Inverse thermoreversible methylcellulose/cellulose nanocrystal nanocomposite hydrogel for fiber spinning

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TAPPI

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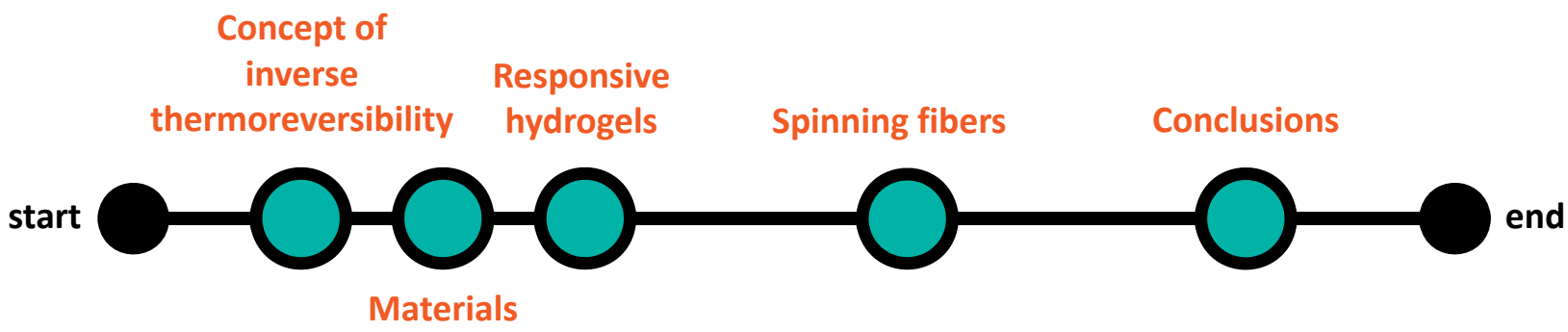

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Inverse thermoreversibility

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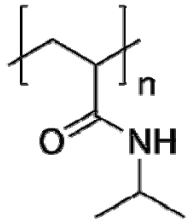
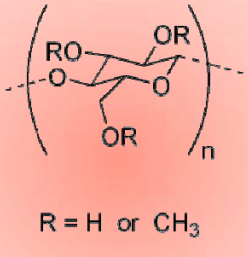
Heating = Melting



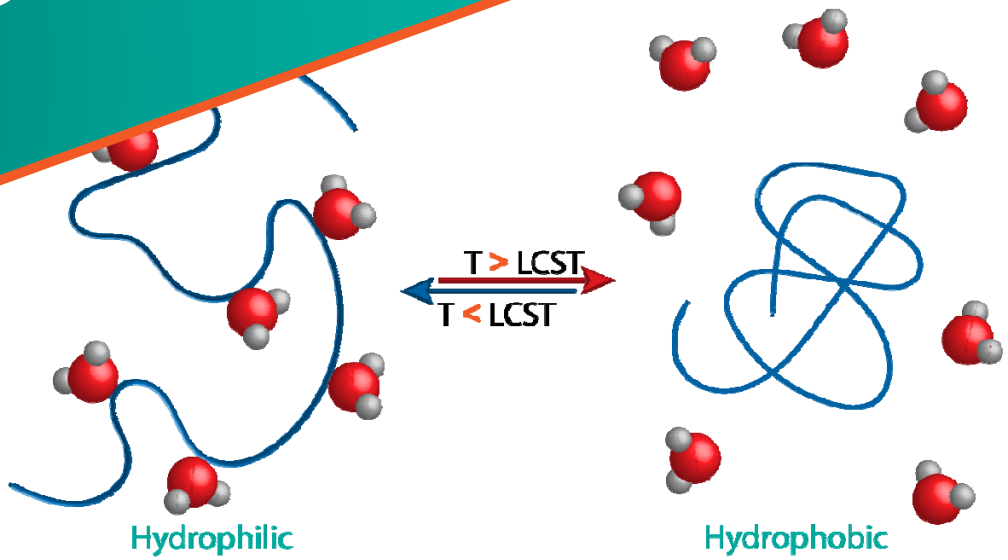
PNIPAM

Thickening



Methylcellulose

Can the mechanical response be tuned?



