NEW SIMULATION APPROACH TO MECHANICAL PROPERTIES OF NANOCELLULOSE AEROGELS

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High mechanical strength and stiffness and large surface area are properties often referred to when nanocelluloses are described. These properties in combination with biodegradability make nanocelluloses tempting raw materials for new bio-based materials. Here we demonstrate the potential of such materials. In particular, we prepared 3-dimensional structures based on pure nanocellulose, characterized their structure and compared their mechanical properties with those obtained by micromechanical simulations.

Highly porous, mechanically stable aerogels [1] were prepared by freeze drying of nano-fibrillar-cellulose (NFC) suspensions. The NFC concentration was varied to alter the morphological structure and mechanical properties of the samples. Three dimensional samples (disks with 15mm thickness and 50mm diameter) were prepared and their compressibility was tested. The increase of NFC content and thus density clearly increased the mechanical strength.

The pore morphology of the structures was investigated with SEM and X-ray tomography. The main feature in the structures was the formation of micron-sized nanocellulose sheets. From the 3D tomography image, we obtained 2D cross-sections that allowed the recording of microscopic geometric features (see Fig. 1). This structure was used to simulate the stresses and strains during compression with a rigid surface. The model considered a microscopic 2D structure formed from thin beams representing the NFC sheet-like layers. The microscopic model was implemented in a commercial FE-code.

We also simulated similar artificial structures obtained by placing beams randomly in a rectangular cell. Orientation, length as well as curvature of the beams obeyed Gaussian statistics. In addition, the porosity, heterogeneity, micro-film-thickness and elastic properties of the beams could be varied. Furthermore, mutual interactions of the beams were taken into account by modeling the mechanical contact behavior of the beams.

The resulting stress-strain curves are consistent with experimental findings. In other words, 2D modeling is sufficient to obtain the main qualitative features of the mechanical behavior of nanocellulose aerogels. The sheet-like layers improve effectively the stiffness of the structures. Yield in stress-strain behavior is related to the heterogeneous distributions of local displacements rather than the local bending of nanocellulose micro-sheets. Stiffness is dominated by structural homogeneity in micron scale. This homogeneity is sensitive to freezing time. The contacts between the micro-sheets affect the overall stress level. However, for moderate strains the qualitative features of the stress-strain behavior are quite well predicted by simulations even when these contacts are omitted.

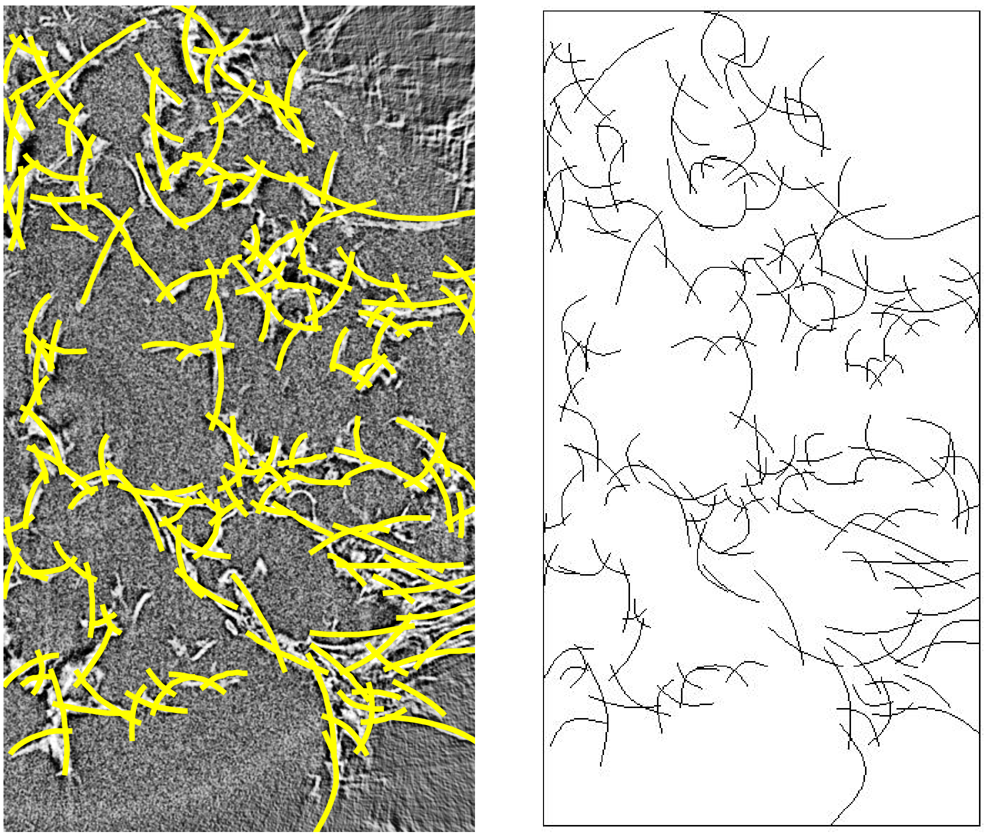

Figure 1. 2D cross-section of the 3D X-ray tomography image of the bulky NFC structure (left) and the corresponding model structure (right).

Reference

[1] Pääkkö et al., Long and entangled native cellulose I nanofibers allow flexible aerogels and hierarchically porous templates for functionalities. Soft Matter 4, 2492 (2008).

