

# Durability of the Wettability Properties of a Polypropylene Film with a Low-Pressure CH<sub>4</sub>-O<sub>2</sub> Plasma Treatment

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**ABSTRACT:** The aim of this work was to study the durability of a polypropylene film plasma-treated with an 80 : 20 methane-oxygen gas mixture. Three different storage conditions were used to evaluate the influence of the relative humidity and temperature on the aging process. The surface functionalization of the polypropylene film was analyzed with X-ray photoelectron spectroscopy and attenuated total reflectance/Fourier transform infrared spectroscopy analysis, and the variations of the surface energy and its polar and dispersive components were also investigated. The effects of this plasma treat-

ment were similar to those of a plasma polymerization process, the ablation and polymerization mechanisms taking place simultaneously at the treated surface, but in this case, we obtained hydrophilic properties. The obtained results indicated an improvement of wettability and high durability of the plasma-treated polypropylene film. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1201–1207, 2008

**Key words:** ageing; cold plasma; films; poly(propylene); (PP); surfaces

## INTRODUCTION

Polypropylene (PP) is a versatile polymer because of its low cost, easy processing, and good mechanical properties; it is used in many applications such as films, fibers, slit tape, containers, closures, and automotive interior trim.

The singular structure of PP is responsible for its chemical inactivity;<sup>1</sup> for this reason, PP is a strongly hydrophobic polymer that is very difficult to paint onto and adhere to other materials.<sup>2</sup> With the aim of improving the low intrinsic wettability and adhesive properties of PP films, the low-pressure plasma treatment has been widely used in recent decades. Also, this technique allows the application of plasma at relatively low temperatures, and in this way, a remarkable improvement of surface activation is obtained without its intrinsic bulk properties being affected. There are two methods of promoting glow discharge: microwave and radio frequency (RF). However, RF excitation is preferred at the industrial level. The activation/functionalization of the surface

is achieved in several ways dependent on the gas and the processing conditions. In this way, activation is achieved by the insertion of active species, surface abrasion, or crosslinking processes.

The surface treatment of polymers by plasma techniques is a method available for improving the adhesive properties of polymers. The effects produced by the plasma treatment are well known, so some works have focused on the plasma treatment of PP.<sup>3–6</sup>

The use of conventional gases such as oxygen, nitrogen, and argon promotes a remarkable increase in surface wettability; nevertheless, because of the high instability of the species generated during and after the plasma treatment, hydrophilic properties achieved by the plasma treatment are rapidly lost. This process is well known as hydrophobic recovery and represents a significant restriction on the use of hydrophilic films in technical areas such as the automotive and aerospace industries (in a laminate form with other films or foams). In past years, some works have focused on the study of the hydrophobic recovery process and minimization of its negative effects.<sup>7–11</sup> In particular, some works have focused on the use of different plasma gas mixtures to ensure good durability, such as CH<sub>4</sub>-O<sub>2</sub> mixtures (with an 80 : 20 ratio), which promote the formation of an ultrathin layer that confers excellent and durable hydrophilic properties.

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On the other hand, the use of a plasma containing an organic monomer such as methane is known as plasma polymerization. In this process, the monomer molecules are activated in the plasma phase and impact with the substrate surface, promoting the dissociation of bonds at the topmost layers, surface etching, and the chemical reaction between the active surface and the reactive species in the plasma.<sup>12–14</sup>

The aim of this work was to study the hydrophobic recovery of a PP film treated by low-pressure plasma with a CH<sub>4</sub>–O<sub>2</sub> gas mixture. The surface functionalization was analyzed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared/attenuated total reflectance (FTIR–ATR) spectroscopy analysis; the variations of the surface energy and its polar and dispersive components were also investigated.

## EXPERIMENTAL

### Materials and sample preparation

The film used in this study was a transparent PP film supplied by Logoplast (Logoplast S.L., Alicante, Spain) with a thickness of 50 μm. Samples that were 20 × 20 cm<sup>2</sup> in size were prepared for the plasma treatment, and after this, samples of different dimensions were cut for different measurements. Before the plasma treatment, the films were washed in an acetone bath for 9 min and then dried in air. The aging processes were carried out in a CTS model C-70/1500 (CTS GmbH, Hechingen, Germany), aging chamber with controlled temperature and relative humidity.

