Sustainable Coatings: Utilizing Lignin for the Development of Biobased Resins

Mojgan Nejad

Associate Professor,

Department of Forestry and Department of Chemical Engineering & Materials Science

Michigan State University

Wood Coating Conference

Sept. 26th, 2024

Have you ever used lignin?

Main Drivers: Together for Sustainability

40 Members in 2023

22 Members in 2020

"Goals: To enhance sustainability within the supply chain of chemicals"

Why Lignin?

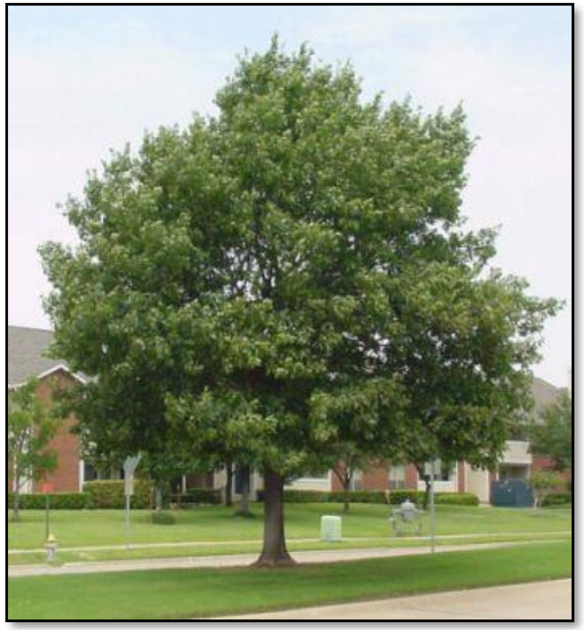
1. Lignin is the second most abundant natural polymer after cellulose in the world, made up 1/3 of dry mass of plants
2. Sustainable, renewable, and biodegradable
3. Produced as byproduct of pulp and paper or bioethanol production, thus the lignin price will not fluctuate with the price of oil and gas
4. Excellent compatibility with wood

Lignin Variations in Biomass

Properties of lignin varies based on biomass source (Hardwood, Softwood, Wheat Straw, Corn Stover, Peanut Shell, Bagasse)

Softwood
25-35%

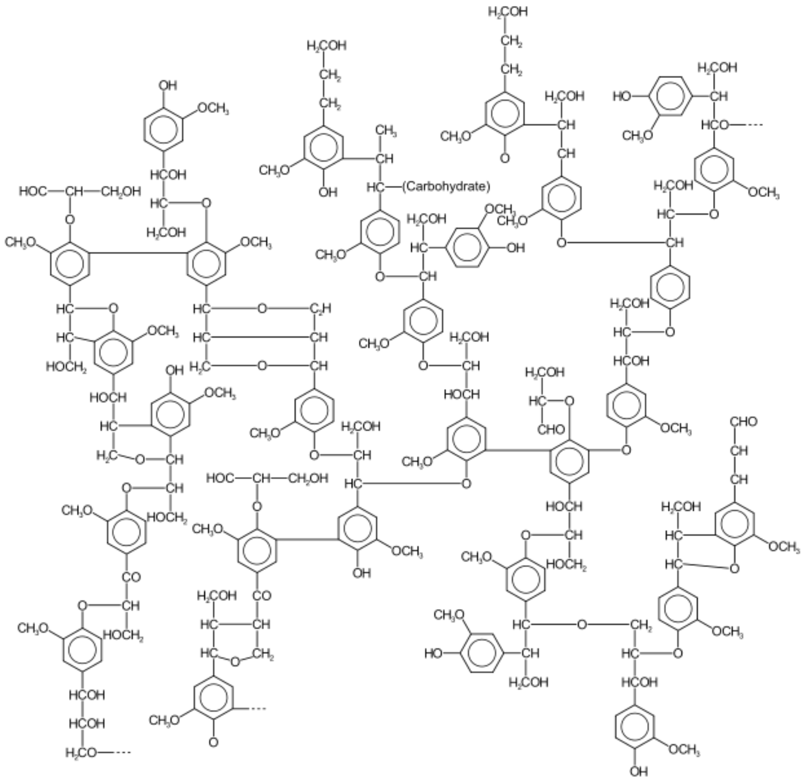
Hardwood
18-25%



Annual Crops
15-25%

Lignin Variations: Isolation Methods

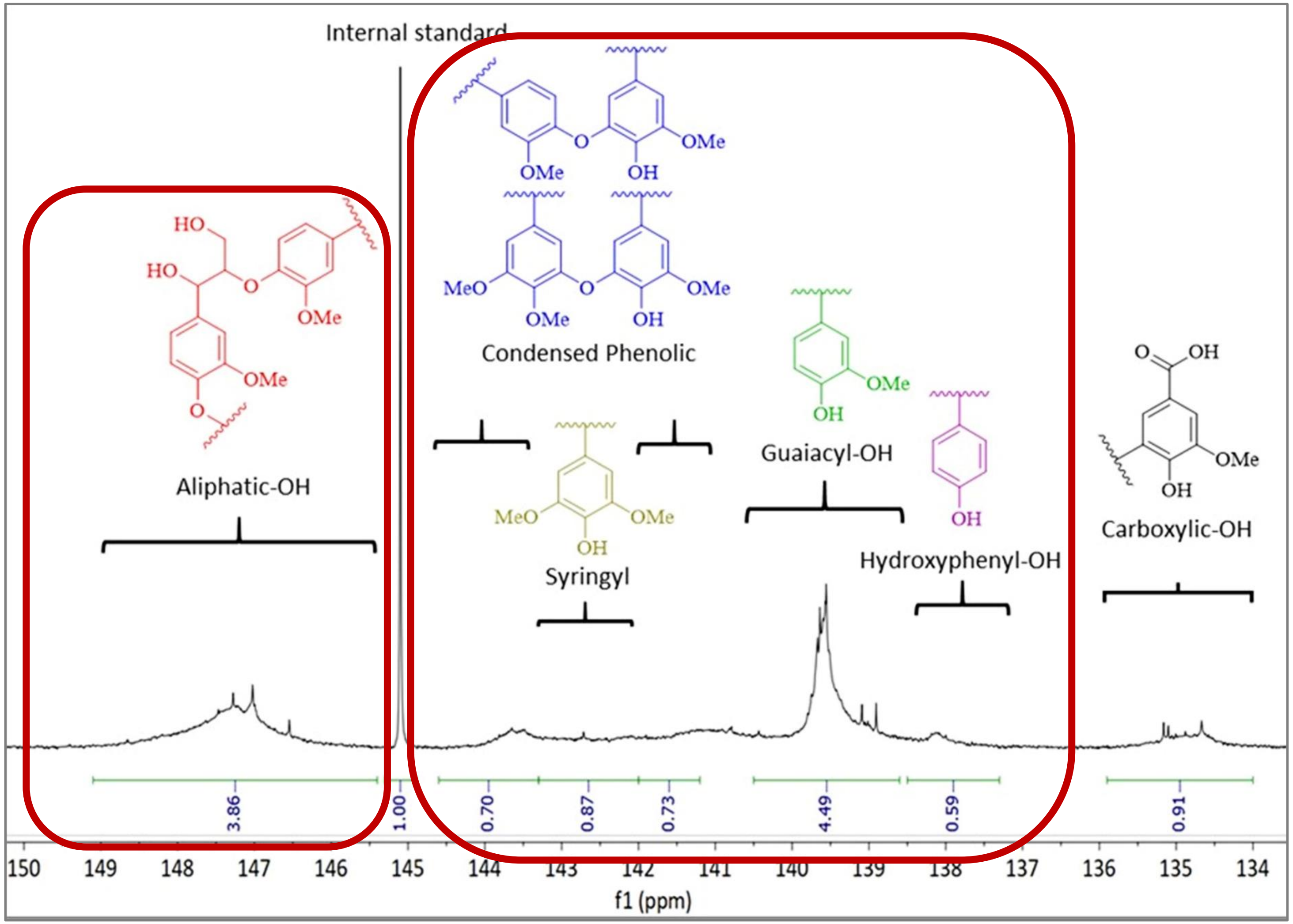
Properties of lignin also varies based on the isolation methods (Kraft, Sulfite, Soda, Organosolv, Ionic Liquid, Enzymatic Hydrolysis)



Lignin Characterization

- **Chemical analysis:** FTIR, ^{31}P NMR, ^{13}C NMR, ^{1}H NMR, 2D-NMR,
- **Thermal analysis:** Glass transition temperature (Tg) using DSC, Thermal stability (TGA)
- **Molecular size:** Molecular weight (Mw), molecular number (Mn) and PDI using GPC (analyzing acetylated lignin)
- **Moisture content:** Gravimetrically and TGA
- **Ash content:** Furnace at 525°C for 4 hrs
- **Elemental analysis:** Percentage of N, S, P, K, Mg, Ca, Na, B, Zn, Mn, Fe, Cu and Al

Hydroxyl Content of Lignin: ^{31}P NMR



Example of Some Measured Lignin Properties

Sample ID	Mw (D)	PDI	S (%)	Na (%)	K (%)	Hydroxyl Value (mmole/g)			
						Aliphatic-OH	Aromatic-OH	COOH	Total-OH
1-KR-SW	6420	3.99	1.93	0.82	0.094	2.00	3.15	0.41	5.56
2-OS-SW	4970	4.02	0.17	0.01	0.004	0.96	2.10	0.45	3.51
3-OS-HW	3790	2.63	0.02	0.01	0.001	1.33	2.68	0.31	4.32
4-KR-SW	6970	3.63	2.56	0.53	0.064	1.70	4.63	0.53	6.86
5-SO-WS	3770	2.77	0.68	0.11	0.044	1.30	3.04	0.75	5.08
6-KR-HW	3070	2.36	2.10	0.19	0.044	1.04	4.38	0.2	5.62
7-KR-SW	6800	4.08	1.87	0.14	0.042	2.03	3.41	0.48	5.92
8-SO-HW	6460	3.51	1.96	0.75	0.902	2.22	3.18	1.16	6.56
9-OS-CS	5410	2.83	0.10	0.01	0.010	0.62	2.53	0.38	3.53
10-KR-SW	9390	4.06	1.43	0.05	0.015	2.18	3.96	0.50	6.64
11-KR-SW	5440	4.94	1.78	0.19	0.027	2.35	3.74	0.45	6.53
12-OS-HW	4070	2.48	0.02	0.01	0.022	0.80	3.07	0.26	4.13
13-OS-WS	4950	2.73	0.09	0.01	0.008	1.11	2.09	0.41	3.61
14-SO-HW	3410	2.61	0.10	0.08	0.013	1.16	3.98	0.62	5.76
15-SO-WS	3889	2.51	0.29	0.37	0.001	1.22	3.14	1.1	5.46

