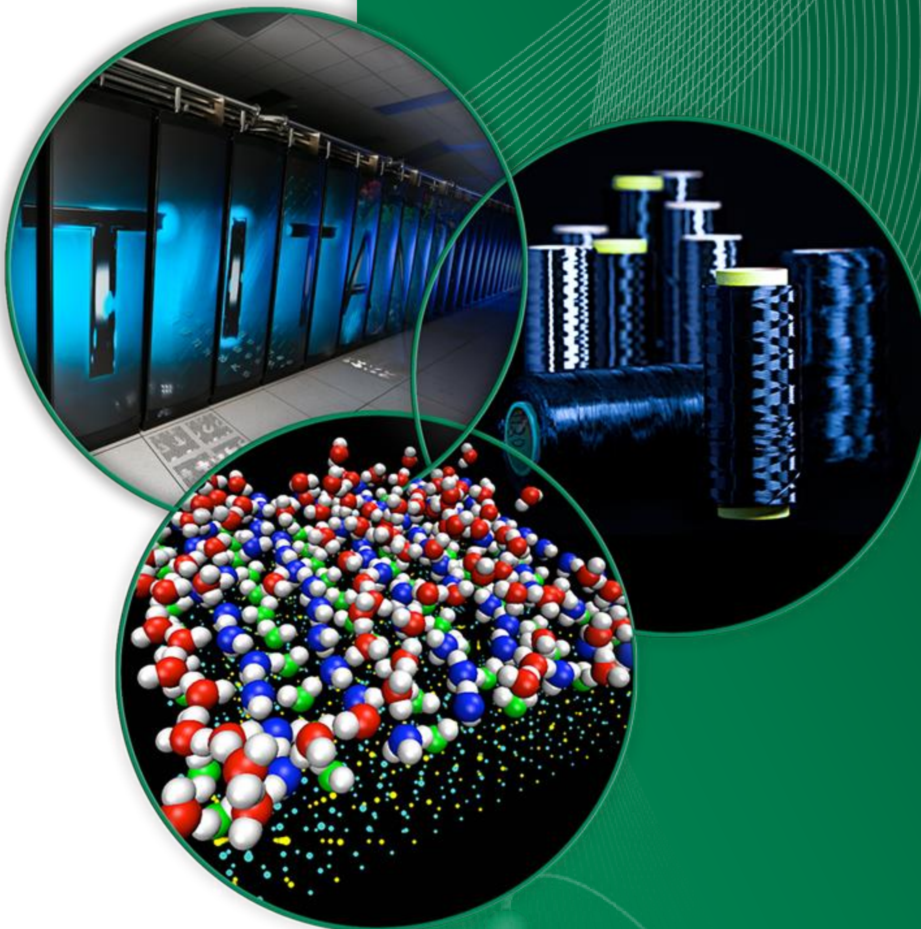
Performance-enhanced polymeric products from lignin



Presented to
Bioeconomy2017
Session — "The Lignin Renaissance: New Approaches to a Century-Old Opportunity"

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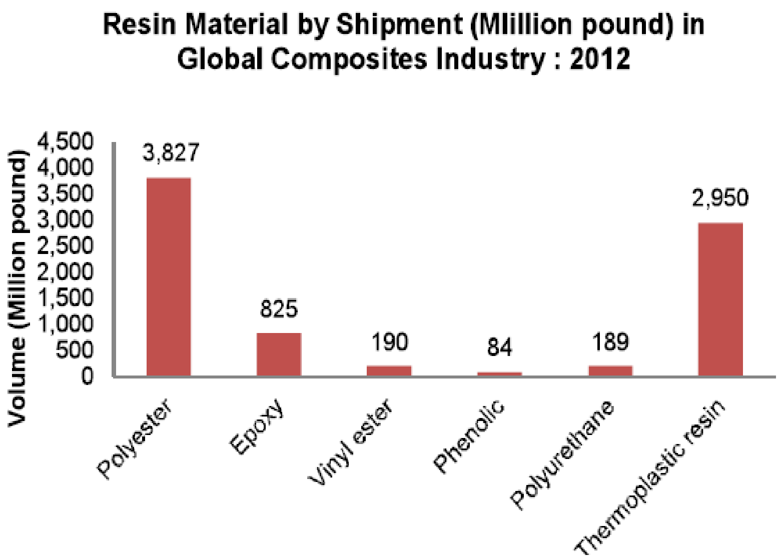
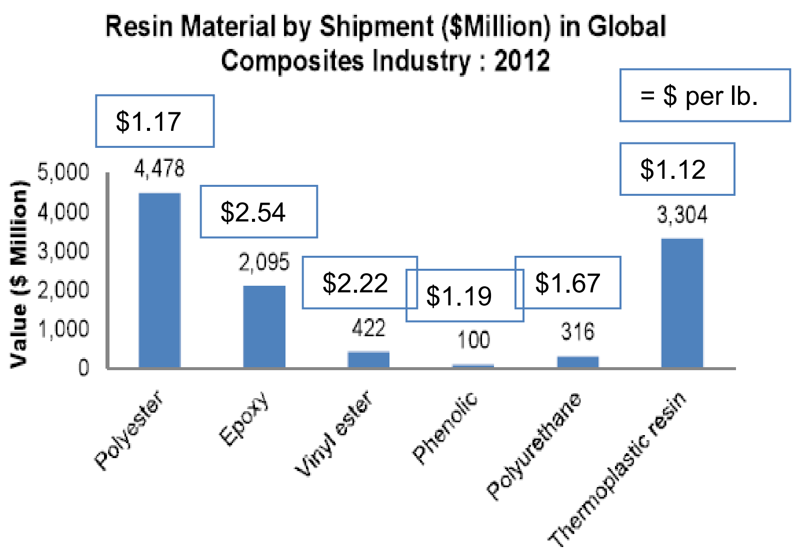
Value proposition