### Plasma surface treatment

PP films were exposed to RF low-pressure CH<sub>4</sub>–O<sub>2</sub> plasma. A type CD 400 MC option PC glow discharge RF generator (Europlasma, Oudenaarde, Belgium), operating at 13.56 MHz with a maximum power of 150 W, was used. 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<sub>4</sub> and O<sub>2</sub> in an 80 : 20 ratio. It had a gas flow rate of 100 cm<sup>3</sup>/min, with the working pressure varying in the 31–32 Pa range. The power was fixed at 150 W.

### XPS surface analysis

The XPS spectra were obtained with a VG-Microtech Multilab electron spectrometer (Thermo Fisher Scientific, Inc., Waltham, MA) using the Mg Kα (1253.6 eV) radiation of a twin anode in a constant analyzer energy mode with a pass energy of 50 eV. The pressure of the analysis chamber was maintained at 5

**TABLE I**  
Constant Values of the Test Liquids Used for the Contact-Angle Measurements

Liquid	γ <sub>l</sub> <sup>d</sup> (mJ/m)	γ <sub>l</sub> <sup>p</sup> (mJ/m)	γ <sub>l</sub> (mJ/m)
Water	22.0	50.2	72.2
Glycerol	34.0	30.0	64.0
Diiodomethane	48.5	2.3	50.8
Formamide	32.3	26.0	58.3

× 10<sup>–8</sup> Pa. The binding energy scale was regulated by the C1s transition being set at 284.6 eV. The accuracy of the binding energy values was ±0.2 eV.

### Contact-angle measurements and surface energy calculations

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) with four different test liquids: water, glycerol, diiodomethane, and formamide. At least six different measurements on the plasma-treated surfaces were obtained, and the average values for the contact angles were calculated. The maximum error in the contact-angle measurement did not exceed ±3%. Surface energies were calculated with the Owens–Wend method derived from the general theory of adhesion work among solid and liquid phases, in which polar and nonpolar (dispersive) contributions are considered to explain interactions among the two phases.<sup>15</sup> In this method, it is possible to determine the solid surface energy as the sum of polar and dispersive contributions with at least two different test liquids. The relationship with the equilibrium contact angle of the liquid phase deposited onto the solid phase is derived from the general Fowkes expression, which considers the polar and dispersive contributions for both the solid surface energy and liquid surface energy, which are designated γ<sub>l</sub> and γ<sub>s</sub> with a superscript *d* or *p* for the dispersive and polar contributions, respectively<sup>16,17</sup>:

$$\gamma_l(1 + \cos(\theta))/2(\gamma_l^d)^{1/2} = (\gamma_s^p)^{1/2} \times \left[ (\gamma_l^p)^{1/2}/(\gamma_l^d)^{1/2} \right] + (\gamma_s^d)^{1/2} \quad (1)$$

Contact values for the four test liquids used for contact-angle measurements can be observed in Table I.

### Infrared spectroscopy (FTIR–ATR) analysis

FTIR–ATR measurements were carried out with a PerkinElmer Spectrum BX infrared apparatus (PerkinElmer España, S.L., Madrid, Spain) equipped with an attenuated total reflection accessory. A hundred

**TABLE II**  
**Contact Angles for Different Test Liquids of PP Films**  
**Treated with CH<sub>4</sub>-O<sub>2</sub> Plasma with Different Exposure**  
**Times**

Exposure time (s)	Water (°)	Glycerol (°)	Diiodomethane (°)	Formamide (°)
0	99.27	84.11	65.99	67.14
15	76.34	72.97	56.56	55.15
30	74.49	69.38	52.25	49.68
60	51.5	57.32	28.83	39.94

scans with a resolution of 4 cm<sup>-1</sup> were carried out for each one of the sample measurements.

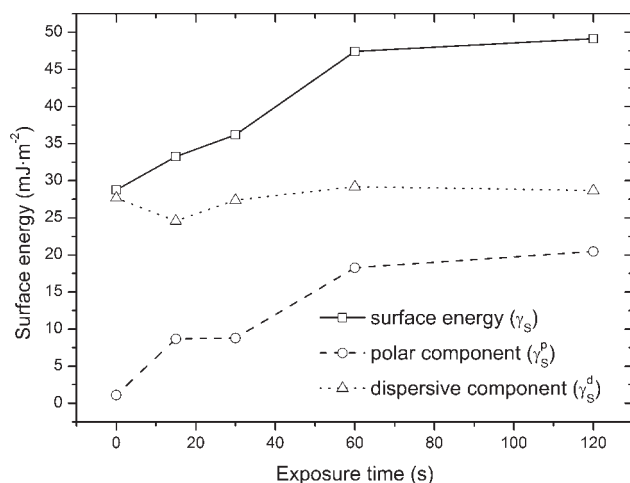
### Weight measurements

The weight change due to plasma modification was calculated with a Mettler-Toledo AL-104 balance (Mettler-Toledo, Inc., Schwerzenbach, Switzerland). The films were weighed before and after exposure to plasma, and an average of five readings was taken for each sample.