Business from technology

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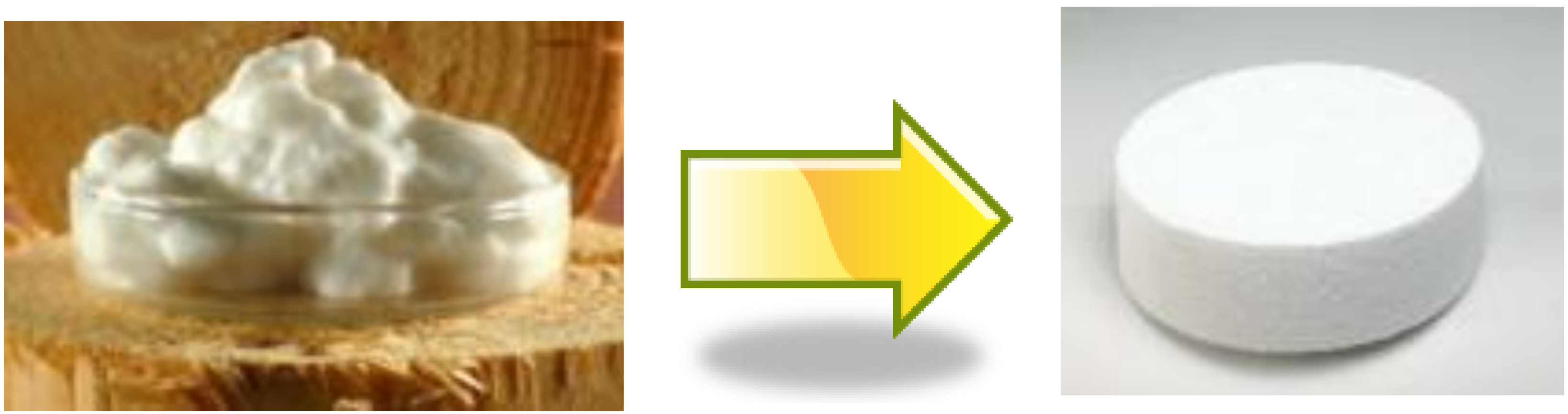
Nanocellulose aerogel:
Interesting structure with simple means

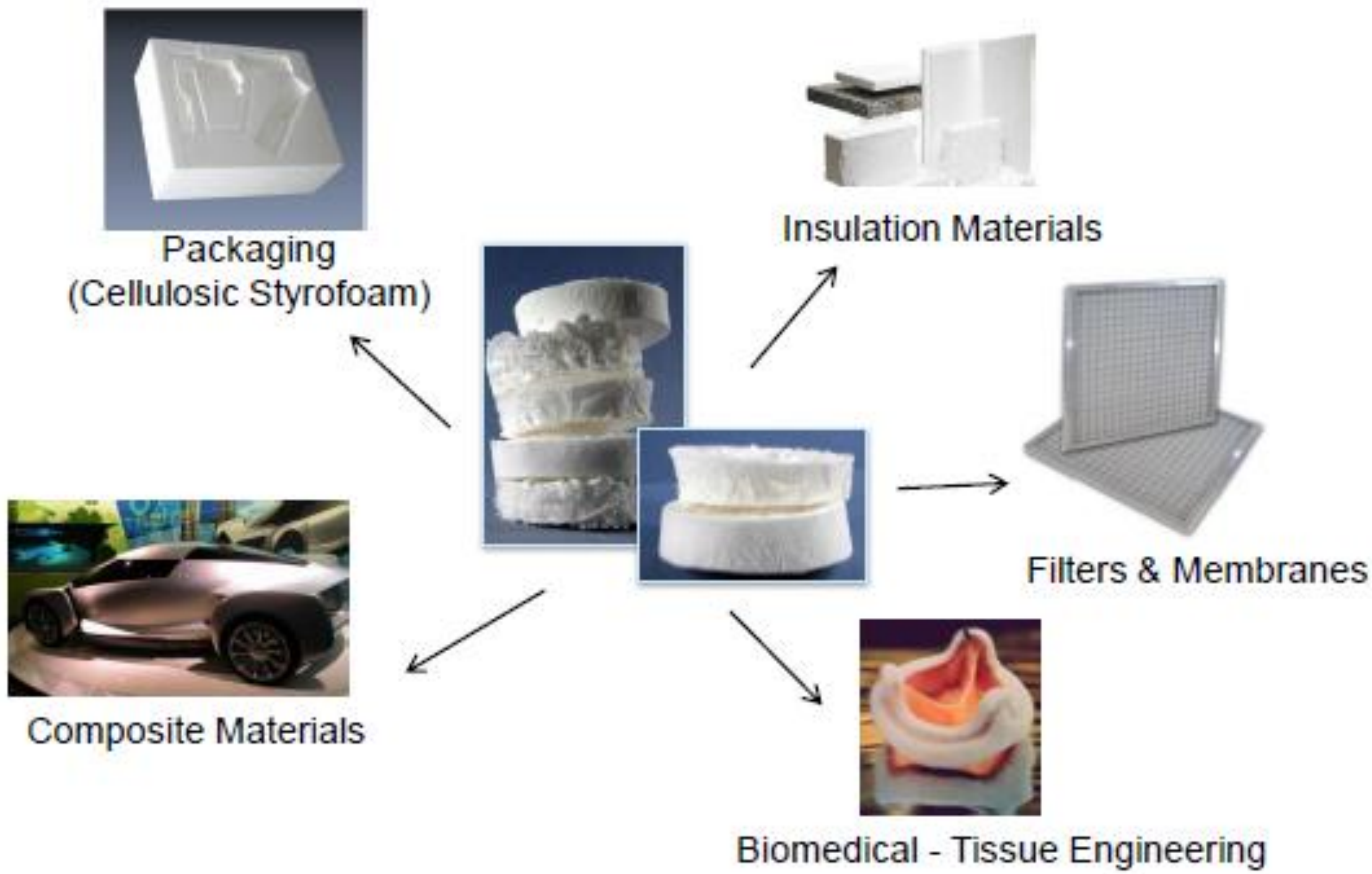
1. Preparation of a homogeneous nano-fibrillar cellulose (NFC) suspension
2. Freezing of the suspension
3. Sublimation of the water by freeze-drying



