Redispersibility of TEMPO Oxidized Cellulose Fibrils via Spray-Freeze Drying

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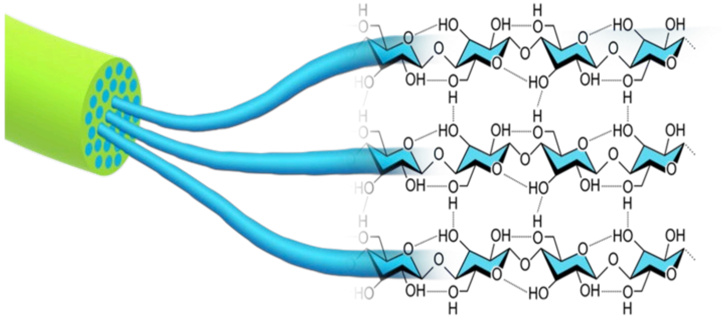
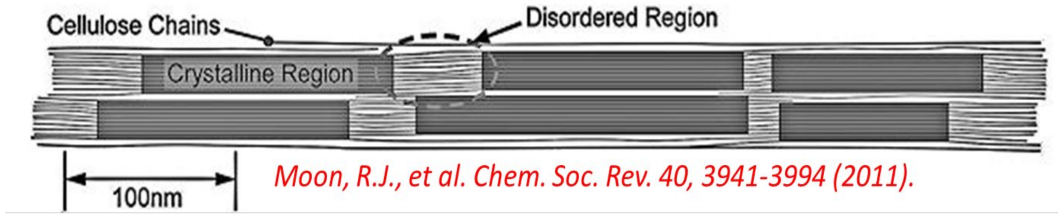
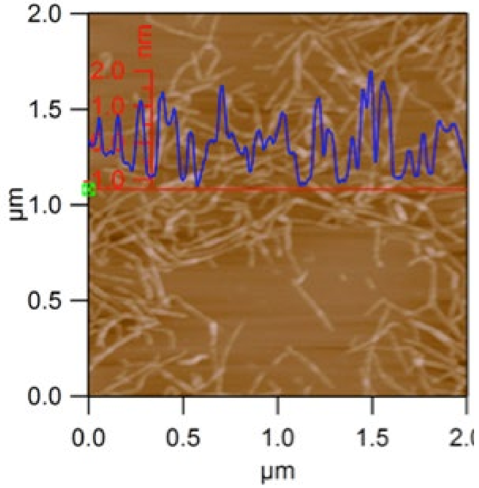
NANOCELLULOSE



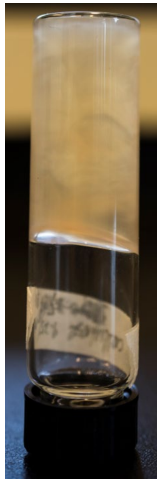
- Highly crystalline cellulose I
- Excellent mechanical properties
- High specific surface
- Abundant surface functional groups

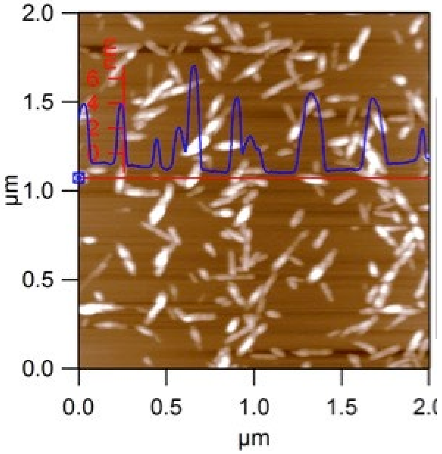


Moon, R.J., et al. Chem. Soc. Rev. 40, 3941-3994 (2011).



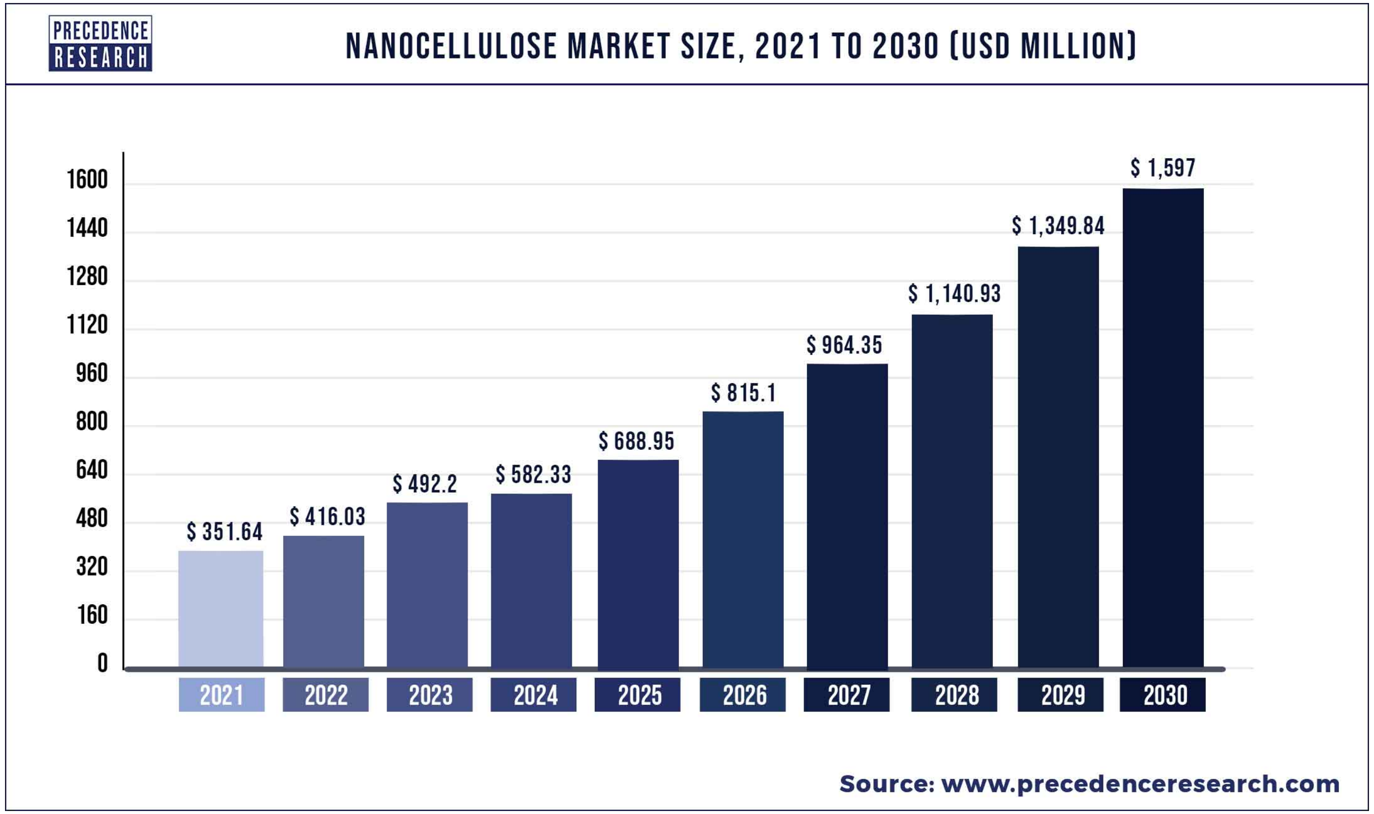
Cellulose nanofibrils





Cellulose nanocrystals

MARKET



NIPPON PAPER GROUP

RISE (INNVENTIA, SP, SWEDISH ICT)

CelluForce

sappi

Kruger

FiberLean Technologies

Innovative by Nature.

