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# Development of Poly(Lactic Acid) Cellular Materials

## Physical and Morphological Characterization

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### Introduction

In this study the chemical foaming of two commercial PLA through extrusion process is investigated. Different processing conditions (extrusion flow rate, temperature and cooling system) as well as different contents of chemical foaming agent (CFA) were considered. The foaming aptitude of the PLA/CFA formulations is assessed on the basis of void content induced by extrusion in the final product. For each PLA, the experimental results allowed defining optimum set of extrusion conditions, leading to a maximal void content. Secondly, in the case of PLA-based foams extruded in optimal process conditions, the cells structure and mechanical properties were investigated as a function of chemical foaming agent content.

### Materials, Processing

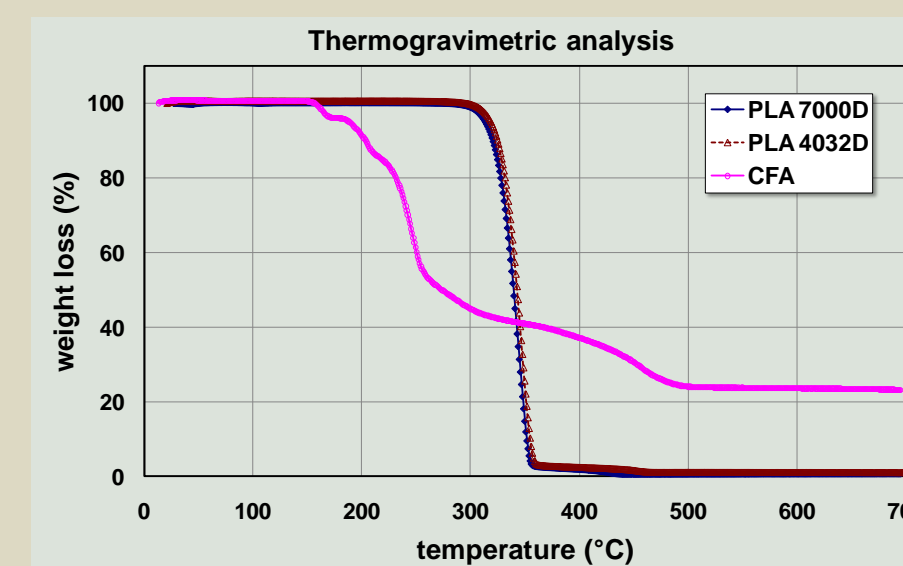
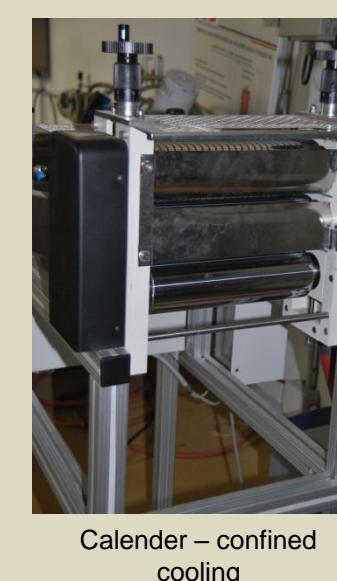
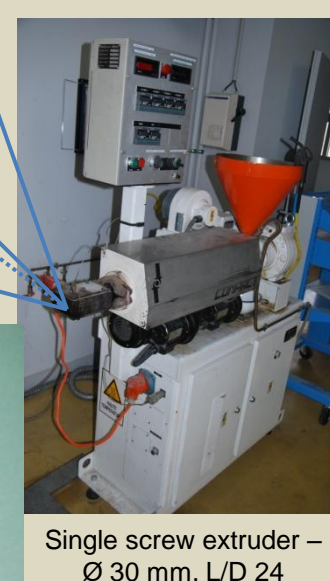
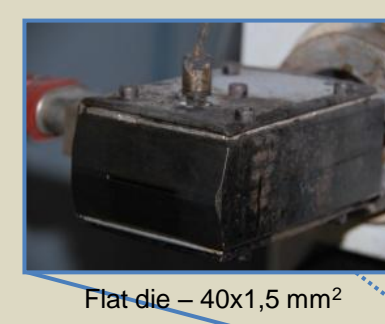
→ PLA 7000D, PLA 4032D (NatureWorks®)

