

# DEVELOPMENT OF NANOCLAY REINFORCED POLY(LACTIC ACID) CELLULAR MATERIALS

Influence Of The Filler Content And The Addition Of Maleic  
Anhydride-Grafted-PLA On Physical Properties And Cell Morphology

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# Outline

- **Background and objectives**
- **Materials and processing method**
- **Results and discussion**
- **Conclusion and perspectives**

# Background

Crude Oil



Environment



**Bio-based & Biodegradable  
Polymers (R&D)**

Reducing !



- Raw materials
- Energy

**(Bio)Foams**

# Background

## Poly(lactic acid) (PLA)

- ✓ Bio-based & biodegradable
- ✓ Eco-friendly alternative
- ✓ Mechanical properties
  - High tensile modulus
  - High tensile strength
- ✓ More reasonable cost (bioplastics)

- × Higher cost (synthetic plastics)
- × Brittleness
- × Impact resistance
- × Melt strength (linear PLA)
- × Service temperature (amorphous)

	PLA	PET	PS
$T_g$ (°C)	55	75	105
Tensile strength at break (MPa)	53	54	45
Tensile modulus (GPa)	3.4	2.8	2.9
Elongation at break (%)	6	130	7
N. Izod impact strength (J/m)	13	59	27
Gardner impact (J)	0.06	0.32	0.51
Cost (\$/lb)	1-1.5	0.70-0.72	0.99-1.01

Adapted from: H. Liu, J. Zhang, Journal of Polymer Science Part B: Polymer Physics 49 (2011) 1051-1083.

# Background

## Solutions to overcome PLA shortcomings

### ❑ Plasticization, copolymerization, melt blending

- **Flexibility and toughening**

- H. Liu, J. Zhang, Journal of Polymer Science Part B: Polymer Physics 49 (2011) 1051-1083.

- **Tensile strength and modulus**

- L.M. Matuana, C.A. Diaz, Industrial and Engineering Chemistry Research 49 (2010) 2186-2193.

### ❑ PLA nanocomposites : organo-modified montmorillonite (OMMT)

- **Physical, chemical and mechanical properties,**

- **OMMT (2.5 wt %) : Higher strain at break (fourfold increase).**

- L. Jiang, J. Zhang, M.P. Wolcott, Polymer 48 (2007) 7632-7644.

### ❑ PLA foams

- **Microcellular foams: impact resistance, strain at break and toughness,**

- **Nanocomposites foams : control cellular structures and properties.**

- L.M. Matuana, Bioresource Technology 99 (2008) 3643-50.

- Y. Di, S. Iannace, E. Di Maio, L. Nicolais, Journal of Polymer Science Part B: Polymer Physics 43 (2005) 689-698.

# Background

## Foam processing

### Physical Blowing Agent

**PBA** : hydrocarbons, CO<sub>2</sub>, N<sub>2</sub>

- Batch process,
- Expanded PLA beads,
- Continuous extrusion foaming,
- Continuous injection foaming.

✓ **Low density foams (R<0.1)**

✓ **Microcellular foams**

× **Specific equipments**

### Chemical Blowing Agent

**CBA**: azodicarbonamide, acid/carbonate

- Continuous extrusion foaming,
- Continuous injection foaming.

✓ **No specific equipment**

× **Low density reduction of 50 %**

#### Few studies (continuous extrusion) :

➤ S.T. Lee, L. Kareko, J. Jun, Journal of Cellular Plastics 44 (2008) 293.

➤ L.M. Matuana, O. Faruk, C.A. Diaz, Bioresource Technology 100 (2009) 5947-54.

# Objectives


## Investigation of the chemical foaming of PLA/clay nanocomposites through extrusion process

Could the foaming of PLA /clay nanocomposites balance the mechanical properties of neat PLA ?

### *Effect of organoclay & maleic anhydride-grafted-PLA (MA-g-PLA):*

- ✓ Void fraction (density reduction),
- ✓ Cell size and cell-population density (SEM image analysis),
- ✓ Tensile and flexural properties.

