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The Effects of Cold Plasma Treatments on LDPE Wettability and Curing Kinetic of a Polyurethane Adhesive

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Summary: A cold plasma feed with either oxygen or nitrogen was used to modify thin Low Density Polyethylene films. The treatment improved both the surface wettability and the curing kinetic of a polyurethane based adhesive spread on the surface. The chemical functionalities responsible of the observed behaviours were investigated and monitored over time by high resolution x-ray photoelectron spectroscopy. Atomic force microscopy were used to compare the effects of the two feeding gases on the surface morphology of films exposed (to the plasma) for equal times. The effect on the treated films of the atmosphere exposure and of the aging time were also considered.

Keywords: hydrophilicity; low density polyethylene; plasma treatment; polyurethanes coating; surface

Introduction

In the last years, the food packaging industry showed a growing interest for easy processable polymers able to substitute traditional materials such as paper, glass and metals. These materials have good bulk properties, are available at low cost and can be modified to show the four main properties required: food containment and preservation, easy availability and last but not least good appearance. Recently, the interest of the market and of the producers is therefore focused on the development of a new class of functional packaging. In addition, surface properties, such as hydrophobicity and chemical reactivity of polymer materials must be modified to fit with the requirements of packaging

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application. This goal can be achieved by surface treatments such as wet chemical functionalization[1], acid etching[2], flame treatment[3], corona and plasma methodologies[4-5]etc.. that can lead to an increase in the reactivity of the surface, improving wettability, dyeing properties, adhesion to other polymers or metals, barrier properties, while bulk properties are usually not affected. The most attractive techniques to carry out these tasks are the physical methodologies because of their low environmental impact and limited degradation of the film. In particular, cold plasma treatment seems to be the more efficient and versatile. The surface energy can be modulated in opposite direction by treating with O_2 or a fluorinated gas[6-8]. Main advantages related to the use of this technique are the chemical modification of only a few tenths of microns in depth, the possibility to modify any polymer material independently of its chemical nature, the absence of solvents and the high uniformity. The main disadvantage is the need of a high-vacuum system.

In this work, O_2 and N_2 cold plasma treatments were applied to LDPE films in order to improve the surface polarity for increasing the polymerization rate of a polyurethane adhesive. The extent of the surface functionalization was evaluated by X-Ray Photoemission Spectroscopy (XPS) analyses, by AFM and contact angle measurements.

Experimental

A blown-LDPE film obtained from low density polyethylene pellets (Exxon Chemical LD 158 JD; density 0.925 g/cm^3, vicat softening point 98 °C, $\overline{M_w} = 70.6 \cdot 10^3$, $\overline{M_n} = 19.0 \cdot 10^3$) was treated by using an excited electron cyclotron wave resonance (ECWR) controlled plasma reactor (COPRA). The reactor allows to control the ion current density and energy, the ionization and the degree of dissociation of the beam independently. It is suitable for various working gases such as, oxygen, nitrogen and air. The source uses a radiofrequency of 13.56 MHz at a work pressure of 10^{-4} mbar. The working plasma conditions used are reported in Table 1. The chemical composition and the electronic properties of the films were measured by XPS analysis. The specimens were measured just after plasma treatment with no atmosphere exposure, thus avoiding any contamination. A non-monochromatized Mg-anode X-ray (hv=1253.6) source was used for exciting the photoelectrons while an hemispherical analyzer, run in the constant pass energy mode, was utilized for the electron kinetic energy analysis. The overall energy resolution (source plus analyzer) was about 1eV. The photoemission spectra were firstly measured up to 1100 eV of binding energy and secondly the spectra of the C1*s*, O1*s* and N1*s* core levels at higher resolution. In addition, the influence of the exposure time, the aging of the film and the homogeneity of the treatment were also investigated.

