International Conference on Nanotechnology for Renewable Materials

Pilot-Scale Preparation of a Surface Modified Cellulose Nanofibrils (CNF) Composite Feedstock

Meghan E. Lamm, R&D Associate Staff Member

Manufacturing Science Division, Oak Ridge National Laboratory

Oak Ridge National Laboratory (ORNL)

The United States' largest multi-program science and technology laboratory

ORNL's Unique Capabilities

Advanced Characterization

SNS: World's most intense pulsed neutron beams

HFIR: world's highest flux reactor-based neutron source

Zeiss Enclosure: comprehensive powder-to-part methodology for manufacturing-born qualified components

Nuclear & Advanced Manufacturing

Manhattan Project: 76 years of nuclear research

Radioisotope: projection, fusion, and fission

TCR Program: revitalizing the nation's capabilities in nuclear power by substantially reducing the cost and accelerating the deployment of new reactors

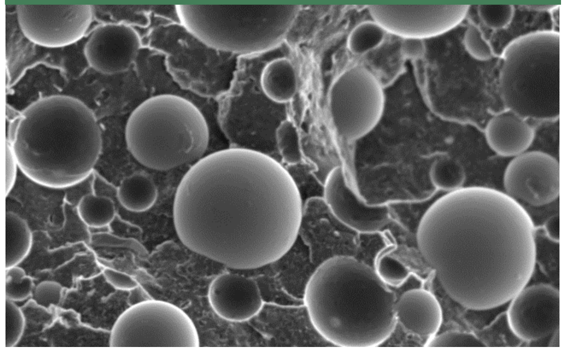
World-Renowned Computing

Frontier: next-level exascale system >1 quintillion calculations per second

Summit: nation's most powerful open-science supercomputer

Visualization Lab: Voxel-based approach to inspecting, evaluating, and understanding AM and composite components

Materials Development



400+ researchers, scientists, and engineers across a range of material systems

Cutting-Edge Research activities in materials for harsh environments, new AI alloys, ceramics, metals, fiber production, and bio-derived polymers

Multiphase, hybrid, and **advanced** materials R&D

Manufacturing Demonstration Facility

Core Research and Development

Leveraging ORNL's fundamental research to solve challenges in advanced manufacturing

- ☐ *FY20 **80%** of the MDF Budget*
- ☐ **80-100** publications annually

Industry Collaborations

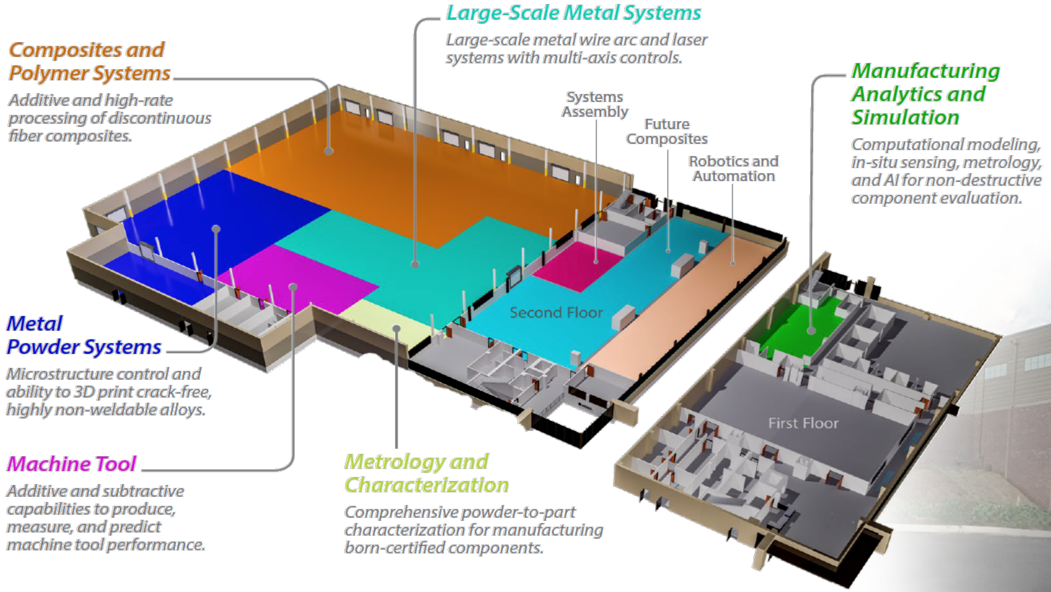
Cooperative research to develop and demonstrate advanced manufacturing with industry and universities

- ☐ *FY20 **10%** of the MDF Budget*
- ☐ **22** licensed technologies; **>50** patent applications

Education and Training

Internships, academic collaborations, workshops, training programs, and course curriculum for universities and community colleges

- ☐ *Incorporated into our projects*
- ☐ **1,000** student internships



Composites and Polymer Systems

Additive and high-rate processing of discontinuous fiber composites.

Large-Scale Metal Systems

Large-scale metal wire arc and laser systems with multi-axis controls.

Manufacturing Analytics and Simulation

Computational modeling, in-situ sensing, metrology, and AI for non-destructive component evaluation.

Metal Powder Systems

Microstructure control and ability to 3D print crack-free, highly non-weldable alloys.

Machine Tool

Additive and subtractive capabilities to produce, measure, and predict machine tool performance.

Metrology and Characterization

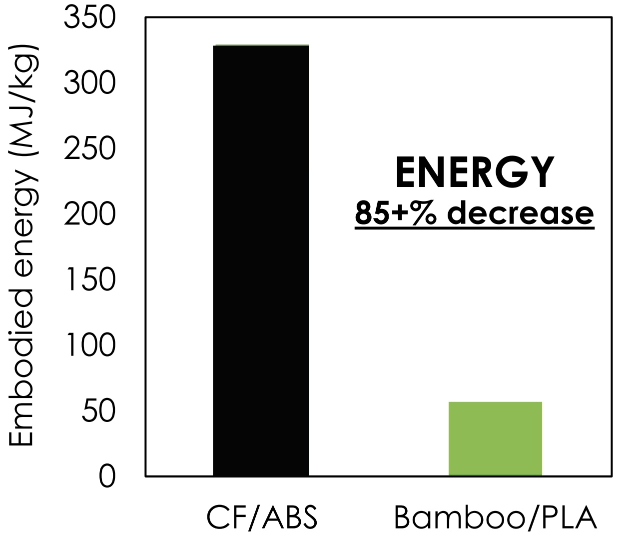
Comprehensive powder-to-part characterization for manufacturing born-certified components.