Polymer	M <sub>v</sub> (g/mol)	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	Residual moisture content (%)	Density (kg/m <sup>3</sup> )
PLA7000D	90438	63 (1,6)	151 (0,8)	500 ppm	1268
PLA4032D	89563	67 (0,5)	170 (0,5)	approximately	1260

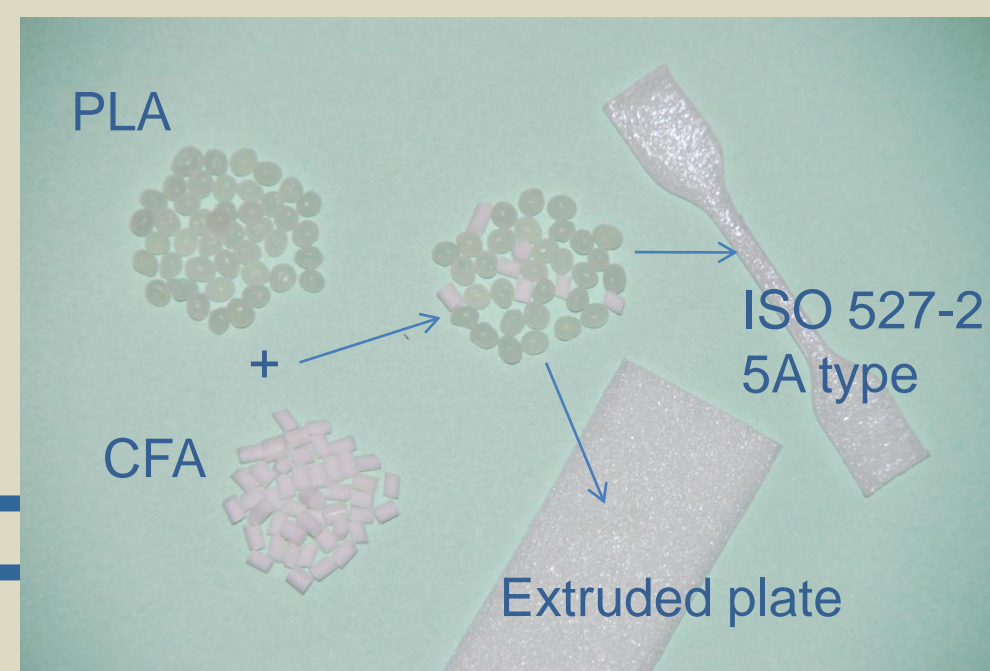
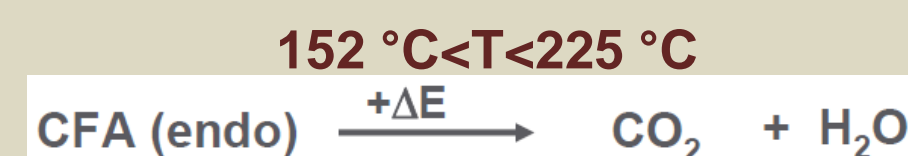
M<sub>v</sub> (molecular weight - Ubbelohde capillary viscometer), T<sub>g</sub> (glass transition temperature - DSC), T<sub>m</sub> (melt temperature - DSC)

→ CFA Hydrocero<sup>®</sup> OMAN 698483 (Clariant Masterbatches)  
: sodium bicarbonate and citric acid encapsulated in PLA

Temperature profile	Barrel (from hopper to die)					Die
	1	2	3	4	5	
A	130	150	165	165	170	180-195-210
B	150	170	170	170	180	195

