Procédés et Ingénierie en Mécanique et Matériaux

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15th International Symposium on Bioplastics, Biocomposites and Biorefining

Guelph, Canada

IMPROVEMENT OF GAS BARRIER PROPERTIES OF POLYLACTIC ACID (PLA) BY LAYER MULTIPLYING CO-EXTRUSION

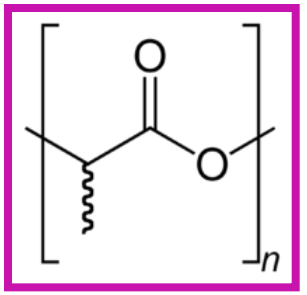
Alain GUINAULT

PIMM laboratory, UMR 8006 ENSAM/CNRS/CNAM, 75013 Paris, France

Introduction

Bio based material → PLA





- Available at the industrial scale
- Classical film or sheet processing
- Good transparency (=PET)
- Interesting for food packaging

→ *replacement of petrochemical based polymer*

Drawback: poor gas barrier properties / PET

→ Needs to divide 10x oxygen permeability

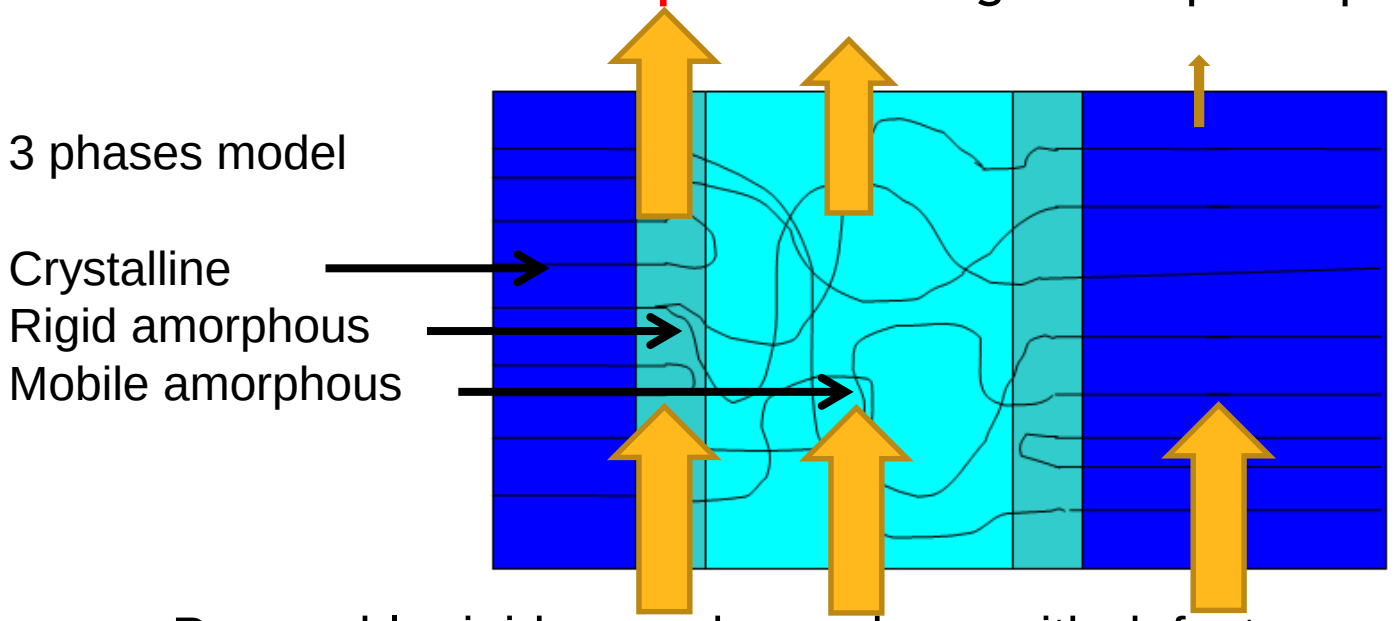
Technical solutions to enhance gas barrier properties

1. Crystallinity: slow crystallisation

Increasing crystallinity degree / orientation by annealing / biaxial stretching in order to increase tortuosity

But effects are often low (improvement barrier factor around 2 to 3)

And for PLA very low and highly dependent on the recrystallization conditions: existence of a **permeable** rigid amorphous phase (RAF)



⇨ Permeable rigid amorphous phase with defects

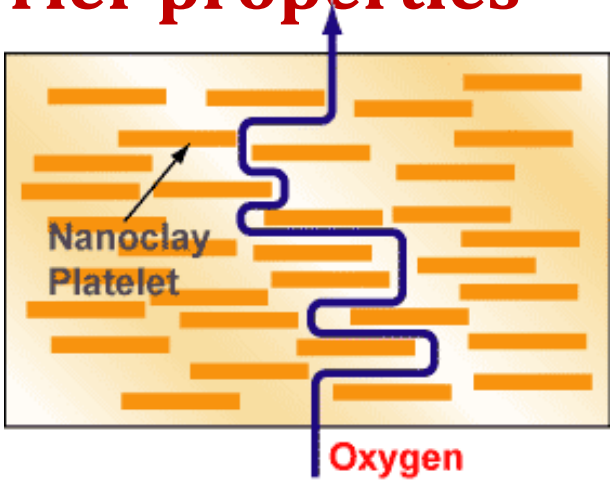
(Guinault et al, European Polymer journal, 2012, vol 48 (4), Pp 779–788)

Technical solutions to enhance gas barrier properties

2. Tortuosity:

Nanofillers

Promising way but results are also low (improvement factor until 2 to 5)



3. Classical multilayers:

2 to 5 to 10 layers with the series model:

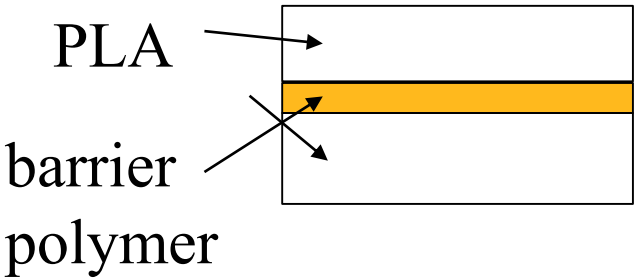
So, for 10x, need to incorporate a polymer with much better gas barrier properties < 0.006 barrer for 0_2 !!

