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Development of an experimental technique to assess the permeability of metal coated polymer films

Géraldine Garnier · Yves Brechet · Lionel Flandin

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Abstract The experimental time required to measure water vapour permeability of barrier film using the cup method is extremely long. In this study, a new technique is proposed, based on light transmission. This fast and accurate method was first validated using model films constituted of aluminized PET (polyethylene terephthalate) with aluminium layers of different thicknesses (<100 nm). It was possible to show that the 'illuminating' method could advantageously be employed to control the film's barrier properties during their fabrication. In a second step, the method was tentatively used to measure the changes in barrier properties over time, when the samples are submitted to severe hydrothermal ageing (70 °C, 90% relative humidity [RH]). It was concluded that the complex degradation mechanism prevents accurate measurement while ageing.

Introduction

Polymer films functionalized with a metallic barrier layer have become increasingly important for the development of protective envelope for vacuum insulation panels [1]. Thanks to the association of contrasted materials, the end use properties of the films have been improved [2]. Typically, polymer films are used for their good mechanical properties (elasticity and tear resistance) while metallic layers (often aluminium) prevent gases and water vapour to diffuse through the film. The association of both would, in principle, provide an attractive combination of mechanical properties and resistance to water permeation. However, it has been shown [3, 4, 5, 6, 7] that numerous defects commonly exist within thin inorganic layers that affect the permeability properties of the packaging. For instance, Chatham [4] reports that coating defects and inhomogeneities such as pinholes routinely occur in vacuum-deposited thin films. The author suggested that these defects result from dust on the polymer surface and from geometric shadowing during growth of the coating from the metallic vapour, due to the surface roughness of the polymer surface. In addition, this author found clear correlations between the permeation rate of aluminized polyethylene terephthalate (PET) and the measured coating pinhole density as well as between the smoothness of the polymer and the reduction in barrier effectiveness due to application of a barrier coating [4]. For Sobrinho et al. [5], microscopic pinholes created in the metallization and the web handling processes contribute substantially to the permeation levels of oxygen and nitrogen in particular. Overall the literature suggests that fabrication process considerably affects the barrier properties, mainly during folding and sealing operations [3]. For the production of ultrabarrier envelopes, the inorganic layer should obviously be deposited with a very low defect density. In addition, the structure should remain effective for very long periods. The main objective of this study is the description of a new experimental method allowing a rapid and reliable characterization of the barrier properties of metallized materials.

In addition, the literature reports that an exposition to atmospheric moisture or a contact of material with liquid water for a long time lead to damages resulting from the

G. Garnier · Y. Brechet
SIMAP, Grenoble-INP, BP75, 1130 rue de la piscine,
38402 Saint Martin d'Hères, France

G. Garnier · L. Flandin (✉)
LMOPS, UMR CNRS 5041, Université de Savoie, Bât IUT,
73376 Le Bourget du Lac, France
e-mail: lionel.flandin@univ-savoie.fr

diffusion of water molecules through out the polymer chains [8]. As a consequence, the influence of hydrothermal ageing on the barrier properties of ultrathin aluminium coatings on PET is of central interest for practical applications. This degradation of materials permeability was investigated using accelerated ageing tests; samples were exposed to 90% relative humidity (RH) and at 70 °C, and the relevance of the proposed characterization method was also addressed.

Experimental

Materials

In this study, thin aluminium coated materials, supplied by Rexor company (38, France), were investigated. These polymer–metal model films were produced using a biaxially oriented PET film of 12 μm thickness as the original material. They were referenced as shown in Table 1. In order to create long lasting materials, PET surface can be pretreated (corona treatment) or coated with an acrylic enduction (chemical treatment); both corona and chemical treatments provide an increasing adhesion of Al to PET [9].

Hydrothermal ageing

In order to investigate the effect of hydrothermal ageing on barrier properties of the coated films, two rectangular samples of each film were kept for about 6 months in a climatic chamber at 70 °C and 90% RH. Samples were extracted from this environment after various ageing time, 12, 24, 48, 96 and 192 days, respectively, noted T1, T2, T3, T4 and T5; T0 is the denomination of the unaged films.

