

DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Melt-stable engineered lignin thermoplastic: a printable resin (WBS: 2.5.6.103)

March 10, 2021

Performance-Advantaged Bioproducts,
Bioprocessing Separations, and Plastics Panel

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

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Project Overview

Goal: *Develop and commercialize lignin-derived, industrial-grade polymers and composites with properties, including processability, exceeding current petroleum-derived alternatives.*

Relevance to the bioenergy industry

Enables high value uses of lignin, a biorefinery waste stream; lignin valorization is CRITICAL to the cost-competitive production of biofuels.

Lignin contributes significantly to reduce cost, enhance stiffness, oxidation resistance, and high dimensional stability in its polymeric derivatives.

Challenge: *Functionalities in lignin vary widely and those depend on the pretreatment and method of isolation*

Project outcome

A group of commercial-ready, lignin-based 3D-printable, self-healing, recyclable composites suitable for high-volume applications.

Utilization of lignin at 30-60 (%) volume to produce engineered plastic materials with values ranging from \$2000-\$5000/metric ton.

Commercialization opportunity got impacted by COVID.

Discussion is going on about commercialization of a new shape memory polymers from lignin.

Potential applications of lignin-derived polymers

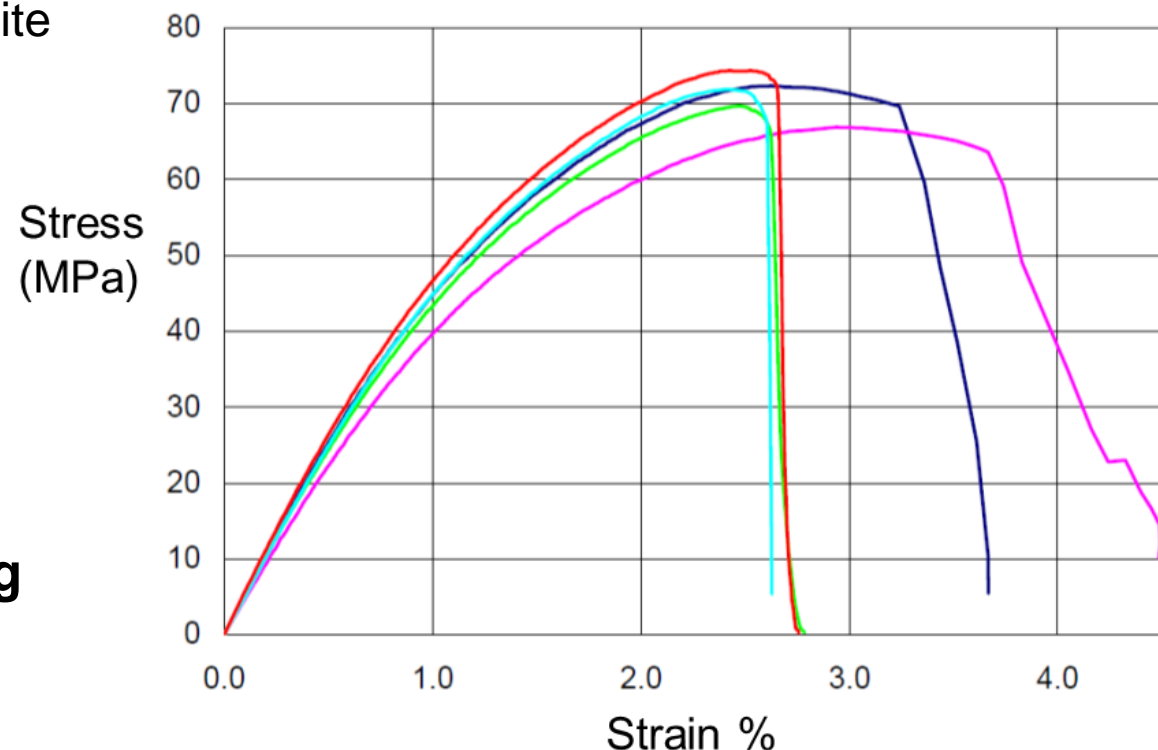
Properties of automotive interior polymer-matrix composite parts (ASTM D 638-2008):

Failure strength: 60-80 MPa

Elongation at break: 3-5%

Young's modulus: 4-6 GPa

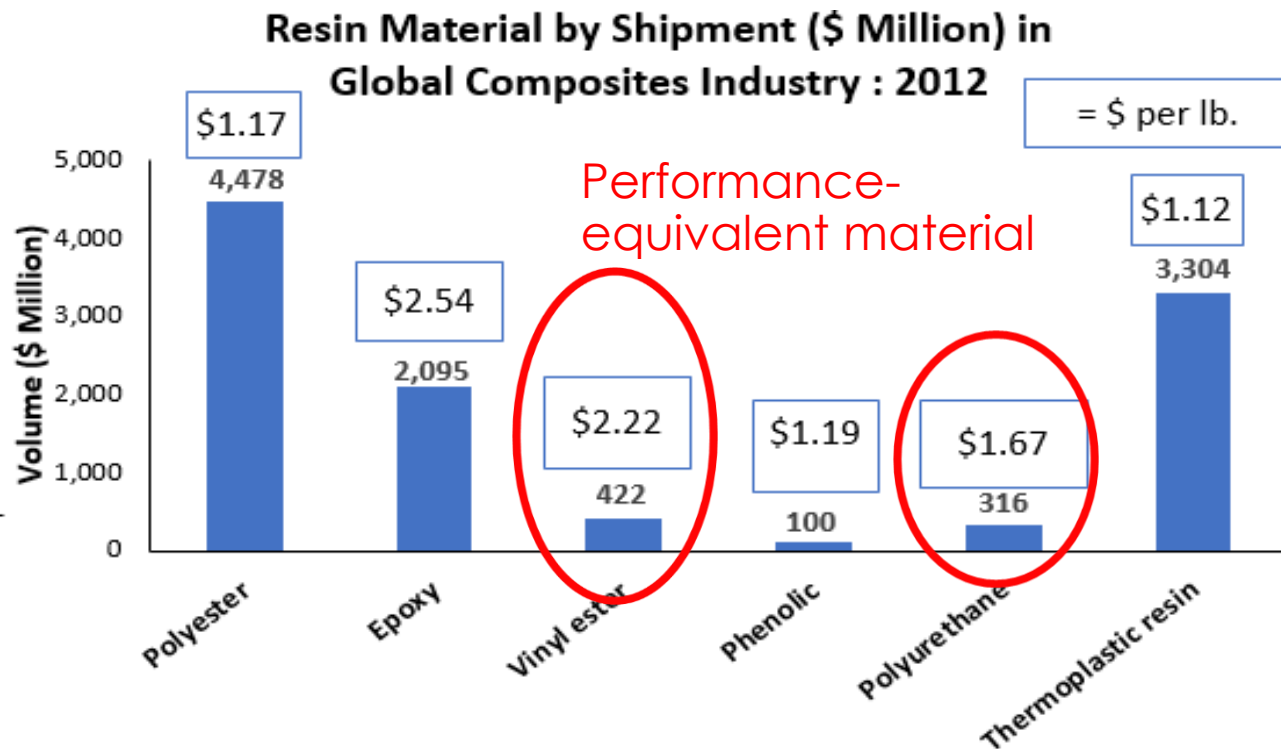
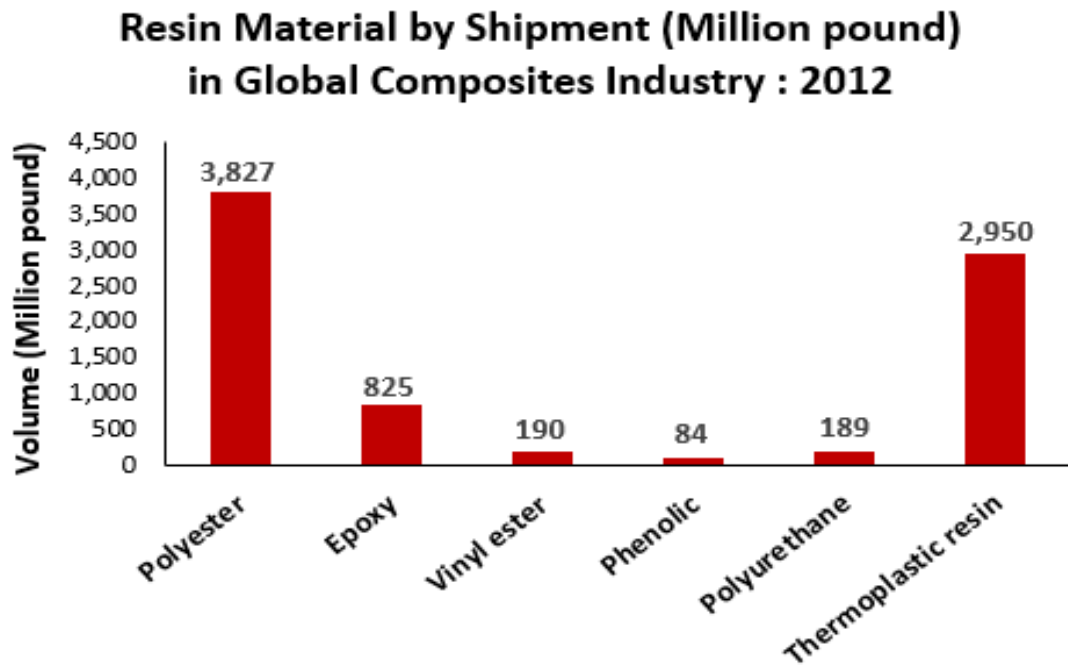
Can we make a product with an equivalent performance (to this commercial product) using available biorefinery lignin at 50% or higher lignin content?



Mechanical property of an automotive interior part containing ~20 wt.% carbon fibers.

This presentation will demonstrate our path to reach such performance goal suggesting potential commercialization opportunity in near future.

Project Overview: Styrene-free polymer products and potential business opportunity



Entire market for these materials is much larger than the composites industry: Epoxy (2 million ton); Nylon (7 million ton); ABS (9 million ton) (~\$22 billion); PVC (40 million ton)

3D printable thermoplastics feedstock has a market value >\$5/lb. (although with little volume)

“Growth Opportunities in Global Composites Industry 2013-2018.” Lucintel. March 2013

1 - Management

The project team involving PI (Naskar), R&D Staff members (Goswami-MD Simulation; Damron-Solid State NMR) and post-doc (Kanbargi-Reactive extrusion) colleagues meet and assess data on a biweekly basis. Outreach to industrial partners is mainly conducted by PI and ORNL partnership members.

