Design Rules for Cellulose Nanocrystal-Stabilized Emulsions & Dry Oil Powders

Sustainable NaNO BiO Composites

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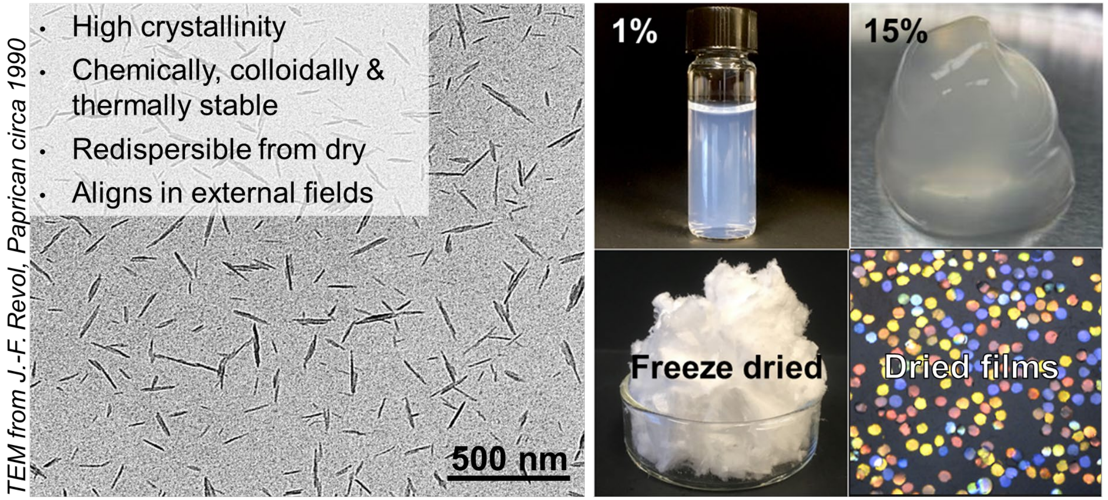
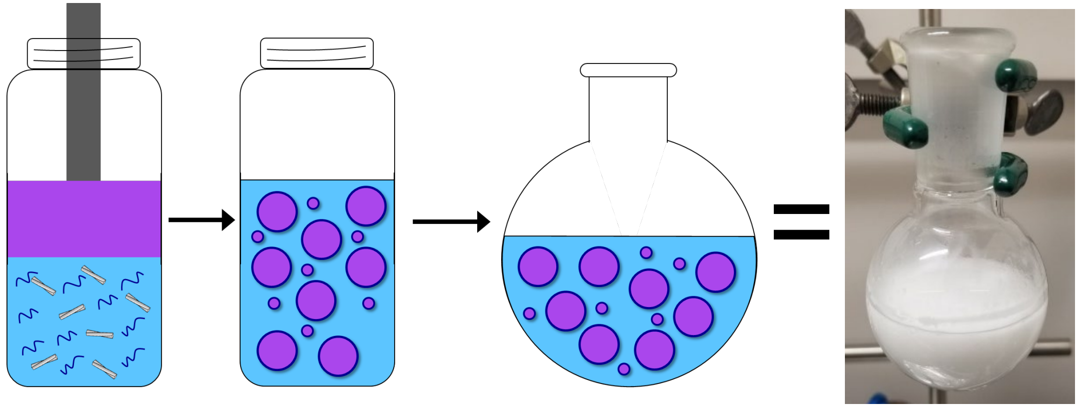
TAPPI NANO DIVISION

Introduction

- Cellulose nanocrystals (CNCs) are bio-based amphiphilic high aspect ratio nanoparticles capable of stabilizing interfaces

- Industrial relevance
  - ✓*Emulsions:* food, cosmetic, pharma & household products
  - ✓*Emulsion-based (a.k.a. latex) polymers:* paints, coatings, adhesives, toners & rubbers



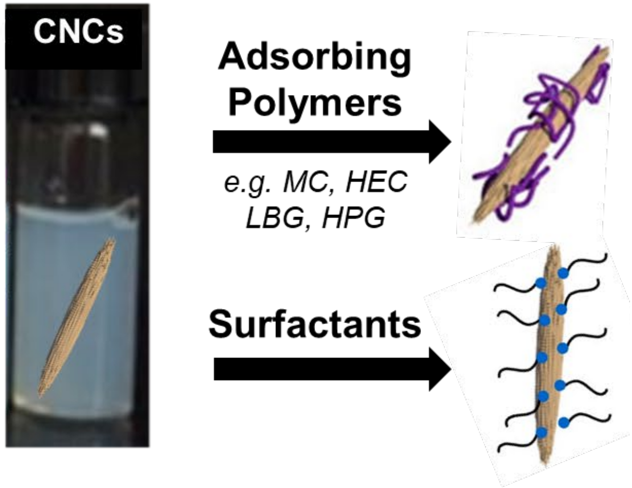


CNC Pickering Emulsions

Zhen Hu

- CNCs (uncharged or with salt) can stabilize oil/water interfaces
  (Kalashnikova, Bizot, Cathala, Capron. *Langmuir* **2011**, *27*, 7471)

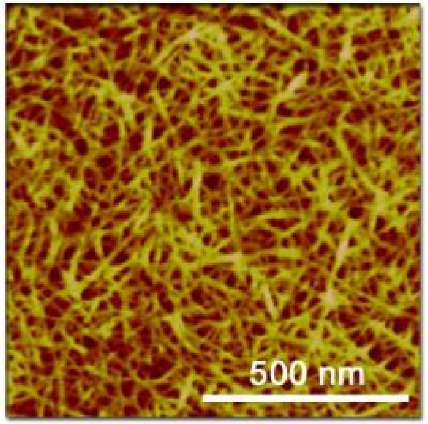
- CNCs + adsorbed co-stabilizers give smaller droplets, good stability, tailorability, and require less stabilizer