## RESULTS AND DISCUSSION

### Effect of the plasma treatment on surface wettability

To evaluate the influence of the plasma exposure time on PP wettability, contact-angle measurements and subsequent surface energy calculations were used. Table II shows the values of the contact angles of nontreated and plasma-treated films for the different test liquids: water, glycerol, diiodomethane, and formamide. As can be observed, for all four liquids, the contact-angle values decrease gradually as the plasma exposure time increases. Figure 1 shows the

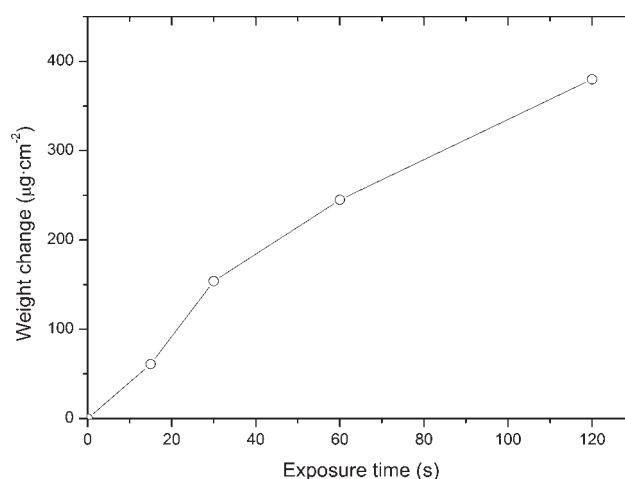


**Figure 1** Variation of the surface energy ( $\gamma_s$ ) and its polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ) components for PP films treated with CH<sub>4</sub>-O<sub>2</sub> plasma as a function of the exposure time.

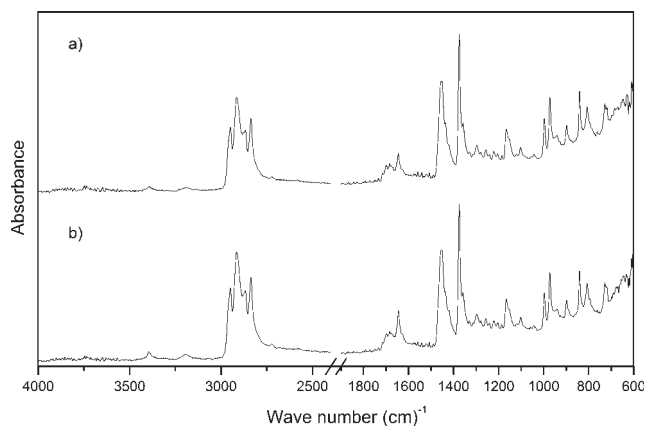
variation of the surface energy and its polar and dispersive components as a function of the CH<sub>4</sub>-O<sub>2</sub> plasma exposure time in the range of 1–120 s. The surface energy increases with the exposure time and levels off for a time of about 60 s. Thus, after the first minute of exposure time, the surface energy increases from 28.7 to 47.4 mJ/m<sup>2</sup>, whereas during the second minute, it increases only up to 49.1 mJ/m<sup>2</sup>.

With respect to the polar and dispersive components, the tendency of the polar component is similar to the tendency of the surface energy, but the dispersive component remains at values close to those of the nontreated film. This behavior shows that the main mechanism of CH<sub>4</sub>-O<sub>2</sub> plasma treatment is surface activation by the deposition of organic polar chains present in the plasma gas; these chains are also activated by the incorporation of activated groups because of the presence of O<sub>2</sub> in the plasma gas. On the other hand, the constant values of the dispersive component indicate, in contrast to other traditional plasma gases (O<sub>2</sub>, N<sub>2</sub>, Ar, etc.), a low effect of the etching mechanism, which contributes to the surface topography modification and higher roughness values.<sup>18</sup> The constant values of the dispersive component indicate that the variation of the roughness surface is scarcely appreciable.<sup>19</sup>

The weight change of a PP film treated with CH<sub>4</sub>-O<sub>2</sub> plasma as a function of the exposure time in the range of 1–120 s is shown in Figure 2. The CH<sub>4</sub>-O<sub>2</sub> plasma treatment produces an increase in weight. The increase is higher at low exposure times; as the exposure time increases, the weight gain is lower. In this case, the weight loss associated with the etching mechanism of plasma is counterbalanced by the deposition of a plasma product typical of the plasma polymerization process due to the nature of the plasma gas with the mixture of an organic gas (CH<sub>4</sub>) and a highly reactive gas (O<sub>2</sub>).<sup>20–22</sup>



**Figure 2** Variation of the weight of PP films treated with CH<sub>4</sub>-O<sub>2</sub> as a function of the exposure time.

