

Universidad Carlos III de Madrid



Institutional Repository

This is a postprint version of the following published document:

N. Encinas, B. Díaz-Benito, J. Abenojar, M.A. Martínez. *Extreme durability of wettability changes on polyolefin surfaces by atmospheric pressure plasma torch*. Surface & coatings technology, vol. 205 issue 2 (2010), pp. 396-402

DOI: [10.1016/j.surfcoat.2010.06.069](https://doi.org/10.1016/j.surfcoat.2010.06.069)

© 2010 Elsevier B.V.



This work is licensed under a Creative Commons Attribution–NonCommercial–NoDerivs
4.0 International License

Extreme durability of wettability changes on polyolefin surfaces by atmospheric pressure plasma torch

N. Encinas^{*}, B. Díaz-Benito, J. Abenojar, M.A. Martínez^{*}

Materials Science and Engineering Department, IAAB, Materials Performance Group. Universidad Carlos III de Madrid. Av. Universidad, 30. 28911 Leganés (Madrid), Spain

A B S T R A C T

In the present work three common polyolefins: high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) have been treated with an atmospheric pressure air plasma torch (APPT) in order to improve their wettability properties. The variations in surface energy (γ_s), as well as the durability of the treatment are determined by means of contact angle measurements for different aging times after plasma exposure (up to 270 days) using five test liquids which cover a wide range of polarities. The introduction of new polar moieties (carbonyl, amine or hydroxyl) is confirmed by Fourier transform infrared spectroscopy in attenuated total multiple reflection mode (ATR FTIR) and X ray photoelectron spectroscopy (XPS). Furthermore, scanning electron microscopy (SEM) provides information on the morphological changes and variation on surface roughness, revealing that smoother, lamellar and semispheric micrometric structures are created on the LDPE, HDPE and PP surfaces, respectively. Results show that APPT treatment enhances both the total and polar components of the γ_s under study, with an unprecedented stability (>8 months) in time.

Keywords:

Atmospheric pressure plasma
Surface energy
Hydrophilic durability
Polyolefins

1. Introduction

In the last decades, the needs of consumption of the world population have promoted a dramatic improvement in the research and manufacture of new materials with optimized industrial features such as processibility, mechanical properties, recycling possibility and others. Polymers [1] fulfil these solicitations, so that it would be possible to designate these years as the age of polymers. Within this group of materials, polyolefins are a strong, lightweight, recyclable [2,3] and inert type of thermoplastic polymers used in a wide range of applications such as healthcare, films, electrical components, pipes, automotive and aircraft industry among others [1,3,4]. Despite their excellent bulk properties, low cost and processibility, the applications of polyolefins are sometimes restricted by their poor wettability, which causes adhesion problems. This is due to their non porous and hydrophobic surfaces, which results in a very low γ_s . In order to circumvent this problem, several classes of pre treatments to transform polyolefins into valuable finished products have been utilized, including chemical etching, corona discharge, plasma etching, UV irradiation, mechanical abrasion or primers [5 10,12]. The aim of these pre treatments is the elimination of low cohesion layers, creation of specific surface groups, introduction of cross linking [10], modification of crystallinity or roughness, increase in

lubrication [11], or protection and enhancement of γ_s of members prior to bonding [8 10,12]. Plasma technology is an active media constituted by energetic neutrals, ions and electrons which act on a surface modifying its physicochemical nature without affecting the bulk properties [13 21]. Depending on the way it is activated and their working power, it is possible to distinguish between cold or non local thermodynamic equilibrium plasmas (non LTE) [19] and thermal or local thermodynamic equilibrium plasmas (LTE)[18]. Non LTE plasmas usually reach low high particles temperatures [17], so materials do not suffer hazardous warming and can be used for applications like coating, cleaning or surface activation. On the other hand, LTE plasmas reach high particles temperatures up to 10,000 K, so their applications are restricted to welding or melting. Whereas the use of chemical solvents or primers involves the generation of toxic waste, and mechanical treatments lead to heterogeneous surfaces, plasma is a fast, environmentally friendly and dry process. Atmospheric pressure plasma torches (APPT) [17,20] are non LTE devices which mainly produce cleaning by means of the breakdown of pollutants, etching and surface activation [22] due to the introduction of different moieties of polar nature [23 25] (OH, COOH, C O, NH) which significantly increase γ_s and therefore, the adhesion properties of polymers [26,40]. The decrease of γ_s to the original values during prolonged storage, due to the fact that all interfaces have a thermodynamic tendency to minimise γ_s through different processes, has been previously studied [27 31,36,39]. Possible mechanisms of aging are the adsorption of atmospheric low energy pollutants, diffusion of substances in the polymer and reorientation of surface polar groups into the bulk [28].

^{*} Corresponding authors. Encinas is to be contacted at Tel.: +34 91 624 88 63; fax: +34 91 624 94 40. Martínez, Tel.: +34 91 624 94 01; fax: +34 91 624 94 40.

E-mail addresses: nencinas@ing.uc3m.es (N. Encinas), mamc@ing.uc3m.es (M.A. Martínez).

The aim of this study was the improvement of the γ_s of HDPE, LDPE and PP using an APPT device operating with air at two treatment speeds (1 and 10 m/min). Contact angle measurements were used to determine wettability properties and to calculate the γ_s values using the Owens Wendt Rabel Kaelble (OWRK) calculus method [32]. The surface chemical modifications induced were characterized by ATR FTIR and XPS analyses. The etching effects of the treatment on the morphology of the surface were analyzed by SEM. Finally, the durability of the treatment was evaluated throughout 9 months of aging studying the evolution of all the contributions to the γ_s (dispersive, polar and total). We found out an important enhancement of γ_s and an astonishing durability of the APPT effects onto the polyolefin surfaces, in contrast with the behaviour of polyolefins modified by air corona treatment [7,27,33].