Intriguing characteristics
(M. Pääkkö et al., Soft Matter 4, 2492 (2008))

- Highly porous (porosity ~98%)
- Ductile and flexible (compressive strain ~ 70%)
- Hierarchical micro- and nanoscale morphology can be modified by the freeze-drying conditions
- Possibilities for various functionalities, e.g. conductivity

Potential applications



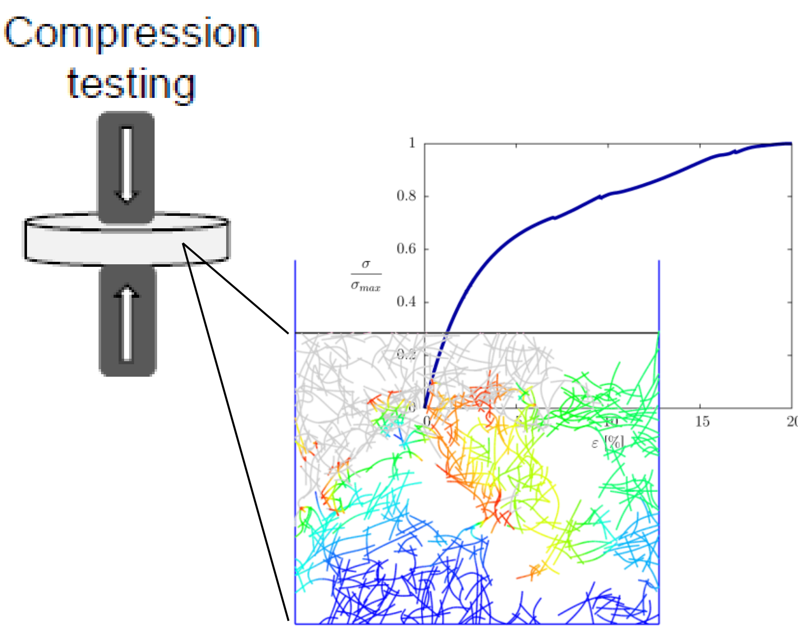
Current work

Experiments

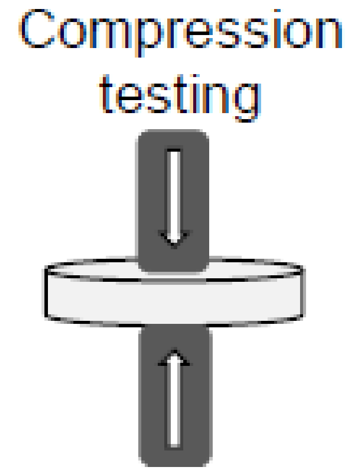
- Commercial nano-fibrillar cellulose (NFC) by J. Rettenmaier und Söhne (JRS), type 100-5
- Glucose as a cryoprotectant
- Both very fast and very slow freezing
- NFC concentration varied to affect overall porosity
- Disks with 50mm diameter and 15mm thickness

Modeling

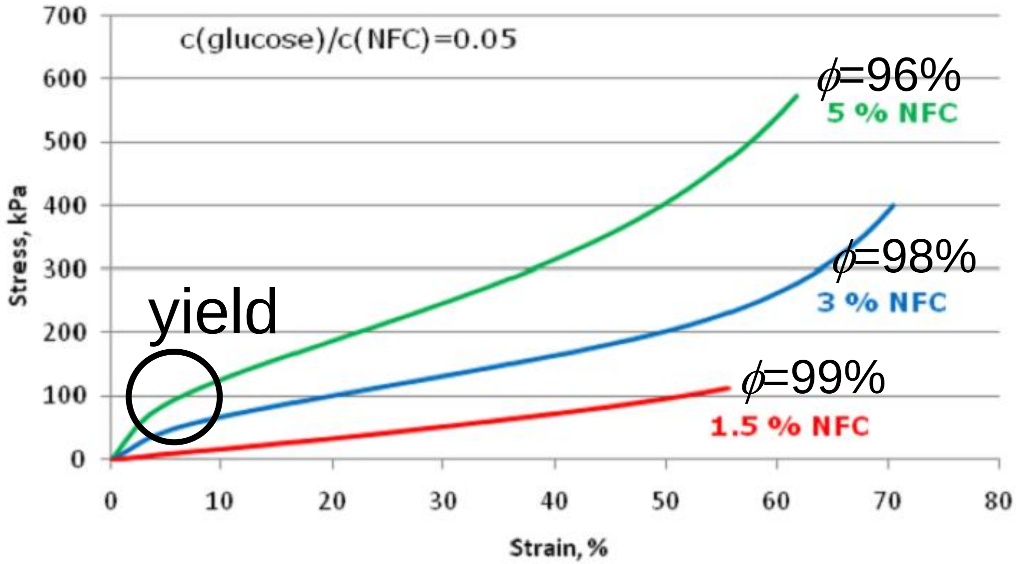
- Goal to understand microscopic structural features that dominate the mechanical behavior of NFC aerogels

