Degradations of barrier multilayer films exposed to high temperature and/ or humidity

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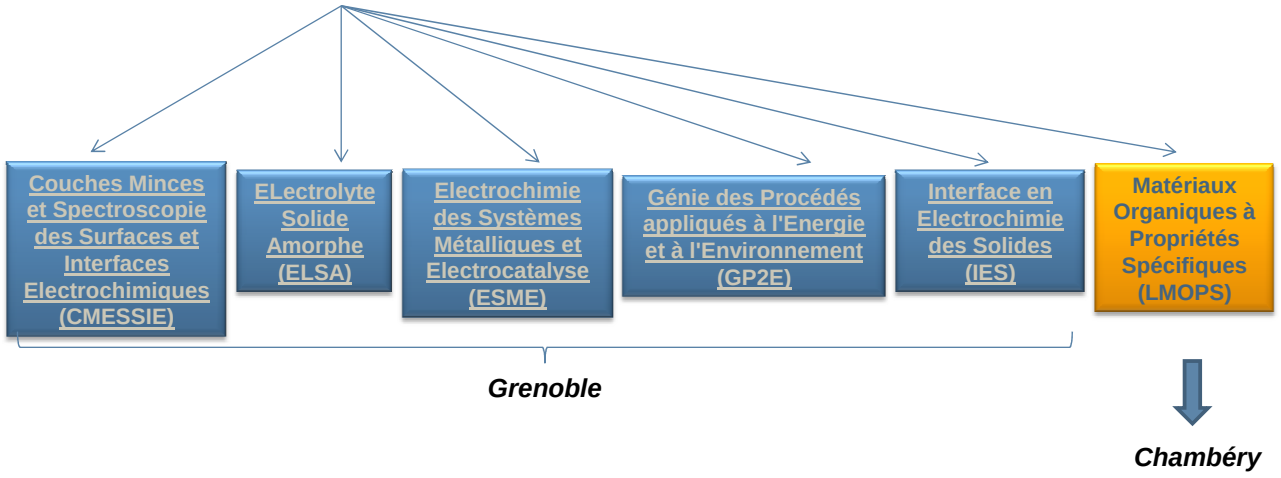
G. Garnier , Y. Bréchet[2], L. Flandin[1], F. Dubelley[1], E. Planès[1], C. Bas[1], E. Pons[4], B. Yrieix[4]

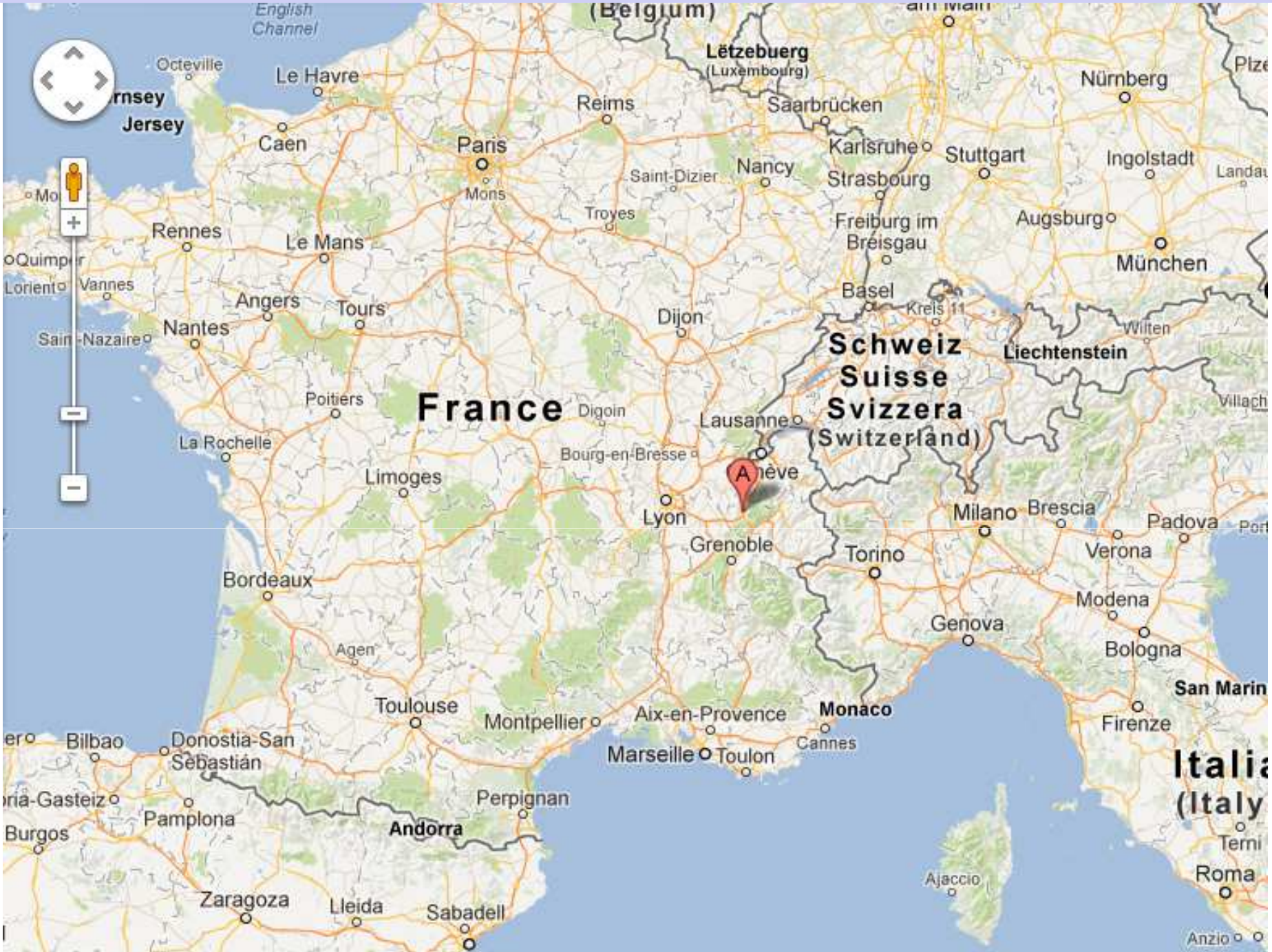
1 - LEPMI - UMR 5279 CNRS - Université de Savoie - France
2 - SIMAP, UMR 5266 - Grenoble-INP, France
3 - CSTB, 38400 Saint-Martin-d'Hères, France
4 - EDF R&D, MMC Moret-sur-Loing Cedex, France

Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces



Director : Prof Ricardo Nogueira

- 80 permanent researchers
- 80 PhD students
- 10 post doc
- 10 administrative people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Nancy
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People @ LMOPS :

- 11 permanent researchers (Prof. and assistant Prof.)
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- 2 post doc
- 3 administrative people

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How about you ?