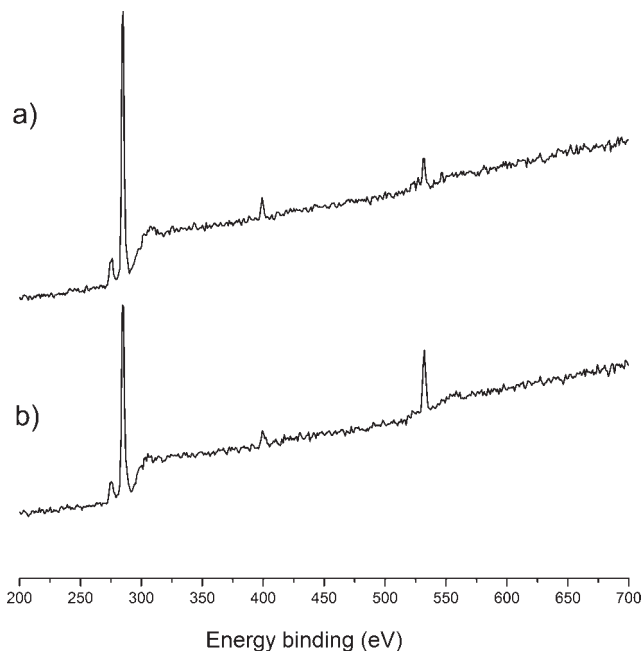


**Figure 3** FTIR-ATR spectra of PP films treated with  $\text{CH}_4\text{-O}_2$  plasma for different exposure times: (a) 0 and (b) 60 s.

Figure 3 shows the FTIR-ATR spectra of nontreated and  $\text{CH}_4\text{-O}_2$  plasma-treated PP films. There are differences between the nontreated and treated films that reveal the evolution of the polar groups with oxygen on the film surface. These polar groups are hydroxyl (O–H) at  $3200\text{ cm}^{-1}$ , carbonyl (C=O) at  $1647$  and  $1720\text{ cm}^{-1}$  (weak), and ester at  $1166\text{ cm}^{-1}$ . The slight increase in the intensity of these peaks indicates the increase in the oxygen-containing functional groups corresponding to the functionalization of the PP surface by plasma treatment. However, because the  $\text{CH}_4\text{-O}_2$  plasma treatment acts on the topmost layers on a nanoscale and the FTIR-ATR technique analyzes at a microscale depth, it is necessary to use other technique such as XPS to obtain results with more accuracy.

Table III shows the results obtained by XPS analysis for PP films treated with  $\text{CH}_4\text{-O}_2$  plasma for different exposure times. Nontreated PP shows an oxygen content of 4.0%, a typical value for industrial PP films because of the content of additives.<sup>18,23</sup> A tendency for the oxygen content to increase can be observed for treated PP samples; in this way, the oxygen content increases up to 11.0% for a plasma-treated sample during 60 s, whereas the nitrogen content remains close to 3.8% in both nontreated and treated samples.

Figure 4 shows the survey (low-resolution) spectra of a PP film treated with  $\text{CH}_4\text{-O}_2$  plasma and a non-



**Figure 4** XPS survey (low resolution) of PP films treated with  $\text{CH}_4\text{-O}_2$  plasma for different exposure times: (a) 0 and (b) 60 s.

treated PP film. The peaks corresponding to carbon (C1s) around 285 eV, oxygen (O1s) around 533 eV, and nitrogen (N1s) around 399 eV are different in the two samples. The plasma-treated sample presents a considerable increase in the O1s peak with respect to C1s, whereas the N1s peak is not affected by the plasma treatment.

With respect to the O/C atomic ratio, the observed tendency is similar to that of the oxygen content, so the O/C atomic ratio increases with the exposure time, indicating the high oxidation level in the deposited layer by plasma polymerization. The N/C atomic ratio remains constant with values around 0.04, and this indicates that it does not participate significantly in the functionalization process. These results are consistent with the FTIR-ATR analysis.

