Rheology and Self-Assembly of Carboxylated Cellulose Nanocrystals

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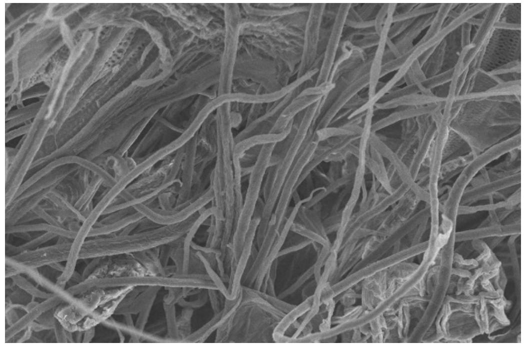
Cellulose Nanocrystals (CNCs)

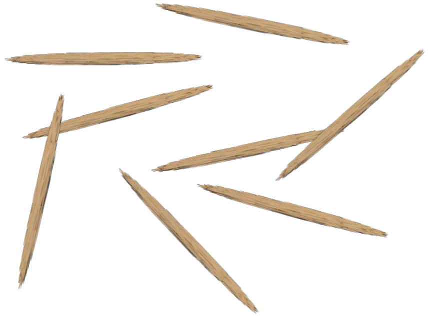
- Cellulose nanocrystals are a renewable, bio-based nanomaterial with a high aspect ratio, high tensile strength, unique optical properties, and low density
- Rod-shaped particles chemically isolated from cellulose