Experimental methods

Scanning electron microscopy

Scanning electron microscopy analyses of the composites were performed on a ZEISS Ultra 55 SEM with X-ray microanalysis. Unaged samples were sufficiently coated with aluminium, so that they conduct electricity and no further preparation was necessary to avoid charge accumulation. A very thin layer of gold was applied to aged samples to prevent charging in the SEM. The defects within the metallic layer were clearly identifiable by SEM and the size of these holes could be analyzed statistically on two coated samples, i.e. PETM1F and PETM2F400 films. The metallized sides of specimens were analyzed in

Table 1 Designation and characteristics of the model films used

Films	Abbreviations	Aluminium thickness (nm)	Treatment	Schematic representation
PET reference (12 μm of thickness)	PET 12 μm	–	–	
PET metallized on one side with 20 nm of aluminium	PETM1F	20	–	
PET metallized on one side with 20 nm of aluminium *Chemical treatment*	PETTCF	20	Chemical	
PET metallized on one side with 20 nm of aluminium *Chemical treatment*	J231	20	Chemical	
PET metallized on one side with 20 nm of aluminium *Corona treatment*	J201	20	Corona	
PET metallized on one side with 30 nm of aluminium	PETM1FRO	30	–	
PET metallized on one side with 40 nm of aluminium	PETM1F400	40	–	
PET metallized on one side with 80 nm of aluminium	PETM1F800	80	–	
PET metallized on two sides with 40 nm of aluminium	PETM2F400	2 × 40	–	

secondary electrons at 4 kV accelerating voltage and with two different magnifications, i.e. ×20,000 and ×50,000. In order to gain a good statistic, 20 samples for analyses were cut with the help of die-cutter ($\varnothing = 10$ mm) for each films and at least three images per magnification for each samples were made. A ×50,000 magnification, well suited for the analysis of a single hole, cannot provide a statistically representative result. A ×20,000 magnification would give a large enough statistics (about 100 holes per photograph), but would not have a resolution to properly characterize a single pinhole. The aim of this study was both to determine the size and number of holes at initial state (T0) and their evolution with ageing time. Microscopy technique was thus combined with image analysis in order to quantify size and number of pinholes in the aluminium layer. ImageJ software [10] was employed in order to distinguish each pinhole separately.

Light transmission measurement by optical microscopy

The samples were analyzed in a light optical microscopy DMLM, from Leica, with the help of ImageJ software. An example of optical micrograph obtained for PETM1F film is given in Fig. 1. SEM analyses (Fig. 3) showed that the typical size of pinholes detected in the aluminium coating was 100 nm. The disks observed, in the optical microscope are lower by an order of magnitude. Several workers studied optical transmission properties of a fabricated subwavelength aperture in metallic layers [11, 12, 13, 14, 15]. Since light passing through an aperture is diffracted and forms a pattern of light and dark regions on a screen some distance away from the aperture due to Fraunhofer diffraction (far-field diffraction), the measurement of the hole diameter is by no way straightforward. The diameter of this disk is related to the wavelength of the illuminating light and the size of the circular aperture (Fig. 1).

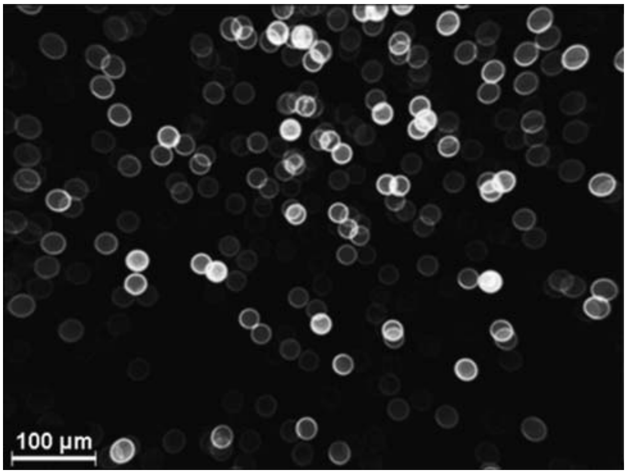

Fig. 1 Example of diffraction on PETM1F film. The light passing through an aperture is diffracted and forms a pattern of light and dark regions on a screen some distance away from the aperture: Airy's disc