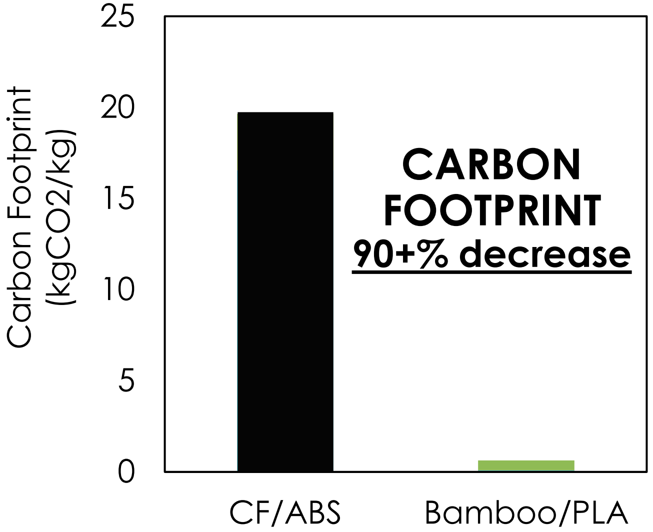
MDF by the numbers

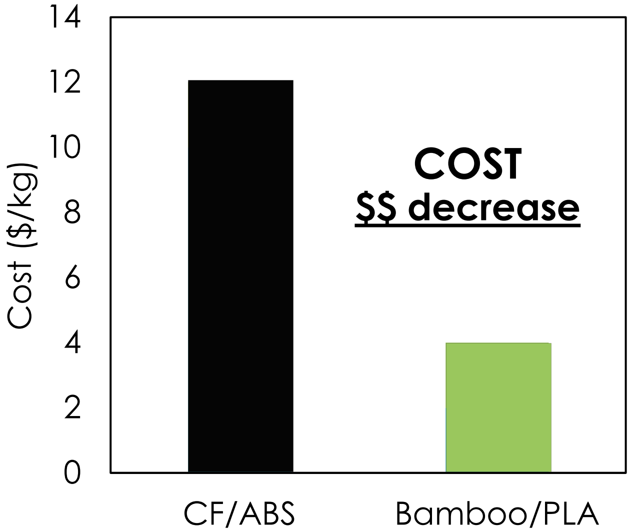
- **>100** staff members and ~200 people total when including interns, students and co-located industry partners
- **1,000** internships from **700** unique students since 2012
- **>180** partnerships
- **>50** university collaborations
- **>130** honors/awards since inception
- **>80** advanced manufacturing systems with 60% placed at the MDF by no-cost leasing (i.e., CRADA)

Benefits of Biomaterials in Manufacturing Applications

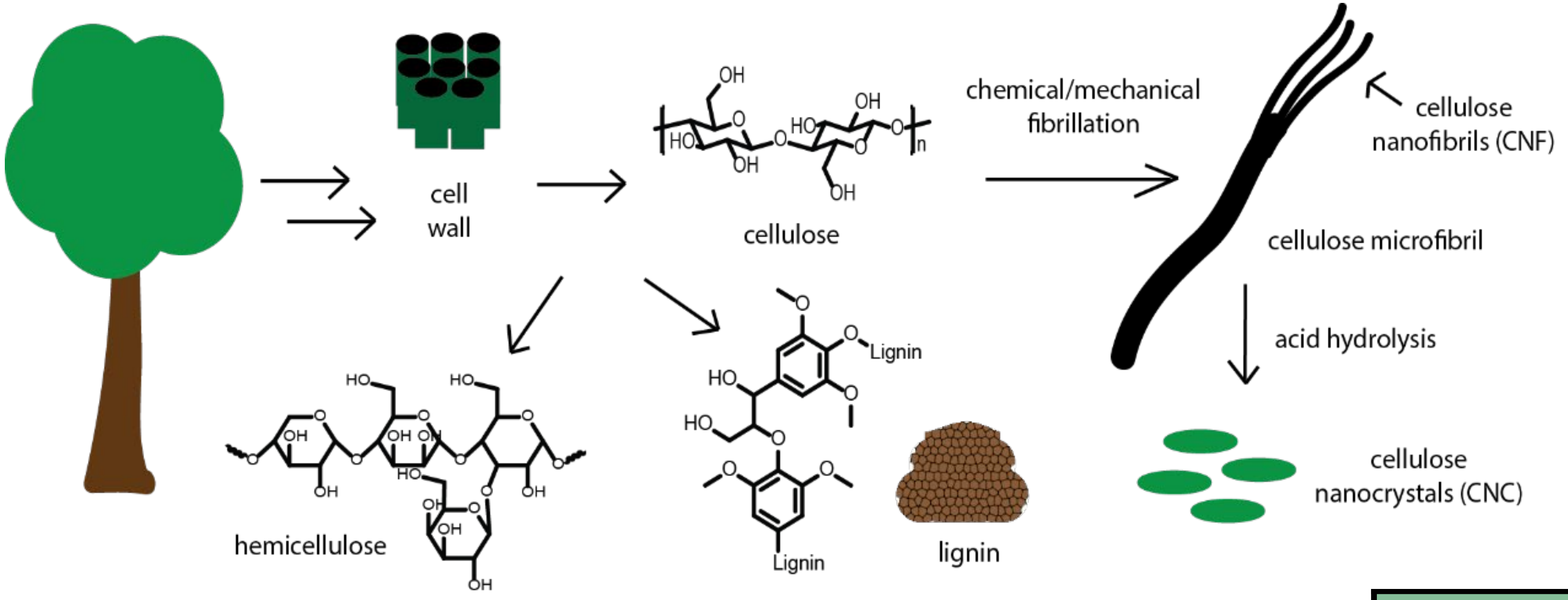
3D Printing Sustainable Structures





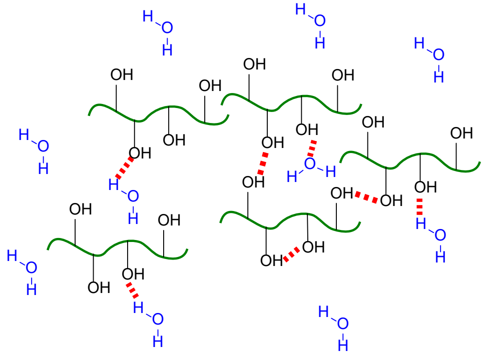


Cellulose as a bio-alternative to fossil-derived materials



Lamm, M.E. et. al. *Polymers*, **2020**, *12* (**9**), 2115.

