# Physical and gas permeation properties of five-layer polyethylene film used as greenhouse roof

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## Abstract

The effect of sand wind ageing simulation performed under different conditions for a five-layer film consisting of polyethylene, poly-vinyl-acetate and various additives has been investigated. The mechanical properties of the five-layer films after several treatments were evaluated, together with their surface morphology - analysed by using Fourier transform infrared and contact angle - and gas permeation properties. The experimental analysis indicated that these treatments had a significant influence on the surface of the film only. An attempt has been done to compare the properties of the five-layer films with the monolayer and tri-layer films with or without air bubble under similar conditions.

## Introduction

Agriculture is the most important sector in which plastic material is employed as a primary building component. Within civil and industrial constructions - where other building materials (*i.e.*, bricks, concrete, steel, wood, *etc.*) are more widespread - the use of this material is limited to complementary applications, as window or door frames, flooring or facing covers, insulation or waterproofing material, rain water goods, *etc.*. Employed as a covering material to protect cultivation, plastic plays indeed a central role, by performing a passive effect - protecting crops from negative weather conditions, dust, animals, birds, insects, *etc.* - and, at the same time, an active effect, contributing to the realisation of a more favourable environment for the cultivations (Picuno, 2014).

The growing use of plastics in agriculture has indeed enabled farmers to increase their crop production. The use of plastics in agriculture results in increased yield, earlier harvest, less reliance on herbicides and pesticides, better protection of food products and more efficient water conservation. Crop protection from hail, wind, snow, or strong rainfall in horticulture, together with the realisation of a confined airspace with controlled microclimatic conditions, is the most common case (Statuto and Picuno, 2017). Plastic films are widely diffused for covering greenhouses, low and medium tunnels, and soil mulching (Figure 1). However, this increasing use creates serious environmental problems connected to the change that the agro-ecosystem may suffer at different scales (Statuto *et al.*, 2013), the alteration of the visual quality of agricultural landscape (Statuto *et al.*, 2016) and the need to collect and dispose high quantities of agricultural plastic waste (Picuno *et al.*, 2012).

Low-density polyethylene (LDPE) is one of the main polymers widely used for the greenhouse cover (Briassoulis, 2006, 2007; Dehbi *et al.,* 2015), to maintain favourable conditions of temperature, lighting, gas composition ($O_2$, $CO_2$, $N_2$) and humidity for optimal photosynthesis, respiration and growth of the plants. In spite of the low cost of these polymeric materials, the economic advantages of plasticulture can be seriously undermined by extreme climatic factors, which decrease the lifetime of the plastic cover (Dehbi and Mourad, 2011; Mourad and Dehbi, 2014). Despite the continuous efforts made by plastic producers (Schettini *et al.*, 2011), this important characteristic is actually limited in Europe and in the US (four to five seasons) and from two to three seasons in Saharan environment (Dehbi *et al.*, 2012a). The specific climatic conditions, besides the high temperature, such as solar radiation, humidity, mechanical constraints, sand wind *etc.* can modify considerably some technical properties like mechanical strength, transparency and gas permeability of the exposed plastic films (Fuina *et al.*, 2016). Moreover, these elements promote the degradation of the polymeric material in its environment resulting into an important residual pollution.

Various researchers were interested in the long-term behaviour of these plastic covers. Some studies (Guenachi *et al.*, 2002) analysed the effect of a sand wind simulation on a LDPE monolayer film, keeping it for 4 h at 40°C. They showed that this creates on the exposed surface a very weak layer of material inlaid with particles of sand. Dehbi *et al.* (2012b) reported that the durability of the material depends on its fitness to resist the erosion. In these studies, variations in the structures were analysed using Fourier transform infrared (FTIR), differential scanning calorimetry and mechanical properties.