Optical system properties have been described by Rayleigh resolution limit [16]. Lateral resolution (r_{lateral}) corresponds to the smallest distance between two objects in the microscope which depends on wavelength (λ) and numerical aperture (NA). It is defined by Eq. 1.

$$r_{\text{lateral}} = \frac{1.22\lambda}{2\text{NA}_{\text{obj}}} = \frac{0.61\lambda}{\text{NA}_{\text{obj}}}. \tag{1}$$

Assuming a wavelength of 500 nm and a numerical aperture of 1.4 (which is near the maximum that is commercially available) one obtains at $r_{\text{lateral}} = 0.22$ µm. This is a fundamental limit that can not be improved, regardless of the magnification of the microscope. So, the airy disk is a clear indication that there is a limit to the size of objects that an optical system can resolve.

Therefore, the determination of realistic size of pinholes was not directly possible by optical microscopy. A new method based on illumination measurements through coated PET films was thus developed. The aim of these experimentations is to quantify the overall light transmitted for each coated films in order to evaluate their performance at initial state and after ageing. This measurement will not provide the size of the holes or their number, but is directly related to the total surface covered by the holes, which is the relevant quantity to evaluate permeation resistance. The measurements were realized using the whole light spectrum, and the intensity of each pixel of the image was considered.

All the films reported in Table 1 were analyzed in their initial state and at different stages of ageing. To prevent biased result from the light source and data treatment, a calibration procedure with a reference film (PETM1F) was employed. The standard deviation in the measurement was estimated to 3%. A total of three images for each test series were realized in the same experimental conditions. The tests were performed in a dark room with an optical microscope adjusted in transmission mode using no polarized white-light with a magnitude of ×20. ImageJ software was employed for image analysis (16-bit in greyscale) with the help of the 'histogram' function. The procedure is as follows: the histogram of the light intensity transmitted at each pixel of the image is given. In most cases, overexposures (corresponding to saturate pixel) was observed but on a limited number of pixels (less than 1%). This phenomenon is unavoidable if one wants to keep the same protocol with all films, and the small proportion of pixels involved ensures that the consequences of this artefact remain negligible.

In Fig. 2, the experimental histograms for a metallized films in its initial state and after ageing are compared. An increase of the intensity of the light transmitted through the aged film is evidenced, and reveals an increase of the total hole area, and therefore a degradation of barrier properties.

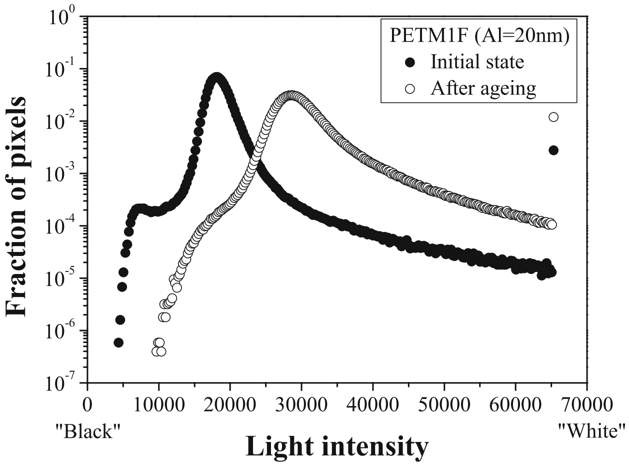

Fig. 2 Example of light transmission measurements histogram for a metallized film PETM1F film (PET: 12 μm, Al: 20 nm), in its initial state and after hydrothermal ageing during 192 days at 70 °C-90% RH

Permeation

The property of interest for these barrier films is the permeance to vapour, not the light transmission. The water vapour permeation test was performed following the permeability cup method [17]. From a total of at least three specimens for each test series, the unaged samples without treatment were stored and regularly weighed in climatic chamber controlled in temperature and relative humidity at, respectively, 25 °C and 90% RH. The mass transfer through the films is caused by the difference in partial pressure inside and outside the cup. Measurements enable to follow the evolution of the mass when a gradient of water vapour pressure is imposed. As a result, the permeance Π (kg/(s m^2 Pa)) can be estimated by the Eq. 2:

$$\Pi = \frac{g}{S \times \Delta P} \tag{2}$$

with g: vapour flow (kg/s) calculated from the slope of the curve of mass changes versus time; S: surface of the specimen (m^2) and ΔP: difference of water vapour pressure (Pa).