Following tasks were undertaken:

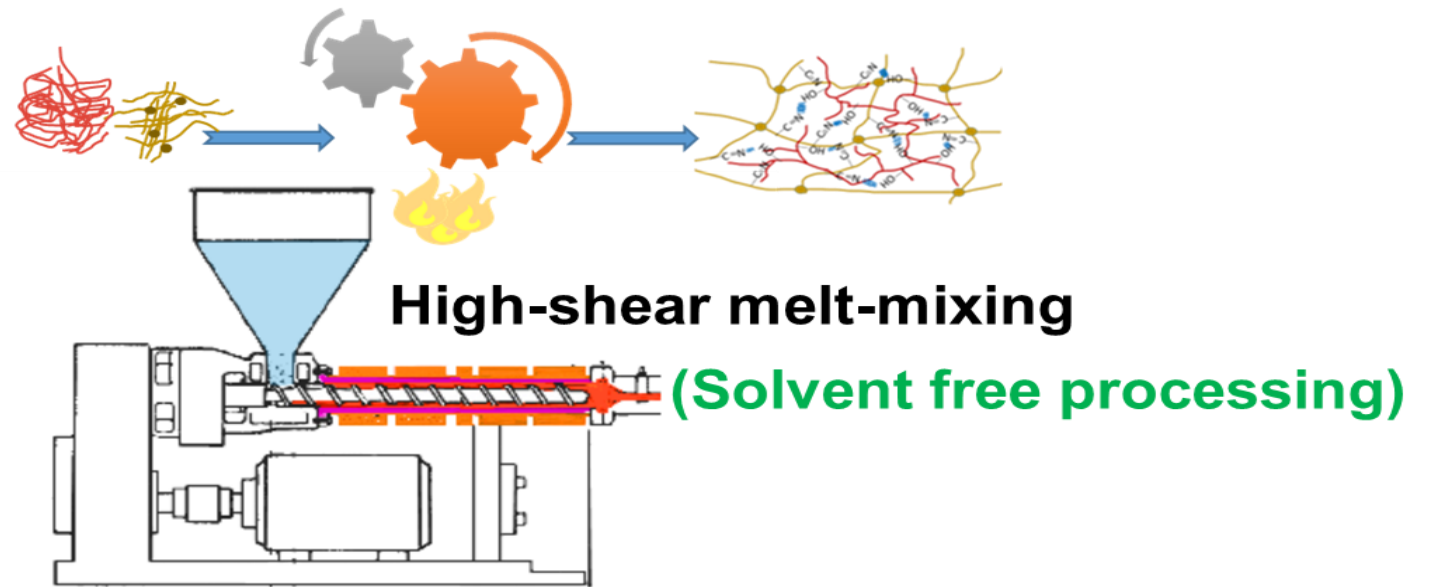
- Synthesis of functionalized lignin (**lignin is prepared in laboratory and sourced from industries**)
- Synthesis of lignin-polymer with characteristic mechanical performance (**solvent-free processing**)
- Understanding lignin-polymer phase morphology and processability (**The task leverages computation and characterization user facilities of ORNL**)

Risks:

Commercialization needs product qualification meeting requirements (Odor testing and mechanical performance require 3rd party testing). We are coordinating efforts with industry experts.

2 - Approach: Solvent-free Synthesis via Reactive processing

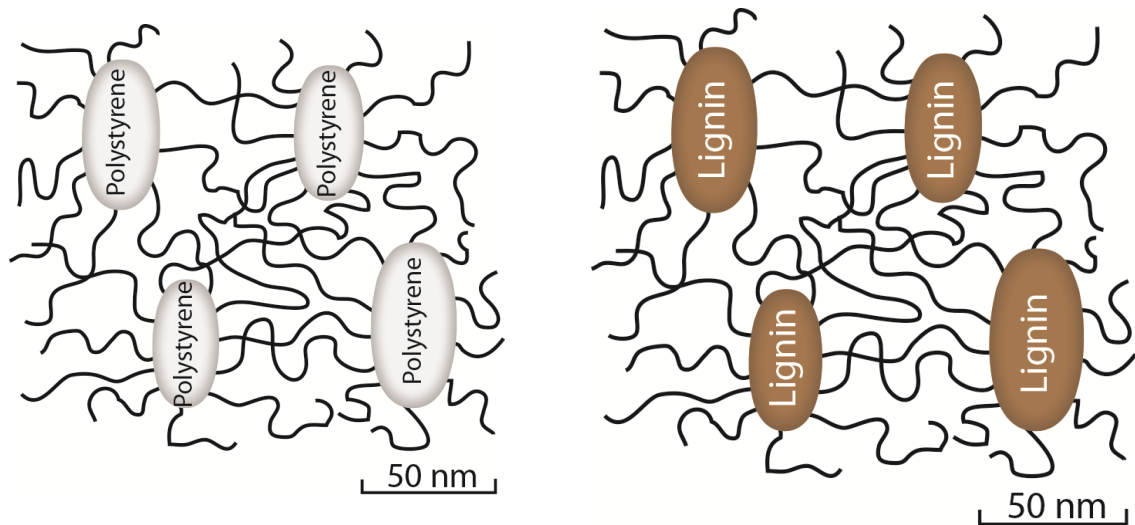
Physical interaction / chemical reaction between lignin and host polymer matrix can be detected from the rise in torque during batch internal mixing or extrusion process (150-200 °C).



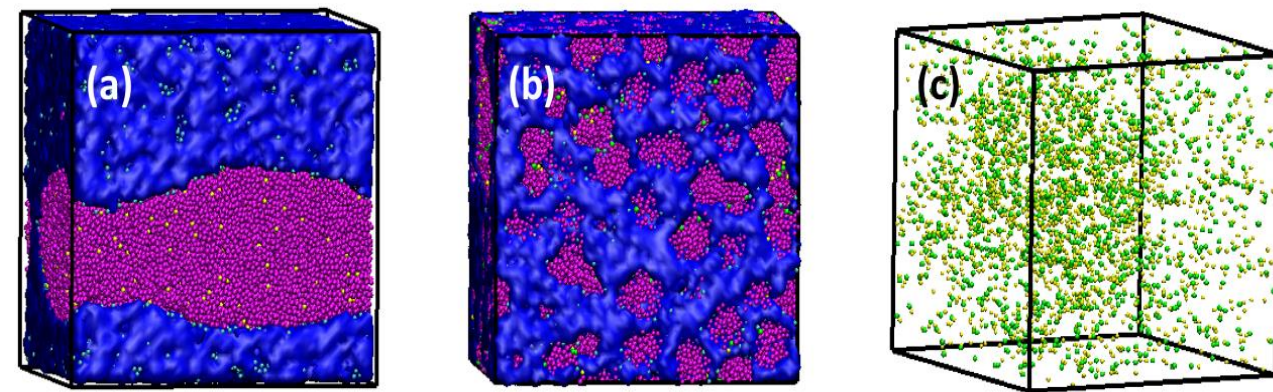
Extrusion and characterization facilities that are utilized to synthesize and analyze the products.

2 - Approach: Lignin-derivatization for new product and market opportunity

Oligomeric lignin (1000-2000 g/mol) with enriched functionalities, when interconnected with polymeric chain extenders, forms multiphase polymers with phase ratio-dependent morphologies and mechanical properties. Nano-scale lignin phase dispersion (10-100 nm) or their co-continuous lamellae forms the high-performance polymeric materials.

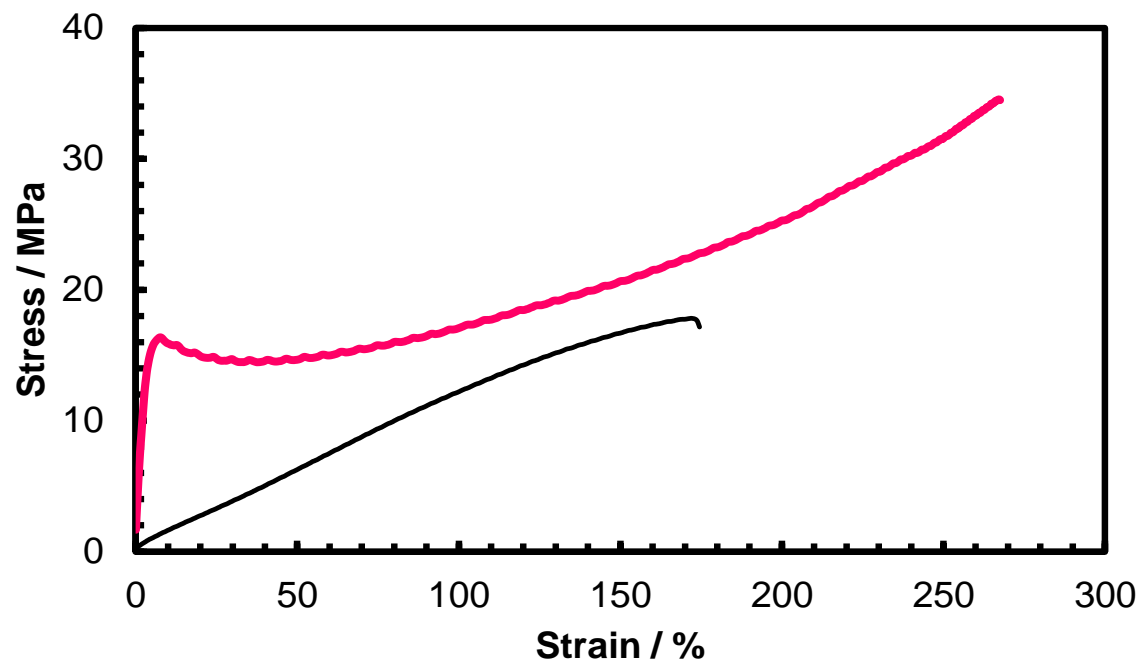


Composition is a group of tough, reprocessable thermoplastic and thermoplastic elastomeric materials.