Earlier, the covers of agricultural greenhouses were made up of monolayer films of LDPE having about 200-μm thickness

(120-200 μm). In spite of its quick thermal transmission nature, poor mechanical properties, and short lifetime, tri-layer films (Youssef *et al*., 2008; Mourad, 2010), typically 220-μm thickness made of LDPE, poly-vinyl-acetate (PVA) with air bubbles entrapped in the middle layer were developed (PROSYN-POLYAN). Due to the air bubble in the middle layer, this is more efficient to maintain the temperature in the greenhouse (Dehbi *et al*., 2017). However, tri-layer films based on LDPE, produced by Agrofilm SA (Algeria) without air bubble show superior mechanical property when compared to the monolayer film. Recently, five-layers films for greenhouse were proposed by Ginegar Plastic Product Ltd. From the literature survey, to our knowledge, no works were reported so far concerning the gas permeation of multilayer films (Dehbi *et al*., 2017) used as covering in the agriculture field. In this paper we propose to analyse the properties of the surface and gas permeability ($O_2$ and $CO_2$) behaviour of a five-layers film in an Saharan environment *i.e.* simulation using sand wind for 8 h at 40°C, under temperature and temperature/UVA condition for 1000 h at 40°C. Since the $O_2$ and $CO_2$ play a significant role for the growth of the plants, it is very important to have a systematic study on the permeability nature of these films. The direct effects of increased carbon dioxide ($CO_2$) on plant growth refers to the change in plant grow with the levels of temperature, precipitation, evaporation and growing season at their present values. The indirect effects include the results of any changes in the other variables which affect plant growth that come as a result of the effect of increased $CO_2$ on global climate. Finally the properties of the five-layer films were compared with the monolayer and tri-layer films with or without air bubbles used in the greenhouse under similar conditions.

## Materials and methods

The material used for this study was supplied by Ginegar Plastic Product Ltd. as a greenhouse cover film called *Sun Selector/Suntherm 4*. The film is obtained by extrusion and has a thickness of 200 mm. It consists of five layers: two external polyethylene (PE) layers and a central PVA (PVAc) layer with two intermediate layers containing adhesives to ensure the cohesion between PE and PVAc. This intermediate layers containing adhesives consists of various additives such as anti-condensation, anti-UV, anti-parasite, anti-virus, anti-dust, anti-drops, *etc*. The real chemical composition of the film was kept confidential by the supplier.

For the ageing tests, the following five-layer films were tested and the 30 Watts lamp being placed 20 cm away above the samples: i) virgin film; ii) film after artificial sand-wind simulation for 8 h at 40°C; iii) film after artificial ageing 1000 h at 40°C; iv) film after artificial ageing by UVA (with wavelength range of 315-380 nm) for 1000 h at 40°C.

The method used for the artificial sand-wind was described in Dehbi *et al*. (2012b). This equipment was composed of a thermostatic tube, a sand-wind chamber and a control keyboard. From an air turbine, the flux was heated up to the target experimental temperature (T=40°C), under a pressure of 100 kNm$^{-2}$, inside the thermostatic tube. This dry air was introduced in the sand-wind chamber where natural sand particles were deposited. A Brownian movement of the sand particles resulted, randomly striking the polymer surface. The five-layers film was subjected to this treatment during 8 h.

The surfaces of the films tested were examined before and after sand-wind ageing by using a Leica DMLM microscope (Japan).

Fourier transform infrared spectroscopic analysis was recorded in total reflection on a Nicolet Avatar 360 instrument equipped with a germanium crystal. A number of 128 scans were accumulated with a resolution of 4 cm$^{-1}$ for each spectrum. IR spectra present absorbance from 3000 to 600 cm$^{-1}$. The calculations were made for the various samples after standardisation, according to a reference peak. The peak at 2920 cm$^{-1}$ was chosen as reference since it remains identical for all the samples.

The changes in the polymeric surfaces have been checked by determining the free surface energy of the different samples by means of contact angle measurements. Three reference liquids, ultra-pure water (milli-Q WaterSystem, resistivity 18 $\Omega$/cm), glycerol and diiodomethane were used. All measurements were carried out at room temperature (23°C). For each liquid deposited on the sample surface, we made an average of five measurements. A drop of 3 mL, deposited with a micro syringe, was photographed with a black and white CCD camera (500×500). Contact angle $\theta$ was determined from a computerised contact angle meter (NFT Communications Company, Tours, France).

