



DEVELOPMENT OF POLY(LACTIC ACID) CELLULAR MATERIALS

Physical and Morphological Characterizations

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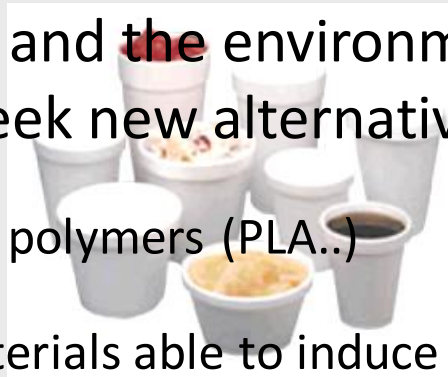
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➤ Sustainable development is nowadays a major priority

➤ The problems related to the management of plastic waste at the end of the lifetime and the environmental impact of these materials lead to seek new alternatives like:

- ✓ The use of bio-based polymers (PLA..)
- ✓ The lightening of materials able to induce important energy profits in various industrial sectors



- ✓ The use of bio-based foams is also a way of progress which a major industrial interest



Definition of Cellular Plastics



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Mines
de Douai

Cellular Plastics:

Polymer (PS, PP, PE etc.)



Foaming agent (gas)



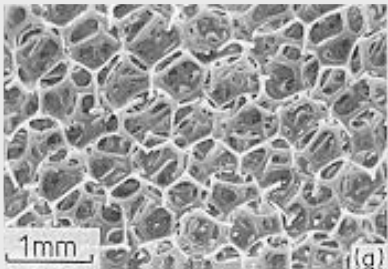
Additives (nucleant agents...)

Physical (PFA): hydrocarbons, CO₂, N₂

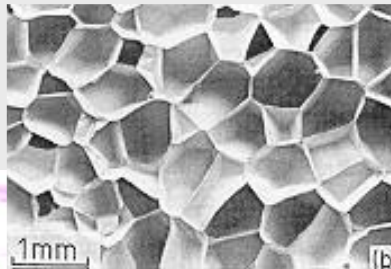
Chemical (CFA): azodicarbonamide, acid/carbonate



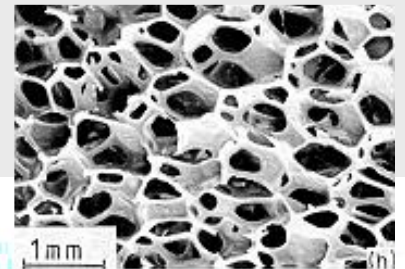
Microstructure:



Open-cell



Closed-cell



Open and closed-cell

Methodology of the study

Chemical foaming extrusion

Optimization of the void fraction

■ Processing conditions

- Die temperature
- Screw speed
- Temperature profile

■ Materials parameters

- PLA type
- CFA content

Measured parameters

- Cell size
- Void fraction
- Bulk density
- Open cell
- Tensile properties

Presentation Outline

➤ **Materials and methods**

➤ **Results**

- ✓ Optimization of the processing conditions
 - Die temperature and screw speed
 - Temperature profile
- ✓ Influence of the material parameters
 - CFA content
 - PLA type
- ✓ - Complementary Results
 - o Effect of the cooling system
 - o Influence of CFA type
 - o Effect of the cooling speed

