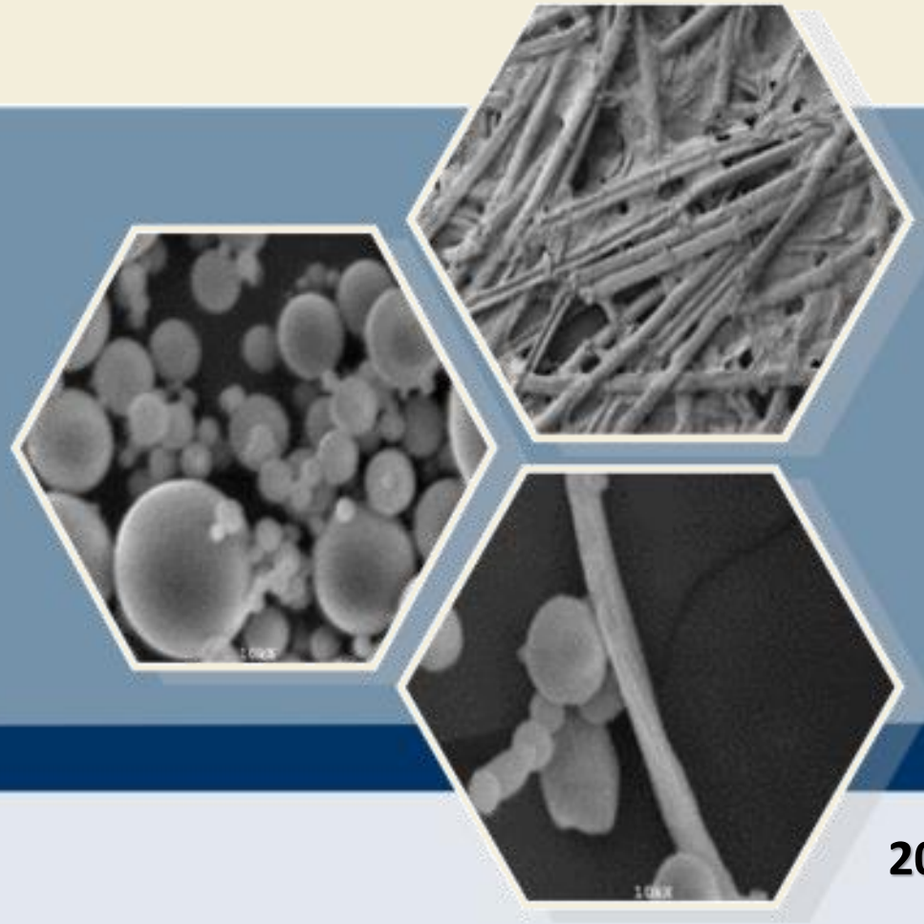
Cellulose Nanocomposites:

Status of development from a commercial perspective



Douglas Gardner, PhD.

Yousoo Han, PhD.

Mehdi Tajvidi, PhD.

2018 SPE Automotive Composites Conference & Exhibition
Sept. 05-07, 2018 Novi, Michigan, U.S.A.

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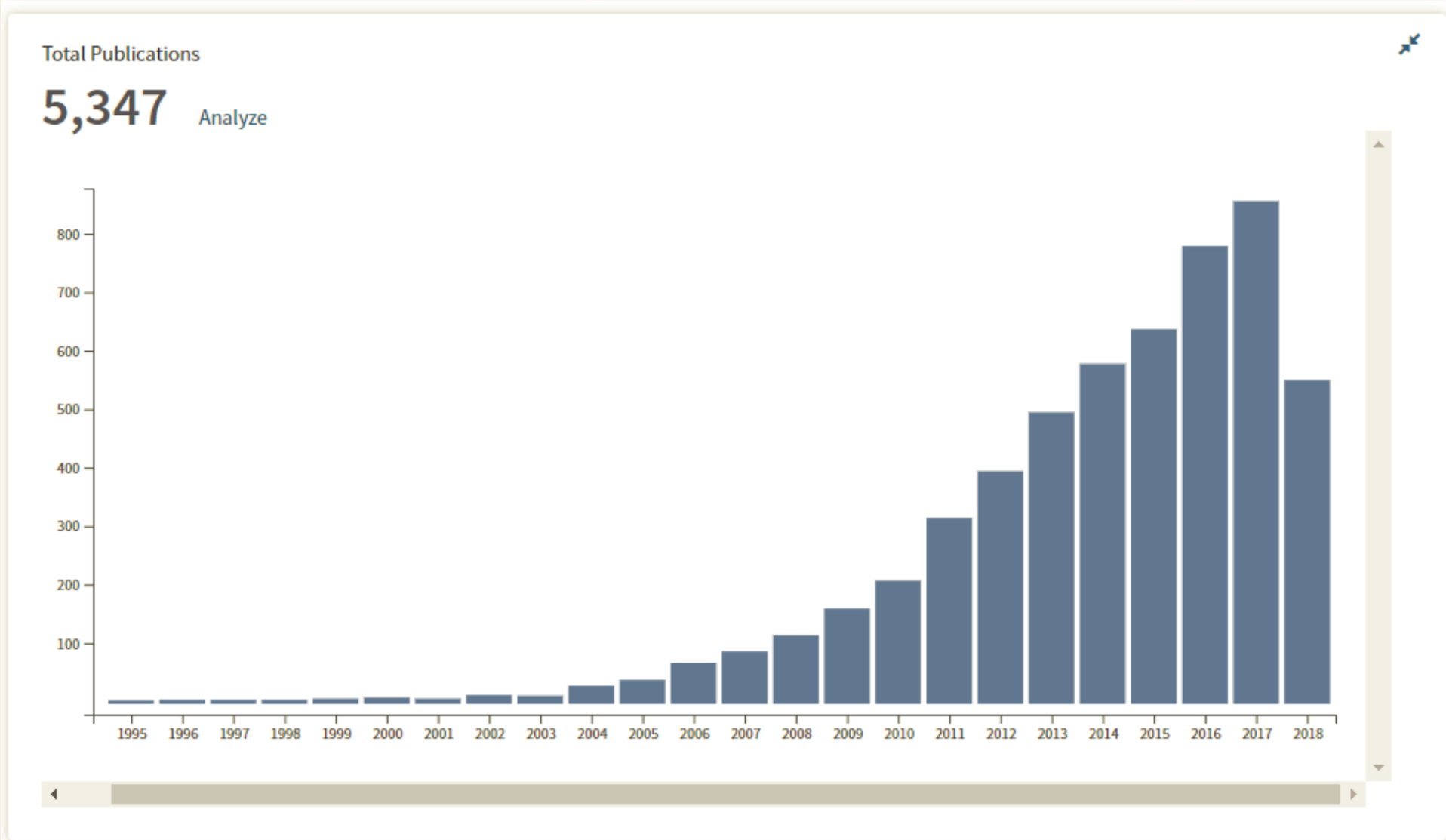
Overview

- Overview of cellulose nanomaterials
- Alternative cellulose feedstocks (lower costs)
- Current applications with commercial potential
- Examples of property enhancement in polymer matrices
- Challenges in scale up from bench to pilot to industrial
- Techno-economic aspects

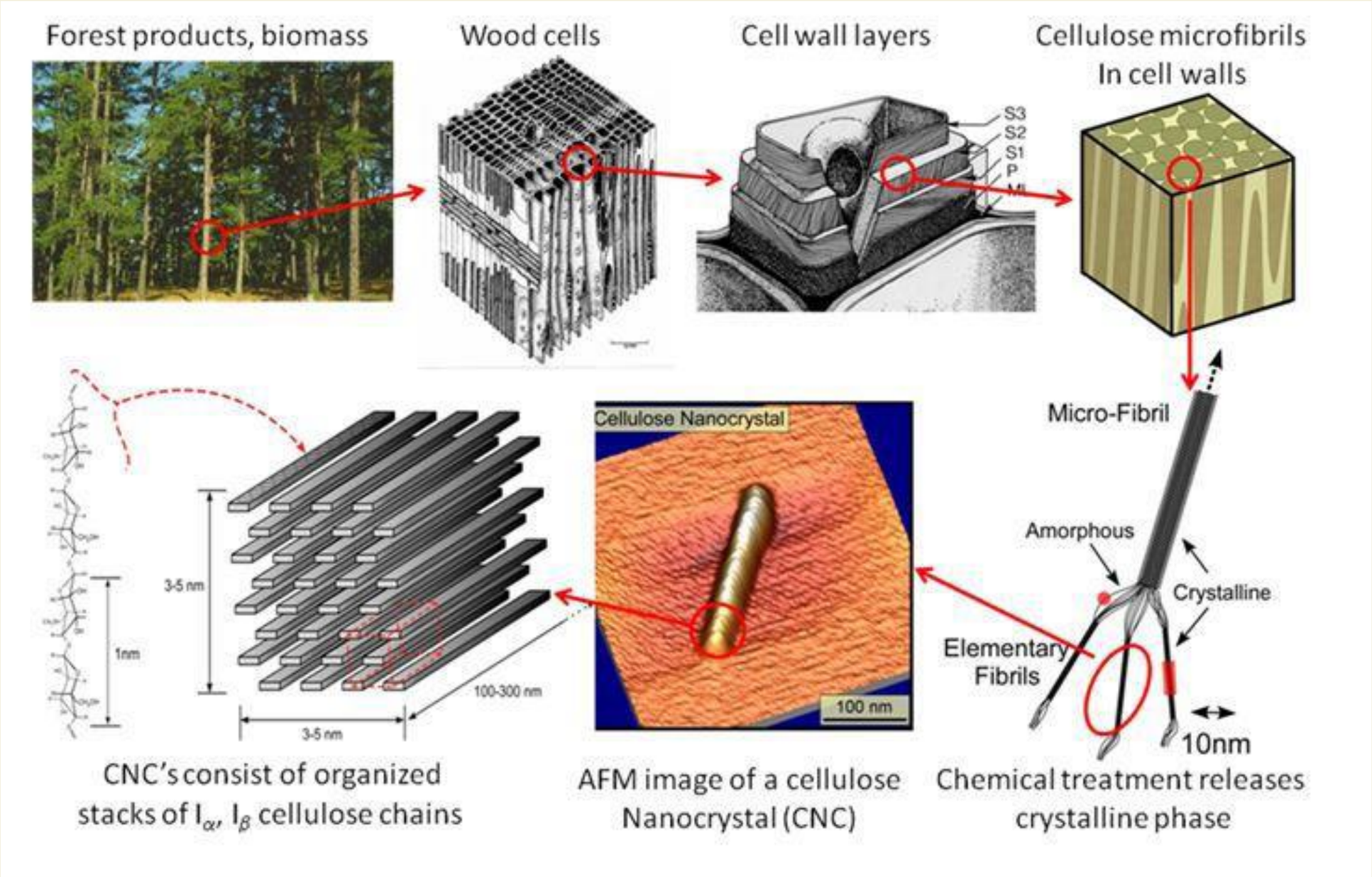
Publication Activity

Publication Activity Cellulose Nanocomposites



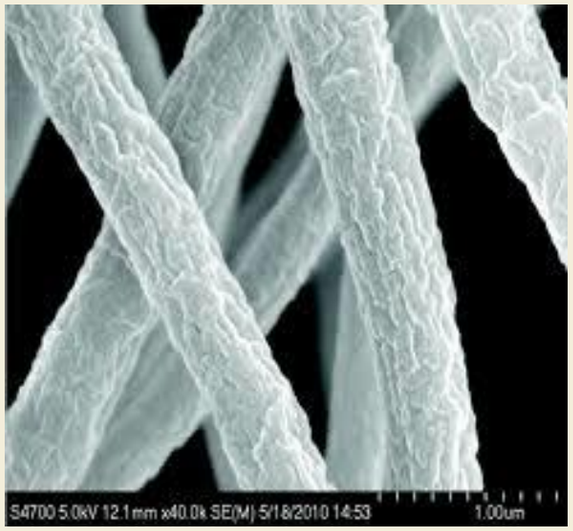
Web of Science July 2018

Size Scale of Lignocellulosics

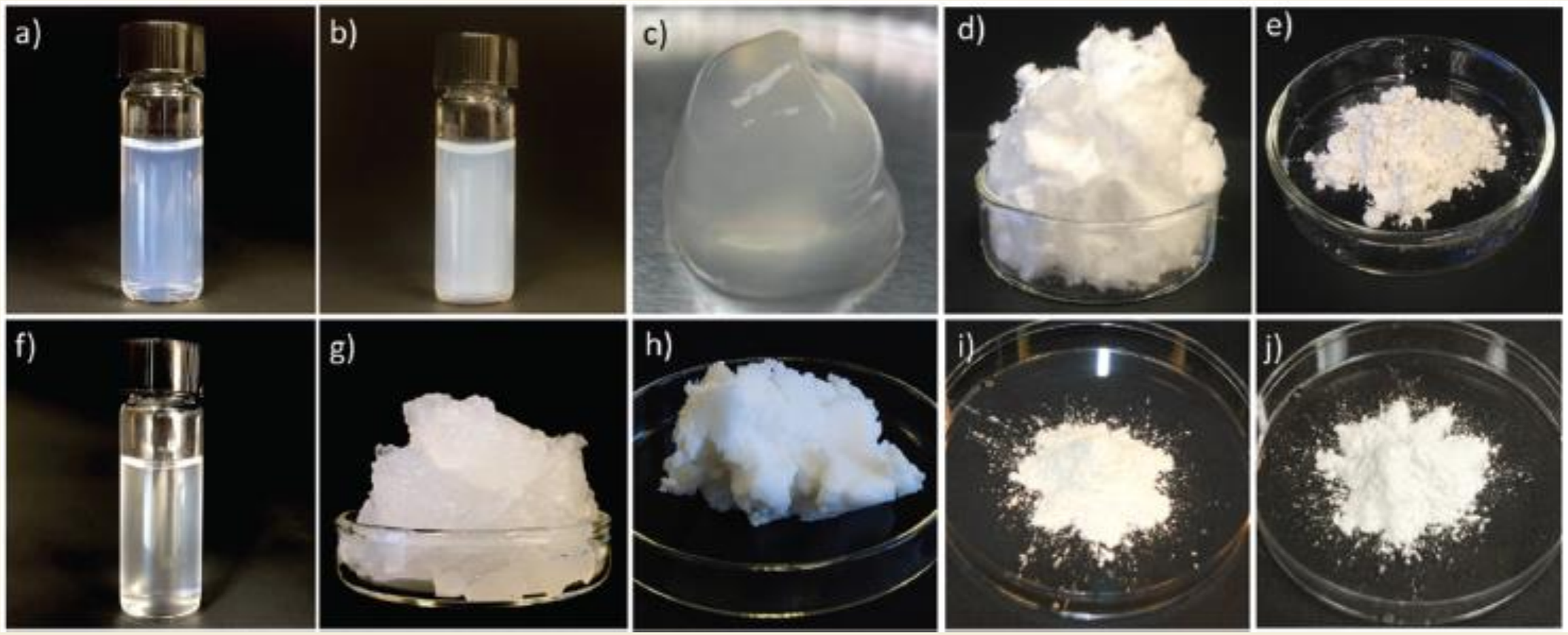


Feedstocks For CNF

- Bleached Kraft Pulp
- Unbleached Kraft Pulp
- Thermomechanical Pulp
- Old Corrugated Containers (OCC)
- Stone Groundwood
- Other Lignocellulosics



