Nanocellulose can reduce carbon emissions in food packaging and construction

Jeffrey P Youngblood

PURDUE MATERIALS ENGINEERING

Current Projects in Youngblood Group

Sustainable Nanotechnology

- PFAS-free surfactants for Fire Fighting Foam (w/ Martinez, MSE)
- Fatty Acid Amides for Sustainable Surfactants, Coatings and Lubricants (w/ Martinez, MSE)
- Sustainable Quench Oils for Austempering (w/ Titus, MSE)
- Cellulose Nanomaterials for Food Packaging
- Recycling of C103 Metal Additive Powders (w/ Titus, Mort, MSE)

Ceramics

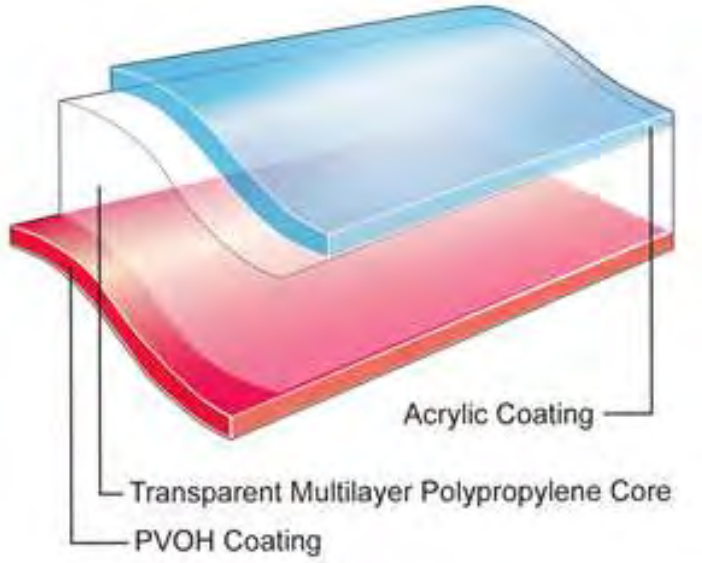
- Aligned Grain Alumina for Enhanced Transparency (w/ Trice, MSE)
- HITEMMP: High Efficiency SiC High Temperature Heat Exchangers for More Efficient Turbine Engines (w/ Trice, MSE; Wang, MIT)
- Direct Ink Writing Additive Layer Manufacturing (3D printing) of Ceramic Matrix Composite (w/ Trice, MSE)

Infrastructure and Other

- Environmental Performance of Water Infrastructure (w/ Whelton, CIVL/EEE)
- Direct Ink Writing Additive Layer Manufacturing (3D printing) of Cement Structures (w/ Zavattieri, Olek, CIVL)
- HESTIA: Cellulose-Cement Composite (C3) for Residential Construction (w/ Weiss, OSU-CIVL; Landis, UMaine, and others)
- CMOS-compatible Aerogels for Extreme Thermal Isolation (w/ Marconnet, ME; Ruan, ME, Wei, ME)

Food packaging

- Lots of concern over single use plastic packaging
- But food packaging is functional
  - Food waste is ~20x larger CO2 than entire plastics industry (~10 gt vs ~0.5 gt)!

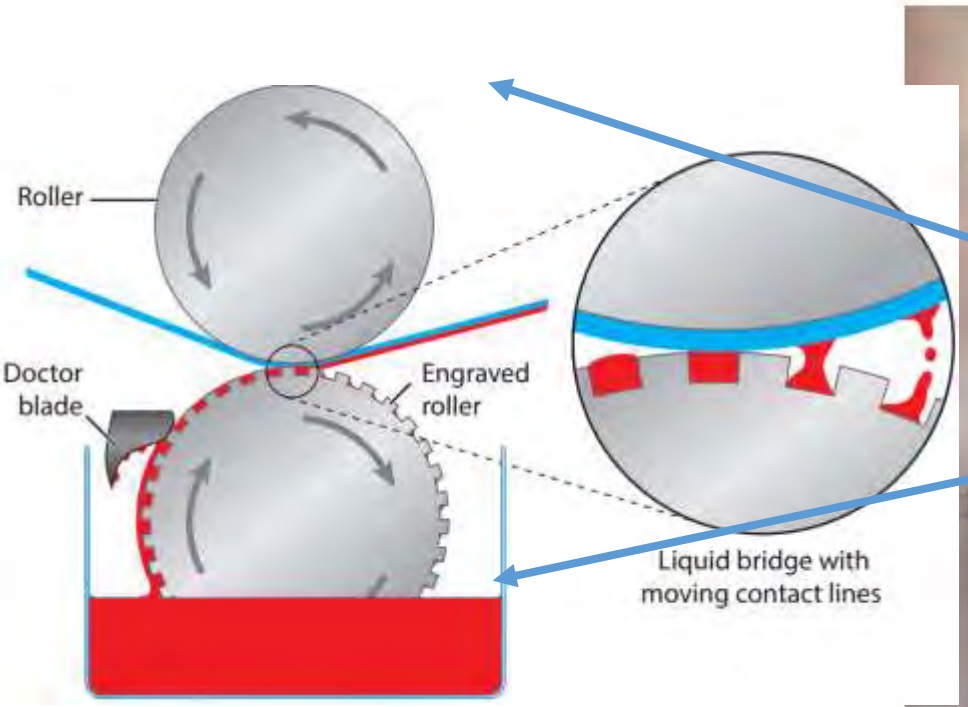


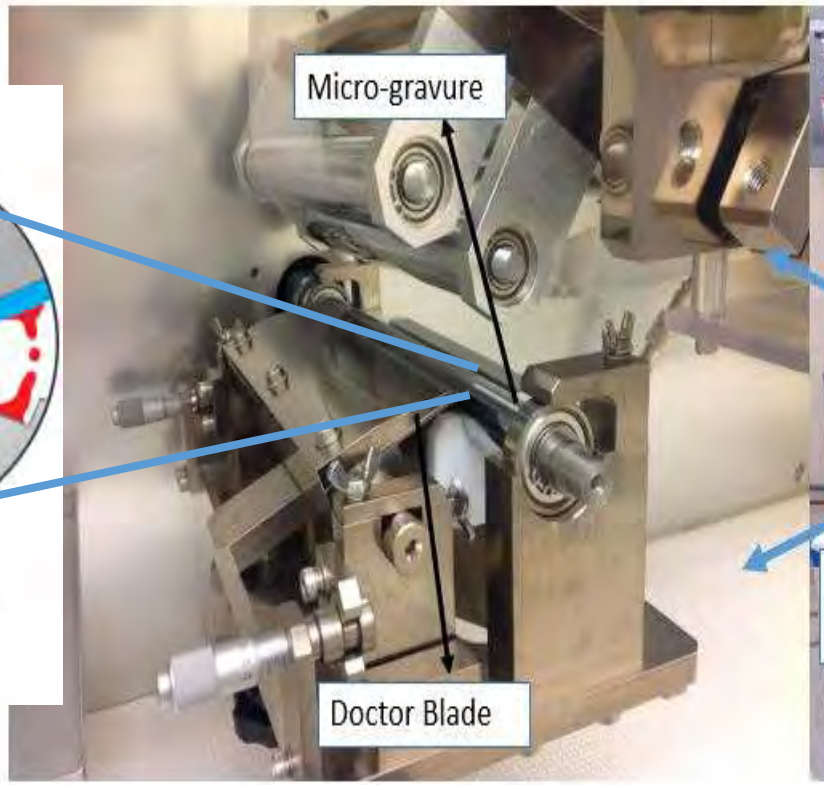
https://www.jindalfilms.com/product-detail/?jpid=239&jpsomid=1

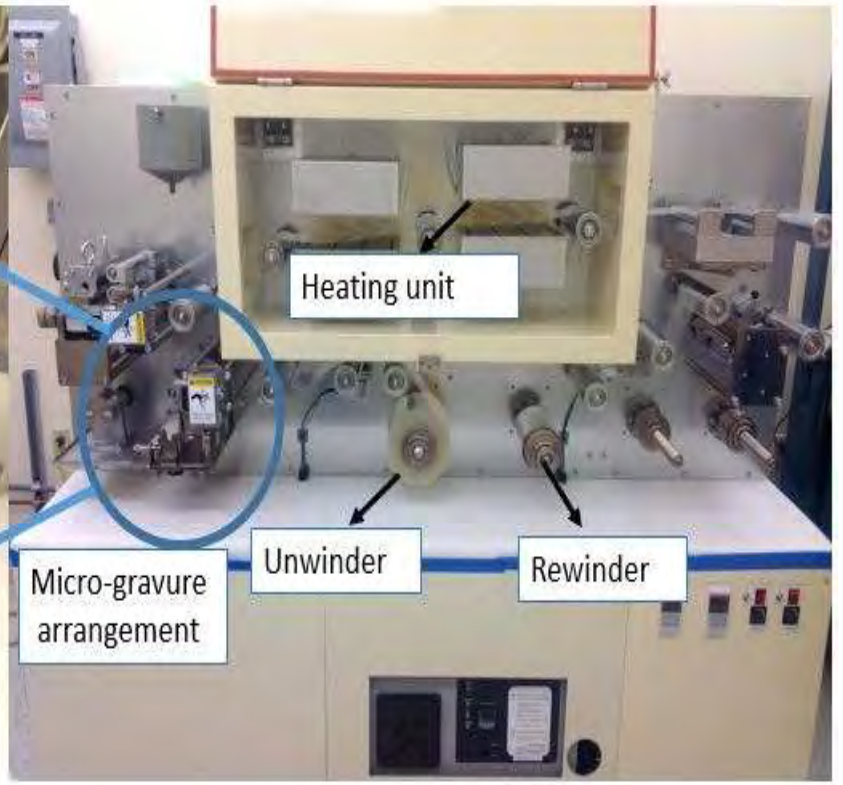
Can we use CNC as a transparent barrier layer?

Microgravure coating is an industrial process

- Liquid transfer rate controls the overall coating quality/thickness.
- Roller speed, substrate speed, ink viscosity control the liquid transfer rate.





