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

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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

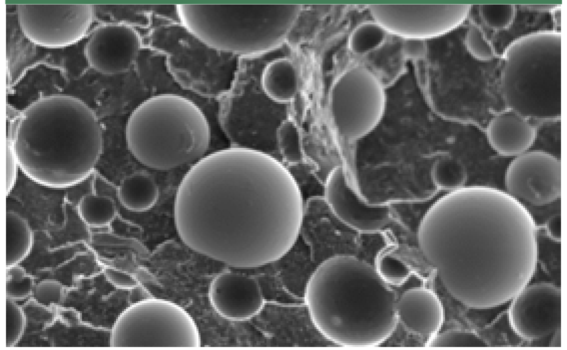
World-Renowned Computing

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 Al 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

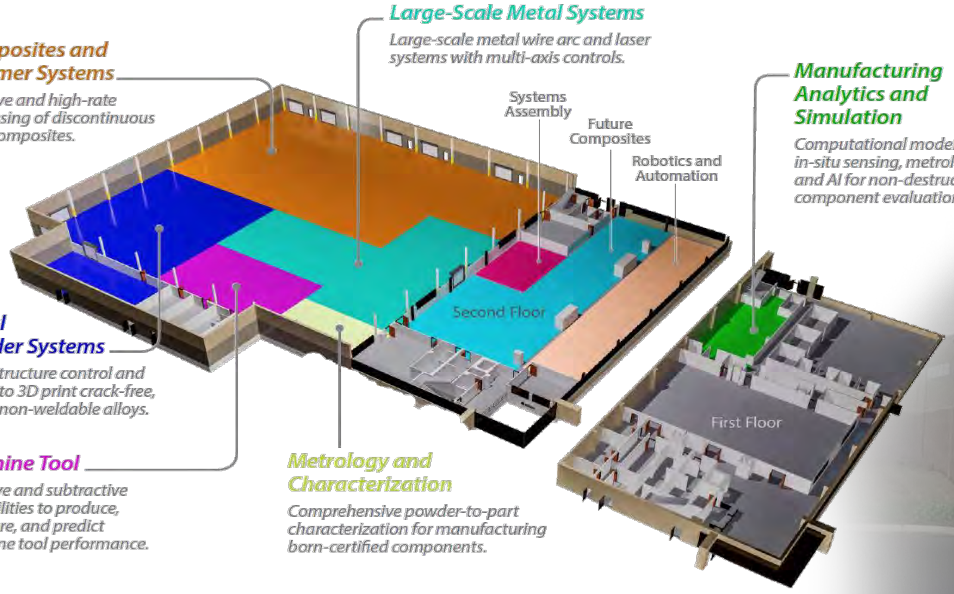
Cooperative research to develop and demonstrate advanced manufacturing with industry and universities

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

Education and Training

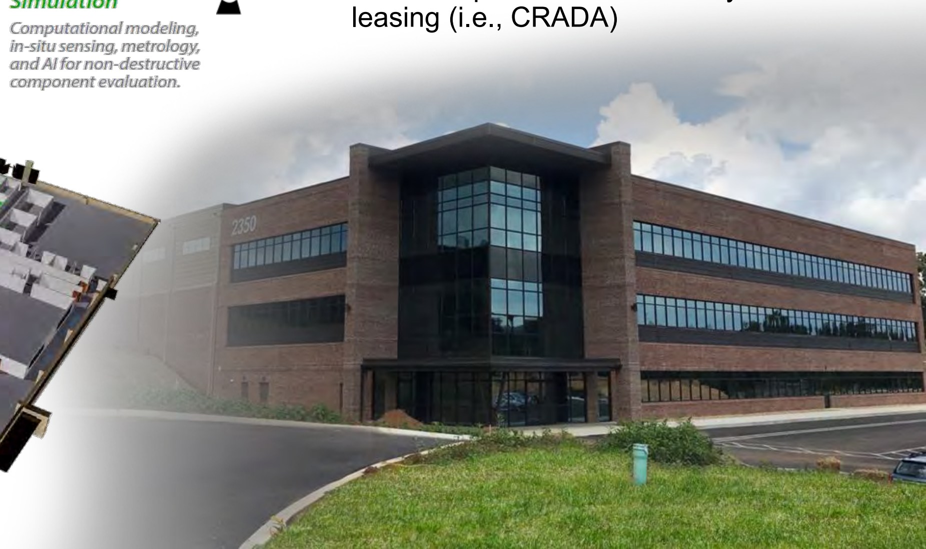
Internships, academic collaborations, workshops, training programs, and course curriculum for universities and community colleges

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



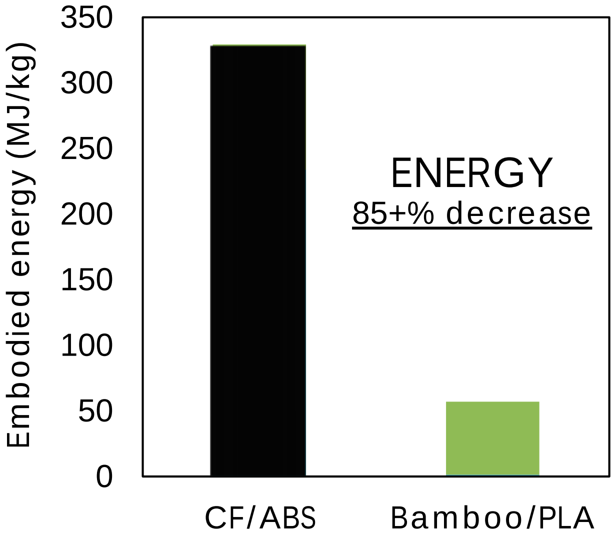
MDF by the numbers

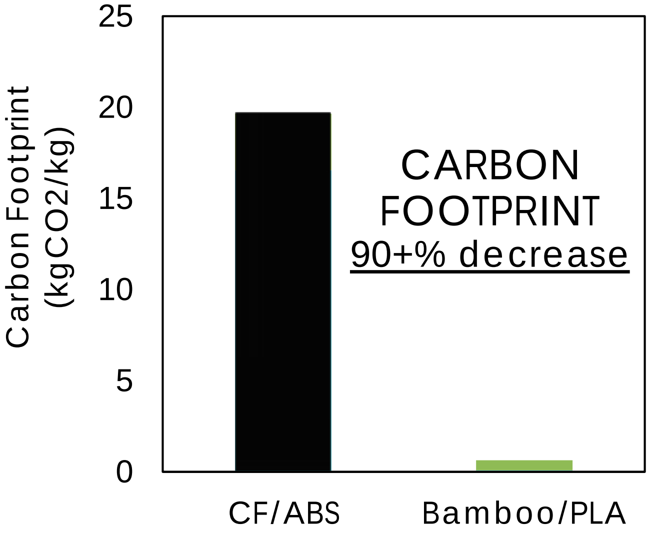
- **>100** staff members and ~200 people total when including interns, students and co-located industry partners
- **1,000** internships from **700** unique students since 2012
- **>180** partnerships
- **>50** university collaborations
- **>130** honors/awards since inception
- **>80** advanced manufacturing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

