

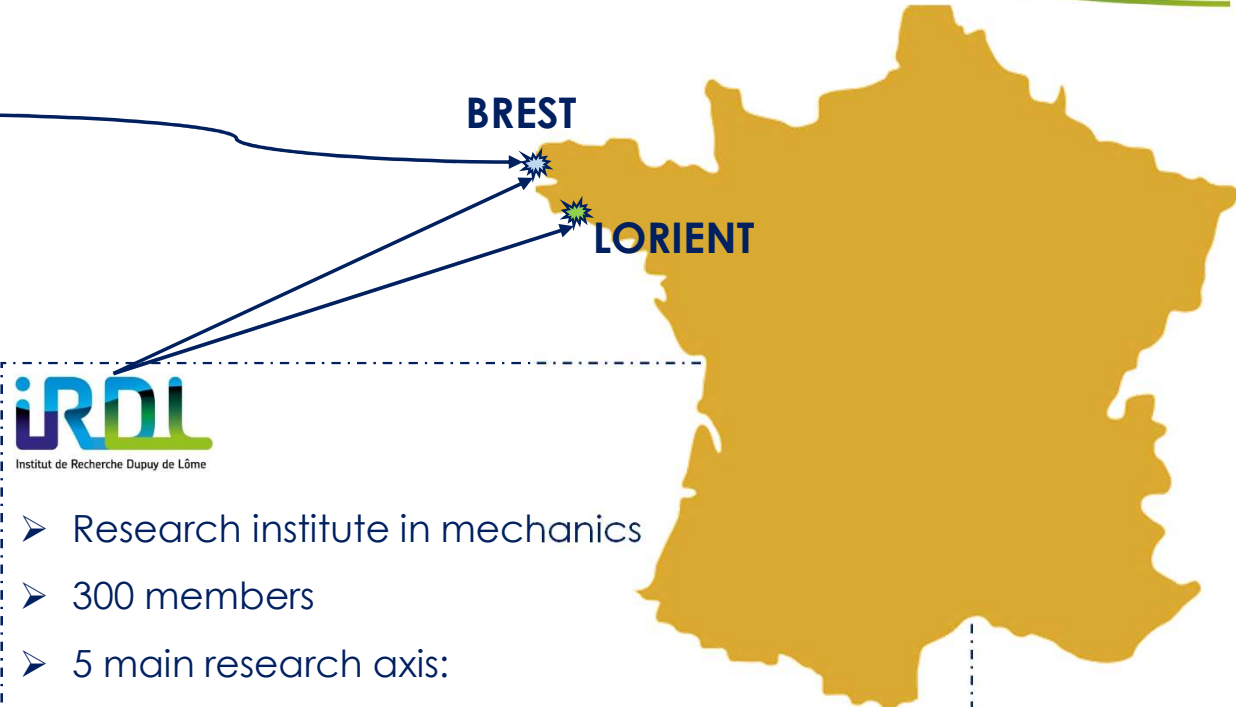


# Combining XRD and nanoindentation to characterize mechanical properties evolution of flax cell walls during controlled heat treatment

*Nanobruecken 2024 – 19/03/2024*

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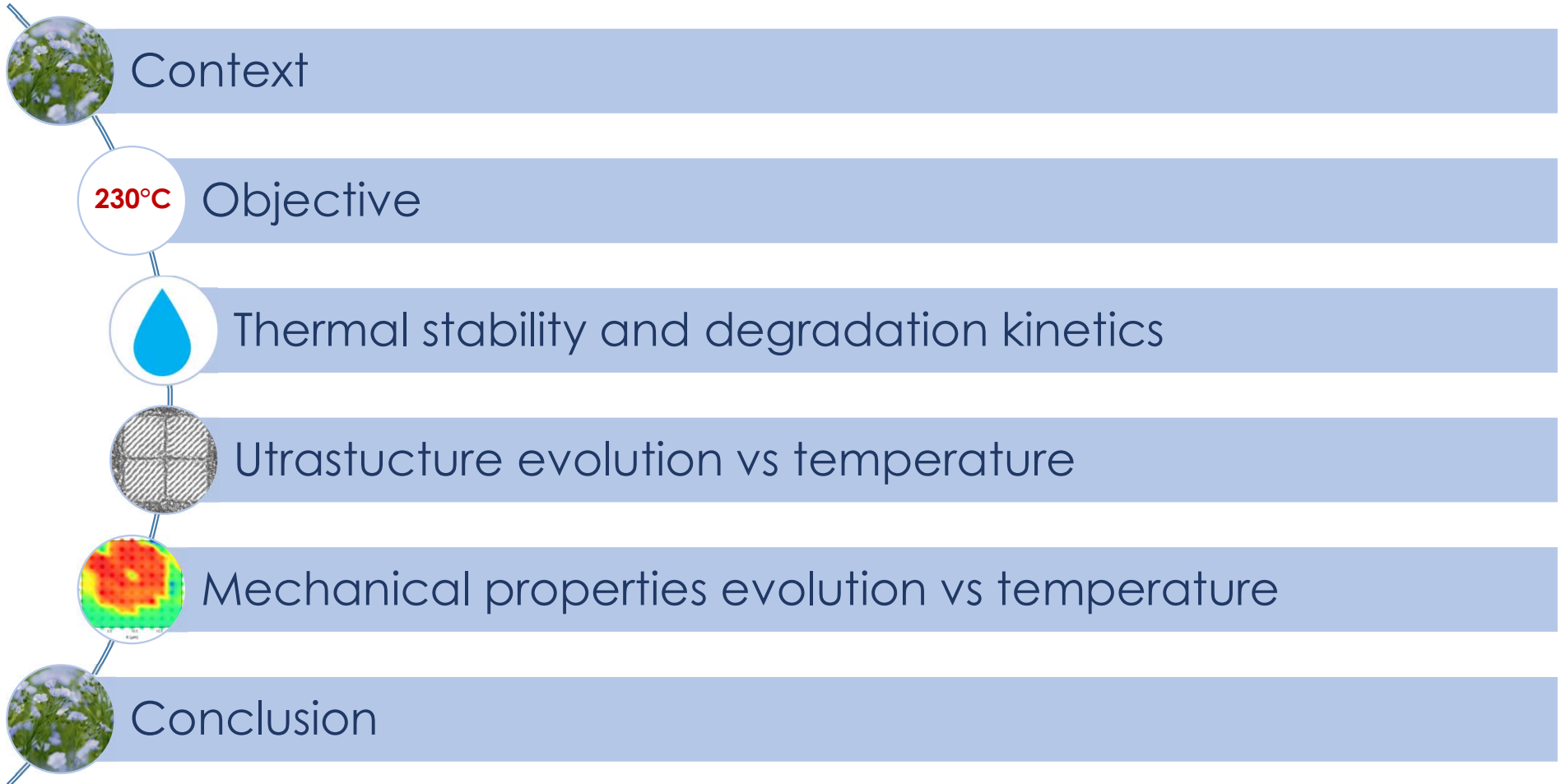


