Physical characterization of sorption and diffusion of water vapor through ultra barrier envelopes for VIP

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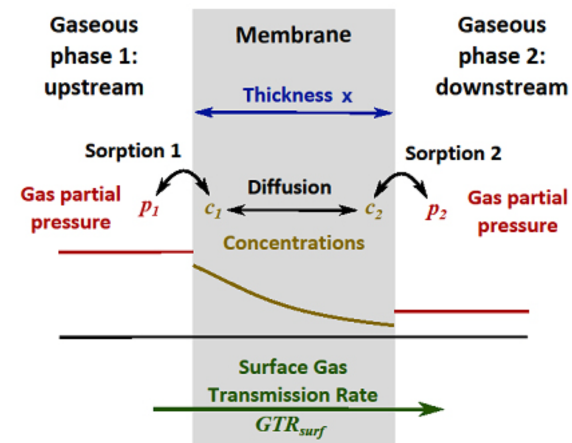
Introduction

- Prediction of VIP lifetime or conductivity => development of models
- Real service conditions: variations of T and R.H.

- Fine-tuned service life prediction: dynamic models are required
  - D_i = f(T, RH) *(i refers to air or water vapor)*
  - s_i = f(T, RH)

Gaseous transfer in a membrane: solution - diffusion model in 3 steps

- Adsorption and dissolution on the upstream side of the membrane
- Diffusion
- Desorption on the downstream side



[M. Bouquerel, Thesis , 2012]

Diffusion: Fick's Law $GTR_{surf,i} = -D_i \frac{\partial c_i}{\partial x}$

Solubility: Henry's law $c_i = s_i p_i$

- In this presentation: only water vapor

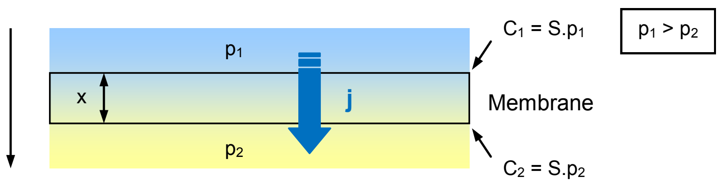
Introduction: permeance, solubility & diffusion

- For a single film: expression of the permeance Π

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

where

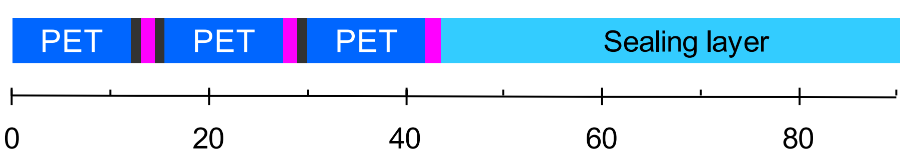
x	=	thickness of the membrane
D	=	diffusion coefficient
s	=	solubility coefficient

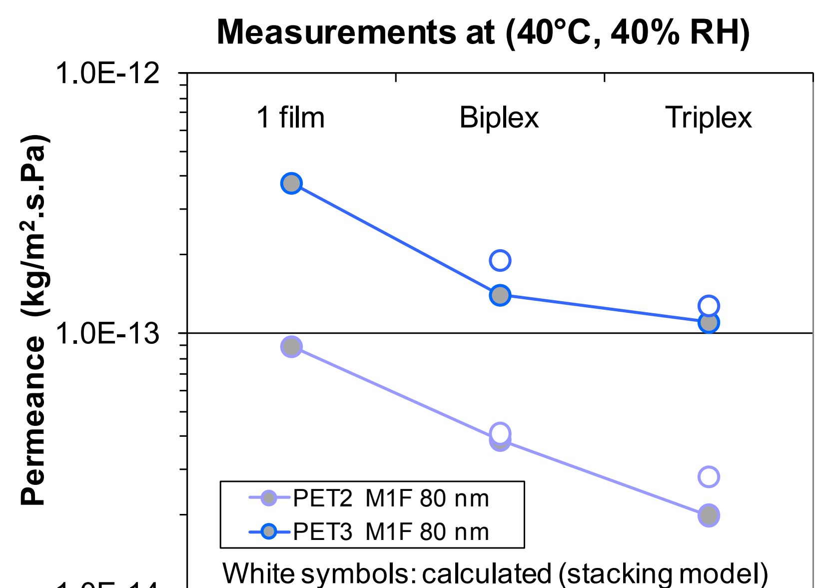


- For a multilayer film: D and s in the previous eq. replaced by the *equivalent* diffusion and solubility coefficients, and a stacking model of “ideal multilayer” was verified for Π by measurements:

$$\Pi = \frac{1}{\sum_{i=1}^{n} \frac{1}{\Pi_i}} = \frac{1}{\sum_{i=1}^{n} \left(\frac{x_i}{D_i . s_i} \right)}$$