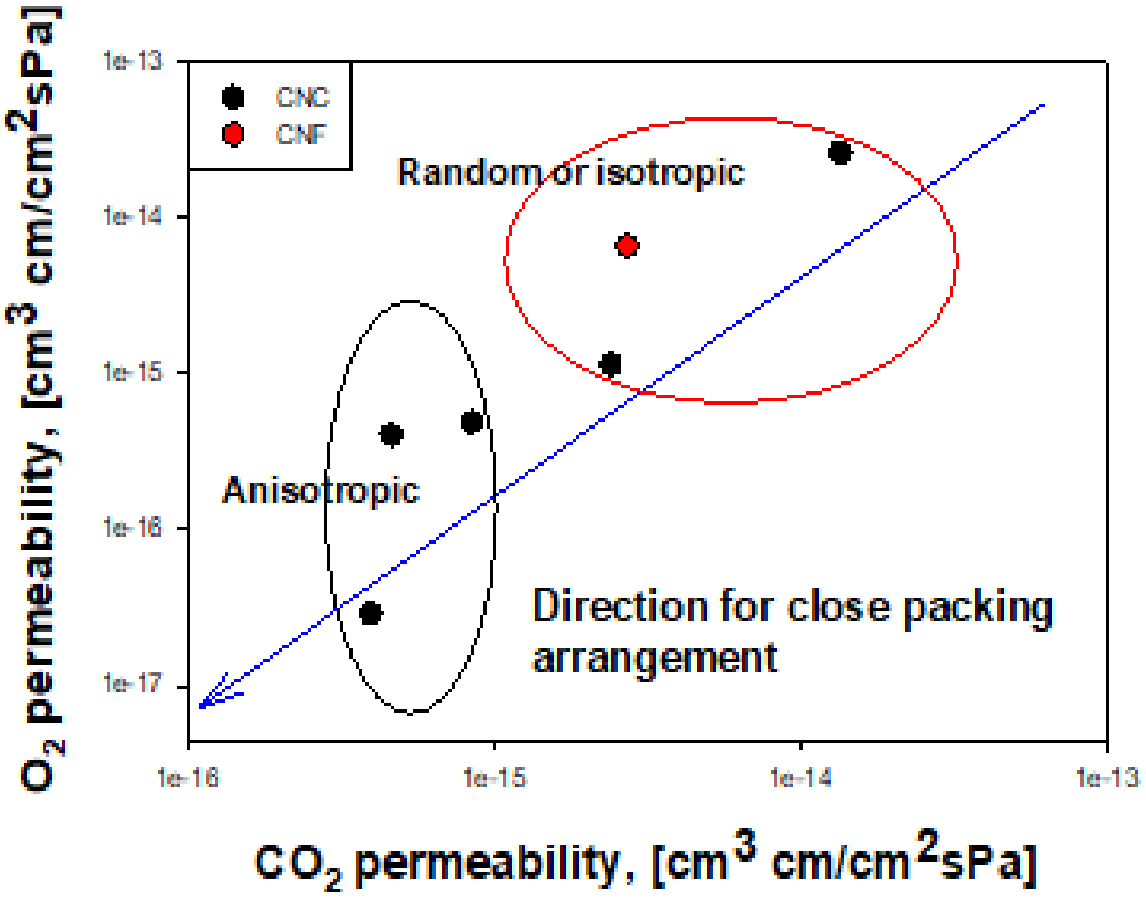


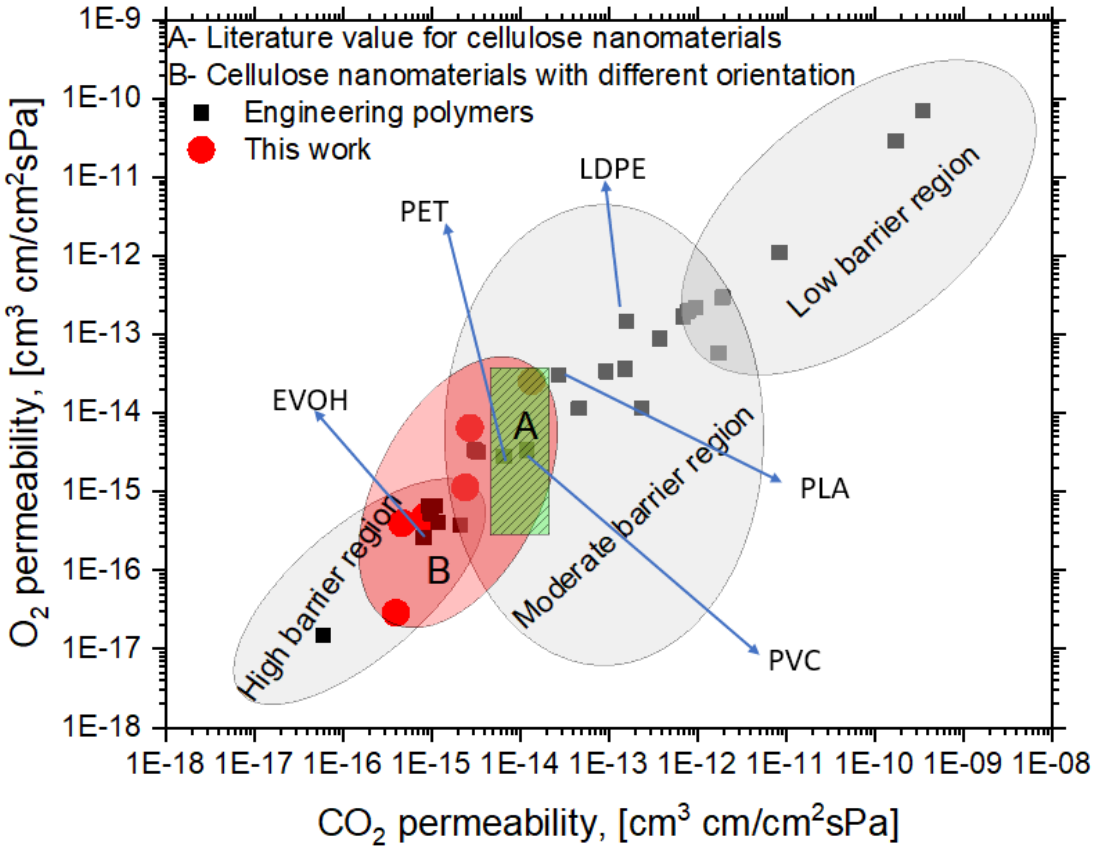
Whatever process is used with sustainable materials (ie nanocellulose) needs to be R2R

R2R gravure coating of CNC is possible

- Low speed (m/s), short run (50-100m) R2R gravure coating of CNC was performed
  - High quality smooth films
  - High transparency
  - Good wet-out with corona treatment, good adhesion

Increasing order parameter enhances the barrier property





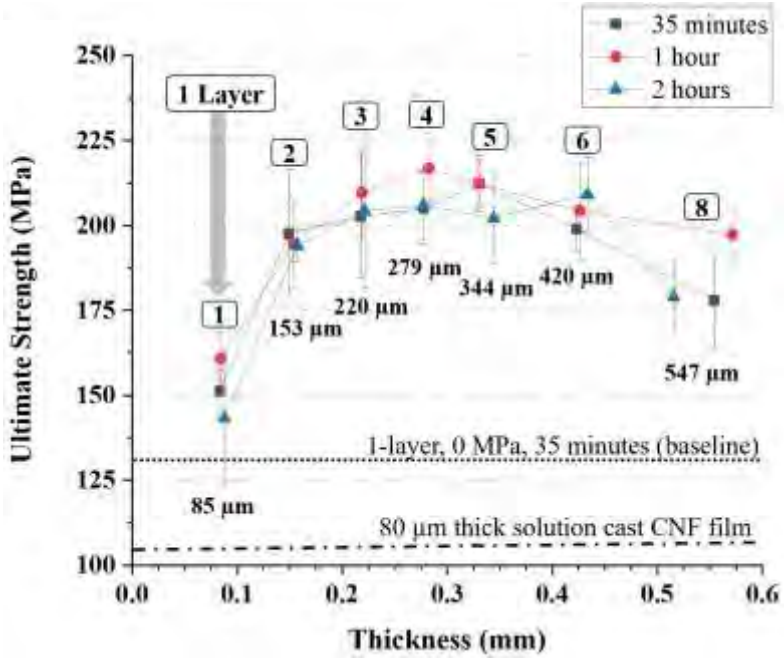
OTR and CO_2TR of aligned CNC is as high as high barrier polymers (EVOH)!

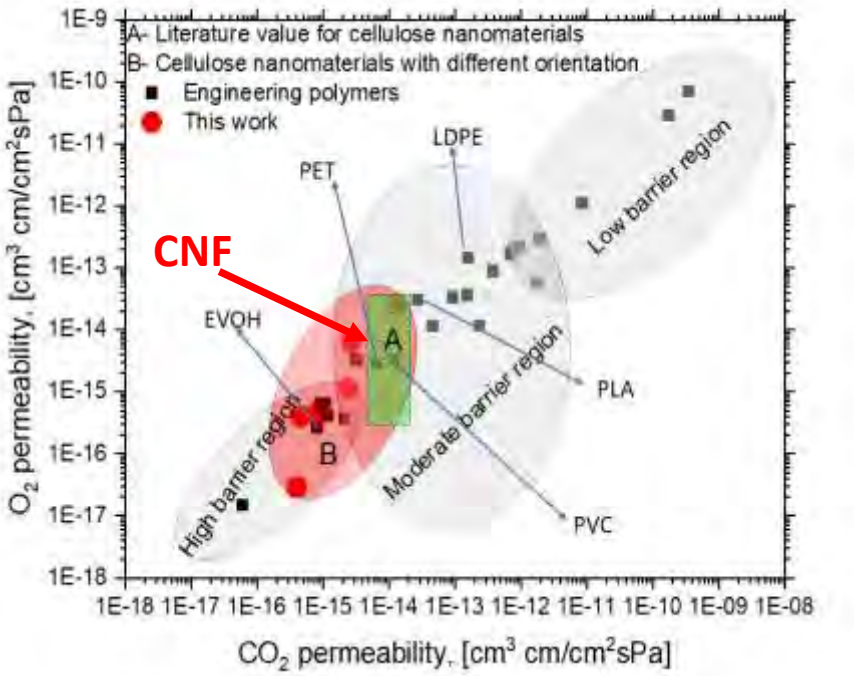
(Not surprising as low OTR needs high hydrophilicity, high crystallinity, and low free volume)

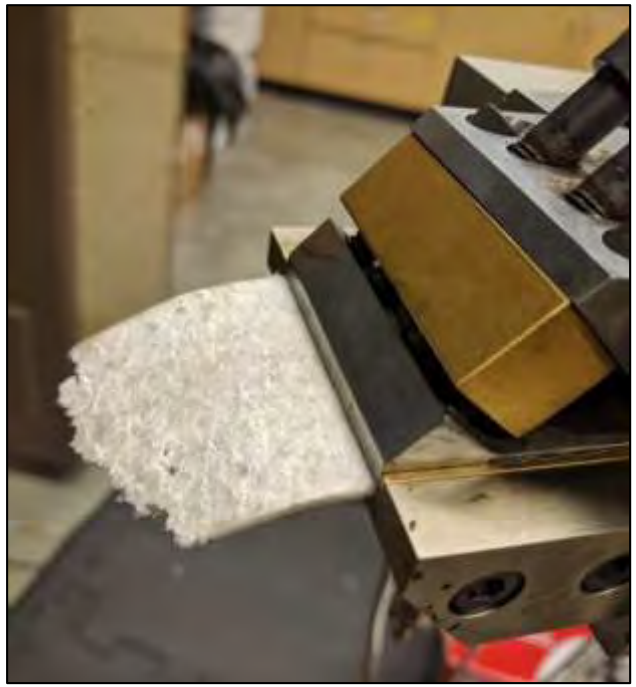
What about CNF?

