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Modification of polypropylene surface by CH_4–O_2 low-pressure plasma to improve wettability

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Abstract The aim of this work is to study the effect of surface treatment of a polypropylene film with low-pressure plasma using CH_4–O_2 mixture gas in an 80:20 ratio. The effect of the variation of the plasma treatment conditions has been studied to optimize the plasma effects. The film wettability has been analyzed by the study of the variation of free surface energy and its polar and dispersive components. The surface functionalization of the PP film was also analyzed by X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance infrared spectroscopy (FTIR-ATR) analysis. The surface topography was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The CH_4–O_2 plasma treatment induces the ablation inherent of a traditional plasma treatment and polymerization mechanisms to take place simultaneously at the treated surface. The PP film treated with CH_4–O_2 plasma shows a remarkable improvement on the surface free energy mainly caused by surface functionalization as XPS reveals. Slight changes in surface topography are observed, but they do not contribute in a significant way to improve wettability.

Introduction

Polypropylene (PP) is a strong hydrophobic polymer with low wettability; due to this reason it is a polymer with problems related to paint and adhesion to other materials [1, 2]. Surface treatment by plasma techniques becomes a useful method for improving its adhesion properties while maintaining its bulk properties.

There are many works focusing on the use of conventional gases such as oxygen, nitrogen, argon, etc. in polymeric films [3–6]. The plasma treatment promotes a remarkable increase in surface wettability. The modification of surface properties is achieved by inserting polar species, surface abrasion, or cross-linking processes. Nevertheless, due to high instability of the species generated during and after the plasma treatment, hydrophilic properties achieved by the plasma treatment are rapidly lost [7–10].

The use of methane–oxygen gas in low-pressure plasma treatment leads to a chemical vapor deposition (CVD) process [11, 12], in which a nanometric layer of activated organic material is deposited on the material surface which confers an improvement in hydrophilic properties and durability due to the presence of an organic gas in the mixture gas [13–15]. In this process, the monomer molecules are activated in the plasma chamber and impact with the substrate surface promoting dissociation of bonds at the topmost layers, surface etching, and chemical reaction between active surface and reactive species in the plasma.

The surface behavior depends on plasma treatment conditions such as plasma exposure time and treatment power. In this work we have characterized the PP film surface treated with low-pressure plasma using a mixture of CH_4–O_2 gas in an 80:20 ratio. In addition to this, the work studies the plasmapolymerization and functionalization phenomena as

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well as surface roughness changes induced by the plasma mechanism. The effect of the variation of the plasma treatment conditions has been studied to optimize the plasma treatment. The film wettability has been analyzed by the study of the variation of the free surface energy and its polar and dispersive components. We have analyzed the surface functionalization by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) analysis. The surface topography was analyzed by scanning electron microscopy (SEM) and the surface roughness was quantified by atomic force microscopy (AFM).

Experimental

Materials and sample preparation

The film used in this study was a transparent polypropylene (PP) film supplied by Logoplast (Logoplast, S.L, Alicante, Spain) with a thickness of 50 μm. Samples of 20 × 20 cm^2 in size were prepared for the plasma treatment and, after this, samples of different dimensions were cut for different measurements.

Low pressure CH_4–O_2 plasma treatment

PP films were exposed to radio frequency (RF) low-pressure CH_4–O_2 plasma. It used a glow discharge RF generator (operating at 13.56 MHz with a maximum power of 150 W) type CD 400 MC option PC (Europlasma, Oudenaarde, Belgium). The plasma chamber consists of four aluminum shelves for a sample holder with a total volume of 64 L. The gas used for the plasma generation was a mixture of CH_4–O_2 in an 80:20 volume ratio. It had a gas flow rate of 100 $cm^3\ min^{-1}$ with the working pressure varying in the 31–32 Pa range. The treatment power varied in the 50–150 W range.

XPS surface analysis

X-ray photoelectron spectroscopy analysis was carried out with a VG-Microtech Multilab (Thermo Fisher Scientific Inc., Waltham, USA) electron spectrometer, using the Mg Kα (1253.6 eV) radiation of twin anode in the 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 284.6 eV. The accuracy of BE values was ±0.2 eV.

