

## Crystallinity Effects in Polylactic Acid (PLA) Based Foams

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## Outline



- Background and objectives
- Methods
  - materials
  - foam processing
  - characterisation
- Results
- Conclusions



## Poly(lactic acid) (PLA)



- Corn → Dextrose → Lactic acid → Lactide → PLA
  - ↙ L
  - ↘ D
- D/L ratio controls:
  - crystallinity
  - crystallisation rate
  - melting temperature
- $T_g$  around 55-60°C

# The Biopolymer Network (BPN) process



Liquid CO<sub>2</sub>  
impregnation



Pre-foaming



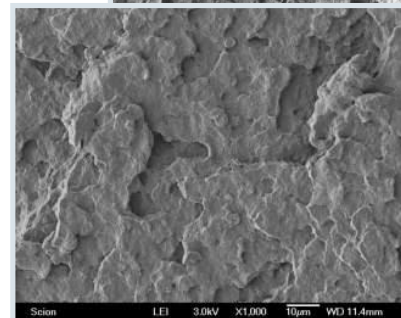
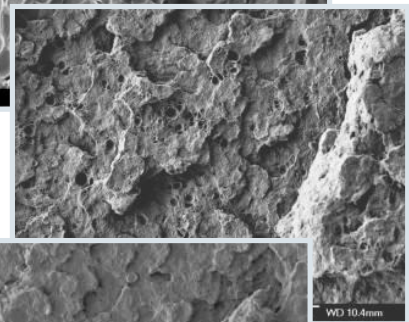
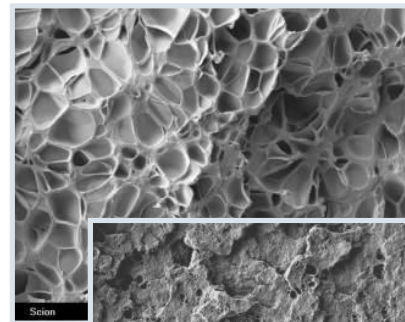
Moulding



Patent # WO 2008/093284 A1

## Crystallinity and foaming

- Higher crystallinity in the starting material means:
  - lower CO<sub>2</sub> solubility
  - higher matrix stiffness
  - more difficult foaming
- CO<sub>2</sub> induces crystallisation
- Expansion also generates crystallinity



## Benefits of crystalline PLA foams



- Effect on mechanical properties?
- Higher dimensional stability?
- Wider processing windows?

## Materials



- Four PLAs with various D-contents
- Samples extruded in 15 mm x 2 mm rods



PLA	D-content (%)	Crystallisation $t_{1/2}$ @ 100°C (minutes)
SC1	1.4	3-4
SC2	4.3	22-23
SC3	7.7	121-124
AM	11.8	-

# Foam processing



Liquid CO<sub>2</sub>  
impregnation



Foaming in hot water  
targeting 40 and 60 g/L



## Characterisation



- Density (fluid displacement)
- Scanning Electron Microscopy (SEM):
  - cross-sections
  - surfaces
- Differential Scanning Calorimetry:
  - 20 to 200°C at 5°C/minute
- Dimensional stability:
  - relative volume change over 24 hours at 70°C

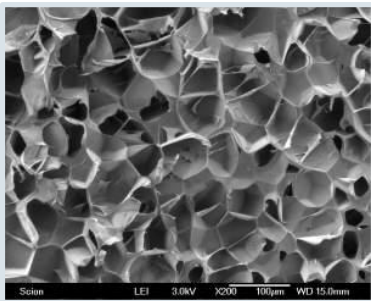
## Mechanical testing



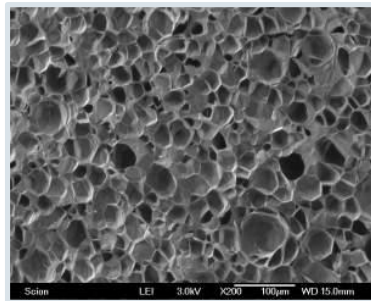
- Samples foamed between two steel plates and cut into rectangular specimens (35 x 4 x 3 mm)
- Three-point bending (DMTA):
  - 28 mm support span
  - 10% per minute strain rate
- Modulus by linear regression



