Ice-templating of gels of cellulose nanofibril (CNF) and cellulose nanocrystal (CNC) for the design of cellular materials

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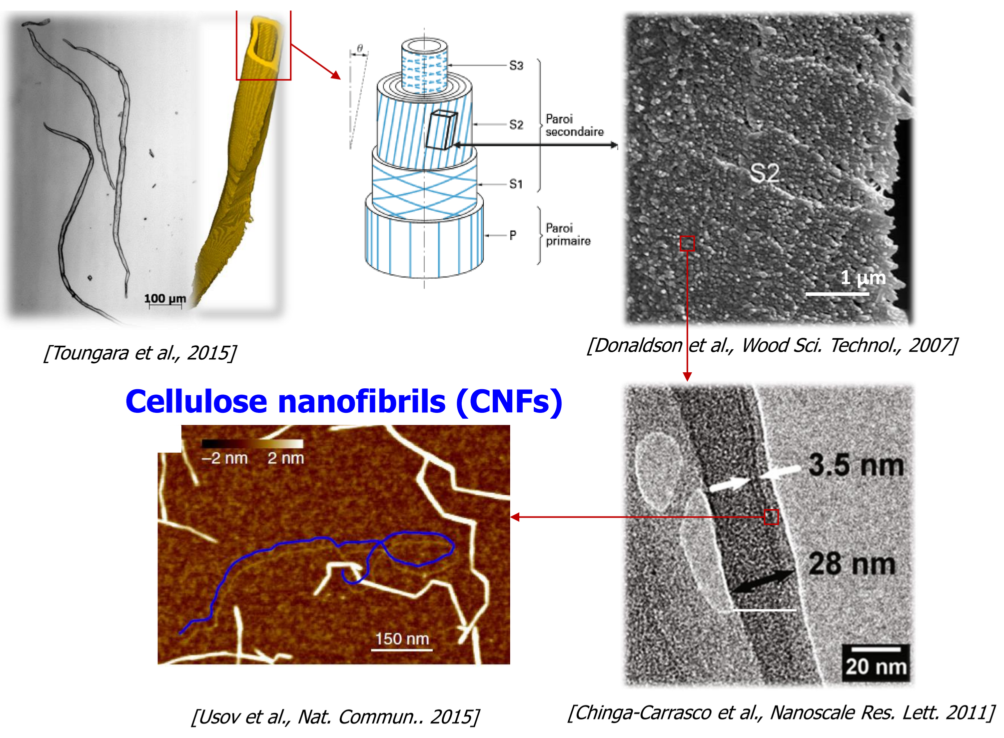
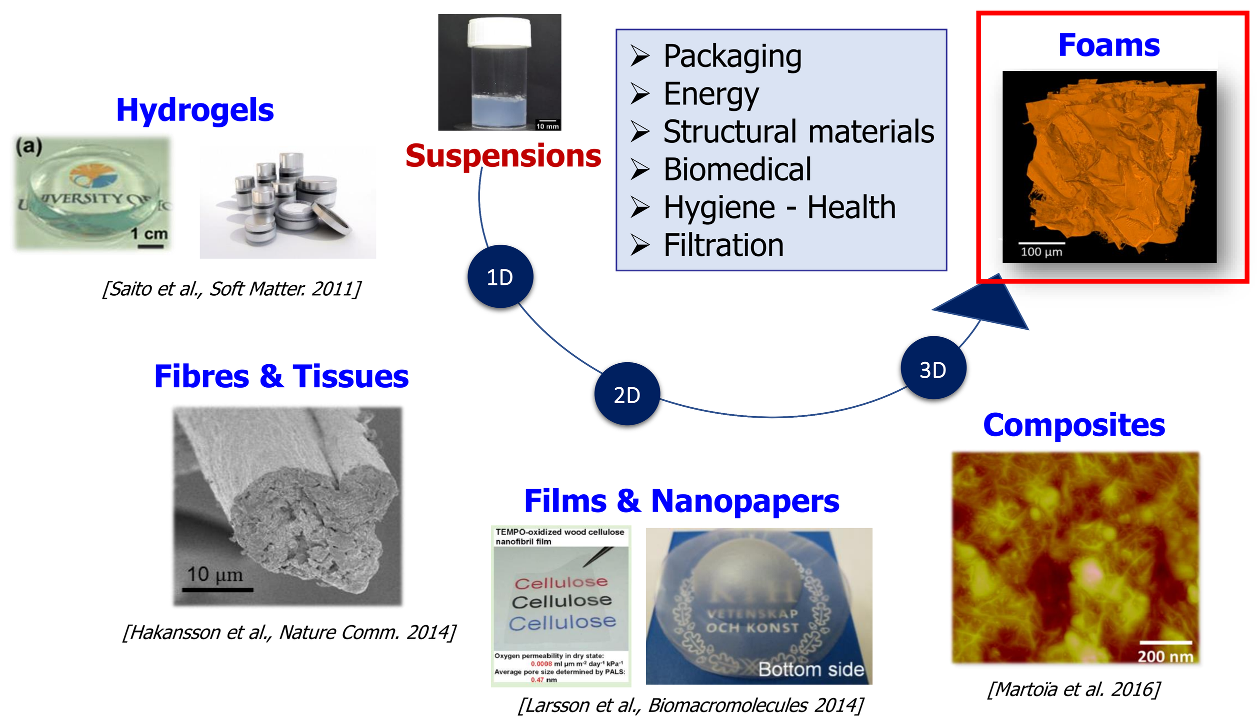
Context and objectives