**ENSTA  
BRETAGNE**

- Graduate and post-graduate Engineering School :
  - **Mechanics of materials, fluids and structures**
  - Information and communication technologies
- ~1000 students (including PhD students) per year

**IRDIL**  
Institut de Recherche Dupuy de Lôme

- Research institute in mechanics
- 300 members
- 5 main research axis:
  - Composites, Bio-composites, Nano-composites
  - Multi-materials Assembly
  - Structures, Fluides & Interactions
  - Energetic Systems
  - Mechanical Behavior and Durability of Materials



## Towards sustainable composite materials

Environmental concern : need for designing bio-based, recyclable, compostable materials

### ▪ Fibers :

Fibre bundles	Young's modulus (GPa)	Tensile strength (MPa)	Density $\rho$ ( $10^{-3}$ kg/m <sup>3</sup> )
<b>E-glass</b> [1]	72-73	3200 - 3400	2.54
<b>Flax</b> [2]	37 - 75	595 - 1510	1.52

**Low density, good mechanical and insulation properties !**

### ▪ Matrix:

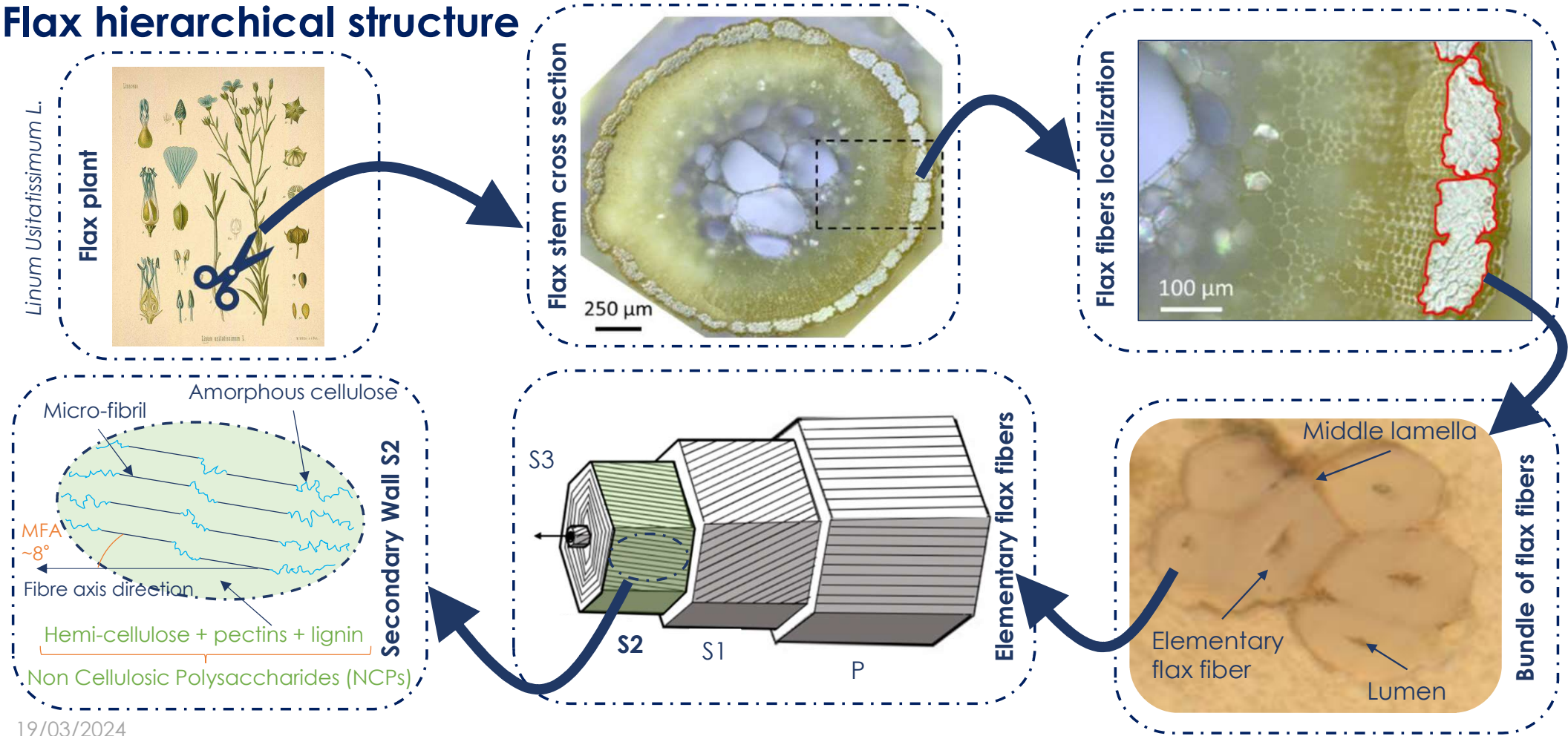
Substituting thermoset matrices for thermoplastic resins