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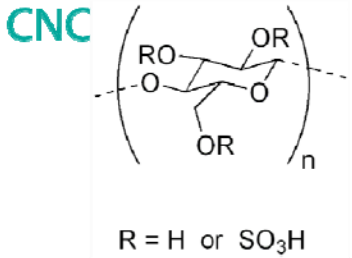
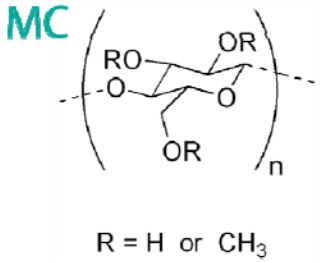
Materials & experimental design

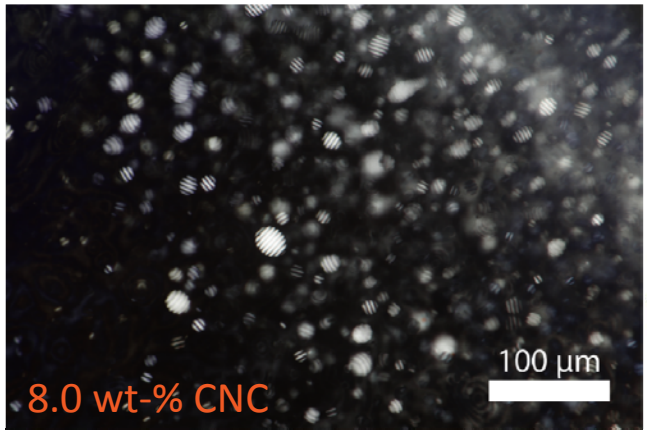
Cellulose nanocrystals (CNC)
- Rigid anionic rods, length ~200 nm
- Lyotropic liquid crystallinity
- Varied in the range of 0 - 3.5 wt-%

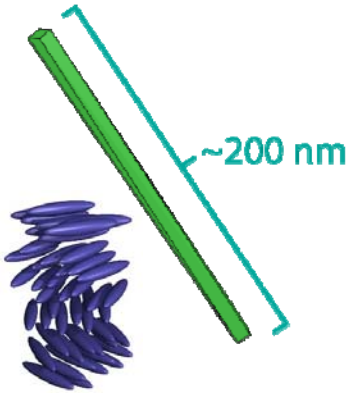
Methylcellulose (MC) (MW 88,000)
- Water soluble cellulose derivative
- Inverse thermoresponsive
- Fixed at 1.0 wt-%

MC/CNC hydrogel
- Physically crosslinked
- Stiffness tunable by MC/CNC ratio
- Mechano-optical thermoresponse









Mechanical properties studied with rotational rheometry at 20 – 60 °C

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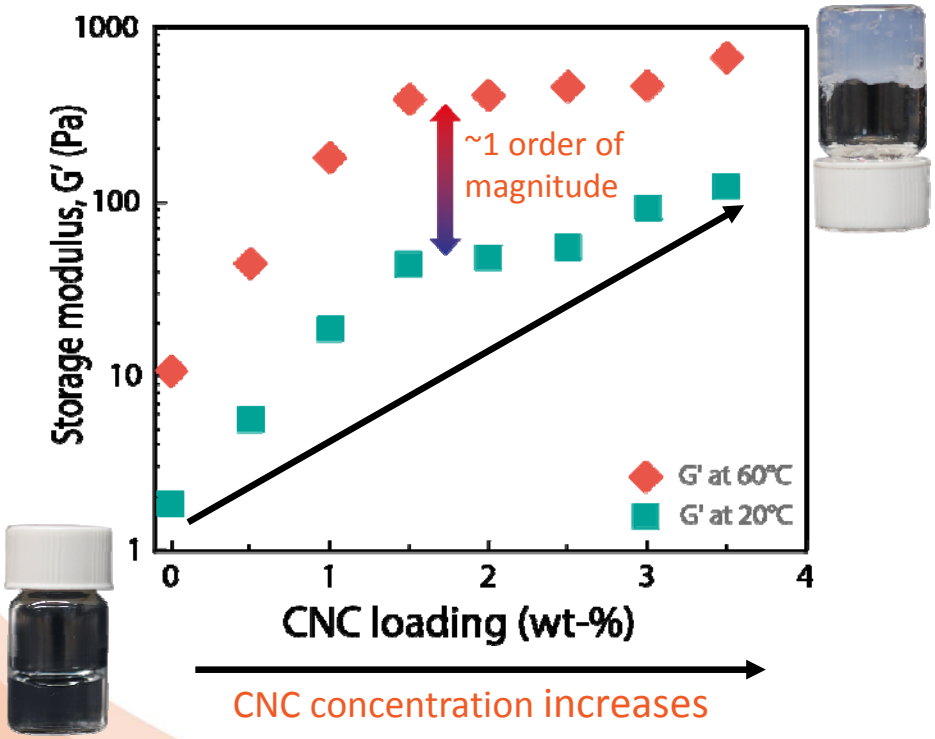
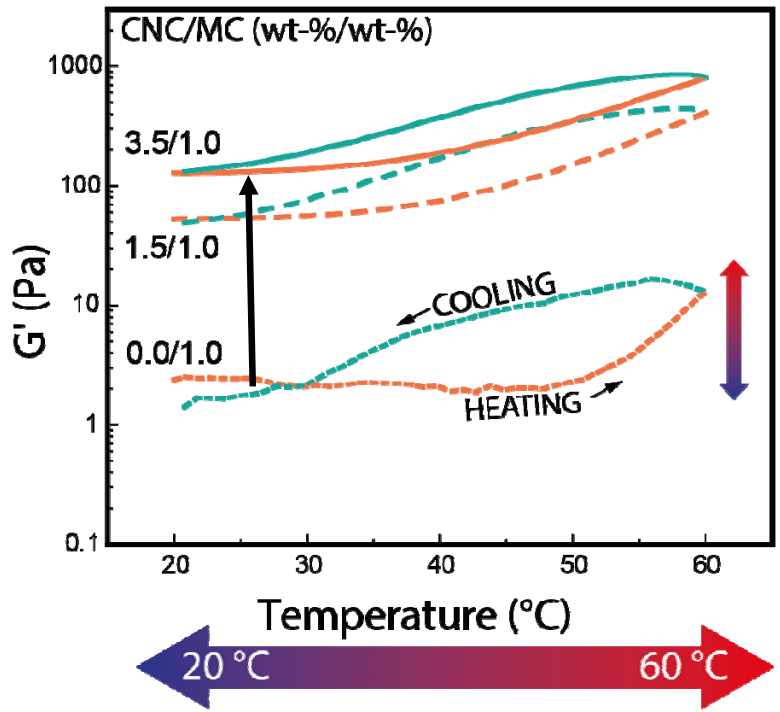
Tactoids photo by Linda Srbova.
Cholesteric phase schematic: Wikimedia Commons © user Kebes