A typical change in mass as a function of time is obtained. The measurement period is controlled by the time to reach the steady state, with metallized samples it is typically of about 12 days. The linear shape clearly allows to define accurately a permeance, which will be correlated to the light transmission measurements.

Results and discussions

Statistical analysis by SEM

The purpose of this section is to propose a local approach to study the hydrothermal ageing of coated PET films. It is based on a mesoscale analysis of the different steps of ageing process. SEM images (three per film) were taken, binarized and analyzed with imageJ software, in order to obtain a representative estimation of density and size of defects in the aluminium layer.

Evolution of pinholes

The effect of hydrothermal ageing on the PET coatings was investigated with two different approaches. On the one hand, a qualitative analysis of SEM images at large magnification permitted to assess the geometrical changes of the individual pinholes (Fig. 3).

On the other hand, a quantitative analysis of SEM images was used to describe the evolution of number, size and surface fraction of pinholes observed with the ageing time. The results concerning the number and area of pinholes with a magnification of ×20,000 are represented (Figs. 4, 5), with the associated error bars.

The number of pinholes per surface unit appeared very important for unaged films with the lowest aluminium thickness. However, it is important to notice that the number of heterogeneities strongly varied from one film to the other depending on aluminium thickness. A systematic study [18], showed that surface fraction occupied by pinholes in the unaged specimens decreases linearly with increasing thickness of the deposited aluminium film. The analysis of the shapes of individual holes for long ageing

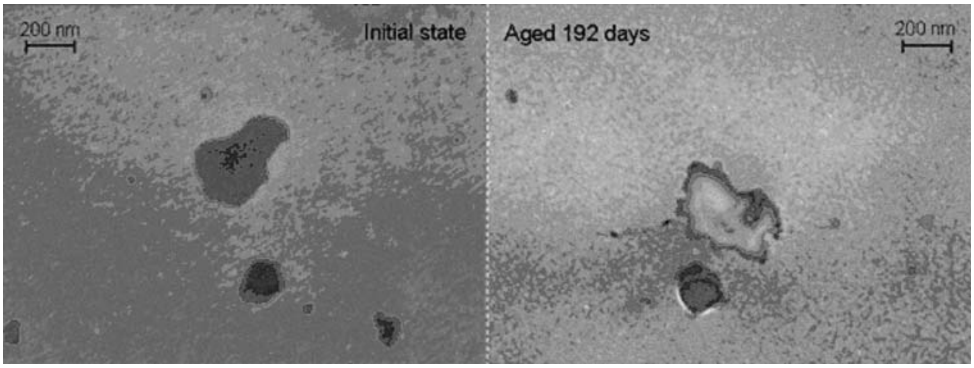

Fig. 3 SEM images of metallized side of PETM1F20 nm film unaged and aged for 192 days at 70°C-90%RH. Mag: × 50,000, EHT = 4KV_InLens