2. Experimental

2.1. Materials and sample preparation

Polymers (75 mm long, 25 mm wide and 3 mm thick) were provided by Ketersa (Spain). The specimens were cleaned and degreased with methyl ethyl ketone (MEK).

2.2. APPT device

An APPT device from Plasma Treat GmbH (Steinhagen, Germany) described in Fig. 1. was used to treat the polymers.

The setup operated at a frequency of 17 kHz and a high tension discharge of 20 kV, and it was provided with a rotating torch ending in a nozzle (1900 rpm) through which plasma was expelled. The system contained an electronically speed controlled platform where the samples were placed. The air plasma was generated at a working pressure of 2 bars inside the rotating nozzle by a non equilibrium discharge and expelled through a circular orifice onto the samples. The speed of the platform was set at 1 and 10 m/min, and the distance between the sample and the plasma torch nozzle was fitted to 6 mm. Polymers were stored during aging process at nearly 25 °C and 50% relative humidity, in dust free conditions up to 9 months.

2.3. Contact angle measurements and γ_s calculations

Contact angle was measured both before and after the plasma treatment in order to evaluate the wettability of the polymers, by using an OCA 15 plus device from DataPhysics (Neurtek Instruments, Eibar, Guipúzcoa, Spain) following the normative UNE EN 828:2009. The samples were placed into an isothermal chamber at (24 ± 2) °C previously saturated with vapour of the corresponding liquid for at least 10 min before placing the drops. Contact angle was measured within 3 min after the liquid drop was attached to the surface. The test liquids used (deionised water, nitromethane, diiodomethane, glycerol

and 1, 5 pentanediol) were chosen covering a wide range of surface tensions and polarities as it is shown in Table 1.

At least six drops per sample were measured and averaged by the sessile drop method. Every component of γ_s were obtained by means of the OWRK [32] method (Eq. (1)), which enables the determination of both additive contributions of the γ_s , dispersive (due to London type forces) and polar [31] (which accounts for the dipole dipole and hydrogen bonding interactions), fitting a linear equation which derives from the Fowkes expression [34].

$$\frac{(1 + \cos \theta) \gamma_l}{\sqrt{\gamma_l^D}} = \sqrt{\gamma_s^P} \cdot \sqrt{\frac{\gamma_l^P}{\gamma_l^D}} + \sqrt{\gamma_s^D} \quad (1)$$

In this expression, θ represents the test liquid contact angle on the surface, γ_l and γ_s are the liquid surface tension and the solid surface energy, respectively. The superscripts *D* and *P* are referred to the dispersive and polar fractions contribution to the surface tension and γ_s parameters.

2.4. ATR FTIR spectrum

A Bruker Tensor 27 (Bruker Optik GmbH, Madrid, Spain) spectrometer was used to obtain the infrared spectra of both untreated and plasma treated samples. The attenuated total multiple reflection technique (ATR) was used to analyze the surface chemical modifications produced to about 5–10 μm depth of the pieces. A diamond prism was used and the incident angle of the IR radiation was 45°. Thirty two scans with a resolution of 4 cm^{-1} were obtained and averaged. Spectra were recorded from 600 to 4000 cm^{-1} .

2.5. X ray photoelectron spectroscopy (XPS) chemical composition analysis

Chemical modifications on the outermost surface layer (about 5 nm) on the APPT treated samples were analyzed with a VG Scientific Microtech Multilab (VG Scientia, Hastings, United Kingdom) spectrometer using a Mg K_{α} X ray source (1253.6 eV) operating at 15 keV and 300 W. The take off angle was 45°. The analysis was performed on 1 \times 1 cm^2 surfaces at a residual pressure below 5×10^{-8} Torr. A survey scan encompassing the 0–1200 eV region was obtained for each sample. High resolution spectra were obtained in a 20 eV range. All binding energies were referred to the C 1s core level spectrum position for C C and C H (hydrocarbons) species at 285.0 eV. Atomic concentrations were calculated using a VGX900 W system.

2.6. Morphology study

The topography of the atmospheric plasma treated surfaces was analyzed using a Philips XL 30 FEI EUROPE SEM microscope (Eindhoven, Holland). The samples were prepared using gold coating

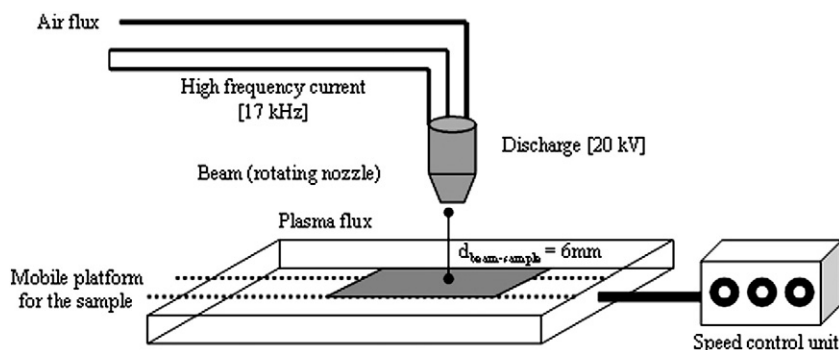


Fig. 1. Scheme of the APPT setup.

Table 1

Surface tension (dispersive, polar and total components) of the test liquids obtained by the pendant drop method both in air and immersed in n-hexane.

Liquid	σ_T (mN/m)	σ_D (mN/m)	σ_P (mN/m)
Water	66.6 ± 0.3	31.5 ± 0.7	35.1 ± 0.7
Glycerol	61.6 ± 0.2	37.8 ± 0.3	23.9 ± 0.4
Diiodomethane	47.5 ± 0.2	42.2 ± 0.6	5.24 ± 0.6
1,5-pentandiol	42.4 ± 0.1	38.6 ± 0.4	3.8 ± 0.4
Nitromethane	35.3 ± 0.4	31.4 ± 0.6	3.9 ± 0.7

in a Polaron high resolution sputter coater in order to obtain a conductor media for electrons and enough contrast in the SEM micrographs. The energy of the electron beam was 20 kV.