Advantages:
Abundant, renewable resource with price stability • compostable •biocompatible • high strength and modulus • lightweight • shear thinning thickener (stable against temperature and salt addition)



3 wt% CNF in water

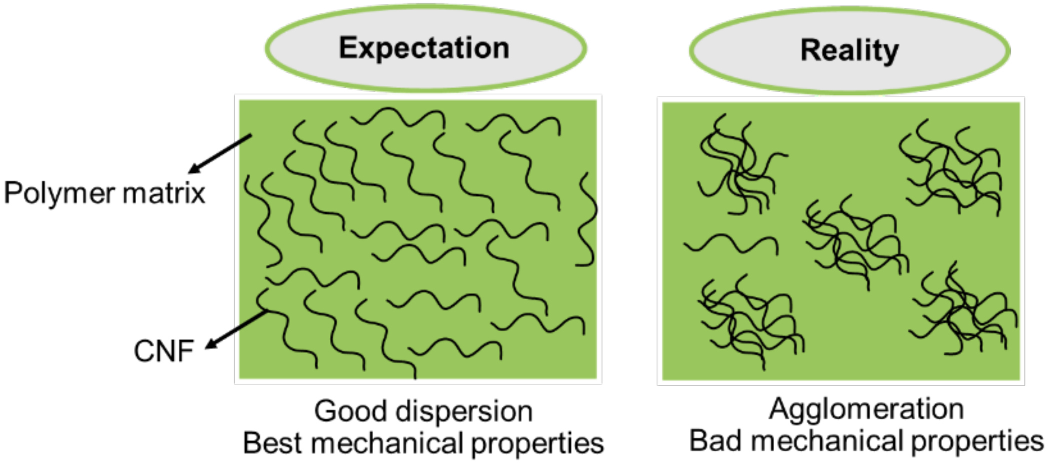
	Carbon Fiber (CF)	**Cellulose nanofibrils (CNF)**	**Cellulose nanocrystal (CNC)**
Density (g/cm^3)	1.8 - 2.2	1.5	1.5
Tensile Strength (MPa)	4000	< 3000	10,000
Modulus of Elasticity (GPa)	235	<150	150
Cost ($/lb)	$$$	$	$
Sustainable	NO	**YES**	**YES**

CNF Composites Challenges

<u>Challenge:</u> Very hydrophilic surface of CNF can lead to incompatibility with hydrophobic polymer matrices

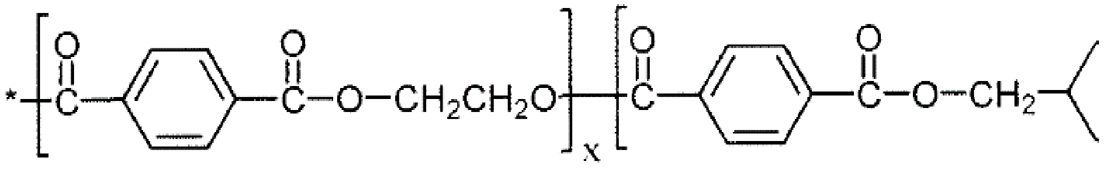
CNF

- Adsorption (interact with surface)
- Molecular grafting (covalently attached small molecules)
- Polymer grafting (covalently attached large molecules)



Good dispersion
Best mechanical properties

Agglomeration
Bad mechanical properties



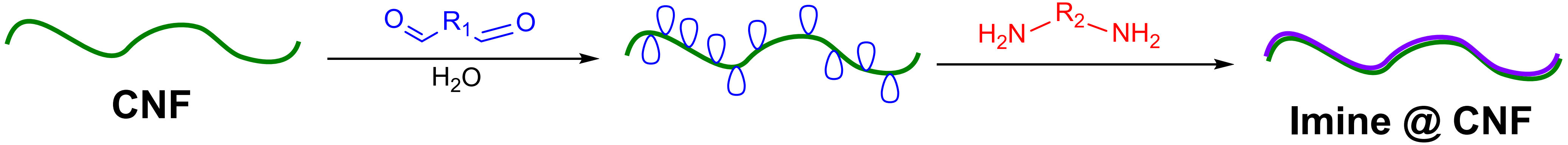
PETG: polyethylene terephthalate-glycol modified

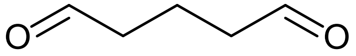
<u>Solution: Surface modification</u>

Modifying the surfaces of CNFs can:

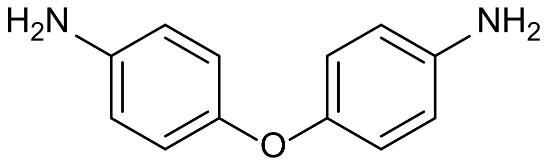
- Reduce surface energy and hydrophilicity
- **Reduce agglomeration** during drying
- **Reduce energy** requirement for drying CNF
- **Improve the compatibility** with polymers and lead to high performance bio-composites

Experimental Design

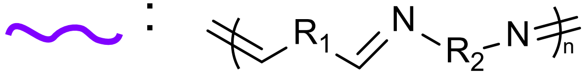




Glutaraldehyde



4,4′-Oxydianiline



hydrophillic: soluble in water, able to interact with CNF in aqueous phase

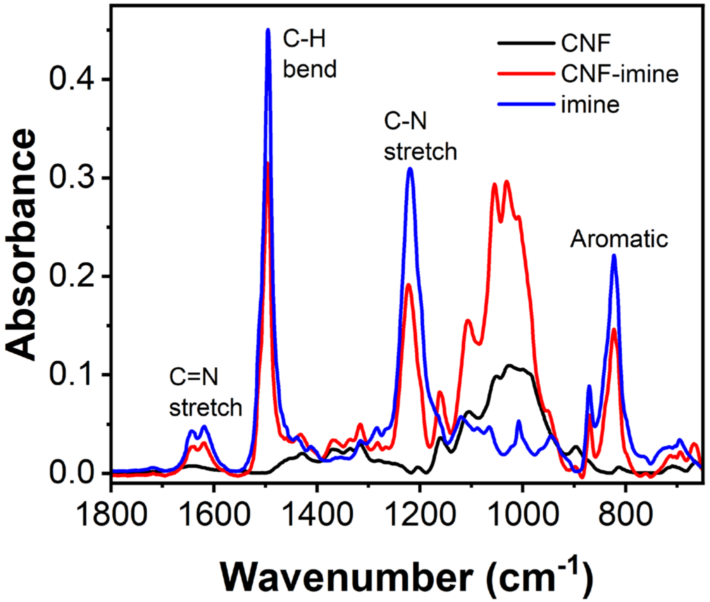
hydrophobic: prevent water solubility of the formed imine

