



# Development of Poly(Lactic Acid) Cellular Materials - Modifications Induced by $\gamma$ -ray Irradiation and Chain Extenders

J.M. Julien<sup>1,2,3</sup>, J.-C. Bénézet<sup>3</sup>, J.-C. Quantin<sup>3</sup>, E. Lafranche<sup>1,2</sup>, A. Bergeret<sup>3</sup>, M.-F. Lacrampe<sup>1,2</sup>, P. Krawczak<sup>1,2</sup>

<sup>1</sup>Univ. Lille Nord de France, 59000, Lille, France

<sup>2</sup>Ecole des Mines de Douai , TPCIM, 941 Rue Charles Bourseul, BP 10838, 59508 Douai, France.

<sup>3</sup>Ecole des Mines d'Alès, CMGD, 6 avenue de Clavières, 30319 Alès, France

CMGD  
Centre des Matériaux



# **OUTLINE**

- **Background**
- **Objectives**
- **Materials and experiments**
- **Results and discussion**
- **Conclusions**
- **Perspectives**

# Background

- PLA

- Aliphatic bio-based polyester
- Eco-friendly (vs. oil-based polymers)
- Biodegradable

- PLA foams

- Weight reduction (energy reduction, specific properties, ...)
- Different possible material engineering applications (packaging, thermal or sound insulation, ...)

Many attention is paid worldwide to this kind of material

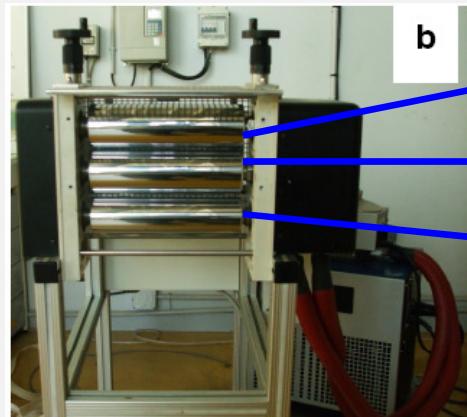
# Background

Jean-Mario Julien, PhD thesis – Ecole des Mines d'Ales

- Optimization of chemical foaming of a linear PLA on a single-screw extruder based on a weight reduction criterion
- Optimized parameters:
  - Barrel temperature profile
  - Die temperature
  - Screw speed
  - CBA content
  - Cooling system
- Advantage: continuous extrusion (or injection molding) foaming on standard equipment
- Drawback: lower weight reduction than physical foaming

# Background

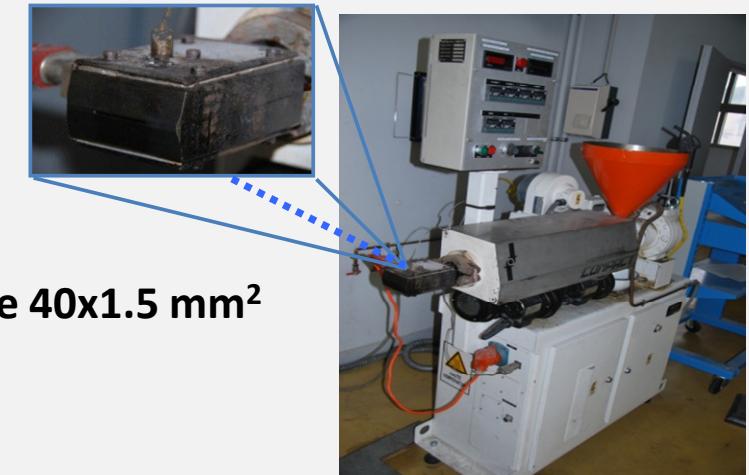
Jean-Mario Julien, PhD thesis – Ecole des Mines d'Ales



Cooling system:

Three-roll calendar

T=-15 °C



Slit Die 40x1.5 mm<sup>2</sup>

Single-screw extruder

Diameter: 30 mm, L/D: 24

Temperature (°C)					
Barrel					Die
1	2	3	4	5	6
130	150	165	165	170	195

CBA content: 4 wt%

49 % weight reduction

(Theoretical maximum: 80 %)

# Background

**Improvements expected from PLA modification:**

- Irradiation
- Chain extender addition
- Melt Strength Enhancer addition (*operates differently than 1 et 2*)

- Higher heat stability
- Higher melt strength (branching, crosslinks, physical interactions)
- Lower in-process degradability (chain scissions limitation, ...)
- Improvement of foam mechanical properties (stiffness, tensile strength, ...)