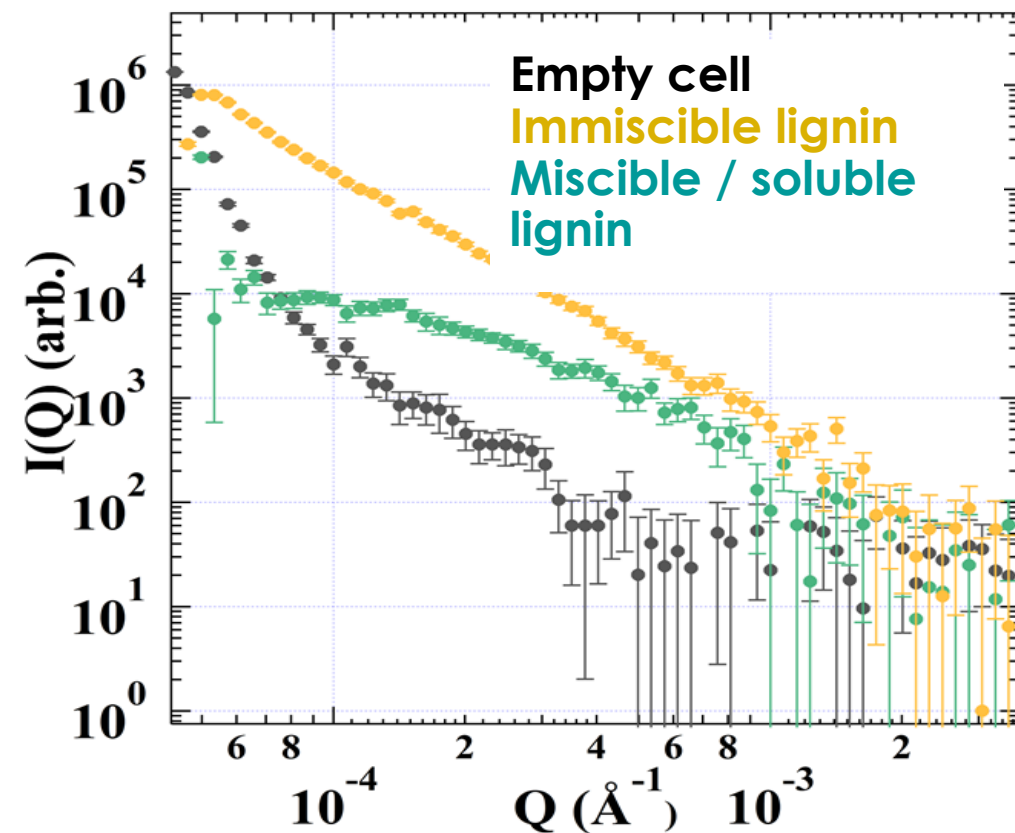


Modeling (a) phase-separated morphology; (b) breakdown of the morphology by additive; (c) percolation of the additive in the system is teaching us general approaches with lignin valorization.

2 - Approach: Controlling lignin properties and phase morphology is needed to achieve mechanical performance



Fractionated lignin showed better morphology and performance in acrylonitrile-butadiene-lignin polymer (ABL).



Very large microphase separation of immiscible-lignin was obtained by USANS. The **NBR-I lignin** sample revealed a straight line with a power law of -4 , indicating the presence of sharp interface between phase-separated domain and surrounding matrix. In contrast, **NBR-S** lignin showed very good dispersion of small phase-separated lignin domains within the NBR matrix.

3 - Impact

- Technologies that enable high-value uses of lignin, a biorefinery waste stream, are essential to allow the cost-competitive production of biofuels. This research develops a novel family of commercial-ready, lignin-based thermoplastic polymers and polymer composites suitable for high-volume applications. Specifically, lignin derivatives that are inherently recyclable, rapidly moldable, and 3D printable, while capable of retaining their superior mechanical properties after thermal reprocessing, are being produced.
- We are developing a green processing technology using various available lignins. New *in-situ* functionalization chemistry for lignin is introduced in this research as separation of functionally graded lignin will be cost intensive. High lignin contents in the polymeric products have been aimed to incentivize the biorefining process.

3 - Impact - BETO program enabled designing multifunctional materials from lignin

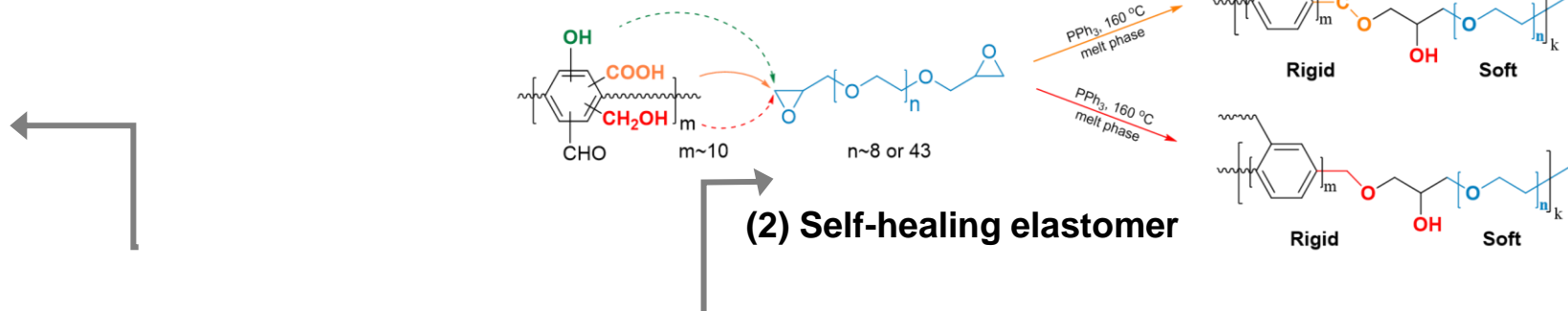
(1) High-shear processable plastics



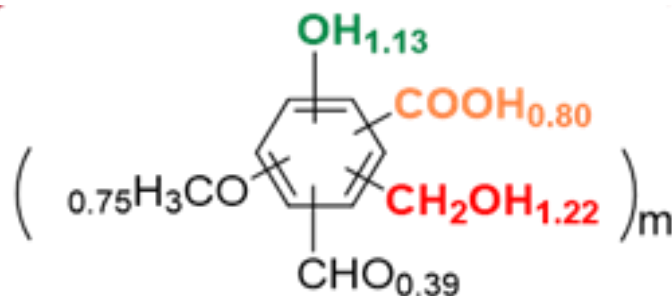
U.S. Patent Application No. 16/911,693 (2020)
 U.S. Patent Application No. 16/829,167 (2020)
 U.S. Patent Application No. 16/257,313 (2019)
 U.S. Patent Application No. 16/257,294 (2019)
 U.S. Patent Application No. 16/277,020 (2019)
 U.S. Patent Application No. 16/014,136 (2018)
 R&D License by Prisma Renewables, LLC

Work with World's 4th largest automotive part manufacturer.

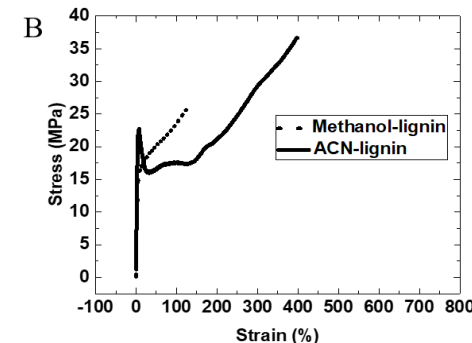
1. *Composite Science and Technology* 199, 108352 (2020).
2. *Materials* 13(8), 1940 (2020).
3. *Advanced Materials Interfaces* 7, 1901751 (2020).
4. *Industrial & Engineering Chemistry Research* 59(1), 9-17 (2020).
5. *Green Chemistry* 21, 4354–4367 (2019).
6. *Macromolecular Rapid Communications* 40, 1900059 (2019).
7. *Polymer* 160, 210-222 (2019).
8. *Science Advances* 4(12), eaat4967 (2018).



