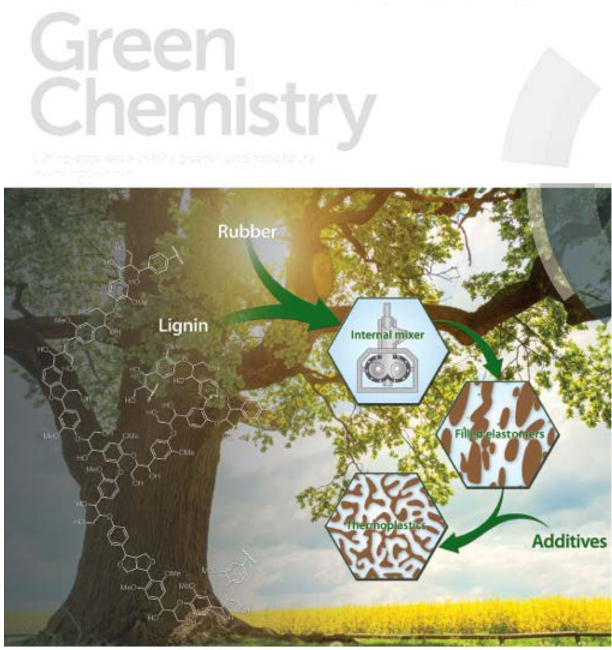
U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review



2.5.6.103 - Melt-stable engineered lignin thermoplastic: a printable resin

March 7, 2017
Thermochemical Conversion Session

Amit K. Naskar
Carbon & Composites Group
Materials Science & Technology Division
Oak Ridge National Laboratory (ORNL)

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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Overarching Goal

- ***Project goal:***
  - Produce and commercialize lignin-derived, industrial-grade composites with properties including 3D printability, rivaling current petroleum-derived alternatives.
- ***Project outcome:***
  - A novel family of commercial-ready, lignin-based 3D-printable composites. Also, suitable for high-volume applications.
  - Recyclable compositions retain their unprecedented mechanical properties.
  - Utilize unmodified lignin at ≥50 (%) volume to produce engineered plastic materials with values ranging $2000-$5000/metric ton.
- ***Relevance to 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.

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Quad Chart Overview

Timeline

- Project start date: 04/2016
- Project end date: 03/2019
- Percent complete: 25%

Budget

	Total Costs FY 12 –FY 14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY 17-Project End Date)
DOE Funded	N/A	N/A	$500k	$1500k
Project Cost Share (Comp.)*				

Barriers

- Feedstock variability
  - Difficulty with monetization of by-products and residual streams
  - Complexity of multi-step separation and purification process steps
- CapEx and OpEx associated with deconstruction of feedstock into intermediates that are then upgraded into products.
  - Inhomogeneity of intermediates causing non-uniform heat and mass transfer during the manufacturing processes
  - To apply new knowledge and tools to innovate beyond current SOT

Partners

- University of Tennessee (polymer characterization)
- Multiple lignin producers
- Other universities
- Potential end users

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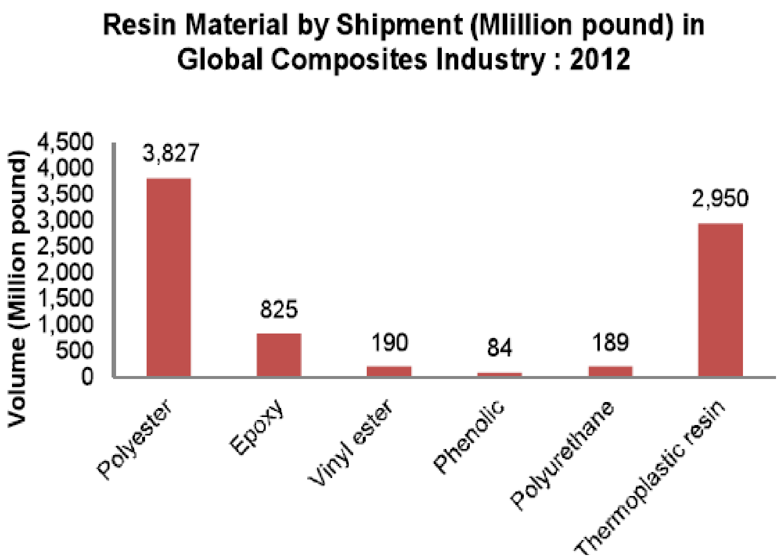
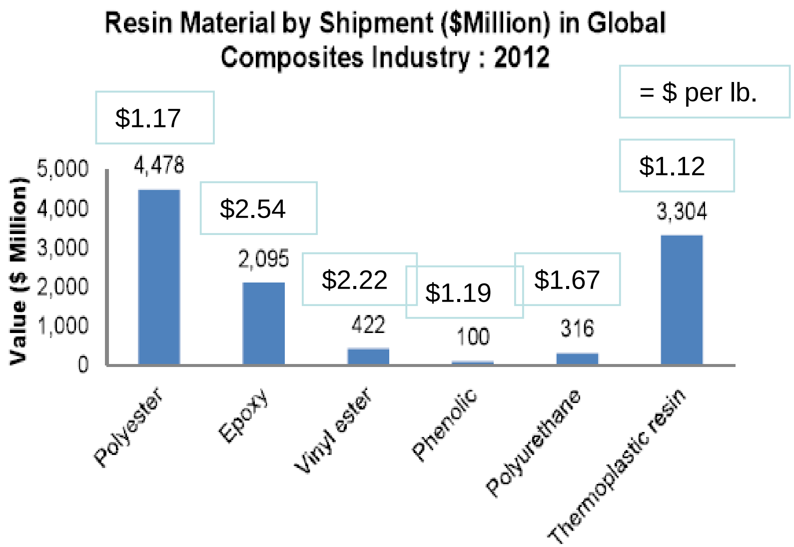
1 - Project Overview

Value proposition:





Polymer industries want alternative (styrene-free) cost-effective solutions for commodity applications.

- We aim to use lignin as substitute for styrenic polymer segment in materials.

Entire market for these materials is much larger than composites industry.

- Current Epoxy market : 2 million ton
- Current Nylon market : 7 million ton
- Current ABS market : 9 million ton (~$22 billion)
- Current PVC market : 40 million ton