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

Market Opportunity

2002 THERMOPLASTIC MARKET
$46.9 B

2012 THERMOPLASTIC MARKET
$87.1 B

TARGET MARKETS

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

Long-term goal

Produce and commercialize lignin-derived industrial-grade fibers, polymers, and their composites, with properties rivaling current petroleum-derived alternatives.

Barriers:

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

Physical characteristics of lignins

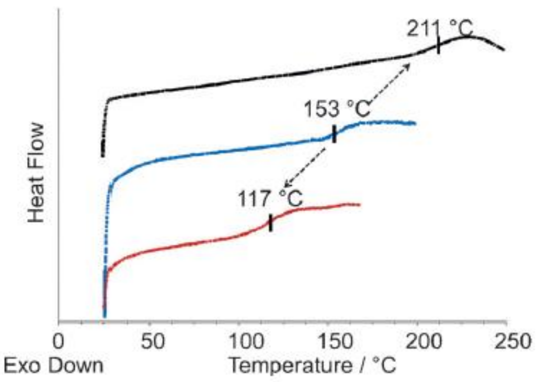
Glassy to rubbery transition : 90 – 200 °C
Some lignins do not exhibit a Tg

Melt viscosity (at 150 – 200 °C): 100 – 5000 Pa.s
Some lignins are not melt-processable. Thermal crosslinking and degradation often cause increase in viscosity of the lignins.

Theoretical Young's modulus: [a] 2.31– 4.65 GPa
PE, PP (1 – 2 GPa), Nylon, PET (2 – 3 GPa),
PS, PVC (2 – 4 GPa)

Molecular weights: 1000 – 5000 Da
(depends on lignin isolation methods used)

