# In situ characterisation of the drying shrinkage of fibres made of cellulose nanofibrils during their extrusion

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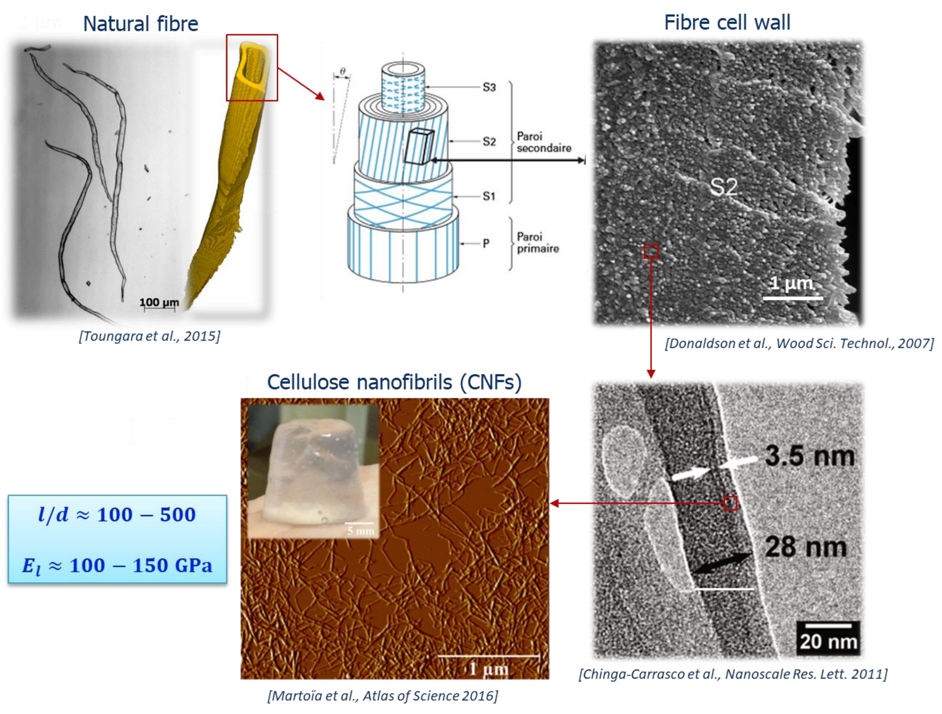
## Context and objectives

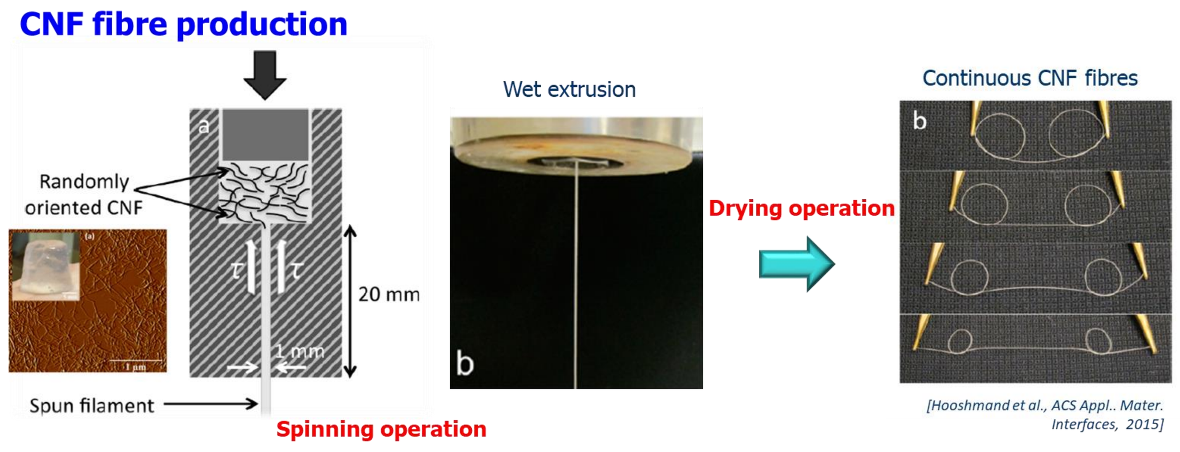
### Cellulose nanofibrils (CNFs)




- Because of their pronounced slenderness and oustanding intrinsic mechanical properties, CNFs constitute promising building blocks for the design of biobased high-performance materials!