# Materials

- ✓ **Linear PLA : Grade Ingeo™ 7000D (NatureWorks® LLC)**  
D content = 6.4 %,  $T_m = 145-155$  °C,  $M_w = 370$  kDa.
- ✓ **Clay : Cloisite® 30B (Southern Clay Products Inc.)**  
organo-modified montmorillonite,  
4 contents : 1, 3, 5, 7 wt % (**CN1, CN3, CN5 and CN7**).
- ✓ **Maleic anhydride-grafted PLA (MA-g-PLA)**  
3 grafting contents : 0.25, 0.41, 0.48 wt % (**g1, g2 and g3**),  
 10 wt % MA-(**g1, g2, g3**)-PLA + 3 wt % Cloisite® 30B  
**CN3-g1, CN3-g2 and CN3-g3**

D. Carlson, L. Nie, R. Narayan, P. Dubois, Journal of Applied Polymer Science 72 (1999) 477-485.

- ✓ **CBA : Hydrocerol® CT 3108 (Clariant Masterbatches)**  
endothermic,  $T_d = 138-216$  °C (TGA),  
CBA content : 3 wt %.



# Foam processing

✓ Single screw extruder (Fairex )

✓ Slit die (1.5 mm x 40)

✓ 2 temperature profiles :

Temperature (°C)	zone 1	zone 2	zone 3	zone 4	zone 5	Slit die
195	130	150	165	165	170	195
155	140	180	195	155	155	155

✓ Fixed screw speed (30 rpm) and cooling system

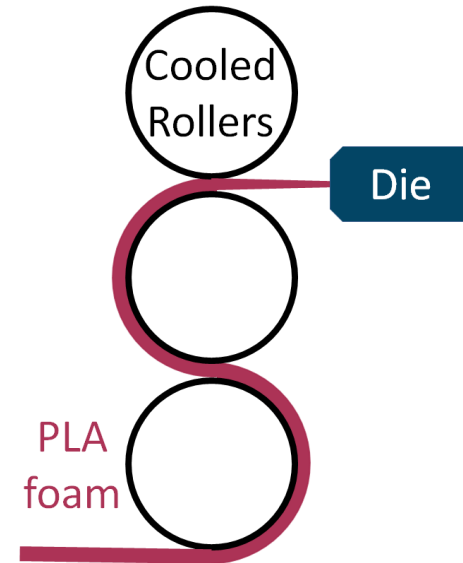
✓ 2 Types of specimens punched :

- T1 : Flexural properties (ISO 178), voids fraction, SEM images

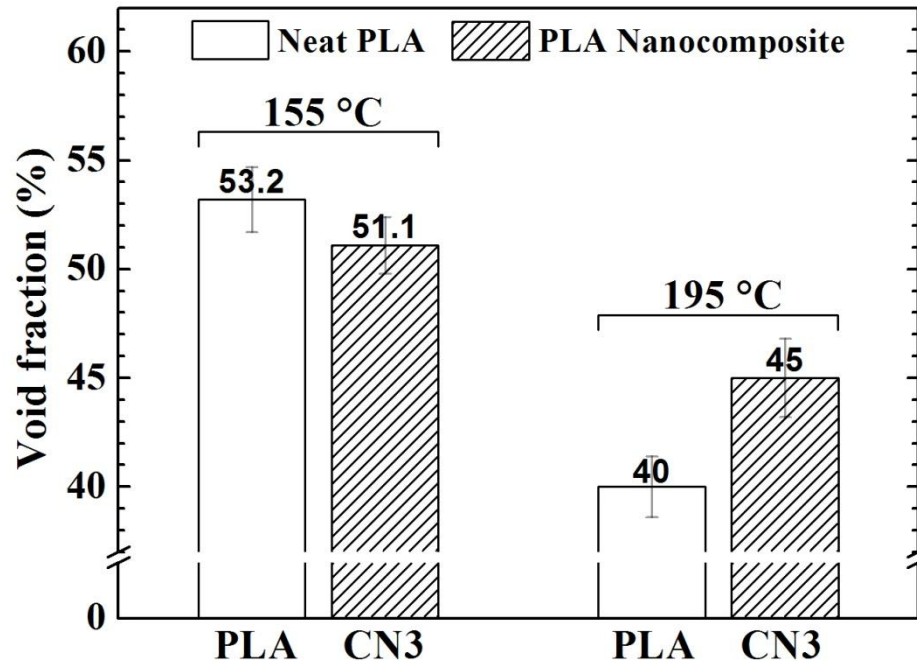
Dimensions : 80 mm x 10 mm x thickness

- T2 : Tensile properties (ISO 527-2)

