International Conference on Nanotechnology for Renewable Materials

Revolutionizing Nanocellulose-Reinforced Composites Through the Manufacturing Renew3D Program

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TAPPI NANO DIVISION

12-16 JUNE 2023 • VANCOUVER, B.C. CANADA

SM^{2}ART

Sustainable Materials and Manufacturing Alliance for Renewable Technologies

- We transform locally sourced bio-materials and the advanced manufacturing processes that utilize them by leveraging world class R&D institutions that share a culture of **commercializing innovative solutions at scale.**

- We demonstrate applications of our **technology platform** in a variety of industries to drive adoption of sustainable materials and decarbonize the manufacturing industry.

SM^2ART

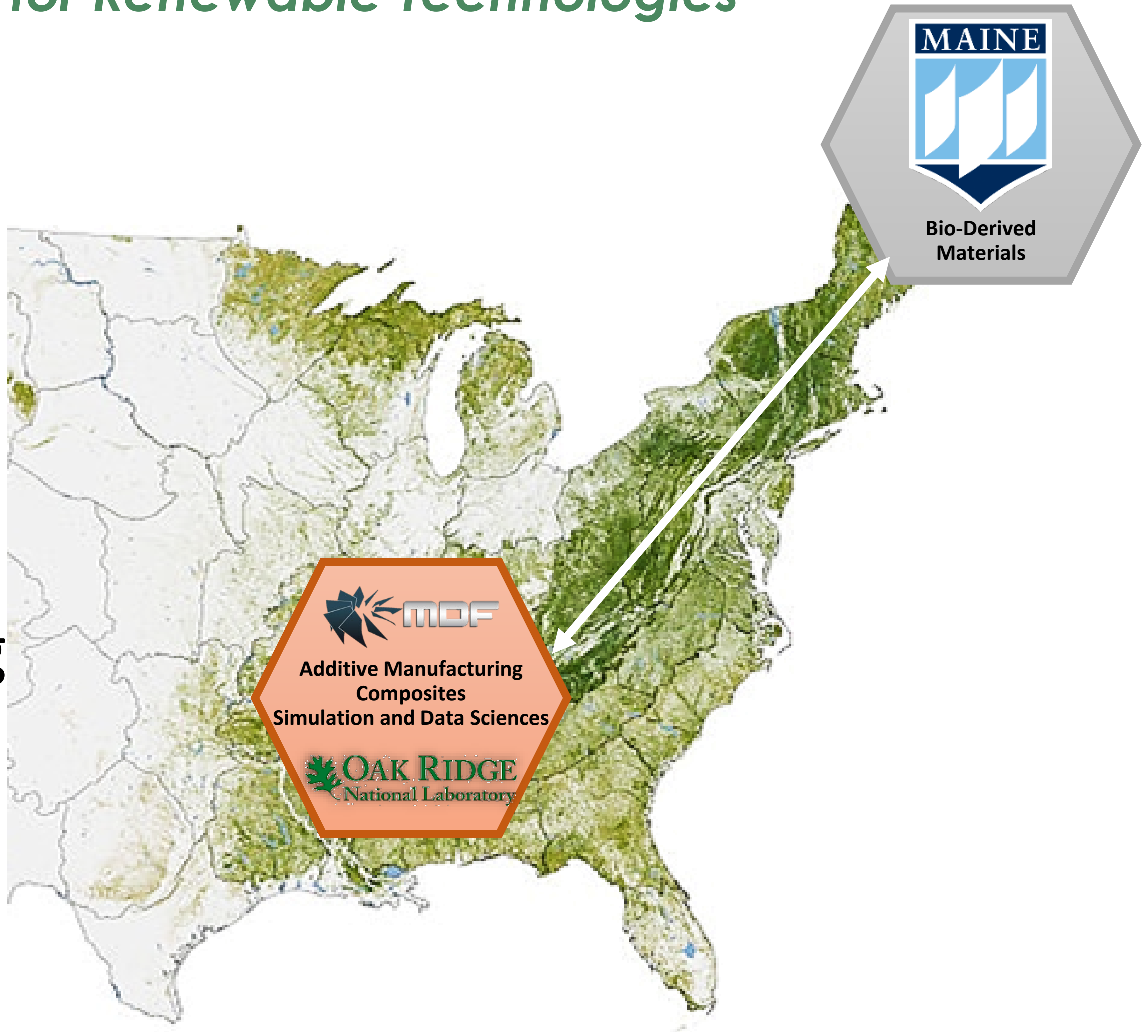
Sustainable Materials and Manufacturing Alliance for Renewable Technologies

- Emphasis of forest resources and advanced manufacturing
- Seek broader input to make the best use of industry resources
- Areas of focus to deliver what industry needs
- Help with the business case
- Seek to de-risk technologies with market pull

SM^{2}ART

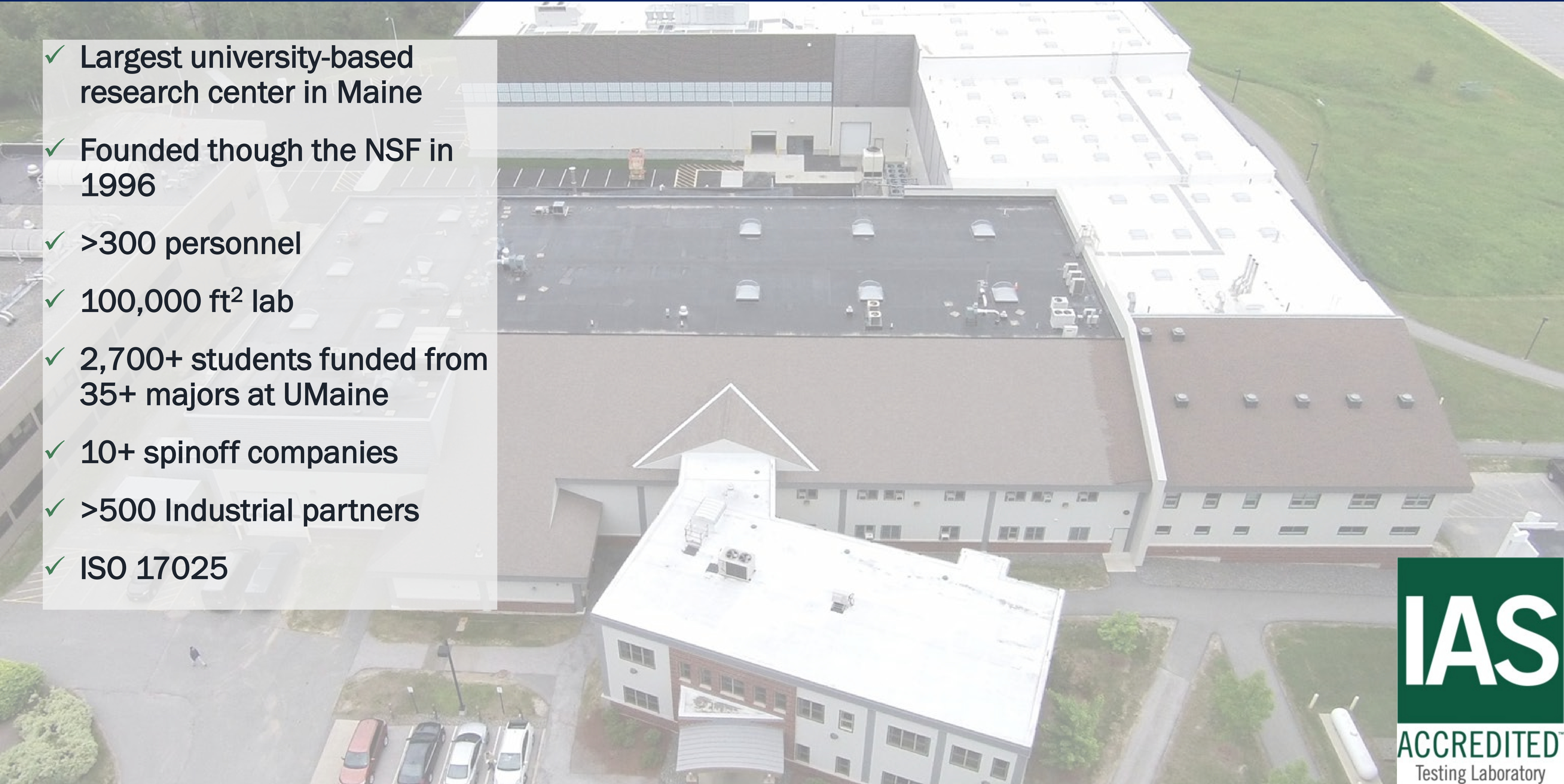
Sustainable Materials and Manufacturing Alliance for Renewable Technologies

- Connecting two world-class research facilities
- Redefining how national laboratories and universities connect with industry while driving U.S. manufacturing to a more sustainable future by accelerating commercialization of crosscutting technologies using biobased composites and advanced manufacturing.



