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Study of the aging process of corona discharge plasma effects on low density polyethylene film surface

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Abstract A study of the durability of corona discharge plasma effects on a polymer surface was investigated in this work. We used the corona discharge plasma technique to modify the wettability properties of low density polyethylene (LDPE) film and evaluated the influence of relative humidity and temperature on the aging process with three different storage conditions. The effects of the aging process on the plasma-treated surface of LDPE film were quantified by contact angle measurements, Fourier-transformed infrared spectroscopy, and X-ray photoelectron spectroscopy. The results obtained with these techniques have allowed us to determine how the aging process promotes changes in the plasma-treated surface by decreasing its wettability and taking place a remarkable hydrophobic recovery process.

Introduction

The use of composite structures based on a film–film or film–foam has grown in a remarkable way in the last decades and involves high demands in technological sectors like automotive, electrics and electronics, aerospace, medicine, etc. Among the wide variety of films, the use of low density polyethylene (LDPE) is widely extensive as a consequence of good balanced properties (mechanical, thermal, chemical, cost, etc.). We have to take into account that this polymer film is characterized by very low surface energy values (lower than 30 mJ m^{-2}) and this represents an important problem during laminates processing.

One of the most interesting industrial treatments, which permits increasing adhesive properties on the polymeric film by improving its surface energy, is corona discharge plasma treatment [1, 2]. The polymeric films treated with corona discharge plasma show a remarkable increase in wettability properties as a consequence of the surface activation, thus increasing surface energy values (γ_s) and promoting a hydrophilic character [3–8]. However, the overall effects induced by the corona discharge plasma treatment are not permanent and this promotes a noticeable loss in hydrophilic character on treated surfaces. This phenomenon is known as hydrophobic recovery or "aging" and it is difficult to avoid since it is related to the unstability of the species formed during and after the plasma treatment [9–13]. The aging process is responsible for decreasing the polarity of plasma-treated LDPE surface and subsequent decrease in free surface energy (γ_s) [11, 13].

It is necessary to take into account that the hydrophobic recovery process is closely related to polymer chains and polar groups (formed during and after the corona discharge plasma treatment) re-arrangement [14–17]. There is a driving thermodynamic force on the treated LDPE surface to tend to decrease the high surface energy reached after the treatment [9, 18, 19]. The aging phenomenon is interpretated for various authors by the combination of four principal mechanisms that occur simultaneously. These mechanisms are the following.

(1) Chemical groups inter-reactions on the LDPE plasma-treated surface; many functionalities achieved during

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and after the plasma treatment have a tendency to react, thus they can promote some specific interactions.

(2) New oxidation and degradation reactions as a consequence of air exposure of plasma-treated surfaces; these surfaces are characterized by the presence of unstable groups such as hydroperoxides and peroxides which tend to react to form the more stable oxidized species such as ketonic and aldehydic groups [20, 21].

(3) Diffusion of low molecular weight oxidized material (LMWOM) from the topmost layers into the bulk film by reaching a more stable thermodynamic state with lower surface free energy (γ_s) values.

(4) Low molecular weight compounds, such as some additives in LDPE, tend to exude from the bulk material to the surface, thus promoting some additional hydrophobic recovery as a consequence of their incompatibility with the polymer and this induces the creation of a low molecular weight layer with lower free surface energy values (γ_s). The non-polar fragments of the processing additives, produced by the corona discharge plasma treatment, remain on the polymer topmost layers and their concentration increases during the aging process.

In this work, due to the relevance of the hydrophobic recovery for industrial purposes (mainly related to durability of adhesion properties), we have analyzed the wettability changes of the polymeric film surface in terms of the aging time for three different storage conditions: aging process in air at room temperature, aging process in a climate chamber at 23 °C and 50% relative humidity (RH), and aging process in a climate chamber at 50 °C and 40% RH, always during 3 weeks of exposure time. These particular conditions have been selected because of their interest in aging tests. Aging in air at room temperature is very close to aging conditions at industrial level without any additional controlled factor such as temperature or RH; aging in a climate chamber at 23 °C and 50% RH is similar to aging in air at room temperature but both temperature and RH are well controlled. The aging in an aging chamber at 50 °C and 40% RH has been selected since these conditions are widely used to characterize aging processes for automotive materials.