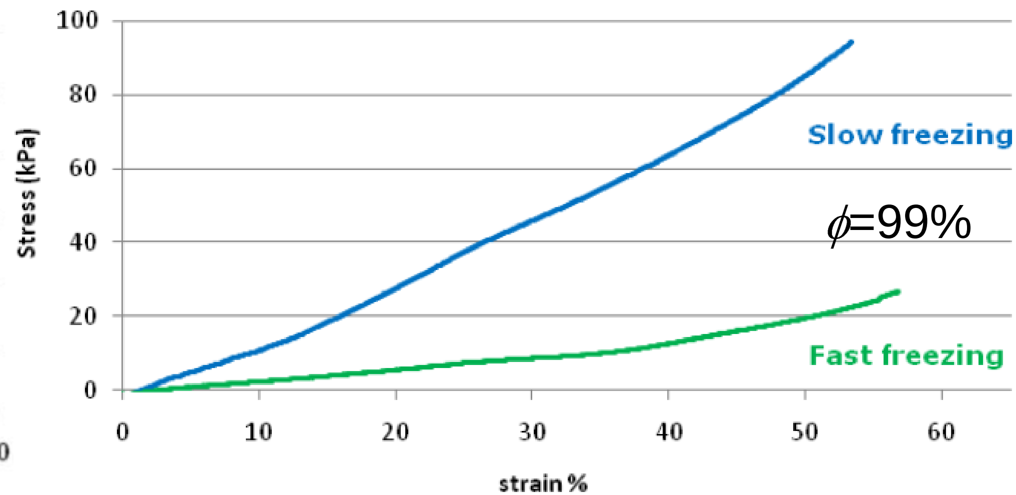


Contrary to previous work…



- Yield behavior observed at 3-5% NFC concentration (porosity 96-98%)
- Compressive stiffness can be quite large at 96% porosity
  - specific compression modulus 55 MPag^{-1}cm^3
- Stiffness and structure are greatly affected by freezing time



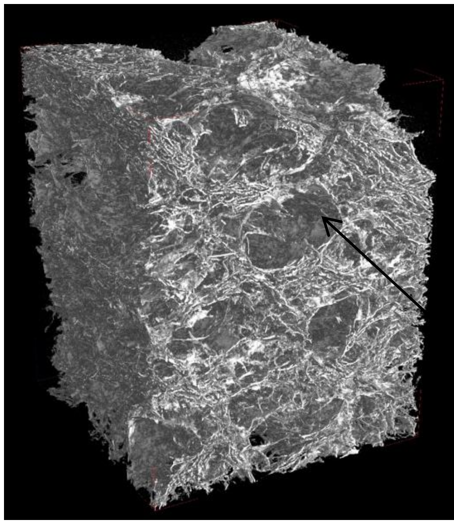


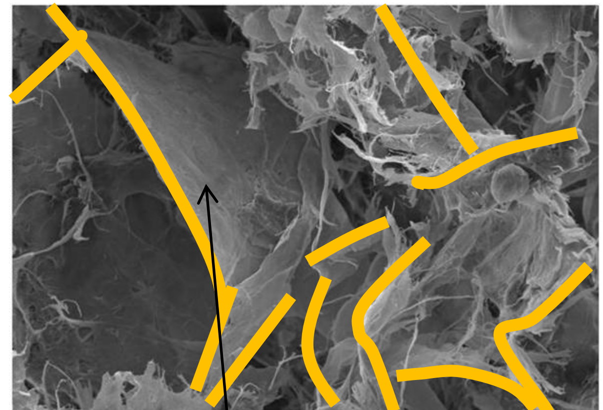
Micro structure of NFC aerogels

X-ray tomography

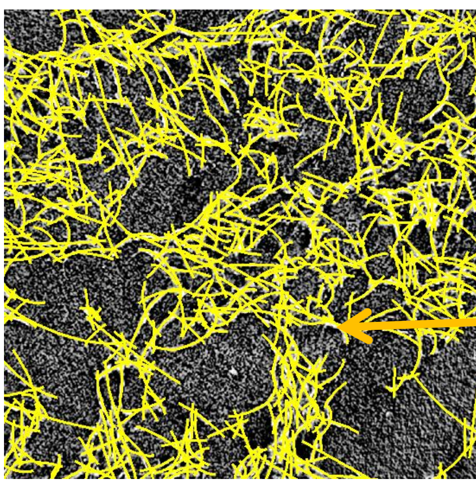
SEM

3D





2D



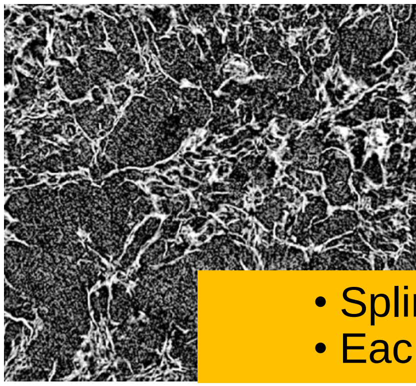
NFC fibrils aggregate to micro sheets/membranes

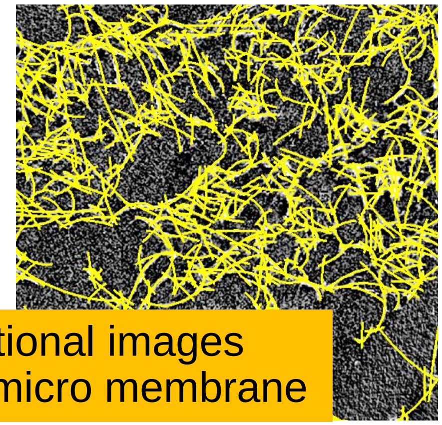
Seen as ”arches” in 2D

Re-construction of the 2D micro structure

A

From real structure





- Splines fitted to cross-sectional images
- Each spline represents a micro membrane

