DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

2.5.6.103 Melt-stable engineered lignin thermoplastic

March 5, 2019

Performance Advantaged Bioproducts and Separations

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Goal Statement

- ***Project Goal***
  - *Produce and commercialize lignin-derived, industrial-grade polymers and composites with properties, including processability, exceeding current petroleum-derived alternatives.*
- ***Project outcome***
  - *A group of commercial-ready, lignin-based 3D-printable, self-healing, recyclable composites. Also, suitable for high-volume applications.*
  - *Utilization of lignin at 30-60 (%) volume to produce engineered plastic materials with values ranging $2000-$5000/metric ton.*
  - *Already created commercialization opportunity with 3 entities and several others are discussing details of innovation with (1) low-modulus self-healing elastomer and (2) high shear processing of engineered lignin thermoplastics.*
- ***Relevance to the bioenergy industry***
  - *Enables high value uses of unmodified lignin, a biorefinery waste stream, and facilitates the cost-competitive production of biofuels.*
  - *Lignin contributes significantly to reduce cost, enhance stiffness, oxidation resistance, and high dimensional stability in its polymeric derivatives.*

Quad Chart Overview

Timeline

- Project start date: 10/2018 (4/2016)
- Project end date: 9/30/2021
- Percent complete: 17% (54)

Barriers addressed

Process Development for Conversion of Lignin

Developing Methods for Bioproduct Production

Identifying New Market Opportunities for Bioenergy and Bioproducts

	Total Costs Pre FY17**	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	N/A	$500k	$600k	$1,600k
Project Cost Share*				$250k*

*** UT-B LCC Royalty Funds and Technology Licensee Cash-in**

Objective

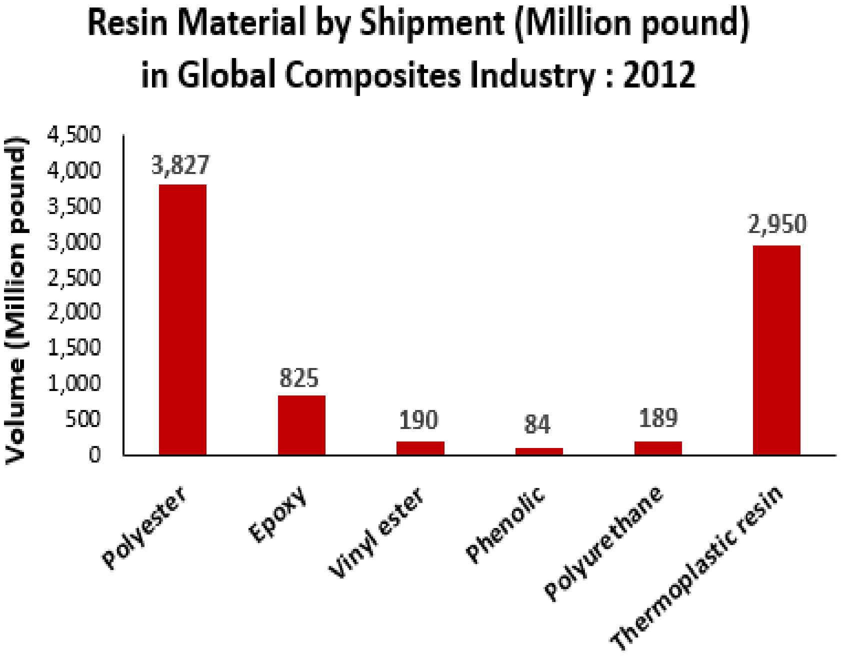
Produce and commercialize lignin-derived, industrial-grade polymers and composites with properties, including processability, exceeding current petroleum-derived alternatives.

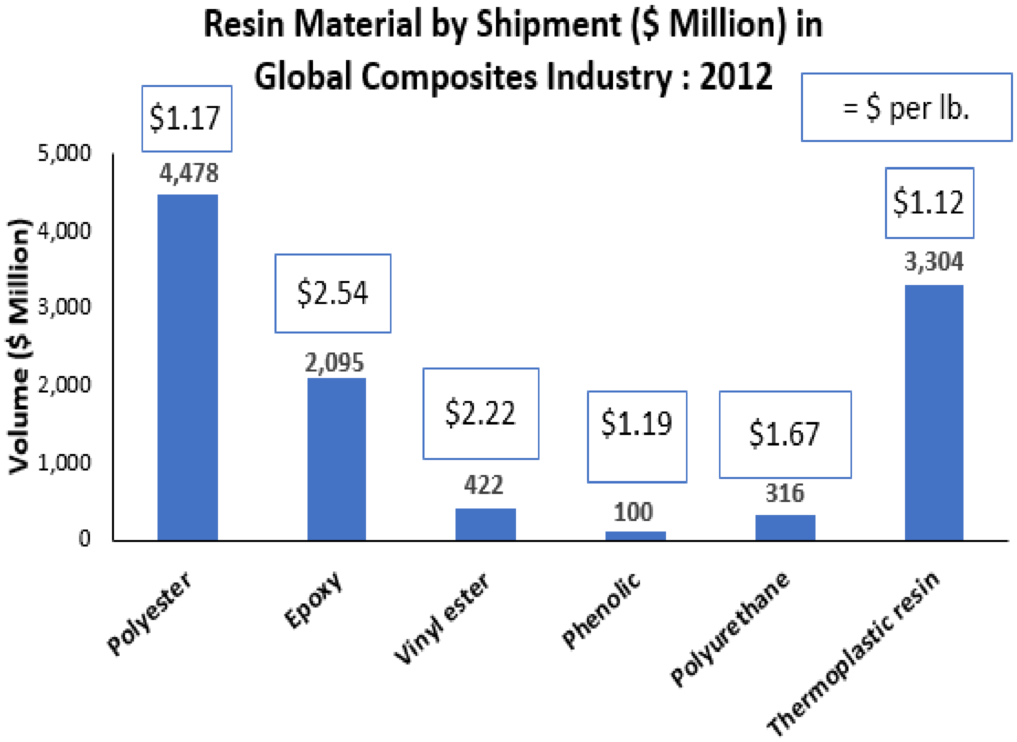
End of Project Goal

A new understanding of different lignin characteristics and their potential impacts on properties of lignin-based thermoplastic that can outperform commodity automotive grade polymers and other petrochemical-derived plastics.

Commercialization of products.

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





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

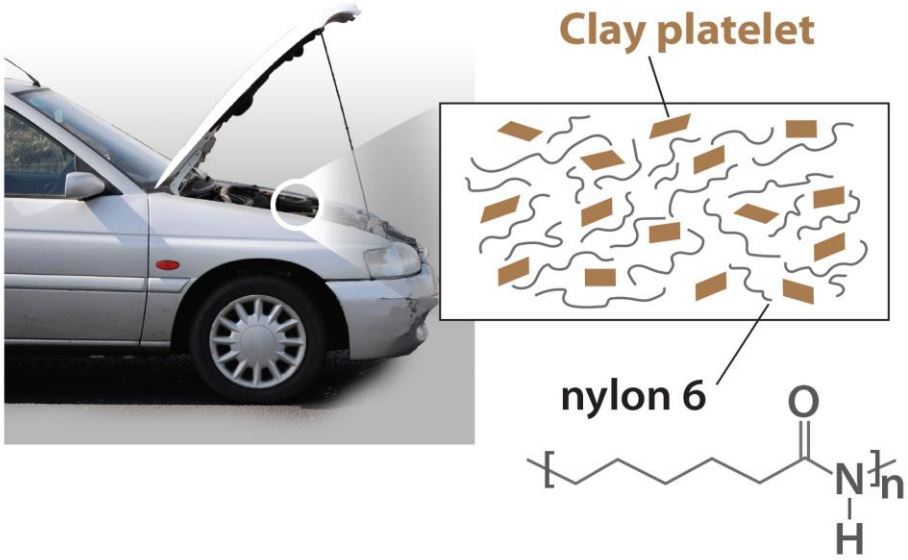
3D printable thermoplastics feedstock has a market value >$5/lb.

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

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

Lignin is a complex macromolecule and not an organic filler!

Presence of co-continuity of a rigid lignin phase (via extended configuration of lignin in a soft matrix) results in tensile yield stress as high as ~40 MPa and a tenfold increase in the rubbery matrix modulus. Formation of lignin-matrix hybrid interphase enhances performances.

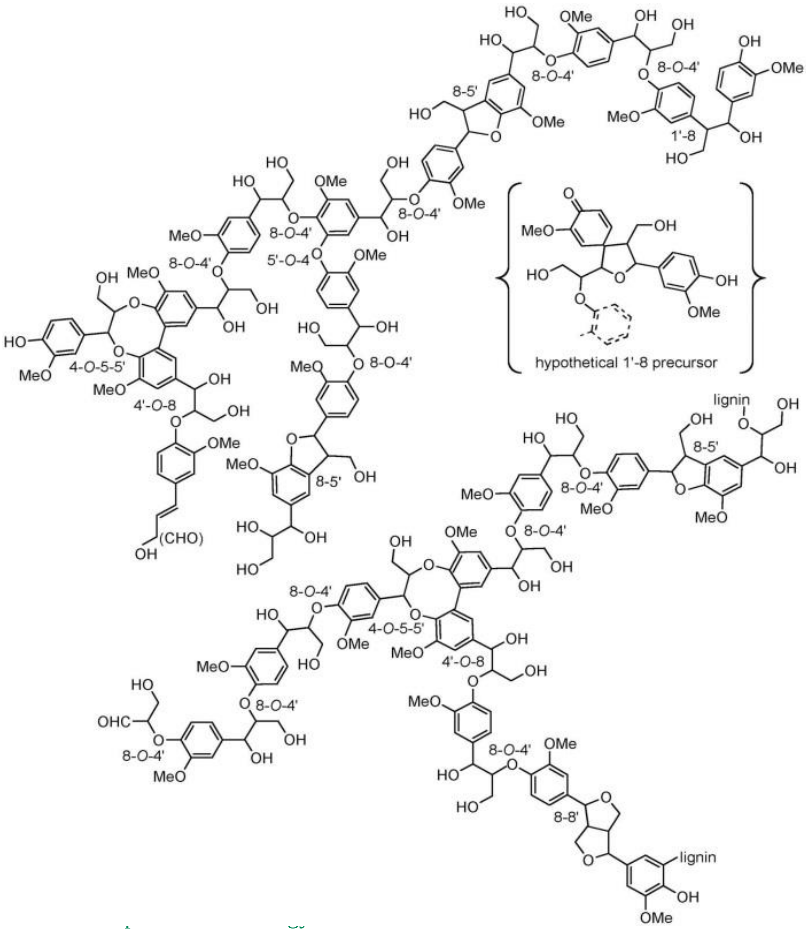


- Dispersed clay in polyamide thermoplastic melts → exfoliated-layered nanocomposites.
  - Tougher and gas impermeable, and has improved heat distortion temperatures.
- Inspires us to develop lignin-based organic-organic nanocomposites.