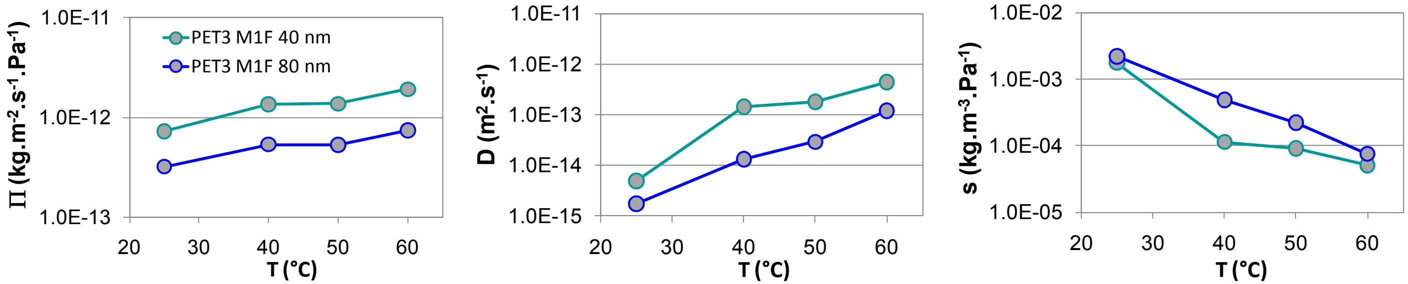
where subscript *i* refers to an individual layer





Goals

- Better comprehension of the evolution of permeance versus T and RH
  - D versus T, RH
  - s versus T, RH



First manometric measurements on single metallized films: Π and D increase with T, s decreases with T (evolution of Π controlled by evolution of D)

- Better comprehension of the role of the different layers which constitute the multilayer film

- Determination of data for modeling
  - D and s of a typical multilayer used for VIP envelope
  - D and s of single films that constitute a multilayer
    - PET films (metalized or not)
    - Sealing layers: PE or PP
    - Upcoming: glue

How do we measure Π, D and s?

Permeance

	Direct measurement	Indirect measurement
Π	Manometric method on foils (Deltaperm, *Technolox*) (water vapor only)	Weight gain on VIPs in climatic chambers (water vapor and air simultaneously)

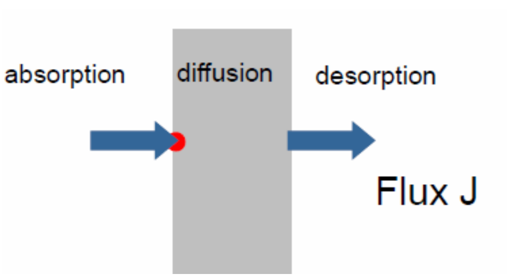
For more details, see:
L. Heymans, B. Yrieix & E. Pons
« Permeation of water vapor through high performance laminates for VIP »

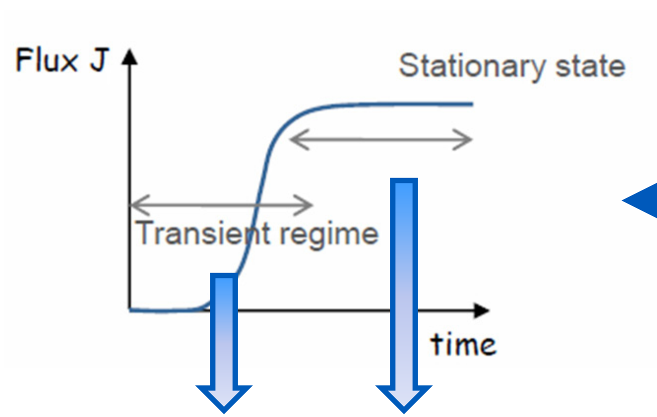
Solubility and diffusion coefficients

	Direct measurement	Indirect evaluation
s	– Water vapor sorption isotherms (Belsorp Aqua, *Bel Japan*) – Dynamic water vapor sorption (IGAsorp DVS, *Hiden Isochema*)	Deduced from Π and D measurements
D	– Permeation on foils (transient regime) (Deltaperm, *Technolox*) – Dynamic water vapor sorption (transient regime)	Deduced from Π and s measurements

Permeation and sorption: cross approaches

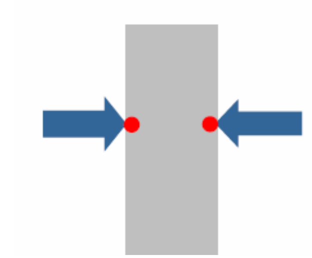
PERMEATION

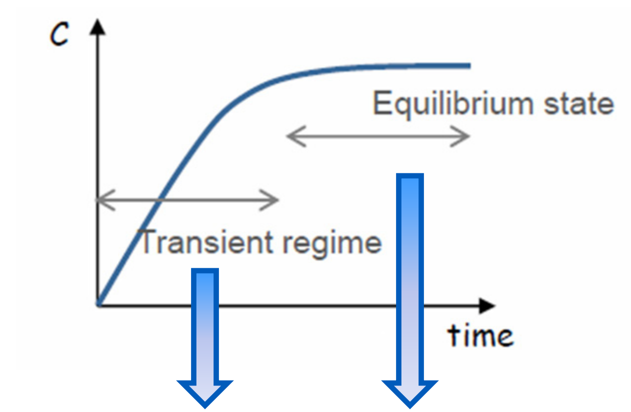




D   Π

DYNAMIC SORPTION





D   C = f(p)