Tunable mechanical properties by composition and temperature

MC concentration fixed at 1.0 wt-%
CNC loading varied 0.0 – 3.5 wt-%





Combined effect from [c] + T → from 1.6 to 850 Pa

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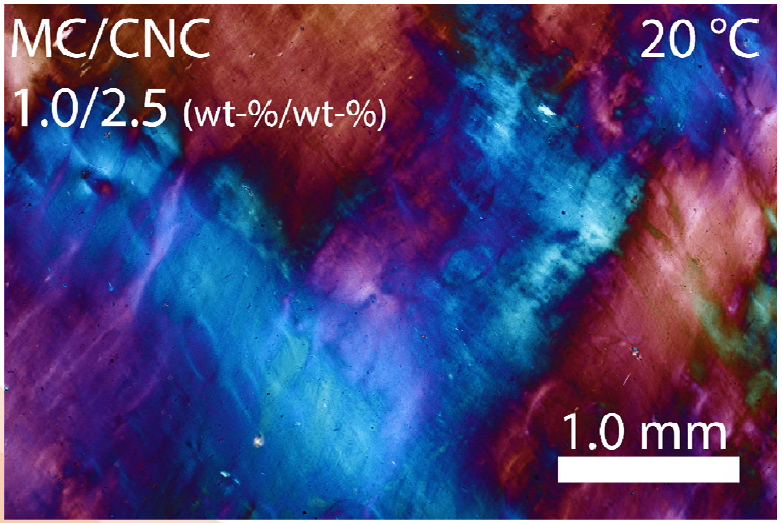
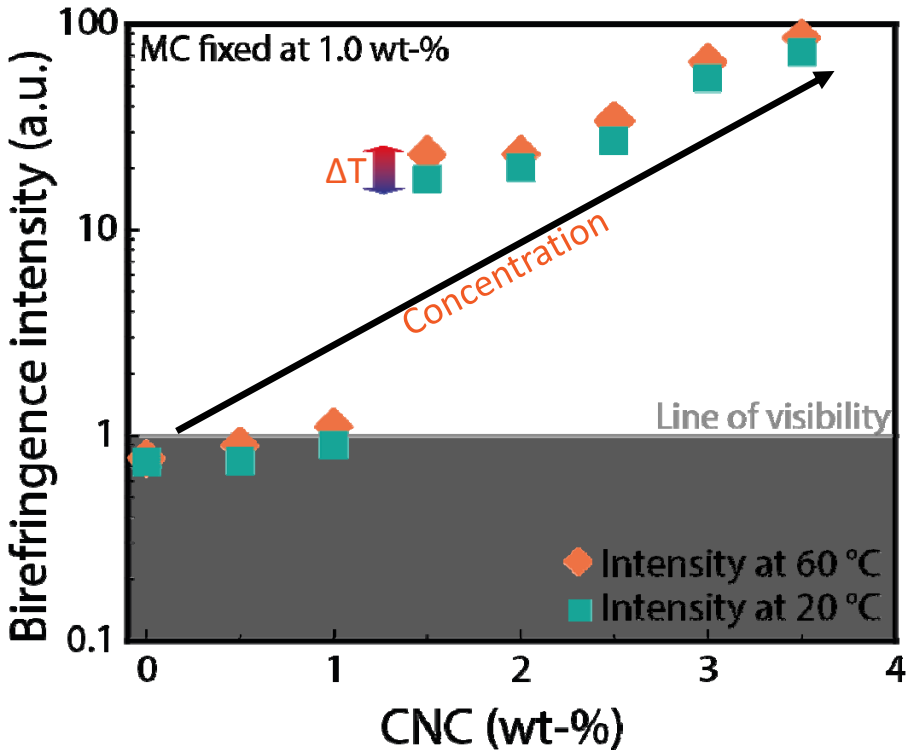
Hynninen et al. Biomacromolecules. 2018;19(7):2795-2804