# Background

## **$\gamma$ -irradiation + crosslinking agent**

➤ Irradiation (electron beam,  $\gamma$ -ray) induces random chain scissions (average molecular weight reduction) correlated with decrease of  $T_m$ ,  $T_g$  and some mechanical properties (stiffness)

- Nugroho P., Mitomo H., Yoshii F., Kume T., *Polymer Degradation and Stability* 2001; 72 (2) : 337-343
- Nijenhuis A. J., Grijpma D. W., Pennings A. J., *Polymer* 1996 ; 37 (13) : 2783-2791

➤ Addition of crosslinking agents could overcome these drawbacks. Polyfunctional monomers as TAIC (triallyl isocyanurate) are very effective for crosslinking of PLA by irradiation technique

- Nagasawa N., Kaneda A., Kanazawa S., Yagi T., Mitomo H., Yoshii F., Tamada M., *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 2005 ; 236 (1-4) : 611-616

# Background

## Chain extenders

➤ Reactive mixing in presence of peroxides or isocyanates makes possible crosslinking of PLA → partial or total gelation

➤ Bo-Hsin L., Ming-Chien Y., *Polymers for Advanced Technologies* 2006 ; 17 (6) : 439-443

➤ Di Y., Iannace S., Di Maio E., Nicolais L., *Macromolecular Materials and Engineering* 2005 ; 290 (11) : 1083-1090

## Melt Strength Enhancers

➤ No reactive mixing is involved. High molecular weight polymers (acrylic, ...) are dispersed in a PLA matrix. The increase in melt elongation viscosity results from entanglements (Biostrength® – Arkema)

➤ Grimes E., Keeley S., *Rubber World* 2010 ; 243 (1) : 28-29, 33

# Objectives

**Two types of modification of a linear PLA are investigated:  $\gamma$ -ray irradiation and addition of chain extenders**

- Effects on the weight reduction (foaming ability)
- Effects on the cellular morphology

# Materials and Experiments

## Materials

### PLA

- Grade INGEO™ 7000D (NatureWorks® LLC – Injection Stretch Blow Molding)
- Linear PLA –  $T_g$ : 55-60 °C –  $T_m$ : 145-155 °C –  $M_w$ : 340 kDa – D content: 6.4 %

### CBA

- HYDROCEROL® CT 3108 (Clariant Masterbatches)
- Sodium bicarbonate, citric acid and nucleating agents - Gaseous output: 50 ml/g – Decomposition liberating CO<sub>2</sub> and H<sub>2</sub>O ( $T_d$ : 138-216 °C) - 4 wt% of CFA for all materials

### Crosslinking agent

TAIC - triallyl isocyanurate (Aldrich) – polyfunctional monomer

### Chain extender

CESA®-extend BLA0050109-ZN based on a styrene/acrylic/glycidyl ethylacrylate terpolymer (Clariant Masterbatches)

# Materials and Experiments

## Processing

### $\gamma$ -ray irradiation + coupling agent (TAIC)

- Two steps: PLA+TAIC (1, 3 wt%) compounding →  $\gamma$ -irradiation (5, 10, 25, 50 kGy – IONISOS - France)
- Coding: PLAx/y (x kGy, y wt% of TAIC)

Or

### Chain extender

- Compounding PLA+CESA<sup>®</sup>-extend
- Coding: PLAxC (x wt% of CESA)

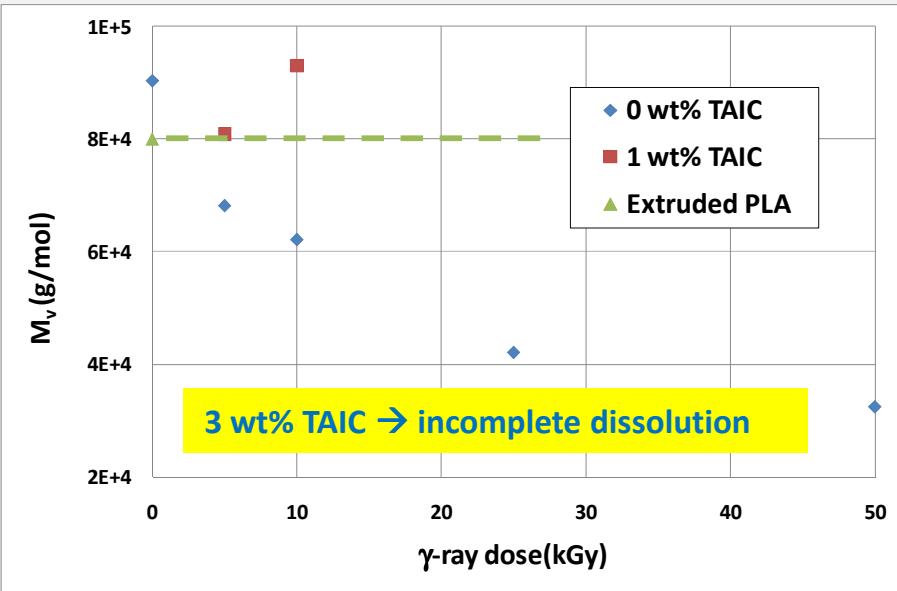
### Compounding (PLA+TAIC, PLA+CESA<sup>®</sup>-extend)

