



Overview of the U.S.

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Thanks to

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Colleen Walker, U. Maine

Michael Goergen, U.S. Endowment

PRESENTED BY:

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Outline



- ▶ American Process Inc. now GranBio
- ▶ University of Maine
- ▶ The U.S. Forest Service
- ▶ Product developments

America Process Inc. → GranBio LLC

- ▶ API is located in Atlanta, Georgia. In addition to a consulting company that does engineering studies, they have a research company working on biobased energy and chemicals, and on cellulose nanomaterials.
- ▶ The biorefinery and cellulose nanomaterial portions of API recently became part of GranBio, a Brazilian based biorefinery company.
- ▶ GranBio also acquired the Thomaston, GA pilot facilities, and the Alpena (Michigan) biorefinery.

GranBio, Thomaston, GA Pilot Plant



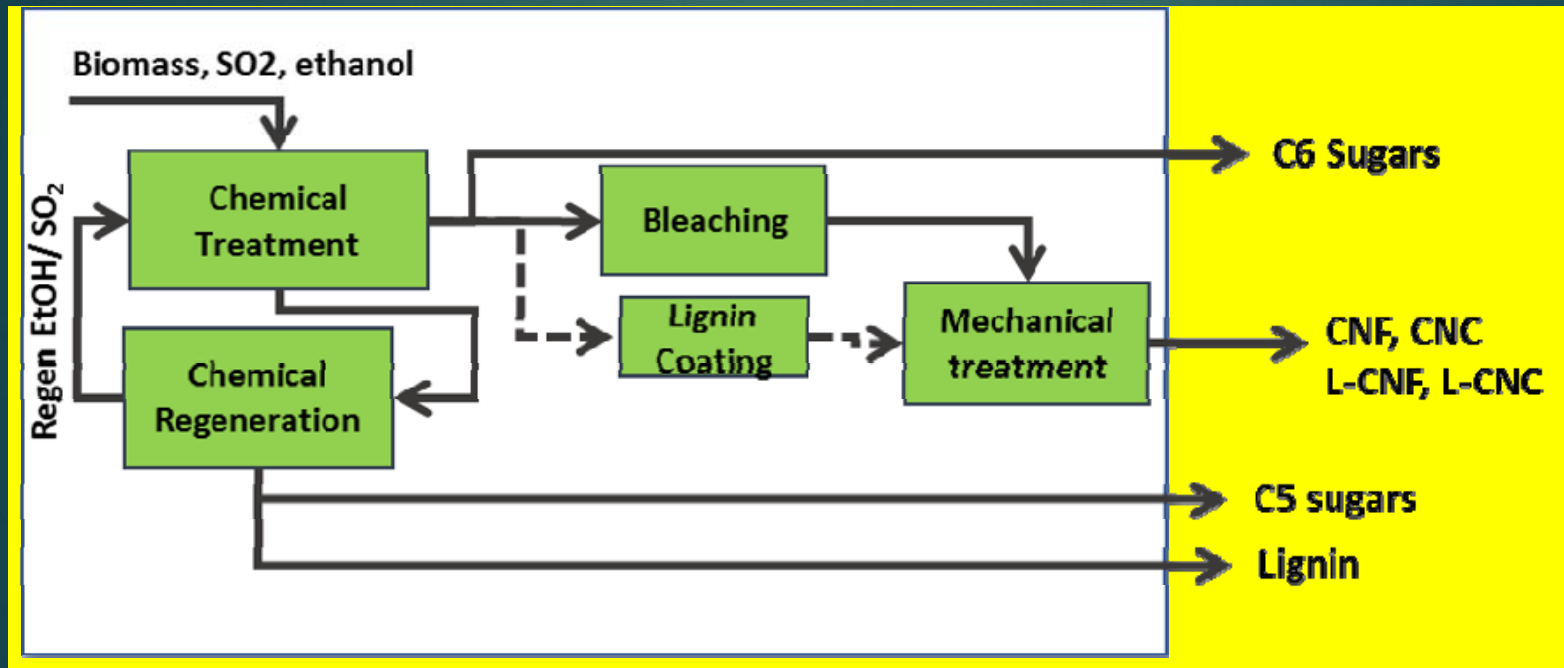
Thomaston

GranBio Thomaston Pilot Plant

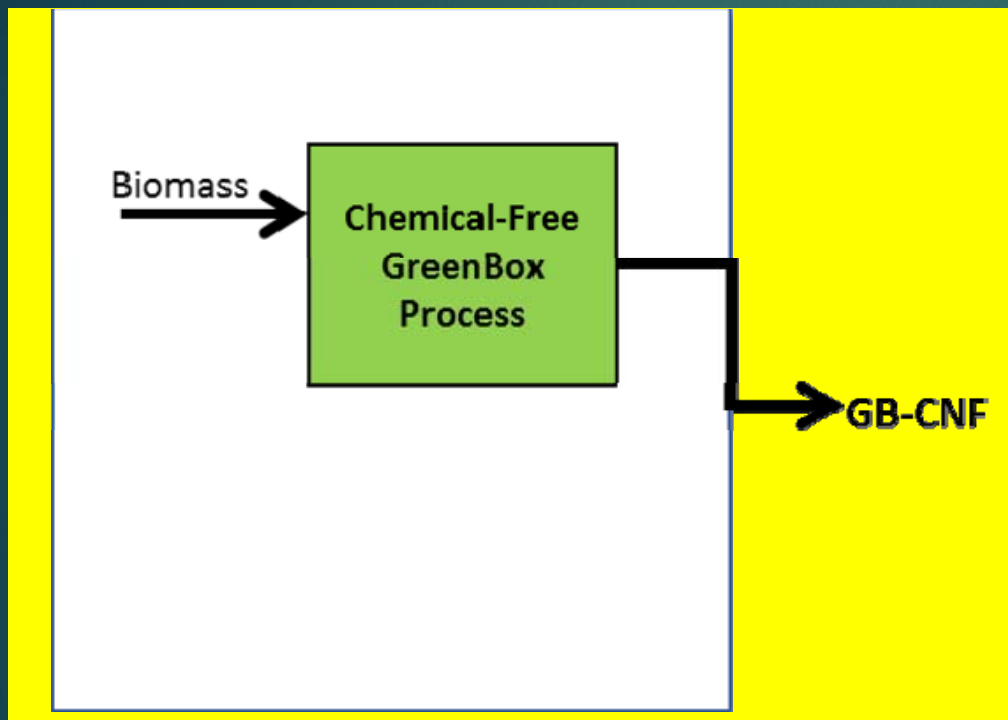


- ▶ 500 kg per day capacity
- ▶ 5 variants of CN
- ▶ BioPlus[®] with AVAP[®]
 - ▶ CNC
 - ▶ CNC with lignin (L-CNC)
 - ▶ CNF
 - ▶ CNF with Lignin
- ▶ BioPlus[®] with GreenBox[®] CNF