Contact angle measurements and surface energy 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 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 contact angles were calculated. The maximum error in the contact angle measurement did not exceed ±3%. Surface energies were calculated using the Owens–Wend method derived from the general theory of adhesion work among solid and liquid phases on which polar and nonpolar (dispersive) contributions are considered to explain interactions among the two phases [16–19]. Contact values for the four test liquids used for contact angle measurements can be observed in Table 1.

FTIR-ATR analysis

The Fourier transform infrared spectroscopy (FTIR-ATR) measurements were carried out using a Perkin Elmer Spectrum BX infrared equipment (Perkin Elmer España, S.L., Madrid, Spain) equipped with an attenuated total reflection (ATR) accessory. Hundred scans with a resolution of 4 cm^{-1} were carried out for each of the sample measurements.

Atomic force microscopy (AFM)

AFM analysis was performed on a Multimode AFM microscope with a Nanoscope IIIa ADCS 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 μm × 5 μm images was evaluated.

Table 1 Constant values of test liquids used for the contact angle measurements

Test liquid	γ_l^d (mJ m^{-2})	γ_l^p (mJ m^{-2})	γ_l (mJ m^{-2})
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

Scanning electron microscopy (SEM)

SEM photographs of different samples were obtained using a scanning electron microscopy JEOL 6300 (JEOL USA Inc., Peabody, USA) with an accelerating voltage of 15 kV and a working distance of 15 mm. Samples were previously coated with a thin layer of gold with a thickness of 20 nm; the coating process was performed in vacuum.

Results and discussion

Changes in surface wettability

The plasma treatment conditions are a critical factor that influences the final performance of film surface. Regarding this subject, the effect of the plasma treatment power as a function of the exposure time has been analyzed to determine the ideal RF power that offers the best wettability properties. In Fig. 1, the variation of surface energy of CH_4–O_2 plasma-treated PP film as a function of the plasma exposure time for different treatment powers can be observed. As can be observed the surface energy increases with the plasma exposure time for all treatment powers (50, 100, and 150 W). An important increase is shown for exposure time around 60 s, and after this the values remain almost constant. Thus, after the first minute of exposure time the surface energy increases from 28.7 to 33.5, 35.1, and 47.4 mJ m^{-2} for treatment powers of 50, 100, and 150 W, respectively; while during the second minute, the increase is significantly lower for treatment powers of 100 and 150 W (up to 35.9 and 49.1 mJ m^{-2}, respectively) and even for treatment power of 50 W a slight decrease is experimented (33.1 mJ m^{-2}).

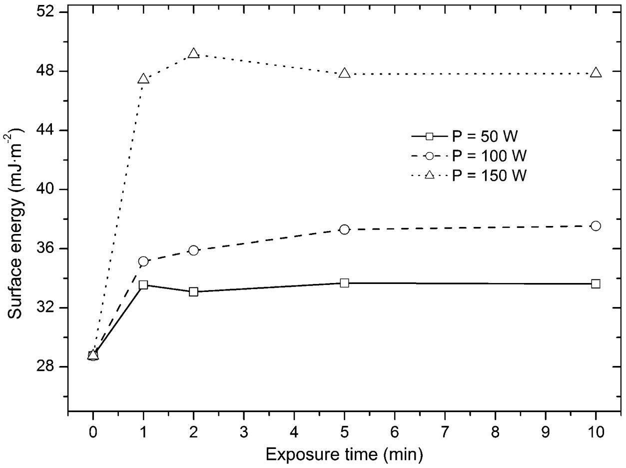

Fig. 1 Variation of surface energy of CH_4–O_2 plasma-treated PP film as a function of the plasma exposure time for different treatment powers