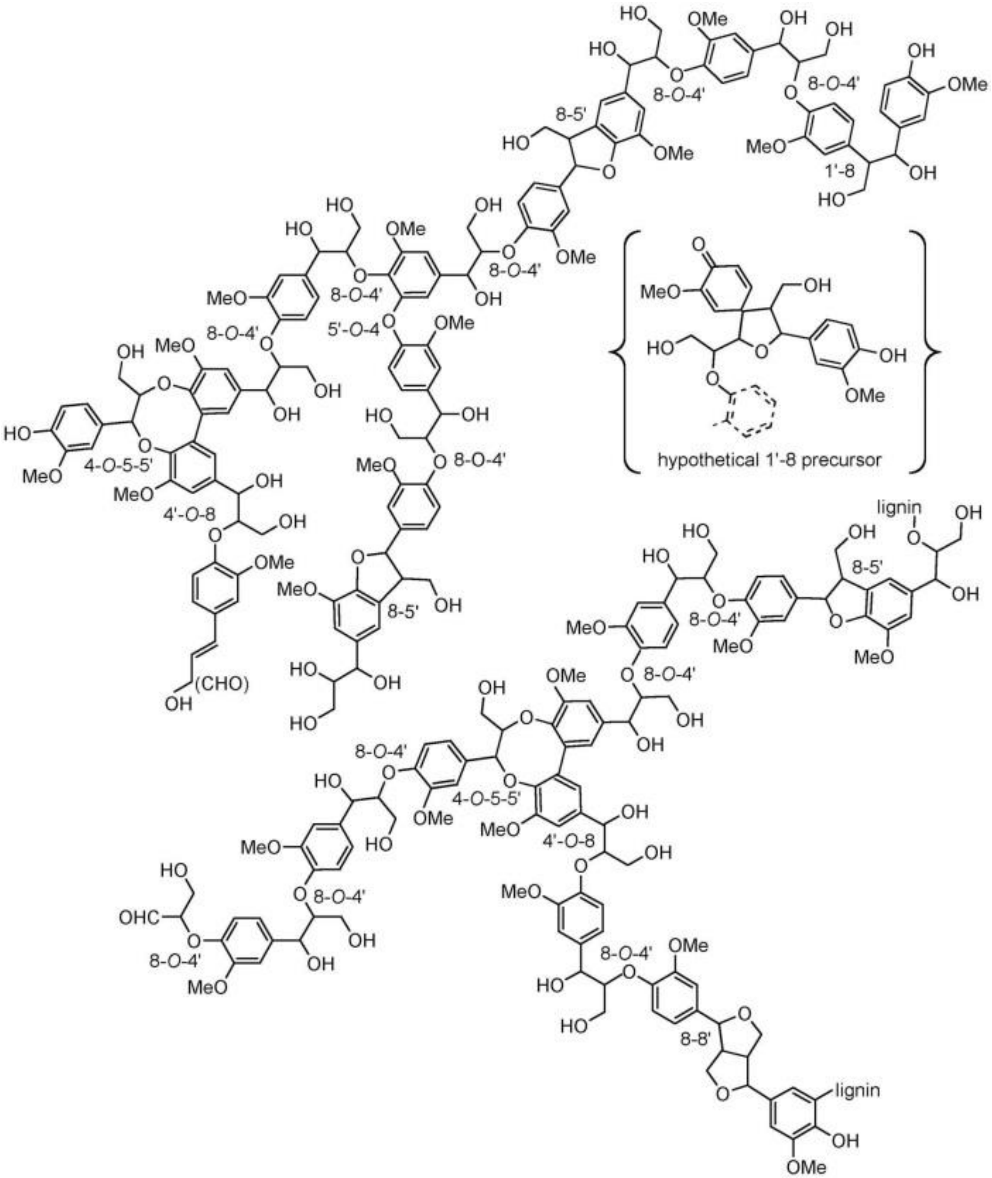
Solubility parameters: [b] 24.3 – 24.6 $MPa^{1/2}$



Isolated lignins have different fractions with variable degrees of functionalities

[a] T. Elder, Biomacromolecules, 2007, 8, 3619–3627
[b] W. Thielemans , R. P. Wool , Biomacromolecules 2005 , 6 , 1895.

Architecture of lignin molecules



Small angle neutron scattering of lignin in solution suggests dissolved lignins' spherical structures consisting of cylindrical building blocks.

With increase in lignin concentration, dimension of cylinders decrease and molecular self-assembly takes 2D shape.

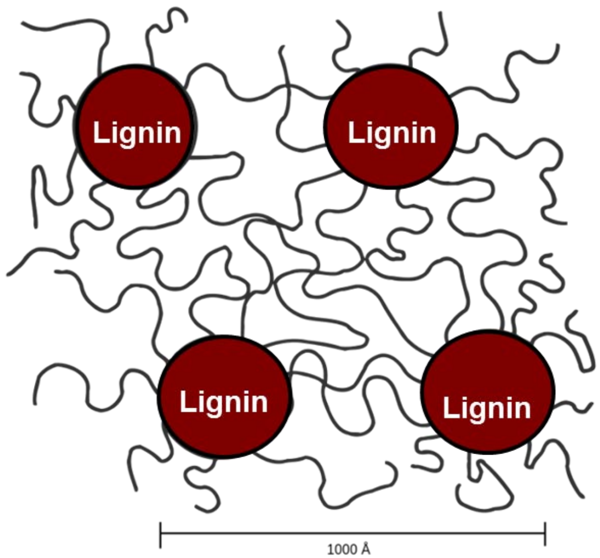
Cylinders of 1 – 2 nm diameter and 2 – 10 nm length. Radii of gyration of the assembly are in the range of 50 – 100 nm.

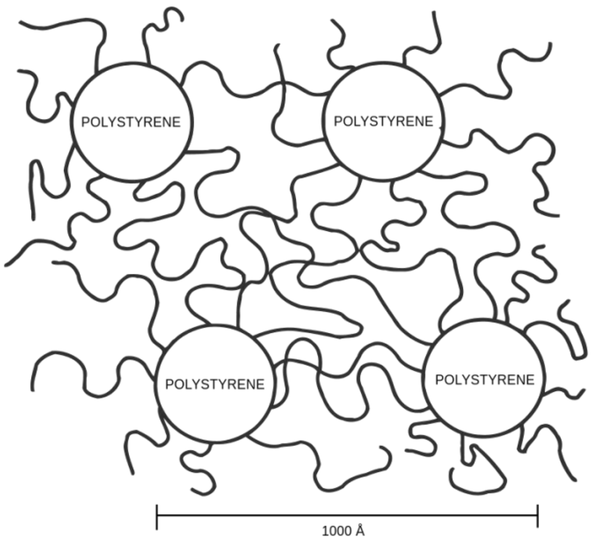
Imel et al. *ACS Appl. Mater. Interfaces* 2016, 8, 3200−3207.
Ratnaweera et al. RSC Adv., 2015, 5, 67258–67266.

