Hierarchical control of swelling in pulp fibers

Thad Maloney*, Sara Ceccherini*, Josphat Phiri*, Hamid Ahadian*, Antti Paajanen**, Paavo Penttilä*, Aleksi Zitting*

* Aalto University, Finland
**VTT, Finland

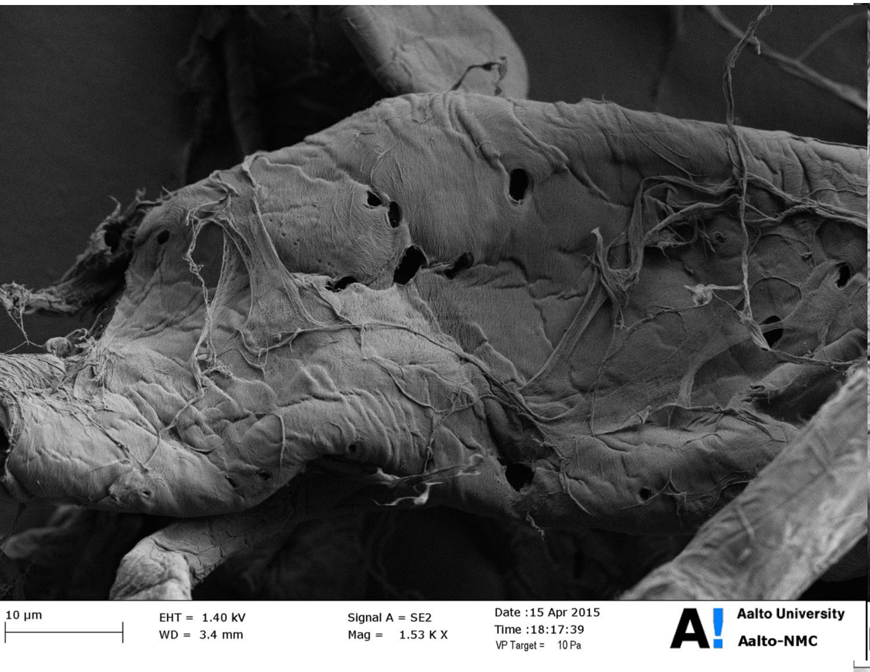
TAPPI NANO DIVISION

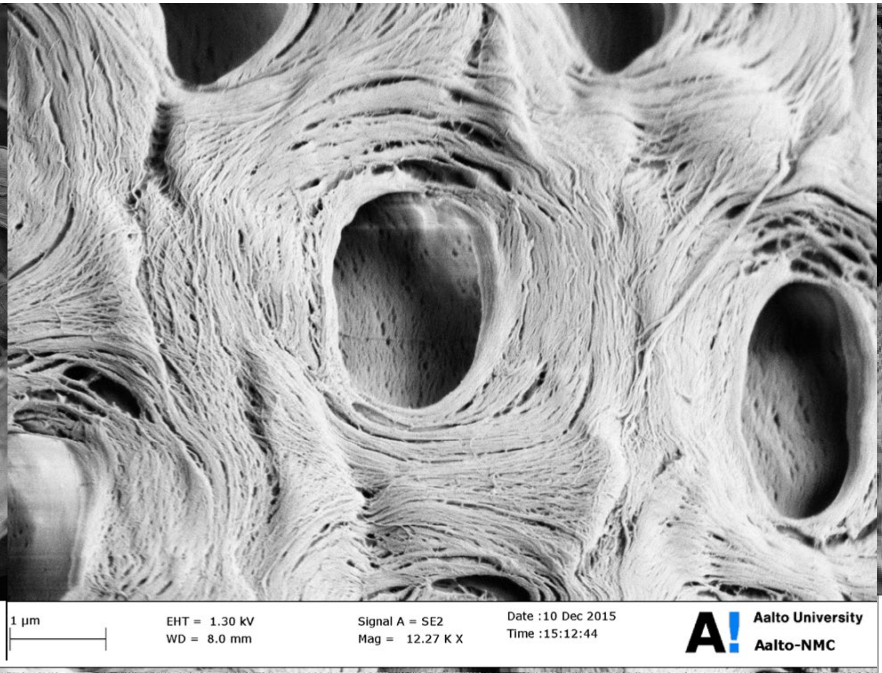
Introduction

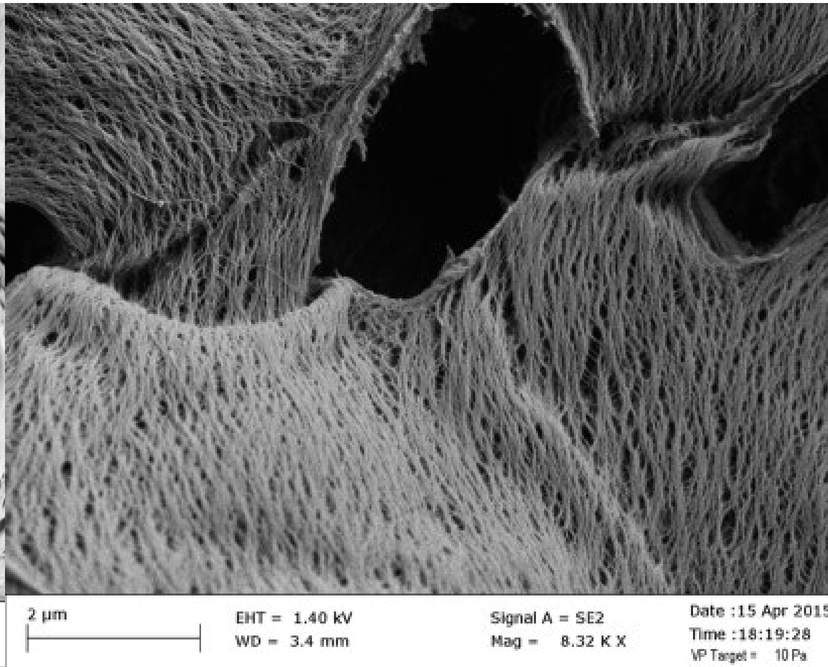
Fiber/water interactions → fiber swelling → product performance