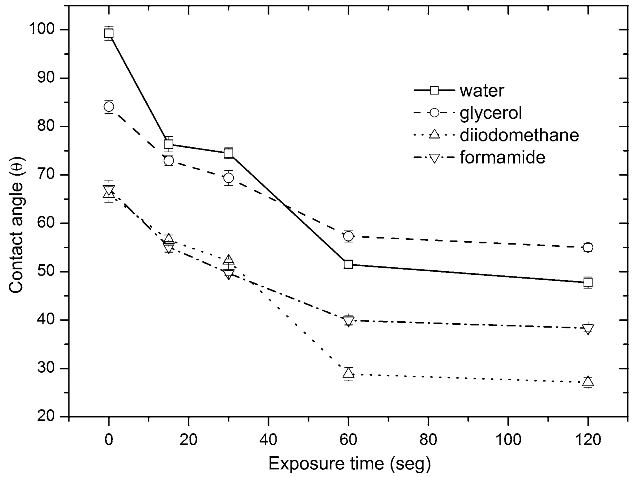

Fig. 2 Variation of the surface contact angle of CH_4–O_2 plasma-treated PP film (150 W) as a function of the plasma exposure time for different test liquids

From these results it can be concluded that a treatment power of 150 W offers higher values of surface energy and as a consequence the higher wettability properties. Also it can be observed the surface energy increases with the exposure time and levels off for a time range up to 60 s.

To analyze in more detail the influence of the plasma exposure time on the PP wettability, contact angle measurements and subsequent surface energy determination were used fixing up the treatment power to 150 W. Figure 2 shows the variation of the surface contact angle of PP film treated with CH_4–O_2 plasma in terms of the exposure time for different test liquids (water, glycerol, diiodomethane, formamide) with different polarity. As can be observed, for all the four liquids, the contact angle values decrease gradually with increasing plasma exposure time but level off from 60 s. Thus, for exposure time of 15 s the contact angle loss is around 23, 13, 14, and 18% for water, glycerol, diiodomethane, and formamide, respectively; while for exposure times from 60 to 120 s the decrease is not significant. From these results it can be concluded that the ideal exposure time is 60 s since higher exposure times do not decrease practically the contact angle.

Regarding the surface energy, in Table 2 it can be observed the values of surface energy (γ_s) and its polar (γ_s^p)

Table 2 Values of surface energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) components of CH_4–O_2 plasma-treated PP film (150 W) for different plasma exposure times

Exposure time (s)	γ_s (mJ m^{-2})	γ_s^p (mJ m^{-2})	γ_s^d (mJ m^{-2})
0	28.75	1.09	27.66
15	33.24	8.68	24.57
30	36.18	8.79	27.39
60	47.44	18.26	29.19
120	49.15	20.47	28.68

and dispersive (γ_s^d) components of the PP film treated with CH_4–O_2 plasma for different exposure times, can be calculated for the four liquids. As it was foreseeable from contact angle values the increase of the surface energy in the first 60 s of treatment is by 65.1%, while during the second minute the increase is only by 3.5%. This wettability increase is associated to surface energy increase. The main contribution to the surface energy increase is attributed to the polar component which increases in a way similar to the surface energy; thus the values suddenly increase from 1.1 to 18.3 when the exposure time varies from 15 to 60 s, while during the second minute they increase up to 20.5. However the dispersive component does not show significant changes during the treatment.

The polar component tendency shows that the main mechanism of CH_4–O_2 plasma treatment is the surface activation by deposition of organic polar chains present in the plasma gas (plasmapolymerization); these chains are also activated by the incorporation of activated groups present in the O_2 gas [20, 21]. On the other hand the constant values of the dispersive component indicate the low effect of etching mechanism [22]. It is important to remark that the etching mechanism is associated to traditional plasma gases (O_2, N_2, Ar, etc.) and contributes to the surface topography modification and higher roughness values, but in this work a mixture of organic gases are used, thus allowing plasmapolymerization to be the predominant process.

Surface functionalization study

Figure 3 shows the FTIR-ATR spectra of CH_4–O_2 plasma-treated PP films for different exposure times. The spectra

