



THERMAL STABILITY IMPROVEMENT IN MODIFIED CELLULOSE NANOCRYSTAL

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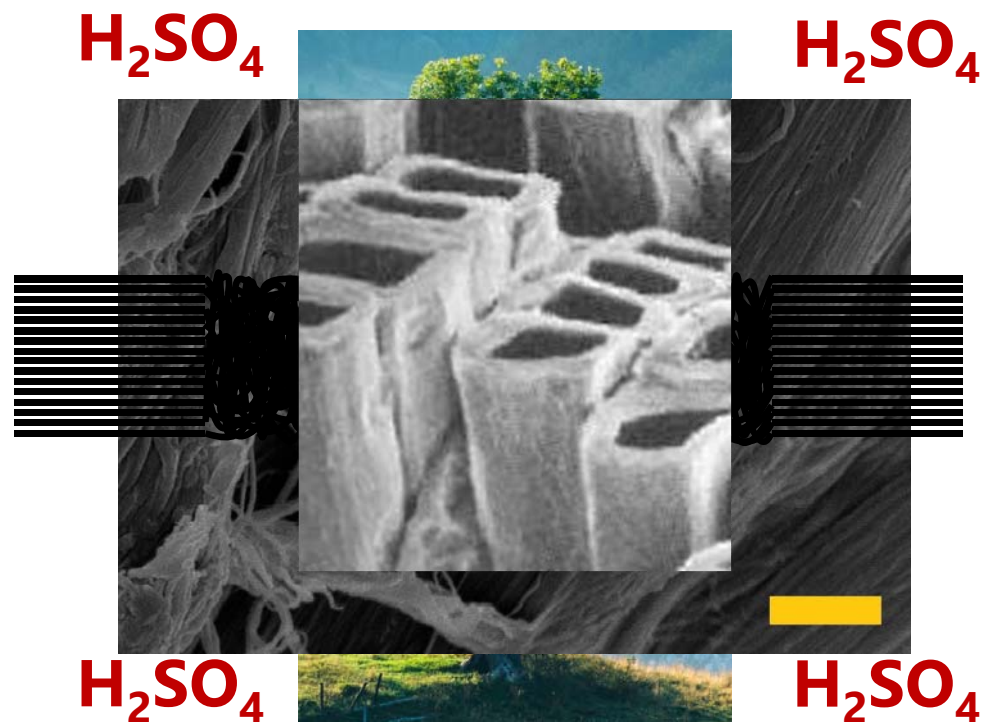
TAPPI Nano 2021, 15-16/06/2021

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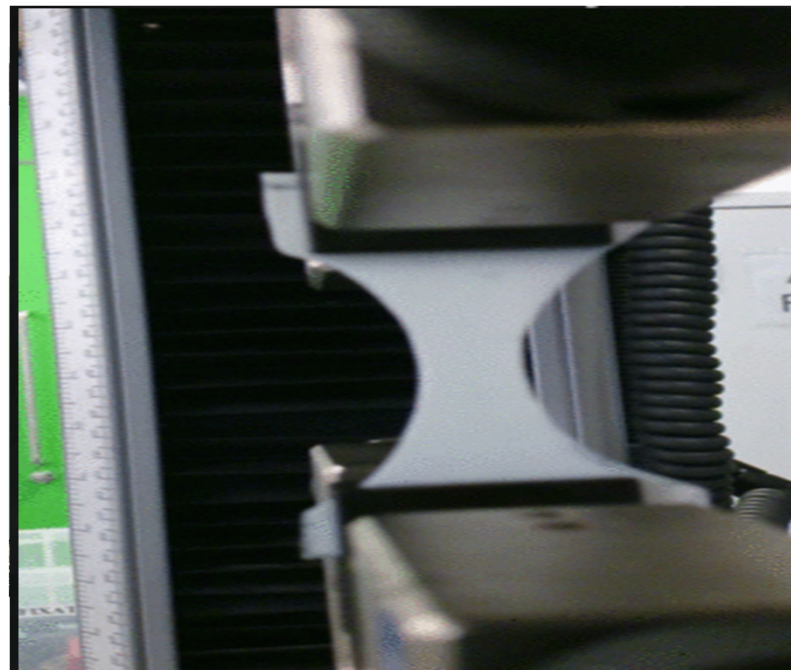
CELLULOSE NANOCRYSTALS (CNC)

- Starting from a tree.
- To one branch.
- To fibrils.
- To microfibrils.
- To nanocrystals.