1865 THE UNIVERSITY OF MAINE

ADVANCED STRUCTURES & composites center



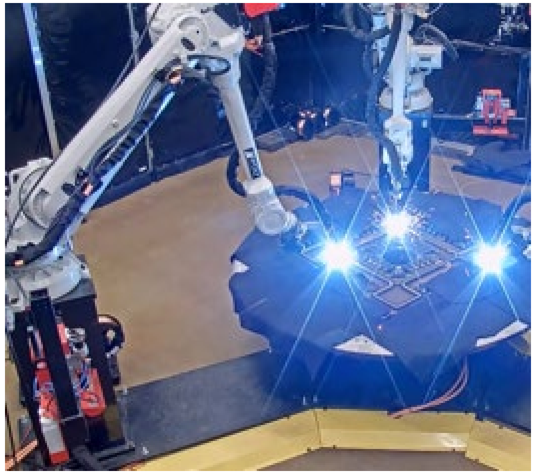
- ✓ Largest university-based research center in Maine
- ✓ Founded though the NSF in 1996
- ✓ >300 personnel
- ✓ 100,000 ft^2 lab
- ✓ 2,700+ students funded from 35+ majors at UMaine
- ✓ 10+ spinoff companies
- ✓ >500 Industrial partners
- ✓ ISO 17025

IAS ACCREDITED Testing Laboratory


Oak Ridge National Laboratory
The SNS is a next-generation spallation neutron source for neutron scattering that is currently the most powerful neutron source in the world.
As the US Department of Energy's largest multi-disciplinary laboratory, we deliver scientific discoveries and technical breakthroughs for complex challenges including:
• Transition to clean energy,
• Mitigation of climate change,
• Improvements to human health,
• Innovation that strengthens economic competitiveness

ORNL Manufacturing Demonstration Facility

A DOE-designated user facility. Established 2011.



DOE's designated user facility focused on early-stage research and development to improve the energy and material efficiency, productivity, and competitiveness of American manufacturers.

Research focuses on additive, composites, machining, hybrid and digital manufacturing.