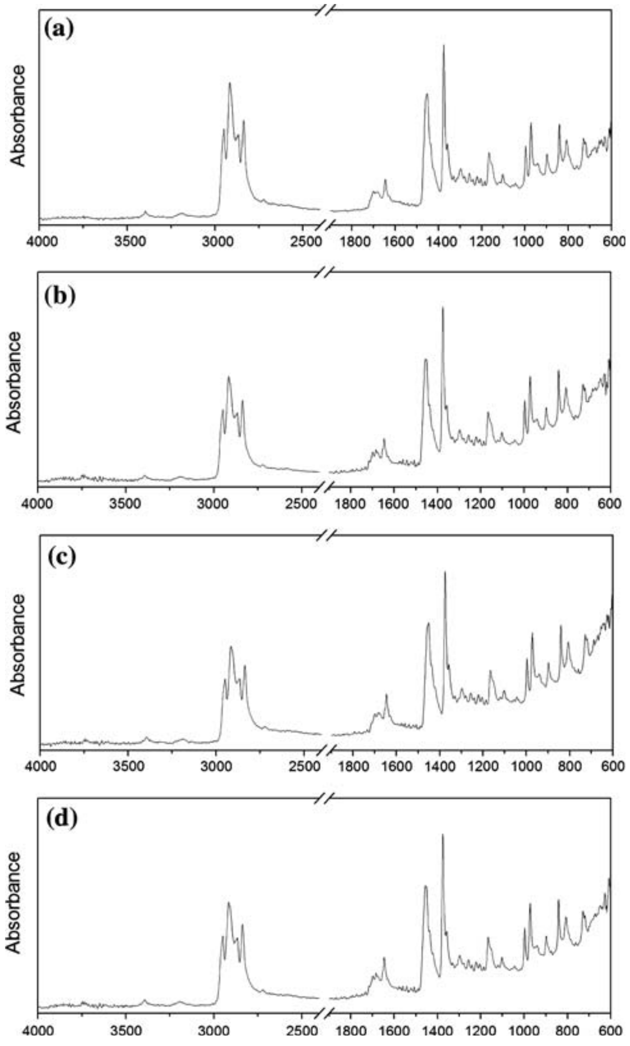

Fig. 3 FTIR-ATR spectra of CH_4–O_2 plasma-treated PP film (150 W) for different exposure times: (**a**) Untreated, (**b**) 30 s, (**c**) 60 s, (**d**) 120 s

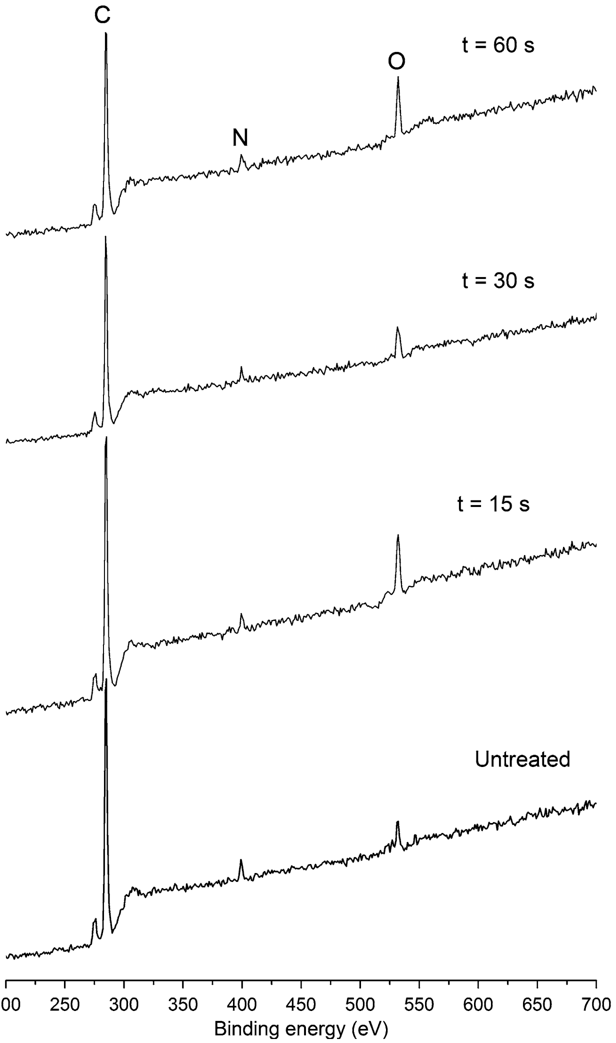

Fig. 4 XPS survey (low resolution) of CH_4–O_2 plasma-treated PP film (150 W) for different exposure times

show the evolution of the peaks associated to functional groups located in the FTIR-ATR spectra at 3,200 cm^{-1}, 1,647 cm^{-1}, 1,720 cm^{-1}, 1,166 cm^{-1} corresponding to hydroxyl [O–H], carbonyl [C=O] (strong and weak) and ester [O=C–O–C], respectively [23, 24]. As can be observed the oxygen-containing functional groups show an increase of intensity as the plasma exposure time increases.