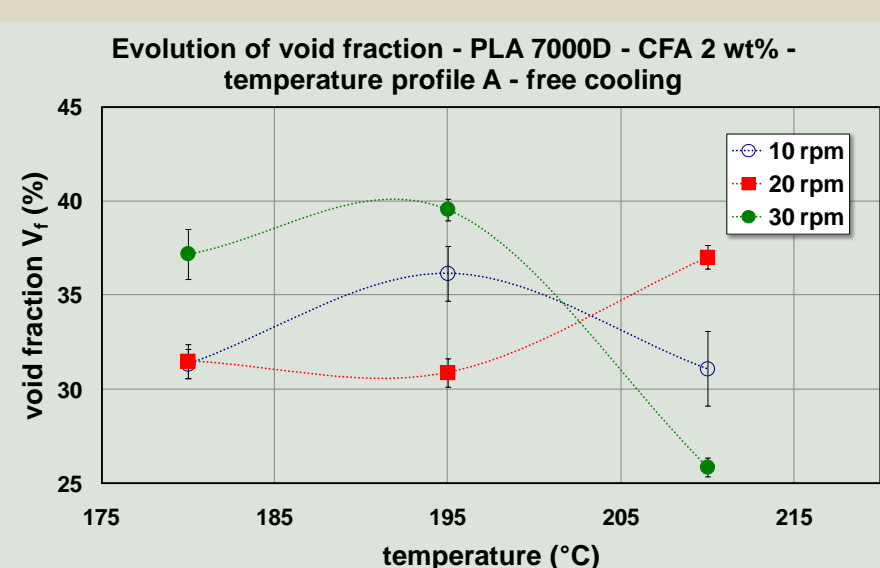


No difference in thermal stability of both PLA

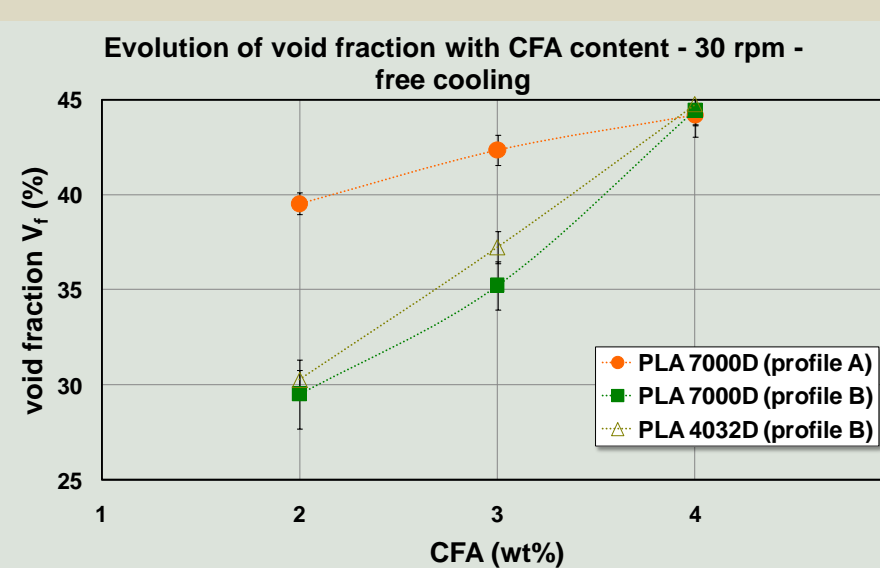


### Results, Analysis

#### Void content



Void fraction is optimized at 30 rpm and 195 °C die temperature.  
→ Competition between degradation and diffusion of CFA.



Both PLA show the same behaviour with temperature profile B. The evolution is controlled by the amount of gas and thus the CFA content.  
Void fraction increases up to 45 % which is quite good for a CFA.

#### Morphology

Environmental Scanning Electron Microscope pictures observed and analysed assuming all cells to have a spherical shape

Cooling system	V <sub>v</sub> (%)	$\bar{d}_n$ (μm)	$\bar{d}_w$ (μm)	PDI	N <sub>c</sub> (cells/cm <sup>3</sup> ) × 10 <sup>4</sup>	δ (μm)
Free at air	44 (1.2)	98 (12.4)	99	0.98	92.93	47.64
confined	46 (0.94)	98 (21.2)	101	0.97	92.50	46.58

Effect of the cooling system on the cellular structure. PLA 7000D (temperature profile A); screw speed 30 rpm; die temperature 195 °C; free cooling. ( ) = standard deviation

Polymer	CFA (wt%)	$\bar{d}_n$ (μm)	$\bar{d}_w$ (μm)	I <sub>c</sub>	PDI	N <sub>c</sub> (cells/cm <sup>3</sup> ) × 10 <sup>4</sup>	δ (μm)	C <sub>o</sub> (%)
PLA7000D	2	104 (31.2)	113	2.05 (0.7)	0.92	68.01	61.12	23.13 (0.5)
	3	100 (19.0)	102	1.50 (0.3)	0.98	81.17	53.58	13.86 (0.6)
	4	98 (12.4)	99	1.64 (0.3)	0.98	92.93	47.64	12 (0.4)
PLA4032D	2	137 (32.6)	145	1.7 (0.3)	0.94	22.51	111.94	19.12 (1.5)
	3	133 (63.8)	157	1.7 (0.4)	0.85	30.09	85.03	24.49 (1.3)
	4	143 (28.1)	151	1.5 (0.3)	0.94	24.32	91.28	26.76 (1.1)