Naskar et al. ***Nature Nanotechnology*** (2016)

1 - Project Overview: Architecture of lignin molecules

Typical lignin derived from an annual plant does not have a uniform shape of self-assembled units in solution. In contrast, the woody biomass-derived lignins have cylindrical units. The radius of gyration of hardwood lignin molecular assemblies is significantly larger than that of the softwood lignin.



With an increase in lignin concentration, the dimension of cylinders decrease, and molecular self-assembly takes 2D shape. This information offers the opportunity of mimicking nylon-clay morphologies.

Cylinders of 1–2 nm diameter and 2–10 nm length. Radii of gyration of the assembly are in the range of 50–100 nm. Can we maintain such solvated nanoscale morphology in the planned polymer products?

Imel, Naskar, Dadmun, ***ACS Appl. Mater. Interfaces*** 2016, 8, 3200−3207

Ratnaweera et al. ***RSC Adv***., 2015, 5, 67258–67266.

1 - Project Overview: Lignin residues to product history

Scientific Achievement

ORNL discovered that lignin dispersion in synthetic polymer matrix can be controlled during facile melt mixing process to produce renewable thermoplastics. This process is solvent-free and compatible with existing polymer processing equipment.

Significance and Impact

This green product consisting of 30–70% of renewable content could offer a revenue stream to reduce the need for synthetic thermoplastics produced from petrochemicals.

The manufacturing process is modular and least capital intensive. Lignin polymer manufacturing site can be located in a biorefinery to avoid transportation of dry, low-bulk density, flammable lignin.

Market Opportunity

2002 THERMOPLASTIC MARKET
$46.9 B

2012 THERMOPLASTIC MARKET
$87.1 B

TARGET MARKETS
BUILDING MATERIALS = $23B
PACKAGING = $17B
MOTOR VEHICLES = $11B

Akato et al. ***ACS Sus Chem Eng.*** 3(12), 3070–3076 (2015)
Tran et al. ***Adv Functional Materials*** 26(16) 2677-2685 (2016).
Bova et al. ***Green Chemistry*** 18 (20), 5423-5437 (2016).

2 – Approach (Management)

❑ **Principal Investigator:**

- Amit K. Naskar

❑ **Collaborators:**

- Center for Renewable Carbon - University of Tennessee (Dr. Nicole Labbe)
- Dr. Jong Keum, Dr. Jihua Chen, Dr. Ken Littrell, Dr. Monojoy Goswami, Dr. Peter Bonnesen (User programs - ORNL)

❑ **Team members:**

- Dr. Mengmeng Cui (Post-Doc, ORNL)→ Supporting lignin characterization: Mw, structures and development of functional lignin and self-healing materials
- Dr. Ngoc A. Nguyen (Staff, ORNL)→ Developing materials with 3D-printability and thermo-responsive characteristics.
- Dr. Chris Bowland (Wigner Fellow)→ Composites of lignin-based polymers
- Sietske H. Barnes (Post- Master, ORNL)→ Lignin compounding
- Hoi-Chun Ho (PhD student, ORNL/UT-Bredesen Center)

❑ **Periodic progress assessment:**

- Biweekly meeting among team members
- Presentation of updates to sponsor

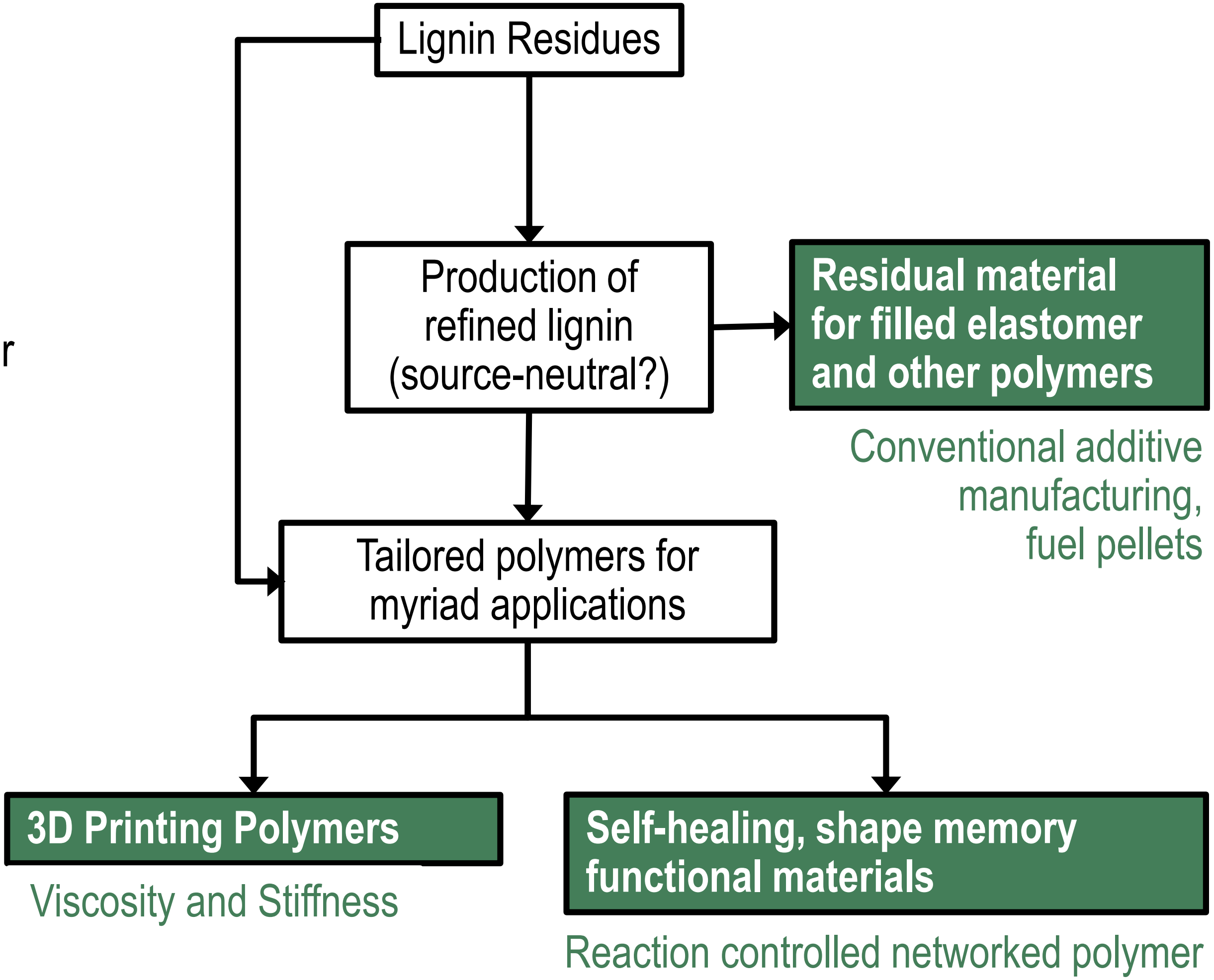
2 – Approach (Technical)

Challenges with lignin to polymeric product R&D:

- All lignins are not the same!
- Lack of control in lignin self-assembly
- Thermal processing is difficult for some lignins

Critical success factors

- Product performance
- Solvent-free synthesis
- Commercialization opportunity
- Diversified product portfolio



Lignin Residues

Production of refined lignin (source-neutral?)

Residual material for filled elastomer and other polymers

Conventional additive manufacturing, fuel pellets

Tailored polymers for myriad applications

3D Printing Polymers

Viscosity and Stiffness

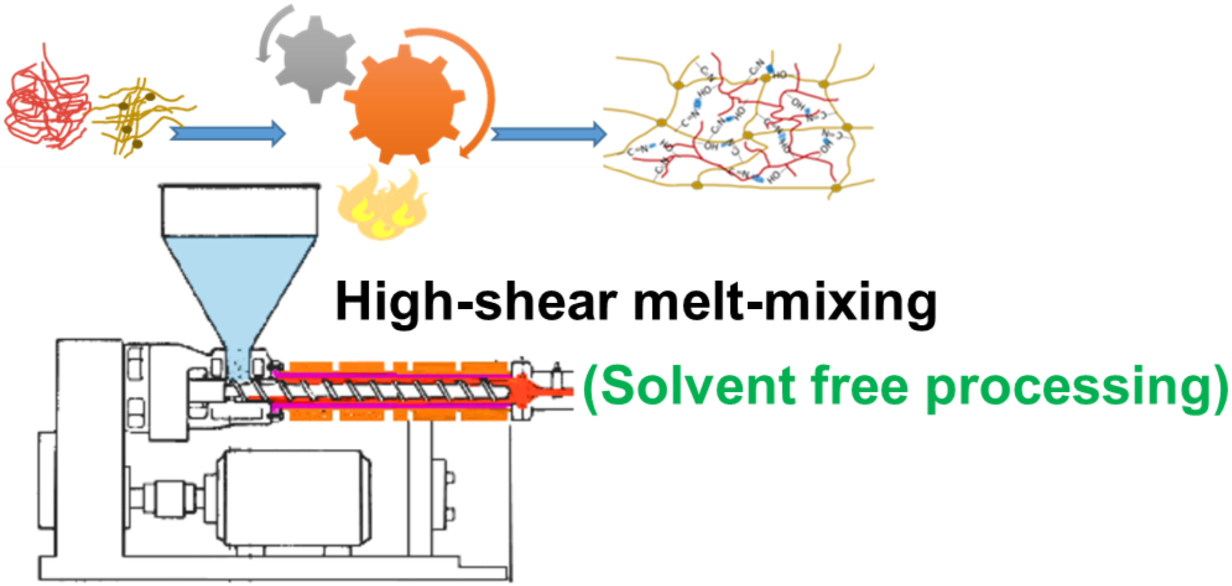
Self-healing, shape memory functional materials

Reaction controlled networked polymer

<u>Source-neutral</u> functional lignin often offers better control on product morphology and performance.