GranBio: BioPlus® with AVAP®



BioPlus® with GreenBox®



Chemical free method with a product more suitable for some commodity product needs.

CN Products Summary

	AVAP® CNC	AVAP® CNF	GreenBox® CNF
Feedstock	Any Biomass		
CN Yield	25%	42%	80-90%
Treatment	SO ₂ and Ethanol	SO ₂ and Ethanol	Water
Cellulose	100% (85%)	100% (94%)	50%
Hemicellulose	0	0	14%
Lignin	0 (15%)	0 (6%)	36%
Market	Performance Materials	Performance Materials	Commodities

Joint Development Agreements

Automotive



Cement



Brown Packaging (x2)



Tires/ Carbon Black



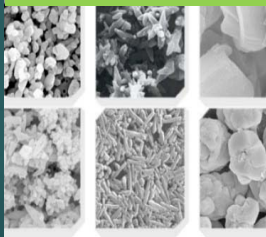
Adhesives & Sealants



Lithium Ion Batteries



Synergy w/ Minerals



Plastics (x2)



Tissue Engineering



Electronic Inks



University of Maine: Orono, ME



U. Maine

Joint Venture with GL&V

- ▶ One ton per day mechanically produced CNF
- ▶ Uses paper industry stock preparation refiners with specialized refiner plates.
- ▶ U. Maine and the Turner Falls installation operated in a batch recirculation mode.
- ▶ The University of Maine is also the retail sales agent for the cellulose nanomaterials produced by Maine, and by the Forest Products Laboratory.

University of Maine - Projects

Review of several U. Maine academic
projects

Nerve regeneration:

Carter and Neivandt

Peripheral Nerve Injuries

- ▶ Severed or crushed nerve segments resulting from physical trauma
- ▶ Currently repaired via nerve grafts or neural conduits
- ▶ Silicon and collagen conduits are non-biodegradable and can constrict the regenerating nerve

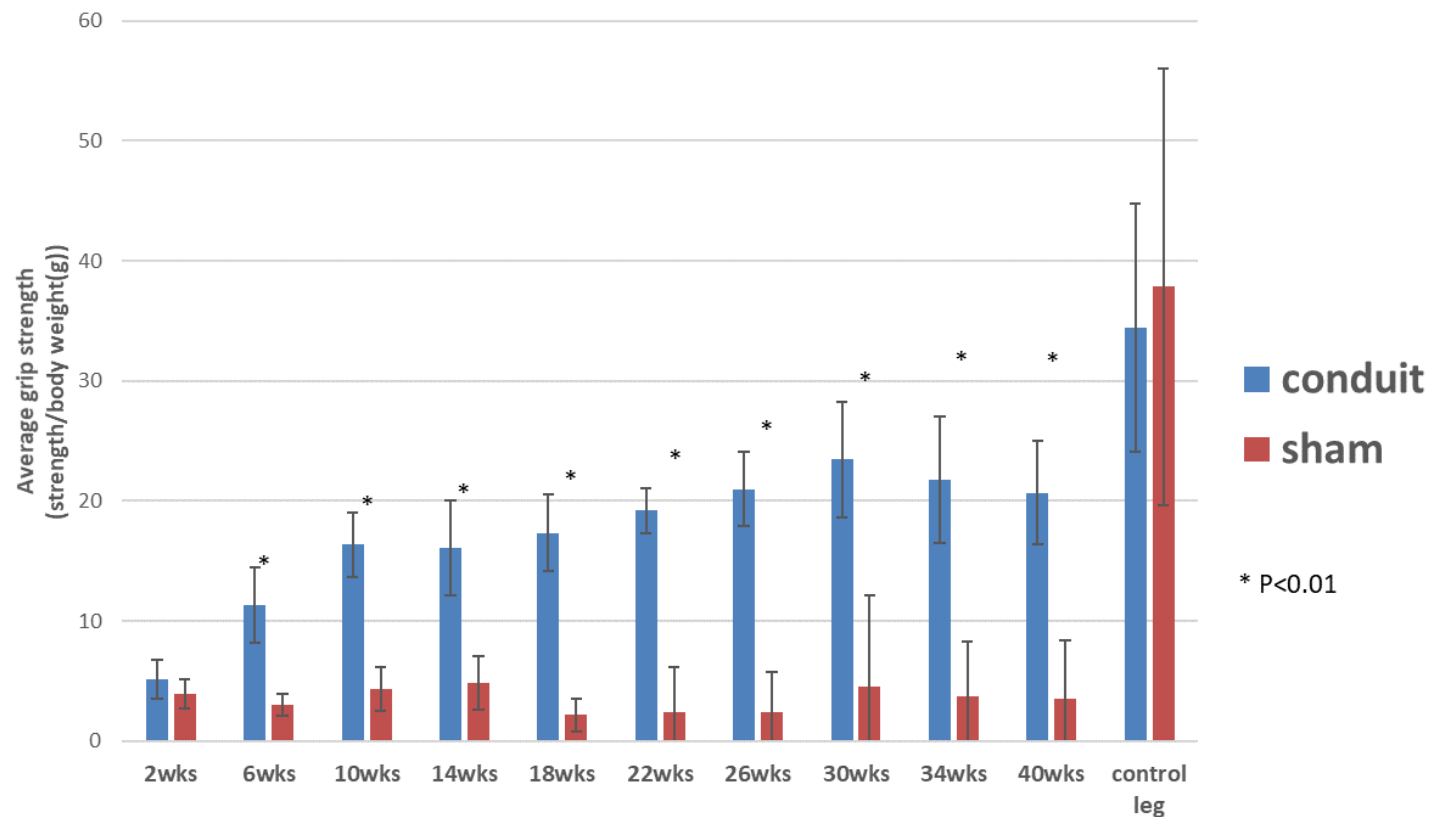
Experimental Methods

- ▶ Films were produced using a diluted CNF slurry from the PDC and air drying on a stainless steel platform
- ▶ Conduits were then cut from the film and formed into a neural conduit around a plastic mandrel