Experimental

Materials

The film used in this study is a LDPE for automotive applications supplied by Logoplast (Logoplast S.L., Alicante, Spain), with 50 μm thickness and a density of 0.92 g cm^{-3}. The test liquids used for contact angle measurements were selected to include a range of liquids with different polar and dispersive constants and correctly measure changes in surface free energy values. The selected liquids were water, glycerol, diiodomethane, and formamide.

Corona treatment

LDPE films were exposed to a continuous corona discharge plasma treatment with a constant film flow of 15 m min^{-1}. The corona plasma equipment was supplied by FABRILEC S.L., mod. GF-100-BADIA (Fabrilec, S.L., Valencia, Spain). This corona discharge generator operates at 50 Hz with a maximum power of 1 kW. The distance between electrodes was fixed at 1.5 mm. The plasma treatment was carried out at a power of 600 W.

Contact angle measurements and surface energy calculation

To evaluate wettability changes, a KSV CAM 200 goniometer was employed to measure contact angles (KSV Instruments, Helsinki, Finland). The initial contact angle measurements were carried out 5 min after the plasma treatment to obtain comparative results. The maximum error in the contact angle measurement did not exceed ±3%.

The Owens-Wendt method was chosen to calculate surface free energies due to its simplicity and also because it takes dispersive and polar components into account [22–24]. The general expression of the Owens-Wend method is as follows:

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

In this equation, θ is the contact angle, γ_l is the surface tension of the liquid, and γ_s is the surface tension of the solid or surface free energy. The terms with the subscripts d and p refer to the dispersive and polar component, respectively. This expression can be written in terms of a linear equation ($y = ax + b$); so if we represent $(\gamma_l^p)^{1/2}/(\gamma_l^d)^{1/2}$ versus $\gamma_l(1+\cos\theta)/2(\gamma_l^d)^{1/2}$ we obtain a linear representation. The slope of the line is $(\gamma_s^p)^{1/2}$ while $(\gamma_s^d)^{1/2}$ represents the intercept of this line on the y axis. Once the polar γ_s^p and dispersive γ_s^d contributions are calculated, the total surface free energy is the sum of these two components ($\gamma_s = \gamma_s^p + \gamma_s^d$).

Spectroscopic characterization

The Fourier transform infrared spectroscopic technique used to evaluate chemical changes induced by plasma

treatment on LDPE film polymers was carried out using a Perkin Elmer BX spectrometer (Perkin Elmer España S.L., Madrid, Spain) equipped with attenuated total reflection (ATR) accessory. For each sample, 150 scans with a resolution of 4 cm^{-1} were performed.

Analysis by X-ray photoelectron spectroscopy of various LDPE film samples treated with corona discharge plasma were carried out with a VG-Microtech Multilab electron spectrometer (VG Microtech Ltd., Uckfield, UK) using the Mg Kα radiation (1253.6 eV) from a twin anode working in constant energy mode at a pass energy of 50 eV. The pressure of the measuring chamber was maintained at 5×10^{-10} mbar. The regulation of the scale of binding energies (BE) was performed according to the C (1s) transition at 284.6 eV. The accuracy of BE values was ±0.2 eV. Binding energy values were obtained using the Peak-fit program installed in the XPS spectrometer control software.

Aging equipment

LDPE films treated with corona discharge plasma were exposed to different aging conditions. One of the aging processes was carried out in air at room temperature and two additional well-controlled aging conditions were performed with a climate chamber at different temperature and RH conditions. The climate test chamber allows controlling temperature in the 10–95 °C range with a fluctuation of ±0.1/0.3 °C temporally, and RH in the 10–98% range with a fluctuation of ±0.5/1.5% RH temporally. This equipment was supplied by CTS GmbH, mod. C-70/1500 (CTS GmbH, Hechingen, Germany). The experimental aging conditions in the climate chamber were the following: aging temperature of 23 °C and 50% RH and aging temperature of 50 °C and 40% RH. For all aging tests, the test time was 21 days.

Results and discussion

Aging in air at room temperature

Figure 1 shows the variation of contact angles in terms of the aging time in air at room temperature. The aging process produces a remarkable wettability loss on the LDPE plasma-treated surface. This effect is quantified with the increase of contact angle values as the aging (or storage) time increases; we can clearly observe the plot evolution for the four test liquids (with different polar and dispersive components) in terms of the aging time in air at room temperature.