The tensile tests of films were carried out using a universal testing machine (Instron model 4301, France). The tests were performed using a 5 kN load cell at a crosshead speed of 2 mm/min. The tensile modulus (E) was obtained from the tangent at the origin of the stress-elongation curve according to the AFNOR NF T54-102. The results obtained represent an average value calculated from five samples.

The gas permeation properties of the films towards oxygen and carbon dioxide were determined by using the time-lag technique based on the variable pressure method (Crank and Park, 1968; Joly *et al*., 1999), During all experiments, the temperature of the permeation apparatus was kept at 25°C in a thermo regulated chamber (Figure 2). Before measurement, the permeation cell (XX45047 Millipore filtration cell adapted for gas permeation) was completely evacuated by applying vacuum (10$^{-3}$ mbar) on both sides of the film for at least 10 h (valves V1 and V3 closed, V2 and V4 open). Then the upstream side was provided with the gas under test at pressure p$_1$ (V2 and V4 closed, V1 open). The increase of pressure p$_2$ in the calibrated downstream volume V was measured and recorded using a sensitive pressure gauge (0-10 mbar, Effa AW-10-T4) linked to a data acquisition system.



**Figure 1. Plastic-covered tunnel with inside plastic soil mulching.**

## Results and discussion

FTIR spectra of the surface of five-layer film kept at different conditions such as after sand wind treatment, keeping at 40°C for 1000 h and UVA/temperature at 40°C for 1000 h is given in Figure 3. The initial film spectrum (Figure 3A) presents bands, which are characteristic of polyethylene: $CH_2$ stretching vibrations (2920 and 2850 cm$^{-1}$), $CH_2$ deformation vibrations (1470 cm$^{-1}$), and $CH_2$ skeleton vibrations (720 cm$^{-1}$).

During ageing (samples kept at 40°C) we observed that the absorption band at 1470 cm$^{-1}$ does not vary before 700 h. After that, new peaks appeared between 650 and 1750 cm$^{-1}$ especially at 1650 cm$^{-1}$, 1390 cm$^{-1}$ and 1029 cm$^{-1}$ that correspond to oxygenated groups, and those at 1540 cm$^{-1}$ and 1450 cm$^{-1}$ which correspond to absorption band of vibrations of $CH_2$-O group (Dilara and Briassoulis, 1998) or C=C double bonds. The intensity of the peak increases as a function of time. Figure 3B presents the variation of the peak of the sample kept at 40°C for 1000 h. Here we noticed a peak at 1740 cm$^{-1}$, which corresponds to the formation of ester groups (Allen *et al.*, 2000). For the samples under UVA/temperature treatment we observed the same phenomenon, but new peaks appeared between 650 and 1750 cm$^{-1}$. The intensity of the peak increases more significantly compared to the samples kept at 40°C. Figure 3C displays the FTIR for the sample kept at UVA at 40°C for 1000 h. The peak at 1740 cm$^{-1}$ observed for the samples kept at 40°C for 1000 h were not seen here.

After sand-wind simulation for 8 h, the same bands of absorptions appear like that of ageing in temperature, with furthermore a band at 875 cm$^{-1}$ and 1110 cm$^{-1}$ (Figure 3D) which corresponds to the vibration of Si groups (Youssef *et al.*, 2008; Dehbi *et al.*, 2012b). Here also we noticed a peak at 1740 cm$^{-1}$ which corresponds to the formation of ester groups as observed for the samples kept at 40°C for 1000 h. Thus, the various bands of absorptions observed after the various ageing constraints show that the surface of film suffered some chemical modifications such as cross linkage, unsaturation and oxidation. Moreover, the chemical modifications observed for the samples kept at 8 h of treatment by sandwind at 40°C and 1000 h of ageing at 40°C are almost similar. A comparison of the FTIR peaks of sand wind treated tri-layer with that of five layer shows similar peaks, but the intensity of peak is more for the tri-layer film (Dehbi *et al.*, 2017). This indicates that additives in the five-layer film are more suitable to resist to the sand wind.