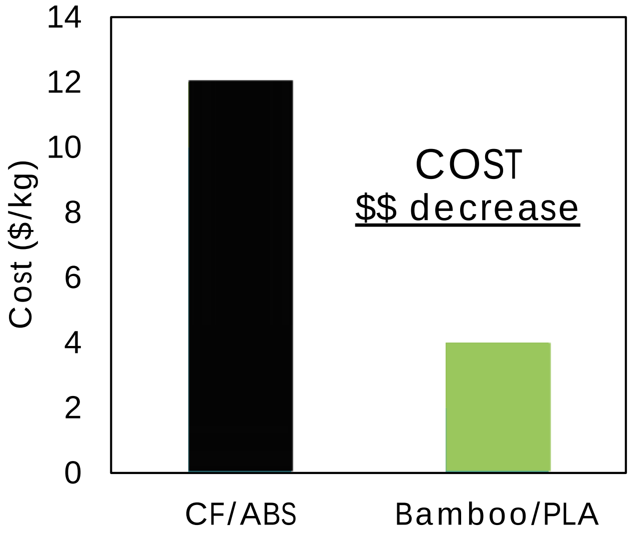


Benefits of Biomaterials in Manufacturing Applications

3D Printing Sustainable Structures

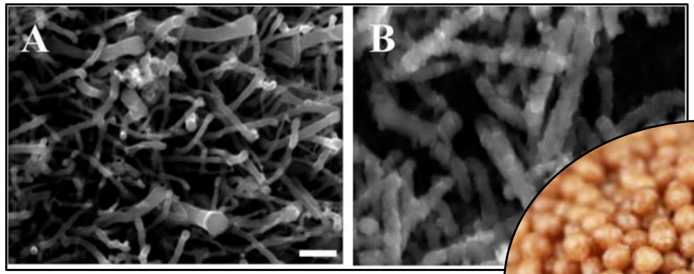


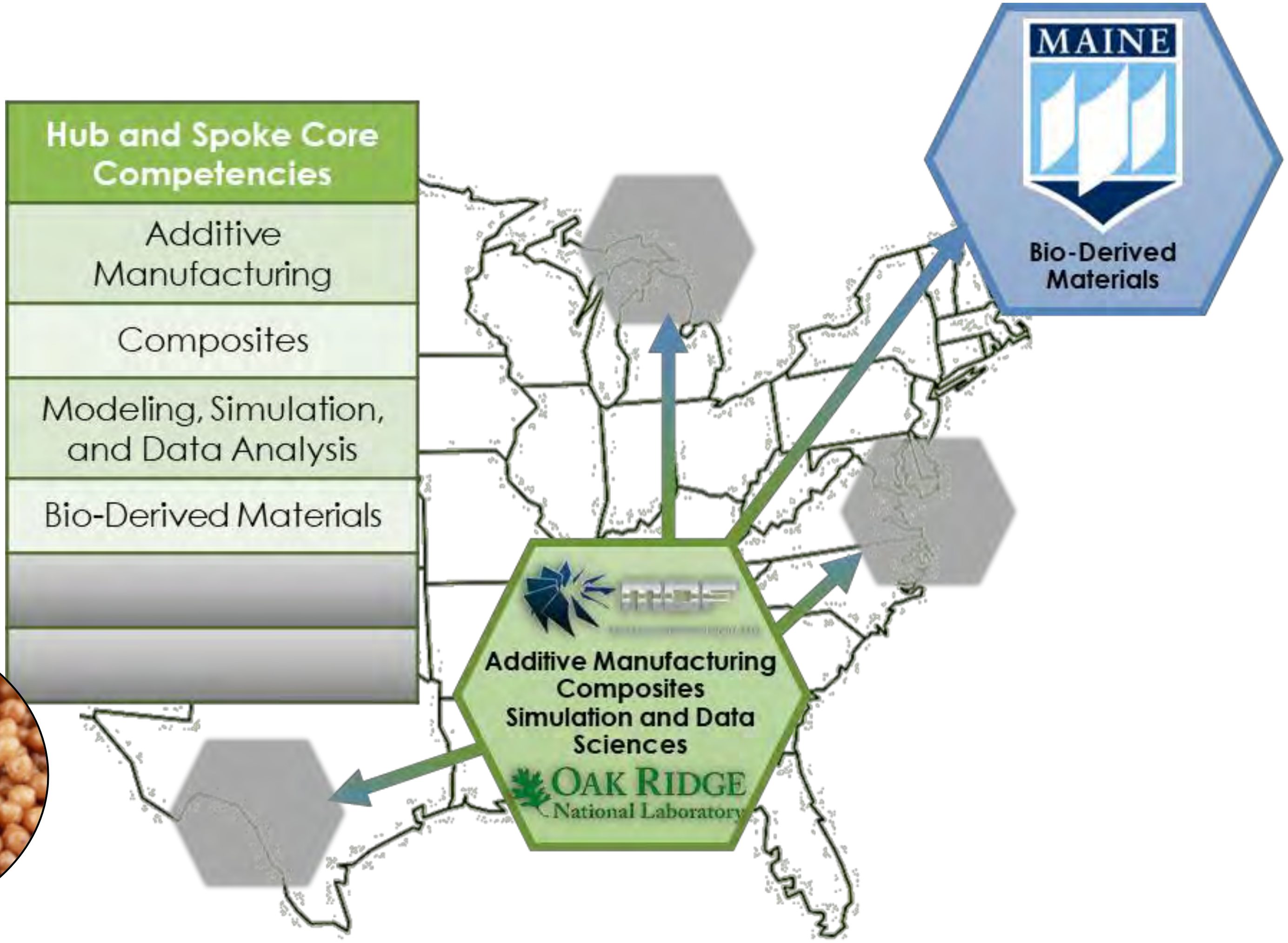




Pilot Hub & Spoke Program with UMaine

The sustainable biocomposite manufacturing research program will enable high stream utilization of forest products & cellulose fibrils to develop renewable, low cost, energy-efficient bio feedstocks for large-scale AM and other composite applications.





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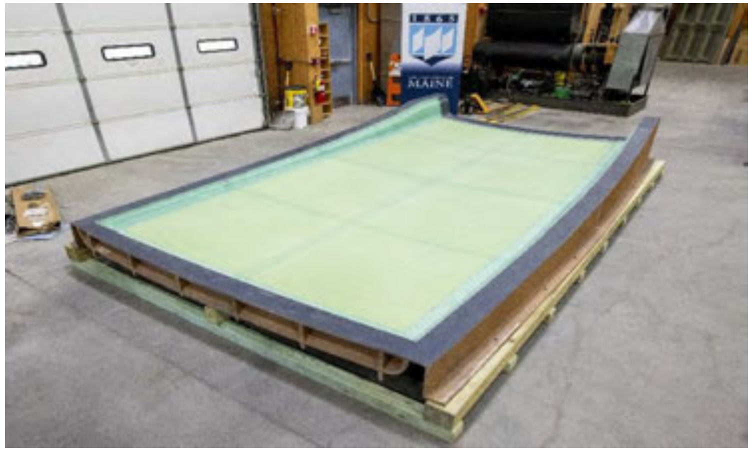
1865 THE UNIVERSITY OF MAINE

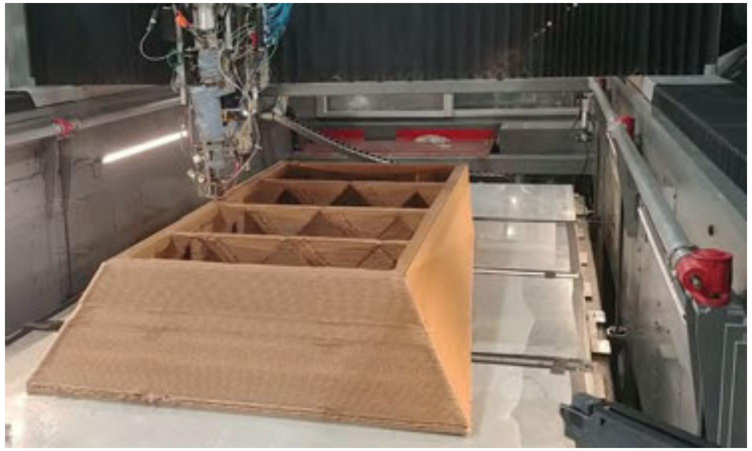
Manufacturing Applications

Building materials

Molds (marine applications)



