DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

1.2.1.9/1.2.1.10
Value-added biocomposite production using off-spec biomass from mechanical fractionation

4/5/2023
Renewable Carbon Resources

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ORNL is managed by UT-Battelle LLC for the US Department of Energy

Project Team

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<u>Summer 2023</u>

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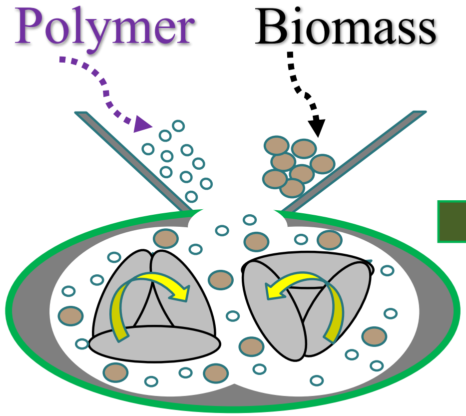
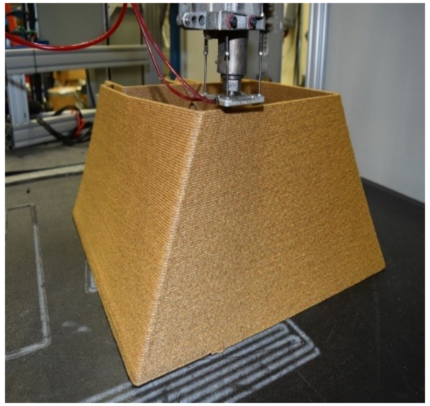
Project Overview

- Biocomposites for large-scale 3D printing offer
  - Reduced carbon intensity
  - Lower cost (biomass/PLA is ~ ¼ cost of CF/ABS*)
  - Recyclability
- Options for biofiber reinforcement
  - Raw, ground biomass
  - Refined biomass polymers (e.g., nanocellulose, lignin)

Biomass

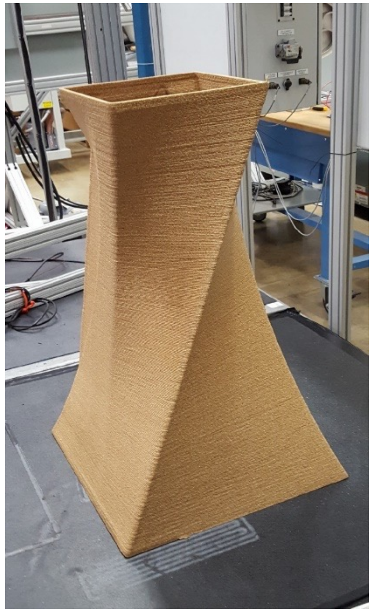


Compounding



Large-scale
3D printing

PLA-biomass products



*CF/ABS = ABS plastic reinforced with carbon fiber
Conventional composite for large-scale additive manufacturing

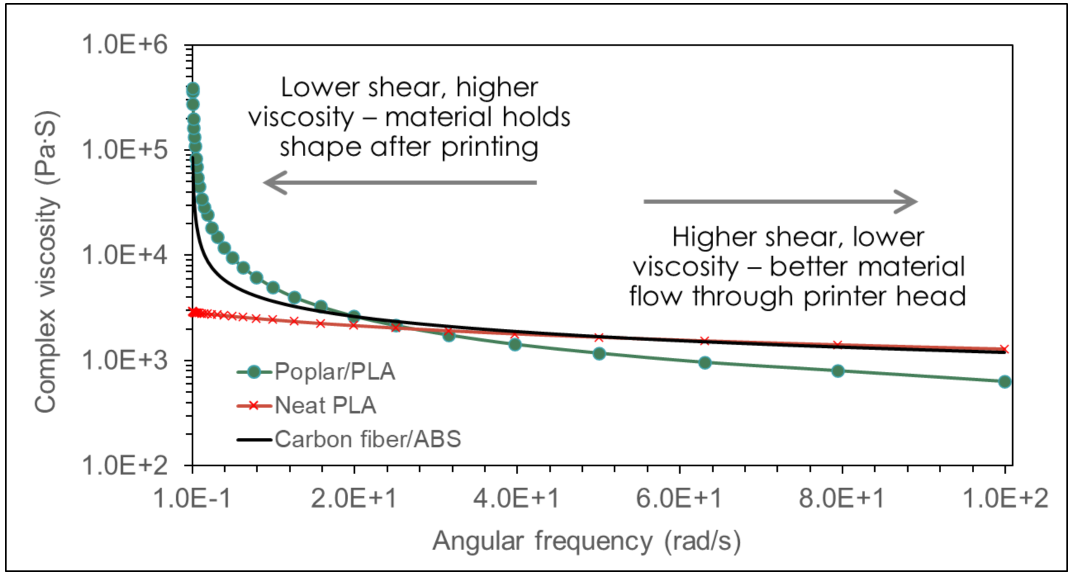
PLA: polylactic acid
ABS: acrylonitrile butadiene styrene

Project Overview

Feasibility of biomass as composite reinforcement

In a prior project using debarked poplar wood, we successfully met technical targets for printability, strength, and cost.

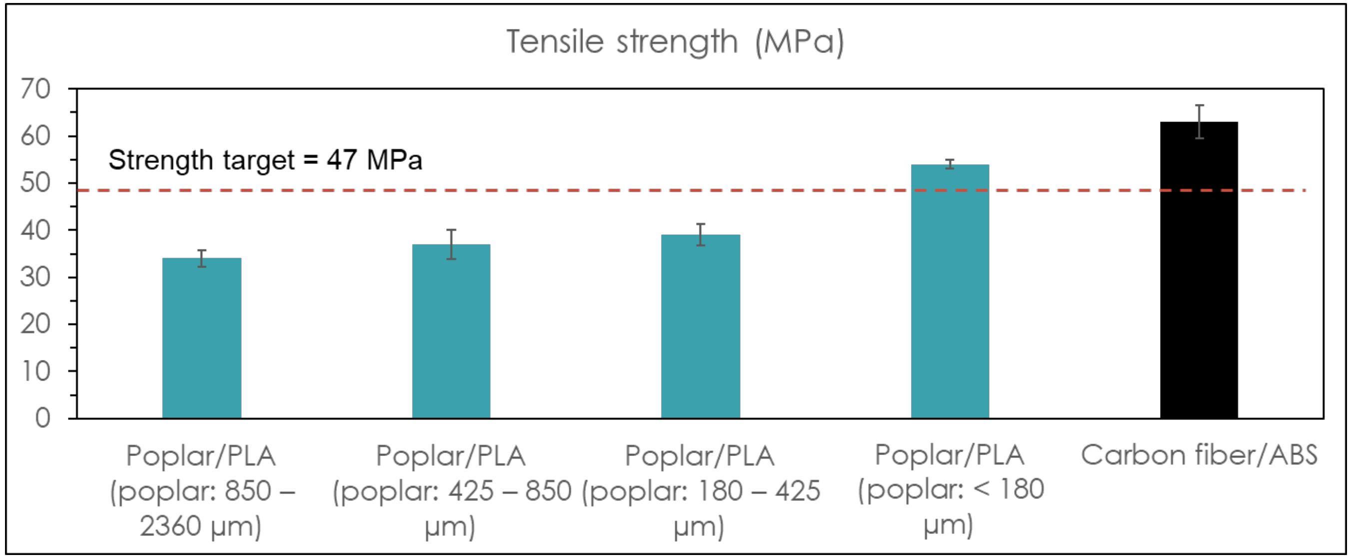
Printability



Composites met the viscous characteristics required for 3D printing

PLA/poplar printability outperforms CF/ABS and neat PLA (no fiber reinforcement)