Dimensions : type 1BA



# Effect of the die temperature and the addition of 3 wt % of nanoclays



## Void fraction : $V_f$

- Temperature :  $V_f$  reduction of both neat PLA and CN3

- Nanoclay addition :

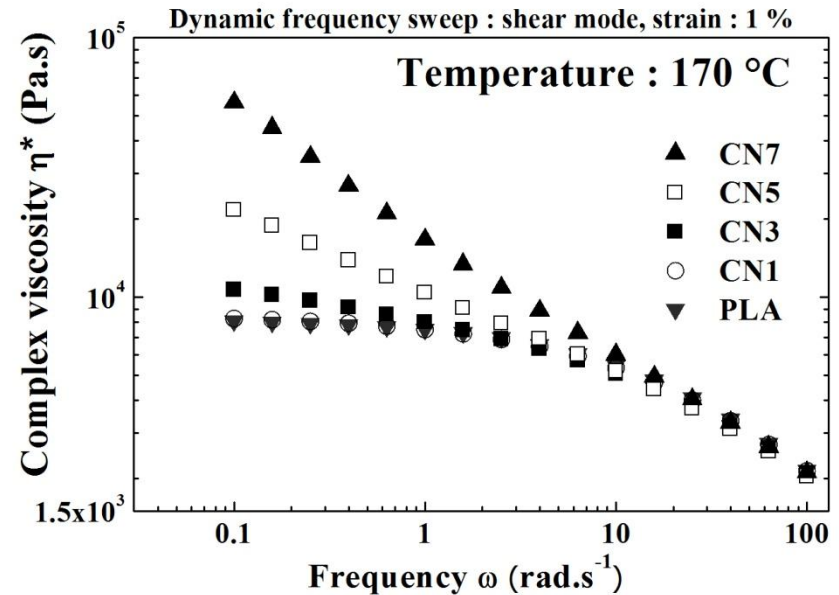
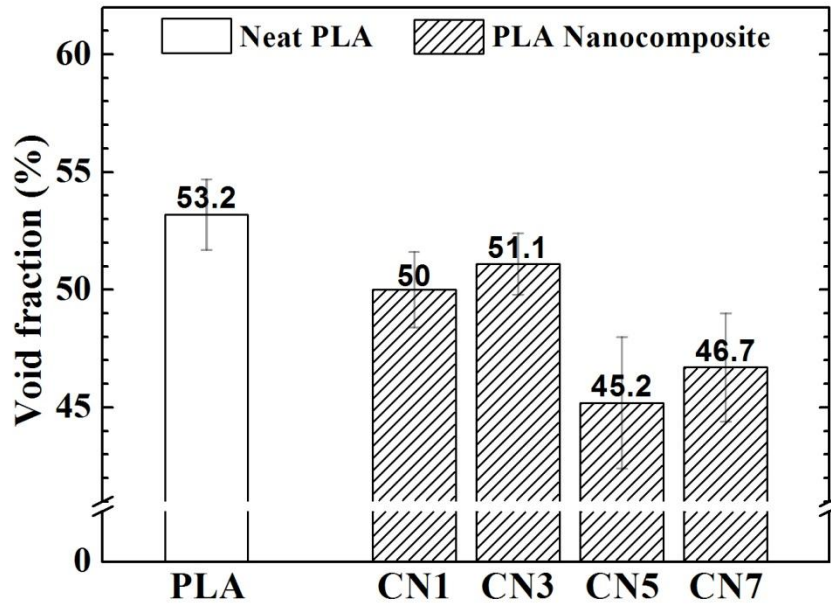
- 155 C : decreased  $V_f$
- 195 C : increased  $V_f$

□ Nanoclay addition increases melt viscosity which will result in increased or decreased void fractions depending on the foaming temperature.

□ A foaming temperature of 155 C was chosen as it leads to higher void fraction.