CNF is great but has its drawbacks

- CNF is mechanically strong (strength = 207 MPa), stiff (E = 11.0 GPa) and light weight (ρ = 1.35 g/cm^3).
- CNF has good OTR, and smaller pore size than typical paper
- However, processing can be difficult due to low solids and paper-based methods.

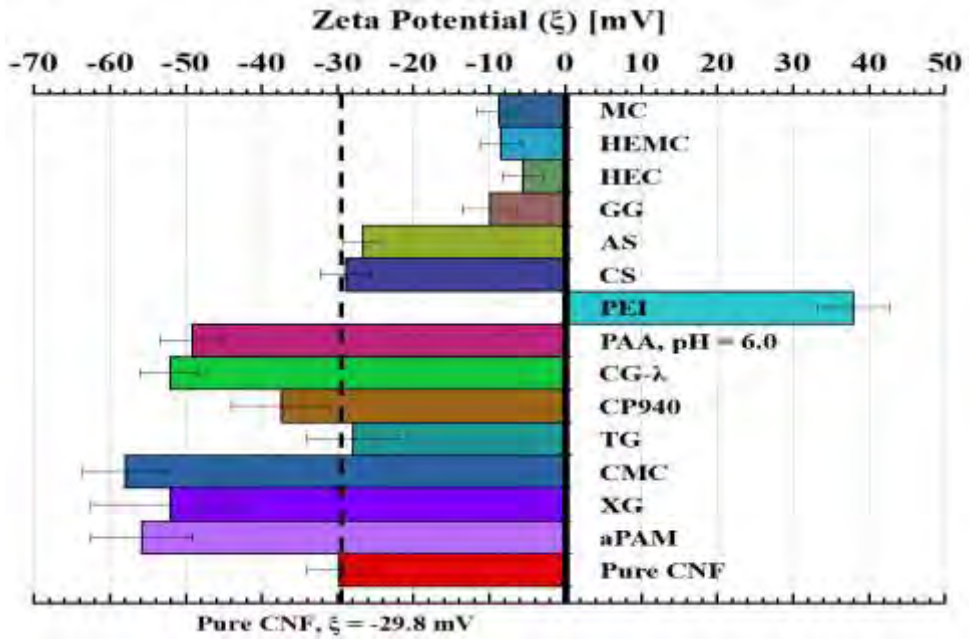


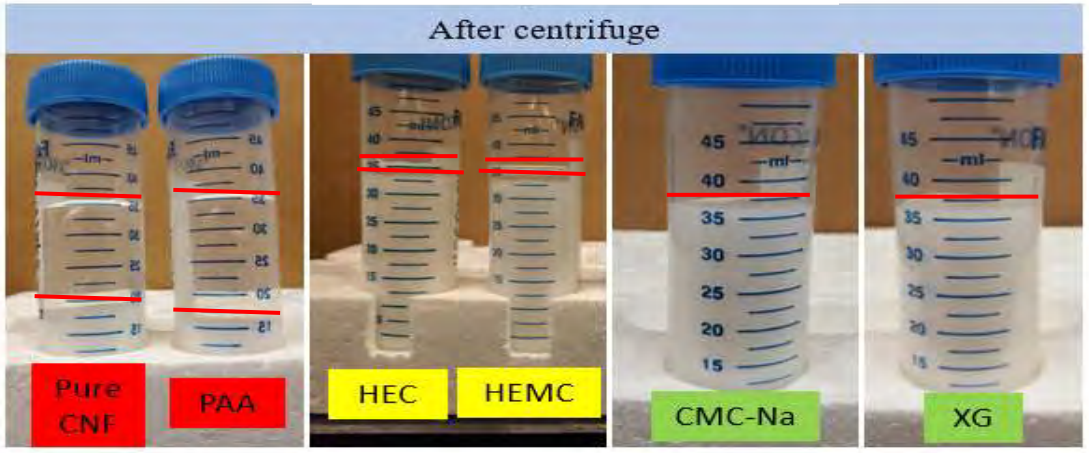




What if we could add something to retain the water in the CNF?

- A variety of water binding polymers were evaluated
- 10:1 CNF:polymer were evaluated ability by centrifugation to speed settling kinetics
  - Red highlighted polymer = more than 20 ml of water extracted
  - Yellow highlighted polymer = ~2.5 ml extracted
  - Green highlighted polymer = no perceivable water extracted
- Large magnitude of zeta seems necessary but not sufficient
  - Possibly a colloidal stabilization effect





Processing Aid	Acronym	Processing Aid	Acronym
Methyl Cellulose	MC	Carrageenan-lambda	CG-λ
Hydroxyethyl methyl Cellulose	HEMC	Carbopol 940	CP940
Hydroxyethyl Cellulose	HEC	Tragancanth Gum	TG
Guar Gum	GG	Carboxymethyl cellulose	CMC
Konjac Flour/Glucomannan	KM	Xanthan Gum	XG
Amphoteric Starch	AS	Anionic Polyacrylamide	aPAM
Cationic Starch	CS		
Poly(ethyleneimine)	PEI		
Polyacrylic Acid sodium salt	PAA		

Selected candidates (in green)

CMC can allow CNF to be processed like a polymer

Brabender mixing of CNF with the addition of CMC
Video is played at 1x speed

~15 wt% CNF/CMC mixture

- CMC disperses CNF and provides a more Newtonian Rheology that, at higher solids (15-30%), is still flowable
  - Allows processing with typical polymer methods: high shear mixing, extrusion, etc.

CNF/CMC has nice properties and is now processable, so can we use it for food packaging?

We can mold it?

But that could be a really expensive package!

How about a coating?

- A coating would lower amount used so lower cost
  - CNF could be used for enhanced strength, stiffness, and barrier properties
- Substrate would have to be VERY cheap to justify expense.
- Ideally, it would be compostable, etc to take advantage of CNF being cellulose

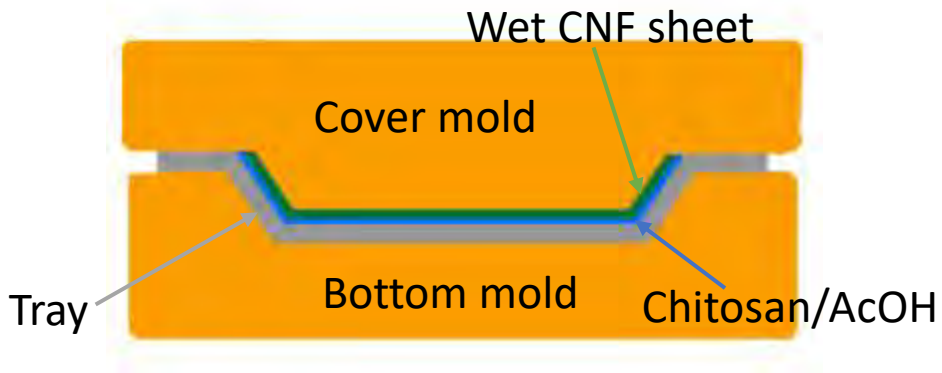
So, What?

Molded Pulp

- MP strengths:
  - Biodegradable, compostable.
  - Sustainable
  - CHEAP!
- MP weaknesses
  - Weakness (ie low strength and stiffness)
  - No barrier properties (about the same as an open container!)

Overmolding of CNF onto MP is possible

- Cellulose-Cellulose bonding can be promoted by cationic polymers
- Wanted to stay "biobased" → Chitosan!
- So now the method is:



Spray chitosan solution onto MP

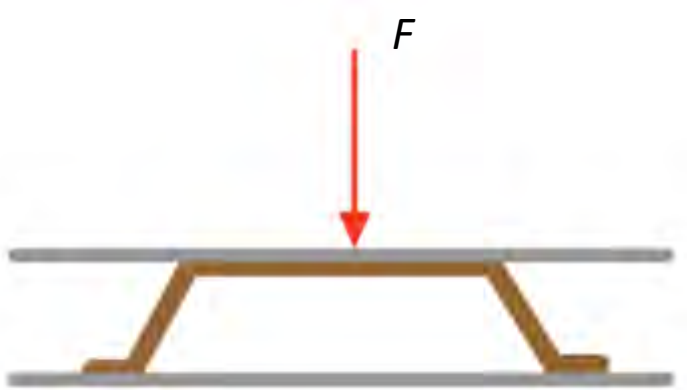
Cover MP with extruded CNF sheet

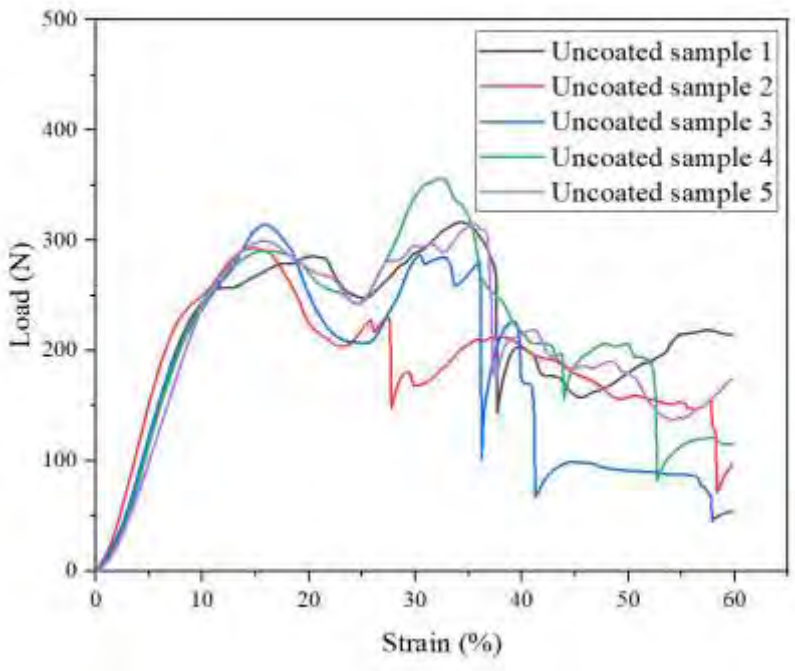
Close mold and heat in oven

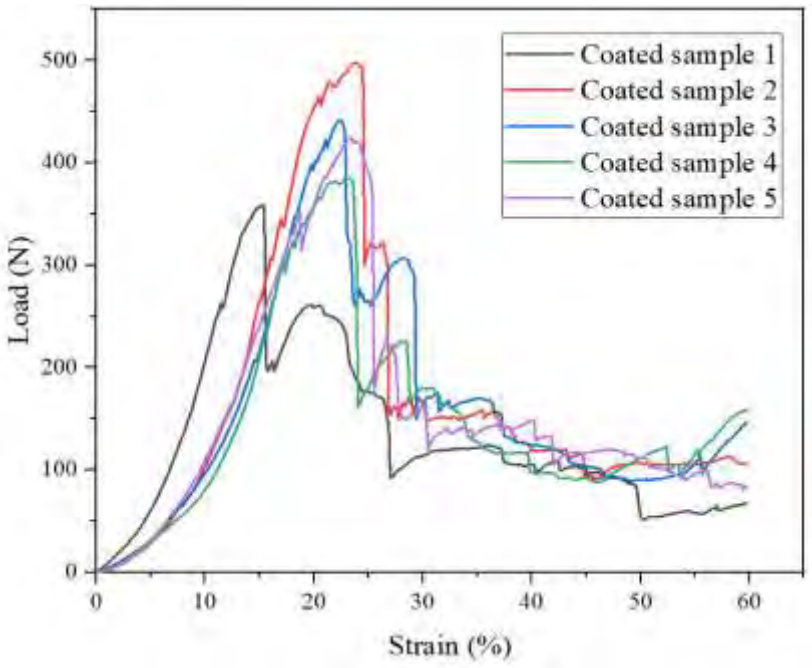
- ~200 μm (dry) CNF coating with no large delaminations
- The coating surface is smoother compared with MP

“Crush-strength” is enhanced by CNF coating

- “Crush-strength” is an important mechanical property of trays, clamshells, etc.
  - MP is particularly weak.
- As it sounds, it is a compression test of an entire package.
- Data is messy as it is geometry dependent with buckling modes







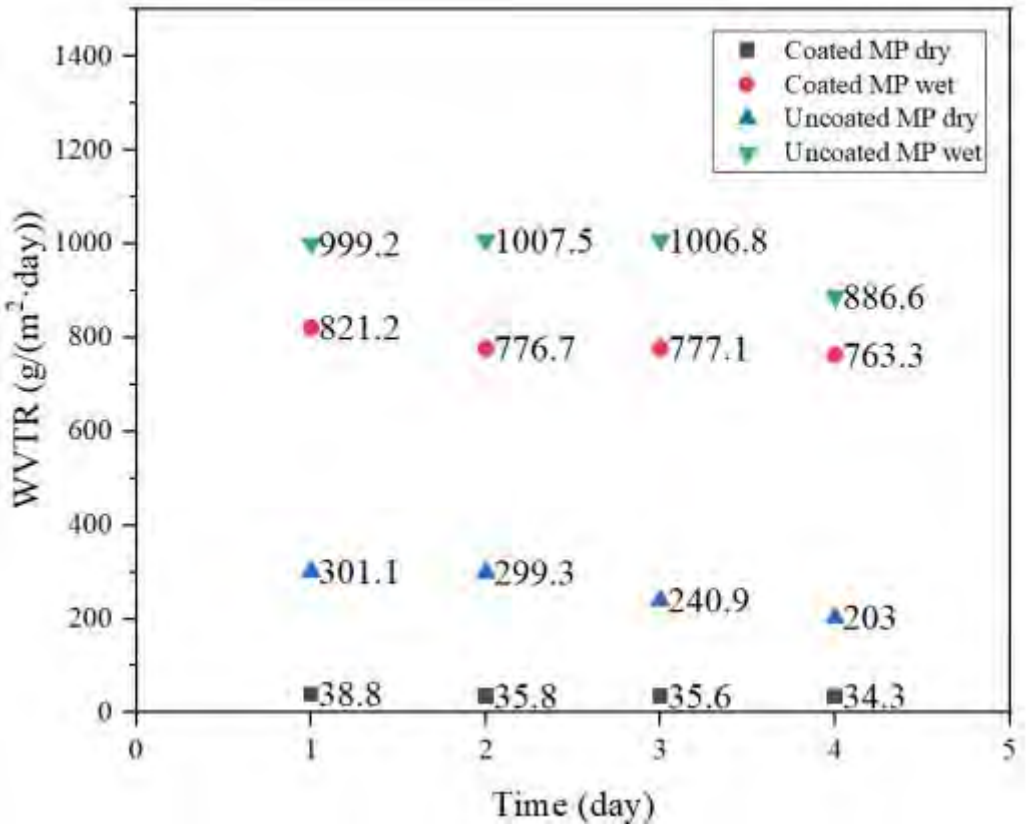
CNF greatly increases crush-strength

CNF also increases stiffness

CNF coating improves grease resistance and moisture barrier

- Grease resistant testing performed under TAPPI T559 standard, AKA the "kit test"
  - Kit = 1 for uncoated MP (ie lowest rating)
  - Kit = 12 for coated MP (hard to do for MP as it is so porous)

- Moisture barrier is a particular issue for fresh foods (fruits, veggies, meat, etc).
  - Moisture barrier can be very humidity dependent
  - MP is particularly poor
- WVTR was measured by perm cup at 20C
  - Dry condition: 0% RH, 50%RH outside.
  - Wet condition: 100% RH, 50% RH.

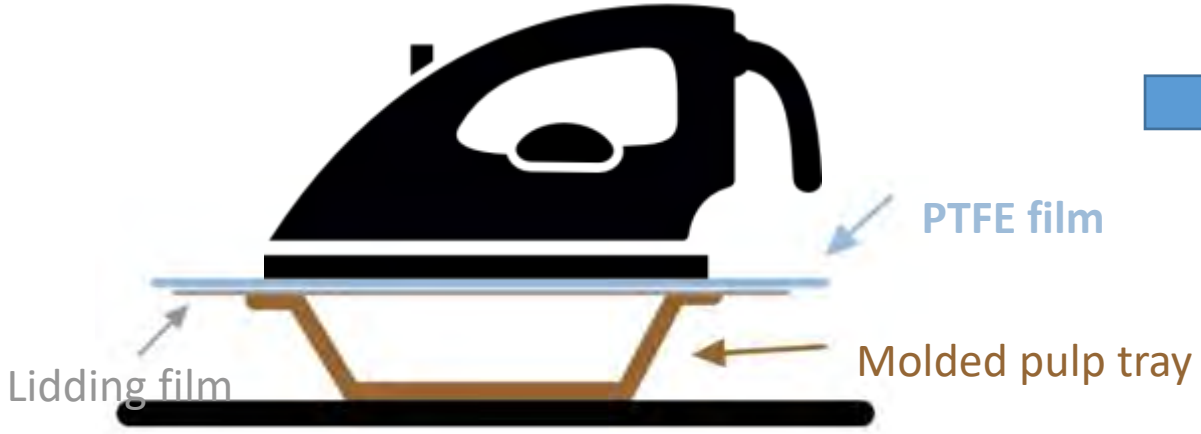


CNF coating caused major WVTR decrease to improve barrier!

(Although most of benefit was lost at high humidity)

Can these trays be “lidded”?

- “Lids” are plastic film tops on trays – hence these are called “lidded trays”
  - Typically, PET, PP, PE.
  - Typically adhered with low MP adhesive thermally or ultrasonically.
- Here two different lidding films used: For
  - Commercial PET lidding film coated with a heat-seal.
  - BOPLA, with starch glue around edge.
- A clothes iron is used for heat sealing (neat trick)



Test in real life! Fruit storage test with berries

- Yuk, sealed berries grew mold

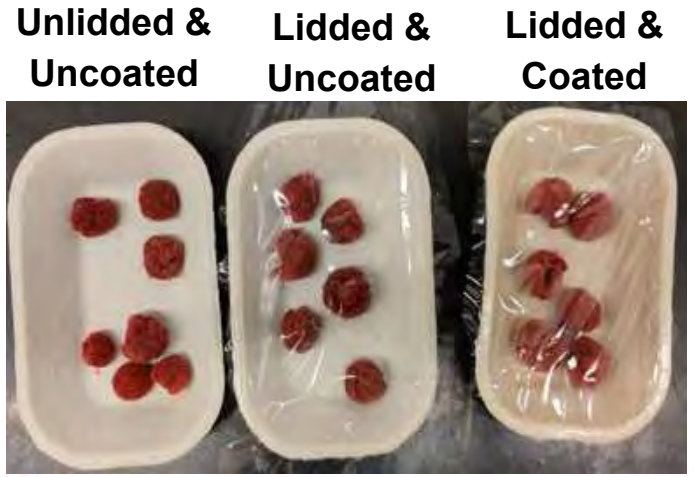
  - There is a reason berry clamshells have holes – to move air through to keep berries dry.