### Fabrication of continuous fibres by extrusion from CNF hydrogels

**CNF fibre production**



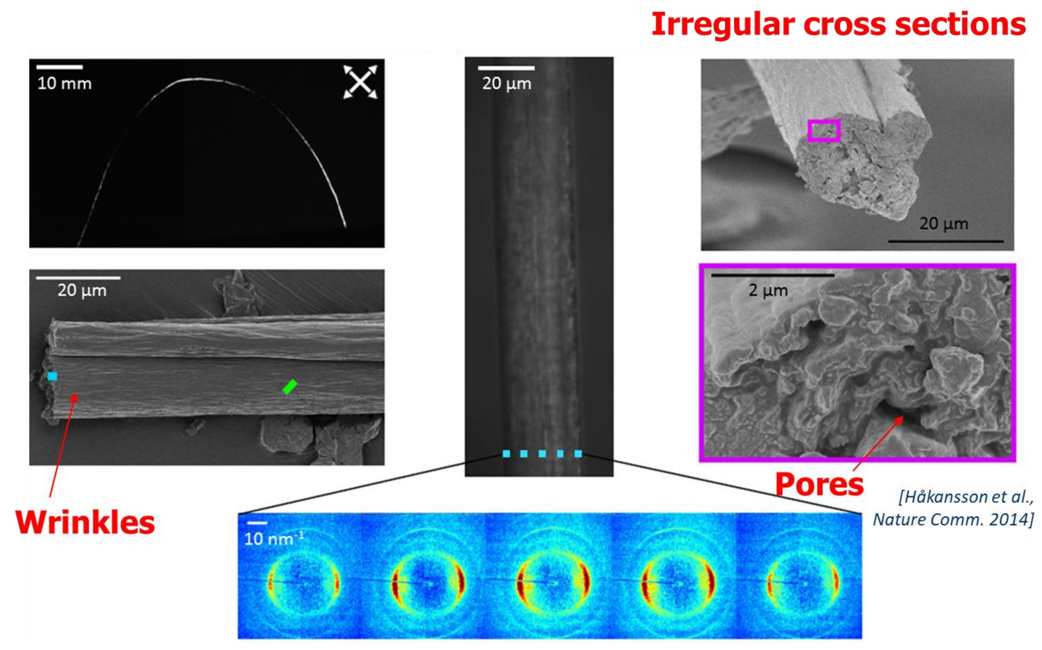

**Longitudinal tensile properties**

| Literature | $\sigma_u$ (MPa) | $\varepsilon_u$ (%) | E (GPa) |
|---|---|---|---|
| Iwamoto et al. | 321 | 2.2 | 24 |
| Walther et al. | 275 | 4 | 23 |
| Torres-Randon et al. | 289 | 1.6 | 34 |
| Håkanson et al. | 490 | 6.4 | 18 |
| Hoosmand et al. | 222 | 3 | 13 |

Promising specific mechanical properties !

- CNF fibres represent a new generation of sustainable and functional continuous filaments that can be used as green reinforcement for high-end composites applications.

### Geometry and microstructure of continuous CNF fibres




- To fully exploit the potential of CNF fibres, the fundamental spinning and drying operations must be better understood and characterised.