- Twin-screw extruder (Clextral BC21 – screw diameter: 25 mm, L/D: 36)
- Temperatures (from hopper to die): 100/165/170-170 °C, screw speed: 250 rpm

→ Single-Screw Extrusion Foaming

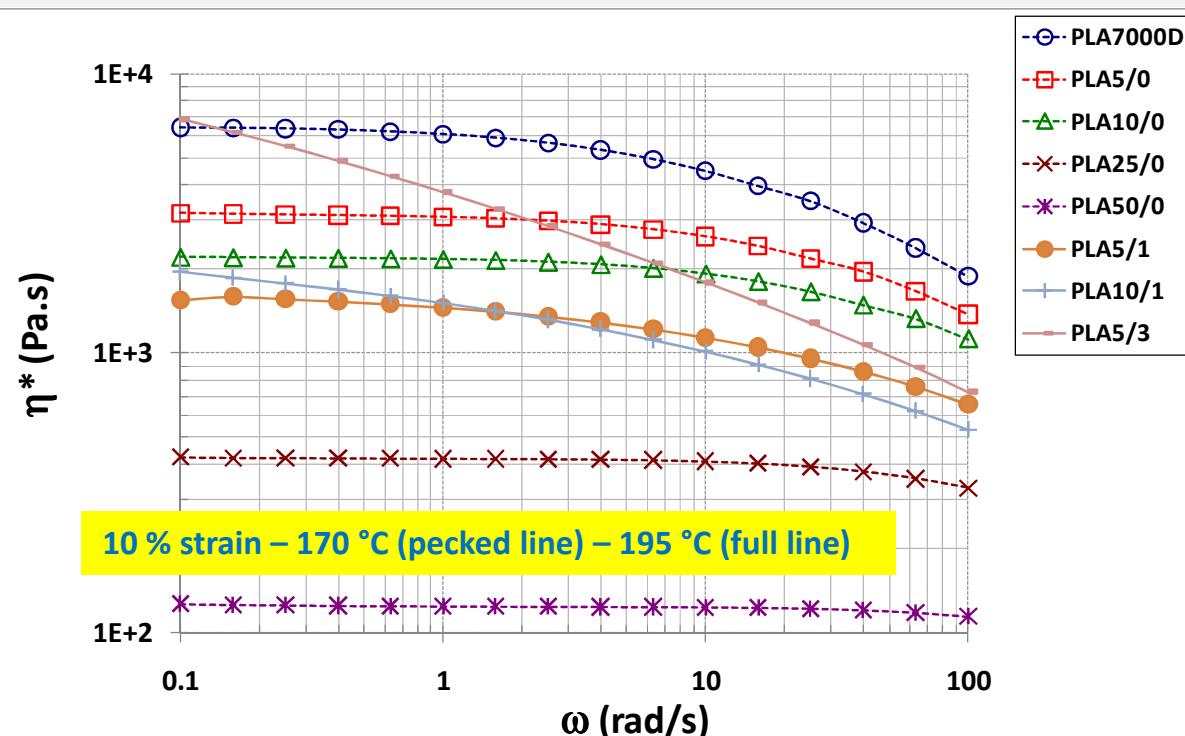
# Results and Discussion

## Rheology – $\gamma$ -ray irradiation



## Solution Viscometry – Viscosity Average Molecular Weight M<sub>v</sub>

- Without TAIC the irradiation causes a decrease of M<sub>v</sub> probably due to chain scissions
- The addition of a little amount (1 wt%) of TAIC increases M<sub>v</sub> → cross-linking limiting PLA degradation