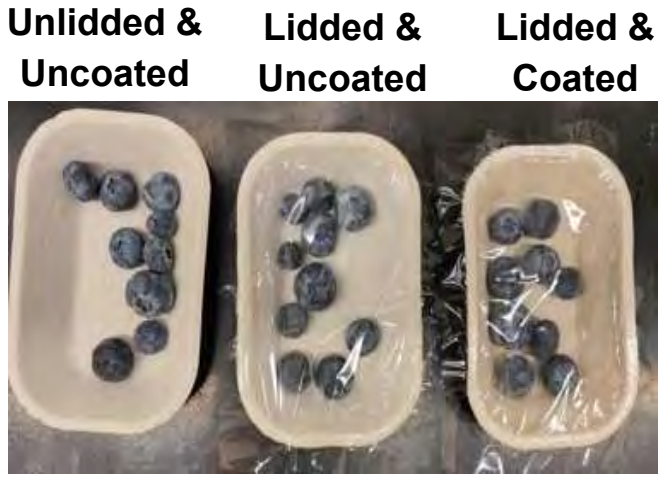
So, what to do?

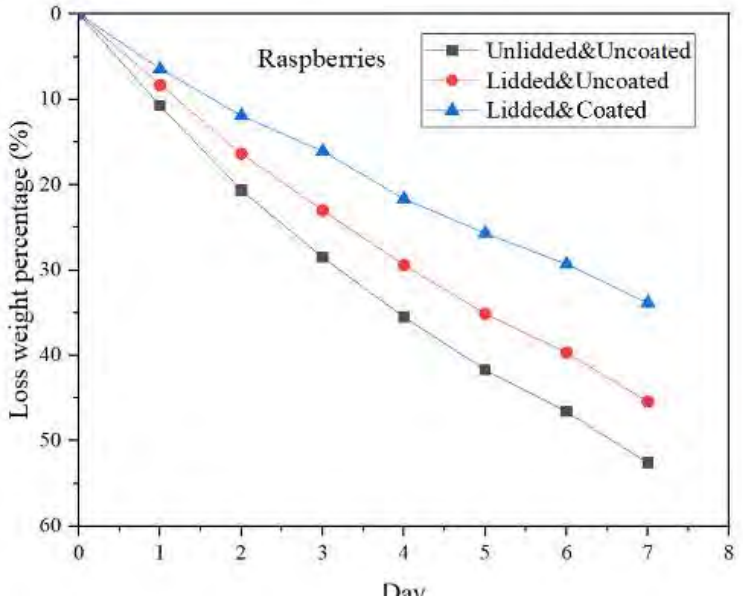
UV-sterilization!

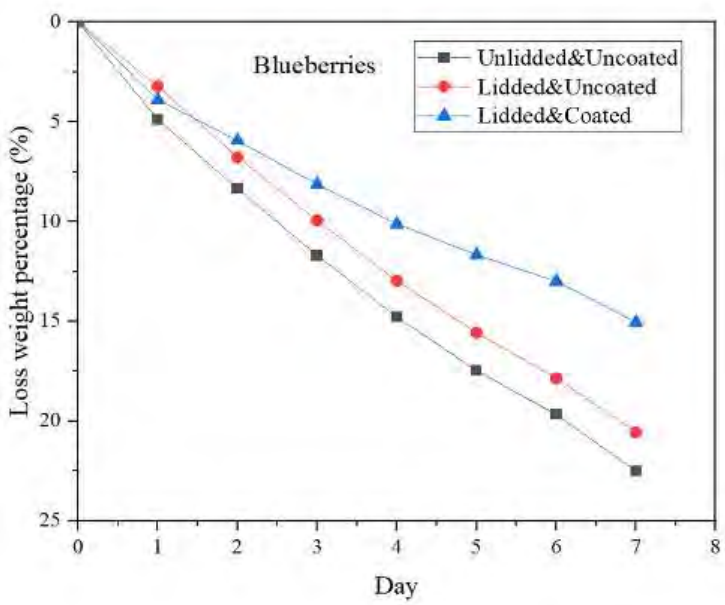
Lidded Coated MP trays can extend berry shelf-life!

- PLA lidding film with and without CNF coating
  - CNF coatings reduce water loss, doubling the time
  - Raspberries visually retained more color and were less "mushy"
- Notes:
  - Berries were UV-sterilized after sealing to prevent fungus growth
  - Films sealed with chitosan slurry and clothes iron.
  - Raspberries are non-climacteric (don't further ripen when picked) and blueberries are semi-climacteric)









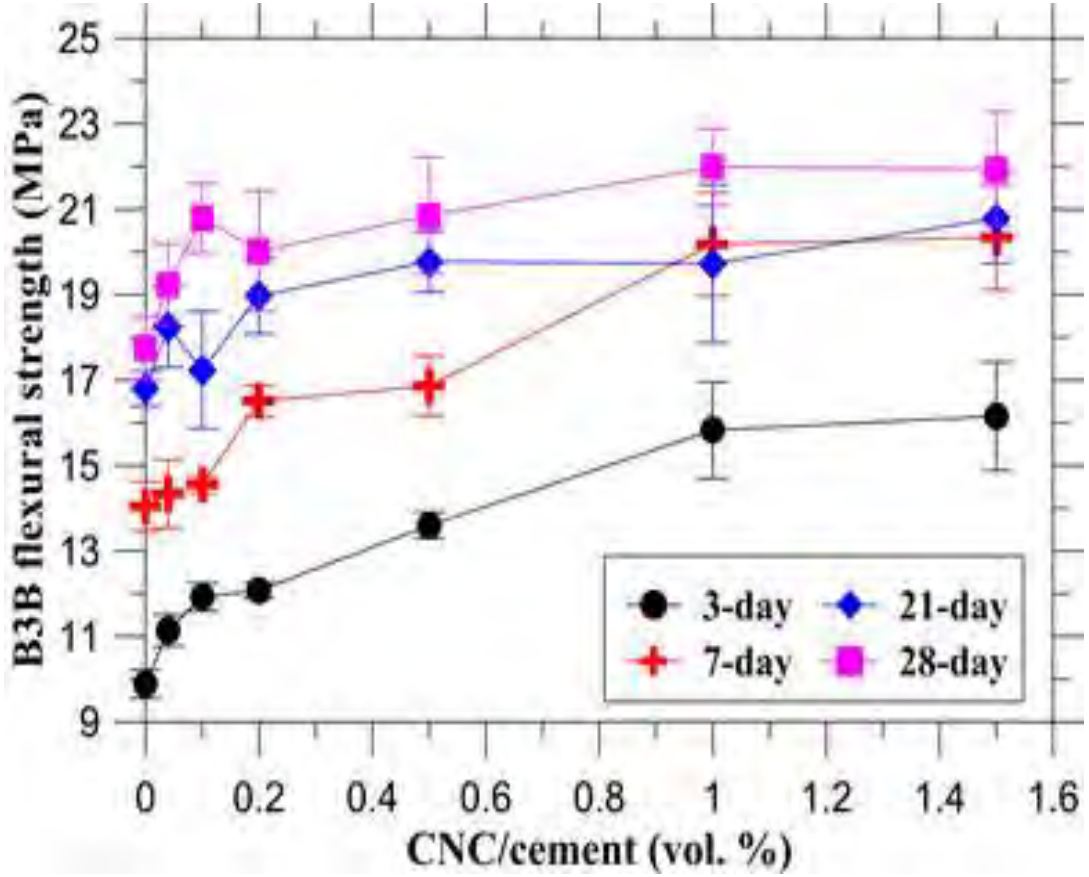
Proof-of-Concept that CNF coated MP lidded trays can preserve food!

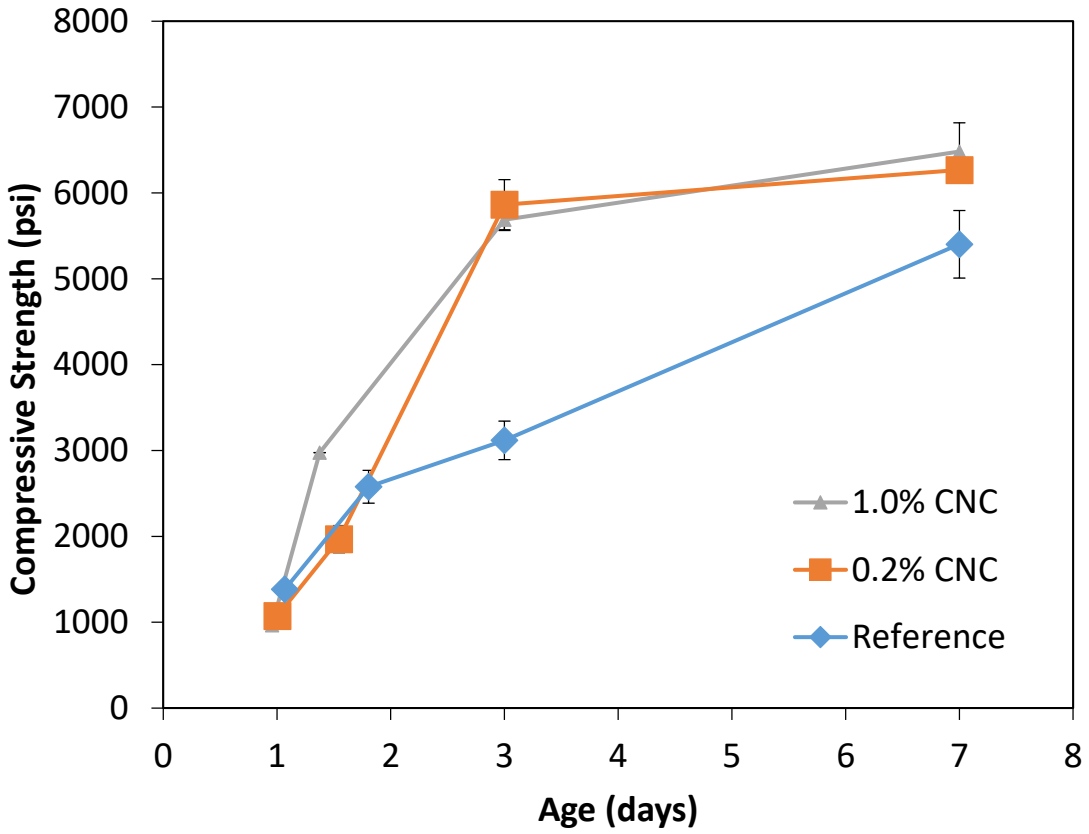
What else can CNM do for us?