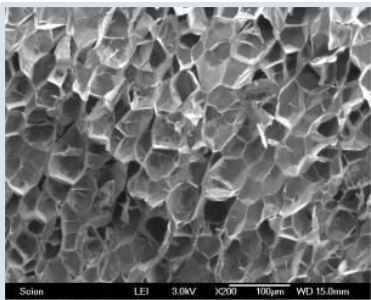
## Foams cross-sections (SEM)



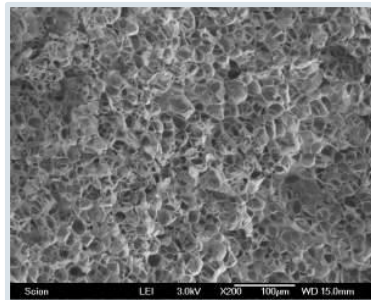
SC1



SC2



SC3

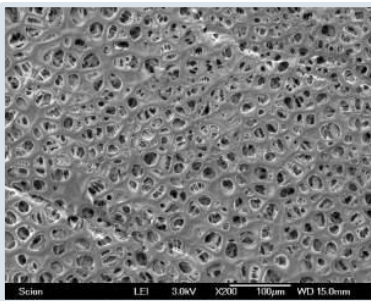


AM

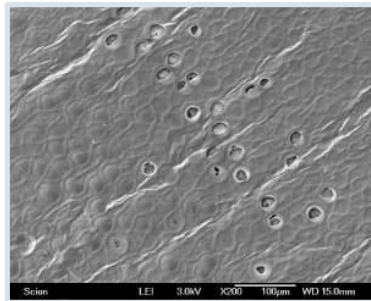
40 g/L

- Closed-cells
- Higher cell density in AM PLA

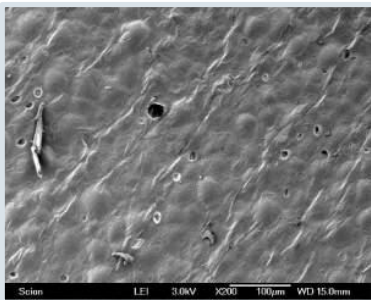
## Foams skins (SEM)