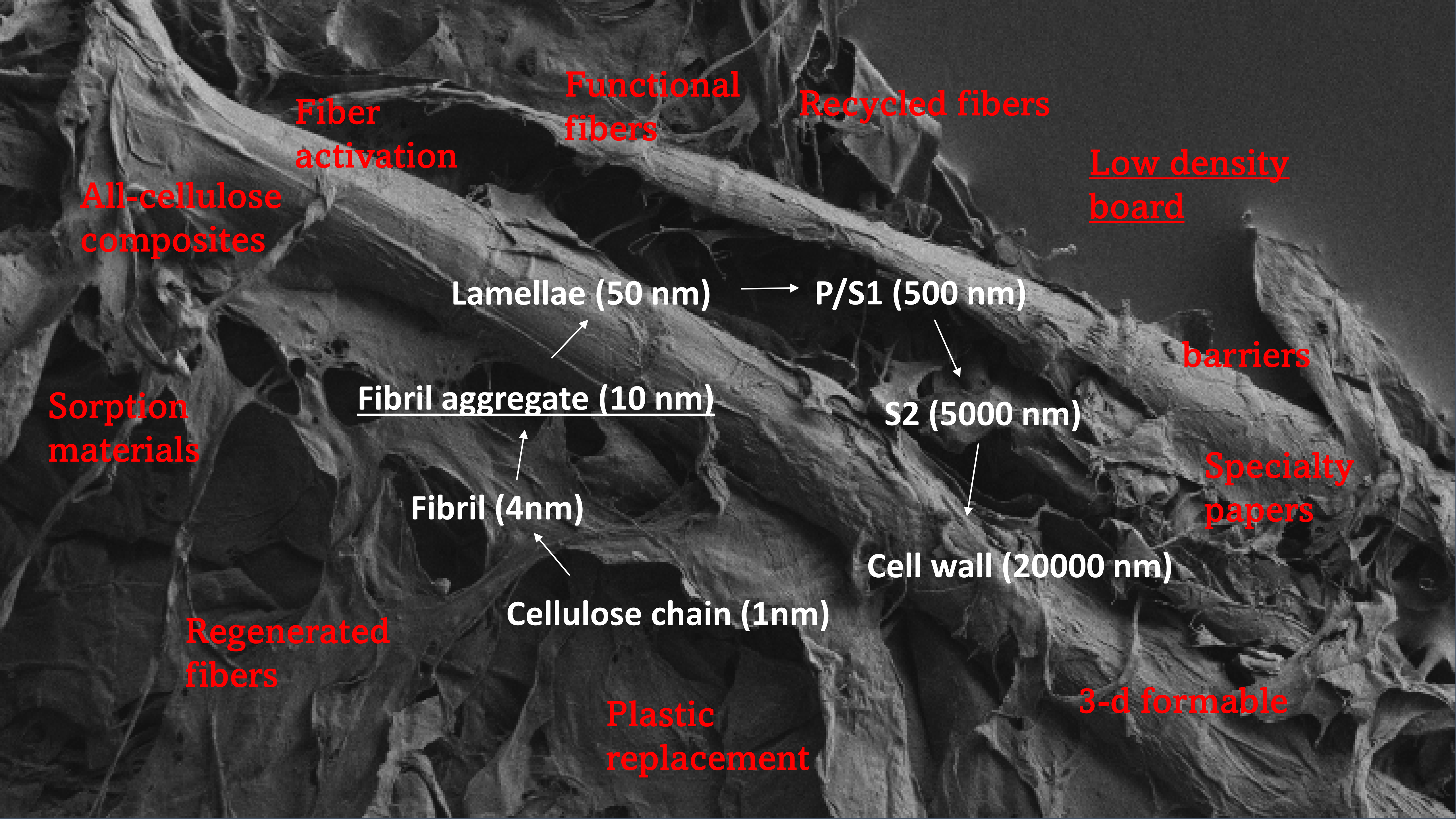
The cell wall is composed of sub-units i.e the hierarchy. Do these swell independently?

Can we “nano-engineer” the cell wall without extracting nanocellulose?








Fiber activation
Functional fibers
Recycled fibers
Low density board
All-cellulose composites
Lamellae (50 nm)
P/S1 (500 nm)
barriers
Fibril aggregate (10 nm)
S2 (5000 nm)
Sorption materials
Specialty papers
Fibril (4nm)
Cell wall (20000 nm)
Cellulose chain (1nm)
Regenerated fibers
Plastic replacement
3-d formable

Hypothesis

Macrofibril swelling can be controlled independently from cell wall swelling.