Goals
1. Small droplets
2. Stability to coalescence
3. No phase separation
4. No oil leakage
5. Low [stabilizer]
6. Heat-cool & freeze-thaw stable

Hu, Ballinger, Pelton, Cranston, *JCIS* **2015**, *439*, 139
Hu, Patten, Pelton, Cranston, *ACS Sust Chem & Eng* **2015**, *3*, 1023

Cellulose Nanocrystals vs. Fibrils



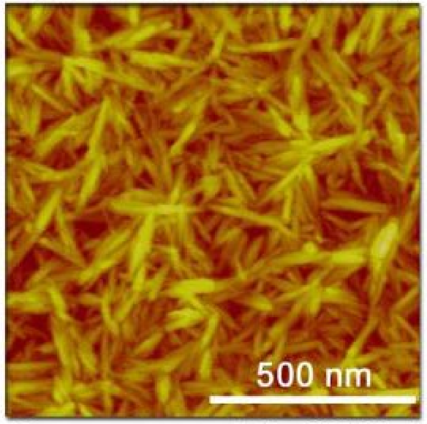
Cellulose nanofibrils (CNFs)

≈

"Spaghetti-like"

Entangled fibrils with lower crystallinity

- ✓ Some interfacial stabilization (size dep.)
- ✗ Heterogeneity means less predictability
- ✓ Network can prevent droplet coalescence
- ✓ Rheological modifier of continuous phase
- ✗ Can bridge droplets → coalescence
- ✗ More energy required to produce emulsion



Cellulose nanocrystals (CNCs)

≈

"Rice-like"

Rigid individual particles with higher crystallinity

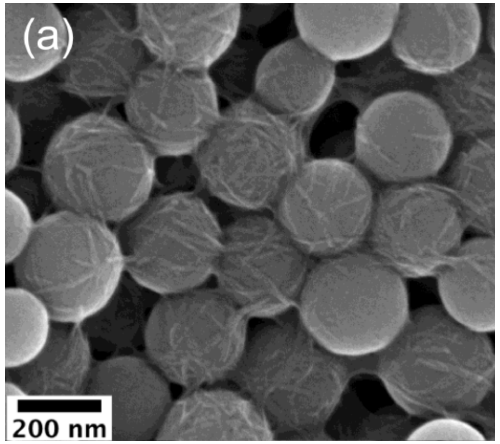
- ✓ Crystallinity → amphiphilicity → good stabilizer
- ✓ Mesh-like network at interface (low [CNC])
- ✓ Discrete particles = discrete droplets
- ✓ Predictability emulsion properties
- ✓ Less energy required to produce emulsion
- ✗ Droplet size limited by CNC rigidity

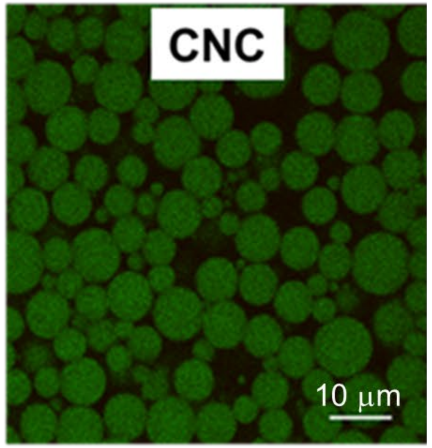
Kedzior, Gabriel, Dubé, Cranston. *Advanced Materials* **2020**, 2002404.

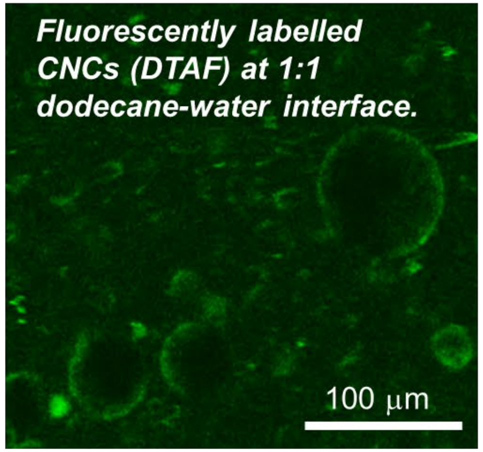
1. **Typically for stable emulsions, small droplets are desired and creaming should be avoided – is this really the case for CNC Pickering emulsions?**

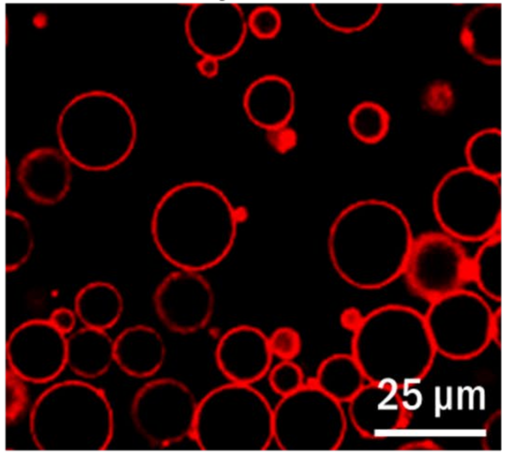
Large(ish) Droplets are OK!