3. Results and discussion

An evaluation of the γ_s of the pristine polyolefins was conducted both on the pretreated and plasma affected polymeric surfaces. None of the test liquids exhibited low contact angles on the original surfaces. These high contact angle results are indicative of the non polar character of the surfaces, which is the main cause of the poor wettability and adhesion difficulties associated to this type of materials.

The values of energy obtained (Table 2) were in agreement with the results previously reported for other polyolefins [35,36], that is to say, low total fractions and an almost purely dispersive behaviour with polar contributions of 3, 0.8 and 2% for HDPE, PP and LDPE respectively.

The surface degradation and durability of the APPT effects in terms of γ_s were evaluated considering the pristine materials, for aging times of 3 min and 1, 8, 21, 31 and 270 days after subjecting the specimens to plasma (Fig. 2).

At the very start of the APPT application a dramatic rise of the polar and total energy fractions for all the polymers was observed, reaching values close to 45 and 65 mN/m, respectively, which involves a significant improvement of hydrophilicity. Similar behaviour has been observed with the application of other plasma [35] or corona [37] techniques applied on polymers, nevertheless, in all previous cases, the recovery of the non wettable nature of all the materials took place in just a few weeks [38] following diverse mechanisms. O'Connell et al. [39] defined a two phased recovery for different biopolymers under UV light, with an initial rapid rate over the first 24 h followed by a slower recovery up to 28 days. Truica Marasescu et al. [28] found out a stable enhancement of γ_s for several months after a decrease in the first week for vacuum ultraviolet/ NH_3 treated LDPE and biaxially oriented polypropylene, and a two phase recovery when the samples were treated by nitrogen atmospheric pressure glow discharge.

Hydrophobic recovery was attributed by Liston et al. [40] to thermodynamic processes including the reorientation of the hydrophilic groups formed by plasma (carbonyl, hydroxyl, carboxyl, etc.), diffusion of substances such as additives from bulk to surface and reaction with free radicals. Considering these precedents, we were surprised to find that both HDPE and PP maintained the improvement in hydrophilicity approximately constant throughout 9 months of aging, exhibiting total γ_s components located around the value of 50 mN/m. It has to be highlighted that, even though the total energy

Table 2

Initial components of the γ_s of the polymers.

Polymer	γ_T untreated (mN m ⁻¹)	γ_P untreated (mN m ⁻¹)	γ_D untreated (mN m ⁻¹)
LDPE	22.68 ± 4.12	0.44 ± 0.08	22.23 ± 4.05
HDPE	26.88 ± 1.22	0.74 ± 0.08	26.81 ± 1.22
PP	23.01 ± 5.35	0.19 ± 0.06	22.82 ± 5.31

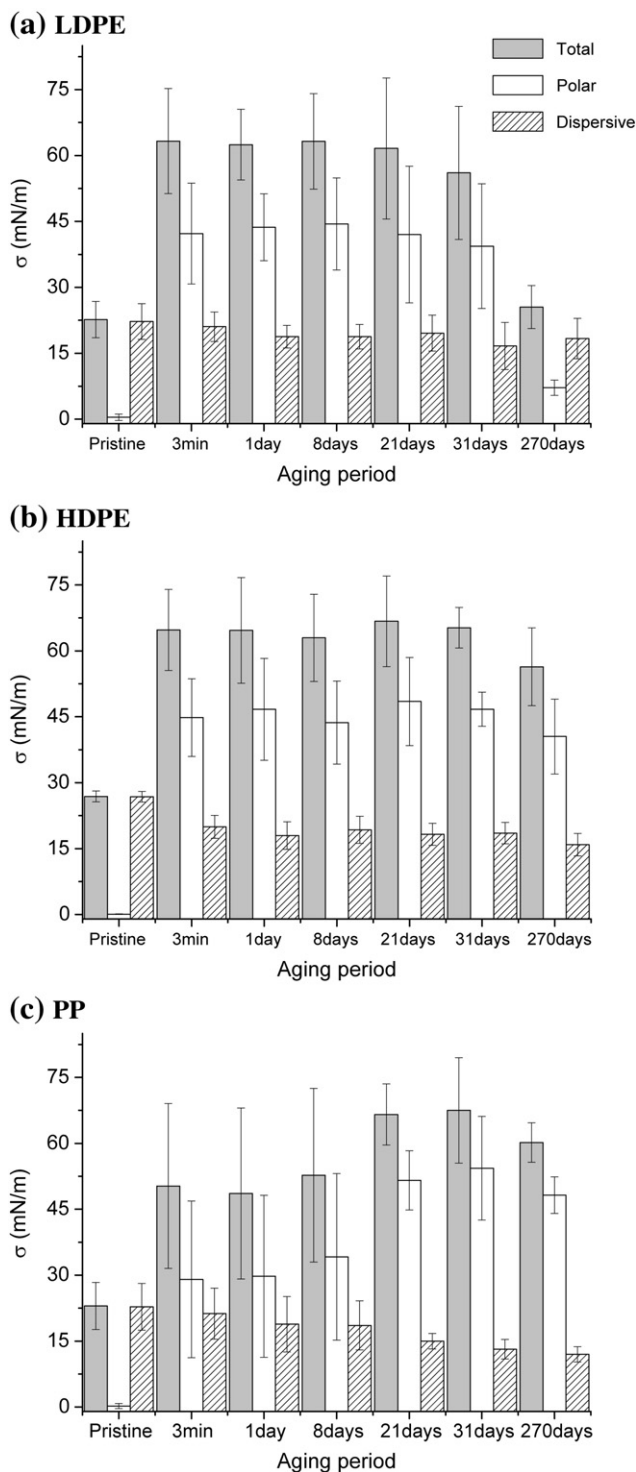


Fig. 2. Evolution of the dispersive, polar and total fractions of the surface energy throughout 270 days of study for (a) LDPE, (b) HDPE and (c) PP.

for the LDPE sample reversed to its initial value of approximately 23 mN/m, the polar fraction was still 91% higher than the one obtained for the untreated surface.