We appreciate to receive résumés, we do have fundings.

We focus on polymeric materials with specific functionalities for energy and their durability.

- Vacuum Insulation Pannels ...

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We appreciate to receive résumés, we do have fundings.

We focus on polymeric materials with specific functionalities for energy and their durability.

- Vacuum Insulation Pannels
- National National Institute for Solar Energy (INES)
- Polymers for fuel cells
- Dielectrics and semi conducting materials

Outline

Goal :

- Optimizing the structure of the envelope (polymer + metal)
  - ✔ Initial state
  - ✔ After aging

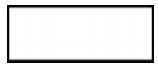
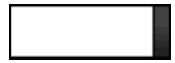
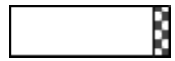
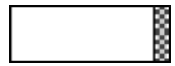
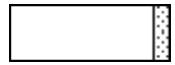
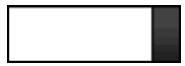
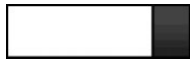
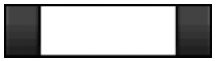
G. Garnier, Y. Brechet, *et al.*, *J Mater Sci*, 44 (2009)(17) :4692

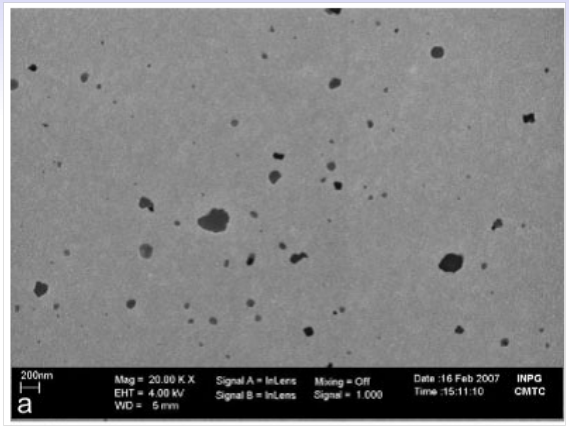
G. Garnier, B. Chehab, *et al.*, *J Mater Sci*, 44 (2009)(20) :5537

G. Garnier, B. Yrieix, *et al.*, *J Appl Polym Sci*, 115 (2010)((5)) :3110

G. Garnier, B. Yrieix, *et al.*, *Polym Adv Technol*, 22 (2011)(6) :847

Outline

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



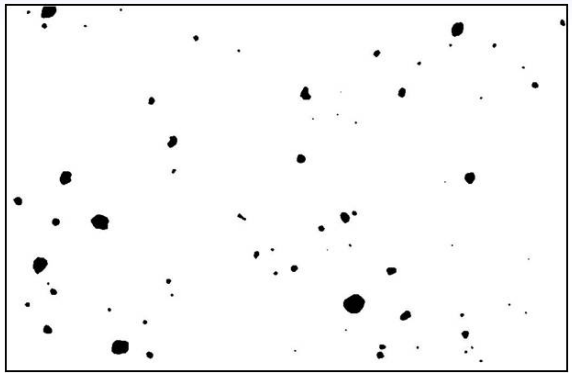
Warning

The aluminum layer might present many pinholes [a]