The variation of peak at 1715 cm$^{-1}$ which represents the bands of vibrations of the carbonyl groups and the peak at 1550 cm$^{-1}$ and 1415 cm$^{-1}$ which corresponds to the presence of $CH_2$-O and/or C=C functions is due to the breaking and branching of double bonds of the polymeric material under different ageing conditions. Under the action of the light and/or heat, the formation of radicals occurs on the film surface, which leads to the reactions of reticulation of chains, reactions with oxygen in air and reactions of scission of chains (Gulmine *et al.*, 2003). The peak at 1740 cm$^{-1}$ found for the samples kept at 40°C for 1000 h indicates that the degradation mechanism is different for the UVA/temperature treatment with the former.

The presence of any chemical modifications in the film surface due to the effects of temperature and UVA radiations were studied through the measurements of the free surface energy (surface polarisation energy plus the triple- layer dispersion energy). The method is based on the measurement of the contact angle (significant element to know the physico-chemical interactions at the surface of a film).

Here we calculated the free surface energy by measuring the contact angle (q) according to the Equation 1:

$$\gamma = \gamma_d + \gamma_p \qquad (1)$$

$\gamma_d$ and $\gamma_p$ are the dispersive and non-dispersive components, $\gamma$ is the total surface energy (MJ/mq). According to the relationship proposed by Owens Went method (Owens and Went, 1969) this surface energy is obtained from the following equation:
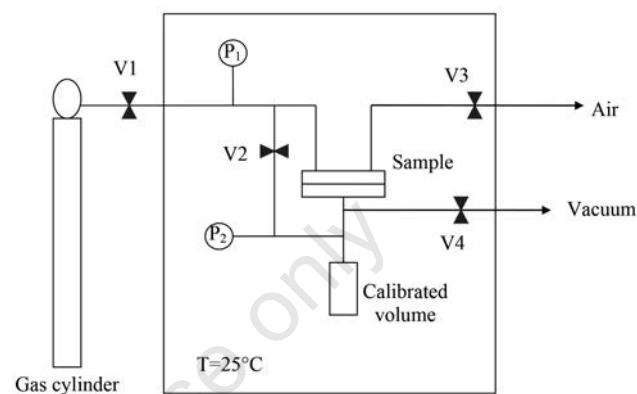


**Figure 2. Diagram of the gas permeation apparatus used for the measurement of the $CO_2$ and $O_2$ permeation properties of the films. Vi are gas valves, p1 and p2 are the upstream and downstream pressures.**
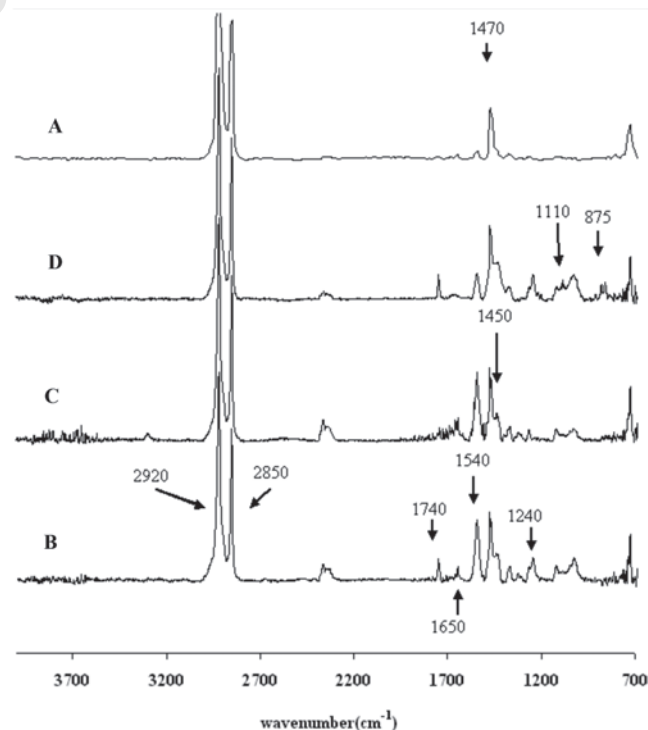