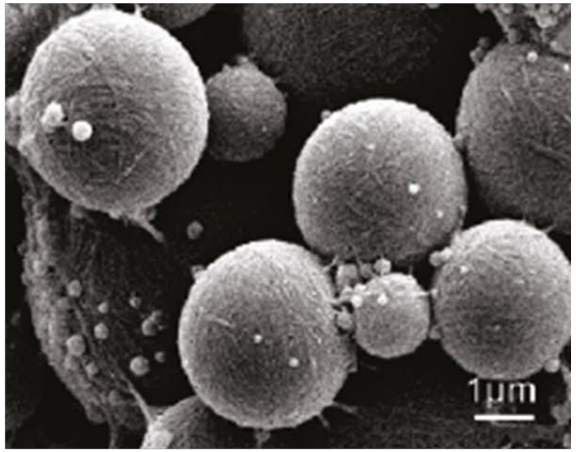
- Literature shows ca. 200 nm to 70 µm droplets but always stable





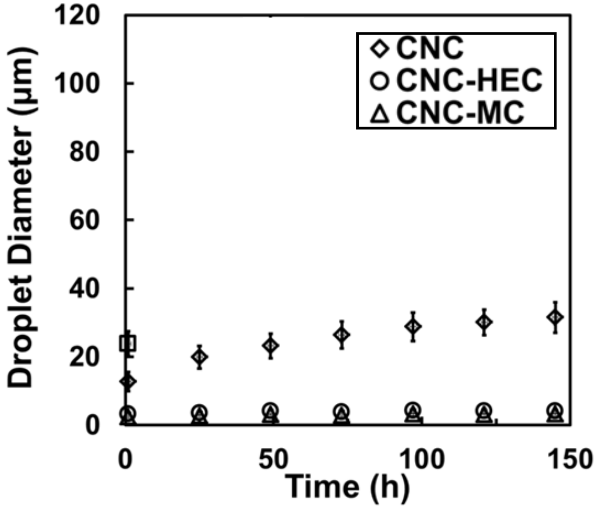






- Zhang and Rowan. *Macromolecules* **2017**, *50*, 6032.
- Kalashnikova, Bizot, Cathala, Capron. *Langmuir* **2011**, *27*, 7471.
- Kalashnikova et al. *Biomacromolecules* **2012**, *13*, 267.
- Kalashnikova et al. *Soft Matter* **2013**, *9*, 952.
- Capron & Cathala, *Biomacromolecules* **2013**, *14*, 291.
- Hu, Patten, Pelton, Cranston, *ACS Sust Chem & Eng* **2015**, *3,* 1023.

While 2 – 7 µm droplets are achievable, 10 – 20 µm are more typical and do not coalesce over years on the shelf @RT.



Emulsion Creaming is Fine

- Creaming is a “destabilization mechanism” but is acceptable in many products and can be controlled through additives

After sonication

After 30 days

Droplets are still intact.

Creaming is due to
- **Density difference**
- **Droplet agglomeration**
- **Low viscosity water phase**

2. **How much salt should be added to screen CNC surface charge and provide the most stable emulsions?**

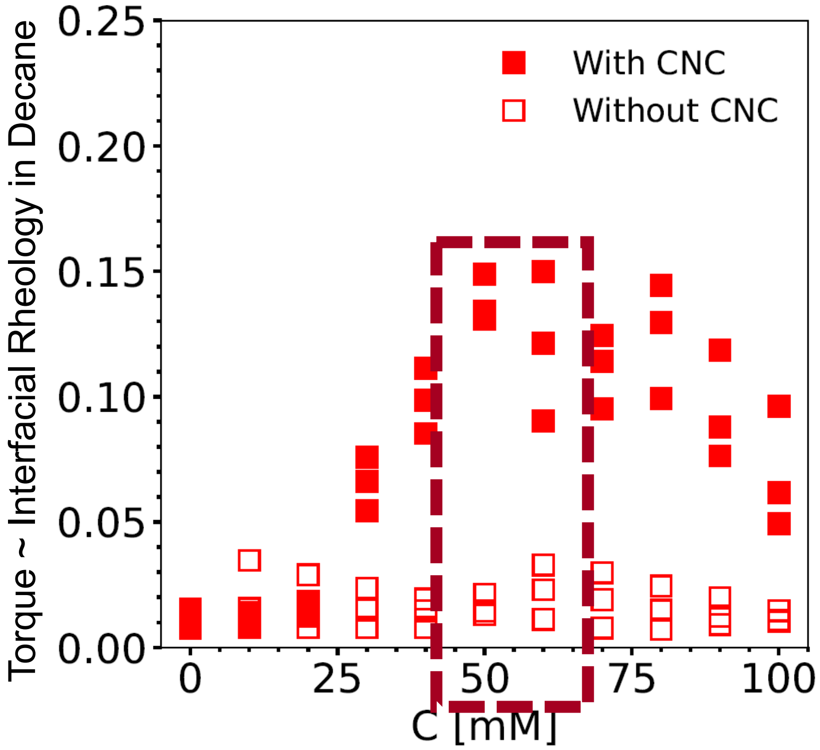
   What is the role of emulsion co-stabilizers and when should they be used?

How Much Salt (NaCl)?

Roxanne Fournier

- Role of salt (screening CNC charge)
  - Allows denser packing of CNCs at the oil-water interface
  - Increases interface & bulk viscosity
  - Too much salt aggregates oil droplets

- Not a one-size-fits-all solution
  - CNC surface charge
  - Surface functionality
  - Oil:water ratio
  - [CNC]
  - Salt type
  - **Oil type**



Our recommendation: 20-50 mM NaCl

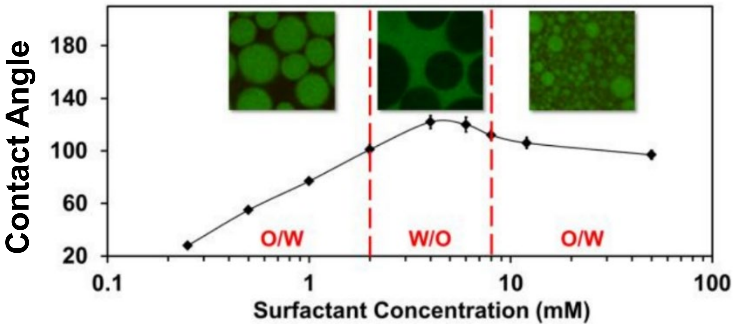
Fournier, Diaz, Cranston, Frostad. *Submitted*.

