

# Improve of adhesion properties of polypropylene film using low pressure plasma containing organic gas

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## INTRODUCTION

Polypropylene (PP) is a strong hydrophobic polymer commonly used in textile industry with a high difficulty to paint and adhere to other materials. With the aim of improving the wettability and adhesive properties of PP the low pressure plasma treatment has been widely used in the recent decades to improve the wettability properties of polymer films. Also this technique allows the application of plasma at low temperature without affecting its intrinsic bulk properties. The surface activation is obtained by several ways in function of the gas used and the conditions of processing [1-3].

Surface treatment of polymers by plasma techniques is an available method for improving the adhesive properties of polymers. The effects produced by the plasma treatment are well know, thus some works are focused on the plasma treatment of polypropylene [4-7]. The use of conventional gases such as oxygen, nitrogen, argon,... promotes a remarkable increase in surface wettability; nevertheless, due to the high instability of the species generated during and after the plasma treatment, hydrophilic properties achieved by the plasma treatment are rapidly lost [8-10].

In this work we have investigated the wettability changes in a polypropylene film treated with low pressure plasma using a mixture of CH<sub>4</sub>-O<sub>2</sub> gas. The effect of the variation of the plasma treatment conditions has been studied in order to optimize the plasma treatment.

The addition of an organic compound to O<sub>2</sub> gas promotes that the ablation inherent of a traditional plasma treatment and the plasmapolymerization mechanisms take place simultaneously at the treated surface. The PP film treated with CH<sub>4</sub>-O<sub>2</sub> plasma shows a remarkable improvement on surface free energy mainly caused by surface functionalization. Slight changes in surface topography are observed but they do not contribute in significant way to improve wettability.

## EXPERIMENTAL

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

x 20 cm<sup>2</sup> in size were prepared for the plasma treatment and after this, samples of different dimensions were cut for the different measurements.

PP films were exposed to radio frequency (RF) low pressure CH<sub>4</sub>-O<sub>2</sub> plasma. It was 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 aluminium shelves for sample holder and a total volume of 64 l. The gas used for the plasma generation was a mixture of CH<sub>4</sub>-O<sub>2</sub> with a 80:20 volume ratio. It was used a gas flow rate of 100 cm<sup>3</sup>min<sup>-1</sup> and the working pressure varied in the 31-32 Pa range. The treatment power was 150 W.

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 [11-15]. Contact values for the four test liquids used for contact angle measurements can be observed in the Table 1

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

Test liquid	$\gamma_l^d(\text{mJ}\cdot\text{m}^{-2})$	$\gamma_l^p(\text{mJ}\cdot\text{m}^{-2})$	$\gamma_l(\text{mJ}\cdot\text{m}^{-2})$
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

SEM photographs of different samples were obtained using a scanning electron microscopy JEOL 6300 (JEOL USA Inc., Peabody, USA). Samples were previously coated with gold; the coating process was performed in vacuum conditions.

## RESULTS AND DISCUSSION

Table 2 shows the variation of the surface energy and the components polar and dispersive, as a function of the exposure time with CH<sub>4</sub>-O<sub>2</sub> plasma. The surface energy values have been calculated from the four liquids considered (water, glycerol, diiodomethane and formamide). As can be observed an increase of surface energy is experimented by the PP film. The main increase is focused in the initial seconds of treatment. As the exposure time increase the increment of surface energy is lower. By this way during the first minute practically all surface energy increment has been generated.

Table 2. Values of surface energy, polar and dispersive components of samples treated with CH<sub>4</sub>-O<sub>2</sub> plasma in function of the exposure time.

<b>Exposure time (s)</b>	<b><math>\gamma_s</math> (mJ·m<sup>-2</sup>)</b>	<b><math>\gamma_s^p</math> (mJ·m<sup>-2</sup>)</b>	<b><math>\gamma_s^d</math> (mJ·m<sup>-2</sup>)</b>
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

The action of other reactive plasma gases produces a loss of weight due to the removal of material as a consequence of the impact of plasmas gas species and the resulting increase of surface roughness. As can be observed in Table 3, the methane-oxygen plasma treatment produces the opposite effect. As the exposure time increase an increase of weight in the sample is promoted. This weight increase is consequence to the plasmapolymerization that take place simultaneously to ablation.