Precast concrete structures

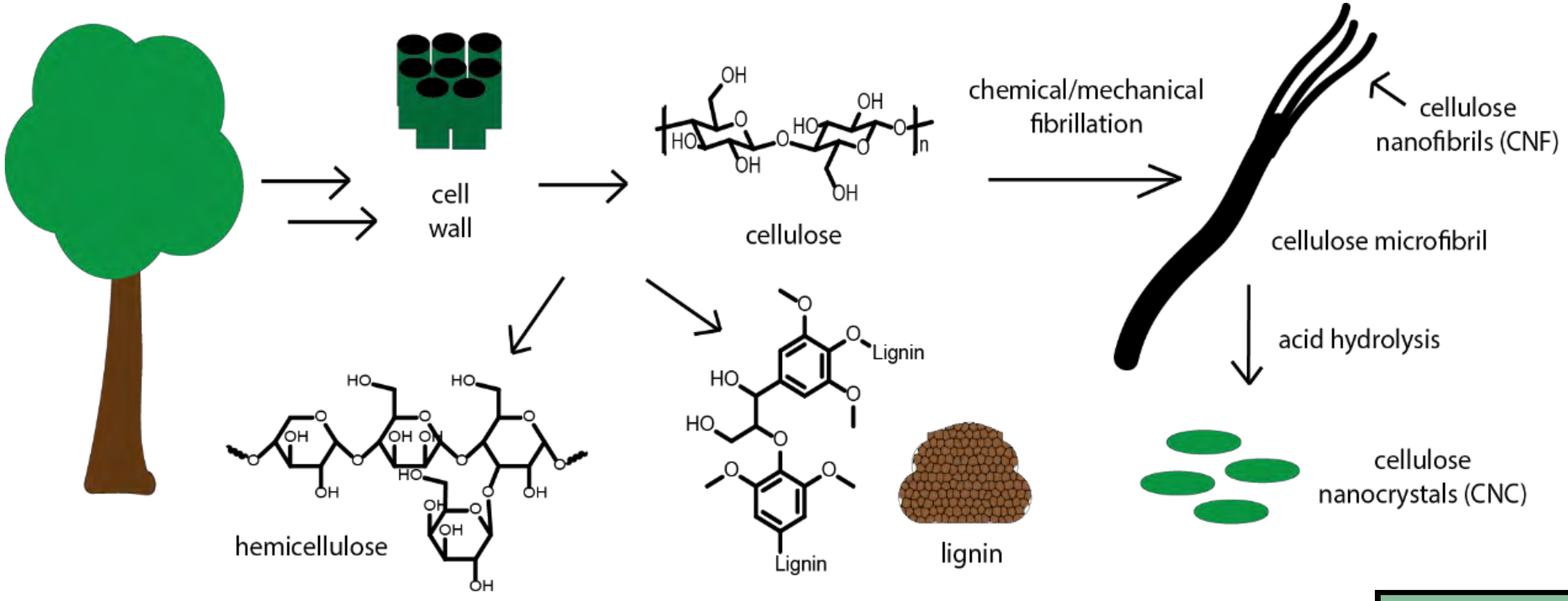


Wind energy

Infrastructure (utility poles)

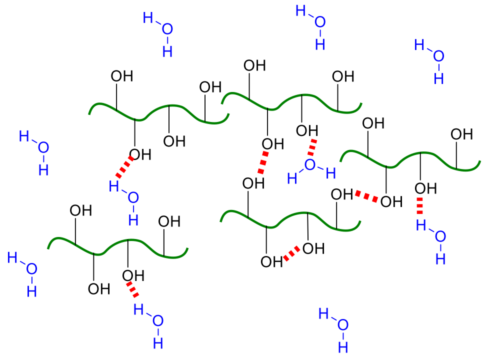
Tooling

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)

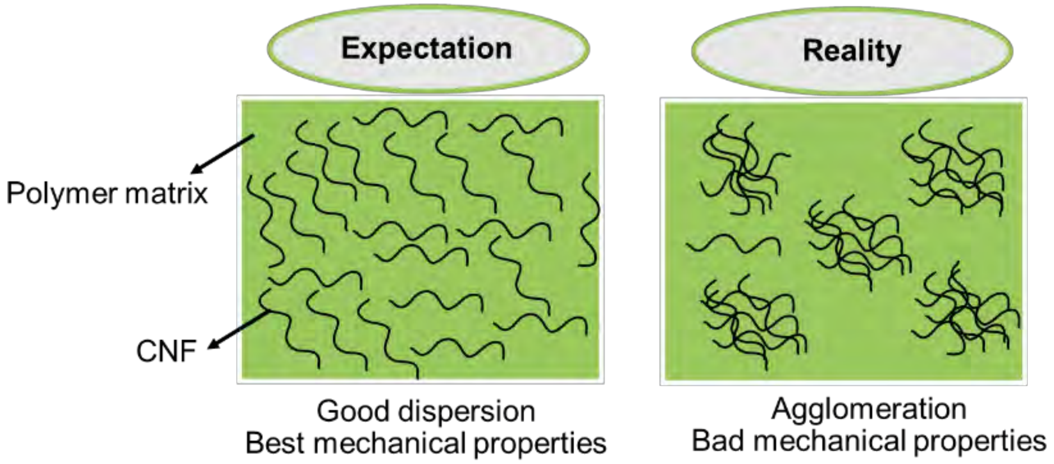


3 wt% CNF in water

	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

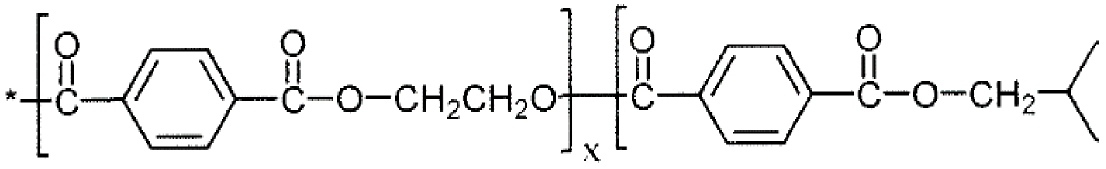
CNF Composites Challenges

Challenge: Very hydrophilic surface of CNF can lead to incompatibility with hydrophobic polymer matrices



Solution: Surface modification

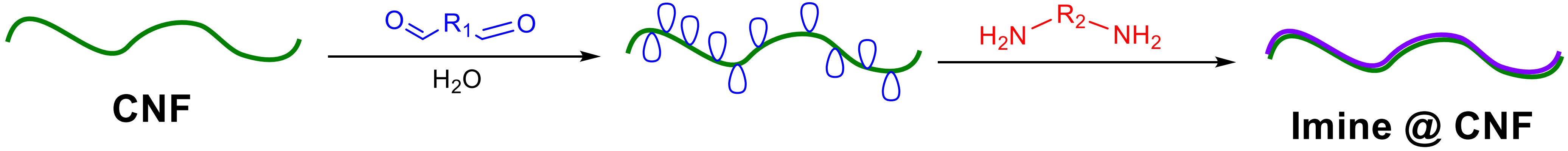
CNF
- Adsorption (interact with surface)
- Molecular grafting (covalently attached small molecules)
- Polymer grafting (covalently attached large molecules)

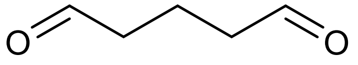


PETG: polyethylene terephthalate-glycol modified

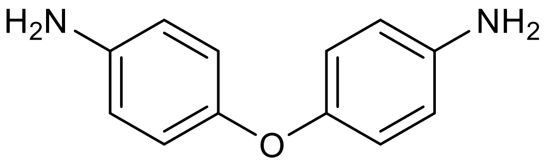
Modifying the surfaces of CNFs can:
- Reduce surface energy and hydrophilicity
- Reduce agglomeration during drying
- Reduce energy requirement for drying CNF
- Improve the compatibility with polymers and lead to high performance bio-composites

Experimental Design

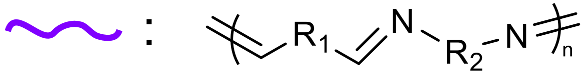




Glutaraldehyde



4,4′-Oxydianiline



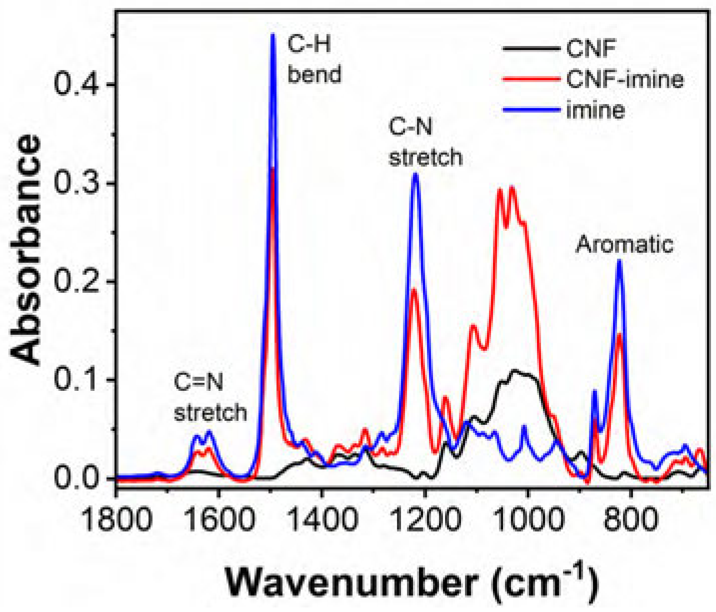
hydrophillic: soluble in water, able to interact with CNF in aqueous phase
hydrophobic: prevent water solubility of the formed imine