Oil & Gas

Personal care products

Nanocomposites

Paints & Coatings

REDISPERSIBILITY OF CNFs

CHALLENGES

Redispersibility

Low solid content

Strategies

Steric stabilization

- Grafting
- Redispersing agents

Surface charge density increment

Drying methods

- Freeze drying
- Spray drying
- Spray freeze drying

MATERIALS AND METHODS

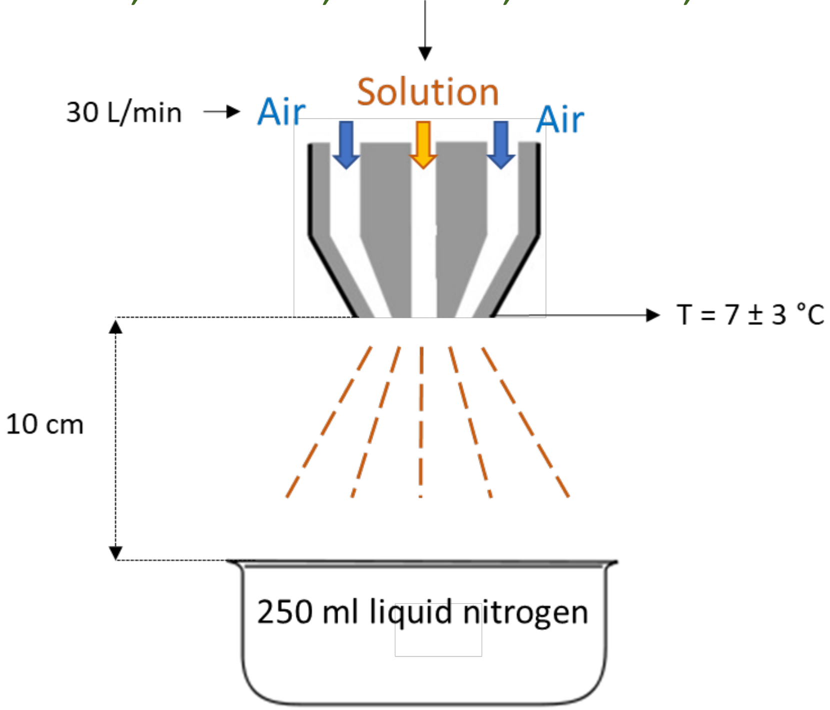
NBSK PULP

TEMPO Oxidation
NaClO 5 mmole/g
pH 10

Dialysis

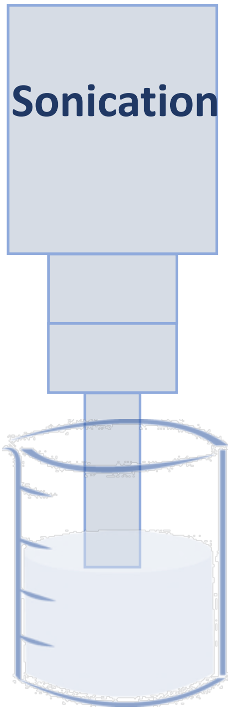
Blending

Initial Concentration
0.5 wt.%, 0.6 wt.%,0.7 wt.%,0.8 wt.%, 0.9 wt.%



Spray-Freeze Drying

Freeze Drying



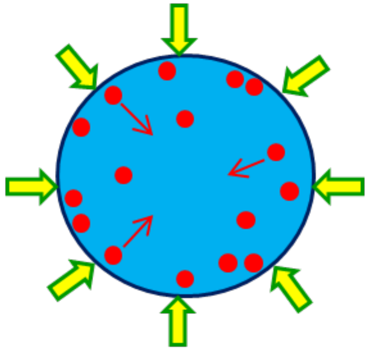
Redispersion
60A, 20 s

SPRAY FREEZE DRYING

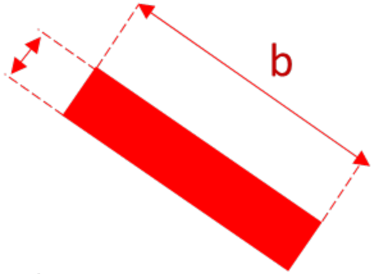
For suspension:

1. $Pe = \frac{R^2}{T_{dry} D}$
2. $D = \frac{k_B T}{6\pi\eta r}$

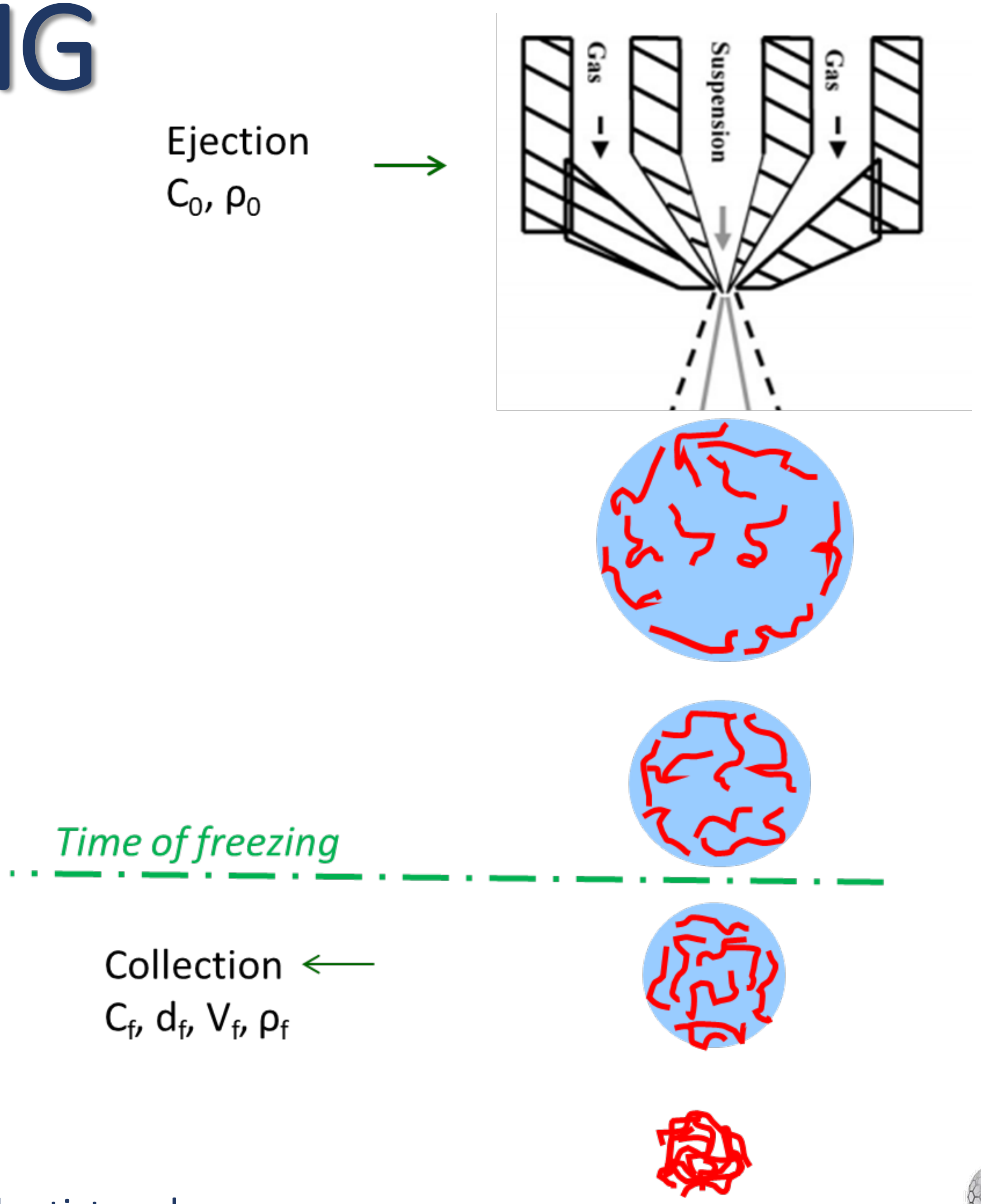
Radius of the solid particles



Cylinder coordinates could be applicable for CNF

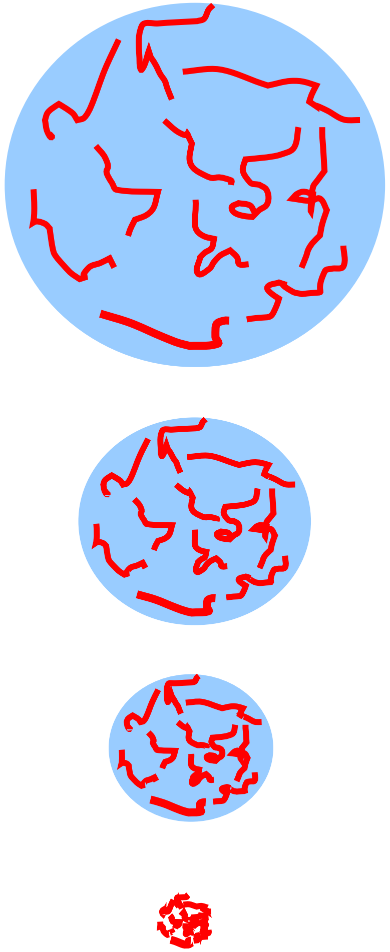


$$D = \frac{kT}{3\pi\eta L}\left(\ln L - \ln d + c_0 + \frac{c_1 d}{L} + \frac{c_2 d^2}{L^2}\right)$$