→ Pave the way for recyclable composite materials

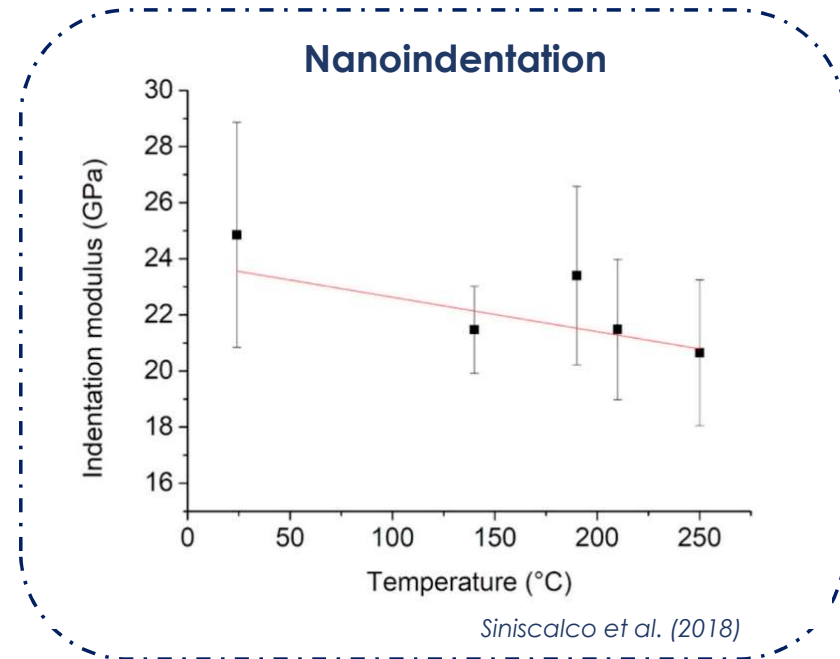
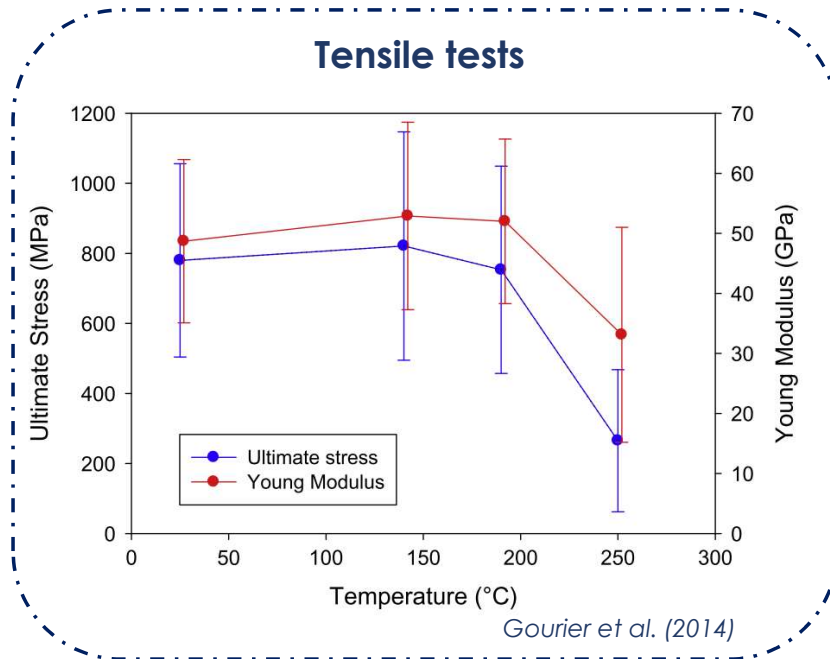


**Thermoplastic processes involve high temperatures (up to 230°C) and long processing times (few to tens minutes)**

# Flax hierarchical structure



## Mechanical tests and temperature on flax fibers



Mechanical tests performed at room temperature AFTER heat treatments  
(post mortem analysis)

**What happens DURING heat treatment?**

## Study « in situ » the effect of temperature on both structure and mechanical properties of flax fibres

### Thermal pattern

- 25°C → 230°C → 25°C

### Thermal stability and degradation kinetics

- Thermogravimetric analysis (TGA)



### Ultrastructure evolution vs temperature

- X-Ray Diffraction (XRD)



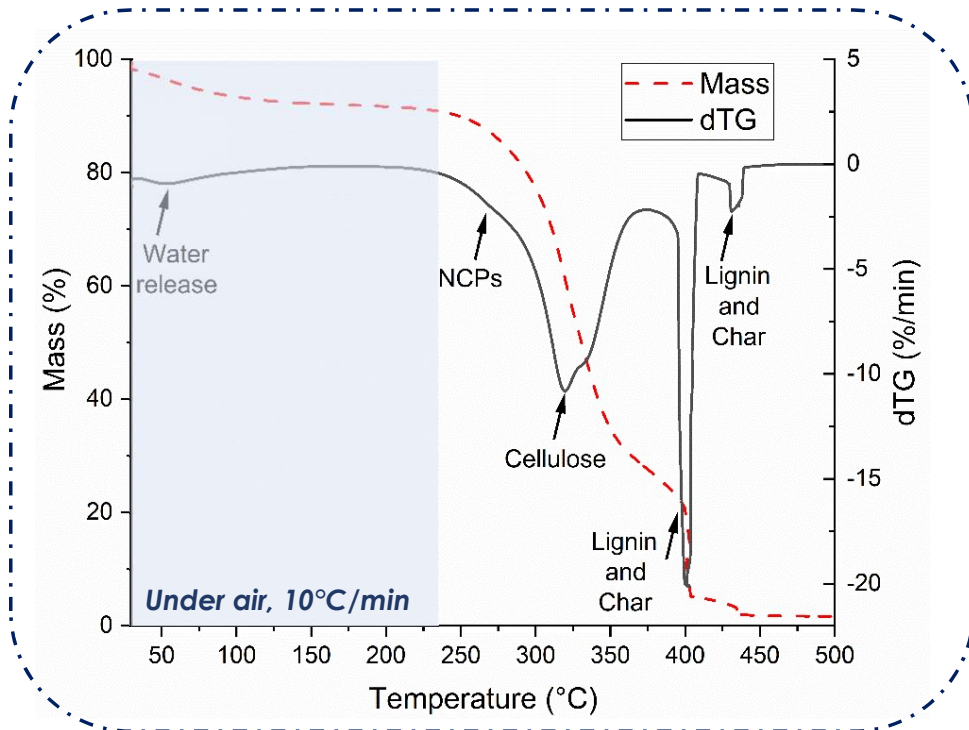
### Mechanical evolution vs temperature

- Nanoindentation



## Results

### Linear heating

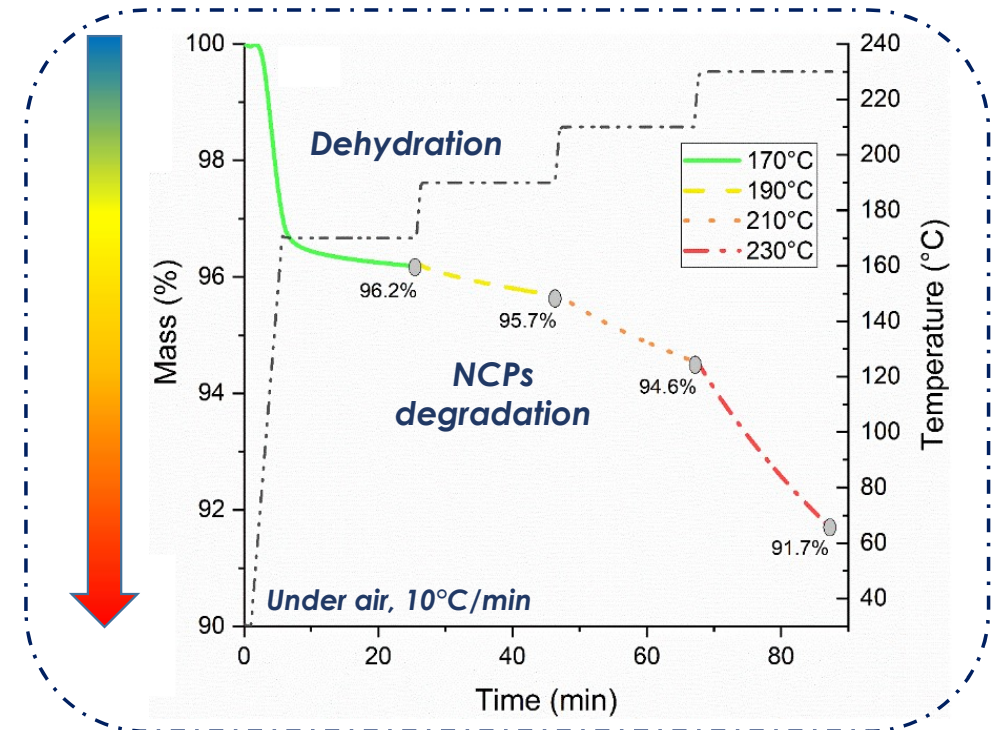


- 2 main events up to 230°C:
  - **dehydration** (50-100°C),
  - **degradation of NCPs** (225-275°C)