Cellulose Fibre

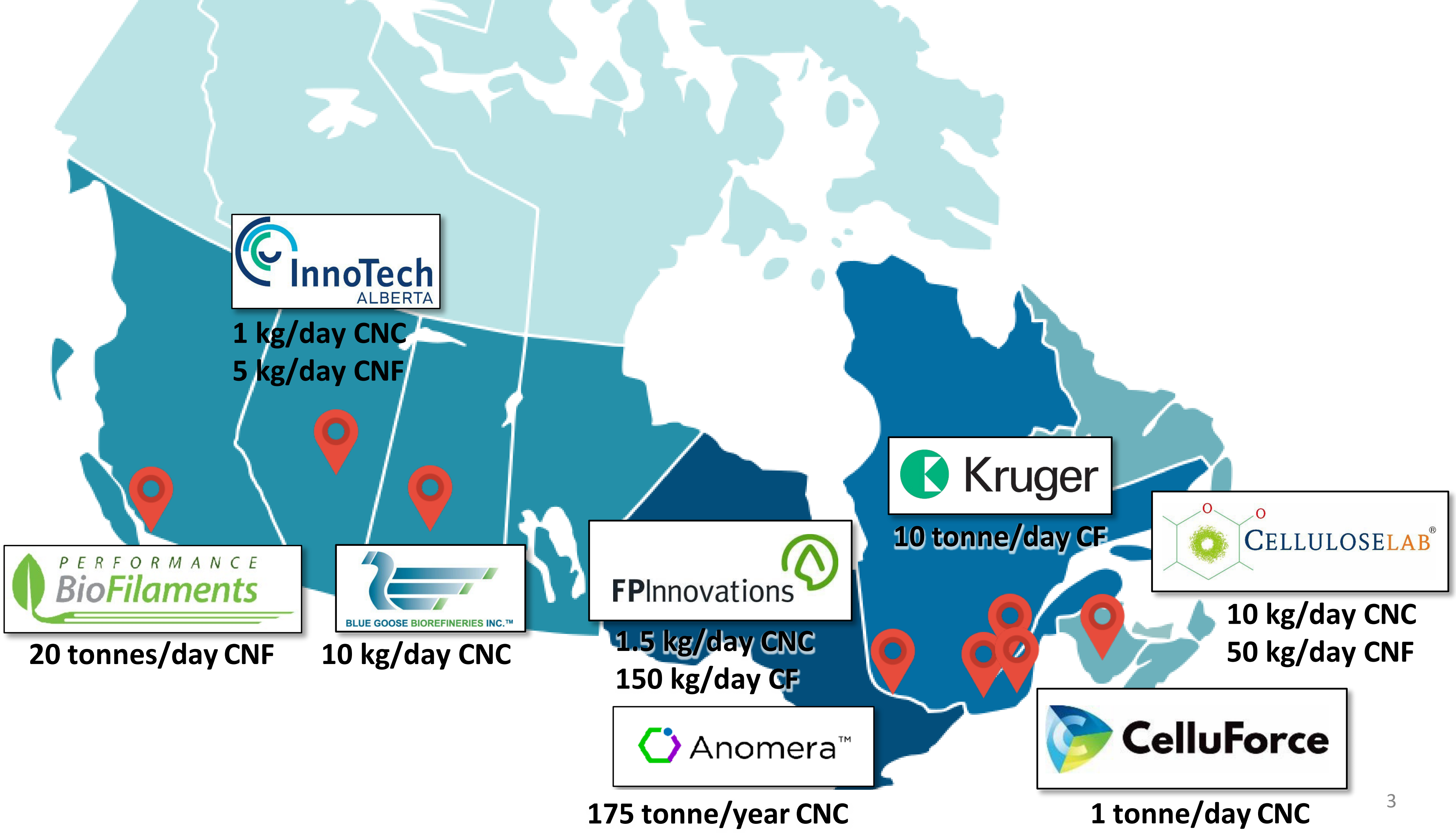


Chemical Degradation

Cellulose Nanocrystals

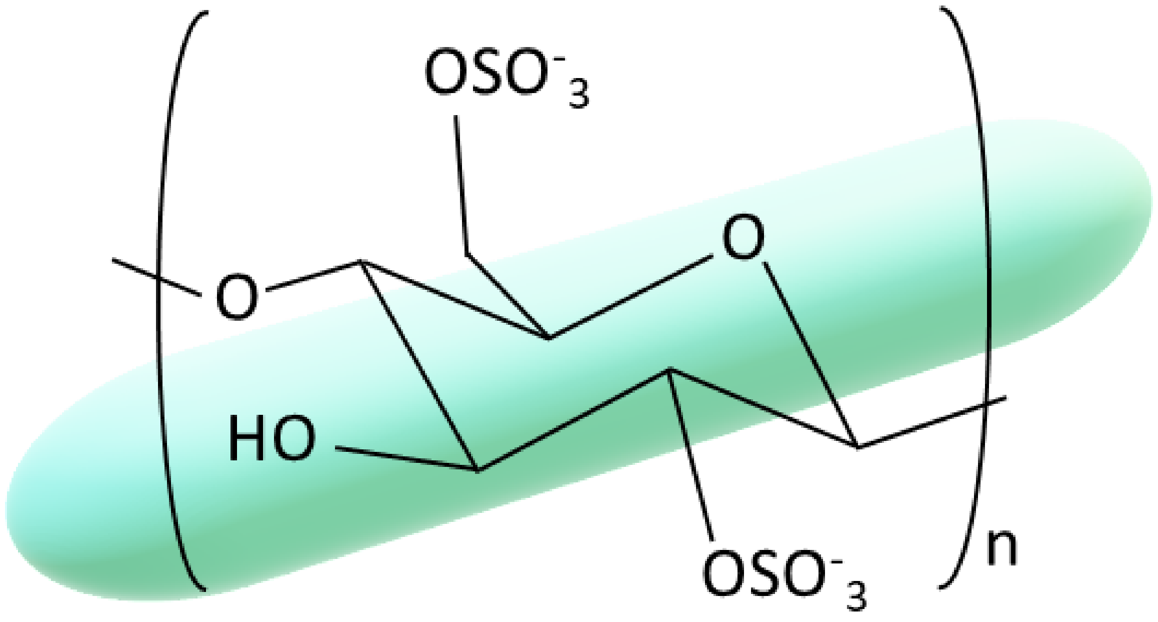


Canadian Nanocellulose Producers



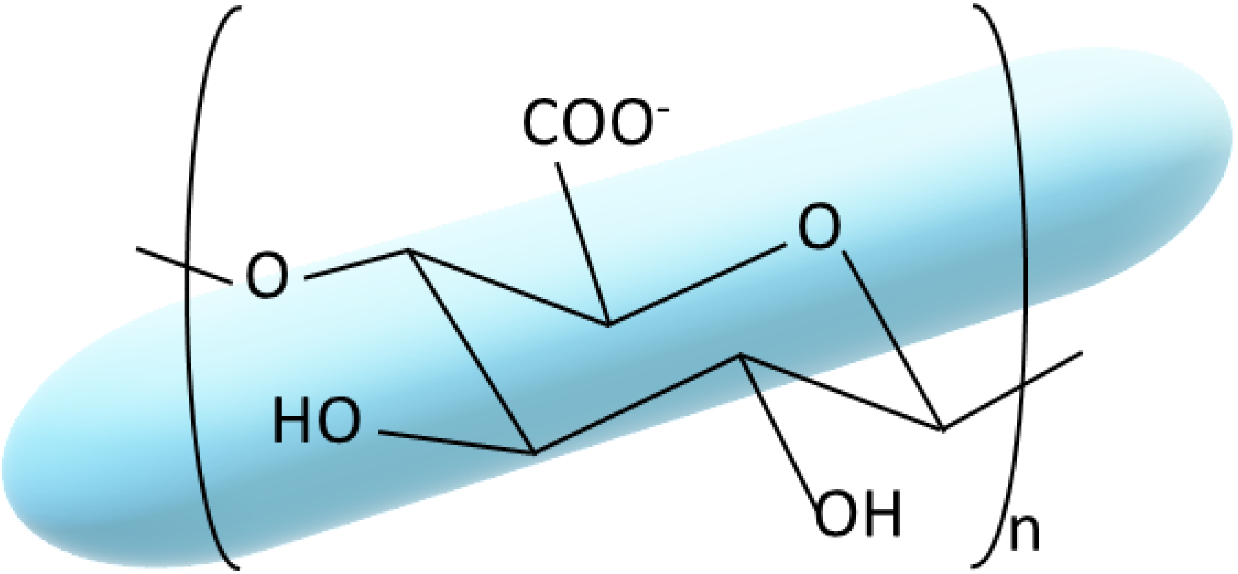
Sulfated CNCs

- CNCs are most often isolated through sulfuric
  acid hydrolysis which results in nanocrystals with charged sulfate half-ester surface groups
- Commercially produced
- Example applications:
  - Reinforcement additives in composite materials
  - Rheological modifiers in food, cosmetics and pharmaceuticals



Carboxylated CNCs

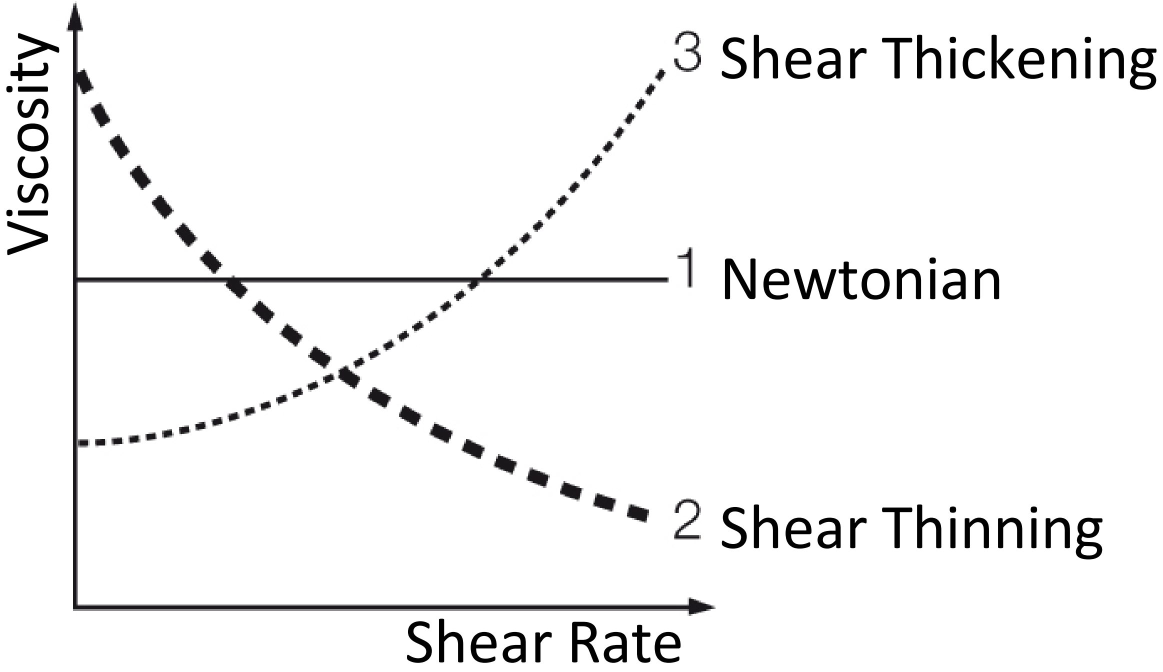
- Commercially produced by Anomera through oxidation using hydrogen peroxide
- Has carboxyl groups on the surface of the CNCs
- No existing work on the rheology of carboxylated CNCs
- Do they have the same useful properties as sulfated CNCs?
- Are they a potential alternative?