Fig. 3. presents a brief scheme of the reactions taking place in the outermost layer of the polyolefinic surfaces when subjected to APPT and aged: firstly, a rapid γ_s enhancement just after treatment took place, due to immediate reactions with plasma species, which imply σ bonds (C C, C H) rupture and creation of oxygen and nitrogen containing moieties. Further reactions of the formed radicals with

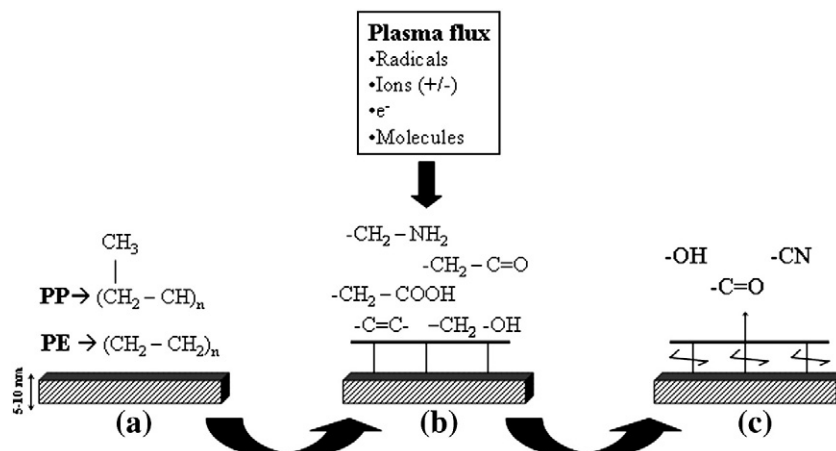


Fig. 3. Reaction scheme of the outermost layer of the polyolefins (about 5 nm): (a) pristine PE and PP composition, (b) possible polar functionalities introduced in the surface by reactions with plasma species (ions, neutral, molecules, and radicals) and (c) loss or reorientation of hydrophilic groups with aging.

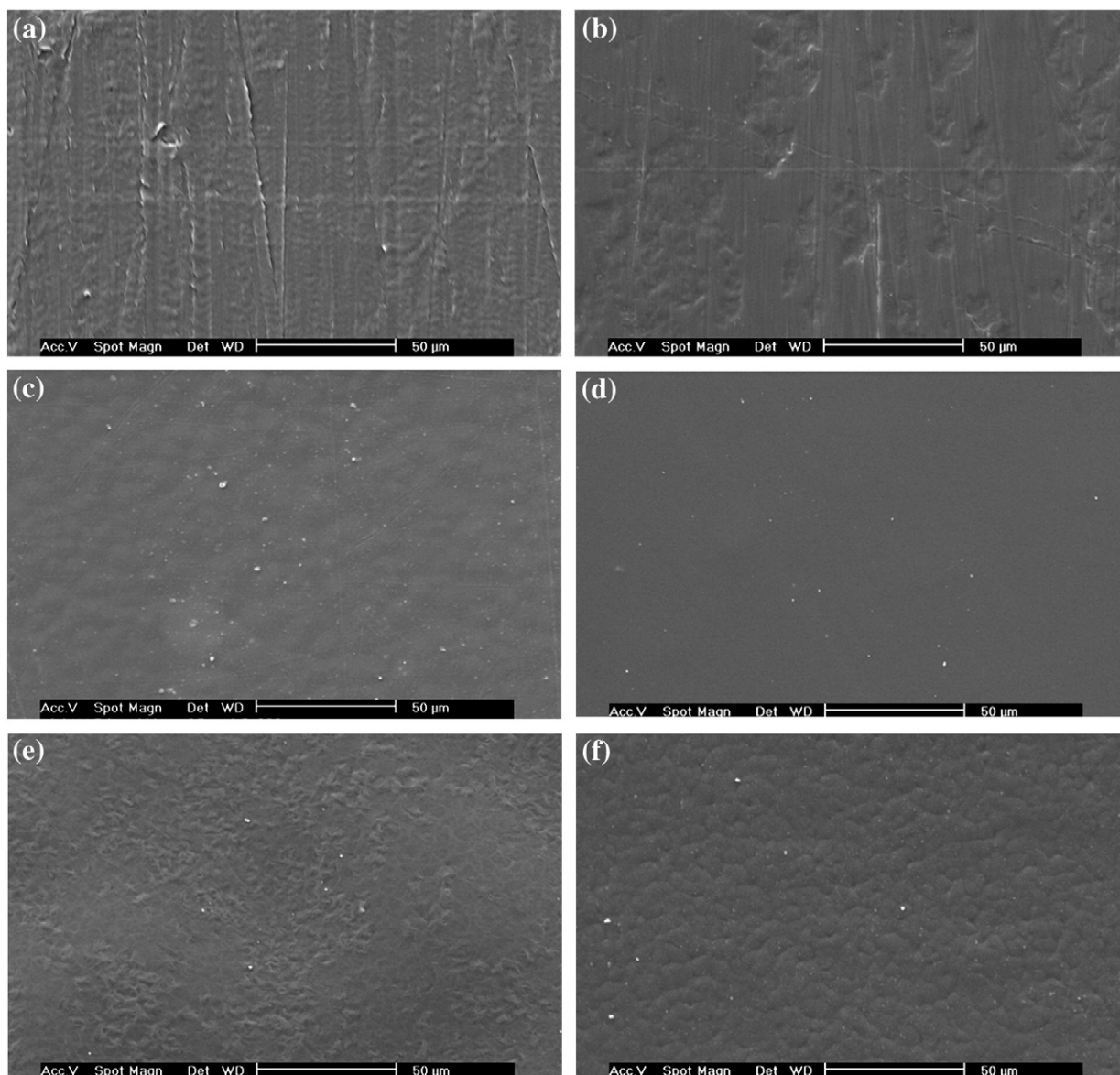


Fig. 4. SEM micrographs of the pristine (a) LDPE, (b) HDPE and (c) PP; immediately after APPT treatment (d) LDPE, (e) HDPE and (f) PP; after 31 days of aging (g) LDPE, (h) HDPE and (i) PP.