19/03/2024

Guillou et al. (2023)

### Multi-step simulation of XRD and nanoindentation protocols



- **Degradation kinetics** :
    - water release up to 170°C ~3.5%
    - followed by NCPs degradation ~4.5%
- pronounced **mass loss up to 8% above 190°C !!**



## XRD samples and methodology

### Equipment

- Bruker D8 Diffractometer ( $\theta$ - $\theta$  configuration  $\text{CuK}\alpha$  radiation)
- High temperature chamber (HTK 1200, Anton Paar)



### Samples

- Pressed flax fibres bundles
- Alumina ceramic sample holder cup



### XRD method

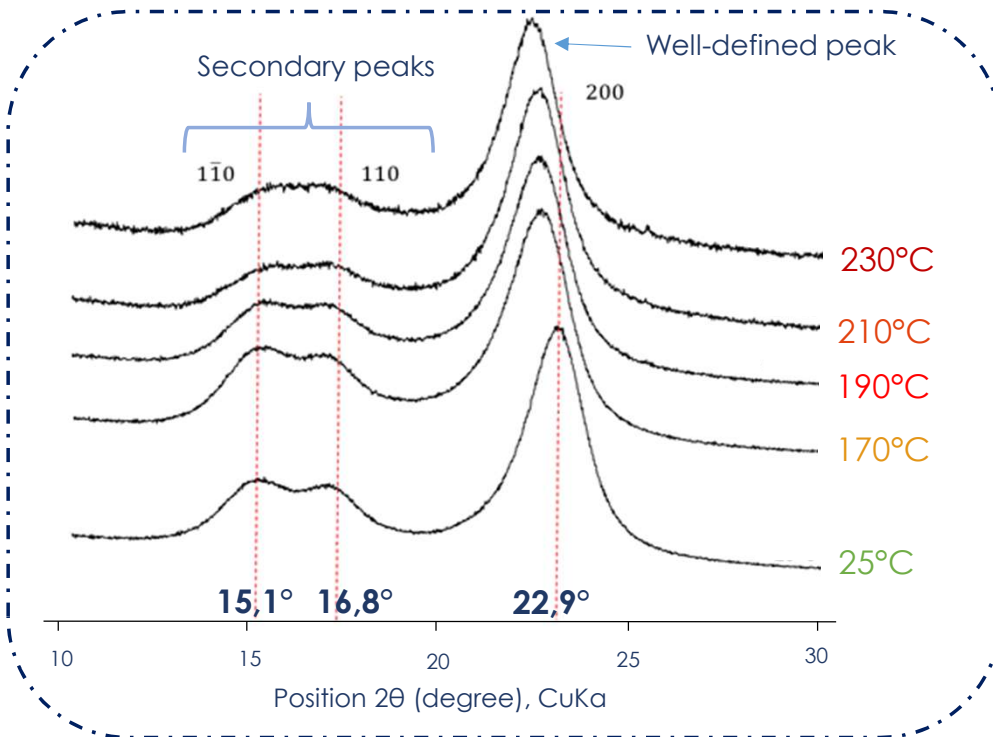
- Scans collected in  $10^\circ$ - $50^\circ$   $2\theta$  range
- d-spacings calculated using Bragg law
- Step size :  $0.009^\circ$
- Based on 200 plane position

### Temperature

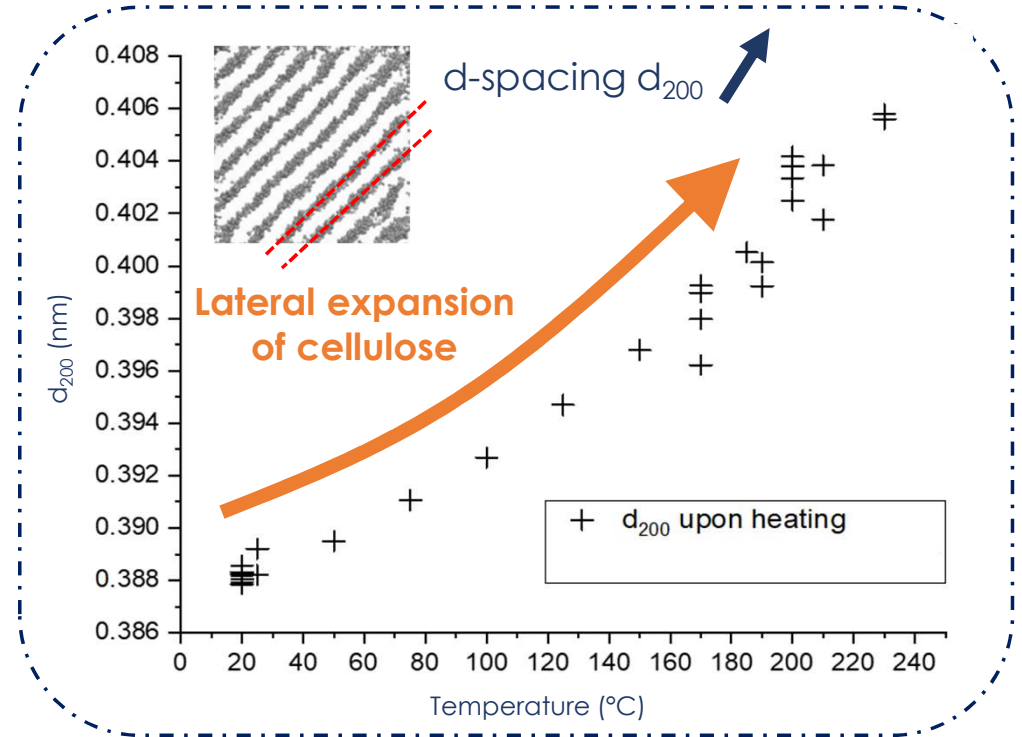
- Heating rate :  $30^\circ\text{C}/\text{min}$
- Isothermal steps for XRD measurements : 16min
- Pre-defined isotherms temperatures :