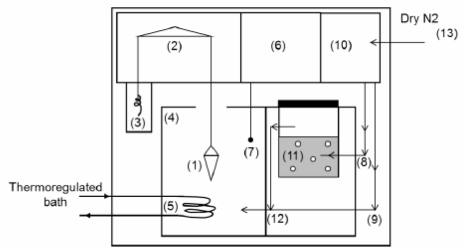
(only for homogeneous membranes)

S

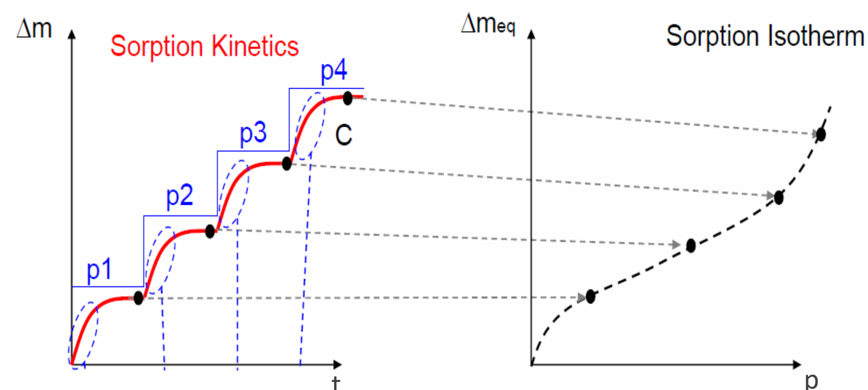
Water vapor sorption: calculation of s

- $\Delta m = f(t)$ or $\tau = f(RH)$ → $\mathbf{C = f(p)}$ → **s**

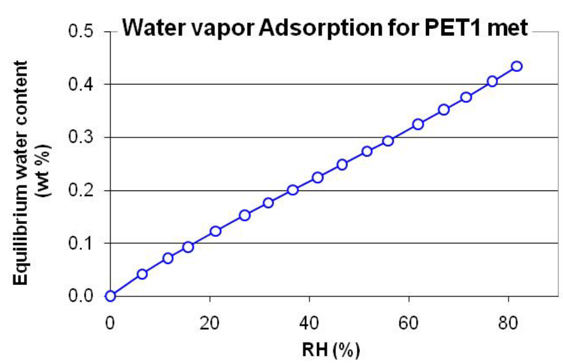
Gravimetric sorption



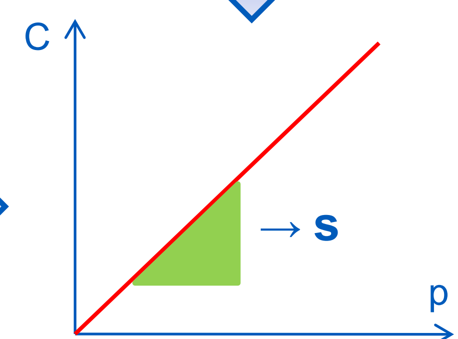
IGAsorp for water sorption



Volumetric sorption



Belsorp aqua for water sorption



s: $cm^3(STP).cm^{-3}(polymer).Pa^{-1}$
or $kg.m^{-3}.Pa^{-1}$

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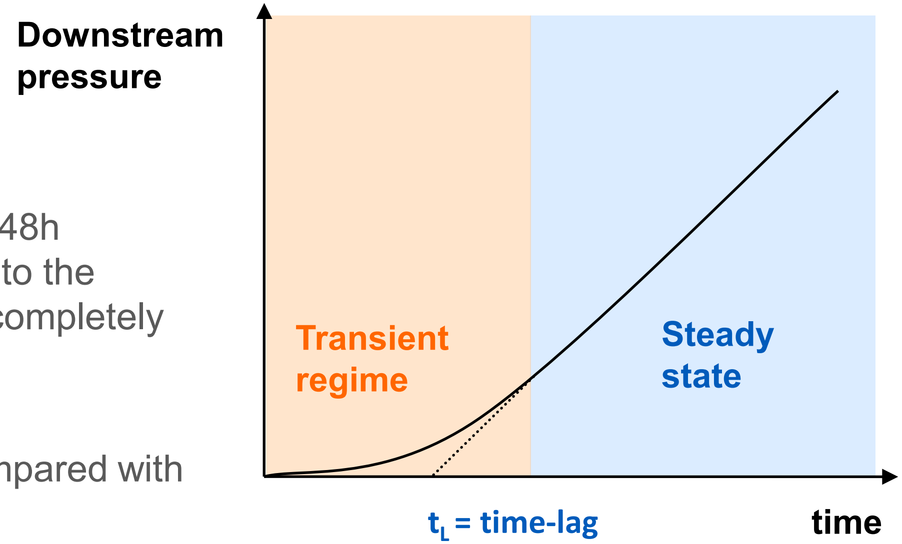
Permeation & Water vapor sorption: exploitation of the transient regime