Table 3 XPS results of CH_4–O_2 plasma-treated PP film (150 W) for different exposure times

Exposure time (s)	O/C ratio	N/C ratio
0	0.04	0.04
15	0.10	0.04
39	0.08	0.04
60	0.13	0.04

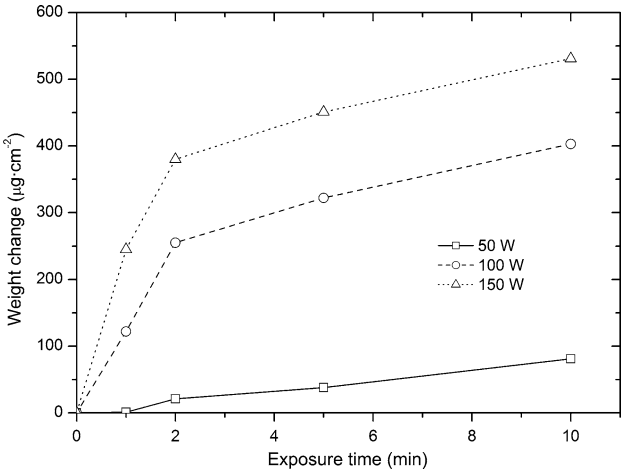

Fig. 5 Weight variation of CH_4–O_2 plasma-treated PP film as a function of exposure time for different treatment powers