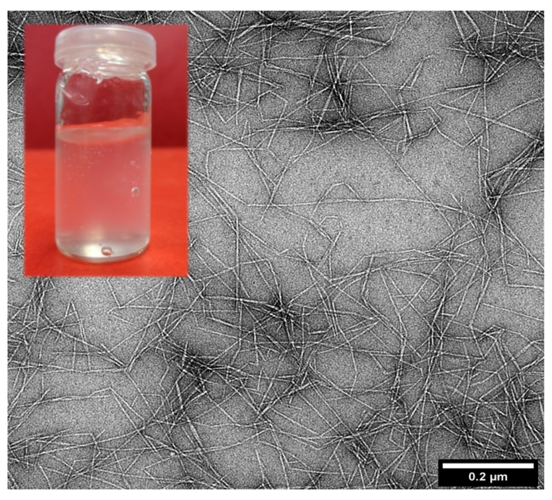
- This study aims to establish the influence of drying conditions on the microstructure and geometry of the extruded CNF filaments.
- The consolidation and shrinkage phenomena that are induced by the drying operation were investigated using 3D in situ and real-time imaging techniques, coupling X-ray microtomography and X-ray diffraction techniques (XRD).

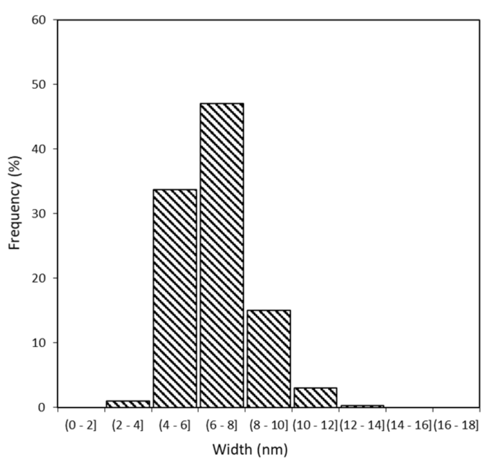
## In situ drying experiments of CNF fibres

### CNF hydrogels

**Extraction of CNFs**

- CNFs extracted from bleached birch kraft pulp using a mechanical fibrillation process. The delamination process of cellulose fibres was combined with a TEMPO-mediated oxidation pretreatment to reduce energy input needed for fibrillation.
- CNFs were extracted in the form of aqueous colloidal gels at a concentration of 1 wt%.



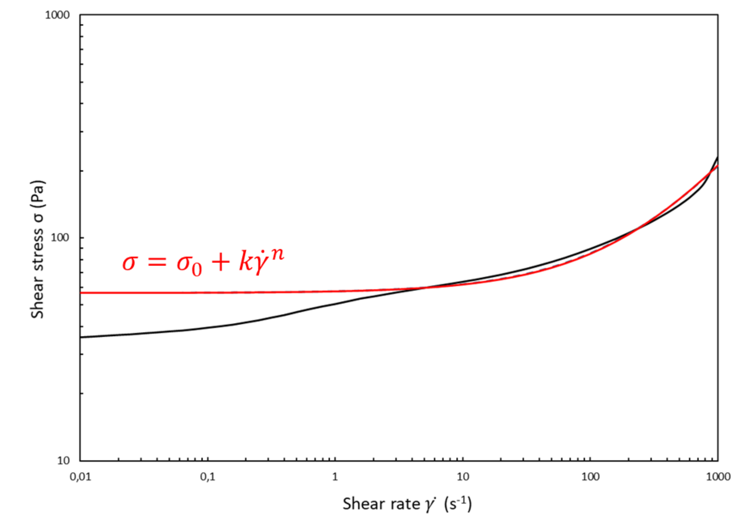



- Homogeneous CNF gels with well-dispersed CNFs.
- Tortuous CNFs (average width ≈ 7 nm and average length ≈ 1000 nm) with a pronounced slenderness!