Strength

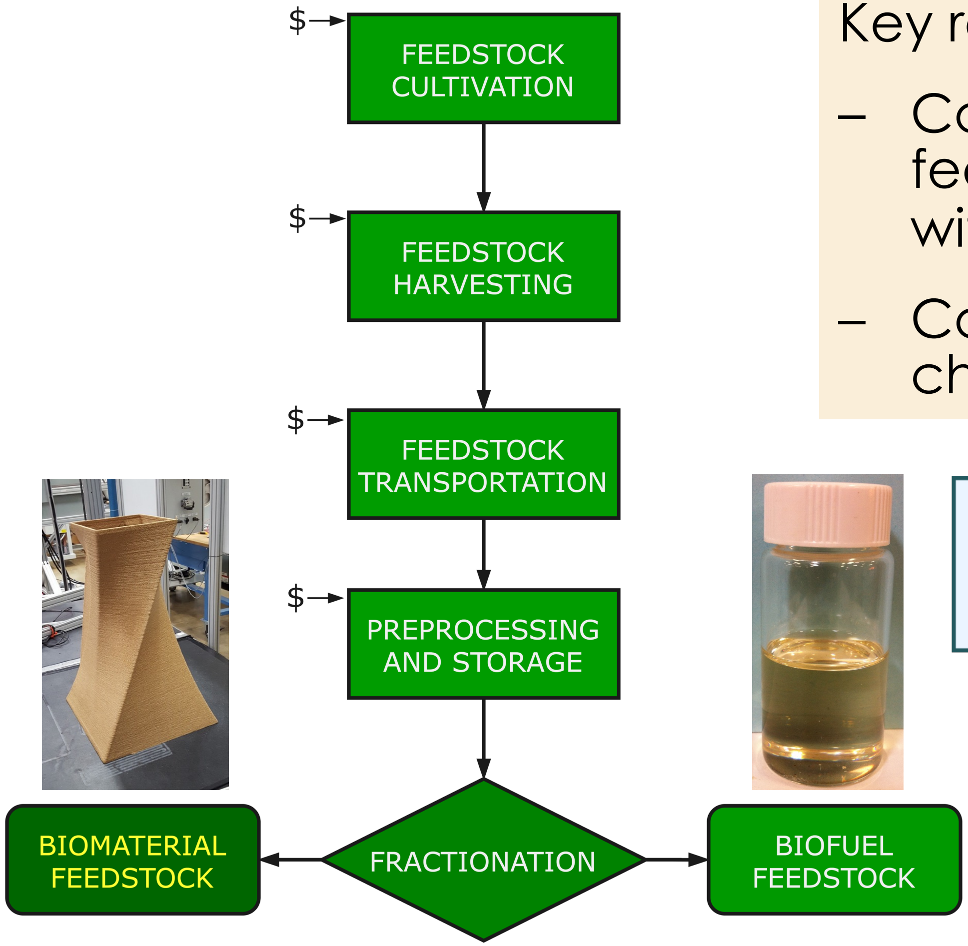


For debarked wood, with particle size <180 µm, composite of 20% poplar and 80% PLA had tensile strength 89% of carbon fiber/ABS

Project Overview

Objectives

Improve the economic viability of biomass supply chains by integrating materials coproducts



Key research questions:

- Can we produce biocomposites from domestic feedstocks in a way that complements, not competes with, the biofuel industry?
- Can biomaterials coproducts improve biofuel supply chain economics?

Year 1: Characterize impacts of ash, particle size, moisture in off-spec biomass fractions on biocomposites

Year 2: Surface treatments to improve biocomposite strength

Year 3: TEA to determine impact of fractionation to create biomaterials feedstock coproduct that improves biofuel feedstock quality on fuel selling price

Biocomposite preparation

Biomass prep

- Samples (e.g., corn stover, pine) collected from light fractions of the INL air classifier
- For some tests, biomass sieved to sort by particle size

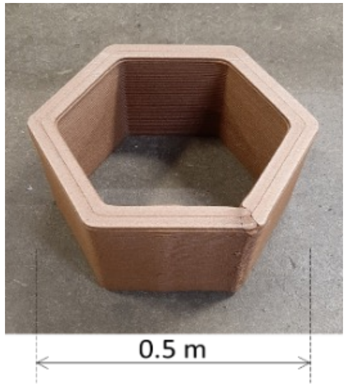
Biomass characterization

- Physical properties (ORNL)
  - Moisture
  - Particle size and shape
  - Flowability
  - Particle densities
  - Surface roughness
- Chemical properties (INL)
  - Ash content, ash species

Particle image analyzer

Composite preparation and testing

- Screening tests
  - Small-batch compounding of biofiber with PLA
  - Bench-scale testing of tensile strength, stiffness, and rheology
- Demonstration prints
  - Compounded by Techmer PM
  - Utilize in large-scale printer

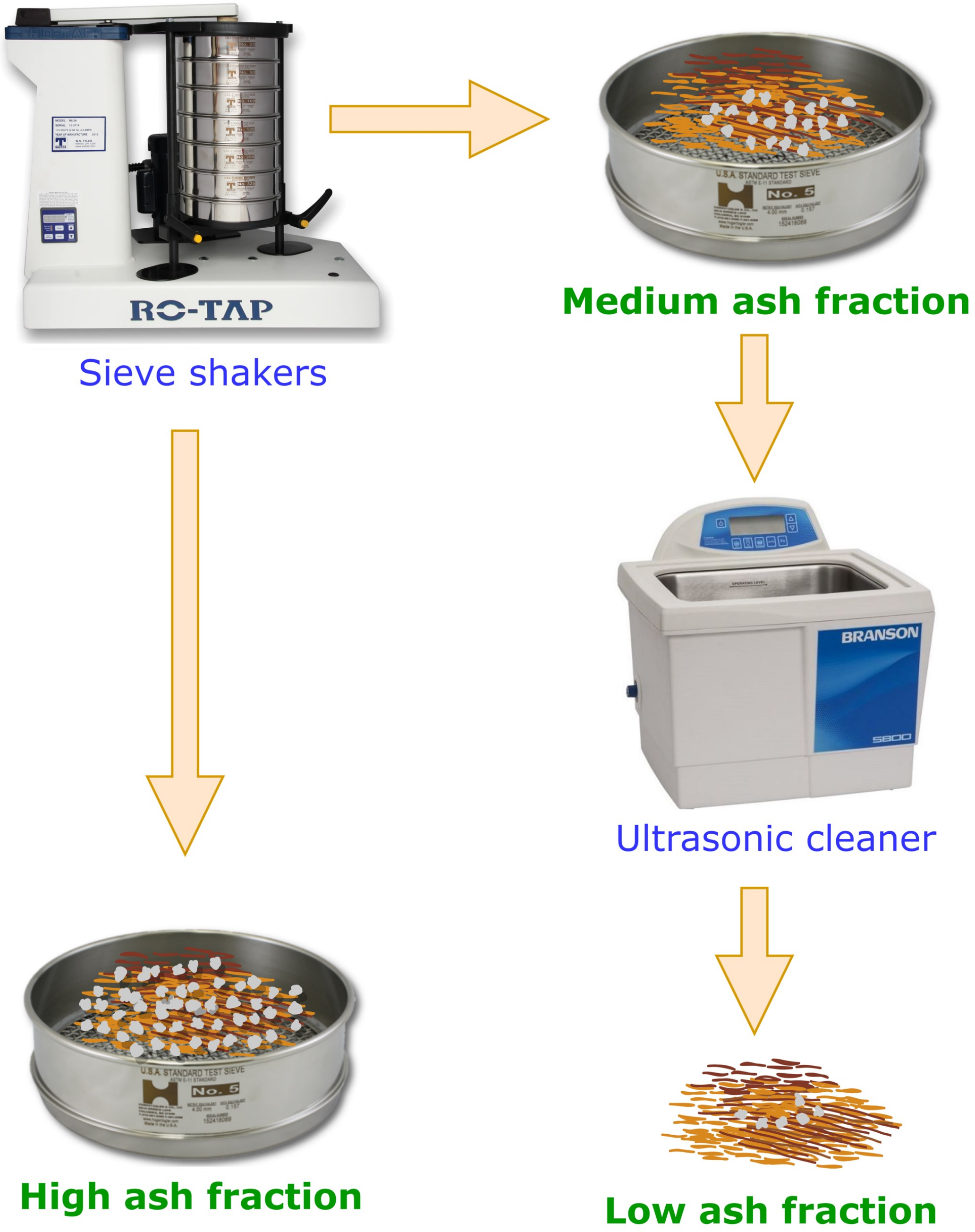


1. Approach
Biomass ash treatments

Feedstock treatments (ash %)