- This can be measured
- Its useful where high specific bond strength is important

Experimental

Materials

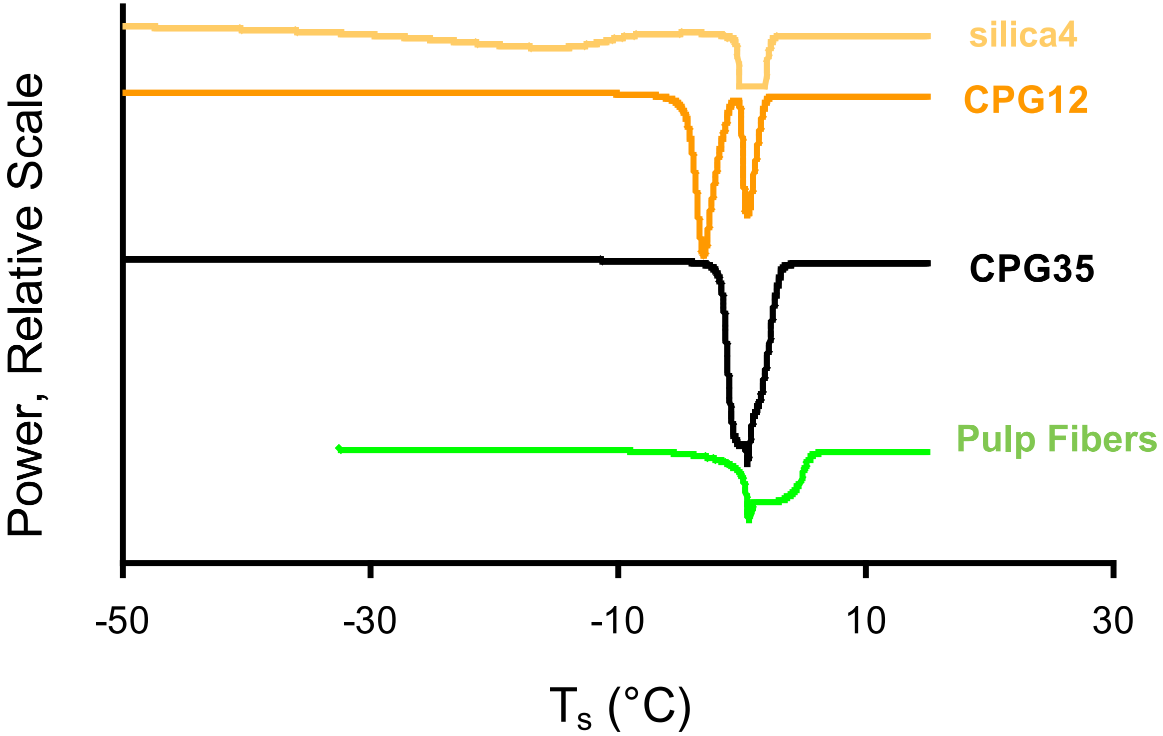
- Pulp: Bleached softwood kraft, never dried, some experiments use an UBSW kraft pulp.
- Functionalization: varying quantities of phosphate groups added to the internal surfaces by drying the pulp from diammonium phosphate/urea aqueous solution under controlled conditions. Exchanged to Na^+ form.

Analytics

- Water retention value (WRV) for measuring cell wall swelling.
- Se exclusion with 3.2 nm dextran probe for measuring macrofibril swelling.
- Thermoporosimetry for macrofibril swelling, pore size distribution and surface area.
- Molecular dynamics simulation for visualizing macrofibril swelling and estimating surface area (Antti Paajanen).
- X-ray scattering for measure fibril separation (another measure of macrofibril swelling) (Paavo Penttilä, Aleksi Zitting).

In thermoporosimetry, the pore size distribution can be accounted calculated from the well-known Gibbs-Tomson eq., except….