RESULTS / DISCUSSIONS

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- ▶ The sciatic nerve in the left leg was severed and the nerve was either sutured in place (sham) or the conduit was sutured over the nerve gap
- ▶ The right leg was used as the control leg



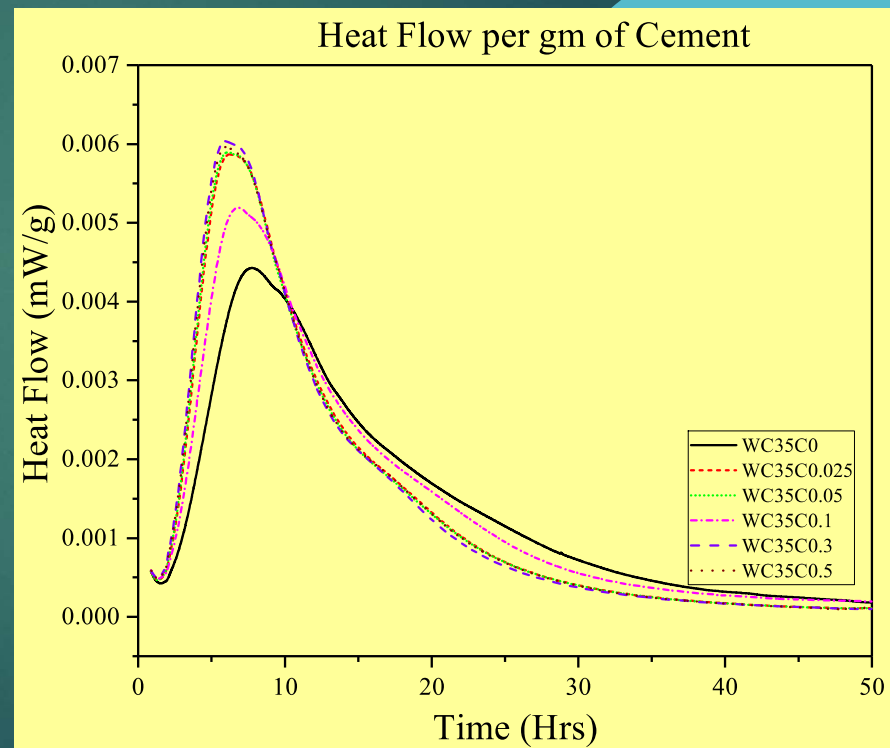
Silica-cellulose in concrete

Shirisha, Landis and Ashraf

- ▶ Use of sol-gel method to add silica to CNF
- ▶ Silica at 0.3% of CNF
- ▶ Result is improved hydration, resulting in an 11% increase in compressive strength.
- ▶ CNF without the silicate has a minimal impact on heat release, but provides some increase in compressive strength

Cement calorimetry

- ▶ Higher heat flow indicates a faster rate of reaction due to improved hydration.
- ▶ All samples at a water to cement ratio of 0.35
- ▶ Heat flow rises as Si-CNF increases to 0.05%
- ▶ Strength optimum is about 0.3% on cement.

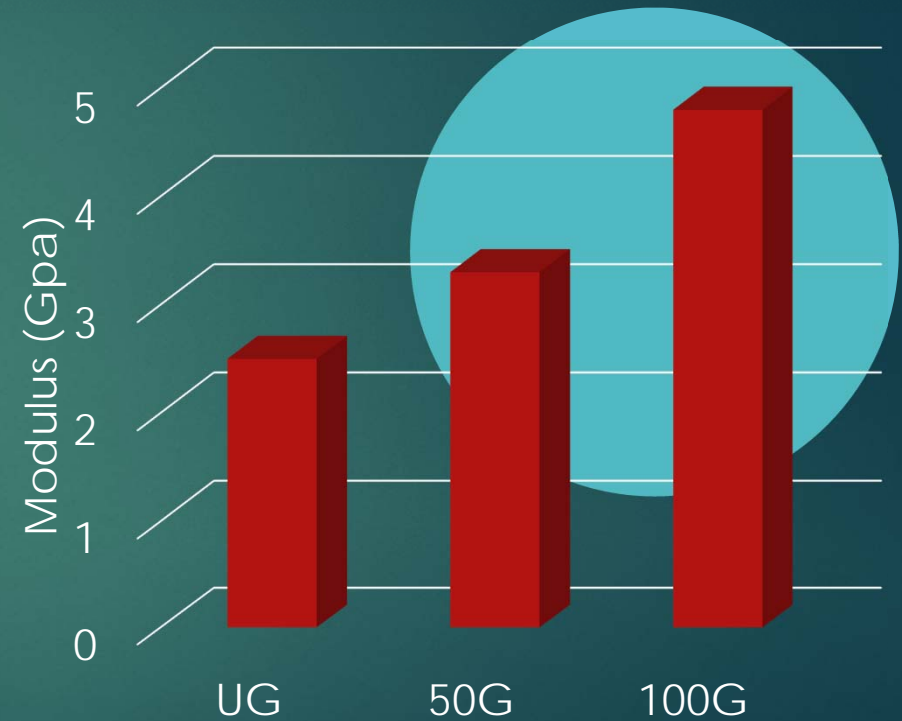
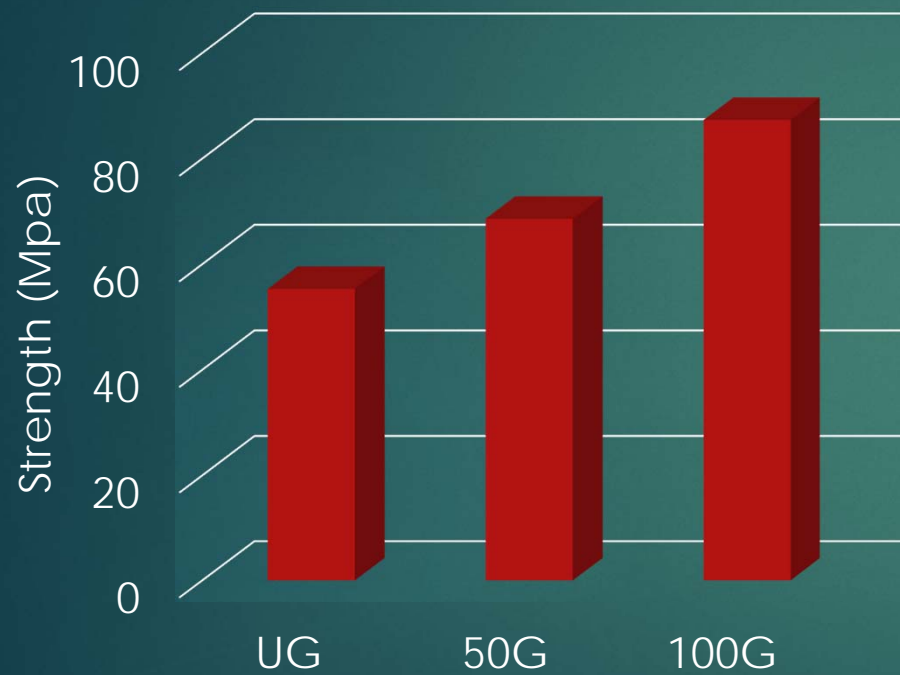