$25^\circ\text{C} \rightarrow 170^\circ\text{C} \rightarrow 190^\circ\text{C} \rightarrow 210^\circ\text{C} \rightarrow 230^\circ\text{C} \rightarrow 25^\circ\text{C}$

## XRD results – from 25°C to 230°C

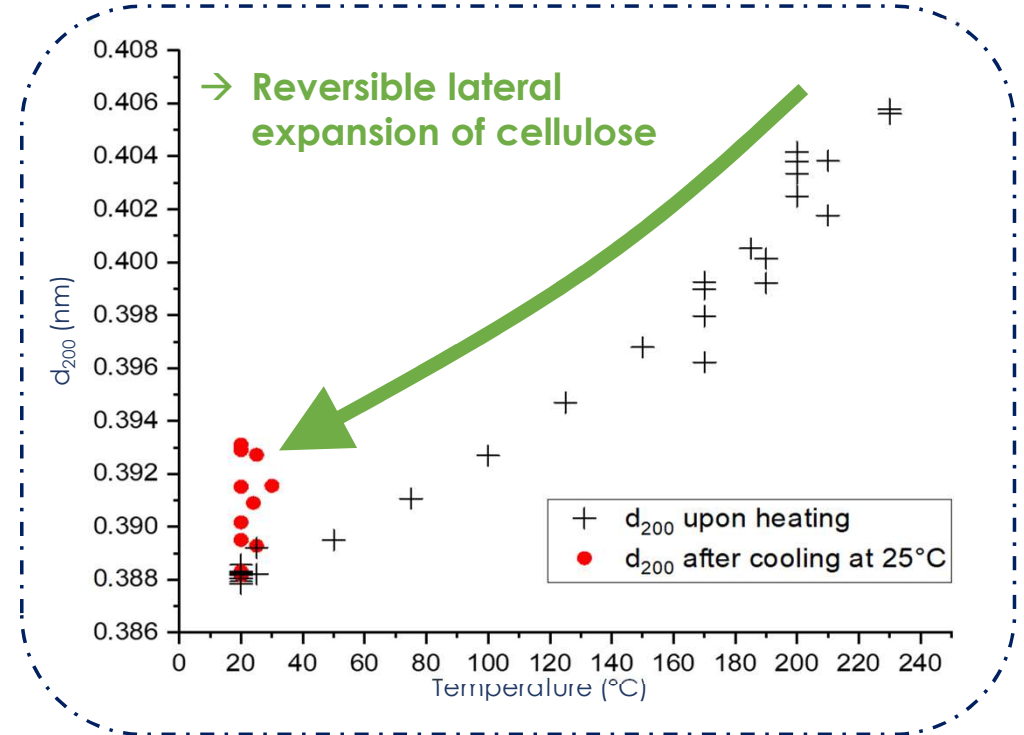
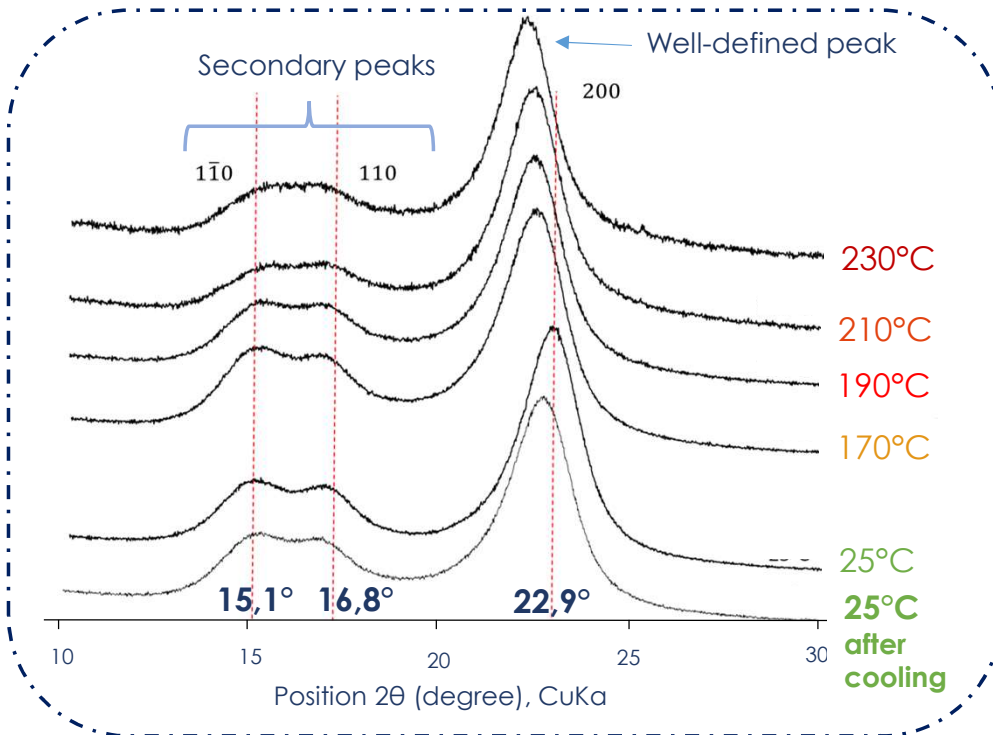


- **Cellulose** peaks
- Shift to lower angle of the 200 peak with rising temperature



- d-spacing  $d_{200}$  increases upon heating

## XRD results – back to ambient



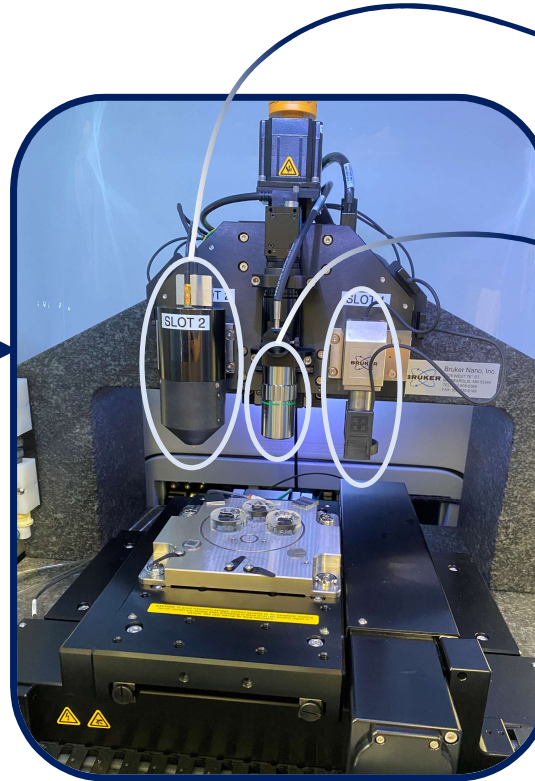
- Position of peak 200 is very close to its initial position upon returning to room temperature