→ No biobased polymer are available today !

$$\frac{1}{P_{film}} = \frac{\phi_{PLLA}}{P_{PLLA}} + \frac{\phi_{barrier}}{P_{barrier}}$$

PHBV	PBS	PLA	PBSA	PCL
0.03	0.20	0.32	0.74	0.9

02 Permeability in barrer (10^{-10}cc(stp).cm^3/cm^2.s.cmHg)



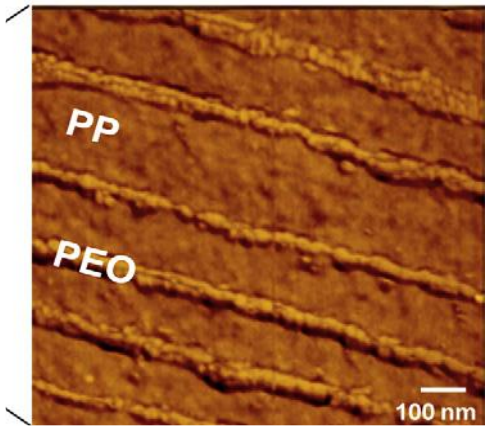
Technical solutions to enhance gas barrier properties

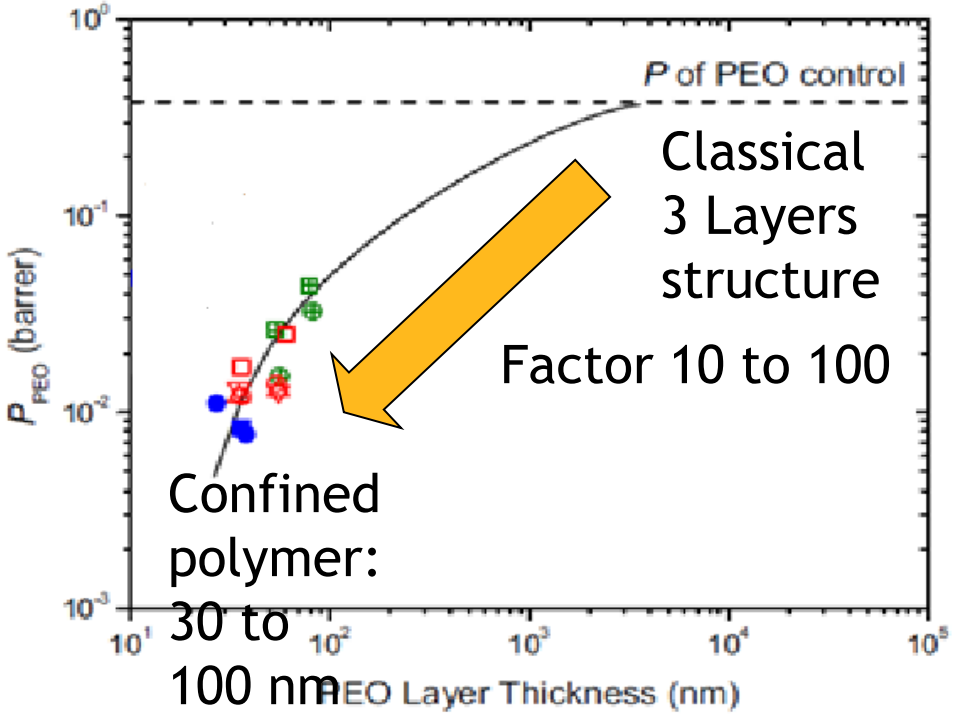
→ a new solution: the geometrical confinement for restricting the space for the molecules and modifying the crystallinity

Effect of layer thickness on the oxygen permeability of the PEO layers – PP/PEO
*Lin Y., Hiltner A., **Baer E.,** Polymer (2010)*

30 to 100 nm confined PEO thick layers

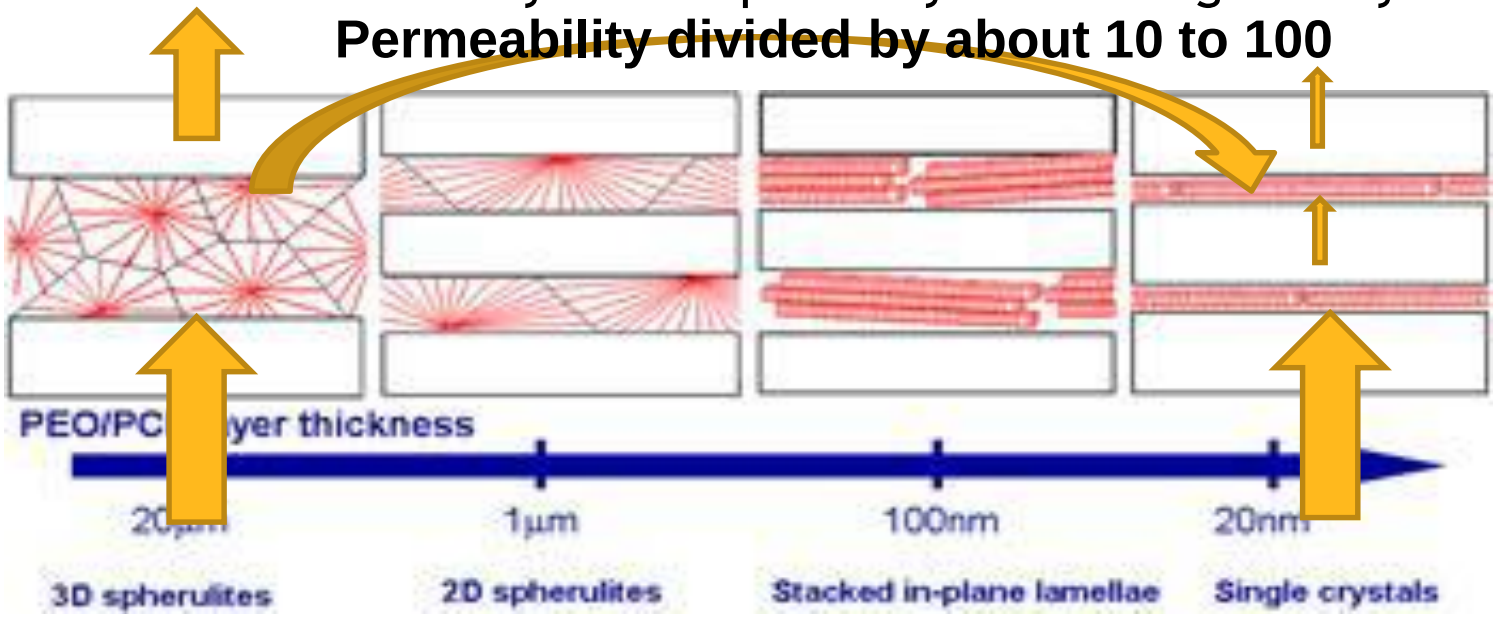
AFM micrograph





Confinement: a major research topic

→ orientation of the crystalline phase by decreasing the layer thickness



J M. Carr, D S. Langhe, M T. Ponting, A Hiltner and E Baer (2012). Journal of Materials Research, 27, pp 1326-1350