# Effect of the filler content

Void fraction :  $V_f$

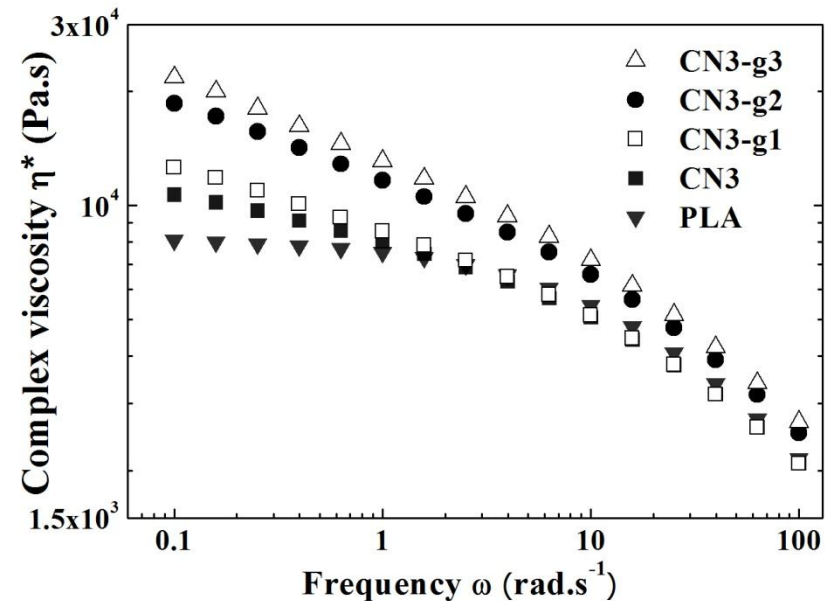
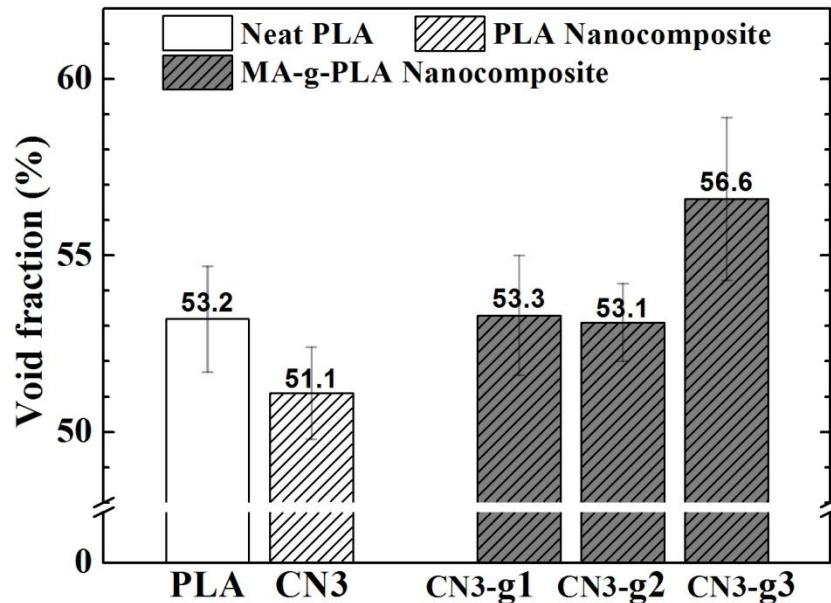


The void fraction of the nanocomposite foams decreases with increasing filler content.

□ Higher viscosity due to organoclays during foaming restricts the expansion of cells

# Effect of the MA-g-PLA addition and content

## Void fraction : Vf

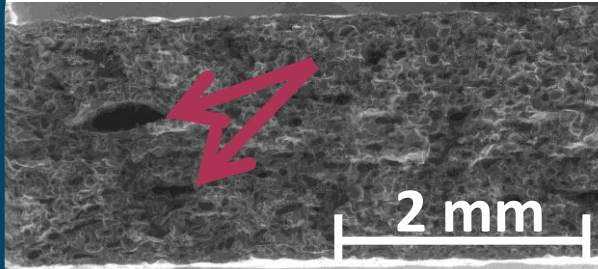


The void fraction of the nanocomposite foams increases with MA-g-PLA addition.