THINGS THAT WORK

- Abundant. 
- Renewable. 
- Biodegradable. 
- Cheap. 
- Easy to make. 
- Colorful films.
- Very **STRONG**.



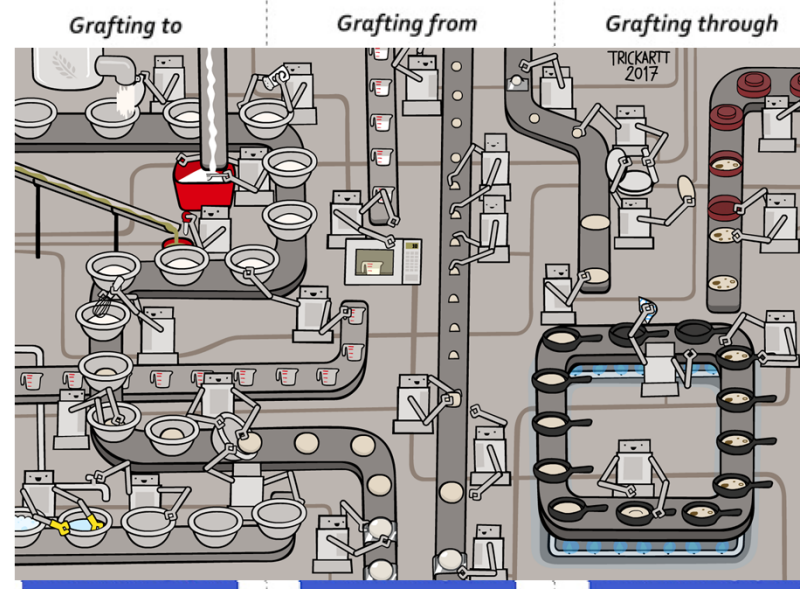
Shopsowitz, et al. 2010.

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THINGS THAT WORK PARTIALLY

- As prepared CNCs are thermally **unstable**.
- Many remedies are long and laborious.
- *Speed* is an industrial requirement for commercialization.



Lizundia, et al. Multifunctional Polymeric Nanocomposites Based on Cellulosic Reinforcements 2016, 61-133.

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PART 1: THERMAL STABILITY ENHANCEMENT IN CNC FILMS THROUGH RAPID MECHANOCHEMICAL METHODS

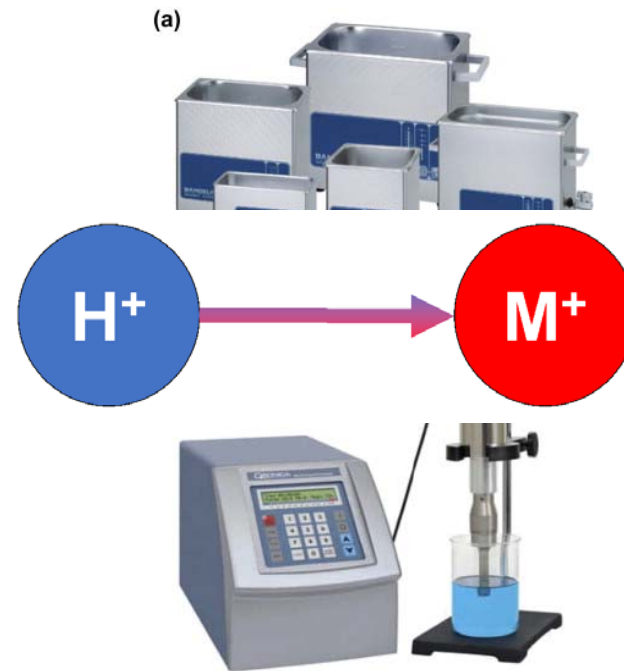
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FAST METHODS TO TREAT CNC

SUSPENSIONS

- **Quickly** treat stored suspensions just before air-drying.
- *Mechanical*: Ultrasonication.
- *Chemical*: Ion exchange.