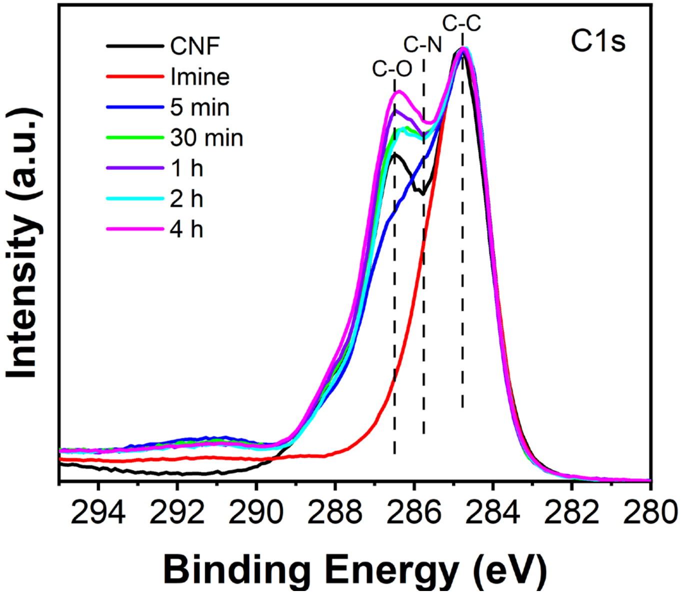
- Fast react rate
- Unstable in water and tend to hydrolyze back into reactant
  - Imine-dynamic covalent bond

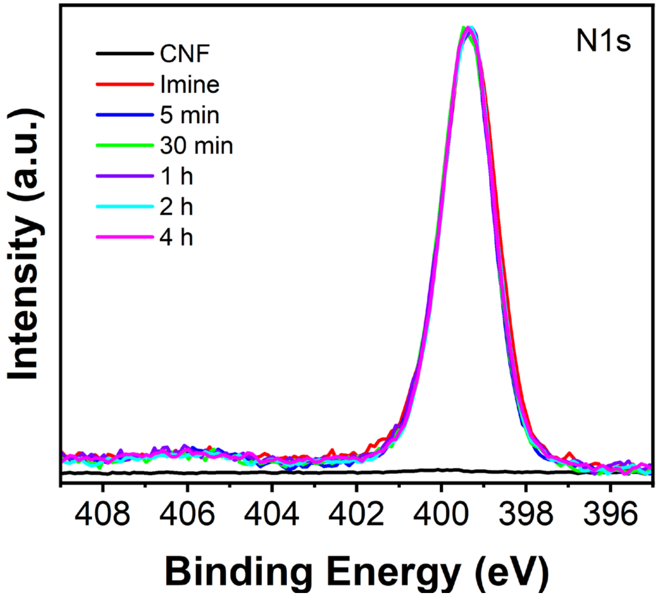
Incorporation of second hydrophobic portion forces the newly formed polyimine to co-precipitate with the entwined CNF, preventing the reverse hydrolysis reaction

Verification of Imine Formation

- FTIR confirmed presence of new bonds consistent with polyimine formation
  - C=N stretch
  - C-N stretch
  - Presence of aromatics C
- XPS changed with polyimine synthesis
  - Appearance of N1s
  - Increase in C-OH