CN string

Ghasemi and Tajvidi

- ▶ Used a syringe pump to produce a CN string which was dried and tested
- ▶ Water suspension, no solvent
- ▶ Tested 3 grades of CNF,
 - ▶ UG is Ultra Ground CNF, the normal U. Maine CNF product.
 - ▶ 50G received additional grinding for 50 minutes
 - ▶ 100G received additional grinding for 100 minutes.

Influence of CN form and process

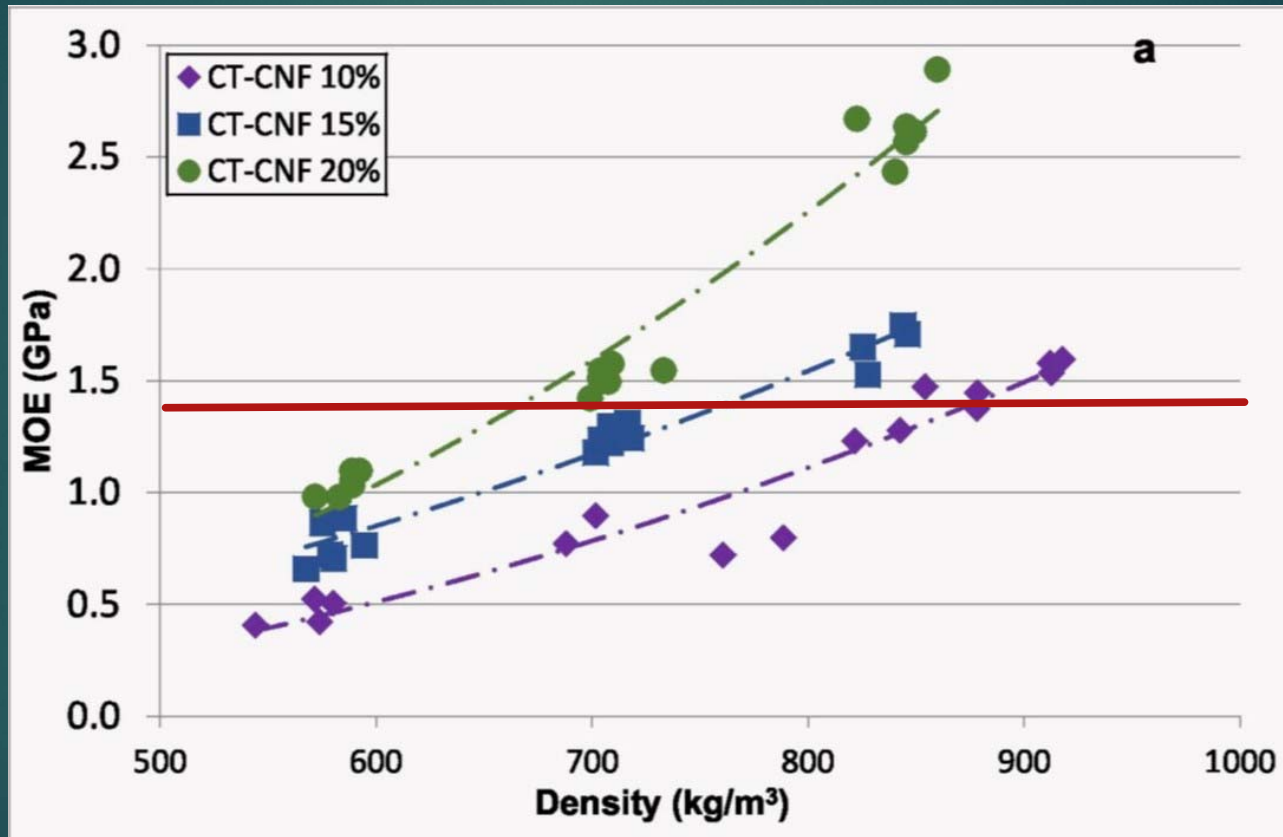


Use of CN in particleboard

Amini and Tajvidi

- ▶ Replacement of phenol-formaldehyde adhesive typically used in particleboard
- ▶ Exceeds stiffness and strength for low density fiberboard
- ▶ Meets internal bond strength of low and medium density fiberboards.
- ▶ Project has transitioned to application in wet-formed particleboard products.