Rheological Applications

- Optimization of processing energy
- 3D printing – viscosity not too low not too high
- Lubrication – hydrodynamic lubrication
- Fast characterization of materials
- Useful rheological properties
  - Shear thinning behaviour – Rheological modifiers
  - Viscoelastic properties – lubrication

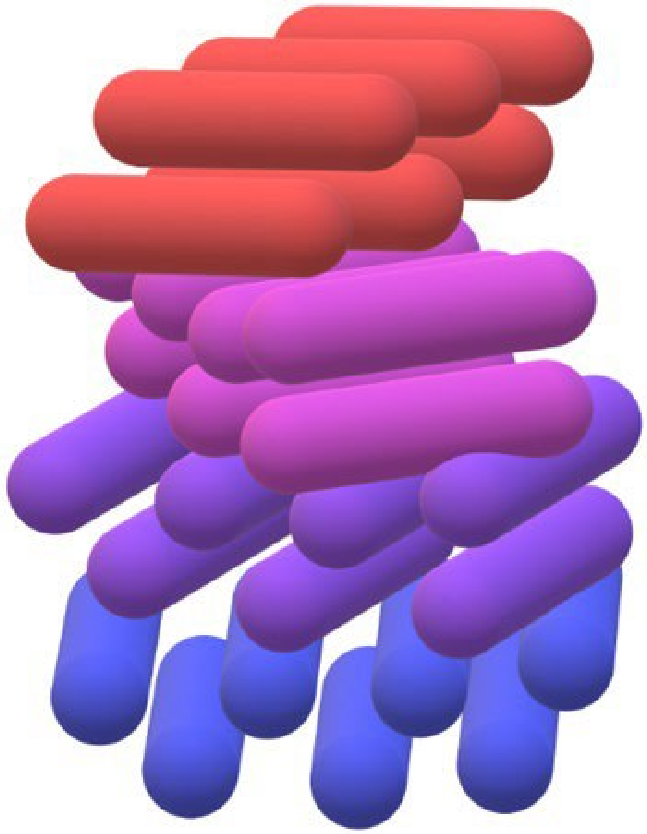
Types of material flow:



https://wiki.anton-paar.com/ca-en/basics-of-rheology/

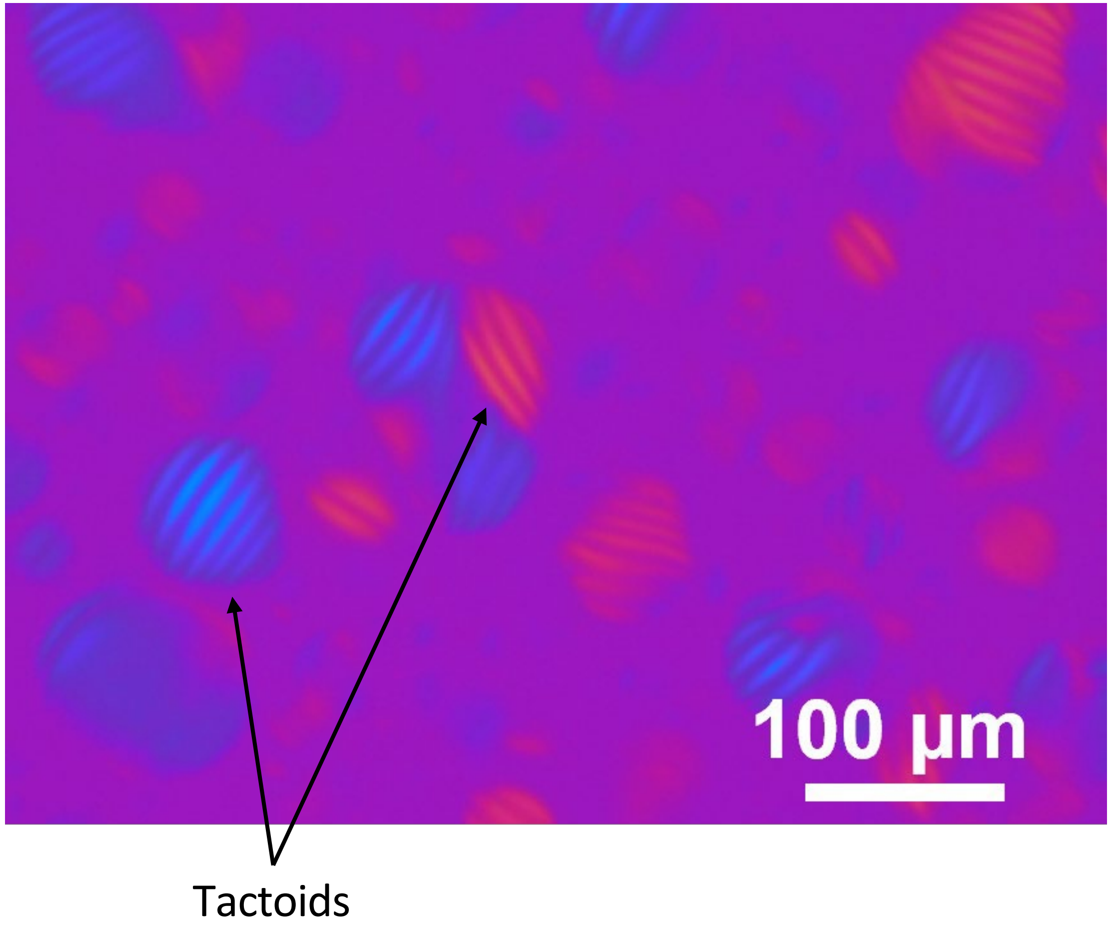
Self Assembly of CNCs

- The concentration above which self-assembly occurs
- CNCs arrange into chiral nematic liquid crystals
- Can be seen under polarized light



Self-Assembly Applications

- The self-assembly of sulfated CNCs are well defined[a]
- Applications of CNC[b]
  - Liquid-crystal phase optical filters
  - Optical films
  - Security paper
- cCNCs also self-assemble

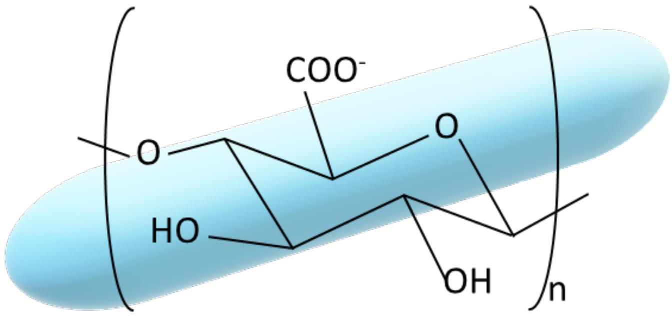


a. Lagerwall, Jan PF, et al. *NPG Asia Materials* 6.1 (2014) e80-e80.
b. https://www.azooptics.com/Article.aspx?ArticleID=1406

CNC Comparison

Property	**Sulfated CNCs**	**Carboxylated CNCs**
Critical concentration through phase separation		
Critical concentration through 3-region-flow		
Change of viscoelastic behaviour		