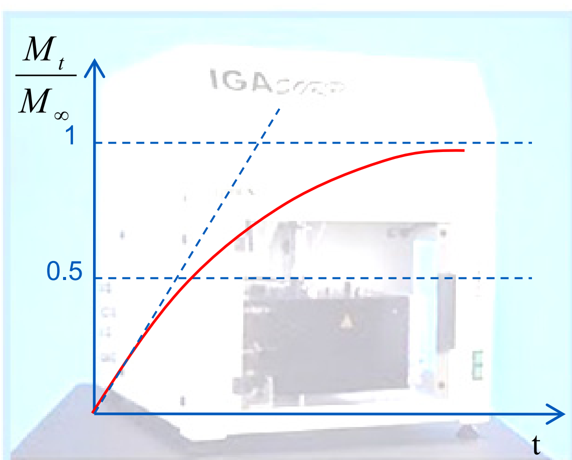
Permeation (Deltaperm)

- Required conditions
  - Preparation: vacuum drying between 3 and 48h according to the operating temperature and to the number of metalized layers to begin with a completely dry sample at initial state
  - Downstream chamber purged: $P_{down\ ini} = 0$
  - Water vapor admission upstream: quick compared with the transient regime duration

$$\boxed{D = \frac{x^2}{6.t_L}}$$

Gravimetric sorption device

- For each RH step: Model ⇒ **D**

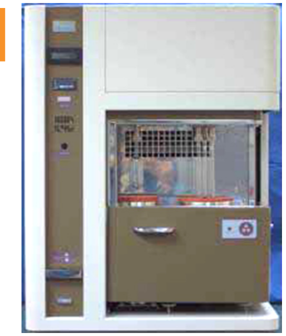


Model

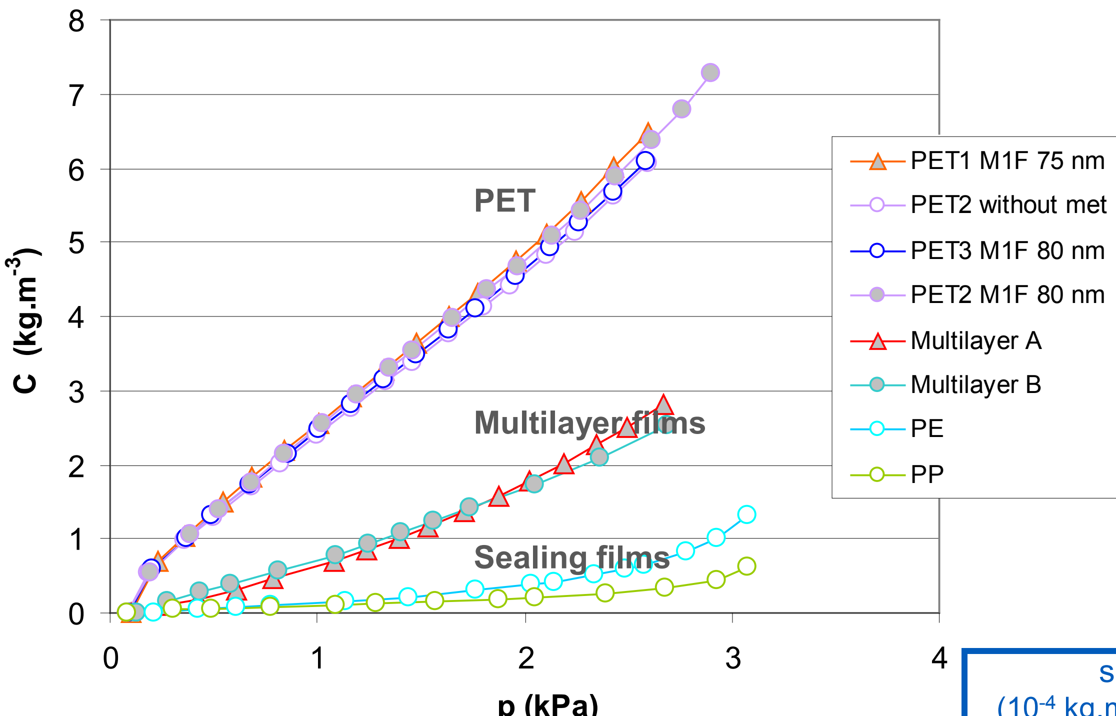
$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2\pi^2 Dt}{x^2}\right)$$

D: $m^2.s^{-1}$

Water vapor sorption: results for single and multilayer films & influence of R.H.



