



# Permeation of water vapor through high performance laminates for VIPs and physical characterization of sorption and diffusion phenomena



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## ARTICLE INFO

### Article history:

Available online 28 August 2014

### Keywords:

Vacuum insulation panels (VIPs)  
Barrier foil  
Laminate  
Water vapor  
Permeance  
Solubility  
Diffusion

## ABSTRACT

Maintaining the long term performance of vacuum insulation panels (VIPs) remains the focus of many technical and scientific investigations. The performance of the barrier laminate is decisive to hold the vacuum level and to resist the permeation of water vapor. This barrier property against water vapor is characterized by the permeance of the laminate. The permeance of several commercially available products was determined by different methods and a good correlation was obtained between the manometric method on laminates and the current reference method on VIPs (weight gain in climatic chambers).

Even if the permeance is appropriate to evaluate the performance of VIPs under stationary conditions, the solubility and diffusion coefficients are required for a fine-tuned service life prediction under real climatic loading conditions. Whereas for the PET the absorption isotherm is linear up to high humidity levels, this is not the case for the sealing layers, nor for the laminates. But this deviation from Henry's law does not impact the modeling of the behavior of current laminates because only the external PET layer is exposed to high humidity. The activation energies of sorption and diffusion have been evaluated. The experimental results on metalized and non metalized PET films confirm that the temperature dependence of the diffusion and of the permeance is driven by the behavior of the polymer.

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## 1. Introduction

The exceptionally high thermal performance of VIPs positions them at the very heart of strategies to achieve energy efficiency in buildings [1,2]. Maintaining the long term performance of VIPs remains the focus of many technical and scientific investigations [3,4]. The performance of the barrier laminate is of course decisive, especially its capability of maintaining the vacuum level as well as its resistance to the permeation of water vapor (WV) [5].

Whatever the technology of the laminate (metallization, mineral layers, metal foil...), permeation through the envelope still remains the key challenge. This barrier property is characterized by the WV permeance of the laminate, which is appropriate to evaluate the performance of VIPs under stationary conditions, namely those conditions where the duration of the climatic stages is greater than

the characteristic time of the transient regime of permeation. Given the very high resistance to permeation of VIP barrier envelopes, this characteristic time (or time-lag) is long, typically 48 h at 40 °C for an efficient laminate. This is addressed in Section 3.1.

As a consequence, the life time assessment of VIPs in many real conditions is only possible relying on dynamic diffusion and solubility models based on accurate physical data. This is necessary to take into account the permeation inertia of the barrier. Determining such data for water vapor is the aim of Section 3.2.

Regarding the long term performance of VIPs, the expectations of the end-users and the manufacturers of the panels remain very similar. These two players need to have methods at their disposal to evaluate the performance of the barrier films already used or for a future use in order to obtain a clear idea of the technical value of the barrier films proposed by various manufacturers.

There exist various techniques, either direct measurements on the barrier laminates or an indirect measurement on VIPs. The former methods are applied to the components of the multilayered laminates as well as to the complete multilayer structure in order

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**Table 1**  
List of notations.

Variables		Units
$D$	Diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
$J$	Flux density	$\text{kg m}^{-2} \text{s}^{-1}$
$n$	Number of metalized layers	
$p_v$	Water vapor pressure	Pa
$p_{SAT}$	Saturation pressure	Pa
$Q$	Activation energy	$\text{kJ mol}^{-1}$
$s$	Solubility coefficient	$\text{kg m}^{-3} \text{Pa}^{-1}$ or $\text{cm}^3(\text{STP}) \text{cm}^{-3}(\text{Polymer}) \text{Pa}^{-1}$
RH	Relative humidity	-
$t$	Time	s
$T$	Temperature	K or °C
$V$	Volume	$\text{m}^3$
$x$	Thickness	m
$X_W$	Water content in the metalized layers	$\text{kg m}^{-3}$
$\Delta H_m$	Mass enthalpy of the polymer specimen	$\text{J g}^{-1}$
$\eta$	Plasticizing coefficient	$\text{m}^3 \text{kg}^{-1}$
$\theta$	Equivalent surface fraction of defect	-
$\Pi$	Permeance	$\text{kg m}^2 \text{s}^{-1} \text{Pa}^{-1}$
$\rho$	Density	-
$\chi_m, \chi_v$	Weight or volume crystallinity ratio	%
Constants		
$R$	Universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )	
Subscripts		
$D$	Diffusion	
$i$	Individual layer (metalized polymer or sealing layer)	
$PET_a$	Amorphous PET	
$SC-PET$	Semi-crystalline PET	
$s$	Solubility	
$0$	Reference or initial	
$1 - met$	Single metalized film	

to separate the influence of the metallization from the laminating operation.

The model commonly used for gaseous transfer in a membrane is the solution-diffusion model, considering adsorption and desorption on the top side, then diffusion through the membrane, and desorption on the bottom side. It is a linear model of mass transfer established for the polymeric homogeneous membranes, where Fick's law is used for the diffusion in the membrane and Henry's law for the solubility.

The permeance in a polymeric membrane is defined as the product of the diffusion coefficient and the solubility coefficient, divided by the thickness (Eq. (1)). A list of notations used is given in Table 1.

$$\Pi = \frac{D \times s}{x} \quad (\text{kg m}^2 \text{s}^{-1} \text{Pa}^{-1}) \quad (1)$$

For a laminate (made from both metalized polymer and sealing layers), the previous equation was extended replacing  $D$  and  $s$  by the equivalent diffusion and solubility coefficients, and a stacking model was used (verified by measurements), also called by other authors ideal laminate theory [6–9]:

$$\Pi = \frac{1}{\sum_{i=1}^n 1/\Pi_i} = \frac{1}{\sum_{i=1}^n (x_i/D_i \times s_i)} \quad (2)$$

In the previous equation, the subscript  $i$  refers to the individual layers that constitute the laminate, considering as individual layers either metalized polymer or sealing layers (the metallization itself is not considered as a layer). For metalized polymers, an equivalent permeance is considered (so-called by Langowski “permeability of the coated substrate” [9], the term permeability being

inappropriately used by this author instead of permeance which is recommended by the ISO and ASTM standards).

The solubility is a volume parameter, thus it can be extended to a coated membrane. The diffusion coefficient of the metalized polymer layers is the equivalent diffusion coefficient, controlled by the aluminum layer (barrier function against gas transfer).

The aim of this paper is twofold:

- first to check the validity of Henry's law;
- then to determine the influence of temperature and relative humidity (RH) on the solubility and on the diffusion coefficients, and to obtain some quantitative data for polymer–aluminium multilayer laminates to be used in various models (the activation energies for diffusion and solubility).

## 2. Experimental

### 2.1. Films and laminates studied

Both single films and laminates were included in this study.

The single films, either PET (polyethylene terephthalate) to be metalized or sealing films (polyethylene or polypropylene) included in this study, are:

- PET film without metallization, supplier B, called “PET2 12  $\mu\text{m}$ ”
- metalized PET films (three different PET films from two suppliers):
  - PET1: thickness of the polymer film = 12  $\mu\text{m}$ , supplier A, metallization thickness = 75  $\text{nm}^1$ , called “PET1 12  $\mu\text{m}$  M1F 75  $\text{nm}$ ”
  - PET2: thickness of the polymer film = 12  $\mu\text{m}$ , supplier B, metallization thickness announced = 80  $\text{nm}$ , determined = 100  $\text{nm}^1$ , called “PET2 12  $\mu\text{m}$  M1F 80  $\text{nm}$ ”
  - PET3: thickness of the polymer film = 12  $\mu\text{m}$ , supplier B, metallization thickness announced = 80  $\text{nm}$ , called “PET3 12  $\mu\text{m}$  M1F 80  $\text{nm}$ ”
- amorphous PET films:
  - 280  $\mu\text{m}$  thick amorphous PET (thickness measured between 250 and 280  $\mu\text{m}$ ), called “A-PET 280  $\mu\text{m}$ ”
  - 900  $\mu\text{m}$  thick amorphous PET, called “A-PET 900  $\mu\text{m}$ ”
  - bi-oriented 250  $\mu\text{m}$  thick PET, called “BO-PET 250  $\mu\text{m}$ ”
  - polyethylene sealing film (PE), 50  $\mu\text{m}$  thick, called “PE 50  $\mu\text{m}$ ”
  - polypropylene sealing film (PP), 50  $\mu\text{m}$  thick, called “PP 50  $\mu\text{m}$ ”

The typical architecture of the additionally studied laminates is composed of two or three metalized aluminum layers (here on 12  $\mu\text{m}$  thick PET) and one sealing layer (>50  $\mu\text{m}$ ). The five different studied laminates are detailed in Table 2.

### 2.2. Experimental methods

The permeance of the films and the laminates is measured by two methods: a direct measurement on laminates applying the manometric method and an indirect one on VIPs through the measurement of the weight increase.

The solubility coefficients are determined from water vapor absorption isotherms, with a volumetric apparatus or with a dynamic gravimetric one. However they can also be deduced from permeance and diffusion measurements.