a. The film quality has now been improved **a lot**

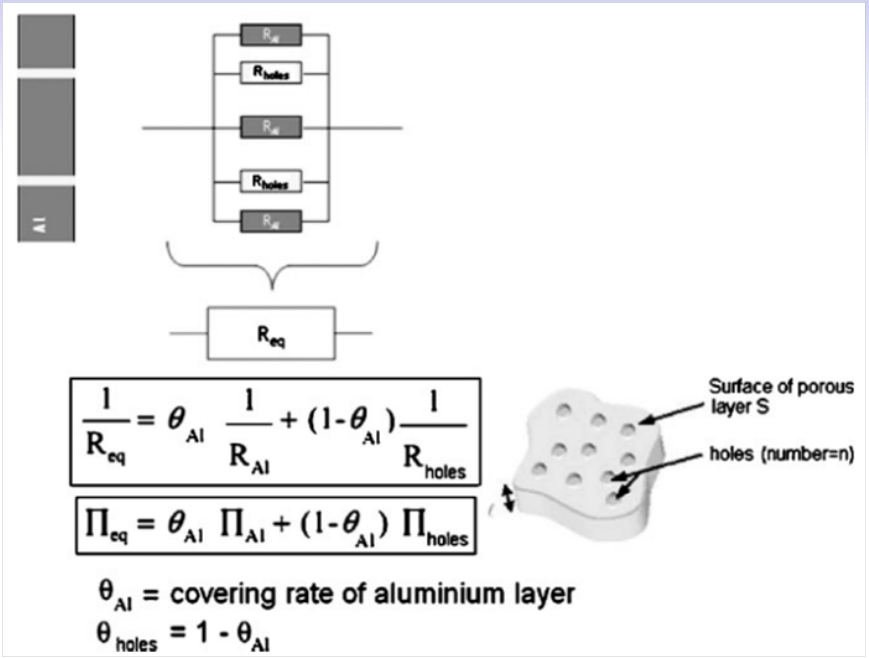
Question

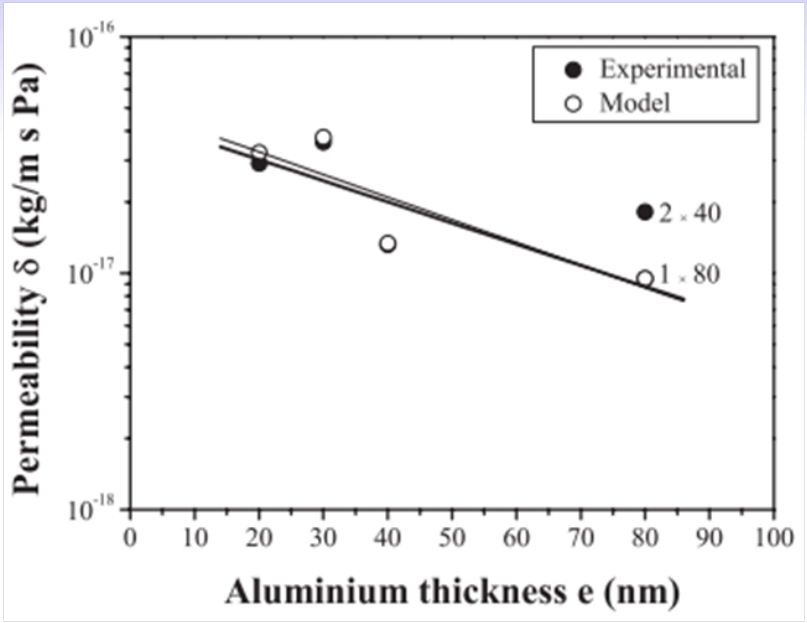
- How do they alter the initial properties ?
- How do they age ?



Method :

1. Count the number pinholes, their sizes and surface fraction.
2. Measure the barrier properties
3. Compare the two





Conclusions :

- ✔ The series + parallel model describes the results
- ✔ The pinholes are primarily responsible for permeation
- ✘ The time to make the measurements is very long

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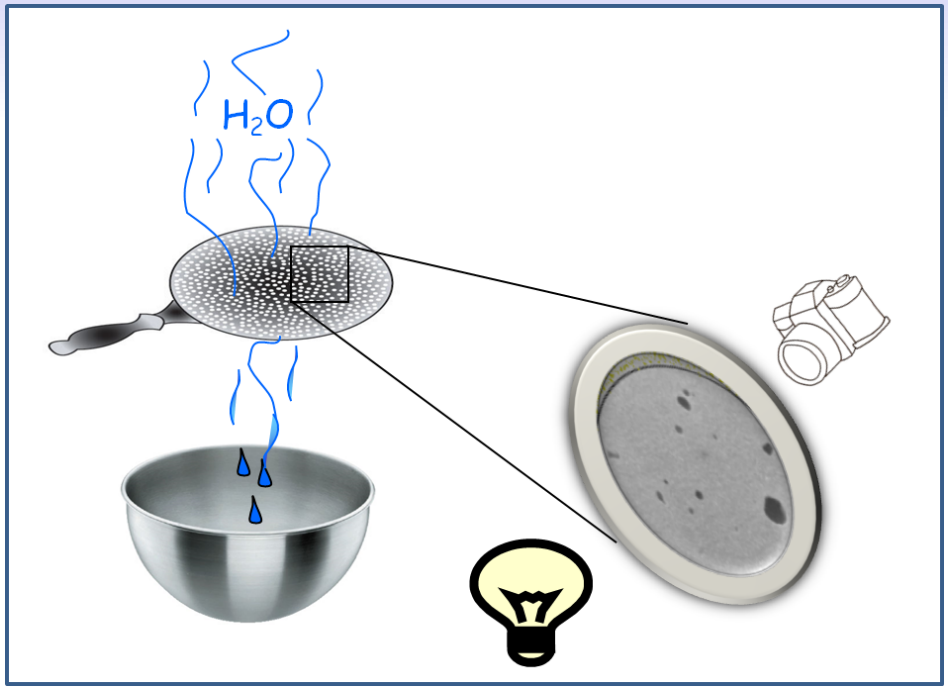
Outline



Another approach :

Try and estimate the permeation (gas or water) by measuring the amount of light that may go through the sample.