The  $\text{CH}_4\text{-O}_2$  plasma treatment permits the formation of a layer of organic chains that contain oxygen, whereas the nitrogen does not participate because the plasma treatment activates the monomer molecules of the film in the plasma chamber and impacts with the substrate surface, promoting the dissociation of bonds at the topmost layers. In addition, the presence of the  $\text{CH}_4\text{-O}_2$  gas mixture in the plasma chamber allows the material deposition of oxygen-containing organic material. The stability of generated groups in the plasma treatment is high; in this way, the latter reactions to the plasma treatment will lower the intensity and help to insert oxygen-containing species because of the reaction with the oxygen existing in the air. Also, with the increase in oxygen-containing species, a decrease in the carbon

**TABLE III**  
XPS Results for PP Films Treated with  $\text{CH}_4\text{-O}_2$  Plasma for Different Exposure Times

Exposure time (s)	C (atom %)	O (atom %)	N (atom %)	O/C ratio	N/C ratio
0	92.3	4.0	3.7	0.04	0.04
15	87.3	8.9	3.8	0.10	0.04
39	89.1	6.7	4.2	0.08	0.04
60	85.1	11.1	3.8	0.13	0.04

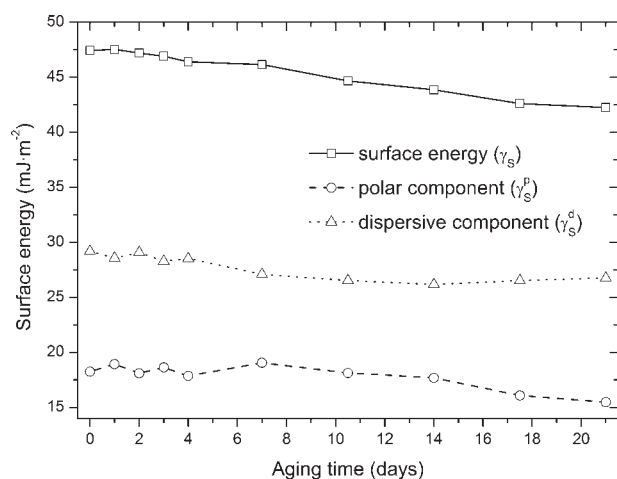
concentration is generated because the deposited polymer on the surface by plasma polymerization has a high content of oxygen.

### Hydrophobic recovery study

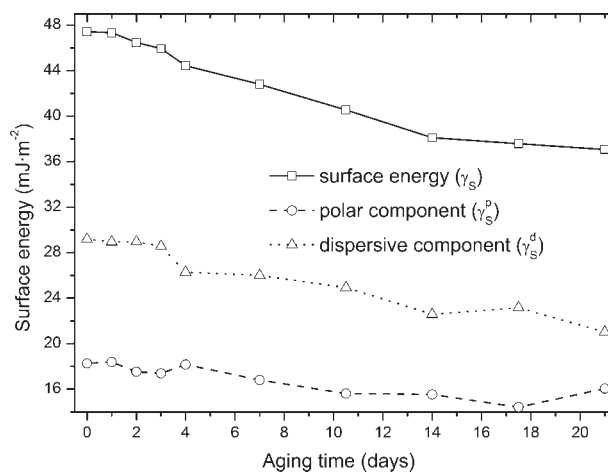
Figure 5 shows the variation of the surface energy and its polar and dispersive components for PP films treated with  $\text{CH}_4\text{-O}_2$  plasma as a function of the aging time in air at room temperature. The surface energy decreases about 8% in 3 weeks of aging. This reduction of wettability is lower than the typical values for other plasma treatments ( $\text{O}_2$ ,  $\text{N}_2$ , Ar, etc.).<sup>24,25</sup> With respect to the polar component, this component shows a slight decrease starting in the second week of aging due to a loss of functionalization by the rearrangement of polar groups, whereas the dispersive component shows no significant decay after 3 weeks of aging.

Figure 6 shows the evolution of the surface energy of PP films treated with  $\text{CH}_4\text{-O}_2$  plasma with respect to the aging time under storage conditions with a temperature of  $25^\circ\text{C}$  and a relative humidity of 50%. As can be observed, the surface energy shows a decrease more evident than that in air, around 20% after 2 weeks of aging, which is mainly promoted by the diminution of the dispersive component, which decreases by 23%, whereas the polar component only decreases by 14%. For a higher aging time, the surface energy values remain constant.