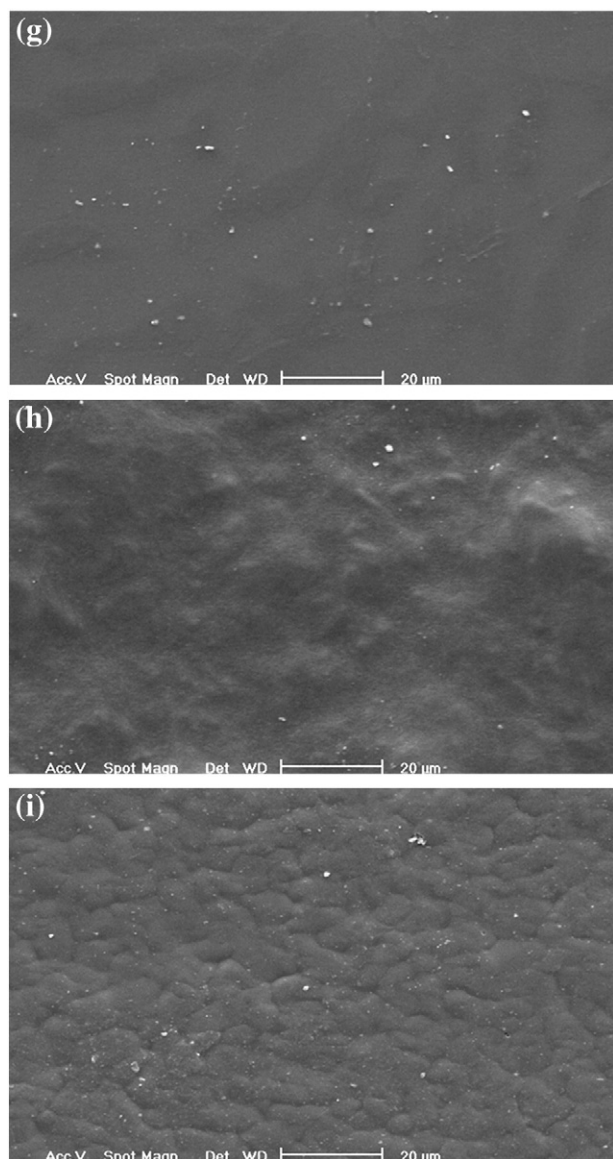


Fig. 4 (continued).

atmospheric elements during storage led to a second slight increase of the γ_s and polarity after 21 days for HDPE and PP. Finally, a total (LDPE) or partial (HDPE, PP) recovery of energy was observed after 270 days, being due to possible recombination of reactive functional groups with environmental species, re arrangement of oxygen and nitrogen containing moieties or reorientation of polar groups from surface to bulk, which led to a diminished hydrophilicity [21].

Besides the change in chemical composition of the surfaces, APPT is also known to promote etching as a consequence of the plasma flux impact onto the surfaces, creating roughness which contributes to the increase in polar properties and their durability. It has been reported that the ablation of the surface layer depends on the chemical structure of the polymer chain [41,42]. To get an insight into the morphological changes produced by APPT treatment, we conducted SEM experiments (Fig. 4). The application of plasma on the LDPE surface led to a rather smooth topography where processing lines disappeared (see Fig. 4a, d, g) due to the strong ablation provoked by the plasma. HDPE surface underwent degradation (Fig. 4b, e, h) when exposed to plasma. This etching effect remained constant for long period of aging (Fig. 4h). PP sample showed the creation of a rougher morphology (Fig. 4b, f), with homogeneous micrometric rounded

areas which became longer with time. The appearance of white coloured particles was observed in all the treated polyolefins. Its analysis by the energy dispersive X Ray probe provided in the SEM device confirmed a carbon, oxygen, titanium and a small atomic percentage of magnesium composition. Carbon and oxygen elements were easily attributed to the hydrocarbonated polymeric backbone chains and to the oxidation associated with the APPT treatment. Magnesium and titanium are part of the Ziegler Natta catalysts, which are commonly used in the manufacturing of these polyolefins.

To properly evaluate the effect of plasma on the polymeric surfaces, we have also studied the changes in chemical composition. The calculation of the polar component of the energy through contact angle measurements showed the introduction of new functionalities on the surfaces which positively affected wettability. To confirm these data, we performed ATR FTIR and XPS analyses.

Very similar results were obtained for all three polyolefins, so the LDPE spectrum, performing plasma with 1 m/min speed, (Fig. 5), was selected to illustrate it.

Typical intense bands for polyolefins [43] are found for pristine surface, such as symmetric stretching vibrations of (C H) and (C C) at 2917 and 2845 cm^{-1} . Peaks located in the range of 1470 cm^{-1} corresponded to methylene deformation, and the absorption band at 723 cm^{-1} was due to the (CH₂) rolling vibration mode. The first approach to the confirmation of an oxidised structure through APPT treatment was the existence of a new sharp line in 1715 cm^{-1} , due to carbonyl stretch vibrations [44,45]. The intensity of this peak increased with aging, thanks to the insertion of environmental oxygen on the activated polymeric surfaces. The mechanism of oxidation was supposed to proceed through the heterolytic breaking of (C H) and (C C) linkages of the polymer chains and subsequent reaction of the free radicals with plasma generated oxygen species in the environment [46]. In both surrounding sides of methylene γ peak two bands rose with aging (655 and 864 cm^{-1}), assigned to out of plane (CH) deformation modes.

Finally, two peaks of increasing intensity appeared in the high frequency region (3188 and 3395 cm^{-1}), which were attributed to water absorption onto the active samples after a large period of storage in ambient conditions and 50% relative humidity.