Melting energy of water in for porous glasses and pulp fibers

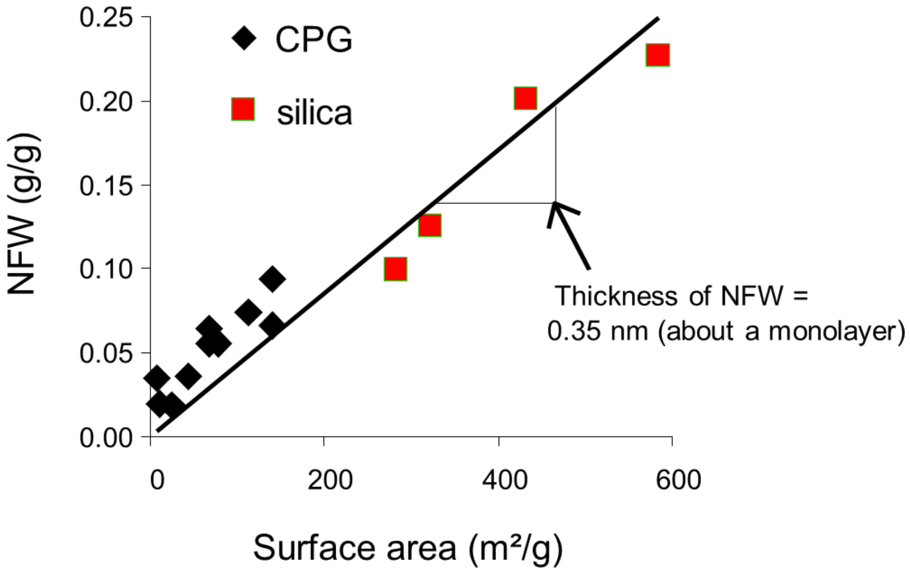


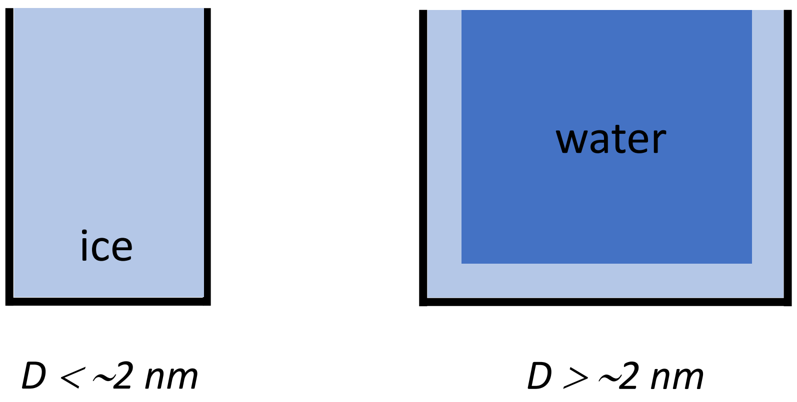
$$D = \frac{k}{\Delta T}$$

$$V_{pore} \propto H_m$$

2 fractions of nonfreezing water (NFW) in pulp fibers

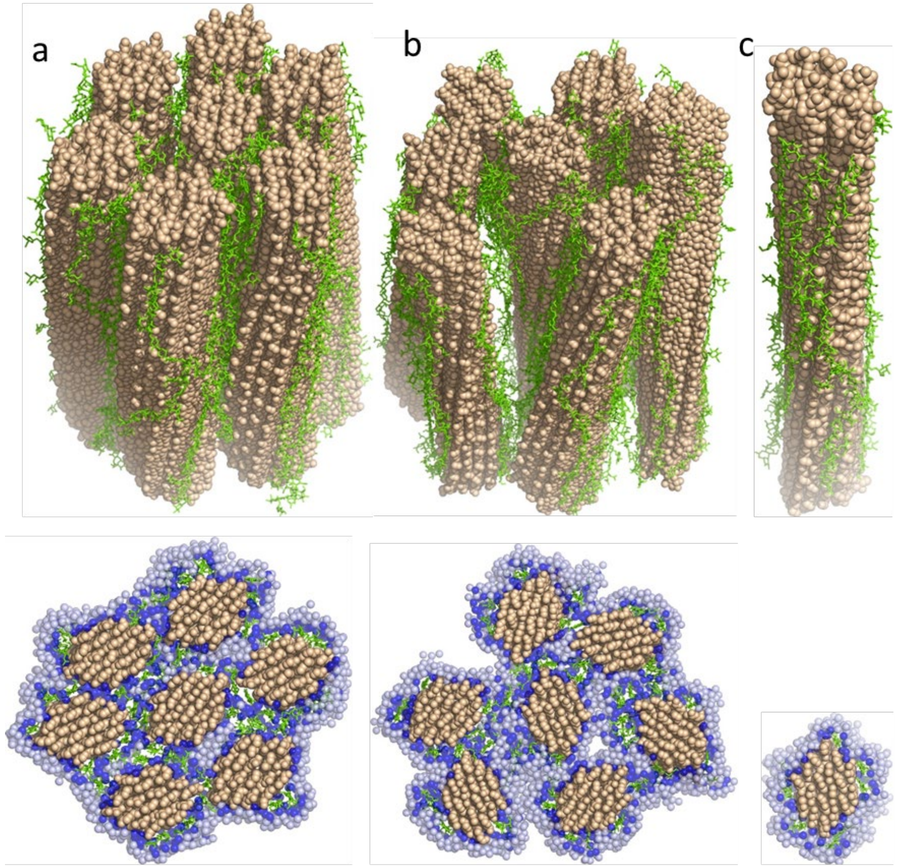
NFW in mesoporous (D>2nm) glasses





Pradzynski, C. , F. R. , Z. T. , S. P. and Bruck. U. (2012). A Fully Size-Resolved Perspective on the Crystallization of Water Clusters. *Science*, *337*(6101), 1529–1532.

Swelling of fibril aggregates



- Molecular dynamics simulation of Spruce S2
- 7 fibril aggregates (macrofibrils with different packing.
- 18 cellulose chains in hexoganol array
- 20% Galactogluccomannan/glucuronoarabinoxylan
- Hornification increases from c to a; deaggregation increases a to c

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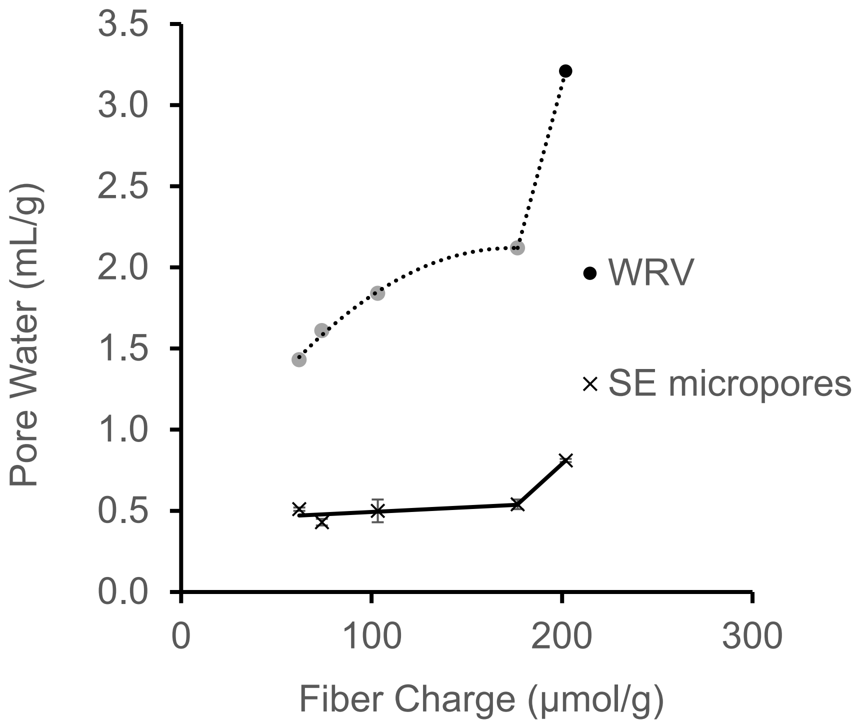
Surface area and bound water volumes from simulations