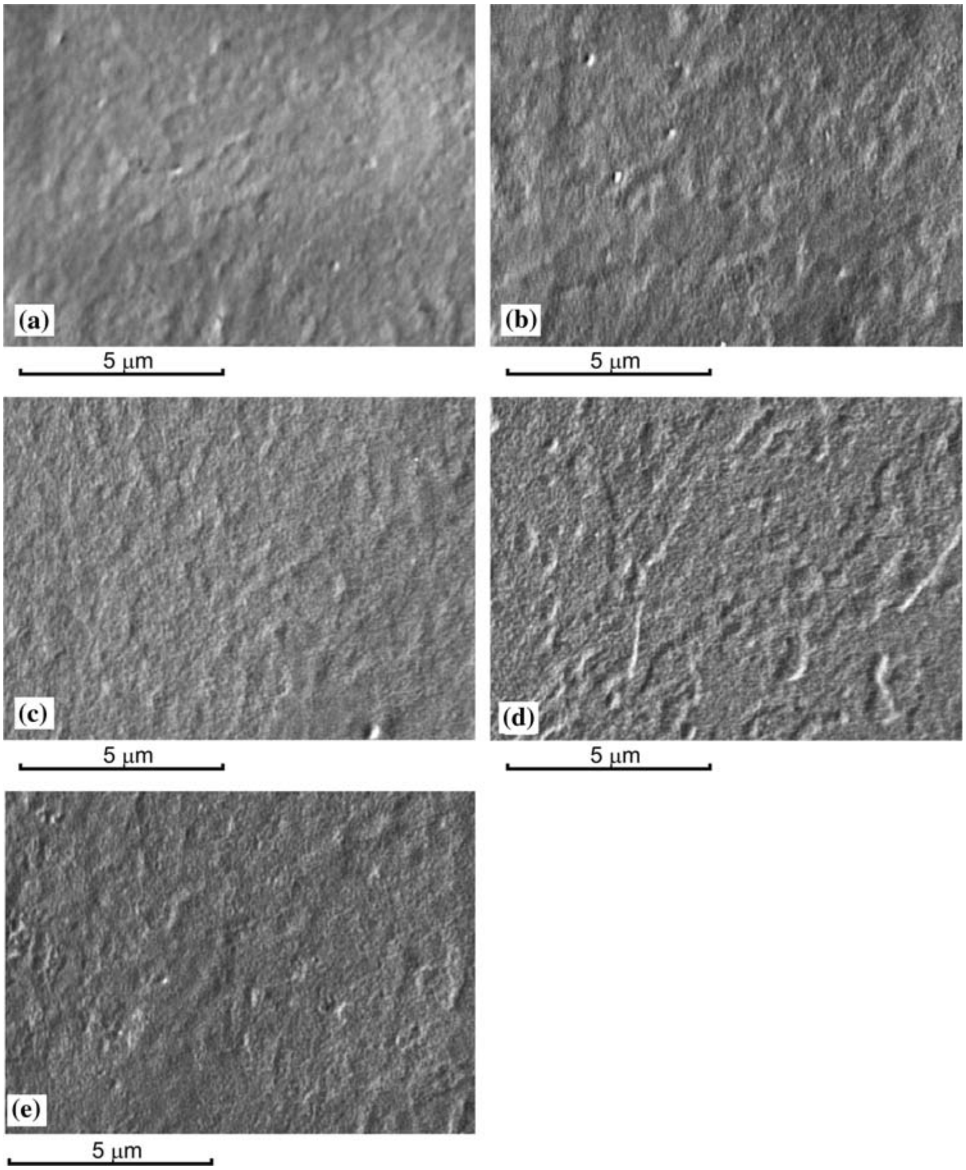

Fig. 6 SEM micrographs of CH_4–O_2 plasma-treated PP film (150 W) for different exposure times (×10,000): (**a**) Untreated, (**b**) $t = 15$ s, (**c**) $t = 30$ s, (**d**) $t = 60$ s, (**e**) $t = 120$ s

This fact corroborates the activation/functionalization effect of CH_4–O_2 plasma treatment on the surface of PP film surface. However the differences between the films with exposure times of 60 and 120 s are not evident. It is remarkable that the functionalization of PP film by plasma treatment remains almost constant for exposure times higher than 60 s, in concordance with the values obtained in the wettability study.

The FTIR-ATR analysis works at micro-scale depth; however, the CH_4–O_2 plasma treatment acts on the topmost layers at nano-scale. In this way it is necessary to use a technique that allows us to obtain results with more accuracy.

Figure 4 shows the survey (low-resolution) spectra of PP film treated with CH_4–O_2 plasma for different exposure times. There are differences in the peaks corresponding to carbon (C 1s) around 285 eV, oxygen (O 1s) around 533 eV, and nitrogen (N 1s) around 399 eV. Plasma-treated samples present a considerable increase of O 1s peak regarding C 1s, while the peaks N 1s are not affected by the plasma exposure time.

Table 3 shows the results obtained by XPS analysis for PP films treated with CH_4–O_2 plasma for different exposure times. The oxygen content increases with the exposure time, while the nitrogen content remains constant; thus the O/C atomic ratio increases with the exposure time up to 60 s, indicating the high oxygen content in the deposited layer obtained by the plasmapolymerization process. The N/C atomic ratio keeps constant, indicating that it does not participate in a significant way.

These results are in concordance with the FTIR-ATR analysis, since the CH_4–O_2 plasma treatment allows the material deposition of oxygen-containing organic material. Also, subsequent reactions to plasma treatment will take place with lower intensity and will help to insert additional oxygen-containing species due to the reaction with the oxygen existing in the plasma chamber. Also the increase of oxygen-containing species drives to a decrease of carbon concentration, since the plasmapolymerized layer has a high oxygen content due to the oxygen presence in the mixture gas.

Changes in surface topography

As described before, the deposition of a polymeric layer with the active species (plasmapolymerization) is one of the plasma-acting mechanisms of low-pressure plasma mixture gas (CH_4–O_2) [22, 23]. This effect is evident from the observation of the weight gain as a function of the plasma exposure time for different treatment powers (Fig. 5). As can be observed the plasma treatment shows an