Challenges

- Impurities, some contain high sulfur content
- Non uniformity, lack of consistency, high molecular size distribution (PDI)
- Lack of functionality or accessibility of functional groups for reaction with other compounds
- Dark color (usually dark brown)
- In some cases, unpleasant odor (Lignoboost Kraft softwood lignin)

Lignin-Based Resins

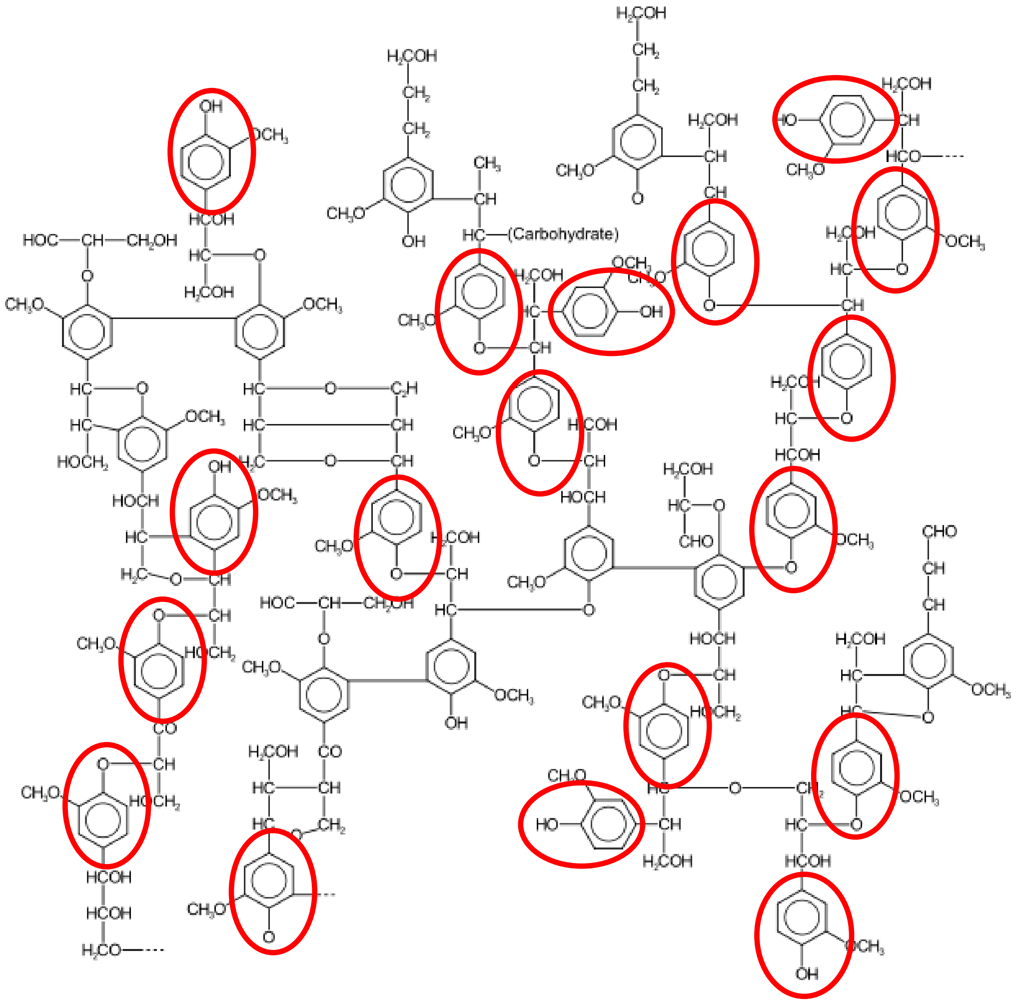
1. **Lignin as Phenol Replacement:** Lignin-Based Phenolic Resin
2. **Lignin as Polyol Replacement:** Lignin-Based Polyurethane Resin
3. **Lignin as Bisphenol-A Replacement:** Lignin-Based Epoxy Resin
4. **Biobased UV-Stabilizer:** Encapsulating Lignin in Halloysite Nanotubes (nanoclay) as natural biobased UV-Stabilizer

Resin Properties Measurements

1. Solid content
2. Viscosity with Rheometer at 1000 1/s shear rate
3. Gelation time (digital viscometer)
4. Curing and Tg (differential scanning calorimeter, DSC)
5. Curing and cross-linking density (Dynamic mechanical analyzer, DMA)

Lignin-Based Phenolic Resins

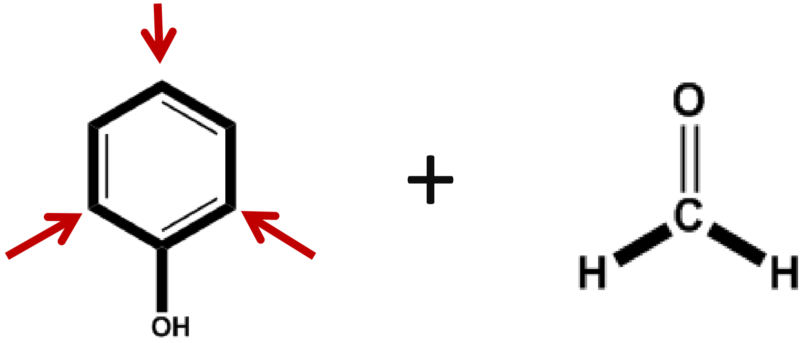
Lignin: Natural Polyphenolic Compound



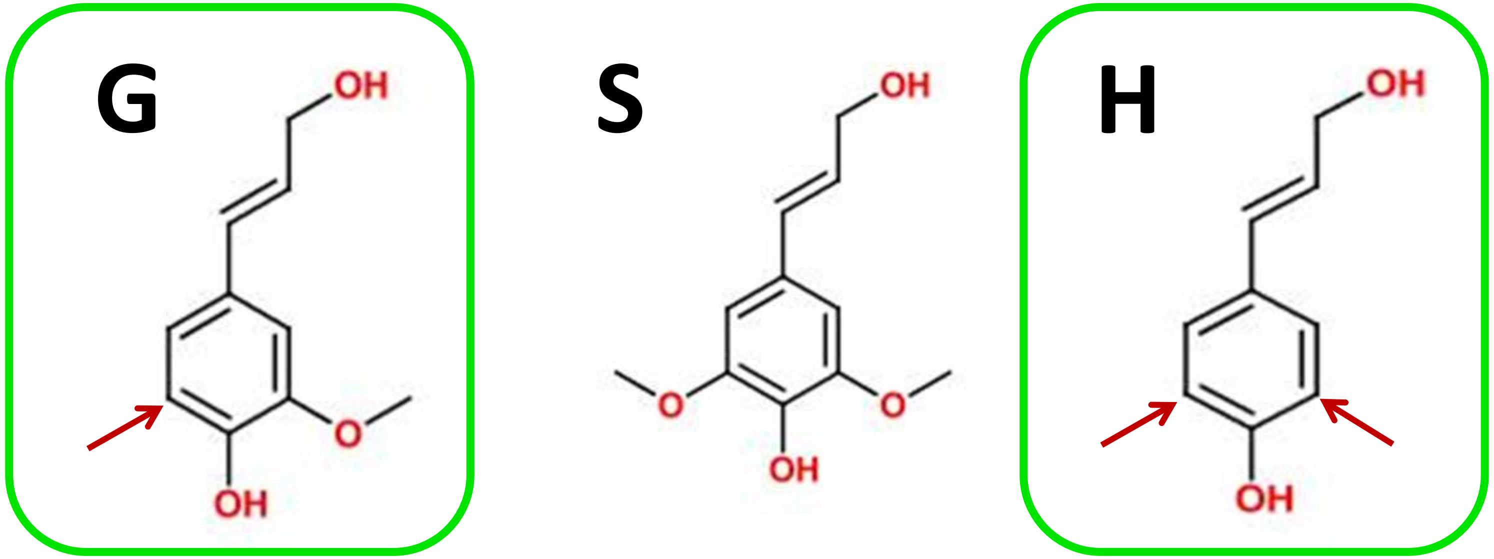
Glazer, A. W., and Nikaido, H. (1995)