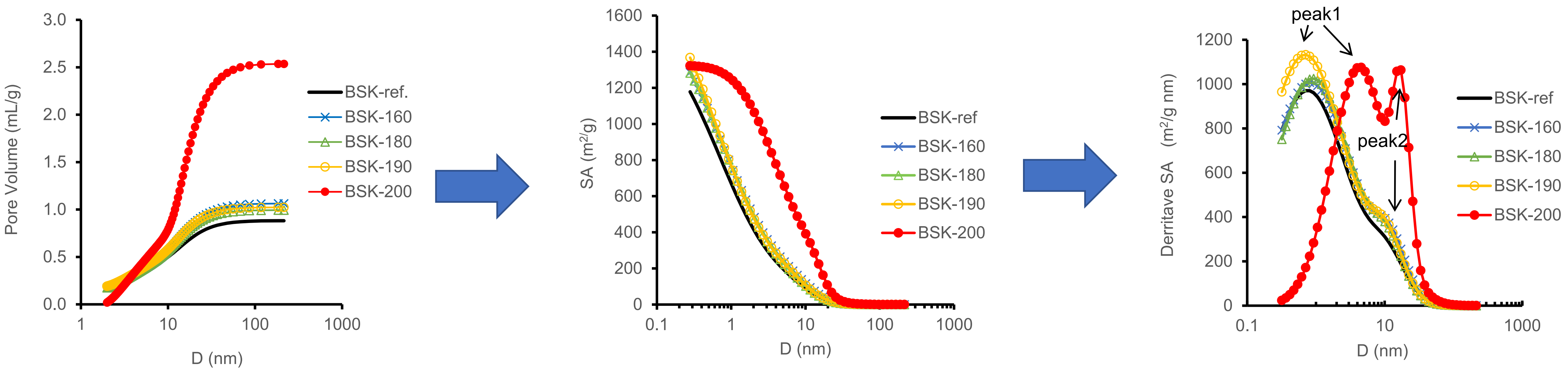
Bond water and surface area	Tight fibril aggregate	Loose fibril aggregate	Single fibril
1st water layer volume, mL/g	0.1585 ± 0.0009	0.197 ± 0.002	0.202 ± 0.004
2nd water layer volume, mL/g	0.205 ± 0.002	0.321 ± 0.007	0.427 ± 0.008
SA, 0.28 nm probe, m^2/g	1050 ± 6	1490 ± 20	1590 ± 30
SA, 3.2 nm probe m^2/g*	536 ± 9	624 ± 9	

Swelling of the cell wall vs swelling of the fibril aggregate



- Adding charge (phosphate groups) increases cell wall swelling elastically up to 180 µmol/g.
- No increase in fibril aggregate swelling in this range.
- At 200µmol/g charge, the cell wall swells dramatically; fibril aggregate swelling increases 35%.

The surface area plot shows dramatic effect of macrofibril swelling



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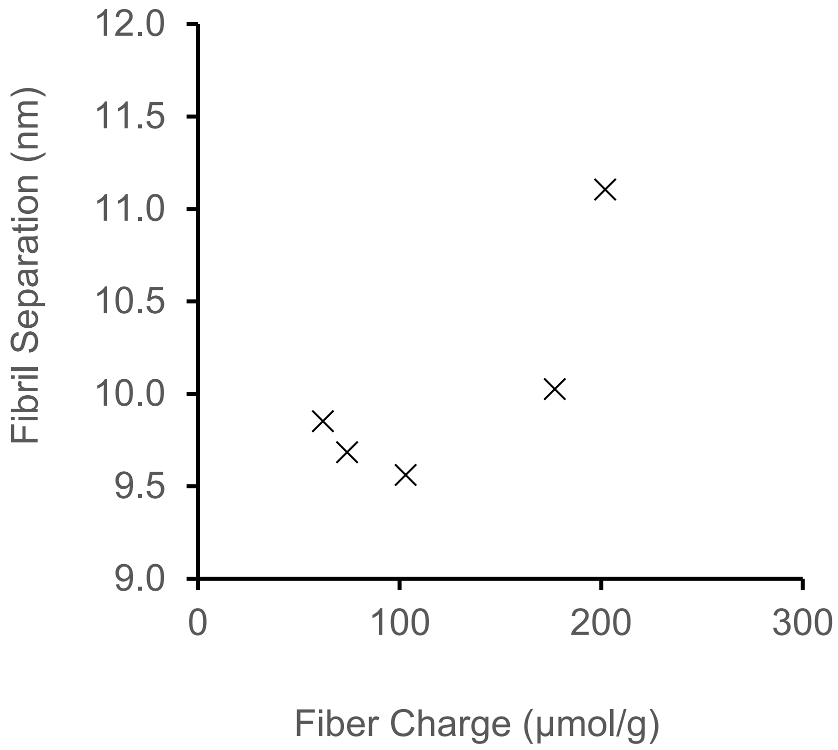
X-ray scattering of phosphorylated pulps



- Results confirm a distinct increase in fibril separation at the highest charge. i.e *deaggregation*.
- No presence of cellulose II or other anomalous crystal structures detected.