The diffusion coefficients are determined by the exploitation of the transient regime of manometric permeation measurements or by the exploitation of the transient regime of dynamic water vapor

<sup>1</sup> Determined by alkaline dissolution and quantitative elementary analysis by atomic emission spectrometry in a plasma excitation device (ICP-AES).

**Table 2**  
Detailed structure of the laminates.

	Supplier	No. of metalized PET films	Determined metallization thickness (nm)	Total thickness ( $\mu\text{m}$ )	Sealing layer	No. of batches
Laminate A1	A	2	75	80	PE <sup>*</sup>	1
Laminate A2	A	3	75	97	PE <sup>*</sup>	3
Laminate B1	B	3	100	90	PP 50 $\mu\text{m}$	5
Laminate B2	B	3	100	90	PE 50 $\mu\text{m}$	1
Laminate C	C	3	100	93	Co-extruded LLDPE <sup>1</sup> /OLLDPPE <sup>2*</sup>	1

\* Not tested as simple film.

<sup>1</sup> Linear low-density polyethylene.

<sup>2</sup> Octene containing LLDPE.

absorption measurements. Furthermore they are also deduced from permeance and solubility measurements.

In order to study the influence of crystallinity on the latter parameters, the crystallinity ratio of different semi-crystalline PET films was determined.

### 2.2.1. Permeation measurements

**2.2.1.1. Manometric method.** The permeance of the films and laminates is directly measured through the manometric method using the Deltaperm tester from *Technolox*. The Deltaperm uses the total pressure method for measuring the rate of permeation as explained in ASTM D-1434-82 (2003) for gases, and in the JIS K-7129A standard for water vapor [10–12]. Between the two sides of a test sample a pressure difference is created, after which the gas or water vapor permeates through the sample.

The apparatus is equipped with a new very sensitive pressure sensor (MKS type 121A Baratron® Capacitance Manometer (ref 121AA-00001 range 1 Torr)) allowing accurate and reproducible measurements; it was modified to fulfill our needs on the laminates. Two samples measuring 50 cm<sup>2</sup> can be tested in parallel with two independent cells or downstream chambers (only one is represented in the operation scheme of Fig. 1). Two nominal identical samples are usually tested during an experiment.

The sample is tightly mounted in the device, and the sample preparation consists in a vacuum drying at 50 °C during 3 h (either a single film or a laminate with up to two metalized layers) and up to 12 h for a laminate with three metalized layers. The sample is then kept under vacuum (<3 Pa) and conditioned at the test temperature for at least one hour (Fig. 1).

Next the water vapor admission valve is opened and the upstream side of the sample is exposed to water vapor (only used in this study, although a mixture of gases can be used). For the single films without metallization, relatively low partial pressure conditions were selected to increase the permeation time: the experiments were performed at 25 °C, currently at 40% RH, but some experiments were carried out at 20% or 60% RH. For the single

metalized films and the laminates, similar conditions were chosen as those for VIP aging in climatic chambers, currently (40 °C, 40% RH) and (50 °C, 90% RH).

The upstream pressures (water vapor in this work or total one in other cases) are regulated during the complete measuring stage of the test. The downstream pressure is measured with an accurate pressure sensor (range 0–130 Pa). From the measured downstream pressure increase per unit of time, the permeation rate (called WVTR for water vapor transmission rate) is calculated taking into account the background noise previously measured at the working temperature (for example  $3 \times 10^{-13} \text{ kg m}^{-2} \text{ s}^{-1}$  at 40 °C). The conversion into permeance is obtained by dividing the WVTR by the partial pressure of water vapor, which is calculated by:

$$p_v = \frac{\text{RH}}{100} \times p_{\text{SAT}} \quad (3)$$

and the saturation pressure is expressed through the Trechsel formula:

$$p_{\text{SAT}} = \exp \left( A + \frac{B}{T} + \frac{C}{T^{1.5}} \right) \quad (4)$$

The coefficients *A*, *B*, and *C* are different for negative or positive temperatures. For positive temperature which is the case of all our tests, the values of the coefficients are the following: *A* = 22.565; *B* = -2377.1; *C* = -33623.

**2.2.1.2. Weight gain on VIPs in climatic chambers.** As indicated earlier the barrier performance of the laminate covering the core of a VIP can also be examined through an indirect measurement on the insulation product itself.

For this purpose VIPs are manufactured with the studied laminates and a standard fumed silica core. They are aged in an environmental chamber at selected temperature and relative humidity conditions, e.g. at 50 °C or 70 °C at 90% RH, and the weight gain due to the water vapor uptake recorded at regular intervals. Under these conditions the weight increase is only considered as water vapor. In previous work, this hypothesis was verified for high

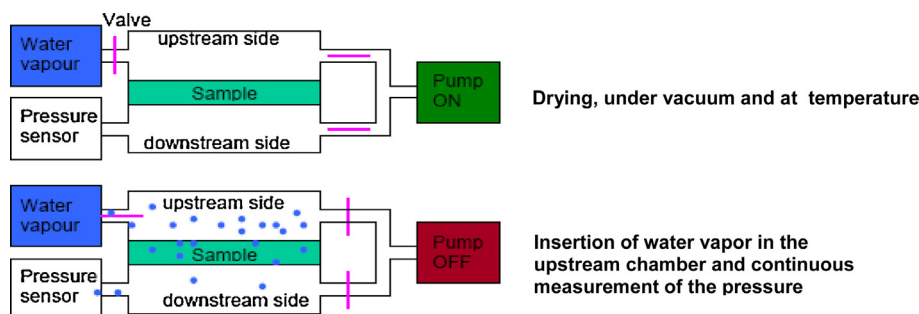


Fig. 1. Deltaperm operation scheme [10].

quality laminates with metalized aluminium layers aged at high RH levels [13]. Typically, the dry air mass is about 2% of the total mass increase for the VIPs of Section 3.1 at their end of life at 50 °C, 90% RH.

As in the case of the manometric method applied either on single films or multilayer metalized laminates, the flux through the surface of the VIP can be determined and thus the apparent permeance of the barrier laminate.

Our experience on VIPs with varying dimensions (from 200 × 200 to 500 × 500 mm<sup>2</sup>) indicates that:

- The interval between two successive weighings must be at least one month; otherwise the global WVTR obtained is smaller due to the drying occurring during the stabilization at (23 °C, 50% RH) before the mass measurement, and to the time necessary to stabilize the sample under aging conditions.
- The dispersion between the weight gains on VIPs is too high with small panels [13] (respectively about 95, 5 and 3% of variance for 200 × 200, 350 × 350 and 500 × 500 mm<sup>2</sup>); therefore panels of at least 350 × 350 mm<sup>2</sup> are hereafter preferred.

### 2.2.2. Absorption measurements (Belsorp Aqua)

The solubility coefficients at a given temperature were determined from water vapor absorption isotherms. These isotherms were established on a very accurate apparatus (Belsorp Aqua) made by *Bel Japan*. This apparatus uses the volumetric method which consists of measuring the volume of dissolved water at different pressures. Measurements were made from 25 to 70 °C on samples of about 0.5 g after vacuum drying at 60 °C during 24 h. Because of no chemisorption (it was checked for the laminate B1-1), only one cycle is performed and the solubility coefficients are calculated from the sorption part of the cycle. The Belsorp Aqua apparatus gives the evolution of the equilibrium water content versus relative humidity. Recording a complete curve (sorption and desorption) takes approximately 2 or 3 days for single thin films (PET, metalized or not, and sealing films) and 5 or 6 days for laminates or thick PET films. The curve is then expressed as the water concentration as a function of water vapor pressure and the solubility coefficient (if it is constant) corresponds to the slope of this curve.

### 2.2.3. Coupled absorption and diffusion measurements (DVS)

Water uptakes were performed on a small section of film (~1 cm<sup>2</sup>, 60–80 mg) using a DVS IGASORP instrument (*Hidden Isochema*). The sample was first dried to 0% RH at 40 °C during 72 h to establish a dry mass. After a stable dry mass was achieved, the sample was exposed to the following relative humidity (RH) profile: 0–90% in %RH increments (by step of 10% RH). The humidity was decreased in a similar manner to achieve a desorption profile. Mass equilibrium was reached at each humidity stage by measuring the percentage change in mass with respect to time. At 99% of stability of mass, the experiment proceeded to the next programmed humidity stage. The water content at equilibrium is used to build absorption and desorption isotherms and estimate solubility according to Henry's law.

Kinetic diffusion coefficients were calculated from the mass uptake curves ( $M_t/M_\infty$ ) by data fitting (using Gnuplot software) Fick's second law for the absorption of water in a film described by Crank [14]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{D(2n+1)^2\pi^2 t}{x^2}\right] \quad (5)$$

where  $M_t$  and  $M_\infty$  represent the amount of water absorbed by the film at time  $t$  and at the equilibrium after infinite time.  $D$  is the kinetic diffusion coefficient,  $t$  the time required to reach  $M_t$ ,  $x$  the thickness of the sample and  $\pi$  is the Pi number.