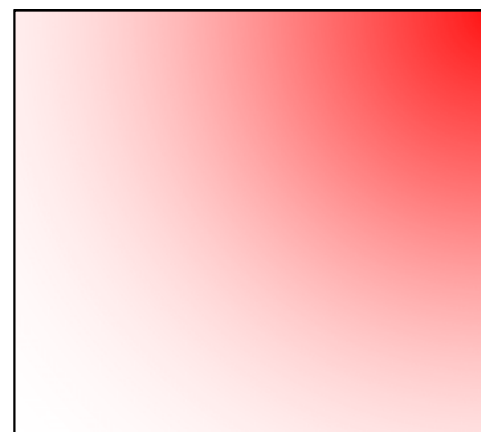


Loos. *Carbon Nanotube Reinforced Composites* **2015**, 171-188.

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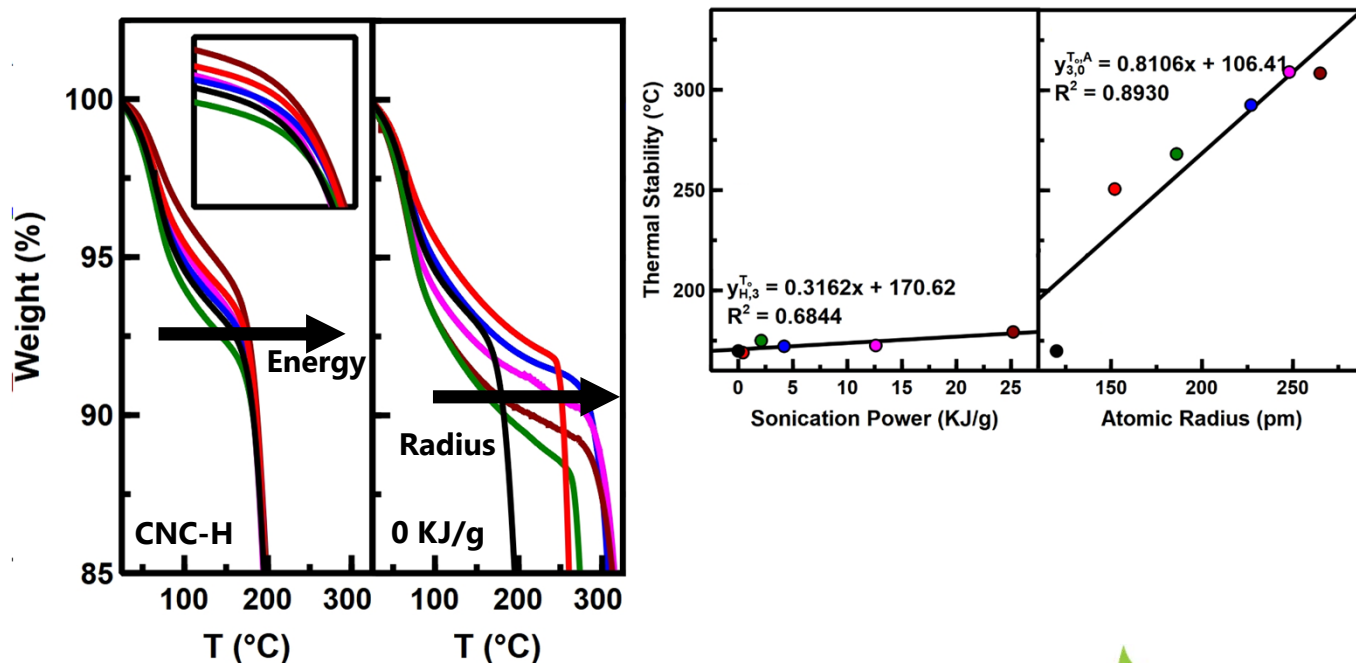
A 2D MATRIX OF SELECTED PARAMETERS

- Ultrasonication (change **energy input**).
- Ion exchange (change **alkali hydroxyl** used).
- Combinations created in MAX.
30 minutes.