- 3 PET films, 2 sealing layers and 2 multilayer films, tested at 25°C



- 3 PET tested: same behavior
- PET2 with or without metalization: no significant influence on s
- PET films: good agreement with Henry's law in the tested R.H. range (up to 82%)
- Sealing films: mismatch with Henry's law for R.H. above 50% => modification of equations defining permeation
- Multilayers: intermediate solubility coefficient value

		s (10^{-4} kg.m^{-3}.Pa^{-1})	R.H. validity interval
PET (met. or not)		around 25	< 82%
Sealing layer	PE	1,5	< 55%
	PP	1	< 55%
Multilayer		5 - 10	< 55 or 75%

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Water vapor sorption

- Solubility coefficient for a multilayer
  - Calculation from the solubility coefficients of the single films that constitute the multilayer

$$s_{multilayer} = \frac{1}{V} \sum_{i=1}^{n} V_i \, s_i$$

with i referring to the individual layers

		T (°C)	Solubility coefficient (adsorption) (kg.m^{-3}.Pa^{-1}) *Linear Reg. through the origin*	R.H. validity interval	Thickness (µm)	S calculated (kg.m^{-3}.Pa^{-1})
PET M1F	PET2 M1F 80 nm	25	2.44E-03	[0 - 86%]	12.1	
		40	1.20E-03	[0 - 81%]	12.1	
Sealing film	PP	25	9.72E-05	[0 - 65%]	50	
		40	8.87E-05	[0 - 82%]	50	
Multilayer film	3-met + PP multilayer	25	8.26E-04	[15 - 75%]	90	1.04E-03
	3-met multilayer	25	2.35E-03	[3 - 77%]	39	2.27E-03
		40	1.34E-03	[2 - 46%]	39	1.12E-03

⇒ Good agreement

- Comparison between methods, and with bibliographical values for PET at 25°C

S	Volumetric method (Belsorp Aqua)	Gravimetric method (DVS)	Biblio
kg.m^{-3}.Pa^{-1}	[$2,3.10^{-3}$ – $2,7.10^{-3}$] PET 12 µm (2 diff)	$3,1.10^{-3}$ amorphous PET	$2,4.10^{-3}$ *Shigetomi et al. (2000), J. App. Pol. Sci.,76*
cm^3(STP).cm^{-3}(polymer).Pa^{-1}	[$2,9.10^{-3}$ – $3,4.10^{-3}$]	$3,9.10^{-3}$	$3,0.10^{-3}$ *Shigetomi et al. (2000), J. App. Pol. Sci.,76*

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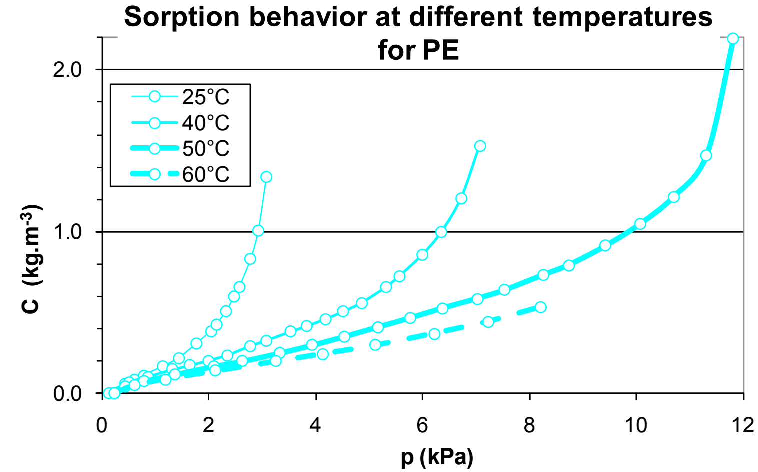
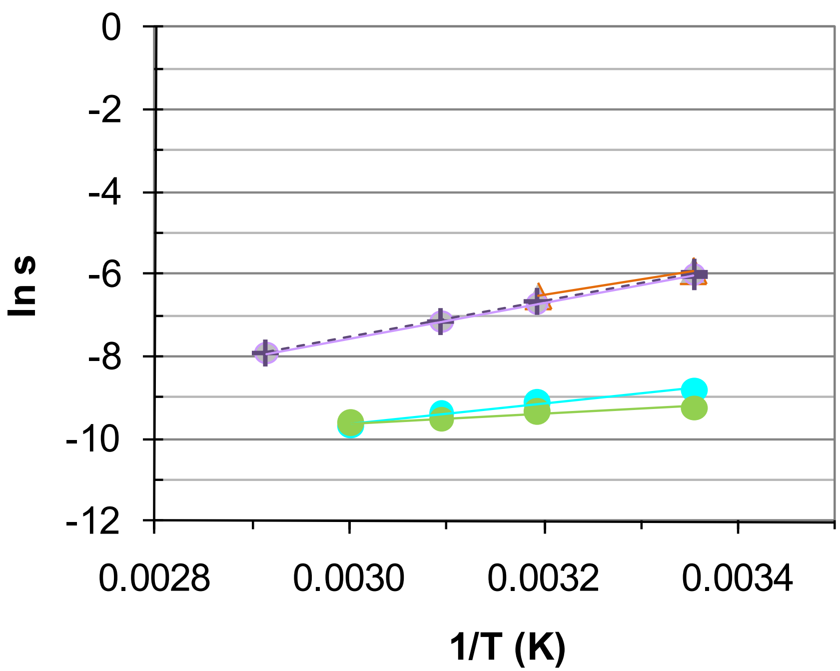
Water vapor sorption: influence of T