Characterization of Anomera's Carboxylated CNCs

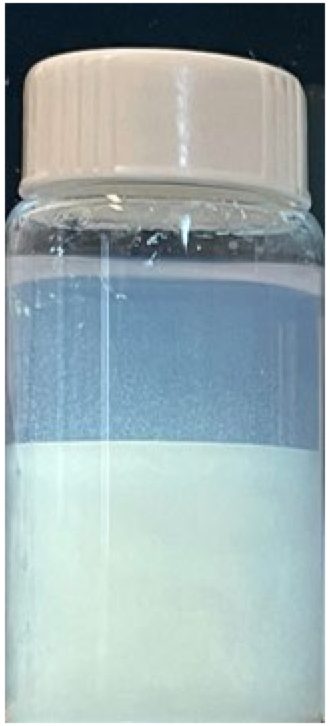


	Low charge cCNCs	High charge cCNCs
Charge content (mmol COOH/ kg)	159 ± 3	217 ± 4
DLS apparent size (nm)	80 ± 1	81 ±1

Methods of Determining Critical Concentration

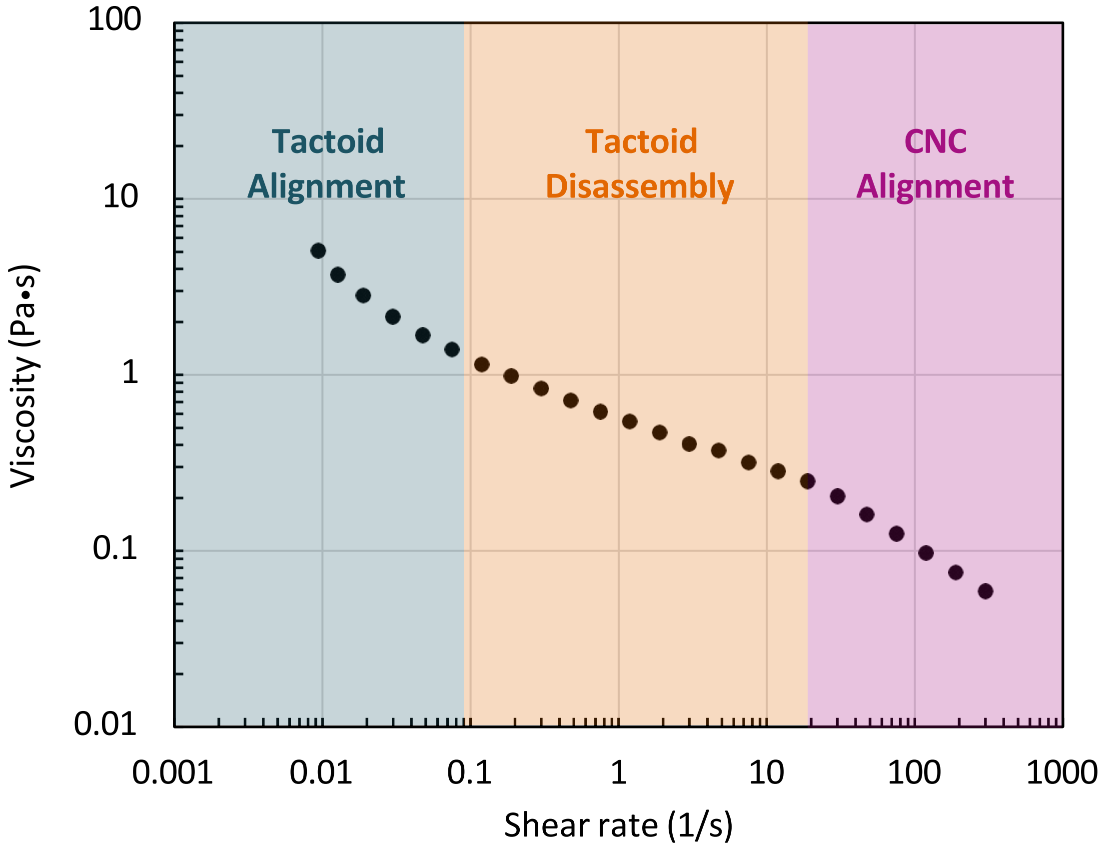
Phase Separation:

- Liquid crystalline region can be seen under polarized light



Rheology:

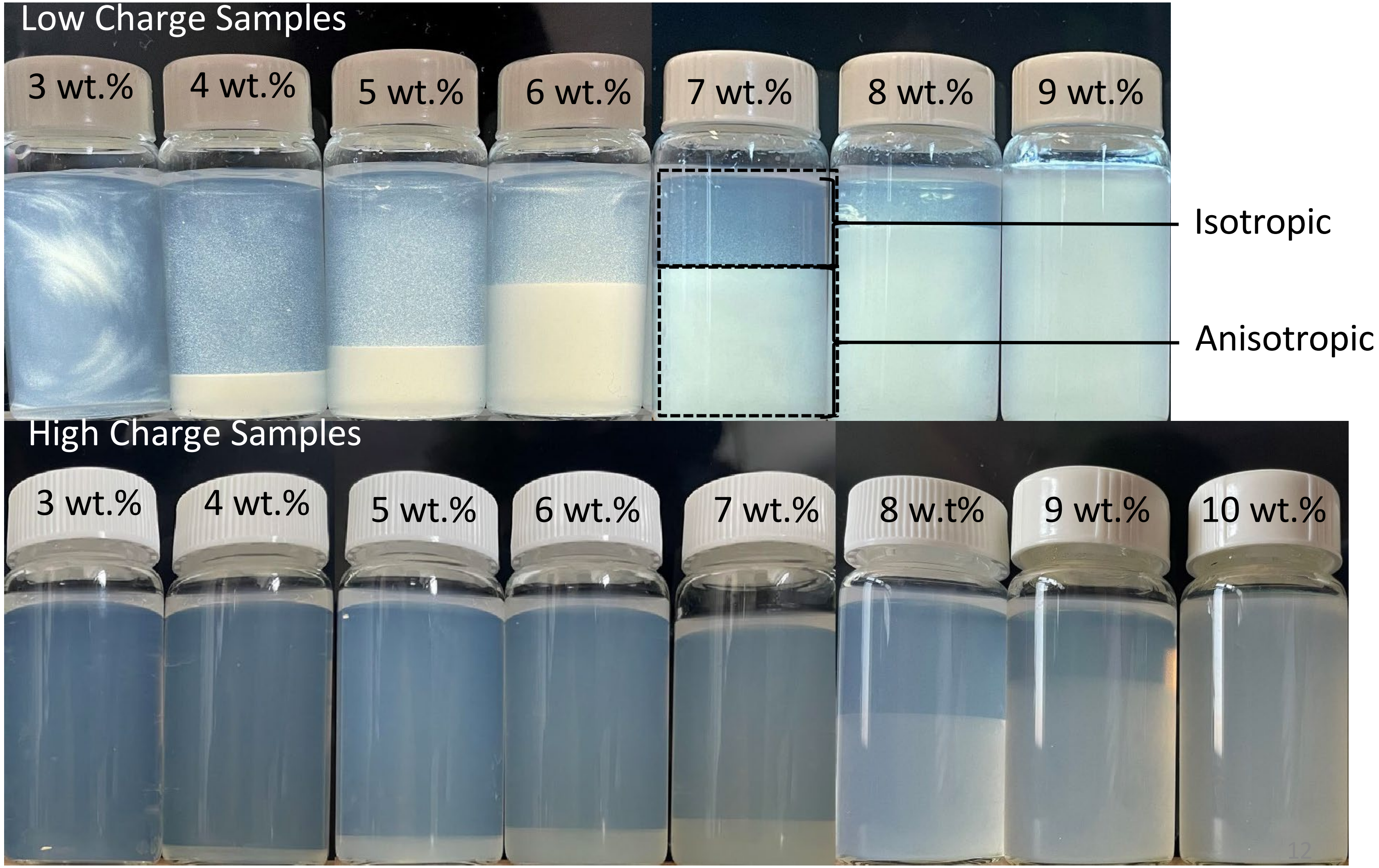
- The presence of liquid crystals results in three-region flow