Clustering of fibrils in delignified Radiata Pine

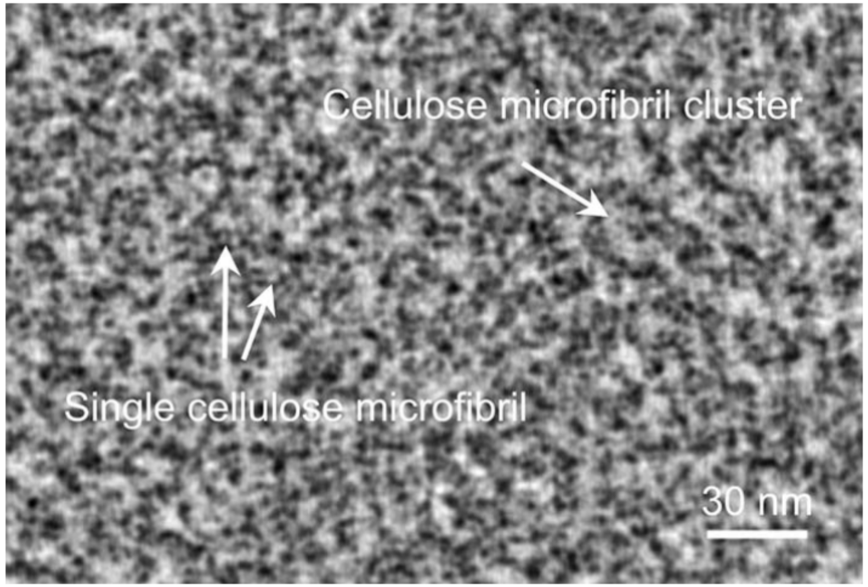


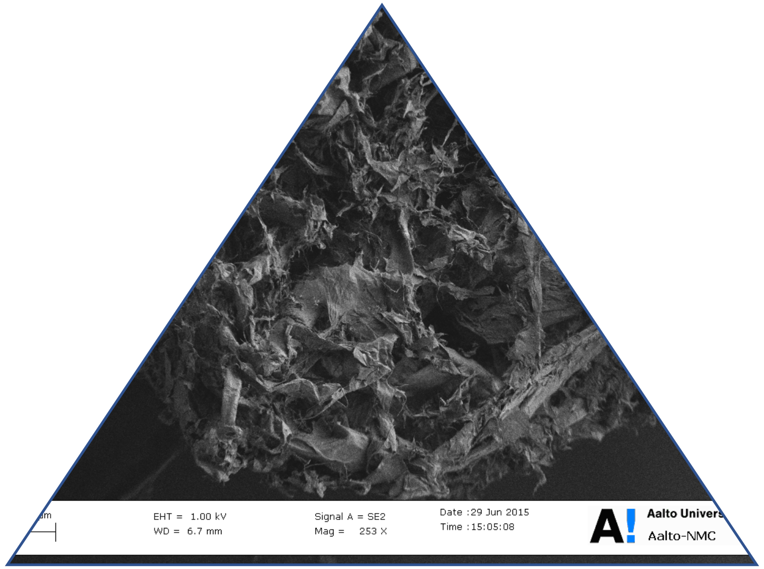
Fig. 1 Tomographic slice image (~ 1 nm thick) of the cross-section of a S2 layer in a delignified early radiata pine wood specimen. The *white/light grey structures* correspond to individual and clustered cellulose microfibrils, and the *surrounding dark grey/black structures* correspond to residual lignin and hemicellulose

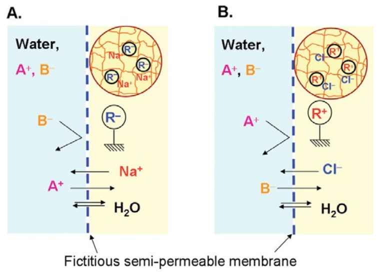
Xu, P., Donaldson, L. A., Gergely, Z. R. & Staehelin, L. A. Dual-axis electron tomography: A new approach for investigating the spatial organization of wood cellulose microfibrils. Wood Sci. Technol. 41, 101–116 (2007).

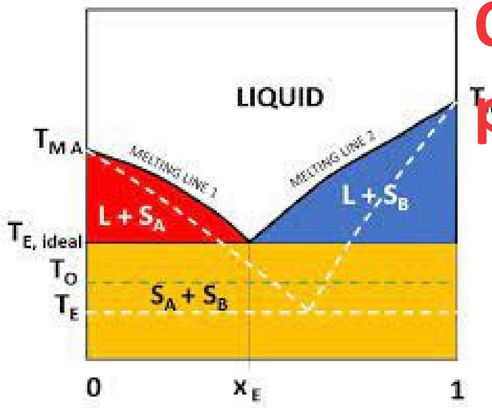
Hierarchical swelling control allows one to decouple important paper property pairs