➤ **Conclusions**

Materials and Methods



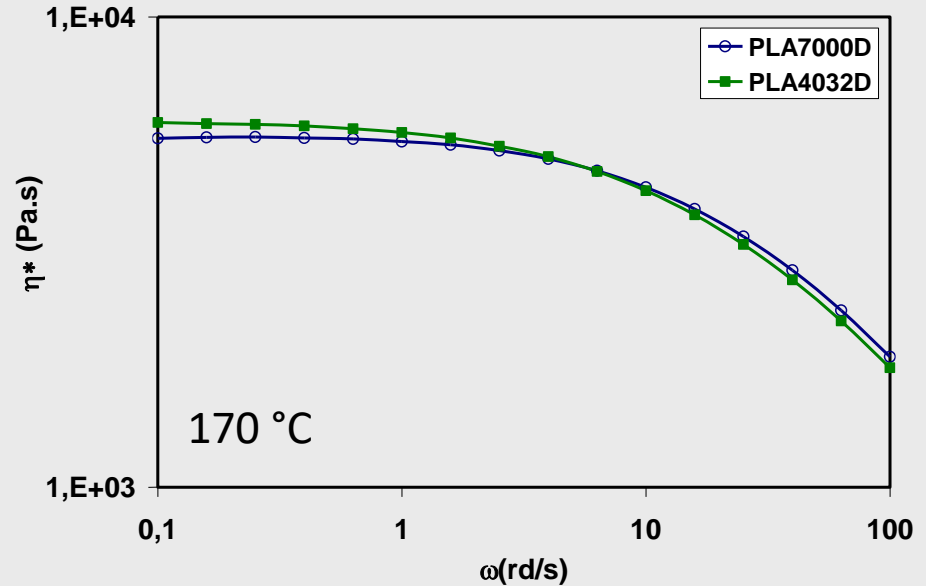
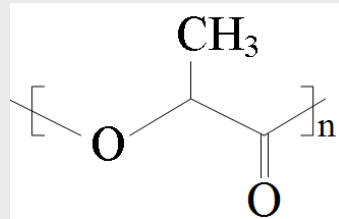
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Materials:

Polylactic Acid (PLA) from NatureWorks: Linear Aliphatic Polyester

■ PLA 7000D®

■ PLA 4032D®



Polymers	M_v (g/mol)	T_g (°C)	T_m (°C)	Density (kg/m ³)
PLA7000D	90438	63 ± 1,6	151 ± 0,8	1329 ± 3
PLA4032D	89563	67 ± 0,5	170 ± 0,5	1332 ± 11

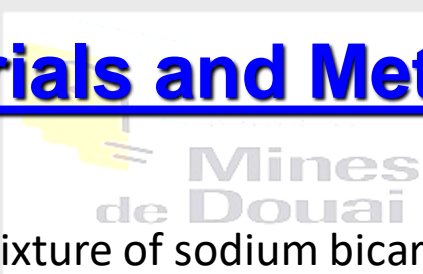
(): Measurement standard deviation

M_v (viscosimetric molecular weight); T_g and T_m (glass transition and melting temperatures respectively)



The only difference lies in the melting temperature of both PLAs

5th International Conference on Modification, Degradation and Stabilization of Polymers, September 5-8, 2010, Lille, France

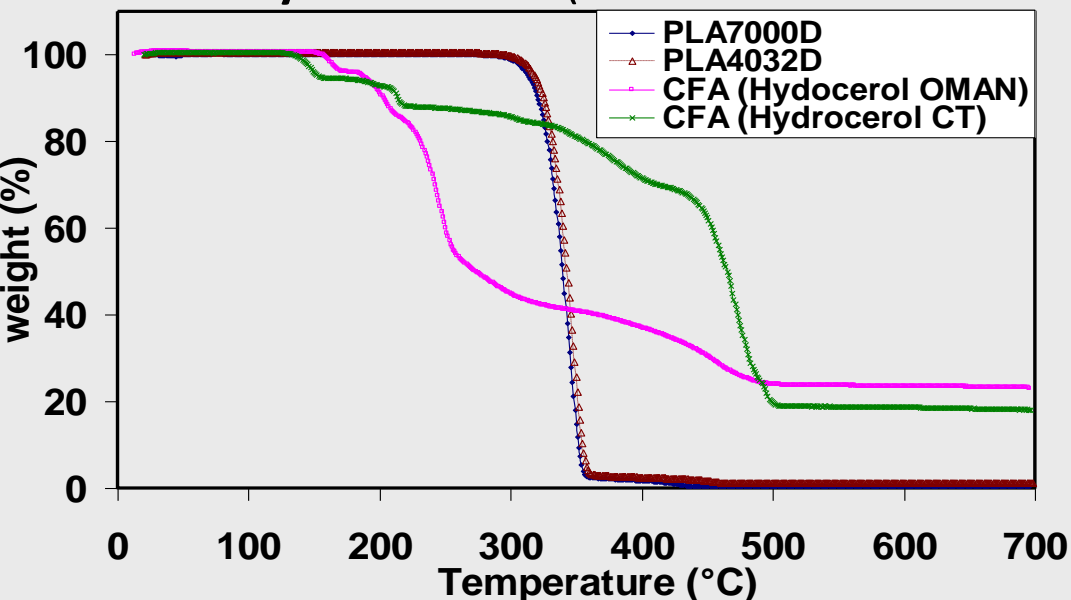


Materials:

Chemical foaming agent (CFA): Mixture of sodium bicarbonate/citric acid which releases CO₂ and H₂O under the temperature effect

■ **Hydrocerol OMAN** (Clariant Masterbatches)

■ **Hydrocerol CT** (Clariant Masterbatches)



- ✓ The thermal stability of both PLAs is similar
- ✓ The initial and final decomposition temperatures as well as the gas yield are slightly different for both CFAs

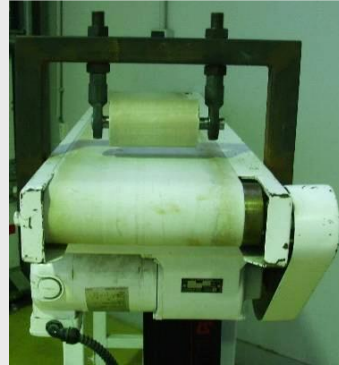
CFAs	T _{in} (°C)	T _{fin} (°C)	Gaz yield (g/ml)
Hydrocerol OMAN	152	211	55
Hydrocerol CT	138	216	50

Materials and Methods

Chemical Foaming process by extrusion:



Calender
(confined cooling)



Drawing frame
(free cooling)

Flat die :
40×1,5 mm²



Single screw extruder
φ 30 mm, L/D 24 mm

Temperature profile	Temperature (°C)					
	Barrel (From hopper to die)					Die
	1	2	3	4	5	6
A	130	150	165	165	170	180–195–210
B	150	170	170	170	180	195
C	170	170	180	180	180	195

Screw speed: 10, 20 and 30 rpm

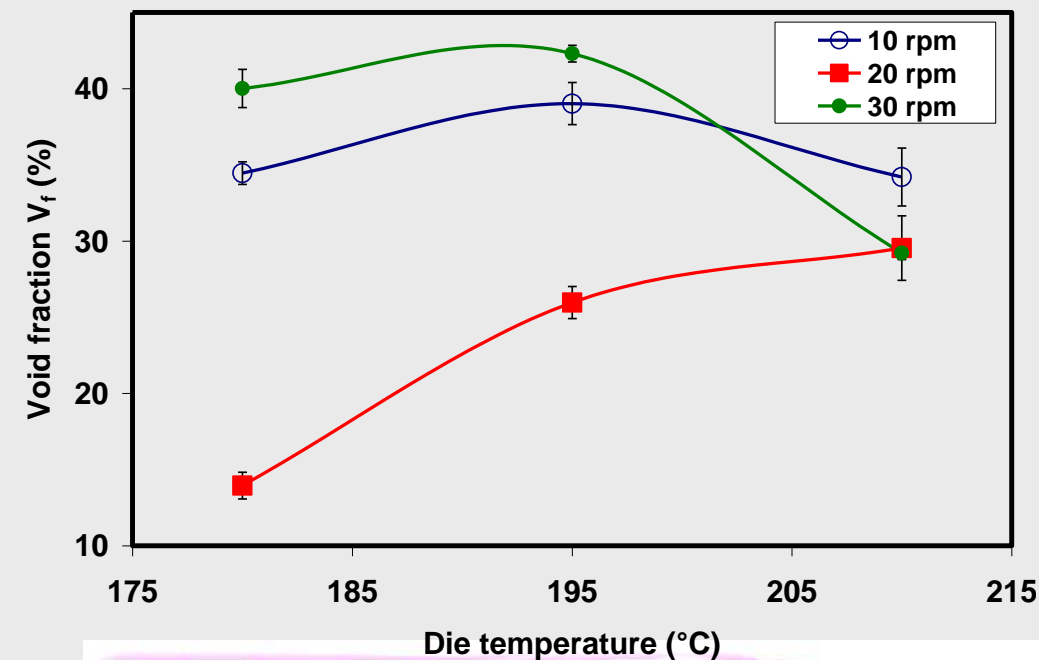
➤ Results

- ✓ Optimization of the processing conditions
 - Die temperature and screw speed
 - Temperature profile
- ✓ Influence of the material parameters
 - CFA content and PLA type
- ✓ - Complementary Results
 - o Effect of the cooling system
 - o Influence of CFA type
 - o Effect of the cooling speed