Modulus of elasticity



DeLeón Cosmetics

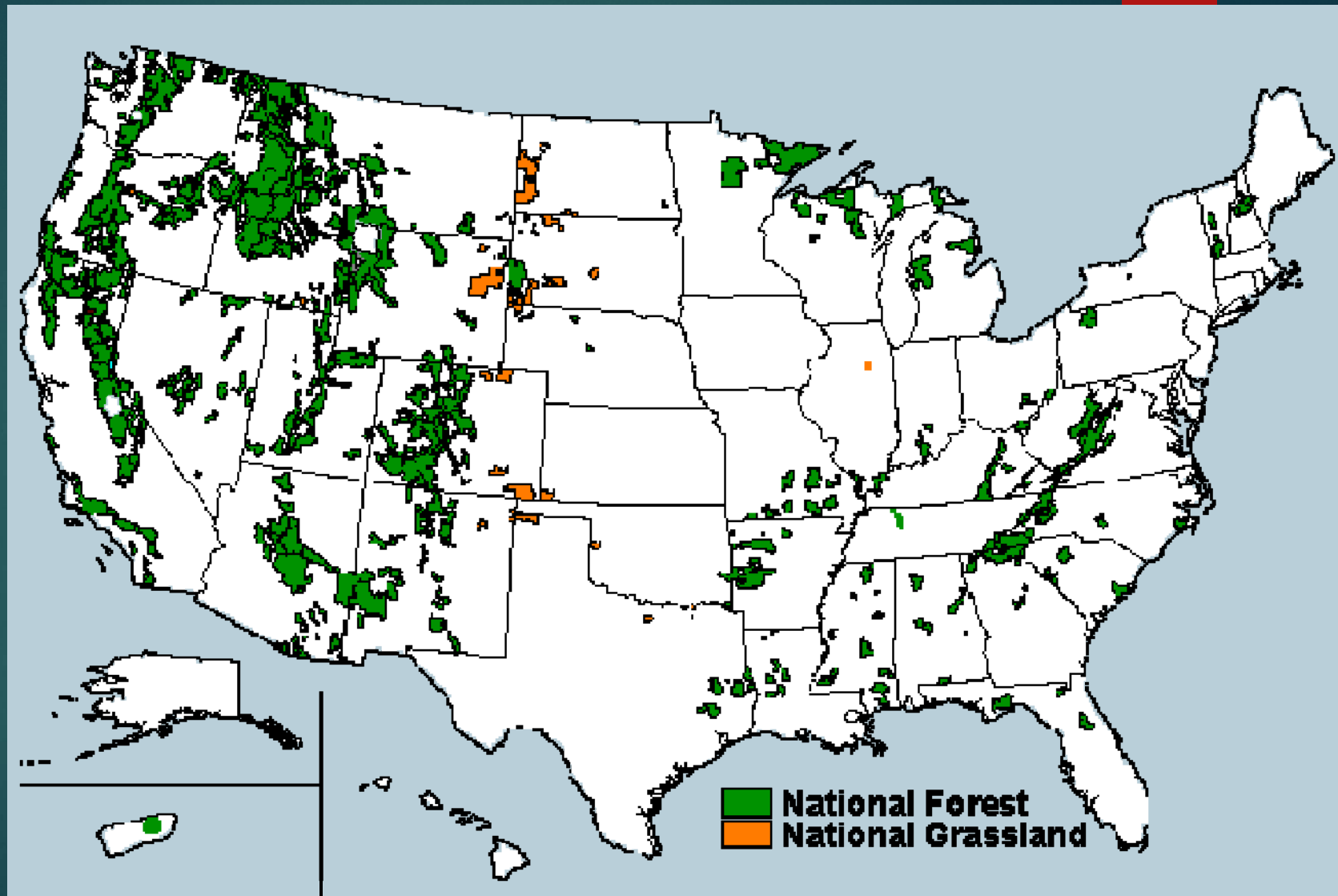


- ▶ The University of Maine CNF is used in the commercial product by DeLeón Cosmetics called Renewal + Hydration.
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U.S. Forest Service

- ▶ Part of the U.S. Department of Agriculture
- ▶ 193 million acres (780,000 km²)
- ▶ 4 million acres is grasslands
- ▶ About 1/4 is mixed hardwood and softwood forests in the Eastern half of the U.S.
- ▶ About 1/4 is mixed softwood forests in the coastal rains region of the Pacific North West.
- ▶ About 1/2 are dry pine forests in the Sierra Nevada and Rocky Mountain regions of the west.

U.S. National Forest Lands



The Forest Products Laboratory




- ▶ Established in 1910 by Gifford Pinchot, the first Chief of the Forest Service.
- ▶ The Forest Products lab's is tasked with helping to develop forest products that make better use of the resource, and provide product applications that support forest management needs.
 - ▶ Products where the value of the trees removed is sufficient to repay the cost of thinning overgrown forests or removing dead trees.

Forest Products Laboratory, Madison, WI



CN Material Availability



- ▶ Forest Service discovered that scientists trying to make composites or other applications of Cellulose nanomaterials were spending more time making the starting CN material than on applications.
 - ▶ FPL had already developed reliable procedures for making s-CNC and t-CNF and was getting many requests to supply other scientists.
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Forest Products Laboratory



- ▶ Pilot plant commissioned in 2012
- ▶ Produces sulfuric acid cellulose nanocrystals at 25 kg per batch
- ▶ Produces the TEMPO form of cellulose nanofibrils at 4 kg per batch
- ▶ FPL has been the bulk supplier of CNC and t-CNF to the University of Maine.

FPL Pilot Plant



Delivery



- ▶ Sold by Maine:
- ▶ 687 pounds (308 kg) of CNC
- ▶ 11 pounds (5 kg) of t-CNF have been sold by Maine.
- ▶ 4 samples of CNC suspension and 10 samples of freeze dried CNC have been purchased by scientists in Japan. 1 sample of freeze dried t-CNF was purchased by a scientist in Japan.