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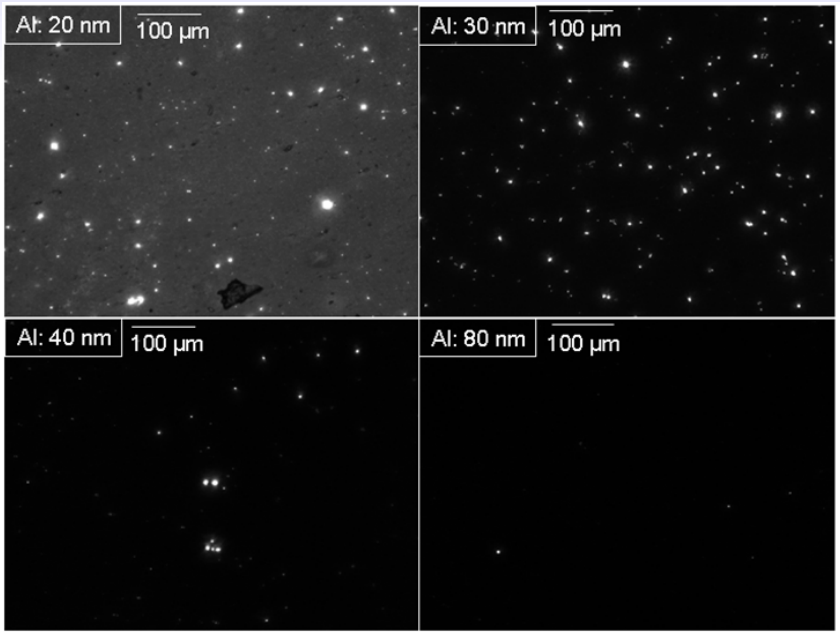
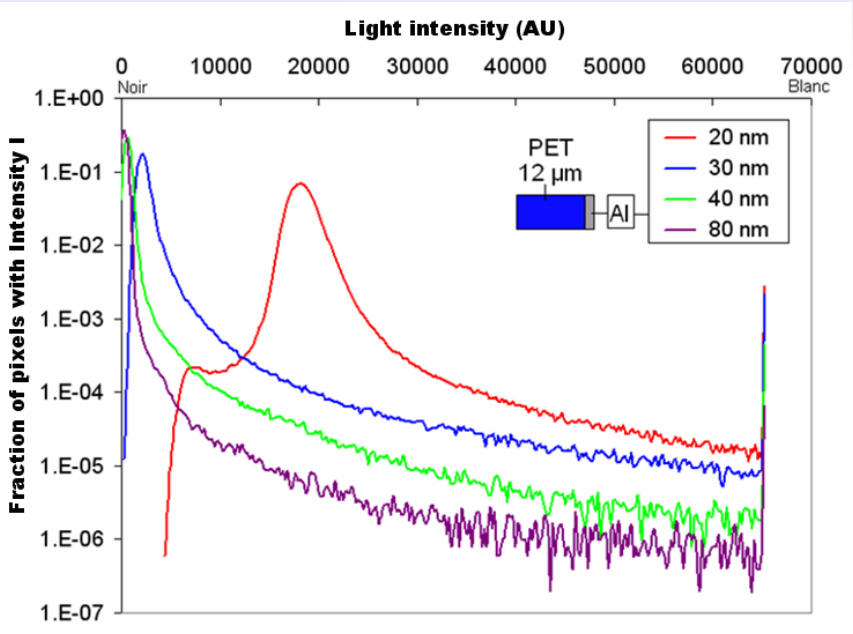
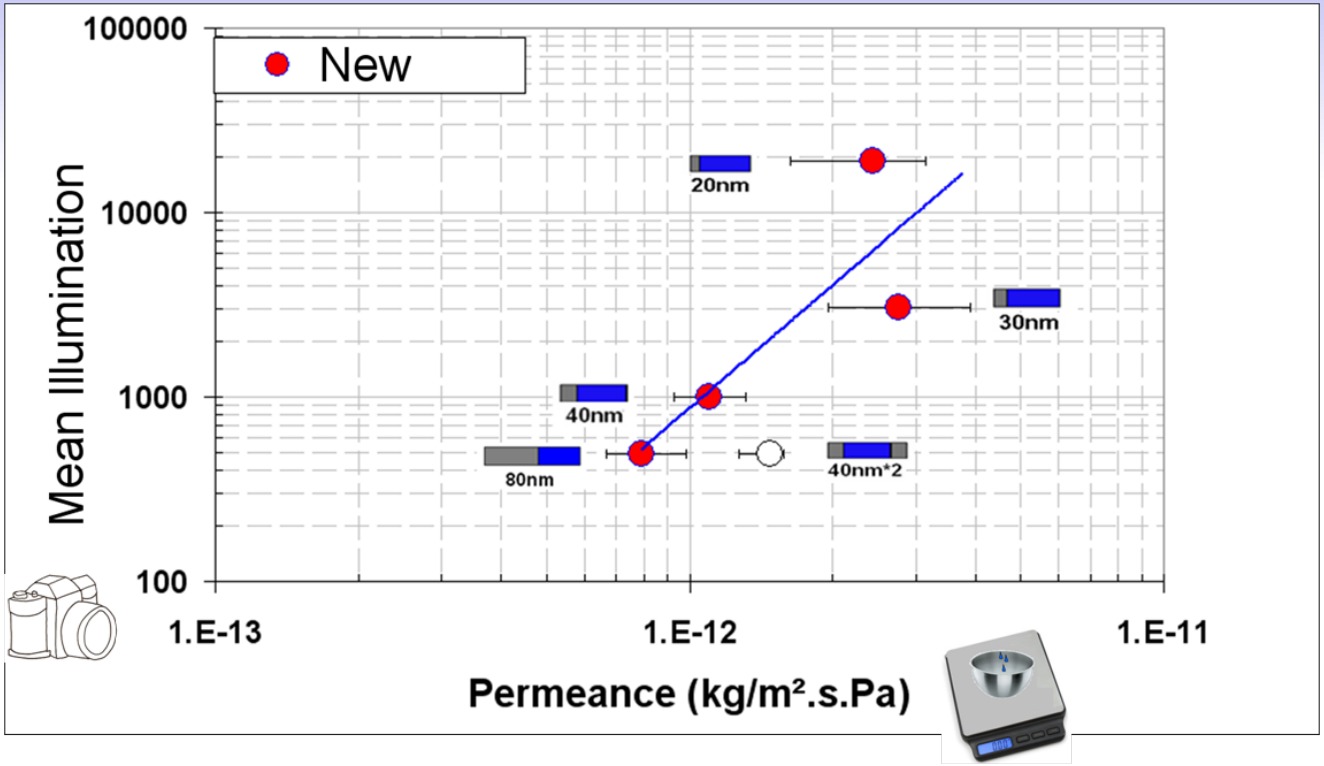
A. Combessis, C. Mazel, *et al.*, *J Appl Polym Sci*, 130-3 (2013) :1778





? Question

- The optical density is commonly employed to estimate the aluminum thickness
- Does it correlate to the permeation ?



Practical applications :

The measurement of the optical density with an OM may help reveal the permeation.

Is it also useful for characterizing the aging ?