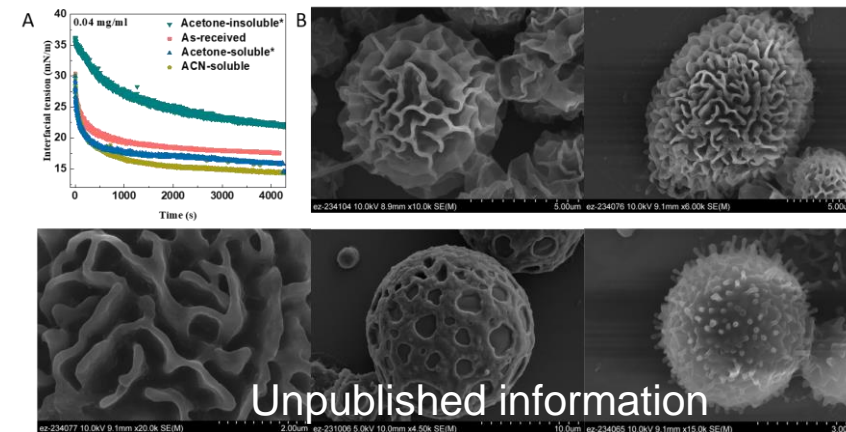
(2) Self-healing elastomer



(3) High-performance ABL

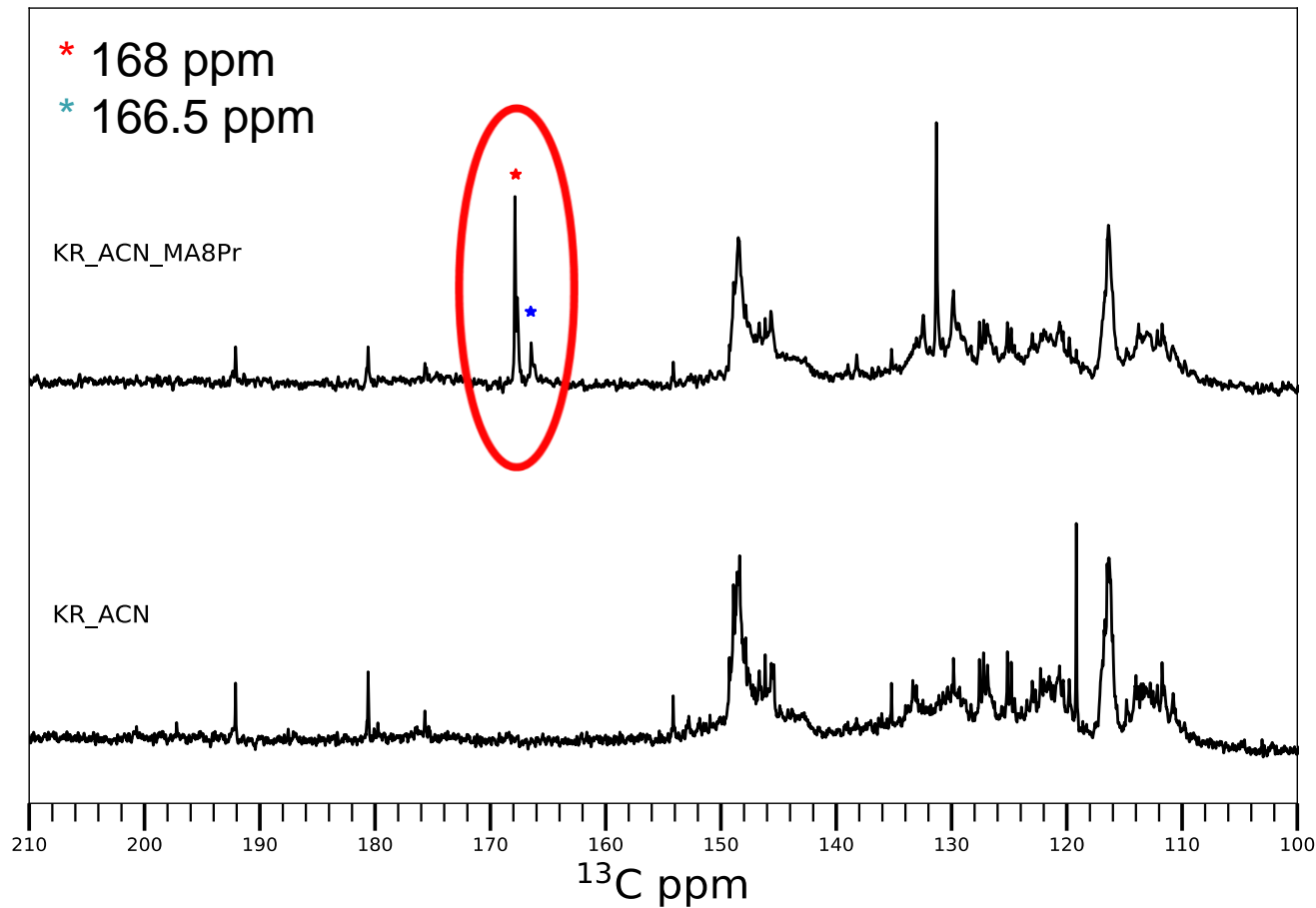


(4) Carbon materials with novel morphologies

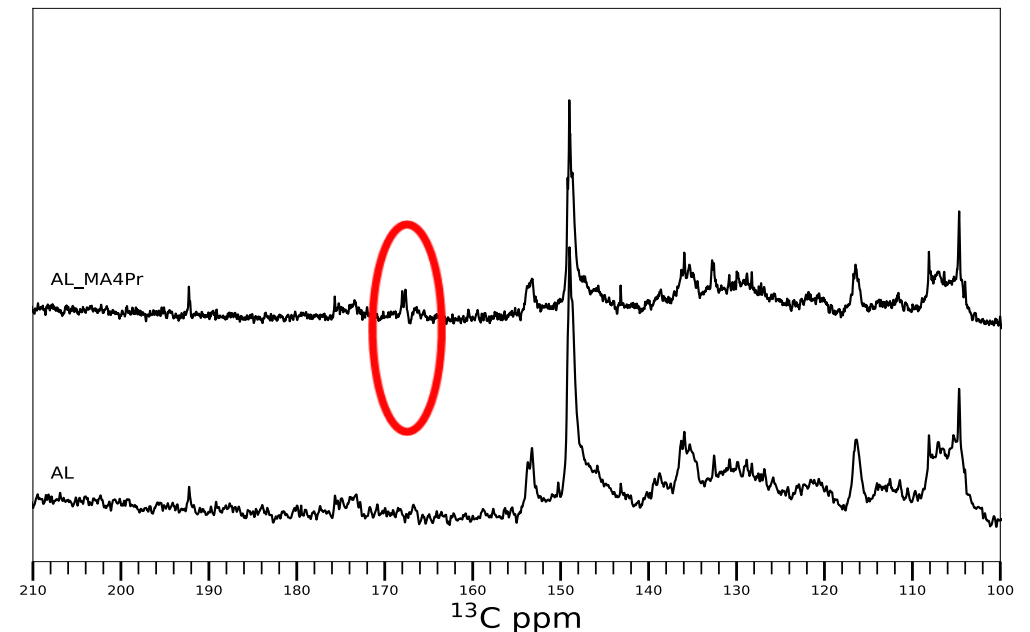


Unpublished information

4 - Progress and Outcomes: NMR data confirm success with solvent-free processing for lignin functionalization

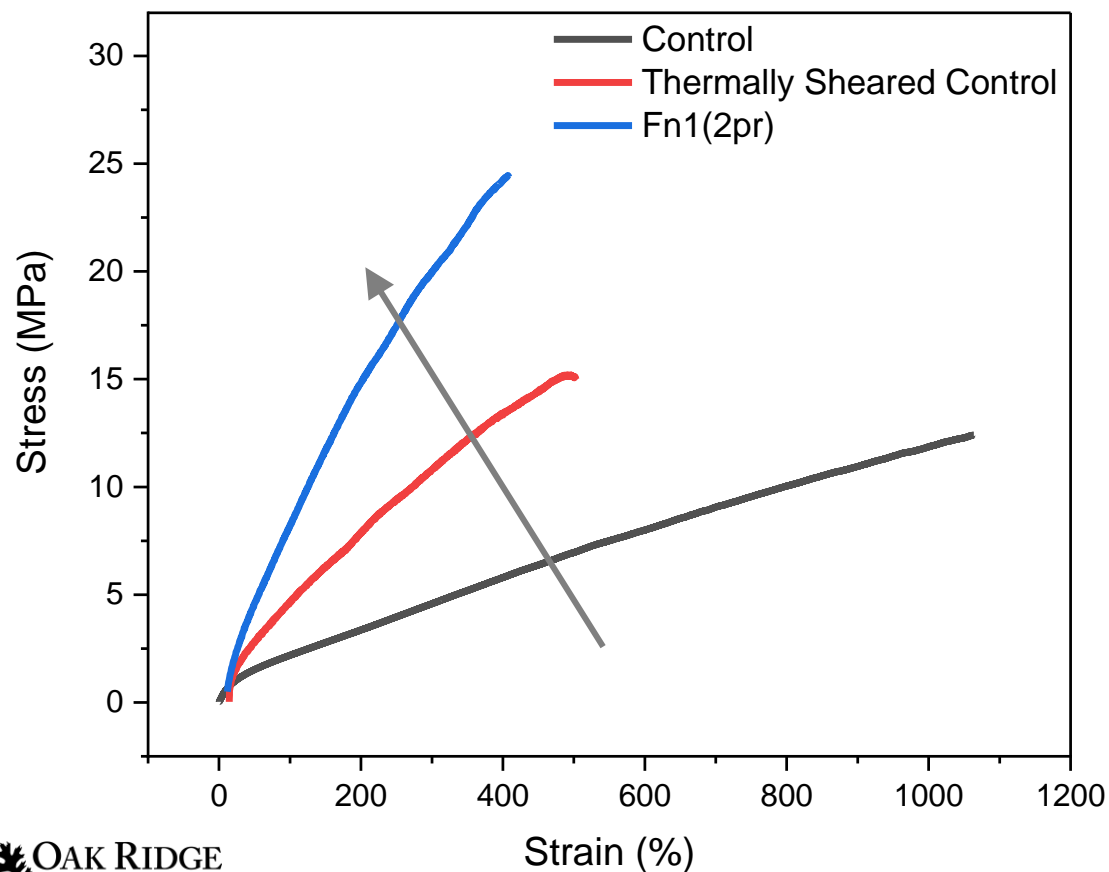


A new method for solvent-free functionalization of lignin has been developed. Improved functionality (as confirmed by solid state NMR data) helps to make a better lignin-based polymer. This method applies to ALL available lignins.

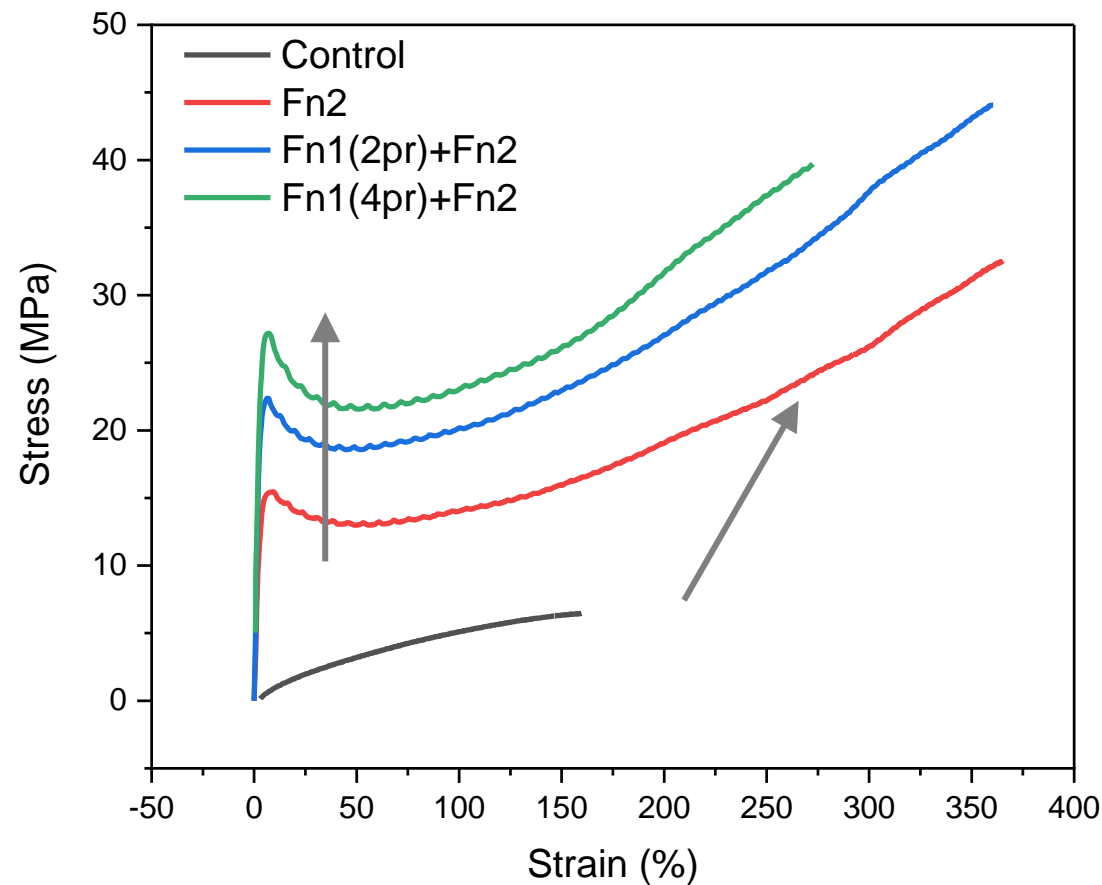


4 - Progress and Outcomes – tougher and stronger ABL produced

Mechanical properties of ABL based on a synapyl-alcohol rich (poplar) lignin show functionalization induced improvement.