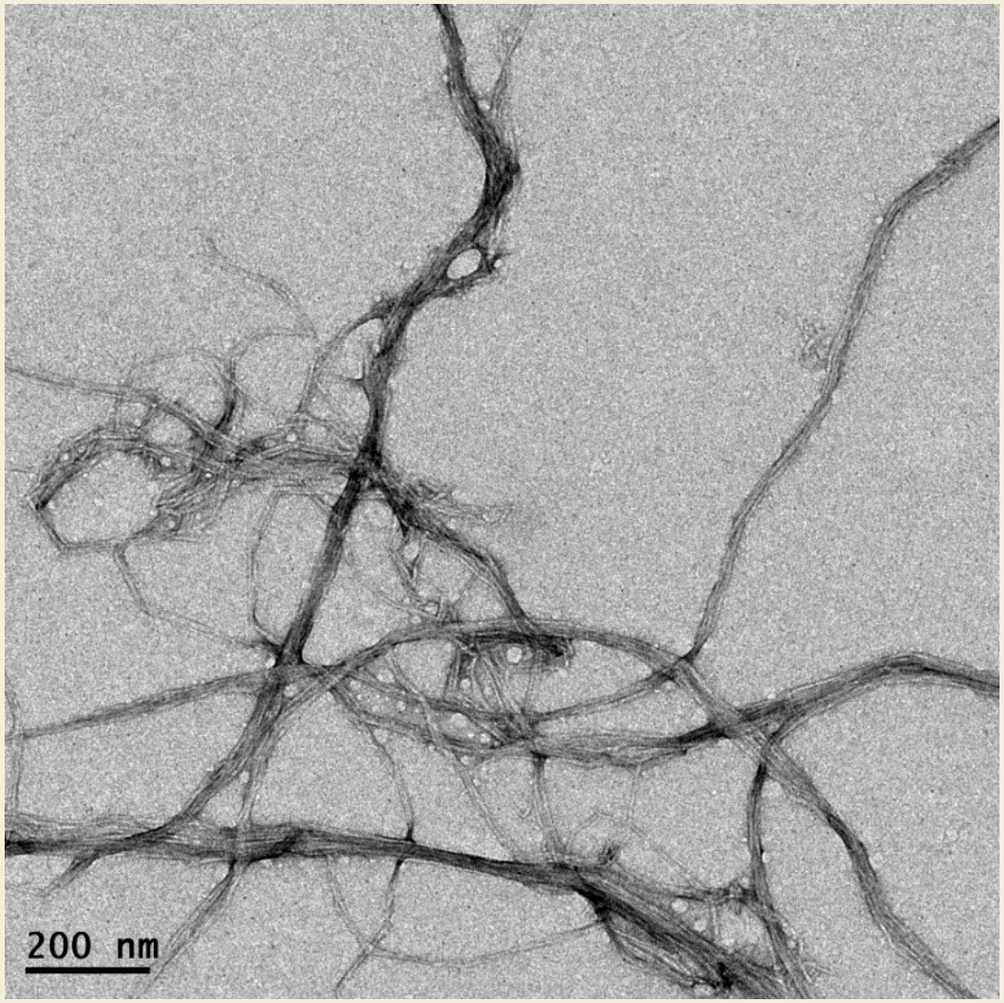
Various Cellulose Nanomaterials



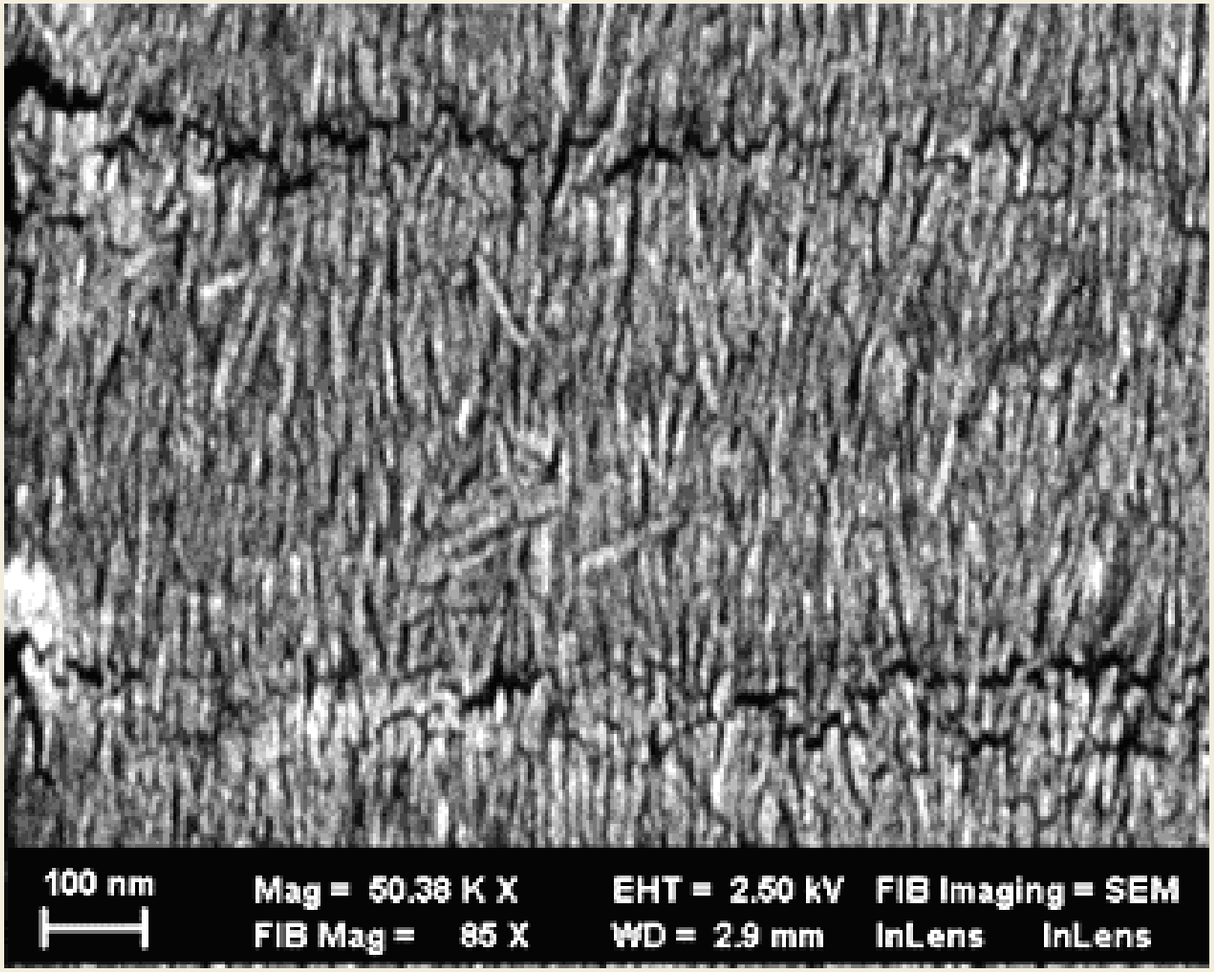
a.1 wt.% CNC in water, b.5 wt.% CNC in water, c. 15 wt.% CNC, d.Freeze-dried CNC, e. Spray dried CNC, f. TEMPO CNF, g. 2 wt.% TEMPO CNF, h. 10% Exliva paste, i. Freeze-dried and Milled CNG, j. Spray dried CNF

Chem. Soc. Rev. 2018, 47, 2609-2679

Cellulose Nanofibrils (CNF)



Cellulose Nanocrystals (CNC)



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UMaine PDC Nanocellulose Distribution

- **Distribution of samples of CNF and CNC**
- Number of countries: 43
- Companies: 240
- Universities: 215
- Other (non-profits, govt.) 49
- Pounds CNF: 7380
- Pounds CNC: 687
- Pounds TEMPO: 10

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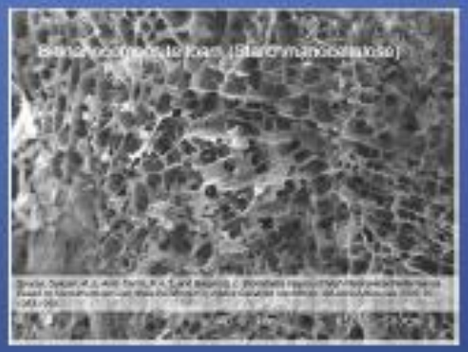
Applications of Cellulose Nanofibrils

- Opportunities for renewable nanomaterials from wood

- Batteries
- Super-Capacitors
- Bio Plastics
- Nano Coatings
- Reinforced Polymers
- Smart Sensors
- High Efficiency Filters
- Light Weight Nano Composites
- Nano Membranes
- Photonic Devices

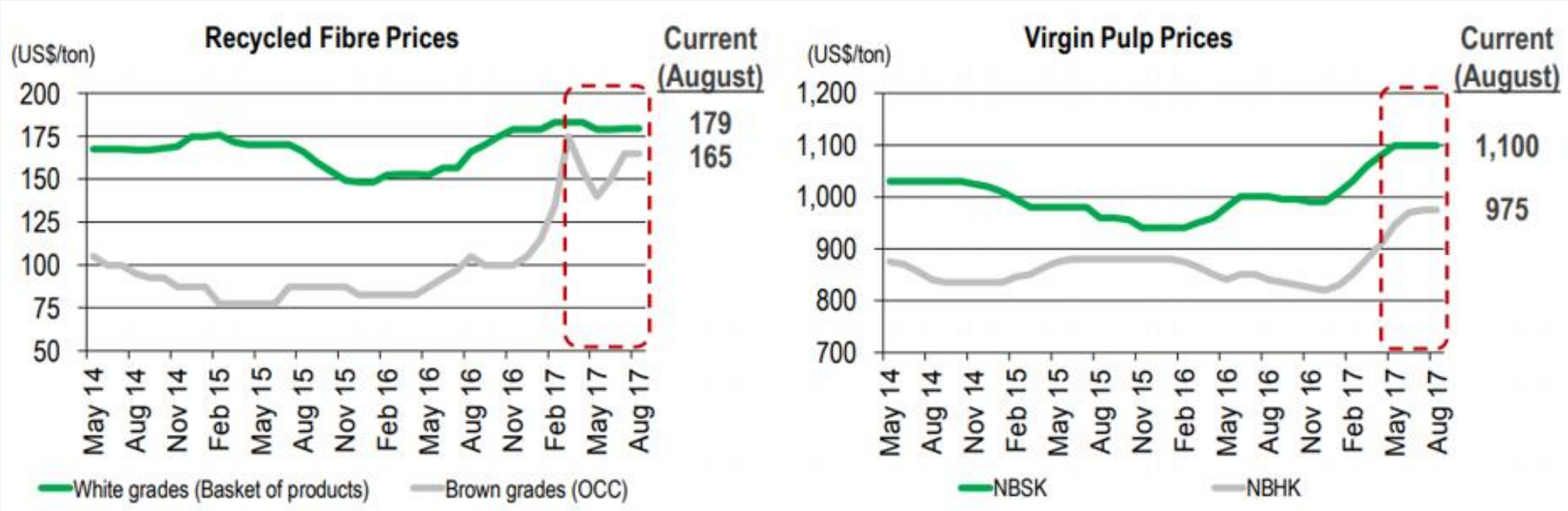


Can be produced in tens of millions of ton quantities

Cost of Cellulose Feedstocks

The prices of the recycled pulp fiber such as old corrugated containers (OCC) are historically significantly lower than other recycled or virgin pulps.