**Figure 3. IR spectra of the five-layer film, virgin (A), aged during 8 h by a sand-wind at 40°C (D), aged during 1000 h at 40°C (B) and aged by UVA at 40°C (C).**

$$\gamma(1+\cos\theta) = 2\sqrt{\gamma_l^d \gamma_s^d} + 2\sqrt{\gamma_l^p \gamma_s^p} \qquad (2)$$

where subscripts s and l denote the solid and liquid phases respectively. From the comparison of the values of γ, $\gamma_d$, and $\gamma_p$ calculated from the experimental values of q for previously studied monolayer, tri-layer (Youssef *et al*., 2008) and for the five-layer film (before and after sand-wind treatment), it was possible to conclude that the low values of $\gamma_p$ obtained for the different films correspond to polyethylene, which is known to be a non-polar polymer (Joly *et al*., 1999) and constitutes the external layers of the two multilayer films. These results indicate the appearance of polar groups in consequence of the attack by oxygen and show also an increase of the surface energy γ of the films treated by the sand-wind with regard to the initial films. It may be due to the physical modification of the film surface because of the sand wind treatment.

For the first heating of the virgin film, as well as of the aged films, several peaks were observed on after the temperature of 80°C. A peak is observed at 40°C due to the ageing of the samples. This phenomenon is well known for several thermoplastic polymers and can be explained by the fact that during such an annealing, the thermal energy brought is sufficient to authorise rearrangements at the level of crystals with meta-stable structures, even the growth of crystals of small size, which had no time to form during the extrusion of the material (Owens and Went, 1969). Since the existence of a mixture of various range of polyethylene with various degrees of crystallinity has been shown, the calculation of the melting enthalpy ($\Delta H_{melting}$) for all crystalline phase has revealed that there is an apparent change in the values. It appears that whatever the type and time of ageing, the melting enthalpy is almost constant so that, globally, there is no visible change of the crystalline fractions. This is because the ageing is concerned principally on the amorphous phase of the polymeric material. Here the modifications are occurring only on the surface of the polymeric material rather than inner part. The additive in and between the layers prevents the effect of ageing to the core of the material. Similar results were obtained for the ageing of tri-layer polyethylene.

Figure 4 presents the mechanical behaviour curves of the five-layer and tri-layer film treated by sand-wind at 40°C. The polyethylene is considered as a hard and firm polymer. We can see that the stress at failure of the aged film is obtained at a higher constraint and with a weaker deformation with regard to the initial film. This phenomenon can be attributed to the cross-linkage, a chemical reaction induced by sand wind and temperature leading to the formation of covalent bridges between the nearby segments of a polymer chain. Considering the mechanical properties, this process usually leads to an increase of the Young modulus and some constraint in the break. So, we can deduce that there was an effective cross-linkage for the films after treatment by sand-wind at 40°C. For comparison the values of the elastic modulus and percentage of elongation of the mono, tri- (Dilara and Briassoulis, 1998; Youssef *et al*., 2008) and five-layer films before and after the sand wind treatment are shown in Table 1. After the sand wind treatment, a slight increase of the elastic modulus and decrease of the elongation at break occur for the samples. With regard to the monolayer film, the multi-layer

films have higher elastic modulus certainly due to the presence of PVAc as central layer. The elongation at break is higher for the five-layer than for the three-layer and monolayer films. The five-layer material is thus more resistant than the three-layer and monolayer films, even after exposure to a sand-wind.

Figure 5 shows the time-lag permeation curves of carbon dioxide and oxygen at 25°C through the virgin and sand-wind aged
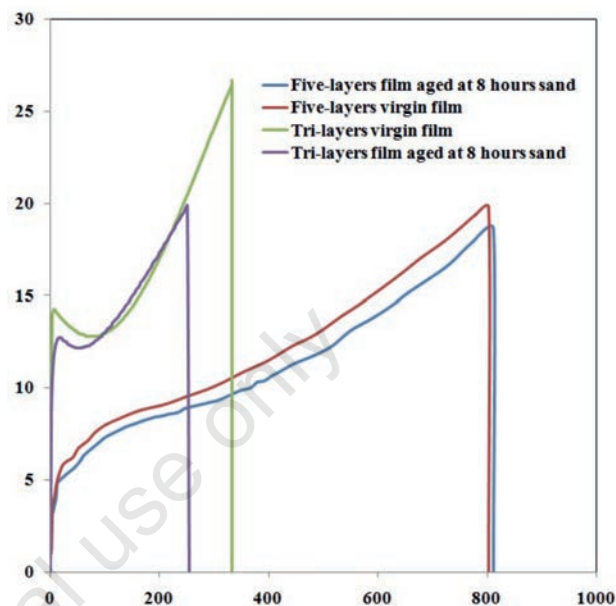