- $d_{200}$  is roughly back to  $(d_{200})^{init}$  after cooling

→ No irreversible plastic mechanism in crystalline cellulose involved by temperature induced strain

# Mechanical properties evolution vs temperature

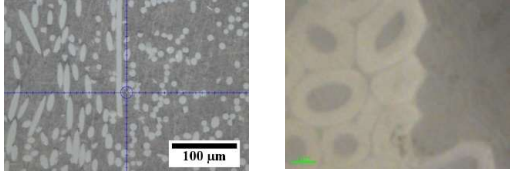
## Our nanoindentation device

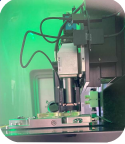



**MRNP Head**  

Load range : 10mN - 10N  
Max. displacement : 80µm

**Numerical microscope**



**NanoDMA Head**  

Max. load QS: 10mN (Dyn.: 5mN)  
Max. displacement : 5µm (Dyn.: 2,5µm)

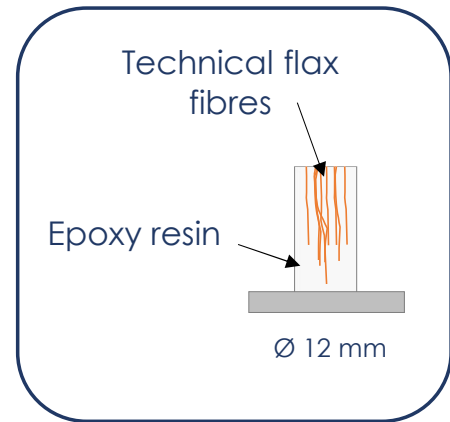
Equipement acquis dans le cadre du CPER ECO-SYS-MER, financé par:

19/03/2024

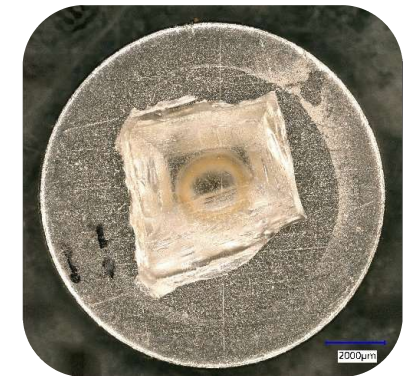


## Nanoindentation – *samples preparation*

- Flax fibres bundles cut to length  $\leq 5\text{mm}$
- Embedded in epoxy resin DP760 (overnight cured :  $50^{\circ}\text{C}$ )
- Glued on a steel disc ( $\varnothing 12\text{mm}$ , thickness :  $0.85\text{mm}$ )



- Cut by ultramicrotome  $\rightarrow$  final thickness  $\sim 2.5 - 3.5\text{mm}$



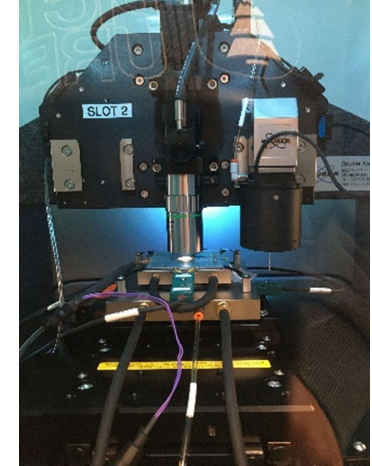
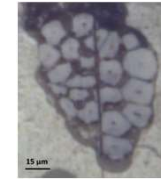
## Nanoindentation – methodology

### Equipment

- TI 980 / NanoDMA III / elongated Berkovich probe
- Xsol 400 heating stage

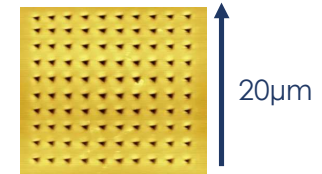
### Samples

- 3 samples tested
- 1 fibre bundle tested on each sample
- 1 fibre = 1 temperature



### Nanoindentation protocol

- Surface detection thanks to a 2µN indentation
- XPM 11x11 load-controlled indents with  $F_m = 180\mu\text{N}$
- Spacing inter-indents : 2µm