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

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

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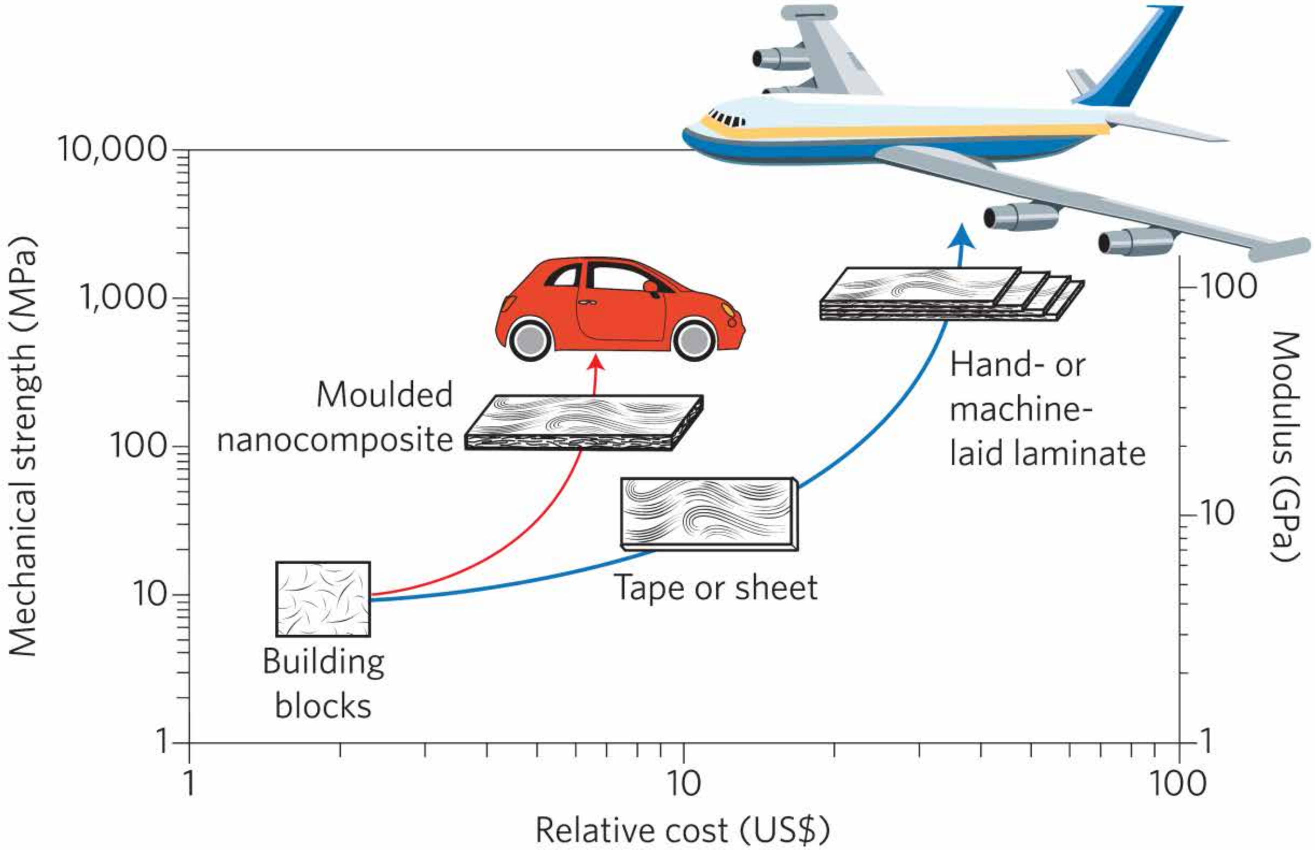
1 - Project Overview (cont'd)



Performance and cost in nanocomposite manufacturing

Naskar, et al. Nature Nanotechnology (2016)

- Attempts to reinforce soft matrices by nanoscale reinforcing agents at commercially deployable scales have been only sporadically successful to date.
- Recently, 3D networked renewable thermoplastics, based on melt-processed blends of nitrile rubber and biomass-derived rigid lignin macromer, have been developed.
    - o Organic-organic nanocomposite.

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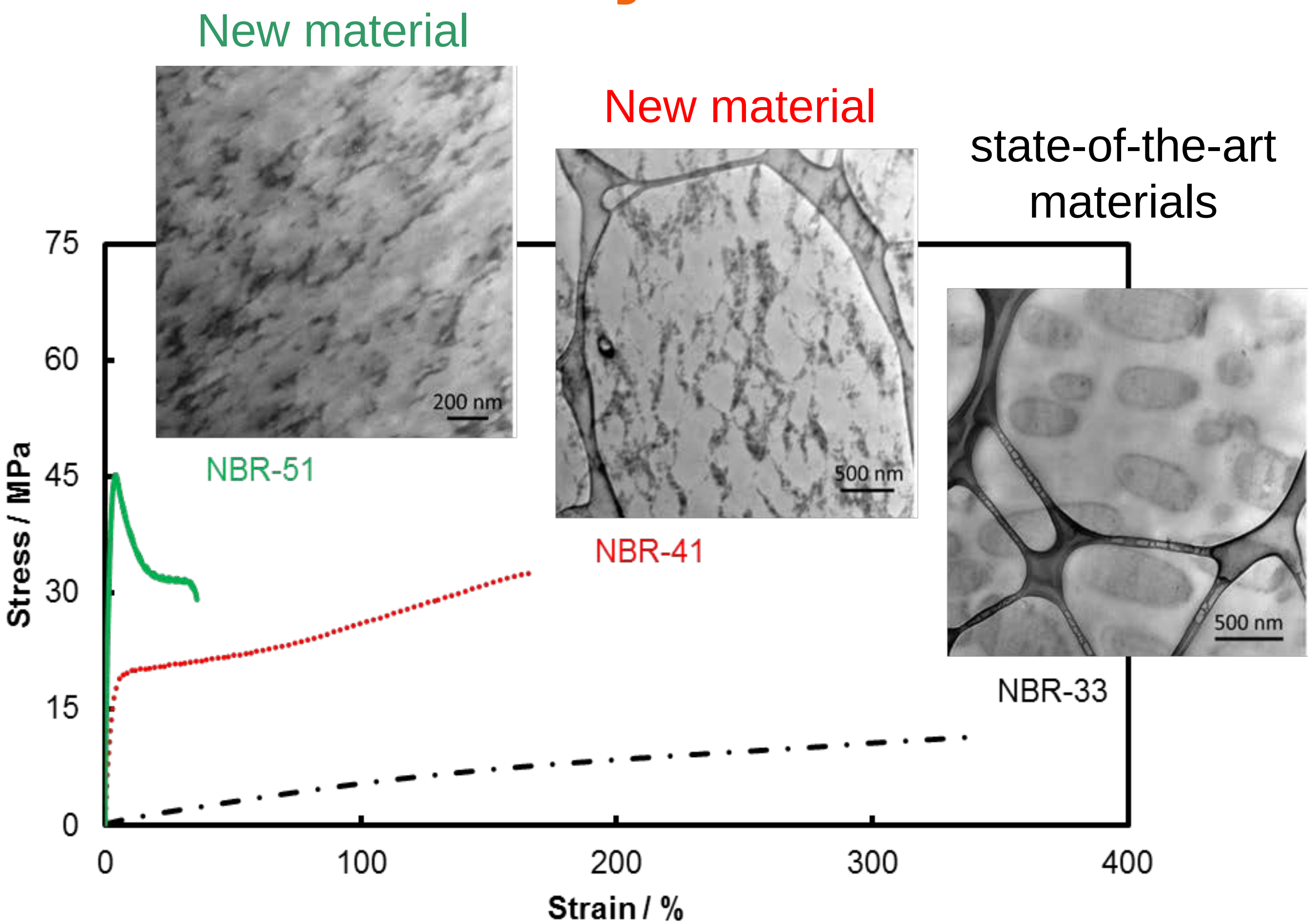
1 - Project Overview (cont'd)



ORNL developed a new methodology of extruding (solvent-free process) lignin with soft matrices that leads to outstanding performance in the product