ORNL Core Team -Sustainable Manufacturing Technologies Group


Halil Tekinalp
Chemical Engineer


Meghan Lamm
Polymer Chemist


Katie Copenhaver
Materials Scientist


Matthew Korey
Materials Scientist


Mitch Rencheck
Materials Scientist


Caitlyn Clarkson
Materials Scientist


Amber Hubbard
Chemical Engineer

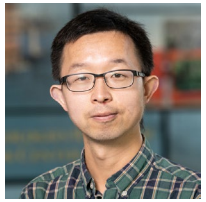

Sena Elyas
Industry collaboration


Dan Coughlin
Chief Officer for Industry Relationship

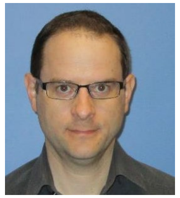

Jody Grace
Administrative Professional


Soydan Ozcan
Group Leader

ORNL team partners


Kai Li
Materials Engineer


Xianhui Zhao
Materials Engineer

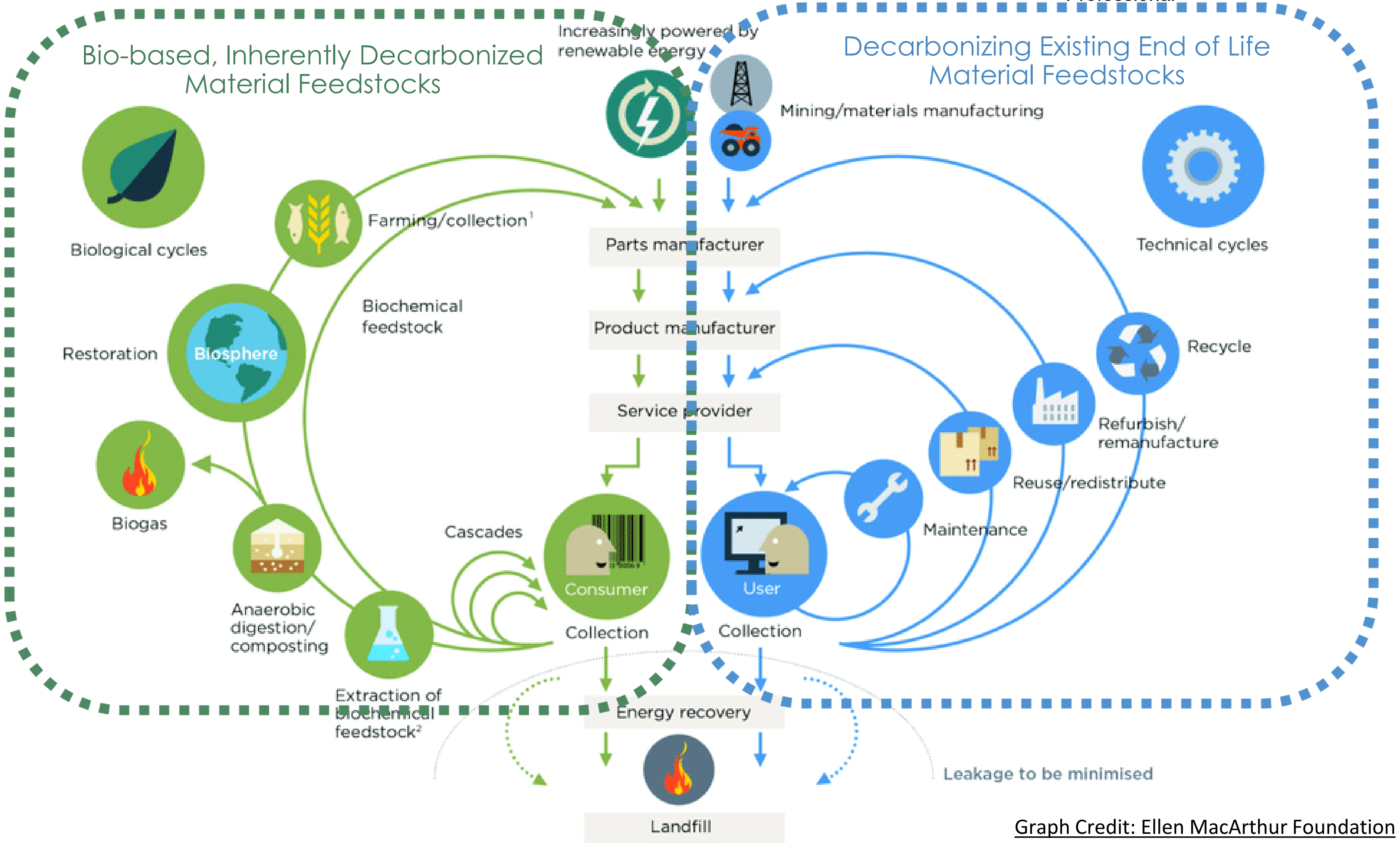

Frederik Vautard
Chemist


Sam Bhagia
Chemist


Art Ragauskas
UTK/ORNL
Governer's Chair


Uday Vaidya
UTK/ORNL
Governer's Chair

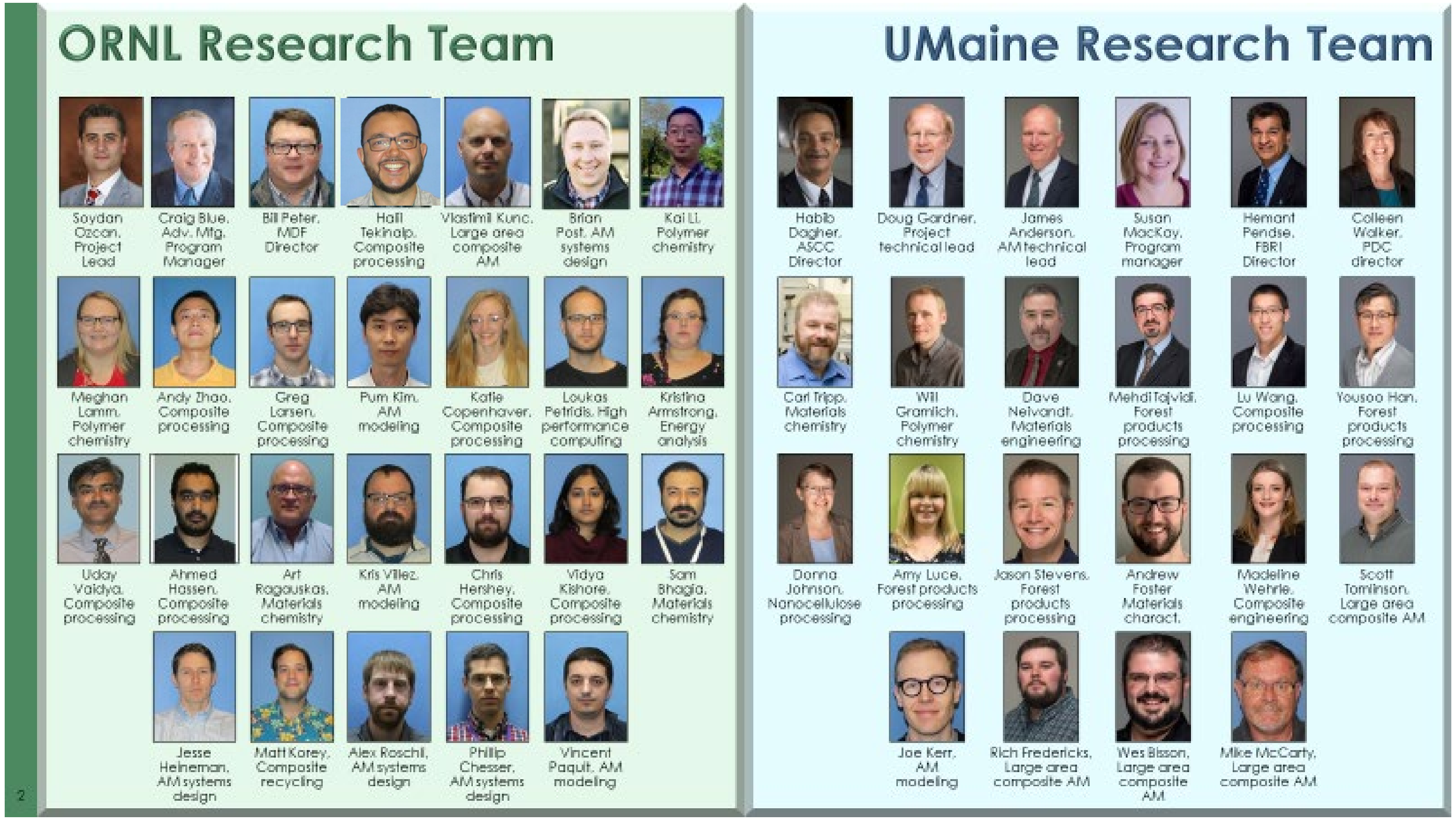

Jeremy Smith
UTK/ORNL
Governer's Chair

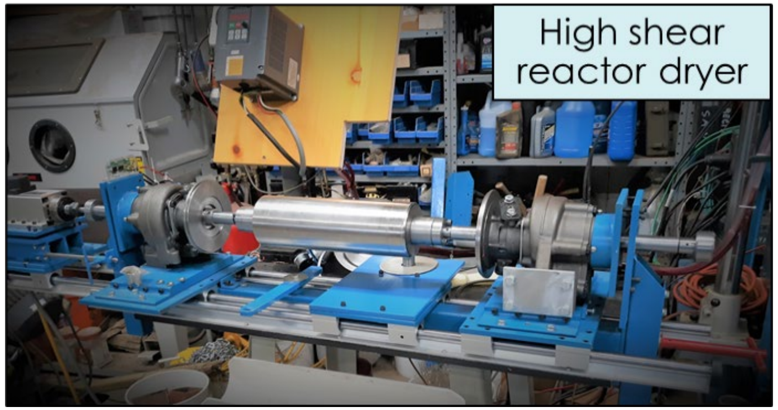


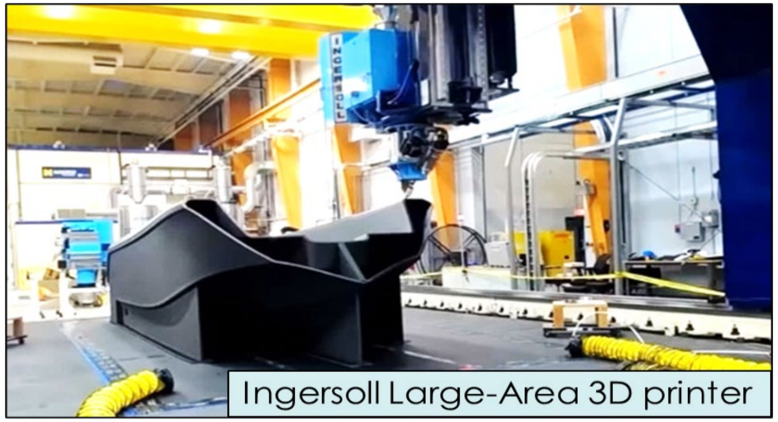
Graph Credit: Ellen MacArthur Foundation

Oak Ridge National Laboratory

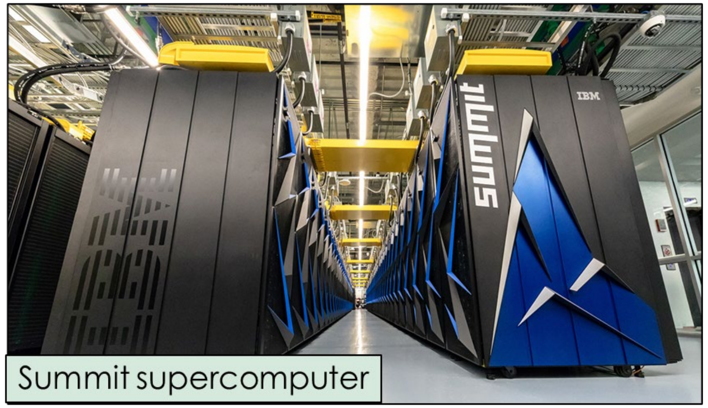
Diverse Skillset, Combined Innovation and Resources




High shear reactor dryer


Ingersoll Large-Area 3D printer


Cincinnati BAAM (Big Area Additive Manf)



Summit supercomputer

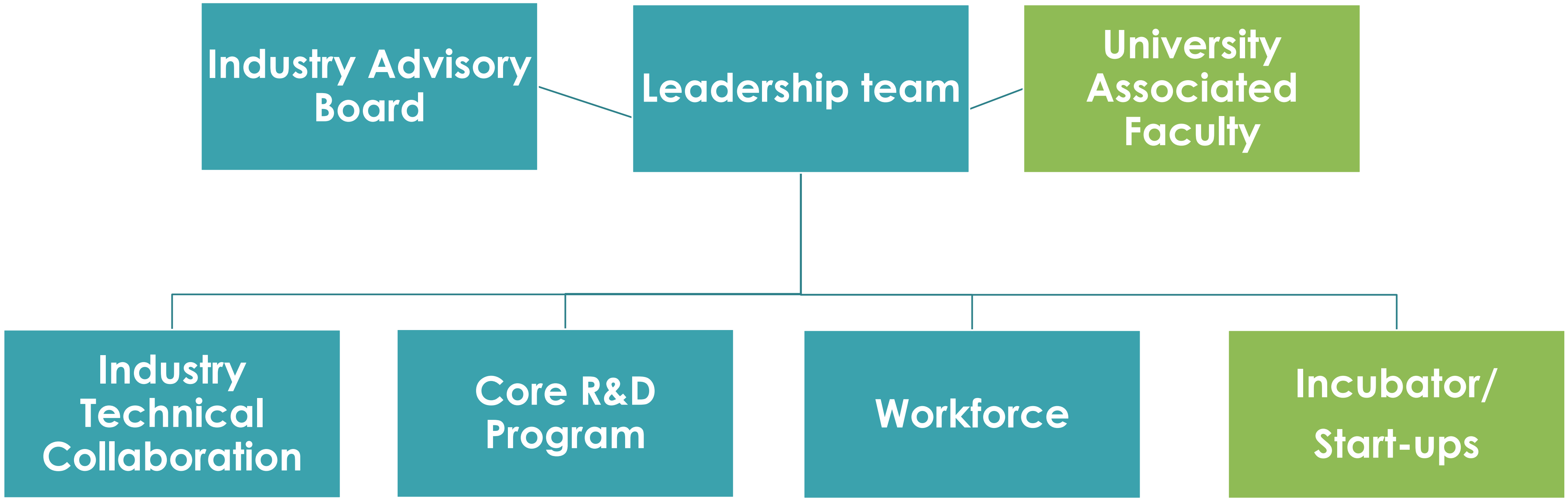

Process Development Center (CNF production)

OAK RIDGE National Laboratory

SM²ART

Sustainable Materials and Manufacturing Alliance for Renewable Technologies

A Public-Private partnership: Sponsored by US. Department of Energy cost shared by the private sector