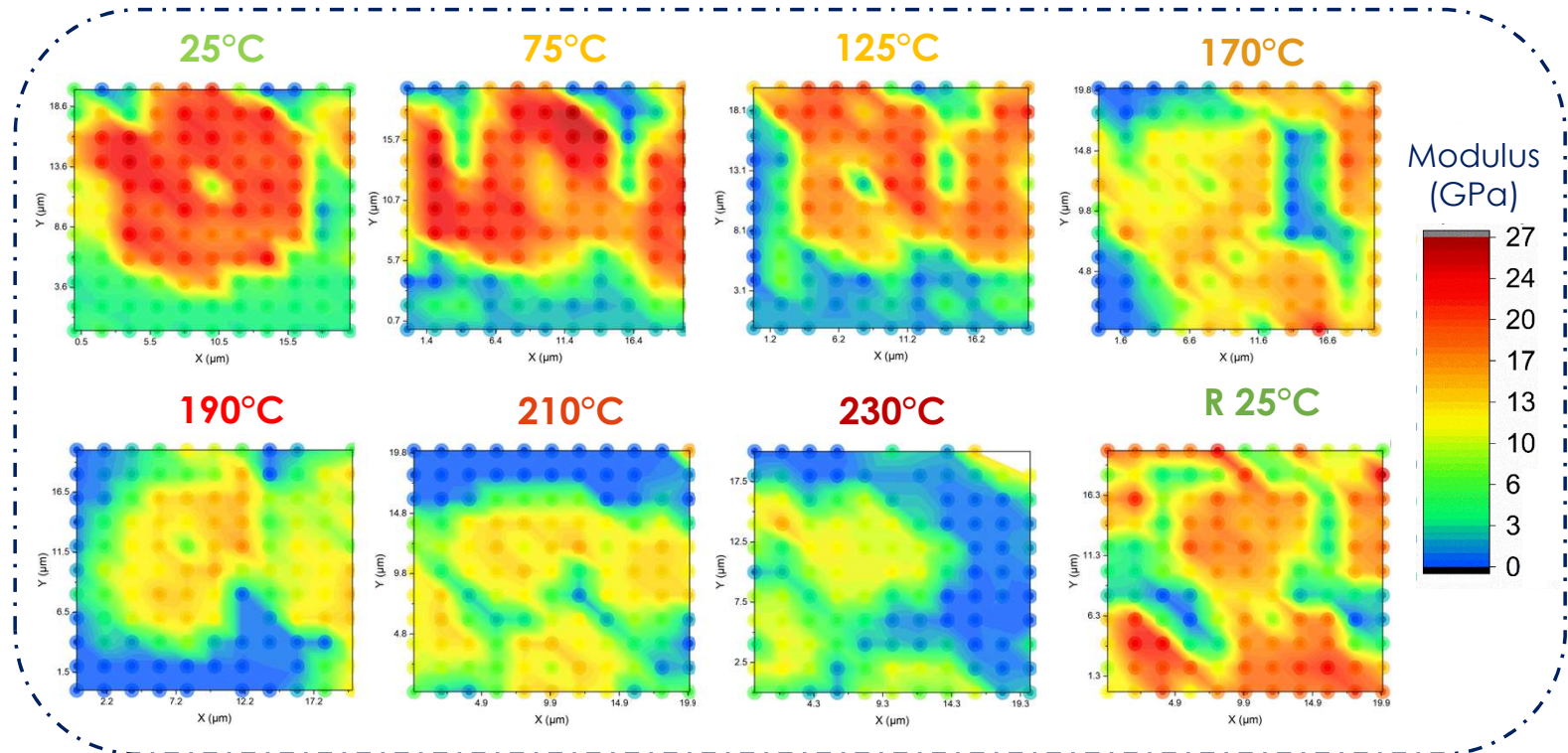
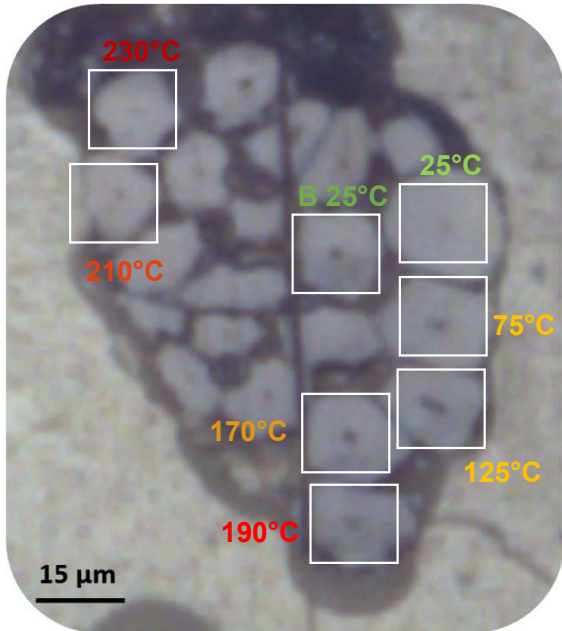


### Temperature

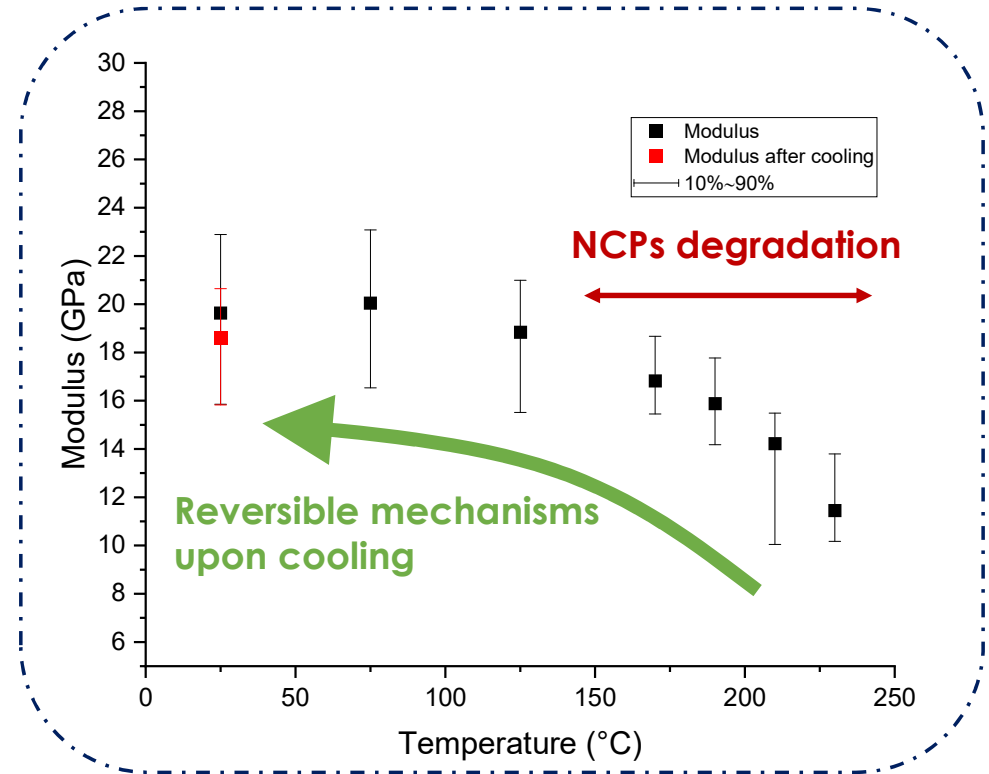
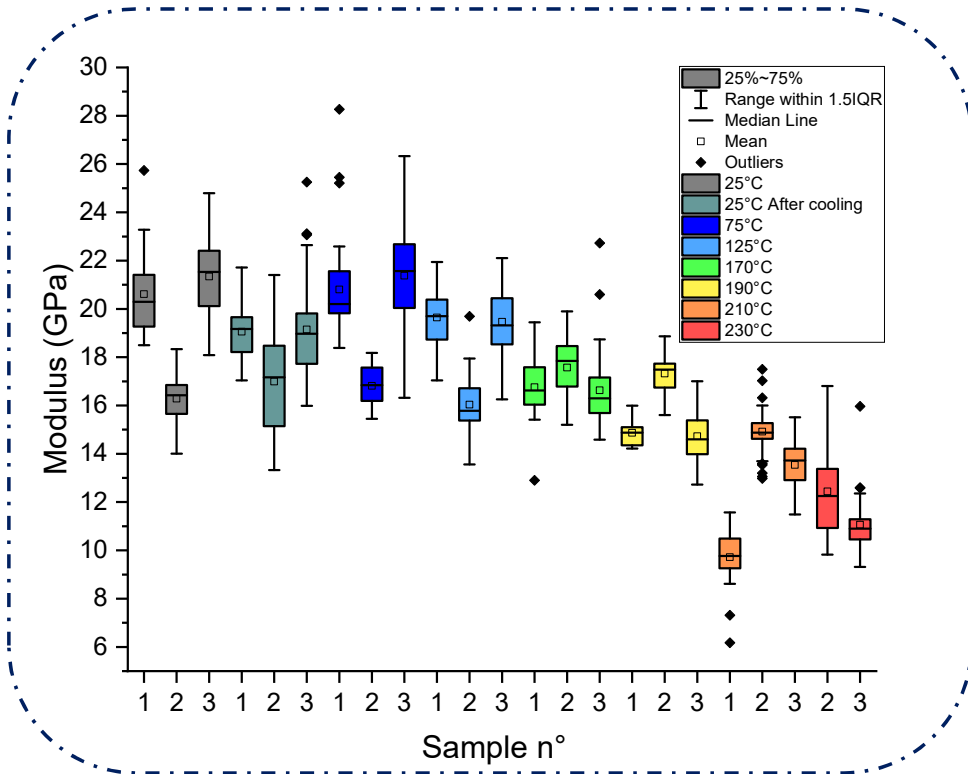
- Heating rate : 20°C/min
- Isothermal steps for nanoindentation measurements : ~20min
- Targeted temperature stops :