Can we retain nanoscale dispersion of lignin in a polymer matrix through irreversible interaction?

The mechanical properties of high-performance commercial copolymer materials like poly(styrene-butadiene-styrene) (SBS) originates from their nanoscale morphology and chemical makeup.

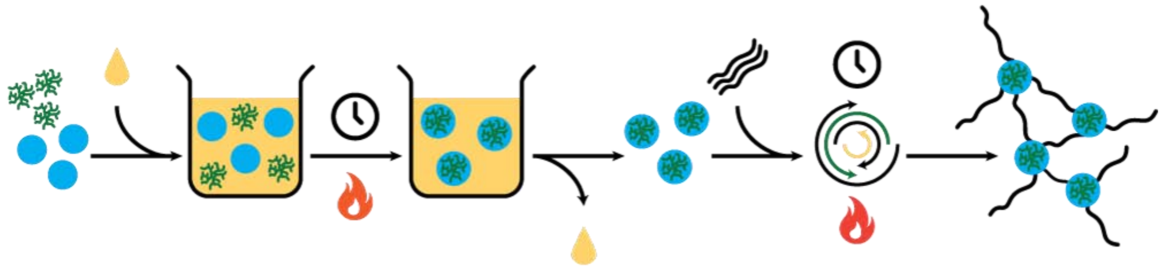
Can we formulate lignin analogue by replacing styrene?



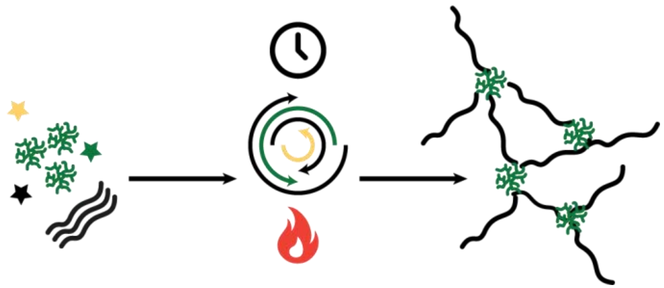


N. R. Legge , G. Holden , H. E. Schroeder , in *Thermoplastic Elastomers: A Comprehensive Review*, Hanser Publishers , Munich, Germany 1987 , p. 47.