Industrial Tech Collaboration: Relevance & Impact

Explore
Opportunity for industry to discover and apply new manufacturing technologies

Engage
Work with manufacturing staff to develop scope of work

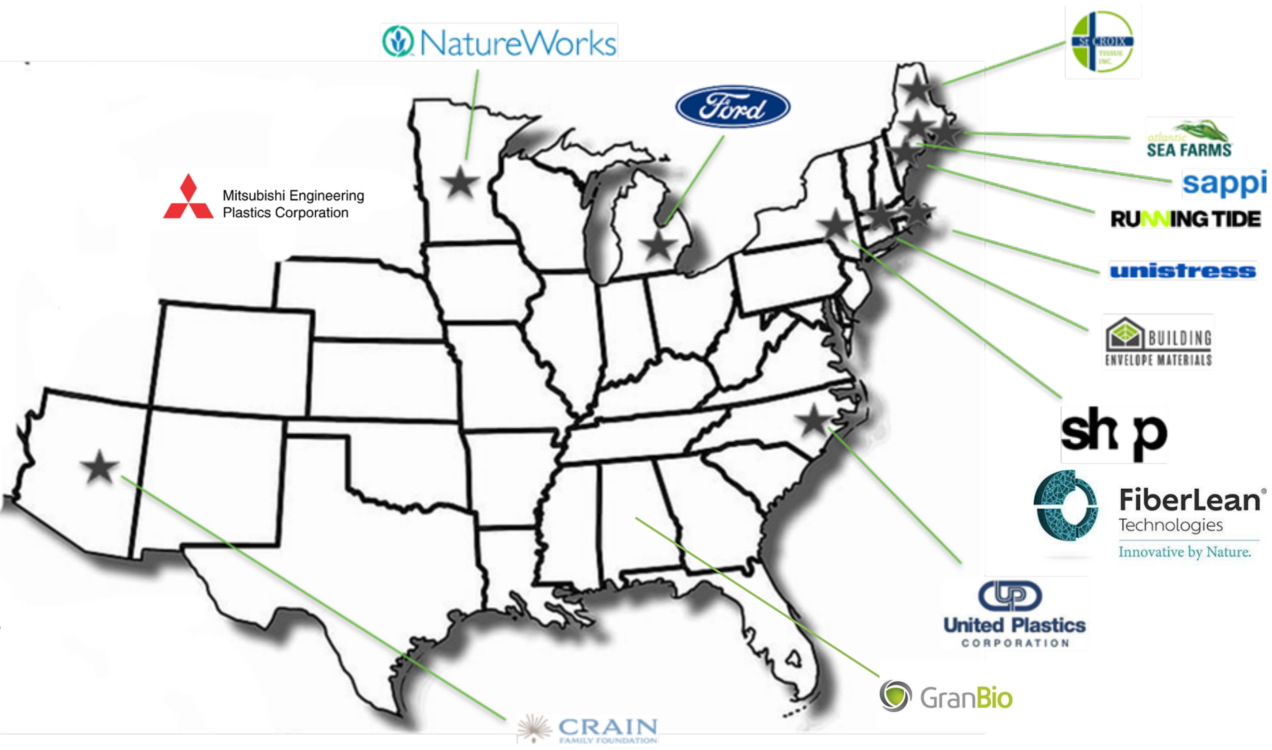
Execute
Phase 1 $40K
Phase 2 $200K
1:1 Cost Match

Technical Collaborations

- Biobased materials- AM Feedstocks
- AM Applications
- Application areas
  - Buildings
  - Packaging
  - Automotive
  - Marine
  - Wind Energy

Value to partners and ecosystem

- First customer connections
- Creating **market pull** for biobased materials
- Identifying **high volume opportunities** for cellulose nanofibrils, wood residuals, and large area additive manufacturing



- Formed a marine consortium with 6 participating marine companies.
- Goal: create industrial clusters focusing on forest products and sustainable manufacturing practices

Workforce Development

REU: building the next generation of sustainable materials and advanced manufacturing leaders

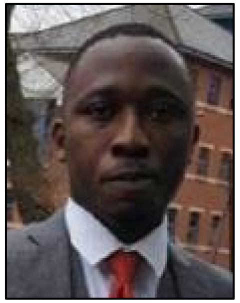
- Promoting **workforce diversity**
- Providing students with active research opportunities
- Increasing student engagement and interest via **research exchange** opportunities

Hub and Spoke program has supported **112 student researchers** and **17** graduate students across **8** academic disciplines

Dr. Chinmoyee Das, Forestry Materials Post Doc

Peter Kelly, Chemistry Grad Student

Dr. Maryam El Hajam, Materials Eng. Post Doc



Jeffrey Eiyike, Electrical and Comp Eng Grad Student

Charles Eme, Chem Eng Grad Student

Sungjun Hwang, Forestry Grad Student

Sanjita Wasti, Mech, Aero, and Biomed Grad Student

ADVANCED STRUCTURES & composites center

COOPERATIVE FORESTRY RESEARCH UNIT CFRU

FBRI FOREST BIOPRODUCTS Research Institute

OAK RIDGE National Laboratory | MANUFACTURING DEMONSTRATION FACILITY

1865 THE UNIVERSITY OF MAINE

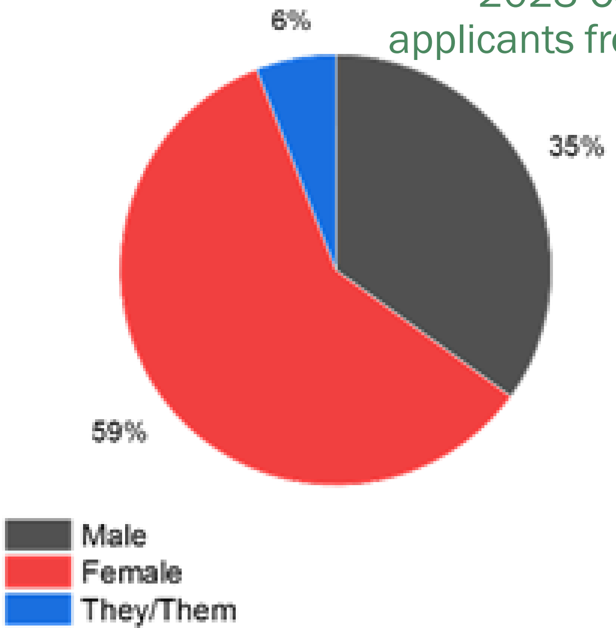
THE UNIVERSITY OF TENNESSEE KNOXVILLE

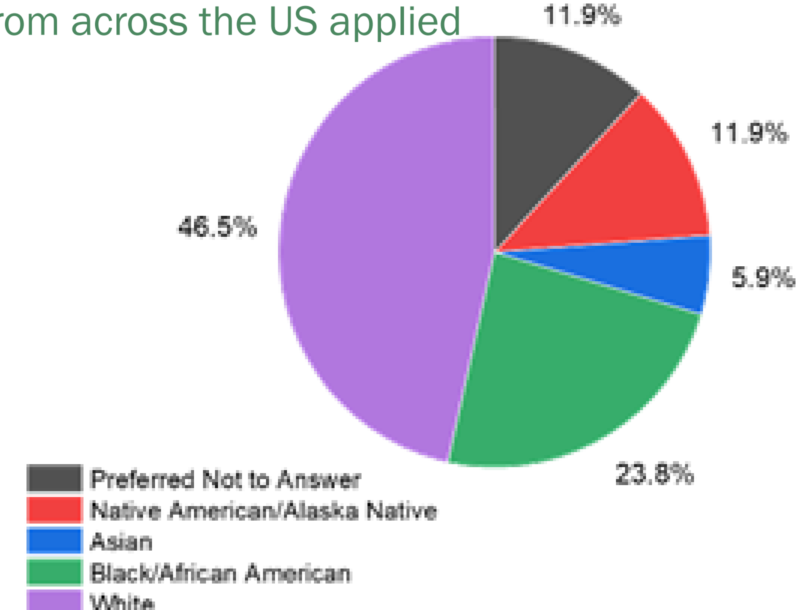
OAK RIDGE National Laboratory

Workforce Development: Research Experience for Undergraduates (REU) with a focus on DEI

- This program provides **12 undergraduates with a 10-week** summer research experience, leveraging the focus areas of the University of Maine-ORNL Hub and Spoke Program.
- The **focus on developing renewable, low-cost, high-performance feedstocks** to replace fossil fuel-derived materials for advanced manufacturing applications is highly topical and of great global importance.
- Objective: Aims for participants to **develop and utilize new knowledge in an ethical manner** to address the development of sustainable composite materials
- A unique Research Experience for Teachers paradigm will be employed. Rather than doing scientific research our RETs take the research that our REUs are conducting and distill it down to appropriate **engineering inquiry activities for secondary school students.**