A KSV, CAM 200, Optical Contact Angle Meter goniometry was used to measure water static contact angle by forming 5μl droplets at a rate of 0.2 μl/s and two different images were recorded for each drop. An average value was obtained from 5 to 7 measurements for each film sample. AFM height images were collected with a self-assembled instrument equipped with a Burleigh Metris 200 controller. Each sample having 9.2 x 9.2 μm of area was analysed at 1, 2, 5, and 10 enlargements in non contact mode with a resonance frequency of 320 kHz and a stabilised/free amplitude of 2u.a./4u.a. A polyurethane adhesive prepared by mixing a polyole (ADOXENE AD 25) and an isocyanate (ADOXENE 91-R) both commercialised by Elchen Adhesive Spa was spread with a Mayer bar on the surface of the O_2 plasma treated LDPE film. The same experiment was carried out on an untreated LDPE taken as a reference. The kinetics behaviour of the consumption of the isocyanate were followed by FT-IR spectroscopy (Perkin Elmer Spectrum One) by monitoring the decrease during the time in the stretching band at 2274 cm^{-1} of the isocyanate group. The rocking band of polyethylene at 720 cm^{-1} was taken as internal reference.

Table 1. Experimental conditions adopted in the plasma treatment of a blown-LDPE film

Experiment N°	**Gas**	**Pressure (torr)**	**Power (W)**	**Ionic discharge (ions/s·cm^2)**	**T_{film} (°C)**
1	O_2	$2.0 \cdot 10^{-2}$	150	10^{15}	45
2	N_2	$2.0 \cdot 10^{-2}$	150	10^{15}	35

Results and Discussion

A LDPE film exposed to the O_2 plasma for a period of time of 180 sec was used as support of a coating resulting from the reaction between the polyol and the isocyanate. The kinetic of the reaction was monitored by the disappearance of the typical stretching band at 2274 cm^{-1} in the FT-IR spectra. As comparison, the same reaction was studied on the surface of an untreated LDPE film. The data are shown in Figure 1, where the ratio between the area of the ν_{NCO} (A_1) and the rocking band of the CH_2 group in polyethylene taken as internal reference (A_2) *vs.* the reaction time is reported and fitted according to a first exponential decay. All data were normalised with reference to the initial time (t_0). The reaction is characterised by a $t_{1/2}$ of 17 hrs on the plasma treated surface and by a $t_{1/2}$ of 23 hrs on the untreated film.

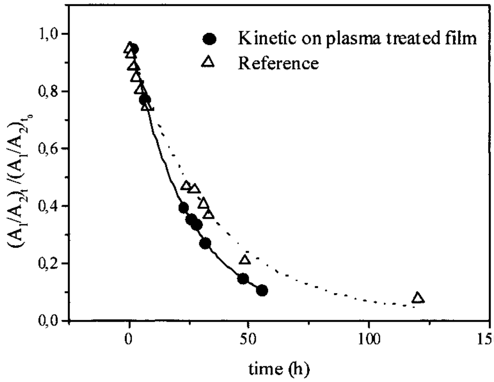
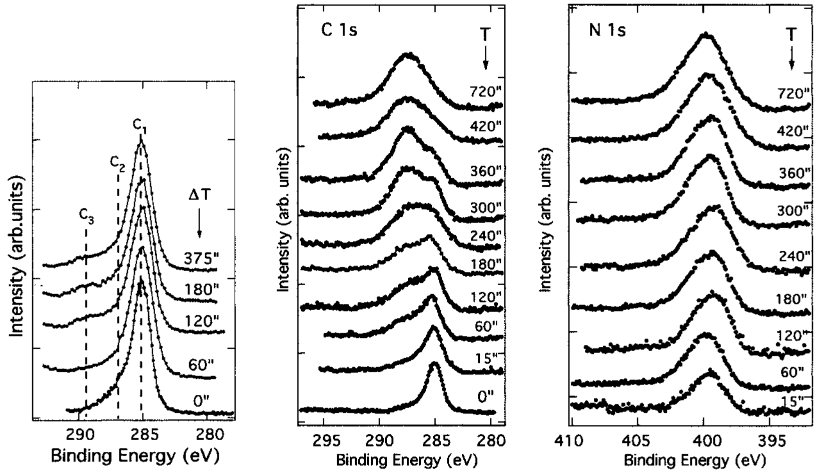


Figure 1: Comparison of the kinetics behaviour of the reaction of polyurethane on the oxygen plasma treated LDPE film and the reference.