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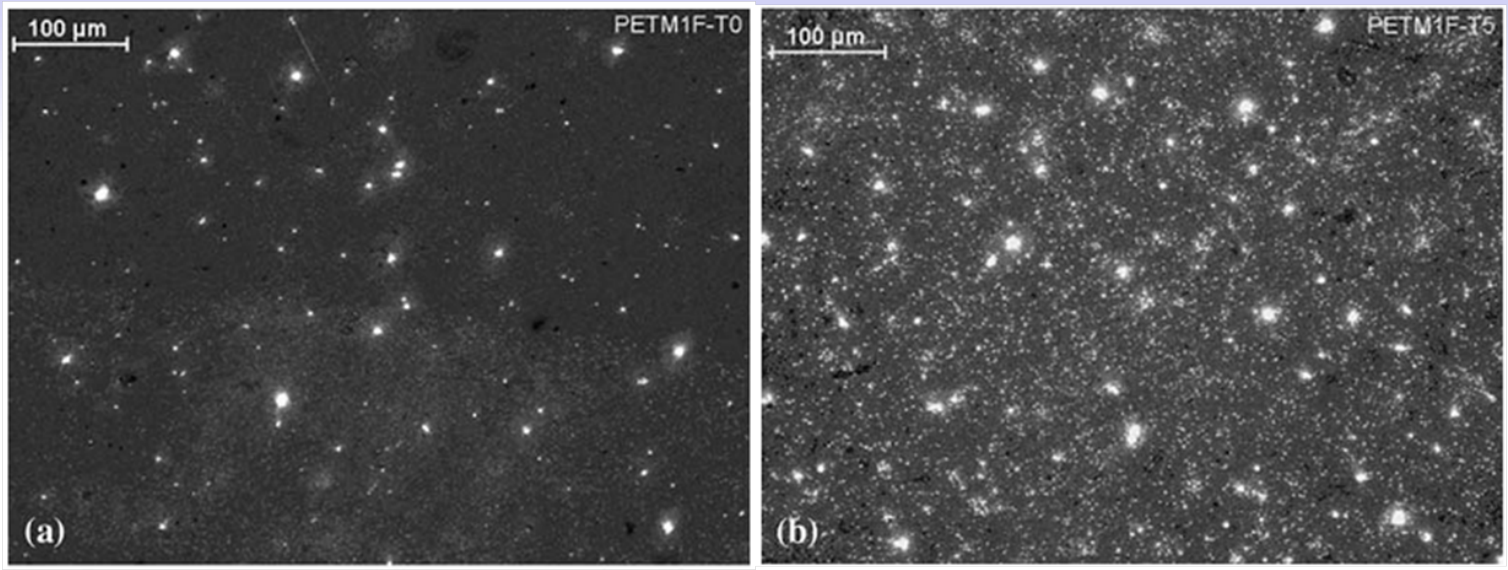
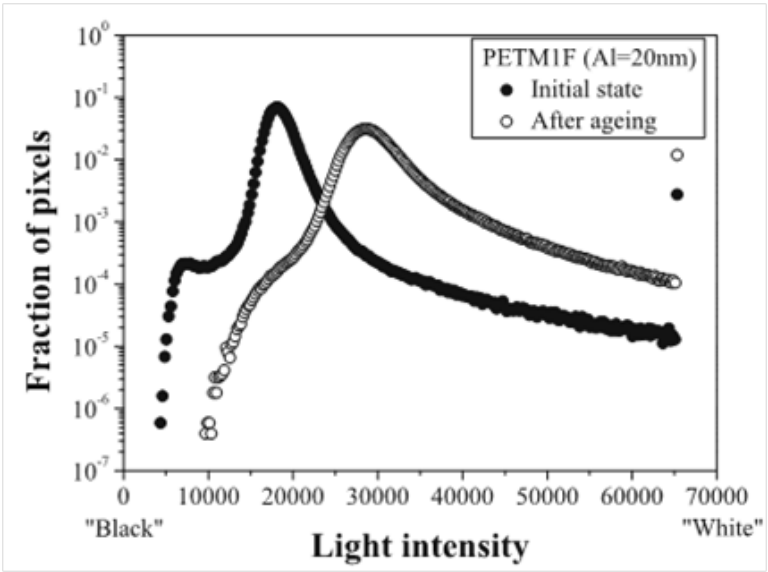
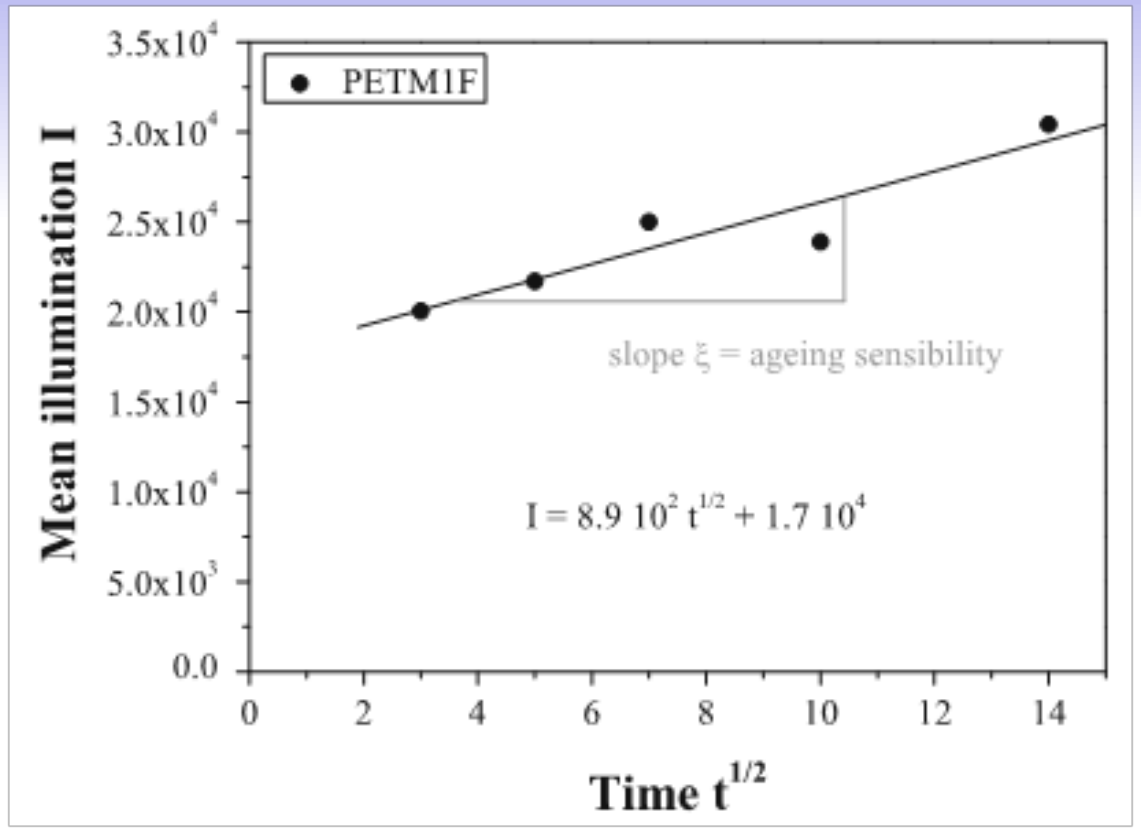