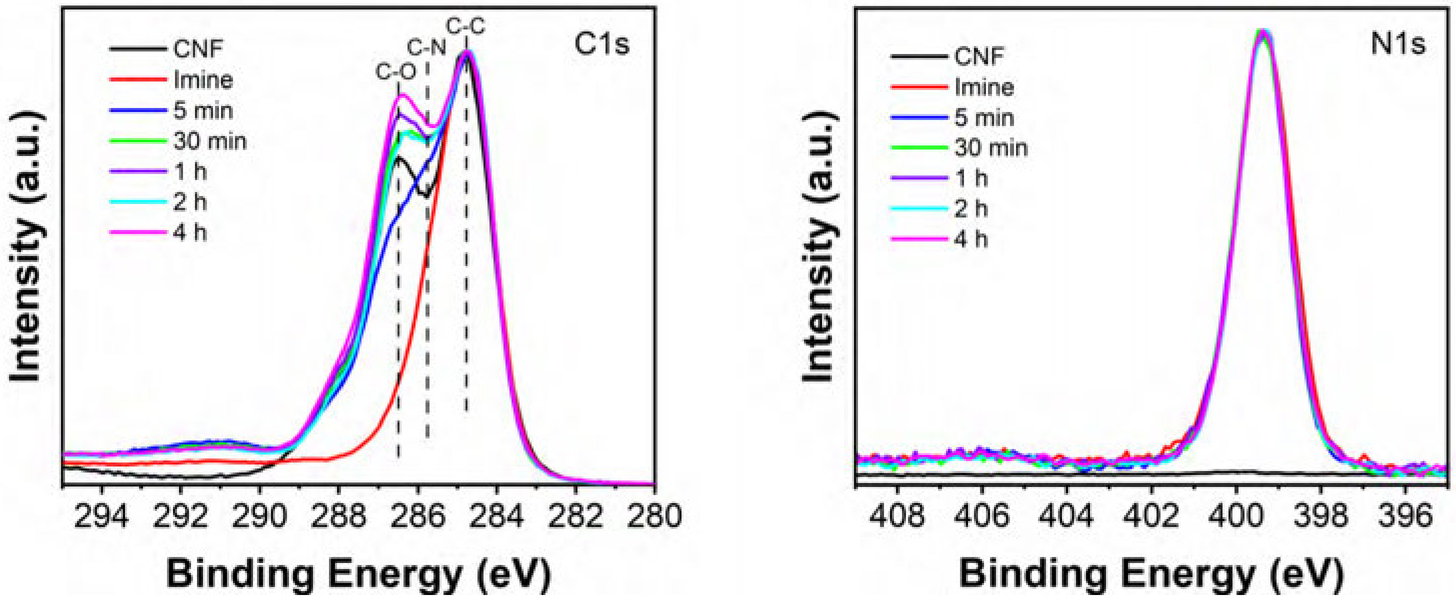
- Fast react rate
- Unstable in water and tend to hydrolyze back into reactant
  - Imine-dynamic covalent bond

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

Verification of Imine Formation

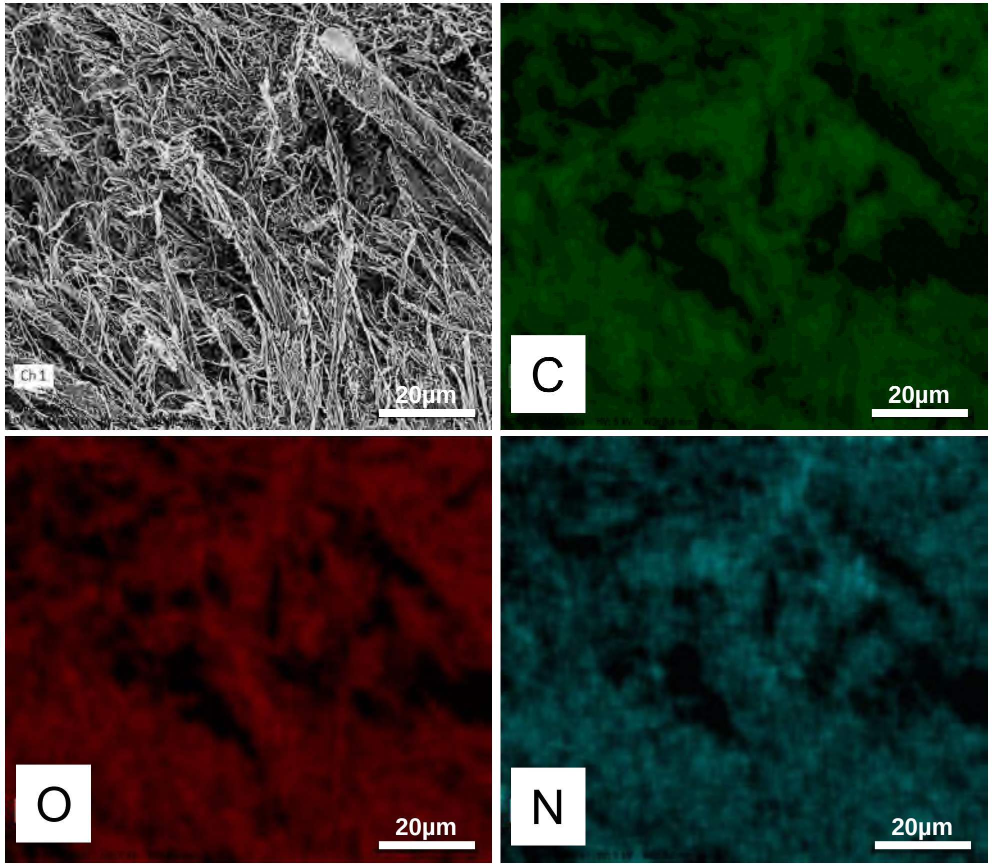
- FTIR confirmed presence of new bonds consistent with polyimine formation
  - C=N stretch
  - C-N stretch
  - Presence of aromatics C
- XPS changed with polyimine synthesis
  - Appearance of N1s
  - Increase in C-OH