Cement

CNM in cement and concrete

- ~15 years ago we found that CNC can increase cement strength

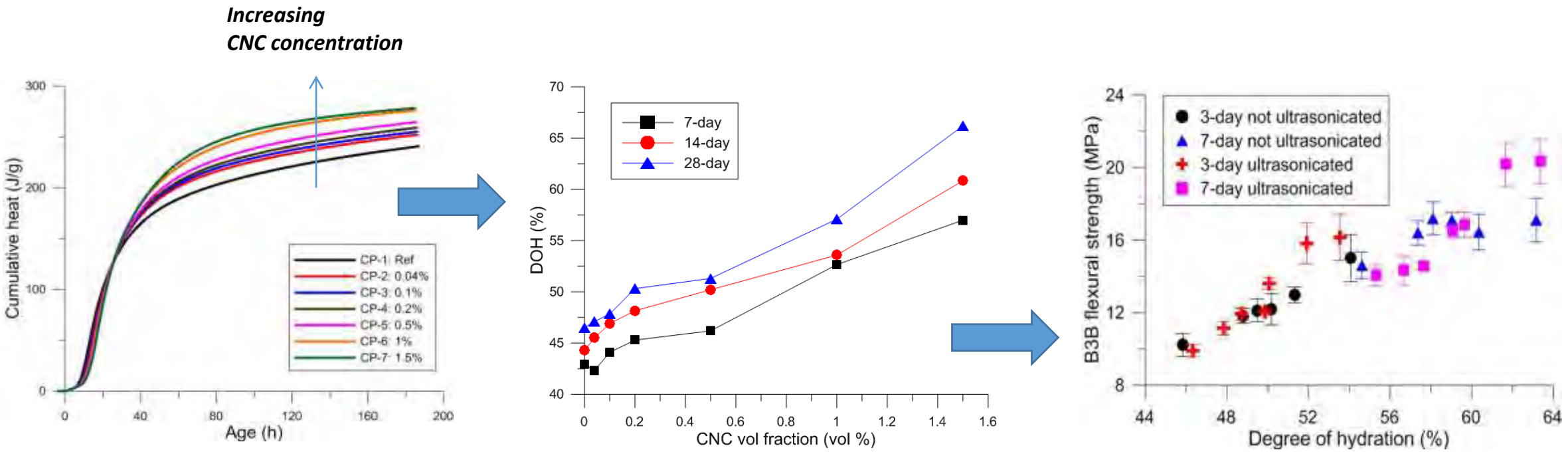




Note: CNC Vol% is relative to initial dry cement powder NOT final material

- Better at early than late strengths

Degree of Hydration (DOH) is increased which leads to higher flexural strength



- Heat release and therefore Degree of Hydration (DOH) is increased with CNC
- CNC induces a delay in onset of cure
- Flexural strength scales with hydration (as expected)

How do CNCs help hydration?

What do we know?

- CNCs are too small to bridge microcracks
- No evidence of IC
- CNCs stabilize particles
- CNCs increase DOH more than SP

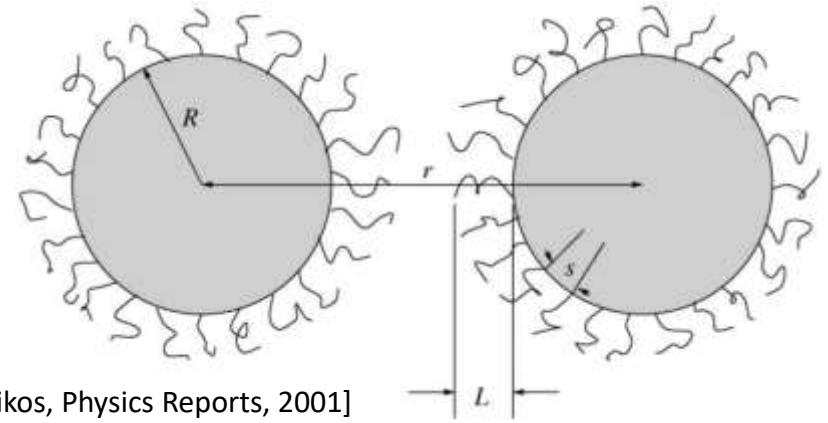
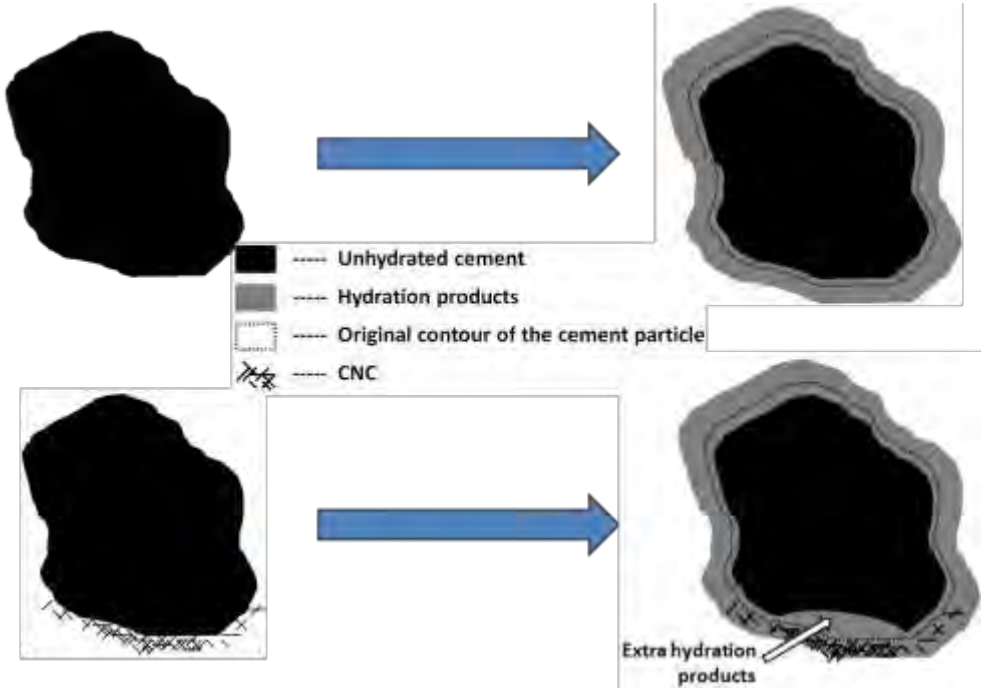


Image from [Likos, Physics Reports, 2001]

Short Circuit Diffusion (SCD)

- Hydration layer around cement particle is dense so diffusion of water is very slow after this layer formed.
- CNCs adhering to cement particles can transport water through the hydration products shell into the unhydrated core, and hence improve DOH.
- The only prerequisite is the attachment of CNCs on to cement and incorporation into hydration layer. No particle separation is needed!



CO2 emissions are a pressing need for infrastructure

2020 TO 2030 - THE DECADE TO MAKE IT HAPPEN

In this key decade, we will accelerate our CO_2 reductions through the following actions and initiatives:

- increased clinker substitution – including fly ash, calcined clays, ground granulated blast-furnace slag (ggbs), and ground limestone.
- fossil fuel reductions and increased use of alternative fuels
- improved efficiency in concrete production
- improved efficiency in the design of concrete projects and use of concrete during construction, including recycling
- investment in technology and innovation
- CCUS technology and infrastructure development

In addition, we will strive for and collaborate in establishing a policy framework to achieve net zero concrete.

2030 CO_2 REDUCTION MILESTONES:

(Compared with 2020 Baseline)

Concrete

25%

CO_2 reduction per m^3 of concrete by 2030

Cement

20%

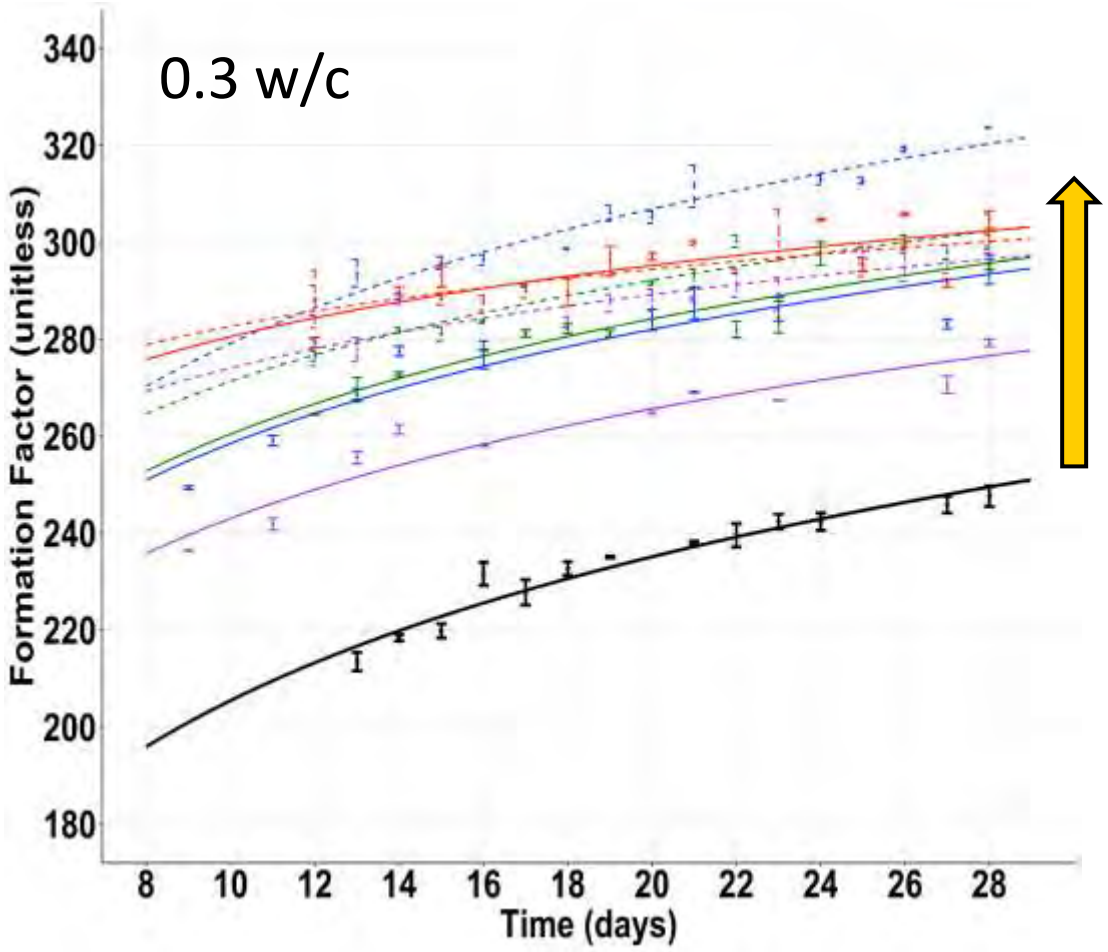
CO_2 reduction per tonne of cement by 2030