Instead of Salt: CNC + Co-Stabilizers

Zhen Hu

Phase Inversion & Enhanced Stability with Surfactants

Hu, Ballinger, Pelton, Cranston.
JCIS **2015**, *439*, 139.



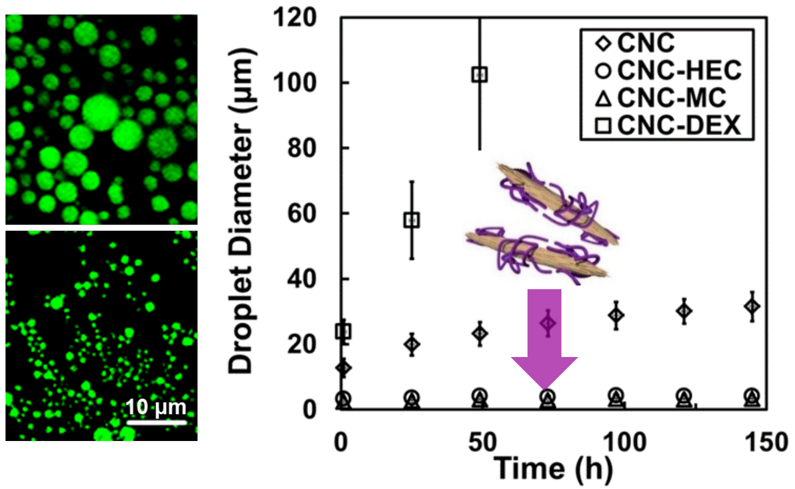
- *Cationic surfactants bind to CNCs = surface active*
- *Controls dispersed phase (either oil or water)*
- *Long term sta*

coalescence

Synergistic stabilization!

Smallest Emulsion Droplets: Polysaccharides + CNCs

Hu, Patton, Pelton, Cranston.
ACS Sust Chem **2015**, *3,* 1023.

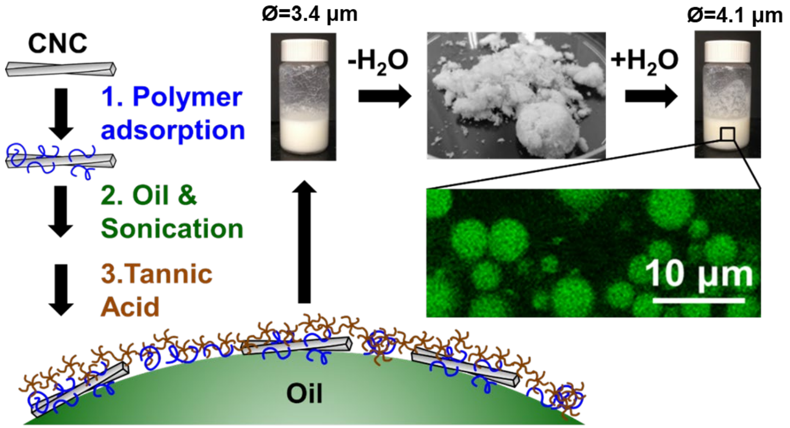


- *Stable to coalescence >1 year, no oil leakage (droplets ~ 2 µm)*

re-responsive emulsion gels (reversible)

Encapsulated Oil Powder

Hu, Marway, Kasem, Pelton, Cranston.
ACS Macro Letters **2016**, *5*, 185.

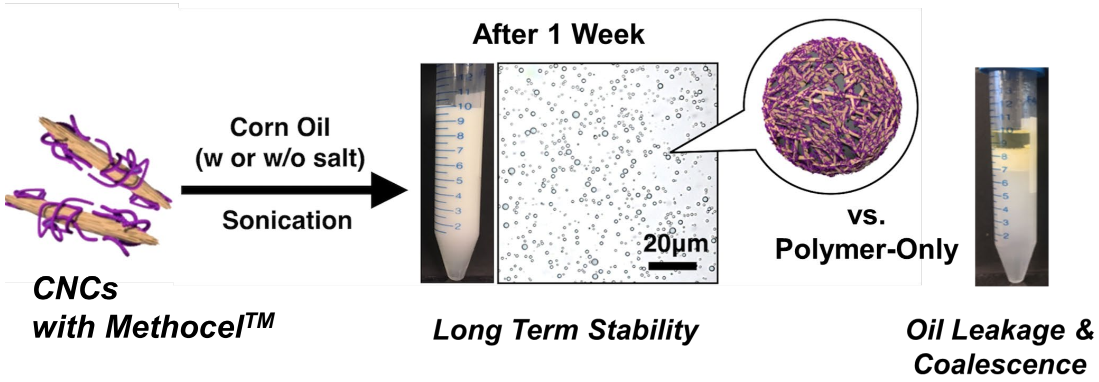


- *Uses plant polyphenol tannic acid to "set" the shell*
- *Stable to oven drying*
- *Dry & redispersible emulsion powder*
- *95% liquid oil (<0.5 wt% H_2O)*