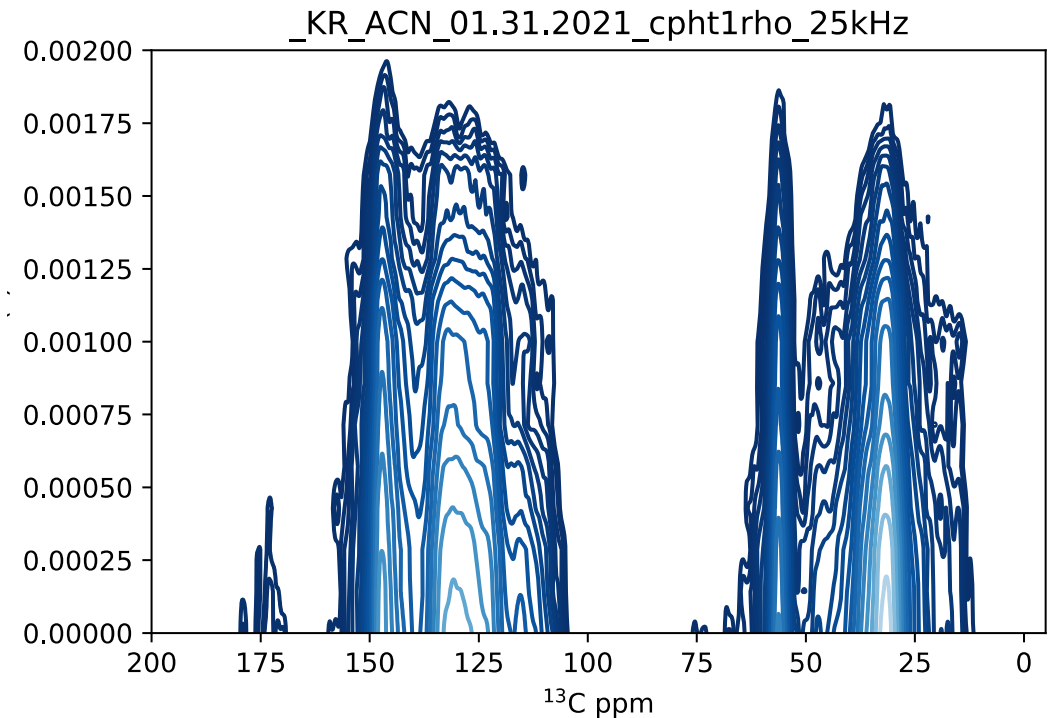
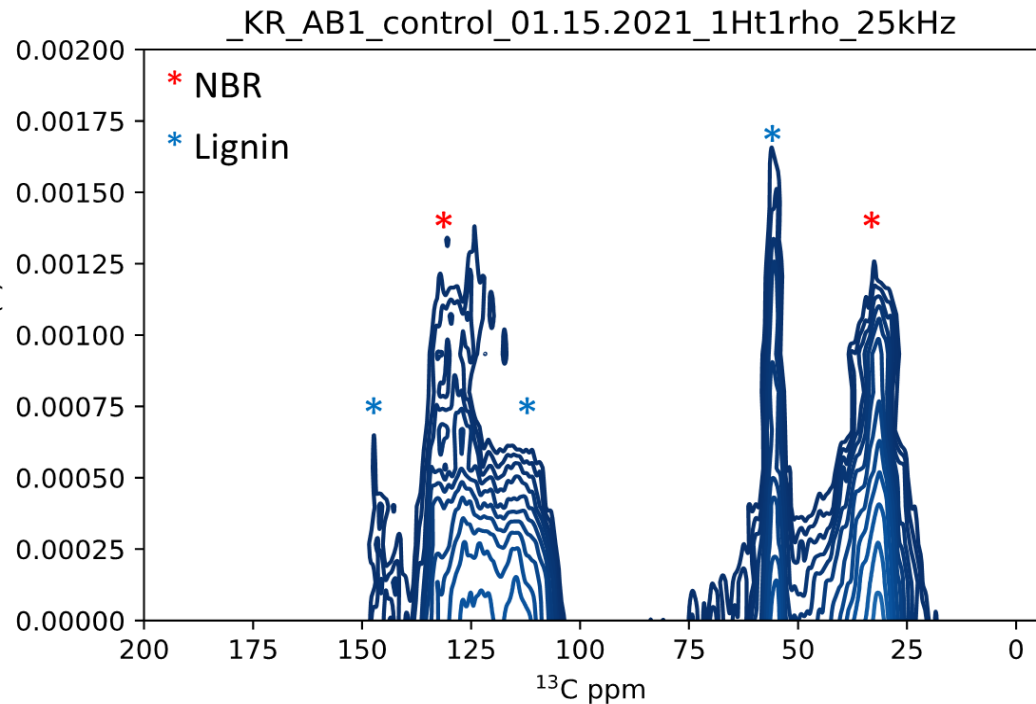


Mechanical properties of ABL based on a guaiacyl-alcohol rich (pine) lignin show functionalization induced improvement.

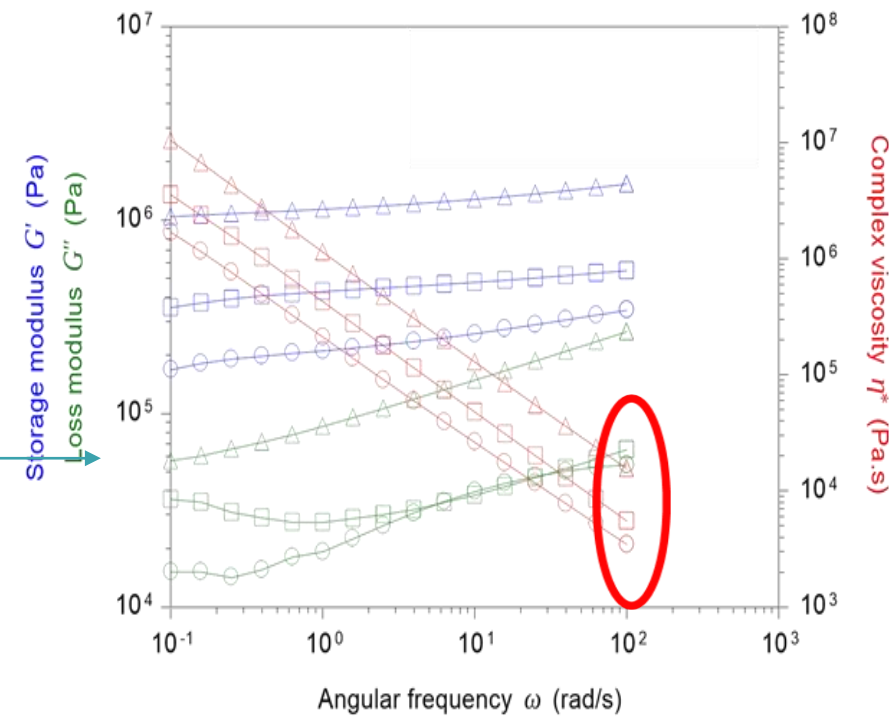
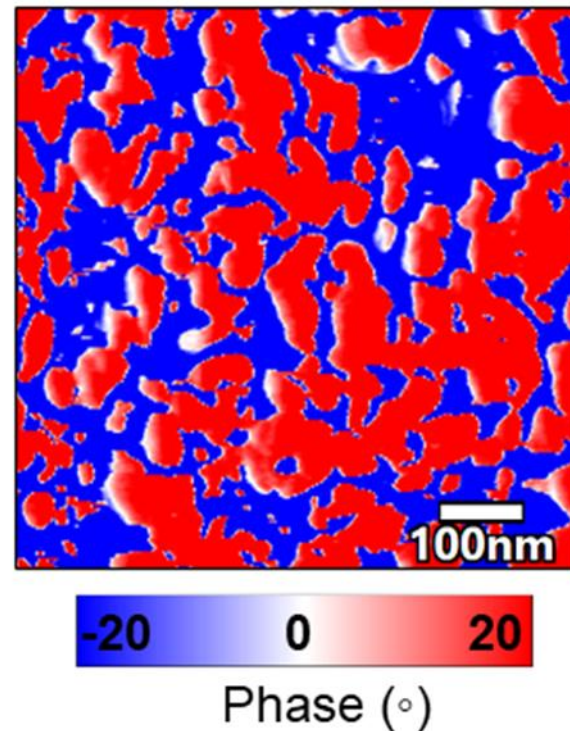
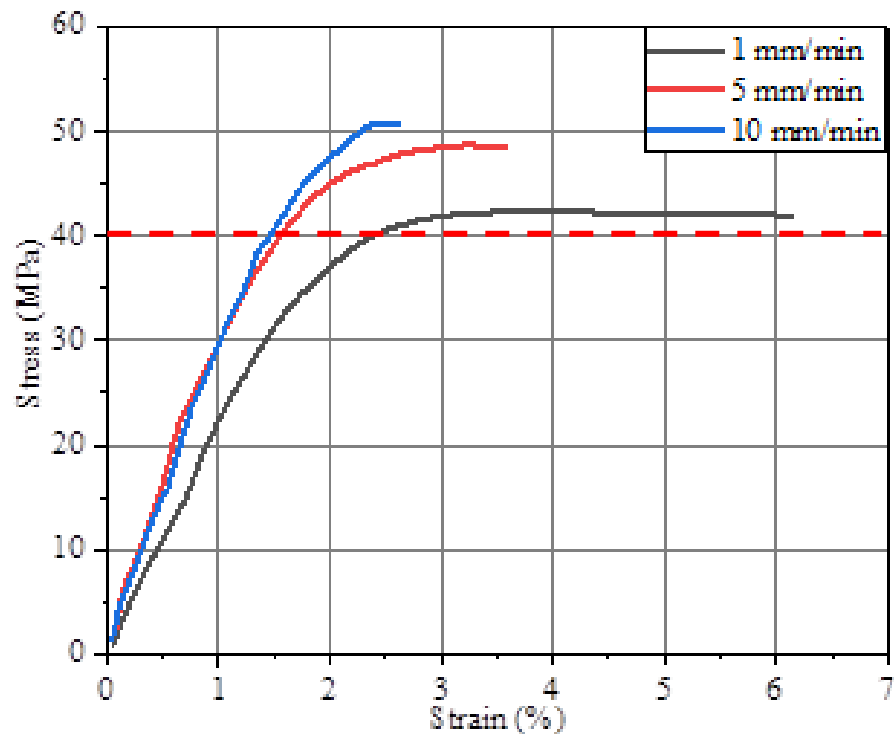


4 - Progress and Outcomes – ABL characterization by solid state NMR confirms successful synthesis of products with unique phase dynamics

NMR ^1H T1rho relaxation experiment detected via ^{13}C , which probes motions on $\sim 25\text{kHz}$ timescale. It dynamically distinguishes the two components, lignin and NBR, quite well for the “control” composition. Overall, the data indicates that the two components are dynamically behaving in an independent manner. However, Func2 lignin-based ABL show longer relaxation times for all species. Except for the unsubstituted Lignin Ar, the groups exhibit nearly identical relaxation behavior. The Func2 ABL composite is more rigid and consists of more intimately mixed components.