→ Major effect with ideal in-plane lamellaes

→ Only few polymers related in the litterature: PE0, PCL, PVDF

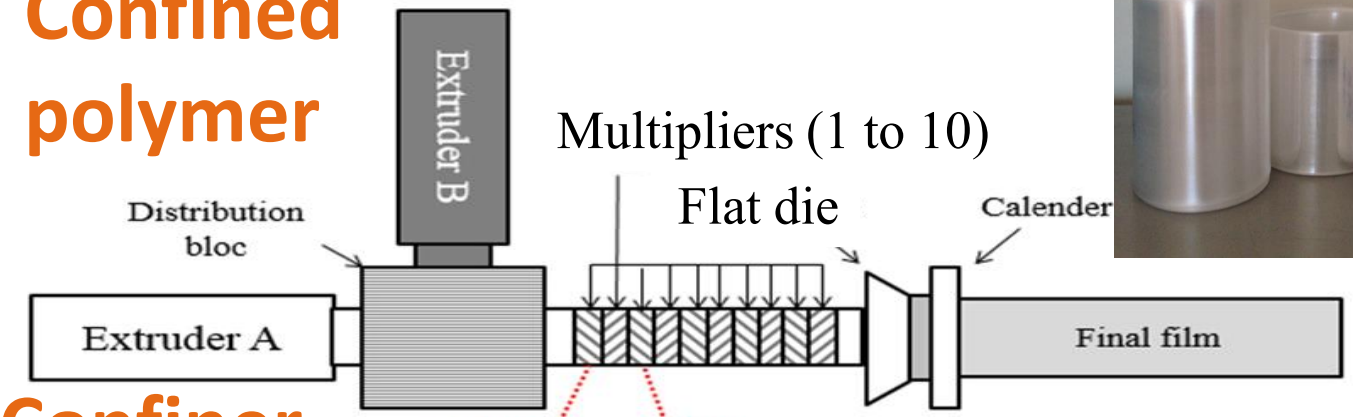
Biobased polymers PLA, PBS, PHBV, PBSA, …: no results ????

The tool: the layer multiplying co-extrusion

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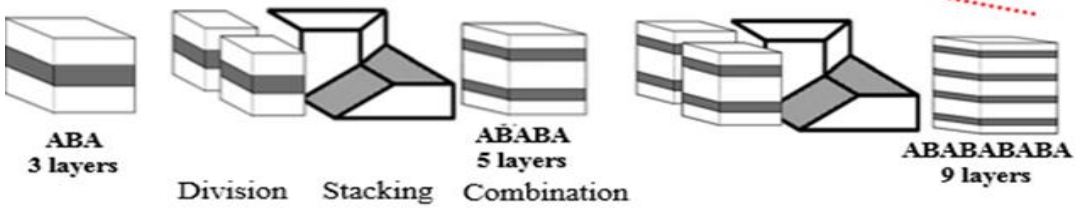
Used to create biobased multinanolayer films with confined continuous layers sufficiently thin (few nanometers thick) and numerous (2000 with 10 multipliers) to be measured by the classical thermal, physical and permeability methods

Confined polymer





Confiner



$$Numbers\ of\ layers = 2^{n+1} + 1$$

n : Multipliers numbers

n = 9 → 1025 layers
n = 10 → 2049 layers

With the same total thickness

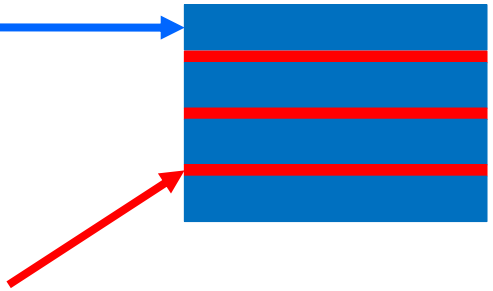
Calculation of the theoretical layers thickness:
Film: 50 µm
50%A-50%B
→ 25 µm B
and 10 M:
1000 layers B
→ theoretical thickness layer = 25 nm

⇨ 2 strategies to produce high barrier PLA films

First solution: Confinement of PLA

PS = confiner polymer

PLA= confined polymer



Objective and challenges:

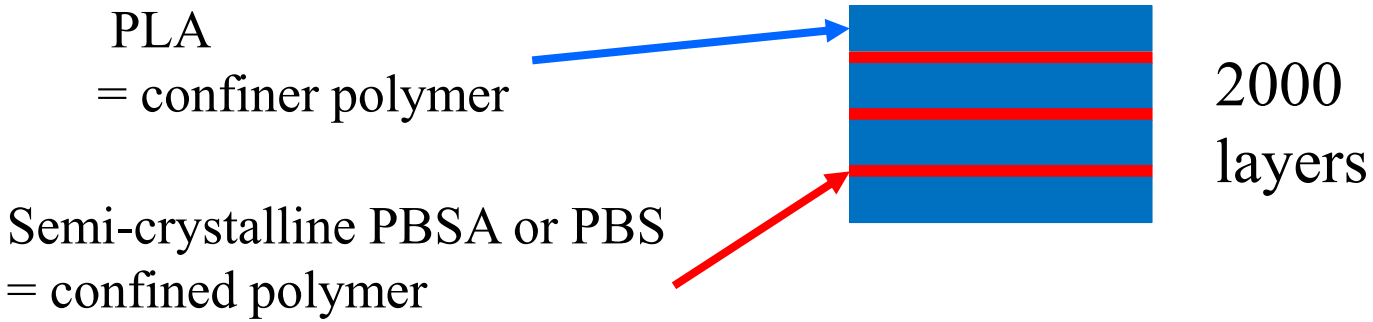
→ Is it possible to create nanometric layers with our process ?

→ Is it possible to create in-plane lamellaes ?

→ What is the improvement in gas barrier properties ?