Lignin as Phenol Substitute in Phenolic Adhesive

Phenol



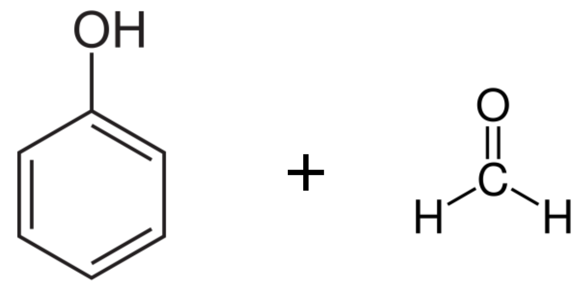
Formaldehyde

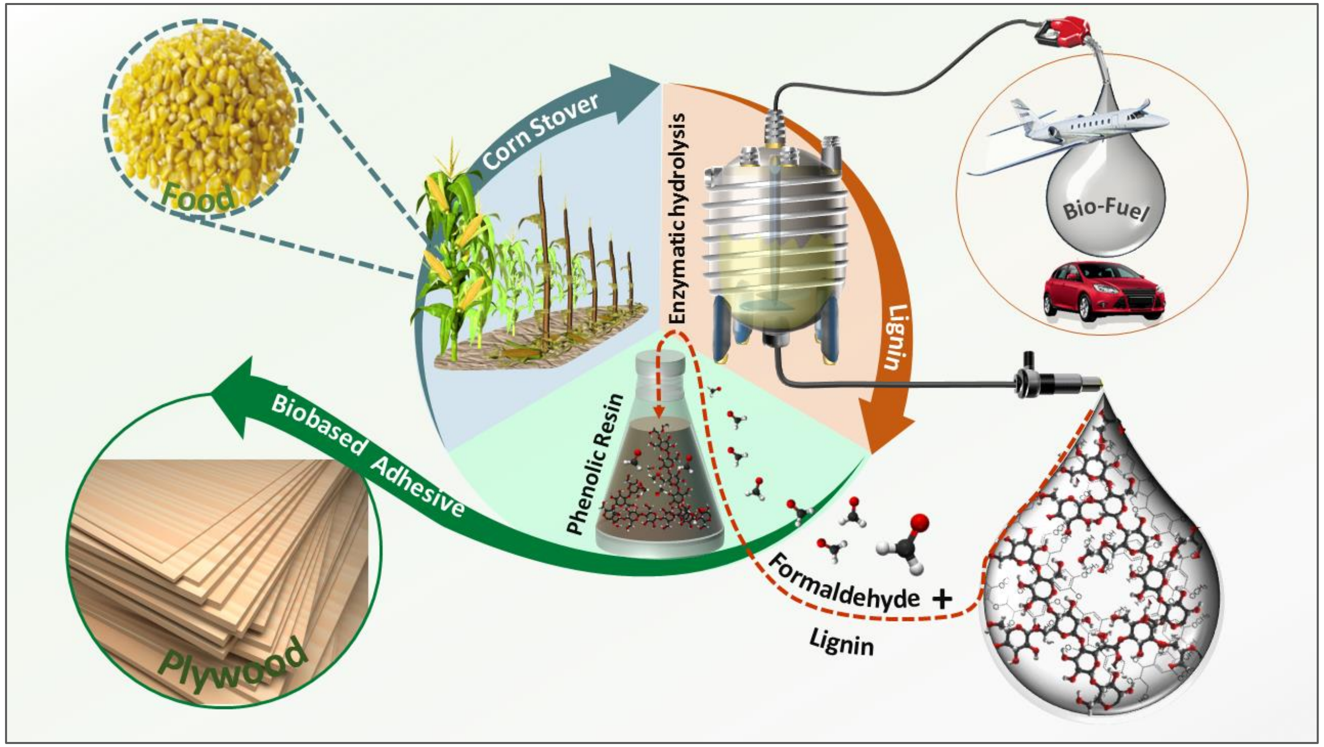


Lignin	G	S	H
Softwood	√		
Hardwood	√	√	
Annual Crops	√	√	√

Lignin as Phenol Substitute in Phenolic Adhesive

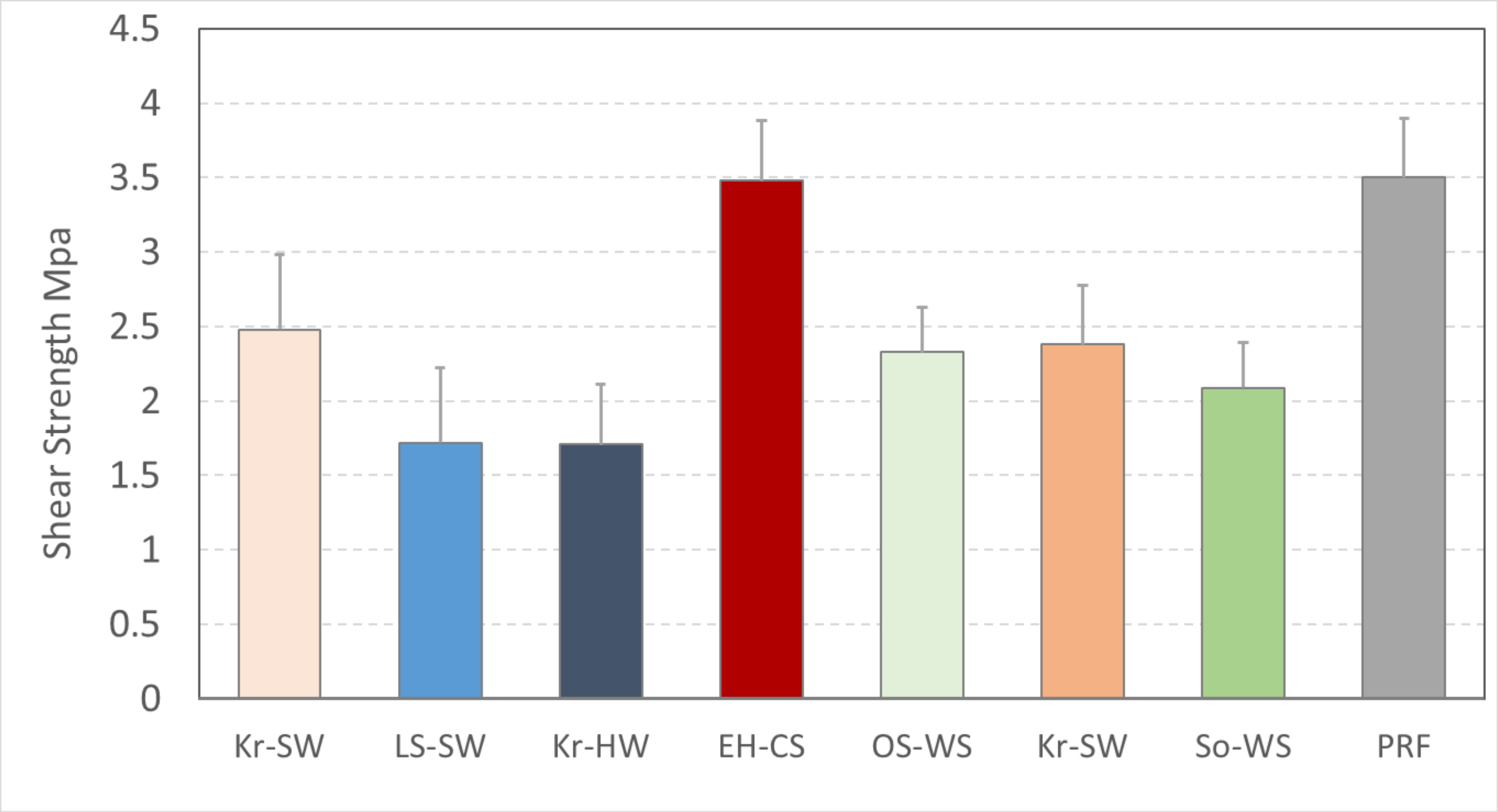
Phenol-Formaldehyde Resin





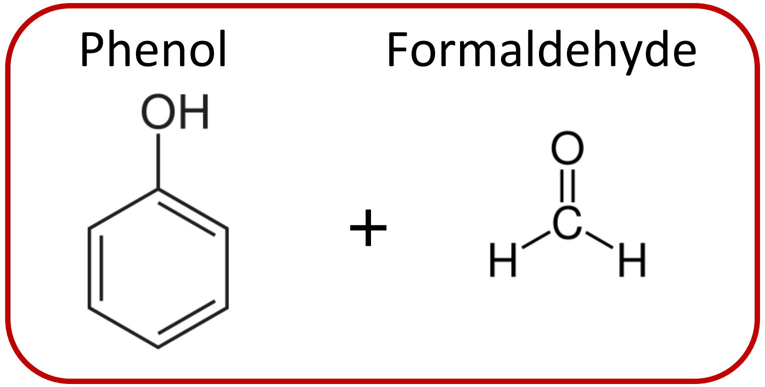
Lignin-based adhesive had 50% less formaldehyde on weight basis than PF

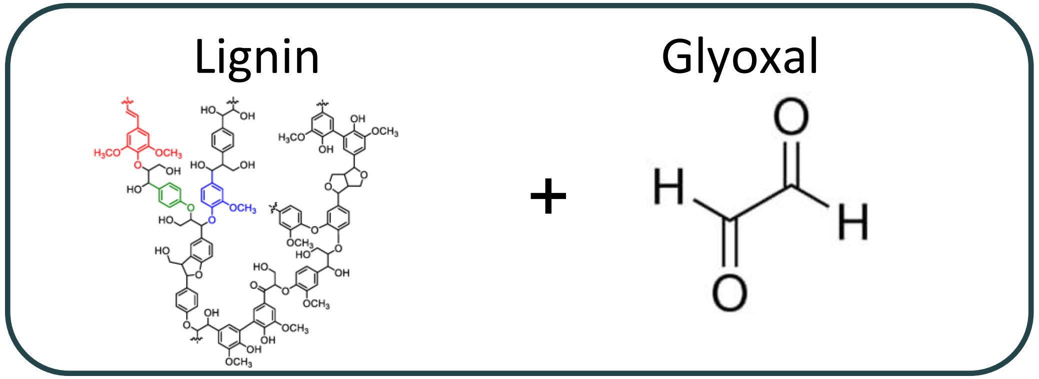
Lignin as Phenol Substitute in Phenolic Adhesive

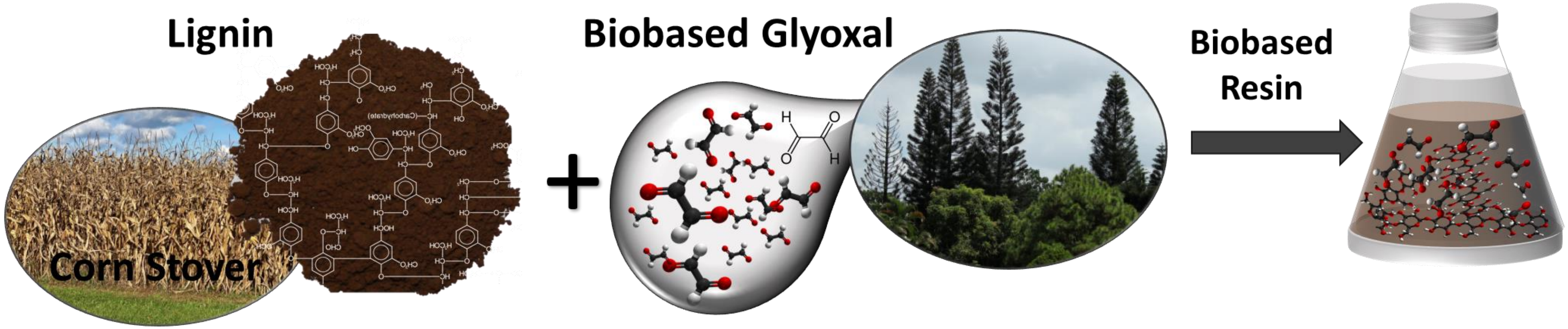


Note: SW=Softwood, HW=Hardwood, CS=Corn Stover, WS=Wheat Straw
Kr=kraft, EH=Enzymatic Hydrolysis, OS=organosolv, So=Soda