DEPENDING ON THE PARTICLE SHAPE

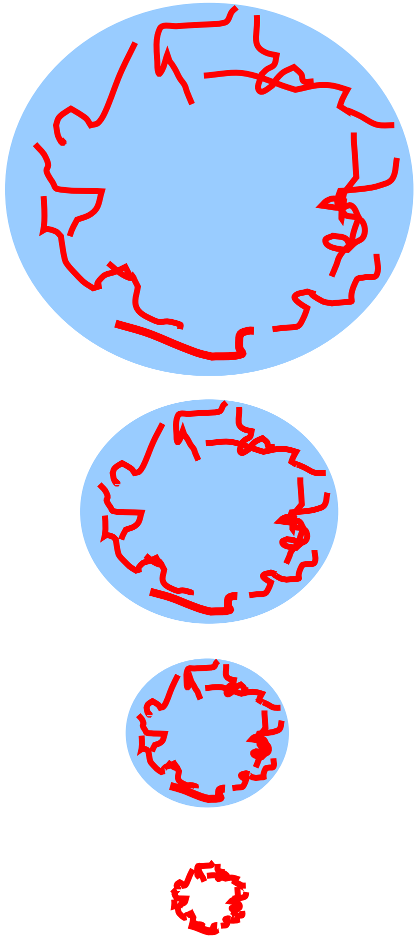
Low
Pe << 1



Diffusive transport

Particle concentration uniform in the droplet

High
Pe >> 1



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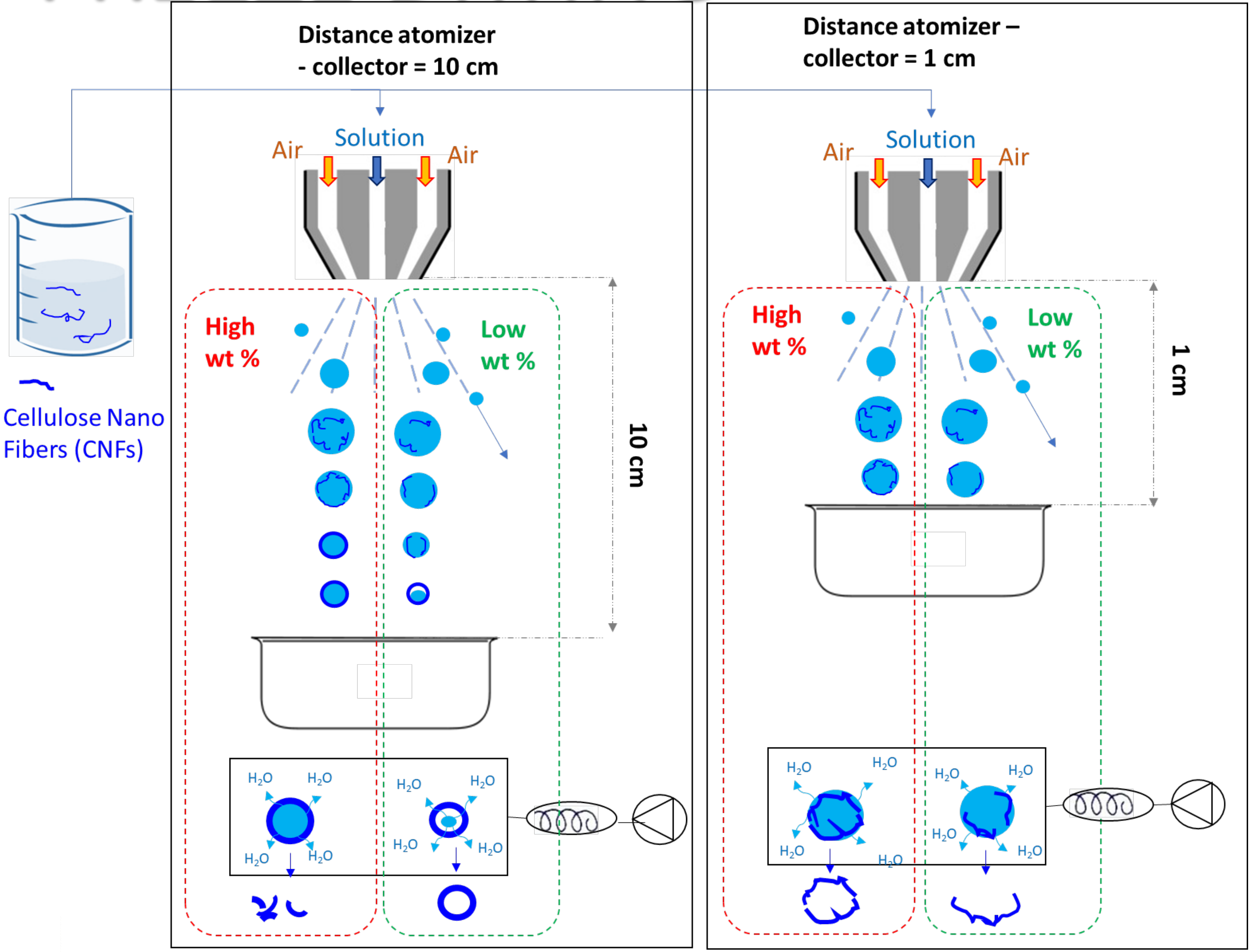
SPRAY FREEZE DRYING



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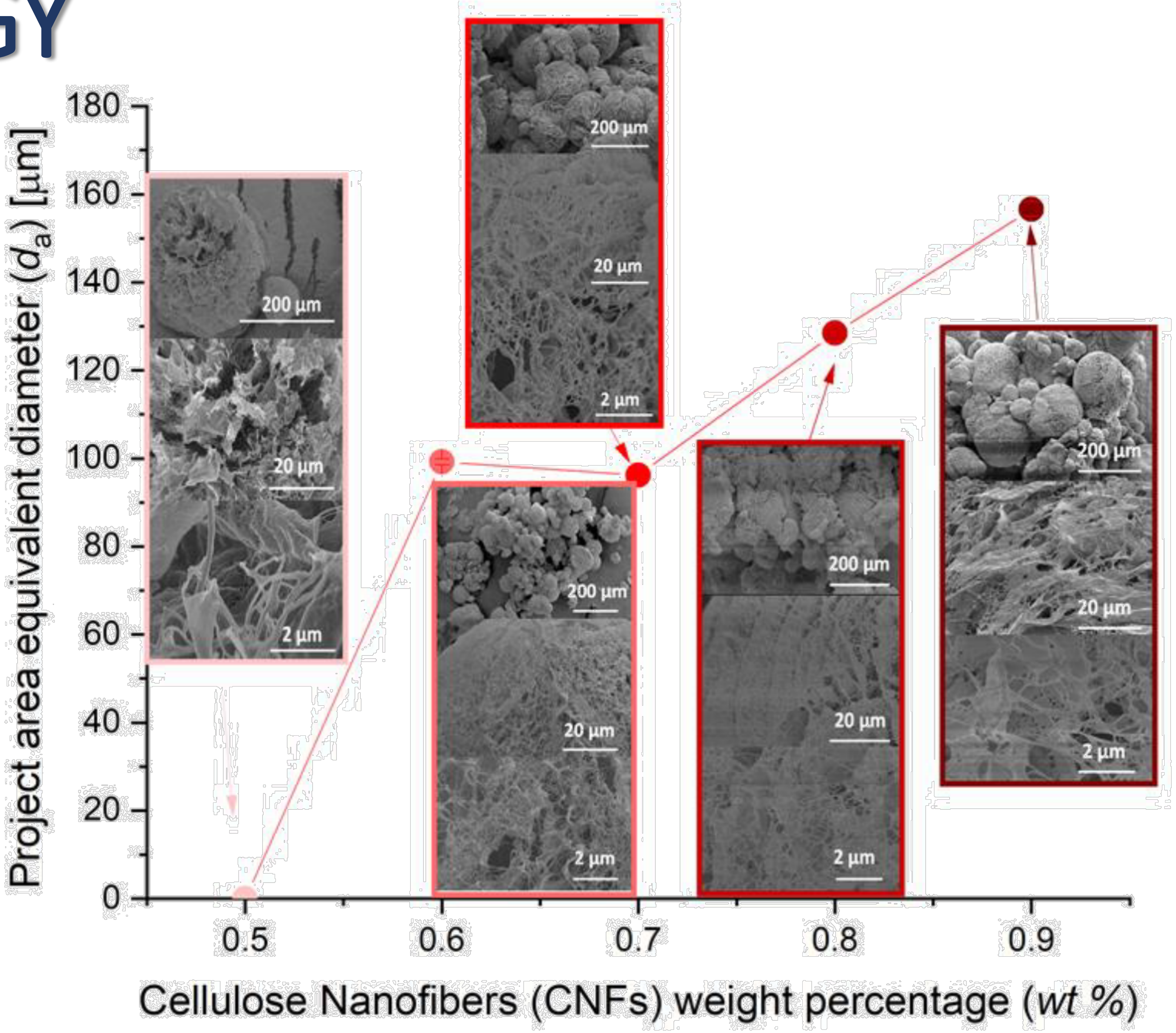
MORPHOLOGY