Using water as a test liquid, the initial contact angle for the untreated film (close to 93.5°) is reduced to a minimum

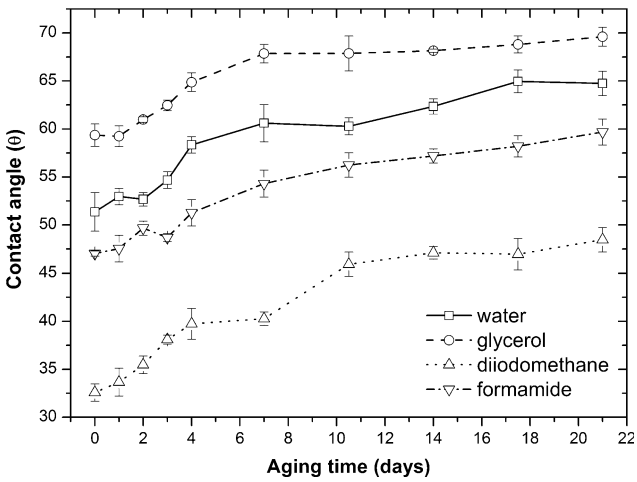

Fig. 1 Variation of the contact angle on LDPE surface for different test liquids on corona discharge plasma-treated samples ($P = 600$ W) aged in air at room temperature in terms of the aging time

initial value of 51.4° for the plasma-treated film (600 W). The aging process promotes a remarkable decrease in surface wettability, thus promoting a partial hydrophobic recovery, so the aged sample (21 days) shows a contact angle of 64.8°, which represents an increase of about 26%. Similar tendency can be observed using glycerol as a test liquid; the contact angle value changes from 59.4° for the plasma-treated material up to 69.6° for the aged sample (21 days) and this represents and increase of 17%. It is important to remark that the film surface does not lose all wetting properties achieved by the plasma treatment since the contact angle for the aged sample with glycerol is still lower than the untreated film with contact angle values close to 79.9°. For diiodomethane, this change varies from 32.6° up to 48.5° for the aged sample, increasing around 49%, but this value is still lower than that of the untreated material with the same test liquid (65.4°). Finally, when using formamide as test liquid, the percentage increase is close to 27%, after 21 days of aging time. So the plot evolution of contact angles in terms of the aging time for different test liquids clearly shows a partial hydrophobic recovery. As we can observe in Fig. 1, this process occurs very quickly at the first stages (aging time lower than 1 week) and seems to reach an asymptotic tendency as the aging time increases.

Graphically, we can observe a quick increase in contact angle values for short aging times (less than 1 week and especially during the 4 days after the plasma treatment for all test liquids). For longer times, the tendency is also increasing but more slowly. The aging effect on the treated surface is promoted by the re-arrange of unstable polar species formed during and immediately after the plasma treatment and subsequent air exposure; these polar groups re-arrange toward the bulk material to a more stable

Table 1 Surface energy (γ_s) and its polar (γ_s^p) and dispersive contributions (γ_s^d) of the LDPE surface treated with corona discharge plasma ($P = 600$ W) in terms of the storage time aged in air at room temperature

Aging time (days)	γ_s (mJ m^{-2})	(γ_s^p) (mJ m^{-2})	(γ_s^d) (mJ m^{-2})
0	45.5	19.1	26.4
1	45.0	18.3	26.7
2	44.1	18.8	25.3
3	43.2	18.1	25.1
4	41.2	15.9	25.3
7	39.5	14.4	25.1
10.5	38.5	16.2	22.3
14	37.6	15.1	22.5
17.5	36.8	13.3	23.5
21	36.2	13.8	22.4

position and this reduces the surface polarity [9, 18]. As a consequence, surface wettability decreases as the aging process takes place.

The contact angle values for different test liquids allow calculating surface free energies (γ_s) on the aged samples. We can quantify polar (γ_s^p) and dispersive (γ_s^d) contributions in terms of the aging (storage) time; as we have observed previously, the contact angle values decrease as the aging process occurs and this promotes a decrease in the surface free energy values for samples aged in air at room temperature (Table 1).