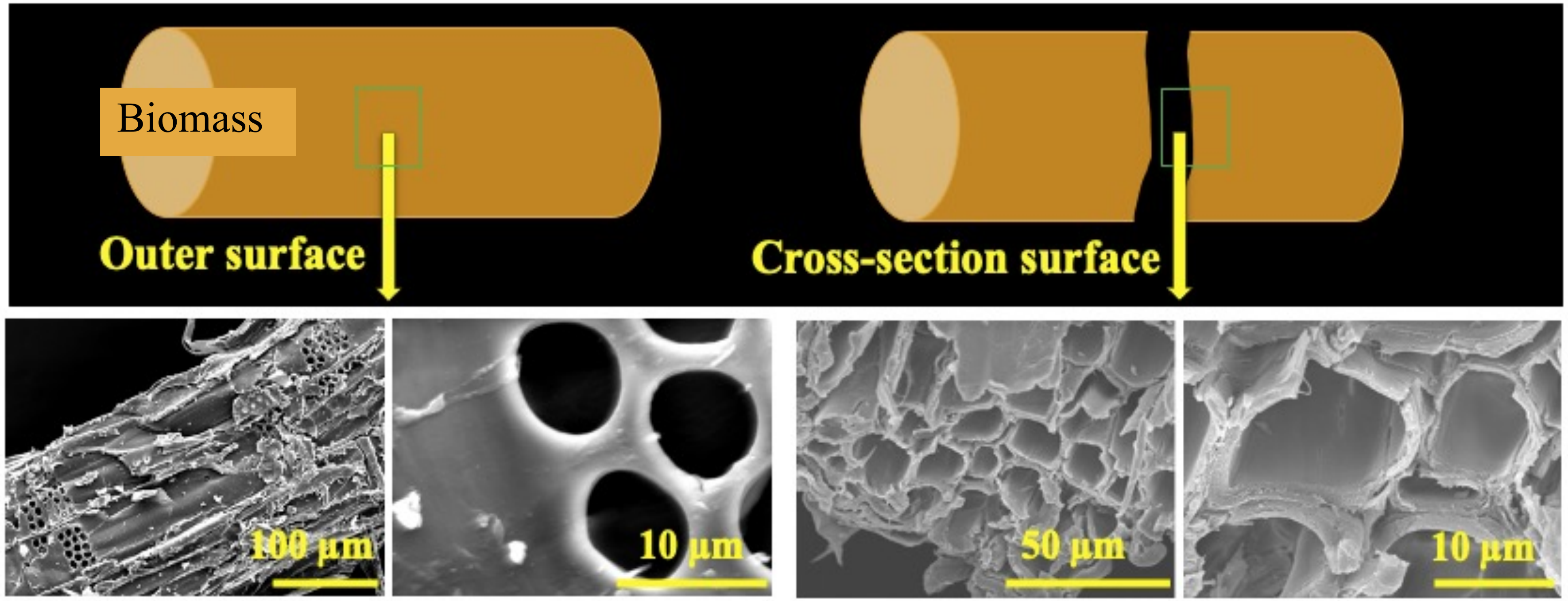
- Switchgrass (0.7 – 2.1%)
- Cornstover (2.2 – 11.9%)

1. Sieving and ultrasonic cleaning were used to adjust the ash content.
2. Sieved fractionated fibers into a “high ash fraction” and a cleaner “medium ash fraction”
3. Ultrasonic cleaning was used to further remove extrinsic ash from the “medium ash fraction.”



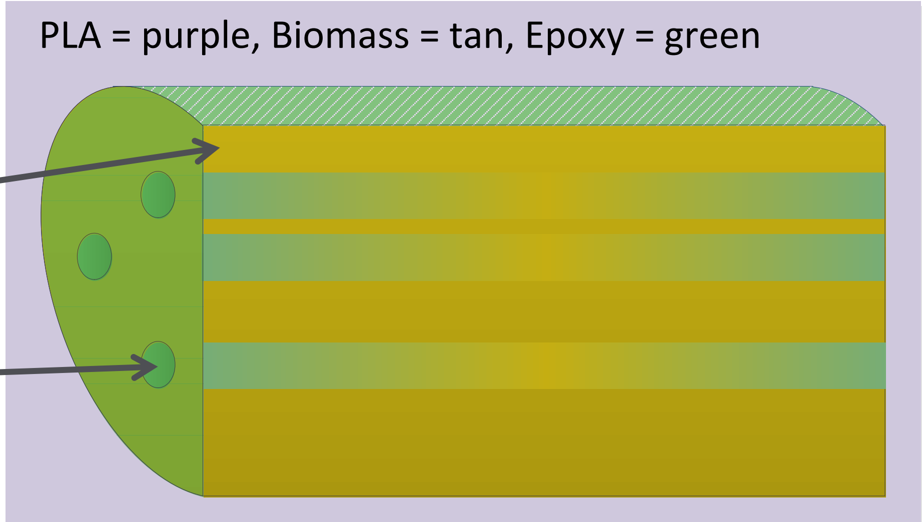
1. Approach

Fiber surface treatments



Hypothesis: Epoxy improves composite performance in two ways:

1. Epoxy reacts with PLA (cross-link fiber and resin)
2. Epoxy molecules penetrate biomass pores and mechanically interlock with biomass fiber