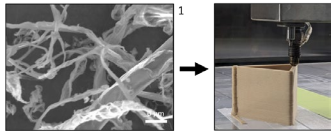
2023 Cohort Demographics
applicants from across the US applied





Program Impact to Date

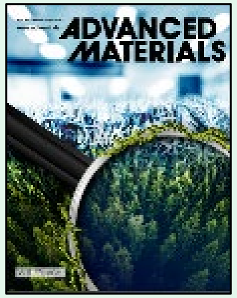
- ✓ **>50% increase** in bio composite strength
- ✓ **>70% energy reduction** in CNF drying
- ✓ **5X state-of-the-art** large format 3D print speed

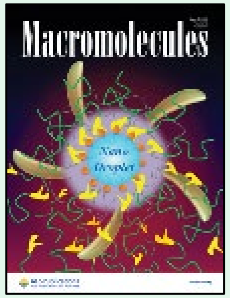


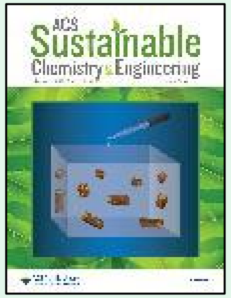
- ✓ **17 graduate students**
- ✓ **112 undergraduate students**
- ✓ **National REU program**

- ✓ **26 Industry partners:** 16 active CRADAS
- ✓ **Annual Industry workshop**
- ✓ **Industrial roadmap**
- ✓ **Webinar series:** 170 registrants

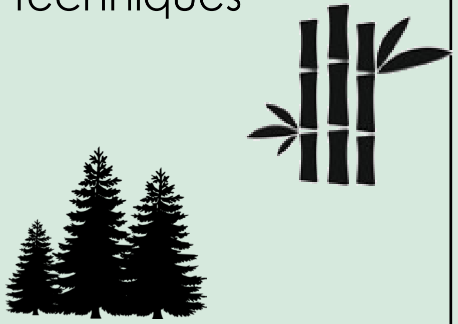
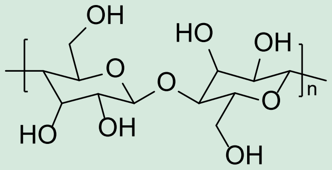
BioHome3D
- ✓ **2023 AM Aubin Case Study Award**
- ✓ **1.76 billion** online views
- ✓ **350 articles**



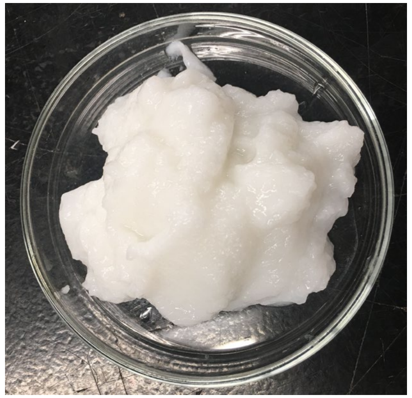




Development of Bio-based Composites for Advanced Manufacturing

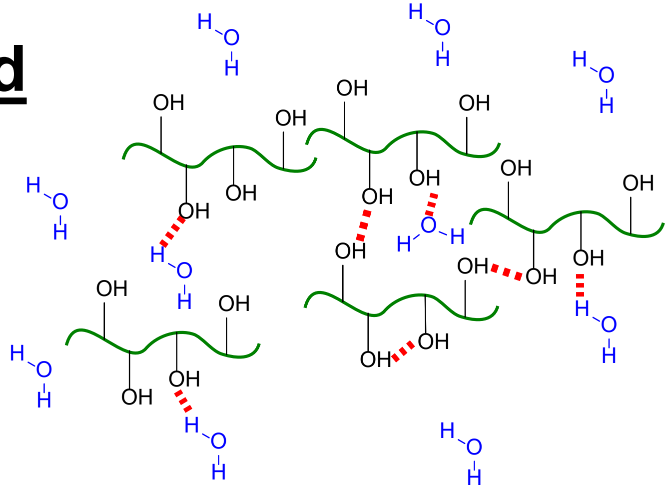
Energy reduction of CNF production	Improved distribution of CNF in composites	Improved performance of bio-based composites	New low-cost bio-based composite alternatives	New applications and higher efficiency for AM
➢ Disk refining process modifications / pretreatments ➢ Using alternate (non-wood) feedstocks ➢ Using alternate fibrillation techniques	➢ Surface treatments for CNF ➢ New, low-energy drying methods ➢ Molecular simulations to predict aggregation and polymer compatibility	➢ Optimizing cellulose fiber content ➢ Developing new bio-based thermosets and foams ➢ Exploring recyclability of bio-based materials	➢ Developing new processing techniques for fibers like hemp, flax, etc ➢ Exploring very highly loaded and hybrid (multi-fiber) composites	➢ Exploring new markets for bio-based materials and AM in general ➢ Increasing throughput and efficiency of AM ➢ Using FEA to predict and account for warpage during printing
		 		