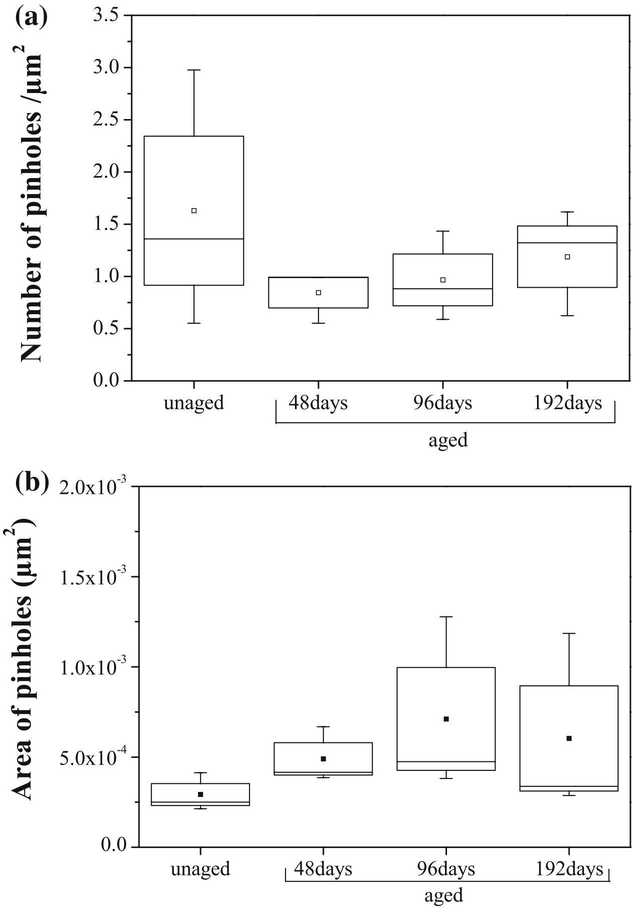

Fig. 4 Evolution of number (**a**), size of pinholes (**b**) from results of PETM1F (Al: 20 nm) and PETM2F400 (Al: 2 × 40 nm) films, as a function of ageing duration at 70 °C-90% RH. Data extracted from SEM pictures (Magnification ×20,000) and represented with the *box* and *whiskers* convention (minimum, 25th quartile, median, mean, 75th quartile and maximum values)

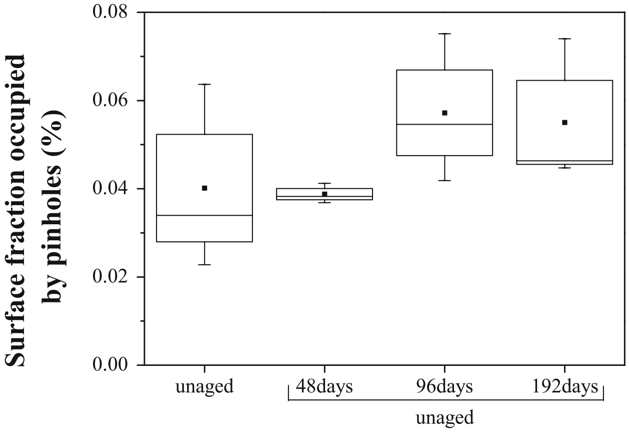

Fig. 5 Evolution of the surface fraction occupied by pinholes with ageing time from results of PETM1F (Al: 20 nm) and PETM2F400 (Al: 2 × 40 nm) films. Data extracted from SEM pictures (Magnification ×20,000) and represented with the *box* and *whiskers* convention

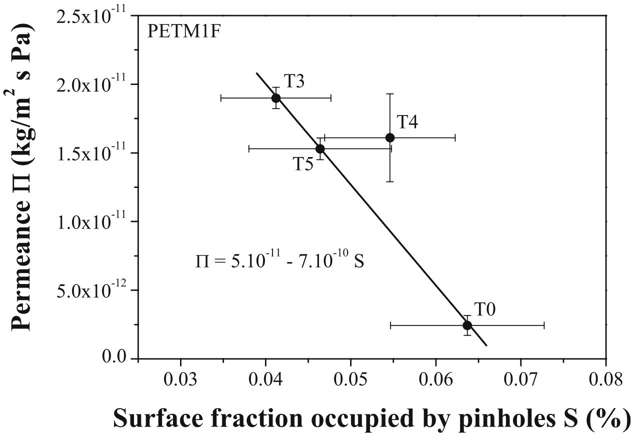

Fig. 6 Relationship between permeance and surface fraction occupied by pinholes. The study was realized with SEM images with a ×20,000 magnification (T0: unaged, T3: aged 48 days, T4: aged 96 days, T5: 192 days)

times shows extremely convoluted shapes, which results very likely from a coalescence process between individual holes.