Polysaccharides & CNCs

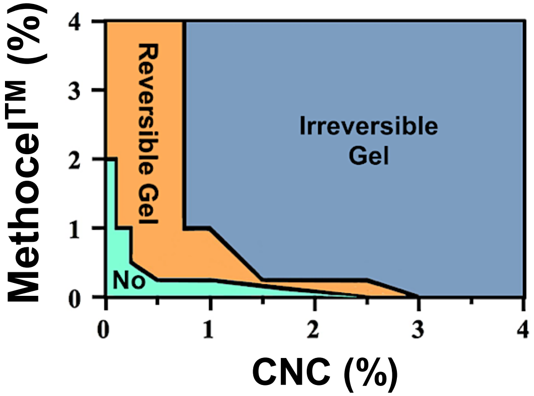
Lingli Liu

- Emulsion **extreme stability** was directly linked to adsorbed cellulose ether amount

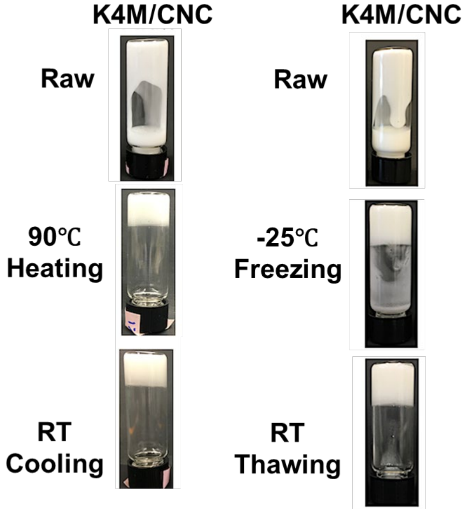


CNCs + Methocel™ make strong & tailorable gels at low concentrations - tendencies extend to emulsions & exhibit no oil leakage with cyclic heating, cooling, and freezing

Thermal Phase Diagram of Mixtures



Thermal Behavior of Emulsions



"Cooked" Vegetarian Patties

"Non-Melting" Ice Cream

Liu, Hu, Sui, Guo, Su, Mao, Cranston. *In preparation.*

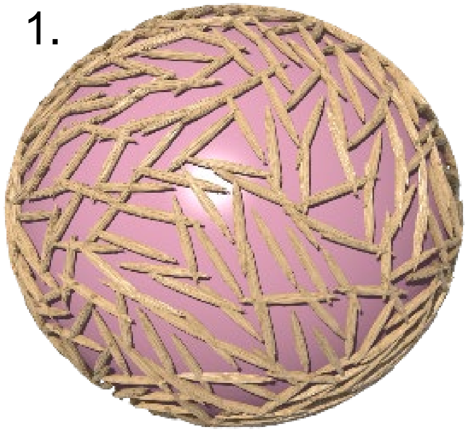
Roles of CNCs in Emulsions

Michael Kiriakou

Stephanie Kedzior

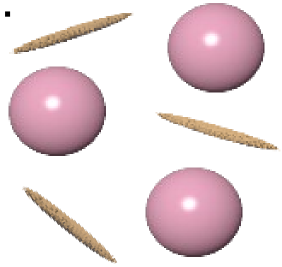
- By choosing your co-stabilizer wisely, you can tailor the role of CNCs in emulsions (and emulsion polymerization)

1.



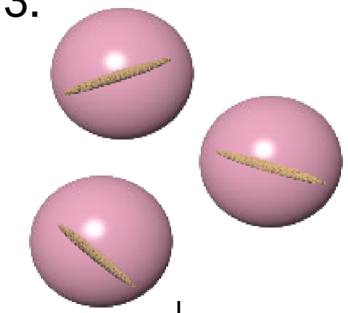
CNCs as droplet stabilizers when no other surfactant is present or if co-stabilizers are <u>attached</u> to CNCs

2.



CNCs in the continuous (water) phase if a non-interacting surfactant is used

3.



Hydrophobic (functionalized) CNCs inside oil droplets if non-interacting surfactant is used