### 2.2.4. Differential scanning calorimetry (DSC)

The measurements were carried out on a DSC-7 instrument (*Perkin-Elmer*, SAS Courtaboeuf Cedex France). All samples were cut off from laminates. The instrument was calibrated with an indium standard ( $T_m = 156.6$  °C;  $\Delta H_m = 28.4$  J g<sup>-1</sup>). The reference was an empty aluminium pan and the average mass of samples was comprised between 5 and 10 mg. The samples were heated from 30 to 300 °C at a scan rate of 10 °C min<sup>-1</sup>, then stopped 2 min at 300 °C, and continued at a negative scan until the initial temperature was reached. Thermal analyses were classically performed to identify the transitions occurring within the polymer layer. In the case of PET, three transition temperatures may be observed during the first heating ramp namely the glass transition temperature close to 80 °C, the cold crystallization temperature and the melting temperature close to 260 °C [15]. The amount of semi-crystalline phase in PET could be determined with the integrated signal of the melting peak. Since the major contribution to the enthalpy of melting comes from the crystalline phase, the area of this peak is proportional to the weight fraction  $\chi_m$  (wt%) of crystalline polymer, as given by the following equation:

$$\chi_m = \frac{\Delta H_m}{\Delta H_m^\infty} \quad (6)$$

where  $\Delta H_m$  is the enthalpy of the polymer specimen and  $\Delta H_m^\infty$  is the enthalpy of completely crystalline PET. The value of  $\Delta H_m^\infty$  for PET found in literature is 125 J g<sup>-1</sup> [16].

Nevertheless, it is necessary to use the volume crystallinity ratio  $\chi_v$  (vol%) to perform a correlation between solubility, diffusion coefficient and this parameter:

$$\chi_v = \frac{\rho_{PETa} \times \chi_m}{\rho_{PETa} \times \chi_m + (1 - \chi_m) \rho_{PETc}} \quad (7)$$

with  $\rho_{PETa}$  and  $\rho_{PETc}$  the density of the amorphous and totally crystalline PET phases.  $\rho_{PETa}$  and  $\rho_{PETc}$  are respectively equal to 1.337 and 1.476 [16].

## 3. Results and discussion

### 3.1. Permeation results

#### 3.1.1. Sensitivity of the experimental methods (& target values)

So far only two methods have been mentioned regarding the measurement of the permeance of the barrier films used in the manufacture of VIPs. However regarding the evaluation of the barrier film or laminate – either of the individual single layer or the multilayer structure – other direct measurement methods have been looked at (Table 3). These include the cup method and the coulometric method. In the so-called cup method – referred to in the ISO 12572 and 2528, and ASTM E 96M-05 norms – the amount of water vapor absorbed or evaporated by a saline solution in the interior of the cup is monitored. The other method implies the use of a coulometric sensor in which the water vapor entering the sensor is converted into a measurable amount of charge. It constitutes the operating mechanism of commercially available equipment such as the one offered by Mocon.

It should be pointed out however that the cup method and the coulometric sensor were not included in the experimental part of this study.

In Table 3, the target values of the permeance are values required to guarantee an acceptable long term performance of VIPs used respectively for interior and exterior insulation applications. These values are calculated on the basis of the severities of these applications described in another paper [17].

**Table 3**  
Comparison of the sensitivities of the experimental methods regarding the measured flux as well as the sensitivity of the permeance calculated with different water vapor partial pressures.

Method	Suitability	Surface analyzed (cm <sup>2</sup> )	Sensitivity (flux), g/(m <sup>2</sup> day)	Sensitivity (Permeance) 10 <sup>-14</sup> kg m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup>
Manometric method	Pressure gradient similar to VIP • Suitable for single films • Limited for high performance barrier films	50	>5 × 10 <sup>-5</sup> [10]	0.002 to 0.02
Cup Method		80	4 × 10 <sup>-2</sup> [6]	1.7 to 17
Coulometric method	• Represents real situation • Many different conditions • Slow method	50	5 × 10 <sup>-5</sup> [18]	0.002 to 0.02
VIP		>800	1.8 × 10 <sup>-3</sup> [6,7,13]	0.06 to 0.6
Target values				0.5 to 1

The sensitivities reported in Table 3 are from:

- our own measurements and the Technolox data [10] for the manometric method;
- previous work for the cup method [6];
- Mocon brochure of new Aquatran® 2 for coulometric method [18];
- our own results for the indirect method on VIP [6,7,13].

The highest value of the permeance indicated in Table 3 corresponds to the minimum flux density (sensitivity) divided by a low water vapor partial pressure (2500 Pa), while the lowest value is for 25 000 Pa.

The indirect method used on several large VIPs is considered as the reference method with the best reliability and representativeness.

The cup method falls short of the required accuracy limit: this technique appears therefore less suitable in light of the superior barrier performance of the barrier laminates, i.e. very low values of the permeance. The temperature range which can be covered with the cup method is also limited.

The manometric and coulometric methods display the required sensitivity to reach the target values [8,10,18,19]. Furthermore the temperature and relative humidity can easily be adjusted when using these methods.

So the manometric method, the coulometric method and the indirect method on VIP are well adapted to the evaluation of the water permeation through the VIP envelopes.

Nevertheless measuring permeance of very tight materials remains a challenge that needs further research and eventual standardization of the appropriate test methods.

### 3.1.2. Results on VIPs and on laminates

In Fig. 2, the experimental results of the aging of VIPs including barrier laminates from different suppliers are presented as the weight gain as a function of time at 50 °C and 90% relative humidity (all VIPs 200 × 200 mm<sup>2</sup>, thickness between 19 and 21 mm). Other aging conditions with regard to temperature and relative humidity can be applied leading to a different water uptake; this property is expressed in g m<sup>-2</sup> in order to allow a direct comparison between the results obtained on the VIPs tested. The area taken into account is the total area of laminate inside the sealing on both faces of the VIP.

The data presented in Fig. 2 clearly demonstrate a varying water uptake behavior between the barrier laminates from different suppliers, identified by A, B and C: the lower the weight gain as a function of time, the lower the permeance and therefore the better the barrier properties of the laminate covering the VIP core. The 3 PET layers barrier laminate from supplier A (ref A2) remains superior to the equivalent products from the other suppliers (ref B2 and C); the latter clearly appears inferior to the other laminates from supplier A and B. At 40 °C and 40% RH, the permeance of

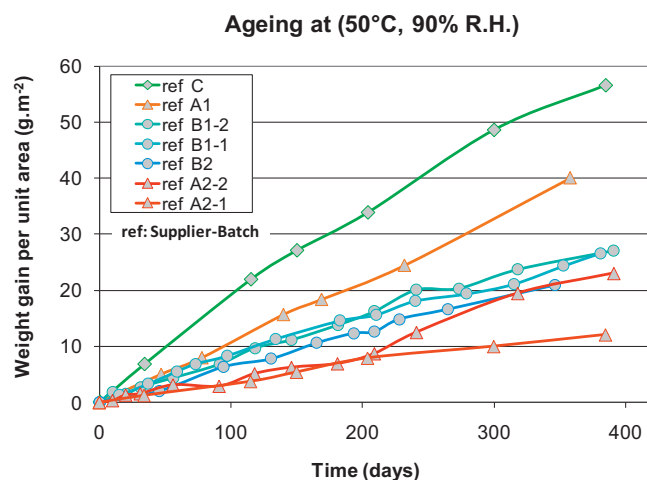
the best laminate A2 is 2.5 × 10<sup>-14</sup> kg m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, the other laminates tested have a permeance about 5 × 10<sup>-14</sup> kg m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, but it should be noted that only high-performance laminates with metalized aluminium layers were tested.

Another observation worth noting includes the variability between different batches of the same product or between samples within the same batch, as exemplified by the results on reference A2, indicated as ref A2-1 and A2-2. This remark points again towards the need for a consistent quality of the metallization and of the lamination of barrier films for VIPs.

Table 4 summarizes the values of permeance determined by this method in different conditions including those of Fig. 2. It is worth noting that the dimension of the VIPs tested did not lead to different results in spite of a different surface/perimeter ratio. This shows that the WV permeation is nearly only operating through the flat surfaces between the sealing areas of the studied laminates.

These results are also reported in Fig. 3 for a better visualization of the influence of the temperature and of the test method.