XPS analysis supports the information on the chemical composition of the surfaces obtained from the ATR FTIR results. As shown in Table 3, a small amount of oxygen was already present in the pristine polymers, attributed to a low level oxidation of the as received surfaces. After 1 day of aging the O/C ratio was dramatically increased, indicating the insertion of oxygen containing species, especially hydroxyl and carbonyl groups.

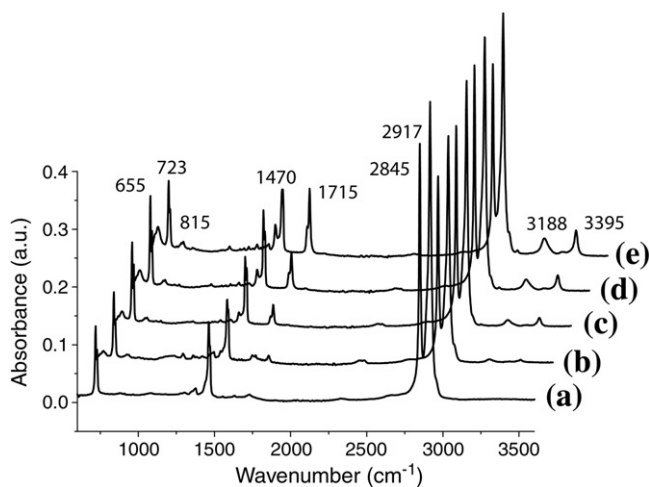


Fig. 5. ATR-FTIR spectra of the LDPE (a) untreated, and aged (b) 1 day, (c) 8 days, (d) 21 days and (e) 31 days after APPT.

Table 3
O/C ratio on the untreated and plasma treated 1 and 21 days aged polymers.

Material	Untreated	1 m/min, 24 h	10 m/min, 24 h	1 m/min, 500 h	10 m/min, 500 h
LDPE	3	7	39	6	29
HDPE	5	67	57	64	43
PP	6	61	56	63	41

Other authors [39] have formulated three possible ways of oxygen insertion: (i) into the polymer chains, (ii) appended to the chain or (iii) appended as hydroxyl group.

The study of the plasma treated specimens is shown in Fig. 6. C 1s core level of the untreated surfaces (Fig. 6c.) consisted of two peaks located around the binding energy values of 284.6 and 285.6 eV [47] due to (C C)/(C H) and (C N)/(C OH) groups [48], respectively (peaks (1) and (2) in Fig. 6.) As we have already commented, the small presence of heteroatoms in the surface of the polymers prior to treatment was attributed to atmospheric partial oxidation of the surface and/or pollutants or additives in their formulation.

The generation of peaks at 287.7 and 288.7 eV (peaks (3), (4) in Fig. 6a and b) corresponding to the oxidised species (CO₂)/(C O) (carbonyl) and (C C(O)OH)/(C C(O)OR) (carboxyl), when applying plasma on the specimens confirmed the oxidation observed in ATR FTIR experiments. The polar nature of these groups should induce an increase in both the polar and total fractions of the surface energy of the polymers. These bands appeared in the C1s core level spectra of the three polymers at similar binding energies.

As expected, the area underneath the peak at 284.6 eV corresponding to (C C) linkages (peak (1) in Fig. 7.) decreased in the initial moments after the application of plasma in the three polyolefins, but began to recover slightly after 21 days.

Obviously, the behaviour of peaks located at 285.6, 287.7 and 288.7 eV (peaks (2), (3), (4) in Fig. 7.) attributed to the new moieties [(C N)]/[(C OH)], [(C O)] and [(C C(O) OR)], respectively, followed the opposite trend, due to the plasma reactions which led to the introduction of oxygen on the surface.

We were surprised to observe that, after the first 1 day, the composition of the polymer surfaces remained more or less constant, conserving their degree of oxidation up to 21 days. This is in contrast with previous findings which indicate that the effect of plasma treatment is much more short lived [27,31].

From the results obtained by ATR FTIR and XPS it was possible to come to the conclusion that, due to the quantity of new functionalities of polar nature introduced in the polymeric surfaces by APPT, not only

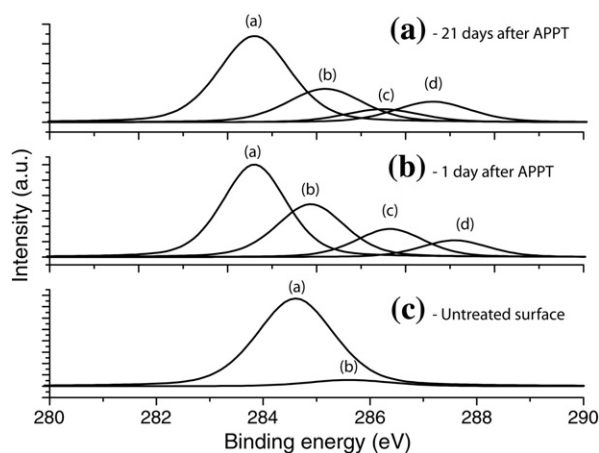


Fig. 6. C1s XPS spectra of the plasma treated specimens at different conditions: (a) after 21 days of aging, (b) after 1 day and (c) untreated polymeric surfaces.