Challenges in Nanocellulose Application

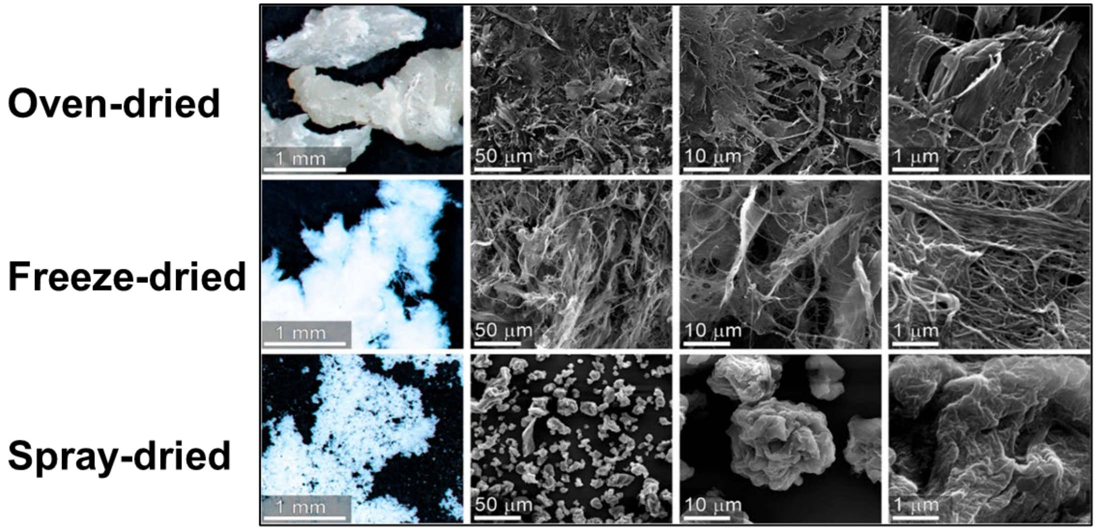


3 wt% CNF in water

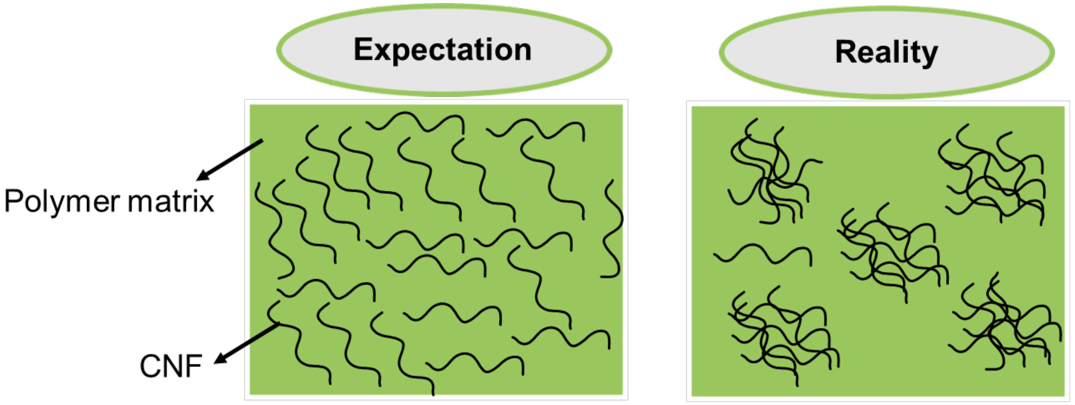
H-bond



➢ Drying



➢ Compatibility

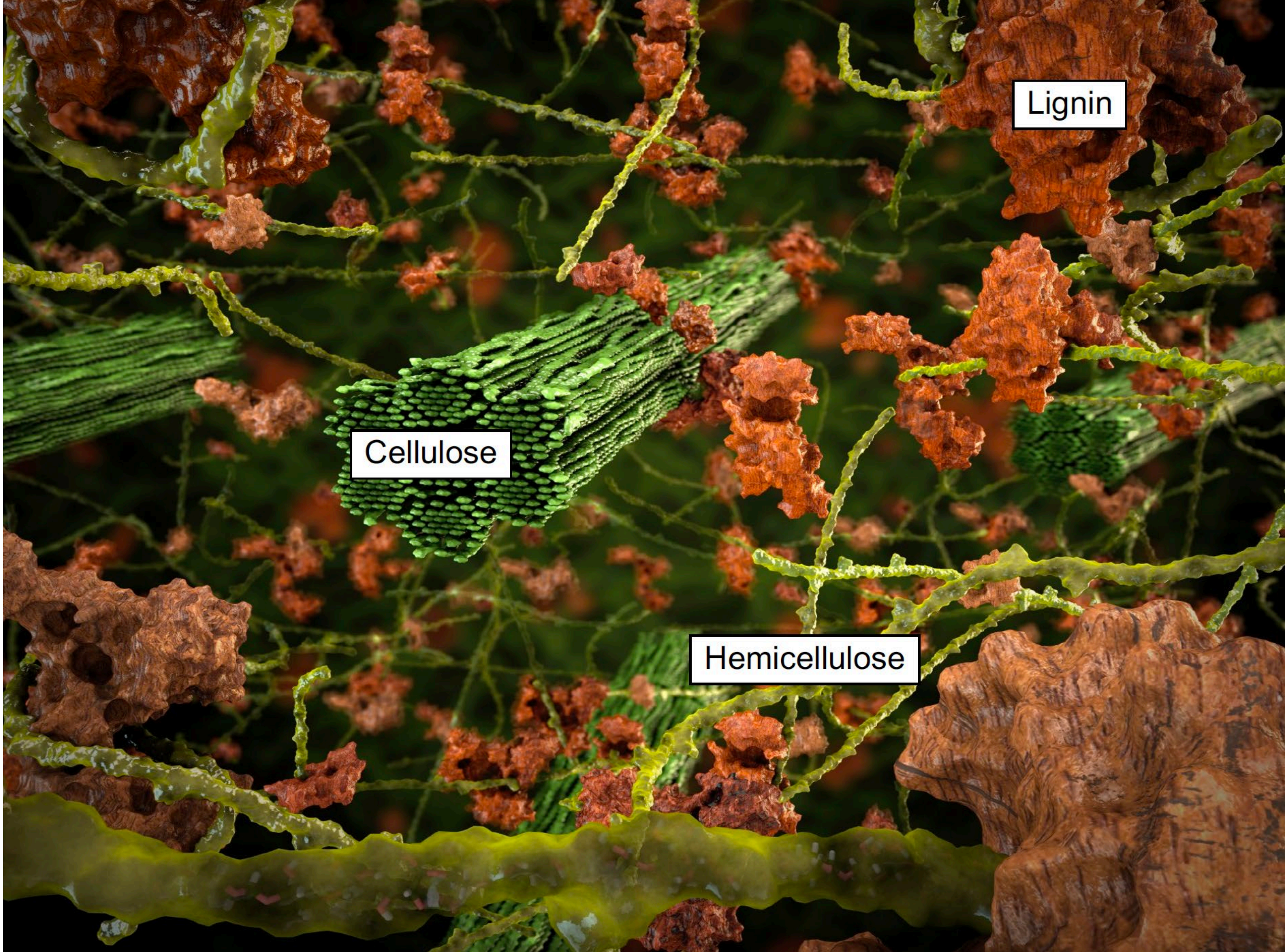


Good dispersion
Best mechanical properties

Agglomeration
Bad mechanical properties

Sinquefield S., Li K., Özcan S., *et al.*, *ACS Sustainable Chem. Eng.* **2020**, 8, 9601-9615.

Prof. Jeremy Smith
ORNL/UTK
Governer’s Chair



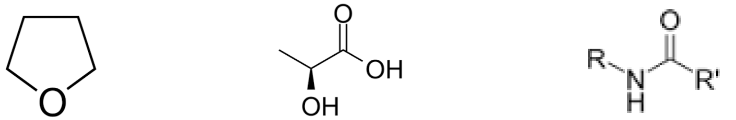
Oak Ridge National Laboratory

High Performance Computing

Alternative fibrillation solvents

- Selected 40 fibrillation solvents from literature
- Screened for CNF interactions (inter-CNF contacts) using HPC
- Determined interaction between CNF and solvent versus water
- Outcome: “enrichment” – increased probability some solvents improve fibrillation and dispersion
- Future: machine learning models/regressions to predict novel fibrillation solvents

solvents



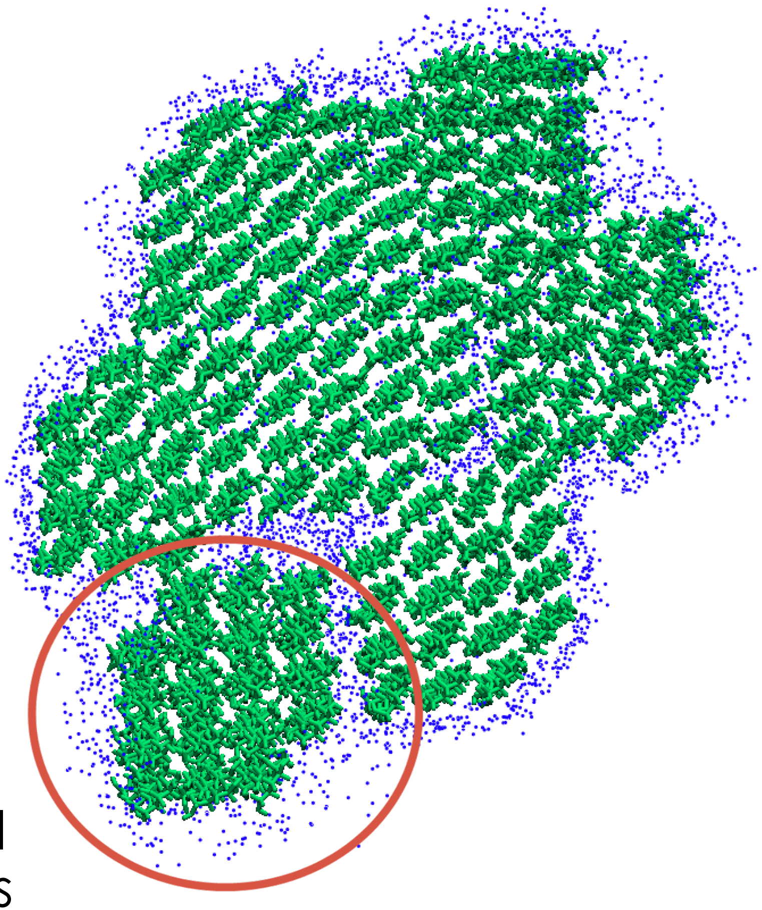
extent of CNF dispersion

Copenhaver, K. *et. al.* Pretreatment of Lignocellulose Feedstocks for Cellulose Nanofibril Production. *Cellulose*. **2022**. *Accepted.*

Alternative fibrillation solvents

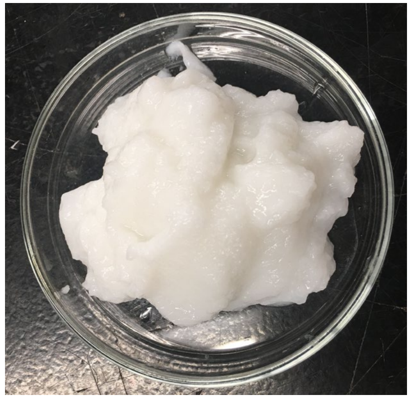
Ranking	Solvent
1	Aqueous NaOH-Urea (7-12 wt%)
2	Aqueous LiOH-Urea (4.2-12 wt%)
3	Glycerol-Water (vol 1:2)
4	Acetone-Water (vol 1:1)
5	Glycerol-Water (vol 2:1)
6	Methyl methacrylate
7	Aqueous KOH-Urea (9.8-12 wt%)
8	Gamma-Valerolactone-Water (vol 1:1)
9	Tetrahydrofuran-Water (vol 1:1)
10	Dimethylformamide-Water (vol 1:1)
11	Dimethylacetamide-LiCl (6 wt%)
12	choline chloride-lactic acid (mol 1:9)
13	Glycerol-Water (vol 1:1)
14	Water
15	Diethyl ether
16	Methanol
17	1-allyl-3-methyl imidazolium acetate
18	Ethanol
19	2-hydroxyethyl methacrylate
20	1-ethyl-3-methyl imidazolium acetate
21	1-allyl-3-methyl imidazolium formate
22	Acetone
23	1-butanol
24	Gamma-Valerolactone (GVL)
25	Ethylene glycol
26	choline acetate
27	1-ethyl-3-methyl imidazolium chloride
28	Tetrahydrofuran (THF)
29	Iso-butanol
30	1-ethyl-3-methyl imidazolium formate
31	choline chloride-oxalic acid (mol 1:1)
32	Ethyl acetate
33	choline chloride-choline acetate (mol 1:1)
34	Acrylamide
35	1-allyl-3-methyl imidazolium chloride
36	Acrylic (2-propenoic) acid
37	Dimethyl sulfoxide
38	Dimethylformamide (DMF)
39	1,4-dioxane
40	Aqueous $CaCl_2$-$ZnCl_2$ (1.85-73.2 wt%)