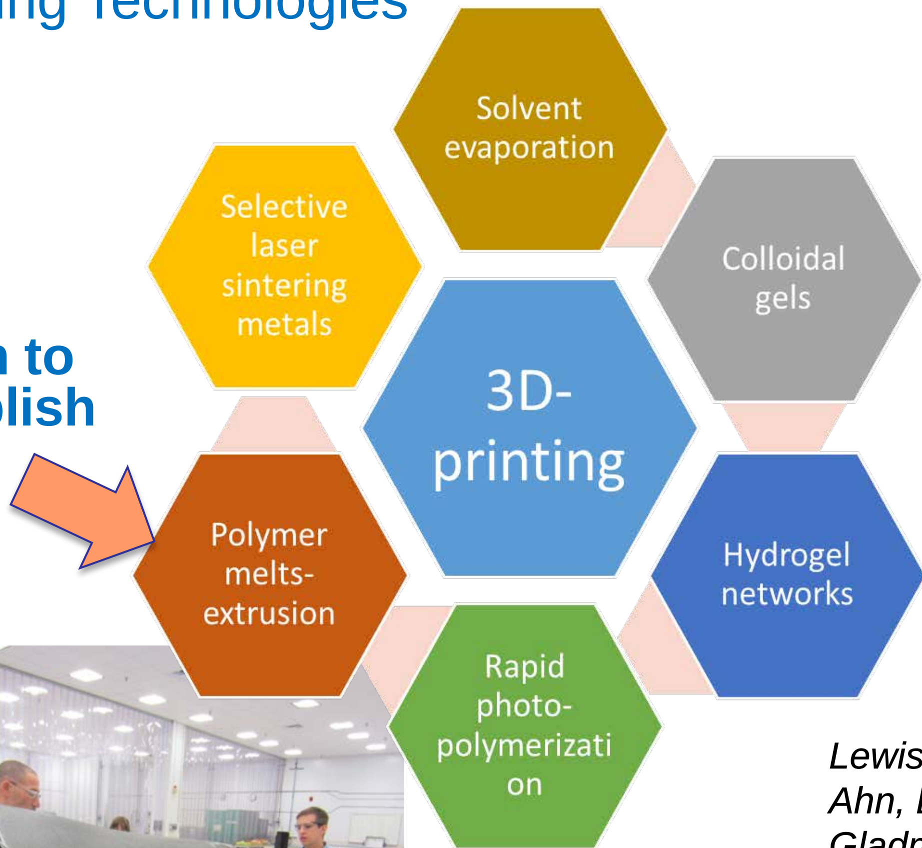
Tran et al. Advanced Functional Material (2016)0

- Lignin-based renewable thermoplastics exhibit an interconnected morphology of lignin lamellae with 6–60 nm thicknesses.
    - The composition is 10 times tougher than the commodity ABS resin.

1 - Project Overview (cont'd)

3D-Printing Technologies

We aim to accomplish



Questions to address:

- How do lignin structure and lignin extraction methods affect properties?
- What are the best lignins (chemistry) for melt-stable materials synthesis?
- Can we induce printability in this material?

Lewis, J. A. Advanced Functional Materials (2006)
Ahn, B. Y. et al. Science (2009)
Gladman, A. S., et al. Nature Materials (2016)

ORNL has developed distinguished capability in polymer extrusion-based 3D printing technology.

1- Project Overview (cont'd)

Specific Goals:

1. Investigate structures and properties of different lignin feedstocks → highly loaded lignin-based composites.
   – Isolation and characterization of melt-stable lignin from biorefinery
2. Melt-synthesize (solvent free) lignin networked polymers in various types of compositions with unprecedented performance.

   → Establish relationship: morphology-thermomechanical-rheological behavior
3. Develop lignin-based (>50% lignin loading) 3-D printable polymer materials: Make printable composites

   → Investigate thermal reprocessibility
4. Develop other functional polymeric materials → Make thermally programmable and responsive composites materials
5. Conduct techno-economic analysis for the systems after process optimization.

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2 - Approach (Management)

- **Principal Investigator:**
  - Amit K. Naskar

- **Collaborators:** (from different groups in/outside ORNL for both characterization of lignins and materials):
  - Polymer characterization lab and center for Renewable Carbon - University of Tennessee
  - Dr. Jong Keum, Dr. Jihua Chen, Dr. Yangyang Wang (User programs - ORNL)

- **Team members:**
  - Dr. Kelly M. Meek (Post-Doc, ORNL)→ Supporting lignin characterization: Mw, structures and functional groups
  - Sietske H. Barnes (Post- Master, ORNL)
  - Tony Bova (PhD student, ORNL/UT-Bredesen Center)
  - Dr. Ngoc A. Nguyen (Post-Doc, ORNL) → Developing high lignin-loaded materials with 3D-printability and thermoresponsive characteristics.

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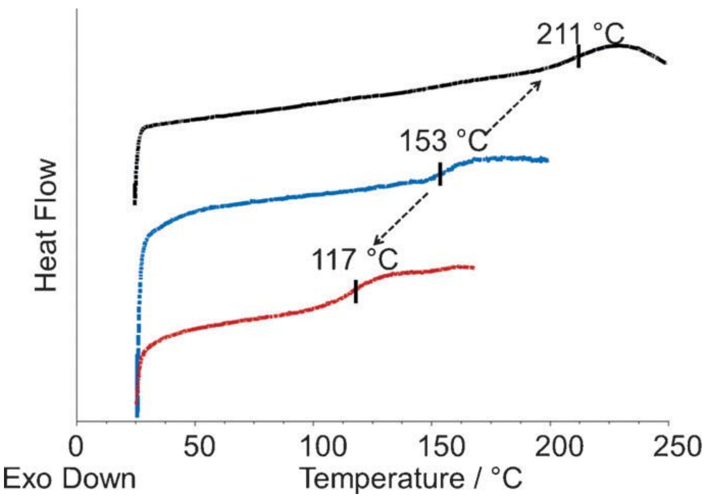
2 - Approach (Technical) **(cont'd)**

Use solvent fractionated lignins from different biomass sources:

- Hardwood (Oak, hybrid Poplar)
- Softwood (Pine)
- Switchgrass

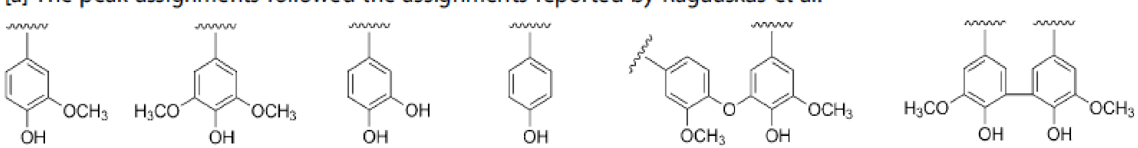
Solvent fractionation conditions offers a tool to tune Tg of lignin.