The model for the permeance of multilayer laminates (Eq. (2)) may be used in two ways. On the one hand, the measurement of the permeance on a single metalized film, which is fast to perform, allows to predict the permeance of laminates composed of several metalized films. As shown in Fig. 4, the calculated values are very close to the measurements, thereby validating the model of ideal stacking layer. Because of the negligible role of the sealing layer, this is also relevant for complete laminates. On the other hand, it is easy to calculate the permeance of the single metalized film composing the laminate. This exercise done for the laminates ref A1 and A2 reveals very different permeances pointing out that the individual performance of the metalized films are very scattered even for the same metallization thickness. Indeed, the metallization quality is

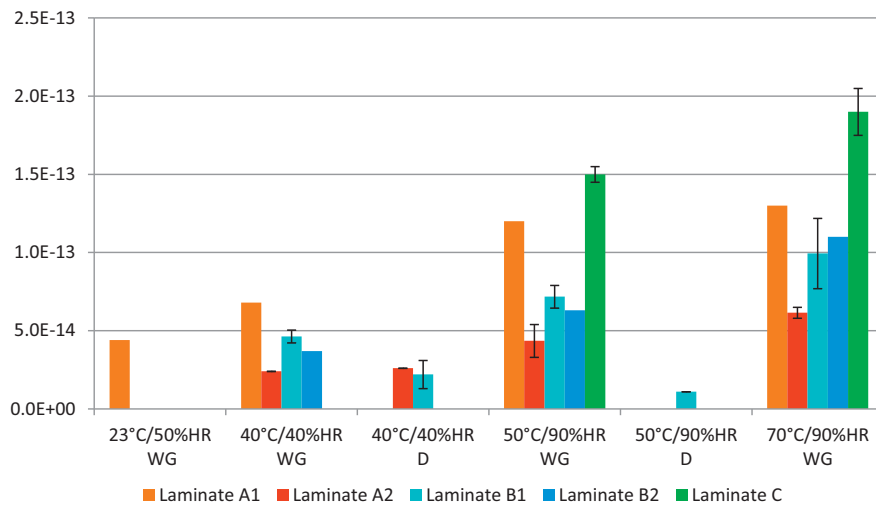


**Fig. 2.** Weight gain per unit area for laminates as a function of time in climatic chambers at (50 °C, 90% RH), all VIPs 200 × 200 mm<sup>2</sup>.

**Table 4**

Permeance ( $\text{kg m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ) of different laminates in different conditions of temperature and relative humidity, deduced from the weight gains on VIPs or from manometric measurements.

Laminate	Technique and dimensions (mm)	$\Pi$ in different conditions ( $\text{kg m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ )			
		(23 °C, 50% RH)	(40 °C, 40% RH)	(50 °C, 90% RH)	(70 °C, 90% RH)
Laminate A1	VIP, 200 × 200	$4.4 \times 10^{-14}$	$6.8 \times 10^{-14}$	$1.2 \times 10^{-13}$	$1.3 \times 10^{-13}$
Laminate A2, batch 1	VIP, 200 × 200			$3.3 \times 10^{-14}$	$5.8 \times 10^{-14}$
Laminate A2, batch 2	VIP, 200 × 200		$2.4 \times 10^{-14}$	$5.4 \times 10^{-14}$	$6.5 \times 10^{-14}$
Laminate A2, batch 3	Deltaperm		$2.6 \times 10^{-14}$		
Laminate B1, batch 1	VIP, 200 × 200			$7.2 \times 10^{-14}$	$7.1 \times 10^{-14}$
	VIP, 500 × 500			$7.2 \times 10^{-14}$	$1.2 \times 10^{-13}$
Laminate B1, batch 2	VIP, 200 × 200		$4.1 \times 10^{-14}$	$6.8 \times 10^{-14}$	$8.1 \times 10^{-14}$
Laminate B1, batch 3	Deltaperm		$3.1 \times 10^{-14}$		
Laminate B1, batch 4	VIP, 200 × 200		$4.7 \times 10^{-14}$	$7.5 \times 10^{-14}$	$9.5 \times 10^{-14}$
	VIP, 500 × 500		$5.1 \times 10^{-14}$	$8.9 \times 10^{-14}$	$1.3 \times 10^{-13}$
Laminate B1, batch 5	Deltaperm		$1.3 \times 10^{-14}$	$1.1 \times 10^{-14}$	
Laminate B2	VIP, 200 × 200		$3.7 \times 10^{-14}$	$6.3 \times 10^{-14}$	$1.1 \times 10^{-13}$
Laminate C	VIP, 200 × 200			$1.5 \times 10^{-13}$	$1.9 \times 10^{-13}$
	VIP, 500 × 500			$1.6 \times 10^{-13}$	$2.2 \times 10^{-13}$



**Fig. 3.** Permeation results ( $\text{kg m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ). Influence of conditions and method (WG: weight gain on VIPs, D: Deltaperm permeation tester).

driven by the defects of the metalized layers [6], in other words as mentioned by Langowski [9], substance transport is mainly localized at defects for inorganic layers which are applied to polymer substrates in thicknesses ranging from about 10 nm to several hundred nanometers. The size distribution and number of defects are decisive and depend on the substrate material, the quality of its surface, and the coating process.

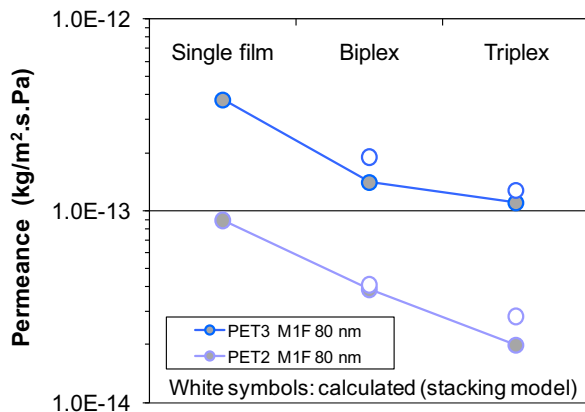
When comparing the permeance data obtained through direct measurements on the barrier laminates themselves with those

generated through the measurement of the water uptake of VIPs as illustrated in Fig. 3, one observes differences in the absolute value of the barrier property. The permeance data generated through the aging of VIPs tend to be higher than those from the direct manometric method. This can be attributed to the mechanical loading history to which the barrier laminate is subjected when the VIP is actually manufactured: this is due to the presence of creases, as a result of folding the barrier laminate around the straight edges of the core material, of core shrinkage, and finally sealing the barrier laminate pouch. In a direct measurement the samples used are small segments of pristine barrier laminate.

### 3.1.3. Influence of temperature and humidity

Fig. 3 shows that the permeance increases with the temperature. To identify this influence of temperature and the potential influence of outer humidity at the VIP scale on the permeation of water vapor, the data base of weight gain recorded during aging at different temperatures and humidities was used:

- eight commercial multilayer laminates of good to very good products from four suppliers (laminates from Table 2 and three other similar materials) presenting a permeance of the single metalized layer (defined in Eq. (8)) at 40 °C and 40% RH:  $0.8 \times 10^{-13} < \Pi_{1-met} < 1.8 \times 10^{-13} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ;
- with one to three metalized layers;
- tested between 23 and 70 °C and from 40 to 90% RH.



**Fig. 4.** Comparison of permeance at 40 °C, 40% RH, measured by manometric method and calculated from Eq. (2) as a function of the number of metalized layers.

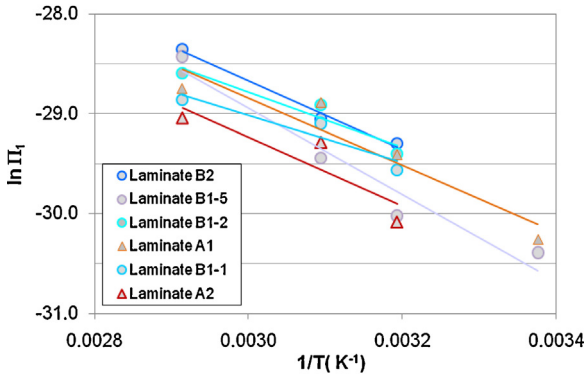


Fig. 5. Permeance of laminates as a function of the inverse of temperature between 23 and 70 °C (RH is different between various conditions).

The model used for the influence of temperature and humidity is given by the following equation [17]:

$$\begin{aligned} \Pi_{\text{Laminate}} &= \frac{\Pi_{1-\text{met}}}{n} = \frac{1}{n} \Pi_1 \times e^{\eta \times X_W} \\ &= \frac{1}{n} \Pi_0 \times e^{-Q_{\Pi}/RT} \times e^{\eta \times s \times p_{\text{SAT}} \times \overline{RH}} \end{aligned} \quad (8)$$

where  $\Pi_{1-\text{met}}$  = permeance of a single metalized layer (taking into account both influences of temperature and relative humidity)

$\Pi_1$  = permeance of a single metalized layer in a dry condition

$s$  = solubility coefficient of the metalized layer

$\overline{RH}$  = mean value of the relative humidity between the two sides of the laminate (up and down for the manometric measurement, or in and out for VIP).

The term  $1/n \Pi_0 \times e^{-Q_{\Pi}/RT}$  in Eq. (8) comes from the ideal stacking layer model (Eq. (2)) and from the thermoactivation of the permeance (cf. Sections 3.2.2 and 3.3.1), while the second part ( $e^{\eta \times X_W} = e^{\eta \times s \times p_{\text{SAT}} \times \overline{RH}}$ ) expresses the potential plasticizing effect of the water linked to its solute content. The water content in the metalized layers is expressed as  $X_W = s \times p_{\text{SAT}} \times \overline{RH}$  (mean value corresponding to the hypothesis of step like gradient of concentration of water into the metalized layers like shown in Fig. 9 explained later in this text).