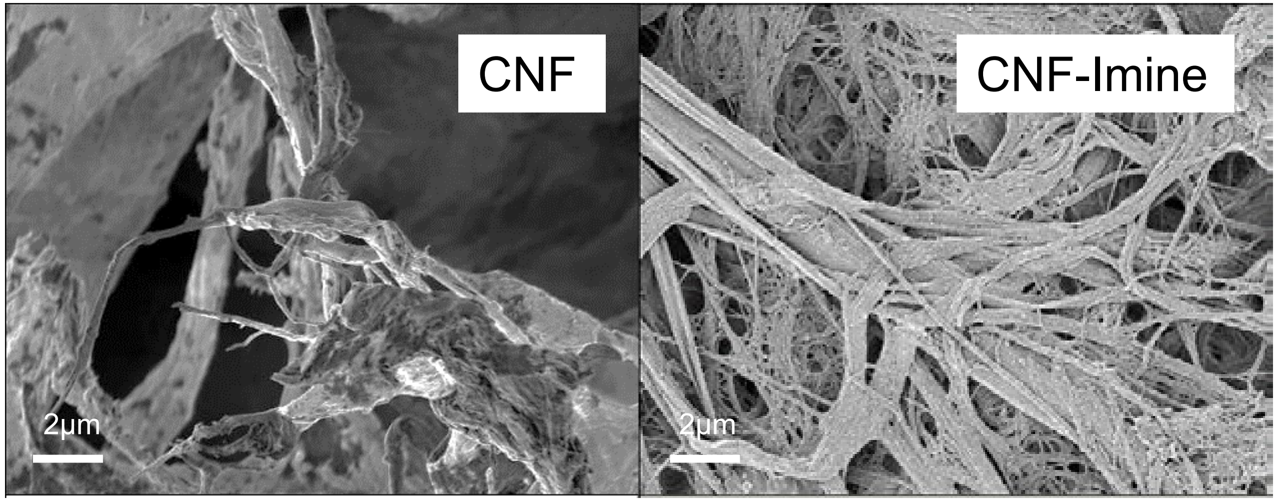




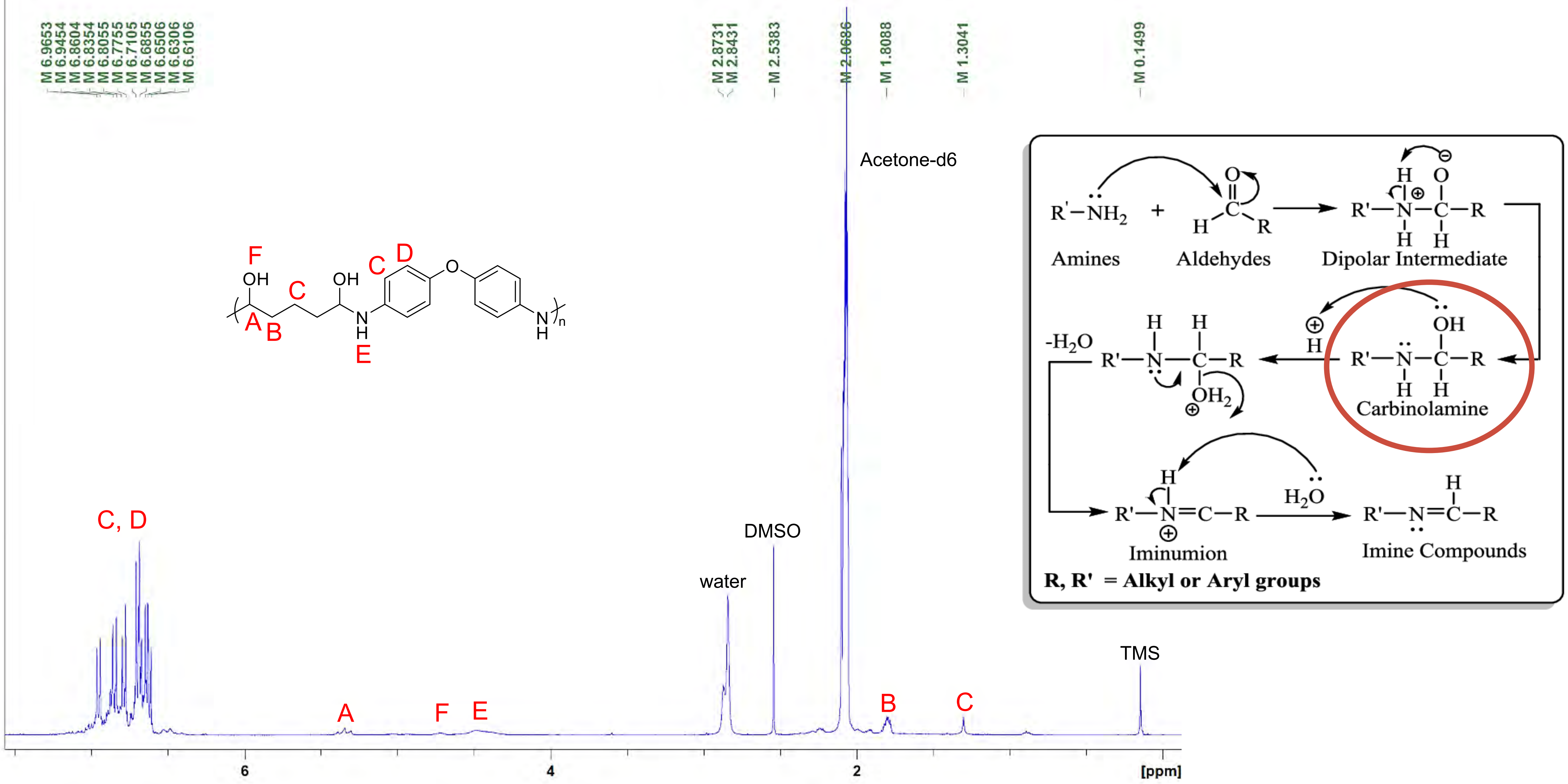
Morphology Changes

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

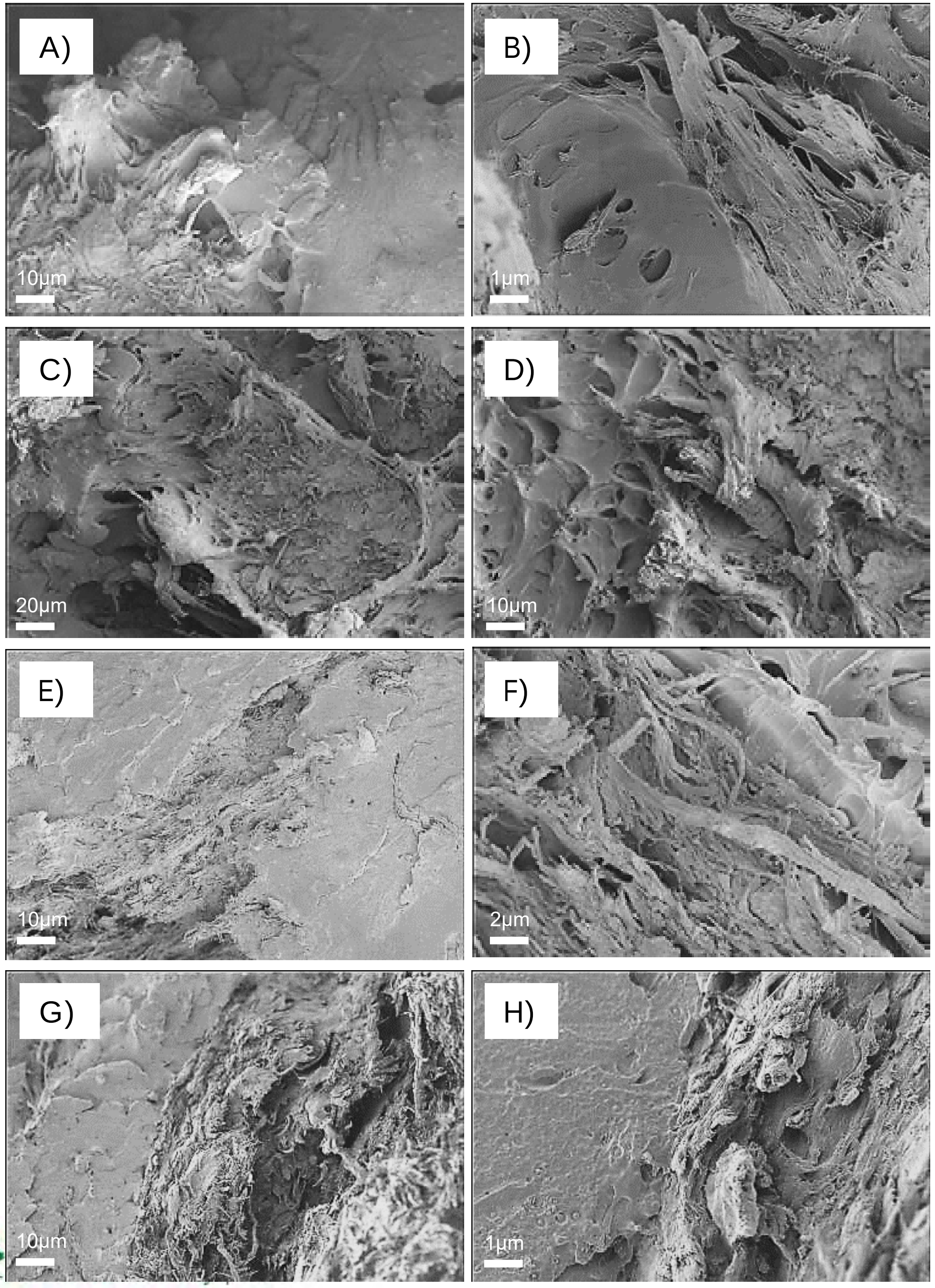




Structure of Polyimine Confirmed by ^{1}H-NMR



PETG composites

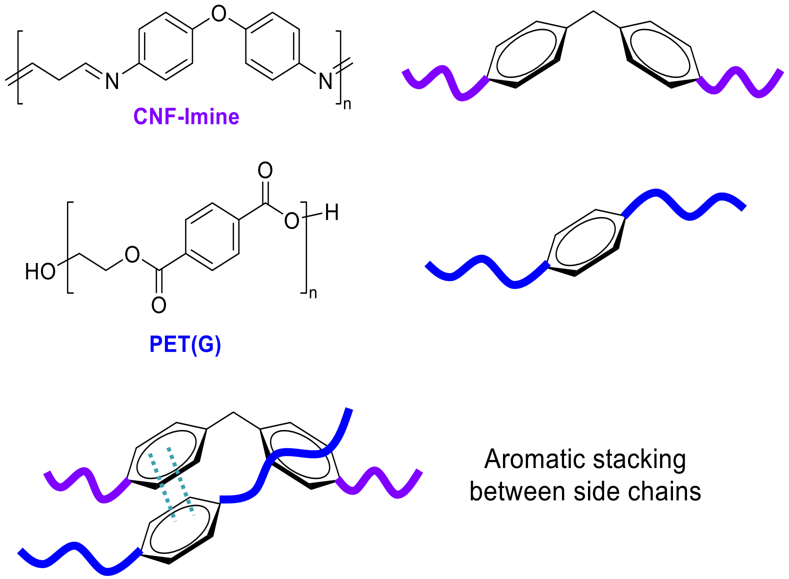


5% CNF-Imine

10% CNF-Imine

20% CNF-Imine

30% CNF-Imine



Aromatic stacking between side chains

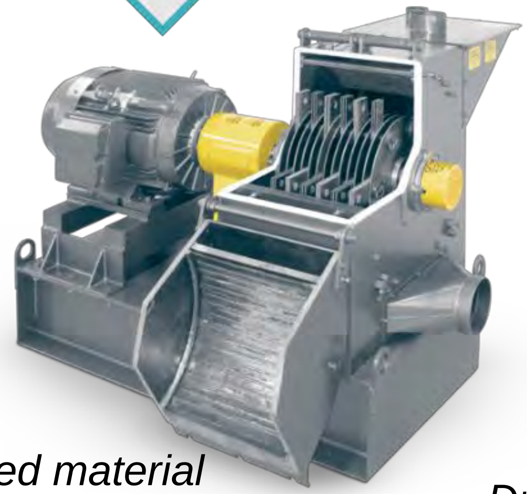
PETG composites feature better interface between fibers and polymer matrix, regardless of fiber content