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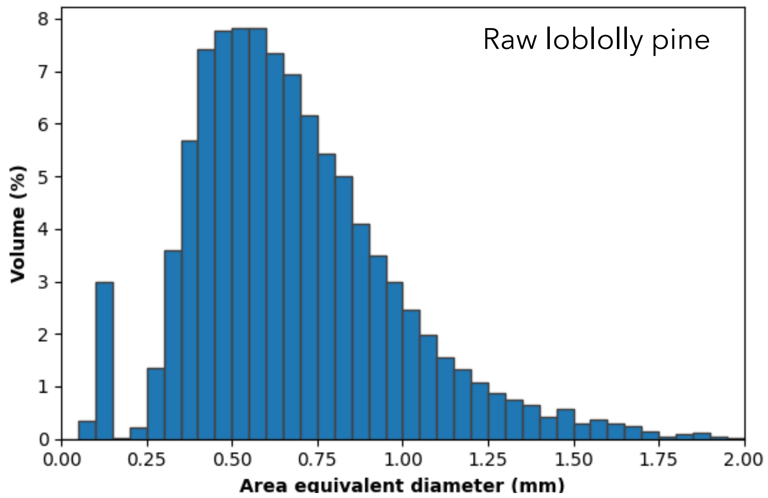
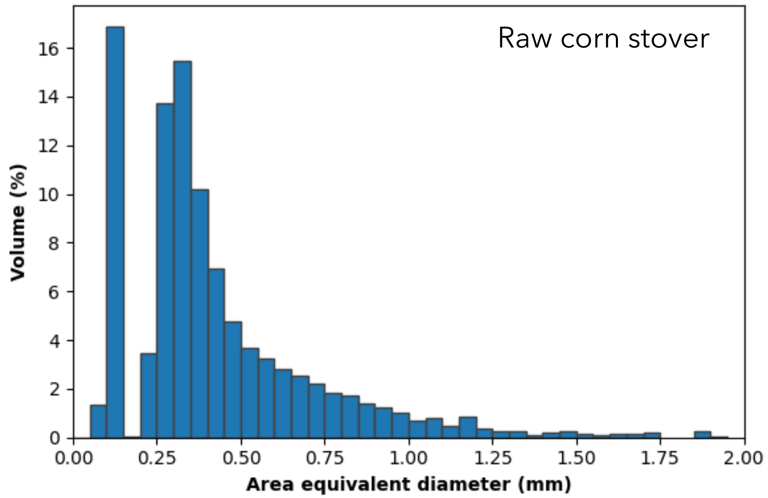
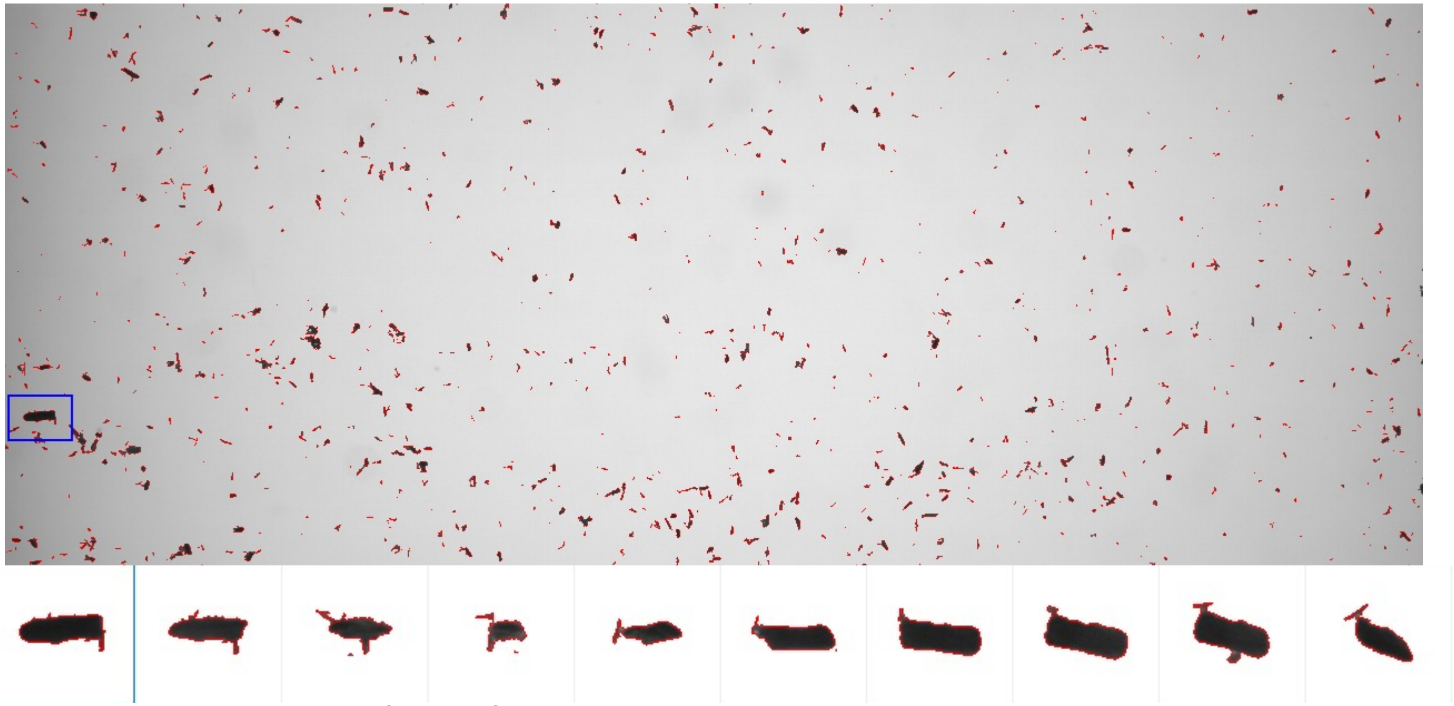
2. Progress and Outcomes
Particle size and distribution





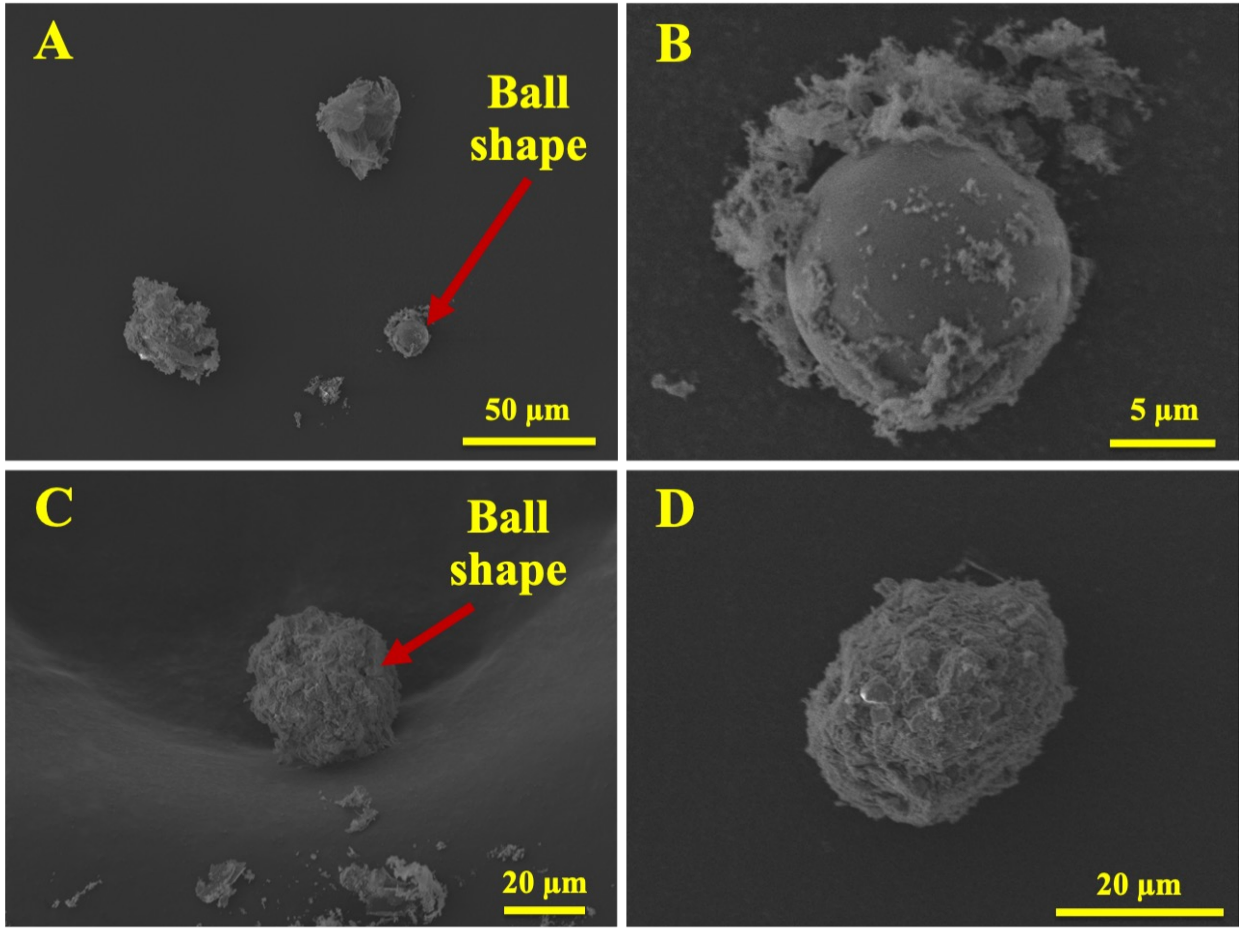
- Fibers screened through 0.2 mm sieves.
- Area equivalent diameter of fibers ranged from <0.1 mm to ~2 mm
- Loblolly pine fiber produced larger particles than corn stover.