**Figure 4. Mechanical behaviour of a five-layer and tri-layer film virgin and aged during 8 h by a sand-wind at 40°C.**
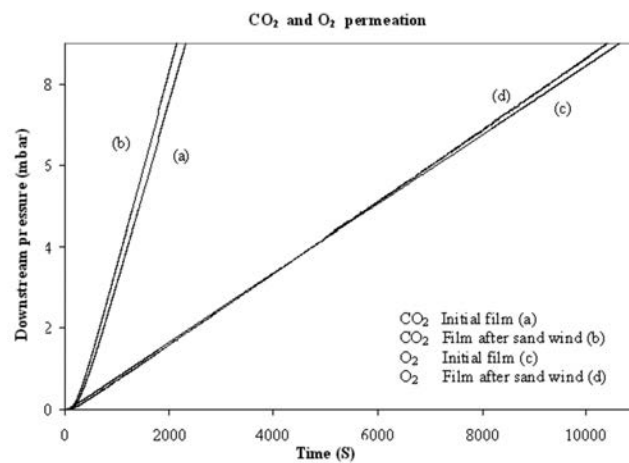


**Figure 5. Permeation of oxygen and carbon dioxide at 25°C through the five-layer film virgin and aged by a sand-wind at 40°C during 8 h. Downstream pressure ($p_2$) as a function of time. Sample thickness = 200±4 μm. Upstream pressure = 4000±mbars.**

**Table 1. Elastic modulus and deformation at break for mono-, tri- and five-layer virgin films and after sand-wind treatment.**

| Type of film | Five-layer initial | Five-layer sand-wind | Tri-layer initial | Tri-layer sand-wind | Mono-layer initial |
|---|---|---|---|---|---|
| Elastic modulus (MPa) | 0.64 | 0.78 | 0.77 | 0.88 | 0.31 |
| Deformation at break (%) | 840 | 820 | 420 | 410 | 260 |

five-layer films. Usually, for a monolayer dense polymer film, the time-lag curve [$p_2 = f(t)$] allows to calculate the permeability coefficient P of the polymer to the gas tested from the slope of the linear part by using (Crank and Park, 1968; Dehbi *et al*., 2012b):

$$P = \frac{L}{A} \frac{V}{p_1} \frac{T_0}{p_0} \frac{dp_2}{T_m} \frac{dp_2}{dt} \qquad (3)$$

where:

L is the thickness of the film (mm);

A the effective film area (mm$^2$);

V the calibrated downstream volume (m$^3$);

$p_1$ and $p_0$ are the upstream and standard (1 Atm.) pressures respectively;

$T_m$ and $T_0$ are the measurement and standard (273.13 K= 0°C) temperatures respectively;

$dp_2/dt$ the slope of the downstream pressure with respect to time stationary straight line.

The intercept of the extrapolated stationary straight line with the time axis is the *time-lag* $t_L$ which is related to the *diffusion coefficient D* of the gas in the polymer which is given by:

$$D = \frac{L^2}{6 t_L} \qquad (4)$$

While the solubility coefficient S of the gas in the polymer is calculated from the ratio:

$$S = P/D \qquad (5)$$

D, S and P are intrinsic properties of a polymer material. In the present case the cover film tested is made of five layers, so that the overall resistance $L/P_m$ of the film to gas permeation is the sum of the resistances of each layer, as for electric resistances in series, according to the following equation (Almanza *et al*., 2005):

$$\frac{L}{P_m} = \sum \frac{L_i}{P_i} \qquad (6)$$

where L and $L_i$ are the film and $i^{th}$ layer thicknesses respectively, $P_m$ and Pi are the mean and $i^{th}$ layer permeability coefficients respectively and $L_i$ and $P_i$ being unknown parameters in the present study. So, by using Equations 3 and 4, the time-lag method allows us to determine the values of the mean and apparent parameters: the overall permeability coefficient Pm of the five-layer film and a mean apparent diffusion coefficient $D_m$.