Lignin-Based Formaldehyde-Free Biobased Resin





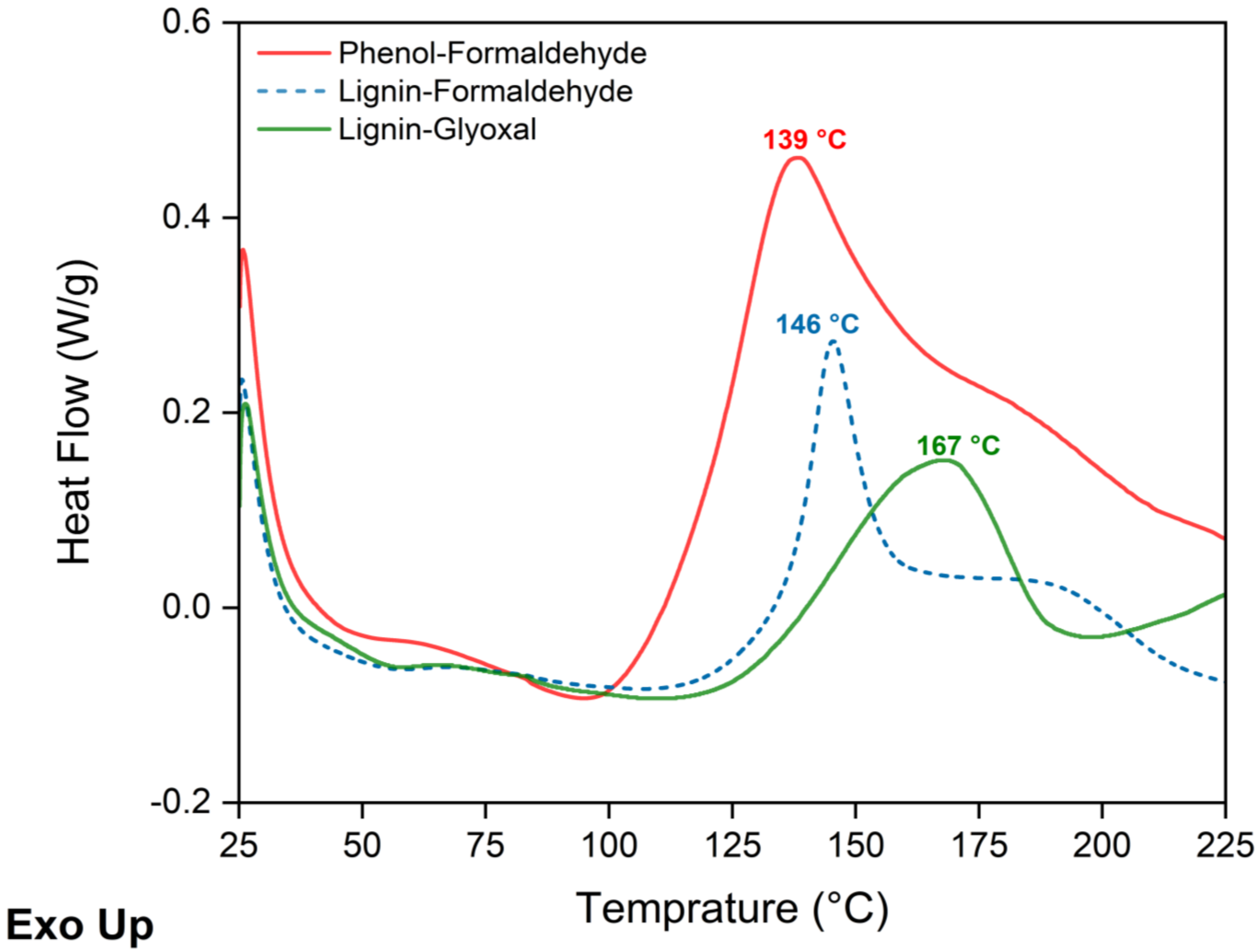


Phenolic Resin Properties

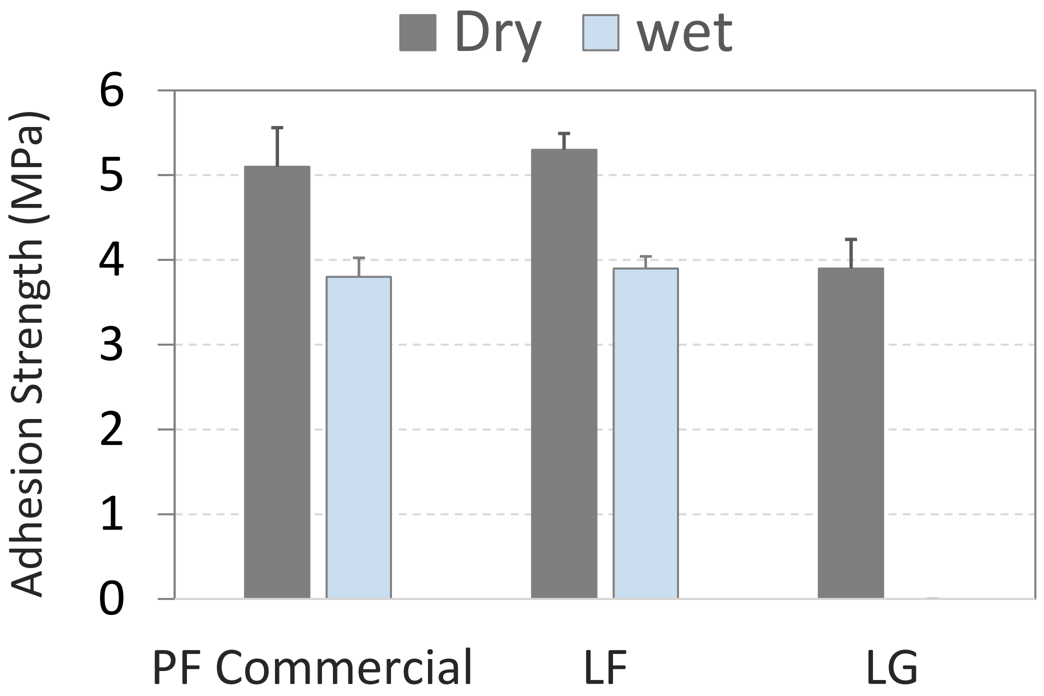
Resin Properties	Phenol-Formaldehyde (PF)	Lignin-Formaldehyde (LF)	Lignin-Glyoxal (LG)
pH	12 ± 0.1	10.9 ± 0.1	9.8 ± 0.1
Alkalinity (%)	5.1 ± 0.1	2.5 ± 0.1	3.6 ± 0.2
Viscosity (mPa.s)	640 ± 6	410 ± 5	200 ± 6
Free Formaldehyde Content (%)	0.17 ± 0.03	0.60 ± 0.02	0
Solid Content (%)	42.3 ± 0.2	25.1 ± 0.1	30 ± 0.2
Gelation Time (min)	11.2 ± 0.4	7.3 ± 0.5	7.7 ± 0.2

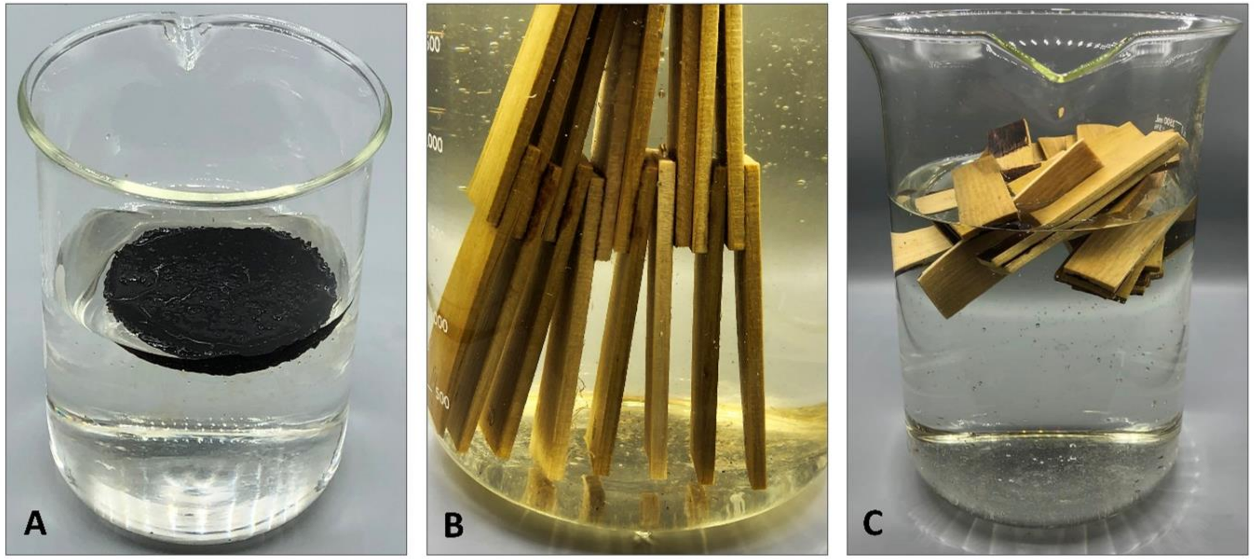
Resin Curing Temperature

- LF resin cured at similar temp. as of PF
- LG required higher temp. curing
- LG resin is only suitable for interior application



Adhesive Performance





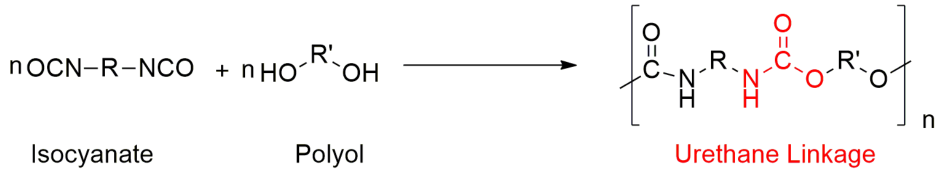
Lignin-Glyoxal for Interior Applications