Cellulose nanofibrils (CNFs)



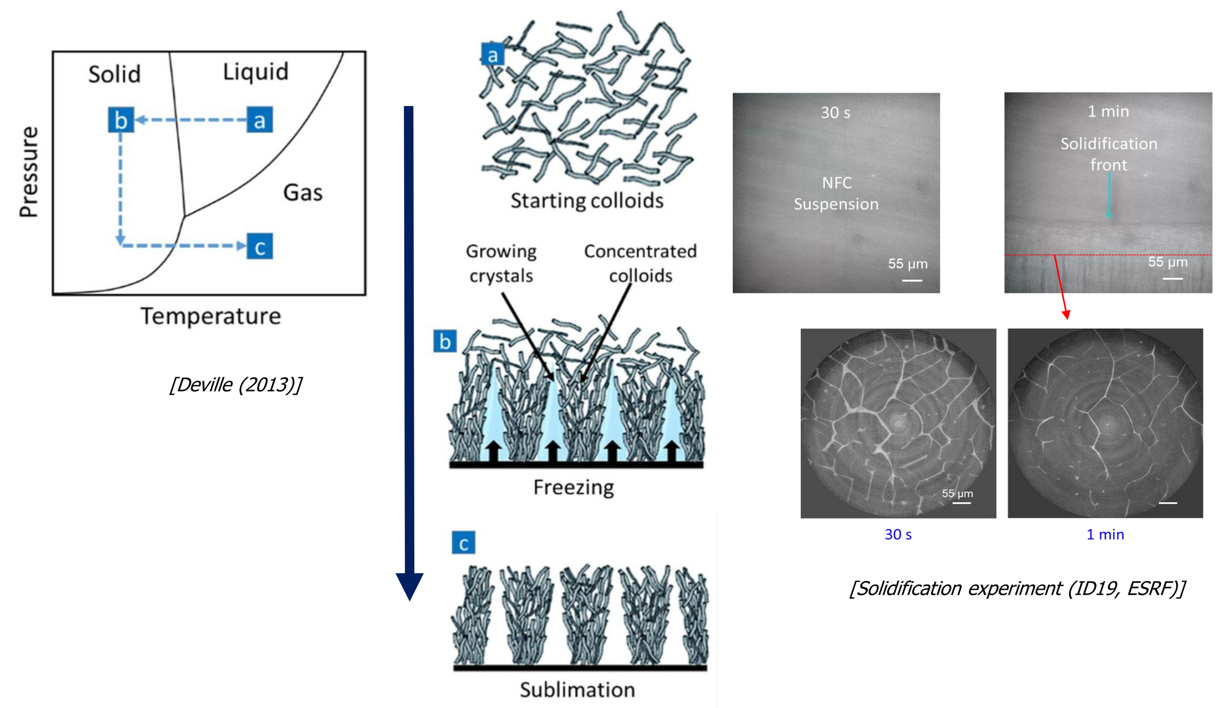
➢ CNFs and CNCs are bio-based nanoparticles extracted in the form of aqueous gels.