2 – Approach (Technical): Reactive processing

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



High-shear melt-mixing

(Solvent free processing)

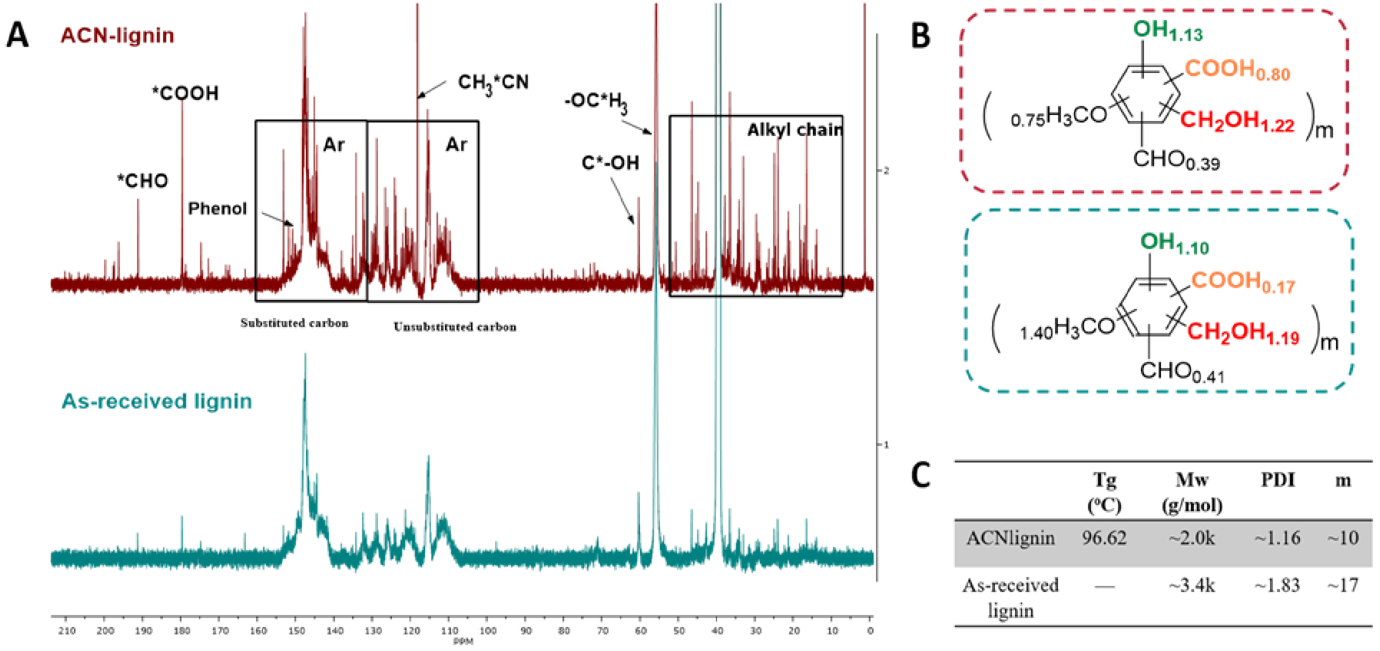
Extrusion and characterization facilities that are utilized to synthesize and analyze the products.

2 – Approach (Technical): Milestones to meet and risks associated with those

Go/No-Go Decision	Description	Criteria	Date
Demonstrate superior performance in renewable polymer that ❖ <u>Contains ~70% lignin from biorefinery source</u> ❖ Demonstrates <5,000 Pa.s viscosity at 100 s^{-1} shear rate for acceptable processability ❖ Possesses >40 MPa tensile strength <u>assured by <100 nm dispersed lignin phase</u>	Produce fractionated biorefinery lignin-based polymer that has (1) ~70% lignin content, (2) ~40 MPa tensile strength, (3) <5,000 Pa.s viscosity at 100 s^{-1} shear rate. Low-viscosity is desired for processing ease; however, low-viscosity tends to reduce mechanical properties.	Demonstrating 40 MPa tensile strength in a polymer that contains 70% lignin will be the first time a printable or injection/compression moldable polymer that incorporates a high volume of lignin, matches the failure strength of commercial automotive thermoplastic, such as nylon.	6/30/20

3 – Technical Accomplishments: Functional Lignin

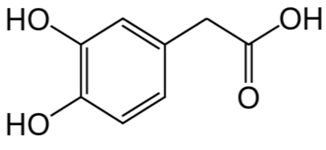
We developed a source-neutral method to produce functionally enriched lignin for producing polymeric materials. Acetonitrile extract of a lignin residue (ACN-lignin) is functionally enriched.



	Tg (°C)	Mw (g/mol)	PDI	m
ACNlignin	96.62	~2.0k	~1.16	~10
As-received lignin	—	~3.4k	~1.83	~17

Chemical structure and characterization of as-received lignin and ACN-lignin. (**A**) ^{13}C-NMR of as-received lignin and ACN-lignin in d^6-DMSO. (**B**) Average degree of substitution (DS) of each functional group per aromatic. (**C**) Comparison between two lignin samples.

ACN-lignin resembles 3,4-dihydroxyphenylacetic acid (DOPAc), a derivate that is responsible for the strong adhesion of mussel and frequently used for self-healing.



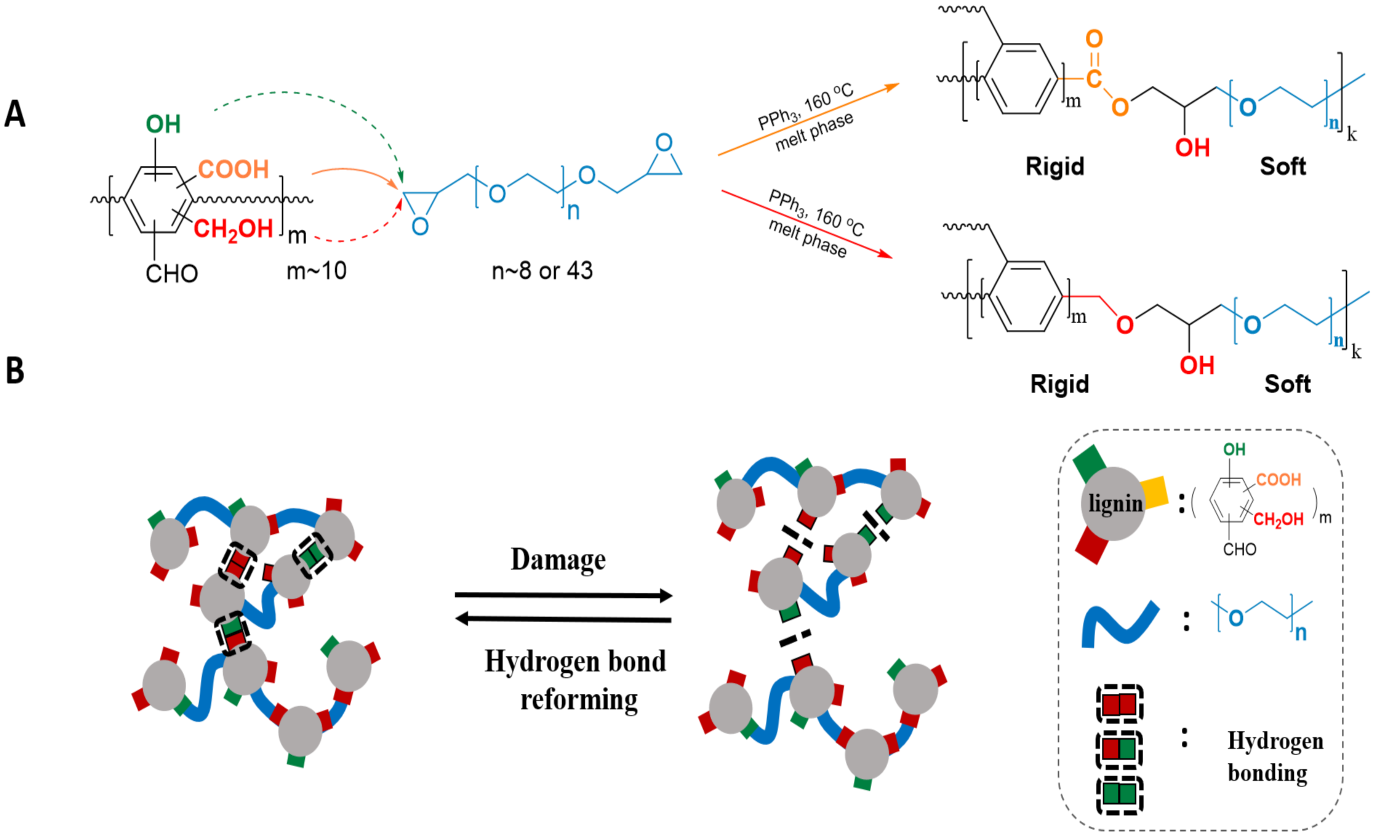
DOPAc

Cui et al. ***ACS Macro Letters*** (2018)
Naskar and Cui**, US Patent Application** (Feb 15, 2019)

J. H. Waite, M. L. Tanzer, ***Science* 212**, 1038-1040 (1981)
N. Holten-Andersen et al., ***PNAS* 108**, 2651-2655 (2011)