So the influences are given for the temperature by the activation energy  $Q_{\Pi}$ , and for the humidity by the plasticizing coefficient  $\eta$ , while the pre-factor  $\Pi_0$  represents the tightness quality of the product (different for each product). The identification of the unknown parameters in Eq. (8) ( $\Pi_0$ ,  $Q_{\Pi}$  and  $\eta$ ) was performed using the least square method. The results are:

- $Q_{\Pi} = 26 \text{ kJ mol}^{-1}$  ( $r^2 = 0.896$ ) meaning only little dispersion for the activation energy for all the tested products;
- $\eta = -0.037$  leading to a median value of  $(e^{\eta \times s \times p_{\text{SAT}} \times \overline{RH}}) = 0.90$ . This means little influence of the outer humidity between 40 and 90% RH, so a very weak influence of the humidity inside the laminate between 20 and 45% RH (the humidity profile inside the laminate is discussed Section 3.2.3).

If one performs the identification of the parameters considering individual activation energies for each product, the mean value obtained is the same ( $26 \text{ kJ mol}^{-1}$ ) and the extreme values obtained are 15 and  $36 \text{ kJ mol}^{-1}$  (Fig. 5).

Nevertheless it has to be highlighted that the aging conditions used mainly concern low temperature associated with low humidity and high temperature associated with high humidity. This set of conditions is suitable for a representative determination of the activation energy but not so much to identify the plasticizing

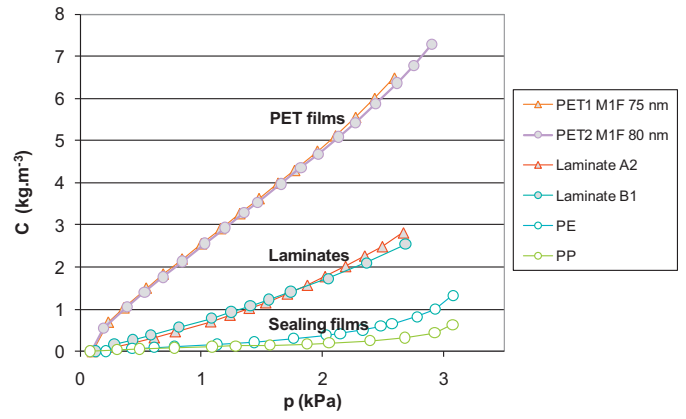


Fig. 6. Concentration versus water vapor pressure for single PET films and laminates at 25 °C with Belsorp apparatus.

coefficient. For this purpose, some additional aging at high temperature and low humidity would be useful.

### 3.2. Water vapor absorption

#### 3.2.1. Results for single and multilayer films

Volumetric absorption isotherms were recorded at 25 °C for two PET films, for laminates and for two sealing layers (one PE and one PP). The results obtained are presented in Fig. 6, and the solubility coefficients are reported in Table 5 which also includes the solubility coefficient for 900  $\mu\text{m}$  thick amorphous PET calculated from the absorption gravimetric isotherm at 23 °C (DVS).

The PET films have the same absorption behavior, in good agreement with Henry's law in the tested RH range, up to 82 or 90%. All the tested 12  $\mu\text{m}$  thick PET films have the same solubility coefficient at 25 °C, about  $2.5 \times 10^{-3} \text{ kg m}^{-3} \text{ Pa}^{-1}$ . The solubility coefficient of amorphous PET is slightly higher. The present values are very close to the bibliographical values given at 25 °C by Shigetomi et al. [20]:  $3.0 \times 10^{-3} \text{ cm}^3(\text{STP}) \text{ cm}^{-3}(\text{Polymer}) \text{ Pa}^{-1}$  or  $2.4 \times 10^{-3} \text{ kg m}^{-3} \text{ Pa}^{-1}$  and by Yasuda and Stannett [21]:  $2.7 \times 10^{-3} \text{ kg m}^{-3} \text{ Pa}^{-1}$  (cf. Section 3.4).

For the sealing films, a deviation from Henry's law is observed for relative humidities above 50%, so the equations defining permeation have to be modified for them. The solubility coefficient is about  $1.10^{-4} \text{ kg m}^{-3} \text{ Pa}^{-1}$  for the tested PP film and 1.5 time higher for the PE film.

For the laminates, the solubility coefficient is intermediate between the coefficient of PET and the one of the sealing films. One has to note that because of the high tightness of the laminates, recording their isotherms at low temperatures could lead to errors due to the difficulty to reach equilibrium. Nevertheless, for two laminates, the solubility coefficient was calculated from the coefficients of the single films (metalized PET and sealing layer) that constitute the laminates by a law of mixtures (Eq. (9)), neglecting the glue, and a good agreement was confirmed between the measurements and such calculations (Table 6). The difference previously observed between the solubilities of the PE and PP sealing films has a limited influence on the solubility of the laminate, because of the law of mixtures, as shown in Table 6 regarding the calculated values of 3-ply metalized laminates with different sealing layers.

$$s_{\text{laminate}} = \frac{1}{V} \sum_{i=1}^n V_i s_i = \frac{1}{x} \sum_{i=1}^n x_i s_i \quad (9)$$

To further explore the possible influence of the solubility coefficient of PET films, water vapor absorption isotherms were

**Table 5**  
Solubility coefficient of single films and laminates at 25 °C (except for A-PET 900 μm, A-PET 280 μm and BO-PET 250 μm at 23 °C).

	$s$ (kg m <sup>-3</sup> Pa <sup>-1</sup> )	RH validity interval (%)	Method
A-PET 900 μm	$3.1 \times 10^{-3}$	0–90	DVS
A-PET 280 μm	$2.9 \times 10^{-3}$	0–90	DVS
BO-PET 250 μm	$1.9 \times 10^{-3}$	0–90	DVS
PET (met. or not)	$2.5 \times 10^{-3}$	0–82	Belsorp Aqua
PE	$1.5 \times 10^{-4}$	0–55	Belsorp Aqua
PP	$1.0 \times 10^{-4}$	0–55	Belsorp Aqua
Laminate (A or B)	$5\text{--}10 \times 10^{-4}$	15–75	Belsorp Aqua

**Table 6**  
Comparison of the solubility coefficients measured and calculated with Eq. (6) for different laminates.

Laminates	T (°C)	s (kg m <sup>-3</sup> Pa <sup>-1</sup> )	
		Measured	Calculated
3-met + PP	25	$8.26 \times 10^{-4}$	$1.04 \times 10^{-3}$
3-met + PE	25	Not measured	$1.06 \times 10^{-3}$
3-met	25	$2.35 \times 10^{-3}$	$2.27 \times 10^{-3}$
	40	$1.34 \times 10^{-3}$	$1.12 \times 10^{-3}$

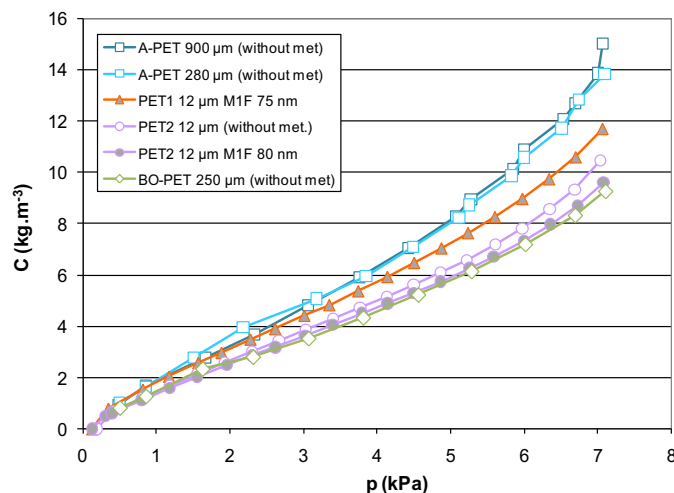
measured at 40 °C for the previously tested references, but also for amorphous or semi-crystalline thicker PET films (at 25 °C the diffusion is very slow). The curves are shown on Fig. 7.

As supposed, it was confirmed that the aluminium has no significant influence on the solubility of PET film. The same reference (PET2), with or without metallization, shows the same isotherm. There is of course no influence of the metallic layer, but also no detectable influence of the metallization itself; so probably no or very little change in the crystallinity.

The two amorphous PET tested show a higher solubility coefficient in comparison with the 12 μm thick PET films (Table 7). Among the tested 12 μm thick PET films, there is a little difference between ref. 1 and ref. 2. Assuming that the water is not soluble in the crystalline phase of semi-crystalline PET, the solubility coefficient of semi-crystalline PET can be expressed as a function of the volume crystallinity ratio  $\chi_v$  and of the solubility of amorphous PET [16]:

$$s_{SC-PET} = (1 - \chi_v) \times s_{PETa} \tag{10}$$

Taking the solubility of the amorphous PET as reference, the volume crystallinity ratio is calculated from  $\chi_v = 1 - s_{SC-PET}/s_{PETa}$  and compared with the measured one in Table 7.



**Fig. 7.** Water concentration versus water vapor pressure for single PET films at 40 °C with Belsorp apparatus.

As it was expected, the determination of the crystallinity ratio through a double measurement of the solubility coefficients is not so accurate as the direct measurement by DSC.