On the other hand the reactive species that are formed on the surface are not all originate by the gas but may be mixed with reactive species of already deposited material.

Table 3. Weight variation of samples treated with CH<sub>4</sub>-O<sub>2</sub> plasma in function of the exposure time.

<b>Exposure time (min)</b>	<b>Working power (W)</b>	<b><math>\Delta</math> Weight (mg)</b>	<b><math>\Delta</math> Weight·cm<sup>-2</sup> (μg·cm<sup>-2</sup>)</b>
1	50	0.1	1
2	50	2.1	21
5	50	3.8	38
10	50	8.1	81
1	100	12.2	122
2	100	25.5	255
5	100	32.2	322
10	100	40.3	403
1	150	24.5	245
2	150	38.0	380
5	150	45.1	451
10	150	53.1	531

The material deposition on the PP film causes changes in the surface topography. Figure 1 shows the SEM micrographs of PP film surface after the methane-oxygen 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, the material etching promotes that surface topography changes; opposite this, in the use of CH<sub>4</sub>-O<sub>2</sub> plasma the material deposition make difficult the observation of significant changes on the surface topography.

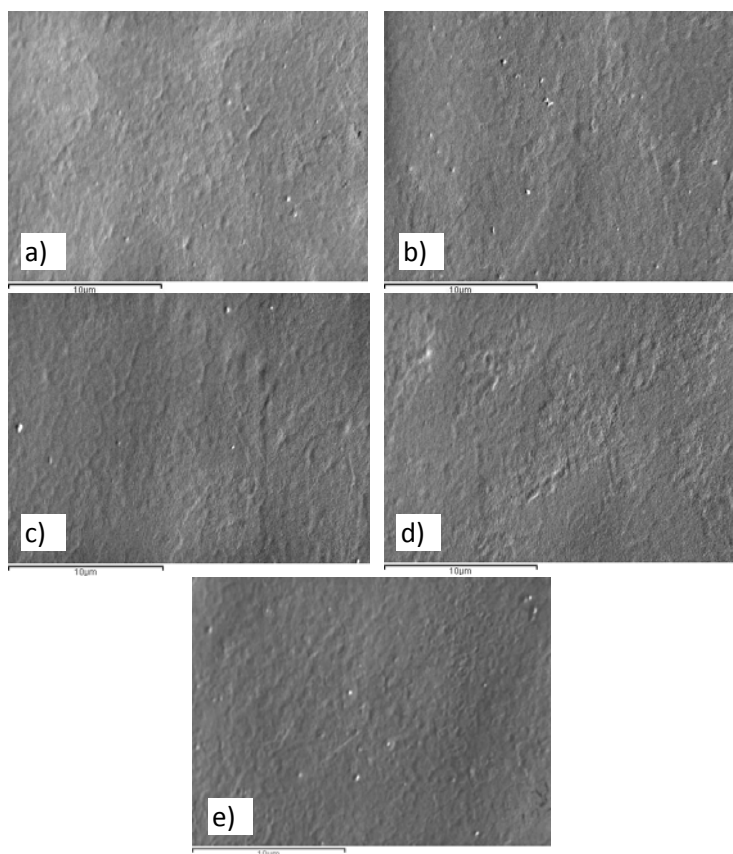


Figure 1. SEM micrographs of CH<sub>4</sub>-O<sub>2</sub> plasma-treated PP film for different exposure times (x 5,000): a) Untreated; b) t=15 s; c) t=30 s; d) t=60 s; e) t=120 s.

## CONCLUSIONS

Plasma treatment with CH<sub>4</sub>-O<sub>2</sub> gas is an adequate technique for improving wettability of polypropylene film. Plasma treatment conditions are considered as a critical factor to take into account since they determine the final wettability performance of PP film. 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 plasmopolymerization 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<sub>4</sub>-O<sub>2</sub> plasma treatment is the surface activation by deposition of organic polar chains, since the abrasion of the material is counterbalanced by the deposition of plasma product typical of plasmopolymerization process due to the nature of the CH<sub>4</sub> gas.

**Acknowledgement:** Authors thank “Ministerio de Ciencia y Tecnología”, Ref: DPI2007-66849-C02-02 for financial support.

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