Birefringence as optical inverse thermoresponse

Birefringence: Orientation dependent differences in refractive index in anisotropic materials





- Birefringence observed at low CNC loadings → anisotropic alignment

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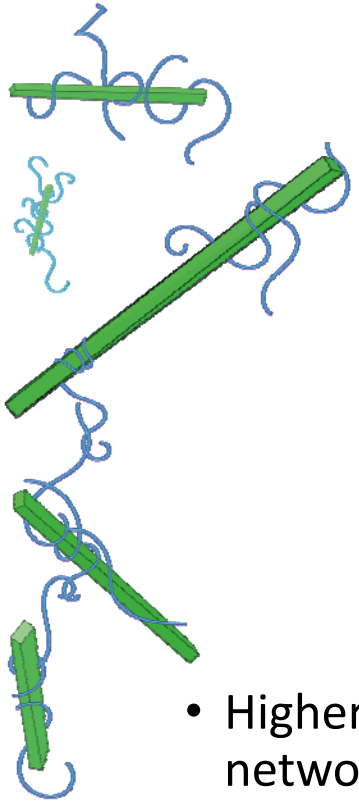
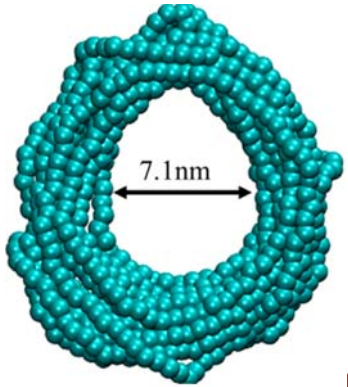
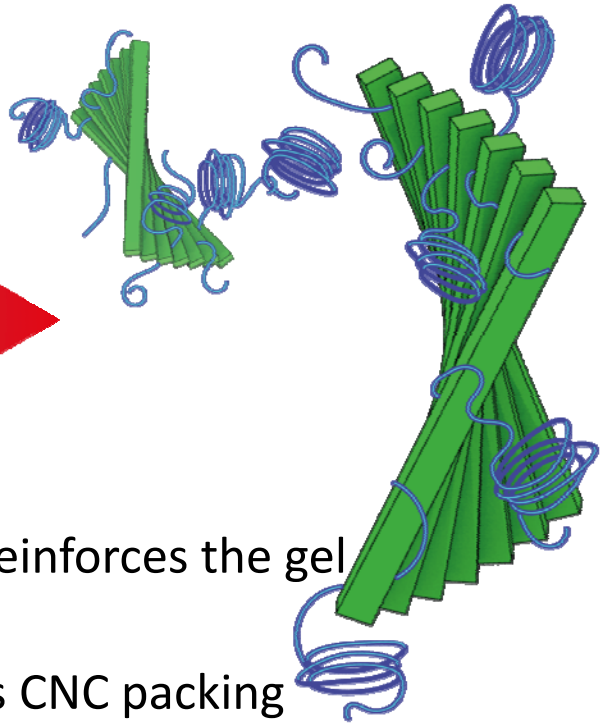
Mechanism

Huang et al. macromolecules. 2016:49:1490-1503.