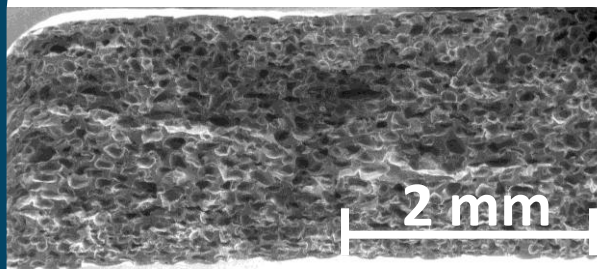
□ Unexpected results as the addition of MA-g-PLA increases the complex viscosity of the modified nanocomposites : Further investigations

# Cell morphology and cell-population density

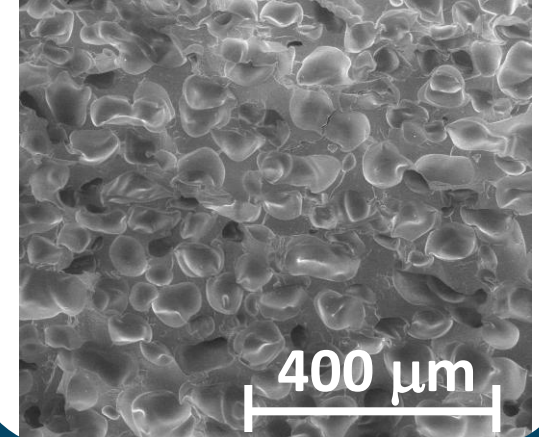
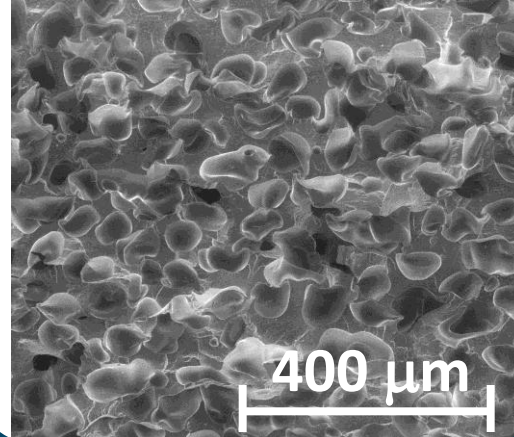
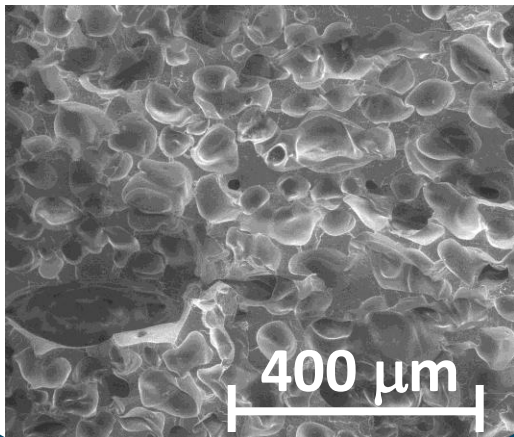
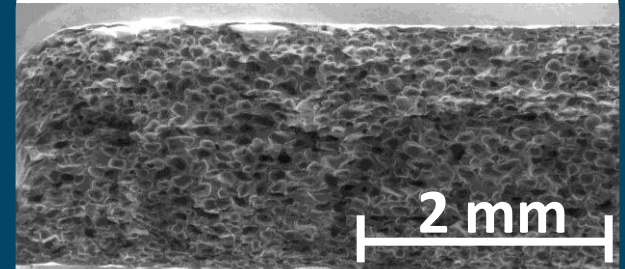
PLA