Distance: 1 cm

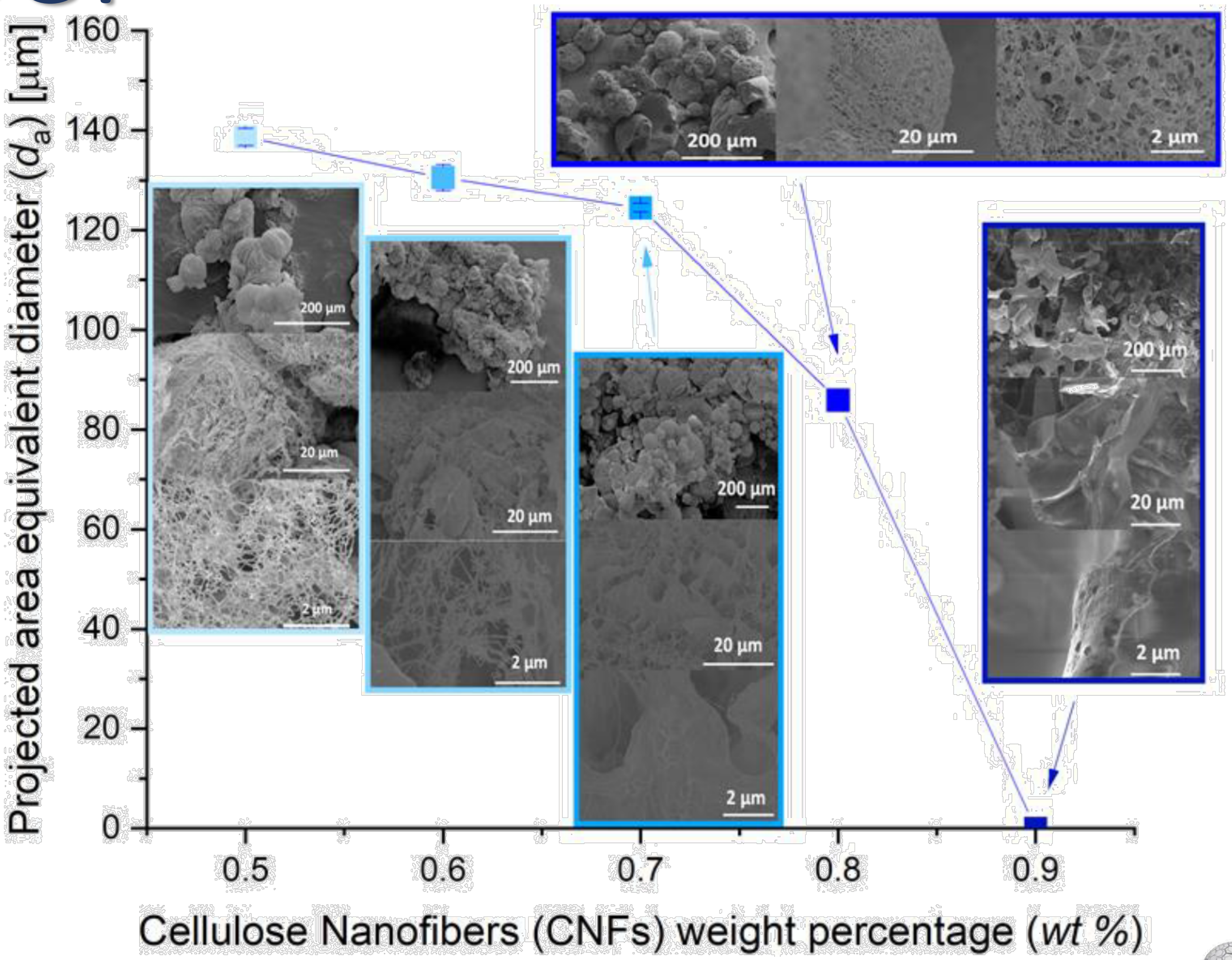
Initial conc. (wt.%)	Yield (%)
0.5	30
0.6	41
0.7	55
0.8	62
0.9	70



MORPHOLOGY

Distance: 10 cm

Initial conc. (wt.%)	Yield (%)
0.5	25
0.6	40
0.7	65
0.8	70
0.9	77



No particle formation

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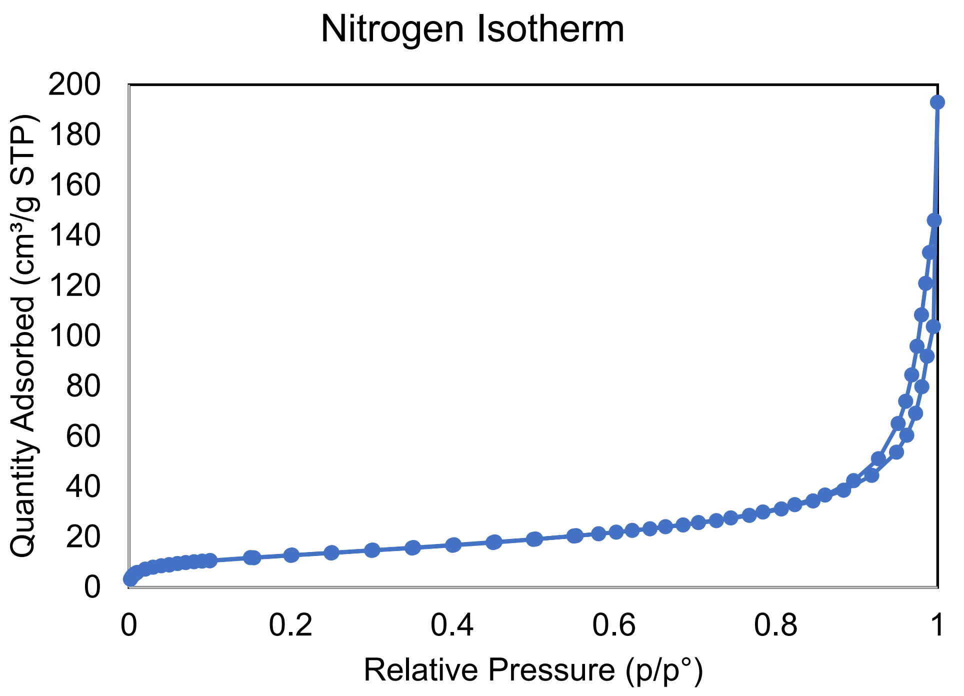
SPRAY FREEZE DRYING

C_i (wt.%)	Distance cm	S_{BET} (m^2/g)	S micro (m^2/g)	V total (cm^3/g)	$V_{micropore}$ (cm^3/g)	$V_{mesopore}$ (cm^3/g)	d pore (nm)
0.5	1	83.2	8.02	0.289	0.004	0.285	5.6
0.5	10	14.1	0	0.065	0	0.065	5.5
0.6	1	110.7	6.29	0.374	0.003	0.371	6.9
0.6	10	33.9	0	0.161	0	0.161	7.7
0.7	1	87.8	5.1	0.3035	0.002	0.3015	5.9
0.7	10	41.3	1.2	0.142	0.0002	0.1418	5.9
0.8	1	76.6	12.73	0.233	0.0105	0.2225	5.1
0.8	10	70.3	2.34	0.244	0.0006	0.2434	6.5
0.8	control	25.4	0	0.098	0	0.098	6.9
0.9	1	83.8	5.17	0.2796	0.0021	0.2775	6.2
0.9	10	46.8	1.41	0.1608	0.0003	0.1605	6