Recycled fibers VS. Virgin pulp

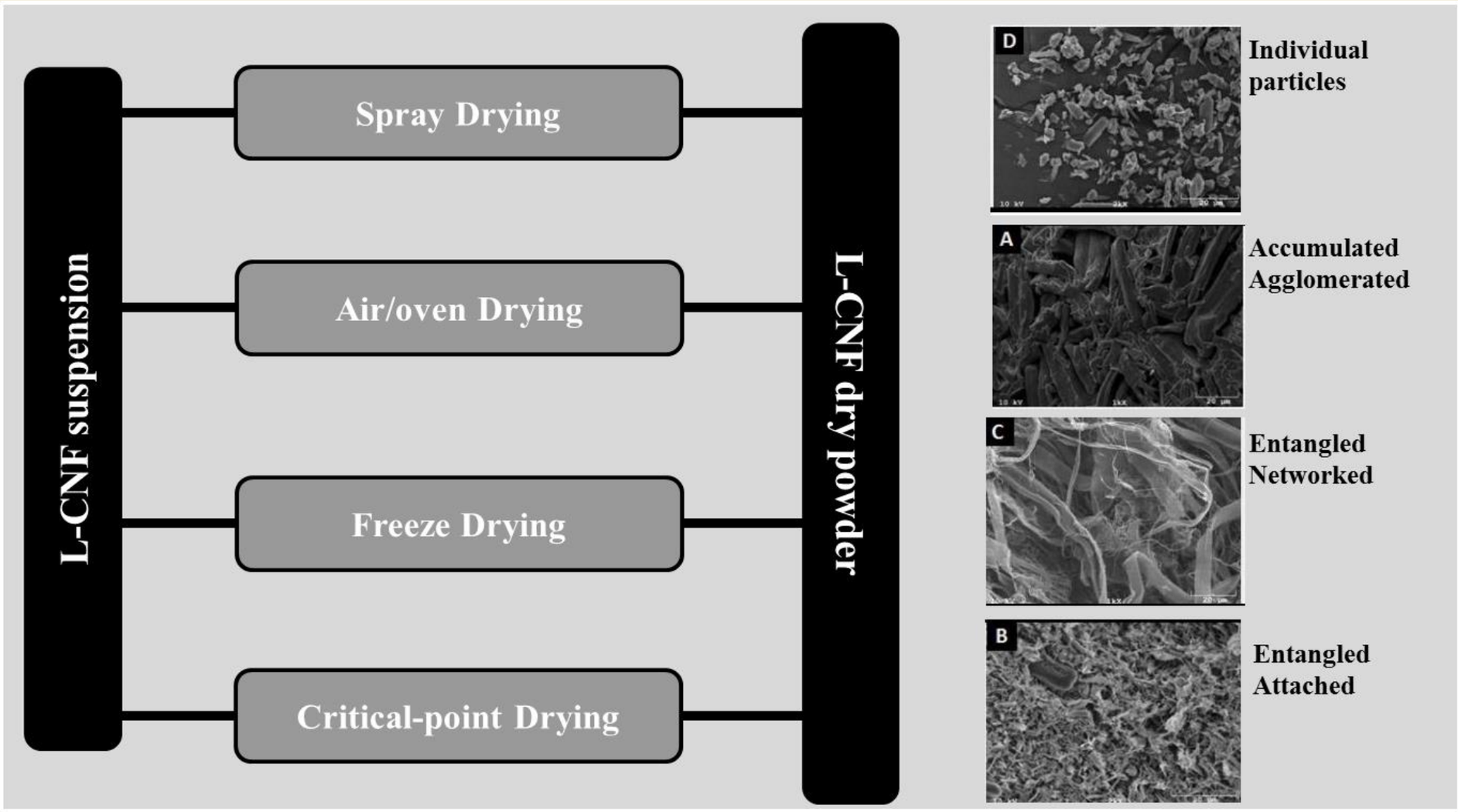


NBSK: Northern bleached softwood kraft pulp
NBHK: Northern bleached hardwood kraft pulp

Source: RISI. [1] Basket of white recycled paper, including grades such as SOP, Hard White Envelope and Coated Book Stock; Northeast average. Weighted average based on Cascades' consumption of each grade.

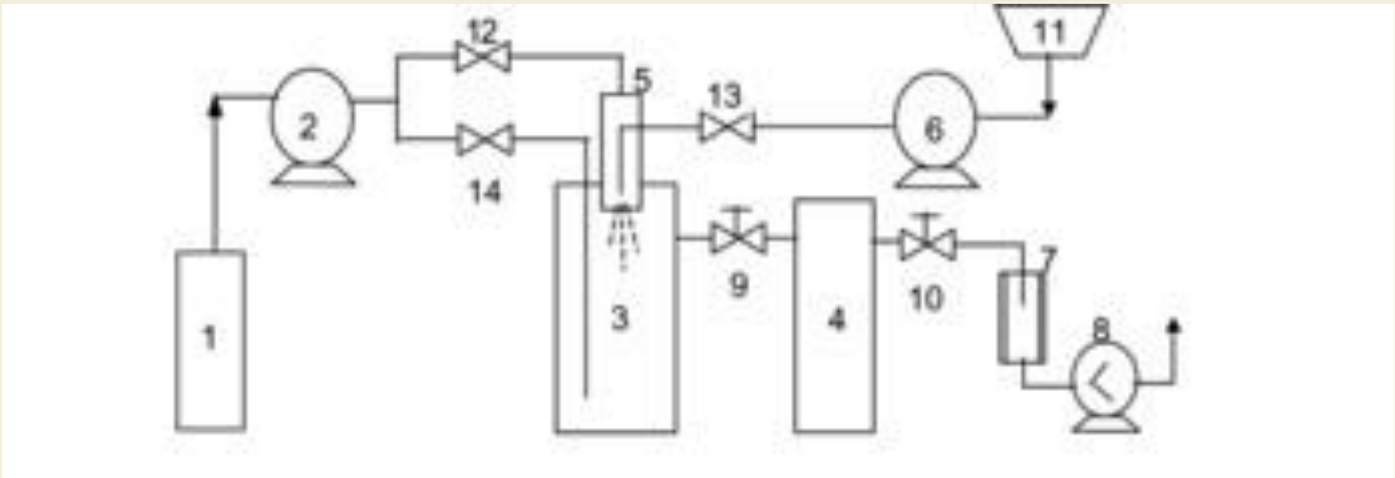
Drying Options in CNF Production

There are technology options for drying *CNF suspensions*. In the polymer processing industry, particulates of CNF are preferred for efficient dispersion and distribution of CNF into the polymer matrices.



Supercritical CO2 Cellulose Spray Drying

- Well explored for pharmaceutical applications
- SAPPI Patent
- Water suspension to organic solvent suspension (ethanol)
- Critical CO2 – Spray Drying Atomization Combination
- Dry, redispersible CNF particles on the nanoscale



1. CO_2 cylinder 2. High pressure pump 3. Precipitation chamber 4. Separation kettle 5. Coaxial nozzle 6. Liquid pump 7. Rotor flowmeter 8. Wet flowmeter 9. Throttle 10. Cut-off throttle 11. Liquid vessel 12, 13, 14. Back pressure throttle

Li, B. G., Zhang, Y., Zhang, W. J., & Hua, Z. Z. (2008). Supercritical CO2 spray drying of ethyl cellulose (EC) for preparing microparticles. *Drying Technology*, *26*(4), 464-469.

Dry Cellulose Particle Feedstocks

There are technology options for production of *CNF suspension* products. The manufacturing options are all conventional and the product quality may be different to each other.

OCC pulp

Mechanical refining

- By disk refining

Pilot disk-refiner at Process Development Center of University of Maine, Orono

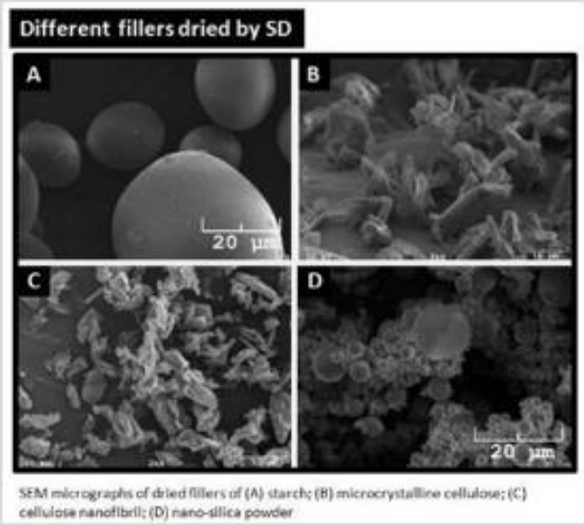
Drying

- By spray drying

Pilot scale spray dryer at TRC of University of Maine, Orono

Dry CNF powder

- Morphology of CNF



SEM micrographs of various powder dried by sprat drying method

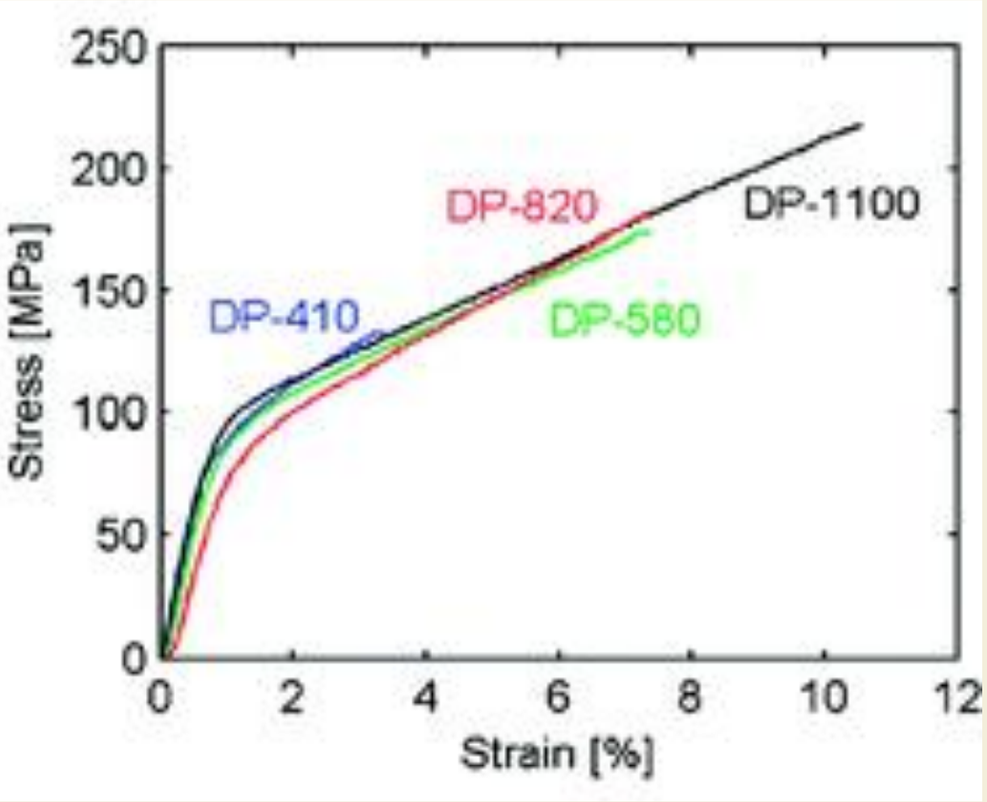
Nanocellulose commercialization

Nanocellulose Close to Commercial Applications?

1. The fruit that grows low on a tree and is therefore easy to reach
2. A course of action that can be undertaken quickly and easily as part of a wider range of changes or solutions to a problem: first pick the low-hanging fruit.
3. A suitable product to exploit as a straightforward investment opportunity.

Disclaimer: *The thoughts expressed are based on the authors' world view.*

Cellulose Nanopaper



- High strength (4 times Kraft, 8 times newsprint)
- High Toughness exceeding plant fibers
- Large strain to failures

Henrikson et al. 2008 Biomacromolecules 9(6)1579-1585.