Nanocellulose applications



➢ Great potential in a wide variety of applications!

Principle of ice-templating process



➢ Rheology at higher concentrations plays a key role on ice-templating process.

➢ To obtain foams with efficient cell walls and pore structures, a better understanding of the rheological properties of nanocellulose gels in hyper concentrated regimes is required !

Objectives of the thesis

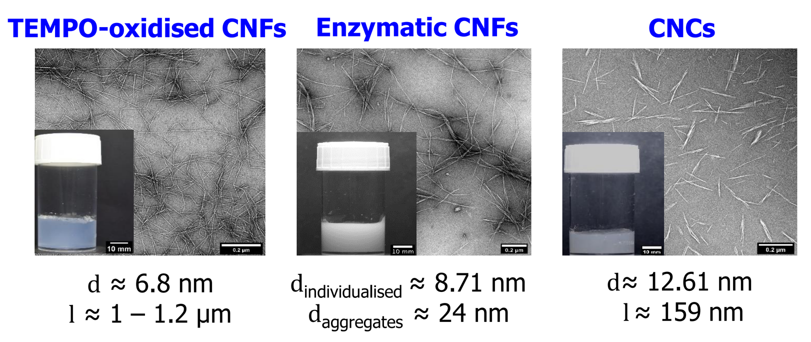
To better understand the correlation between the rheology of concentrated and hyper-concentrated CNF and CNC gels and the effect of freezing conditions on the microstructures and the mechanical properties of ice-templated foams.

Methodology

Material processing

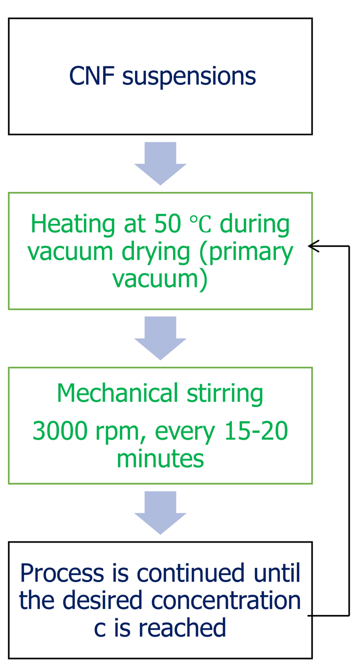
Studied nanocellulose gels

➢ Nanocellulose suspensions: CNCs, TEMPO-oxidized CNFs and enzymatic CNFs aqueous suspensions, i.e., suspensions with three different types of nanofibers and colloidal stabilities.



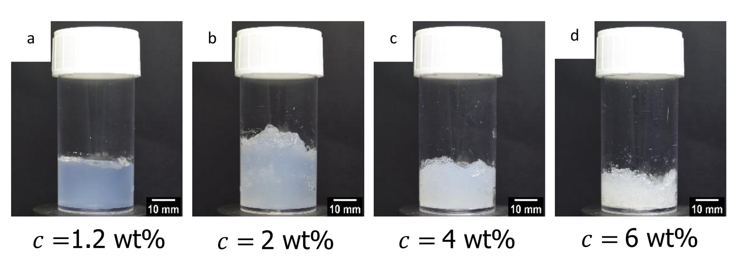
➢ Due to the high aspect ratio of CNFs, their suspensions tend to form hydrogels at low nanofibre contents.

Processing of CNF gels at various nanofiber concentrations



→ An original method to prepare hyper concentrated nanocellulose suspensions was developed.