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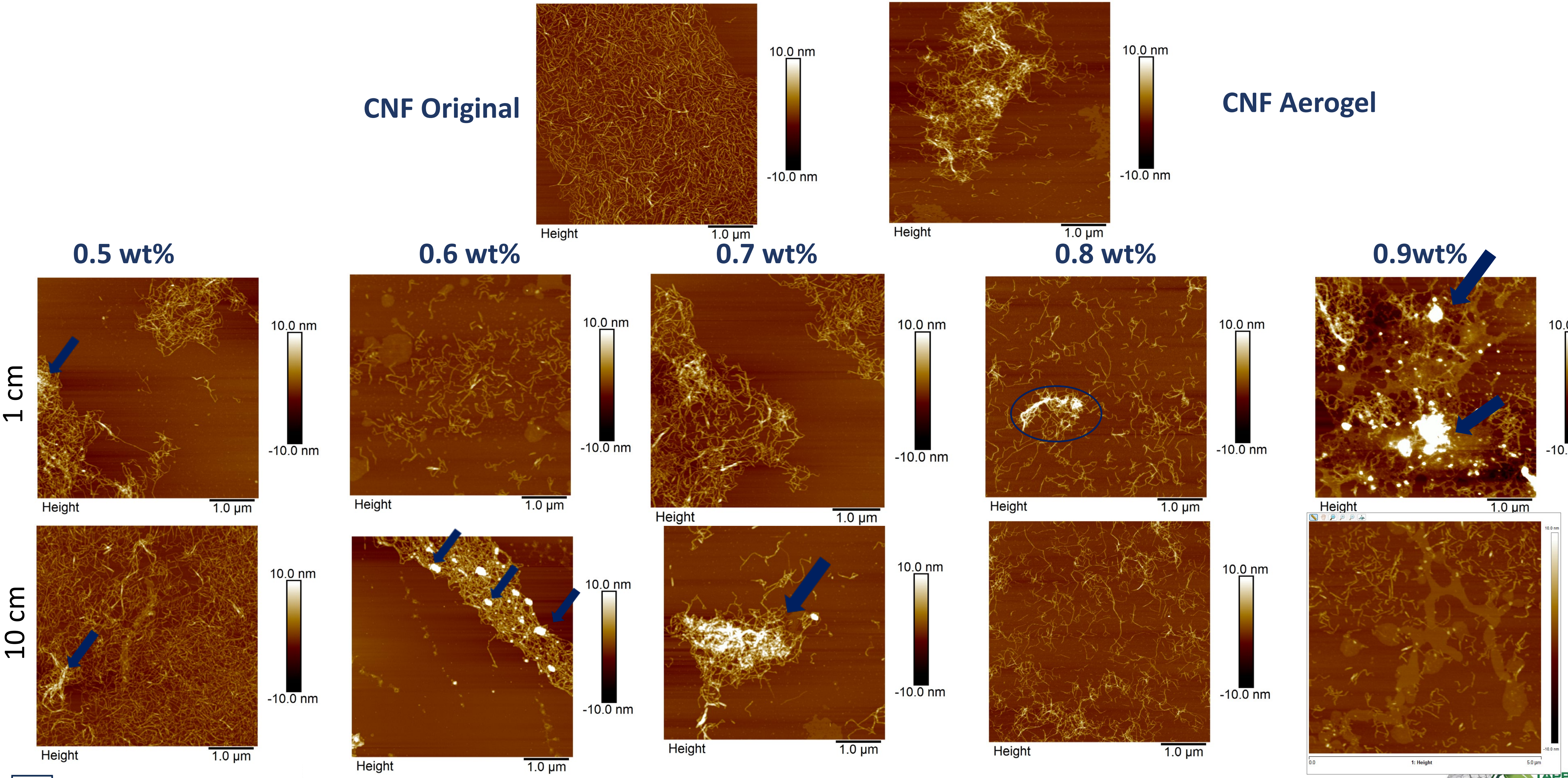
MESOSTRUCTURE



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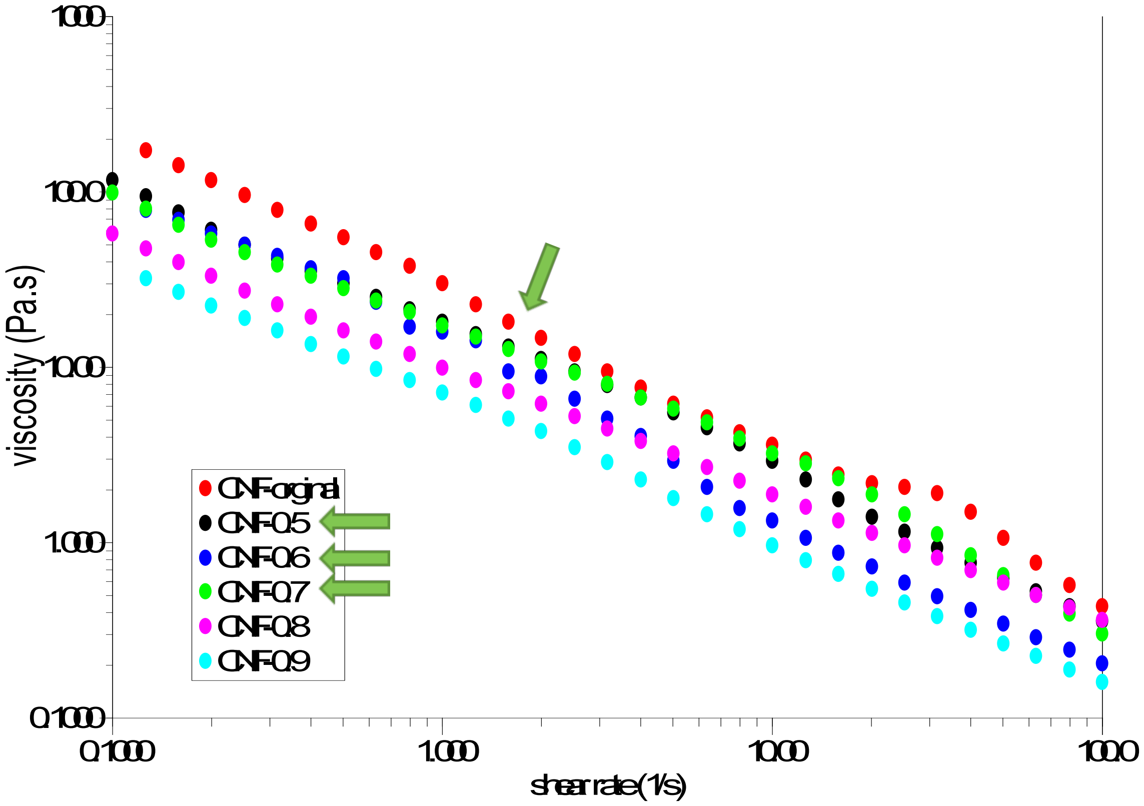
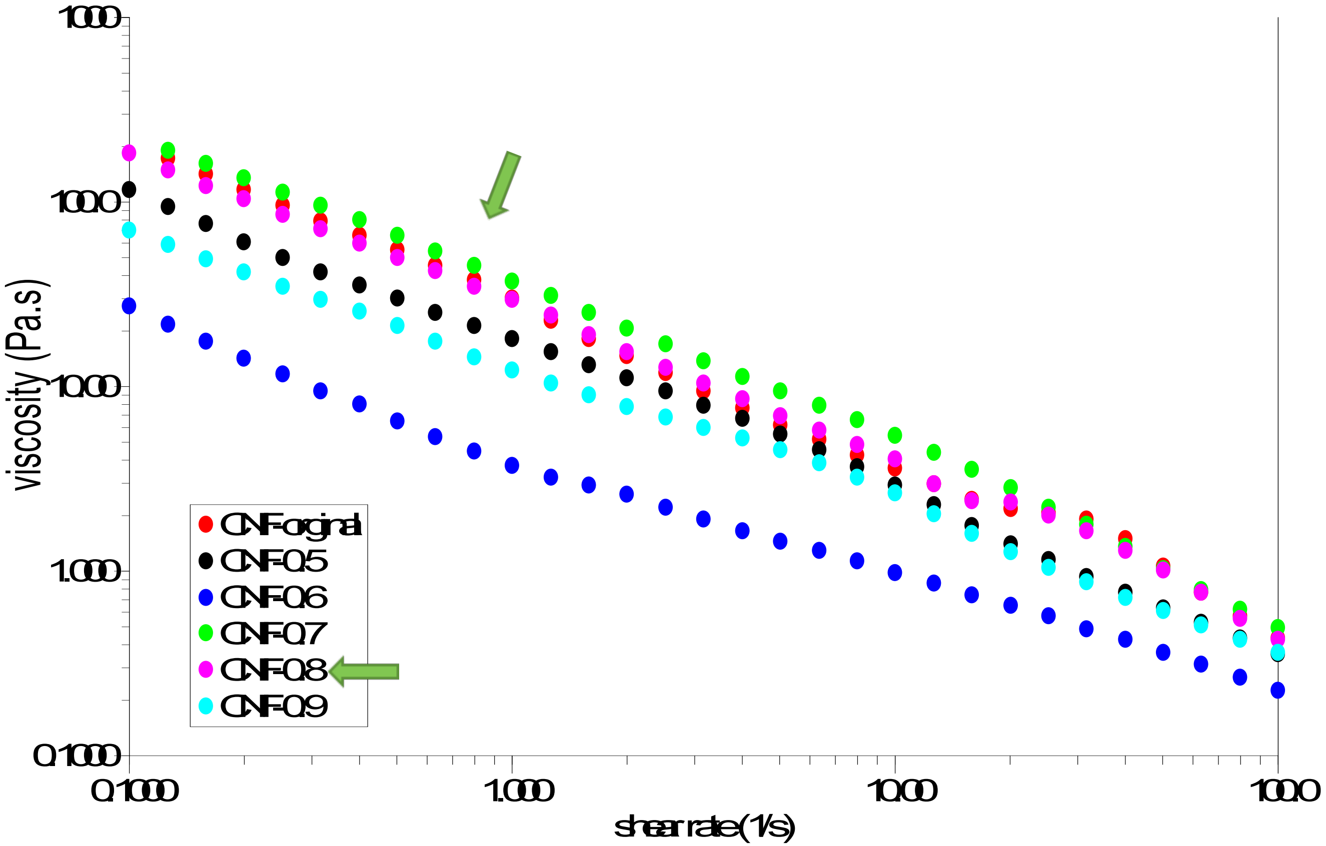
COMPARISION OF SHEAR VISCOSITY