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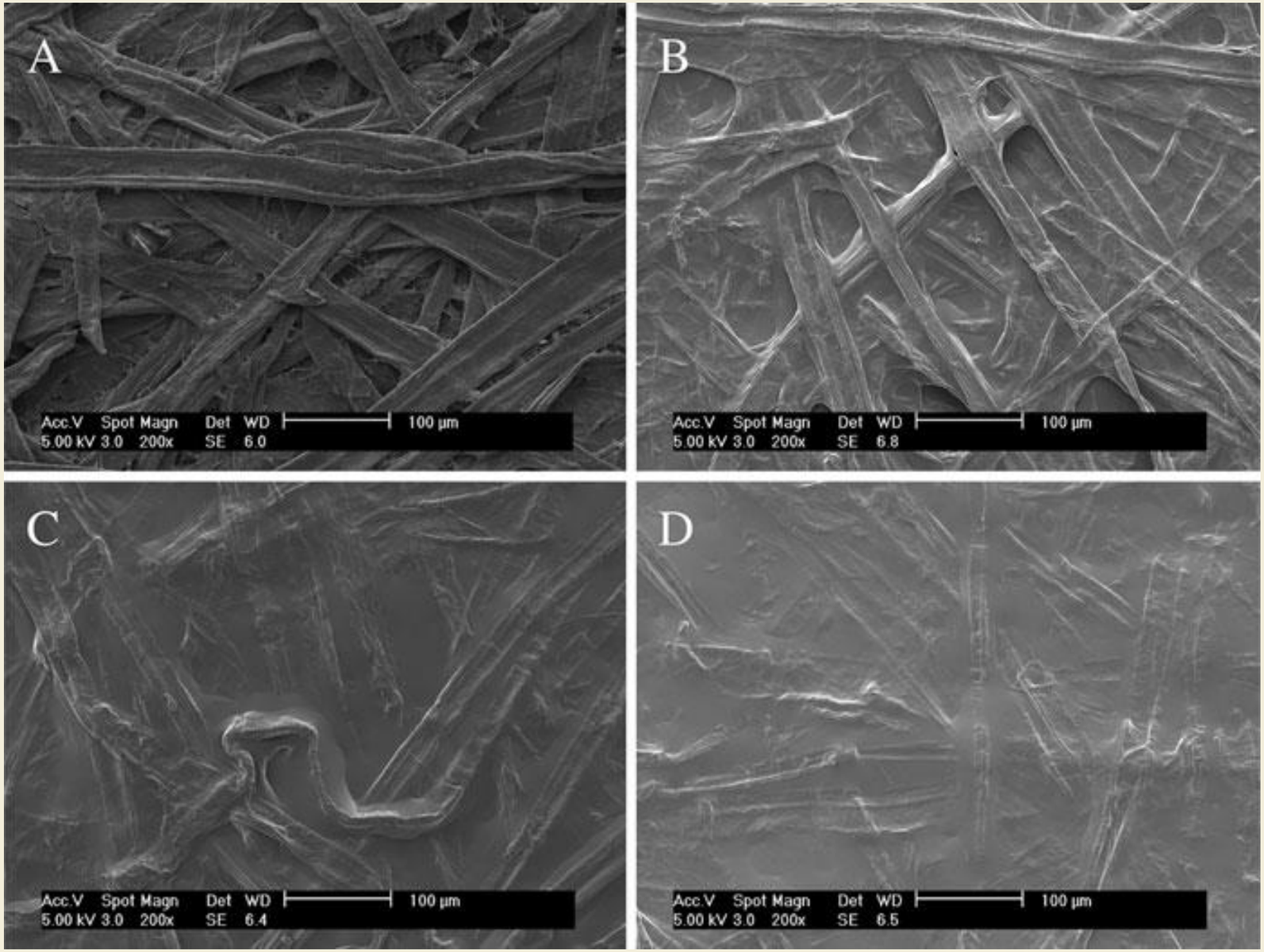
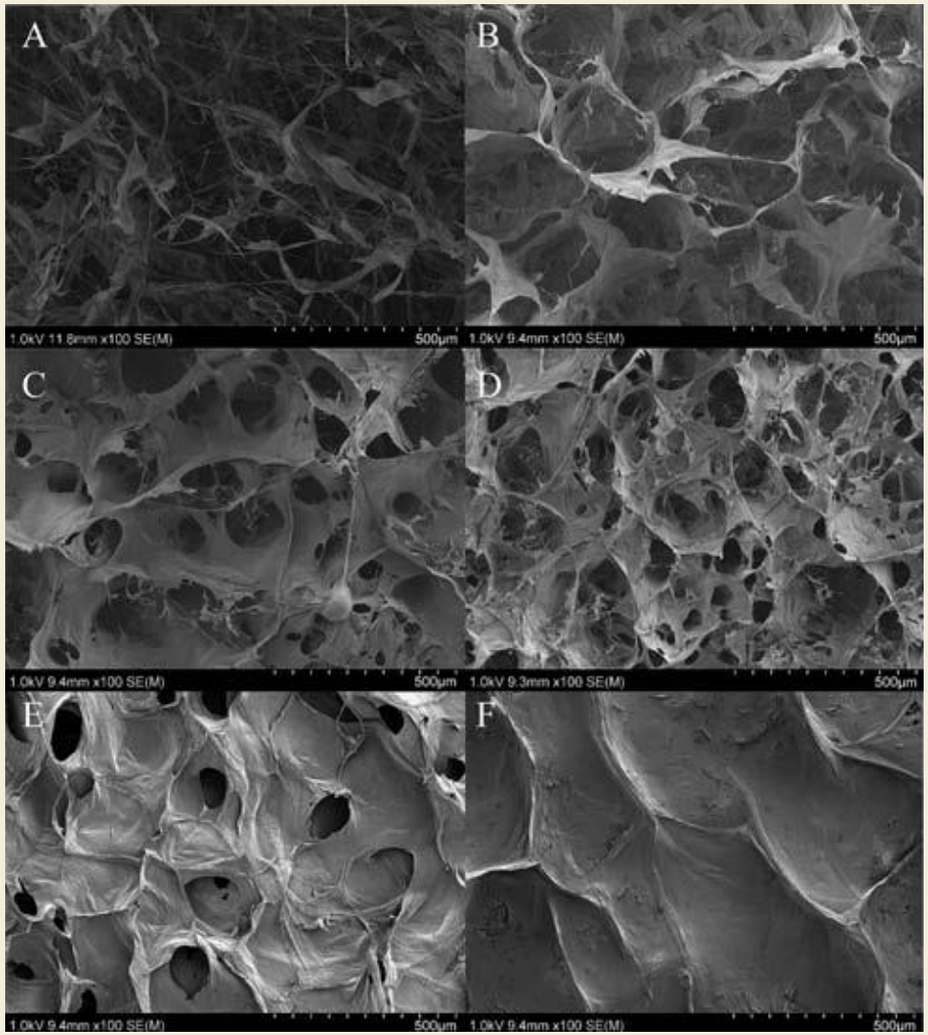
Paper or Board Coatings



E-SEM micrographs of uncoated and NFC-coated papers Aulin et al. 2010 Cellulose 17,559-574

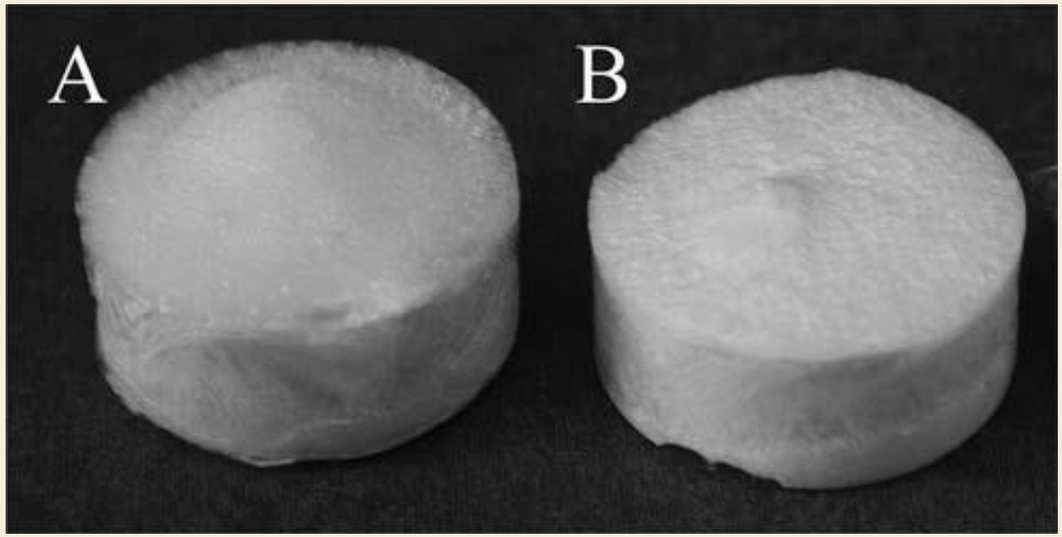
CNF Aerogels/Foams

Low mag. SEM micrographs



Aulin et al. Soft Matter 2010 6:3298-3305

Freeze-dried CNF aerogels



UMaine spin off company *Revolution Research* 2015: received NSF funding for commercialization of NFC foam technology.

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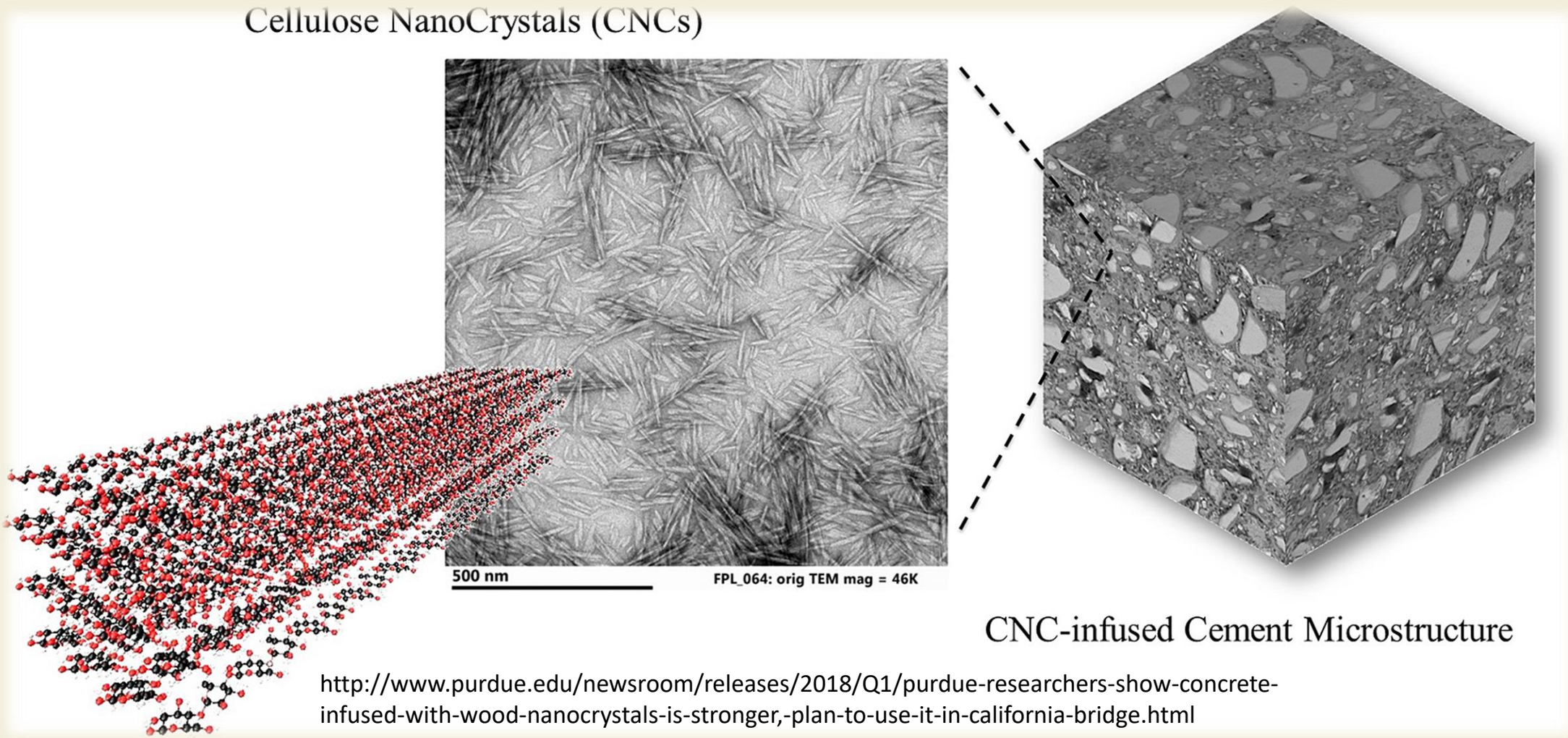
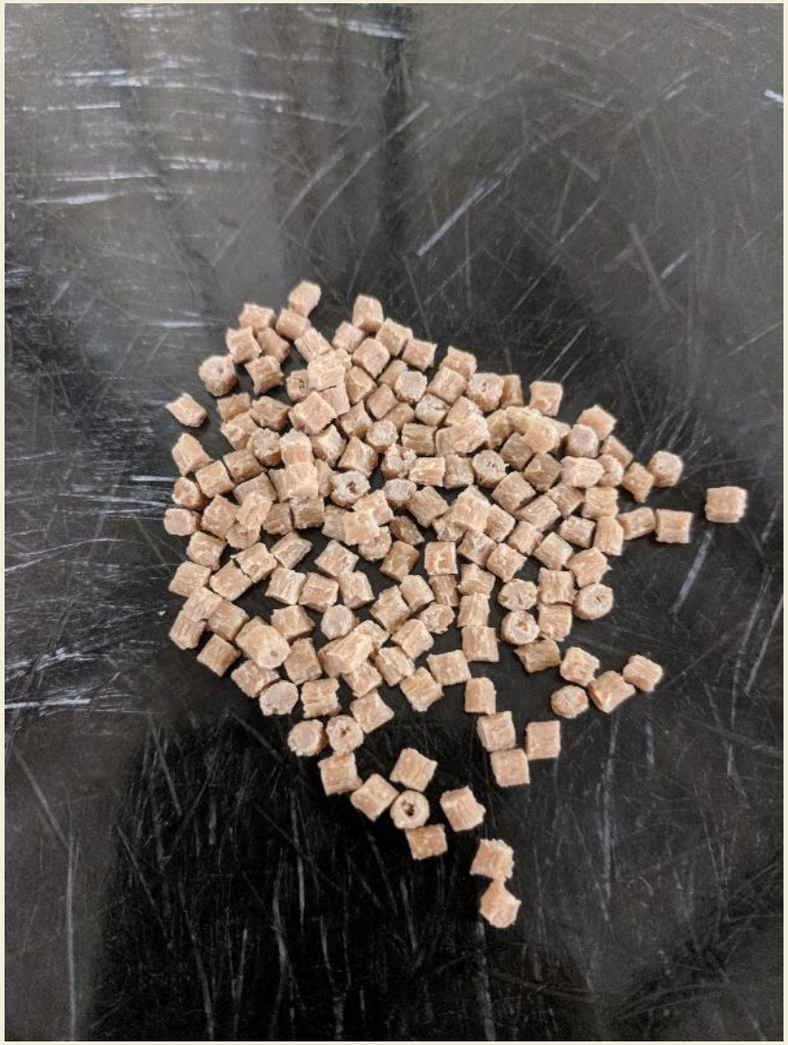
Reinforcement for Concrete



http://www.purdue.edu/newsroom/releases/2018/Q1/purdue-researchers-show-concrete-infused-with-wood-nanocrystals-is-stronger,-plan-to-use-it-in-california-bridge.html