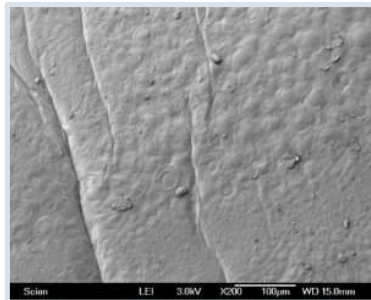
SC1



SC2



SC3

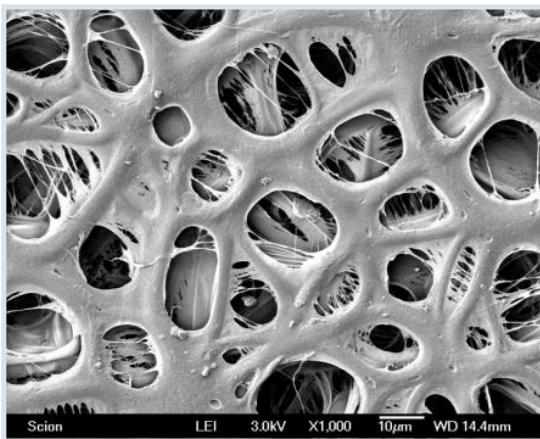


AM

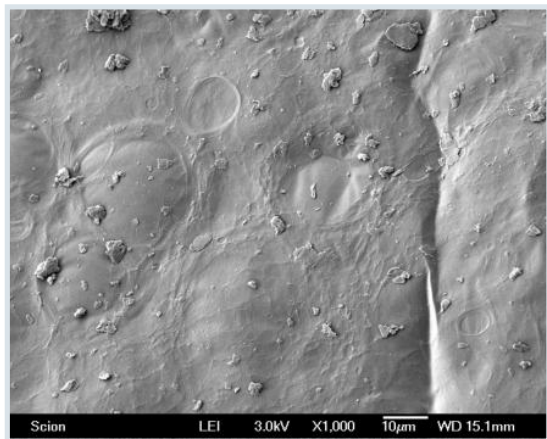
40 g/L

- Porous surface in SC1 PLA
- Smooth surface in AM PLA

## Foams skins (SEM)



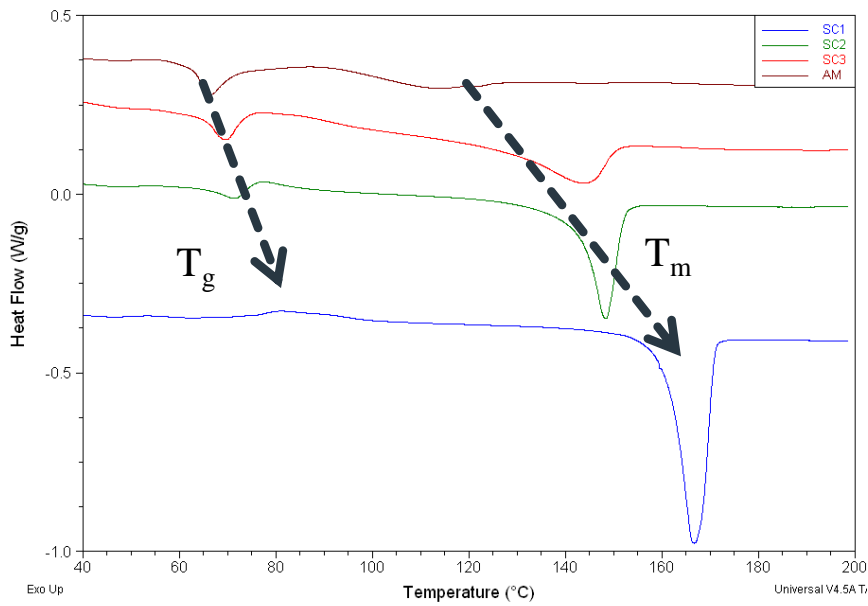
SC1



AM

- Higher open-cell content in SC1 foams?
- Cell wall rupture due to small crystals