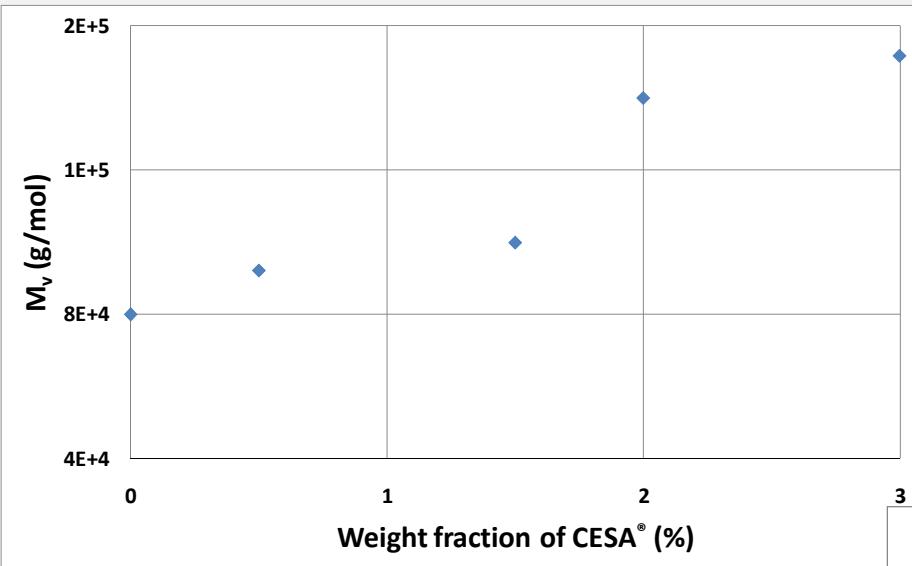


## Oscillatory Rotational Shear Viscometry – Complex Viscosity Modulus

- Without TAIC the irradiation causes a decrease in complex viscosity (non extruded samples)
- Addition of TAIC induces an increase in complex viscosity
- Both results are consistent: TAIC compensates degradation caused by irradiation

# Results and Discussion

## Rheology – Chain extender



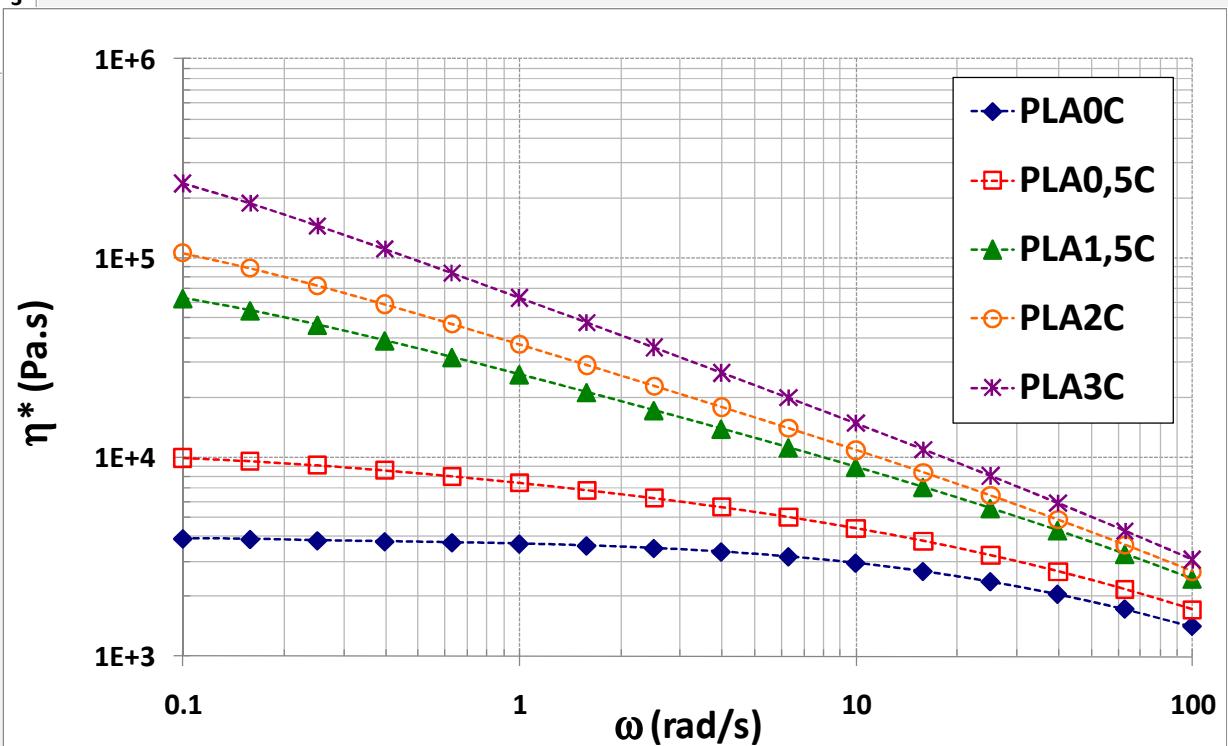
### Solution Viscometry – Viscosity Average Molecular Weight $M_v$

➤  $M_v$  increases when the weight fraction of chain extender increases (47 % increase with 3 wt% of CESA®-extend). So the incorporation of CESA into PLA is a reactive phenomenon which induces longer macromolecular chains in the PLA 7000D.