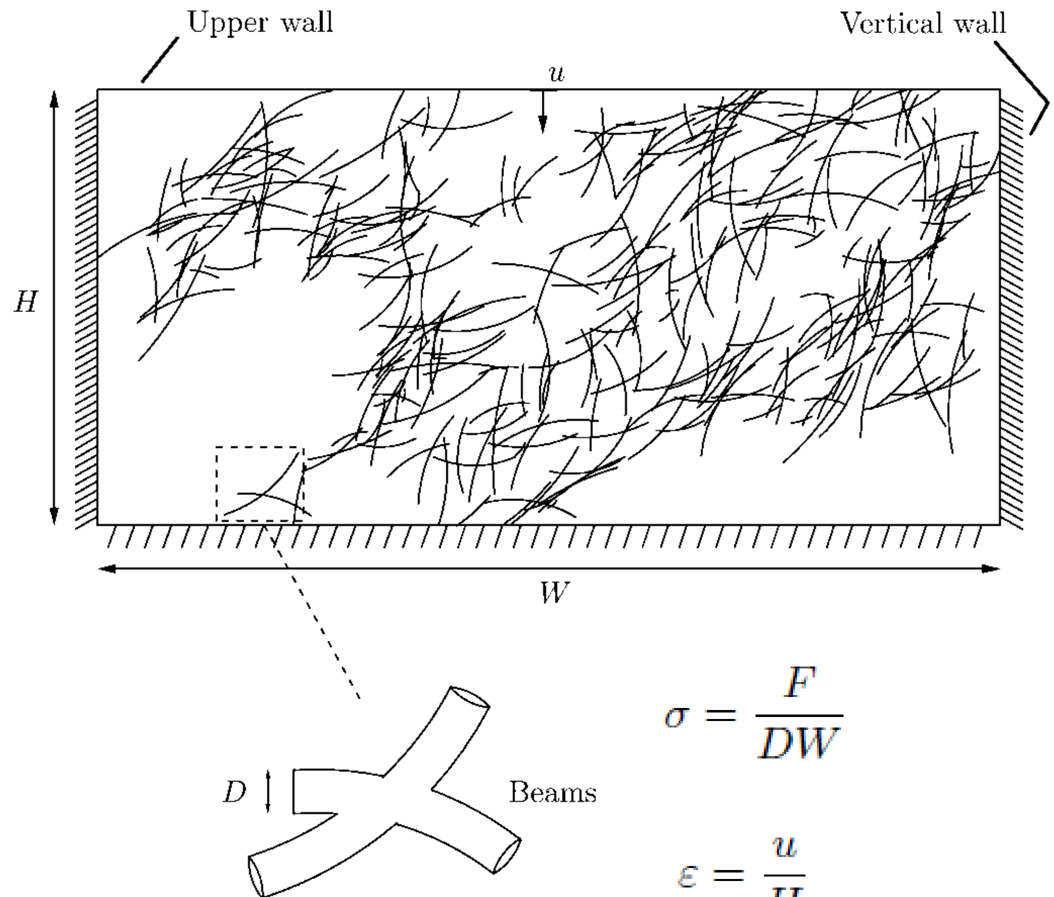
B

Artificial structure

- Random generation of circular arches whose properties follow Gaussian statistics

Compression simulation

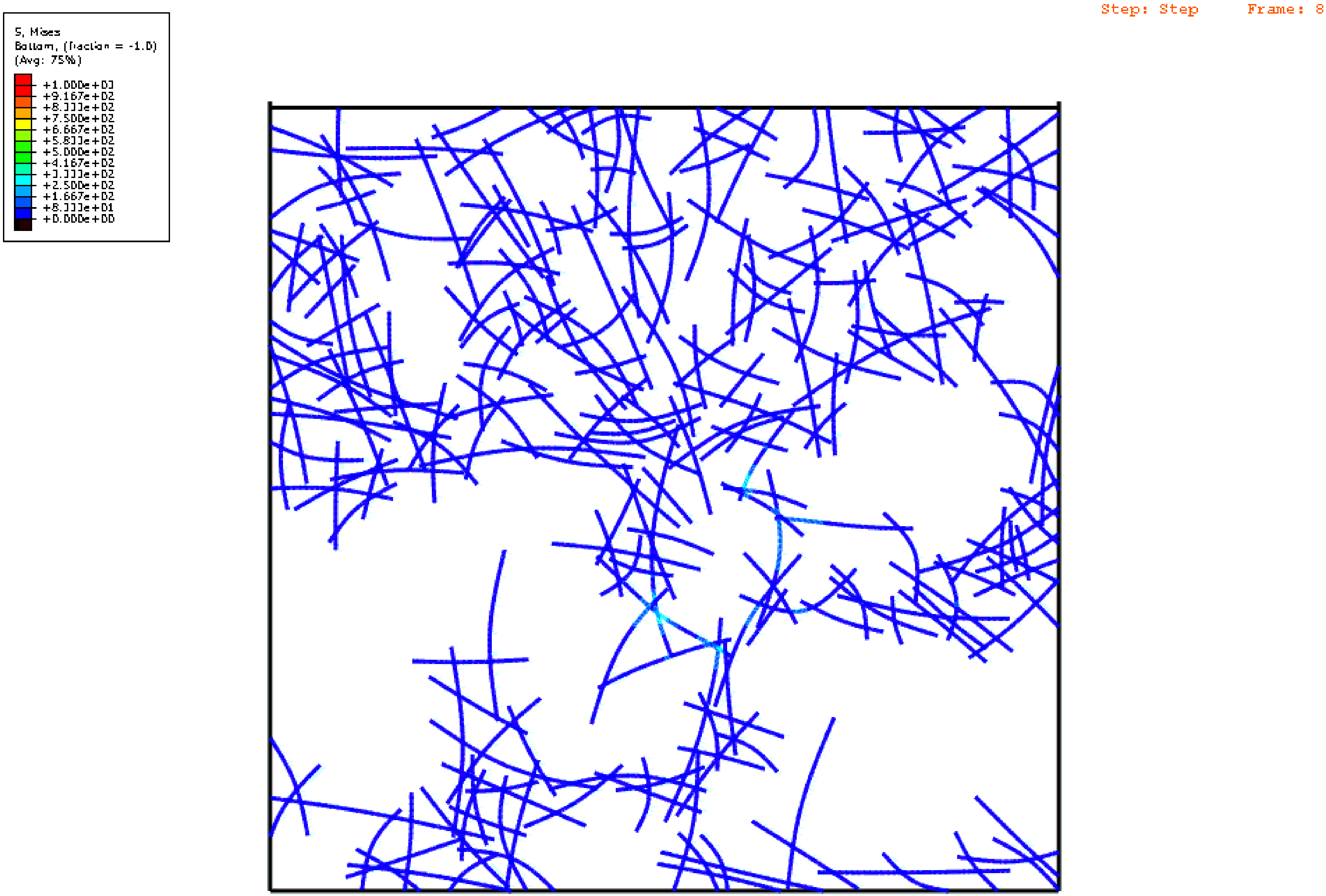
- 2D network is tranferred to commercial FEM code and meshed with beam elements describing NFC micro membranes
- Beams are clambed to horizontal walls but are free to slide against vertical walls
- Upper wall is compressed against the network
- Induced stress and strain are followed