CNF-Imine modification scaleup

100L reactor

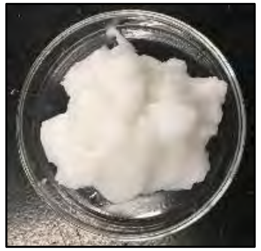
Filter press

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) at a time.

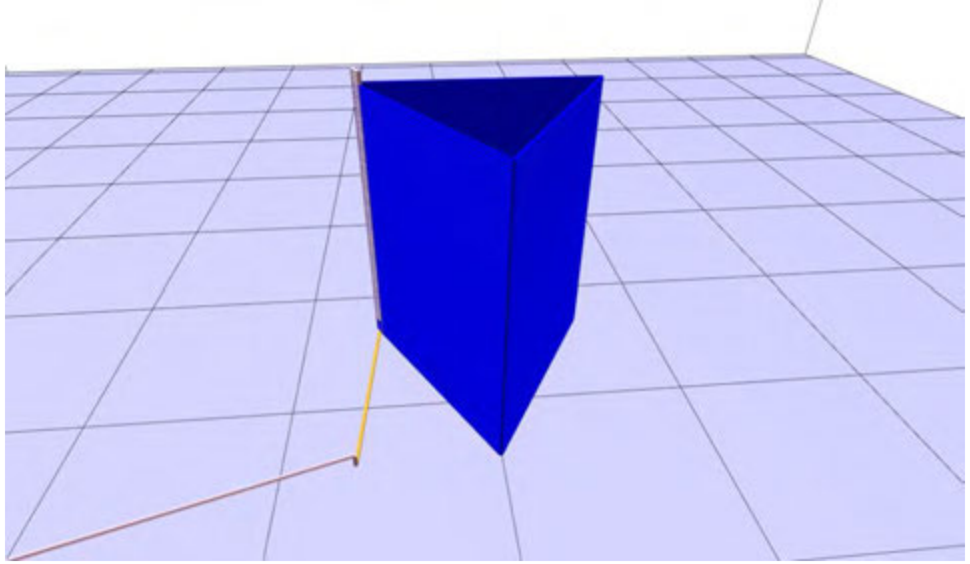
Compounding and Pelletization

Compounding Conditions

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

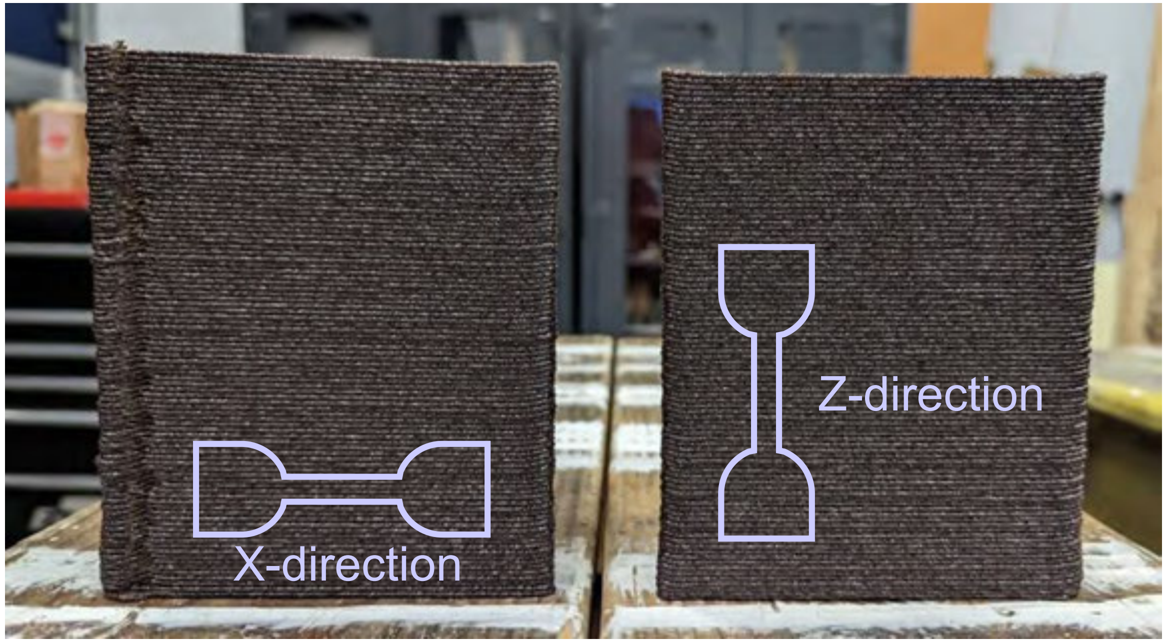
__Produced 10 kg. of composite pellets__