Saito et al. ChemSusChem 2014, 7, 221 – 228

δ [ppm]	Assignment	Hydroxyl group content [mmol g^{-1}] in lignin		
		as-received	MeOH-insoluble	MeOH-soluble
150.0–145.5	aliphatic OH	1.71	1.68	1.24
144.7–145.5	cyclohexanol	–	–	–
136.6–144.7	phenols	3.43	3.45	4.21
140.0–144.7	C5-substituted "condensed" and syringyl	1.57	1.84	1.83
139.0–140.0	guaiacyl	1.45	1.23	2.04
138.2–139.0	catechol	0.28	0.25	0.22
137.3–138.2	*p*-hydroxyphenol	0.17	0.11	0.10
133.6–136.6	carboxylic acid OH	0	0.18	0.25
	total OH	5.15	5.31	5.70

[a] The peak assignments followed the assignments reported by Ragauskas et al.[26]



Guaiacyl Syringyl Catechol *p*-Hydroxyphenol Examples of C5-substituted "condensed"

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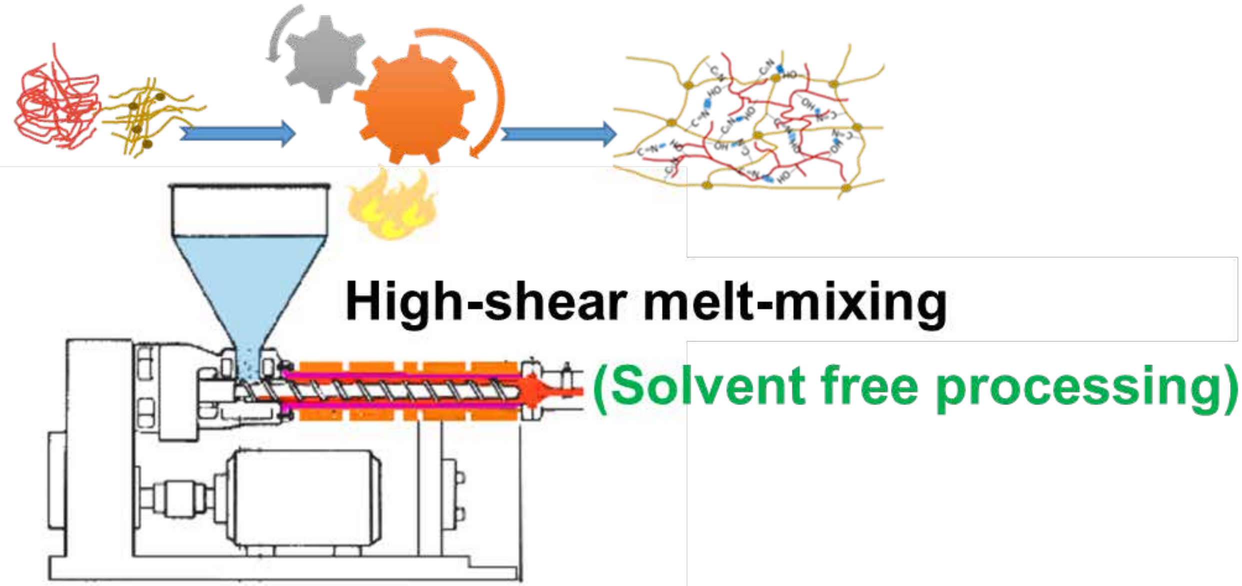
2 - Approach (Technical) (cont'd)

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).



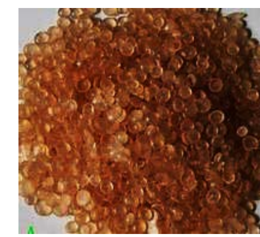
ORNL's core facilities are utilized to synthesize and characterize:
ORNL's unique macromolecular characterization capabilities (spectroscopy, microscopy, rheology, scattering) are accessed.

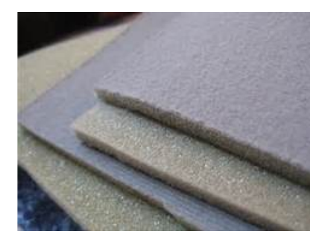
2 - Approach (Technical)

Grand Challenge:

Biorefineries and biomass processing industries want new revenue streams
Automotive part manufacturers want hydrolytically stable, uv-resistant, and renewable polymers

- Effort requires an integrated and interdisciplinary research approach involving:
    - lignin feedstock analysis (lignin rheology, reactivity, and thermal stability)
    - ability to control lignin self-assembly in polymer matrix
    - process engineering (and incorporation of printability)





Techno-Economic Analysis will be needed once tentative material formulations and applications (including extrusion process parameters) are identified.

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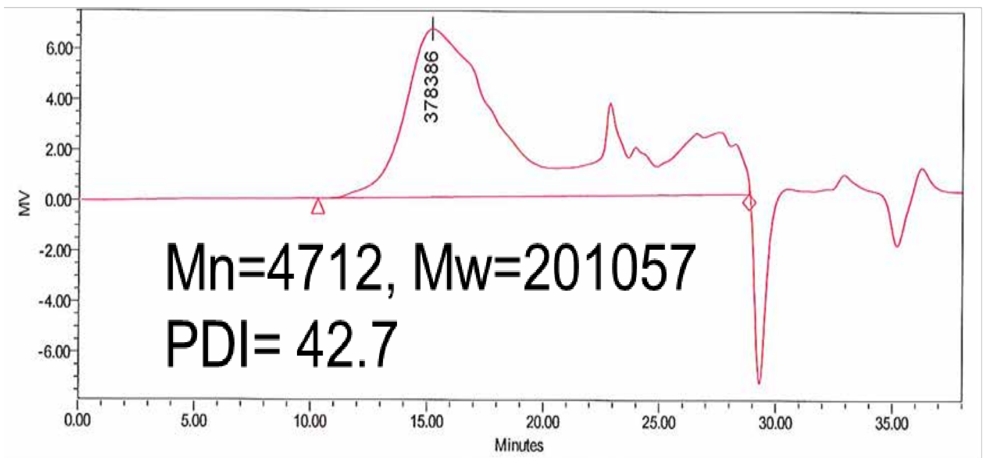
3 - Technical Accomplishments/ Progress/Results

3.1 - Lignin characterization

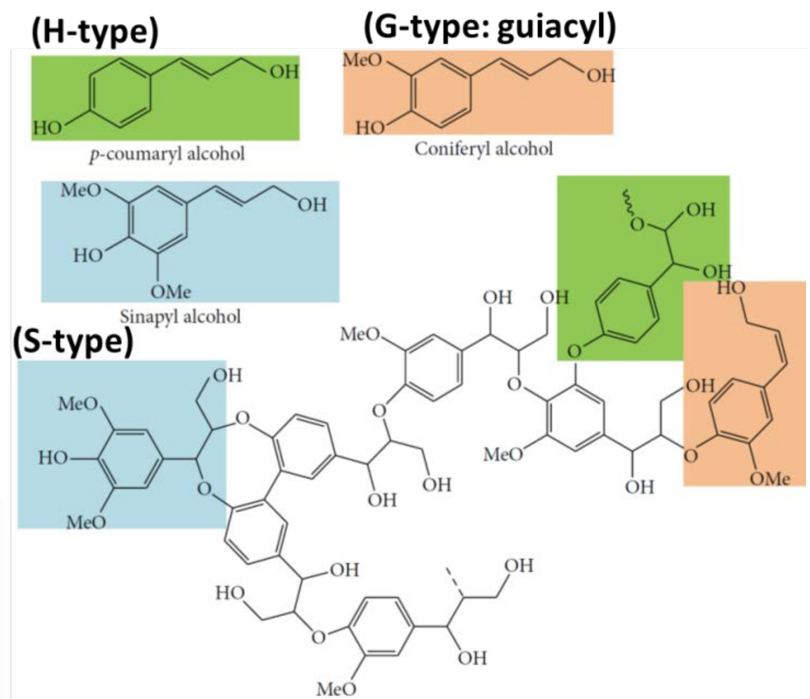
Investigate structures and properties of different lignin feedstocks
→ Utilize to make high loading lignin based composites