**3.2.2. Influence of the temperature**

The solubility coefficient is often expressed as follows, depending on temperature according to an Arrhenius' law [13,22,23]:

$$s(T) = s_0 \times e^{-Q_s/RT} \tag{11}$$

where  $s_0$  = limit value of the solubility coefficient for an infinite molecular agitation ( $T \rightarrow \infty$ )

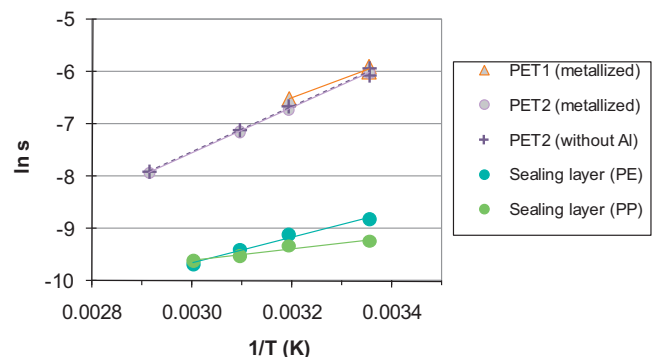
$Q_s$  = apparent heat of solution or dissolution enthalpy of water in the polymer

For single films (PET and sealing films), the solubility coefficient is represented in Fig. 8 according to  $1/T$ , for temperatures ranging from 25 to 70 °C.  $Q_s$  and  $s_0$  were determined from these experimental results (Table 8). As  $Q_s$  is negative, a decrease in the solubility is observed with an increasing temperature. This expresses the fact that the water vapor has less and less sites available in the structure of the film when the temperature increases.

**3.2.3. Influence of the relative humidity**

For the tested PET films to be metalized, the absorption isotherms follow Henry's law in the tested interval ( $C=f(p)$  is linear up to 82% RH), so a linear approximation passing through the origin was used. For the sealing layers and the multilayer laminates, there is a deviation from Henry's law for relative humidity levels above 50–55% RH (excepted for one laminate, which has a linear behavior up to 75% RH). Therefore for the laminates it was expected to evidence a deviation from Henry's law, because of this observation on the polyolefins.

But this influence of the relative humidity on the solubility coefficient has to be moderated by a simple assessment of the real humidity that is seen by the different layers in a typical laminate architecture used in a VIP envelope (3 metalized layers and a sealing layer). Knowing the different solubility and diffusion coefficients, the permeance of the laminate, and the inner and outer water vapor pressures, it is possible to calculate the profile of the water



**Fig. 8.** Solubility of single films as a function of the inverse of temperature between 25 and 70 °C.



**Table 7**  
Solubility coefficients for PET films at 40 °C and calculated and measured volume crystallinity ratio.

Reference	s Measured (kg m <sup>-3</sup> Pa <sup>-1</sup> )	χ <sub>v</sub> (vol%)	
		Calculated (Eq. (10))	Measured by DSC
A-PET 900 μm (without met.)	1.63 × 10 <sup>-3</sup>	-	-
A-PET 280 μm (without met.)	1.64 × 10 <sup>-3</sup>	-	-
PET1 12 μm M1F 75 nm	1.47 × 10 <sup>-3</sup>	10	-
PET2 12 μm (without met.)	1.27 × 10 <sup>-3</sup>	22	31 ± 2
PET2 12 μm M1F 80 nm	1.20 × 10 <sup>-3</sup>	27	32 ± 2
BO-PET 250 μm (without met.)	1.19 × 10 <sup>-3</sup>	27	32 ± 2

**Table 8**  
Q<sub>s</sub> for different single films (PET and sealing layers).

	Q <sub>s</sub> (kJ mol <sup>-1</sup> )
PET1 (metalized)	-32
PET2 (metalized)	-36
PET2 (without Al)	-36
Sealing layer (PE)	-20
Sealing layer (PP)	-9

concentration through the laminate. For this purpose, Eq. (2) is used, together with Eq. (12) which gives the flux density in the laminate, equal to the flux density in each layer *i*:

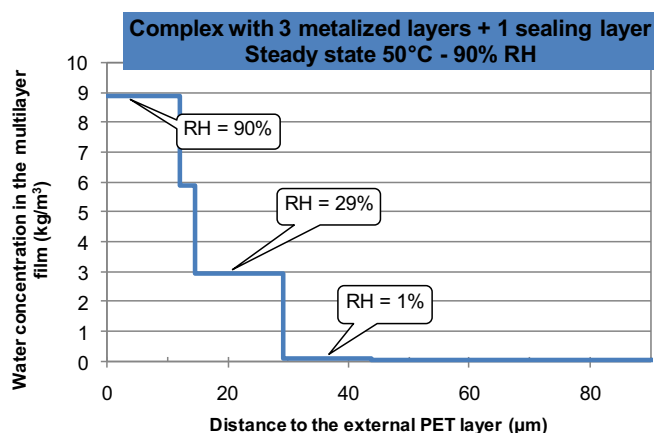
$$J = \frac{D_i \times s_i}{x_i} (P_{i \times \text{upstream}} - P_{i \times \text{downstream}}) = \Pi (P_{\text{ext}} - P_{\text{int}}) \quad (12)$$

where  $P_{i \times \text{upstream}}$  and  $P_{i \times \text{downstream}}$  = upstream and downstream water vapor pressure of each layer *i*

$P_{\text{ext}}$  and  $P_{\text{int}}$  = outside and inside VIP water vapor pressures

The calculated profile is shown in Fig. 9. The step like profile is the consequence of the continuity of the ratio of the concentration to the solubility, which corresponds to a pressure, and of the different values of *s*. It indicates that only the external PET layer is exposed to a relative humidity above 50% when the laminate is in an environment at 50 °C and 90% RH. So the polyolefins, excepted if added on the outside face, will never see a high relative humidity in a VIP.

Another consequence is that the mean pressure or humidity, loading the full thickness of the laminate during real service, or experiments such as weight gain on VIP or permeameter tests, is well below the external value. So for material characterization purposes, the mean value through the laminate is a more convenient value than the upstream (permeameter) or external (test on VIP) pressure or humidity.



**Fig. 9.** Evolution of water concentration in the different layers of a 3 ply metalized multilayer in stationary conditions (50 °C, 90% RH).

### 3.3. Water vapor diffusion

As explained above the diffusion coefficients are obtained either directly (dynamic gravimetric sorption or permeameter) or indirectly by using permeance (permeameter) and solubility (sorption). The results are given in Table 9. In this table the relative humidity indicated is:

- the relative humidity at the end of each step of a RH increment (10%) for the measurements with DVS;
- the mean value between the upstream and downstream sides for direct measurements with Deltaperm or outside and inside VIP for indirect evaluation (weight gain on VIPs).

The values of the diffusion coefficient obtained for the 280 μm thick amorphous PET are in good agreement whatever the technique used: Deltaperm or DVS. The value obtained for BO-PET with a similar thickness is less important than the one obtained for an amorphous polymer. This result can be explained by the presence of a crystalline phase in the polymer. In fact, the crystallinity ratio of BO-PET is equal to 32 ± 2%.

The values obtained for laminates are smaller than the ones obtained for single non-metalized films, showing the effects, first of the metallization and secondly of the multilayer structure on the diffusion and also on the permeation.

#### 3.3.1. Influence of the temperature

For one laminate with three metalized layers, the apparent diffusion coefficient was deduced from the water vapor transmission rate in the transient state of the permeation phenomenon recorded with the *Technolox* Deltaperm tester. The value was 9.2 × 10<sup>-15</sup> m<sup>2</sup> s<sup>-1</sup> at 40 °C.

For four other laminates (three with three metalized layers, one with only two, from two different manufacturers), the diffusion coefficient was deduced from permeance measurements and absorption isotherms (from Eq. (1)). It varies between 2.5 × 10<sup>-15</sup> m<sup>2</sup> s<sup>-1</sup> at 23 °C for a commercial laminate with two metalized layers and 6.6 × 10<sup>-14</sup> m<sup>2</sup> s<sup>-1</sup> at 70 °C for another laminate with three metalized layers.

In order to determine the parameters  $D_0$  and  $Q_D$  (activation energy for the diffusion) from the experimental results on laminates at different temperatures (23, 40, 50 and 70 °C), Eq. (13) and the Arrhenius plot shown in Fig. 10 were used. But because of the different structure of the studied laminates, the single metalized film was considered (Eq. (14)) where the resistance against permeation of the sealing layer is neglected.

$$D(T) = D_0 \times e^{-Q_D/RT} \quad (13)$$

$$D_{1-\text{met}} = \Pi_{1-\text{met}} \times \frac{x_{1-\text{met}}}{s_{1-\text{met}}} = n \times \Pi_{\text{Laminat}} \times \frac{x_{1-\text{met}}}{s_{1-\text{met}}} \quad (14)$$

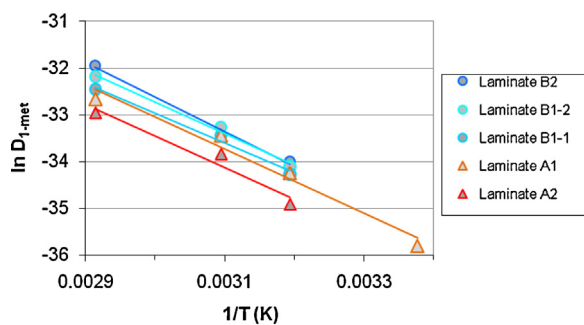
For the different laminates, the same activation energy for the diffusion process was found to be 54 kJ mol<sup>-1</sup>.