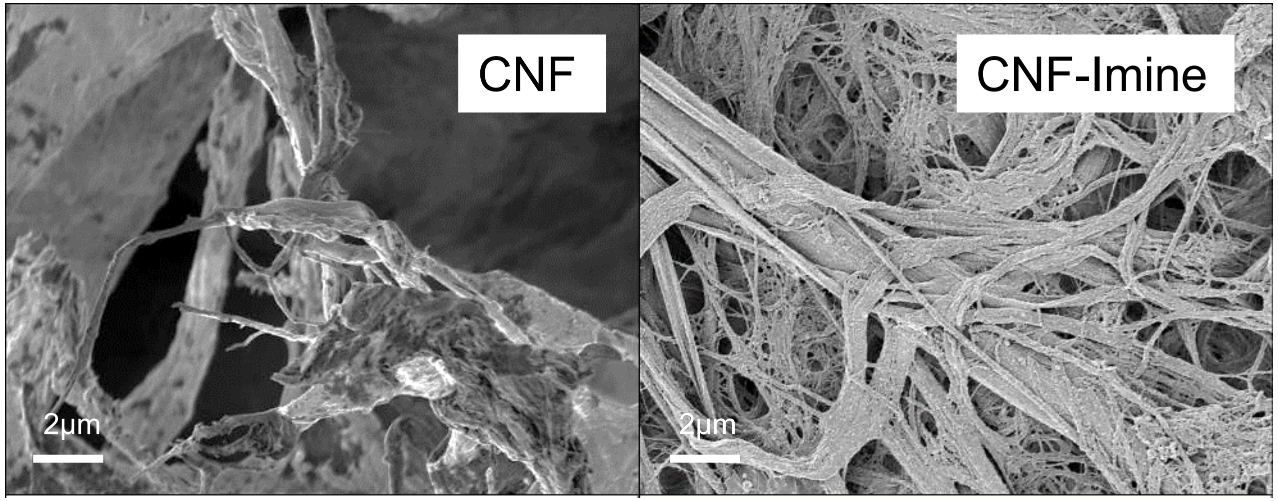


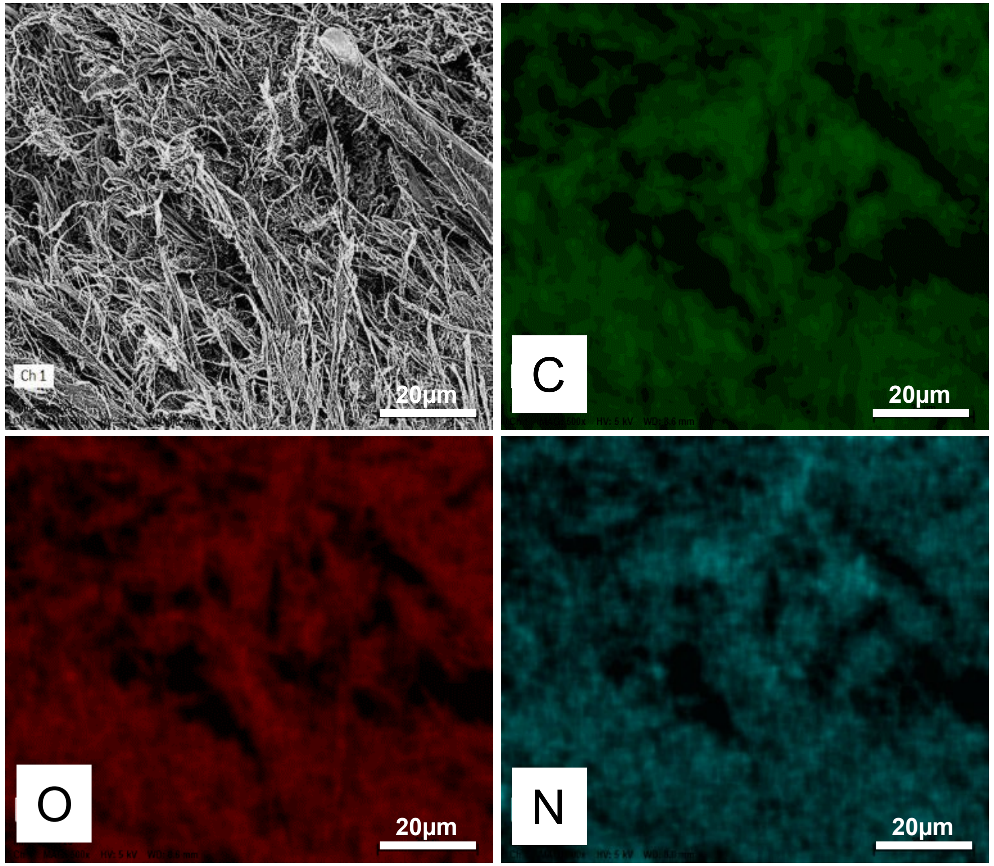




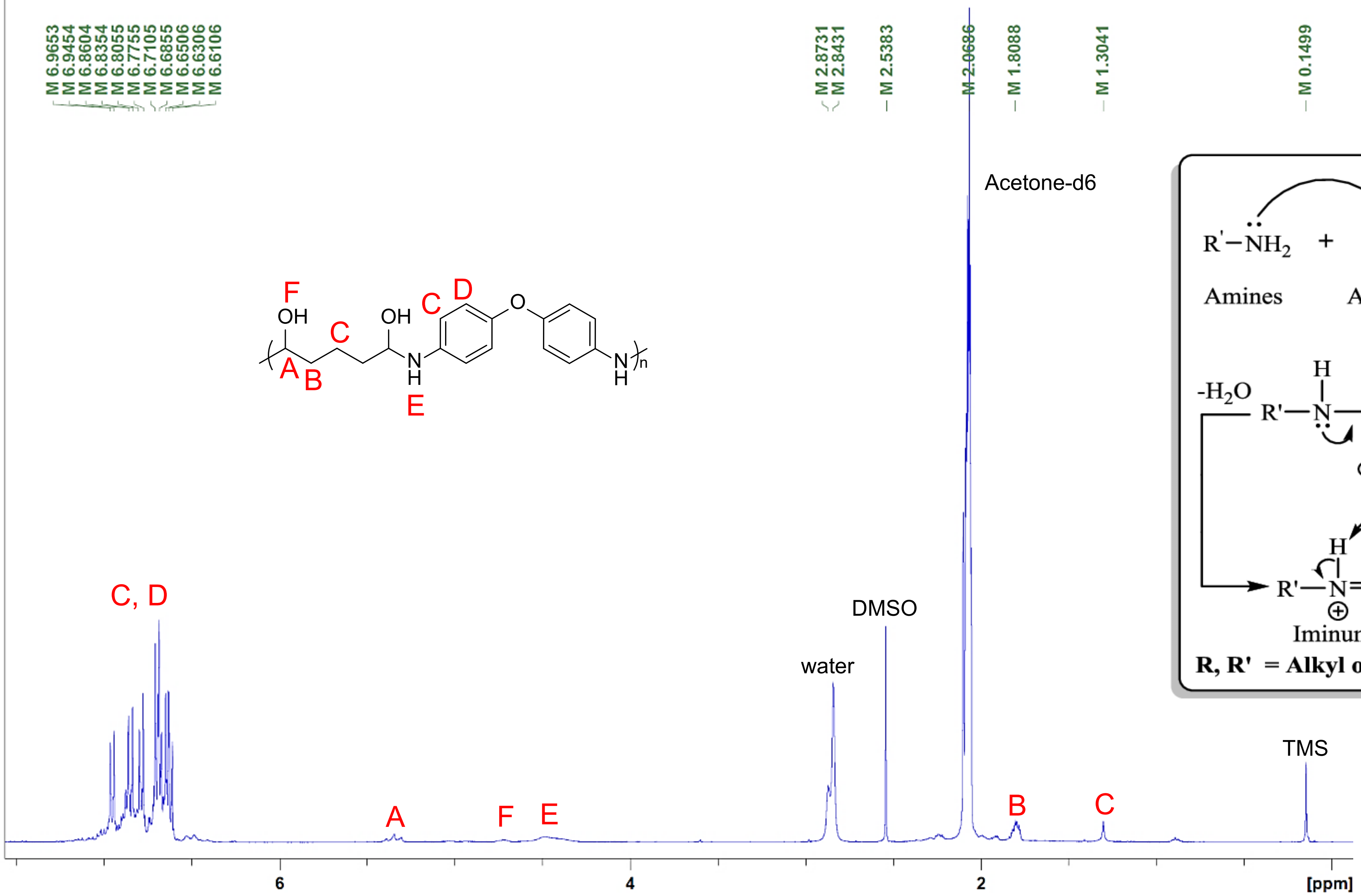
Morphology Changes

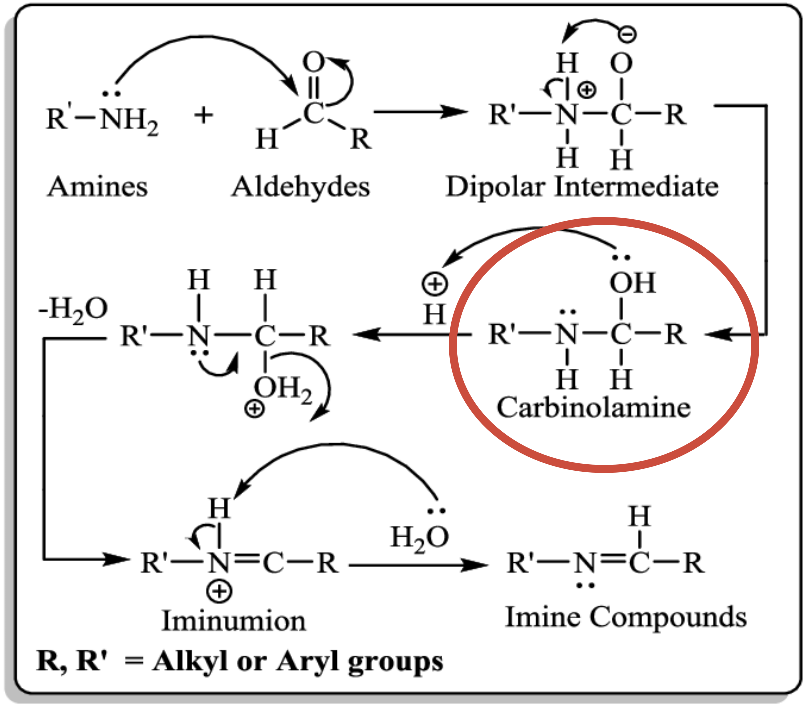
- Incorporation of polyimine produced more fibrillar morphology in drop-cast samples
- Presence of N confirmed using EDX