Conclusions :

With 20 nm Al a 192 days at 70 ^{o}C-90% RH dramatically reduces the optical density

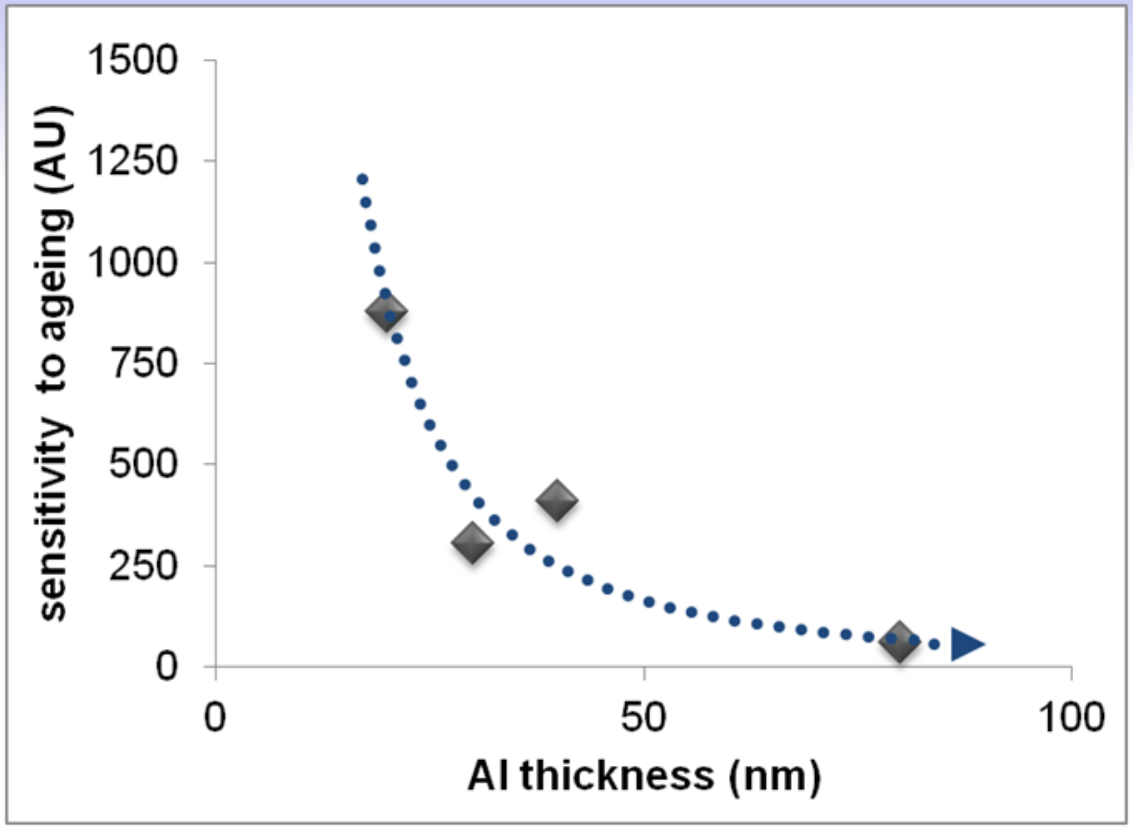


Practical applications :

The "mean illumination" (OD) increases like $t^{\frac{1}{2}}$

✔This is a simple way to probe the degradation

✔One may compare the slopes between samples (sensitivity parameter)



Conclusions :

Thicker Al layer improves the durability [a]

a. K. Rao, K. Rao, *Trans Indian Instit Met*, 57 (2004) :593,

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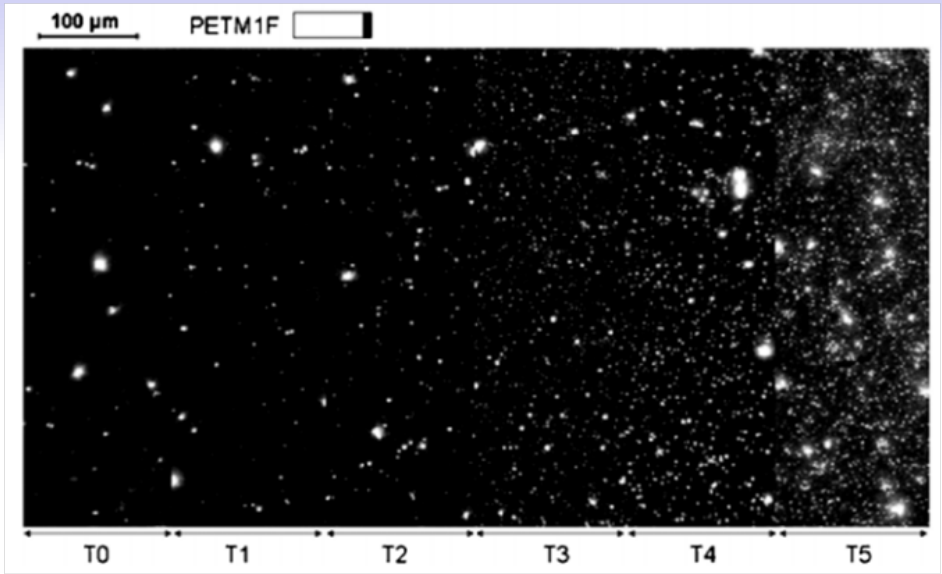
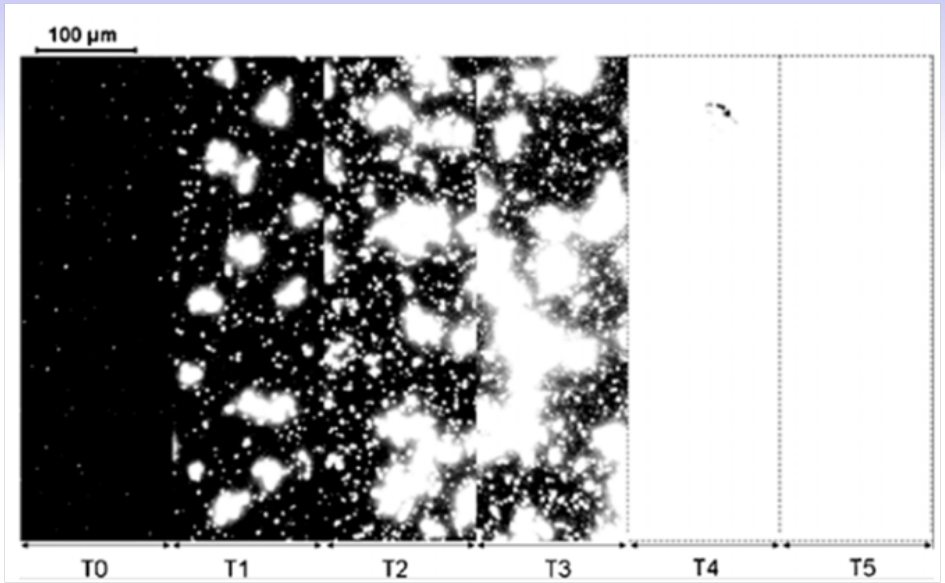
Outline