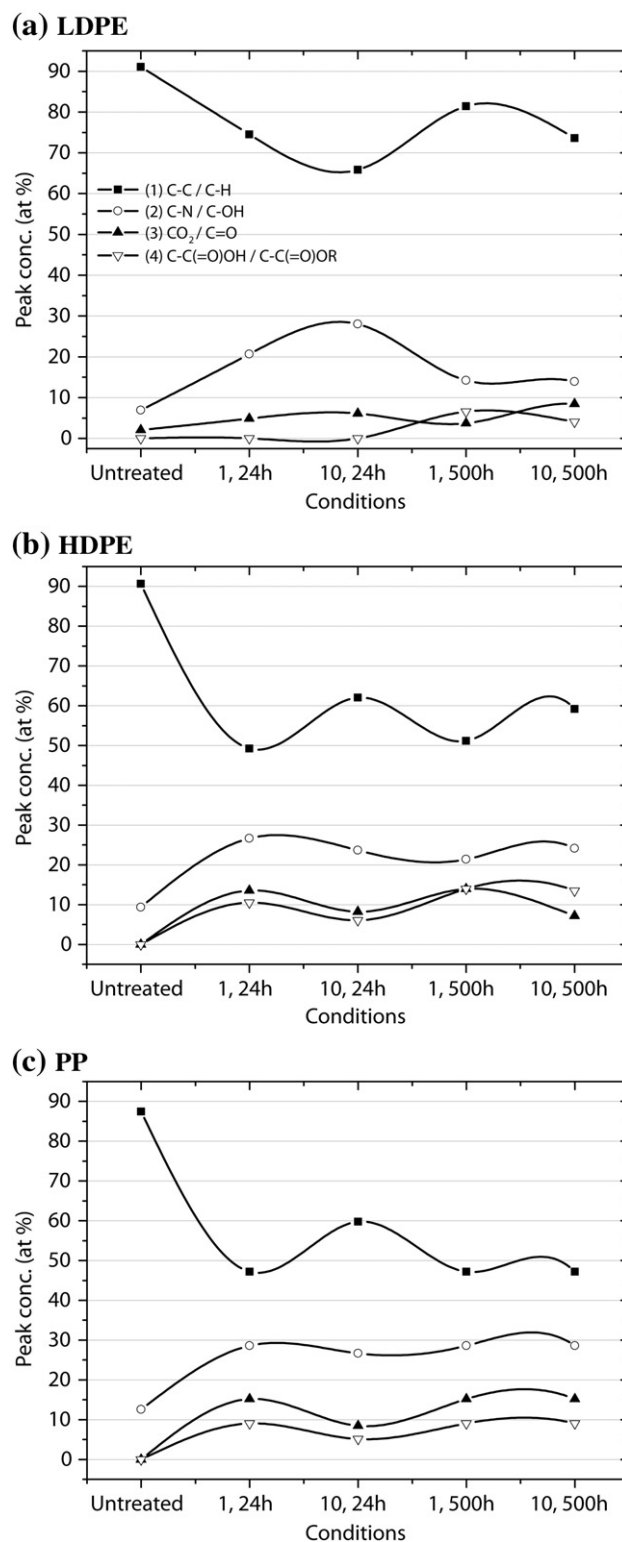


Fig. 7. Variation of the C1s core level XPS peaks concentration for: (a) LDPE, (b) HDPE and (c) PP.

the total component of the γ_s but also the polar fraction should be enhanced, resulting in an improvement of the wettability properties.

4. Conclusions

We have confirmed that APPT treatment considerably activates the surface of the polyolefins HDPE, LDPE and PP by means of γ_s and wettability enhancement. This fact can be attributed to both the

insertion of chemical moieties of polar nature (carboxyl, carbonyl, hydroxyl, amide, etc.) and etching due to the plasma flux impact. The polar component of the γ_s was increased to a great extent up to approximately 96% in all the cases after 31 days of aging due to the creation of these hydrophilic groups, which was demonstrated by ATR FTIR and XPS studies, and subsequently confirmed by γ_s evaluation through contact angle measurements.

The etching effect caused by the impact of the air flux onto the polymeric surfaces was analyzed by SEM, revealing the creation of a visible morphology. A rather smooth surface due to strong ablation was achieved for the LDPE, while HDPE and PP showed a plasma etching effect. In the first case a lamellar structure was created. PP presented homogeneous distribution of rounded areas. In both cases the created morphologies remained constant up to months of aging.

Remarkably, we have observed an unprecedented stability of the effect of plasma treatment, even after long periods of storage under atmospheric conditions. In contrast with previous investigations, the effects achieved by plasma remained almost constant after 9 months of aging. Our results suggest that APPT treatment could be applied to improve the adhesion properties of commercially available polyolefins, enabling to transport materials and postpone the joint process.

Acknowledgements

Financial support from the Fundación Universidad Carlos III de Madrid e Instituto Tecnológico de Química y Materiales “Álvaro Alonso Barba” is acknowledged. Authors also acknowledge MCI for the financial support to the project MAT2006 11614 C03 02.