### Shear Oscillatory Viscometry – Complex Viscosity Modulus

- $\eta^*$  increases as CESA fraction increases.
- Transition in the range 0 to 10 rad/s from a Newtonian (3 wt% CESA) to a power law behavior (<3 wt % CESA)

→ Both results are consistent



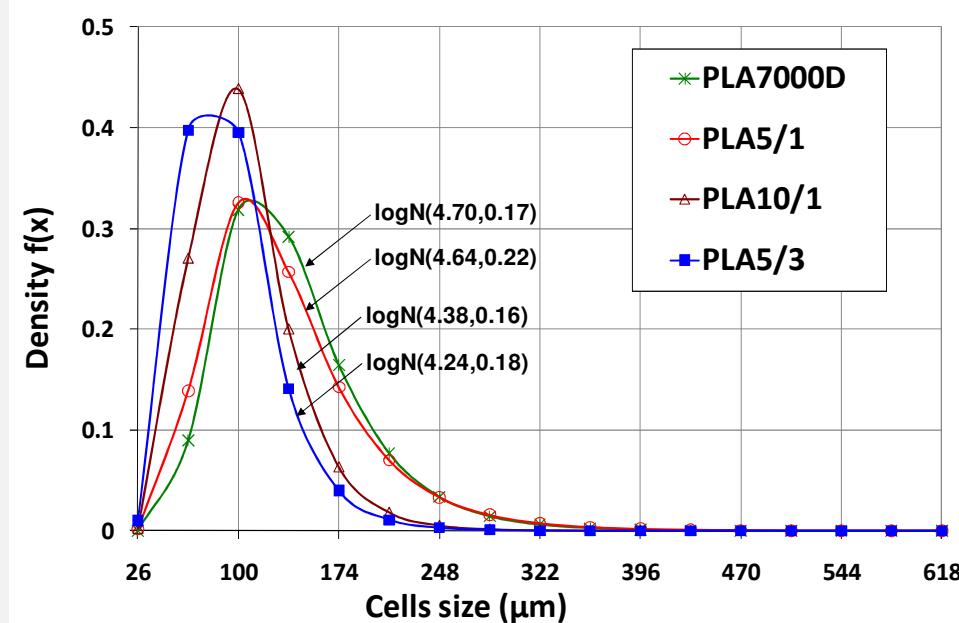
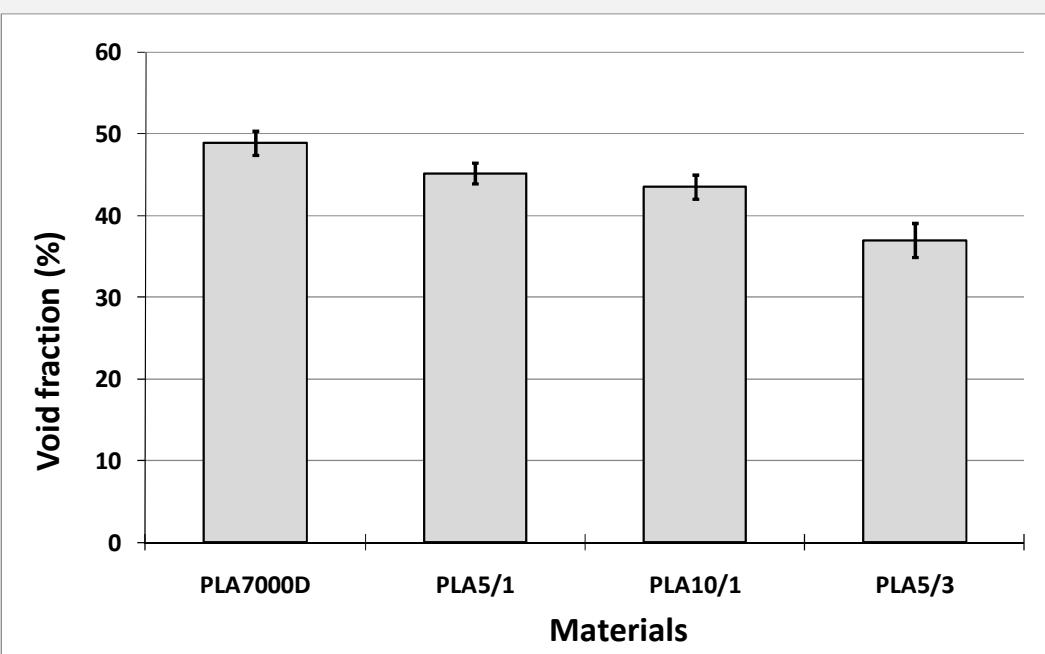
# Results and Discussion

## Void fraction /Cellular Morphology – $\gamma$ -ray irradiation

- All irradiated materials could not be foamed: viscosity either too low, either too high (presence of unmelted parts) - Foamed materials: PLA5/1, PLA10/1, PLA5/3