Produced characterization data of lignins from different biomass feedstocks

Representative data



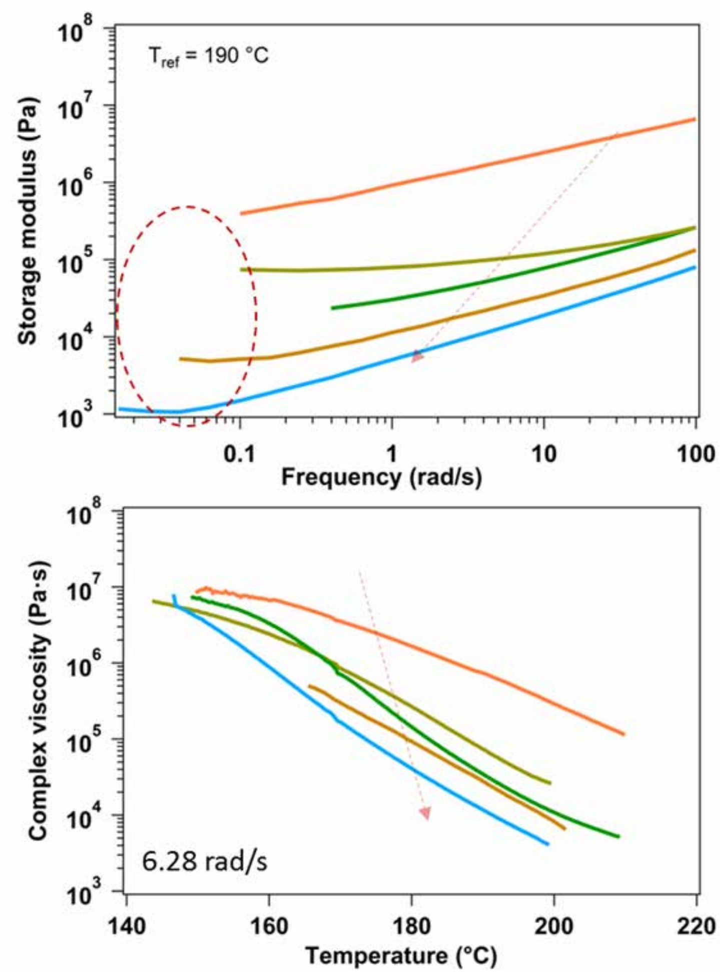
Sample	aliphatic OH	PhOH				Total OH	COOH
		5-subst	G-non condensed	H	PhOH-total		
SW-01	2.17	1.83	2.16	0.16	4.16	6.33	0.57
HW-01	1.76	3.07	0.95	0.07	4.10	5.86	0.71



Lee, H. V., et al. The Scientific World Journal (2014)
Bova, T., Naskar, A.K., et al. Green Chemistry (2016)*

3.1 - Lignin characterization (cont'd)

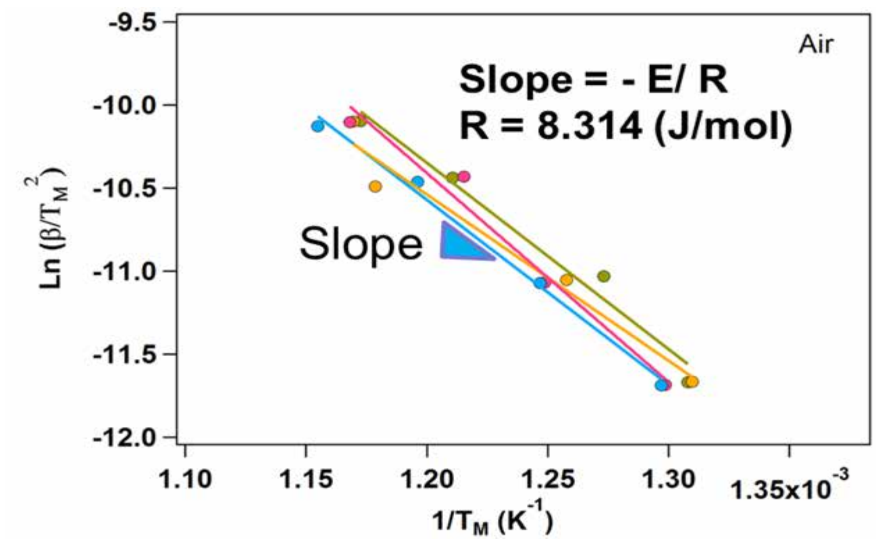
Various functional groups, hyper-branching and complicated structures, low Mw and high polydispersity index affect processibility



N. A. Nguyen et al. (unpublished data)

Varied thermal stability

Activation energy (E, KJ/ mol) - Air			
ID 1	ID 2	ID3	ID4
92.4	83.3	93.2	104.5

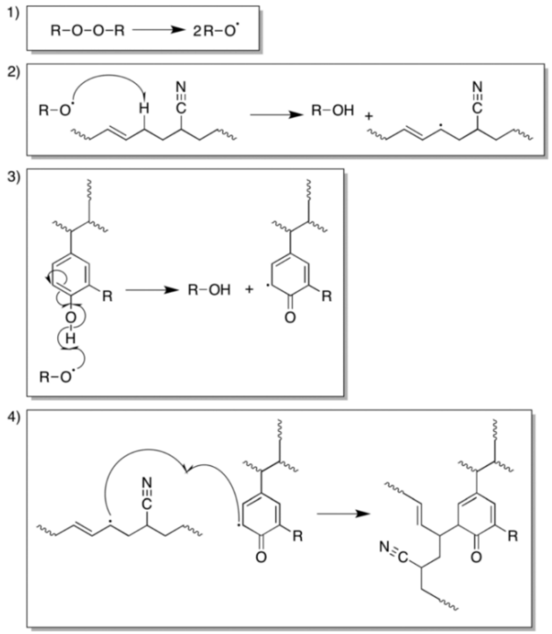


N. A. Nguyen, Naskar, A.K., et al. (in preparation)

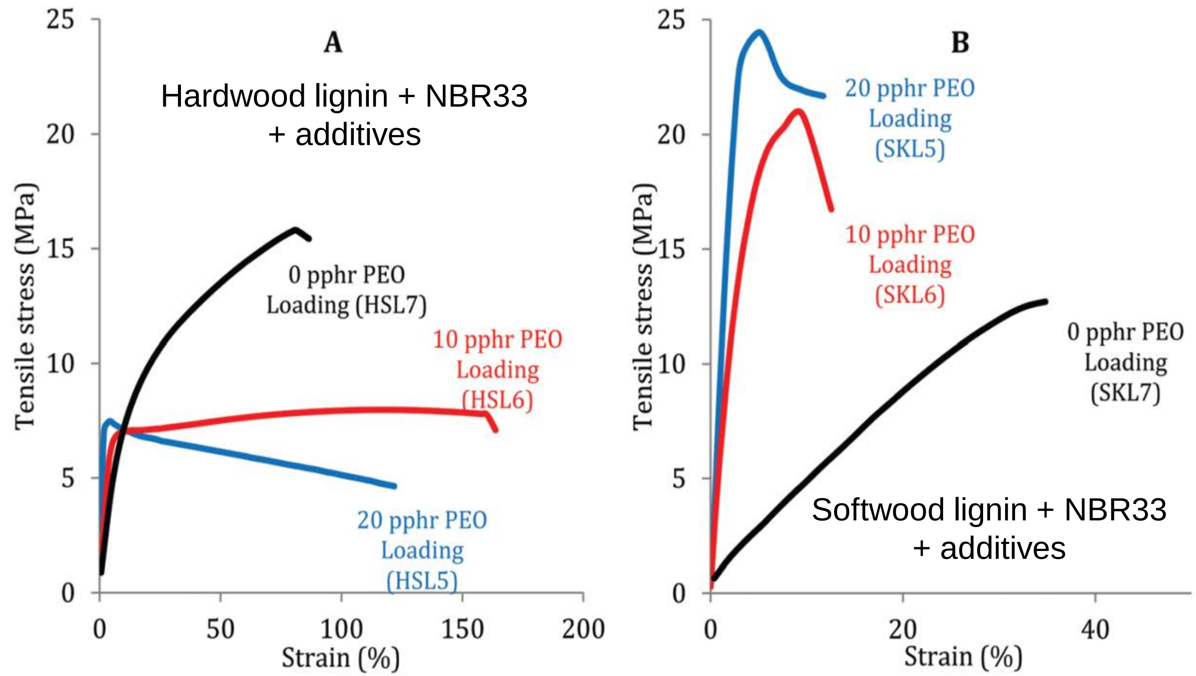
How shall we exploit this melt-stability vs. thermal reactivity?