- Solvents included
  - salts
  - co-water mixtures
  - deep eutectic solvents (DES)
  - organic solvents
  - liquid monomers
  - ionic liquids
- 13 solvents modeled likely to interact better with CNF than water
- Exploring experimental validation with solvents across the ranking

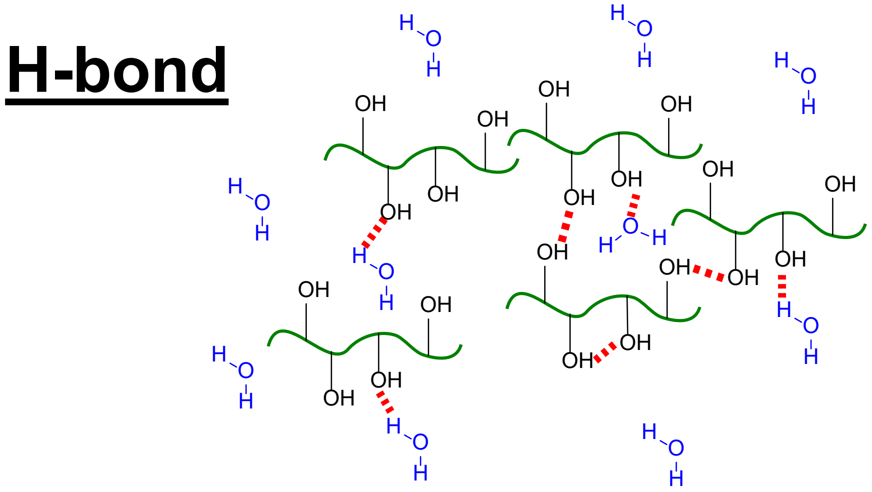


Example of a solvent decreasing CNF interactions in MD simulations

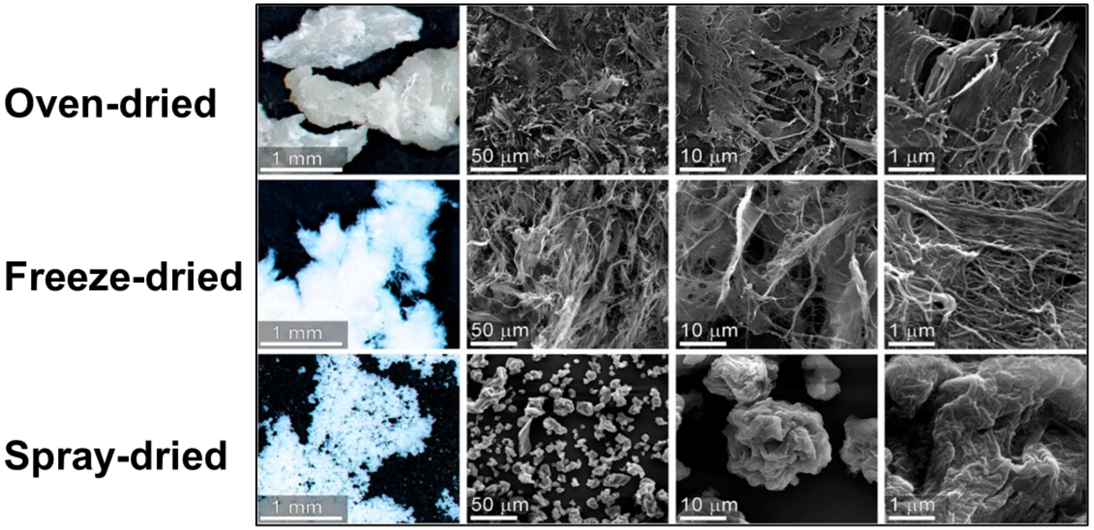
Challenges in Nanocellulose Application



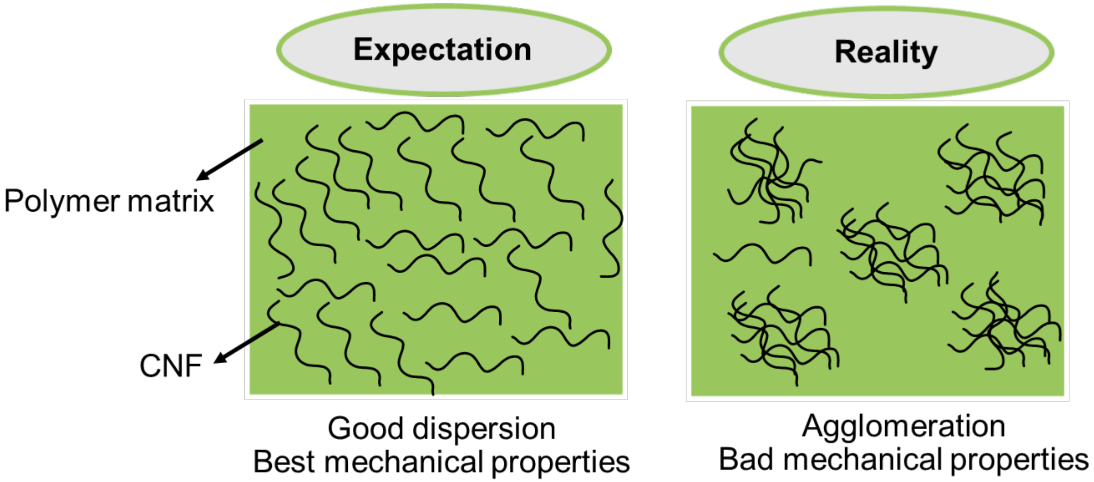
3 wt% CNF in water



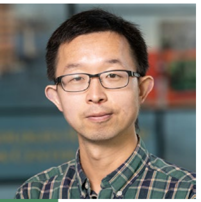
➢ Drying



➢ Compatibility



Sinquefield S., Li K., Ozcan S., *et al.*, *ACS Sustainable Chem. Eng.* **2020**, 8, 9601-9615.

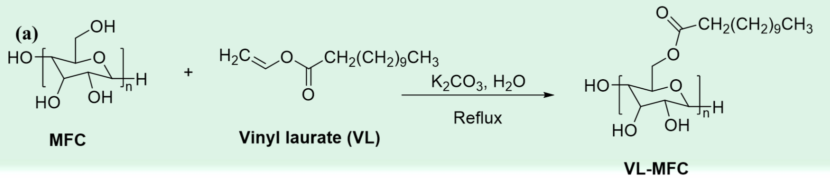


Dr. Kai Li

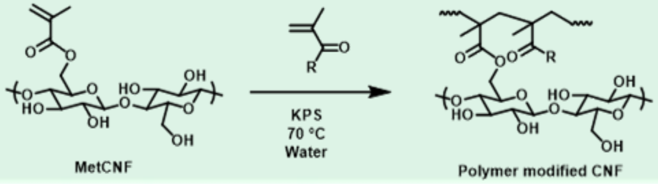
CNF Surface Modifications

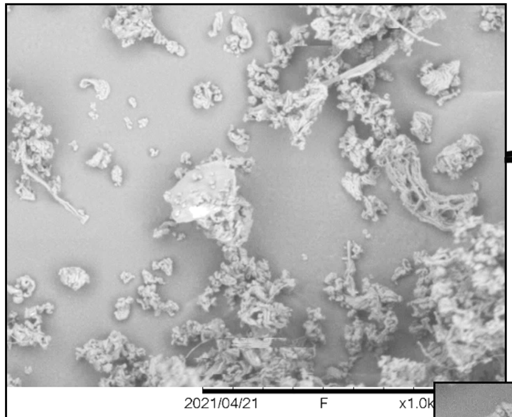
Retain Fibrillar Morphology, Mitigate Agglomeration, and Improve Tensile Properties