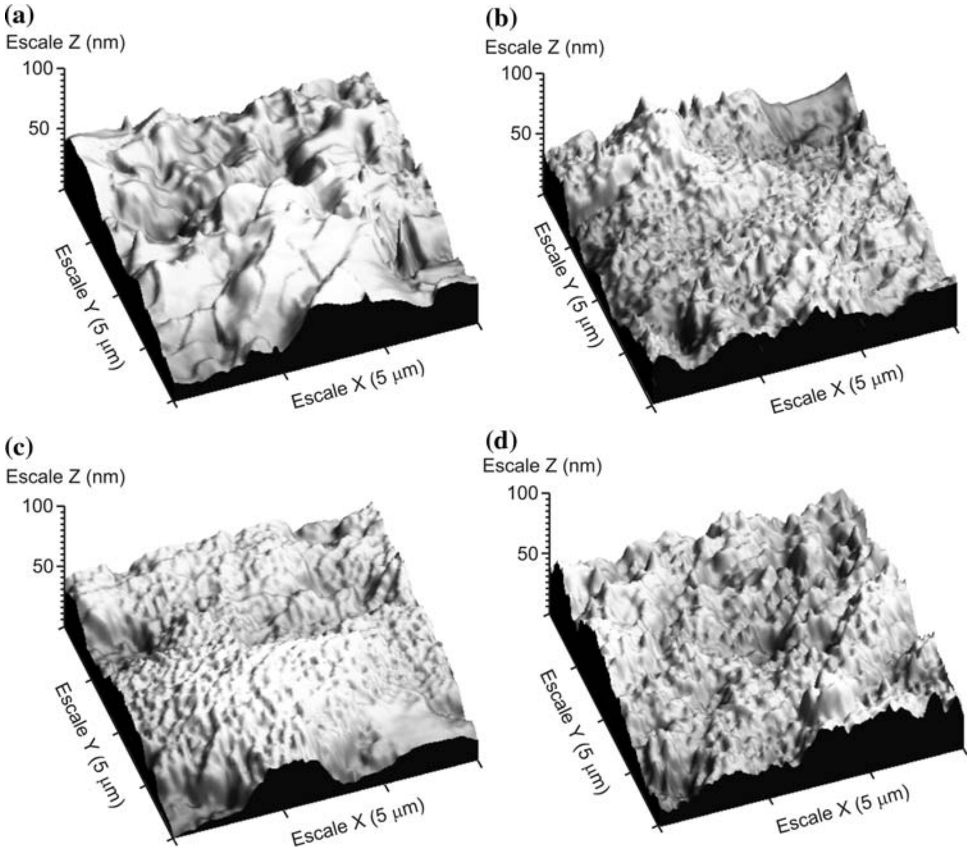

Fig. 7 AFM 3D representation of the surface topography (5 µm × 5 µm) of CH_4–O_2 plasma-treated PP film (150 W) for different exposure times: (**a**) untreated, (**b**) 30 s, (**c**) 60 s, (**d**) 120 s

increase in the sample weight with an increase in the exposure time. Also for higher power treatment the weight increase is more evident since the deposition is promoted by the RF power. This fact demonstrates that the effect of the deposition of plasma product typical of plasmapolymerization process is higher than the material removing associated to other conventional plasma gases (O_2, N_2, Ar, etc.) [25, 26].

The material deposition on the PP film causes changes in the surface topography. Figure 6 shows the SEM micrographs of the PP film surface after the CH_4–O_2 plasma treatment for different exposure times. No significant changes can be observed for films with different exposure times. In the plasma treatment with conventional gases, material etching promotes surface topography changes; opposite to this, in the use of CH_4–O_2 plasma the material deposition makes difficult the observation of significant changes on the surface topography. However AFM is a more adapted technique for the characterization of plasma-treated surface, allowing to obtain a 3D representation of the surface topography and roughness measurements.

Figure 7 shows the variation of the surface topography by means of the 3D representation of PP film untreated and treated with CH_4–O_2 plasma for different exposure times. As it can be observed a topography change is evident as a function of the plasma exposure time. At first, the film surface is smooth with not many peaks. As the plasma treatment acts the number of small peaks increases and the surface becomes more abrupt. The appearance of small peaks is related to the deposition of the material on the film surface due to the plasmapolymerization process. This material deposition promotes a slight increase of the surface roughness.

Table 4 shows the root-mean-squared roughness (R_{rms}) and maximum roughness (R_{max}) values determined by AFM of the PP film treated with CH_4–O_2 plasma for different exposure times. The values of R_{rms} remain constant as the exposure time increases despite the changes observed in 3D AFM figures. As can be observed in Fig. 8, this fact is due to the lower height of the peaks that appears as a consequence of the plasma treatment; thus the CH_4–O_2 plasma treatment increases the peak number but decreases the peak height, and as a result the roughness remains almost constant.