References

- [1] M. Friedman, G. Walsh, *Polym. Eng. Sci.* 42 (8) (2002) 1756.
- [2] M.D. Wiles, G. Scott, *Polym. Degrad. Stab.* 91 (2006) 1581.
- [3] D.S. Achilias, C. Roupakias, P. Megalokonomos, A.A. Lappas, E.V. Antonakou, *J. Hazard. Mat.* 149 (2007) 536.
- [4] F.R. Teles, L.P. Fonseca, *Mat. Sci. Eng.* 28 (8) (2008) 1530.
- [5] M.D. Green, F.J. Guild, R.D. Adams, *Int. J. Adhes. Adhes.* 22 (2002) 81.
- [6] R. Oosterom, T.J. Ahmed, J.A. Poulis, H.E.N. Bersee, *Med. Eng. Phys.* 28 (2006) 323.
- [7] M. Strobel, V. Jones, C.S. Lyons, M. Ulsh, M.J. Kushner, R. Dorai, *Plasmas Polym.* 8 (1) (2003) 61.
- [8] S. Bhowmik, T.K. Chaki, S. Ray, F. Hoffman, L. Dorn, *Int. J. Adhes. Adhes.* 24 (2004) 461.
- [9] M. Noeske, J. Degenhardt, S. Strudthoff, U. Lommatzsch, *Int. J. Adhes. Adhes.* 24 (2004) 171.
- [10] D. Hegemann, H. Brunner, C. Oehr, *Nucl. Instrum. Meth. Phys. Res. Sect B-Beam Interact. Mater. Atoms* 208 (2003) 281.
- [11] H.S. Chen, *Metals Handbook* 10th ed., 1996, p. 89, 18.
- [12] S. Debnath, R. Ranade, S.L. Wunder, G.R. Baran, J.M. Zhang, E.R. Fisher, *J. Appl. Polym. Sci.* 96 (5) (2005) 1564.
- [13] Y.H. Kim, Y.H. Choi, J.H. Kim, J.K. Park, W.T. Ju, K.H. Paek, et al., *Surf. Coat. Technol.* 174–175 (2003) 535.
- [14] H. Conrads, M. Schmidt, *Plasma Sources Sci. Technol.* 9 (2000) 441.
- [15] N.S.J. Braithwaite, *Plasma Sources Sci. Technol.* 9 (2000) 517.
- [16] P. Fauchais, A. Vardelle, B. Dussoubs, *J. Therm. Spray Technol.* 10 (1) (2004) 44.
- [17] C. Tendero, C. Tixier, T. Pascal, J. Desmaison, P. Leprince, *Spect. Acta* 61 (Part B) (2006) 2.
- [18] R.W. Smith, D. Wei, D. Apelian, *Plasma Process. Polym.* 9 (1989) 1355.
- [19] B. Eliasson, U. Kogelschatz, *IEEE Trans. Plasma Sci.* 19 (1991) 1063.
- [20] A. Schütze, J.Y. Jeong, S.E. Babayan, J. Park, G.S. Selwyn, R.F. Hicks, *IEEE Trans. Plasma Sci.* 16 (1998) 1685.
- [21] M.R. Sanchis, V. Blanes, M. Blanes, D. Garcia, R. Balart, *Eur. Polym. J.* 42 (2006) 1558.
- [22] A.N. Bhoj, M.J. Kushner, *IEEE Trans. Plasma Sci.* 33 (2) (2005) 250.
- [23] A.C. Fozza, J.E. Klemberg-Sapieha, M.R. Wertheimer, *Plasmas Polym.* 4 (1999) 183.
- [24] C. Mühlhan, S. Weidner, J. Friedrich, H. Nowack, *Surf. Coat. Technol.* 783 (1999) 116.
- [25] R. Snyders, O. Zabeida, C. Roberges, K.I. Shingel, M.P. Faure, L. Martinu, J.E. Klemberg-Sapieha, *Surf. Sci.* 601 (2007) 112.
- [26] K. Gotoh, Y. Nakata, M. Tagawa, *Colloids Surf. A: Physicochem. Eng. Aspects* 224 (2003) 165.
- [27] S. Guimond, M.R. Wertheimer, *J. Appl. Polym. Sci.* 94 (2004) 1291.
- [28] F. Truica-Marasescu, S. Guimond, P. Jedrzejewski, M.R. Wertheimer, *Nucl. Instr. Meth. Phys. Res. B.* 236 (2005) 117.
- [29] S. Yang, M.C. Gupta, *Surf. Coat. Tech.* 184 (2004) 172.
- [30] J. Abenojar, R. Torregrosa-Coque, M.A. Martínez, J.M. Martín-Martínez, *Surf. Coat. Tech.* 203 (2009) 2173.
- [31] T. Murakami, S. Kuroda, Z. Osawa, *J. Colloid. Interf. Sci.* 202 (1999) 3744.
- [32] D.K. Owens, R.C. Wendt, *J. Appl. Polym. Sci.* 13 (1969) 1741.
- [33] S. Guimond, I. Radu, G. Czeremuszkín, D.J. Carlsson, M.R. Wertheimer, *Plasmas Polym.* 7 (2002) 71.
- [34] F.W. Fowkes, *J. Phys. Chem.* 67 (1963) 2583.
- [35] A. Kaminska, H. Kaczmarek, J. Kowalonek, *Eur. Polym. J.* 38 (9) (2002) 1915.
- [36] D.J. Upadhyay, N.V. Bhat, *Plasmas Polym.* 8 (4) (2003) 237.
- [37] M. Matsunaga, P.J. Whitney, *Polym. Degrad. Stab.* 70 (3) (2000) 325.
- [38] C. Sun, D. Zhang, L.C. Wadsworth, *Adv. Polym. Tech.* 18 (1999) 171.
- [39] C. O'Connell, R. Sherlock, M.D. Ball, B. Aszalús-Kiss, U. Prendergast, T.J. Glynn, *Appl. Surf. Sci.* 255 (2009) 4405.
- [40] E. Liston, L.M. Martinu, M.R. Wertheimer, *J. Adhes. Sci. Technol.* 7 (1993) 1091.
- [41] P.K. Chu, J.Y. Chen, L.P. Wang, N. Huang, *Mater. Sci. Eng. R.* 36 (2002) 143.
- [42] V. Svorčík, K. Kolářová, P. Slepická, A. Machová, M. Novotná, V. Hnatowicz, *Polym. Degrad. Stab.* 91 (2006) 1219.
- [43] D.O. Hummel, *Polymer Spectroscopy*, Verlag Chemie, 1974, p. 83.
- [44] H. Drnovska, L. Lapcik, V. Bursikova, J. Zemeck, A.M. Barros-Timmons, *Colloid Polym. Sci.* 281 (11) (2003) 1025.
- [45] R. Mishra, S.P. Tripathy, K.K. Dwivedi, D.T. Khathing, S. Gosh, M. Müller, D. Fink, *Rad. Meas.* 33 (2001) 845.
- [46] J. Yip, K. Chan, M. Kwan, S.L. Kai, *Appl. Surf. Sci.* 205 (2003) 151.
- [47] Y. Kusano, H. Mortensen, B. Stenun, S. Goutianos, S. Mitra, A. Ghanbari-Siahkhalil, P. Kingshott, B.F. Sorensen, H. Bindsle, *Int. J. Adhes.* 27 (2007) 402.
- [48] L. Mathieson, R.H. Bradley, *Int. J. Adhes. Adhes.* 16 (1996) 29.