Formaldehyde LD_{50} : 500–800 mg/kg

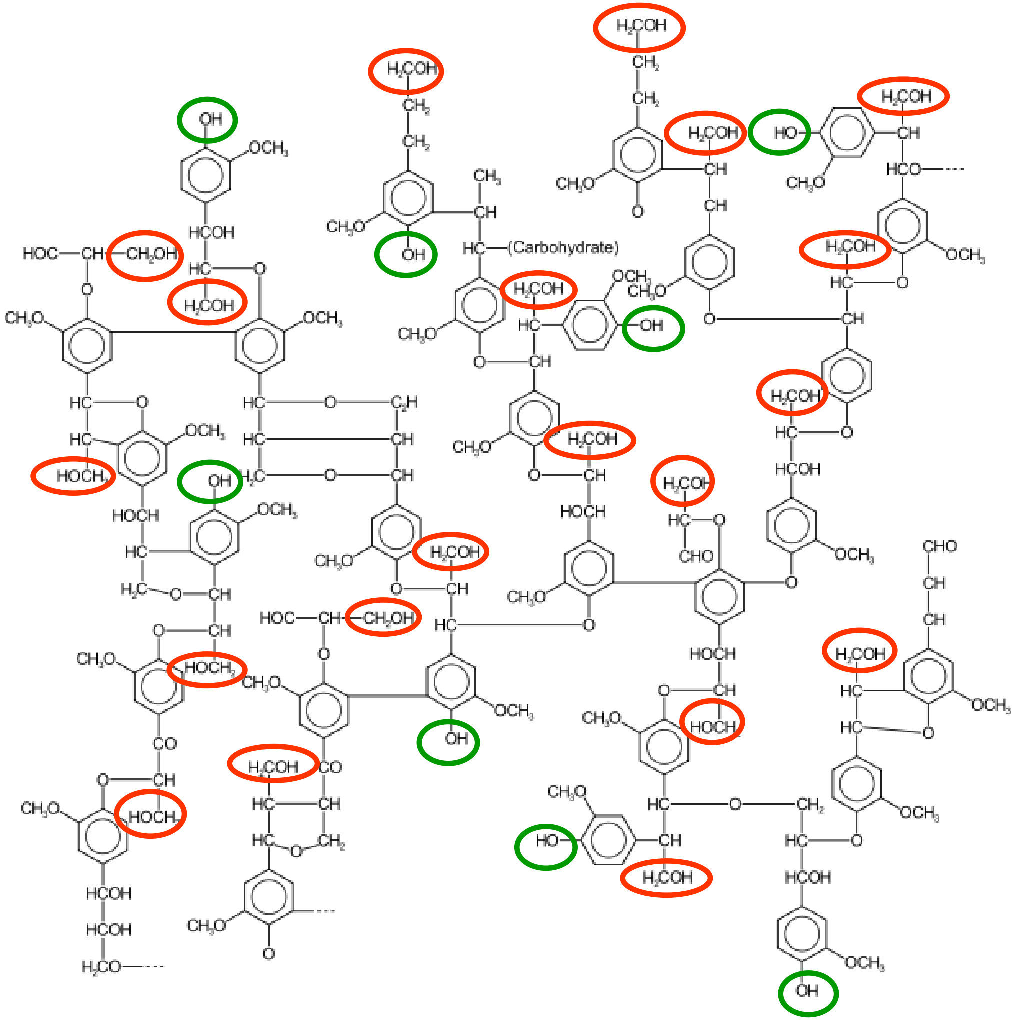
Glyoxal LD_{50} : 2960–8979 mg/kg

Lignin-Based Polyurethane

Lignin: A Natural Polyol



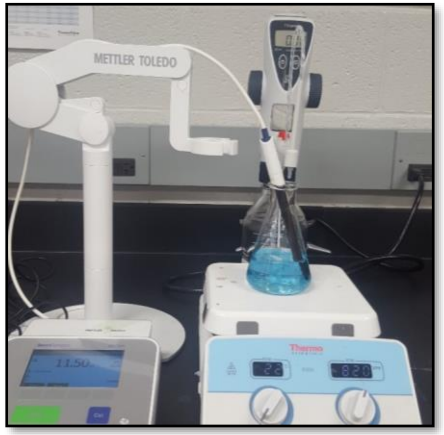
Lignin is a Natural Polyol

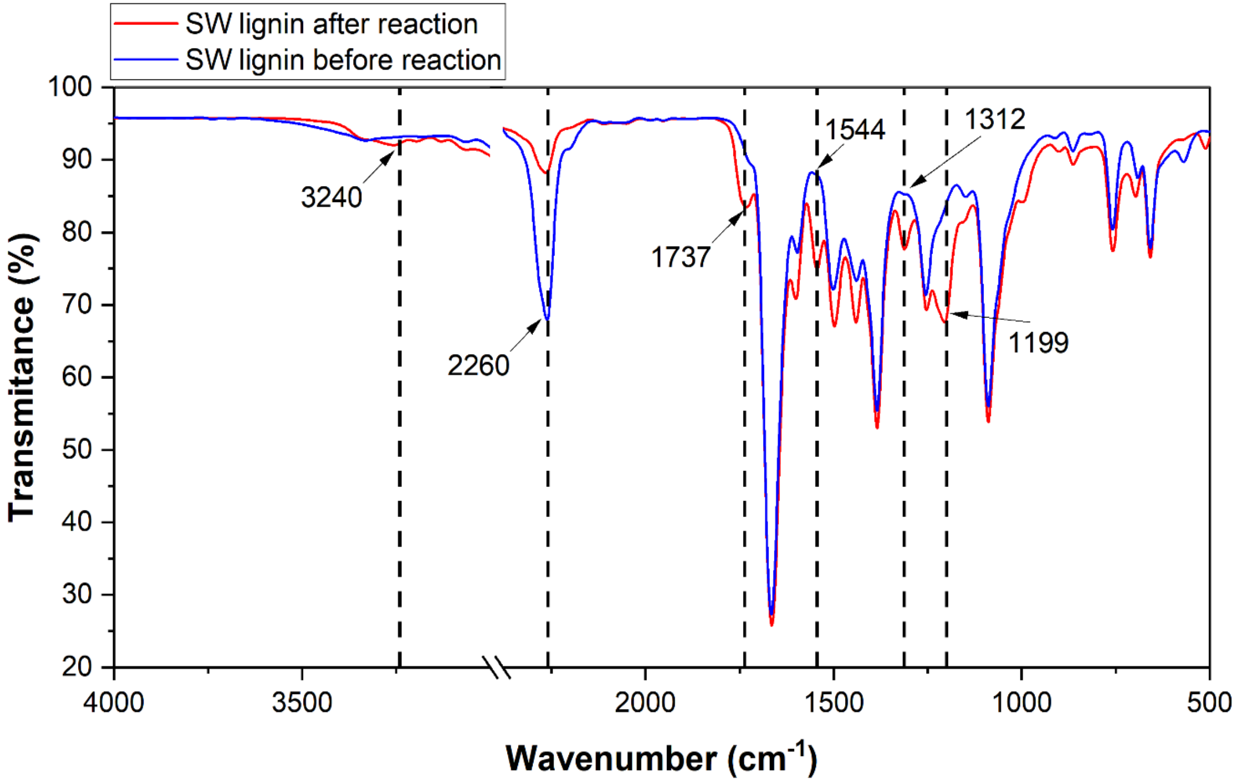


Glazer, A. W., and Nikaido, H. (1995

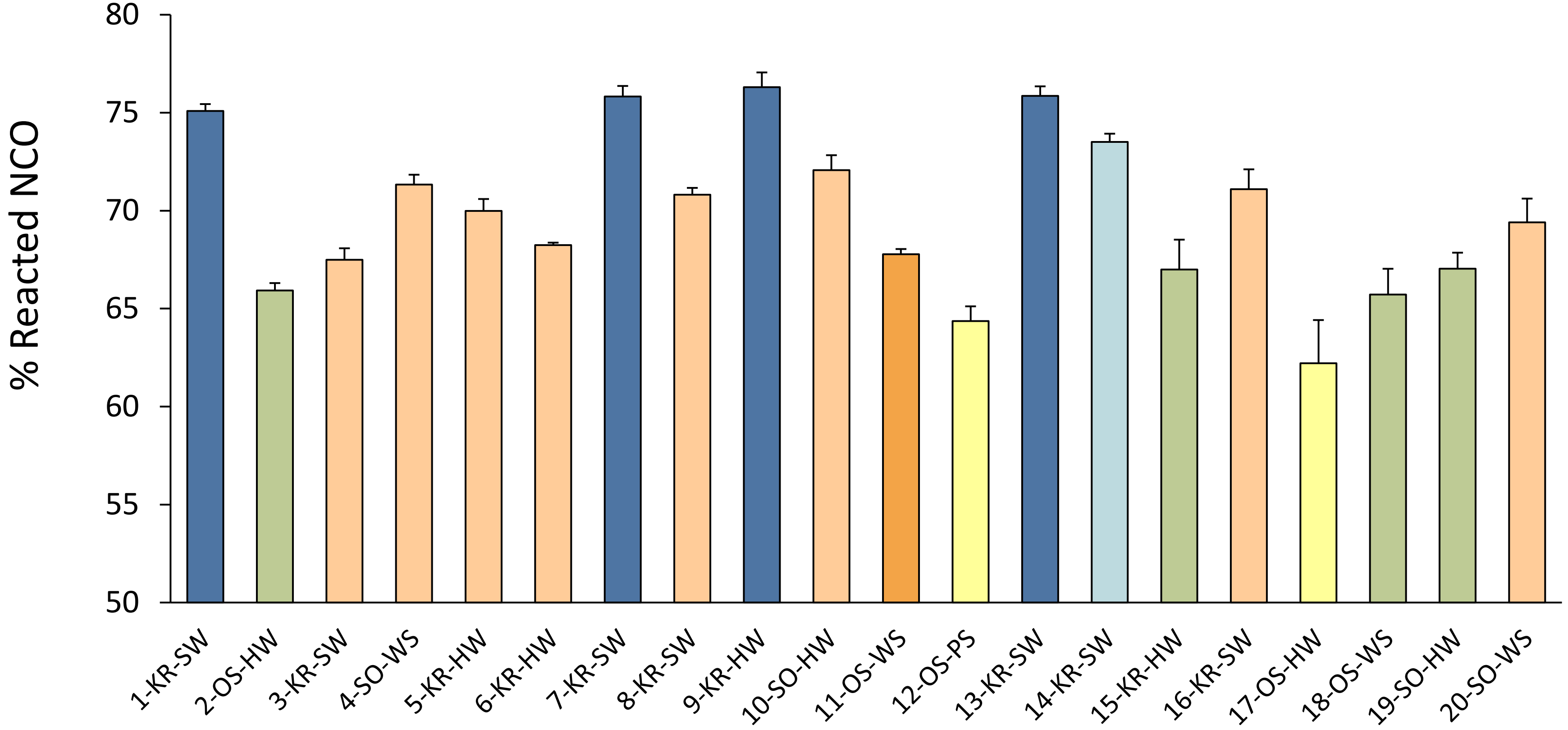
Lignin Reactivity Analysis

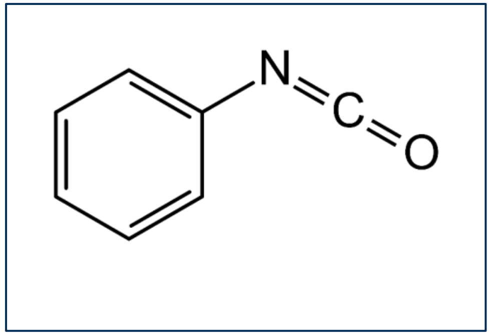
- Heated samples at 50°C for 1hr
- Analyzed with FTIR and titration **(D5155)**