The analysis of surface free energies in Table 1 corroborates the wettability loss as a consequence of the partial hydrophobic recovery related to the aging process. So the initial surface energy, close to 45.5 mJ m^{-2}, is reduced after the aging process (21 days in air at room temperature) up to values close to 36.2 mJ m^{-2}, which represents a decrease of about 20% in wetting properties. The polar component of the surface energy varies from 19.1 mJ m^{-2} up to 13.8 mJ m^{-2} for aged samples (21 days in air at room temperature), which represents a percentage decrease of about 28%. On the other hand, the dispersive component changes from 26.4 mJ m^{-2} for plasma-treated and non-aged samples up to 22.4 mJ m^{-2} for aged samples at the end of the aging cycle, and this represents a percentage decrease around 15%. This decrease in surface energy values with the exposure time is promoted by a surface functionalization loss as a consequence of the polar groups re-arrangement toward the bulk to find a more stable position. This process promotes a decrease of the neat functionalization (with oxygen-based species) of the topmost surface layers on the film.

Figure 2 shows the FTIR-ATR spectra of LDPE film untreated and treated with corona discharge plasma together with corona-treated film aged in air at room temperature for 21 days. The main polar groups attributable to plasma

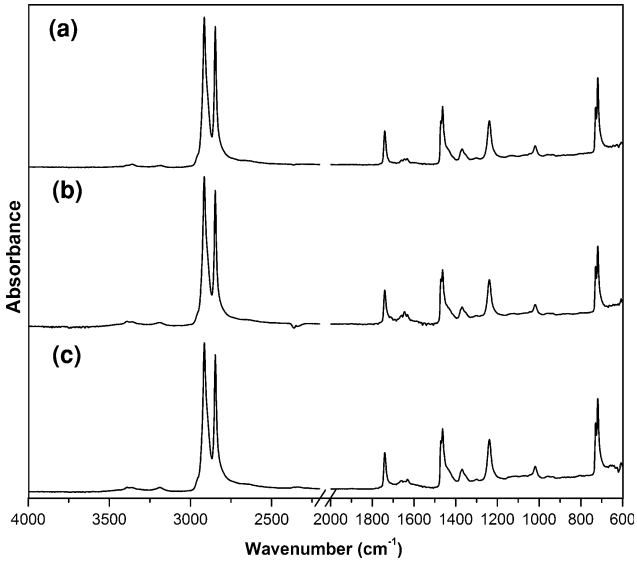

Fig. 2 FTIR-ATR spectra of (**a**) untreated LDPE film, (**b**) corona discharge plasma-treated LDPE film, and non-aged (**c**) corona discharge plasma-treated LDPE film and aged in air at room temperature for 21 days

treatment are hydroxyl [O–H] at 3200 cm^{-1}, carbonyl [C=O] at 1647 cm^{-1}, and ester [O=C–O–C] at 1166 cm^{-1}. The decrease in the neat intensity of these peaks indicates the decrease of oxygen-containing functional groups corresponding to the action of the different aging mechanisms.

These results can be better studied using XPS analysis since the deep of the XPS analysis is similar to the film zone in which the aging mechanism acts. The XPS allows quantifying the surface changes in terms of the surface composition and oxidation ratio. As we have described previously, the different aging mechanisms act as a consequence of the natural tendency of different polar groups (oxygen-based groups which are interlocked during and immediately after the plasma treatment with subsequent air exposure) to re-arrange in order to reach a more thermodynamically stable state. Together with the previous aging mechanism, chain scission occurs during plasma treatment and this promotes the formation of LMWOM that slowly diffuse to the bulk material, thus contributing to decrease the amount of oxygen on the topmost layers of the surface film [25, 26]. At the end of the aging cycle in air at room temperature, the XPS analysis shows a good balance of oxygen-based polar groups on the polymer surface, around 8.5%, and the real oxidation level (expressed as the O/C % atomic ratio) decreases from 0.12 for the non-aged film up to values around 0.10 for the aged sample (Table 2). On the other hand, the N/C atomic ratio during the aging process is very low, close to 0.03, and remains almost constant with the aging time, thus indicating that nitrogen does not take place directly during the aging process or hydrophobic recovery.

Table 2 Surface composition of LDPE film surface treated with corona discharge plasma ($P = 600$ W) as determined by XPS analysis at the beginning and end of the aging cycle in air at room temperature

Aging time (days)	% Atomic C	% Atomic O	% Atomic N	O/C ratio	N/C ratio
0	86.7	10.3	2.9	0.12	0.03
21	88.7	8.5	2.8	0.10	0.03

Aging in climate chamber at 23 °C and 50% RH

The same comparative study about hydrophobic recovery has also been carried out in a climate chamber with controlled and invariant conditions at 23 °C and 50% RH during 21 days. In these conditions, the polymer surface is also subjected to an aging process (but in this case with controlled temperature and RH) that decreases the wettability properties achieved during and immediately after the corona discharge plasma treatment.