Compostable Packaging/Films

Large Scale Additive Manufacturing



PLA 20% Wood Flour + 1% CNF

- Gantry Speed: 2.2 in/sec, Layer Time: 2 min 18 sec
- Temp Profile (°C): 130, 170, 170, 195, 200
- Melt Temp (°C): 209
- Layer Height: 0.15 in/Bead Width: 0.335”/Nozzle size: 0.3”

* Photos courtesy ORNL

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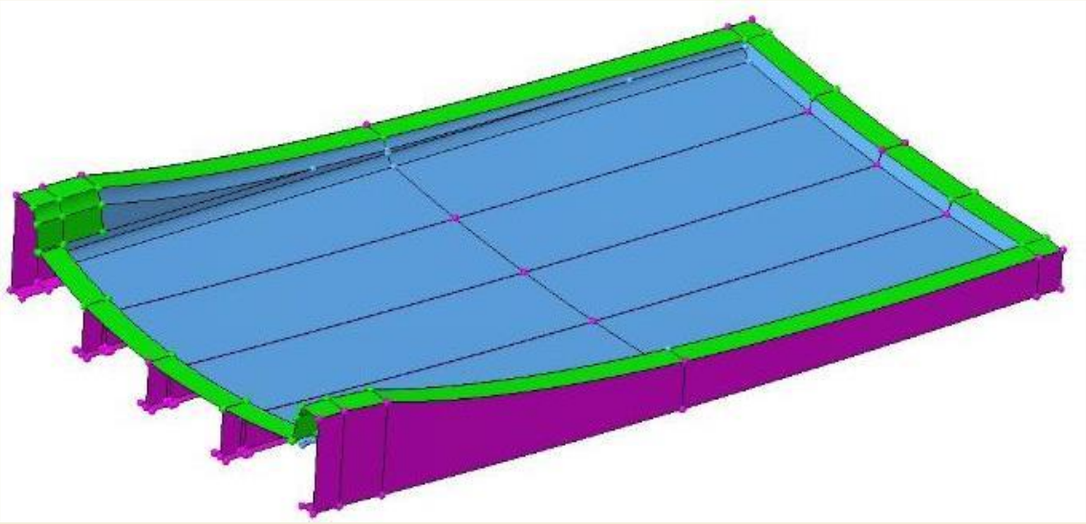
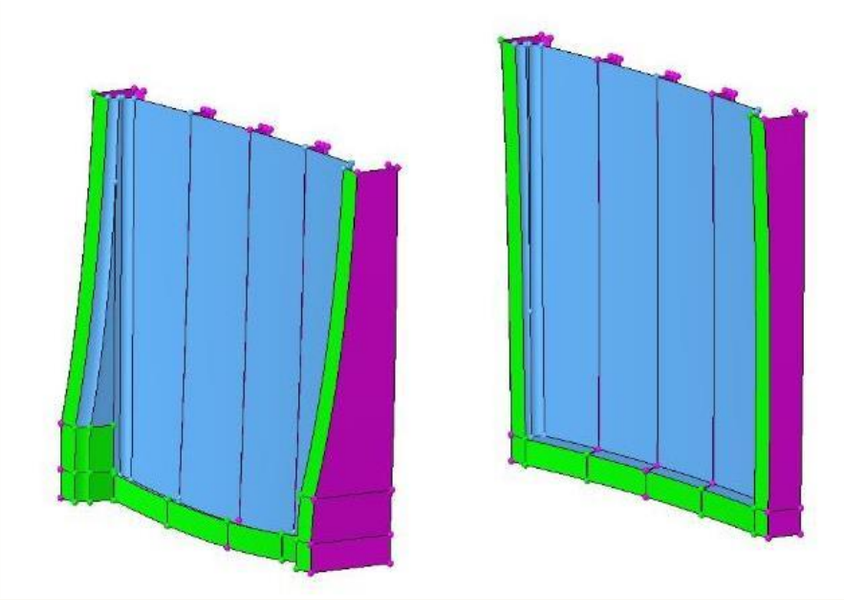
Hodgdon Boats 10.5m Limo Roof Mold

16’ x 8’, approx. 1200lb material





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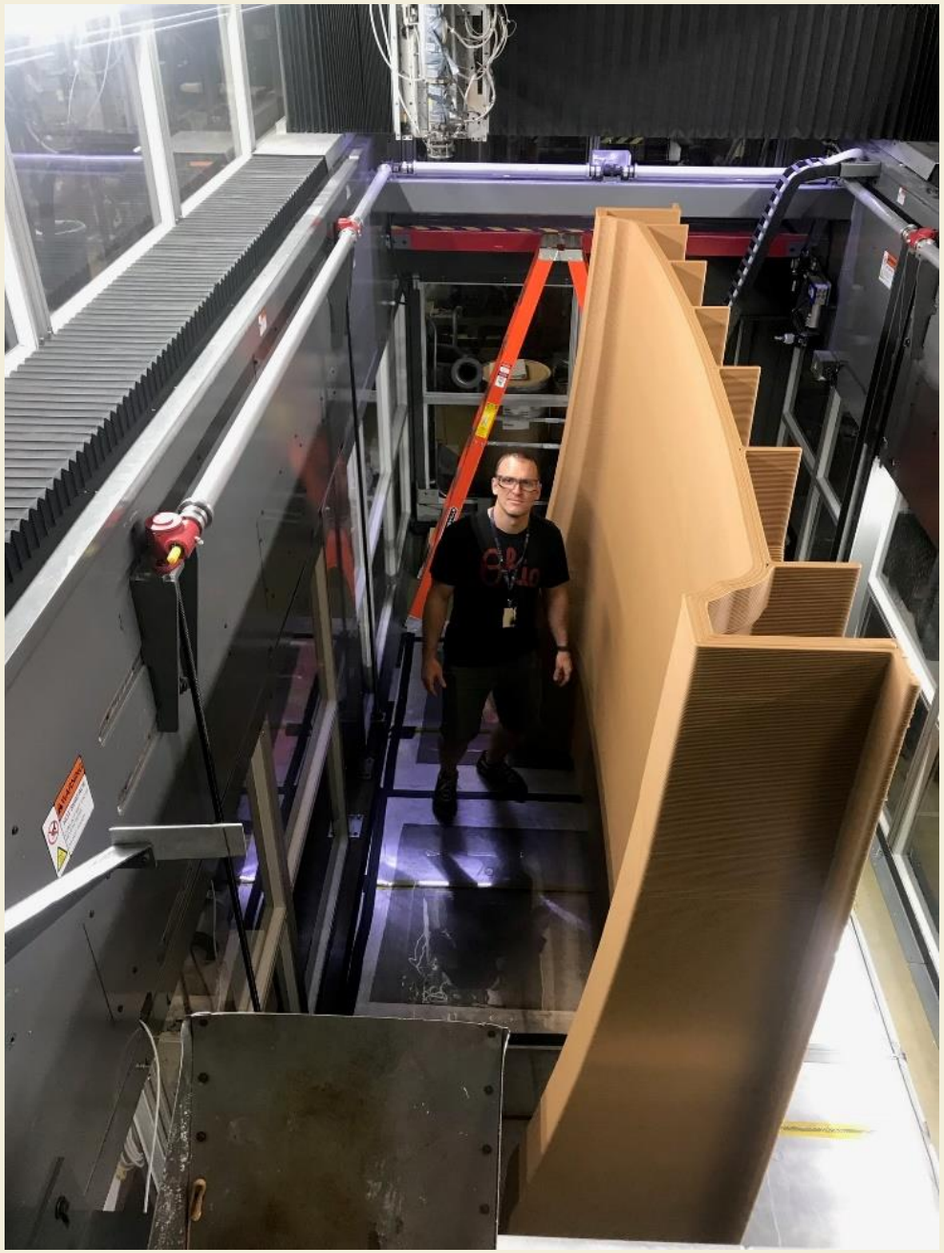
Printing Roof Mold Wood/CNF/PLA Composite



Joint Project between the University of Maine and Oak Ridge National Labs

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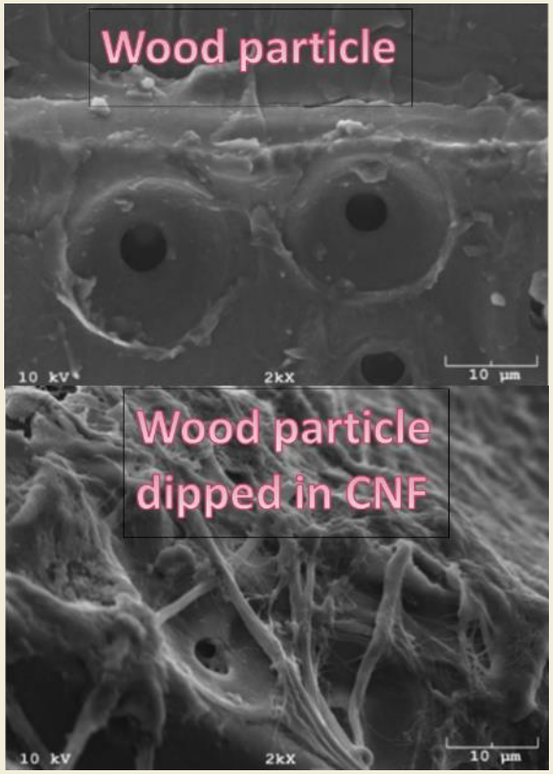
CNF as adhesives for composites

- Production of new composites such as particle board made of CNF adhesives rather than synthetic thermosetting resins

Researcher:
Mehdi Tajvidi, PhD.



Materials
- 3 wt.% CNF slurry
- Southern pine

Methods
- Forming
- Cold pressing
- Hot pressing

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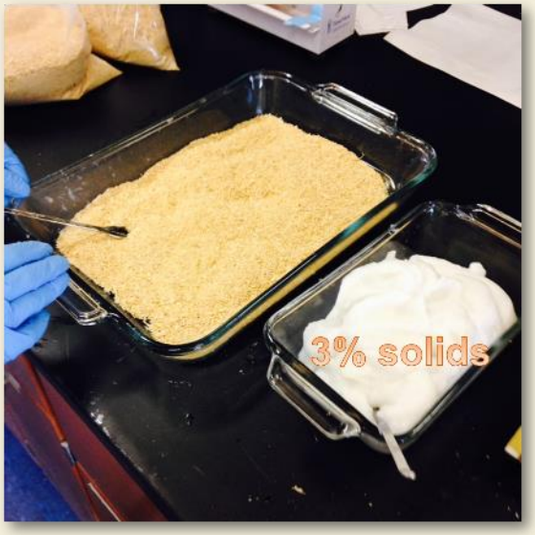
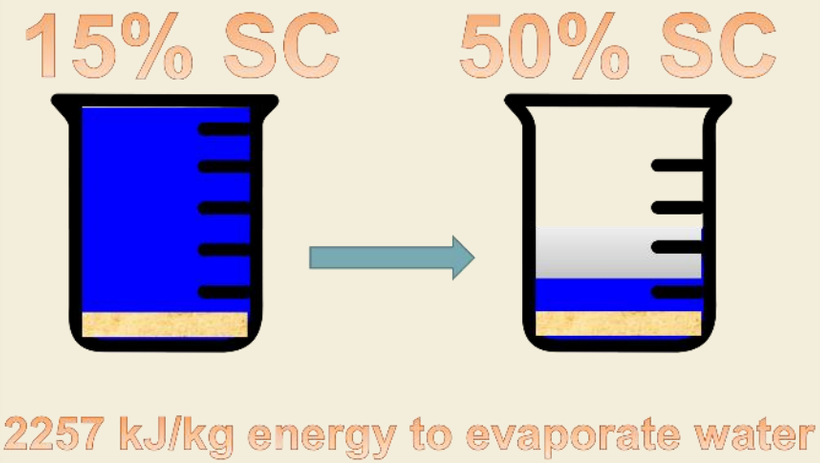
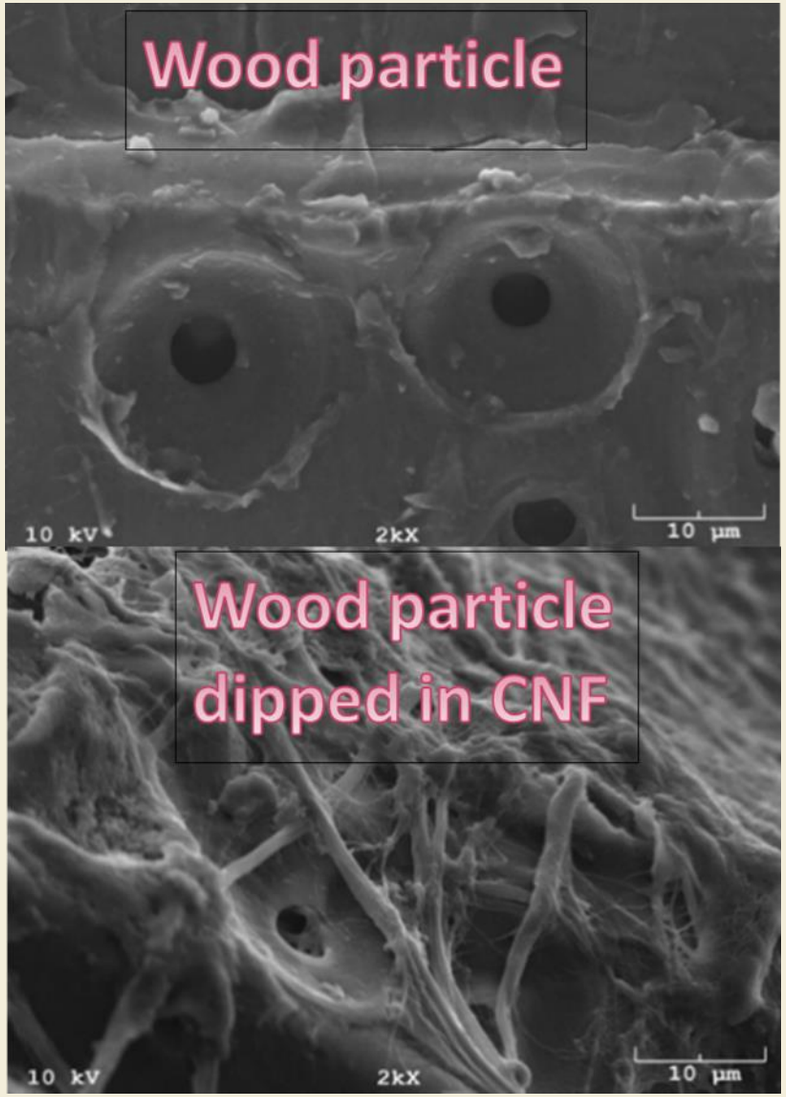
CNF as adhesives for composites