The computed values are shown in Table 2. First, it can be noticed that the five-layer film is about five to six times more permeable to carbon dioxide than to oxygen (5.3 <$P_{mCO2}/P_{mO2}$<5.9) while the carbon dioxide and oxygen apparent diffusion coefficients are of the same order of magnitude. Carbon dioxide is in fact much more soluble (about 12 times) than oxygen in this film as it is usual in the case of most of the polymers. The permeability values obtained are comparable to the values usually measured for LDPE films, *i.e.* 6 to 12 Barrer and 1.5 to 2.1 Barrer, for carbon dioxide and oxygen respectively (Guenachi *et al*., 2002) or Dow LDPE films (Braudrup and Immergut, 1989).

Secondly, the carbon dioxide permeability of the sand-wind treatment film seems to be slightly higher than that of the initial film. The slope $dp_2/dt$ is in fact slightly higher for the aged film with regard to the initial film. This could be due to a minimal and not easily measured diminution of the film thickness attributable to the surface abrasion and formation of micro-cracks ($P_m$ has been calculated considering the same thickness (200 mm) for both films). Owing to the measurement uncertainties, the increase of $P_m$ is not really convincing.

## Conclusions

The effect of simulation using sand wind for 8 h at 40°C, under temperature and temperature/UVA condition for 1000 h at 40°C for a five-layer polymer cover film has been studied by using several physicochemical characterisation methods. The optical analysis show distinctly the deterioration on the surface of the tri-layer then the five layers film after 8 h of exposure to sand-wind at 40°C. The FTIR spectra and free surface energy calculated using contact angle method indicated all the three test conditions modified the film surface due to cross-linkage, oxidation and chain scission reactions. In FTIR a band vibration of Si groups appeared after the sand-wind simulation.

The mechanical test showed a slight increase of the elastic modulus and a decrease in the elongation at break after treatment, attributed by the superficial cross-linking occurred on the film. Due to the deterioration of the superficial layers of the material, the gas permeability flow increased slightly through the aged films. Finally we can conclude that the surface properties of the films were more affected by these treatments and the properties of the five-layer film are better when compared to mono- or tri-layer films after exposure. Technical aspects about the performance of these materials during the working life are usually poorly reported and further experimental analysis should be conducted. The limited life of agricultural plastic films would indeed be enhanced

**Table 2. Mean apparent diffusion coefficient ($D_m$) and overall permeation coefficient ($P_m$) of $O_2$ and $CO_2$ through the five-layer film virgin and aged by a sand-wind at 40°C during 8 h.**

| Gas/film | $10^{12} \times D_m$ (m$^2$ s$^{-1}$) | $P_m$ (Barrer)* | $P_{CO2}/P_{O2}$ |
|---|---|---|---|
| $CO_2$ (initial five layer film) | Undetermined | 11.1 | 5.3 |
| $CO_2$ (five layer film, sand-wind) | 26 | 23.7 | 5.9 |
| $O_2$ (initial five layer film) | 27 | 2.1 | - |
| $O_2$ (five layer film, sand wind) | 33 | 4.0 | - |
| $O_2$ (initial LDPE film)° | 25 | 2.2 | - |
| $O_2$ (LDPE film, sand wind)° | 26 | 2.2 | - |

*1 Barrer = $10^{10}$ cm$^3$STP cm$^{-2}$ s$^{-1}$ cm cmHg$^{-1}$. Uncertainties are estimated to 10%; °for comparison, monolayer LDPE film. Permeability measurements made by using the differential permeation method.

thanks to new more efficient customised formulations, performed with the support of suitable equations, able to predict their useful lifetime considering the meteorological characteristics of the area where this material will be exposed and the operative conditions (contact with pesticides/agrochemicals, external pollution, contact with structural frames, *etc*.).

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