THERMAL STABILITY OF CNC FILMS AFTER ULTRASONICATION AND ION EXCHANGE

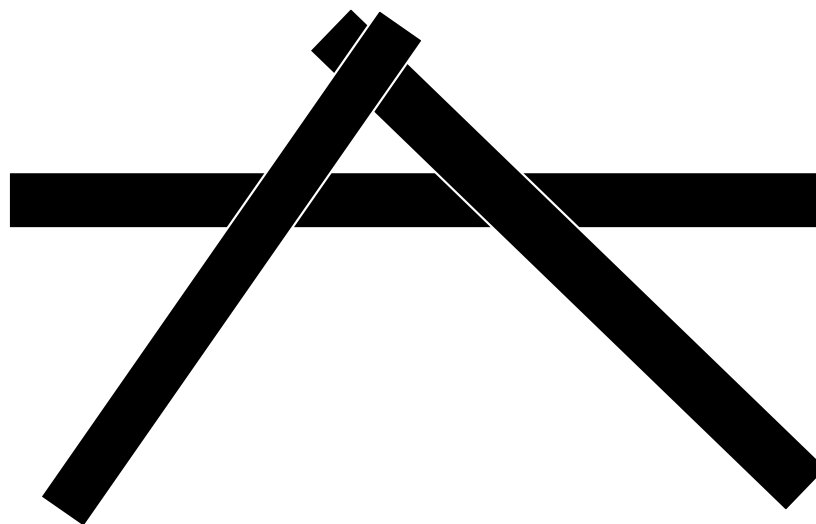
- **Ultrasonication** enables **mild** thermal improvement.
- Very **high enhancement** for ion **exchange**.



D'Acierno, et al. *In preparation*.

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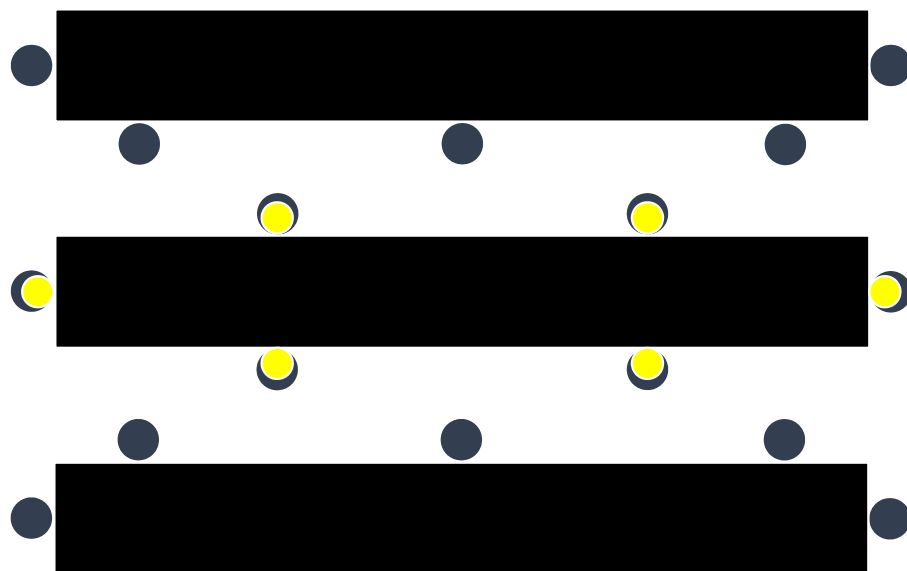
ULTRASONICATION AND THERMAL STABILITY