### Rheology of CNF hydrogels

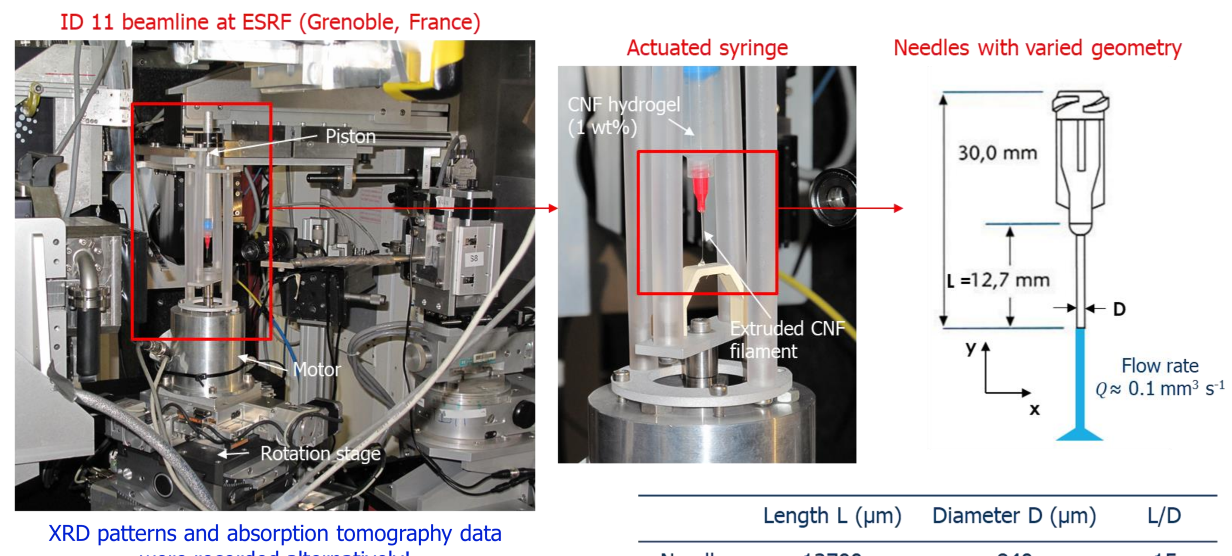
**Shear rheology**

- The rheology of CNF hydrogels was studied using a strain-controlled rheometer (ARES, TA) equipped with a plate-plate geometry (diameter 25 mm, gap 1 mm).
- Flow curves were obtained by sweeping down the shear rate $\dot{\gamma}$ from $10^3$ s$^{-1}$ to $10^{-2}$ s$^{-1}$ in 50 logarithmically-spaced steps for times of $\delta t$ =50 s. All the measurements were performed at 20°C with suspensions pre-sheared at $10^3$ s$^{-1}$ for 60 s.




- Yield stress fluid that exhibits a solid-like behaviour at low shear rates and a shear thinning behaviour at high shear rates
- The flow curves of CNF gels can be seen from a phenomenological standpoint as a Herschel-Bulkley fluid ($\sigma_0$ = 57 Pa, $k$ = 4.32 Pa s$^n$ and $n$ =0.74)