Relationship between permeance and surface fraction occupied by pinholes

The results provided by SEM analyses permit to give a correlation between the evolutions of permeance and surface fraction occupied by pinholes (noted S (%)) with increasing ageing time (Fig. 6). According to other results [19], this correlation can in a first approximation be adjusted with a linear function.

Although SEM is a reliable method to measure the size of pinholes without the diffraction problems associated with optical microscopy, the number of images required to obtain a representation sample is time consuming. It thus seemed important to develop another method related to the barrier properties.

Light transmission measurement

The technique measuring light transmission could provide information on the permeance values. Illumination measurements provide thus a new technique to rapidly estimate the water vapour permeance of polymer–metal model films.

Relationship between mean illumination and permeance at initial state

When the barrier materials are of good quality, a very low water vapour transmission rates largely increases duration for the permeance measurement. In most occurrences, 3 weeks of measurement are required to obtain satisfactory results. To overcome this drawback, a correlation between

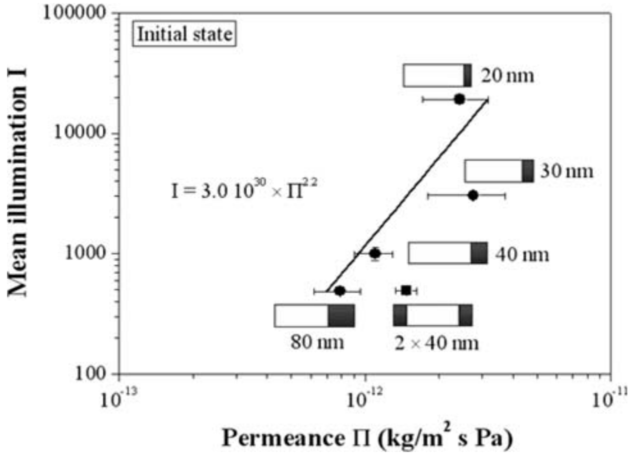

Fig. 7 Relationship between mean illumination and permeance at initial state

the meso (related to illumination) and macrostructural analyses (related to the permeation) was tentatively established (Fig. 7); indeed evidences a very strong correlation between the permeance and the light transmitted in the initial stage. This relationship could plausibly be adjusted with a power law function for the films metallized on one side.

This correlation is very important on the application point of view because the implementation of the illuminating technique is so easy that it could be employed to qualify films in situ during the metallization process. In other words, it would be quite simple to measure the illumination within the coating machine in order to tailor the appropriate quality of the metallic coating films depending on the applications.

Variation of illumination with ageing time

A comparison of optical microscopy images realized with a white-light source on unaged and aged coated PET films is presented in Fig. 8. The white spots correspond to zones where the light could pass through the film. Hydrothermal ageing leads to a clear degradation of the aluminium coating.