Cell dimensions ( $\bar{d}_n$ ,  $\bar{d}_w$ ), circularity index (I<sub>c</sub>), cell density (N<sub>c</sub>), cell size polydispersity (PDI), cell-wall thickness (δ) and open-cell ratio (C<sub>o</sub>) as function of CBA content - PLA 7000D temperature profile A and PLA 4032D temperature profile B; screw speed 30 rpm; die temperature 195 °C - free cooling. ( ) = standard deviation

- Cellular structure is rather homogeneous (PDI≈1) and low open-cell ratio (<26 %).
- Both PLA are different on the open-cell evolution with CFA content.
- Cell density of PLA 7000D is higher than that of PLA 4032D (especially under 4 wt% CFA content).
- The type of cooling has little effect on the morphology (except presence of macro-voids with air cooling).

$$d_i = 2\sqrt{A/\pi}$$

$$\bar{d}_n = \frac{\sum d_i n_i}{\sum n_i}$$

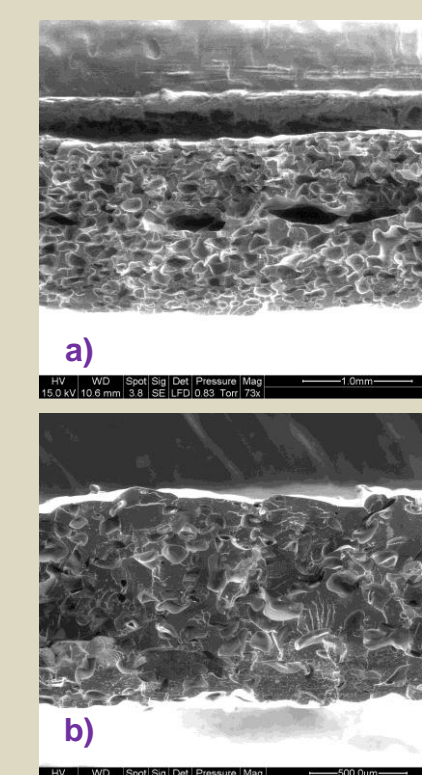
$$\bar{d}_w = \frac{\sum d_i^2 n_i}{\sum d_i n_i}$$

$$PDI = \frac{\bar{d}_w}{\bar{d}_n}$$

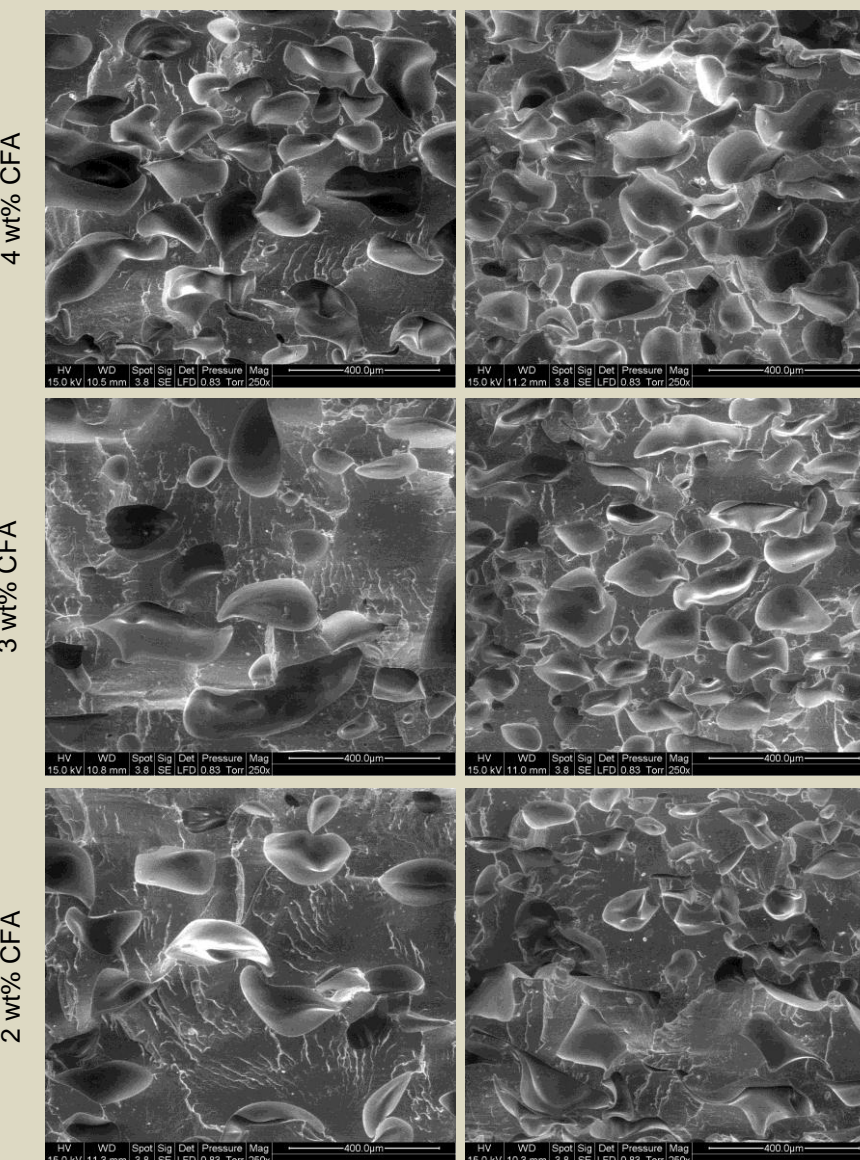
$$I_c = \frac{\text{perimeter}^2}{4\pi \cdot \text{surface}}$$