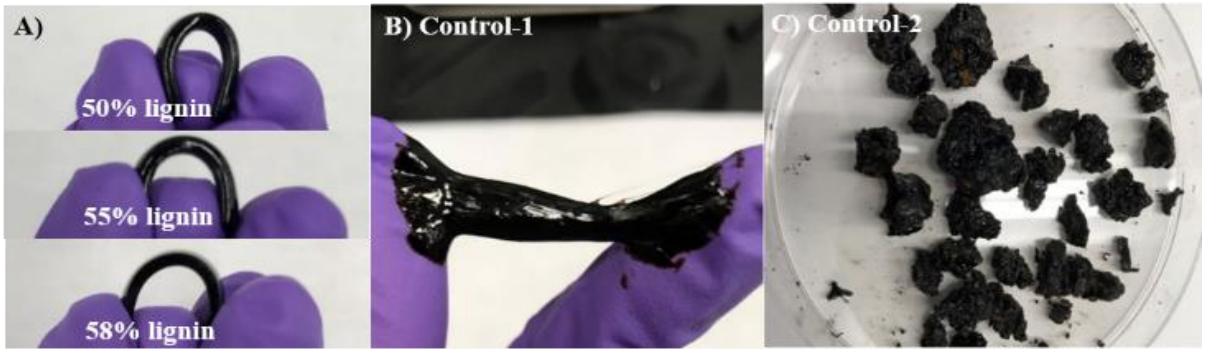
New Self-Healing Elastomer via Solvent-Free Copolymer Synthesis from ACN-lignin

Many self-healing materials rely on supramolecular interactions (hydrogen-bonding, π-π stacking, metal-ligand, and ionic interactions). These weak interactions afford quick and spontaneous self-healing but also lead to unsatisfactory mechanical properties. Our solution to this problem is to introduce multiple phases into the material (Figure below), a hard phase bringing in stiffness and a soft phase for self-healing.



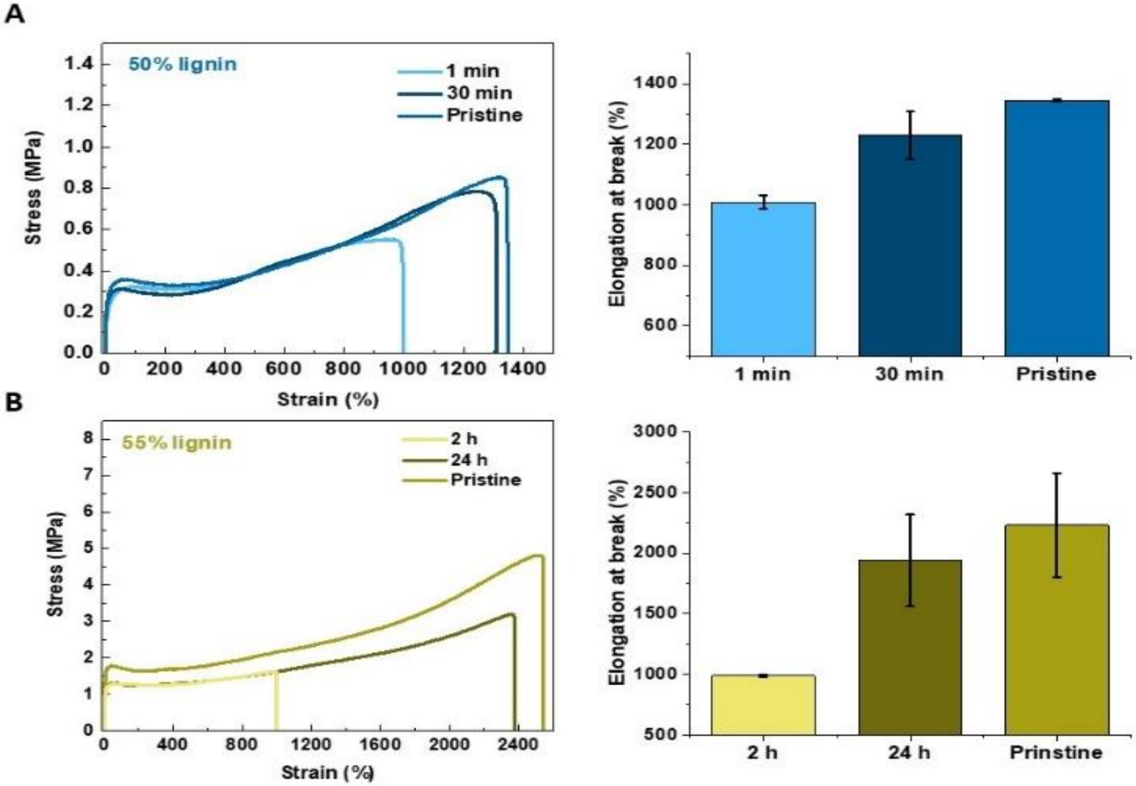
Preparation, characterization and schematic illustration of the self-healing material from ACN-lignin. (**A**) Two dominant reactions between ACN-lignin and diglycidyl ether polyethylene glycol (PEG) at melt-phase. (**B**) Schematic illustration of a network formed by coexisting covalent bonds and non-covalent bonds.

The copolymer elastomers exhibit yield strength, ultra-high toughness, and instant healing



Physical appearance of products from reactions between diglycidyl ether PEG and: (**A**) ACN-lignin, (**B**) DOPAc, and (**C**) as-received lignin.

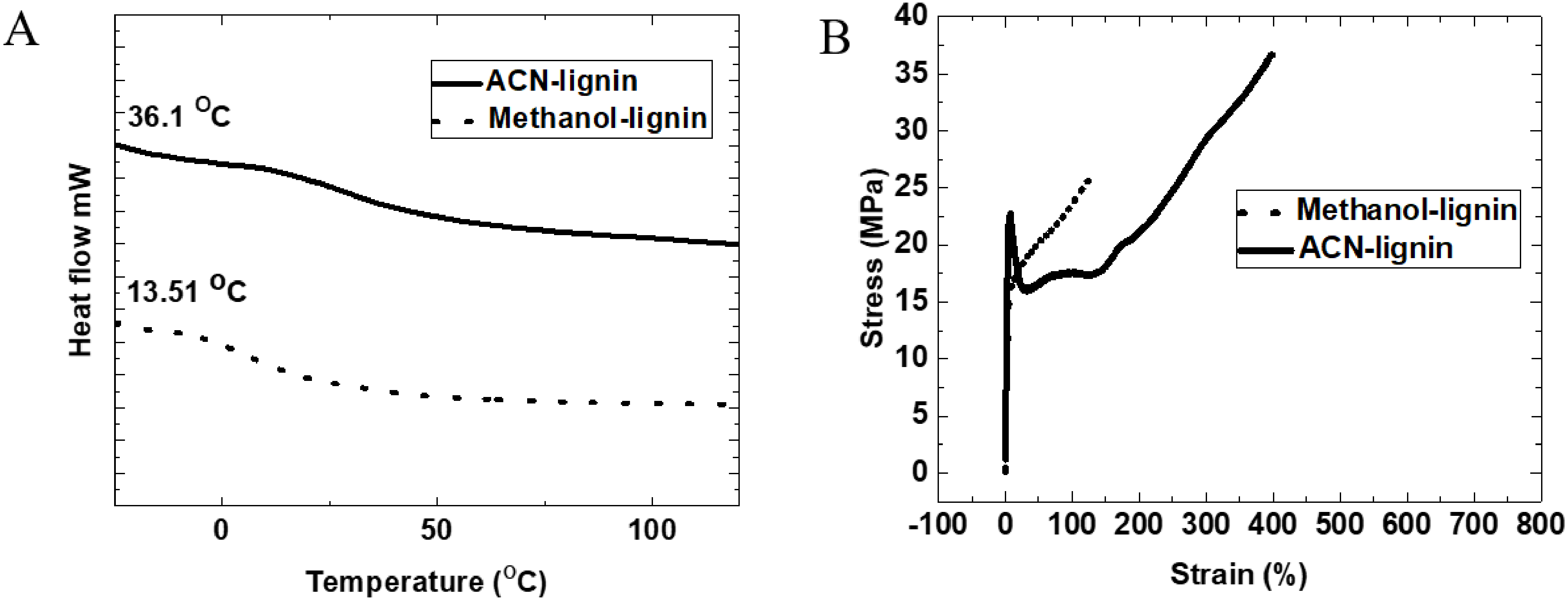
ACN-lignin delivered the best product!



Stress-strain curve and recovery performance of (**A**) the elastomer with 50% ACN-lignin in 1 min and 30 min healing time at room temperature, and (**B**) the elastomer with 55% ACN-lignin in 2 h and 24 h healing at 37°C.

As the lignin content increased, the self-healing became slower due to an increased T_g.