**Table 9**Comparison of the diffusion coefficients  $D$  and uncertainty  $\Delta D$  obtained for single films and laminates from direct and indirect measurement methods.

	Method	$T$ ( $^{\circ}\text{C}$ )	$RH$ (%)	$D$ ( $\text{m}^2 \text{s}^{-1}$ )	$\Delta D$ ( $\text{m}^2 \text{s}^{-1}$ )
A-PET (280 $\mu\text{m}$ )	DVS	23	50	$5.5 \times 10^{-13}$	$8.3 \times 10^{-15}$
	Deltaperm	25	20**	$5.3 \times 10^{-13}$	$3.6 \times 10^{-13}$
A-PET (900 $\mu\text{m}$ )	DVS	23	10–80	$6.2 \times 10^{-13}$ *	
	Deltaperm	25	10**	$5.4 \times 10^{-13}$	
		25	20**	$9.1 \times 10^{-13}$	
		25	30**	$1.1 \times 10^{-12}$	
BO-PET (250 $\mu\text{m}$ )	Deltaperm	25	20**	$3.2 \times 10^{-13}$	
	DVS	23	50	$4.5 \times 10^{-13}$	$4.0 \times 10^{-14}$
Laminate B1 bis(3-met + SCE)	Deltaperm	40	20**	$9.2 \times 10^{-15}$	
Laminate A1 (2-met + SCE)	Indirect evaluation***	23	25*	$2.5 \times 10^{-15}$	
		40	20**	$1.2 \times 10^{-14}$	
Laminate A2 (3-met + SCE)	Indirect evaluation***	40	20**	$3.9 \times 10^{-15}$	
Laminate B1, batches 1 & 2 (3-met + SCE)	Indirect evaluation***	40	20**	$7.6 \times 10^{-15}$	
Laminate B2 (3-met + SCE)	Indirect evaluation***	40	20**	$8.9 \times 10^{-15}$	

\* Mean value on the RH interval.

\*\* Mean value between upstream and downstream humidities for Deltaperm or outside and inside VIP for indirect evaluation.

\*\*\* Weight gain on VIPs and  $s$  calculated from Belsorp Aqua WV isotherm measurements.**Fig. 10.** Diffusion coefficient (deduced from permeance and solubility) of PET M1F in laminates as a function of the inverse of temperature between 23 and 70  $^{\circ}\text{C}$ .

### 3.3.2. Influence of the humidity

From the direct measurements obtained on 900  $\mu\text{m}$  thick amorphous PET, keeping in mind that a factor 2 on diffusion coefficients is not a significant variation (Table 9), one can observe a slight increase of  $D$  at 25  $^{\circ}\text{C}$  with the increase of humidity between 10 and 30% RH.

### 3.4. Discussion

A first point to note is the validity range of the determined activation energies for each mechanism. Because the barriers are largely made up of polymers, it has to be kept in mind that their validity domains are restricted to a temperature domain where no phase transition occurs. In fact, for the commercial products studied made with PET, one has to consider separately the temperatures below 70  $^{\circ}\text{C}$  and above 80  $^{\circ}\text{C}$ , because the glass transition temperature of PET is around 75  $^{\circ}\text{C}$ .

There are very few data available in the public literature on solubility and diffusion in the ultra barriers for VIPs and only a little bit more about permeation. More data can be found about pure polymers or about mineral layers coated on polymer films for the packaging applications. So the next sections are focused on VIP laminates to make comparisons about permeation and on pure polymers regarding solubility and diffusion.

#### 3.4.1. Solubility

Concerning solubility in PET, our results are in good agreement with the literature data about polymer films; this is true for the activation energies as well as for the influence of humidity. Table 10 compares the main results with the bibliographic data [20,21].

The values of the solubility coefficient must be compared taking into account the crystallinity; indeed the solubility coefficient is proportional to the volumetric content of the amorphous phase (Eq. (10)) considering the range of pressure covered. Very good agreements are observed for PET with the results from Shigetomi [20] and Yasuda and Stannett [21]; this concerns the values and the very good reported match with Henry's law [21]. For the first one, this agreement is in fact a little bit trickier because two opposite factors influence the value:

- on the one hand the low pressure (2000 Pa) considered by Shigetomi [20] leads to an overestimation of the global solubility coefficient due to the role of the Langmuir adsorption mode neglected in the present work done at higher pressure;
- on the other hand, the very high crystallinity of PET studied by Shigetomi leads to a lower solubility coefficient.

One therefore compensates the other.

The decrease of the solubility with the increase of the temperature is also observed but with a higher negative activation energy ( $-33 \text{ kJ mol}^{-1}$ ) than Shigetomi ( $-22 \text{ kJ mol}^{-1}$ ). This could be due to the differences highlighted above.

The comparison with literature data for the other films needs to be pursued but the data are very rare about water vapor. A comparison with results from Yasuda and Stannett [21] shows a poor agreement with our results concerning the solubility coefficient (Table 10): surprisingly for PE and PP this author reports a good match of the solubility of water vapor with Henry's law (absorption determined by a method using tritiated water).

#### 3.4.2. Diffusion

Concerning diffusion in PET, our results are also in good agreement with the literature data about polymer films; this is true for the activation energies as well as for the influence of humidity. Table 11 compares the main results with the bibliographic data [20,21,24,25]. The values must be compared taking into account the crystallinity, as the diffusion coefficient varies greatly with it, in the following equation [25].

$$D = D_{\text{PETa}} (1 - \chi_v^{0.5}) \quad (15)$$

The temperature dependence is expressed by the activation energy  $Q_D$ , found equal respectively to 36 and 43  $\text{kJ mol}^{-1}$  by Shigetomi [20] and Yasuda and Stannett [21], which can be compared to the mean value of 54  $\text{kJ mol}^{-1}$  obtained in the present work on metalized PET.

**Table 10**  
Comparison of author's results and data from literature ( $s$  in  $\text{kg m}^{-3} \text{Pa}^{-1}$ ,  $Q_s$  in  $\text{kJ mol}^{-1}$ ).

Material	Coefficient	Author's results		Literature data		
		Conditions	Value	Conditions	Value	Ref.
PET	$s$	25 °C, 0–82% HR <sup>1</sup>	$2.17 \times 10^{-3}$ , $2.54 \times 10^{-3}$	25 °C	$2.4 \times 10^{-3}$	[20] <sup>3</sup>
		40 °C, 0–81% HR <sup>1</sup>	$1.20 \times 10^{-3}$ , $1.32 \times 10^{-3}$	35 °C	$1.9 \times 10^{-3}$	[20] <sup>3</sup>
		50 °C, 0–76% HR <sup>1</sup>	$7.65 \times 10^{-4}$ , $7.98 \times 10^{-4}$	45 °C	$1.4 \times 10^{-3}$	[20] <sup>3</sup>
		70 °C, 0–40% HR <sup>2</sup>	$3.61 \times 10^{-4}$	25 °C	$2.7 \times 10^{-3}$	[21]
	$Q_s$	12 $\mu\text{m}$ films	–36, –32	1500 Pa	–21.9	[20] <sup>3</sup>
PE	$S$	BO-PET 250 $\mu\text{m}$	–33			
		25 °C, 0–45% HR	$1.48 \times 10^{-4}$	25 °C	$3.1 \times 10^{-5}$	[21] <sup>4</sup>
		40 °C, 0–66% HR	$1.10 \times 10^{-4}$			
		50 °C, 0–67% HR	$8.31 \times 10^{-5}$			
		60 °C, 0–41% HR	$6.20 \times 10^{-5}$			
PP	$s$	25 °C, 0–65% HR	$9.72 \times 10^{-5}$	25 °C	$1.8 \times 10^{-5}$	[21] <sup>4</sup>
		25 °C, 0–82% HR	$8.87 \times 10^{-5}$			
		25 °C, 0–72% HR	$7.31 \times 10^{-5}$			
		25 °C, 0–41% HR	$6.69 \times 10^{-5}$			

<sup>1</sup> PET 12  $\mu\text{m}$ , mean value for 2 ref. (PET1 and PET2, the latter metalized or not) and BO-PET 250  $\mu\text{m}$ .

<sup>2</sup> PET2 12  $\mu\text{m}$  (mean value for this ref., metalized or not).

<sup>3</sup>  $\chi_c = 52\%$ .

<sup>4</sup> Method using tritiated water.

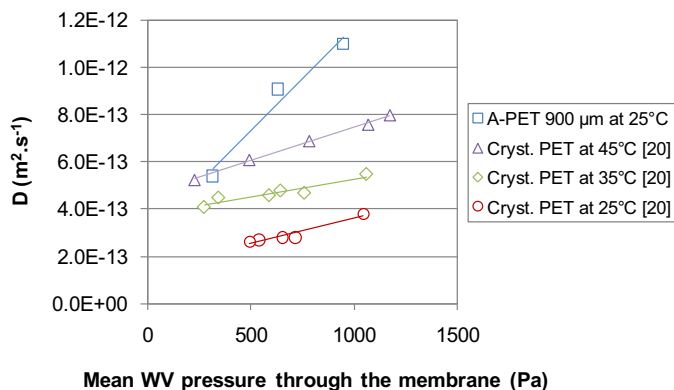
**Table 11**  
Comparison of author's results and data from literature ( $D$  in  $\text{m}^2 \text{s}^{-1}$ ).