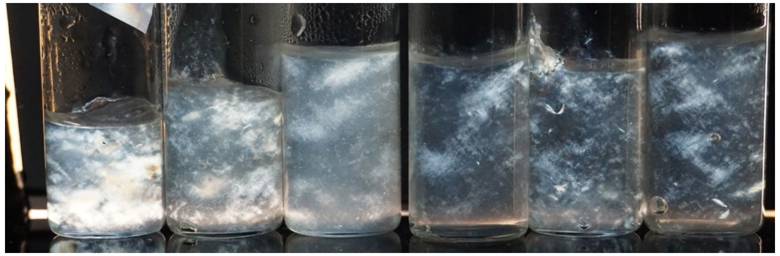
Distance: 1 cm



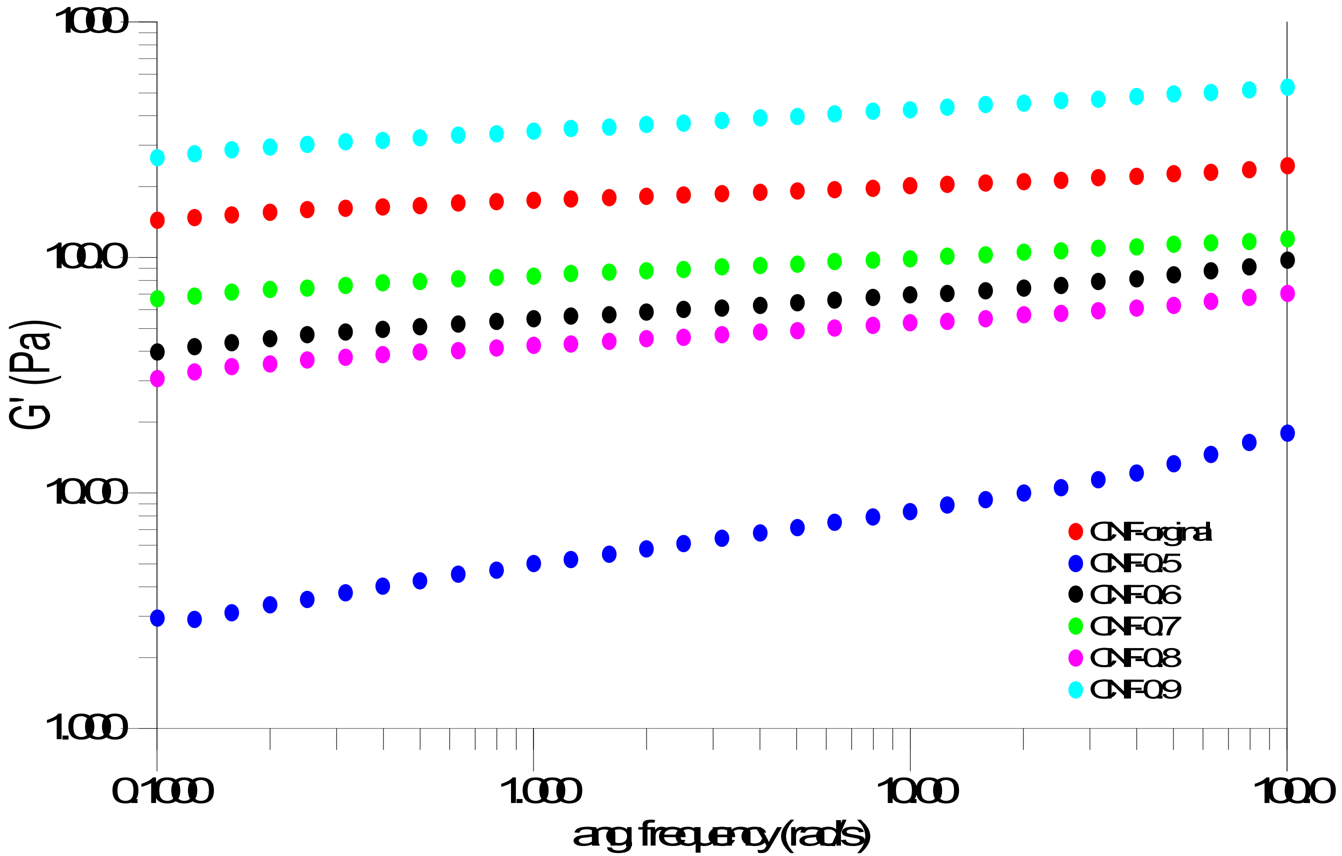
Distance: 10 cm

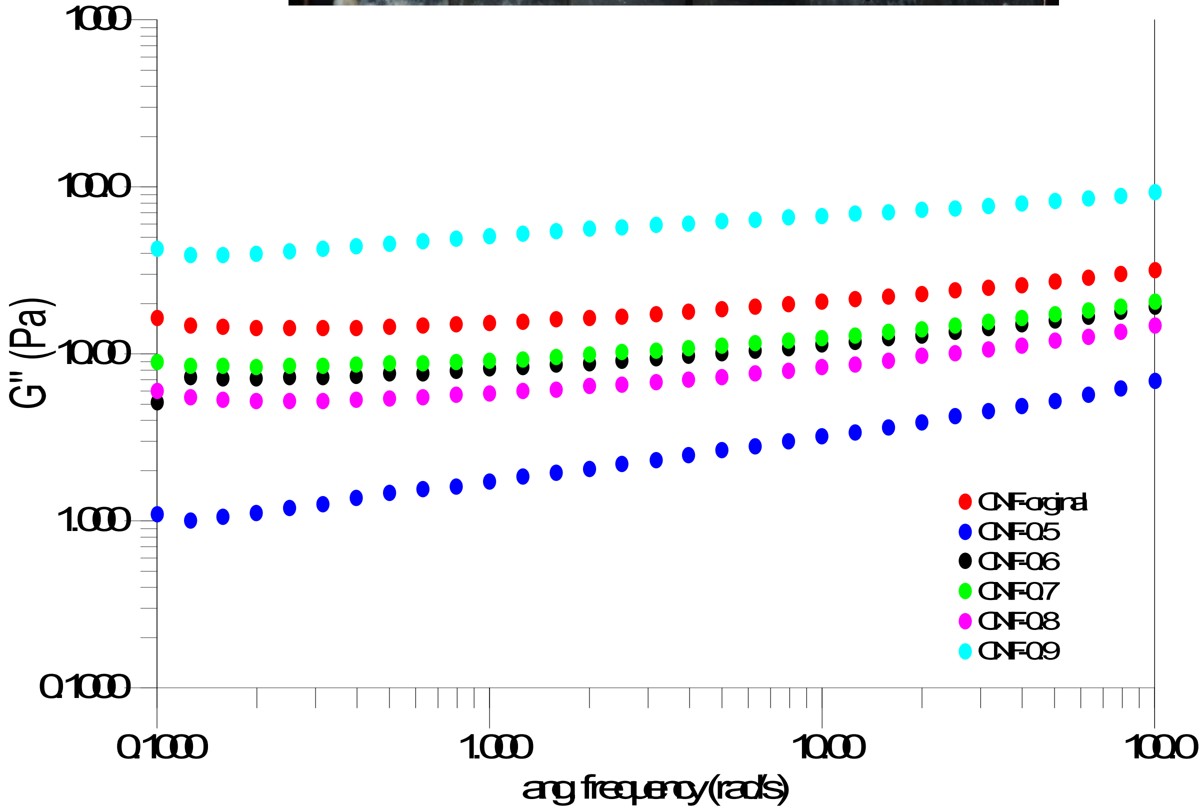


RHEOLOGY



Distance: 1 cm