Glue D



Glue A

Conclusions :

The chemical nature of the interface strongly alters the degradation mechanism

Presence of chlorine ? [a]

a. K. Rao, K. Rao, *Trans Indian Instit Met*, 57 (2004) :593

	Elementary chemical analyses				
Products	Cl (ppm)	C (%)	H (%)	N (%)	O (%)
A	30	58.68	5.74	10.16	25.03
B	45	63.34	6.11	8.91	21.46
C	25	61.50	7.26	<0.30	31.13
D	17	61.89	9.04	2.34	25.19
E	34	58.94	5.75	9.87	25.56
F	<10	70.04	8.08	4.46	15.02
G	<10	61.68	7.03	<0.30	29.23

Conclusions :

✔ The presence of chlorine favors the degradation

✘ It is however not necessary nor sufficient

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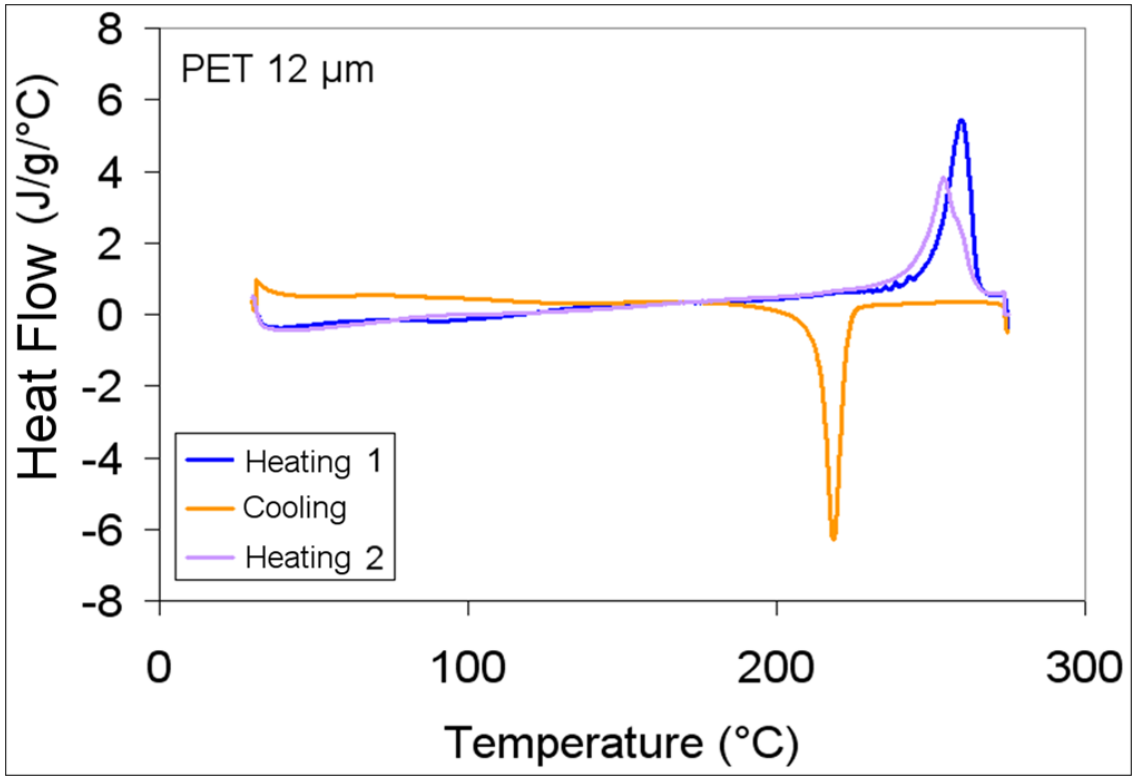
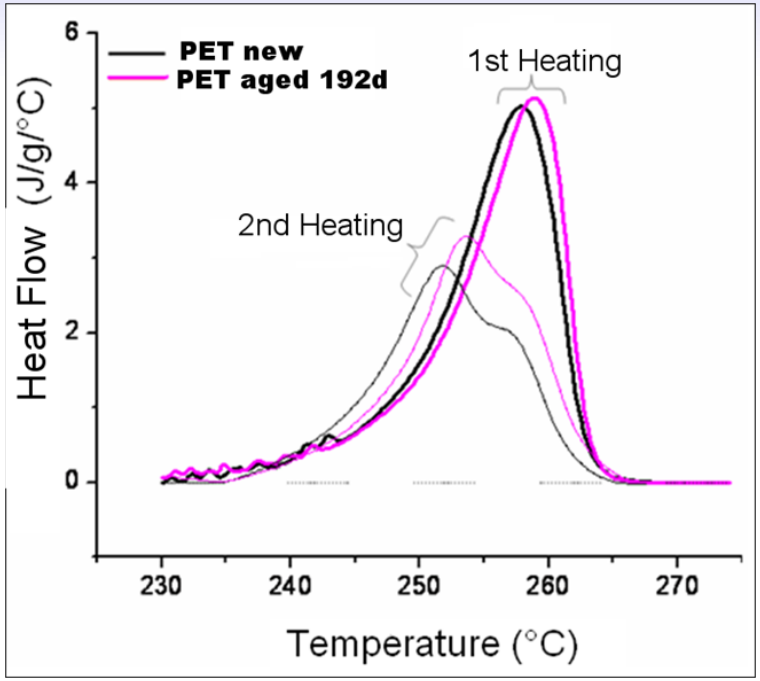
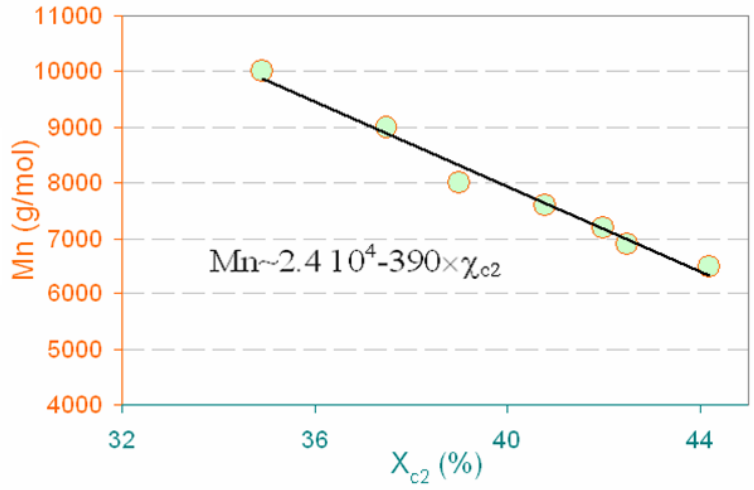
Outline