Sample	Density kg/m^3	Tensile index Nm/g	E-Modulus GPa	Light scattering (cm^2/g)
BSK-ref	360	16.6 ± 4.6	3.9	35.5 ± 0.5
BSK-160	519	26.7 ± 3.1	5.7	30.7 ± 1.4
BSK-180	611	43.0 ± 2.4	3.8	24.9 ± 0.6
BSK-190	611	44.9 ± 7.9	13.7	24.8 ± 0.3
BSK-200	614	59.7 ± 11	16.7	19.1 ± 4.9

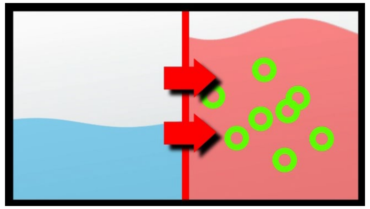
Controlling the hierarchical swelling

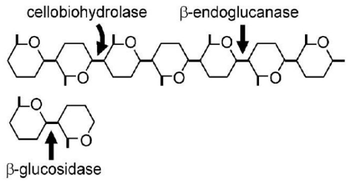


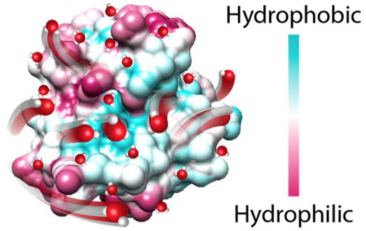




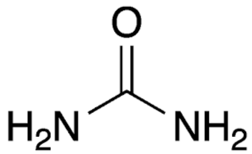
Osmotic pressure

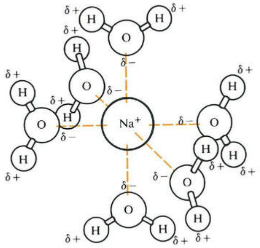


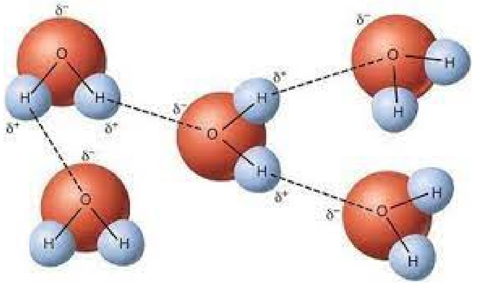




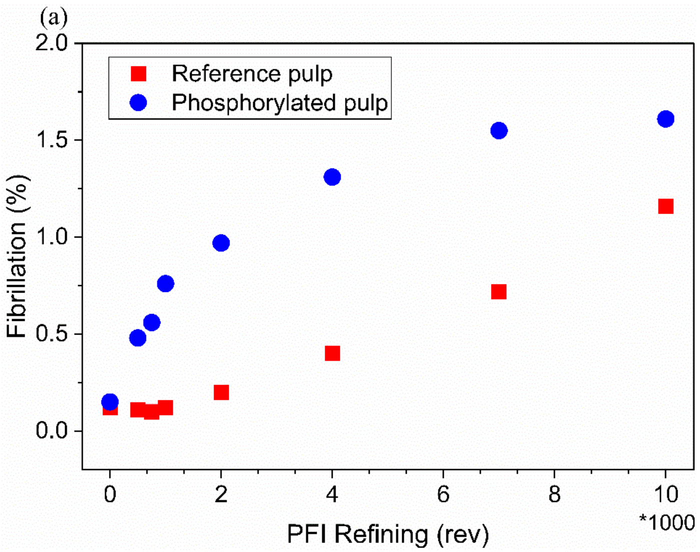
H-bond disruptors

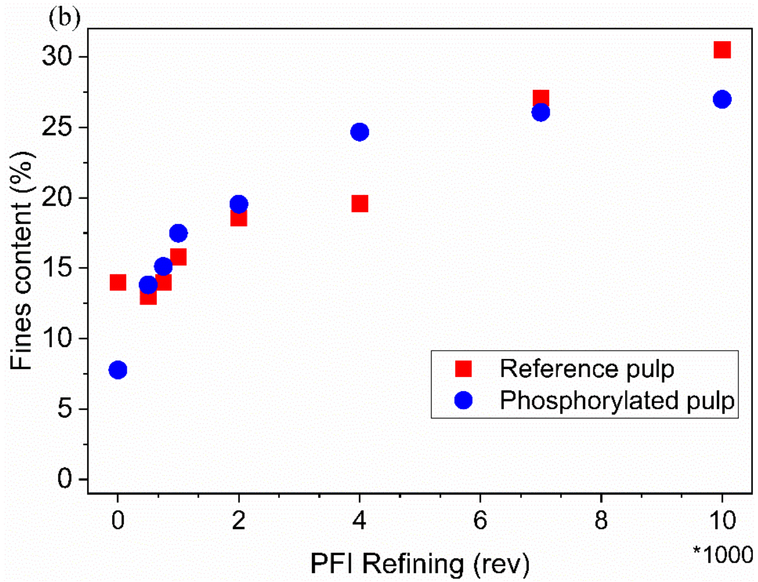


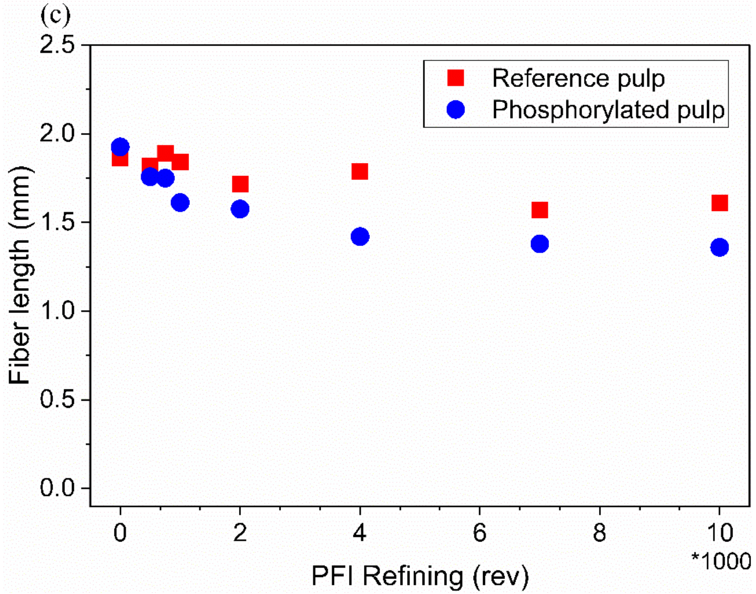




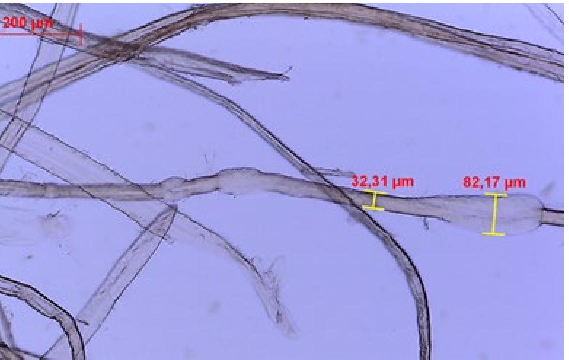
Phosphorylated pulps fibrillate but don’t degrade in refining







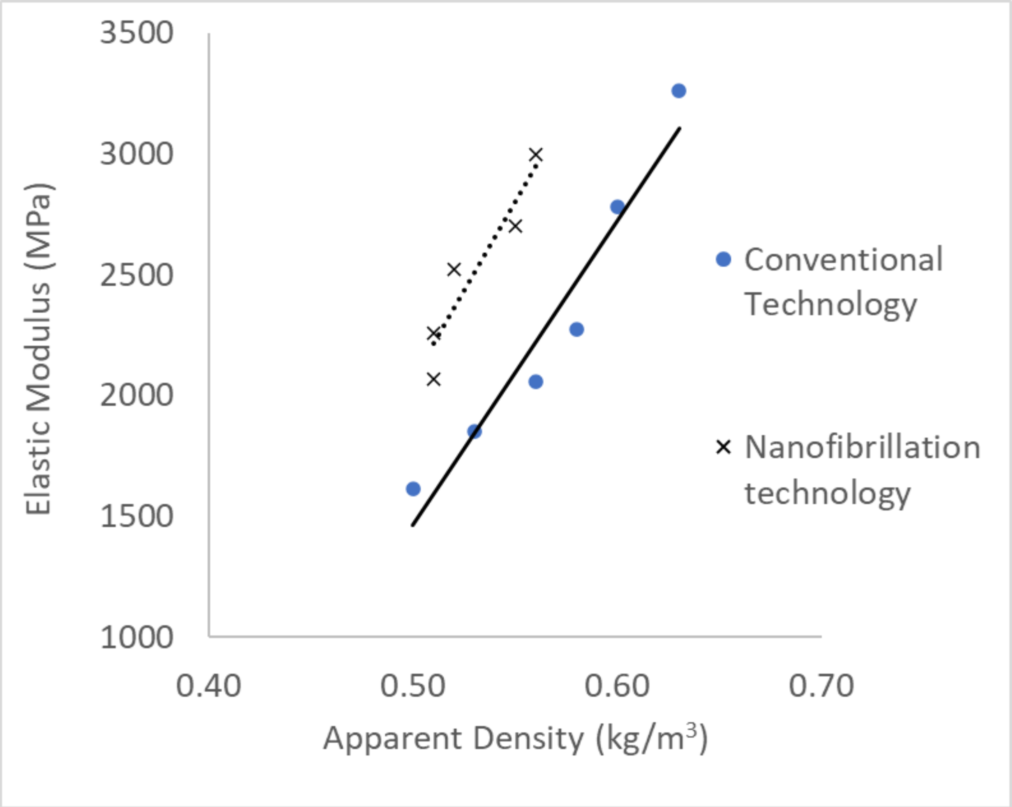
Phosphorylated USWK, unrefined



Phosphorylated USWK, refined

High strength/density paper by controlling hierarchical swelling

- SA or macrofibril ~500 m2/g
- SA microfibril ~1600



Hamid Ahadian, doctoral thesis

Conclusions

- Its possible to control the macrofibril swelling independently from the cell wall swelling and more broadly to manipulate the swelling hierarchy of pulp fibers.
- Increased electrostatic repulsion, disruption Van der Waals and H-bonds, mechanical shear are relevant tools.
- Thermoporosimetry is a good tool for measuring the fiber structural effects.
- In some cases, nano-engineering the fiber is more favorable than producing and adding nanocellulose.

Allocation of nonfreezing water between micropores and mesopores

Sample	Total NFW (mL/g)	Monolayer NFW in mesopores (mL/g)	NFW in subfreezing micropores (mL/g)
BSK-ref	0.25 ± 0.07	0.10	0.15
BSK-160	0.27 ± 0.06	0.11	0.16
BSK-180	0.27 ± 0.05	0.12	0.16
BSK-190	0.29 ± 0.08	0.11	0.18
BSK-200	0.27 ± 0.03	0.27	0.00