Additive Manufacturing

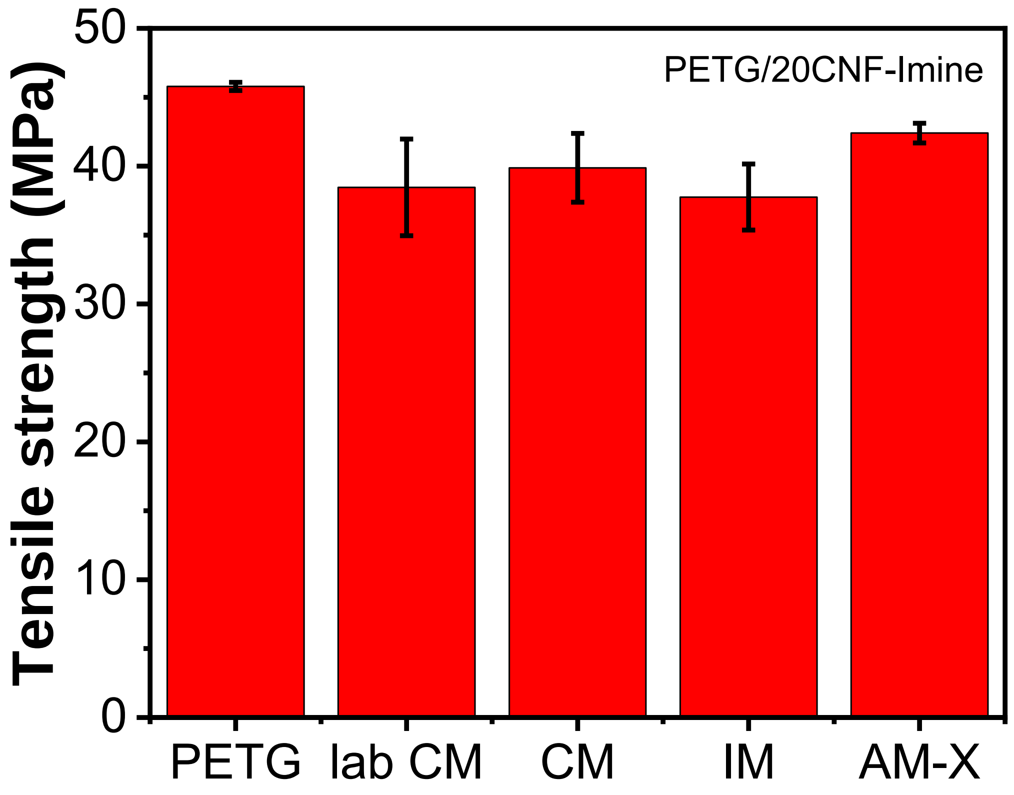


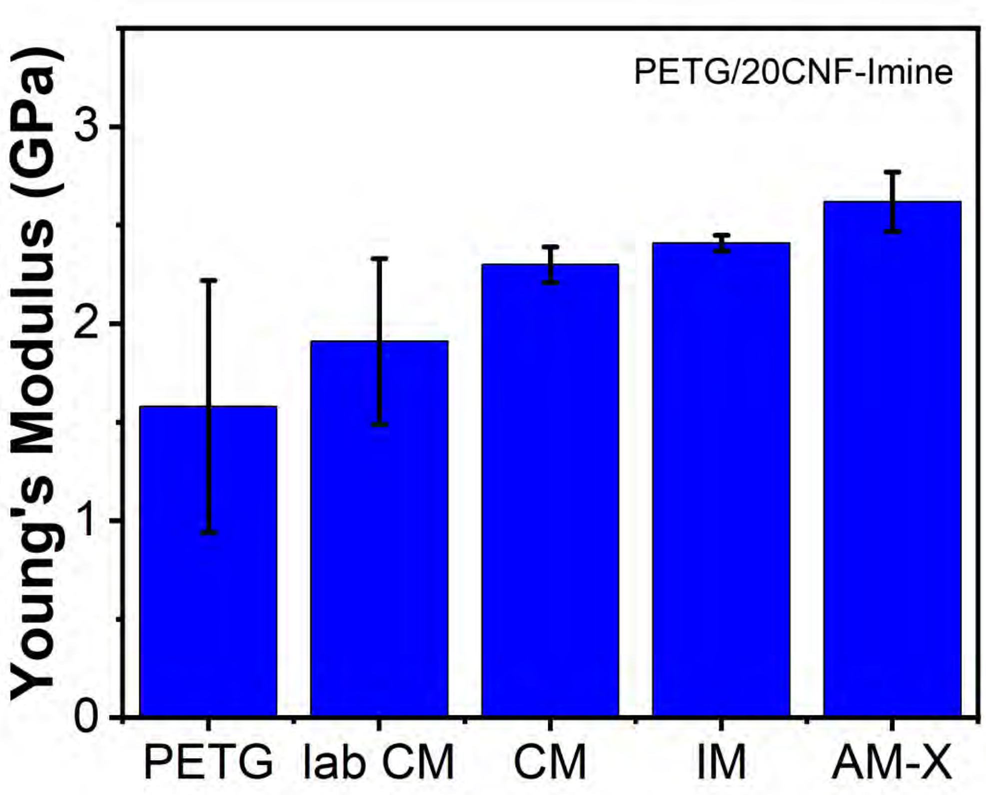
Print Slice Setup

- 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
- Need to optimize injection molding procedure

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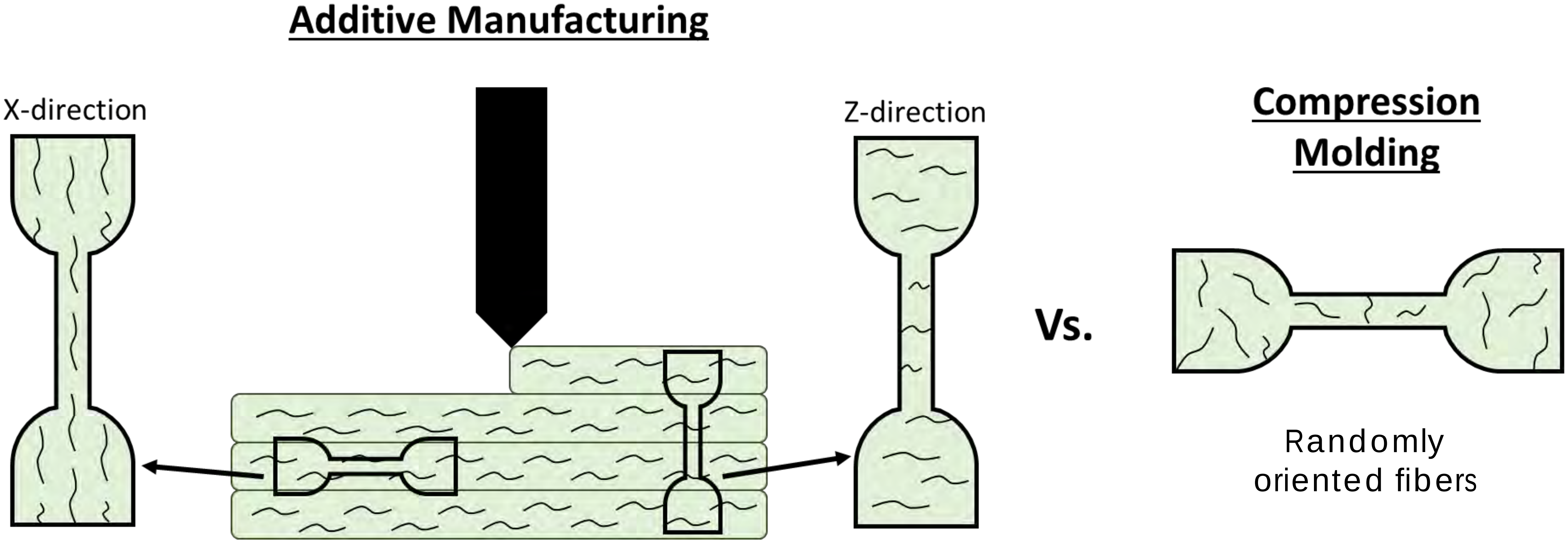
Fiber Alignment