The plot evolution of the contact angle for the different test liquids follows similar tendency as observed with the aging process in air at room temperature. The contact angle variation in terms of the aging time using water as test liquid changes from a minimum initial value of 51.4° for the non-aged film up to 68.6° for the aged film in these conditions; this contact angle variation represents an increase of about 33.5%. In a similar way, using glycerol as a test liquid, the increase is close to 18%; with diiodomethane this increase is high with values around 68% and using formamide as a test liquid the increase is around 22.6%, always at the end of the aging cycle (21 days) with controlled temperature and RH. Figure 3 shows the contact angle variation in terms of the aging time, for each one of the four test liquids. As observed with the previous aging cycle in air at room temperature, it is important to remark a quick contact angle increase for short aging time (lower than 1 week and mainly in the first four days). For longer aging times, we can observe an asymptotic behavior.

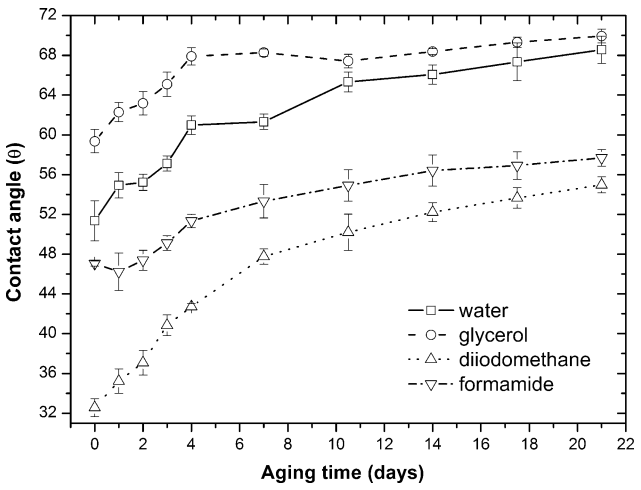

Fig. 3 Variation of the contact angle on LDPE surface for different test liquids on corona discharge plasma-treated samples ($P = 600$ W) aged in a climate chamber at 23 °C and 50% RH in terms of the aging time

The analysis of the information shown in Table 3 allows the observation of surface free energy (γ_s) changes on a plasma-treated LDPE film aged in a climate chamber at 23 °C and 50% RH. The surface free energy changes from 45.5 mJ m^{-2} (non-aged material) up to values around 34.7 mJ m^{-2} at the end of the aging cycle with controlled temperature and RH. This change represents a percentage decrease of about of 23%, thus indicating a partial hydrophobic recovery related to different aging mechanisms. The overall effects of this aging cycle are similar to those obtained with the aging cycle in air at room temperature since temperature and relative fluctuations are very low. The polar component of the surface free energy varies from 19.1 to 13.2 mJ m^{-2} for aged samples at the end of the aging cycle and this represents a percentage decrease of about 30%. On the other hand, the dispersive component changes from 26.4 mJ m^{-2} for non-aged samples up to 21.5 mJ m^{-2} for aged samples at the end of the cycle, which represents a percentage decrease of 18%. This decrease with the exposure time is promoted by a decrease in the overall surface activation as a consequence of the aging mechanisms.

Table 3 Surface energy (γ_s) and its polar (γ_s^p) and dispersive contributions (γ_s^d) of the LDPE surface treated with corona discharge plasma ($P = 600$ W) in terms of the storage time aged in a climate chamber at 23 °C and 50% RH

Aging time (days)	γ_s (mJ m^{-2})	(γ_s^p) (mJ m^{-2})	(γ_s^d) (mJ m^{-2})
0	45.5	19.1	26.4
1	43.9	17.2	26.7
2	43.2	17.4	25.8
3	41.7	17.1	24.6
4	39.6	14.8	24.8
7	38.4	16.0	22.4
10.5	37.1	14.0	23.1
14	36.2	14.1	22.1
17.5	35.4	13.6	21.8
21	34.7	13.2	21.5