- Better dispersion → breaking aggregates
→ more thermally stable

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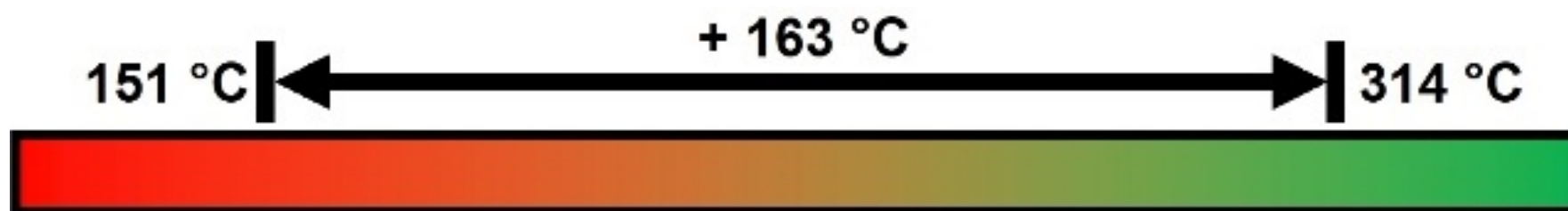
ION EXCHANGE AND THERMAL STABILITY



- Bigger ions → lower polarization of sulfate groups → **more thermally stable**

THERMAL STABILITY OPTIMIZATION

- Ultrasonication can be used for **fine** optimization.
- Ion exchange can be used for **extensive** optimization.
- Combined together the thermal stability can be improved by **163 ° C**.





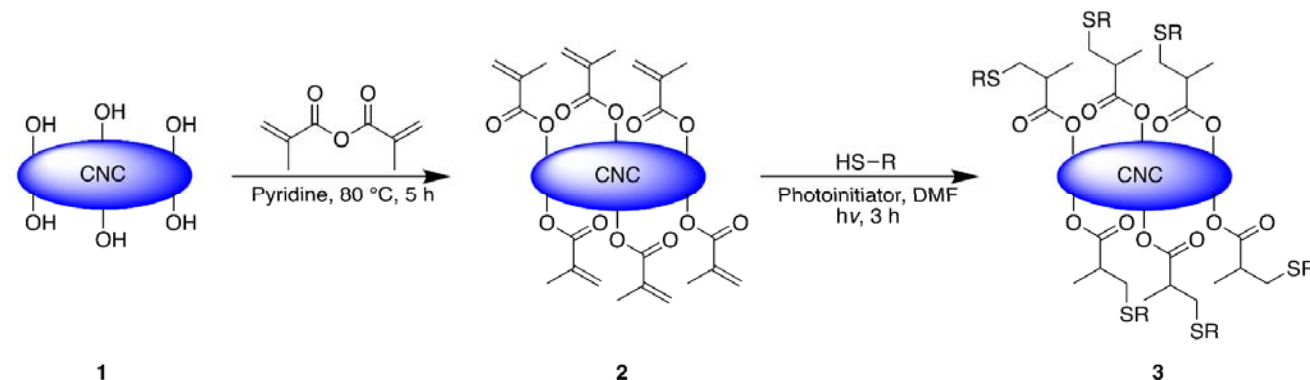
PART 2: THERMAL STABILITY ENHANCEMENT IN CNC AEROGELS THROUGH THIOL-ENE CLICK CHEMISTRY

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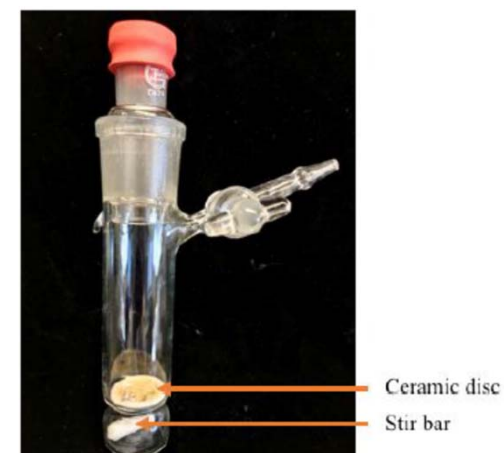


SYNTHESIS OF HYDROPHOBIC CNC AEROGELS

- **Esterification** in dry state.
- Thiol-ene «click» (**radical** addition).
- Thiol-ene «click» (**Michael** addition).