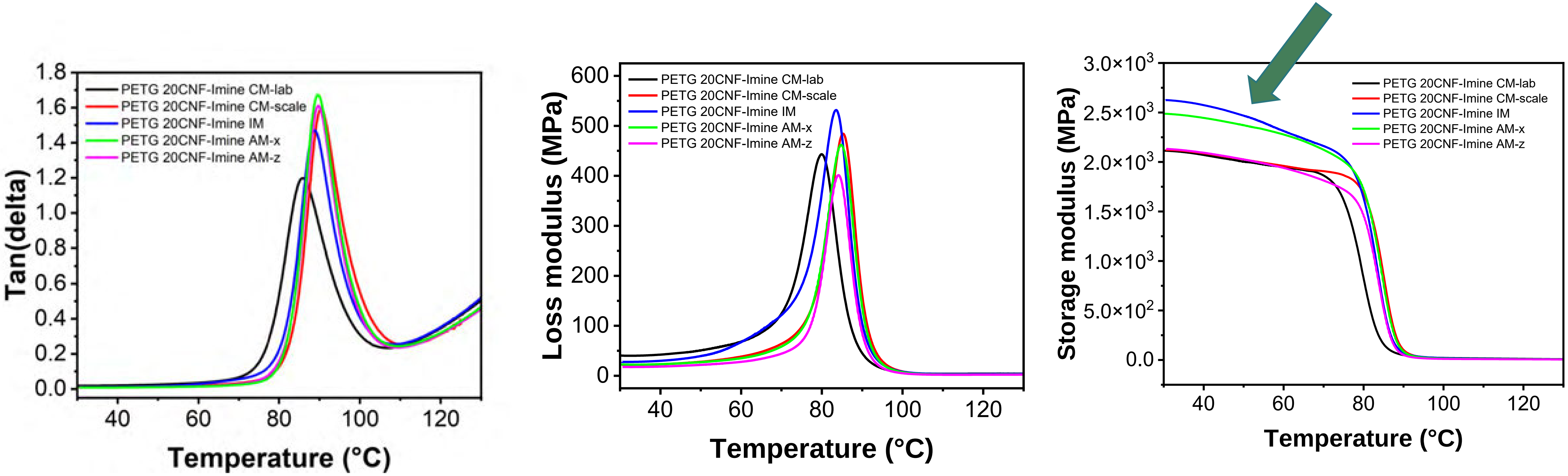


Aligned parallel to print direction

Aligned perpendicular to print direction

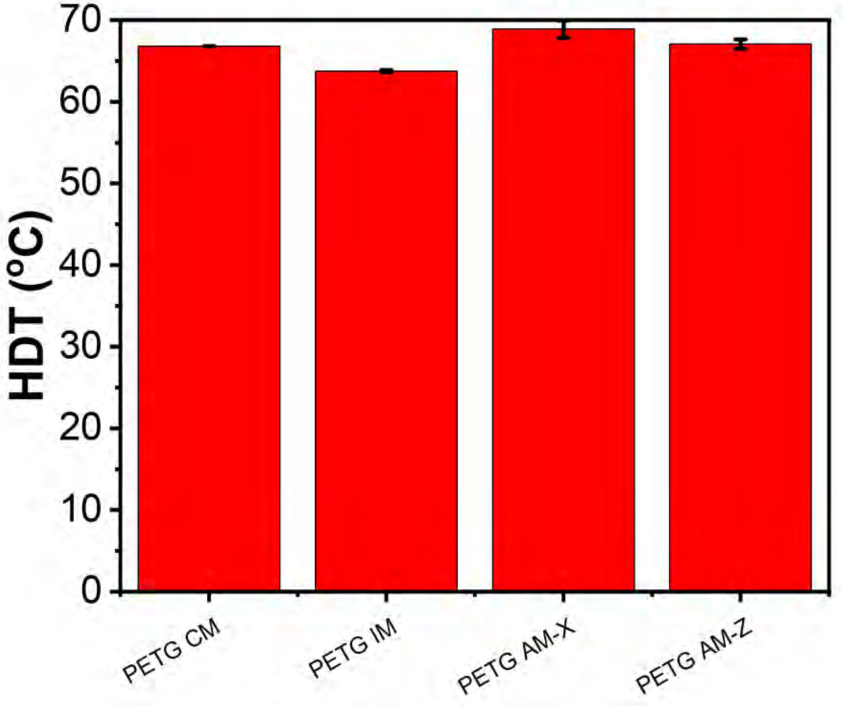
Randomly oriented fibers

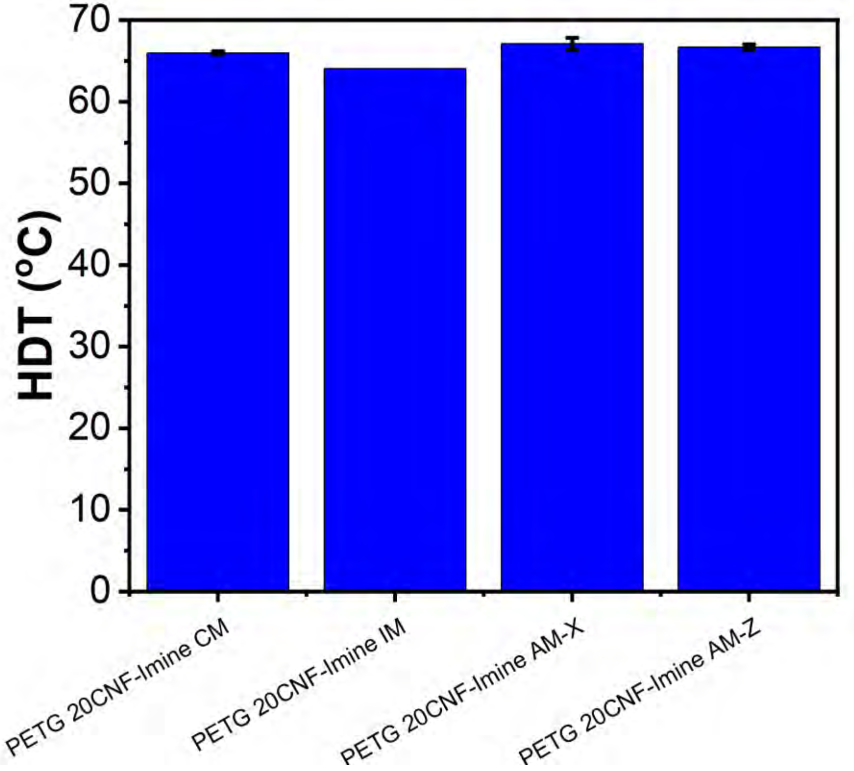
DMA Properties



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

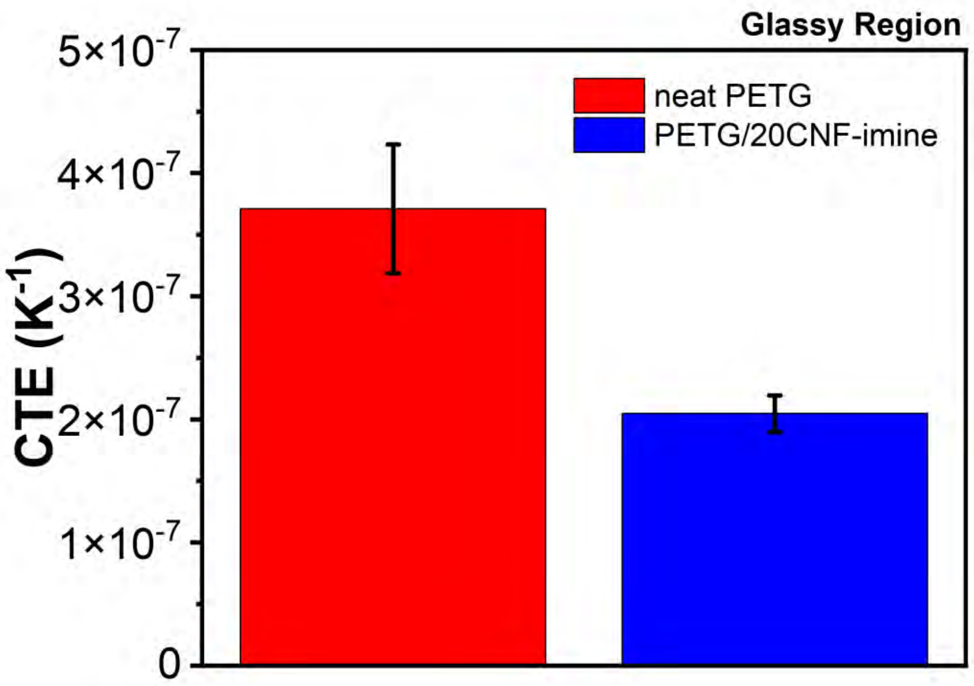
HDT Properties

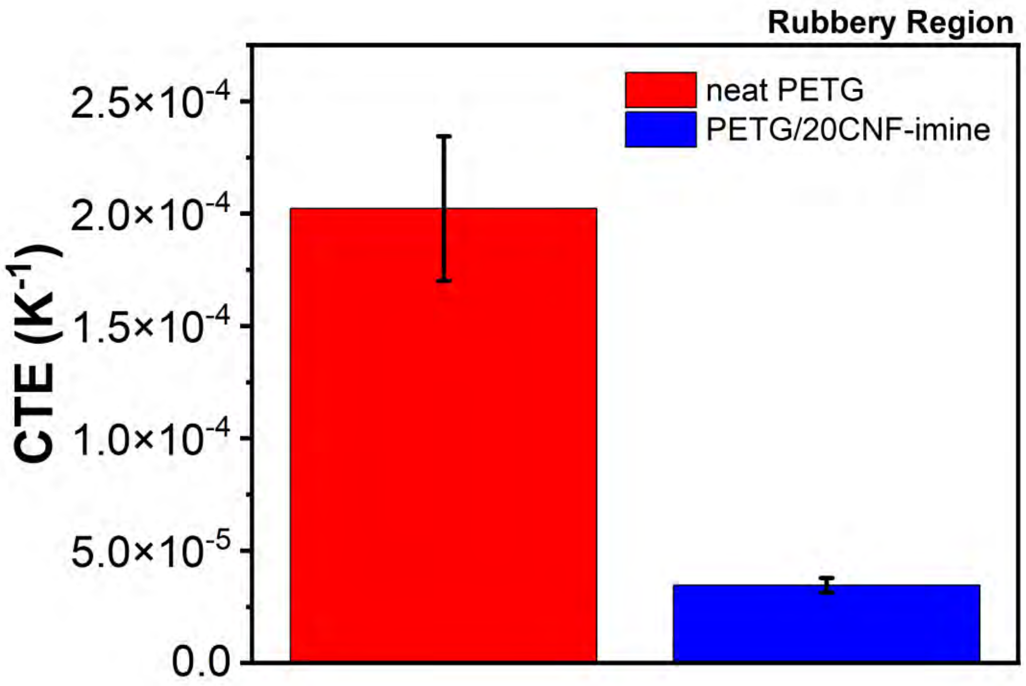




- HDT: heat deflection temperature
- Increased minimally with fiber alignment during printing

CTE Properties





- CTE: coefficient of thermal expansion
- Decreased significantly with addition of fibers
- Provides more applications for this material

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

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- University of Maine, ASCC

Thank you for your attention!