ACN-Lignin produces tougher, stronger acrylonitrile-butadiene-lignin (ABL) polymer than previous report

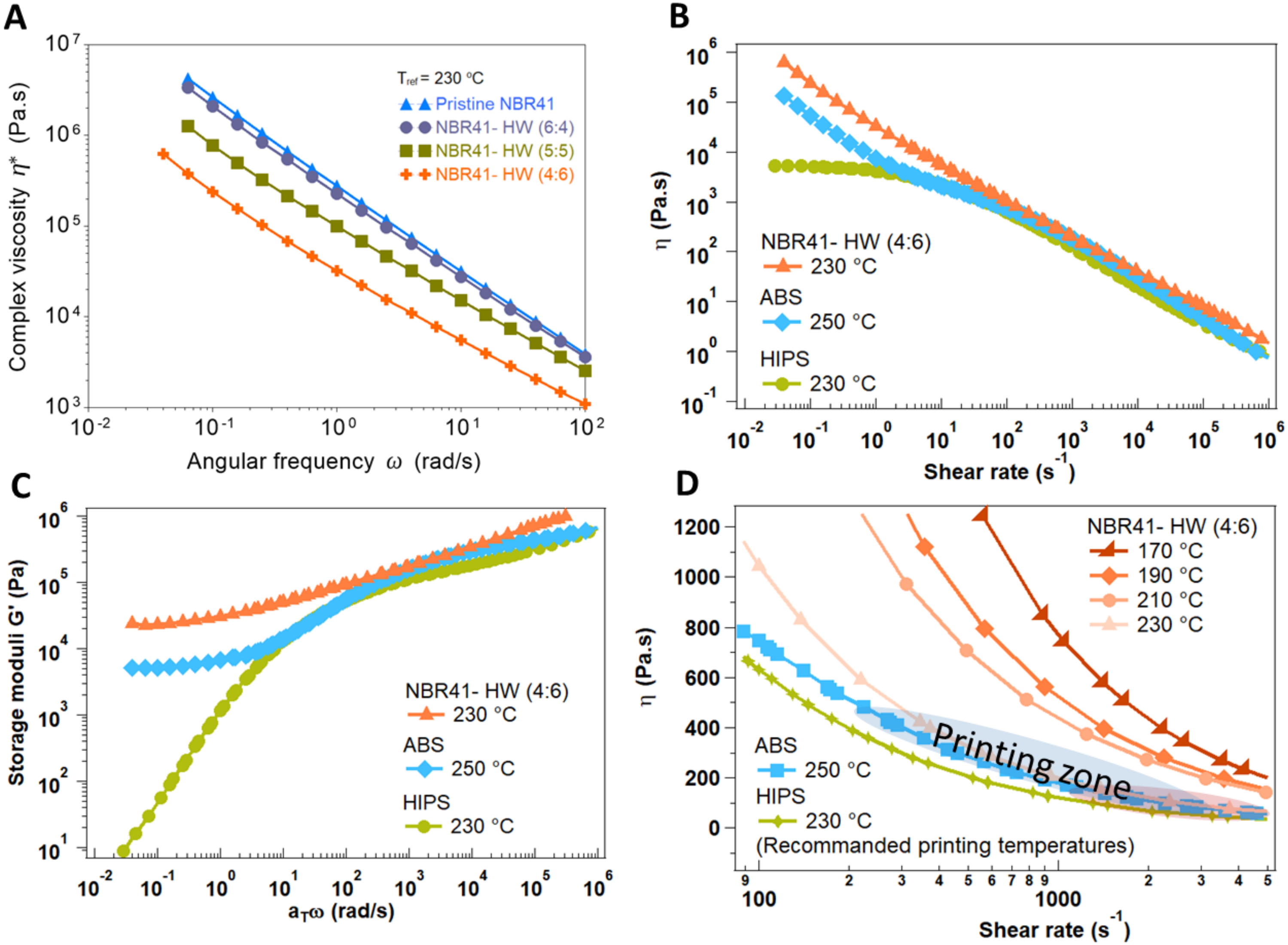


The melt-stable methanol extract of softwood lignin is known to produce a blend with nitrile rubber with desirable properties. However, (Fig. B) unexpectedly demonstrates that the ACN-lignin-nitrile rubber blend is a significantly tougher and stronger product than the state of the art control ABL material.

Tran et al. **Advanced Functional Materials**, 26(16), 2677-2685, 2016.
Naskar and Cui, **US Patent Application** (Feb 15, 2019)

3 – Technical Accomplishments: 3D printability

3D printable polymers must have appropriate viscosity profile and resistance to deformation both in solid and melt-state at the zero-shear condition.

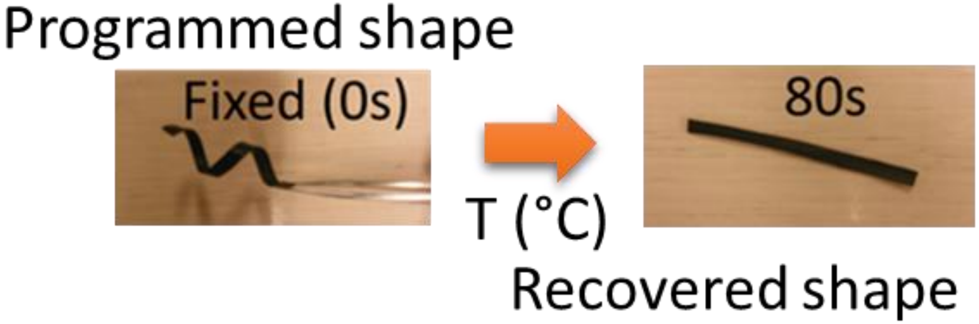


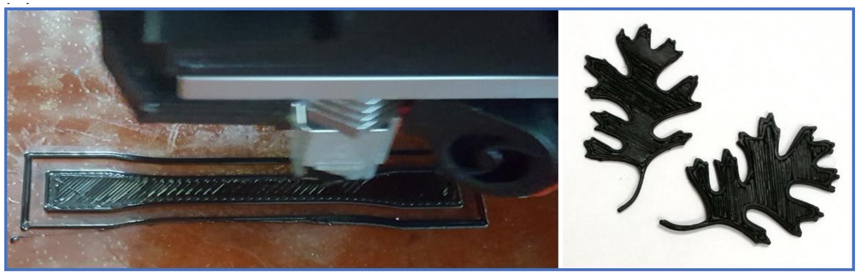
Rheological properties of ABL based on sinapyl alcohol rich units (40-60 wt%). The blue shaded region presents viscosity and shear rate window for ABS when it shows good printability. The red shaded region indicates the overlapped printing viscosity range for ABL, ABS and HIPS samples.

Nguyen et al. ***Science Advances*** *4(12), eaat4967 (2018)*

Application of ABL: Shape Memory Polymers and Printable Composites

Lignin (30–60 wt.%) forms both covalently and hydrogen bonded networks within a Nitrile rubber matrix for shape memory, stress/strain sensing, and 3D printing applications.

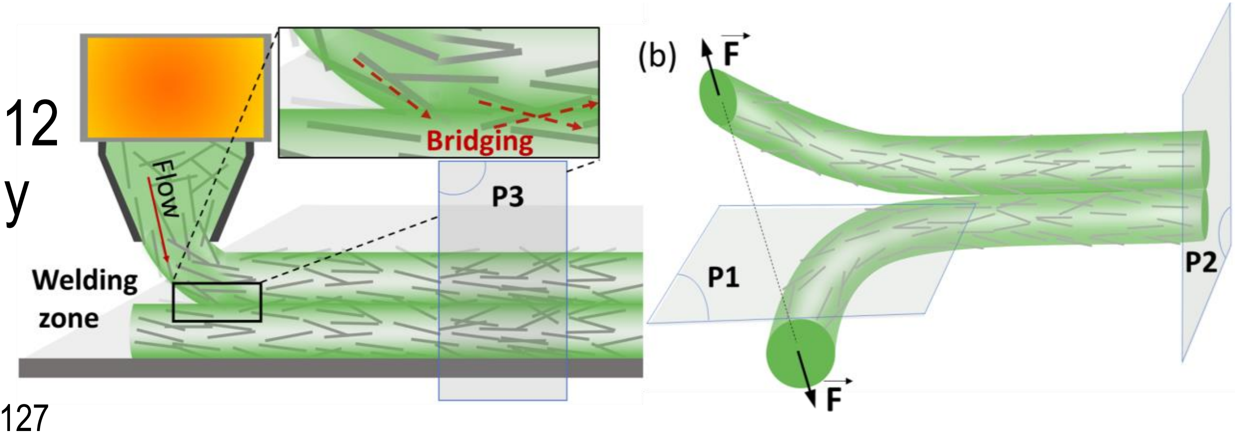




U.S. Patent Application No. 16/014,136 (June 21, 2018).

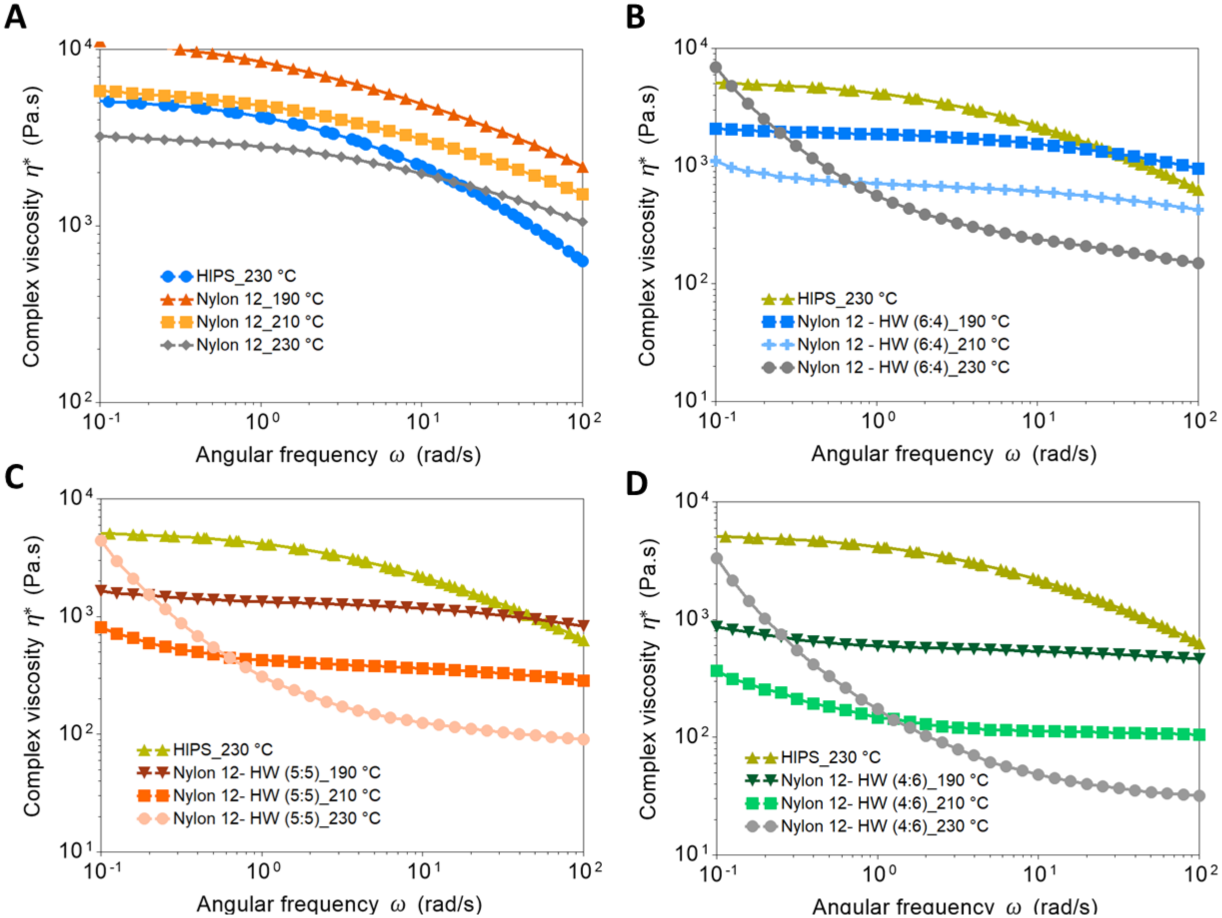
U.S. Patent Application No.: 16/257,313 (Jan 25, 2019).