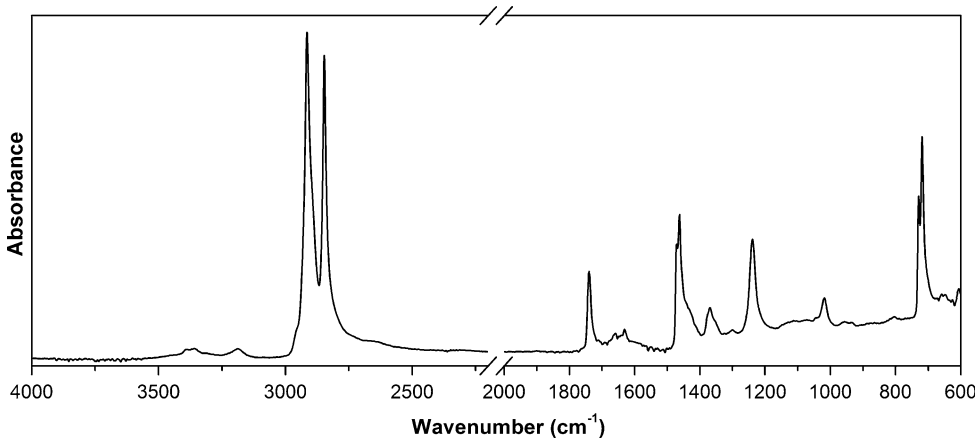

Fig. 4 FTIR-ATR spectrum of LDPE film treated with corona discharge plasma ($P = 600$ W) and aged in a climate chamber at 23 °C and 50% RH for 21 days

Figure 4 shows the FTIR-ATR spectrum of a corona plasma-treated LDPE film aged for 21 days at 23 °C and 50% RH. As described previously, the different species present in the plasma gas promote chain scission and these points act as interlock points for polar species (mainly oxygen-based species). The main polar groups observed in FTIR-ATR spectra are hydroxyl [O–H] at 3200 cm^{-1}, carbonyl [C=O] at 1647 cm^{-1}, and ester [O=C–O–C] at 1166 cm^{-1}. In Fig. 4 we can observe a slight decrease in the peak intensity of some functional groups regarding the plasma-treated and non-aged film.

At the end of the aging cycle with controlled conditions ($T = 23$ °C; RH = 50%), XPS analysis still shows a good balance of oxygen-based polar groups on the topmost surface layers, around 8%. The real oxidation level of LDPE surface, expressed as the O/C atomic ratio, remains with small variations regarding the non-aged material, with values around 0.09 (Table 4), thus indicating that not all the wetting properties achieved by the plasma treatment are lost during aging. On the other hand, the N/C atomic ratio remains at low values close to 0.03; this indicates that nitrogen does not take place directly in the functionalization process achieved by the plasma treatment nor in the aging process.

It is important to remark that the RH used in the climate chamber is quite low and has not a relevant influence on additional functionalization as a consequence of some reactions with water vapor and oxygen. In fact, the post-plasma functionalization process in air exposure is similar to this and it is produced immediately after the plasma treatment; so the overall effects are similar. The action of the plasma gas promotes chain scission and functionalization during plasma discharge but also, after plasma treatment and subsequent air exposure, a post-plasma functionalization process occurs in a very low range time (in a few seconds range); so by FTIR-ATR and XPS we see the overall effects of functionalization on LDPE film, but as we have described there are two overlapped functionalization processes.

Aging in climate chamber at 50 °C and 40% RH

The hydrophobic recovery phenomenon study is completed with the use of more aggressive aging conditions usually employed for automotive testing. In this case, we have defined a thermal aggressive aging process characterized by use of high temperatures (50 °C) and similar RH (40%).

Figure 5 shows the contact angle evolution for each one of the four test liquids, in terms of the aging time. In a similar way to the previous aging cycles, it is important to remark a quick increase in the contact angle values, but in this case the increase is reached by very short aging times (practically 1 day) compared to previous non-aggressive aging cycles. For long aging times, we observe a slow hydrophobic recovery and after 14 days, we see asymptotic behavior. So we can conclude that temperature is one of the main influencing parameters in the aging of plasma-treated surfaces. This could think us that the hydrophobic recovery related to polar groups re-arrangement and LMWOM movement is governed by diffusion laws.