- No formaldehyde added
- No need to dry CNF prior to manufacture
- Phenomenon of CNF –wood particle contact dewatering
- Rely on Hydrogen Bonding







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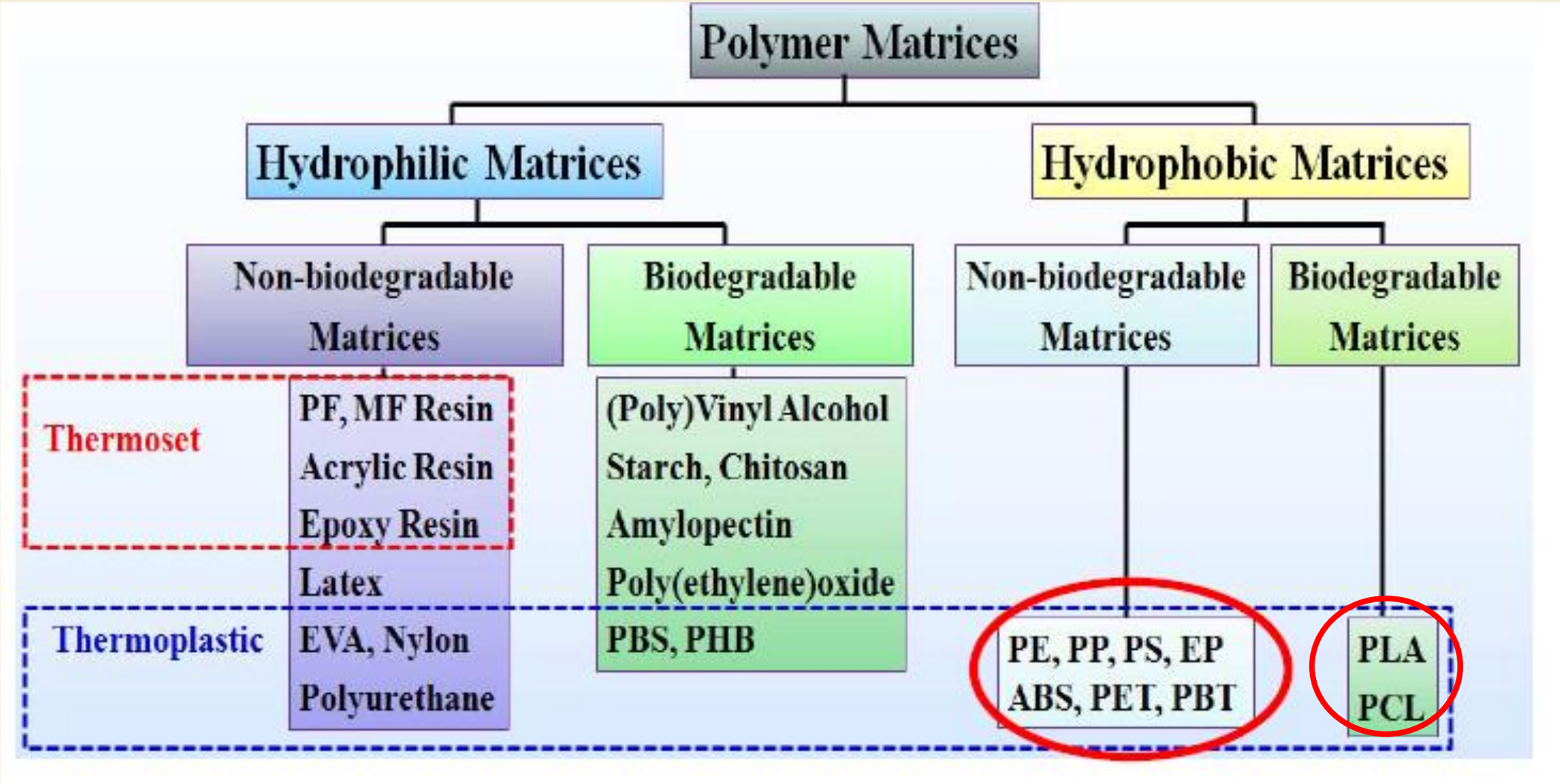
Challenges using CNF

- Poor Adhesion and Dispersion in Hydrophobic Matrices
- Processing challenges for commercially relevant production processes.



Nanocomposite manufacturing

Nanocomposites:

Material composed of polymeric matrices reinforced with *nano-sized fillers or additives* for improved properties, including physical & mechanical properties.

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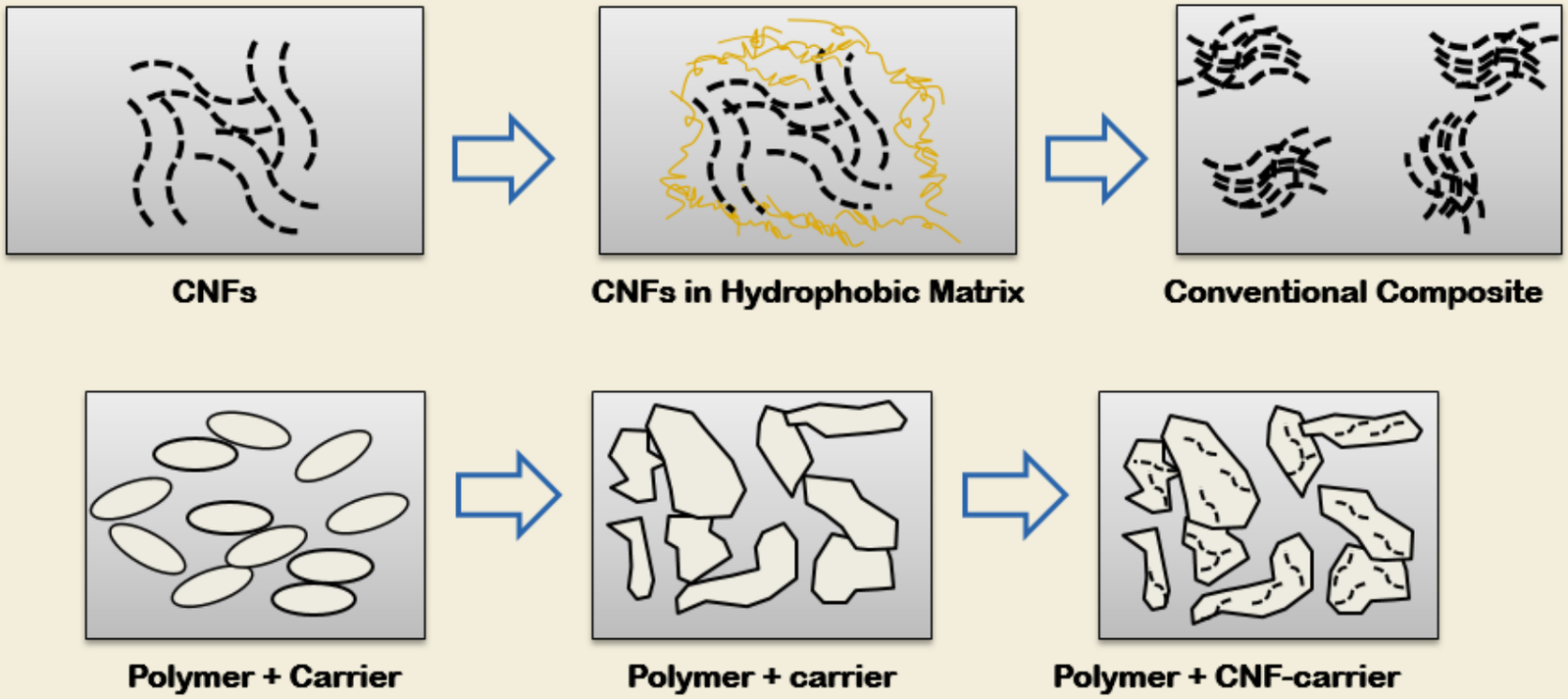
One approach:

Base Polymer (Hydrophobic Matrix) + **Nanoscale Additive (Filler, Dispersed Phase CNFs)** + **Functionalized Carrier System**

=

Hydrophobic Thermoplastic Composites with Better Dispersion and Improved properties



Kiziltas, A. 2014. Carrier Systems For Cellulose Nanofibers In Hydrophobic Polymer Composites. Doctoral dissertation. University of Maine, Orono, ME. 202 pp.

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Cellulose Nanocomposite Production

Carrier

CNF

Polymer

Speed Mixer

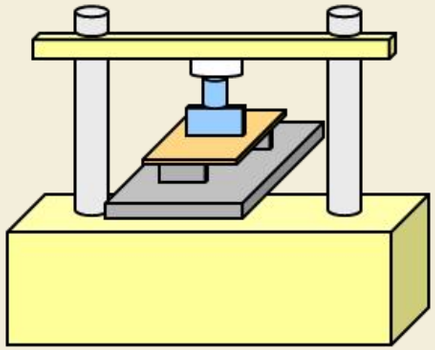
Brabender Bowl Mixer or Twin Screw Extruder