$$N_c = \frac{6 \left(1 - \frac{\rho_f}{\rho_p}\right)}{\pi \bar{d}_n^3}$$

$$\delta = \bar{d}_n \left( \frac{1}{\sqrt{1 - \frac{\rho_f}{\rho_p}}} - 1 \right)$$



Cellular structure of PLA 7000D foam temperature profile A; screw speed 30 rpm; die temperature 195 °C a) free cooling, b) confined cooling



PLA 4032D - Temperature profile B - 30 rpm - free cooling PLA 7000D - Temperature profile A - 30 rpm - free cooling

#### Mechanical behaviour

Polymer	CBA (wt%)	Void fraction (%)	σ <sub>max</sub> (MPa)	ε <sub>max</sub> (%)	σ <sub>r</sub> (MPa)	ε <sub>r</sub> (%)
PLA 7000D	2	39.54 (0.57)	36.00 (2.84)	8.41 (0.32)	33.38 (2.18)	9.95 (0.71)
	3	42.36 (0.81)	25.65 (1.33)	8.84 (0.39)	21.51 (1.72)	11.59 (0.92)
	4	44.21 (1.16)	23.71 (0.90)	8.37 (0.55)	20.49 (1.08)	10.28 (1.16)
PLA 4032D	2	30.28 (0.49)	40.54 (3.27)	10.24 (0.89)	37.91 (3.90)	11.51 (1.23)
	3	37.25 (0.85)	30.68 (2.40)	8.61 (0.70)	27.14 (3.44)	10.43 (1.11)
	4	44.77 (1.05)	26.77 (1.24)	9.44 (1.36)	22.87 (1.12)	11.50 (1.60)

PLA-foams tensile properties. Processing conditions: PLA 7000D (temperature profile A) and PLA 4032D (temperature profile B); screw speed 30 rpm; die temperature 195 °C; free cooling. (σ<sub>max</sub>: yield stress, ε<sub>max</sub>: elongation at yield stress, σ<sub>r</sub>: tensile strength, ε<sub>r</sub>: elongation at break. ( ) = standard deviation

- Samples are cut from extruded parts in a direction parallel to die axis.
- Tensile tests are performed.
- CFA content has little effect on maximal and ultimate strains.
- Increase in CFA content induces a reduction of yield stress and tensile strength of both PLA. This is correlated with increase in void fraction and thus reduction in effective sample cross-section.

### Conclusion

- Optimized foaming extrusion leads to 45 % void fraction and homogeneous cellular structures with two PLA which differ at least by melt temperature.
- Free and confined cooling cause similar morphologies except the presence of macro voids with free (air) cooling
- Tensile strength is well correlated with CFA content and thus with void content
- A better understanding of the foaming process is necessary to explain particular trends
- Further achievements will be carried out: injection molding, alternative methods to quantify the morphology, ...