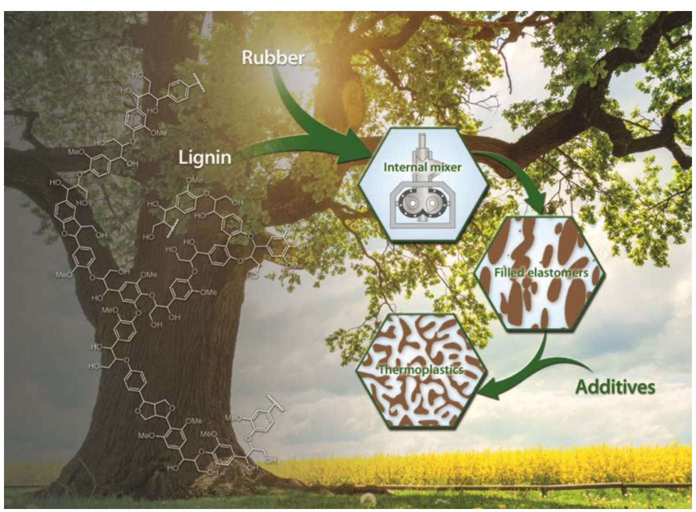
3.2 - Lignin- nitrile rubber

Melt-synthesize (solvent free) selected lignins in various types of elastomeric nitrile butadiene rubber (NBR)→ improve material performance



Effects of lignin structures and additives



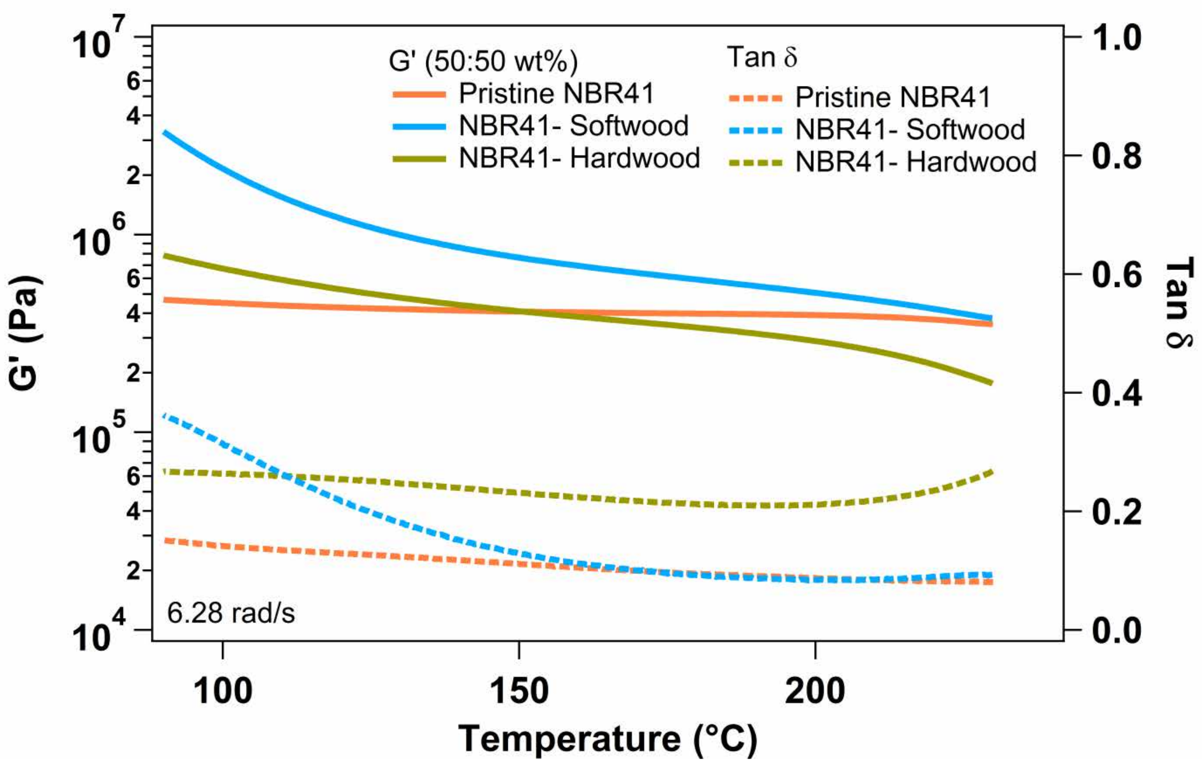


Preliminary neutron scattering data and reactivity differences offer the explanation for such contrasting results!

Bova, T., Naskar, A.K., et al. Green Chemistry (2016)

3.2 - Lignin- nitrile rubber (cont'd)

Networked material:
wide temperature independent G'



Rheology data supports higher degree of interactions between NBR and SW lignin.

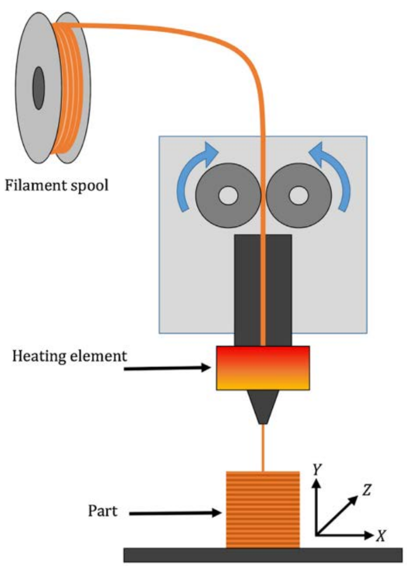
Crosslinked structures → high viscosity → offers challenges for processing

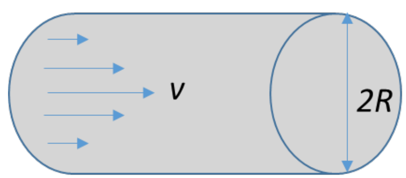
N. A. Nguyen et al. (unpublished data)