Table 4 Surface composition of LDPE film surface treated with corona discharge plasma ($P = 600$ W) as determined by XPS analysis at the beginning and end of the aging cycle in a climate chamber at 23 °C and 50% RH

Aging time (days)	% Atomic C	% Atomic O	% Atomic N	O/C ratio	N/C ratio
0	86.7	10.3	2.9	0.12	0.03
21	88.9	8.1	3.0	0.09	0.03

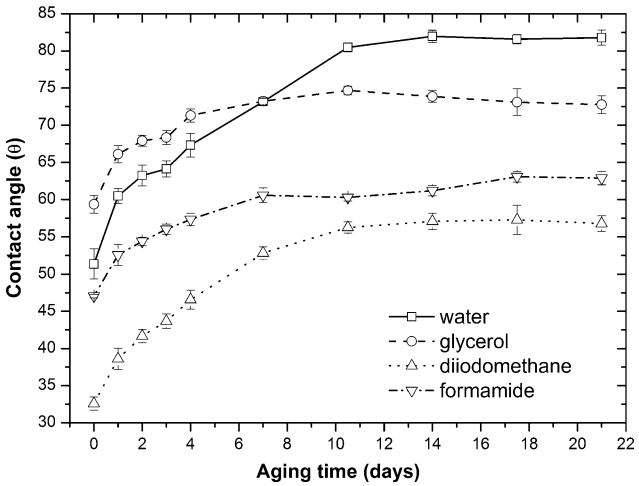

Fig. 5 Variation of the contact angle on LDPE surface for different test liquids on corona discharge plasma-treated samples ($P = 600$ W) aged in a climate chamber at 50 °C and 40% RH in terms of the aging time

Table 5 Surface energy (γ_s) and its polar (γ_s^p) and dispersive contributions (γ_s^d) of the LDPE surface treated with corona discharge plasma ($P = 600$ W) in terms of the storage time aged in a climate chamber at 50 °C and 40% RH

Aging time (days)	γ_s (mJ m^{-2})	(γ_s^p) (mJ m^{-2})	(γ_s^d) (mJ m^{-2})
0	45.5	19.1	26.4
1	40.5	14.2	26.3
2	38.9	13.1	25.8
3	38.0	13.0	25.0
4	36.2	11.6	24.6
7	33.3	9.6	23.7
10.5	32.0	6.3	25.7
14	31.9	5.8	26.1
17.5	31.6	6.1	25.5
21	31.9	5.9	26.0

The change in contact angles in terms of the aging time using water as test liquid varies from a minimum initial value of 51.4° up to 81.8°, which represents a percentage increase of about 59% (much higher than the values obtained for the previous aging cycles). Same tendency can be found when using glycerol as test liquid (with a percentage increase of about 22.5%), diiodomethane (percentage increase of 74%), and formamide (percentage increase of about 33%), always measured at the end of the aging cycle (21 days).

Changes in surface free energy values obtained using the Owens-Wend method with four different test liquids show some differences regarding the previous aging conditions (air at room temperature and $T = 23$ °C; RH = 50%). The initial surface free energy of the non-aged film (45.5 mJ m^{-2}) decreases up to values near 30 mJ m^{-2}, which represents a percentage decrease of about 30% (Table 5). Changes in the polar component of the surface energy are highly relevant and we can observe a change from high values for the non-aged film (19.1 mJ m^{-2}) up to very low values for the aged film with thermal aggressive conditions (5.9 mJ m^{-2}); on the other hand, the dispersive component varies in a very narrow range, so we can ensure that temperature has a negative effect on the wetting properties of plasma-treated surfaces since it accelerates the aging mechanisms (re-arrangement of polar groups and LMWOM diffusion as the main mechanisms).

Figure 6 shows the FTIR-ATR spectrum of a corona plasma-treated LDPE film aged for 21 days in a climate chamber at 50 °C and 40% RH. The decrease in the intensity of the peaks related to oxygen-based species achieved during and immediately after the plasma treatment is indicative of a decrease in the overall amount of oxygen-based species on the topmost polymer layers as a consequence of aging mechanisms. At the end of aging cycle with thermal aggressive conditions ($T = 50$ °C; RH = 40%), XPS analysis still shows a good balance of