### In situ drying experiments coupling X-ray synchrotron microtomography and X-ray diffraction (XRD)



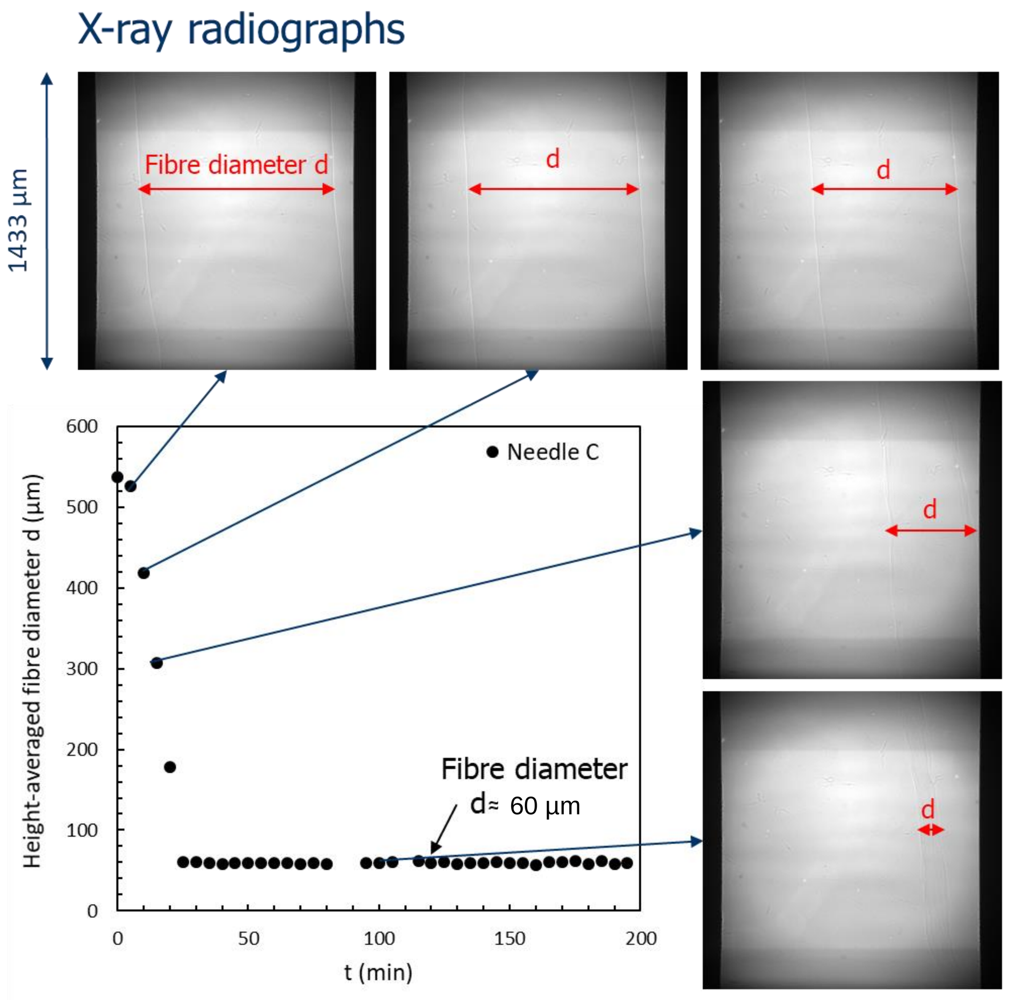

XRD patterns and absorption tomography data were recorded alternatively!

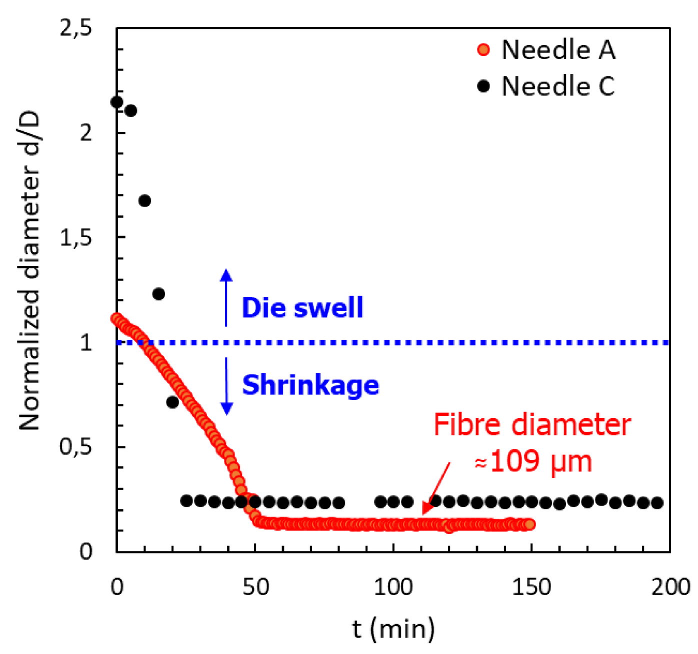
| | Length L (µm) | Diameter D (µm) | L/D |
|---|---|---|---|
| Needle A | 12700 | 840 | 15 |
| Needle C | 12700 | 250 | 51 |