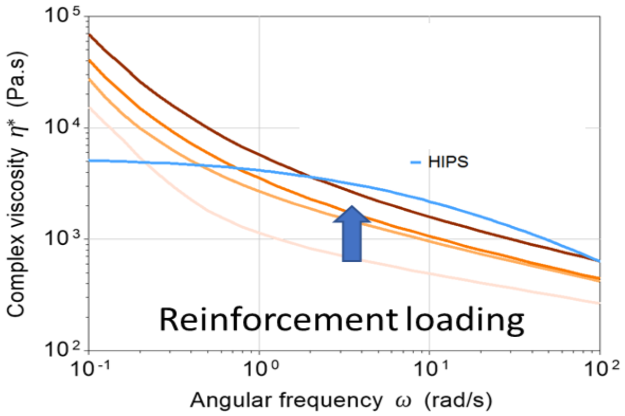
Use of little carbon fiber (4-12 wt%) enhances weld energy between printed layers.



Nguyen et al. ***Macromolecules*** 51 (2018) 115–127
Nguyen et al. ***Applied Materials Today*** 12 (2018) 138–152
Nguyen et al. ***Polymer*** 160, (2019)

Lignin enables outstanding processability (3D printing) in the nylon products



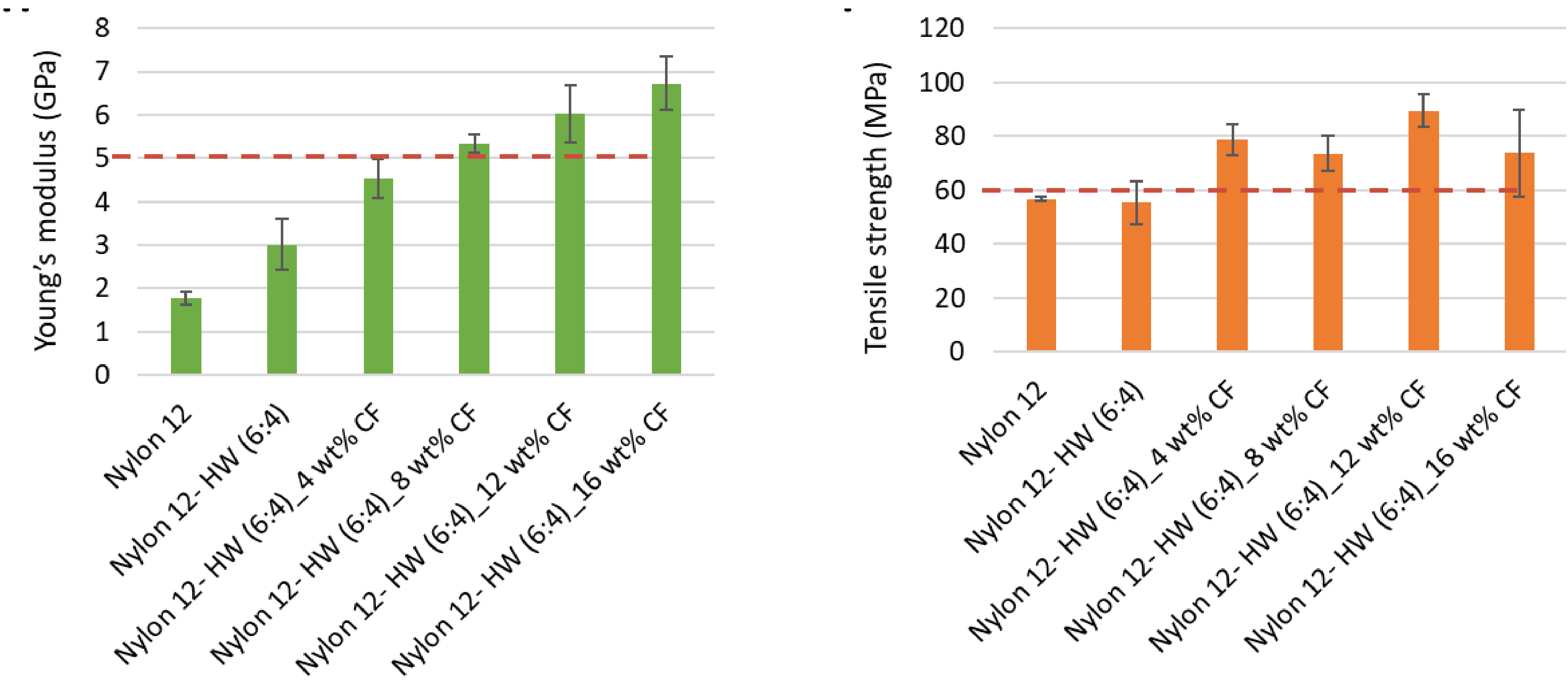


The increase in viscosity after adding 4-16 wt.% CF in the lignin-thermoplastic melt is still favorable compared to the neat styrenic 3D printable resins.

Key Discovery: Low-shear viscosity is very high but the high shear viscosity is very low

Mechanical properties of lignin-based composites

Young's modulus and tensile strength of selected nylon/lignin samples.

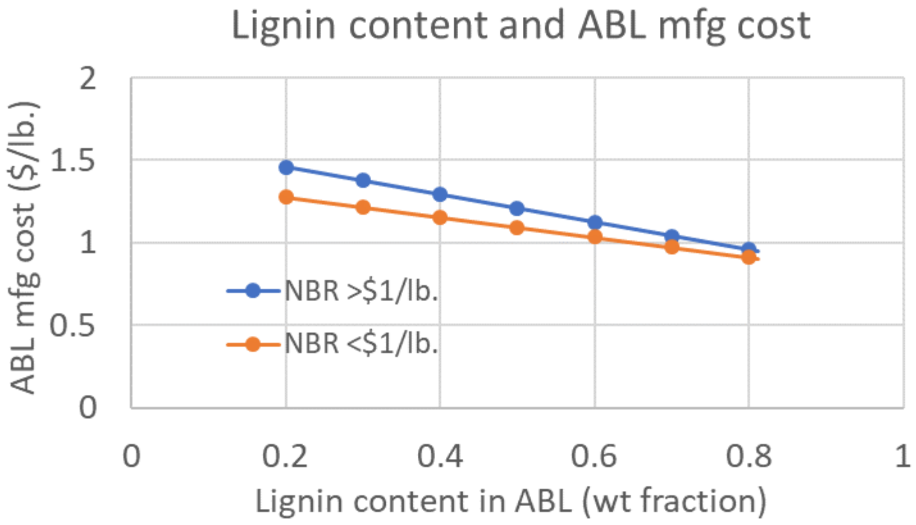


Selected compositions meet initial performance goal (red dotted line above) of automotive composites (5 GPa modulus and >60 MPa strength to failure).

4 - Relevance

Goal: Produce and commercialize lignin-derived and industrial-grade composites. The project objective is driven by an initial economic assessment that encourages the use of unmodified lignin.

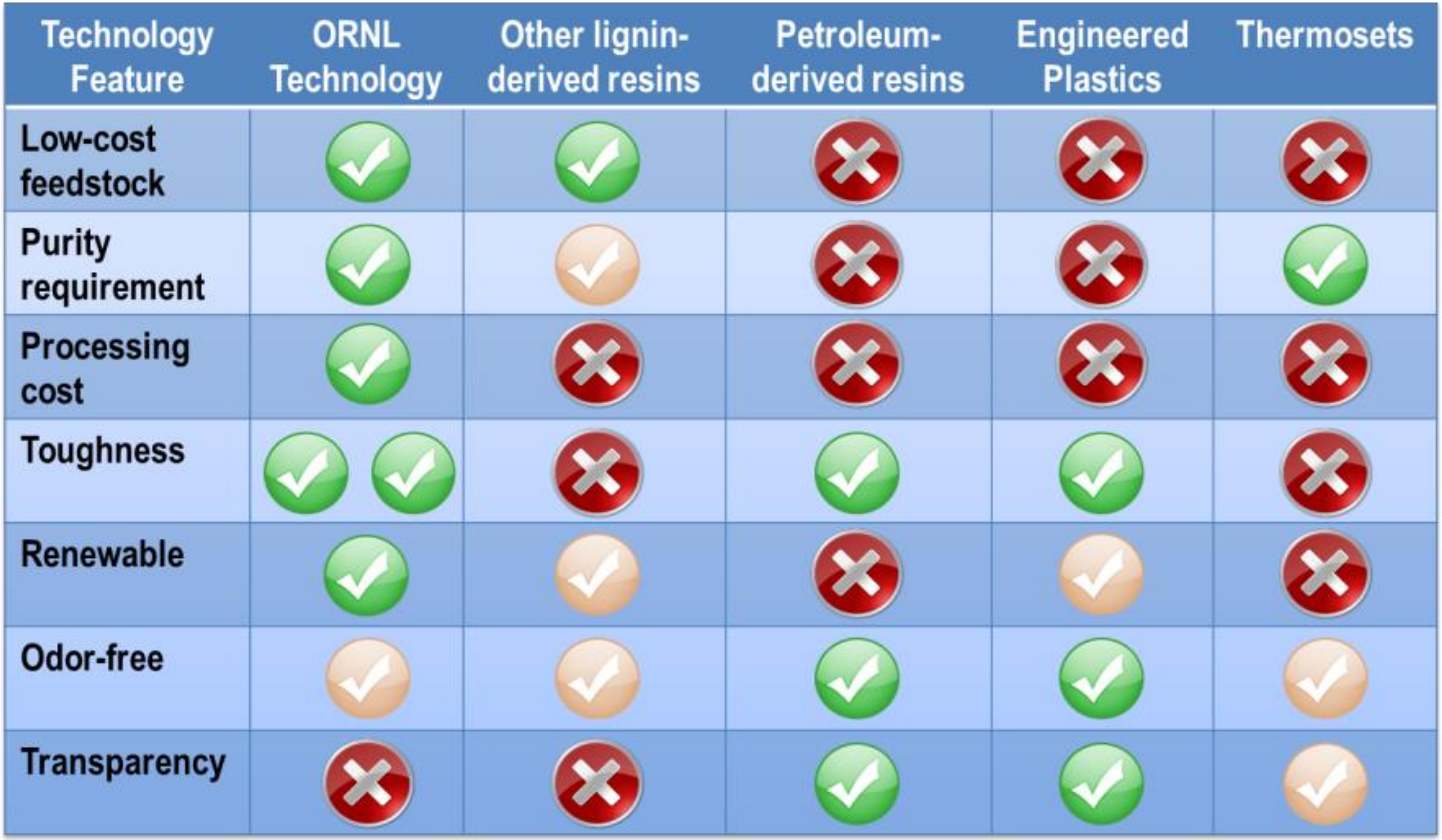
To meet the 2022 cost goal of $3/GGE, BETO aims to utilize a high-value co-product derived from lignin. A successful synthesis of novel renewable engineered thermoplastic materials will open a new pathway to biomass utilization and making such value-added materials (>$2000/metric ton, based on the preliminary estimate, see Figure in the right) is an important economic objective for future biorefineries.