Approach

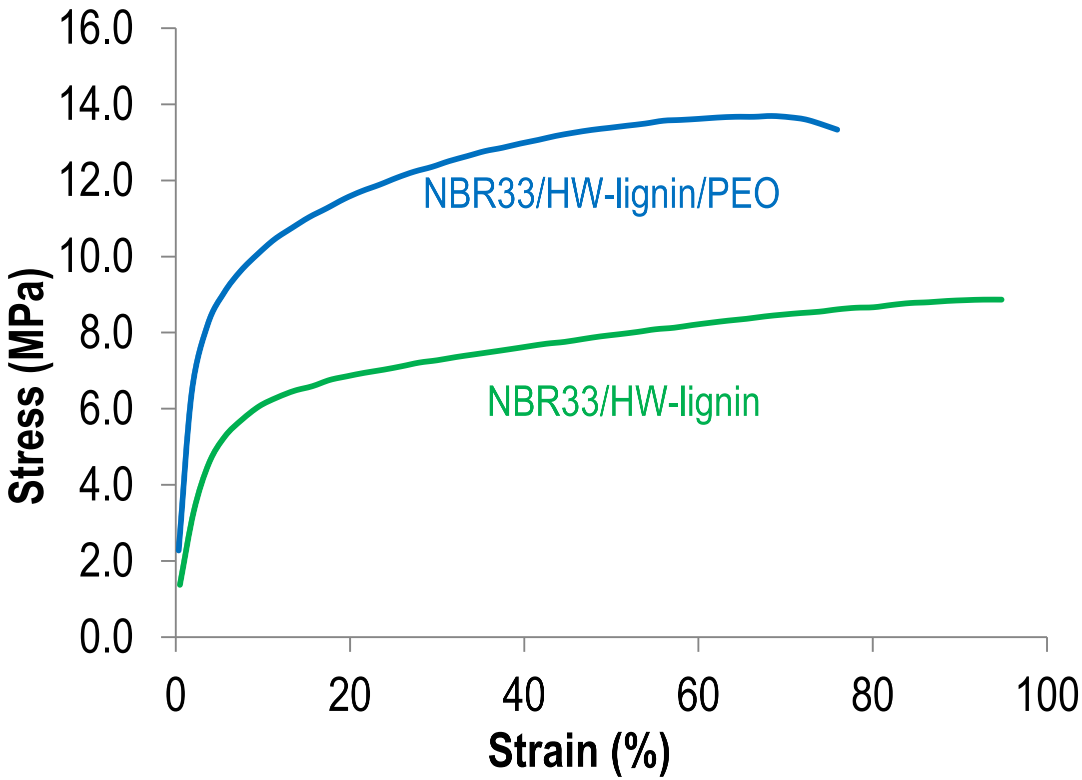


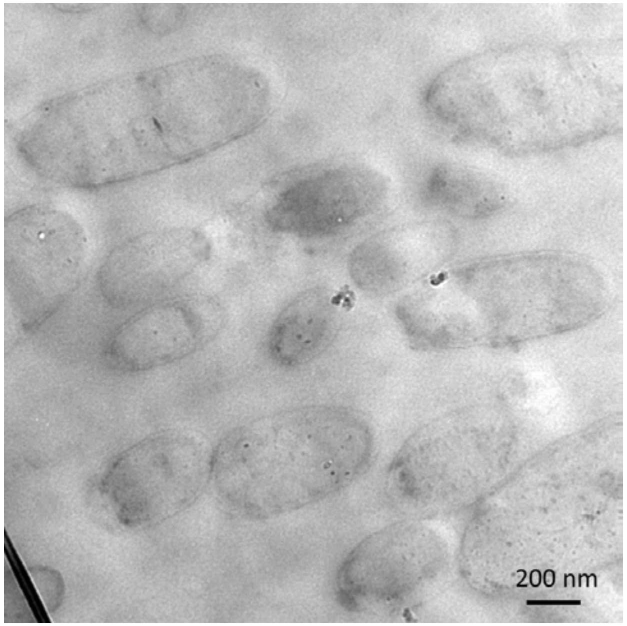
Conventional methods to create lignin–polymer blends or multiphase lignin copolymers required batch chemical modification of lignin in organic solvents, creating waste, followed by reaction with other organic polymer substrates in solution or melt.