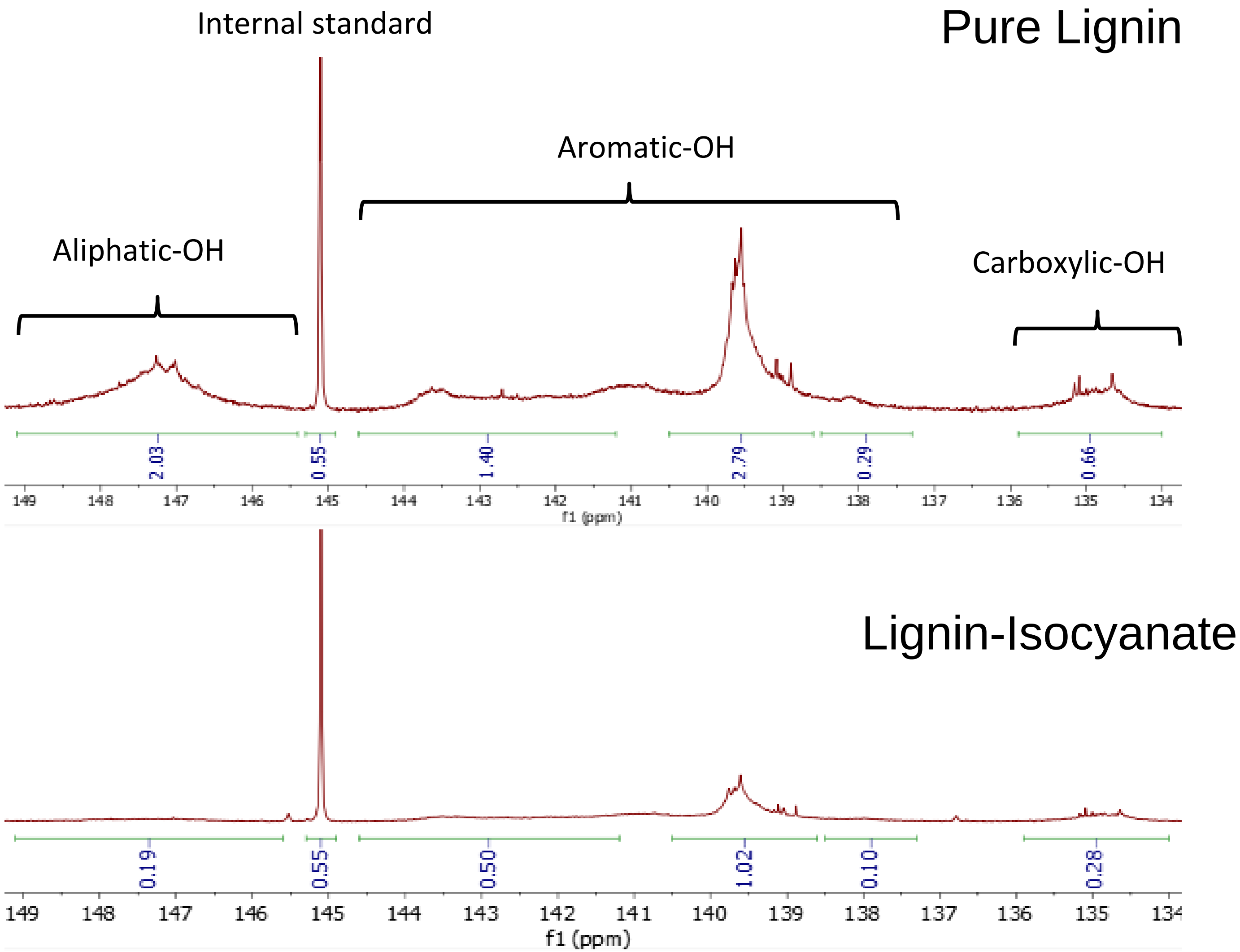


Reactivity of Different Lignins with Phenyl Isocyanate





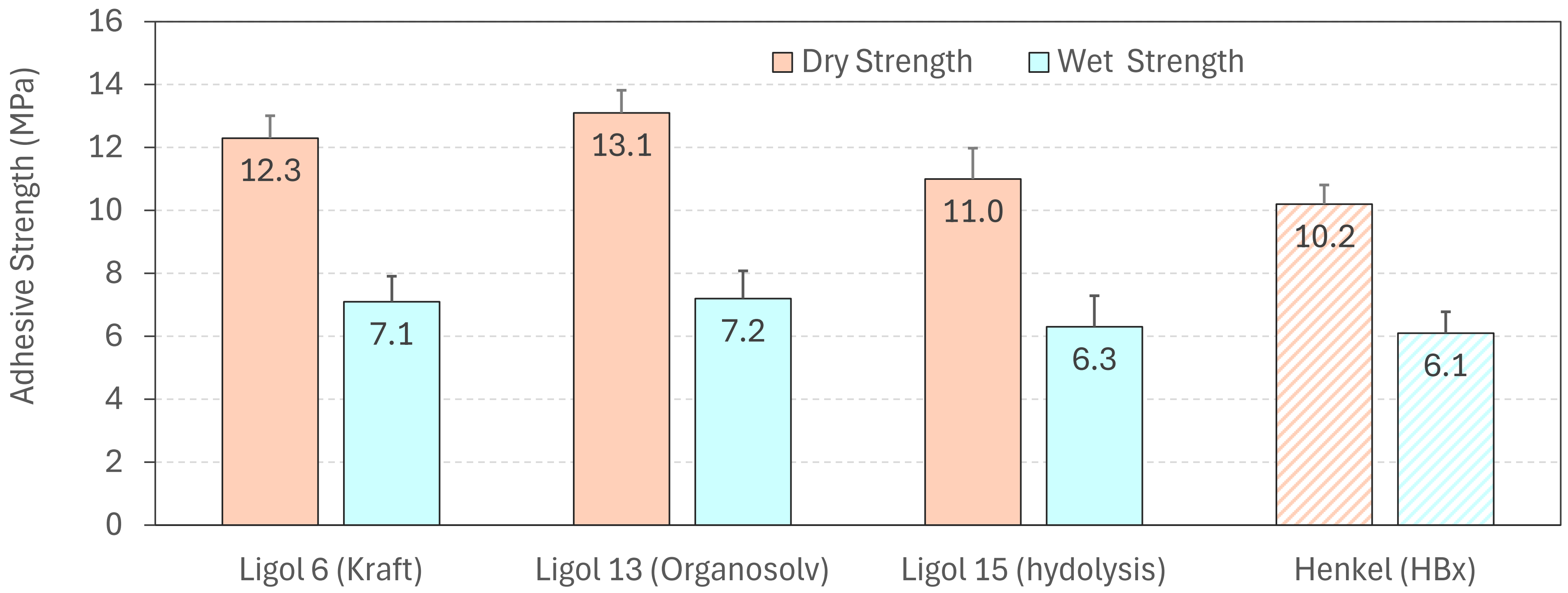
Lignin Reactivity with Isocyanates (^{31}P NMR)



Functional groups	% OH Reduction ± STDEV
Aliphatic	88 ± 1
Guaiacyl	77 ± 2
p-Hydroxyl	76 ± 1
Syringyl	81 ± 1
Carboxylic acid	61 ± 0

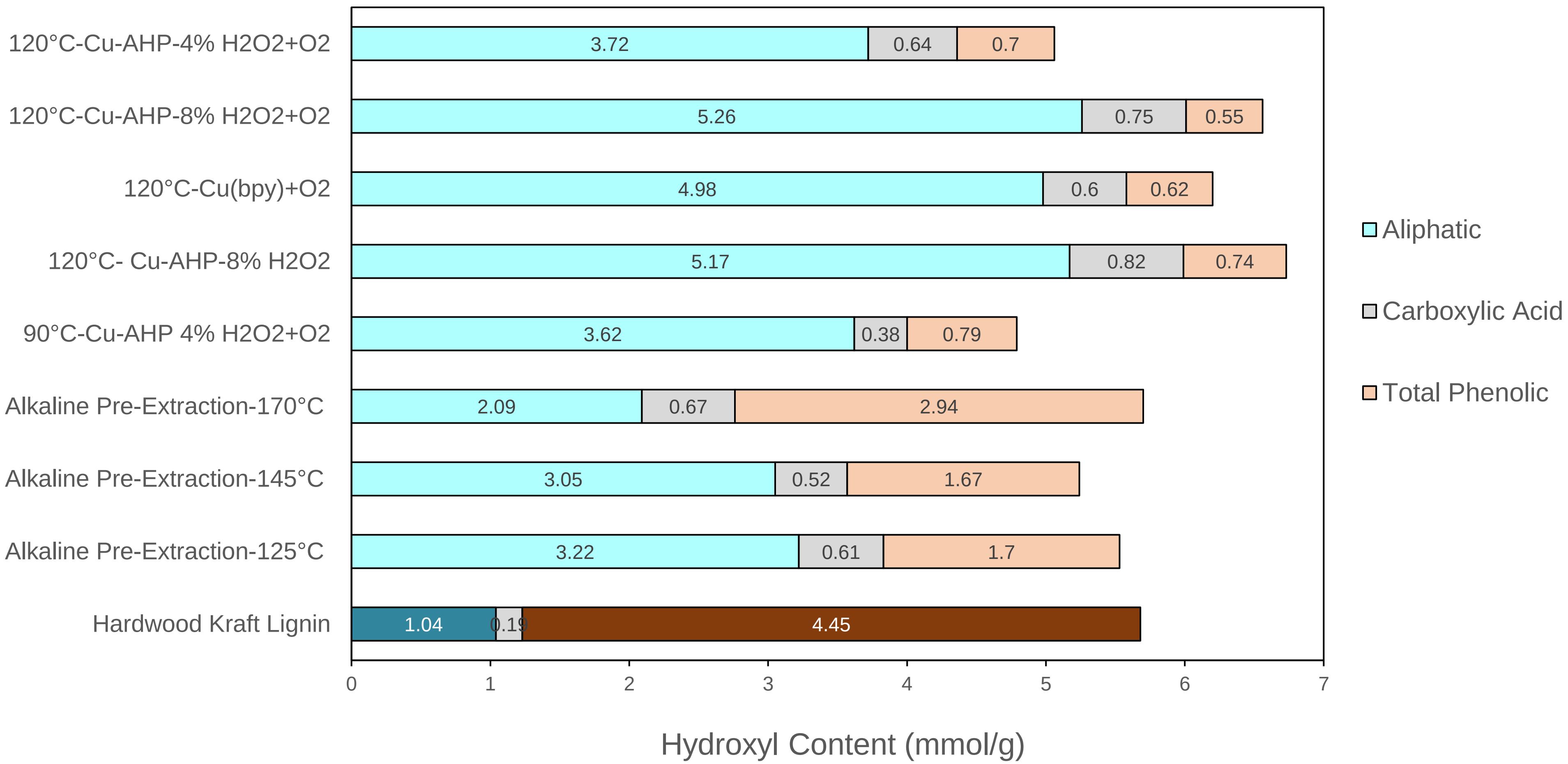
Lignin-Based Polyurethane Adhesive

- Replaced 100% of petroleum-based polyol with lignin
- High-solid, zero VOC, contains more than 30% lignin (on weight basis)
- Can be cured at room temperature or higher