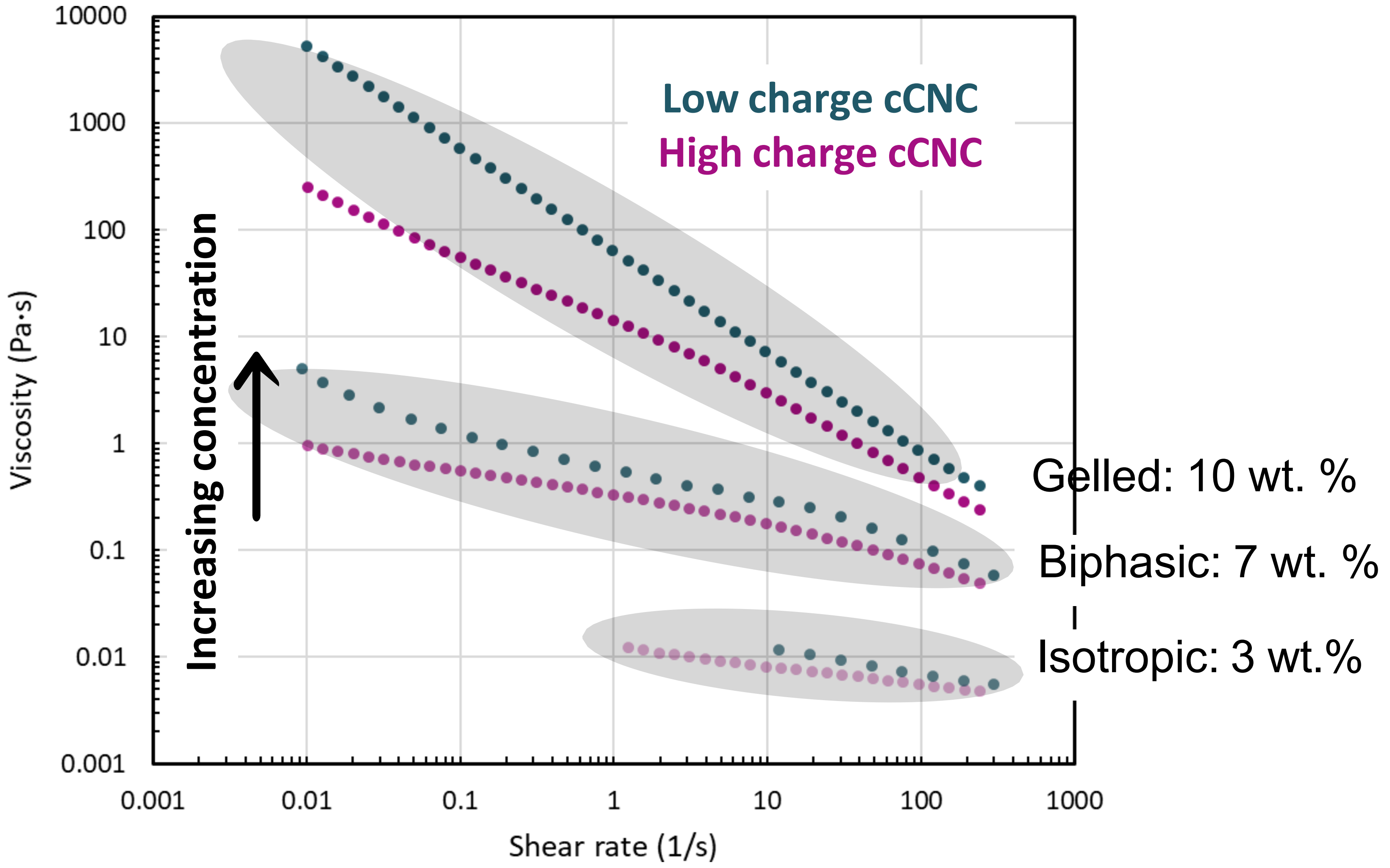
Critical Concentration Determination Through Phase Separation

Critical concentration:
Low charge: 2.4 wt.%

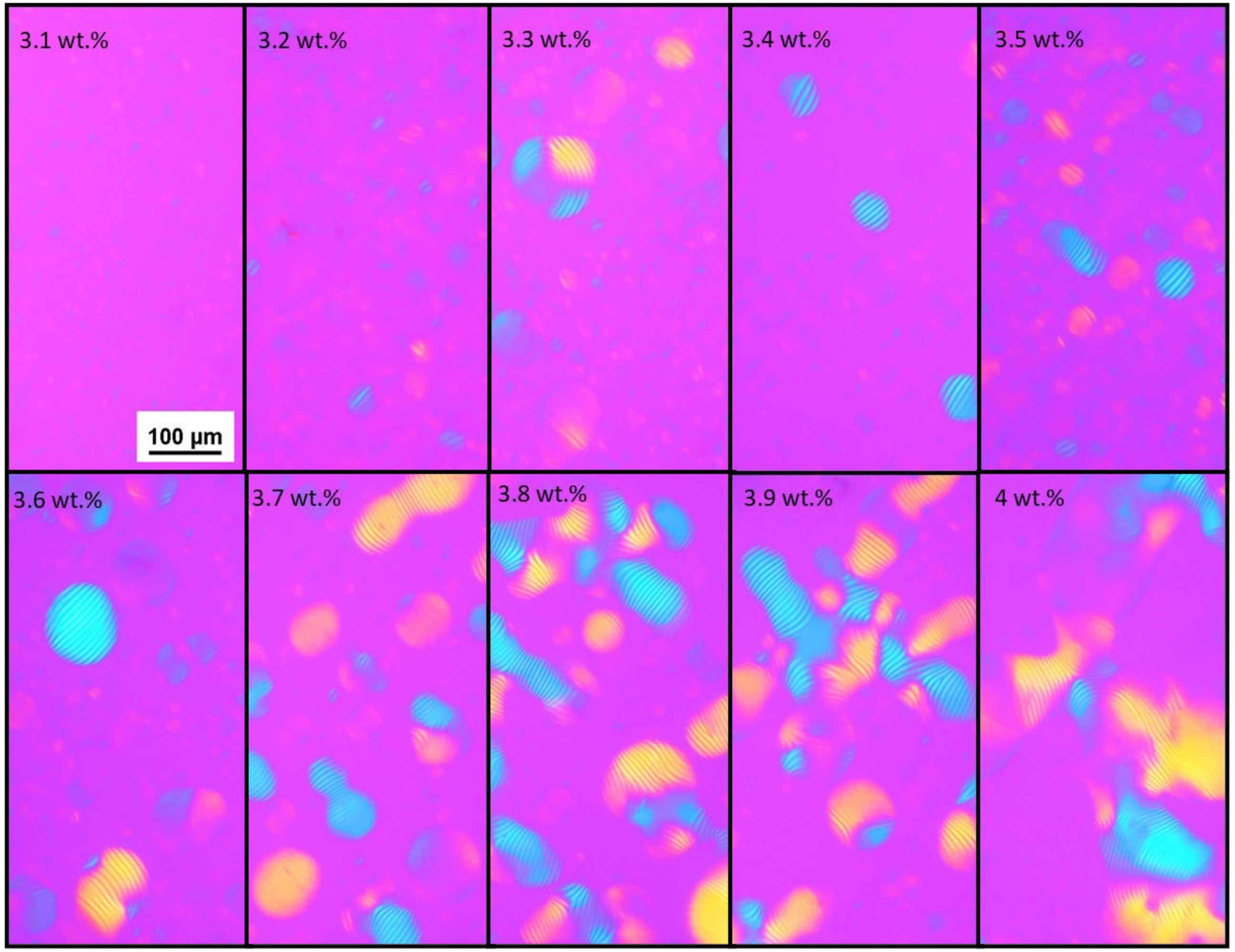
Critical concentration:
High charge: 3.6 wt.%