MC at high T:





- Higher CNC concentration promotes alignment and reinforces the gel network
- MC network constricts CNC movement and enhances CNC packing
- At high temperature MC stiffens and bundles into coils, which further reduces of CNC freedom and promotes mutual templating and organization

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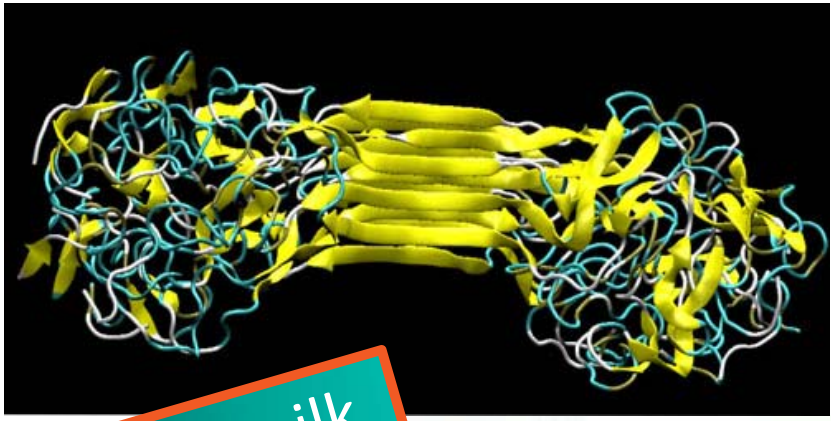
Spinning fibers

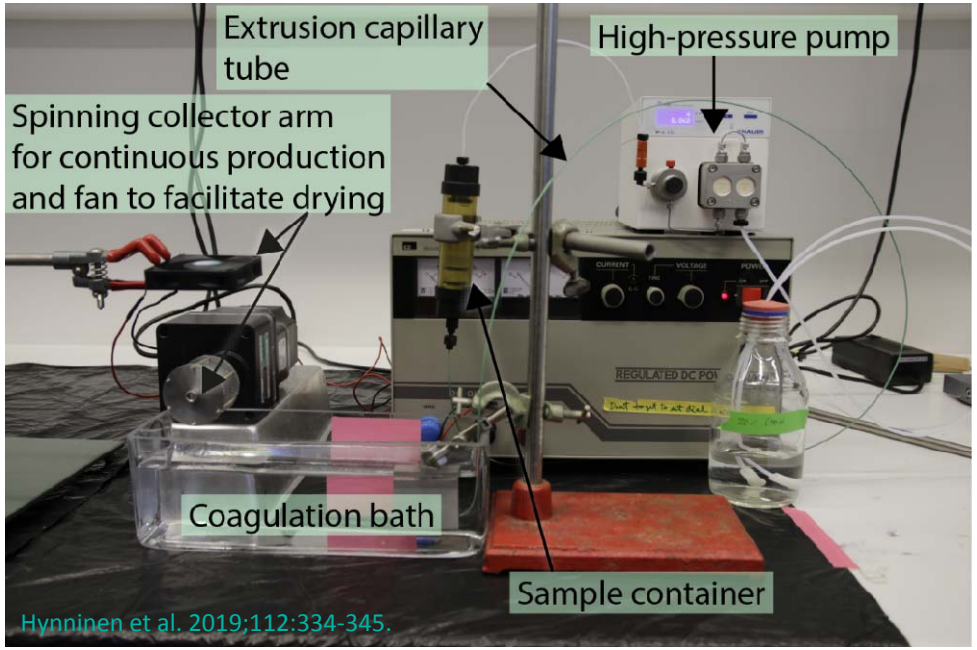
Crystalline-like regions within amorphous polymer matrix



Spider silk, anyone?

Images:
https://www.iltalehti.fi/kotimaa/a/1b1f840a-f8ed-4a78-97f7-8ecba03c93d3
https://aip.scitation.org/doi/10.1063/1.3385388