- This work has produced 5 invention disclosures with 4 non-provisional patent applications filed. The background work (co-funded by ORNL's LDRD and royalty dollars) already developed a significant IP portfolio. A new product, named ABL, is being scaled up. Three companies have licensed the technology. A recent report on 3D printing resin has received tremendous interest from industries.
- The method uses reactive extrusion of lignin in combination with soft macromolecules.

4 - Relevance

Competitive Differentiation



Technology Feature	ORNL Technology	Other lignin-derived resins	Petroleum-derived resins	Engineered Plastics	Thermosets
Low-cost feedstock	✅	✅	❌	❌	❌
Purity requirement	✅	✓	❌	❌	✅
Processing cost	✅	❌	❌	❌	❌
Toughness	✅ ✅	❌	✅	✅	❌
Renewable	✅	✓	❌	✓	❌
Odor-free	✓	✓	✅	✅	✓
Transparency	❌	❌	✅	✅	✓

Lignin derivatives are commercially appealing

5 - Future Work

Main focus:

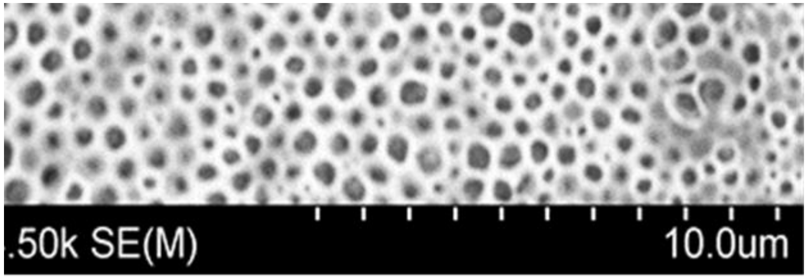
Develop high-performance lignin-based materials using source-neutral chemistry and >90% utilization of available lignin via graded functionality.

→ Discover the key links between lignin chemistry, morphological, mechanical, thermal, and rheological properties for 3D-printing and functional composite applications.

→ Produce filaments and test on a 3D-printing machine.

→ Develop the best candidate for 3D-printing, a self-healing polymer, and functional particles.

Interfacial chemistry of functional lignin to deliver soft matter with novel functionalities: shape memory, 3D printability, ultra-high toughness in composites, and hyperbranched morphology that are difficult to mimic via synthetic chemistry.



Key Pending Milestones

- **Demonstrate >50% tensile strain to failure in epoxy thermoplastic materials to ensure toughness equivalent to engineered thermoplastics. (3/30/2019)**
- **Demonstrate >15% yield during fractionation of functional lignin containing ~1 [-COOH] group per aromatic ring. (6/30/2019)**

5 - Future Work (cont'd)

Key Milestones

- Produce solvothermally upgraded functional lignin oligomer from source-neutral feedstock exhibiting direct reactive synthesis of ABL with engineering thermoplastic-like performance (>40 MPa failure strength). The lignin without upgrading shows LDPE like average mechanical performance (~20 MPa tensile strength). Thus, demonstrating 100% performance enhancement caused by lignin upgrading via solvothermal separation.
- Deliver a new group of high-performance engineering polymer products with 70% renewables in their compositions.
- Demonstrate fractionation path that enhances the value of lignin >$0.45/lb. (compared to current cost ~$0.30/lb.) as a chemical feedstock for self-healing thermoplastic elastomeric product manufacturing (50 g scale molded component). Thus, increase potential lignin value by 50%.

Scale-up Goal

- Demonstrate molding of lignin-derived high-performance products with commercial value > $4000/metric ton that assures a value of lignin residues >$990/metric ton to a biorefinery. These products include automotive interior part and siding of residential buildings.

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: Published 7 articles (1 cover art in *ACS Macro Letters*), 2 data articles; Filed 1 US patent application and 3 US patent applications are being drafted. Raised $250k non-Federal funds and established 1 CRADA, developed a composition for 3D printing and functional lignin-derivatives.

Need*:* Valorization of lignin to high-performance materials is an important economic objective for future biorefineries.

Coming up: Our future work focuses on fundamentally understanding lignin rheology, its interaction with polymer matrices, controlling morphology and performance, and developing a case for high-performance materials from biorefinery lignin.

Risk Assessment

Risk Name	Classification	Description	Probability	Risk Severity
Meeting morphology criteria for the polymer to be prepared.	Cost Schedule	Meeting structure-property-processability criteria for the polymer to be prepared for 3d printability along with functional need.	Medium	Medium
Meeting high yield functional lignin fractionation requirement.	Cost	If natural lignin does not meet high functionality need, chemical functionalization (with succinic acid or adipic acid) will be attempted.	Medium	Medium

Publications, Patents, Presentations, Awards, and Commercialization

Publications (2018)

1. Nguyen NA*, Meek KM, Bowland CC, Naskar AK*. Responsive lignin for shape memory applications, ***Polymer*** 160, 210-222 (2019).
2. 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).
3. 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).
4. 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]
5. 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).
6. Ho HC, Goswami M, Chen J, Keum JK, Naskar AK*. Amending the Structure of Renewable Carbon from Biorefinery Waste-Streams for Energy Storage Applications, ***Scientific Reports*** 8, 8355 (2018).
7. 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).
8. Nguyen NA, Meek KM, Bowland CC, Barnes SH, Naskar AK*, An acrylonitrile-butadiene-lignin renewable skin with programmable and switchable electrical conductivity for stress/strain-sensing applications, ***Macromolecules*** 51(1) 115-127 (2018).

Publications, Patents, Presentations, Awards, and Commercialization

Patents

- Naskar Ak, Nguyen NA, Shape Memory Polymer Blend Materials (ORNL ID 3857), **U.S. Patent Application No. 16/014,136** (filed on June 21, 2018).
- Naskar AK, Nguyen NA, Lignin-Based Polymers with Enhanced Melt Extrusion Ability (ORNL ID 4110), **U.S. Patent Application No.: 16/257,313** (filed on Jan 25, 2019).
- Naskar AK, Nguyen NA, Lignin-Based Polymers with Enhanced Melt Extrusion Ability (ORNL ID 3895), **U.S. Patent Application No.: 16/257,294** (filed on Jan 25, 2019).
- Naskar AK, Cui M. A Beneficial Chemical from Lignin Waste Stream and its Applications. **Patent Application No. XX/XXX,XXX** (filed on February 15, 2019).

Awards

- 2017 ORNL Inventor of the Year (A. K. Naskar)
- 2017 Outstanding Technical Paper Award CAMX 2017 (Orlando, FL; Dec 11-14, 2017)
- 2018 ORNL Post-Doc of the year (N.A. Nguyen)

Commercialization

- Based on Background IP (predates BETO sponsored work) initiated CRADA with Prisma Renewable Composites (Sponsored by UT-B LLC Royalty Funds)

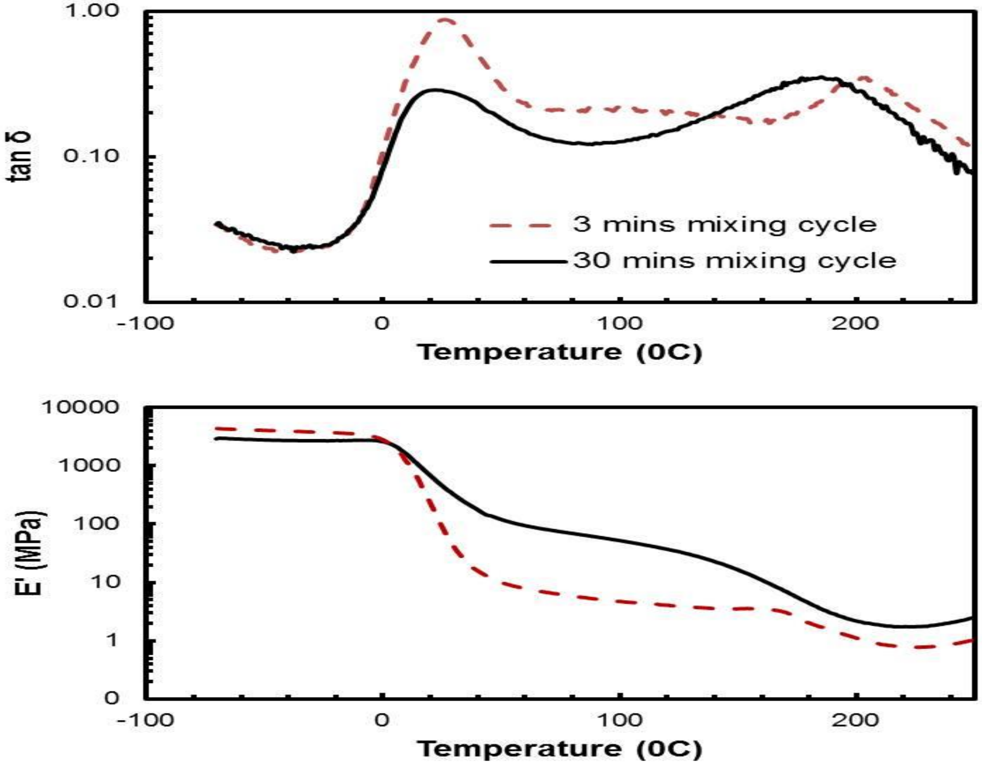
2 – Approach (Technical): How does it work?