➤ Conclusions

Optimization of the processing conditions:

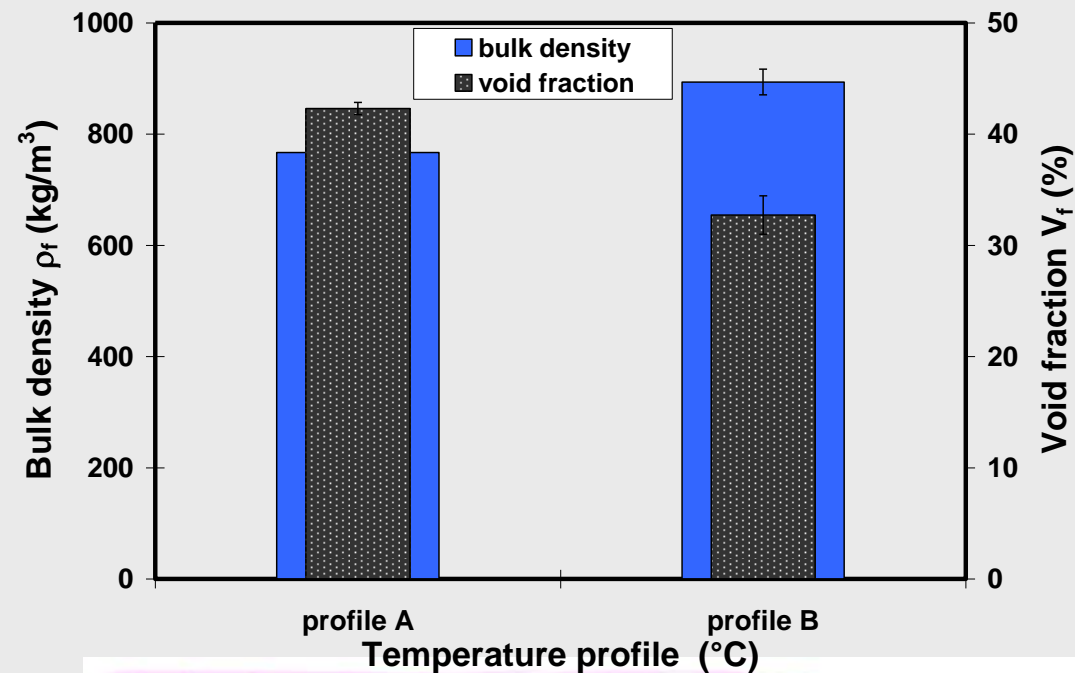
Effect of the die temperature and the screw speed: Evolution of the void fraction as a function of the die temperature and screw speed – PLA7000D, CFA content 2 wt%, temperature profile A, free cooling



- Maximum value for an intermediate die temperature of 195 °C and 30 rpm
- Competition between two antagonist mechanisms :
 - ✓ An increase in the temperature accelerates the CFA decomposition (increasing of the void fraction)
 - ✓ An increase in the temperature decreases the blend viscosity (decreasing of the void fraction)

Optimization of the processing conditions:

Effect of the temperature profile: Evolution of the void fraction or the bulk density as a function of temperature profile (A and B) – PLA7000D; CFA content 2 wt%; screw speed 30 rpm; die temperature 195 °C, free cooling



- The bulk density of the foam extruded with the temperature profile A (766 kg/m³) is 14 % lower than the bulk density of the foam extruded with the temperature profile B (893 kg/m³).