As with DOH and strength, Formation Factor increases with CNC addition to Type V cement

- Durability = resistance to deterioration processes
- Durability is determined by transport processes at pore level
  - Permeability which is from diffusivity which is from porosity

Formation Factor (FF)

- A property used to describe concrete durability by quantifying transport of porous materials
- A higher formation factor *indicates* slower ions movement, lower porosity and/or porosity tortuosity



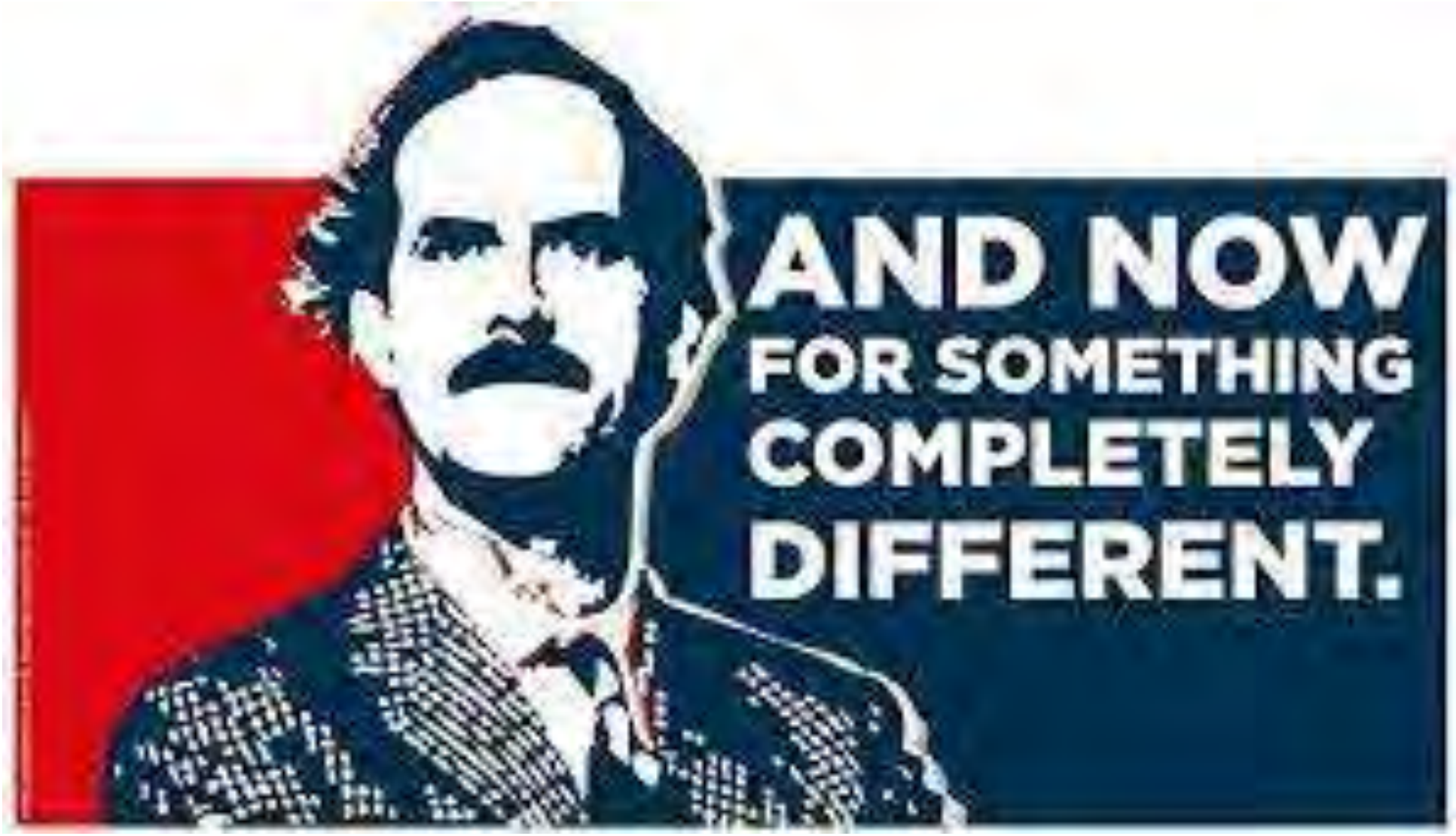
CNC Park: Bigger, Longer & Unrut

- A CNC-concrete parking lot was poured at the US Endowment in Greenville, South Carolina
- 60 cubic yards of CNC concrete were poured at 0.2% dosage (and 10 yards of standard concrete
- What we learned during the pour:
  - The CNC concrete behaved as well as standard concrete during placement
  - No apparent adverse effects when using heated water for batching CNC concrete
  - No apparent adverse effects on CNC concrete placement due to the cold weather

Concrete: The Revenge - this time it's structural!

- CNC-cement enabled bridge was precast at Knife River (Oregon) and placed in Siskiyou Co, CA USA
- Driven over every (most? Some?) days

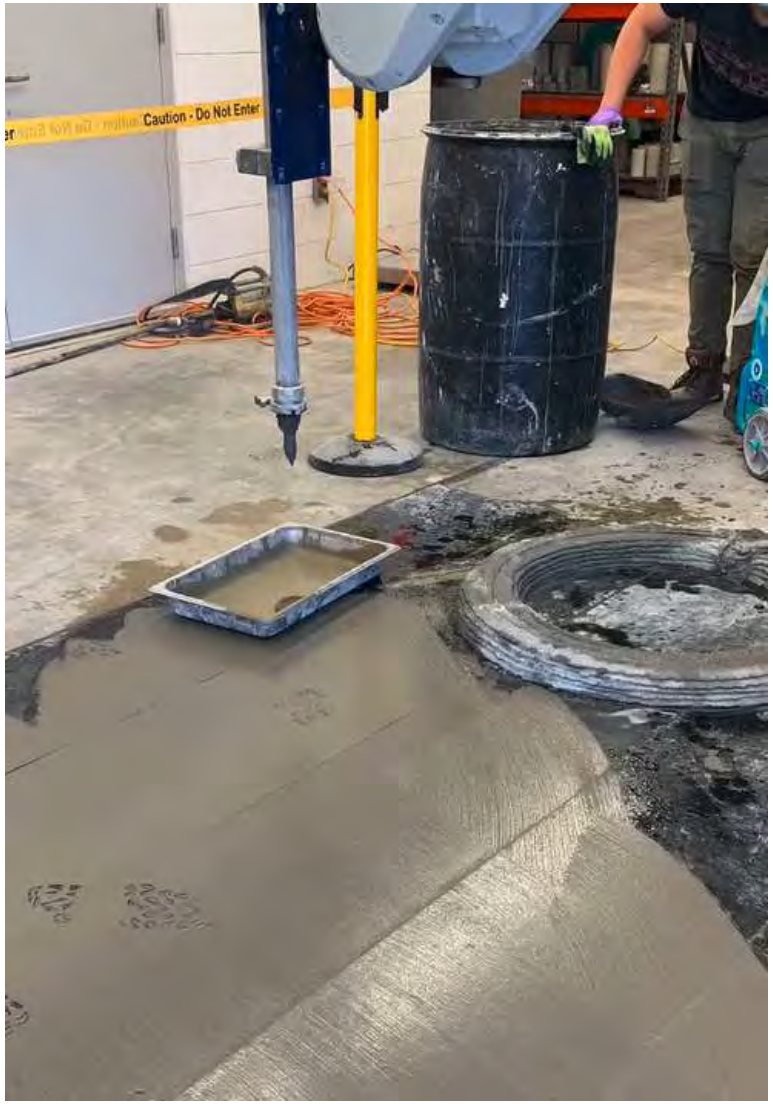
Next up: That Dam Project!


AND NOW
FOR SOMETHING
COMPLETELY
DIFFERENT.

Additive Manufacturing of Cement, Mortar and Concrete.

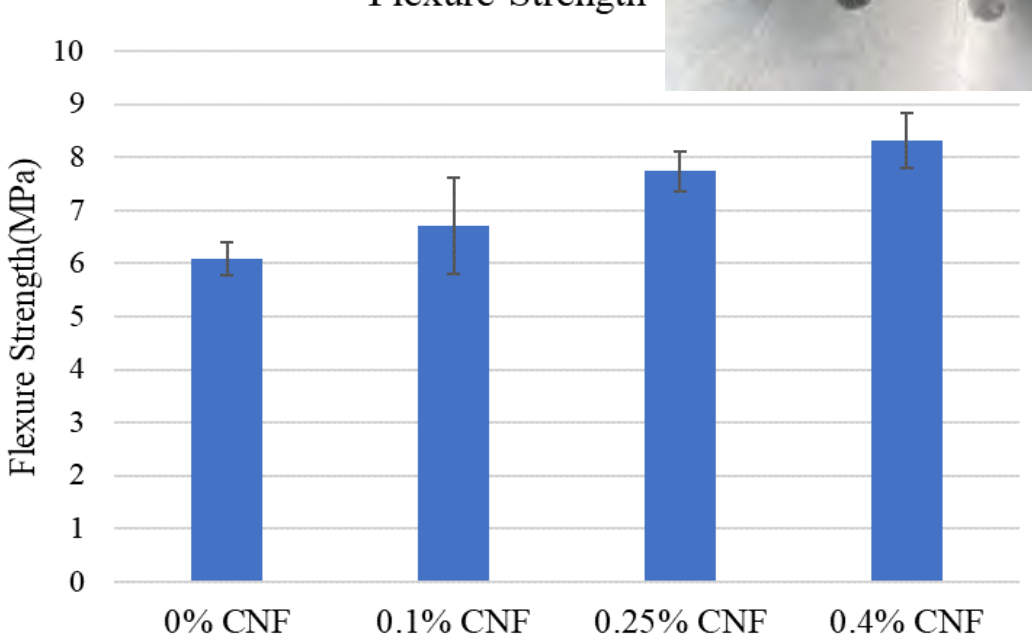
Purdue Concrete 3D Printing

Prof. Jan Olek,
Prof. Pablo Zavattieri,
Prof. Jeffrey Youngblood,
Prof. Christopher S Williams,