Spinning the hydrogel into ethanol coagulation bath through thin capillary



MC concentration fixed at 1.0 wt-%
CNC loading varied 0.10 – 3.0 wt-%

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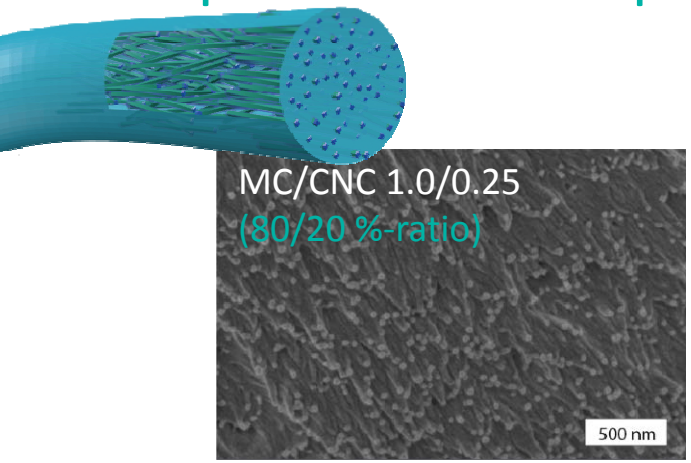
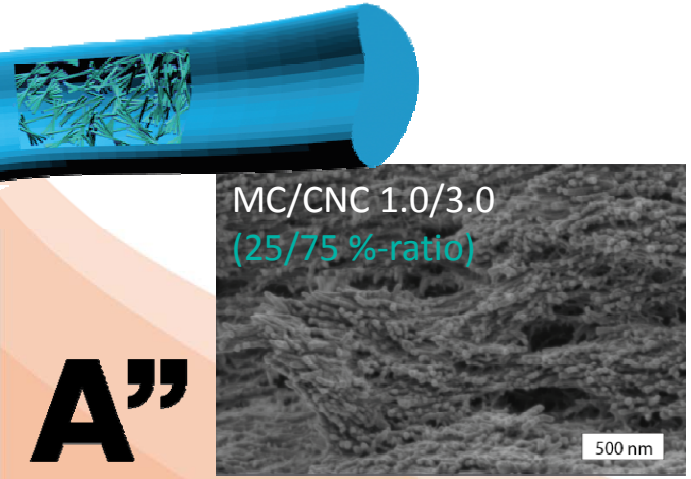
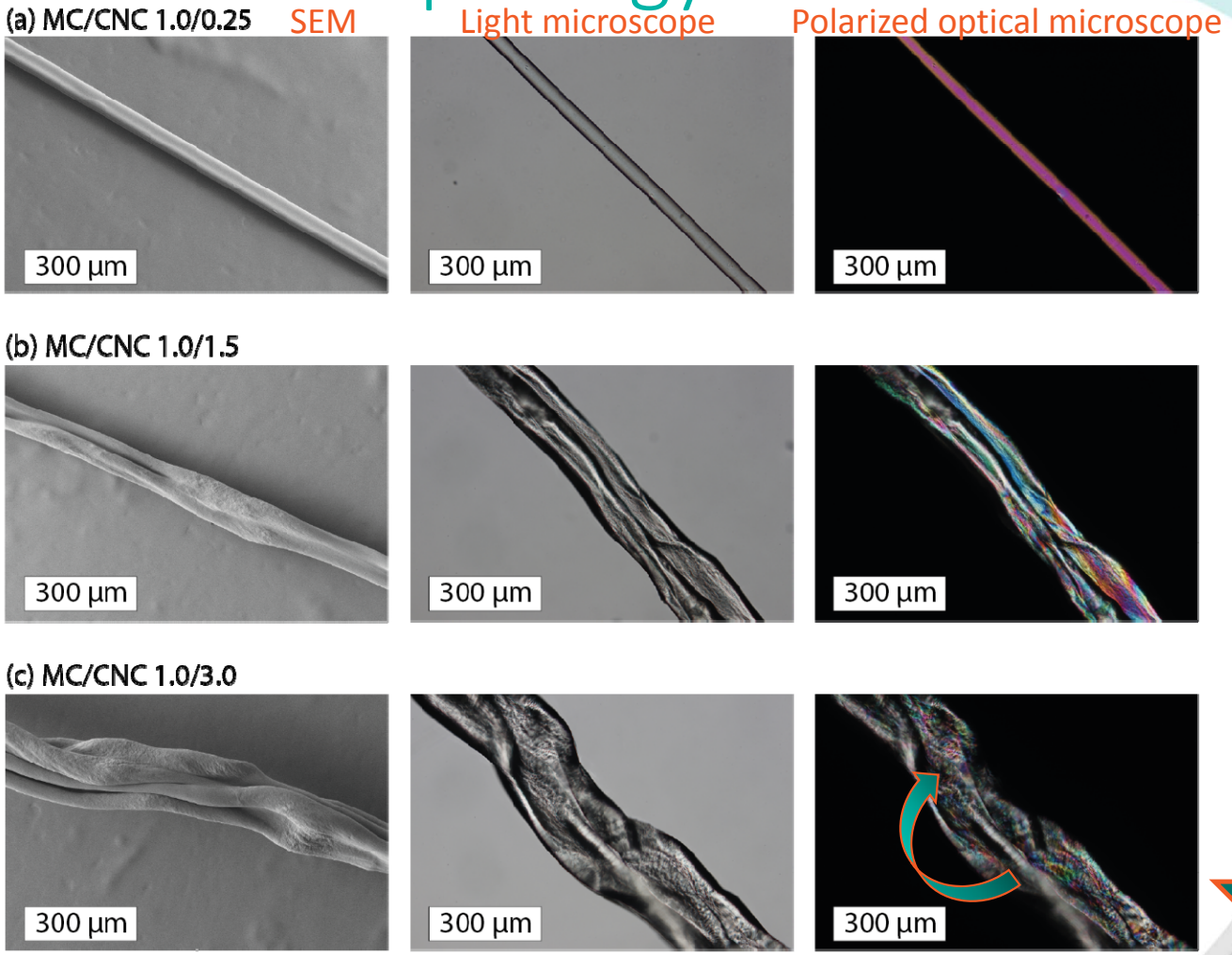
Composition dependent morphology







Increasing CNC content

Hynninen et al. 2019;112:334-345.