The variation of the surface energy of PP films treated with  $\text{CH}_4\text{-O}_2$  plasma under storage conditions of  $50^\circ\text{C}$  and 40% relative humidity can be observed in Figure 7. A remarkable decrease in the surface energy can be observed. In comparison with the storage conditions described before, a similar



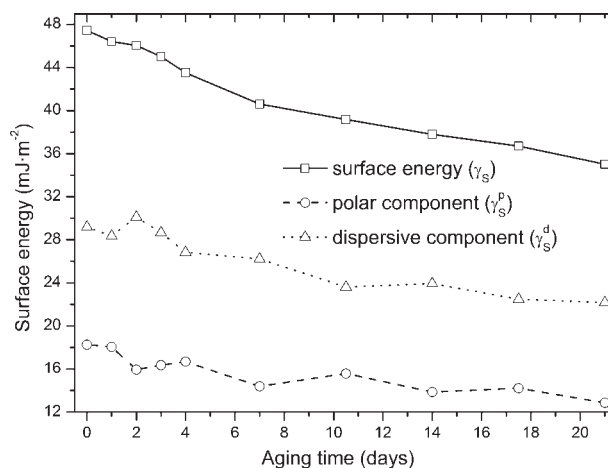
**Figure 5** Variation of the surface energy ( $\gamma_s$ ) and its polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ) components for PP films treated with  $\text{CH}_4\text{-O}_2$  plasma as a function of the aging time in air storage.



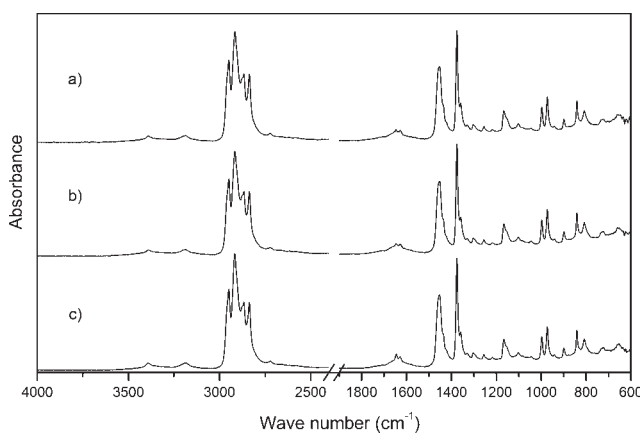
**Figure 6** Variation of the surface energy ( $\gamma_s$ ) and its polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ) components for PP films treated with  $\text{CH}_4\text{-O}_2$  plasma as a function of the aging time under certain storage conditions ( $25^\circ\text{C}$  and 50% relative humidity).

diminution of wettability is observed; however, in this case, an evident hydrophobic recovery continues after 3 weeks of aging.

The hydrophobic recovery consists of a rearrangement of polar groups toward the bulk material, a rearrangement of nonpolar groups from the bulk material toward the surface, and a migration of low-molecular-weight oxidized materials (LMWOMs) from the surface to the bulk.<sup>26-29</sup> The mobility of polar groups on the film surface decreases because of a crosslinked structure at the surface; however, in the aging process, the rearrangement of these groups is allowed, although in a slight way.<sup>18</sup> On the other hand, the migration of LMWOMs is due to a



**Figure 7** Variation of the surface energy ( $\gamma_s$ ) and its polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ) components for PP films treated with  $\text{CH}_4\text{-O}_2$  plasma as a function of the aging time under certain storage conditions ( $50^\circ\text{C}$  and 40% relative humidity).



**Figure 8** FTIR-ATR spectra of PP films treated with  $\text{CH}_4\text{-O}_2$  plasma aged for 21 days under different storage conditions: (a) air, (b)  $25^\circ\text{C}$  and 50% relative humidity, and (c)  $50^\circ\text{C}$  and 40% relative humidity.

thermodynamically more stable state being reached with lower values of the surface energy.<sup>30</sup>

The aging rate is faster in the initial stage of the aging process because rearrangements and migration processes are directly related to the diffusion mechanism, so in the first 4 days, an important decrease in the wettability is observed, and after this time, the aging ratio decreases because diffusion is more difficult. In high-temperature storage, the aging ratio is longer because temperature contributes to the diffusion.