3A = R¹ = CH₂CH₂COOH
3B = R² = (CH₂)₅CH₂OH
3C = R³ = (CH₂)₁₁CH₃
3D = R⁴ = CH₂CH₂(CF₂)₇CF₃

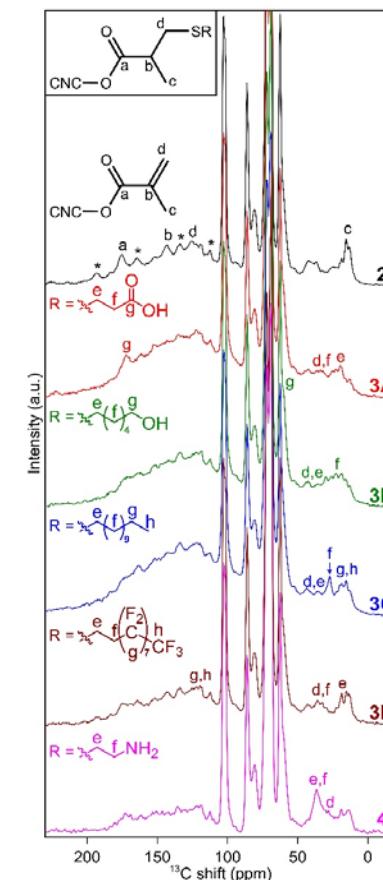
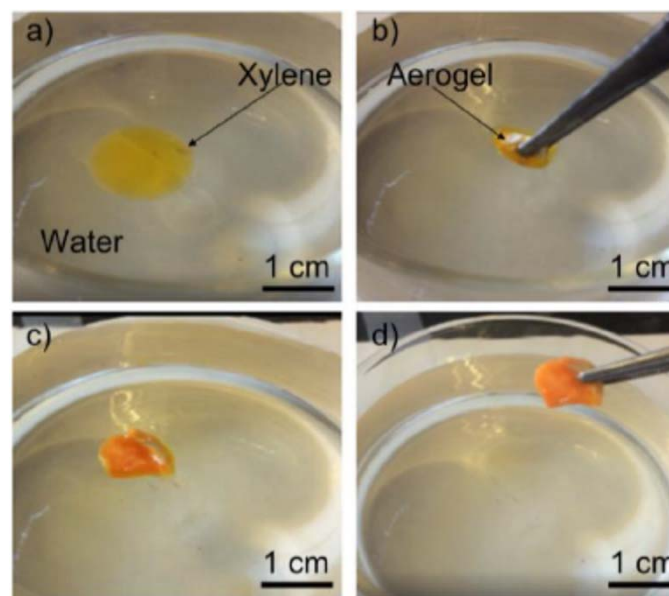


Aalbers, Boott, et al. *Biomacromolecules* **2019**, 20, 2779-2785.

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^{13}C SS-NMR CHARACTERIZATION OF HYDROPHOBIC CNC AEROGELS

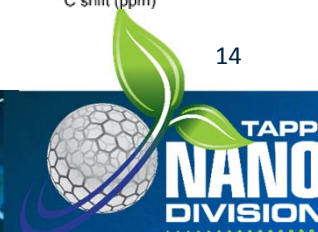
- Successful surface **functionalization**.
- **Cellulose** structure not modified.
- Used as **oil absorbents**.



Aalbers, Boott, et al. *Biomacromolecules* **2019**, *20*, 2779–2785.

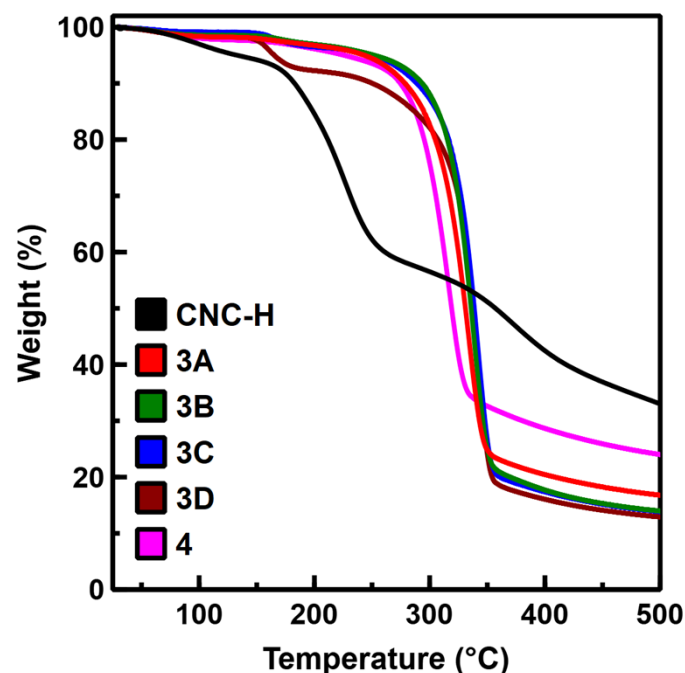
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THERMAL STABILITY OF HYDROPHOBIC CNC AEROGELS