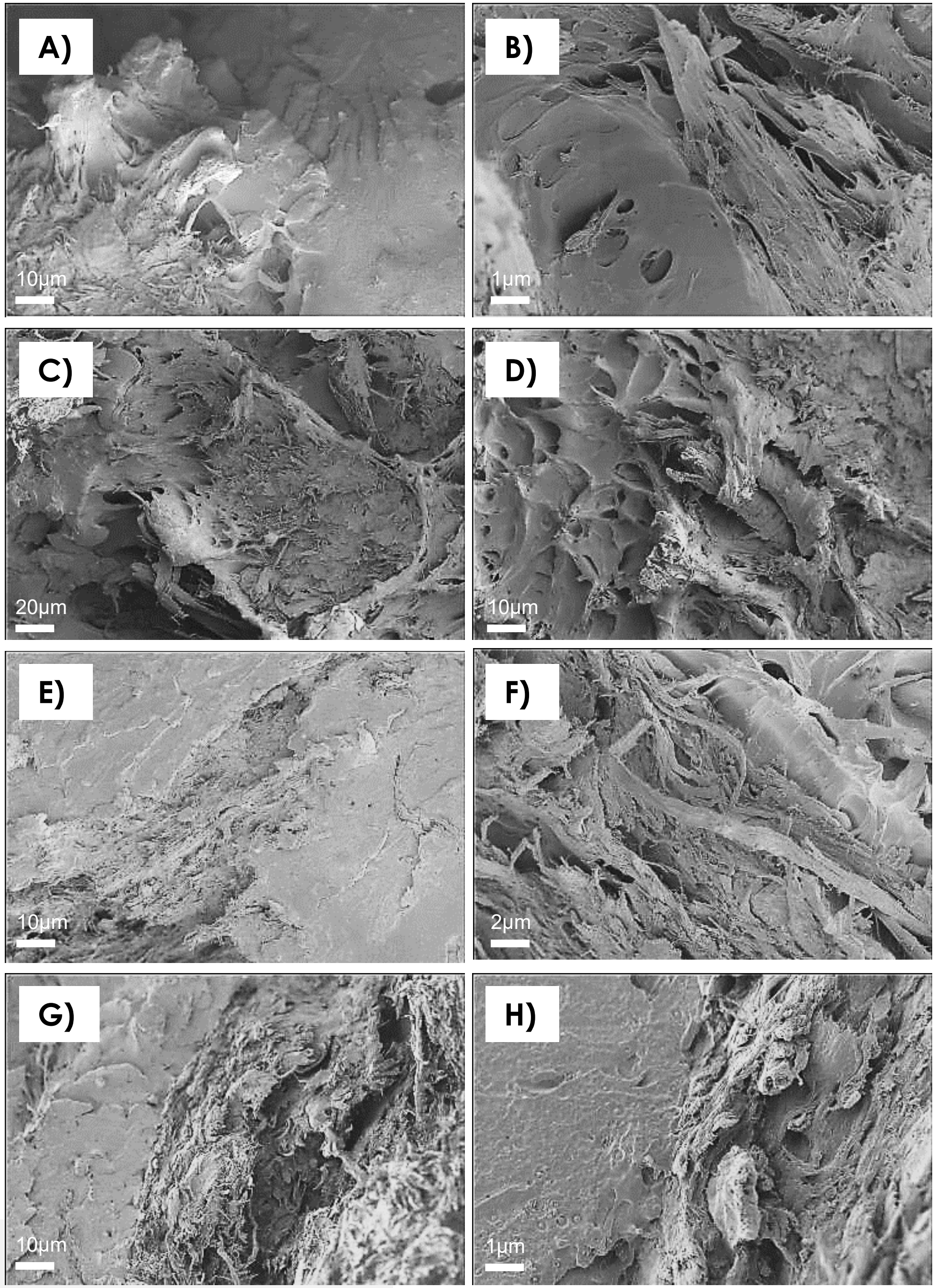


Structure of Polyimine Confirmed by ^{1}H-NMR





PETG composites

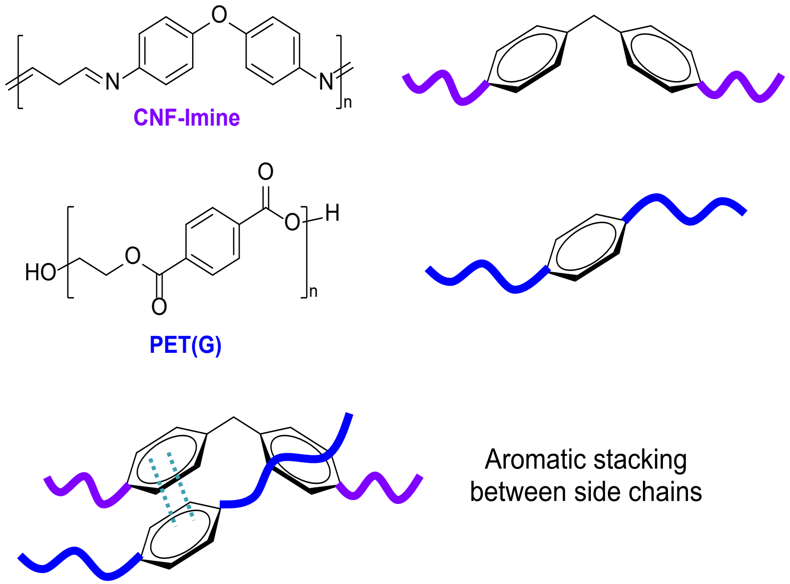


5% CNF-Imine

10% CNF-Imine

20% CNF-Imine

30% CNF-Imine



Aromatic stacking between side chains

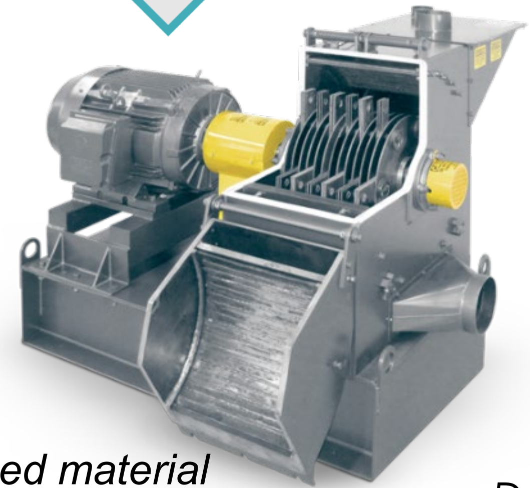
<u>PETG composites feature better interface between fibers and polymer matrix, regardless of fiber content</u>

CNF-Imine modification scaleup

100L reactor

Filter press

Wash material and press to 20% solids



Mill

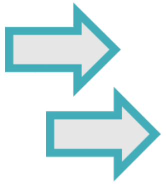
Grind oven-dried material in fluffy fibers

3 wt.% CNF in water

Dried, modified CNF ready for melt compounding

Allows us to surface-modify up to 3 lbs. of CNF (solid content, wt.%) at a time.