Figure 8 shows the FTIR-ATR spectra of PP films treated with  $\text{CH}_4\text{-O}_2$  plasma during 3 weeks under different storage conditions. A decrease in the number of oxygen-containing functional groups is detected; in this way, a decrease can be observed in the hydroxyl peak (O-H) at  $3200\text{ cm}^{-1}$  and the carbonyl peak (C=O) at  $1647\text{ cm}^{-1}$ . In PP films, a slight diminution of the intensity can be observed, whereas in the PP films aged under high humidity and temperature storage conditions, the diminution is more evident. However, under the highest temperature storage conditions, a lower intensity of functional groups is shown, indicating a higher loss of functional groups on the film surface, which promotes a decrease in the surface energy.

**TABLE IV**  
XPS Results for PP Films Treated with  $\text{CH}_4\text{-O}_2$  Plasma for Different Aging Times in Air Storage

Aging time (days)	C (atom %)	O (atom %)	N (atom %)	O/C ratio	N/C ratio
0	85.1	11.1	3.8	0.13	0.04
7	84.7	11.3	4.0	0.13	0.04
21	85.6	10.9	3.5	0.12	0.04

**TABLE V**  
XPS Results for PP Films Treated with  $\text{CH}_4\text{-O}_2$  Plasma for Different Aging Times Under Storage Conditions ( $25^\circ\text{C}$  and 50% Humidity)

Aging time (days)	C (atom %)	O (atom %)	N (atom %)	O/C ratio	N/C ratio
0	85.1	11.1	3.8	0.13	0.04
7	86.3	10.8	2.9	0.12	0.03
21	86.7	9.7	3.6	0.11	0.04

Table IV shows the results obtained by XPS analysis for PP films treated with  $\text{CH}_4\text{-O}_2$  plasma for different aging times in air storage. The O/C atomic ratio of the polymeric layer deposited in the plasma polymerization treatment is around 0.13, whereas the N/C atomic ratio is close to 0.04. This supports the results obtained for the surface energy. The PP film treated with  $\text{CH}_4\text{-O}_2$  plasma maintains good wettability in air storage. On the other hand, these results reveal that the aging process does not promote significant changes in the film surface. It is necessary to take into account that the hydrophobic process is closely related to the migration of LMWOMs from the surface to the bulk and the rearrangement of polar groups from the surface to the bulk; the rate of these processes is influenced by the time and temperature. In this way, storage at room temperature does not promote major changes in the wettability, and the surface composition remains constant during the aging time.

With respect to aging under storage conditions with a relative humidity of 50% and a temperature of  $25^\circ\text{C}$ , Table V shows the results obtained by XPS analysis for PP films treated with  $\text{CH}_4\text{-O}_2$  plasma for different aging times under the aforementioned conditions. As can be observed, the oxygen atomic content experiences a slight decrease. On the other hand, the O/C atomic ratio of the deposited layer in the plasma polymerization maintains relatively high values (0.11 for 21 days of aging), whereas the N/C atomic ratio maintains the initial values. This fact corroborates the results obtained for the surface energy and its polar and dispersive component.

In Table VI, we can observe the results obtained by XPS analysis for PP films treated with  $\text{CH}_4\text{-O}_2$

**TABLE VI**  
XPS Results for PP Films Treated with  $\text{CH}_4\text{-O}_2$  Plasma for Different Aging Times Under Storage Conditions ( $50^\circ\text{C}$  and 40% Humidity)

Aging time (days)	C (atom %)	O (atom %)	N (atom %)	O/C ratio	N/C ratio
0	85.1	11.1	3.8	0.13	0.04
7	87.5	8.4	4.1	0.10	0.04
21	89.0	7.8	3.2	0.09	0.04

plasma for different aging times under storage conditions of 50°C and 40% relative humidity. There is a decrease in the oxygen atomic content with a consequent reduction of active oxygen-containing species, the O/C atomic ratio decrease from values close to 0.13 to 0.09, and the N/C atomic ratio remains constant around 0.04. With respect to this, it is possible to think that the effect of the temperature is a negative referent to the durability treatment because it makes easier the rearrangement of nonpolar groups from the bulk material toward the film surface. Also, the temperature simultaneously accelerates the rearrangement process of polar groups deposited on the film surface by the plasma treatment and migration of LMWOMs from the surface to the bulk.