The increase in the reaction rate must be ascribed to the plasma treatment. It is well known[4] that plasma produces a limited oxidation of the polymer surface. In order to understand the chemistry of the phenomena involved, a series of samples were prepared by changing the exposure time to the cold plasma source and analyzed by XPS immediately after the preparation. In addition, a plasma treatment with a N_2 on a LDPE film was also performed.

The details of the photoemission spectra of the C1*s* and N1*s* core levels acquired for each sample after O_2 or N_2 treatments are compared in Figure 2. The spectra were analysed assuming that C1*s*, O1*s* and N1*s* core levels are composed by a number of gaussian peaks superimposed to a polynomial background. From the mathematical deconvolution, four peaks resulted for the C1*s* core level (C_i, i=1,4) and three peaks for the N1*s* core level (N_i, i=1,3). Only one component, labelled with the O symbol, was used to fit the O1*s* core level because the different contributions can not be resolved in the spectra. The binding energy scale (see Table 2) was calibrated by assuming the C1*s* binding energy of the carbon atoms in saturated hydrocarbons to be equal to 285 eV.

According to this calibration, the components C_i (i=1,2) were assigned to the carbon atoms naturally present in the sample before the treatment, C_3 to the carbon atoms chemically bound to oxygen (for this reason indicated as C_o), and C_4 to a shake-up loss in the case of the O_2 treatment, while it was assigned to the carbon atoms bound to nitrogen (for this reason indicated as C_N) in the case of the N_2 treatment. With a similar approach, N_1 was assigned to C-N or C≡N groups, N_2 to C=N groups and N_O to the presence of nitrogen bound to oxygen[9-10]. For each gaussian curve obtained from the fitting, the intensity I_i, the energy E_i, and the width at half-height $FWHM_i$ were estimated. A typical result of a core line fit relative to a C1*s* spectrum taken after 120 sec of O_2-treatment is shown in Figure 3.



(a) (b) (c)

Figure 2: Photoemission spectra at different exposure time of the C1s core levels acquired for O_2-treated LDPE films (a), N_2-treated LDPE films (b) and N1s core levels acquired for N_2-treated films.

Table 2. Binding energies of the 1*s* core levels as resulting from the XPS spectra fitting

Core levels					**Binding energy** (eV)
	O_2 treatment		**N_2 treatment**		
C1*s*	C_1	C_i	C_1	C_i	285
	C_2		C_2		286
	-		C_3	C_o	287
	C_3	C_o	C_4	C_N	289
	C_4	C_{pl}	-		295
N1*s*	-		N_1		399
	-		N_2		401
	-		N_o		404
O1*s*	O		O		532

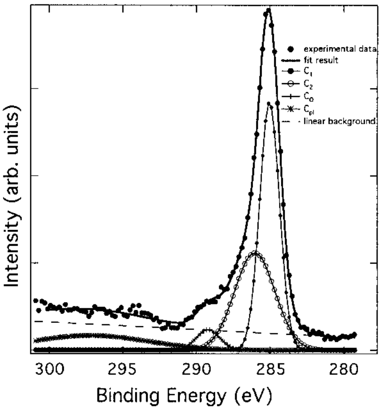


Figure 3: Core line fit relative to a C1*s* XPS spectrum taken after 120 sec of O_2 plasma treatment. (see text for more details).

According to this analysis, the formation of chemical functionalities on the film surface mainly due to the ester [-O-C(O)-C-], carboxylic [HO-C(O)-C] and anhydride [-C(O)-O-C(O)-] groups was observed for exposure time to O_2 plasma longer than 60 sec. The maximum extent of modification was reached after 180 sec of treatment coupled with a decrease in the concentration of the C_i species (Figure 4). For exposure time longer than 180 sec, the amount of functionalization starts to decrease whereas the concentration of non-oxidised carbon atoms increases again. This result could be explained by the formation of a carbon layer on the surface of the LDPE film at long exposure times as a result of degradation/combustion phenomena.