CNC
March, 2013

75 Kg
suspension

15 Kg freeze
dried



The materials: Cellulose nanoCrystal

- ▶ Initially – 1949: Low concentration sulfuric acid to what was referred to at the time as the limiting degree of polymerization.
- ▶ Currently – 60-65% sulfuric acid
 - ▶ Concentrated sulfuric acid is a solvent for cellulose. 60-65% is the range where it will dissolve amorphous cellulose but not the crystalline regions.

CNC

- ▶ Currently, any material with a rod shaped particle and dimensions of 60-400 nm length and 5-50 nm width is generally referred to as a cellulose nano-crystal.
- ▶ Should be in the range of 90% crystalline or higher
- ▶ Properties are not consistent across forms, some will not form the chiral nematic phase and some have higher thermal decomposition temperature

TEMPO CNF



- ▶ FPL uses a scaled up version of the process developed by Professor Isogai at the University of Tokyo.
- ▶ 400 Liter stirred reactor
- ▶ 800 Liter pressure filter for collecting and washing the TEMPO treated wood pulp
- ▶ 3-valve homogenizer
- ▶ Membrane filtration system to concentrate.

Advanced Product Development



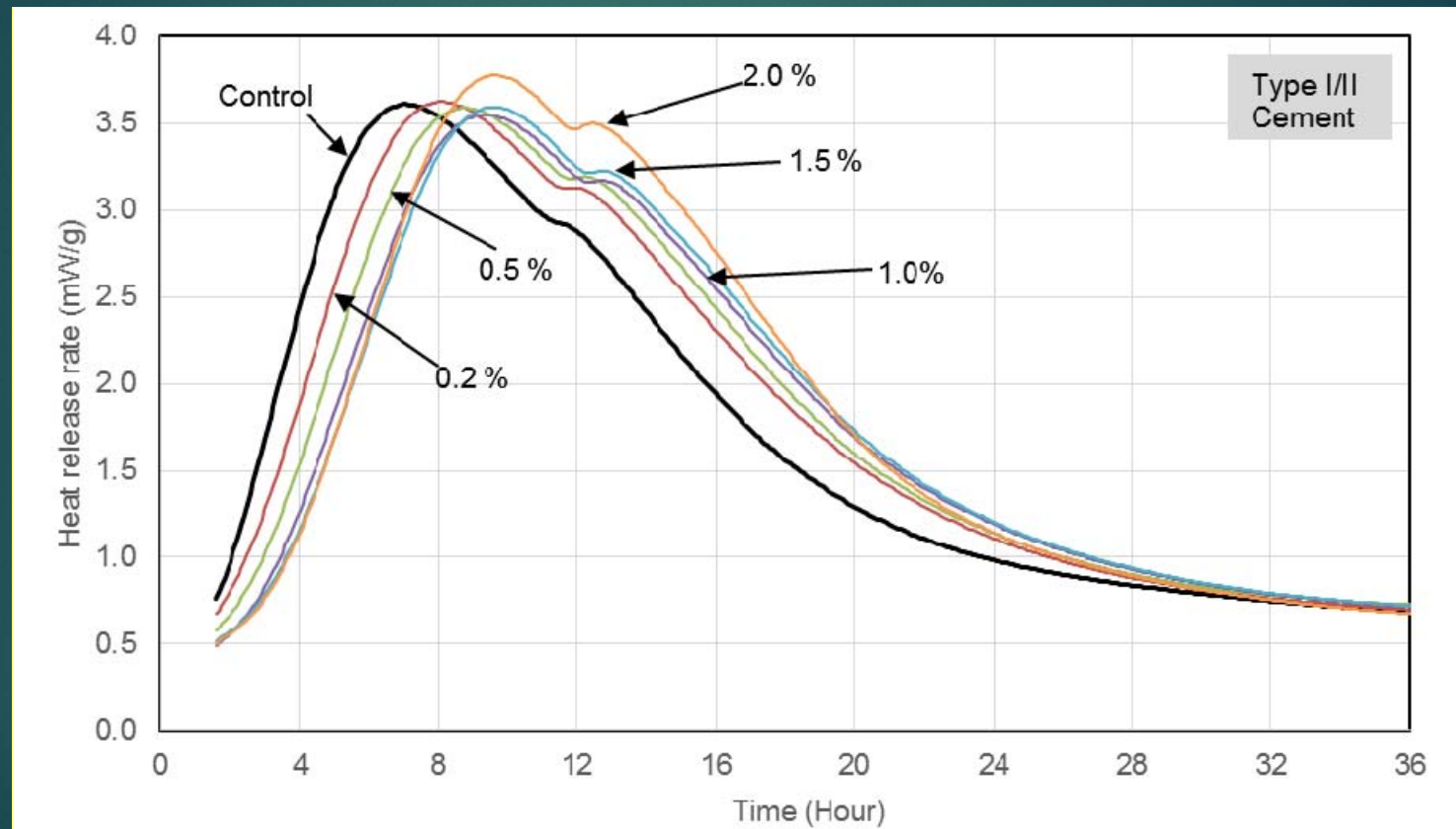
- ▶ Concrete: Oregon State University and Purdue University
- ▶ Fiberglass: Georgia Institute of Technology
- ▶ Particleboard: University of Maine