Our method involves the proper selection of host polymer and/or additives in the molten state to form unique polymer morphologies having superior performance in a semi-continuous operation without the use of solvents.

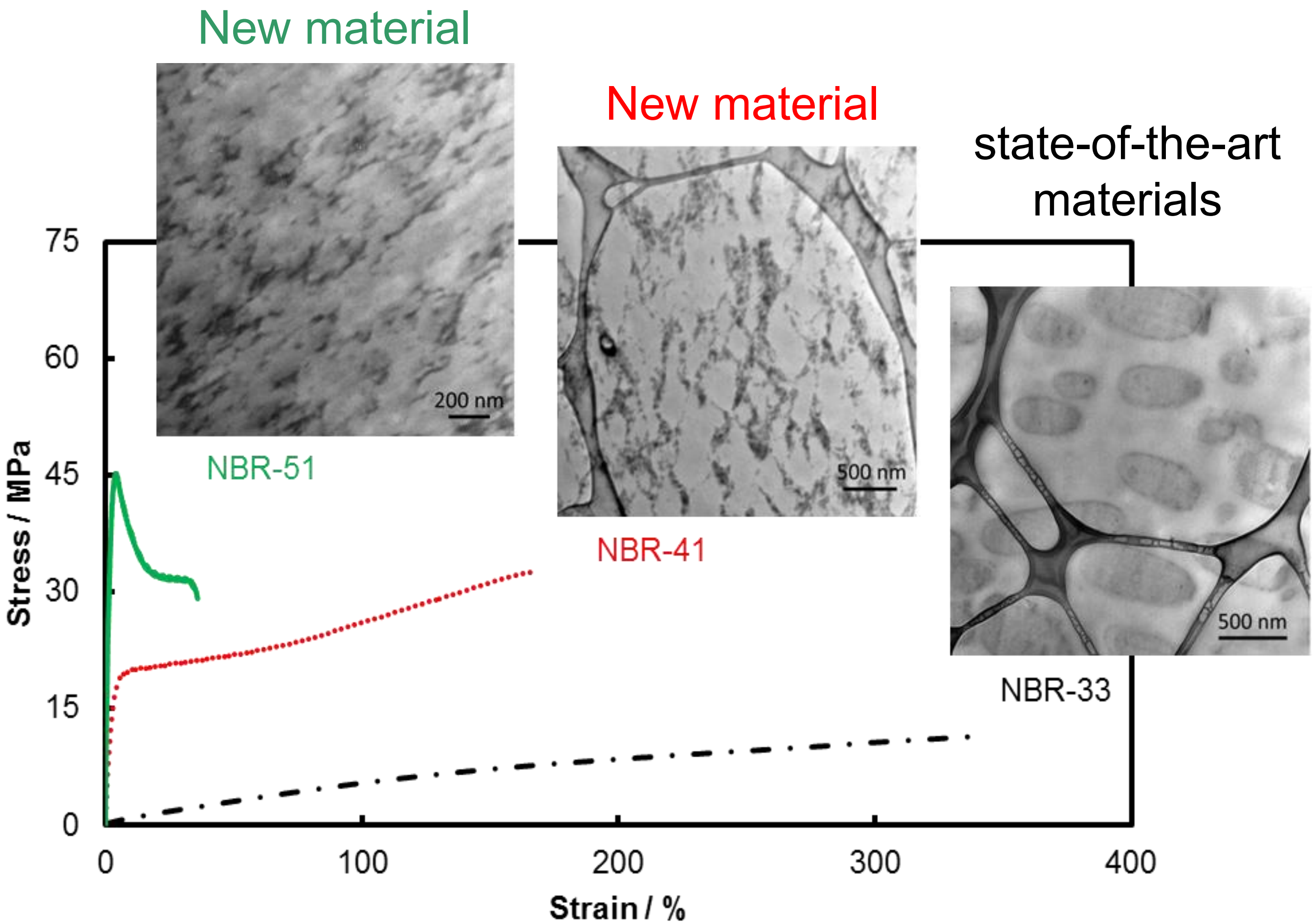
Mechanical performance of reactively extruded products