To better understand the phenomenon, PLA was confined by an amorphous polymer PS in this study

Second solution: consists to introduce PBS or PBSA as confined nanolayers between PLA layers with expected better barrier properties due to confinement



→ preparation of a 2000 layers PLA based multinanolayer film with a small amount of PBS or PBSA

Objective:

- Creating continuous nanolayers of PBS and PBSA between PLA layers
- increasing the gas barrier properties of PBS or PBSA by confinement in order to reach 0.006 barrer in 0_2

First strategy: PLA confinement and its effect on its gas barrier properties

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[d] UMR 8207, UMET, Unité Matériaux Et Transformations, Université Lille 1, Villeneuve d'Ascq, France

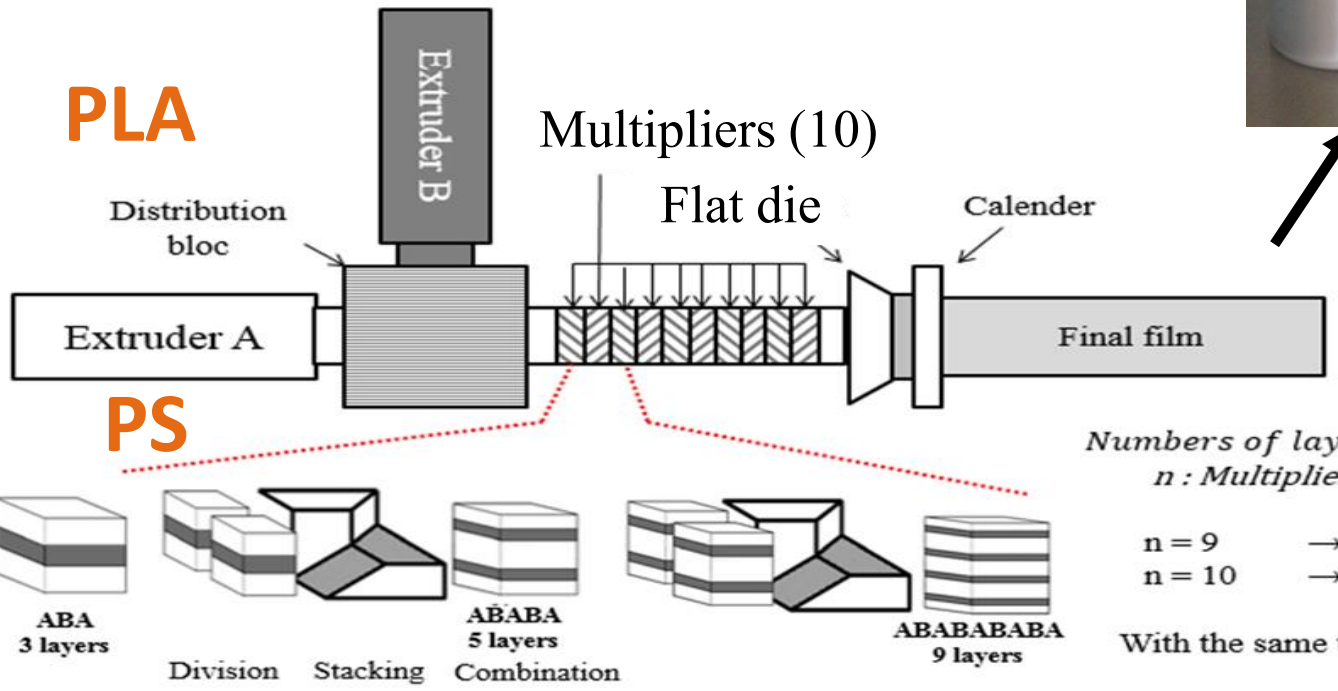
The configuration

PLA is confined by PS (weight ratio 25%/75%)

- PLLA Revode 9000
- PS Total 1540



100 µm films



$Numbers\ of\ layers = 2^{n+1} + 1$

n : Multipliers numbers

n = 9 → 1025 layers

n = 10 → 2049 layers

With the same total thickness

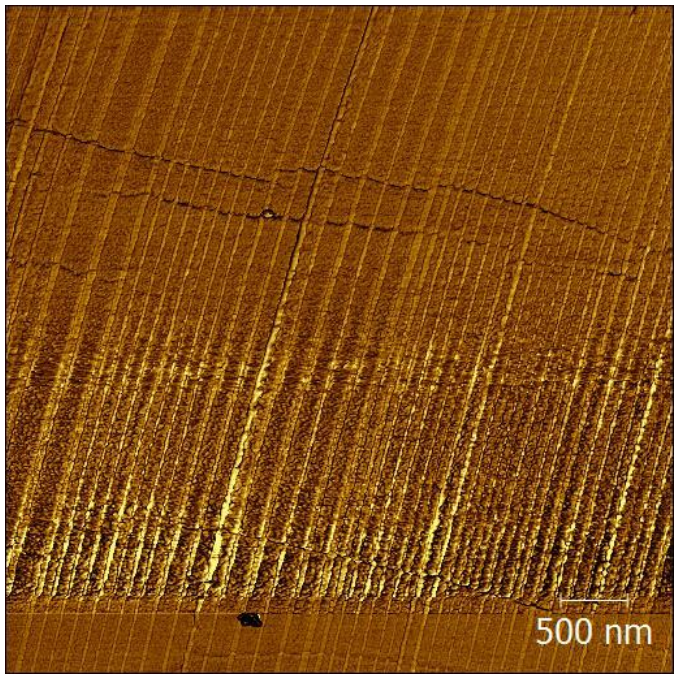
Expected: 1000 continous 25 nm PLLA layers between 75 nm PS layers

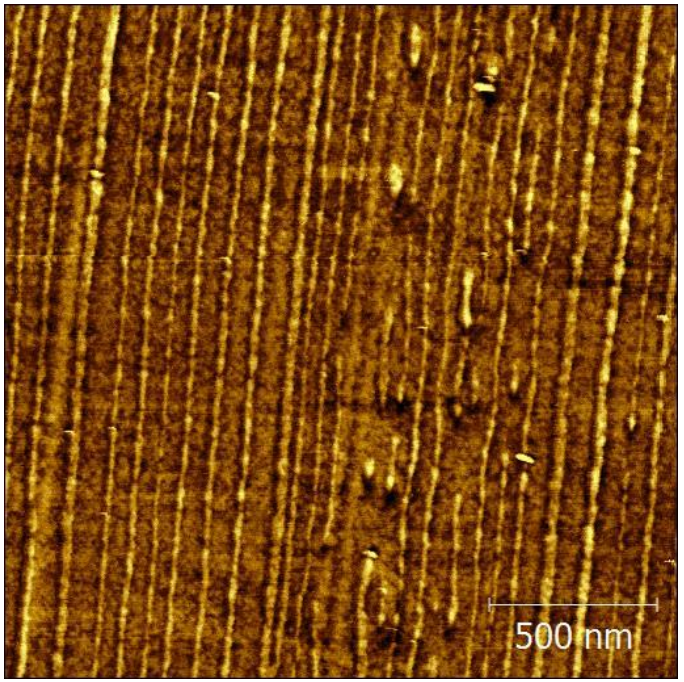
Nanolayer observation

Different methods to observe the nanometric layers:

SEM, TEM and AFM

- The best one: AFM after ultramicrotomic preparation



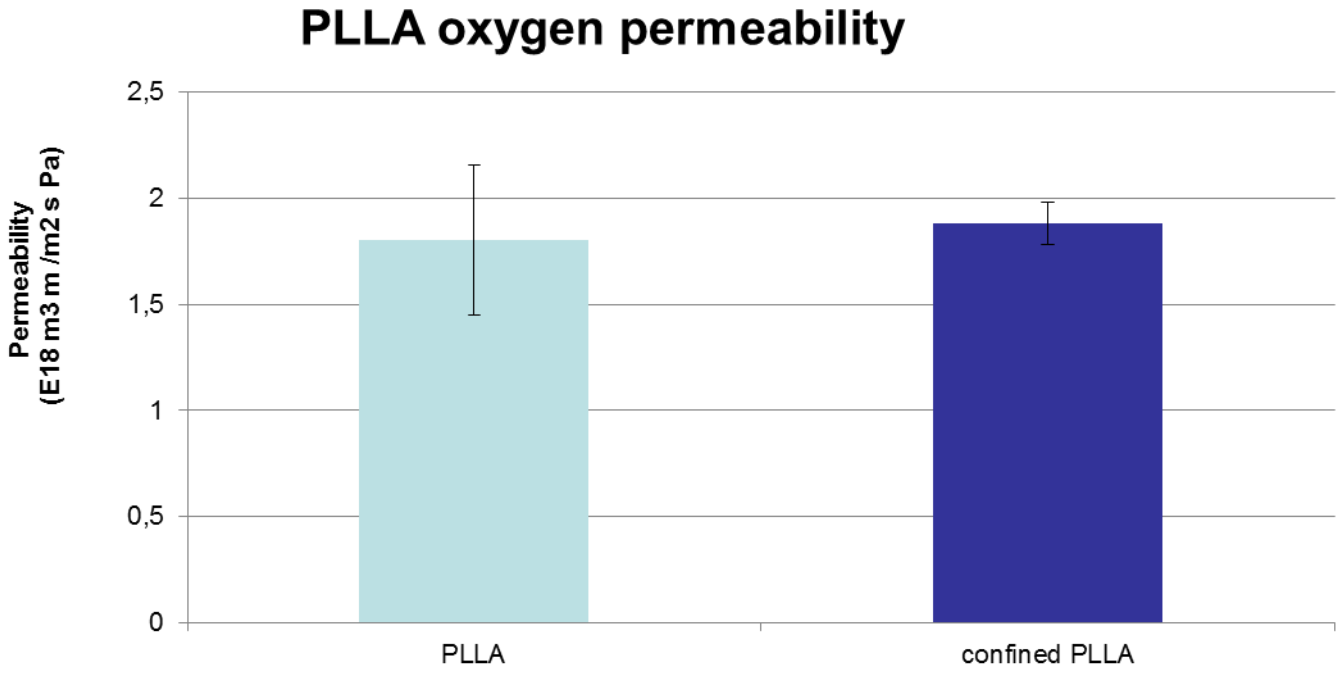


→ Continuous and homogeneous layers (more than 90%)

layer around 25 nm in thickness

O_2 permeability of PLLA in bulk and in PLLA/PS films

$$P_{PLLA} = \frac{\varphi_{PLLA}}{\frac{1}{P_{Film}} - \frac{\varphi_{PS}}{P_{PS}}}$$



→ After extrusion, without post-crystallisation, no modification of PLLA oxygen permeability by confinement

→ No effect of the confinement on the PLA crystallisation rate (stays slow)

Cold crystallization of PLLA-PS films

2 conditions for PLA:

85°C / 3 hours and 9 hours (at higher temperature, loss of the structure)