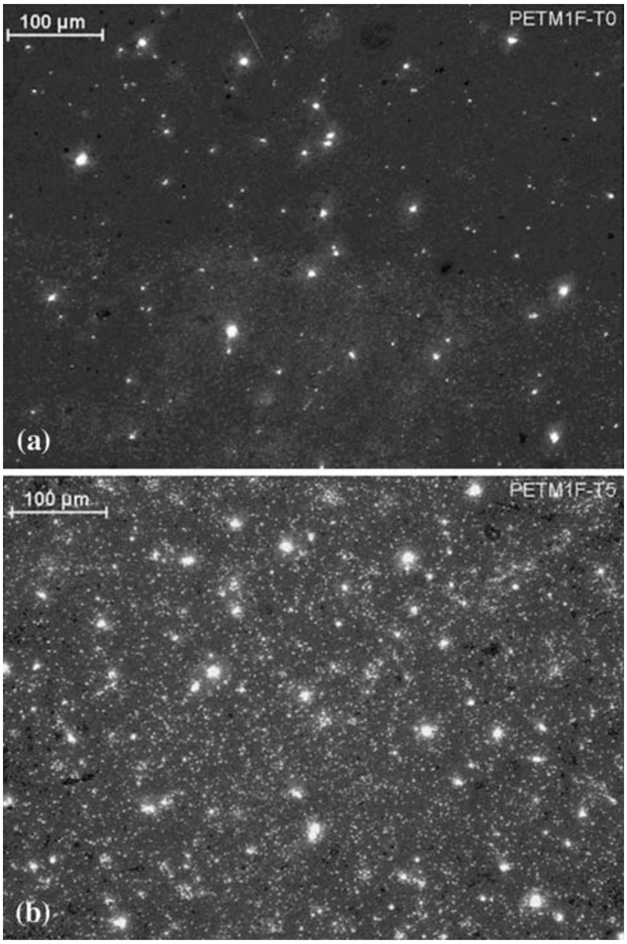

Fig. 8 Optical microscopy images in transmission mode for the PETM1F (Al : 20 nm) film, **a** initial state (T0), **b** after an ageing time of 192 days at 70 °C-90% RH (T5)

The variations of the optical properties of all PET composites listed in Table 1 during the ageing test are shown in Fig. 9 in order to give a global tendency. A loss of barrier properties is evidenced that started after 12 days of ageing. An increase of light intensity is related to the modification of the metallic surface with ageing time. Theses changes could be directly linked to substrate material. By testing various coated films aged in the same experimental conditions, different behaviours were observed. In particular, the films with the lowest aluminium thicknesses (20 nm) show the most important increase in light transmission. In other words, this thin coating is strongly degraded by the ageing procedure (Fig. 9). For instance, the hydrothermal ageing realized in severe exposure conditions ($T = 70$ °C, RH $= 90$ %) leads to an increase of the intensity for all the measured samples.

Ageing of metallized thin films has therefore a major influence on light transmission, and light transmission is closely related to permeability. Measurements of light transmission evolution with ageing time are therefore a very sensitive manner to follow materials degradation. In order to better quantify the degradation process, a new parameter (ξ) named 'sensitivity parameter' and corresponding to the slope of mean illumination versus $t^{1/2}$ (Fickian process) was defined (Fig. 10). The measured values from ξ are reported in Fig. 11. As already noticed, thin metallization with 20 nm of aluminium not only gives poor initial properties in terms of permeability, but also lead to the fastest degradation. Figure 11 shows that 10 nm of additional thickness considerably improve the durability of the films. Ageing sensitivity decreases following with the aluminium thickness

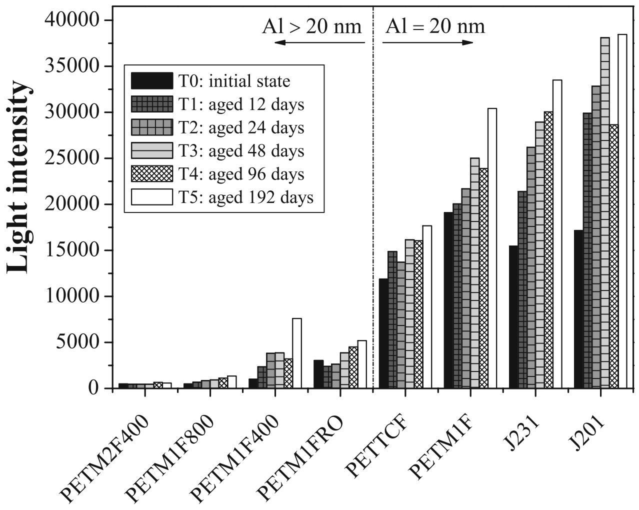

Fig. 9 Light intensity transmitted through metallized films at initial state and after different ageing time