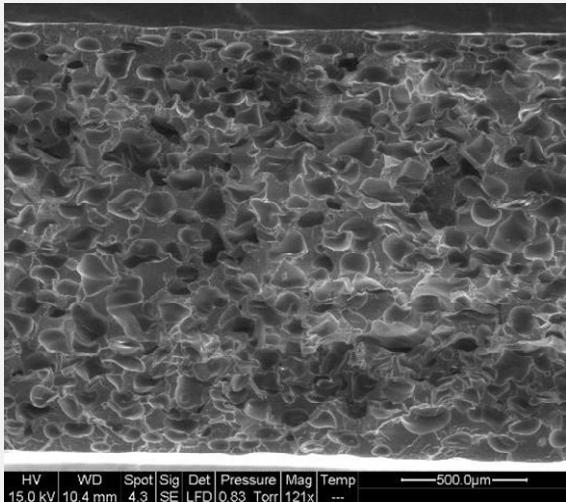
Material	$\bar{d}_n$ ( $\mu\text{m}$ )	$\delta$ ( $\mu\text{m}$ )	$N_c$ (cells/ $\text{cm}^3$ ) $\times 10^5$	$C_o$ (%)
PLA7000D not extruded	$95 \pm 2$	$41 \pm 1$	$10.76 \pm 0.75$	$21.35 \pm 1.74$
PLA5/1	$92 \pm 2$	$45 \pm 1$	$11.07 \pm 0.77$	$17.55 \pm 2.83$
PLA10/1	$72 \pm 2$	$37 \pm 1$	$22.06 \pm 1.53$	$12.65 \pm 0.85$
PLA5/3	$65 \pm 2$	$42 \pm 1$	$25.37 \pm 1.76$	$20.65 \pm 1.00$

- $d_n$ : number average cell size
- $\delta$ : average cell's wall thickness
- $N_c$ : cell's density
- $C_o$ : open-cell content

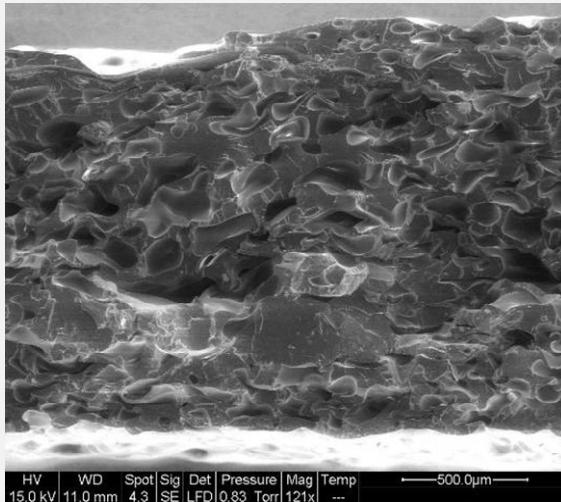


# Results and Discussion

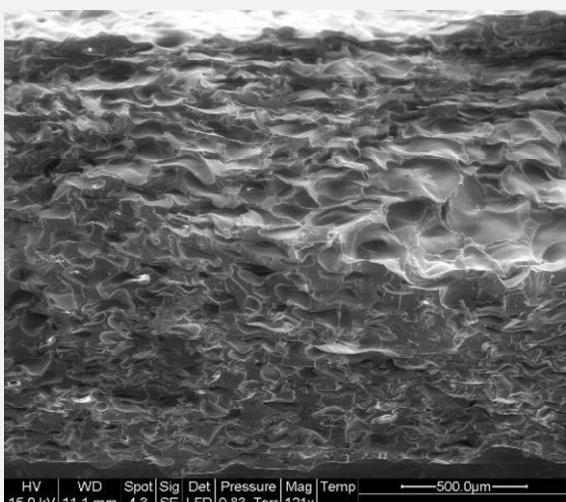
## Void fraction /Cellular Morphology – $\gamma$ -ray irradiation



PLA 7000D

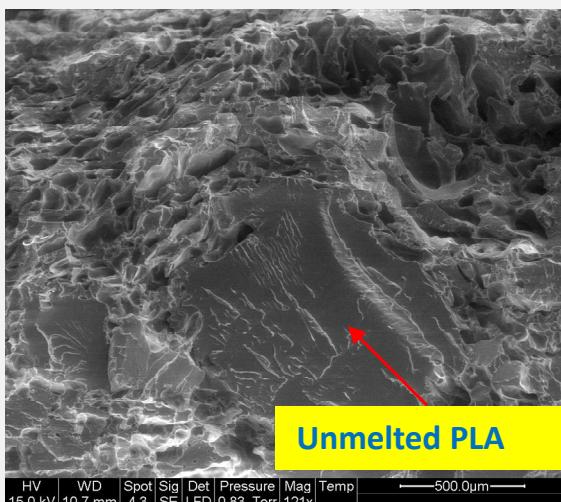


PLA5/1



PLA10/1

500  $\mu$ m



PLA5/3

- Irradiation+TAIC induces a reduction of the void fraction
- Cell size is reduced
- Open-cell content is reduced (except at 3 wt% TAIC)
- Cell wall thickness is quite constant