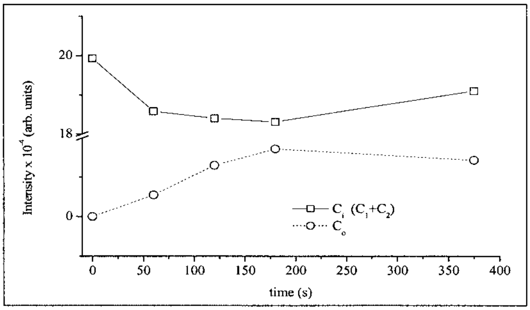


Figure 4: Intensity of the XPS lines of an O_2 plasma treated LDPE surface *vs* exposure time.

A much more marked decrease in the concentration of the C-C bond (C_i) was observed by increasing the exposure time during the N_2 treatment (Figure 6). A limited oxidation of the film, which seems to be independent from the exposure time, was evidenced from the formation of a small amount of oxygen atoms and C-O bonds probably because of the presence of traces of air in the plasma reactor[11-12] (Figure 5). The functionalization of the surface by N-groups seems to proceed rapidly in the first 60 sec of treatment. In particular, a larger amount of N_1 groups (single and triple C-N bonds) than N_2 (double C-N bonds) is formed.

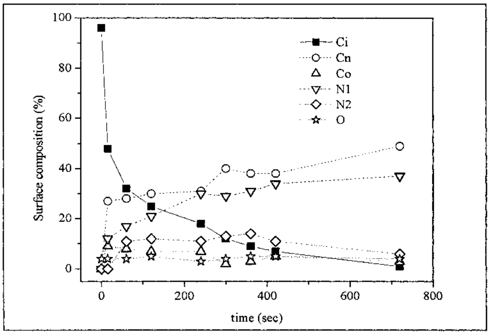


Figure 5: XPS analysis: LDPE surface composition *vs* N_2 plasma exposure time.

A sample treated for 180 sec with N_2 plasma was successively exposed to the laboratory atmosphere for 12 hrs and then analysed again in order to investigate the chemical stability of the induced N-groups. From the data reported in Figure 6 it seems that the nitrogen atoms itself introduced with the treatment (180 sec) is barely substituted by oxygen atoms, whereas an appreciable increase in the oxidised groups and oxygen atoms is observed.

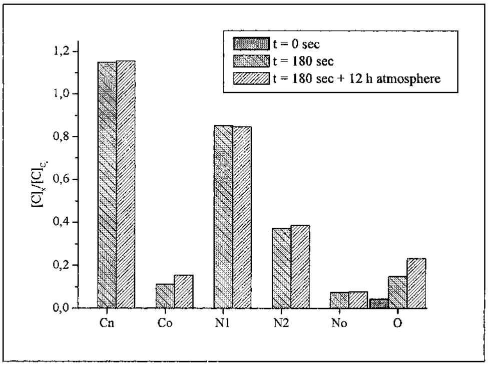


Figure 6: Effect of the atmosphere exposure on the concentration of the functional groups relative to the concentration of the saturated C-C bond (N_2 plasma treatment).

Because of the higher polymerization rate of the polyurethane adhesive observed on the O_2 treated sample, a uniform modification of the surface was invoked. In order to confirm this conclusion, the amount of C_i, C_0 and O species was monitored on two different points on the surface of the sample exposed for 120 sec to the O_2 plasma. The data, summarized in Table 3, indicate an homogeneous modification of the surface. On the same sample, the stability of the treatment-induced surface changes with time was also evaluated. In any case, the induced polarity does not seem to be largely affected by the ageing of the surface as indicated by the concentration of the polar groups that remains practically unmodified (difference <0.5%) 15 hrs after the end of the treatment (t = 0 h, Table 3).