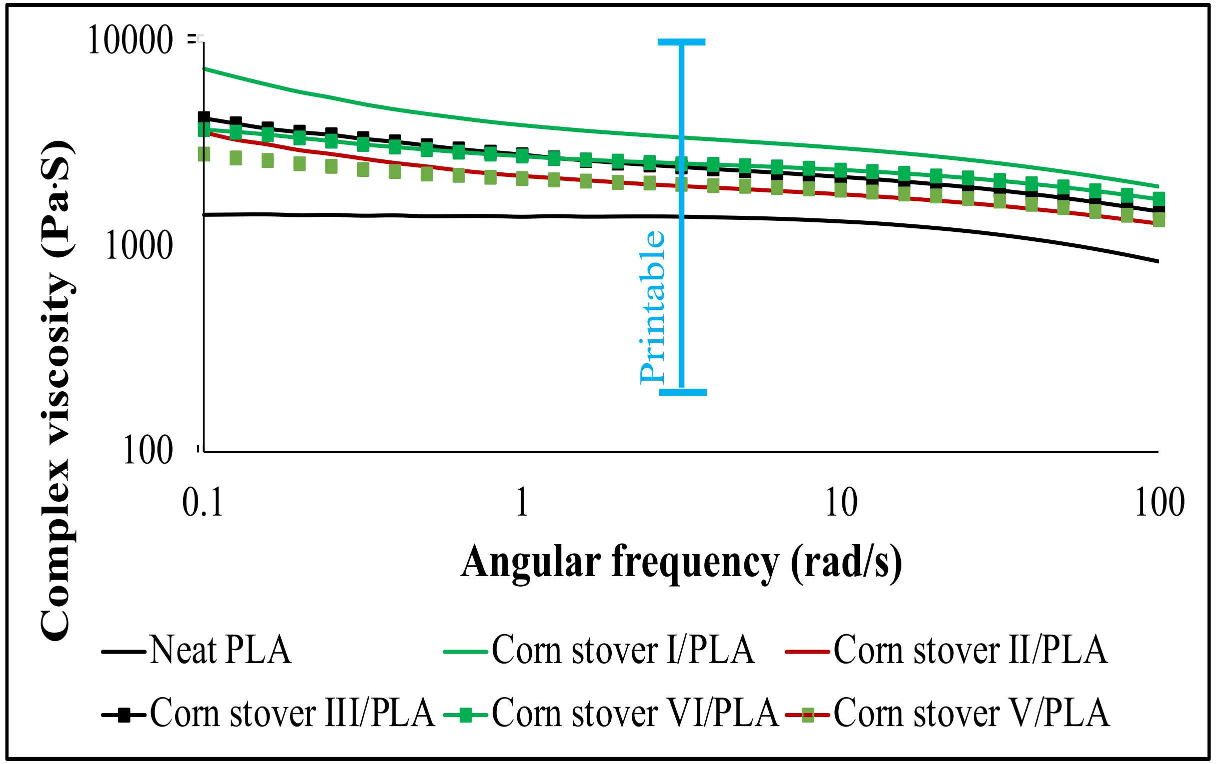


Measurement field of Microtrac's PARTAN 3D analyzer

2. Progress and Outcomes

Impact of ash on rheology

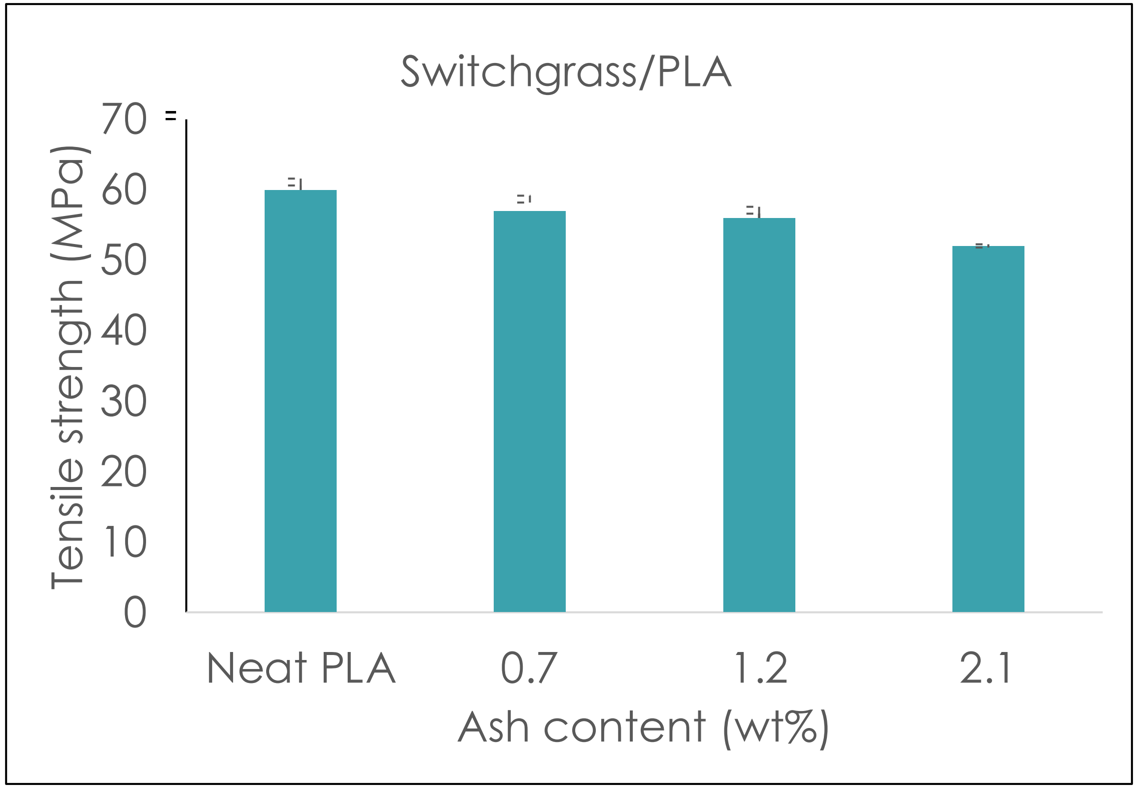


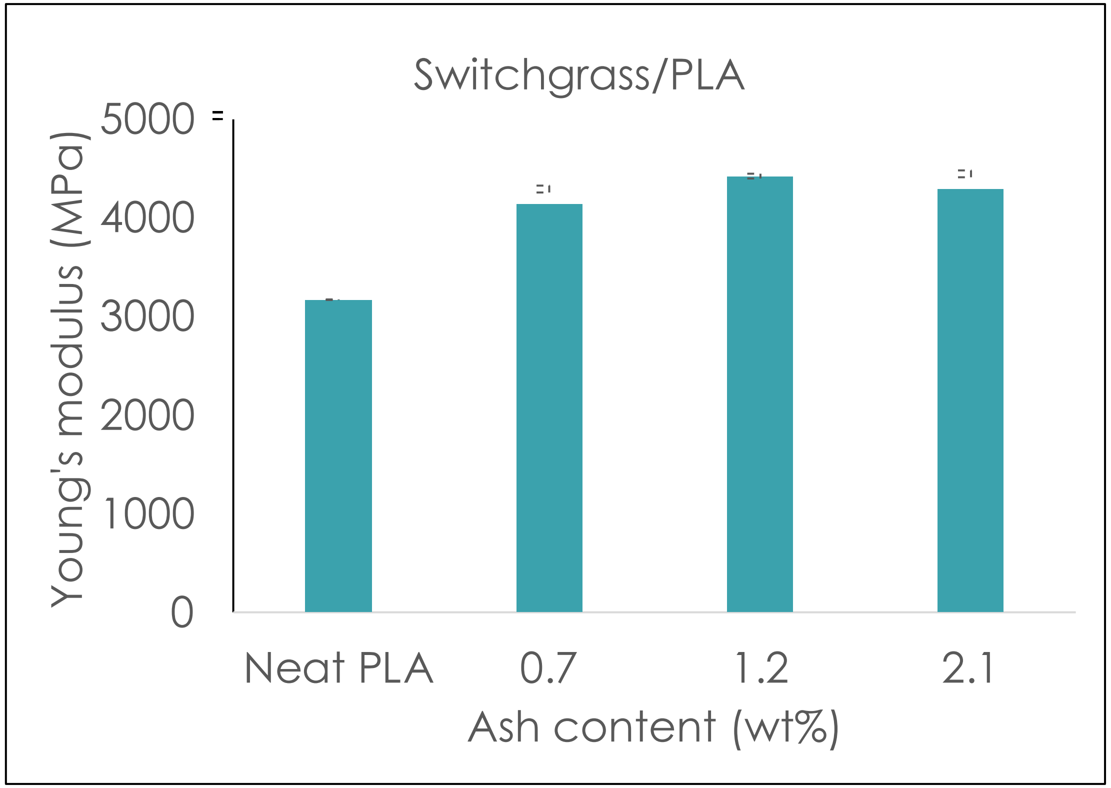


Ball shapes of some ash particles may have a ball-bearing effect

Switchgrass: Impact of ash on strength and stiffness