Lignin-Based Polyurethane Waterborne Coating

^{31}P NMR Data of Isolated Lignin Samples

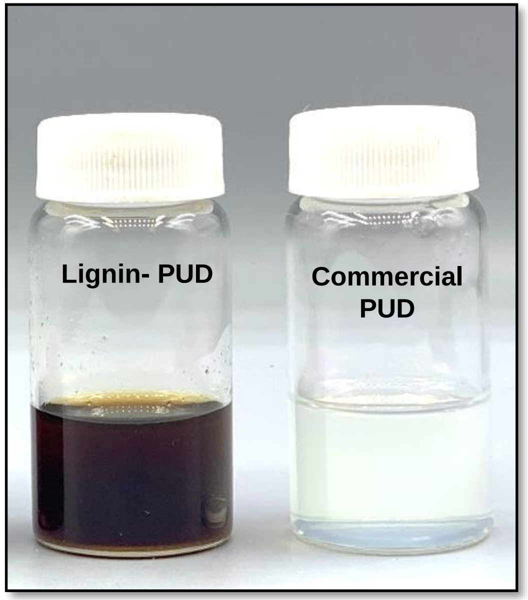


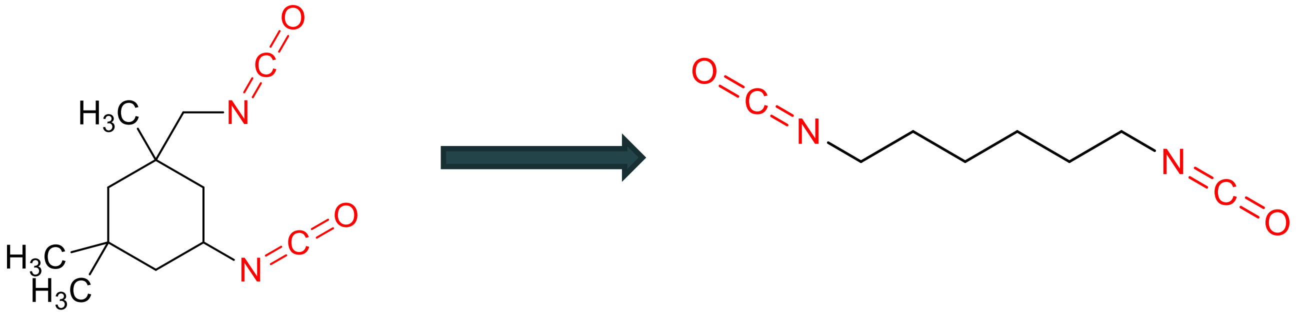
Cu-AHP Lignin

Prof. Eric Hegg

Prof. David Hoge

Lignin-Based PU Dispersion Resins





Isophorone diisocyanate (IPDI)

Hexamethylene diisocyanate (HDI)

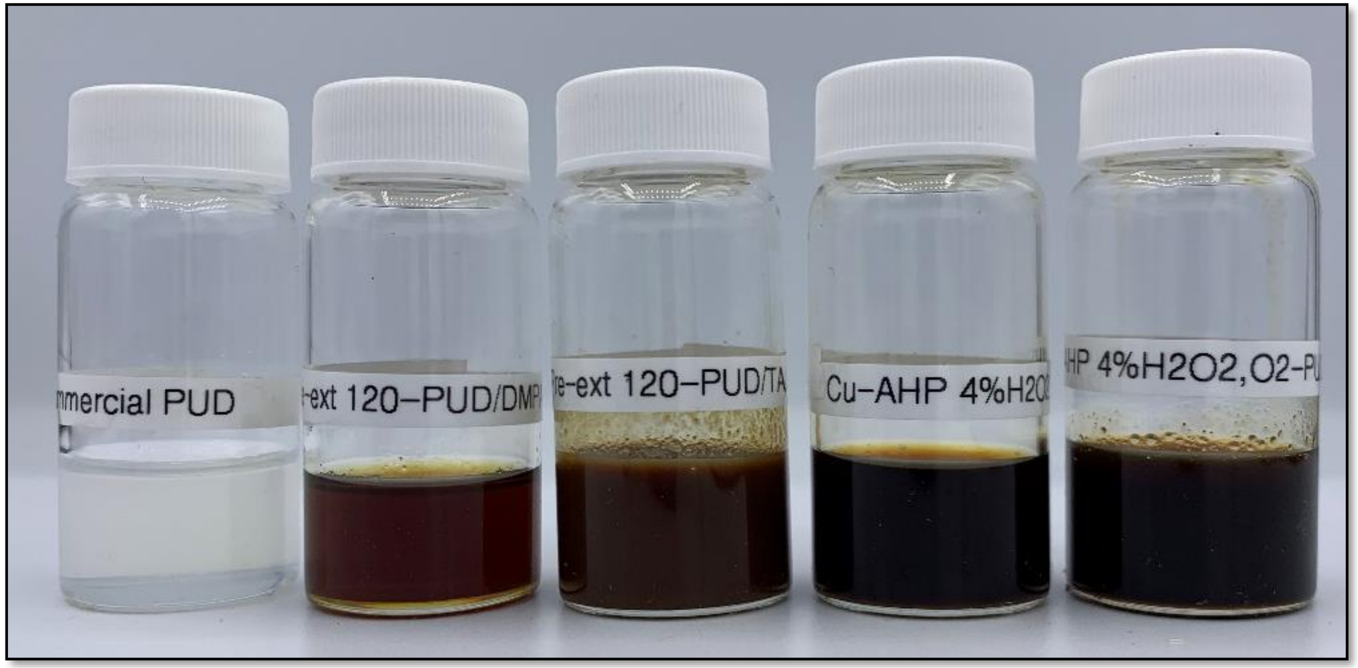
Dimethylol propionic acid (DMPA)

Tartaric acid (TA)

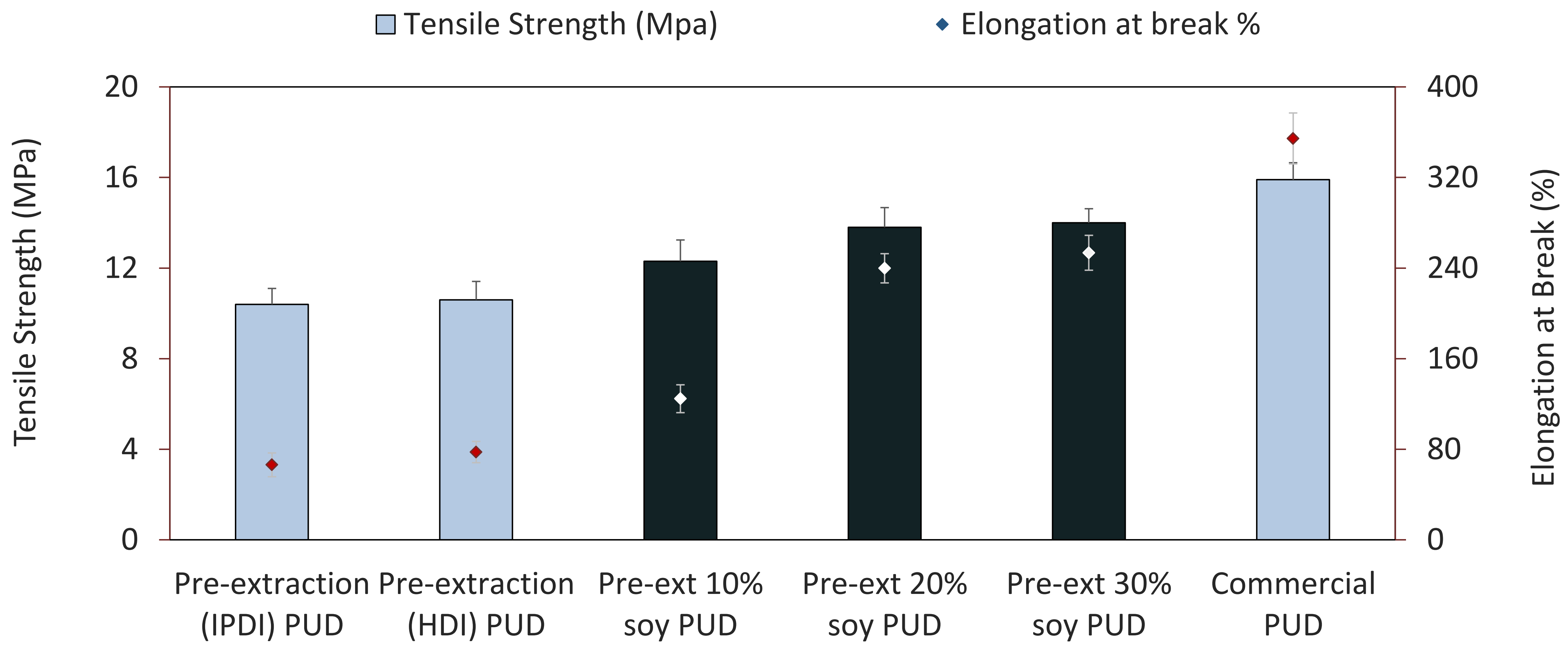
Lignin-Based Polyurethane Waterborne Coating

- Replaced 100% of petroleum-based polyol with Lignin (80%) and soy-polyol (20%)

- Used biobased internal Emulsifier and Solvent



Lignin-Soy Based PUD Resins



Soy polyol: Cargill 5100, OH-Value: 40 mg KOH/g

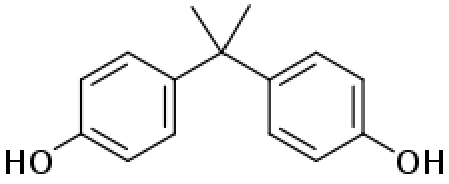
Lignin-Based Polyurethane Waterborne Coating

Lignin-Based PUD Resins

Commercial PUD

Lignin-Based Epoxy Resins

Lignin Epoxidation



Bisphenol-A (BPA)

Lignin+ DMF (Acetone now) + Epichlorohydrin + TBAB

Stir at 60° C for 3hrs, then cool down to room temp

Add NaOH Gradually

Stir Overnight

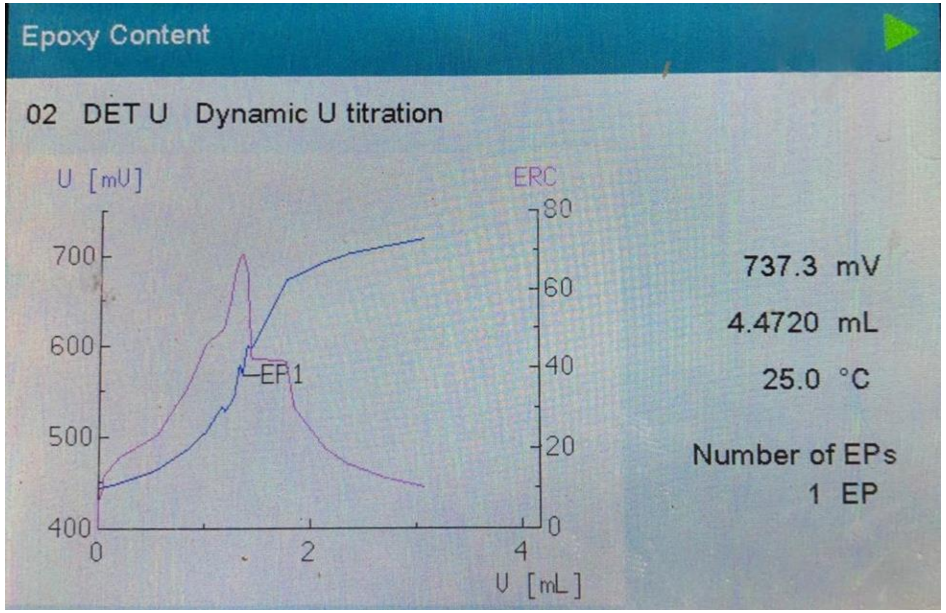
Add water to precipitate epoxidized lignin