Photographs showing TEMPO-oxidized CNF gels at various concentrations



Prepared gels:

➢ TEMPO-oxidized CNF gels: c from 1.2% to 6.3 wt%

➢ Enzymatic CNF gels: c from 3% to 14 wt%

➢ CNC gels: c from 7.5% to 25 wt%

Rheology of CNF and CNC gels

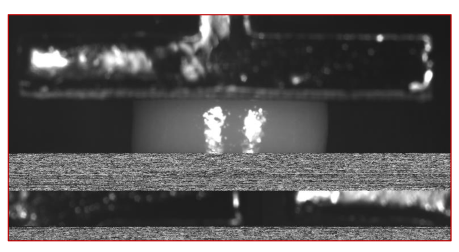
➢ Effect of physicochemical properties (repulsive or attractive systems).

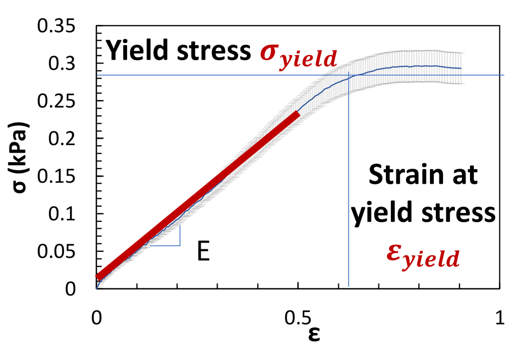
➢ Effect of nanofiber slenderness.

➢ Effect of nanofiber concentration.

→ On the rheological response of nanocellulose gels under simple lubricated compression.

Compression tests coupled with optical visualizations





Testing procedure

➢ Prepared gels were casted into a cylindrical mould with height h_0 = 3 mm and diameter d_0 = 13 mm.

➢ The cylindrical samples were then subjected to uniaxial compression experiments using an universal tensile testing machine (Shimadzu) equipped with a 100 N load cell.

➢ Samples were placed between two horizontal and parallel platens, which were lubricated with silicone oil with a very low viscosity of 0.02 Pa s.

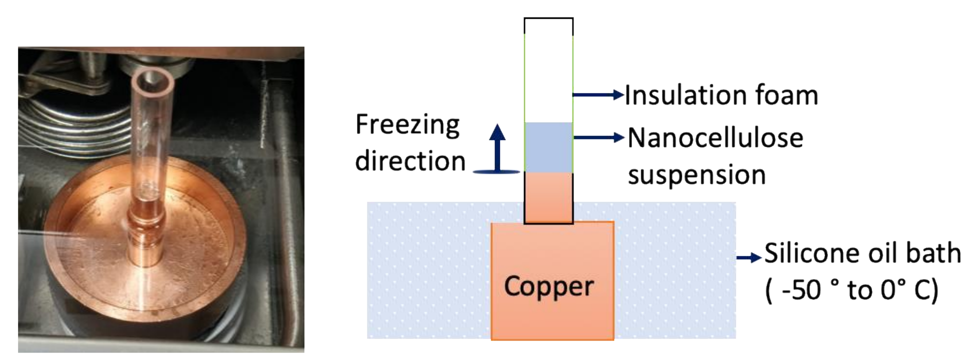
➢ Samples were compressed with initial strain rates varying from 0.001 s^{-1} to 0.8 s^{-1} and axial strain levels up to 0.9.

Ice templating of CNF and CNC gels

Freezing experiments

➢ Effect of freezing conditions on CNC suspensions (7.5 – 25 wt%).

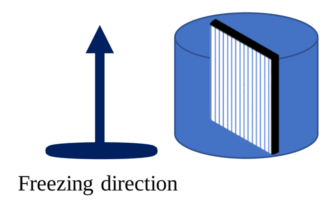
1D solidification setup



➢ Then, frozen nanocellulose suspensions were put into a freeze-dryer (Christ Martin, Alpha 2-4 LD plus) for 24 h at 10^{-3} mbar.

Microstructure analysis of CNC foams

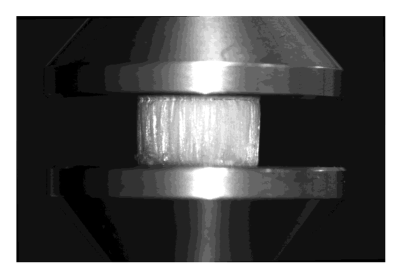
➢ The microstructure of the CNC foams were analysed using SEM.