Compounding and Pelletization

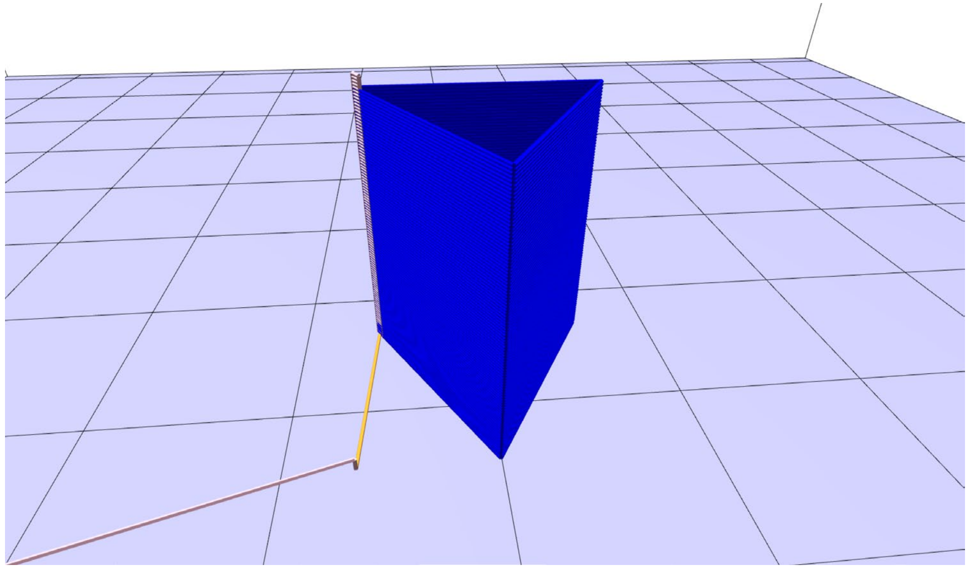


Compounding Conditions

- Temperature: 150-220 C
- Torque: 50-65
- Melt Temperature: 220-225 C
- Throughput: ~8 kg/hr

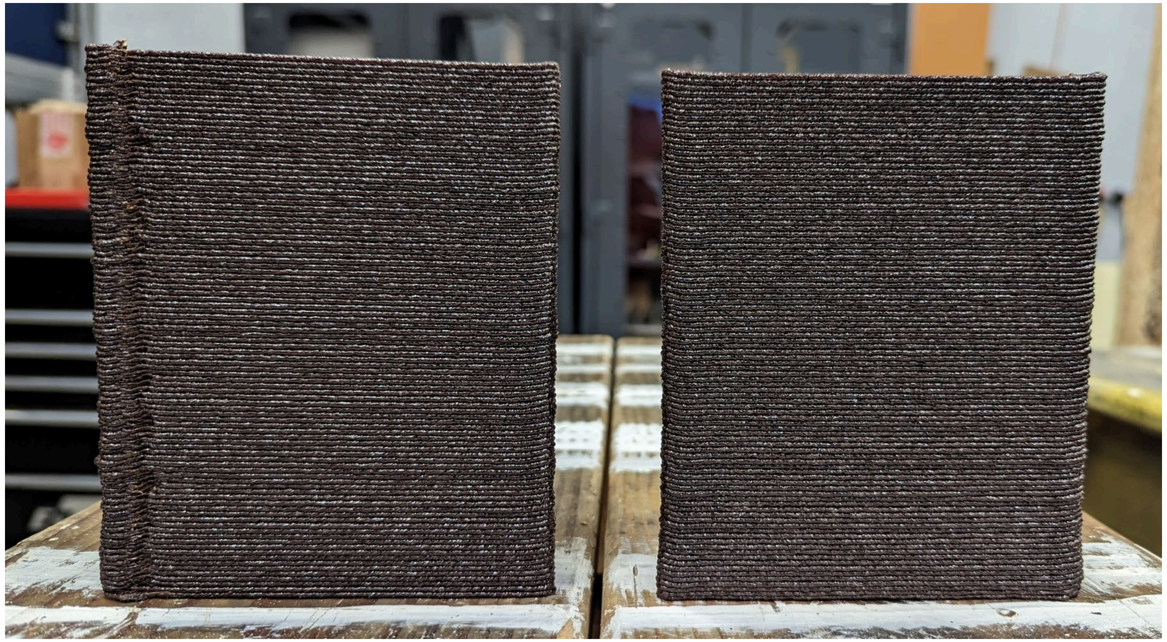
<u>Produced 10 kg. of composite pellets</u>

Additive Manufacturing

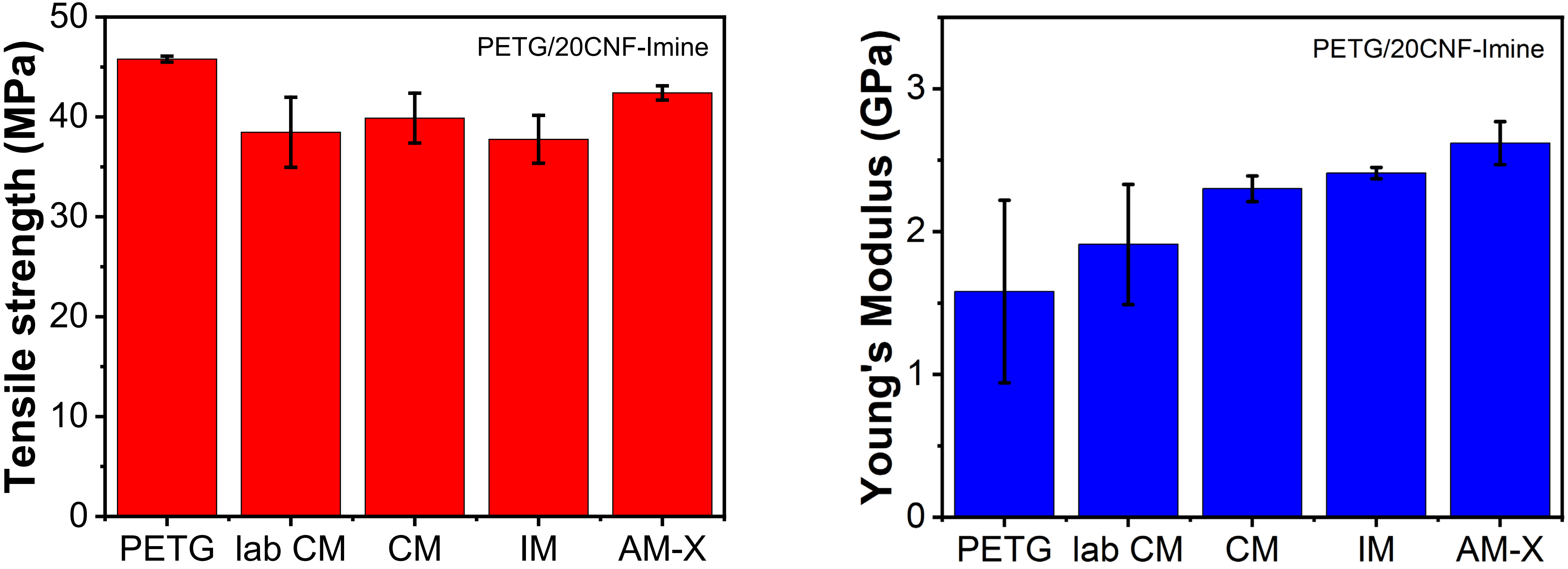


Print Slice Setup

- Nozzle Size: 4mm
- Bead profile: 6mm x 1.5mm
- Feed rate: 850mm/min
- Screw speed: 10 rpm
- Forward Tip Wipe: 0.25”
- Wipe speed: 350.00mm/min
- Travel Lift: 0.25”