Compounded Materials

Production Flow Process

Grinder

Injection Molder



ASTM Tests Samples
Tensile, Flexure, Impact

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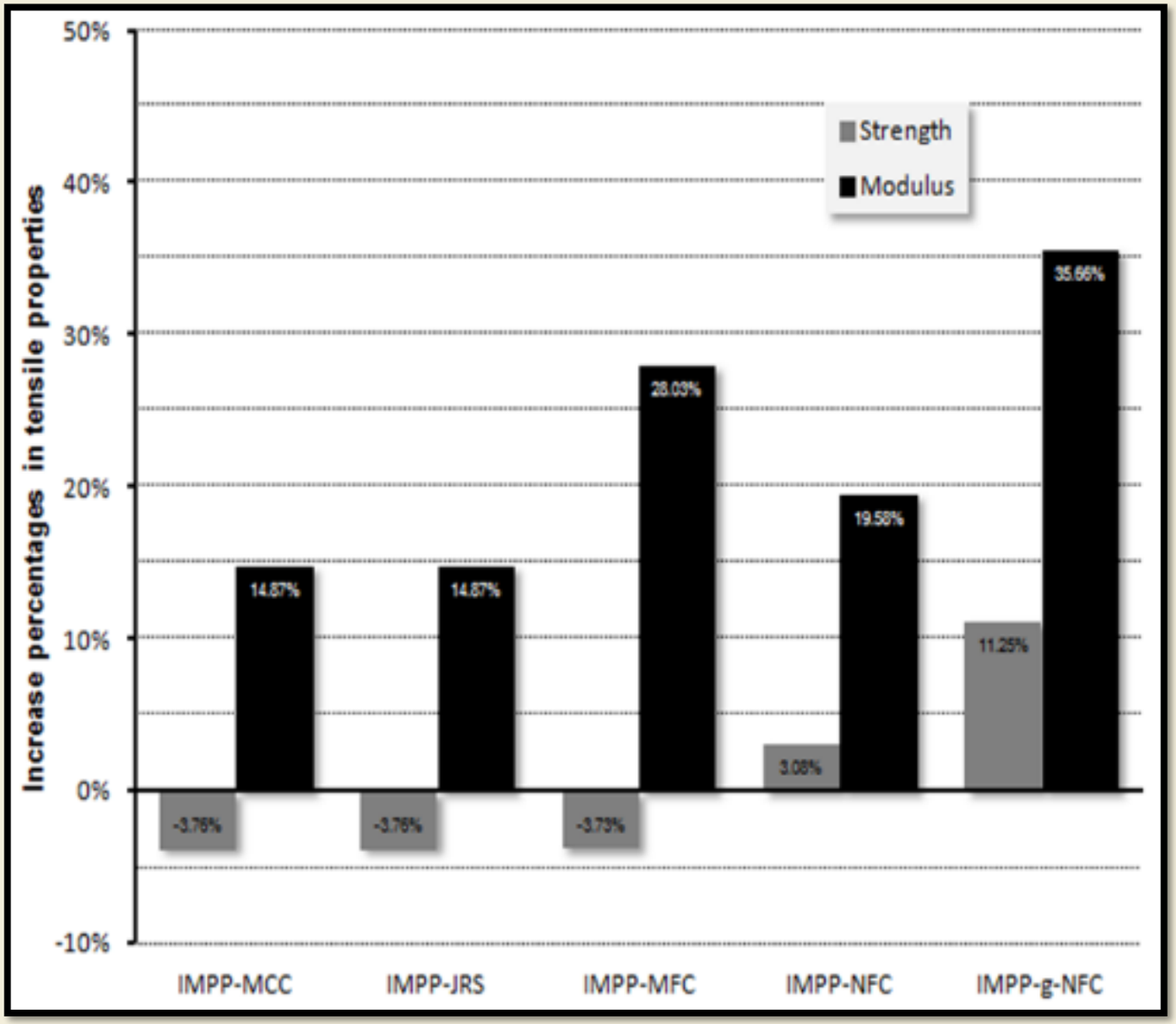
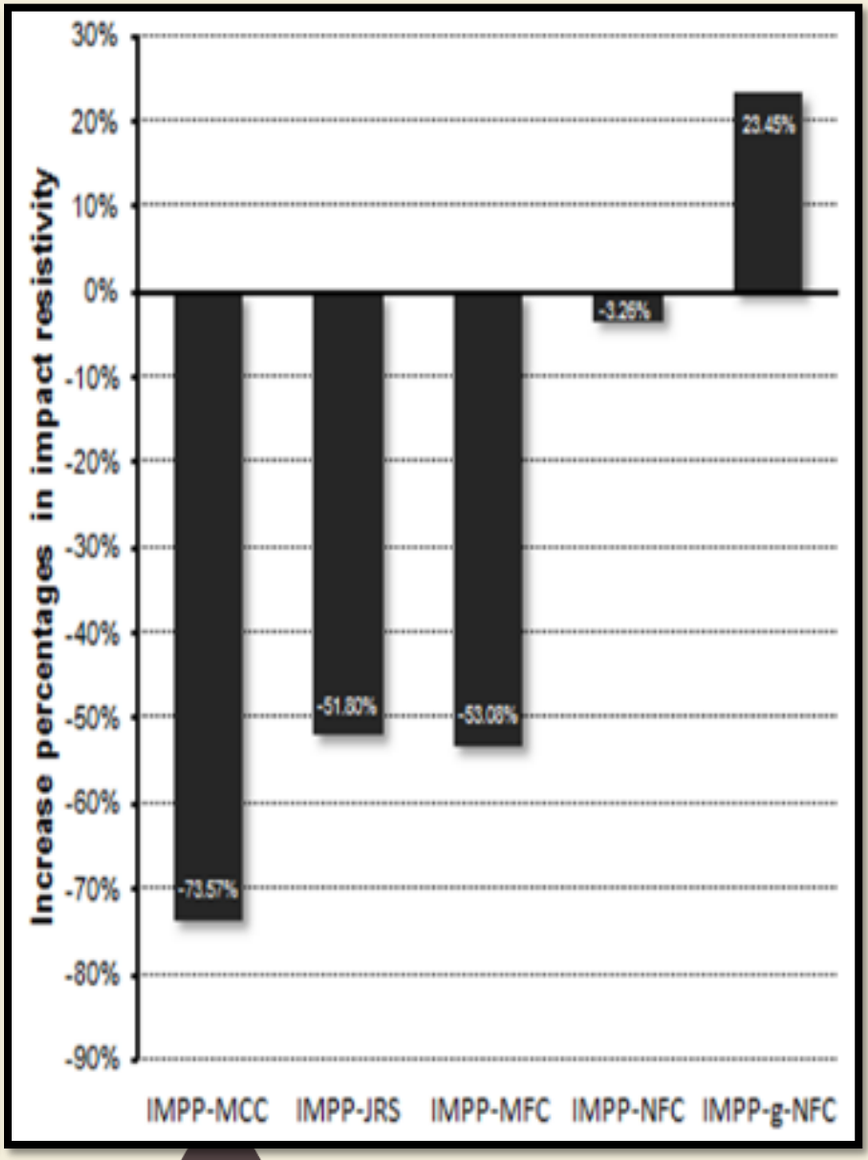
Nanocomposites with Cellulose Nanofibers

UMaine Polypropylene Nanocomposites with spray dried CNF





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Thermoplastic Cellulose Nanocomposites Mechanical Properties

- Reasonable increases in tensile and flexural properties at modest CNF loading levels
- Maintaining or increasing impact strength is more challenging

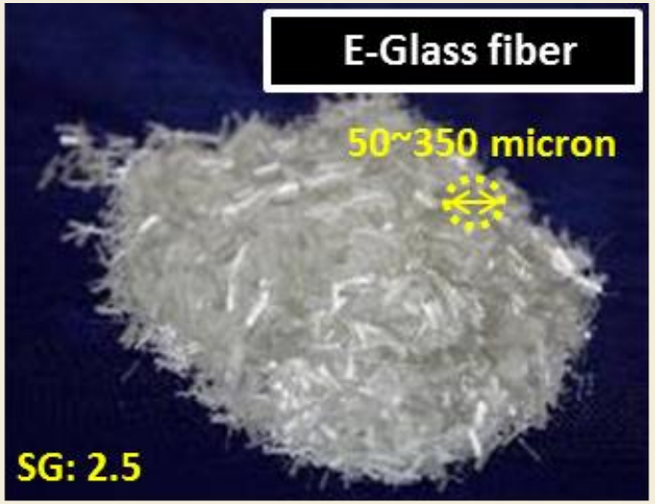
Polymer Matrix	Processing Aid/ Surface Treatment	CNF Added (%)	Tensile MOE Increase (%)	Tensile MOR Change (%)	Flexure MOE Increase (%)	Flexure MOR Change (%)	Izod Impact Change (%)
PP	MAPP	6	36	11	21	7	23
PA 6	POSS	5	25	10	13	0	-38
PE	PVA	5	40	25	20	12	-53
PMMA*	None	0.5			23	5	
SMA	Glycerin	5	6	5	7	-5	
PLA	PHB	5	10	-6	12	1	10

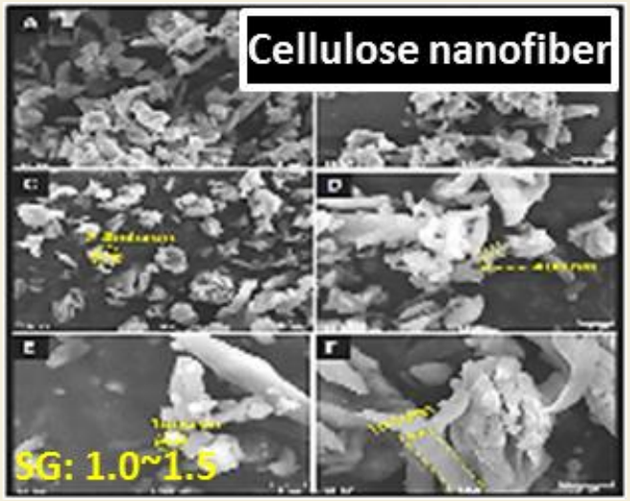
*Samples made by solvent casting.

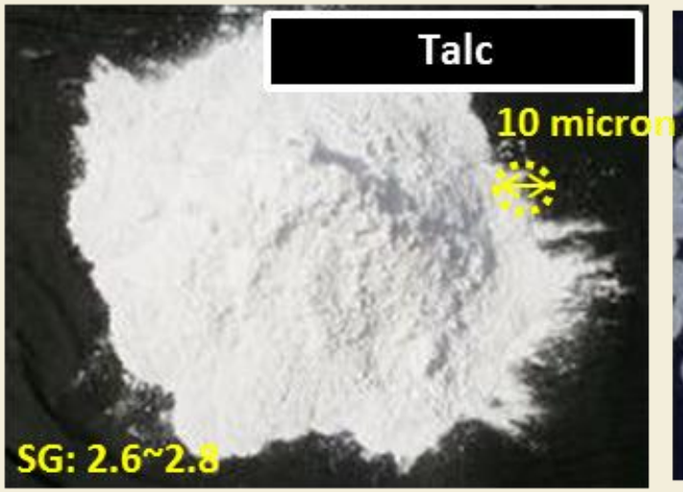
Hybrid Cellulose Nanocomposites

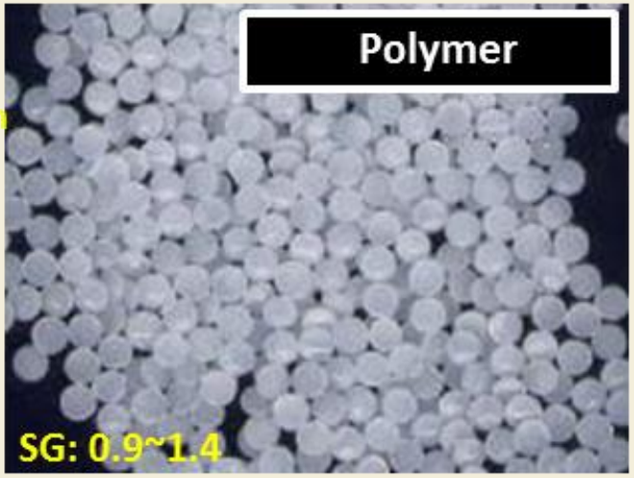
Hybrid Nanocomposites:

Composite materials composed of polymeric matrices reinforced with mixtures of *nano-additives* and *conventional fillers* for economic competitiveness and improved properties



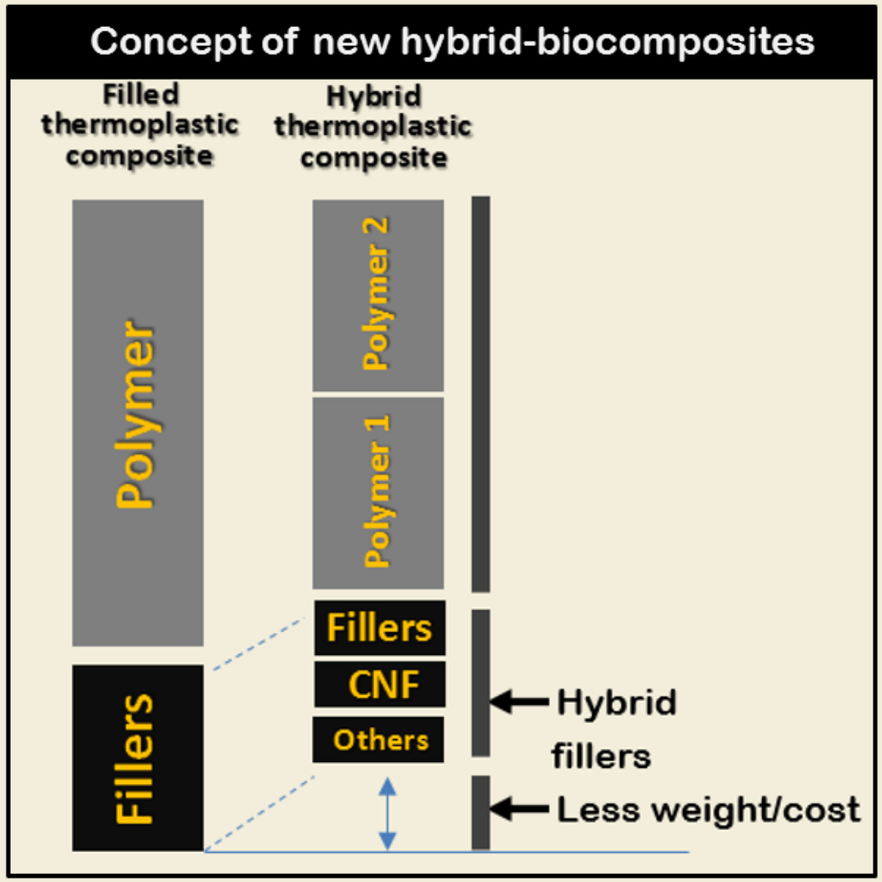


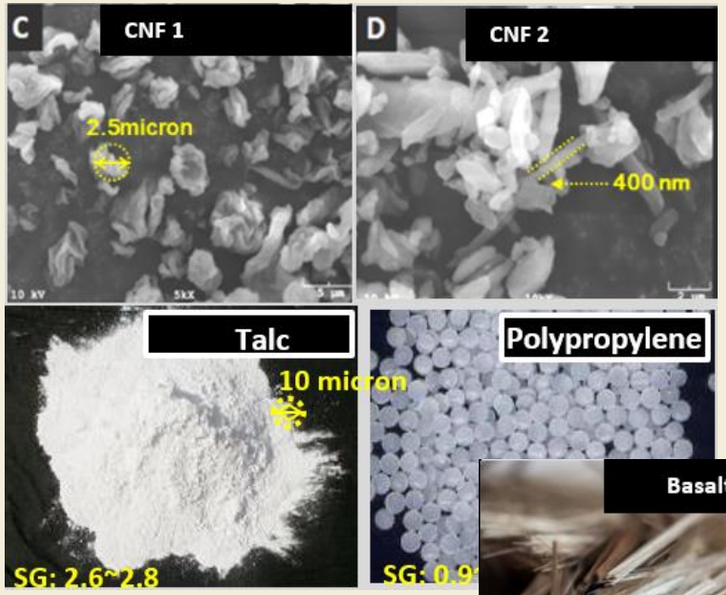




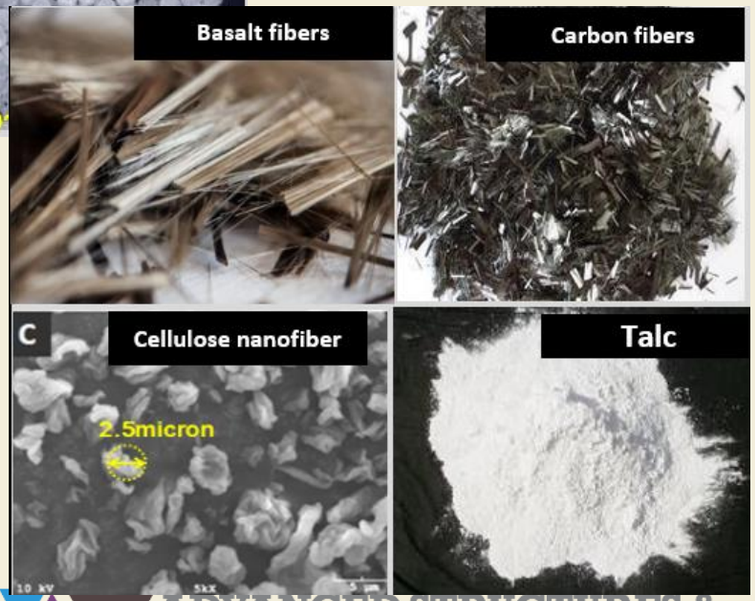
Hybrid Cellulose Nanocomposites

- Hybridization of functional additives in polymer blends to improve the properties by synergetic effects of the components