CN3

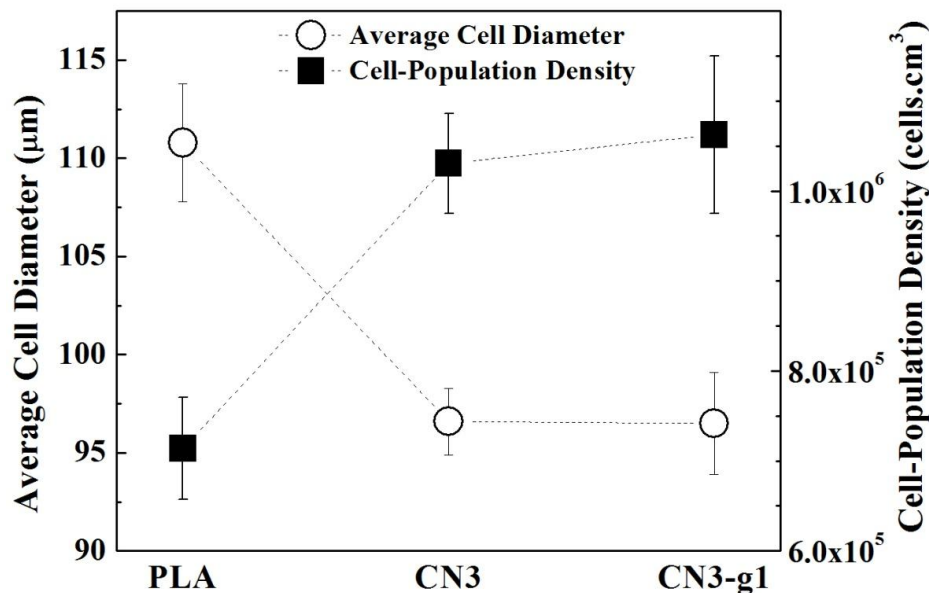


CN3-g1



- PLA foams show large-scale inhomogeneities,
- Nanocomposites : improvement in quality, no significant differences for the modified and unmodified nanocomposites

# Cell morphology and cell-population density



- Filler addition: decreases cell size and increases the cell population density

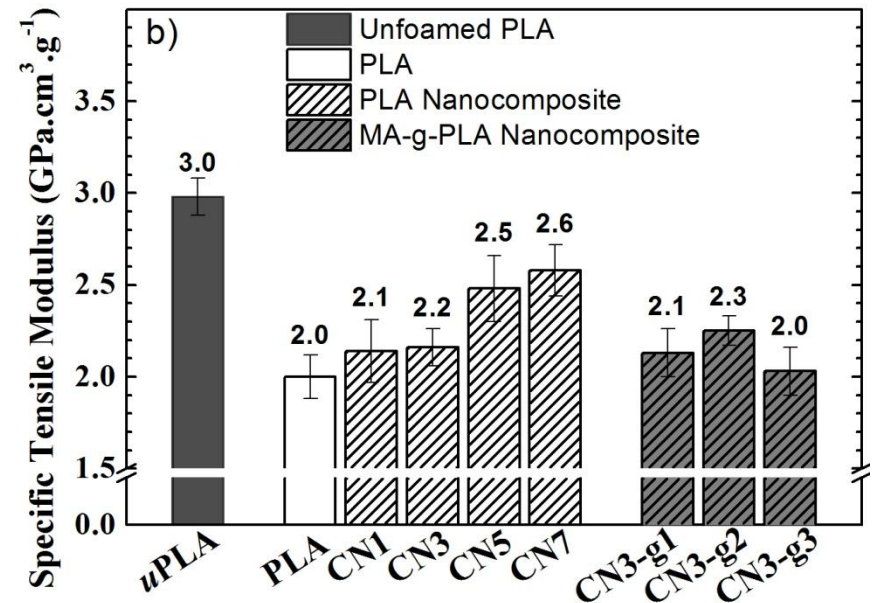
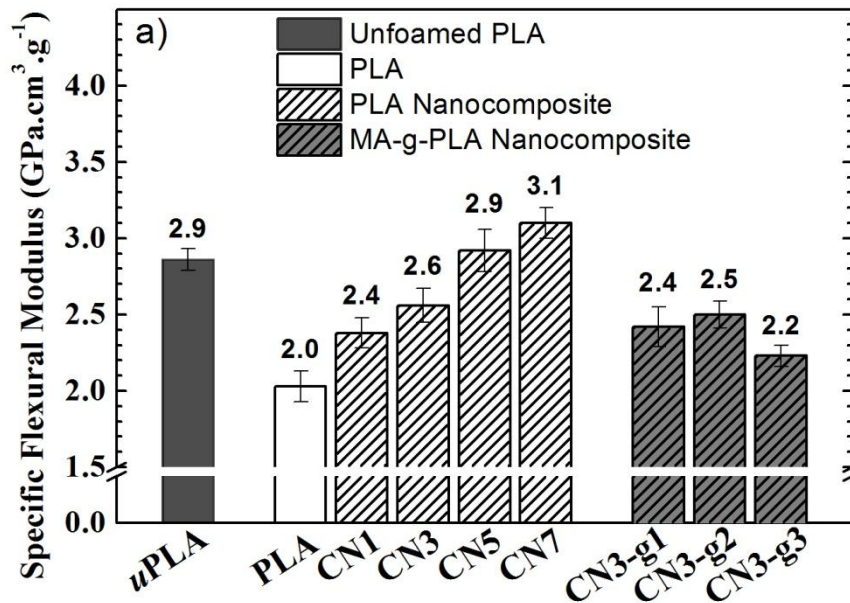
- MA-g-PLA addition: no significant changes in comparison with CN3