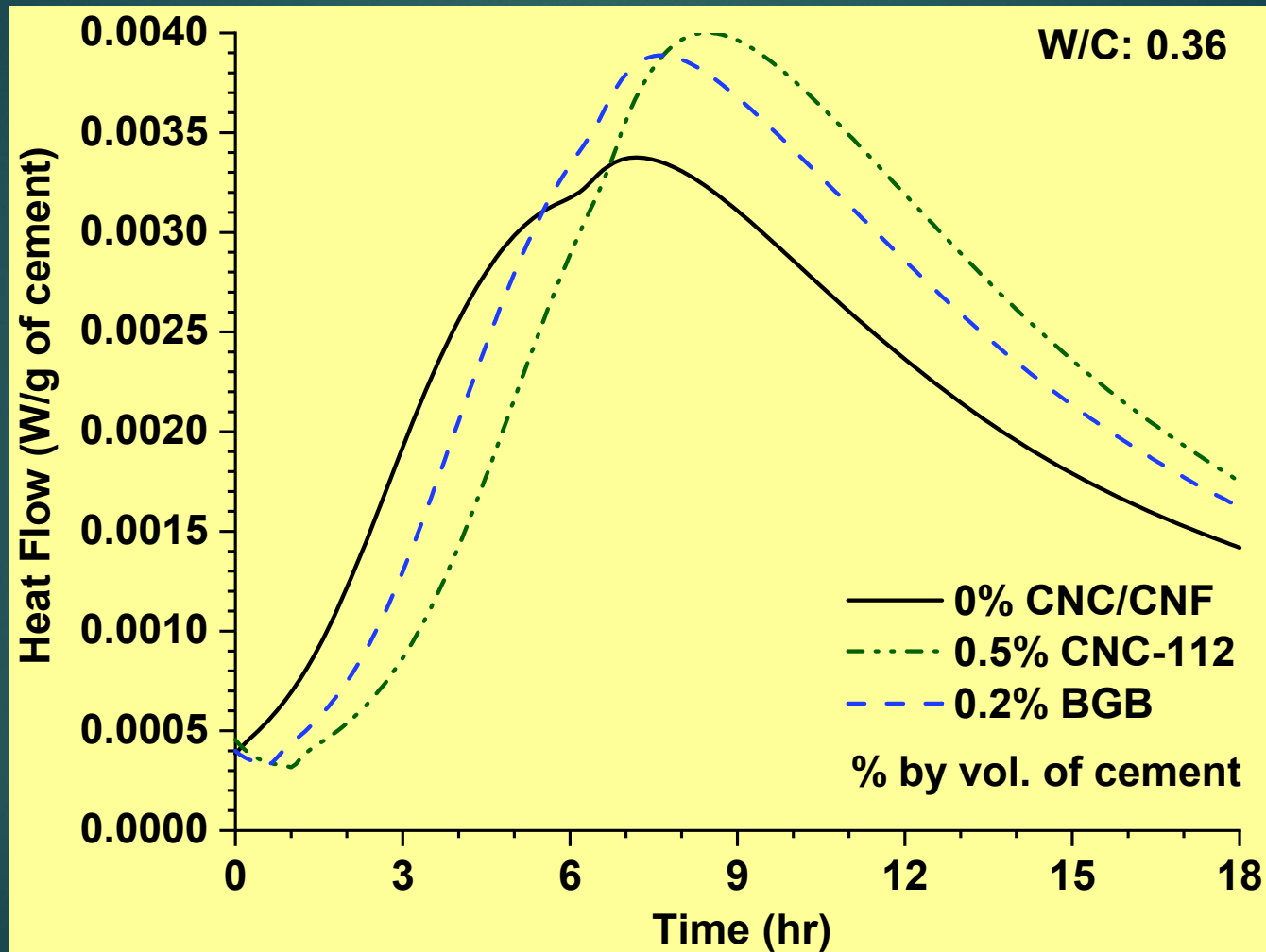
Concrete

Jason Weiss and Jeff Youngblood

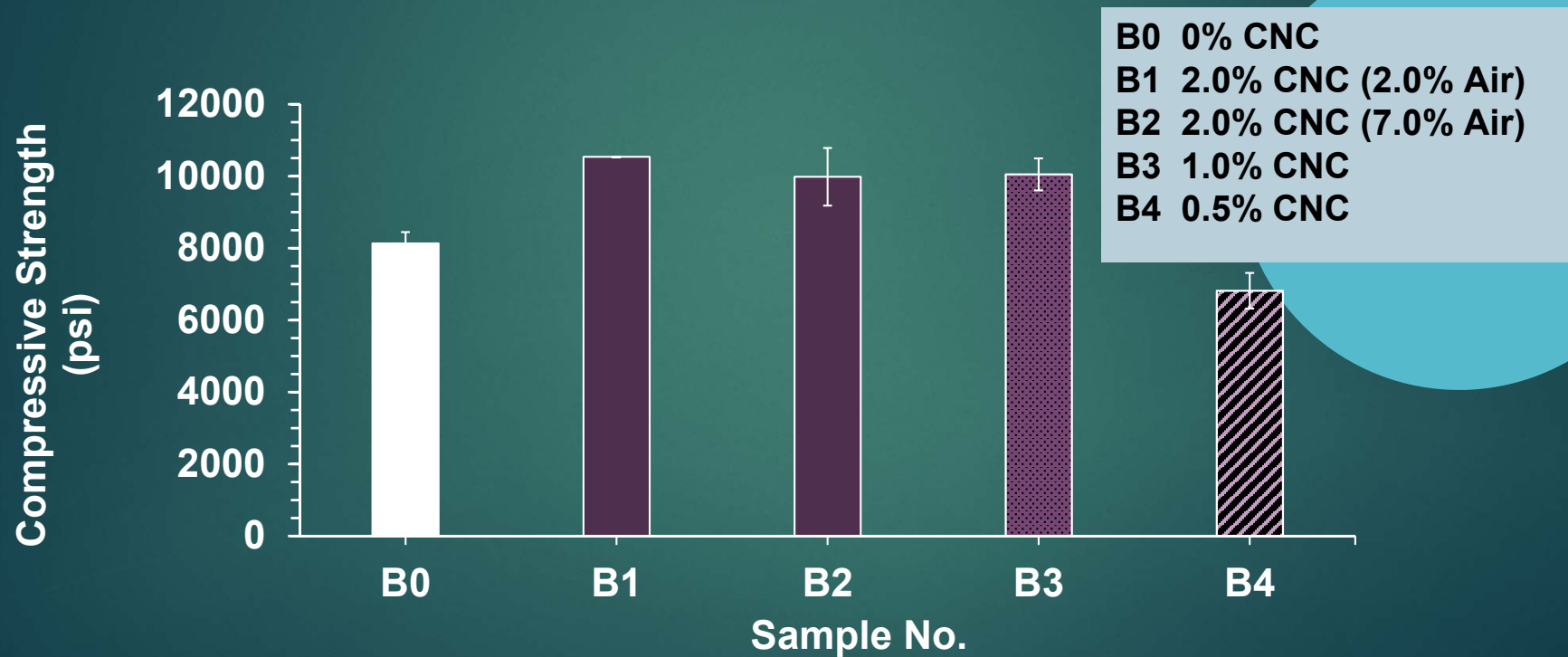
- ▶ Cellulose nanocrystals increase the rate at which concrete cures and extends the curing reaction.
- ▶ Charges – 0.2% by volume of cement (~ 20% of concrete) for Type V
 - ▶ ~1% on cement for type I, II and III
- ▶ Typical strength gains of 20% or more are observed