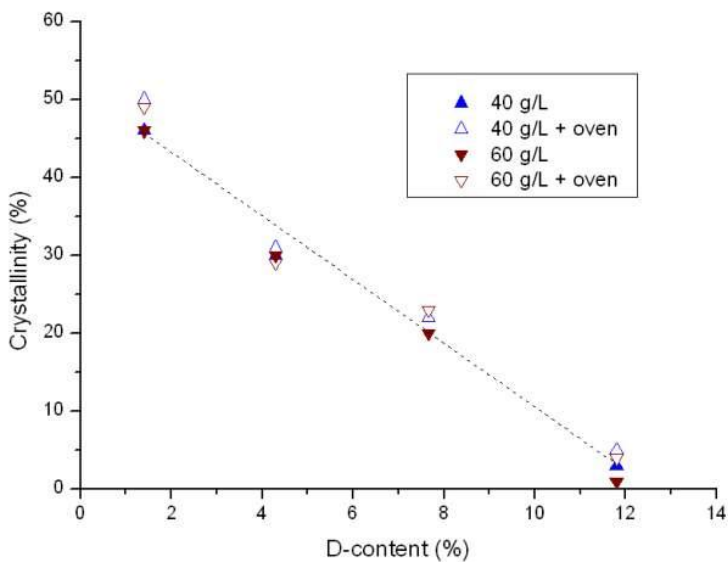
# Thermal behaviour



Foamed at  
60 g/L

- Increasing  $T_m$  and  $T_g$  with decreasing D-content

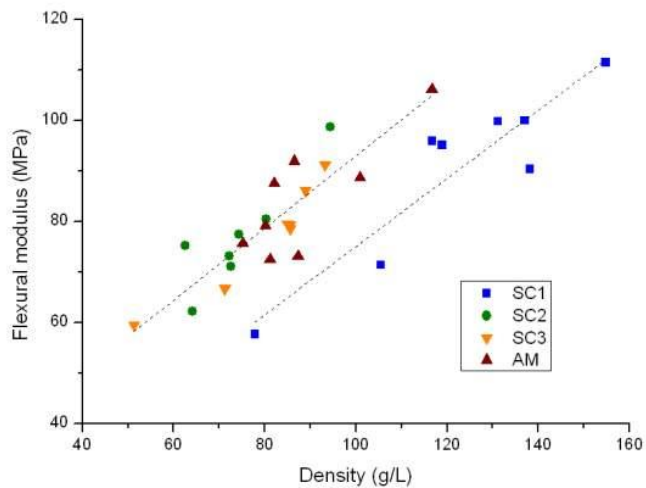
# Thermal behaviour



Crystallinity calculated from DSC

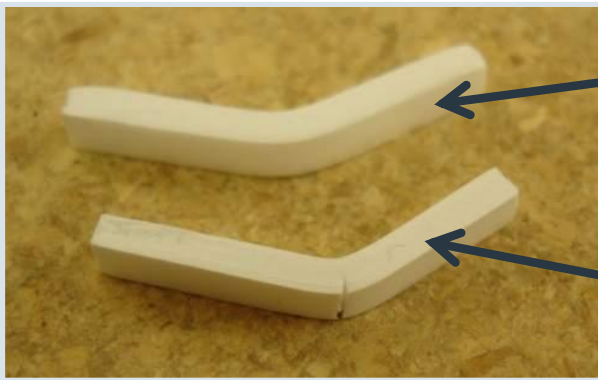
- Linear relationship
- No density effect
- Slight increase due to oven-treatment

## Mechanical testing



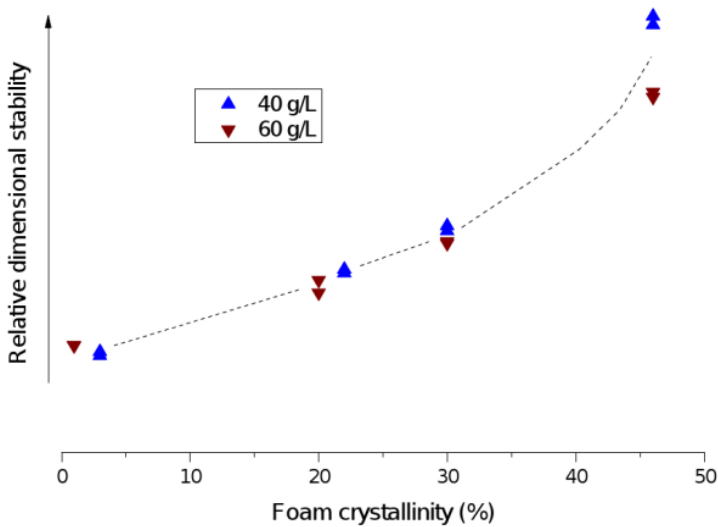
- SC2, SC3 and AM show the same behaviour.
- SC1 PLA foam has lower modulus  
→ due to open-cell content?

## Mechanical testing



- Fracture occurred in some SC1 PLA samples

## Dimensional stability (70°C for 24 hours)



- Not a linear relationship
- Large increase in stability above 40% crystallinity
- Significant density effect

## Conclusions



- PLAs with a wide range of D-contents can be foamed using the BPN process.
- Cellular structure and mechanical properties are affected by the PLA grade used.
- Up to 50% crystallinity in the foams in the foams made by the BPN process.
- Increased crystallinity can significantly improve dimensional stability.

## Acknowledgements



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**THE UNIVERSITY OF AUCKLAND**  
**NEW ZEALAND**