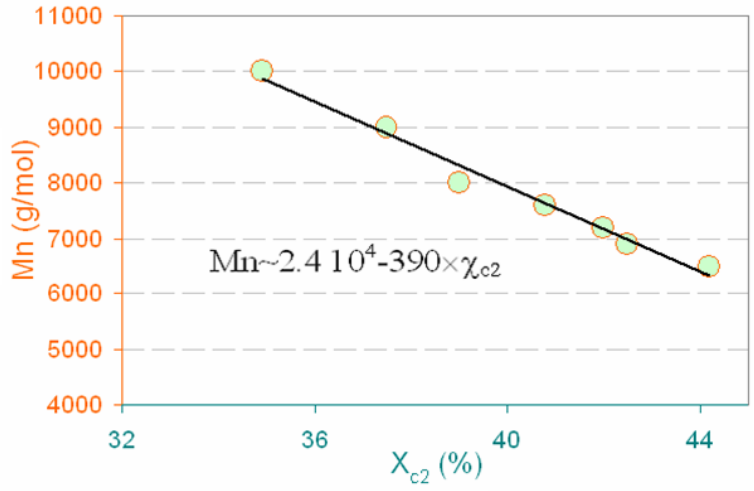

PET 12 µm
Heat Flow (J/g/°C)
8
6
4
2
0
-2
-4
-6
-8
Heating 1
Cooling
Heating 2
0
100
200
300
Temperature (°C)

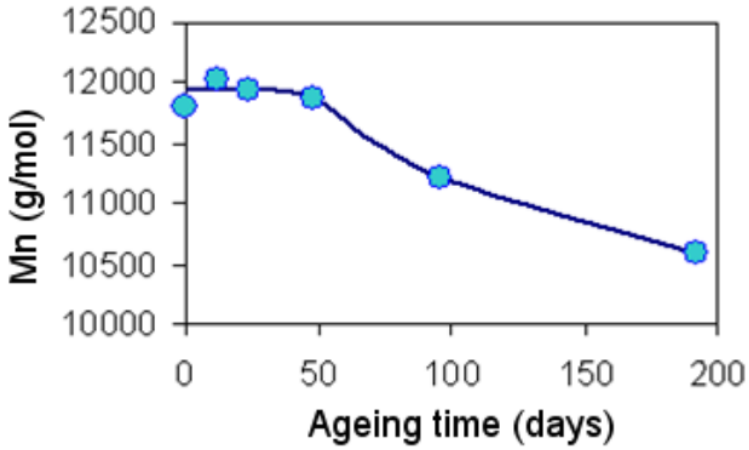


Conclusions :

The first and second ramps are different (Biaxially stretched)
Aging alters the crystallinity in second heating ramp (polymer)


11000
10000
9000
8000
7000
6000
5000
4000
Mn (g/mol)
Mn~2.4 10^4-390×χc2
32
36
40
44
Xc2 (%)

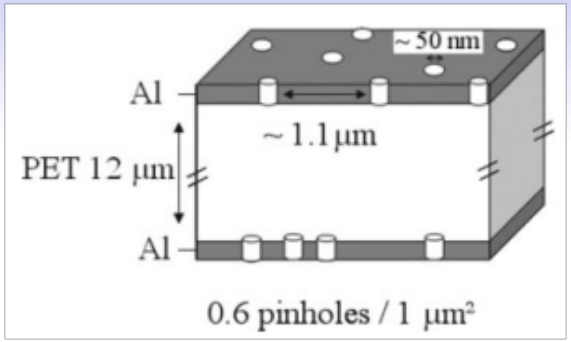




Conclusions :

The molecular weight of PET is reduced by about 20 % (chains scissions)
No difference in IR and Raman spectra

Outline



Conclusions :

- Metalized PET may contain pinholes
- Permeation may be followed with light
- The Al degradation is favored by :
  - ✗ temperature,
  - ✗ humidity
  - ✗ chlorine
  - ✗ thin Al layers
- PET itself degrades (chains scissions) evidenced in the molten state

Aknowledgements :

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- S Kerrouf ADEME
- D Quénard, C Pompéo CSTB
- V Robin, P Rousset and M Chauvois Rexor
- ADEME for sponsorship
- ANR through the BARISOL

Acknowledgments

Thanks to the organizers :-)

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Thanks to the reviewer for thoughtful comments!

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Thank you for your attention, I will be happy to try and answer your questions