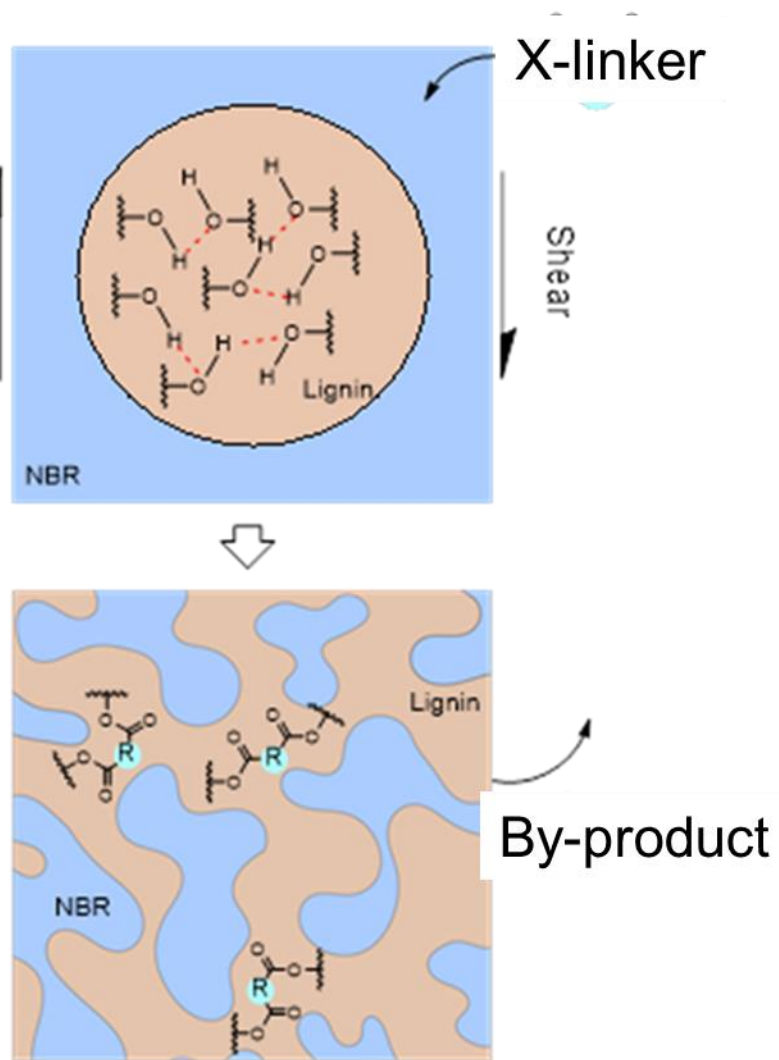
4 - Progress and Outcomes – Go/No-Go criteria met



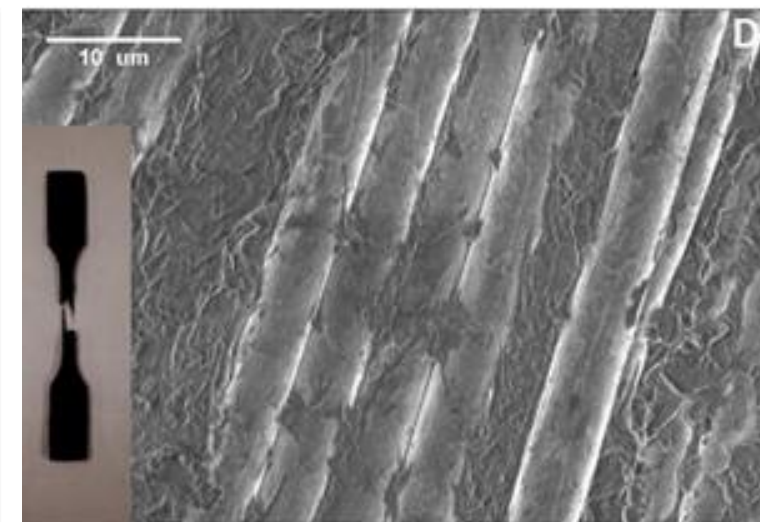
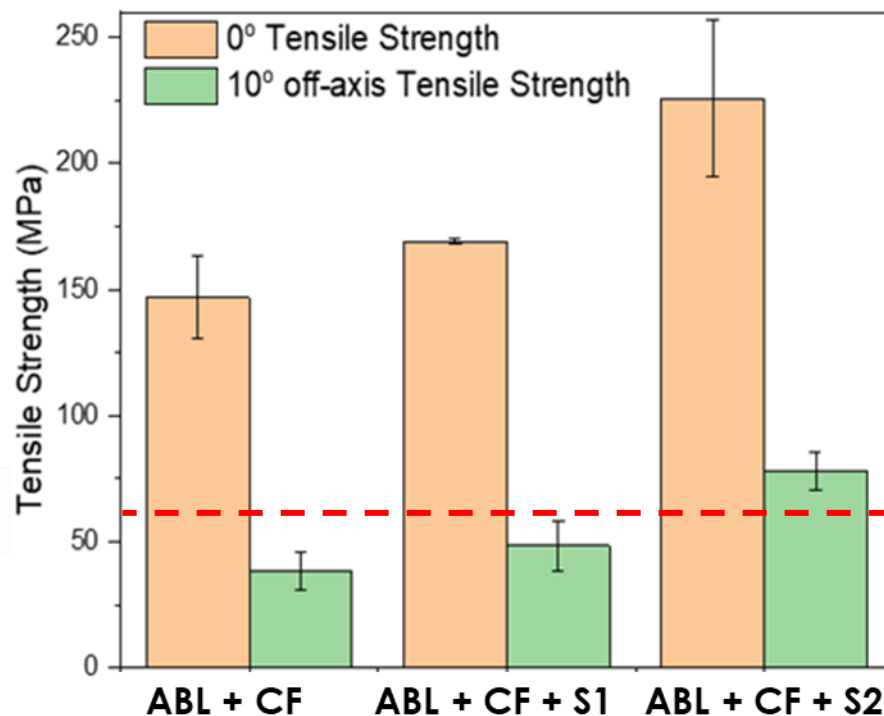
We developed a composition with superior performance in a renewable polymer that

- contains ~70% lignin from biorefinery source (composition of prepared material)
- demonstrates $<5,000$ Pa.s viscosity at 100 s $^{-1}$ shear rates for acceptable processability
- possesses >40 MPa tensile strength assured by <100 nm dispersed lignin phase

4 - Progress and Outcomes – Composite properties



The crosslinking chemistry was useful to tailor CF-reinforced composites for improved composite performance. The material would qualify for the automotive interior specification discussed earlier.



SEM showing the best interfacial adhesion and inset showing the sample failing by fiber fracture.

Adequate interfacial bonding between fiber and lignin-based polymer was developed.

Kanbargi et al., ACS Applied Polymer Materials, (in press)

4 - Progress and Outcomes – Success with fabrication of composite materials motivates us to conduct preliminary TEA

- Earlier it was difficult to claim a certain application or a specific end use of the derivatized lignin. Current lignin products and 10 wt.% carbon fiber composites meets performance goal of an automotive interior part.
- Assumptions: Equal mass composition of ABL from lignin and polymer additive. Say target lignin cost recovery is \$ x /lb.

Cost of lignin \$ 0.5x /lb. of ABL

Polymer additive \$1.5 /lb. (i.e., \$ 0.75 /lb. of ABL)

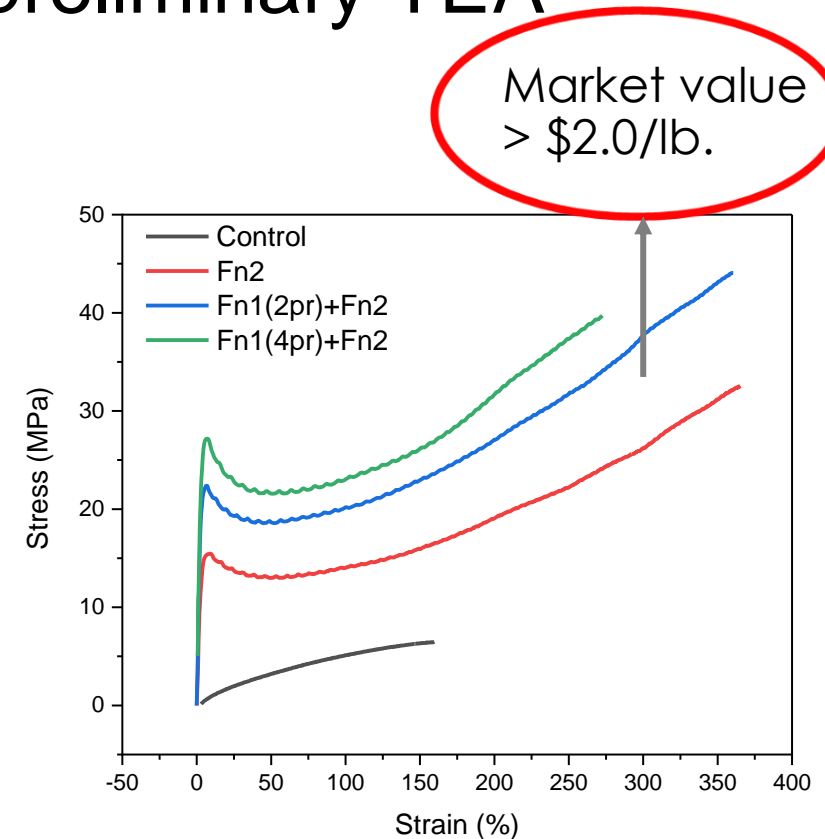
Reactive extrusion cost \$0.25 /lb. (including job work without capital investment via renting a compounding facility)

Materials cost per lb. of ABL

$$0.5x + 0.75 + 0.25 = 2.0$$

Or, $x = \$2$ per pound

The product will yield a value of lignin \$2 /lb. or \$ 4,400 / metric ton.



Summary

Goal: Produce and commercialize lignin-derived and industrial-grade composites with properties including processability and exceeding current petroleum-derived alternatives.

Approach: Use of lignin as a macromolecule component for reactive extrusion of a soft matrix for a solvent-free synthesis of high-performance materials.

Accomplishments: Developed a new understanding of lignin oligomeric molecules at polymer-polymer interface. Used this understanding to design new polymer and composite that can deliver new revenue stream in future biorefinery. Published 10+ articles, Filed 6 US patent applications. Raised \$250k non-Federal funds and initiated 1 CRADA, developed a composition for 3D printing and functional lignin-derivatives.

Need: Lignins from biorefineries.

Coming up: Our future work focuses on the fundamental understanding of lignin functionalities created during biomass processing.

Quad Chart Overview

Timeline

- Project start date: 10/1/2018
- Project end date: 9/30/2021

	FY20	Active Project
DOE Funding	(10/01/2019 – 9/30/2020) \$497,863	(negotiated total federal share overactive project): \$1,750,00

Project Partners*

Engaged with two industrial partners, including one startup company.