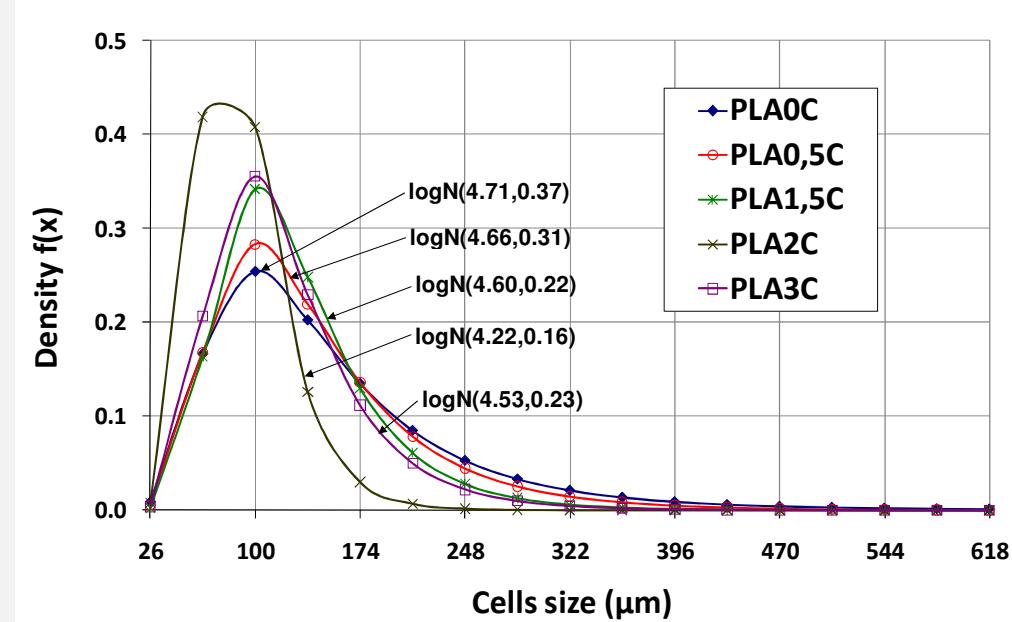
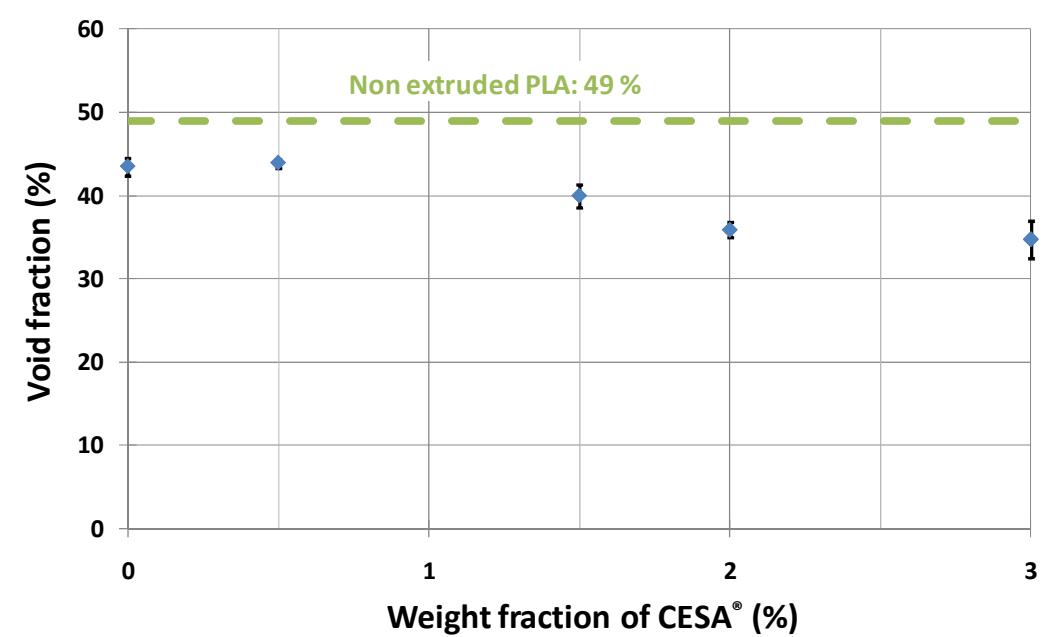
→ All results are quite consistent: TAIC compensates degradation caused by irradiation → increase in melt strength, but this causes no noticeable improvement in foaming efficiency