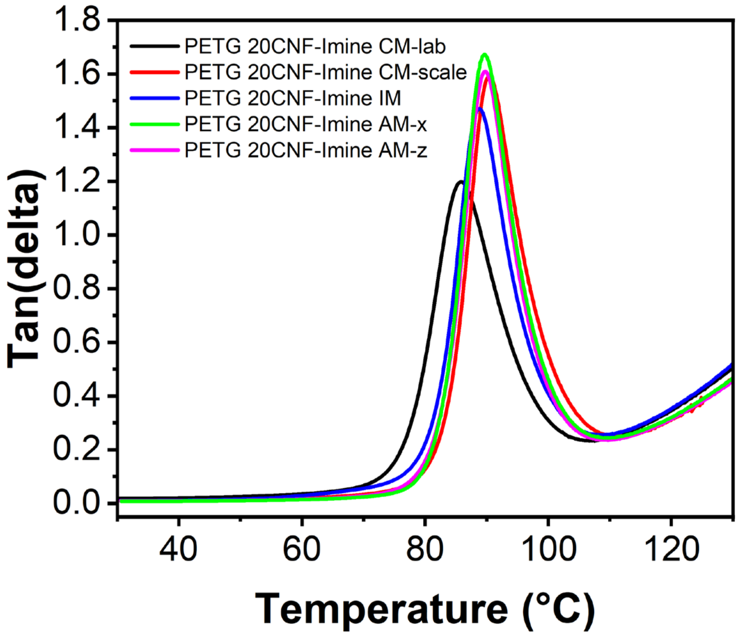


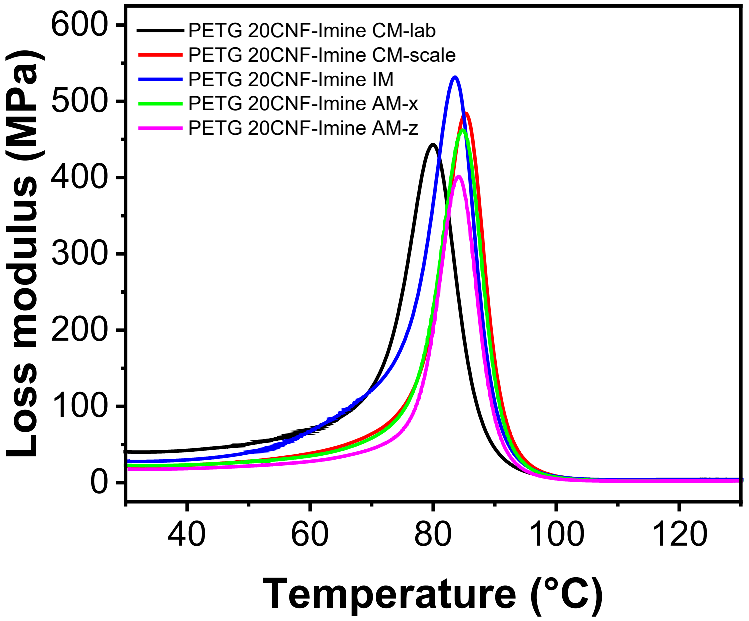
Tensile Properties

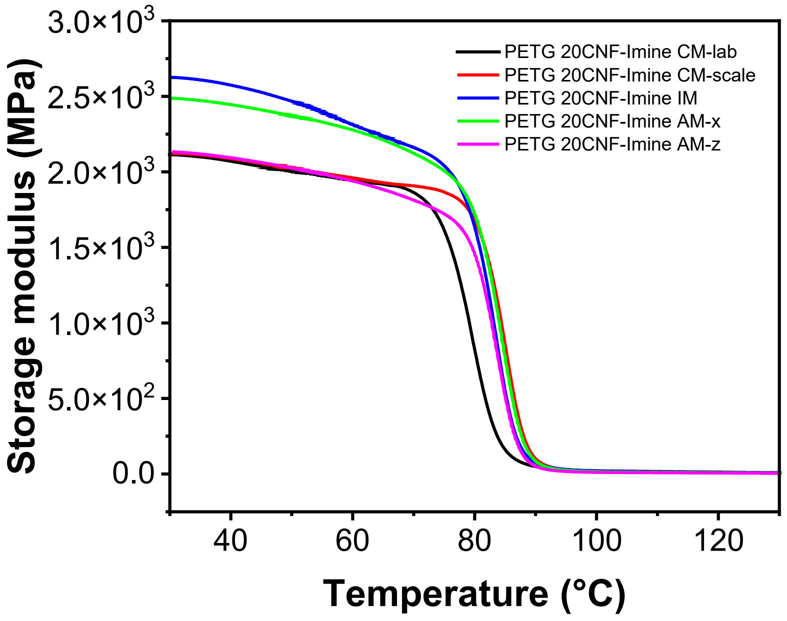


- Scale-up produced no difference in properties
- Fiber alignment observed in printed samples

DMA Properties







- Agrees with tensile properties
- Scale-up produced no difference in properties
- Fiber alignment observed in printed samples

Conclusions

- Polyimine formed and entangled with the surface of CNF as the presence of the imine prevented agglomeration and maintained fibrillar morphology
- Synthesis was scaled-up to produce > 3 kg of modified fibers and ~10 kg of composite pellets for 3D-printing trial
- Scale-up produced similar properties
- Properties compared between compression molding, injection molding, and 3D-printed
  - 3D-printed samples and injection molded samples displayed fiber alignment

Acknowledgements

- U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, AMMTO
- Center for Nanophase Materials Sciences (CNMS), ORNL
- High Temperature Materials Laboratory (HTML), ORNL
- Sustainable Manufacturing Technologies Group, Advanced Composites Science and Technology Section, Manufacturing Sciences Division, ORNL
- University of Maine, ASCC

Thank you for your attention!