- Single films (PET and sealing layers): 25 < T < 70°C
  - When T increases, s decreases
    - strongly for PET
    - less for PE and more weakly for PP
  - s follows an Arrhenius law $s(T) = s_0 . e^{-\frac{Q_s}{RT}}$

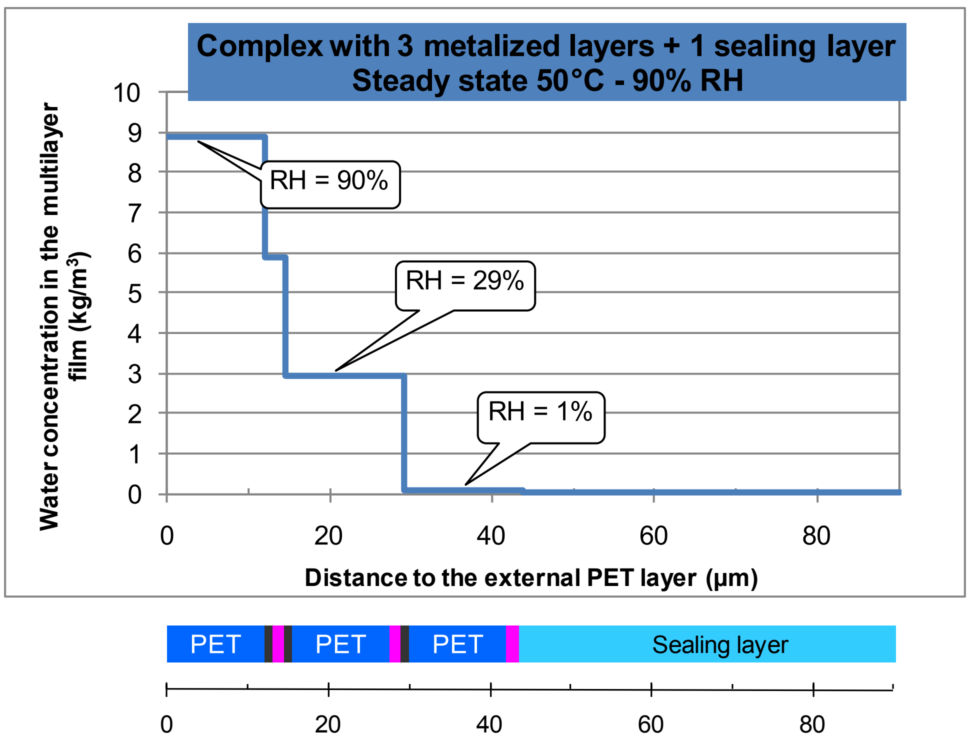




	s_0 ($kg.m^{-3}.Pa^{-1}$)	Q_S ($kJ.mol^{-1}$)
PET1 (metallized)	6.10^{-9}	−32
PET2 (metallized)	1.10^{-9}	−36
PET2 (without Al)	1.10^{-9}	−36
Sealing layer (PE)	4.10^{-8}	−20
Sealing layer (PP)	2.10^{-6}	−9

Water vapor sorption

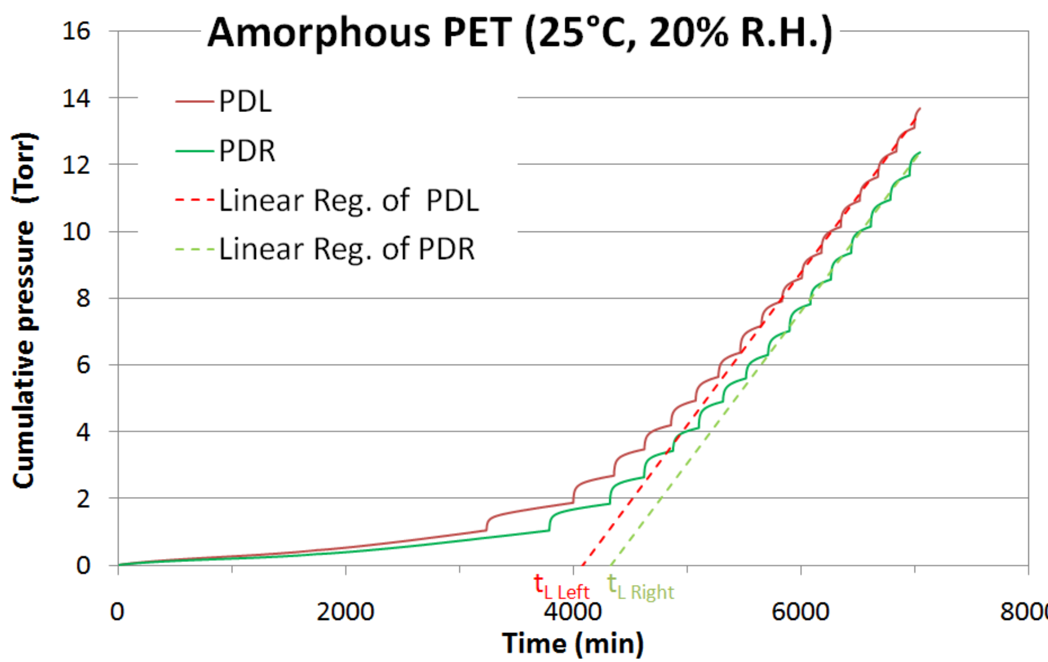
- Mismatch with Henry's law for sealing layers: do we need to change the model?
- Evolution of water concentration in the different layers of a 3 ply metalized multilayer
  - In stationary conditions (50°C, 90% R.H.)