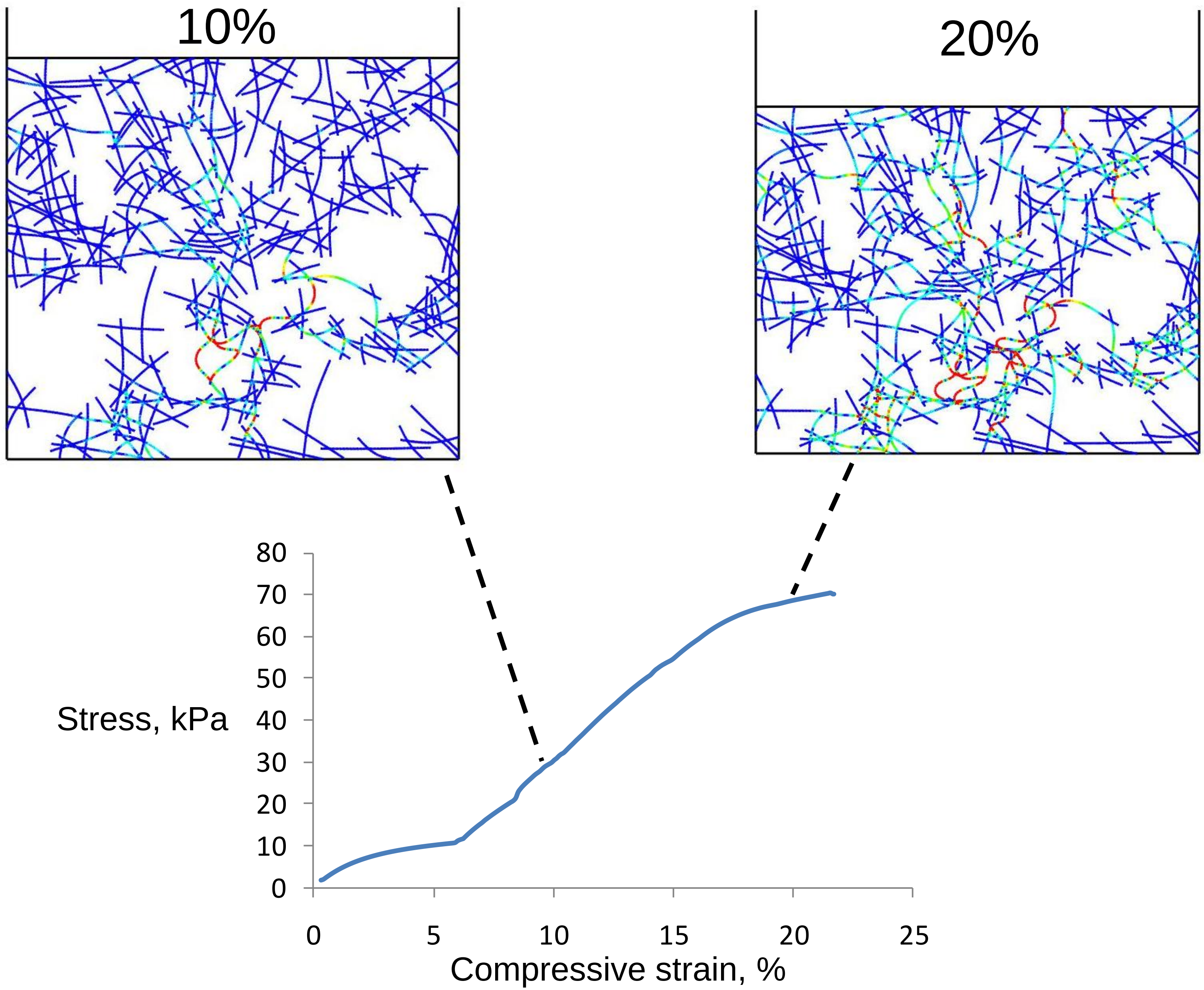
$$\sigma = \frac{F}{DW}$$

$$\varepsilon = \frac{u}{H}$$

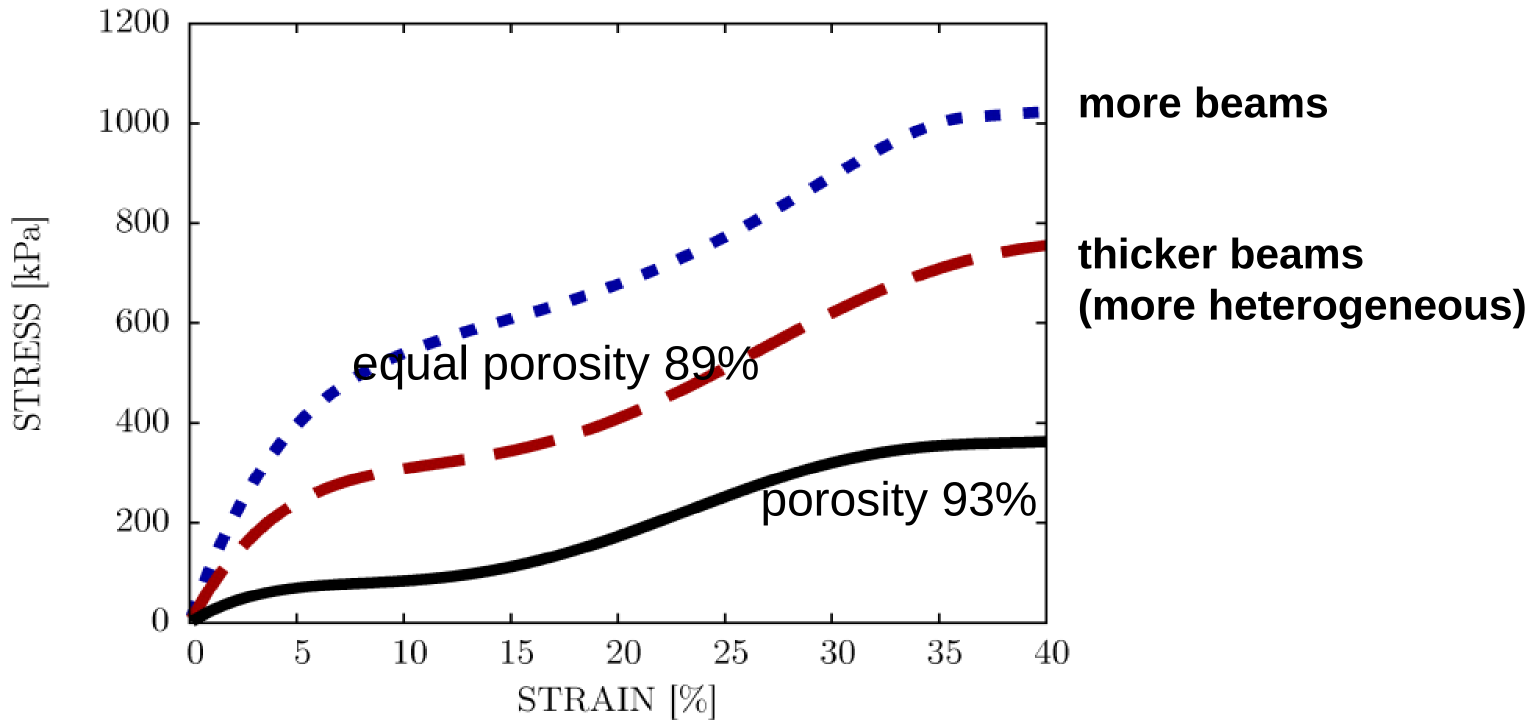
E_{mod}=100GPa



S, Mises
Bottom, (fraction = -1.0)
(Avg: 75%)
+1.000e+03
+9.167e+02
+8.333e+02
+7.500e+02