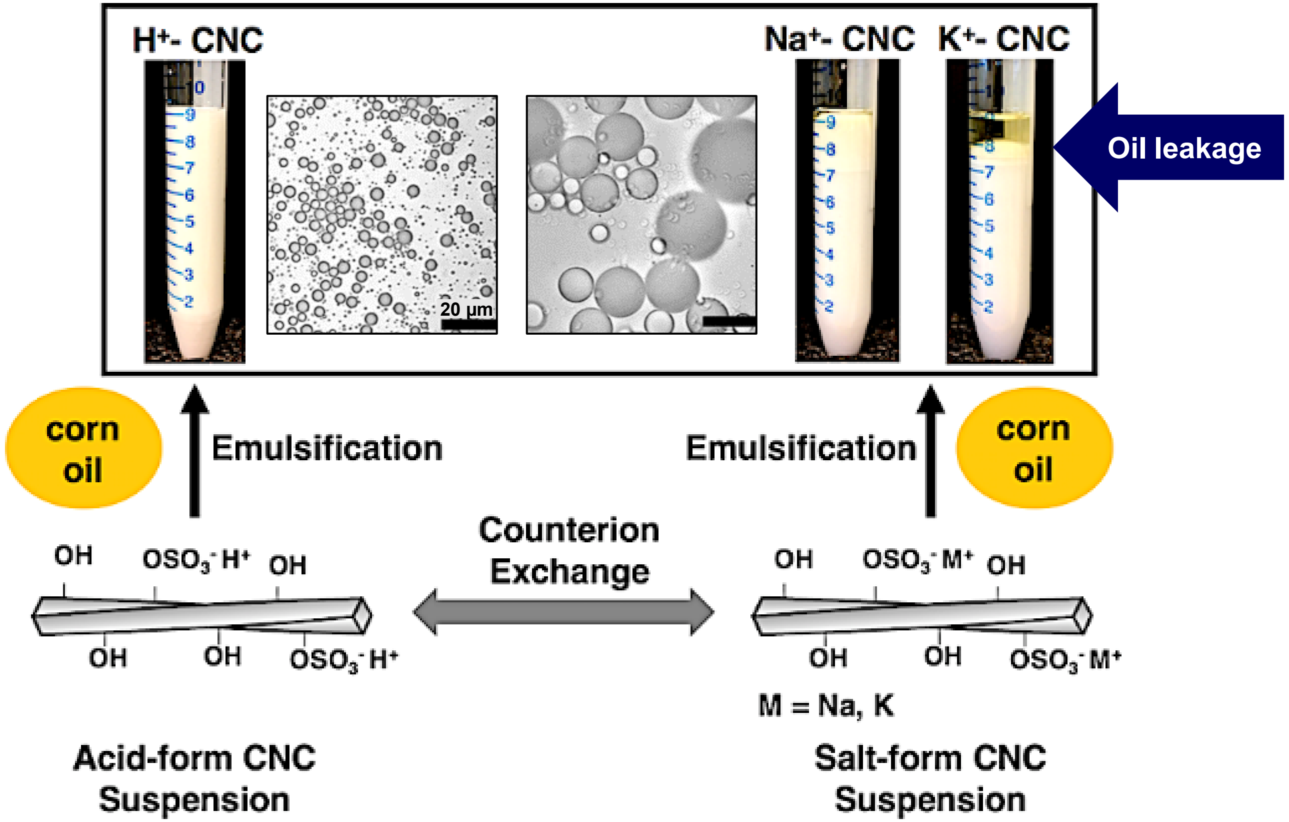
Kiriakou et al. *ACS Materials Au* **2022**, *2*, 176.
Kedzior, Kiriakou et al. *ACS Macro Letters* **2018**, *7*, 990.
Kedzior, Marway, Cranston, *Macromolecules* **2017**, *50*, 2645.
Kedzior, Cranston, *ACS Sustain Chem & Eng.* **2017**, *5*, 10509.

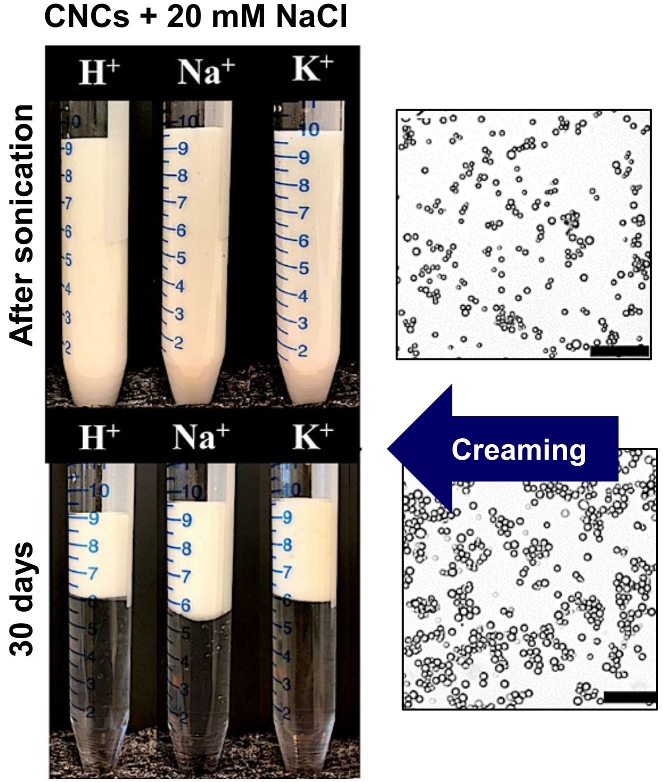
3. Do the counterions associated with CNCs matter to emulsion stability?

CNC Counterion Affects Emulsions

Lingli Liu

- We know counterion on sulfate half-ester affects CNC redispersibility, rheology, self-assembly, thermal stability: **What about emulsions?**





>20 mM NaCl makes emulsions equivalent & leads to creaming from density difference & droplet agglomeration

Yes! Counterion matters but adding salt masks the effect

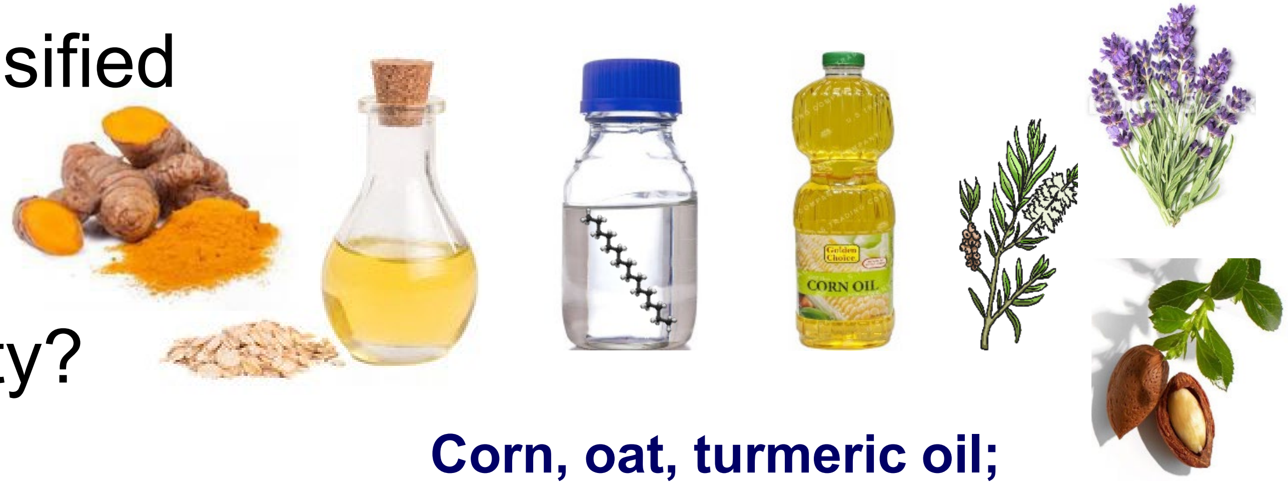
Liu, Hu, Sui, Guo, Cranston, Mao. *Industrial & Engineering Chemistry Research* **2018**, *57*, 7169.