Impact of CNC on Curing Exotherm





Strength at 28 days



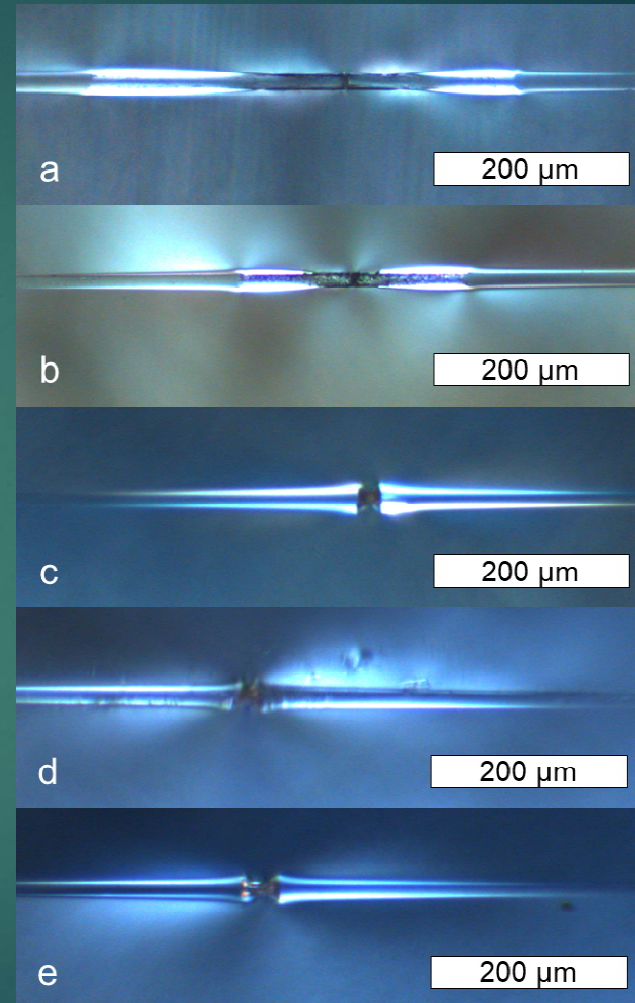
Sheet Molding Compound

Kyriaki Kalaitzidou

- ▶ Addition of CNC by dipping glass fiber into a CNC suspension and drying.
- ▶ Glass fiber is cut and embedded in epoxy sheets
- ▶ SMC with added CNC gives 7% improvement in strength and nearly X2 improvement in bond strength between glass fibers and epoxy resin

Glass-epoxy interface

Label	Composition
GF0	As received
GF1	1% s-CNC
GF2	1% P-CNC
GF4	5% Surfactant
GF5	5% polymer



Yreka; A Forest Service Initiative

- ▶ Most cellulose nanoparticles are prepared from a cellulose source: bleached wood pulp and cotton linters as examples.
- ▶ To provide products that can help in forest management in parts of the US, the FPL teamed up with the National Forests in California to test methods of producing cellulose nanoparticles directly from wood

Yreka Project: Five methods

- ▶ Sulfuric acid CNC FPL
- ▶ TEMPO CNF FPL
- ▶ Carboxylated CNC BlueGoose Biorefinery
- ▶ Mechanical CNF and GL&V University of Maine
- ▶ Sulfonated CN GranBio

CN From Wood

API BioPlus: BGB Ultra:



t-CNF:



S-CNC:



t-CNF:



Control:



Maine CNF



Outcomes

- ▶ BGB and TEMPO require a lot of sodium hypochlorite because of the lignin in the wood.
- ▶ The C-6 carbon in the cellulose crystals of green wood are disordered. This results in a low yield of CNC, and heat treatment only raises the CNC yield to ~13%
- ▶ The higher chemical cost of BGB and low yield for s-CNC make these three methods high cost relative to starting from market pulps.

Better Outcomes



- ▶ The sulfonation process used by GranBio is a modified sulfite pulping process. It works well on wood.
- ▶ The mechanical process used by the University of Maine needs wood particles from a hammer mill or willey mill but works well and is the lowest cost method to produce a CN or CM type particle.

Next Steps



- ▶ Decide between the API and U. Maine methods for further characterization and techno economic evaluations
- ▶ Evaluate a wider range of methods to try to increase crystal yield in sulfuric acid treatments.

Summary



- ▶ The U.S. program is not very large but making progress on several large scale applications
 - ▶ Use in concrete
 - ▶ Use in fiberglass
 - ▶ Use in wet formed particleboard
- ▶ In the U.S., there is need for products that can grab the attention of larger companies and generate more corporate research activity.



Thank you

PRESENTED BY

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References on projects

- ▶ Concrete: Cao, Y., Zavattieri, P., Youngblood, J., Moon, R. and Weiss, W.J., The influence of cellulose nanocrystals on the structure of cement paste and hydration. *Cement and concrete composites*, 56(2): 73-83(2015).
- ▶ SMC: Asadi, A., Millar, M., Singh, A., Moon, R. and Kalaitzidou, K., Lightweight sheet molding compound (SMC) composites containing cellulose nanocrystals. *Composite Structures*, 160: 211-219(2017).
- ▶ MDF: Hunt, J.F., Leng, W. and Tajvidi, M., Vertical density profile and internal bond strength of wet-formed particleboard bonded with cellulose nanofibrils. *Wood and Fiber Science*, 49(4): 413-423(2017).