Barriers addressed

Process Development for Conversion of Lignin
Developing Methods for Bioproduct Production
Identifying New Market Opportunities for Bioenergy and Bioproducts

Project Goal

Produce and commercialize lignin-derived, industrial-grade polymers and composites with properties, including processability, exceeding current petroleum-derived alternatives.

End of Project Milestone

Demonstration of lignin product. Demonstrate molding of lignin-derived high-performance products with commercial value > \$4000/metric. These products include automotive parts and building materials.

Funding Mechanism

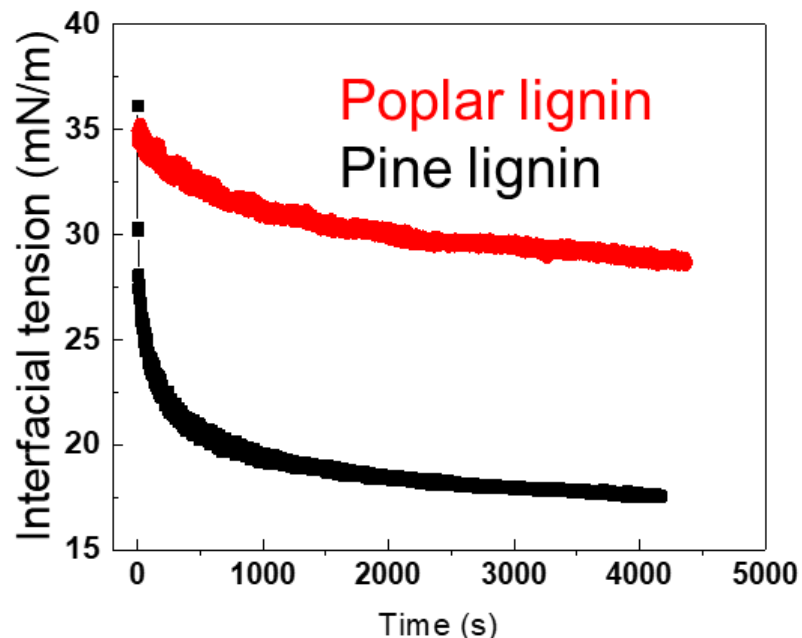
Lab call DE-LC-000L054

Topic area: Conversion

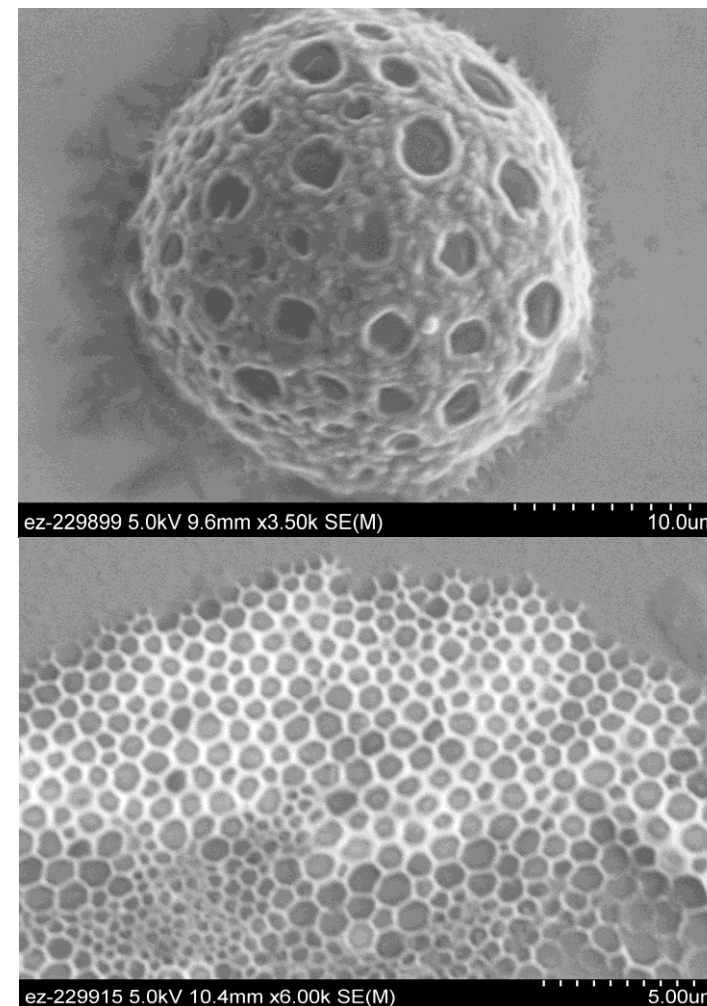
Additional Slides

4 - Progress and Outcomes – Lignin as an amphiphilic surfactant

Understanding instability of lignin – an amphiphilic oligomer at liquid-liquid interface delivers a new route to make porous hierarchical particle.



We use lignin oligomers as renewable surfactant particles that form a 2D surfactant sheet via spontaneous unfolding at the polar-nonpolar liquid interface—just like a cast net thrown onto the interface. Due to the significant interfacial activity, these amphiphilic molecules exhibit unique behavior in jamming, wrapping, and shaping novel non-equilibrium morphologies.



FY19 Peer Review Comments

- Comment: The PIs presented described comparisons between two lignins, but the presentation would be strengthened with comparison of performance and properties to commercial elastomers. Such information would help understand whether a new material stands up to commercial products. Some broader benchmarks would be helpful.
- Answer - We have compared the properties against commercial elastomers such as natural rubbers, elastomers used in tires, and silicones, etc. However, we are preparing materials better than the simple elastomers (20-25 MPa failure stress and have several orders of magnitude lower Young's modulus). Our material failure stress is comparable to engineering products like nylons (30-50 MPa failure stress + it has a high Young's modulus and a characteristic Yield stress). These materials can be used to make a fiber-reinforced composite. Traditional elastomers have very low single T_g (-10 to -70 C). Courtesy of the lignin phase, our materials have both low and high temperature T_g (+10 and +70 C). Therefore, we claim new class of polymers that performs like precision-control-synthesized block copolymers made from petrochemicals.

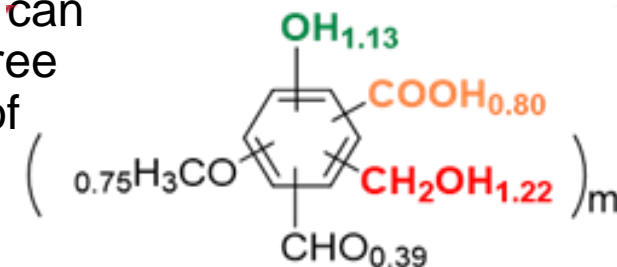
FY19 Peer Review Comments

- Comment: A better understanding of the true target cost of these composites, and whether it will be low enough to compete would be useful. For example, the presentation suggested competition with resins at \$1.12/lb. But the complexity of the process suggests that the cost may be significantly higher for this process. Thus, a clear, simple presentation of targets and economic assumptions is needed.
- Answer: Thermoplastic elastomer equivalent material showing 50 MPa tensile strength while retaining 400% elongation would compete against polyamides. Regular ABL with 40+ MPa tensile strength would compete against toughened polyurethane or engineering plastic like nylon. All these materials will find a market price of >\$2/lb. The market value will increase if we can deliver a composite using either natural fiber or recycled carbon fiber at 10% loading. Such a product will have a market value of \$4-5/lb. We aim to work with a commercialization partner to target the manufacturing of an industrial part/component and a proper TEA analysis.

FY19 Peer Review Comments

- Comment: A weakness – the lignin structure displayed in the slides represents native lignin. Later in the presentation, the PI indicated that the lignin under investigation was organosolv lignin, which is a technical (i. e., isolated) lignin. Technical lignin such as organosolv will be structurally much different, depending on biomass and means of isolation, and thus, hypotheses surrounding the reactivity of this material should reflect those structural differences. Do hypotheses and experiment (for example, research to determine lignin's shape) remain valid if the structure of organosolv is considered instead of native lignin? In addition, the actual steps needed to generate the organosolv products were not described. These will also contribute to the overall cost. The slides indicated the use of PPh₃ during the polymerization. That will likely be unacceptable at larger scale.
- Answer: Agreed, it was a mistake showing native lignin structure. It also showed a generalized structure of lignin containing various functionalities attached to an aromatic moiety. It is a technical lignin or isolated lignin. Our hypothesis is to utilize the malleability of a softened lignin and its amphiphilicity to exploit interaction with a polar rubber where the rubber polar group interacts with phenolic –OH or it's salt. It is an ionic bonding that does NOT inhibit melt-processability.

The material composition we have developed can use any lignin with a substantial phenolic OH group. Soda, sulfite, Kraft, Alcell, residues from IBR, butanol fractionated lignin all yield useful ABL composition. The properties do vary from 20 MPa (better than LDPE) to 50 MPa (better than nylon 6) depending on the lignin backbone structure. All these products can further be upgraded by making their fiber-reinforced composites. PPh₃ as a metal-free catalyst was used for a specific self-healing product simply to demonstrate a proof of concept. It can also be done with tetrabutylammonium iodide.



FY19 Peer Review Comments

- Comment: How is it a source neutral method if lignin from various sources changes? CAN lignin resembles 3, 4 dihydroxyphenylacetic acid DOPAc. A self healing elastomer. It was not clear how would this "self healing" applies when you have a final product like a building material that is damaged over time. Can you elaborate on the self healing aspects and how they improve performance specifically of building materials.
- Answers: Indeed, the lignin compositions vary among sources. However, if a lignin fraction enriched with a functional group be made available from any source, we can call it a source neutral. Essentially, our method extracts a common functional lignin from different sources for higher-performance ABL and an epoxy-based self-healing elastomer application. Self-healing material is not intended for building application. It can be used in thermosets as impact modified to minimize crack initiation. The details for the self-healing aspects are published in ACS Macro Letters 7, 1328-1332 (2018).
- Recently, we have modified the method. We don't fractionate lignin anymore. Rather, we attach a functional group for its enhanced reactivity. The functionalization method is solvent-free.