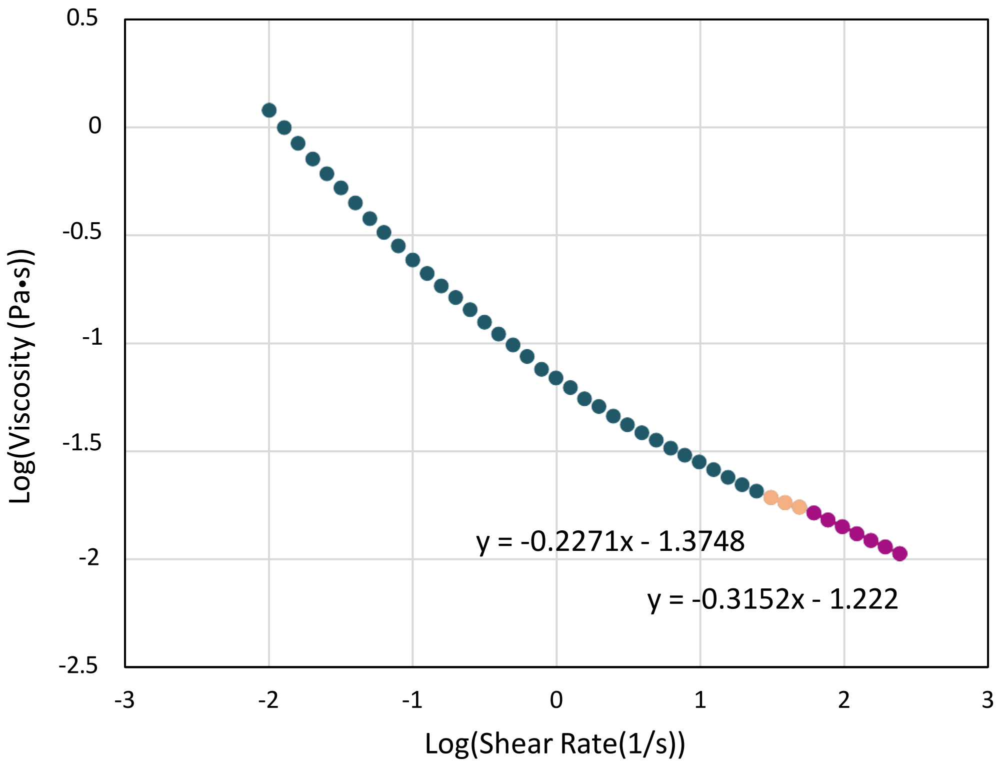
Critical Concentration Through Rheology



Critical Concentration Through Rheology – Tactoid Progression



Critical Concentration Through Rheology



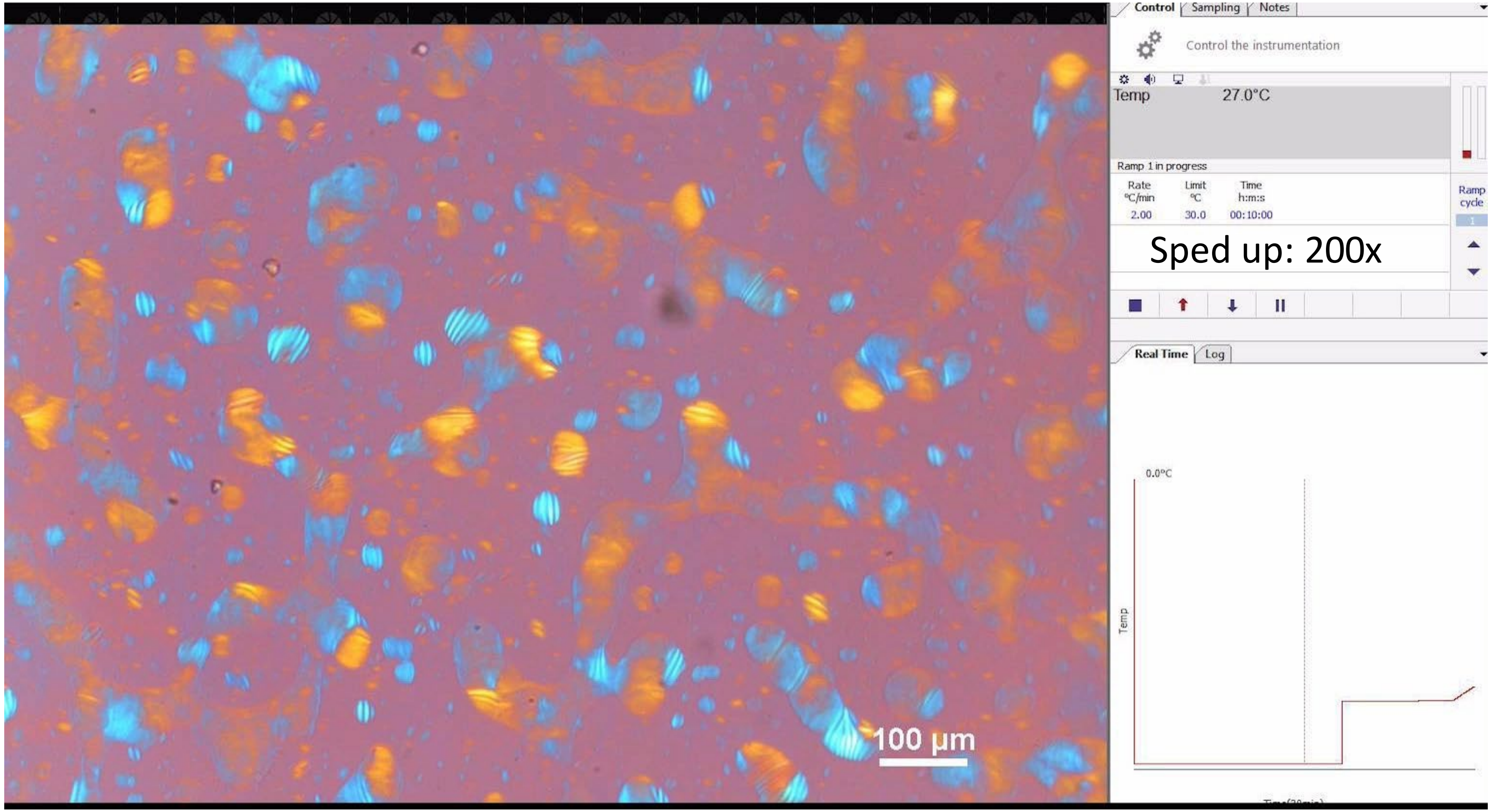
$$\sigma = K\gamma^{n}$$

σ – Shear Stress

γ – shear Rate

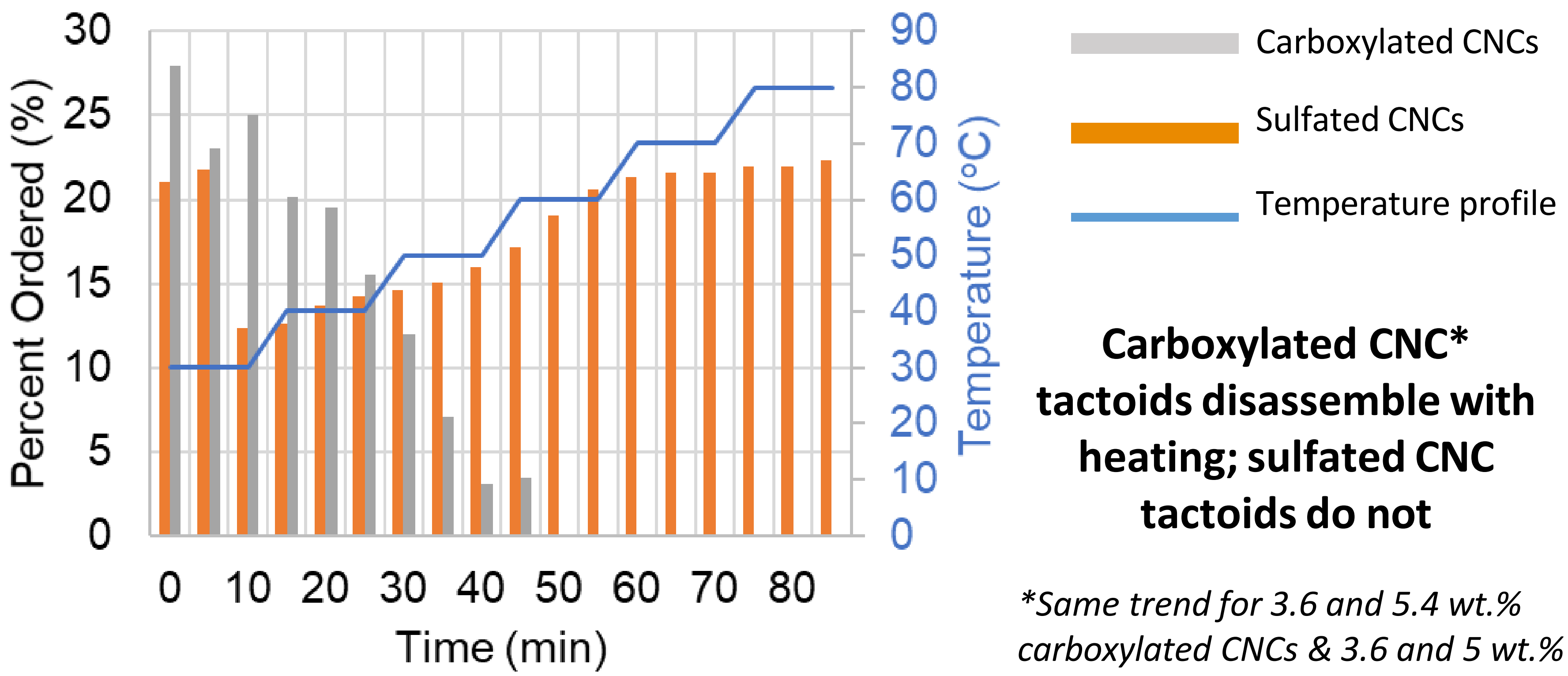
3.1 wt.%		3.2 wt.%		3.3 wt.%		3.4 wt.%		3.5 wt.%	
n_1	n_2	n_1	n_2	n_1	n_2	n_1	n_2	n_1	n_2
0.714	0.714	0.793	0.744	0.776	0.741	0.729	0.739	0.757	0.751
Δn=0		0.049		0.035		0.01		0.06	
3.6 wt.%		3.7 wt.%		3.8 wt.%		3.9 wt%		4.0 wt.%	
n_1	n_2	n_1	n_2	n_1	n_2	n_1	n_2	n_1	n_2
0.766	0.739	0.764	0.740	0.756	0.736	0.737	0.690	0.773	0.685
Δn=0.027		0.024		0.02		0.047		0.088	

Tactoid Disassembly With Heating



- Some tactoids disappear quickly
- Some merge
- Others go out of focus
- By 50 °C there are no tactoids left

Tactoid Disassembly with Heating



Carboxylated CNC* tactoids disassemble with heating; sulfated CNC tactoids do not

**Same trend for 3.6 and 5.4 wt.% carboxylated CNCs & 3.6 and 5 wt.% sulfated CNCs*

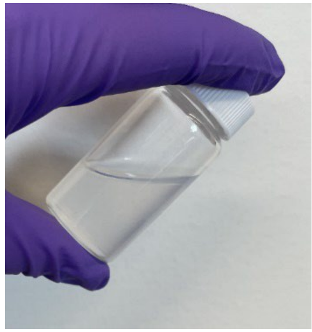
Critical Concentration Summary – Sulfated and Carboxylated CNCs