The control on lignin product phase morphology and the performance rely on how we offer lignin to reach a solvated state (and the desired architecture) with a minimal value of lignin-matrix interaction parameter (χ). Increased time and temperature during reactive processing lower lignin-phase T_g and the volume fraction of free soft segment, also enhances the product’s modulus at 20-100°C.

Statistical thermodynamics of polymer-polymer mixing suggests free energy of mixing (ΔG_m) at temperature T:

$$\frac{\Delta G_m}{\mathrm{RT}} = \frac{V_A}{N_A} lnV_A + \frac{V_B}{N_B} lnV_B + V_A V_B \chi + \frac{\Delta}{\mathrm{R}}$$

$$\chi = \frac{V_m}{RT} (\delta_A - \delta_B)^2$$



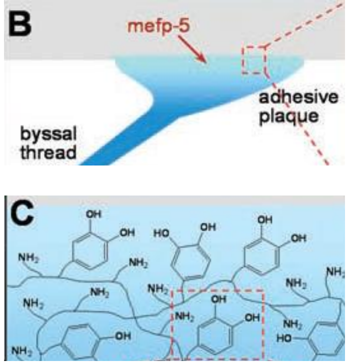
Plots of tan δ (**top**) a measure of damping characteristics of the product and E’ (**bottom**) the stiffness of the product versus temperature for mixtures of solvent fractionated Kraft softwood lignin and a reactive rubber with different mixing time at 160°C.

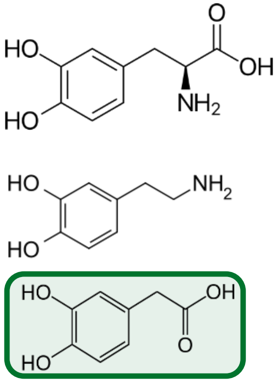
Rigid, oligomeric lignin resembles DOPAc

The only large-scale biomass source of an aromatic functionality.

From a chemistry perspective:

structurally like DOPAc

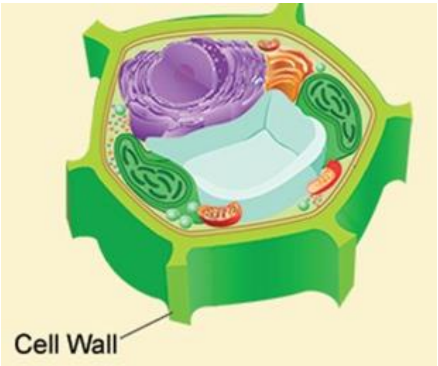




Waite et. al., *Science* **212**, 1038-1040 (1981). Lee, et. al., *Science* **318**, 426-430 (2007).

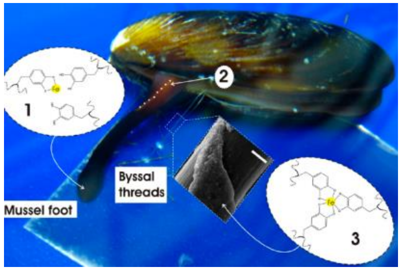
From a materials perspective:

Rigidity



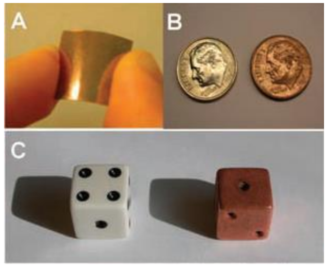
A lot of applications…

Adhesives



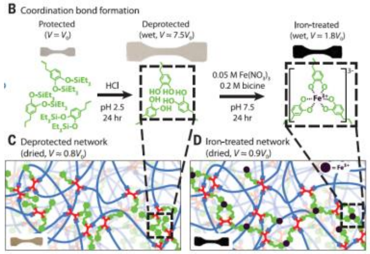
Holten-Andersen *et al.*, *P Natl Acad Sci USA* **108**, 2651-2655 (2011).

Coating



Lee, et. al., *Science* **318**, 426-430 (2007).

Tough elastomer



Filippidi et al., *Science* **358**, 502-505 (2017).

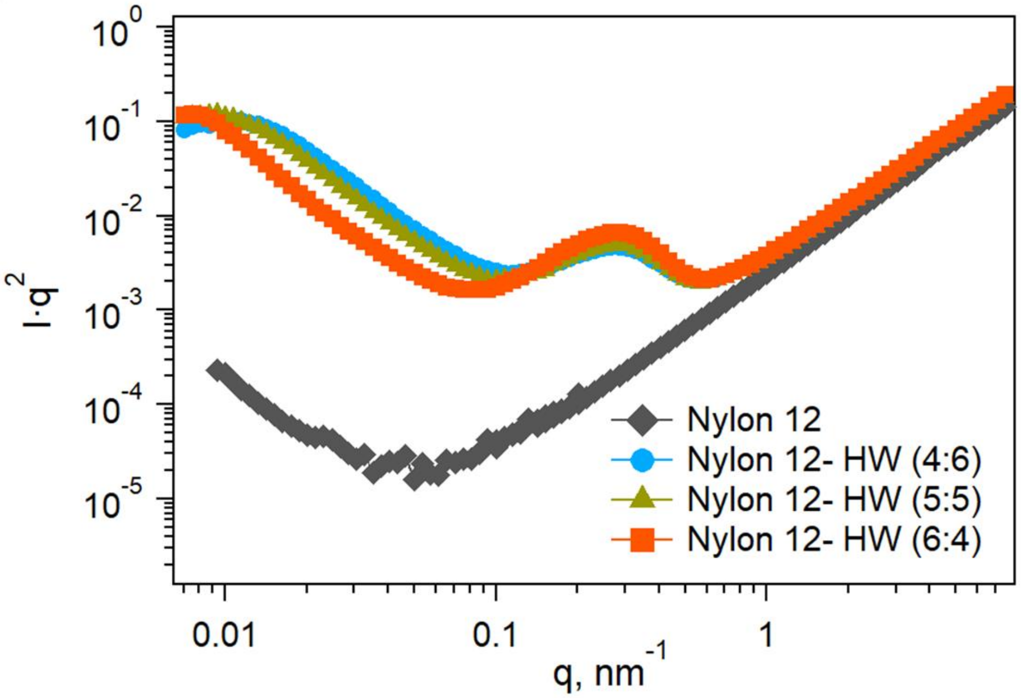
A high theoretical Young's modulus of 2.31~4.65 GPa

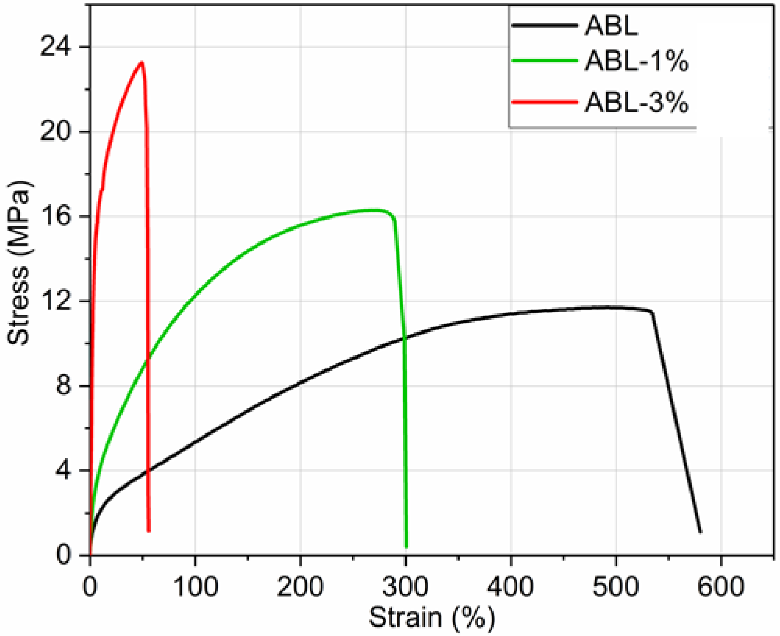
*W. Thielemans , R. P. Wool , Biomacromolecules 2005 , 6 , 1895.

Mechanical Properties of self-healing elastomers

Lignin content (wt%)	**Tg (^oC)**	**Tensile Stress (MPa)**	**Elastic Modulus (MPa)**	**Elongation at break (%)**
50	-5.4	0.96 ± 0.11	4.26 ± 0.22	1345.44 ± 2.03
55	6.9	4.48 ± 0.33	18.70 ± 1.55	2230.84 ± 432.52
58	16.8	12.20 ± 0.75	86.13± 13.21	353.58 ± 51.96
DOPAc (control)	-5.0	~0.011	~ 0.43	~230

Lignin self-assembly in the compositions





Morphology of lignin/nylon suspension. Lorentz-corrected small angle neutron scattering (SANS) data of the lignin-modified nylon samples.

Example: Enhancing performance of ABL composition

Our ability to control the dimension of dispersed lignin phase in a soft matter via matrix-lignin controlled interaction/bonding assure 90% utilization of lignin that can be isolated from any process (refinery).