25°C → 75°C → 125°C → 170°C → 190°C → 210°C → 230°C → 25°C

## Nanoindentation results – indentation modulus mappings



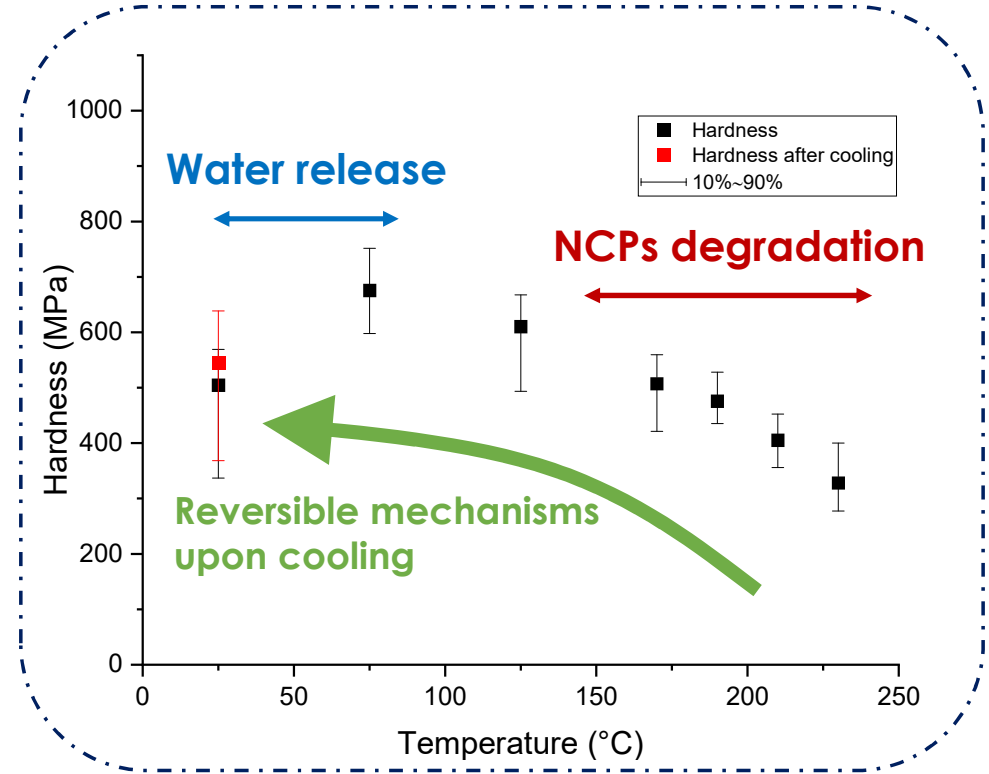
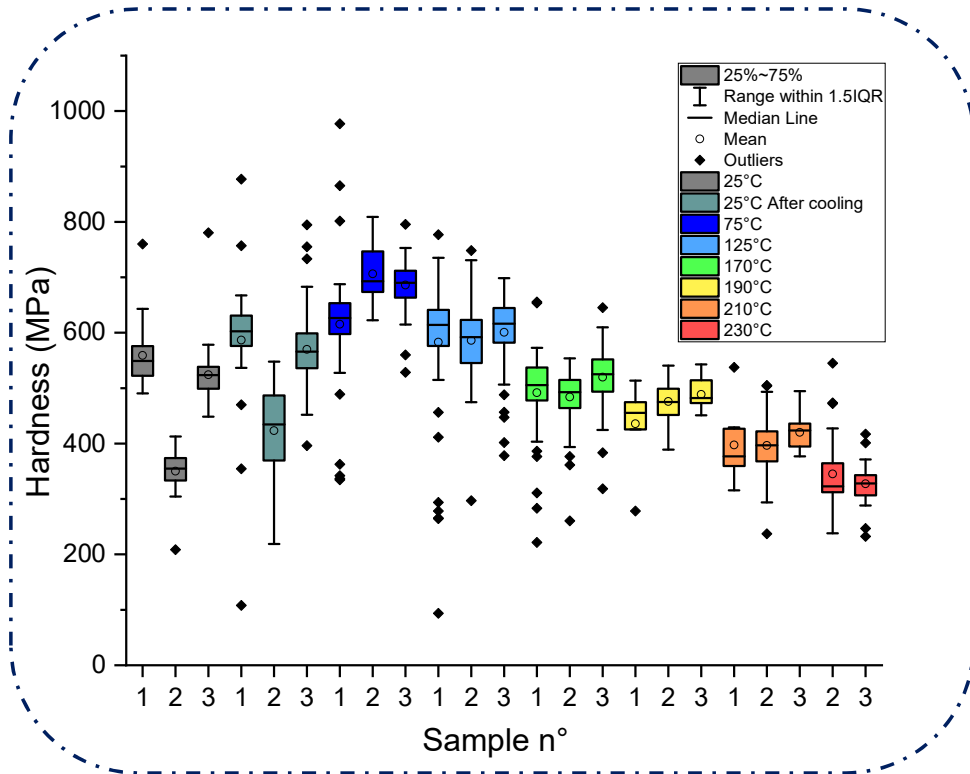
## Nanoindentation results – indentation modulus evolution with temperature



- Indentation modulus remains stable until approximately 125°C and then significantly decreases



## Nanoindentation results – hardness evolution with temperature



- Hardness increases until approximately 75°C : water release followed by regular decrease

- Monitoring of the evolution of ultrastructure and local mechanical properties of flax cell walls during dynamic heating from 25°C to 230°C by XRD and nanoindentation
- Dehydration and degradation of NCPs with increasing temperature but reversible expansion of cellulose
- Reversible softening of flax cell walls due counterbalancing effects
- Limited effect of temperature on elastic properties of flax cell walls

Next step :

- Same protocol applied to a simple heating to 230°C

**Thank you for your attention**