Crosslinked structures and networks may find other functional applications

3.3 - Lignin-based 3D-printable materials

Shear Thinning Behavior and Shear Rate Control → Flow properties

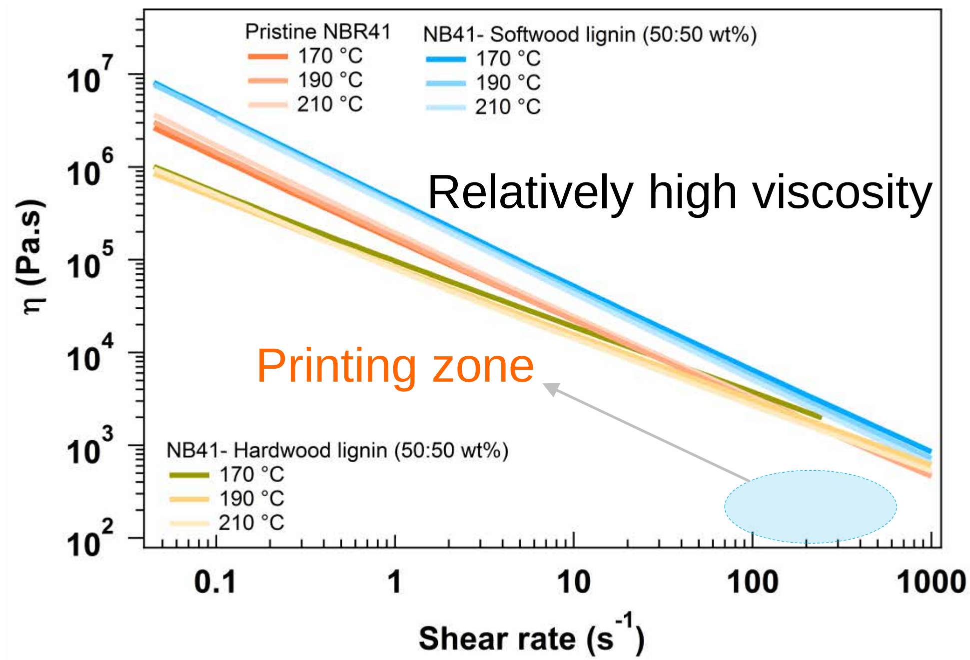




Extrusion and Capillary

$$\dot{\gamma} = \frac{4Q}{\pi R^3}, \quad Q = v \times \pi R^2 \quad \Rightarrow \quad \dot{\gamma} = \frac{4v}{R}$$

Poor printability in rubber composites



Stansbury, J. W. et al. *Dental Materials* (2016)

N. A. Nguyen et al. (unpublished data)

The team needed to find alternative solutions to address high viscosity of the reactive alloys

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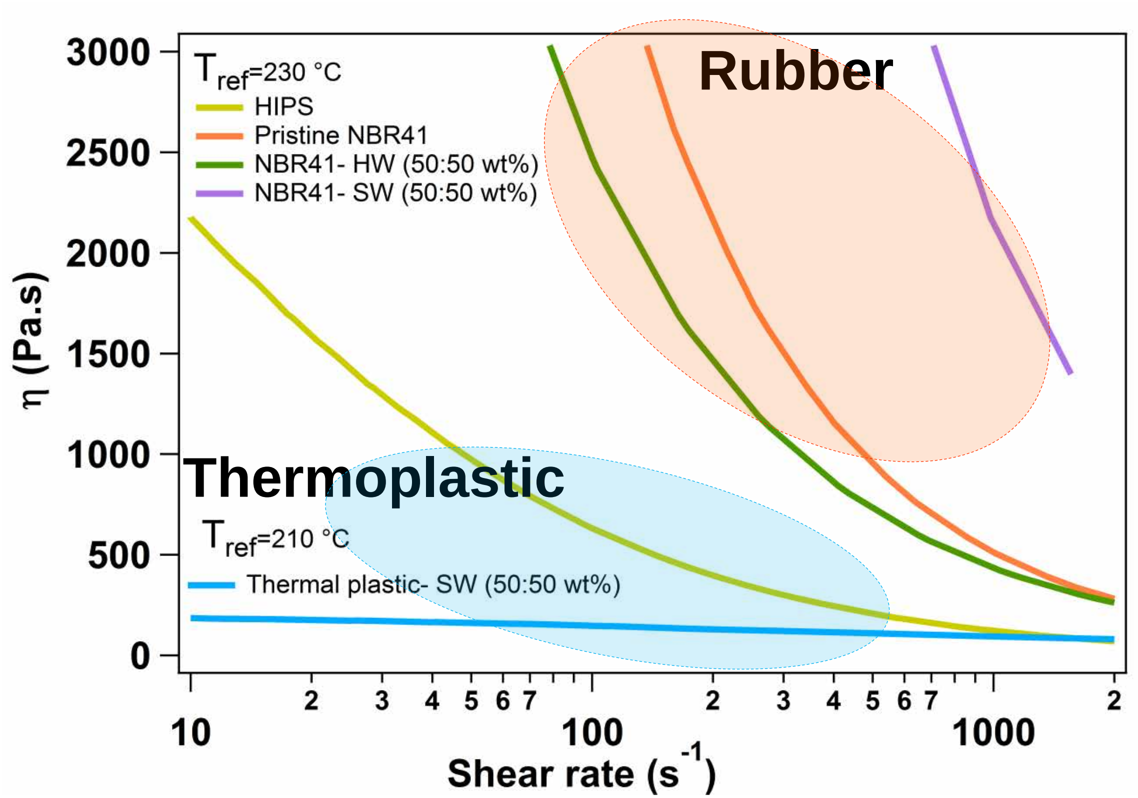
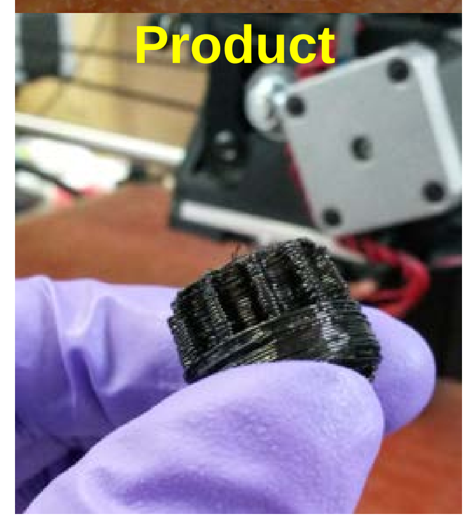
3.3 - Lignin-based 3D-printable materials (cont'd)