- Switchgrass biofiber reinforcement slightly decreases tensile strength, but significantly increases Young's modulus (stiffness) over neat PLA
- Increased ash content had a slightly negative impact on the tensile strength of switchgrass/PLA biocomposites and a negligible impact on stiffness





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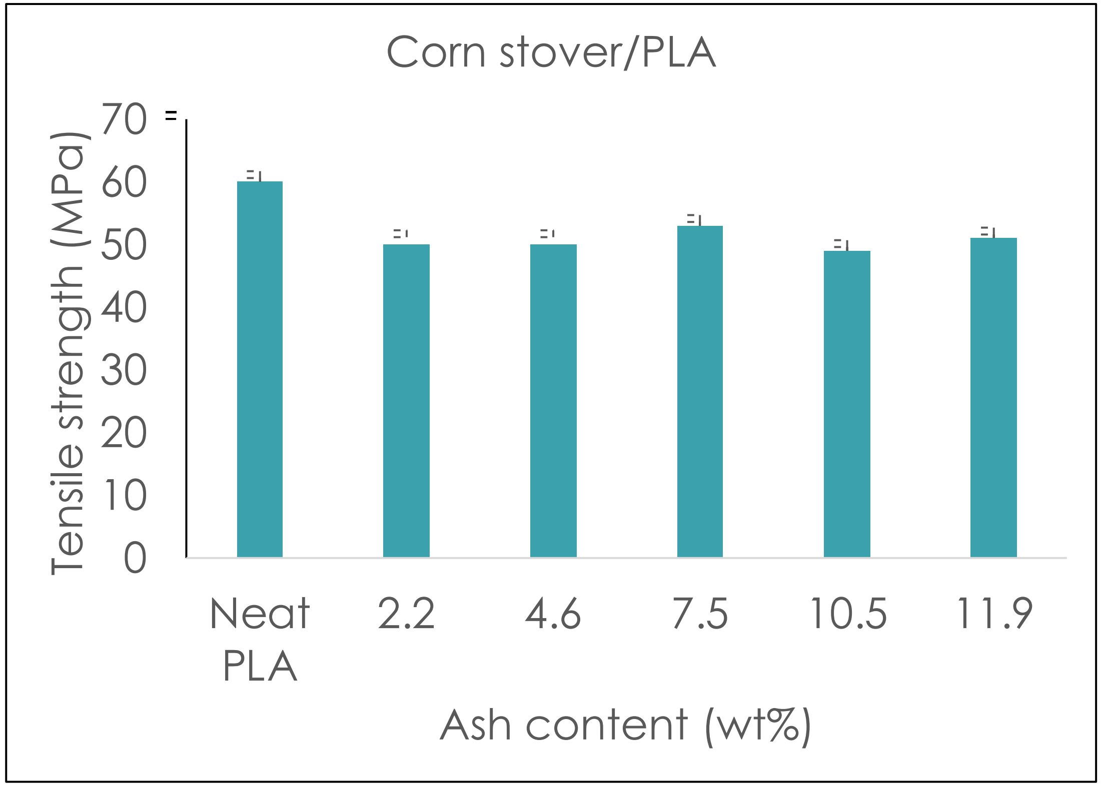
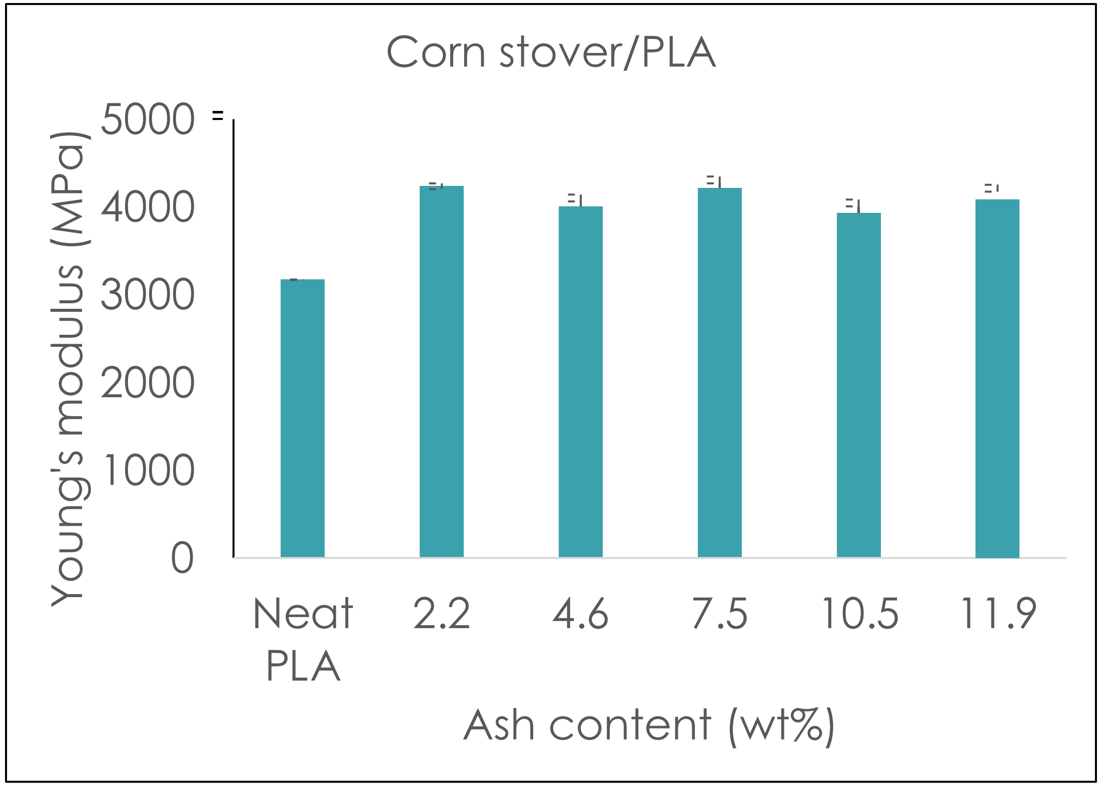
2. Progress and Outcomes