## Organoclay contribution :

- ❑ promotes heterogeneous nucleation
- ❑ increases the melt strength
  - stabilizes the cell wall
  - limits cell coalescences

# Effect of the filler content and MA-g-PLA addition

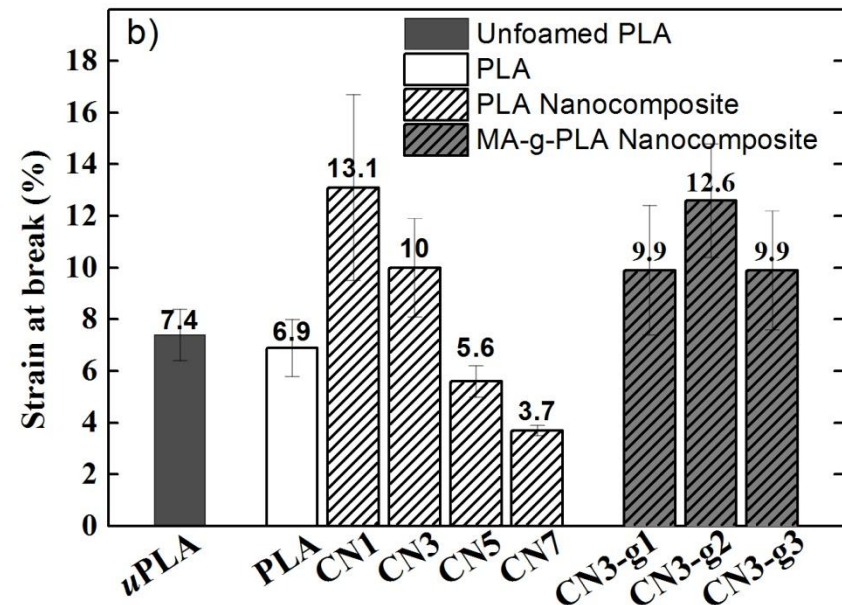
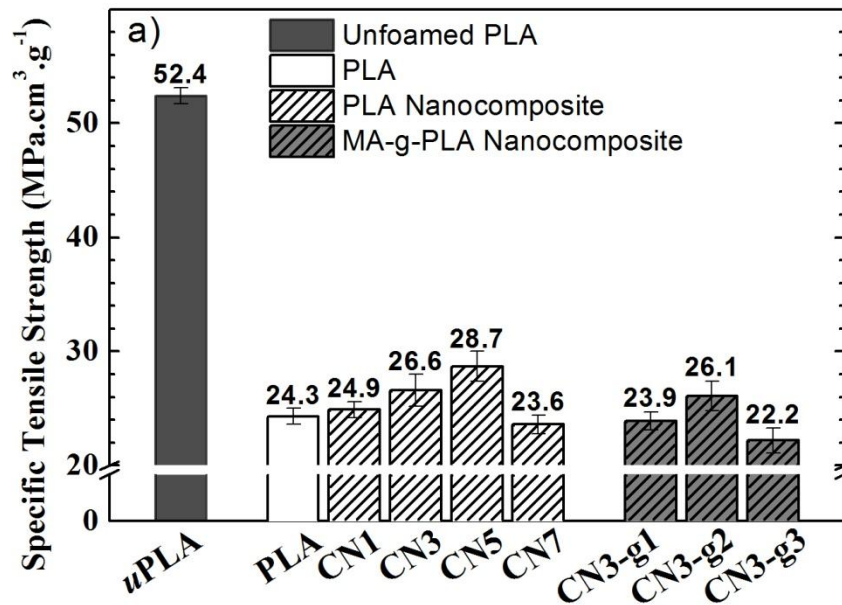
## Mechanical properties: Specific flexural and tensile Moduli