- annealing by hot stage

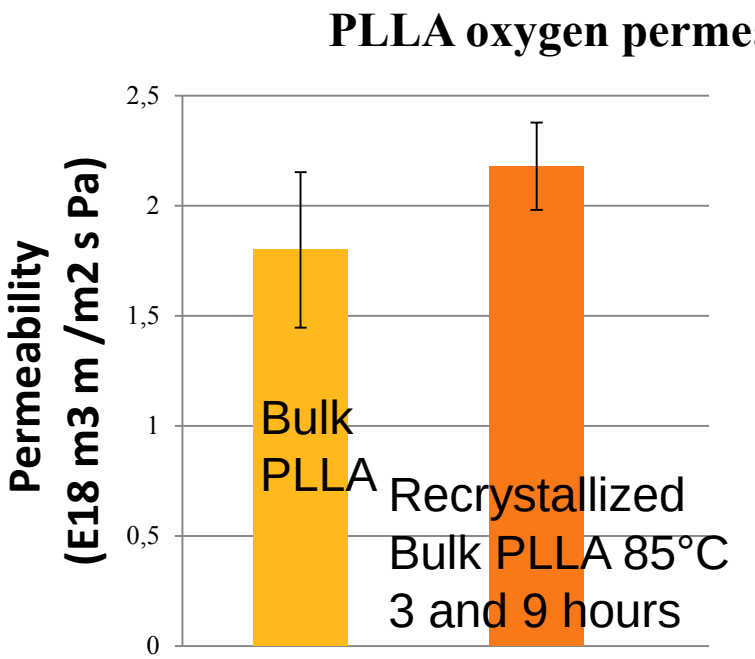
Extruded films

thermocompression recrystallisation @ T°C and time and air cooling



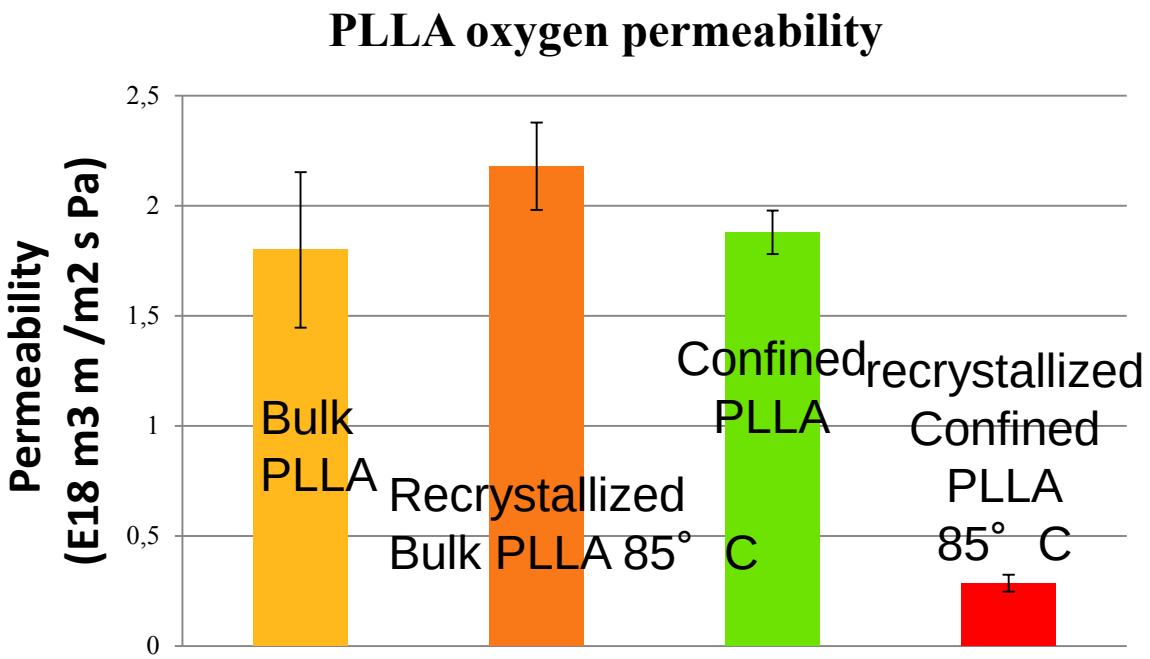
Recrystallised (or annealed) extruded films

O_2 permeability of PLLA in PLLA/PS films



→ As waiting, no effect of cold crystallization at 85°C on bulk PLLA with even with 9 hours: quick RAF formation

O_2 permeability of PLLA in PLLA/PS films



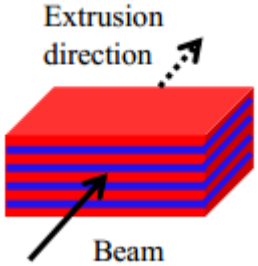
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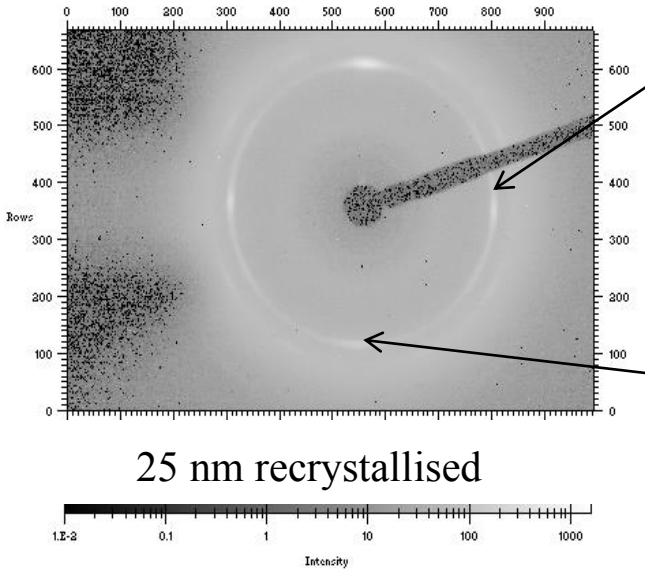
→ Surprisingly, decrease by a factor around 6 of the confined PLLA layer permeability when recrystallized @ 85°C during 3 hours

How explain such barrier improvements

Effects :
- Crystallinity degree increase
- RAF formation is delayed by confinement
- But only factor 6 (≠ 10 to 100 as expected)

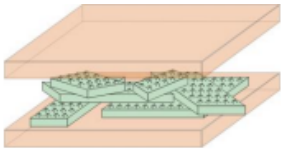
	X_{am} (%)	X_c (%)	RAF (%)
Recrystallised bulk	**34**	**28**	**38 ± 5**
Recrystallised 25 nm	**59**	**44**	**0 ± 5**



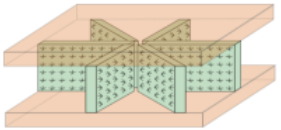


25 nm recrystallised

IN-PLANE



ON-EDGE



Unfortunately both in-plane and on-edge crystalline lamellaes

New works in progress

Second strategy: PLA/PBS and PBSA multinanolayer with expected PBS and PBSA highly improved in gas barrier properties by confinement by PLA

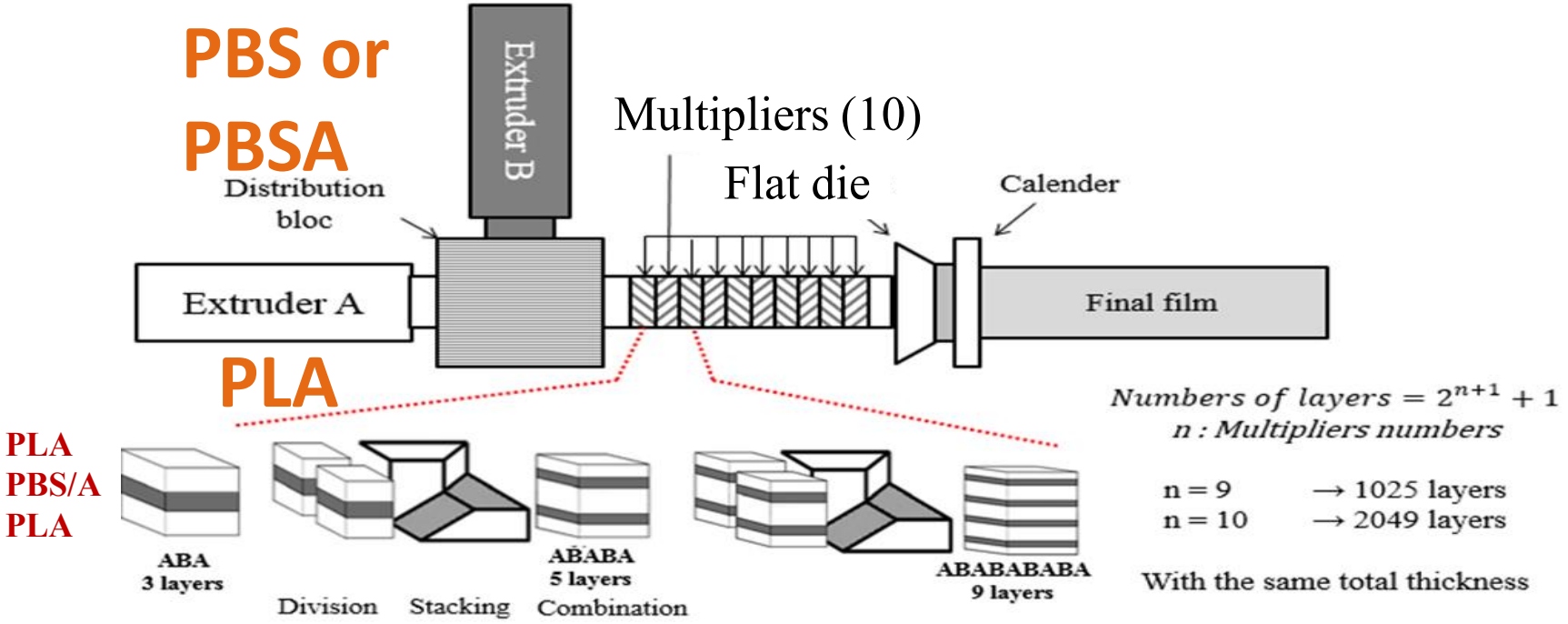
T. Messin [1], N. Follain [1], A. Guinault [2], G. Miquelard-Garnier [2], C. Sollogoub [2], N. Delpouve [3], S. Marais [1]