Chemical foaming extrusion

Optimization of the void fraction

■ Processing conditions

- Die temperature : **195 °C**
- Screw speed: **30 rpm**
- Temperature profile: **A; B**

■ Materials parameters

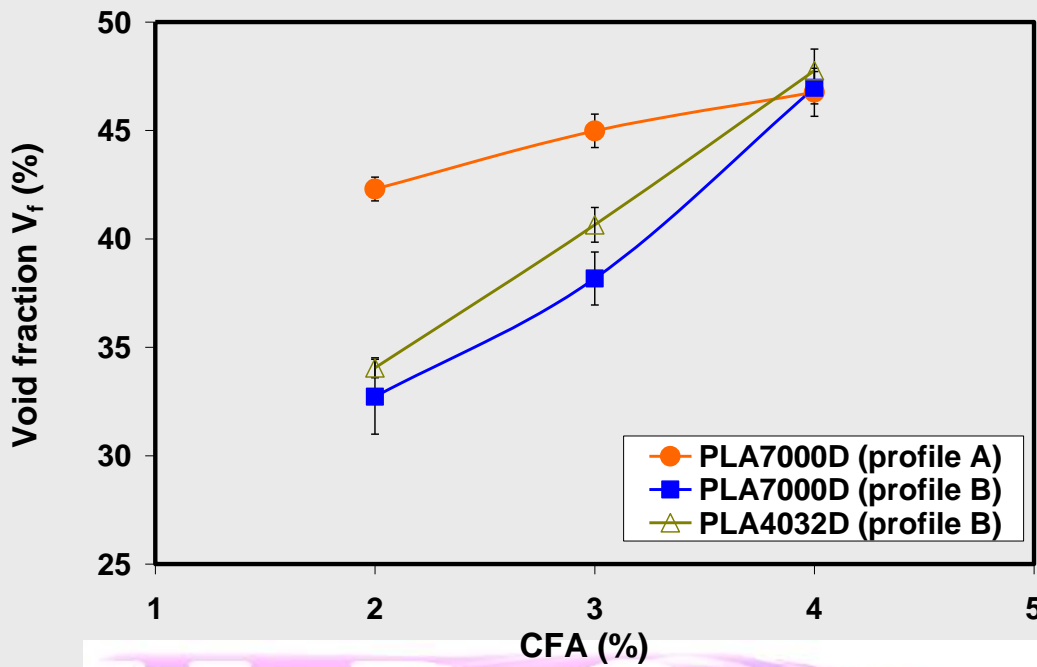
- PLA type
- CFA content

Measured parameters

- Cell size
- Void fraction
- Bulk density
- Open cell
- Tensile properties

Influence of the material parameters:

Influence of CFA rate and PLA type on the void fraction : Evolution of the void fraction as a function of CFA content for PLA 7000D and PLA4032D – two temperature profiles (A and B), screw speed 30 rpm, die temperature 195 °C ; free cooling



- Similar behavior for both PLAs regardless the temperature profile
- The void content increases gradually with the CFA content
- Increases in the void fraction up to 47 %

Results



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Influence of the material parameters: Influence of CFA rate and PLA on the cellular structure:

Polymers	CFA (wt%)	\bar{d}_n μm	\bar{d}_w μm	PDI	N_c (cells/cm ³) $\times 10^5$	δ μm	C_o (%)
PLA 7000D	2	90 (37,2)	105	0,86	11,25	48,14	10,91 \pm 0,2
	3	95 (30,3)	104	0,91	10,13	46,46	14,72 \pm 1.1
	4	107 (40,6)	122	0,88	7,38	49,26	19,22 \pm 0,7
PLA 4032D	2	134 (36,7)	144	0,93	2,72	95,39	19.12 \pm 1.5
	3	125 (78,8)	174	0,72	4,02	70,80	24.49 \pm 1.3
	4	130 (54,3)	152	0,86	4,19	57,89	26.76 \pm 1.1