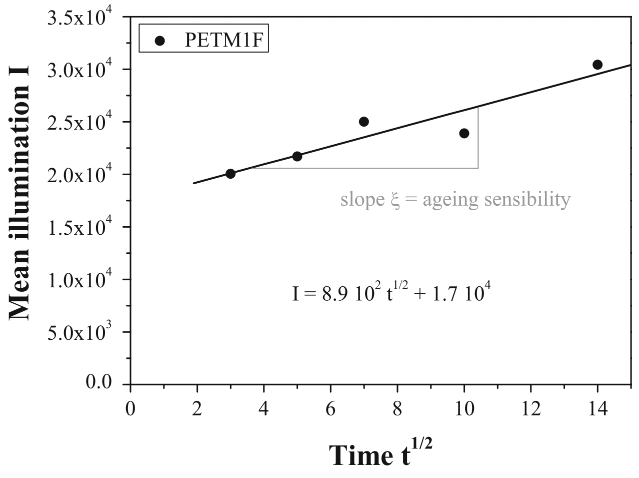

Fig. 10 Determination of the ageing sensitivity for metallized films

according to a power law. Although an acrylic enduction appeared to improve the initial properties, this treatment also induced a lower resistance to severe ageing. Figure 11 shows that the ageing sensitivity of films coated with 80 nm of aluminium is reasonable. For an equivalent overall aluminium amount, it is preferable to metallized the substrate on two sides, i.e. 2 × 40 nm rather than 1 × 80 nm, in order to improve the durability.

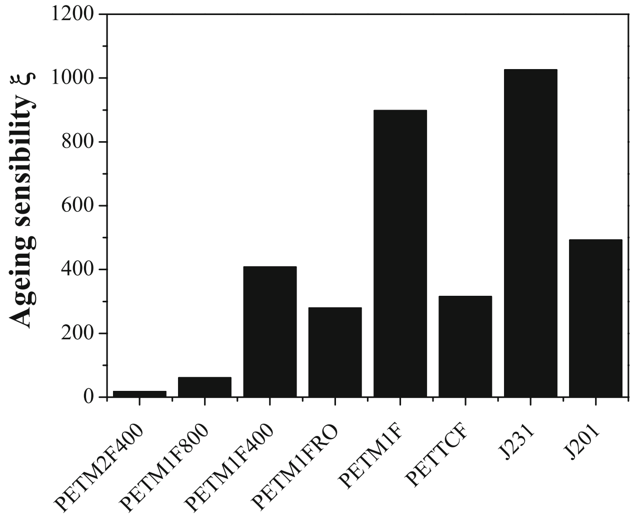

Fig. 11 Bar chart presenting the results of ageing sensitivity for models materials. The exact sensitivity values are shown on the top of each bar

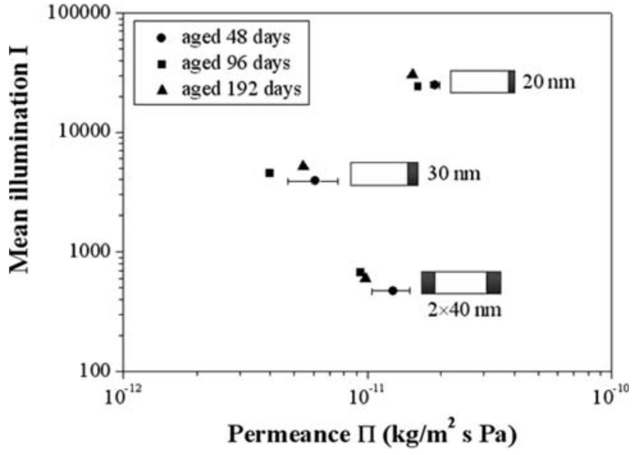

Fig. 12 Relationship between mean illumination and permeance after ageing

Relationship between mean illumination and permeance after ageing

The degraded films were also tested for permeation, and the results were examined versus illumination performance. Unlike the initial material (Fig. 7), the aged specimen departed from the established correlation for unaged specimens (Fig. 12). This seems to indicate that the degradation process is not simply a matter of pinhole evolution, but that a degradation of the polymer film itself plays a role, and that degradation is of course not accounted for in the correlation between permeability and light transmission in the initial state.

Conclusion

Illumination method applied with the optical microscopy was found to be a valuable tool for determining water barrier properties of Al–PET systems; no ageing model was developed in this study. With this method, the initial permeability of films with thicknesses of 12 μm was determined with an excellent reproducibility. The illumination measurement is a simple method that permits after calibration to obtain a good estimation of the water vapour permeance, which is usually measured using very lengthy techniques such as the permeability cup method. This optical method could be used for an in line production to make a quality control during the film's fabrication.

The technique, however, failed to qualitatively estimate a reduction of barrier properties with time, when the permeance becomes too high. It can therefore provide a production testing device, but not a non destructive testing of the degradation in service.

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