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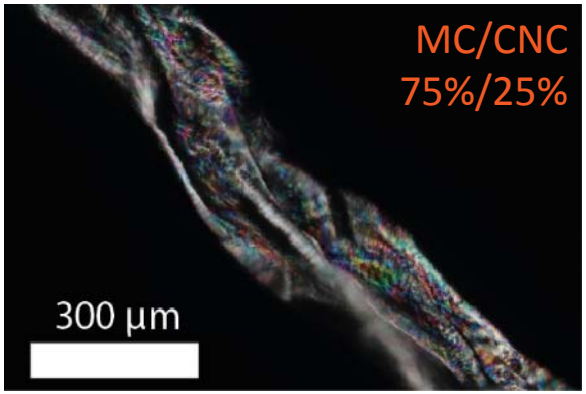
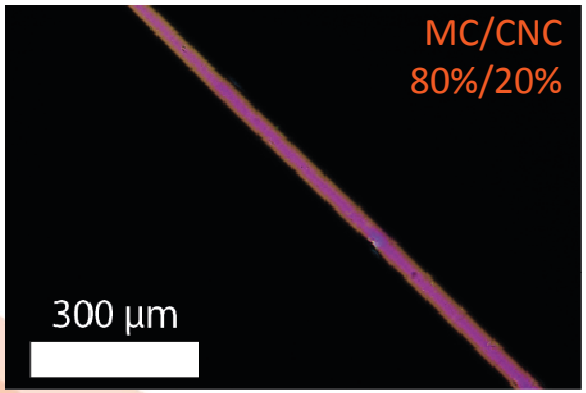
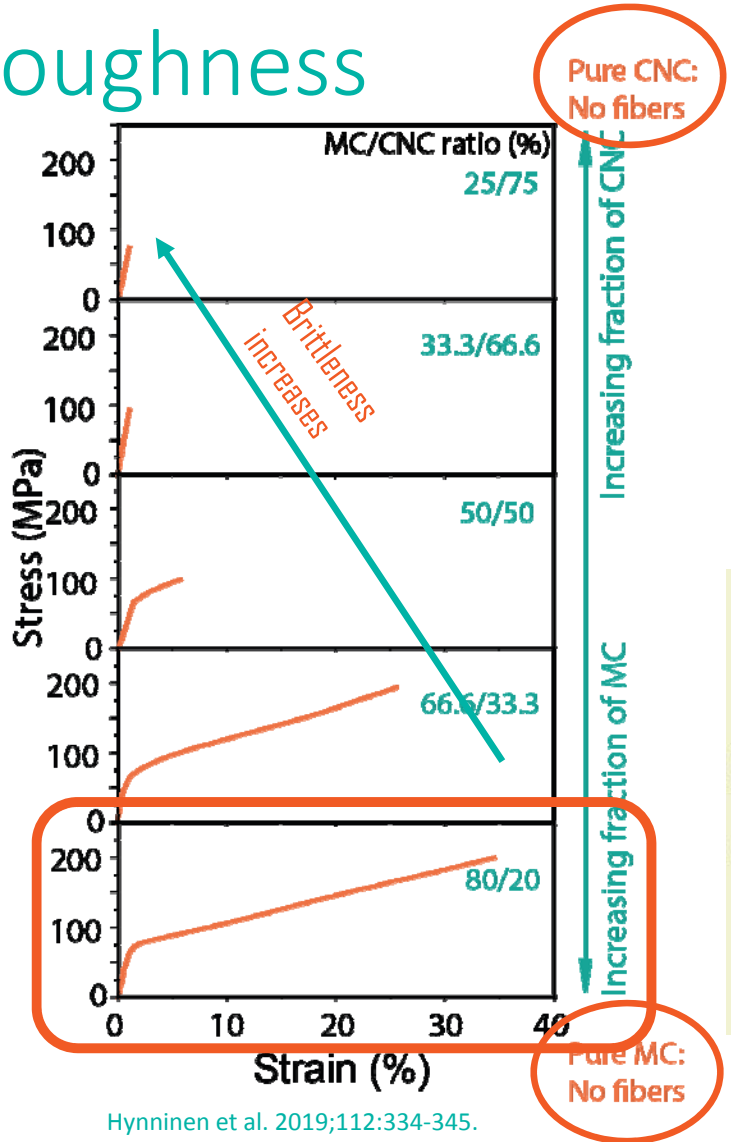
High ductility and toughness







Hynninen et al. 2019;112:334-345.