+6.667e+02
+5.833e+02
+5.000e+02
+4.167e+02
+3.333e+02
+2.500e+02
+1.667e+02
+8.333e+01
+0.000e+00
Step: Step
Frame: 8

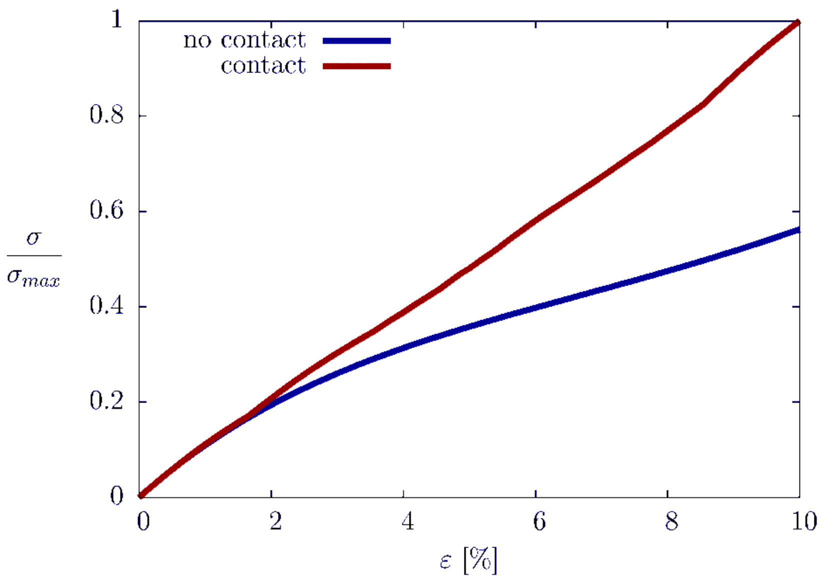

10%
20%
Stress, kPa
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
Compressive strain, %