Addition of functional surface groups

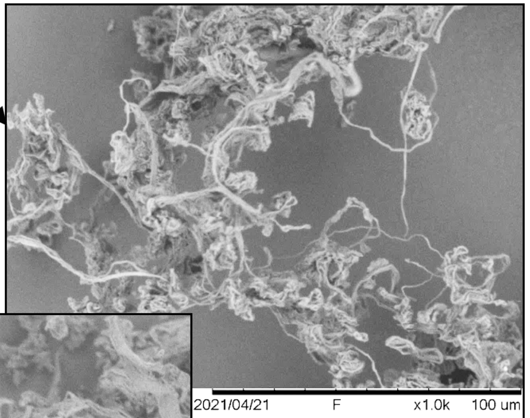


Polymerization on cellulose surfaces

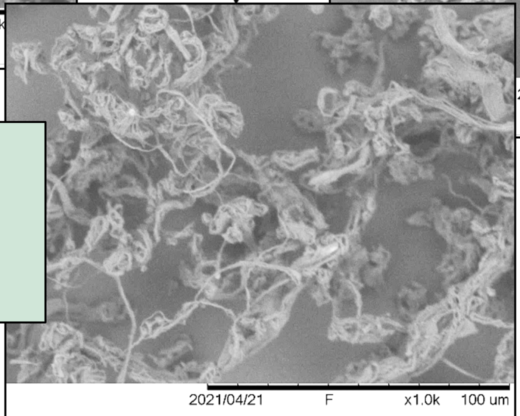




CNF

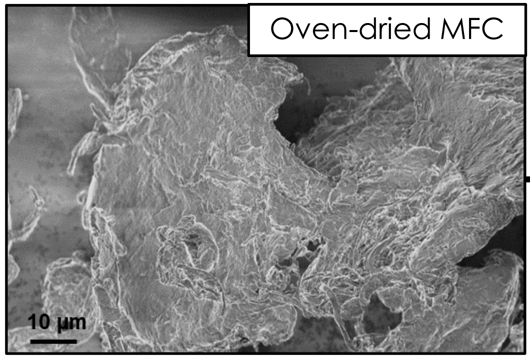


NIPAM

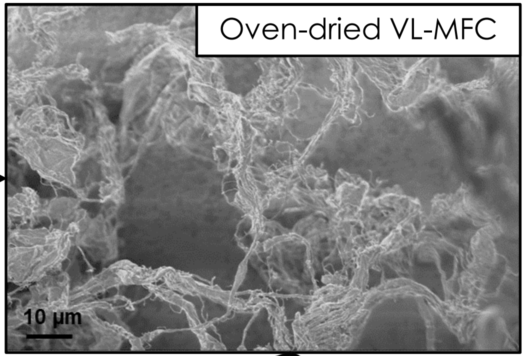


HEMA

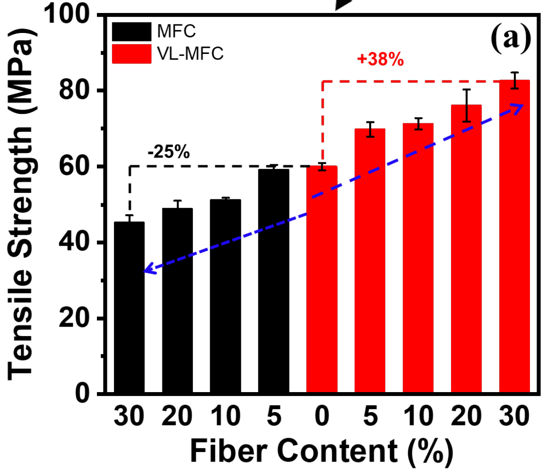
Surface modification allows CNF to retain fibrillar structure after spray drying

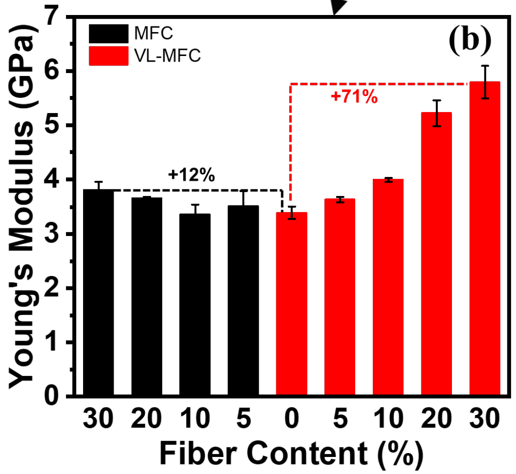


Oven-dried MFC



Oven-dried VL-MFC





38% and **71%** increases in tensile strength and modulus in PLA composites after surface modification

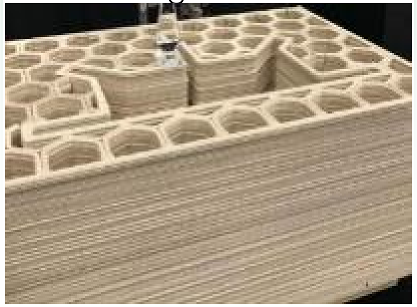
Li, K. *et al.*, *Carbohydrate Polymers. 2021, 256, 117525.*
U.S. Patent Application No. 63/051,614.

R&D Results Drive Industry Adoption

Packaging

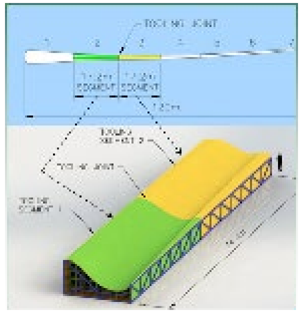
Replacing single use plastic with highly filled, cellulose-reinforced plastic. offset 250,000lb/yr petroleum-based resin at 15% cost savings

3D printed lightweight packaging. using low carbon biofoams. CAMX 2021 Innovation in Green Composites Design Award



Wind

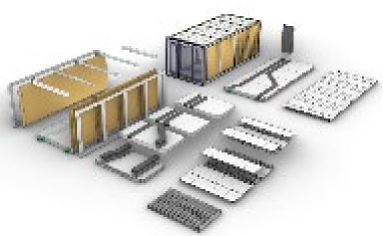
Bio-reinforced, recyclable thermoplastic 3D printed tooling for Wind Blade Root



3D printed integrated heating channels are more energy efficient and using biobased material decreases the embodied energy of the mold

Construction

3DP biobased floor assembly for productized construction. Offsite manufacturing and rapid assembly on-site for mid-rise residential buildings



1000 floor cassettes/building, 39 parts reduced to 1, >3000 hr labor savings, 100% biobased cassette displaces concrete and

Building Materials

Replacement for foam insulation, net shape, 100% biobased to reduce embodied energy and replace with local supply chain materials

Cellulose nanofibers and mycelium foam, near net shape, density optimized for energy efficiency

Marine

Bio-reinforced, semi-structural 3D printed transom door for marine craft

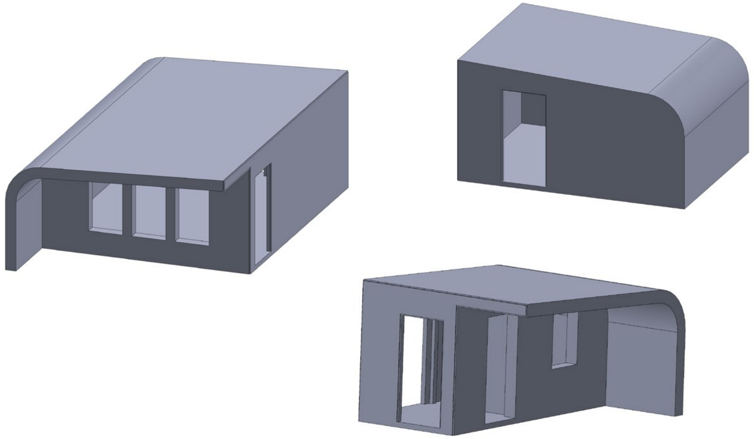
50% cost savings, lighter, bio-reinforced out of recyclable thermoplastic, integrated hinges and latch recess

3D-Printed Bio-based House

Showcasing volumetric modular construction using large format AM

100% Biobased House

- Designed for structural and insulation performance
- Ongoing research on building envelope for material and design improvements
  - Structural and weathering studies



600 sq. ft. biobased home printed as three separate but complete modules (floor, walls and roof)

Modules printed at 45 degrees – entire structure (roof/walls/floors) printed using 4 beads but with programmed start/stop times

UMaine/ORNL Unveiling World's First 3D-Printed Bio-based House

OAK RIDGE National Laboratory

SM²ART

Sustainable Materials and Manufacturing Alliance for Renewable Technologies

BioHome3D

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