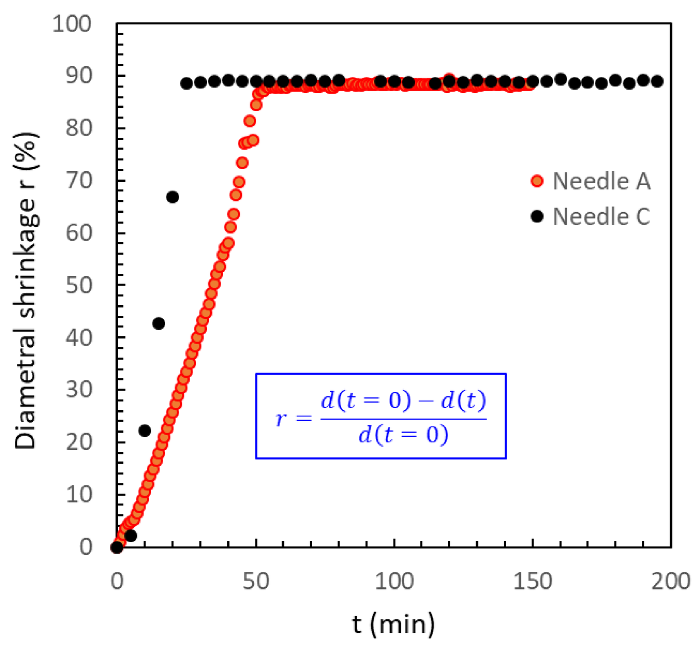
- X-ray microtomography (voxel size of 0.7³ µm³) provides an overall description of the variations in the geometry of the filament.
- XRD with a focused beam (size spot of 20 µm) provides depth-resolved information on the overall orientation of CNFs in the filament