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The configuration

PBS or PBSA are confined by PLA: weight ratio 20%/80%

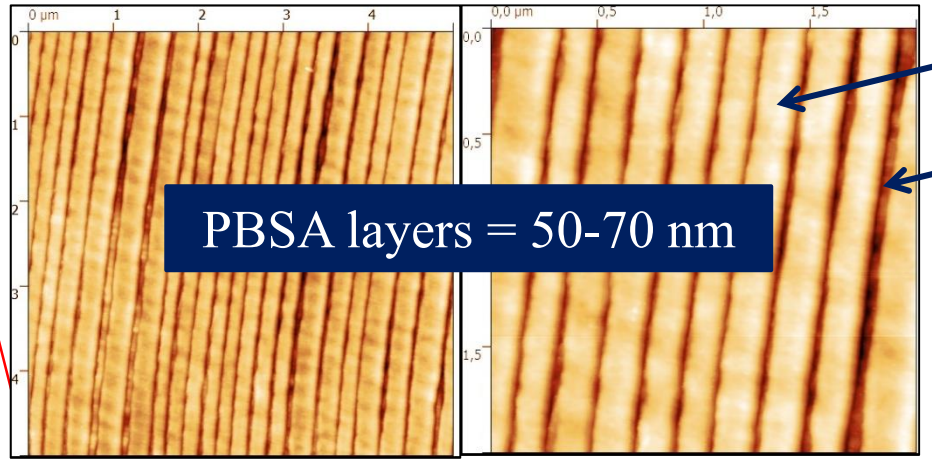
Total film thickness: 250 µm → ≃ 50 nm: not possible to put more multipliers