4. What differences in emulsion stability and processability should be expected with different oil types?

Oil Types & Emulsion Stability

- All oils tested to date can be emulsified into stable oil-in-water emulsions

- What affects droplet size & stability?
  - Viscosity (a bit is good, too much is bad)
  - Polarity (can physically bond with CNCs)
  - Volatility (can be fixed with carrier oil)
  - Additives
  - Supplier(!)



Corn, oat, turmeric oil; essential oils (lavender, tea tree, jojoba); hydrocarbon oils (hexadecane, decane, dodecane)

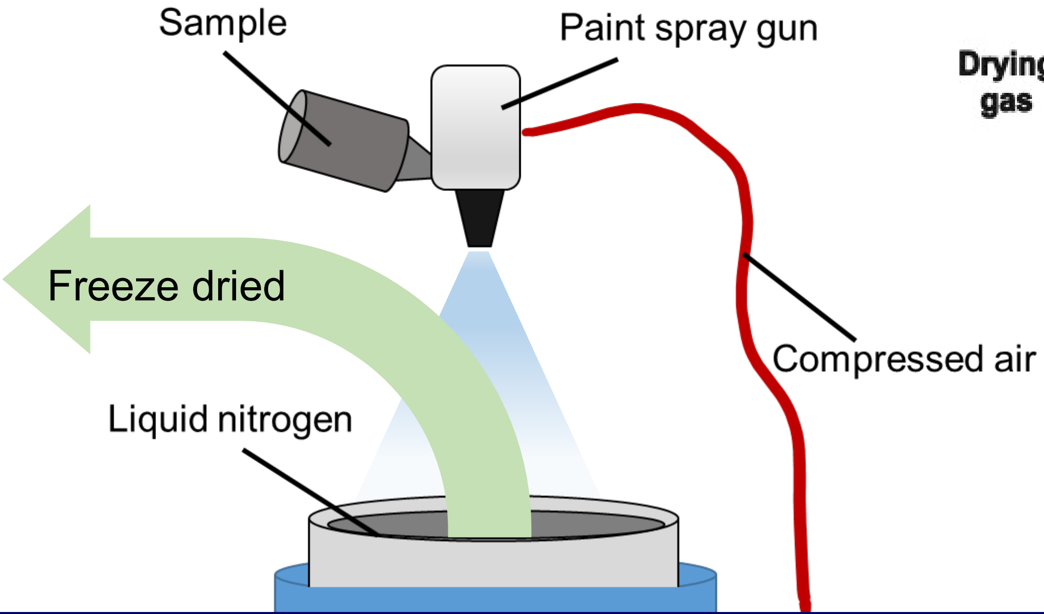
Liu, Hu, Sui, Guo, Cranston, Mao. *Industrial & Engineering Chemistry Research* **2018**, *57*, 7169.
Massicotte & Cranston. *ACS Sus. Chem. & Eng.* **2022**, *10*, 14914.

Scale-up of Dry Oil Powders

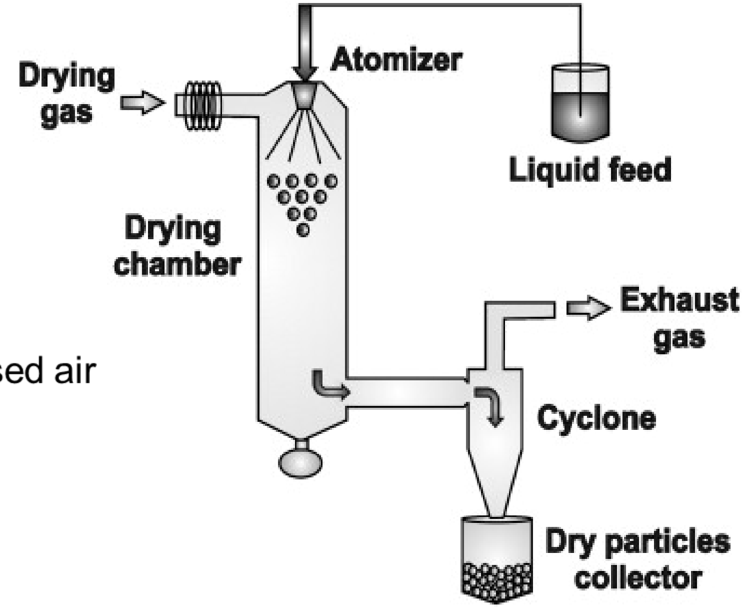
Marc Massicotte

1. Freeze drying (FD)

2. Spray freeze drying (SFD)



3. Spray drying (SD)



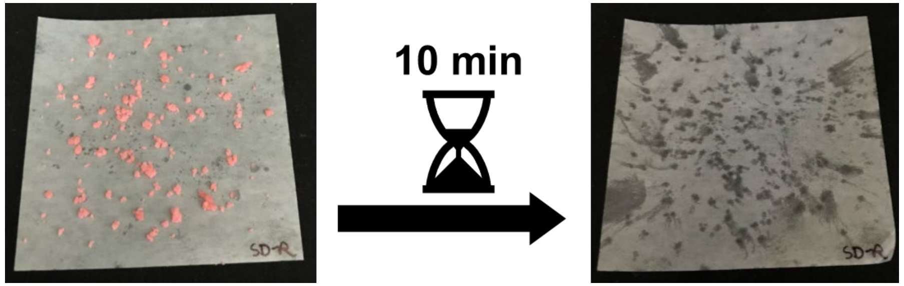
Spray drying = Fastest, least energy intensive, least droplet agglomeration (no freezing), but temperature and shear sensitive