MC/CNC 80/20

(1.0/0.25)

Young's modulus

- 8.5 GPa

Max stress:

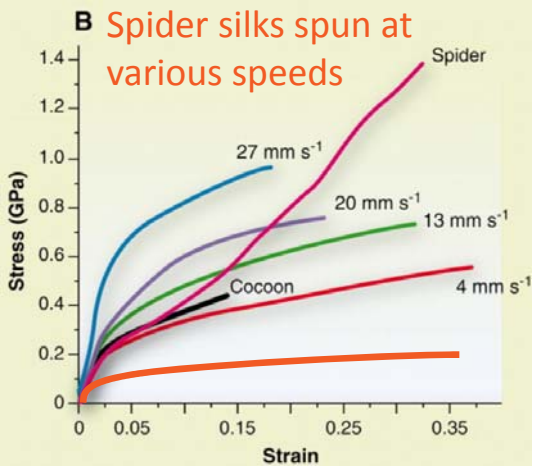
- 190 Mpa

Ultimate strain:

- **36 %**

Modulus of toughness:

- **48 MJ/m³**



Omenetto and Kaplan. Science. 2010;30:329:528-531.

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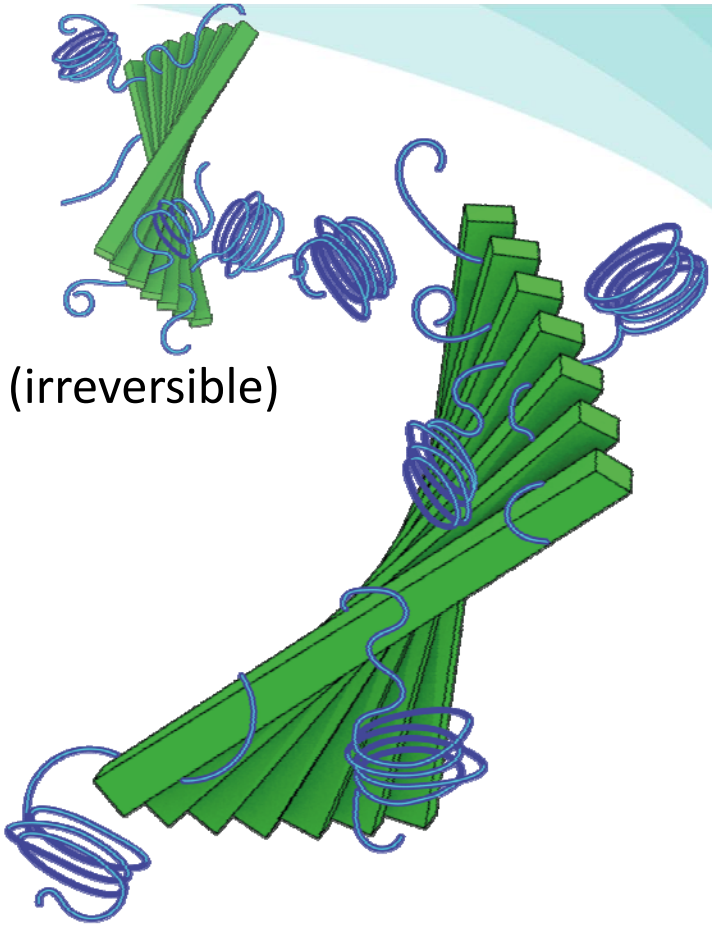
Conclusions and future steps

- MC/CNC hydrogels
  - Mechanical and optical response
  - Tunable by temperature (reversible) and concentration (irreversible)
- MC/CNC fibers
  - Structure and properties depend on composition
  - High ductility and toughness achievable
  - Interaction of MC and CNC required
  - Scalable production possible
- Where to next
  - Optimizing and adding properties to fibers
  - Fiber spinning at high T



Hynninen et al. Inverse thermoreversible mechanical stiffening and birefringence in a methylcellulose/cellulose nanocrystal hydrogel. Biomacromolecules. 2018;19(7):2795-2804.
Hynninen et al. Methylcellulose/cellulose nanocrystal nanocomposite fibers with high ductility. European Polymer Journal. 2019;112:334-345.

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Thank you

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