The layer thicknesses

PLA/PBSA (80/20) multilayer



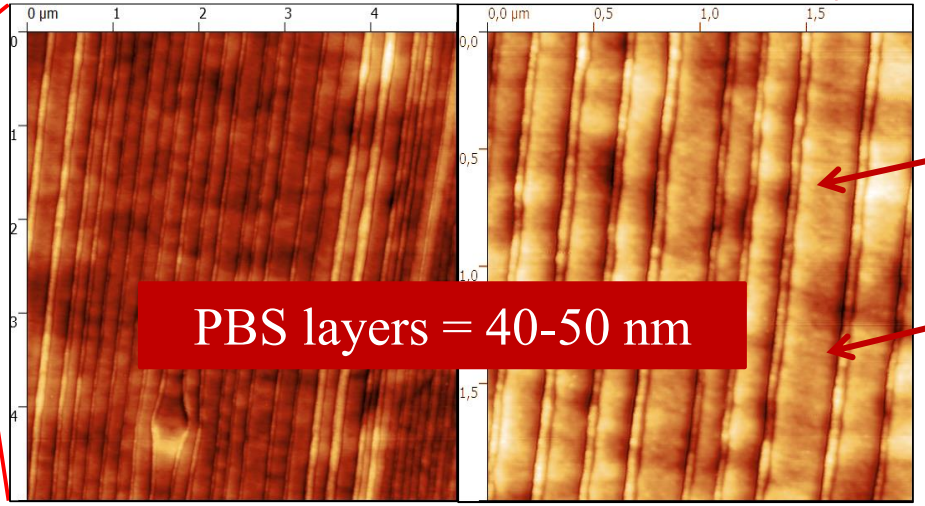


PLA

PBSA

PLA/PBS (80/20) multilayer





PLA

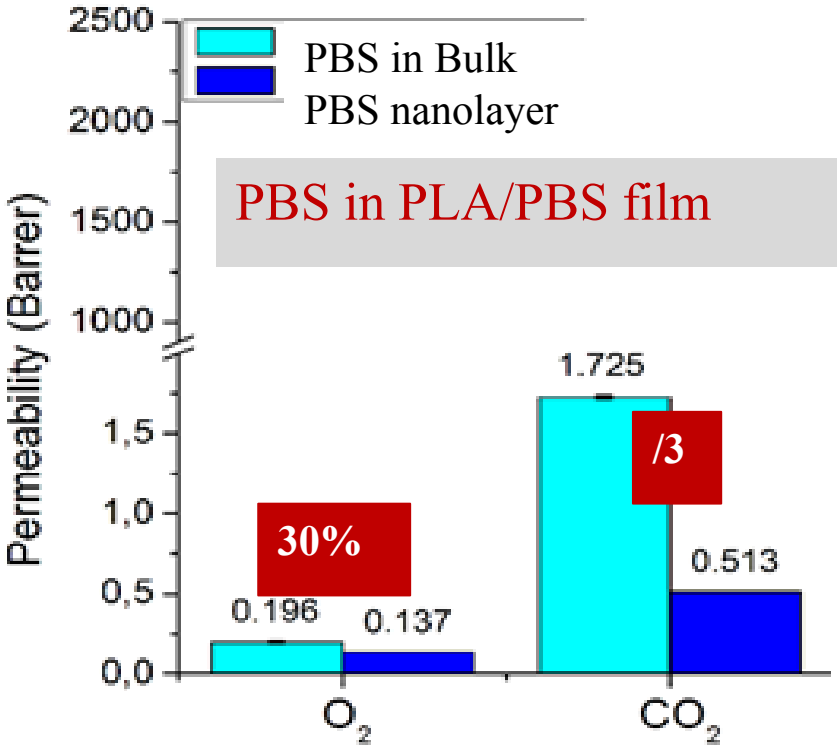
PBS

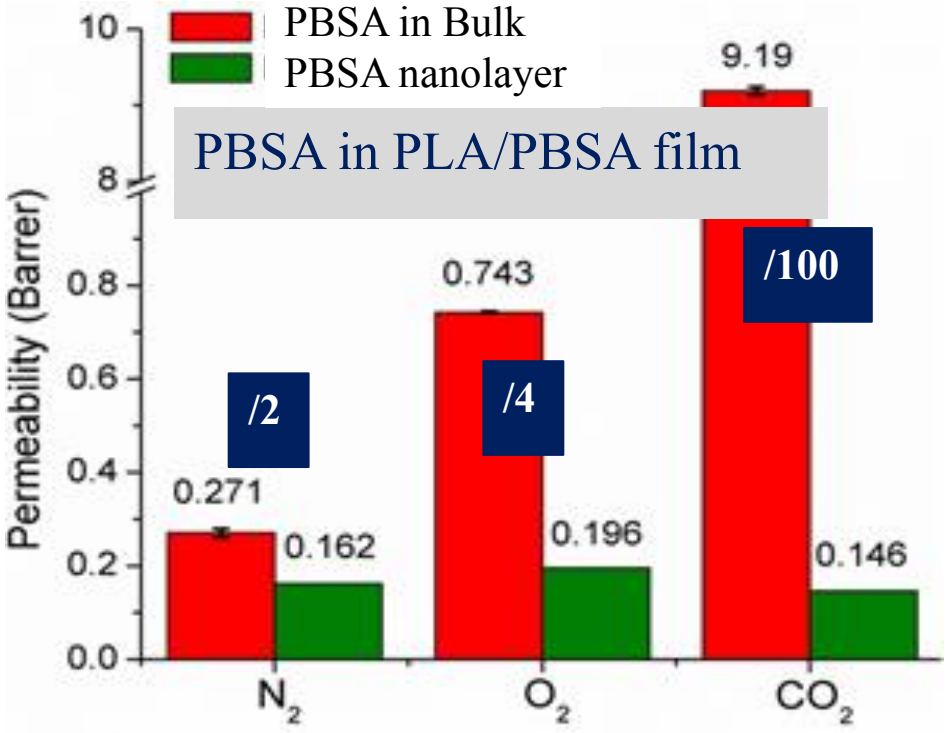
AFM observations
⇨ homogeneous structure with continuous layers

Effect on gas barrier properties

Evaluation of confinement effect on $P_{PBSA\ or\ PBS\ layers}$

✓ Direct comparison with the experimental P_{bulk}





⇨ Slight effect for PBS (factor 3 for CO_2)

⇨ Strong improvement of PBSA CO_2 permeability by the confinement effect /100 even if φ_{N2} (3.64 Å)> φ_{O2} (3.46 Å) > φ_{CO2} (3.30 Å) ⇨ structural changes ??

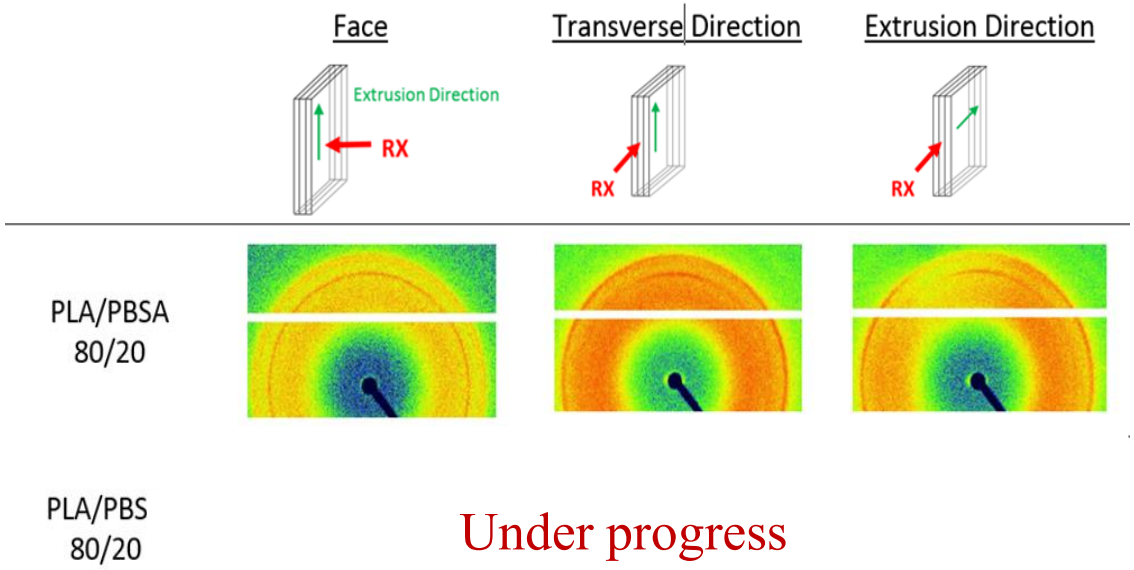
How explain such barrier improvements

Thermal analysis

	Temperature (°C)				
	Tg PBSA	Tg PLA	Tc PBSA	Tm PBSA	Xc PBSA (%)
Bulk PLA	-	55	-	-	-
Bulk PBSA	-46	-	67	90	38
PLA/PBSA nanolayer film	-46	53	71	91	40

NO significant change

How explain such barrier improvements



slight crystal orientation, but perhaps NOT only in-plane orientation in confined polymer layers as for PLA

% RAF for	In bulk	In multinanolayer
PBSA	9	21

Effect of impermeable RAF for PBSA with a defined free volume ? Only CO_2 stopped ??

Conclusion

- Possible to create films containing 25 to 70 nm thin PLA or PBS or PBSA continuous layers with layer multiplying co-extrusion process but with some layer thickness heterogeneities for PLLA: confinement effect !
- Principal confinement effects:
  - Increasing the crystallinity degree, decreasing the RAF formation but crystal orientation not only in-plane for PLA → gain 6 in O_2 permeability
  - Slight orientation of the crystals and increasing of the probable impermeable RAF phase → gain 100 in CO_2 for PBSA but only 4 for 0_2
- Very low gas permeability improvements compared to the litterature for other polymers → orientation of the crystals must be improved
- So Next studies:
  - Chosing a more compatible confiner for PLA to reach in-plane crystals
  - Decrease the PBS and PBSA thickness layers in order to expect a higher in-plane orientation of the lamellaes by adding a sacrificial layer or by biorientation stretching

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Thank you for your attention

ARTS ET MÉTIERS ParisTech cnrs le cnam INSTITUT CARNOT ARTS FEDERATION FRANCILIENNE DE MECANIQUE