➢ Micrographs were obtained parallel to the freezing direction, in the middle part of the foams.

Mechanical properties of CNC foams

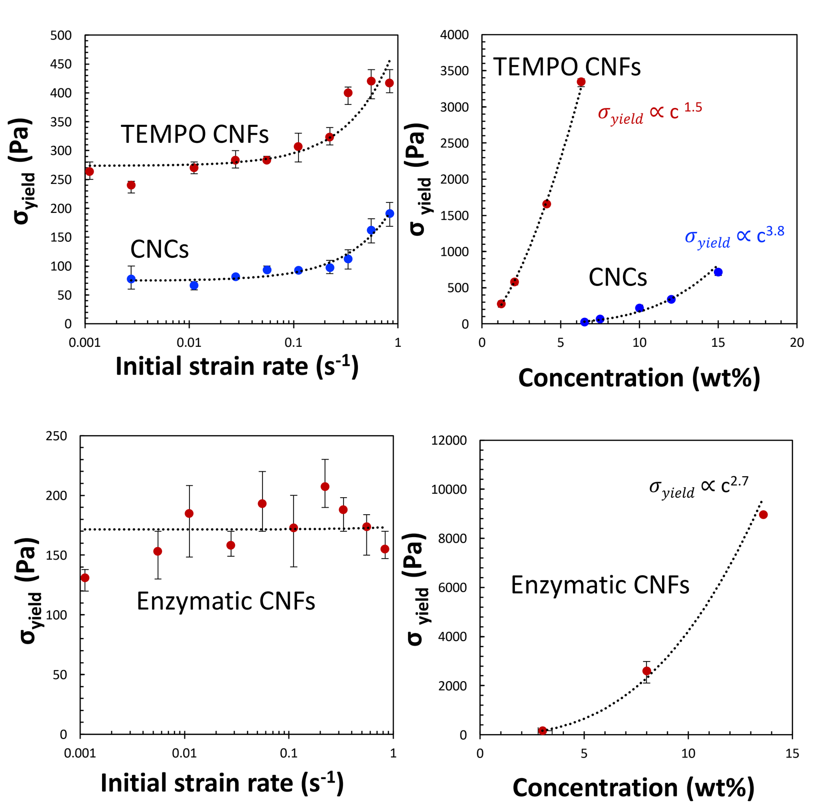
➢ Compression experiments were performed on CNC foams (h_0 =5 mm and d_0 = 5 mm) using a tensile machine (Shimadzu) equipped with a 2 kN load cell.



Main results

Rheology: effect of strain rate and concentration

Rheological properties of CNC and CNF gels



➢ Nanocellulose gels show various types of compression behaviour depending on their colloidal stability and their meso- and microstructures.

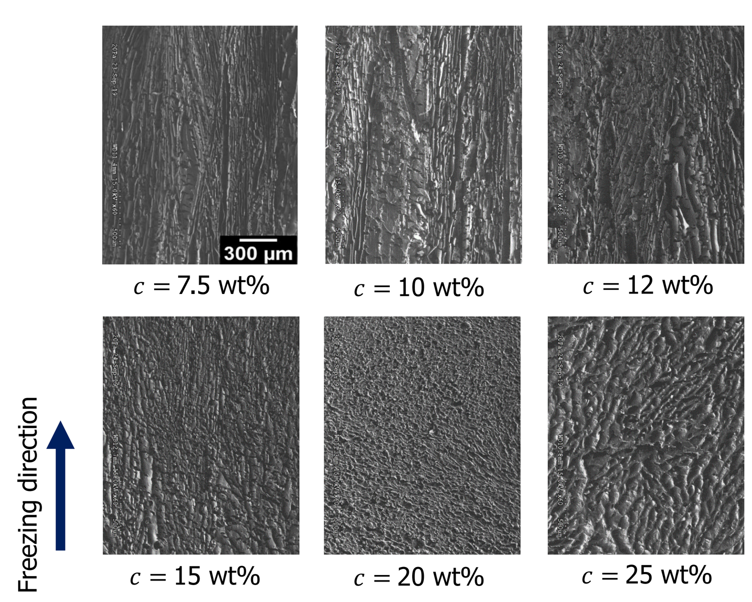
➢ Enzymatic CNF gels are flocculated gels that exhibit high water segregation, especially at low strain rates.