Massicotte & Cranston. *ACS Sus. Chem. & Eng.* **2022**, *10*, 14914.

Scale-up of Dry Oil Powders

Marc Massicotte

- >90% oil in the “dry” powder
- Drying method affected morphology, oil release & redispersibility



SD powder (dyed oil) | Powder removed

	Mass released
Freeze dried	0.9%
Spray freeze dried	2.8%
Spray dried	1.0%

Highly volatile oils needed carrier oils for effective spray drying, dilution reduced shear during drying → high spray drying yields

Massicotte & Cranston. *ACS Sus. Chem. & Eng.* **2022**, *10*, 14914.

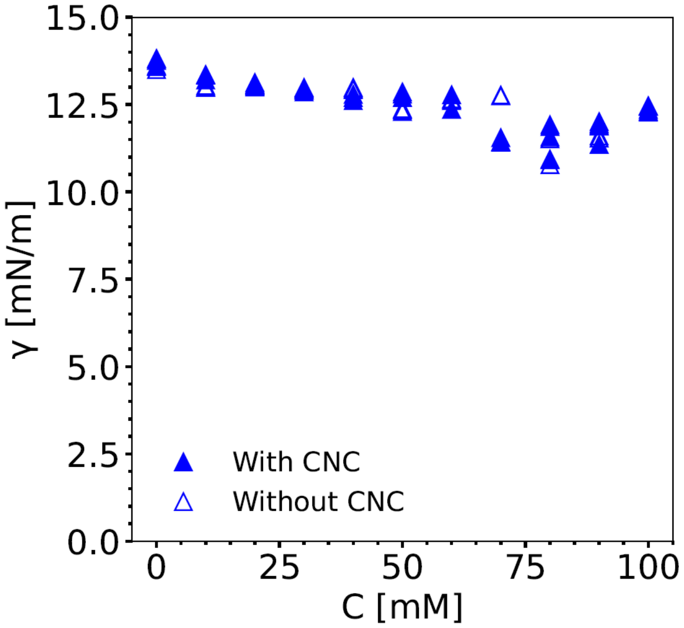
5. What are the best (and easiest) characterization methods to predict emulsion stability?

Large Toolbox – Interpretation Issues

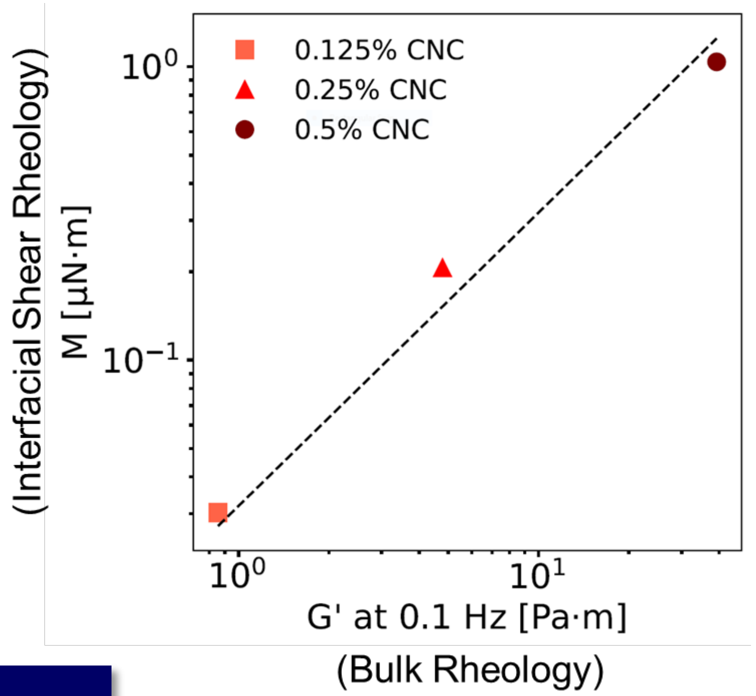
Roxanne Fournier

Microscopy
Light diffraction/scattering
(Mastersizer)
Light transmittance
(Lumisizer/Turbiscan)
Interfacial tension
Interfacial shear rheology
Bulk rheology
Neutron/x-ray scattering

Interfacial tension: noisy and natural occurring surface active species swamp effect of CNCs



Hard to separate the bulk rheology from the interfacial rheology



Our recommendation: Light diffraction with optical microscopy & bulk rheology

Fournier, Diaz, Cranston, Frostad. *Submitted.*

Conclusions

- CNCs with co-stabilizers extend the performance and tailorability of emulsions
- We can control the location and role of CNCs in emulsions
- Emulsion stability to coalescence (even with very low [CNC]) lends itself to a large range of processing methods and characterization techniques

CNCs can be part of a more sustainable approach to emulsions and latex-based formulated products!

Acknowledgements

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- Drs. Kevin Yager & Mike Reid – graphics
- Collaborators: Profs. Bob Pelton, Todd Hoare, John Frostad

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