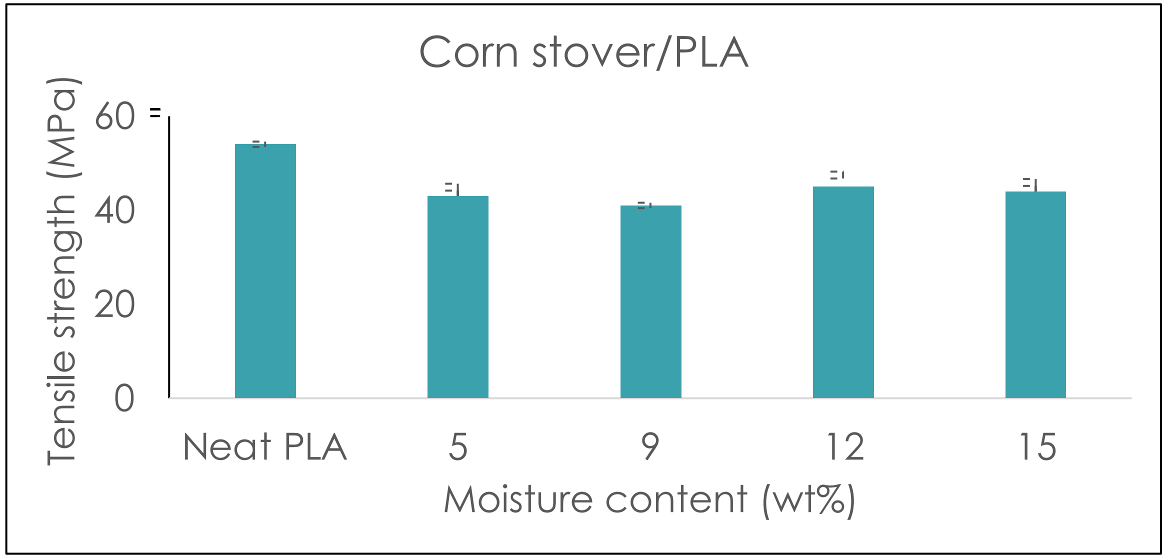
Corn stover: Impact of ash on strength and stiffness

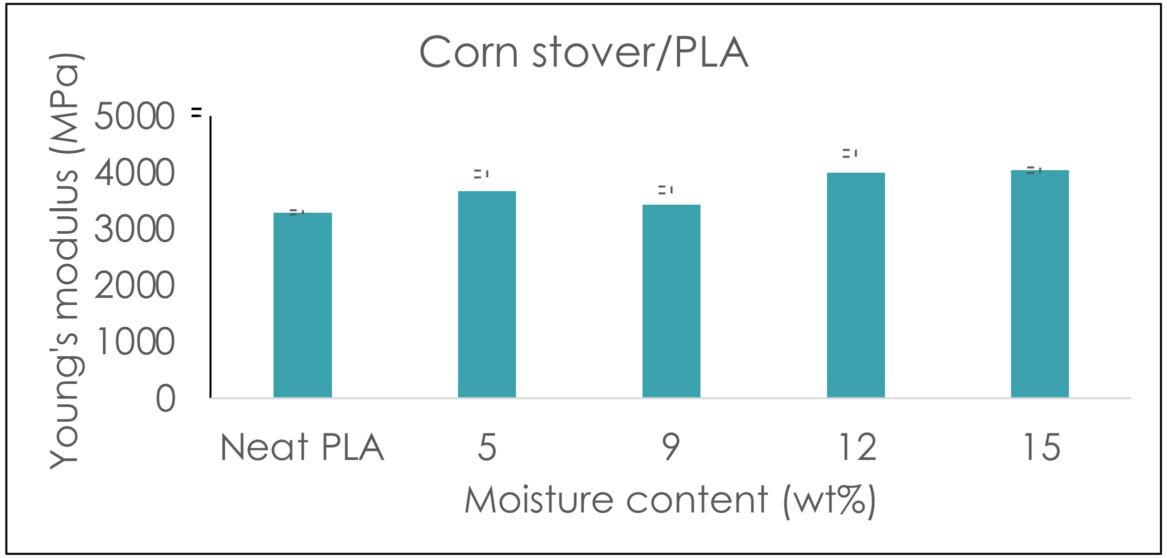
- Stover biofiber reinforcement decreases tensile strength, but significantly increases Young's modulus (stiffness) over neat PLA
- Increased ash content had negligible impacts on the tensile strength and stiffness of stover/PLA biocomposites





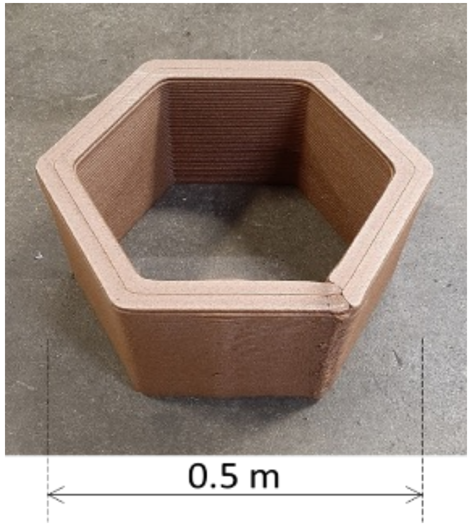
2. Progress and Outcomes
Impact of moisture





Particle size < 0.18 mm

- Moisture increasing from 5-15% did not significantly affect strength or Young's modulus
- Hypothesis: Moisture tolerance of biocomposites reduces the energy requirements of drying biofiber preparation

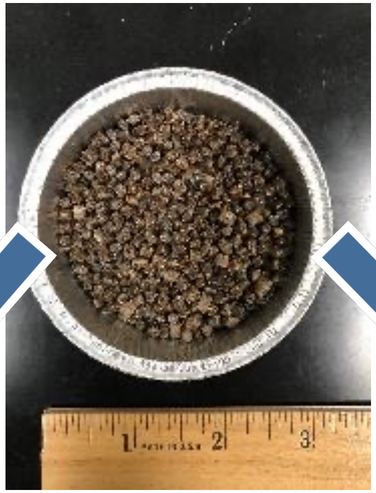


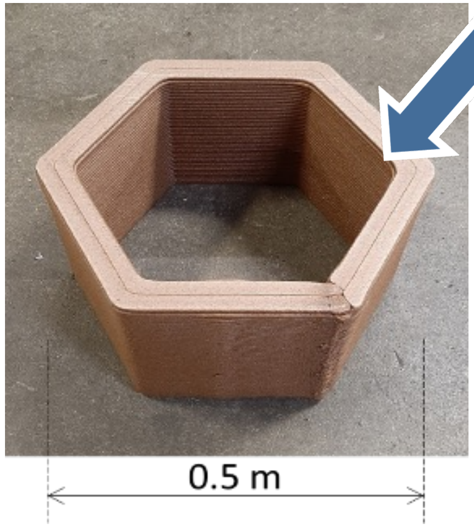
Young's modulus important for maintaining stability of printed product