() : Distribution standard deviation & \pm : Measurement standard

Equivalent diameter	$d_i = 2\sqrt{A/\pi}$
Number average diameter	$\bar{d}_n = \frac{\sum(d_i n_i)}{\sum n_i}$
Weight average diameter	$\bar{d}_w = \frac{\sum(d_i^2 n_i)}{\sum(d_i n_i)}$
Polydispersity index	$PDI = \frac{\bar{d}_w}{\bar{d}_n}$
Cell density	$N_c = \frac{1 - \left(\frac{\rho_f}{\rho_p}\right)}{\left(\frac{\pi d^3}{6}\right)}$
Wall cell thickness	$\delta = \frac{1}{\sqrt{\left(1 - \frac{\rho_f}{\rho_p}\right)}} - 1$
Open cell content	$C_o = \frac{(V_g - V_r)}{V_g} \times 100$

- Homogeneous cellular structure (PDI \approx 1)
- PLA7000D : An increase in the CFA content leads to an increase in the cells size.
- PLA4032D: The cells size passes by an extremum
- The cells density of the PLA 7000D is higher than that of the PLA 4032D
- The open cells ratio increases with the CFA quantity



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Results



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Influence of the material parameters:

Influence of CFA rate on tensile Properties (ISO 527-2): Evolution of the specific tensile strength as a function of the CFA content for both PLAs

Polymers	CFA (wt%)	V _f (%)	σ _{max} (MPa/g.cm ³)	ε _{max} (%)	σ _r (MPa/g.cm ³)	ε _r (%)
PLA 7000D	0	—	45.5 ± 1.6	10.3 ± 0.9	43.2 ± 1.4	11.1 ± 0.9
	2	42 ± 0.5	46.9 ± 2.8	8.4 ± 0.3	43.5 ± 2.2	9.9 ± 0.7
	3	45 ± 0.8	35.1 ± 1.3	8.8 ± 0.4	29.4 ± 1.7	11.6 ± 0.9
	4	47 ± 1.1	33.5 ± 0.9	8.4 ± 0.6	28.9 ± 1.1	10.3 ± 1.2
PLA 4032D	0	—	44.7 ± 2.3	9.4 ± 0.4	41.0 ± 4.9	10.2 ± 0.6
	2	34 ± 0.5	46.1 ± 3.3	10.2 ± 0.9	43.1 ± 3.9	11.5 ± 1.2
	3	41 ± 0.8	38.8 ± 2.4	8.6 ± 0.7	34.3 ± 3.4	10.4 ± 1.1
	4	47 ± 1.0	38.5 ± 1.2	9.4 ± 1.4	32.9 ± 1.1	11.5 ± 1.6

±: Measurement standard deviation

- The increase in CFA content leads to a reduction in the specific stresses at yield (σ_{max}) and break (σ_r)
- The specific stresses at yield and break are similar for the solid PLAs and the foamed PLAs up to 2 % of CFA
- The strain at yield (ε_{max}) and break (ε_r) are independent of the CFA content



Complementary parameters :

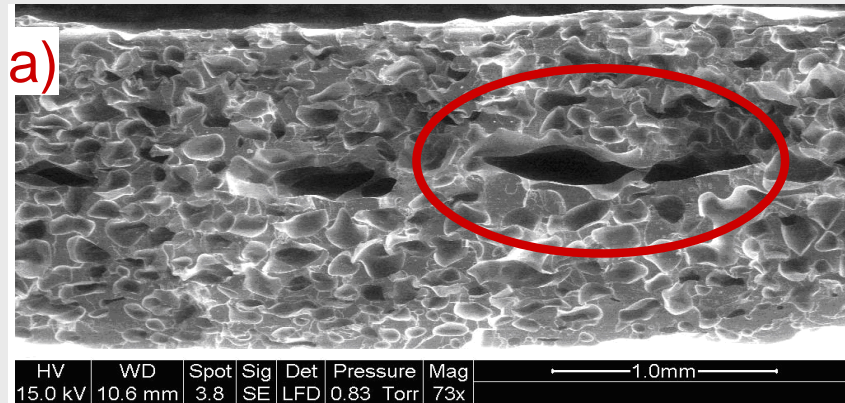
- ❖ Cooling system
- ❖ CFA type
- ❖ Cooling speed