### CONCLUSIONS

Low-pressure plasma in a gas based on a methane and oxygen mixture can be used to improve the wettability and durability of PP films. In particular, the durability of the plasma treatment in terms of the storage temperature and relative humidity conditions has been evaluated. Temperature is a critical factor because the hydrophobic recovery process is governed by diffusion laws. On the other hand, it is important to take into account the relative humidity because water and oxygen can react with active species achieved by the plasma treatment. The obtained results show good durability of the plasma-treated PP with the use of 80 : 20 methane–oxygen plasma gas. The effects of the plasma are similar to those of a plasma polymerization process, the ablation and the polymerization mechanisms taking place simultaneously at the treated surface, but in this case we obtain hydrophilic properties. Furthermore, a good response against temperature and relative humidity can be observed. In conclusion, the use of a mixture of an organic gas (CH<sub>4</sub>) and a highly reactive gas (O<sub>2</sub>) considerably reduces the aging process related to the hydrophobic recovery. This plasma gas mixture promotes molecule formation, thus producing a plasma polymerization process that induces functionalization and durability.

### References

1. Carrino, L.; Moroni, G.; Polini, W. *J Mater Process Technol* 2002, 121, 373.
2. Bhat, N. V.; Upadhyay, D. *J Appl Polym Sci* 2002, 86, 925.
3. Cui, N. Y.; Brown, N. M. D. *Appl Surf Sci* 2002, 189, 31.
4. Huang, C. Y.; Chen, C. L. *Surf Coat Technol* 2002, 153, 194.
5. Kang, M. S.; Chun, B.; Kim, S. S. *J Appl Polym Sci* 2001, 81, 1555.
6. Kwon, Y. A. *Fiber Polym* 2002, 3, 174.
7. Everaert, E. P.; Vandermei, H. C.; Devries, J.; Busscher, H. J. *J Adhes Sci Technol* 1995, 9, 1263.
8. Fritz, J. L.; Owen, M. J. *J Adhes* 1995, 54, 33.
9. Guimond, S.; Wertheimer, M. R. *J Appl Polym Sci* 2004, 94, 1291.
10. Occhiello, E.; Morra, M.; Cinquina, P.; Garbassi, F. *Polymer* 1992, 33, 3007.
11. Occhiello, E.; Morra, M.; Garbassi, F.; Johnson, D.; Humphrey, P. *Appl Surf Sci* 1991, 47, 235.
12. Forch, R.; Zhang, Z. H.; Knoll, W. *Plasma Process Polym* 2005, 2, 351.
13. Yasuda, H. *Nucl Instrum Methods Phys Res Sect A* 2003, 515, 15.
14. Yasuda, H.; Yasuda, T. *J Polym Sci Part A: Polym Chem* 2000, 38, 943.
15. Owens, D. K.; Wendt, R. C. *J Appl Polym Sci* 1969, 13, 1741.
16. Fowkes, F. M. *J Colloid Interface Sci* 1968, 28, 493.
17. Fowkes, F. M. *Ind Eng Chem* 1968, 60, 8.
18. Kwon, O. J.; Tang, S.; Myung, S. W.; Lu, N.; Choi, H. S. *Surf Coat Technol* 2005, 192, 1.
19. Garcia, D.; Sanchez, L.; Fenollar, O.; Lopez, R.; Balart, R. *J Mater Sci* 2008, 43, 3466.
20. Kim, I. Y.; Hong, S. H.; Consoli, A.; Benedikt, J.; von Keudell, A. *J Appl Phys* 2006, 100, 6.
21. Martinu, L.; Poltras, D. *J Vac Sci Technol A* 2000, 18, 2619.
22. Zijlmans, R. A. B.; Gabriel, O.; Welzel, S.; Hempel, F.; Ropcke, J.; Engeln, R.; Schram, D. C. *Plasma Sources Sci Technol* 2006, 15, 564.
23. Rahel, J.; Simor, M.; Cernak, M.; Stefecka, M.; Imahori, Y.; Kando, M. *Surf Coat Technol* 2003, 169, 604.
24. Carrino, L.; Polini, W.; Sorrentino, L. *J Mater Process Technol* 2004, 153, 519.
25. Novak, I.; Florian, S. *J Mater Sci* 2004, 39, 2033.
26. Lawton, R. A.; Price, C. R.; Runge, A. F.; Doherty, W. J.; Saavedra, S. S. *Colloid Surf A* 2005, 253, 213.
27. Olah, A.; Hillborg, H.; Vancso, G. *J Appl Surf Sci* 2005, 239, 410.
28. Rangel, E. C.; Gadioli, G. Z.; Cruz, N. C. *Plasmas Polym* 2004, 9, 35.
29. Walther, F.; Davydovskaya, P.; Zucher, S.; Kaiser, M.; Herberg, H.; Gigger, A. M.; Stark, R. W. *J Micromech Microeng* 2007, 17, 524.
30. Novak, I.; Florian, S. *Macromol Mater Eng* 2004, 289, 269.