Table 3. Influence of the O_2 plasma treatment on the homogeneity and effect of the ageing time on the surface composition

	C_i (C_1+C_2)	**C_0**	**O**
	Homogeneity		
Point 1	0.72	0.05	0.23
Point 2	0.72	0.04	0.21
	Ageing		
t_{ageing} = 0 h	0.72	0.05	0.23
t_{ageing} = 15 h	0.72	0.05	0.23

The influence of the hydrophobic recovery with time was also analyzed by the measurement of the static contact angle values performed four months after the end of the treatment on samples exposed for 120 sec to either oxygen or nitrogen plasma. The values are compared in Table 4 with those of both a non-treated film and of a corona treated one, taken as references.

The corona treatment induced, as expected, an increase in the polarity with respect to the non-treated LDPE film and this effect is limited only to the treated film side exposed to the electromagnetic field. On the contrary, smaller values of the static contact angle continue to be observed for both plasma modified films, even if oxygen treatment seems to be slightly more effective than nitrogen in terms of initial higher induced polarity or limited hydrophobic recovery. In addition, a general increase in the wettability was observed on both sides of the films. This result could be explained by taking into account that, even if during the plasma treatment the film is leaned against the reactor floor, this is completely filled with stationary and not flowing plasma. The reactive species, at the treatment conditions, had a very high average life time and they were effective in modifying also the not directly exposed side.

These observations found a confirmation by the atomic force microscopy investigations (Figure 7).

Table 4: Water static contact angle

Film treatment	ϑ *Directly Exposed side*	ϑ *Not directly exposed side*
Not treated	-	95.1 ± 2.5
Oxygen plasma treated*	43.4 ± 8.3	54.9 ± 2.3
Nitrogen plasma treated*	50.4 ± 3.5	75.69 ± 0.43
Corona treated**	72.2 ± 3.1	91.22± 0.94

*Measure performed four months after the plasma treatment

**Measure performed few days after the corona treatment

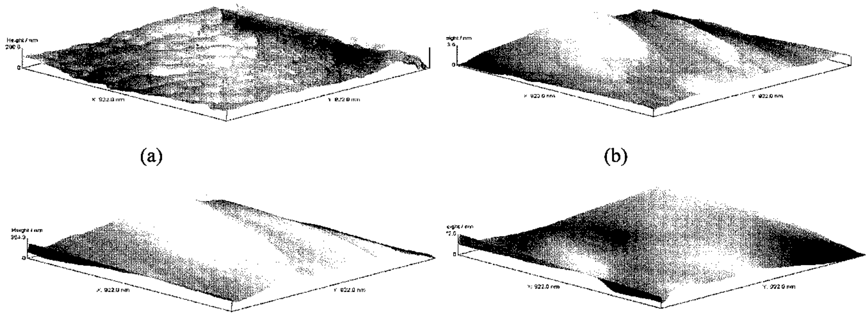

(a) (b) (c) (d)

Figure 7: AFM images at 10 enlargements of the oxygen plasma treated film (a: exposed side, b: non exposed side) and of the nitrogen plasma treated one (c: exposed side, d: non exposed side)

The oxidative gas induced a much more irregular surface morphology on the modified film than nitrogen. This affect was more remarkable in the case of the not directly exposed side. In particular, a quite sharp surface morphology was observed on N_2 treated films and a bumpy morphology on O_2 treated ones. The latest phenomenon is usually observed on thin polymeric film exposed to aggressive plasma treatment[13-16] as a result of the degradation of the surface with the formation of a carbon layer.

Final Remark and applications

LDPE films were surface modified with oxygen and nitrogen cold plasma. The extent of modification was in both cases quite high and sufficient to increase the wettability of the hydrophobic film as it resulted from the measure of the static contact angle. AFM images of the O_2 treated surface showed an etched morphology as a consequence of the use of a more aggressive gas. However, the oxygen atmosphere produces the highest chemical modification of the surface and the degradation observed is limited to a thin layer, especially for exposure time lower than 180 sec. This result allowed to anticipate that the mechanical properties of the bulk are not significantly affected. The functional group introduced with the O_2 treatment act probably as Lewis acid catalyst in the polymerization reaction of a polyurethane adhesive. This results together with the good uniformity of the treatment and the stability with time of the induced funtionalization were positively interpreted in view of potential industrial application of the process.

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