Case study 1



Case study 2

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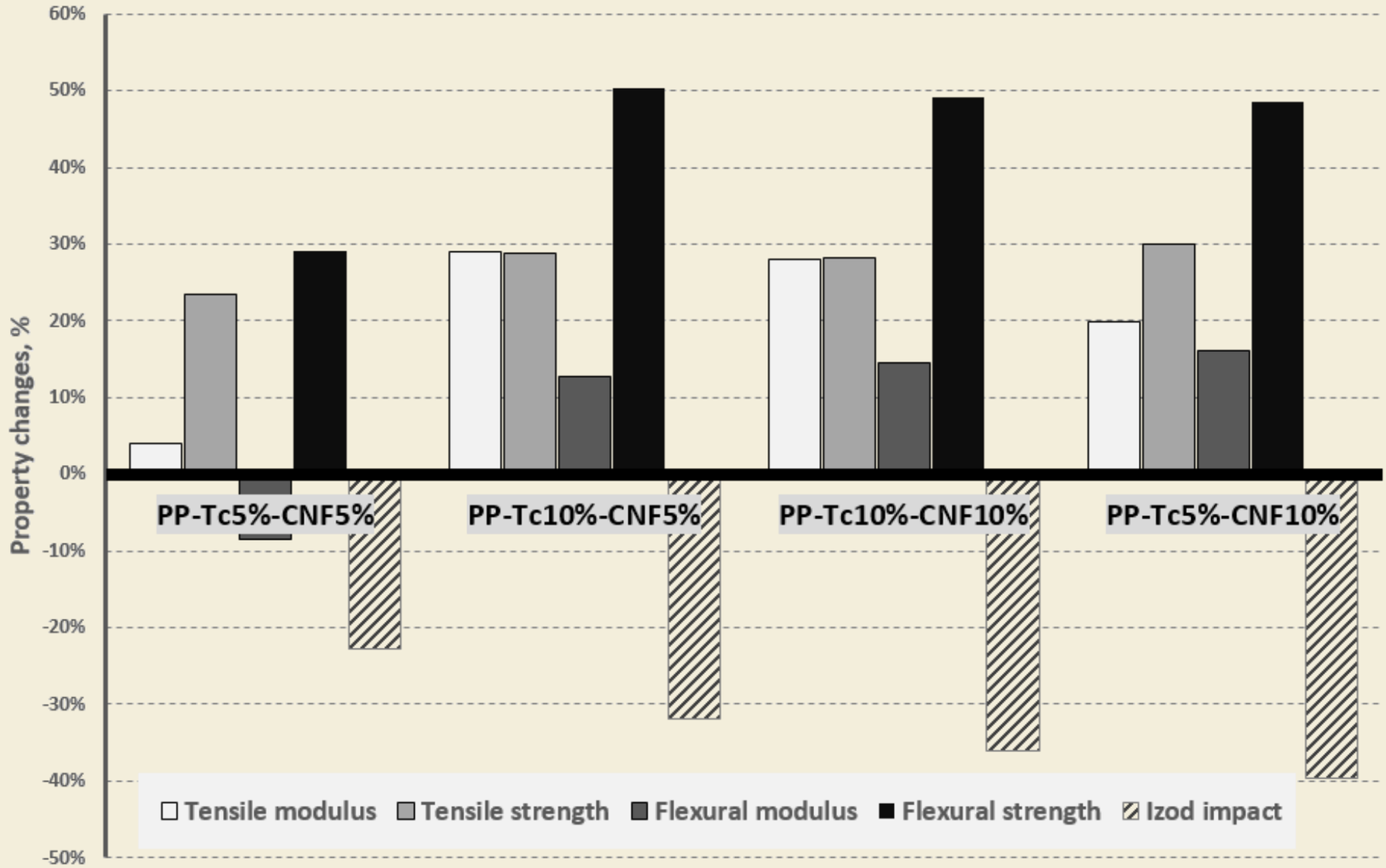
Expectations from Hybrid Nanocomposites

- Combinations of fillers can provide ***enhanced material property performance*** in polymer matrix composites
- Addition of fillers can also typically ***reduce the cost of the resulting composite*** especially with the application of nature-derived fillers such as cellulose nanofibers
- Filler combination chosen to provide ***improved mechanical properties*** and ***reduced composite density***
- Manufacturers are looking at ***automotive composites for lighter weight materials*** to provide better fuel economy and lower carbon dioxide emissions

Hybrid Cellulose-Talc Nanocomposites

Improvements in mechanical properties



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CNF(CMNF) Techno-Economic Analysis

Material	Price per ton pulp ($)	Price per pound ($)
Bleached Softwood Kraft	1016	0.51
OCC	105	0.05
CMNF-Bleached Kraft	1893 - 2440	0.95-1.22
CMNF-OCC	712	0.36
CNC	4380 - 5900	2.19-2.95
TEMPO	187,720 - 220,692	93.86-110.34
Lyocell	2440 - 2727	1.22-1.36

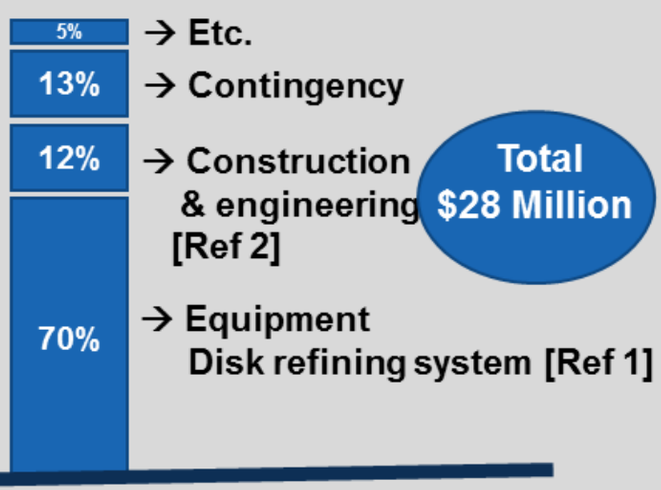
Selected Scenario of Capital Investment

There are few options for the capital investment, depending on the operation methods of facilities and the manufacturing scale. In this study, the medium investment scenario was selected without consideration of new investment for a spray drying facility.

Investment scenario

Co-location facilities

- The manufacturing facilities locate multiple area.
- The investment scale is smaller than the case of stand-alone facility



Breakdown of capital investment

Manufacturing data

- Estimated process data & financing assumptions [Ref 1]

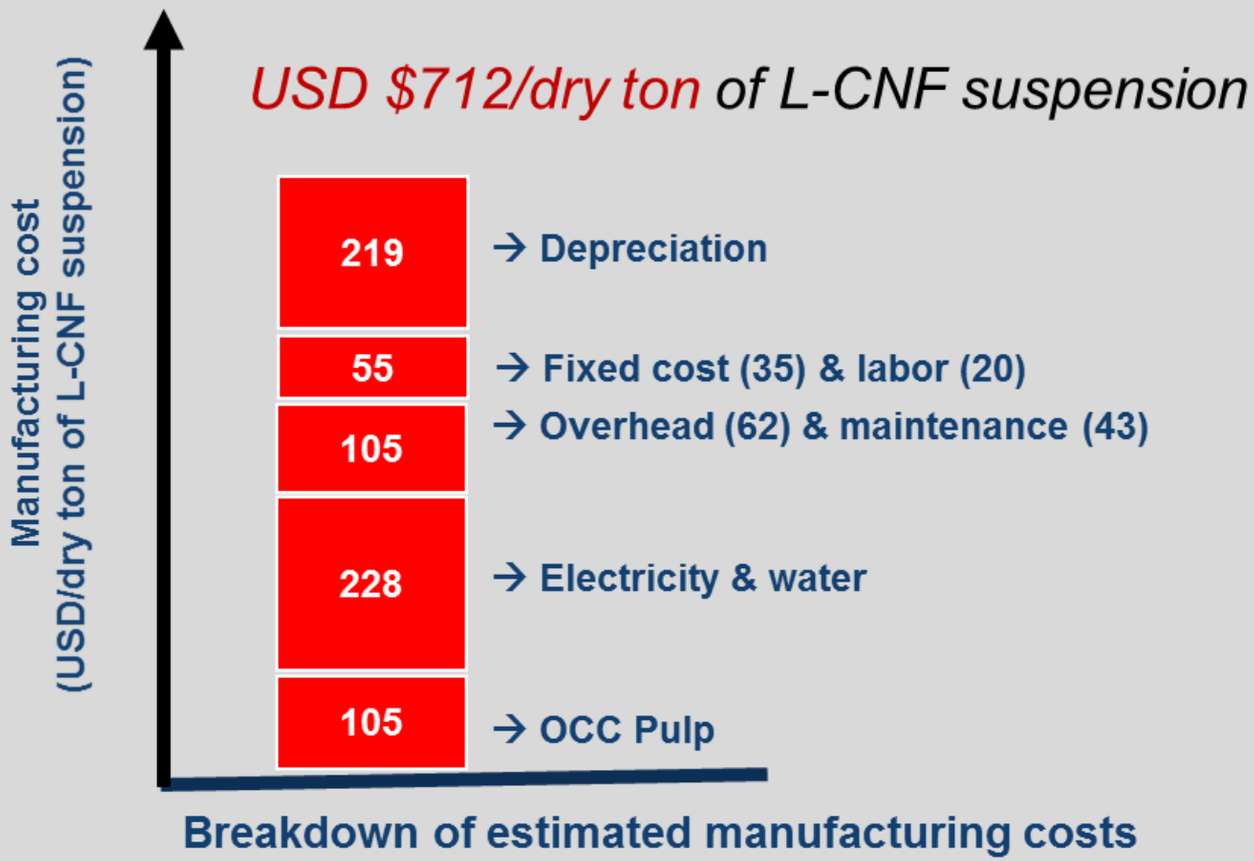
Production rate	50 dry ton/day
Electricity	3,000 kWh/dry ton
Process yield	100%
Solid content	3 wt.%
Production	100% of capacity
Depreciation	10 years
Operating days	340
Staffs	8 persons

Ref 1. de Assis CA, etc. Cellulose micro-and nanofibrils manufacturing-financial and risk assessment. Biofuels Bioprod Bioref 12:251-264 (2018)

Ref 2. de Assis CA, Houtman C, Phillips R, Bilek T (E.M.), Rojas OJ, Pal L, et al. Conversion Economics of Forest Biomaterials:Risk and Financial Analysis of CNC Manufacturing. Biofuels Bioprod Bioref 11:682–700 (2017).

Manufacturing Cost of LCNF

Estimated manufacturing costs of mechanical refining of L-CNF



Manufacturing cost

USD $712 per dry ton of L-CNF suspension

Manufacturing Cost of LCNF

UMaine collaborated with a spray drying company to estimate the manufacturing costs of spray drying. The estimated cost depends on the final solids content of the products in suspension. The target solids content of CNF was set at 2 wt.%. **(Still needs additional processing research and techno economic analysis)**

Commercial scale spray drying

Resource #1

SPRAY-TEK®
QUALITY, SERVICE, RELIABILITY

- **UMaine collaborated with the company to run a commercial scale trial of spray drying of CNF.**
- **Three (3) batches of suspension were utilized in a commercial spray dryer system.**
  (4,500 lbs of suspension processed /day)
- **Commercial Scale Spray Drying Cost Estimates were high $45 to $85/ lb.**

Resource #2

Alfredo Domínguez-Niño, etc. (2018)
Energy requirements and production cost of the spray drying process of cheese whey
Drying Technology, 36:5, 597-608
[DOI:10.1080/07373937.2017.135086]

- **Bench Scale analysis**
- **USD $7.7/lb of products, estimated**
- **The cost depends on the operating conditions.**
  (yield, solid contents, energy consumption, moisture contents, etc.)
- **Solids content in this study: 8.4 wt% in water**

Spray Drying cost

USD $15,000* per ton of CNF

- **Not included with material costs**
- **Expected solids content 2 wt.%**
- **Fixed costs, from capital investments, not included**

Conclusions

- Select applications of cellulose nanomaterials in composite materials are either being explored for commercial production or are far enough along the technology readiness level to be soon implemented.

- Large scale applications where dry CNM are needed for production still requires R&D to lower production costs.

- Dewatering and control of agglomeration are still major challenges for the application of CNM.

Thank you!

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