Better flow control in thermoplastic polymers



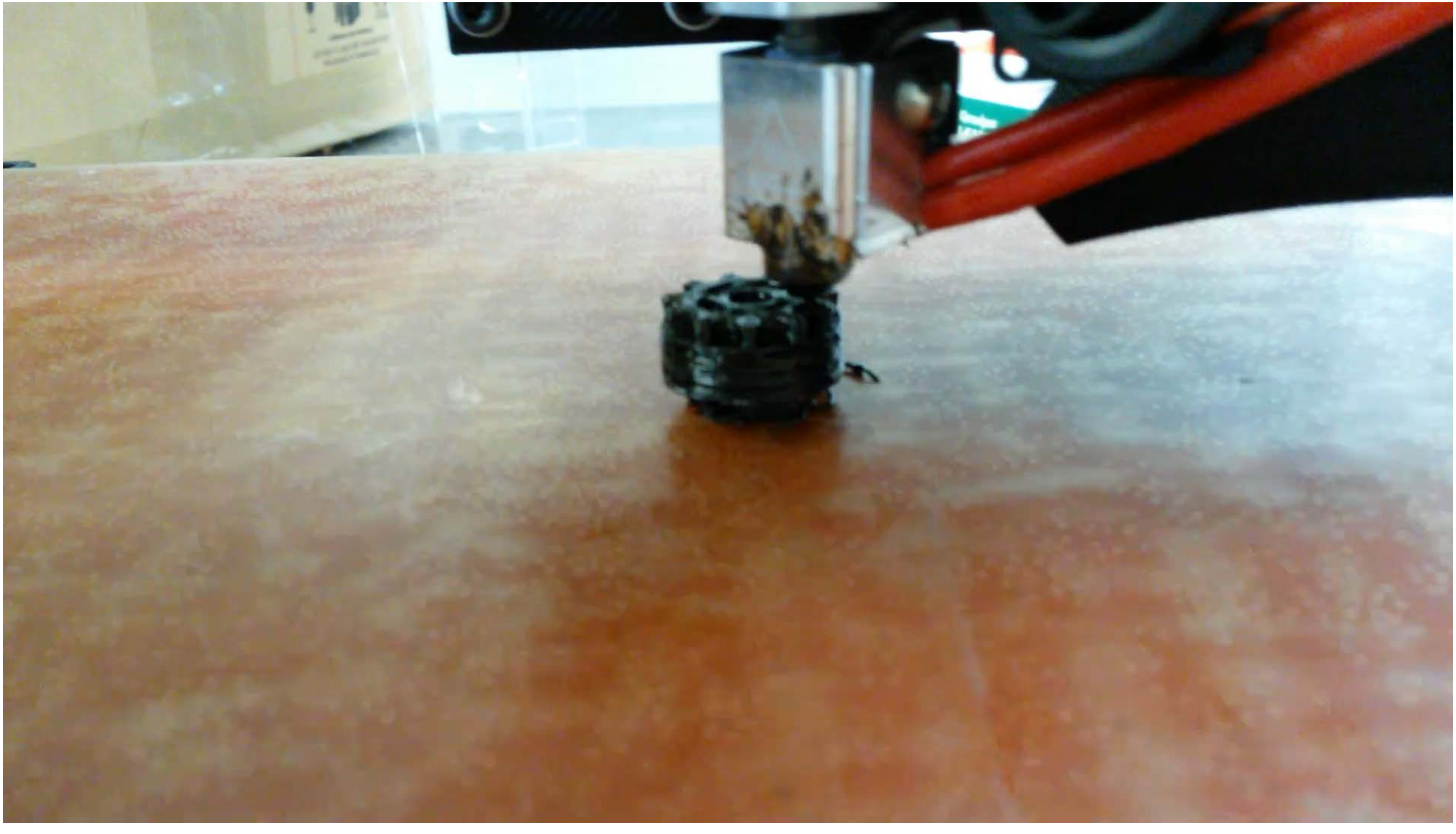
Good printability



<u>HIPS:</u> high impact polystyrene filament (recommended printing temperature: 230 °C and corresponding viscosity)

N. A. Nguyen et al. (unpublished data)

3.3 - Lignin-based 3D-printable materials (cont'd)



3.4 - Lignin-based thermo-responsive materials

What shall we do with high viscosity rubbery formulations with high elastic recovery?

Tailored material containing 50% lignin, however, show shape-memory characteristics that can be exploited for sensor, actuator, or other functionality.

Programmed Shape Fixity

3.4 - Lignin-based thermo-responsive materials (cont'd)

Shape Recovery at 100 °C

A new invention has been disclosed ORNL: ID 3857

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4 - Relevance

Goal:

- Produce and commercialize lignin-derived and industrial-grade composites. The project objective is driven by initial economic assessment that encourages 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) is an important economic objective for future biorefineries.
- This work has produced 1 invention disclosure (ORNL ID: 3857). The background work (co-funded by ORNL's royalty dollars) developed a significant IP portfolio including the product named ABL. Three companies are negotiating licensing opportunities with ORNL.
- The method uses reactive C-C coupling of lignin on rubber macromolecules.

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	✗	✗	✓	✓	(✓)

5 - Future Work

Main focus:

Developing 3D-printable materials employing selected polymers containing lignins with different functionality and having different structural characteristics

→ Discover the morphological, mechanical, thermal and rheological properties for 3D-printing applications.
→ Produce filaments and test on a 3D-printing machine
→ Develop the best candidate for 3D-printing

Key milestones
Correlate mechanical properties of polymer with of lignin functional groups.
Quantify melt viscosity of the series of polymers and report critical lignin functionality that causes polymer strength enhancement and factors that cause minimal viscosity for ease of melt-processing
Demonstrate < 5,000 Pa.s viscosity of a polymer at 100 s^{-1} shear rate. This viscosity range is required to assure printability

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5 - Future Work (cont'd)

Key milestones
Demonstrate printability of resin and produce 3D-printed "dog bone" specimen for materials characterization
Produce TEA reports based on the proposed technology that outline the cost of developing this material and quantify the impact on the biorefinery economics
Demonstrate ~100 nm lignin interphase in the matrix required for critical performance (yield stress and strain hardening) in printed specimen
Demonstrate 40 MPa tensile strength in the polymer at 50% or higher lignin, a yield stress >5 MPa, and strain hardening
Go/No-Go milestone: Demonstrate 35 MPa tensile strength in a polymer that contains 50% or higher lignin from biorefinery source and demonstrates <5,000 Pa.s viscosity at 100 s-1 shear rate. We are on the right track to demonstrate unmodified lignin filled 50% plastics with viscosity lower than that of high impact poly styrene. This is a very encouraging result and we are optimistic of obtaining better than ABS mechanical properties —35 MPa tensile failure stress.

Summary

1. Goal: We aim to produce and commercialize lignin-derived and industrial-grade composites with properties including printability, rivaling current petroleum-derived alternatives.
2. Approach: Use of lignin as a macromolecule component for reactive extrusion of rubbery matrix for a solvent-free synthesis of high performance materials.
3. Accomplishments: Published one article (cover art in Green Chemistry); developing composition for 3D printing and functional composites.
4. Need*: Valorization of lignin to high-performance materials is an important economic objective for future biorefineries.*
5. 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.

Publications, Patents, Presentations, Awards, and Commercialization

- Bova T, Tran CD, Balakshin MY, Chen J, Capanema EA, **Naskar AK***, “An Approach towards Tailoring Interfacial Structures and Properties of Multiphase Renewable Thermoplastics from Lignin–Nitrile Rubber”, ***Green Chemistry*** 18 (20), 5423-5437 (2016). [***Featured on the OUTER FRONT COVER of the issue***]
- Tran CD, Akato K, Bova T, Chen J, Keum JK, Naskar AK,* Renewable thermoplastics from lignin with exceptional properties and their composites, CAMX2016 Composites and Advanced Materials Expo, September 26-29, 2016, Anaheim, California. Outstanding Technical Paper Award.
- Tunable Thermo-responsive Properties of Renewable Composites (ORNL ID: 3857)
- The work (co-funded by ORNL’s royalty dollars) has developed a significant IP portfolio including the product named ABL. Three companies have already applied for licensing and two others are discussing this with ORNL.