➢ TEMPO-oxidized CNF and CNC gels are stable gels that exhibit a yield stress fluid behaviour at low strain rates followed by strain-thinning behaviour at higher strain rates

➢ At low strain rates, the yield stress σ_{yield} of enzymatic CNF, TEMPO-oxidized CNF and CNC gels show a power-law dependence with the nanofibre concentration.

Ice templating: effect of unidirectional freezing

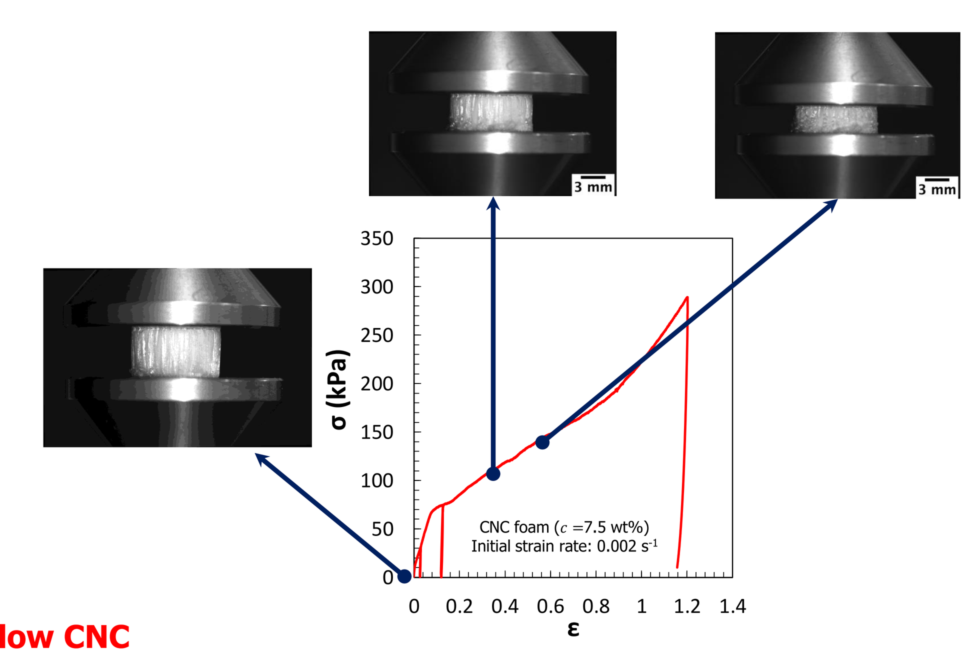
Microstructure of CNC foams



➢ The pore structure is highly anisotropic at low CNC contents, with slender pores aligned along the freezing direction. The anisotropy progressively diminishes and disappears with increasing the CNC content.

➢ The pore size diminishes with increasing the CNC content, except for the sample processed at 25wt%: this trend must be confirmed.

Typical compression behaviour of CNC foams



➢ The mechanical behaviour of the CNC foams is mainly elastic-fragile, with consolidation mechanisms mainly induced by the localised foam damage, with weak elastic recovery upon unloading, even during the early stages of compression.

➢ In this study we have developed an original methodology to prepare concentrated to hyper concentrated nanocellulose gels with enzymatic CNFs, TEMPO-oxidized CNFs, and CNCs. To find out the rheological properties of these suspensions, we have subjected these gels to uniaxial compression under prefect slip conditions. These experiments revealed the effect of the nanocellulose types and concentrations as well of strain rates on the rheological properties.

➢ Freezing experiments on nanocellulose gels and then microstructure analysis on nanocellulose foams as well as compression experiments have been carried out. These experiments revealed the effect of freezing conditions, nanofiber concentration on the resulting microstructures and mechanical properties of the nanocellulose foams.