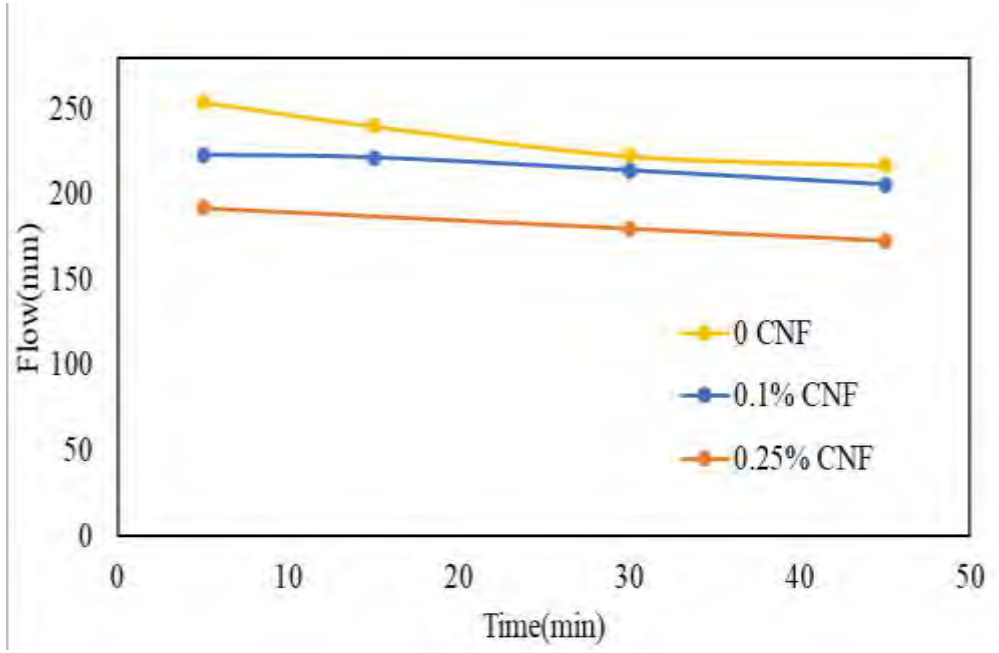


Could we combine the two?: CNM and AM of cement? Yes…Yes, we can!

- CNF can enhance the flexure strength by 30% at 7 days



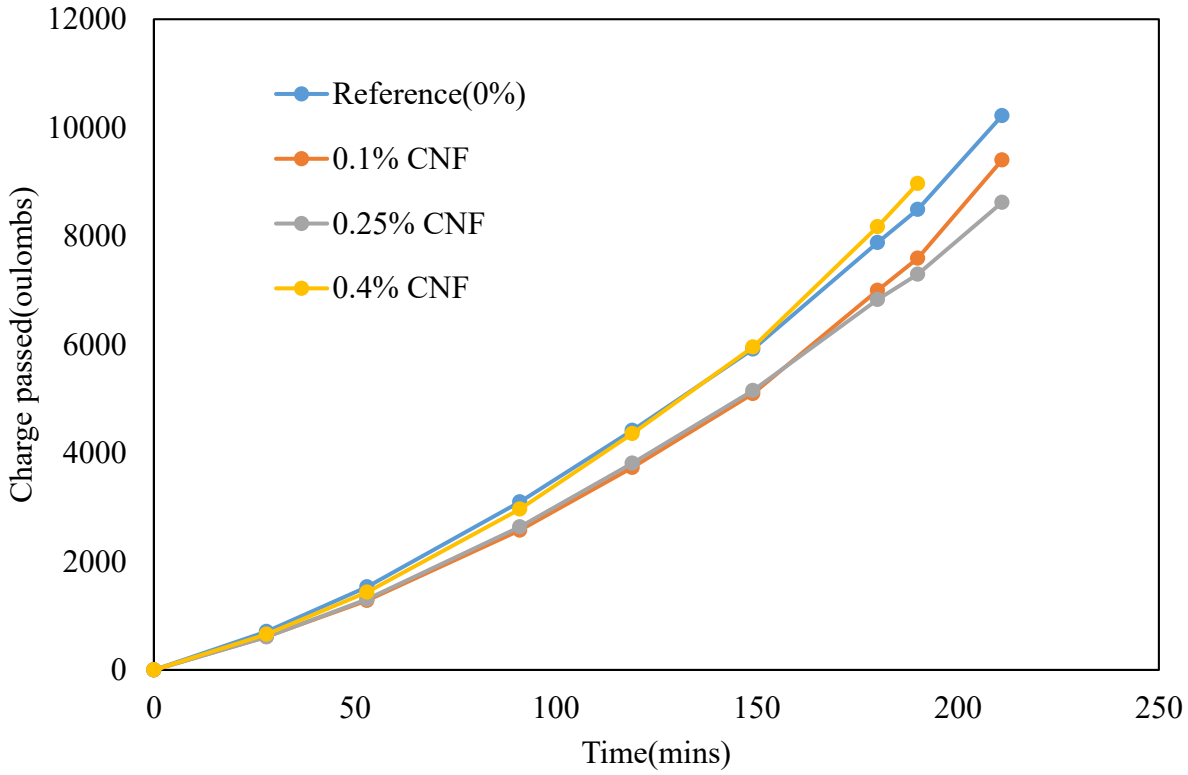
- The results show that increasing CNF content will reduce flow and workability. (like adding VMA)
- Importantly, the material has a more consistent flow by adding CNF.

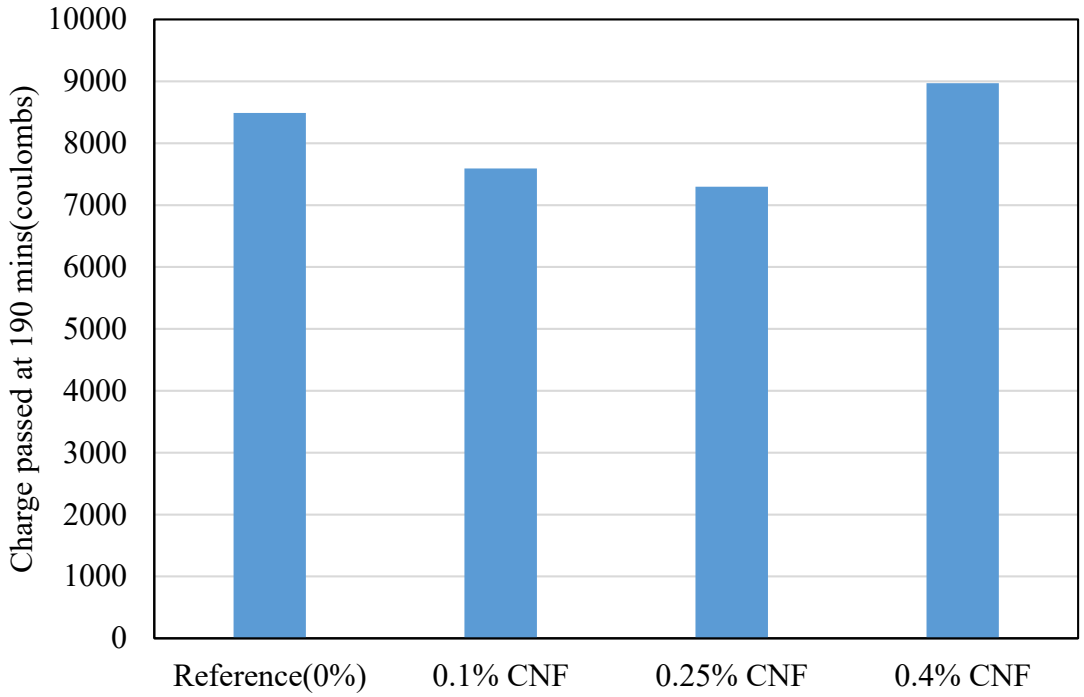


CNF has promise as alternative VMA for 3DCP

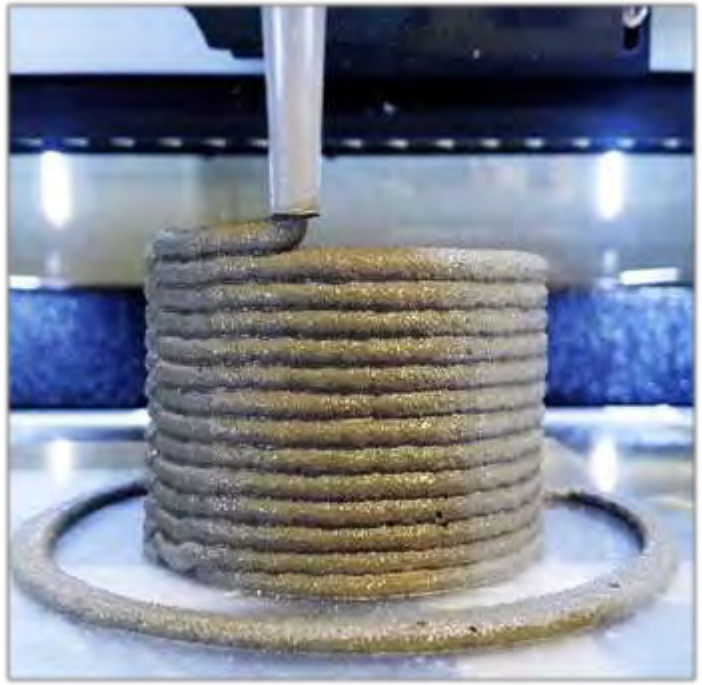
CNF may also improve durability to chloride attack

- Samples with three dosage of CNF were tested at 28 days.
- Samples with 0.1% and 0.25% of CNF shows better chloride permeability
- The results of 0.5% CNF does not help the chloride permeability , it might relate to the dispersion of fibers





PRINT QUALITY IS EXCELLENT!



Summary (stick a fork in him, he's done)

- Yes, Cellulose Nanomaterials are still awesome!
- CNC has PVOH like barrier properties
- CNF coated MP trays can extend the RT shelf life of fresh fruit
- CNM can enhance cement and concrete properties and are particularly promising for low carbon concrete
- CNM can even improve cement AM

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RCAM Technologies

The Youngblood Group 2022

Not Pictured:

- **Rodrigo Orta (PhD)**
- **Yu Wang (PhD)**
- **Ashwin Sivakumar (PhD)**

So Long and Thanks for All the Fish (Lobster???)!