- Improvement by more than **120 °C** with respect to CNC-H aerogel.
- **3B** is the least thermally stable.
- **3D** is the least thermally stable.



Material	Thermal stability (°C)
CNC-H	189
3A	305
3B	310
3C	309
3D	149
4	288

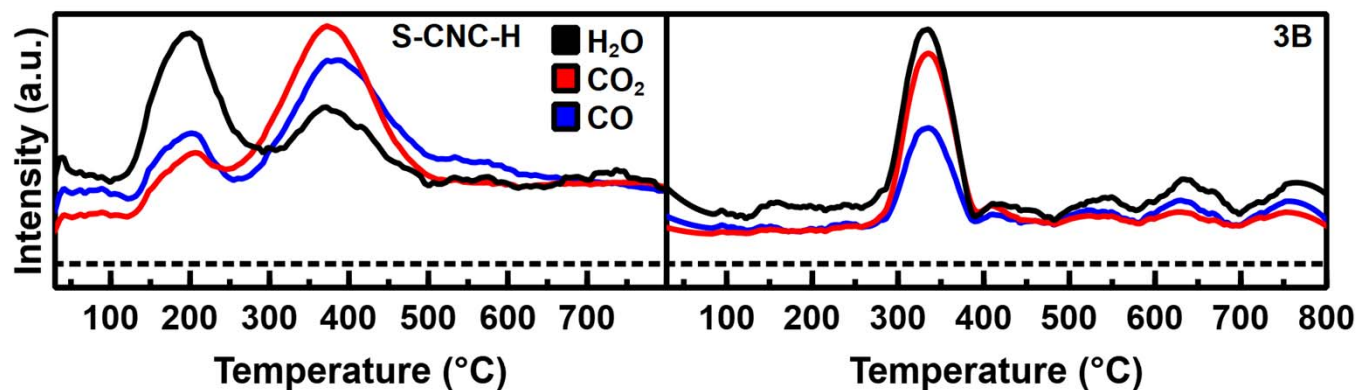
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GAS RELEASE OF HYDROPHOBIC CNC AEROGELS

- **CNC-H** releases a lot of **water** at the main pyrolysis stage.
- Preventing dehydration through **hydrophobic functionalization** is the key to high thermal stability.



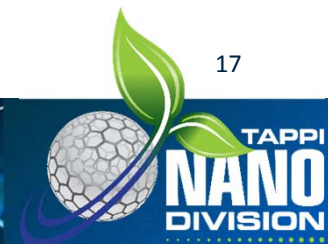
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CONCLUSIONS

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CONCLUSIONS

- Increasing ultrasonication **energy** input and **radius of alkali** counterion in CNC **suspensions** improve thermal stability.
- CNC **aerogels** with **aliphatic chains** grafted to the surface are resistant to heat due to high **hydrophobicity**.
- The thermal stability of CNC can potentially **approach** and even surpass that of **native cellulose**.

ACKNOWLEDGMENTS



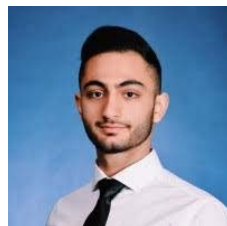
Prof. Mark **MacLachlan**



Prof. Carl **Michal**



Dr. Wadood
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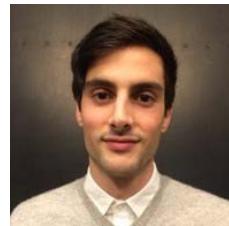
Kiavash
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Guus
Aalbers



Dr. Charlotte
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Dr. Lev **Lewis**



Joseph **Ho**

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THANK YOU.

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