It is difficult to obtain a correlation between the R_{rms} and the surface energy since the main mechanism of CH_4–O_2 plasma is surface activation by deposition of an organic polar layer.

Contrary to conventional plasma treatments, the observation of topography changes of the film treated with

Table 4 Morphology parameters as determined by AFM analysis of CH_4–O_2 plasma-treated PP film (150 W) for different exposure times

Exposure time [s]	R_{rms} (5 μm × 5 μm) [nm]	R_{max} [nm]
0	12.55	94.63
15	12.33	93.91
30	14.08	97.30
60	13.25	91.48
120	13.23	93.70

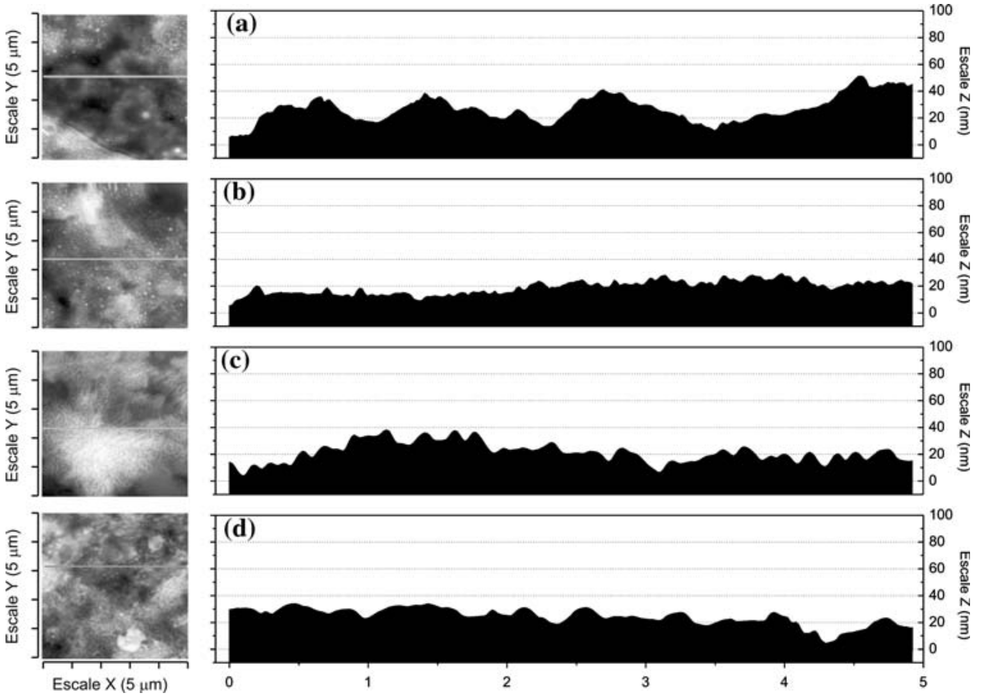

Fig. 8 Roughness profiles (5 μm × 5 μm) of CH_4–O_2 plasma-treated PP surface (150 W) for different exposure times: (**a**) untreated, (**b**) 30 s, (**c**) 60 s, (**d**) 120 s

CH_4–O_2 plasma does not show a behavior associated to etching mechanism due to the absence of a substantial increase of surface roughness [27–29].

Conclusions

Plasma treatment with CH_4–O_2 gas is an adequate technique for improving wettability of polypropylene films. Plasma treatment conditions are considered as a critical factor to take into account since they determine the final wettability performance of PP films. An increase in power treatment and exposure time promotes an increase in wettability; however, the main increase is located at short exposure times. Thus, for exposure times higher than 1 minute the wettability remains in constant values.

The effects of the plasma treatment are similar to a plasmapolymerization process, the ablation and the polymerization mechanisms taking place simultaneously at the treated surface. However contrary to plasma treatments with conventional gases the main mechanism of CH_4–O_2 plasma treatment is the surface activation by deposition of organic polar chains, since the abrasion of the material is counterbalanced by the deposition of a plasma product typical of the plasmapolymerization process due to the nature of the CH_4 gas.

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