## Main results

### In situ drying experiments

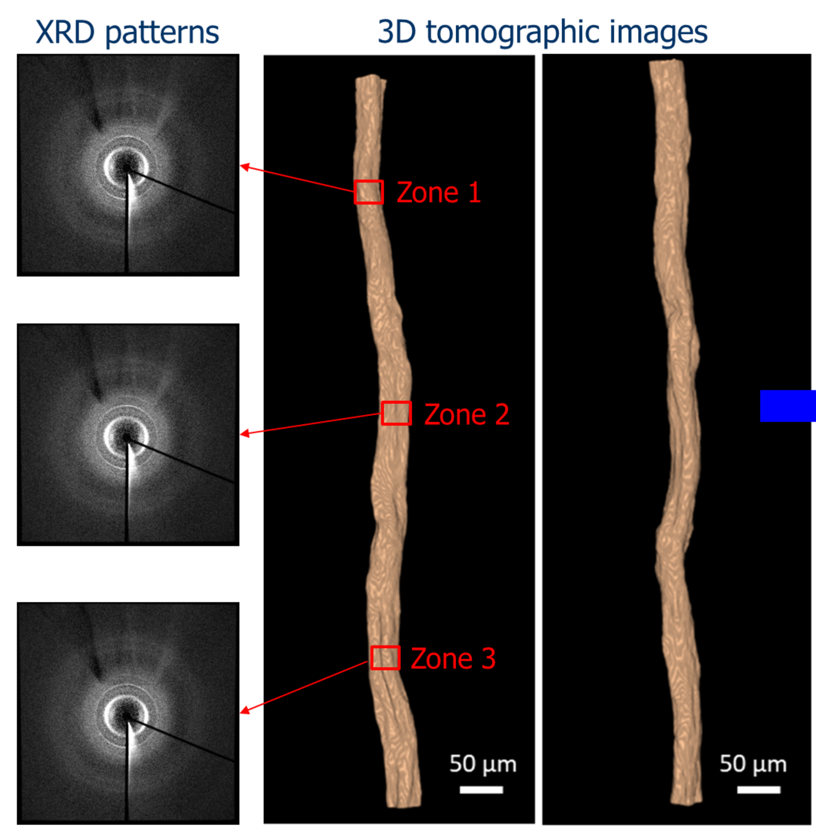


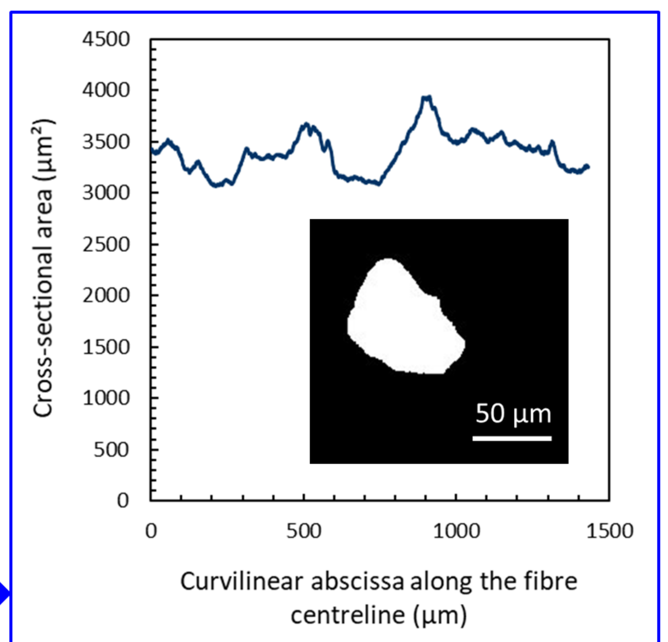



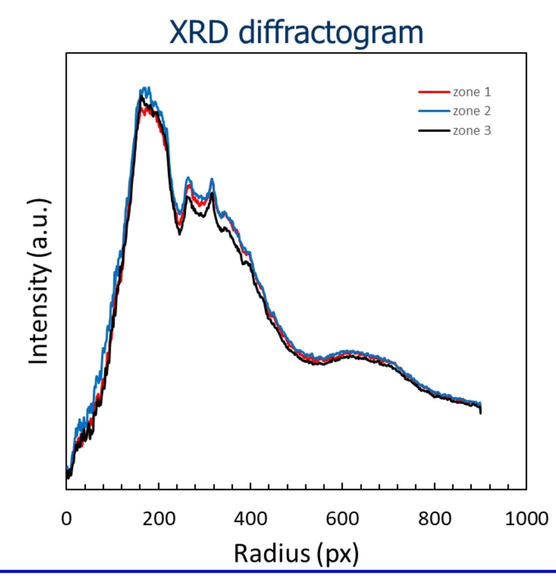




- The set of X-ray radiographs obtained during the in situ extrusion and drying experiments revealed that the extruded CNF fibres swelled just after exiting the die. This so-called 'die swell phenomenon' was then followed by a pronounced shrinkage of the fibre diameter.
- The swelling behaviour and the skrinkage kinetics of the spun CNF fibres was found to depend on the length $L$ and inner diameter $D$ of the needles. In contrast, the ultimate drying shrinkage of CNF fibres was not affected by the geometry of the needle.

### 3D images of CNF fibres after drying




- 3D microtomography images provided a set of microstructure descriptors for the quantitative analysis of the defects of CNF fibres (e.g. cross-sectionnal area profiles, curvature maps, fibre twisting).
- XRD patterns revealed that CNF fibres exhibited anisotropic fibrous microstructures with a preferred orientation of CNFs parallel to the fibre axis.
- XRD patterns also showed that the overall orientation of CNFs was nearly homogeneous along the fibre centreline.

- In this study unprecedented 3D X-ray microtomography and diffraction images of filaments during in situ extrusion experiments were obtained. Image analysis was then performed, allowing the shrinkage of the spun fibres to be measured and unveiling the evolution of their microstructures during drying.