- Only the external PET layer is exposed to high R.H.
- The internal sealing layer is exposed to R.H. << 50%

Water vapor diffusion: first results for single films

- Comparison between 2 methods and bibliographical values for amorphous PET: good agreement
- No influence of R.H. was observed on PET film between 10 and 80% => to continue

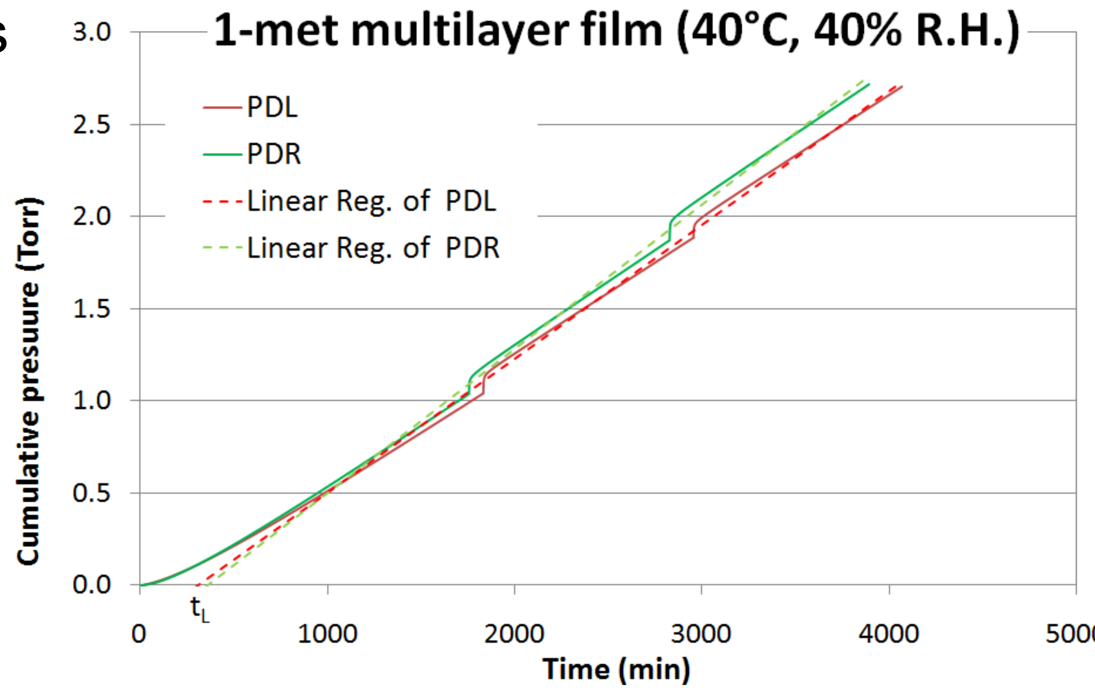


D ($m^2.s^{-1}$)	Dynamic water vapor sorption (deduced from model)	Permeation on foils (transient regime)	Biblio	
PET	**$6,3.10^{-13}$** (23°C, 10% < R.H.< 80%) Amorphous PET (900 µm thick)	**$5,4.10^{-13}$** (25°C, 20% R.H.*) Amorphous PET (900 µm thick)	**$3,5.10^{-13}$** (25°C)	*Shigetomi et al. (2000), J. App. Pol. Sci.,76*
			5.10^{-13} (20°C)	*Launay et al. (1999), J. App. Pol. Sci., 73*

* on the upstream side of the film

Water vapor diffusion: first results for multilayer films

- Permeation through foils



D ($m^2.s^{-1}$)	Permeation on foils (transient regime)
1-met + sealing multilayer	$5{,}2.10^{-14}$ (40°C, 40% R.H.*)
3-met + sealing multilayer	$9{,}2.10^{-15}$ (40°C, 40% R.H.*)

* on the upstream side of the film

Water vapor diffusion: first results for multilayer films

Influence of T

- Indirect evaluation of D, between 23 and 70°C, from Π (measured on VIPs) and s measurements