# Results and Discussion

## Void fraction /Cellular Morphology – Chain Extender

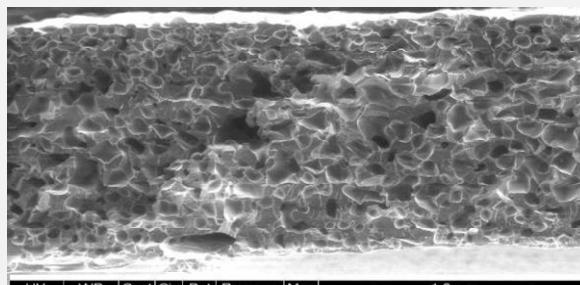
- All materials were foamed
- Foamed materials: PLA0C, PLA0.5C, PLA1.5C, PLA2C, PLA3C

Material	$\bar{d}_n$ ( $\mu\text{m}$ )	$\delta$ ( $\mu\text{m}$ )	$N_c$ (cells/ $\text{cm}^3$ ) $\times 10^5$	$C_o$ (%)
PLA0C	$106 \pm 2$	$41 \pm 1$	$6.98 \pm 0.48$	$21.68 \pm 2.31$
PLA0.5C	$97 \pm 2$	$55 \pm 1$	$9.20 \pm 0.64$	$6.84 \pm 1.63$
PLA1.5C	$90 \pm 2$	$49 \pm 1$	$10.50 \pm 0.73$	$7.58 \pm 1.14$
PLA2C	$64 \pm 1$	$52 \pm 1$	$26.60 \pm 1.85$	$6.41 \pm 2.3$
PLA3C	$84 \pm 2$	$43 \pm 1$	$11.04 \pm 0.77$	$6.38 \pm 1.15$

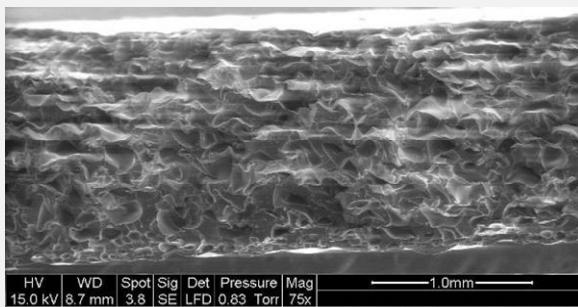


# Results and Discussion

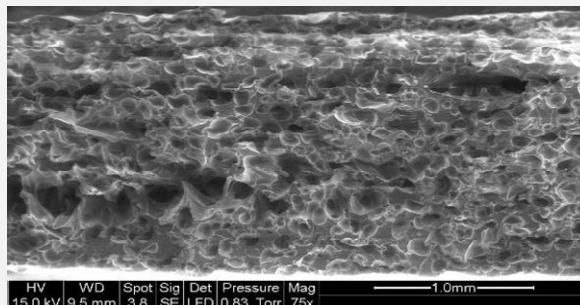
## Void fraction /Cellular Morphology – Chain Extender



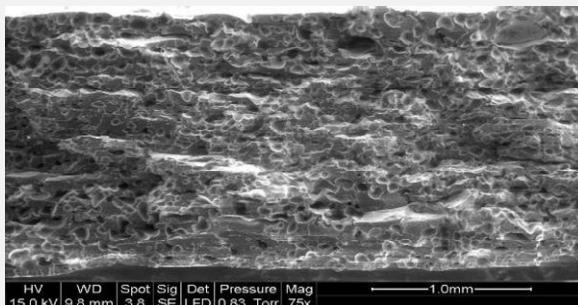
0 % CESA



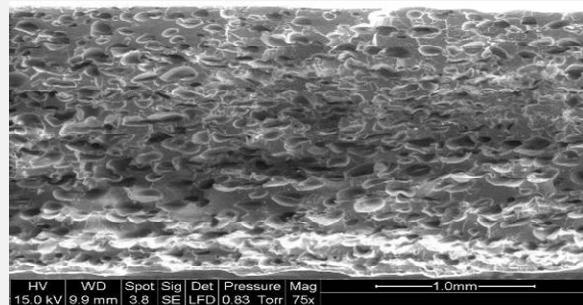
0.5 % CESA



1.5 % CESA



2 % CESA



3 % CESA

1 mm

- First extrusion of neat PLA degrades its foaming ability (void fraction 49 to 43 %)
- Addition of CESA induces a reduction of the void fraction
- Cells size is reduced
- Open-cell content is reduced
- Cells wall thickness is increased

→ All results are consistent: addition of CESA favors chain branching → increase in melt strength → nucleation rather growing of cells is promoted  
→ No noticeable improvement in foaming efficiency

# Conclusions

## Effects of PLA modifications on foaming efficiency and final structure

- High melt strength induced by chain branching may slow down the cell growing
- Both types of modification induce finer cellular morphologies and higher cell density
- For PLA7000D no higher weight reduction is observed. Moreover  $\gamma$ -ray irradiation or addition of chain extenders could be a way to better control the final foam morphology

# Perspectives

- **Introduction of cellulose fibers (conserves the bio-based character, improvement of mechanical characteristics)**
- **Introduction of nanoclays → Vincent Masson PhD Thesis**