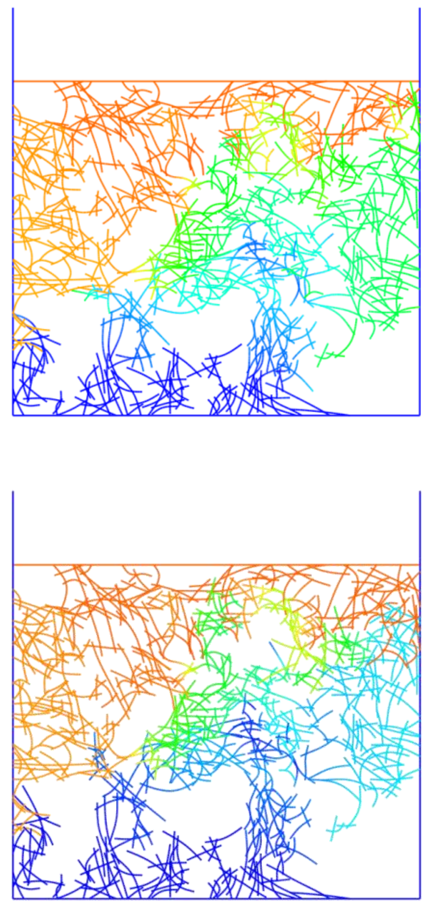
Density affects stiffness
Heterogeneity underlies yield



10 parallel artificial networks (no contacts)

Effect of beam-beam contact



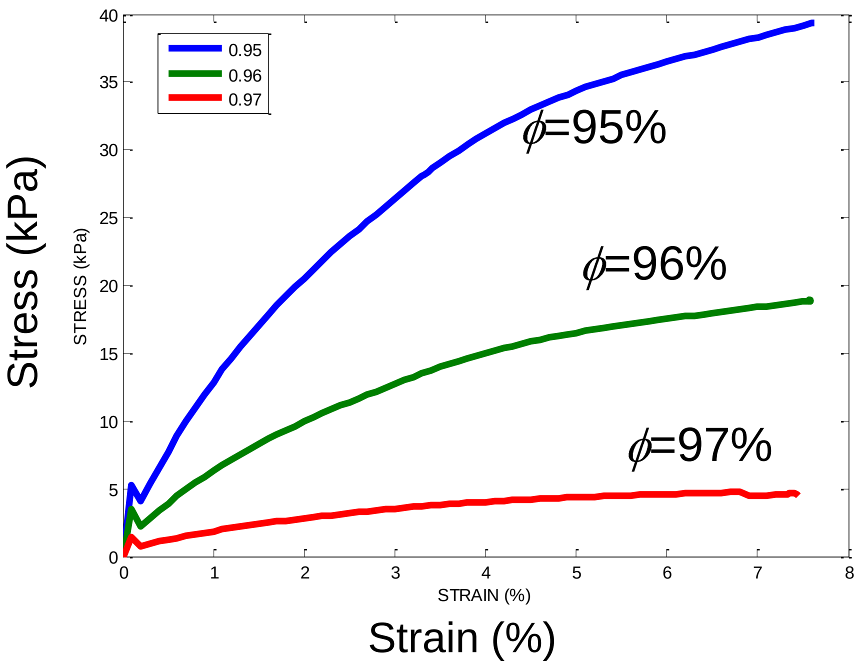


Contact

No contact

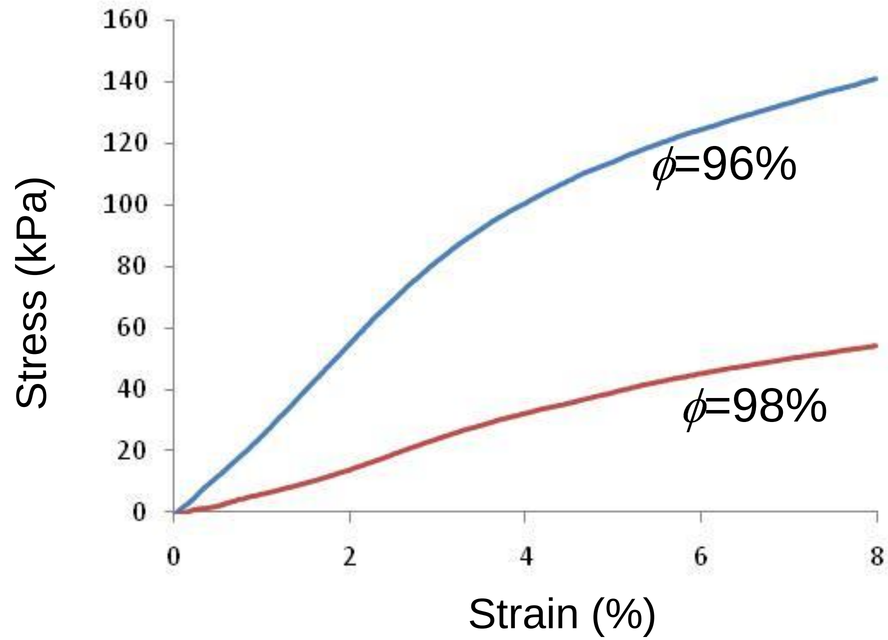
Modeling vs experiment: effect of porosity

MODEL



One fixed network

EXPERIMENT



Conclusions

- 2D model reproduces qualitatively the mechanical behavior of nanocellulose aerogels
- Stiffness is affected both by density and structural homogeneity in micron scale (sensitive to freezing time)
- Yield in stress-strain behavior is related to the structural heterogeneity, not local bending
- ”Hybrid” approach speeds up model analysis considerably
    - complexity of simulation of the process that is used to form the structure can be avoided

Thanks to

Metsäliitto Group

m-real

BOTNIA

MYLLYKOSKI

STORAENSO

UPM