	T (°C)	R.H. (%)	Π ($kg.m^{-2}.s^{-1}.Pa^{-1}$)	$D_{1\text{-met}}$ * ($m^2.s^{-1}$)	$D_{multilayer}$ ($m^2.s^{-1}$)
Multilayer A1	70	90	1.3E-13	6.52E-15	5.35E-14
	50	90	1.2E-13	2.99E-15	2.55E-14
	40	40	7.9E-14	1.34E-15	1.17E-14
	23	50	3.4E-14	2.84E-16	2.54E-15
Multilayer A2	70	90	6.5E-14	4.89E-15	2.63E-14
	50	90	5.4E-14	2.02E-15	1.12E-14
	40	40	2.7E-14	6.89E-16	3.85E-15
Multilayer B1	70	90	8.4E-14	8.05E-15	3.85E-14
	50	90	6.8E-14	2.98E-15	1.54E-14
	40	40	4.6E-14	1.31E-15	6.99E-15
Multilayer B2	70	90	1.1E-13	1.05E-14	5.05E-14
	50	90	8.2E-14	3.59E-15	1.86E-14
	40	40	5.4E-14	1.54E-15	8.20E-15
Multilayer B3	70	90	1.4E-13	1.34E-14	6.56E-14
	50	90	7.1E-14	3.11E-15	1.59E-14
	40	40	6.0E-14	1.71E-15	8.92E-15

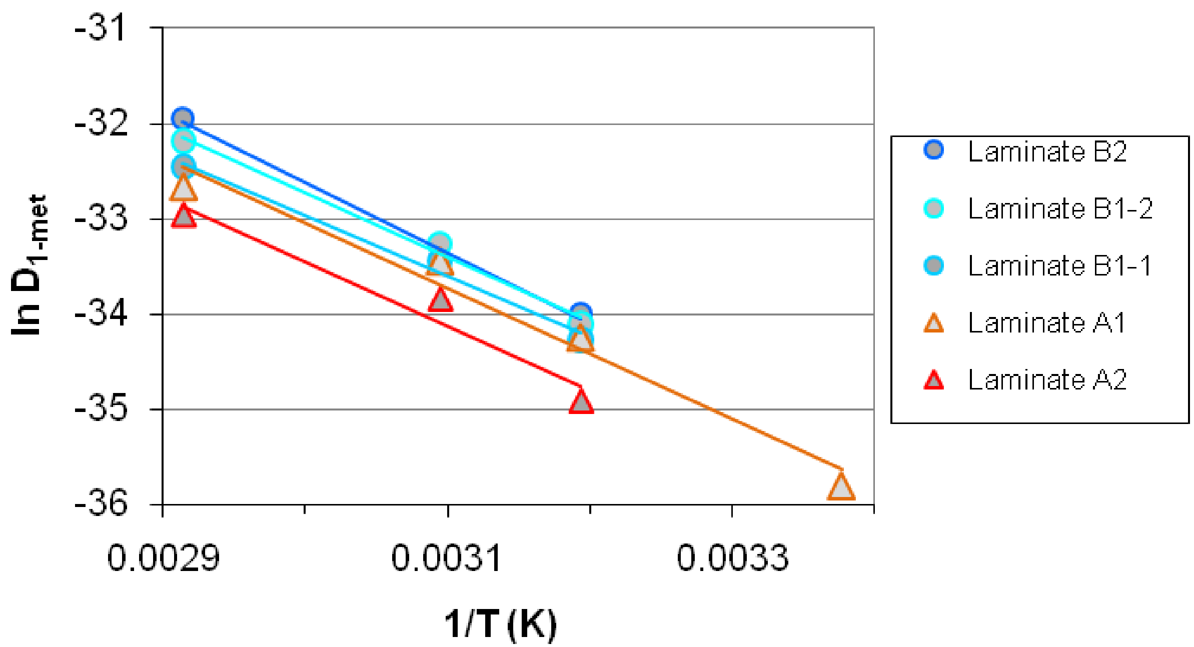
* based on experimental measurements $\Pi_{multilayer(n)} \sim \Pi_{n\text{-met}}$ (and validated relation: $\Pi_{n\text{-met}} = \frac{\Pi_{1\text{-met}}}{n}$)

- Good agreement with permeation tests on foils

Water vapor diffusion: first results for multilayer films

Influence of T

- Indirect evaluation of D, between 23 and 70°C, from Π (measured on VIPs) and s measurements



- Evaluation of the activation energy for PET M1F of 5 tested multilayers

$$D(T) = D_0 . e^{-\frac{Q_D}{RT}}$$

$\boldsymbol{Q_D}$ **= 53 to 62 kJ.mol^{-1}**

- D_0 depends on the multilayer

Conclusions and outlook

- The solubility coefficient was determined for PET and sealing films and also for multilayer films
  - The law of mixtures allowed to estimate the multilayer solubility
- Henry's law
  - OK for PET: the sorption isotherm is linear up to high R.H.
  - Not valid for the sealing layers and as a consequence for the multilayer films above 50% R.H.
  - However this deviation does not impact the studied multilayer films because only the external PET layer is exposed to high R.H.
- Both coefficients follow Arrhenius' law
  - $Q_S < 0$ and $Q_D > 0$
  - Good agreement with the activation energy determined for permeance: $Q_\Pi \sim 26$ kJ.mol^{-1}

Mean values for 1-met	Q_D	Q_s	Q_Π
kJ.mol^{-1}	57	-35	26

- Some quantitative data of s and D are given
  - Solubility: for simple films (determination for multilayer films by law of mixtures)
  - Diffusion: first measurements for PET (good agreement between the methods) and first evaluation from Π and s for multilayer films => to be consolidated

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Special thanks to industrial partners:

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