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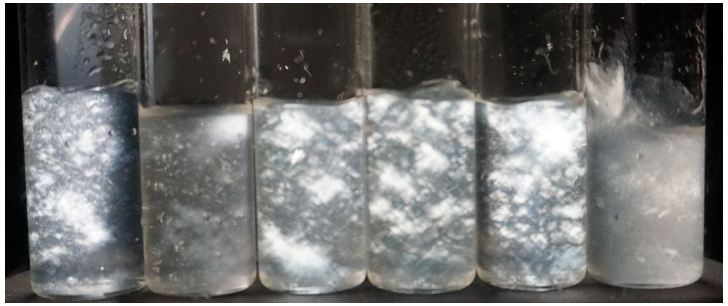
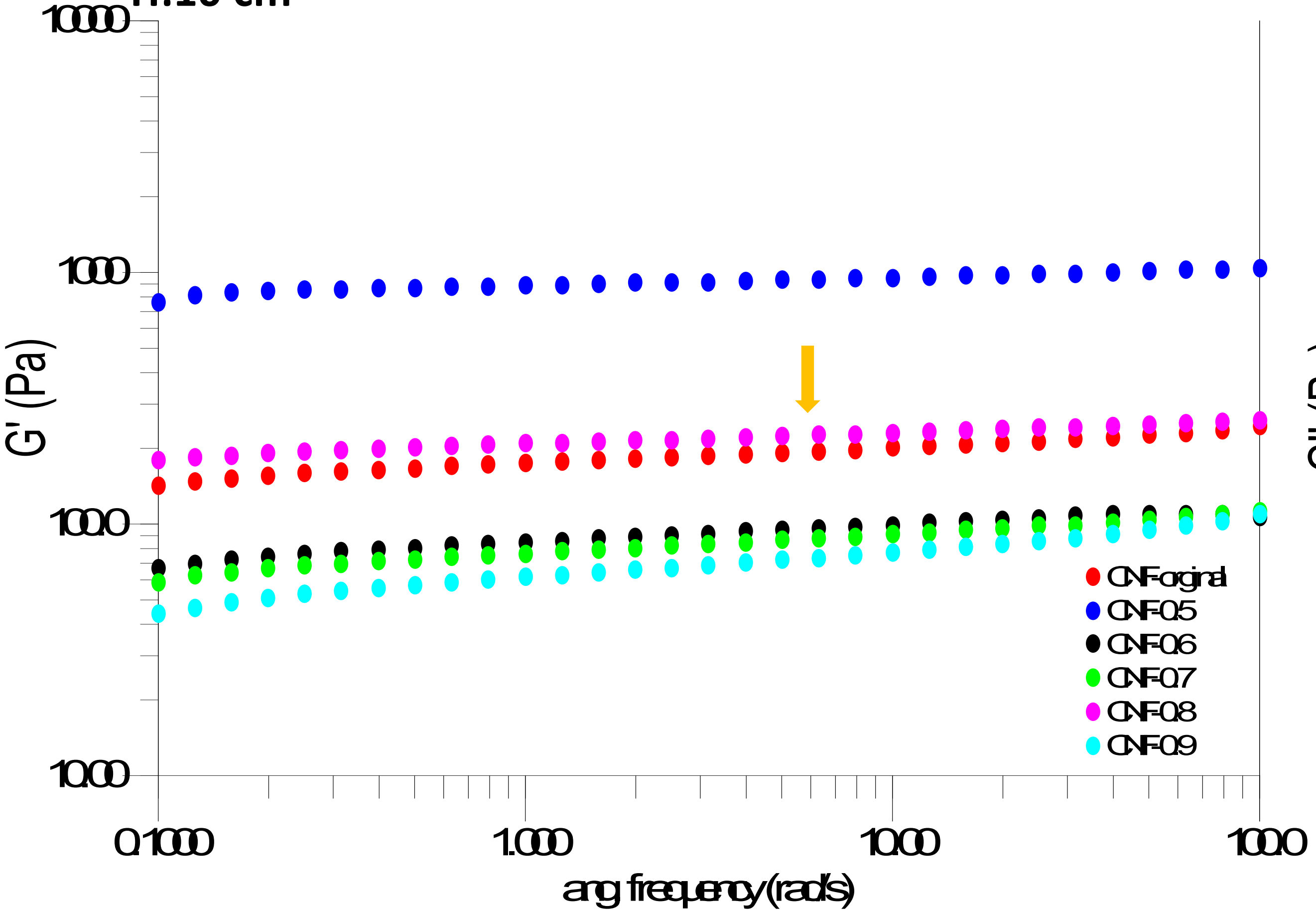
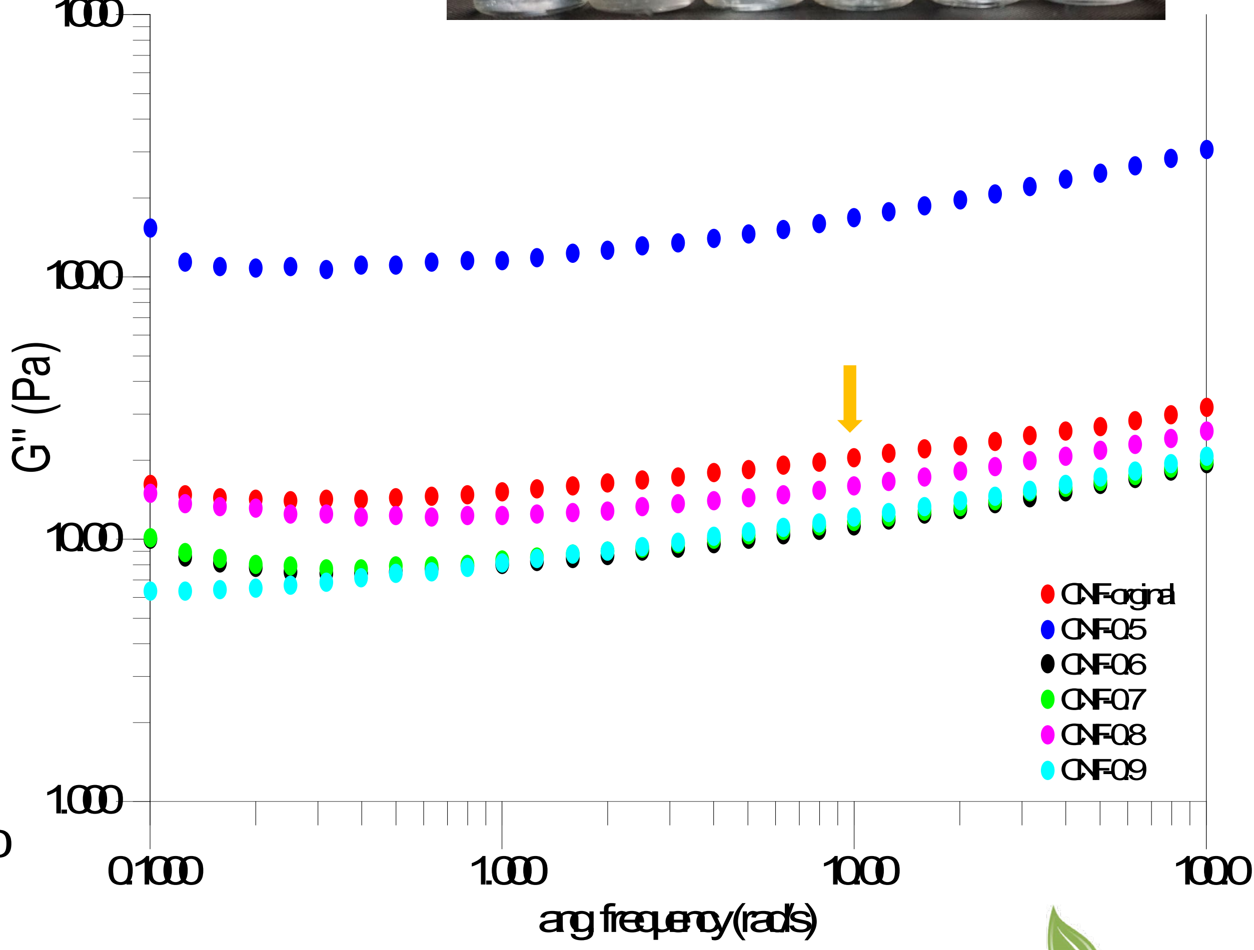
RHEOLOGY