FY19 Peer Review Comments

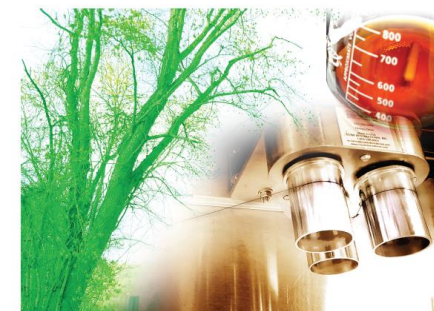
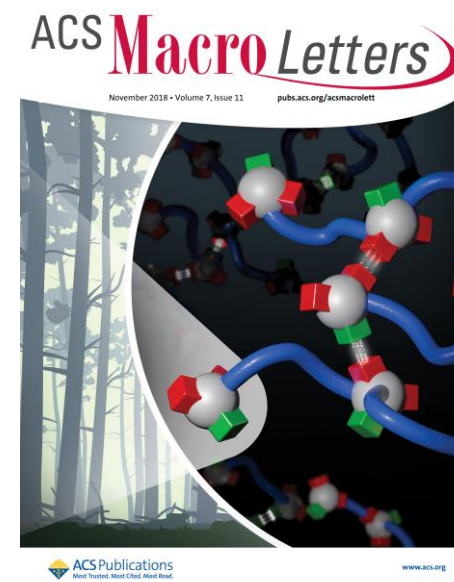
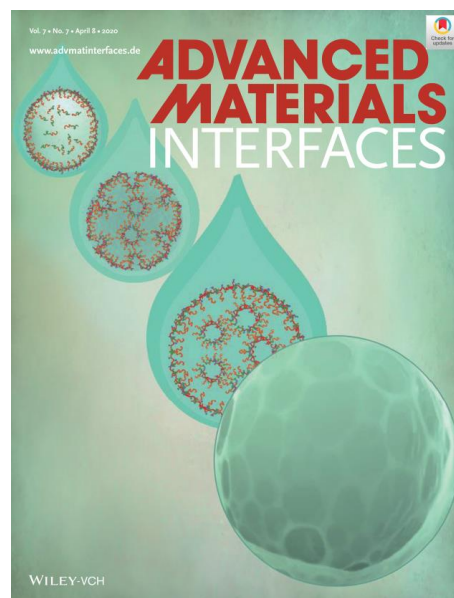
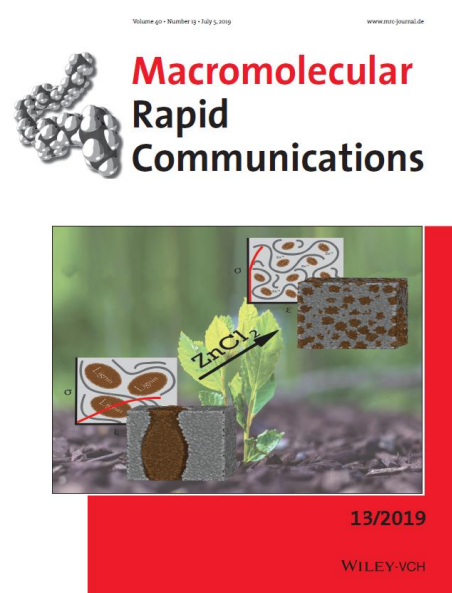
- Comment: Need a more robust TEA for various feedstocks and yield changes / downstream chemistries.
- Answers: Agreed. The yield issue has been resolved. We can use any lignin 100% via a functionalization chemistry without needing a solvent during reactive extrusion itself. We would conduct TEA on a specific automotive product from an industrial partner. Until a scale-up method is demonstrated, and a specific part is designed, it will not be a robust TEA. Fortunately, we could eliminate the need for a solvent fractionation of technical lignin and develop a functionalization chemistry that does not require additional steps and will be functionalized during reactive extrusion. We have presented a slide on arguments for a favorable TEA output.

Journal Publications

1. Kanbargi N,* Goswami M, Collins L, Kearney LT, Bowland C, Kim K, Rajan K, Labbe N,* **Naskar AK**.* Synthesis of High-Performance Lignin-based Inverse Thermoplastic Vulcanizates with Tailored Morphology and Properties. **ACS Applied Polymer Materials** (in press).
2. Jang GG, Nguyen AN, Bowland CC, Ho HC, Keum JK, **Naskar AK***. Effects of graphene surface functionalities towards controlled reinforcement of a lignin based renewable thermoplastic rubber. **Composite Science and Technology** 199, 108352 (2020).
3. Nguyen NA*, Bowland CC, Bonnesen PV, Littrell KC, Keum JK, **Naskar AK***. Fractionation of Lignin for Selective Shape Memory Effects at Elevated Temperatures. **Materials** 13(8), 1940 (2020).
4. Cui M*, Gao Q, Bowland CC, Burgeson EM, Hong K, Yue P, **Naskar AK***. A cast net thrown onto an interface: wrapping 3D objects with an interfacially jammed amphiphilic sheet. **Advanced Materials Interfaces** 7, 1901751 (2020). [**Featured as the BACK COVER of the issue**]
5. Nguyen NA, Kim K, Bowland CC, Keum JK, Kearney LT, André N, Labbé N, **Naskar AK**. A Fundamental Understanding of Whole Biomass Dissolution in Ionic Liquid for Regeneration of Fiber by Solution-Spinning. **Green Chemistry** 21, 4354–4367 (2019). [**Featured as the BACK COVER of the issue**]
6. Barnes SH, Goswami M, Nguyen NA, Keum JK, Bowland CC, Chen J, **Naskar AK**. An Ionomeric Renewable Thermoplastic from Lignin-Reinforced Rubber. **Macromolecular Rapid Communications** 40, 1900059 (2019). [**Featured as the BACK COVER of the issue**]
7. Nguyen NA*, Meek KM, Bowland CC, **Naskar AK***. Responsive lignin for shape memory applications. **Polymer** 160, 210-222 (2019).
8. Nguyen NA*, Meek KM, Bowland CC, **Naskar AK***. Data of thermally active lignin-linkages and shape memory of lignin- rubber composites. **Data in Brief** 22, 392-399 (2019).

Journal Publications

9. Nguyen NA*, Barnes SH, Bowland CC, Meek KM, Littrell KC, Keum JK, **Naskar AK***. A Path for Lignin Valorization via Additive Manufacturing of High-Performance Sustainable Composites with Enhanced 3D-Printability. **Science Advances** 4(12), eaat4967 (2018).
10. Cui M*, Nguyen NA, Bonnesen PV, Uhrig D, Keum JK, **Naskar AK***. A Rigid Oligomer from Lignin in Designing of Tough, Self-Healing Elastomers. **ACS Macro Letters** 7, 1328-1332 (2018). [**Featured as the COVER of the issue**]
11. Nguyen NA*, Bowland CC, **Naskar AK***. Mechanical, thermal, morphological, and rheological characteristics of high-performance 3D-printing lignin-based composites for additive manufacturing applications. **Data in Brief**, 19, 936-950 (2018).
12. Nguyen NA*, Bowland CC, **Naskar AK***. A general method to improve 3D-printability and inter-layer adhesion in lignin-based composites. **Applied Materials Today** 12, 138-152 (2018).



Showing research from the group of Anik K. Naskar of Oak Ridge National Laboratory, Tennessee, USA.
A fundamental understanding of whole biomass dissolution in ionic liquid for regeneration of fiber by solution-spinning.
An environmentally friendly roll-to-roll process for converting waste wood chips into biomass fibers by solution spinning was developed. Results on rheology, solution spinnability, and structure formation under external stress and flow of the biomass-ionic liquid solutions established significant missing details of early stage solution spinning. The findings will catalyze more important studies in this new direction.



See Ngoc A. Nguyen, Nicole Labbe, Anik K. Naskar et al. Green Chem., 2019, 21, 4354

Patent applications (pending)

1. **Naskar AK**, Cui M. Hierarchically assembled particles of lignin and methods to make those. (ORNL ID 4342), **U.S. Patent Application No. XX/XXX,XXX** (filed on September 4, 2020).
2. Bova T, **Naskar AK**. Phenol-containing polyester multiphase polymer blend materials. (ORNL ID 4300), **U.S. Patent Application No. 16/911,693** (filed on June 25, 2020).
3. Naskar AK, Bowland CC, High strength lignin-acrylonitrile polymer blend materials, (ORNL ID 4308), **U.S. Patent Application No. 16/829,167** (filed on March 25, 2020).
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4 - Progress and Outcomes – Success with fabrication of composite materials motivates us to conduct preliminary TEA

- Earlier it was difficult to claim a certain application or a specific end use of the derivatized lignin. Current lignin products and 10 wt.% carbon fiber composites meets performance goal of an automotive interior part.
- Assumptions: Equal mass composition of ABL from lignin and polymer additive. Say target lignin cost recovery is \$ x /lb.

Cost of lignin \$ 0.5x /lb. of ABL

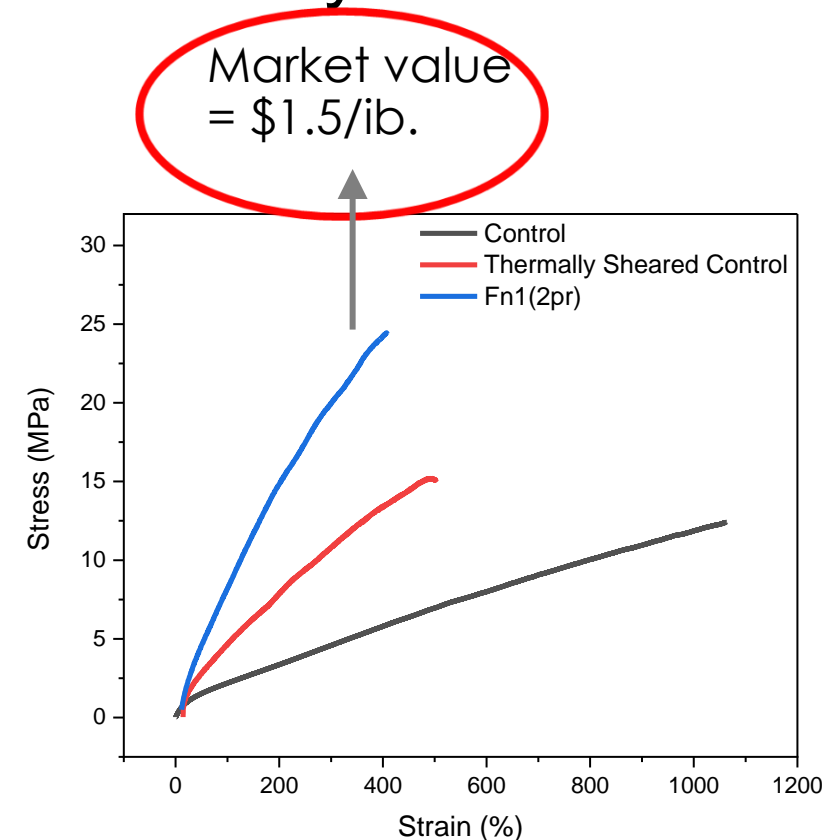
Polymer additive \$ 0.75 /lb. of ABL

Reactive extrusion cost \$0.25/lb. (including job work without capital investment via renting a compounding facility)

Materials cost

$$0.5x + 0.75 + 0.25 = 1.5$$

Or, $x = \$1$ per pound



The product will yield a value of lignin \$1 /lb. or \$ 2,200 / metric ton.