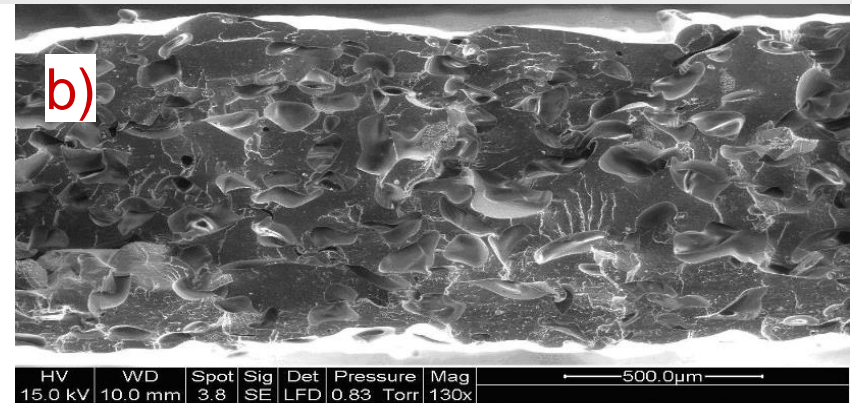


Influence of the cooling system:

Effect of the cooling system: PLA7000D foam cooled to free air with a drawing frame and to 10°C with a calender



a) PLA 7000D / 4 % CFA – 30 rpm – die temperature 195 °C – Drawing frame (free cooling)

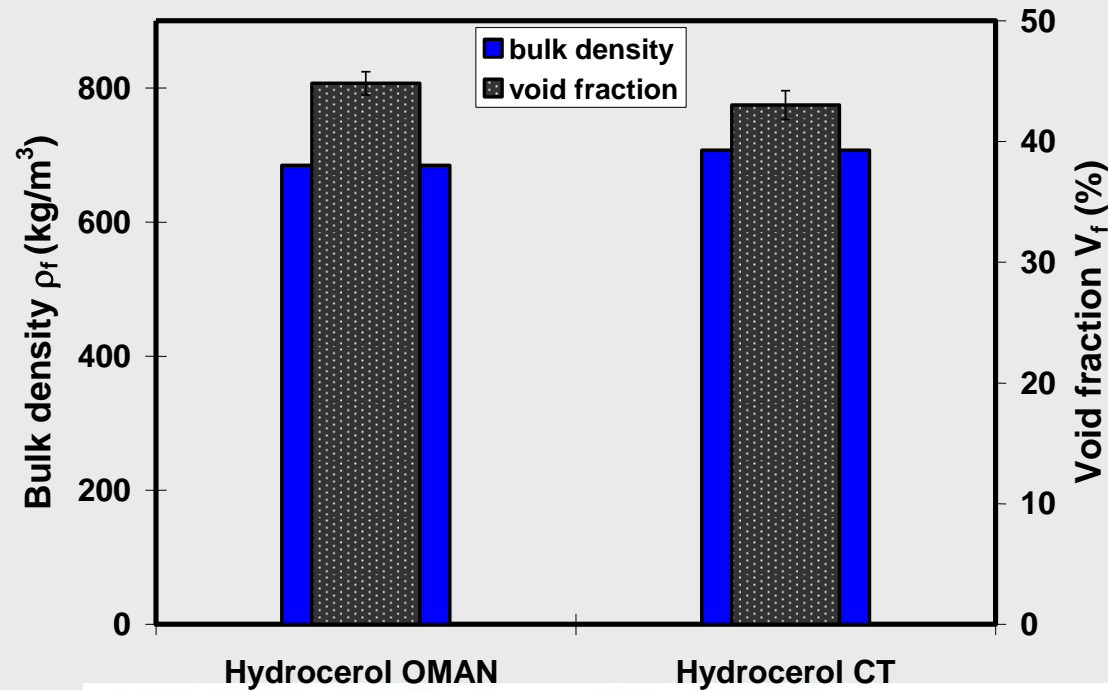


b) PLA7000D / 4 % CFA – 30 rpm – die temperature 195 °C – Calender 10 °C (confined cooling)

- Macroscopic holes in the center of the cooled extruded product with free air
- Disappearance of the cells coalescence with the use of the calender
- Void fraction is similar for both cooling types (47 % and 45 % for the free cooling and the confined cooling respectively)

Influence of the CFA type:

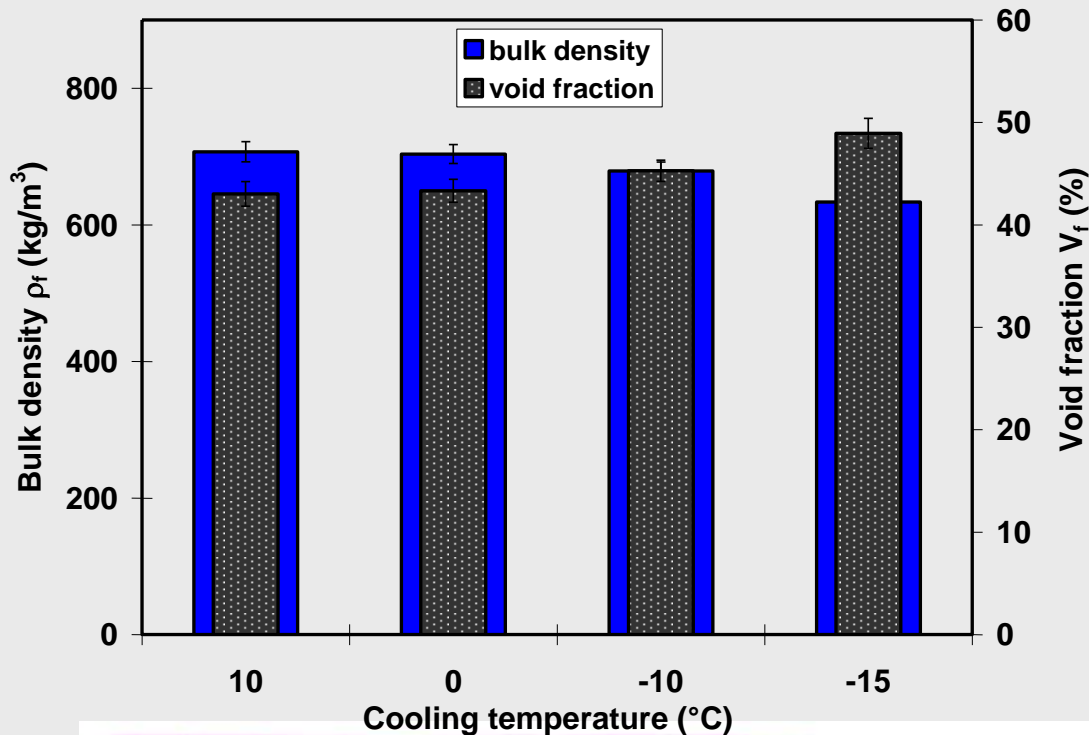
Effect of the CFA type on the void fraction : Evolution of the void fraction and the apparent density of PLA7000D foams as a function of CFA type (**Hydrocerol OMAN et Hydrocerol CT**) to 4 wt% – Confined cooling with the calender (10 °C) – die temperature 195 °C and 30 rpm



- Almost similar void fraction and apparent density (different from 4%) for both CFAs

Influence of the cooling speed:

Effect of the cooling speed on the void fraction for the Hydrocerol CT : Evolution of the void fraction of PLA7000D foams as a function of the cooling temperature (10 °C to -15 °C) – die temperature 195 °C and 30 rpm – confined cooling with the calender



■ Increasing of the void fraction (43% to 49%) with the reduction in the cooling temperature of the calender

Conclusions

- Processing conditions: die temperature 195 °C; screw speed 30 rpm
- Homogeneous cellular structure for both PLAs (**PDI ≈ 1**)
- Low open cell ratio (**between 10 to 26 %**)
- Significant mechanical properties for foams extruded compared to the neat PLA (**$\sigma_{\max} = 47$ and 46 MPa/g.cm^{-3} respectively**)
- The void fraction is similar for both CFAs (**45% et 47%**), nevertheless a reduction of the cooling temperature of materials makes possible to increase it

- Void fraction: **49 %**

Perspectives

- ❖ **Extensional viscosity is an important parameter for the foaming.**
 - ✓ PLA/chain extenders blends
 - ✓ Irradiation of the PLA by γ -rays



Thank You !!!

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