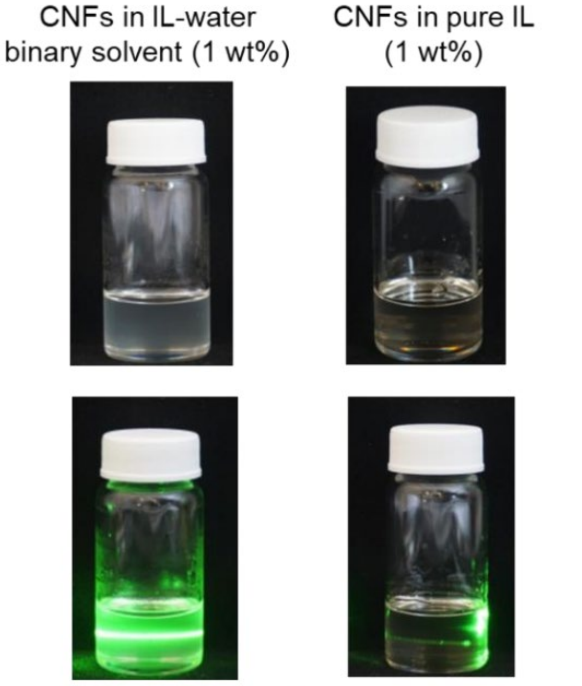


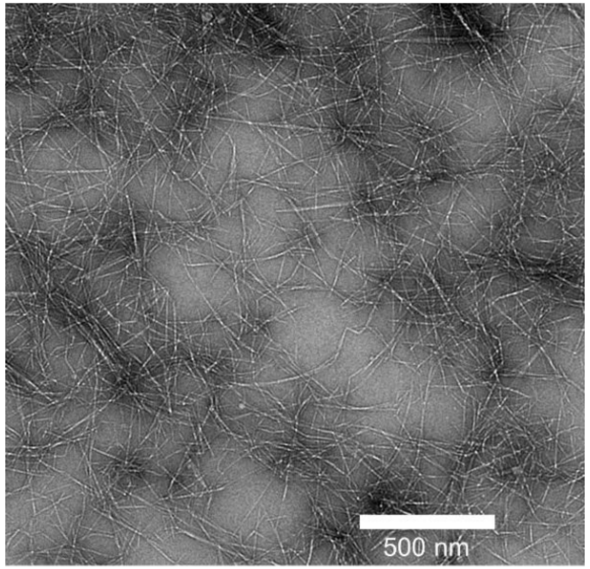
H:10 cm

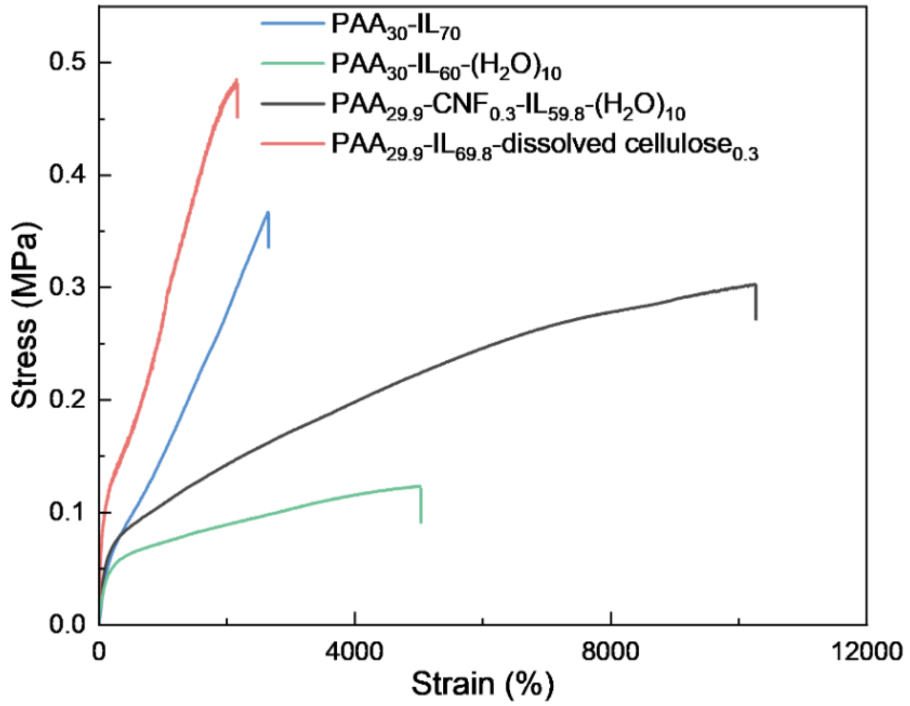




APPLICATION







Ye, Y., Oguzlu, H., Zhu, J., Zhu, P., Yang, P., Zhu, Y., Wan, Z., Rojas, O. J., Jiang, F., Ultrastretchable Ionogel with Extreme Environmental Resilience through Controlled Hydration Interactions. *Adv. Funct. Mater.* 2023, 33, 2209787. https://doi.org/10.1002/adfm.202209787

CONCLUSION

- Initial concentration and distance between liquid nitrogen and nozzle are affecting parameter to control diffusion of TO-CNF through the droplet during drying.
- At shorter distance, lower concentrated suspensions cannot form particles due to not having enough time to diffuse TO-CNF through the surface of the droplet.
- At longer distance, formed droplet from higher concentration burst due to evaporation of water.
- Sonication is needed to disperse spray-freeze dried TO-CNF suspension efficiently.
- Shear viscosity and moduli values of gels from microparticles that formed from 0.8 wt.% CNF solution at 10 cm distance matching the AFM images.

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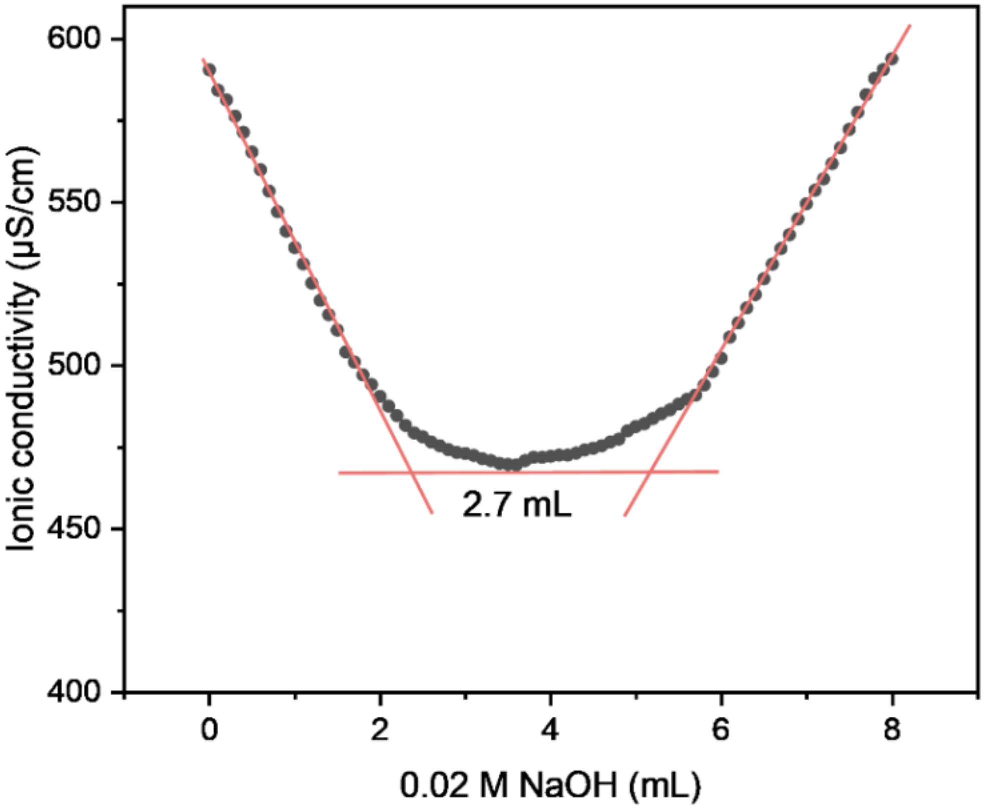
Q&A



600
550
500
450
400
Ionic conductivity (µS/cm)
0
2
4
6
8
0.02 M NaOH (mL)
2.7 mL