Representative tensile stress–strain plots of nitrile rubber, reactive blends containing hardwood lignin and transmission electron micrograph of the compound.

Enhancing mechanical performance of reactively extruded products and formation of ABL material

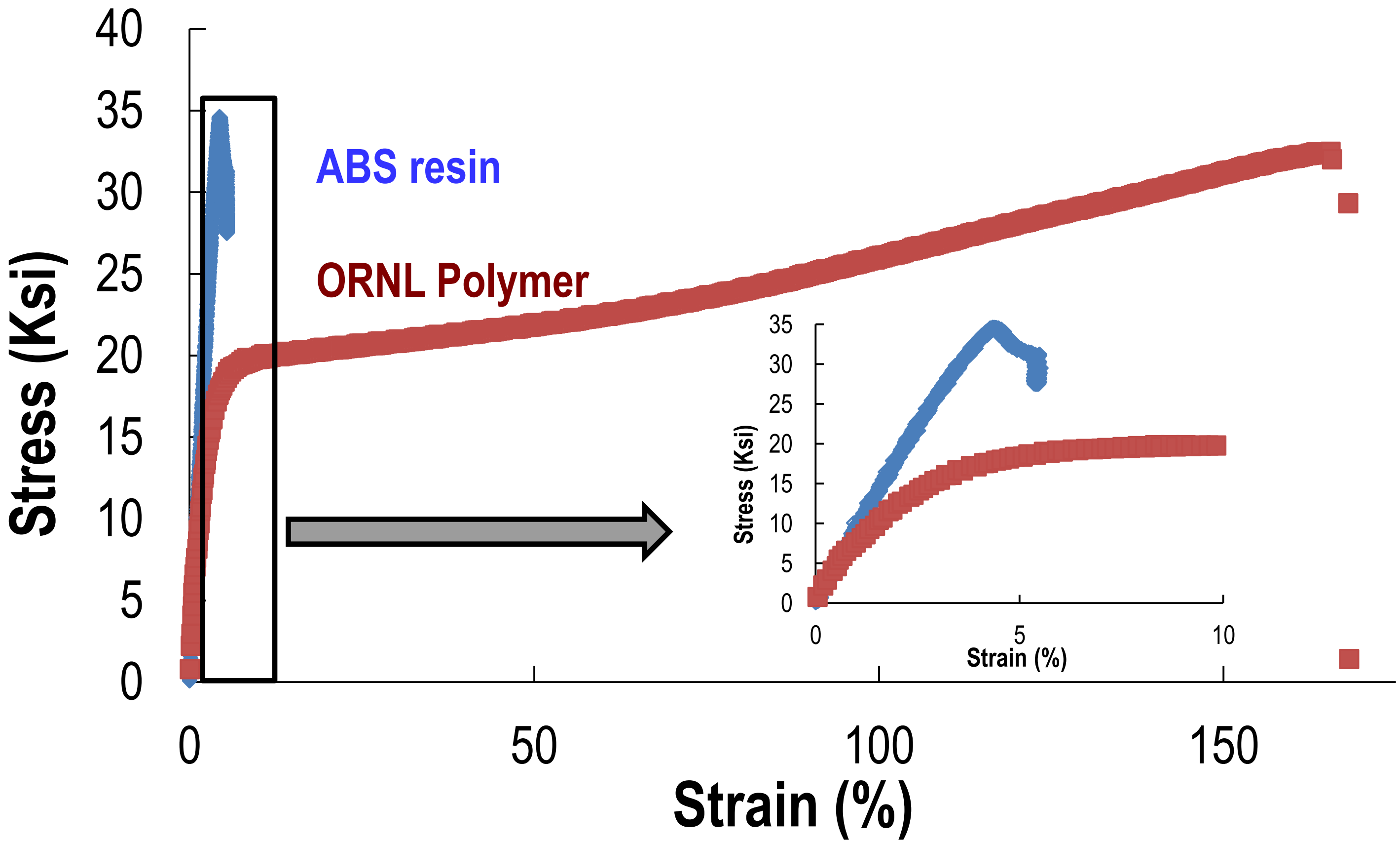


Recently developed methodology of extruding (solvent-free process) lignin with soft matrices that leads to outstanding performance in the product.

Lignin-based renewable thermoplastics exhibit an interconnected morphology of lignin lamellae with 6–60 nm thicknesses.

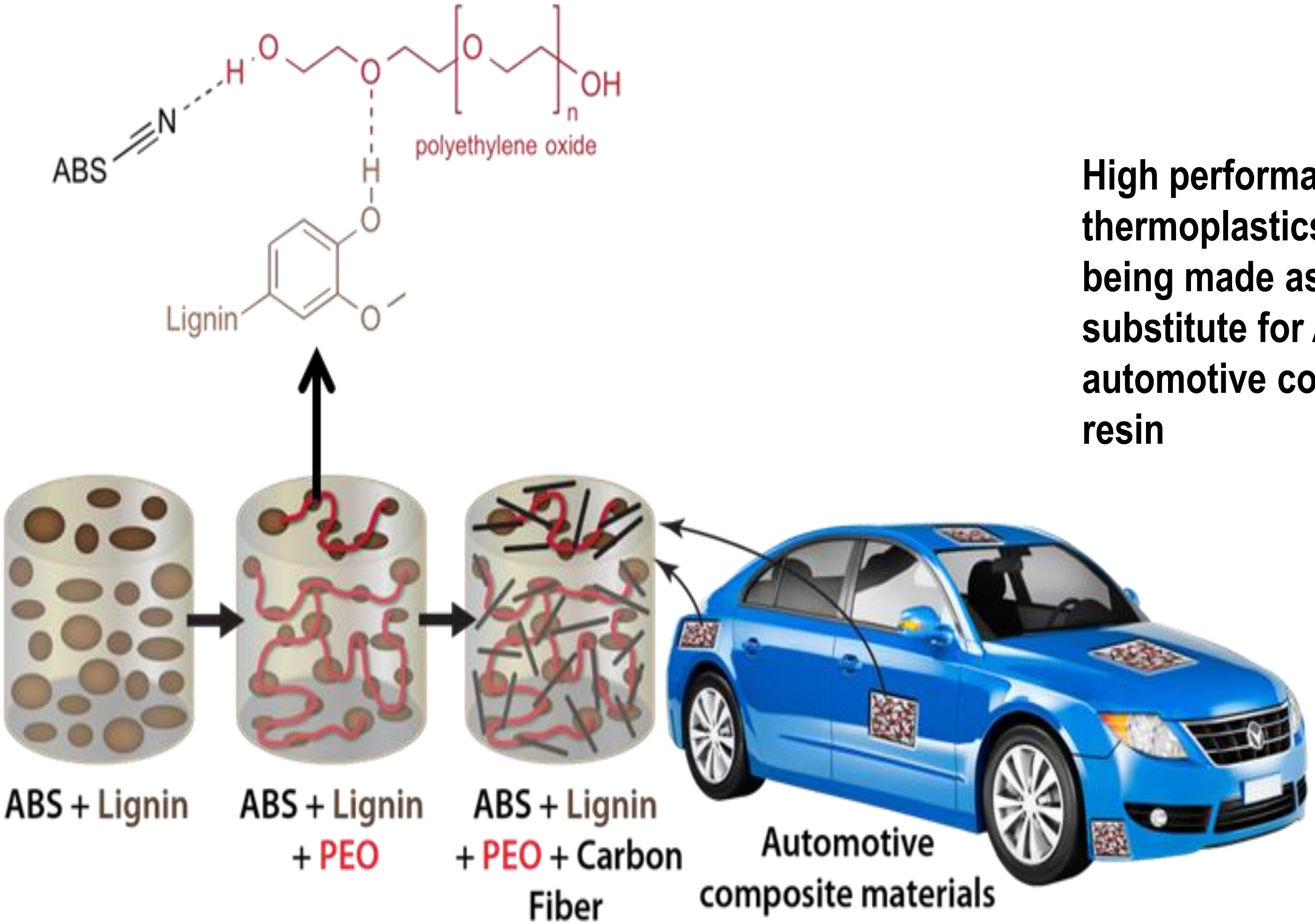
Tran et al. Advanced Functional Material (2016)