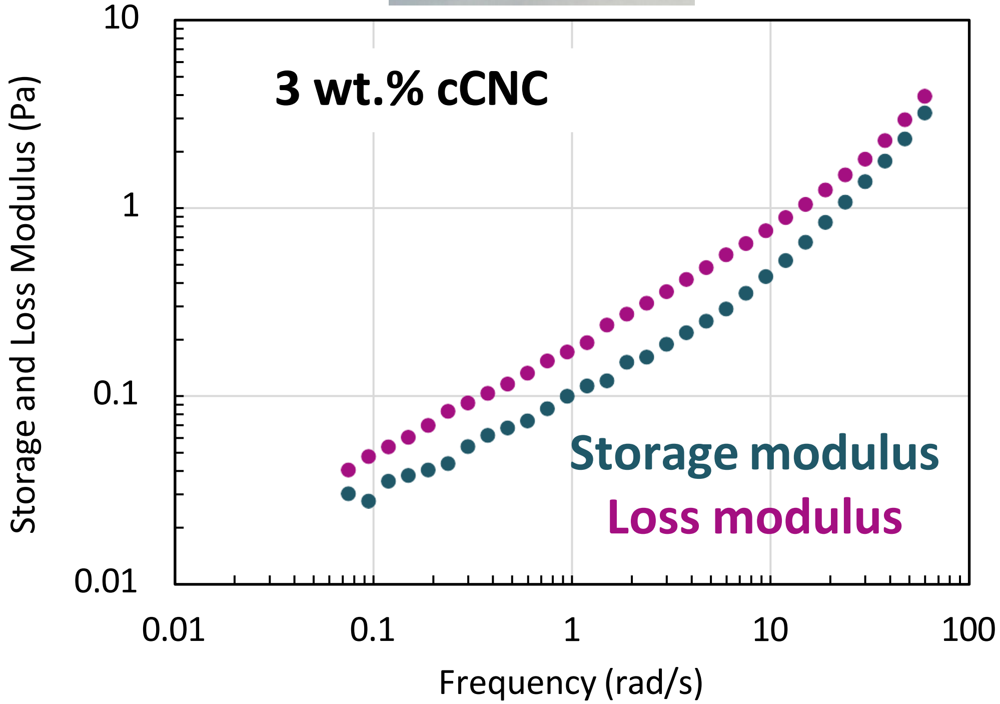
Property	Sulfated CNC	Carboxylated CNC
Critical concentration through phase separation	3 wt.%[a] 0.6 wt.%[b] 4.3 wt.%[c]	2.4 wt.% (low charge) 3.6 wt.% (high charge)
Critical concentration through 3-region-flow	0.6 wt.%[b] 4.8 wt.%[c] 0.4 wt.%[d] 1.5 wt.%[d] 3 wt.%[e] 4 wt.%[e]	4 wt.% (low charge) 5 wt.% (high charge)
Change of viscoelastic behaviour	**Next**	

a. Honorato-Rios, Camila, et al. Frontiers in Materials (2016): 21.
b. Qiao, Congde, et al. Food Hydrocolloids 55 (2016): 19-25.
c. Liao, Jianshan, et al. Cellulose 27.7 (2020): 3741-3757.
d. Wu, Qiang, et al. Journal of Applied Polymer Science 131.15 (2014).
e. Shafeiei-Sabet, Sadaf, et al. Rheologica Acta 52 (2013): 741-751.

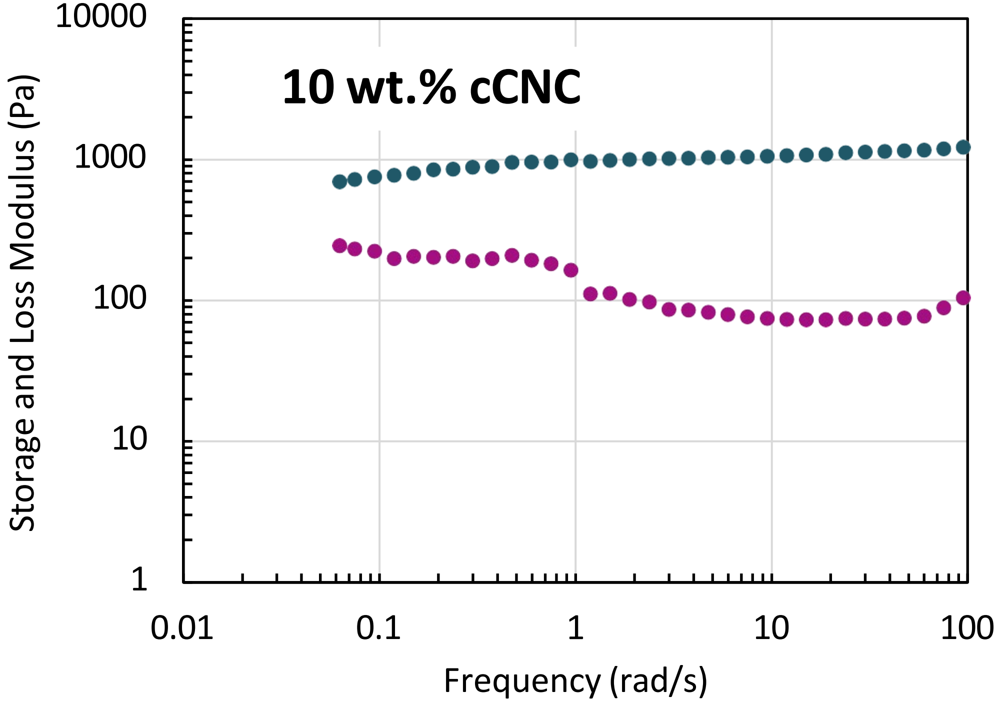
Storage and Loss Modulus of cCNCs

Storage modulus < Loss modulus





Storage modulus > Loss modulus



Summary of Viscoelastic Properties of Sulfated and Carboxylated CNCs

Property	Sulfated CNC	Carboxylated CNC
Critical concentration through phase separation	0.6 - 4.3 wt.%[a,b,c]	2.4 wt.% (low charge) 3.6 wt.% (high charge)
Critical concentration through 3-region-flow	0.6 - 4 wt.%[b-e]	4 wt.% (low charge) 5 wt.% (high charge)
Change of viscoelastic behaviour	3 wt.%[b]	7 wt.% (low charge) 8 wt.% (high charge)

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Summary

Property	Sulfated CNC	Carboxylated CNC
Critical concentration through phase separation	0.6 - 4.3 wt.%[a,b,c]	2.4 wt.% (low charge) 3.6 wt.% (high charge)
Critical concentration through 3-region-flow	0.6 - 4 wt.%[b-e]	4 wt.% (low charge) 5 wt.% (high charge)
Change of viscoelastic behaviour	3 wt.%[b]	7 wt.% (low charge) 8 wt.% (high charge)

- Carboxylated CNCs have a viscosity in the same range as sulfated
- Shear thinning behaviour is present
- The critical concentrations are in the same range as sulfated CNCs
- Viscoelastic properties are not in the same range

Carboxylated CNCs shows two critical concentrations: phase separation and impact on flow

a. Honorato-Rios, Camila, et al. Frontiers in Materials (2016): 21.
b. Qiao, Congde, et al. Food Hydrocolloids 55 (2016): 19-25.
c. Liao, Jianshan, et al. Cellulose 27.7 (2020): 3741-3757.
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e. Shafeiei-Sabet, Sadaf, et al. Rheologica Acta 52 (2013): 741-751.

Thank You

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