Future work

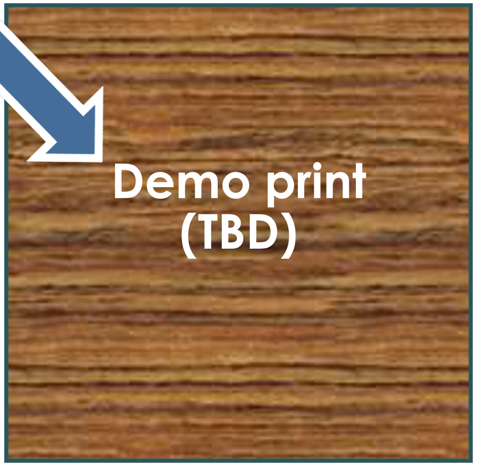
- Complete surface treatment testing
- Test additional feedstocks as they come available
- Large-scale printing demonstration
  - Select item to be printed
  - Prepare composite with fiber selected based on prior screening tests

3D-print hexagon to check printability performance





15 lb



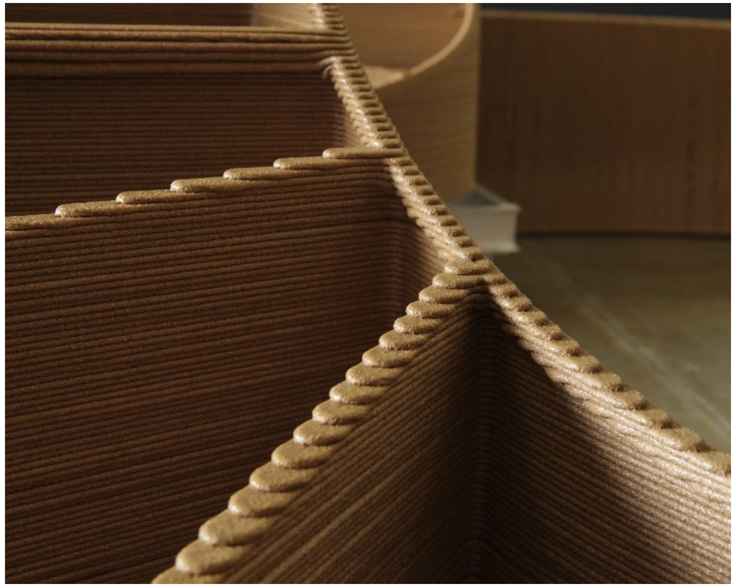
Print demonstration ideas under consideration

Animal enrichment items (Disney's Animal Kingdom)

Playground map for visually impaired children (credit: LSU)

3. Impact

- Biomaterials offer a high-value, high-volume market for off-spec feedstocks
- Biomass for materials can either compete with or complement biofuel feedstock supply chains
- By correlating biomass properties with composite properties, we can design composites using biofuel off-spec feedstock
  - Moisture: no significant impact < 15%
  - Ash: minor decrease in strength, significant improvement in stiffness, some improvement in rheology
  - Particle size: smaller the better
- Surface treatments offer opportunity to improve the performance of biocomposites



Quad Chart Overview

Timeline
- *October 1, 2022*
- *September 30, 2024*

	FY22 Costed	Total Award
DOE Funding	*ORNL $450K* *INL $250K*	*ORNL $1,350k* *INL $750K*

TRL at Project Start: 3
TRL at Project End: 4

Project Goal
Develop feedstock biomaterials coproducts that improve the economic viability of biomass fractionation technologies to produce higher quality biofuel feedstocks.

End of Project Milestone
Demonstrate viability of using off-spec biofuel feedstock with a large-scale 3D printing demonstration. The demo piece will use >100 lb of off-spec biomass residues recovered from air classification. TEA will quantify the economics of this integrated biomaterial and biofuel feedstock streams over baselines. Biocomposite technical target: 80% of the tensile strength of carbon fiber/ABS composites at 33% the cost.

Funding Mechanism
2021 Lab Call

Project Partners
- ORNL Manufacturing Demonstration Facility
- Techmer PM

Additional Slides

Presentations

- Zhao, X. “Developing biomaterials for large-scale additive manufacturing from low-value high-ash biomass”. Poster presented at SBFC 2022 Symposium on Biomaterials, Fuels and Chemicals.
- Zhao, X. “Developing biocomposites for large-scale additive manufacturing from low-value biomass fractions”. 2022 ASABE Annual International Meeting
- Zhao, X., O. Oyedeji, L. Williams, S. Ozcan, and E. Webb. “Moisture management of biomass fibers to reduce carbon intensity of biocomposites”. 2023 ASABE Annual International Meeting. Omaha, Nebraska, July 2023 (Abstract submitted).

Publications

- Publication: X. Zhao, K. Li, Y. Wang, H. Tekinalp, G. Larsen, D. Rasmussen, R.S. Ginder, L. Wang, D.J. Gardner, M. Tajvidi, E. Webb, S. Ozcan, High-strength polylactic acid (PLA) biocomposites reinforced by epoxy-modified pine fibers, ACS Sustain Chem Eng, 8 (2020) 13236-13247.
- Publication: X. Zhao, O. Oyedeji, E. Webb, S. Wasti, S. Bhagia, H. Hinton, K. Li, K. Kim, Y. Wang, H. Zhu, U. Vaidya, N. Labbe, H. Tekinalp, N. Gallego, Y. Pu, A. Ragauskas, S. Ozcan. Impact of biomass ash content on biocomposite properties. Composites Part C: Open Access. 9: 100319, 2022.
- Publication: X. Zhao, K. Copenhaver, L. Wang, M. Korey, D. Gardner, K. Li, M. Lamm, V. Kishore, S. Bhagia, M. Tajvidi, H. Tekinalp, O. Oyedeji, S. Wasti, E. Webb, A. Ragauskas, H. Zhu, W. Peter, S. Ozcan. Recycling of natural fiber composites: Challenges and opportunities. Resources, Conservation & Recycling. 177: 105962, 2022.
- Publication: X. Zhao, Y. Wang, X. Chen, X. Yu, W. Li, S. Zhang, X. Meng, Z. Zhao, T. Dong, A. Anderson, A. Aiyedun, Y. Li, E. Webb, Z. Wu, V. Kunc, A. Ragauskas, S. Ozcan, H. Zhu. Sustainable bioplastics derived from renewable natural resources for food packaging. Matter. 6 (1): 97-127, 2023.
- Publication: L. Wang, P. Kelly, N. Ozveren, X. Zhang, M. Korey, C. Chen, K. Li, S. Bhandari, H. Tekinalp, X. Zhao, J. Wang, M. Seydibeyoglu, E. Alyamac-Seydibeyoglu, W. Gramlich, M. Tajvidi, E. Webb, S. Ozcan, D. Gardner. Multifunctional polymer composite coatings and adhesives by incorporating cellulose nanomaterials. Matter. 6: 344-372, 2023.
- Book chapter: X. Zhao, S. Lu, W. Li, S. Zhang, K. Li, K. Nawaz, P. Wang, G. Yang, A. Ragauskas, S. Ozcan, E. Webb. Epoxy as filler or matrix for polymer composites. “Epoxy-based composites”. Samson Jerold Samuel Chelladurai, IntechOpen. 2022. ISBN 978-1-80355-160-9.
- Book chapter: S. De, B. James, J. Ji, S. Wasti, S. Zhang, S. Kore, H. Tekinalp, Y. Li, E. Urena-Benavides, U. Vaidya, A. Ragauskas, E. Webb, S. Ozcan, X. Zhao. Biomass-derived composites for various applications. “Advances in Bioenergy”. Yebo Li, Elsevier. 2023.
- Provisional Patent: X. Zhao, O. Oyedeji, E. Webb, S. Ozcan, H. Tekinalp. Biomass processing for biocomposites and biofuels. U.S. Provisional Patent, Application No. 63/289,218, 2021.
- Magazine: S. Bhagia, K. Copenhaver, X. Zhao, O. Oyedeji, E. Webb, H. Tekinalp, S. Ozcan, A. Ragauskas. 3D Printing of Natural Fiber-Polylactic Acid Composites to Decarbonize Structural Composites. ORNL Review Magazine. 2023