- ❑ Foaming : specific moduli reductions
- ❑ Specific moduli increase with the filler content
- ❑ MA-g-PLA : no significant improvement

# Effect of the filler content and MA-g-PLA addition

## Mechanical properties: Specific tensile strength and strain at break

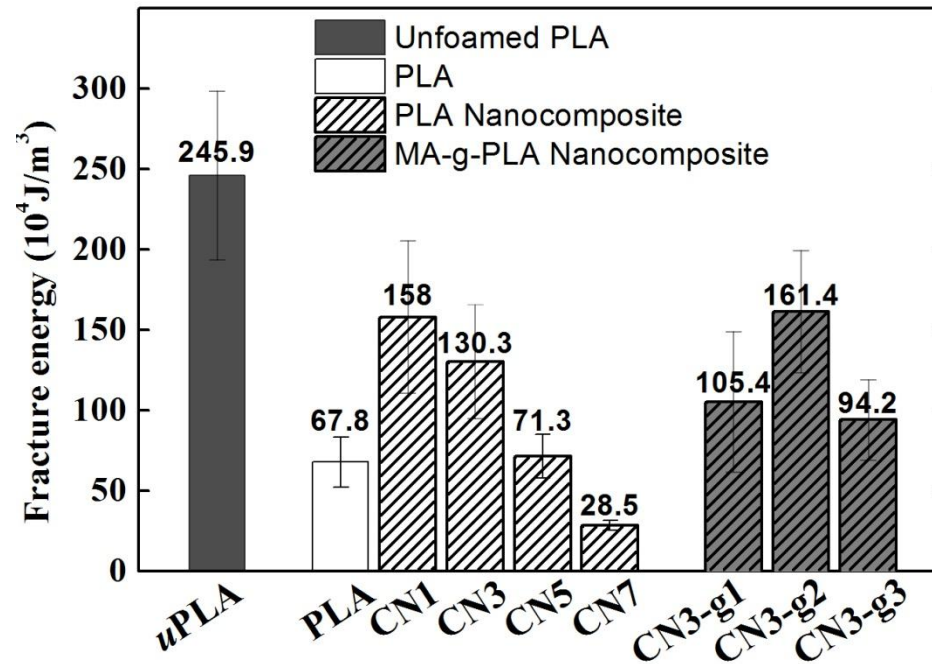


- Slight increase of the tensile strength with the filler content
- Low filler content : prevent propagation of cracks
- High filler content : flaws (agglomerates) trigger early failure
- MA-g-PLA : Enhanced plastic deformation (g2)



# Effect of the filler content and MA-g-PLA addition

## Mechanical properties: Fracture energy



- ❑ Significant reduction of the fracture energy after foaming.
- ❑ Enhanced fracture energy at low nanoclay content
- ❑ Beneficial effect of the compatibilizer g2 in comparison with CN3

# Conclusions

- ✓ **Chemical foaming of PLA leads to reasonable void fraction (50 %)**
- ✓ **Foaming :**
  - **reduces mechanical properties (ultimate and specific)**
- ✓ **Addition of nanoclay (foaming temperature : 155 °C)**
  - **decreases the void fraction**
  - **lower cell size and higher cell population density**
  - **globally balances mechanical properties : enhanced specific moduli, fracture energy (except for the tensile strength)**
- ✓ **Addition of a compatibilizer**
  - **increases the void fraction (up to 56 %)**
  - **Mechanical properties : no significant changes except for the fracture energy (g<sub>2</sub>)**

# Perspectives

- ✓ **Extensional viscosity measurement might help us to understand the effect of maleic anhydride-grafted-PLA on the void fraction**
- ✓ **Impact tests : Higher speed tests are more realistic than tensile testing and the results might differ because high strain rate testing can change a ductile material into a brittle one**
- ✓ **Morphological characterizations : transverse direction to the extrusion flow**

**Thank you for your attention**