Material	Coefficient	Author's results		Literature data		
		Conditions	Value	Conditions	Value	Ref.
A-PET	$D$	23 °C–10 to 80% RH	$6.2 \times 10^{-13}$	20 °C–100% RH	$5 \times 10^{-13}$	[24]
		23 °C–50% RH	$5.5 \times 10^{-13}$	30 °C–100% RH	$14 \times 10^{-13}$	[24]
		25 °C–20% RH	$5.3 \times 10^{-13}$	25 °C	$8.2 \times 10^{-13}$	[25]
		25 °C–10% RH	$5.4 \times 10^{-13}$			
		25 °C–20% RH	$9.1 \times 10^{-13}$			
		25 °C–30% RH	$1.1 \times 10^{-12}$			
PET	$D$	25 °C–20% RH	$3.2 \times 10^{-13}$	25 °C–66% RH	$3.8 \times 10^{-13}$	[20] <sup>1</sup>
				25 °C–33% RH	$2.6 \times 10^{-13}$	[20] <sup>1</sup>
				35 °C–40% RH	$5.5 \times 10^{-13}$	[20] <sup>1</sup>
				35 °C–28% RH	$4.5 \times 10^{-13}$	[20] <sup>1</sup>
				45 °C–25% RH	$7.5 \times 10^{-13}$	[20] <sup>1</sup>
				45 °C–12% RH	$6.1 \times 10^{-13}$	[20] <sup>1</sup>
				25 °C	$3.7 \times 10^{-13}$	[21]
PE	$D$	25 °C–20% RH	$4.8 \times 10^{-13}$	25 °C	$2 \times 10^{-11}$	[21]
PP	$D$	25 °C–20% RH	$5.0 \times 10^{-13}$	25 °C	$2 \times 10^{-11}$	[21]

<sup>1</sup>  $\chi_c = 52\%$ .

Another interesting point to note is that Shigetomi [20] finds like us a slight influence of the humidity on the diffusion coefficient of water vapor in crystallized PET.

Both results show a linear dependence of the diffusion coefficient (Fig. 11). Our results on amorphous PET (Table 9) show a positive slope of  $9 \times 10^{-16} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$  and the results from Shigetomi on a hardly crystallized PET ( $\chi_c = 52\%$ ) a mean slope of



**Fig. 11.** Dependence of the diffusion coefficient with the mean water vapor pressure in membrane of PET (A amorphous; for [20]  $\chi_c = 52\%$ ).

$2.2 \times 10^{-16} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$ . This positive slope is compatible with a slight plasticizing effect of the water molecule on PET, but the effect observed here is of the opposite sign of the one identified from the permeation through VIP laminates (Section 3.1.3). This discrepancy cannot be explained at the moment and other authors like Yasuda [21] found no influence at all of the humidity on permeation and diffusion at 25 °C.

Concerning diffusion in other films (PE and PP), some further work is planned, including the determination of the activation energies in all the single films studied. As for solubility, the few results available from Yasuda and Stannett [21] are not in agreement with our first ones (Table 11).

### 3.4.3. Overall influence of temperature and humidity

Concerning first the influence of the temperature, the direct determination of  $s$  and the indirect determination of  $D$  give values corresponding to the permeance measured through the weight gain on VIPs.

Second this allows to use with confidence the activation energies to evaluate both the severity of the different applications or conditions, and the acceleration factor of accelerated aging tests [17]. Indeed:

- The two methods used for the diffusion measurement agree on non metalized films, and match with the literature data, therefore

the method based on the transient stage of the permeation test is relevant;

- This last method, based on the exploitation of the transient regime of permeation tests, is the only relevant one for metalized films and laminates because of the single flux imposed through all the layers;
- The activation energy  $Q_{\Pi}$  ( $26 \text{ kJ mol}^{-1}$ ) is based on a large number of tests made with the VIPs.

Nevertheless, some improvement remains needed because the agreement between the activation energies corresponding to Eq. (16), obtained by mixing Eqs. (1), (11) and (13) ( $Q_{\Pi} = 26$ ,  $Q_s = -34$  and  $Q_D = 54 \text{ kJ mol}^{-1}$ ) is a bit artificial; if the two first are obtained by independent tests, the identification of  $Q_D$  needs at the moment the input of  $s$  values. Further work is planned to perform independent measurements of  $D$  on laminates at different temperatures and thus an independent evaluation of  $Q_D$ .

$$\exp\left(\frac{-Q_{\Pi}}{RT}\right) = \exp\left(-\frac{Q_D + Q_s}{RT}\right) \quad (16)$$

Concerning the influence of humidity, contradictory results were found between permeation through the laminates and diffusion through non metalized PET films. This point needs additional work either with additional conditions of aging entire VIPs or direct measurements through experiments dedicated to this question.

#### 3.4.4. Permeation

Concerning permeation, some data from ZAE Bayern (Bayerisches Zentrum für Angewandte Energieforschung) are reported [3,5]. They are obtained in the same temperature interval as ours ( $25$  to  $65^\circ\text{C}$ ) on three laminates: one with a laminated aluminum layer (ref. AF), and two with two metalized layers of respectively low and high quality (ref. MF1 and MF2). These results show little influence of the temperature, and a strong influence of the relative humidity, so the exact opposite of our results. One can conclude that the behavior of the laminates relative to water vapor permeation at the VIP scale could greatly vary from a product to another.

The present experimental results exhibit no influence of the metallization on the solubility but a strong one on the diffusion. As explained earlier, the relation given in Eq. (16) appears very well verified but needs another approach to be completely reliable. If the values were confirmed, the remaining difference could be explained either by the measurement uncertainty or by the plasticization effect taken into account for the permeation and not for the diffusion.

These two points lead to the following conclusions:

- validation of the whole mechanism of permeation driven by partial pressure for water vapor; report of the work by Bouquerel for other alternatives [13].
- the model of proportionality between the permeation/diffusion coefficients of a polymer film and those of the same film metalized, governed by the equivalent surface fraction of defect  $\theta$  [6,7] and expressed by Eq. (17), is compatible with the presented results. This does not exclude other influences like the geometrical one, which is equivalent to consider not the real size of the defect but an equivalent size, taking into account the diffusion into the polymer in front of the defect. The relation of Eq. (17) corresponds also to the one written by Langowski, replacing  $1/\theta$  by what he calls the barrier improvement factor (BIF) [9].

$$\Pi_{\text{Met-PET}} = \Pi_{\text{PET}} \times \theta \Rightarrow D_{\text{Met-PET}} = D_{\text{PET}} \times \theta \quad (17)$$

Finally it has to be pointed out that the level of permeance reached at the moment by the laminates with three metalized layers (typically  $3 \times 10^{-14} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ) is obtained through a very

low apparent diffusion coefficient (typically  $2.5 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ ). As a consequence, their hygric inertia is huge: around ten days are required to reach the stationary conditions. This has already been mentioned [3] but the increase of the performance of the envelope enhances this behavior. This time to reach stationary conditions is far over the typical time constant of climatic loading, so there is a strong need for a dynamic model of water vapor permeation, the aim of further investigations.

## 4. Conclusions and outlook

The suitability of different measurement techniques aimed at determining the permeance of barrier films for VIP has been examined. For the characterization of barrier films, the manometric method with recent devices appears to be the most useful and reliable approach as it duplicates the best the real exposure conditions. The good correlation with the current reference method on VIP forms an incentive to further optimize this manometric technique.

The solubility coefficient was determined for PET and sealing films, and also for laminates. The law of mixtures allowed to estimate the solubility of the laminates, in good agreement with the measurements. As for the PET, metalized or not, the sorption isotherm is linear up to high RH, however this is not the case for the sealing layers, and as a consequence for the laminates. But this deviation from Henry's law does not impact the laminates used as VIP envelope because only the external PET layer is exposed to high RH, and the polyolefins, except if added on the outside face, will never see a high relative humidity in a VIP.

Some quantitative data of solubility and diffusion coefficients and of their activation energies are given for laminates, but they have to be consolidated, particularly concerning diffusion and also the coherence of the three activation energies of solubility, diffusion and permeation.

An important point to note is that the activation energy of diffusion is the same for metalized or non metalized PET films. As a consequence, where our previous work has shown that the metallization quality drives the permeance of the laminates, the relation between the permeance of the metalized and non metalized PET films shows that the temperature dependence of the permeance is driven by the behavior of the polymer, in other words by its diffusion and solubility behavior.

## Acknowledgments

The authors acknowledge the ANR (French National Research Agency) and the ADEME (French Agency for Environment and Energy Management) for their financial support of the BARISOL and EMMA-PIV projects, as well as IWT (the Belgian Agency for Innovation by Science and Technology) for its financial contribution to the project. They thank the industrial partners of both projects: Rexor (P. Rousset, V. Robin, B. Larriue, E. Perrin) and Microtherm (P. Van de Velde, K. de Mulder).

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