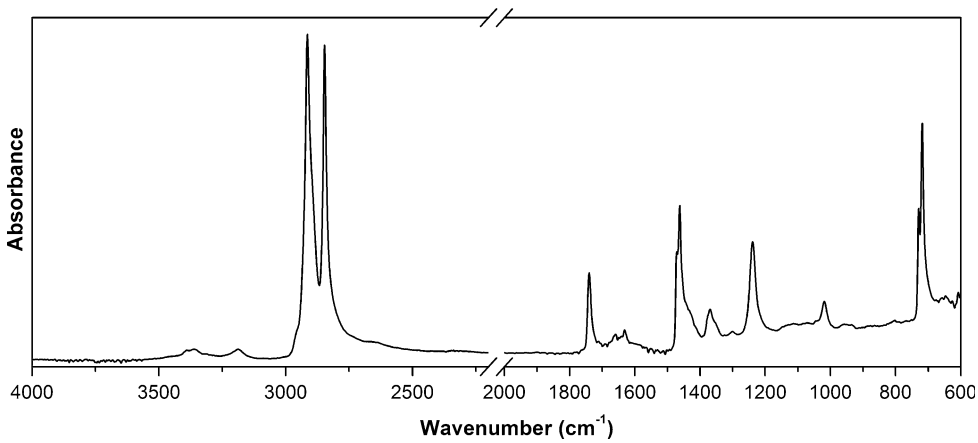

Fig. 6 FTIR-ATR spectrum of LDPE film treated with corona discharge plasma ($P = 600$ W) and aged in a climate chamber at 50 °C and 40% RH for 21 days

Table 6 Surface composition of LDPE film surface treated with corona discharge plasma ($P = 600$ W) as determined by XPS analysis at the beginning and end of the aging cycle in a climate chamber at 50 °C and 40% RH

Aging time (days)	% Atomic C	% Atomic O	% Atomic N	O/C ratio	N/C ratio
0	86.7	10.3	2.9	0.12	0.03
21	89.8	7.1	3.1	0.08	0.03

oxygen-based polar groups present in the topmost layers, around 7%. The real oxidation level of the polymer surface, expressed as the O/C, is slightly reduced up to values close to 0.08 (Table 6). In this case, we can see an intensive wettability loss regarding the previous aging conditions. This is due to the relevance of temperature which accelerates diffusion processes during aging test on corona discharge plasma-treated samples, thus accelerating re-arrangement of polar groups and LMWOM diffusion to the bulk material.

The study of the evolution of the total surface free energy (γ_s) and its polar (γ_s^p) and dispersive (γ_s^d) contributions is interesting to corroborate the aging phenomena. In the three cases, we can observe a remarkable decrease in surface free energy (γ_s) for short aging times (Tables 1, 3, and 5). After the first day of the different aging cycles, we can see that the surface energy is reduced in a small (1.2–3.5%) way for non-aggressive conditions (air at room temperature, $T = 23$ °C; RH = 50% respectively), but in the case of thermal aggressive aging conditions, the surface free energy is reduced in a remarkable way up to values close to 11%. This high decrease promoted by thermal aggressive conditions is due to the negative effect of temperature on wetting durability; temperature promotes diffusion processes that control the re-arrangement mechanism of polar groups and diffusion of LMWOM from the plasma-treated polymer surface toward the bulk material. The use of aggressive thermal aging conditions causes the acceleration of the aging process. We can observe similar effect on the comparative evolution of polar (γ_s^p) and dispersive (γ_s^d) contributions to total surface free energy. The decrease in the polar component is practically the same that was observed for the total surface energy (γ_s) of LDPE film treated with corona discharge. These results reveal that high temperatures during the aging process promote higher decrease in polar surface energy contribution (γ_s^p), around 69%, due to the negative effect of temperature on wetting durability since it accelerates some processes related to aging or hydrophobic recovery (polar groups re-arrangement and LMWOM diffusion). On the other hand, the decrease in dispersive component (γ_s^d) of the surface free energy is relatively low in comparison to the changes observed in the polar component. These results reveal that the aging process do not promote significant changes in the film topography.

Conclusions

The corona discharge plasma treatment can be used to improve wettability on LDPE films, and then their surface free energy. But this effect has a very high thermodynamically unstability. The durability of the plasma treatment in terms of the storage temperature (T) and RH conditions has been evaluated in this work. Temperature is a critical factor since the hydrophobic recovery process is related to diffusion processes as one of the possible aging mechanisms. The obtained results show poor durability properties of the LDPE film corona discharge plasma treated on storage conditions. Because of this, to optimize this polymeric surface treatment we have to take into account that the plasma treatment is not permanent; it is subjected to an important aging process related with a re-arrangement of the polar groups generated during and immediately after the plasma treatment that together with diffusion of LMWOM toward the bulk material reduce surface free energy values in a few days. This must be taken into account when using plasma-treated films for laminates preparation, since adhesion properties are rapidly lost as a consequence of the aging process.

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