Compositions outperforms commodity/ industrial thermoplastic resin



Our resin demonstrates significantly higher impact resistant without loss of mechanical strength compared to commercial industrial-grade ABS.

Lignin-extended high performance thermoplastics: composites applications

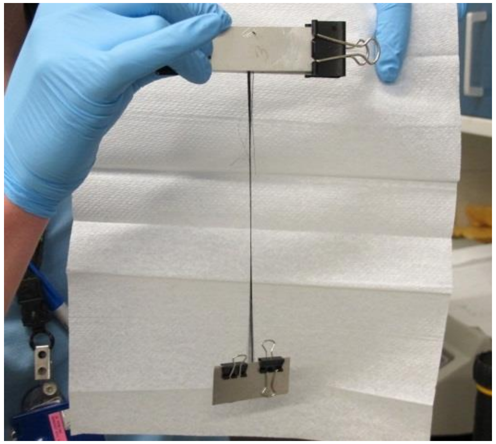


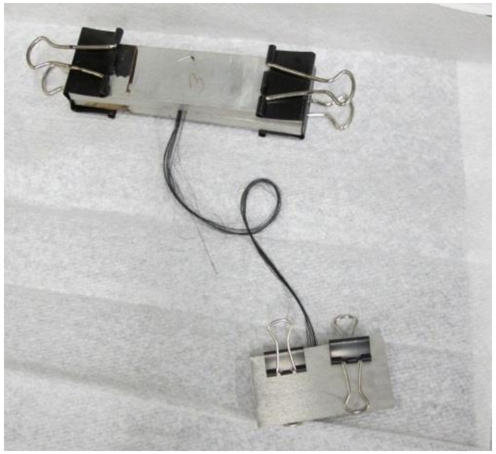
High performance thermoplastics are being made as substitute for ABS, a automotive composite resin

Akato, Tran, Chen, Naskar, ***ACS Sustainable Chemistry & Engineering*** 3(12), 3070–3076 (2015).

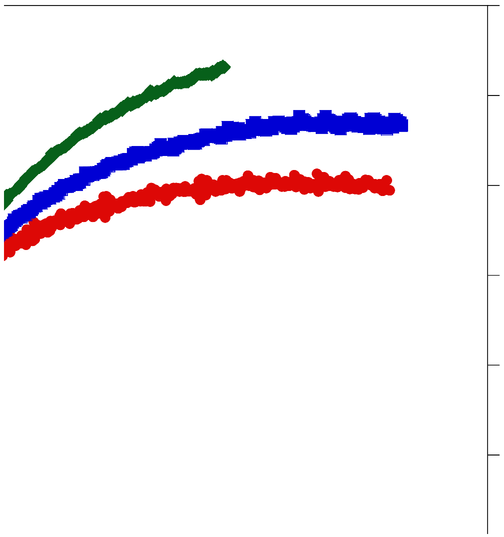
Infusible lignin fiber products

Melt-spun lignin fiber from controlled compositions could be stretched and converted to infusible thermoset fibers





Mechanical properties of lignin polymers can be enhanced significantly if flow-induced orientation in the material is established and retained by converting those to thermosets



- Tailored formulations after significant crosslinking reactions exhibit characteristics of toughened thermoset plastics

Concluding remarks

- We have demonstrated the successful development of a path for loading a sustainable industrial co-product, lignin, to several nitrile-containing thermoplastic matrices, resulting in a new family of high-performance and versatile engineering materials.
- Our work has proven to extend acrylonitrile-butadiene-styrene with as much as 27% low cost lignin with no deleterious effect on mechanical strength, while retaining the ability to incorporate chopped carbon fiber to create rigid parts suitable for automotive applications.
- In addition, we have presented two works in which high-performance thermoplastic materials were produced with lignin contents in excess of 40%, without the need for costly chemical modification of lignin – to our knowledge, the first of their kind.

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