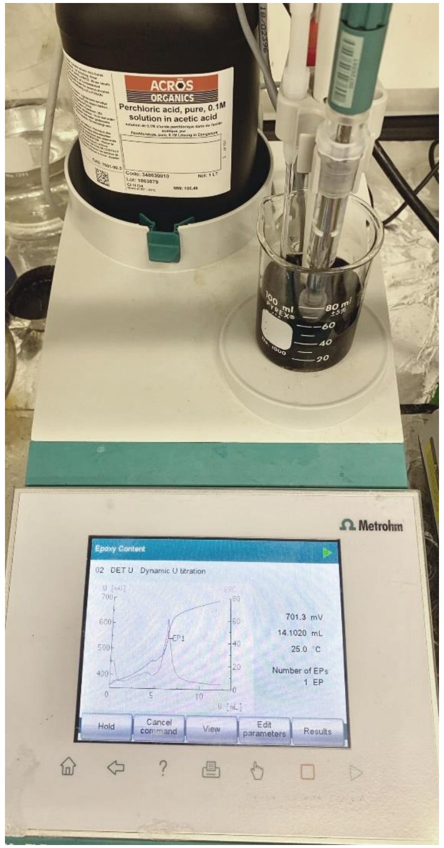
Washing, then drying overnight in vacuum oven at 40˚C

Measuring Epoxy Content

1. **Auto- Titration:** According to modified ASTM – D1652-11. the epoxidized lignin should have been soluble in dichloromethane.

2. **[1]H NMR:** Using Proton NMR with 1,1,2,2 Tetrachloroethane as internal standard

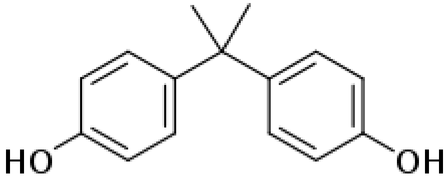




Epoxy Content of Different Lignins

Sample ID	Description	%Epoxy Content (Titration)	**EEW (Titration)**	%Epoxy Content (H NMR)	**EEW (HNMR)**
1	Kraft softwood	9.56 ± 0.3	450 ± 12	9.72	442
2	Kraft hardwood	6.79 ± 0.1	633 ± 11	7.00	614
3	Soda hardwood	8.59 ± 0.4	500 ± 20	8.21	524
4	**Organosolv Wheat Straw**	**12.40 ± 0.3**	**347 ± 9**	**12.53**	**343**
5	Organosolv bagasse	5.93 ± 0.1	725 ± 14	5.87	732
6	Organosolv peanut shell	5.18 ± 0.1	830 ± 19	4.93	872
7	Organosolv hardwood	8.75± 0.2	491 ± 10	8.93	481
8	Kraft softwood	7.97 ± 0.1	540 ± 11	7.88	546
9	Kraft softwood	10.01± 0.2	430 ± 10	9.81	438
10	Kraft hardwood	11.27 ± 0.3	382 ± 9	11.50	374
11	**Kraft hardwood**	**12.14 ± 0.1**	**354 ± 4**	**11.98**	**359**
12	Organosolv wheat straw	4.35 ± 0.1	988 ± 17	3.81	1128
13	Kraft softwood	8.63 ± 0.2	498 ± 10	8.98	479

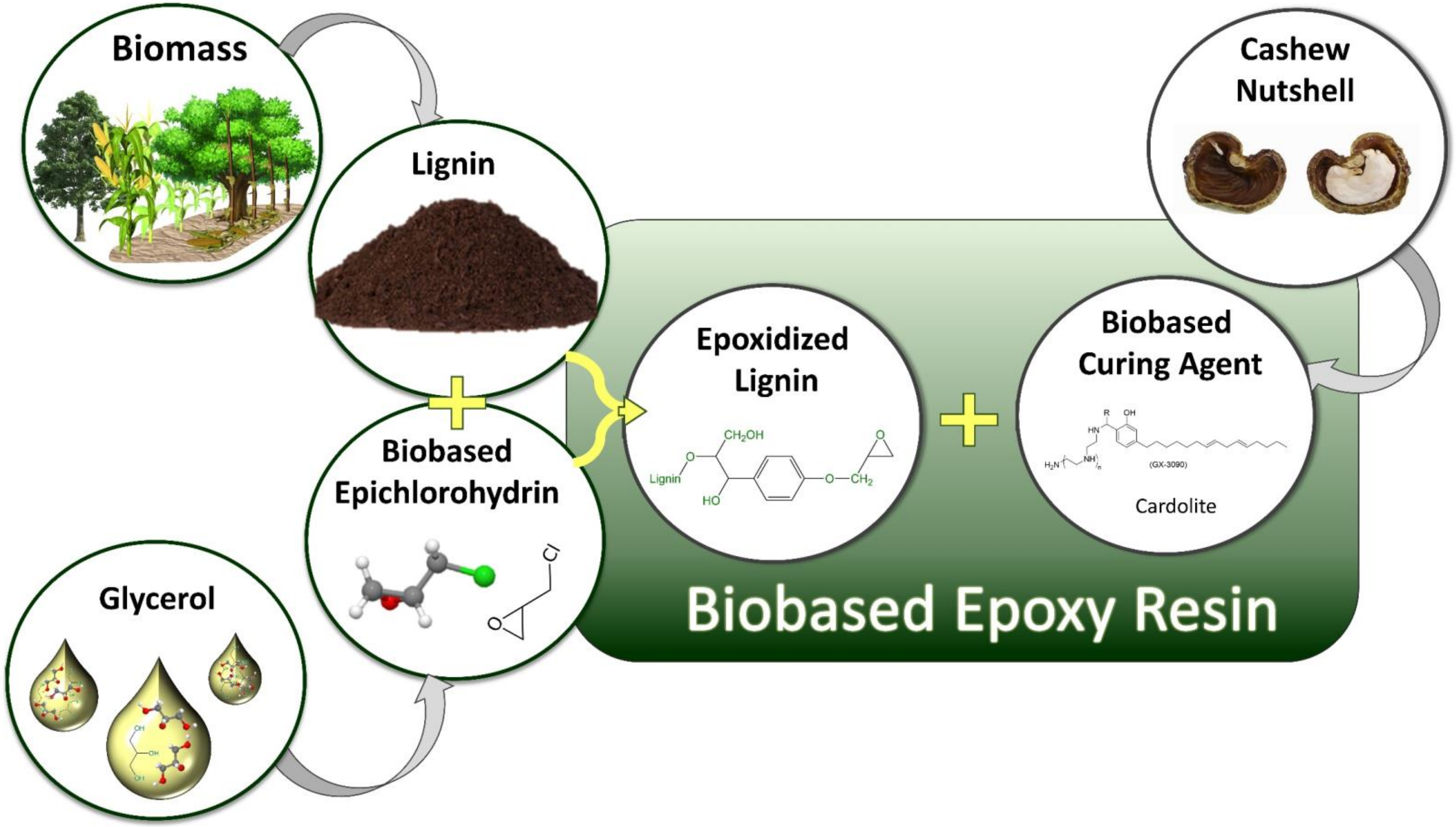
Lignin-Based Epoxy



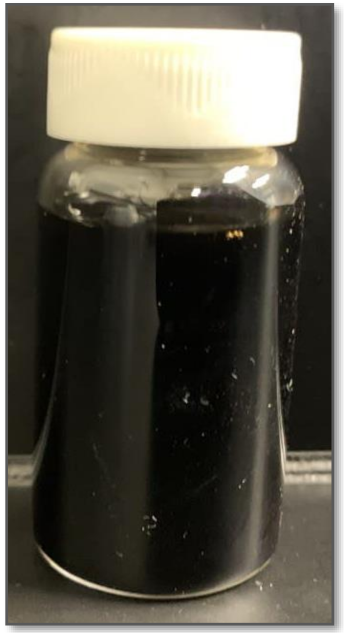
Bisphenol-A (BPA)

Biobased

Epichlorohydrin



Water Dispersion Fully Biobased Epoxy Resin

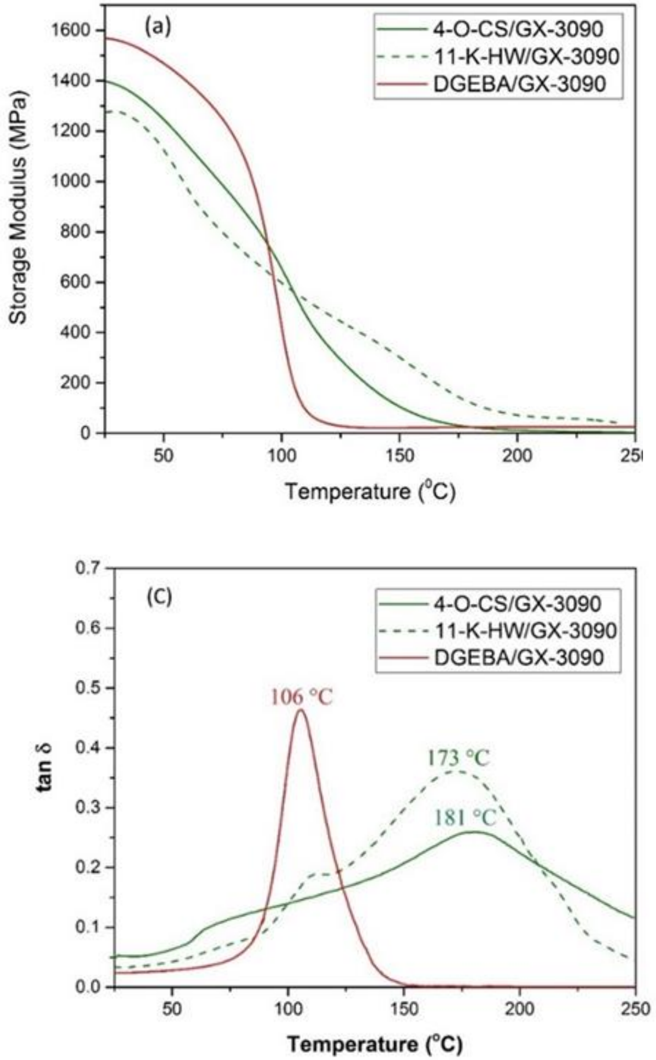


Uncoated Wood

Coated AL with Commercial Epoxy

Coated Wood with Biobased Epoxy

Coated AL with Biobased Epoxy

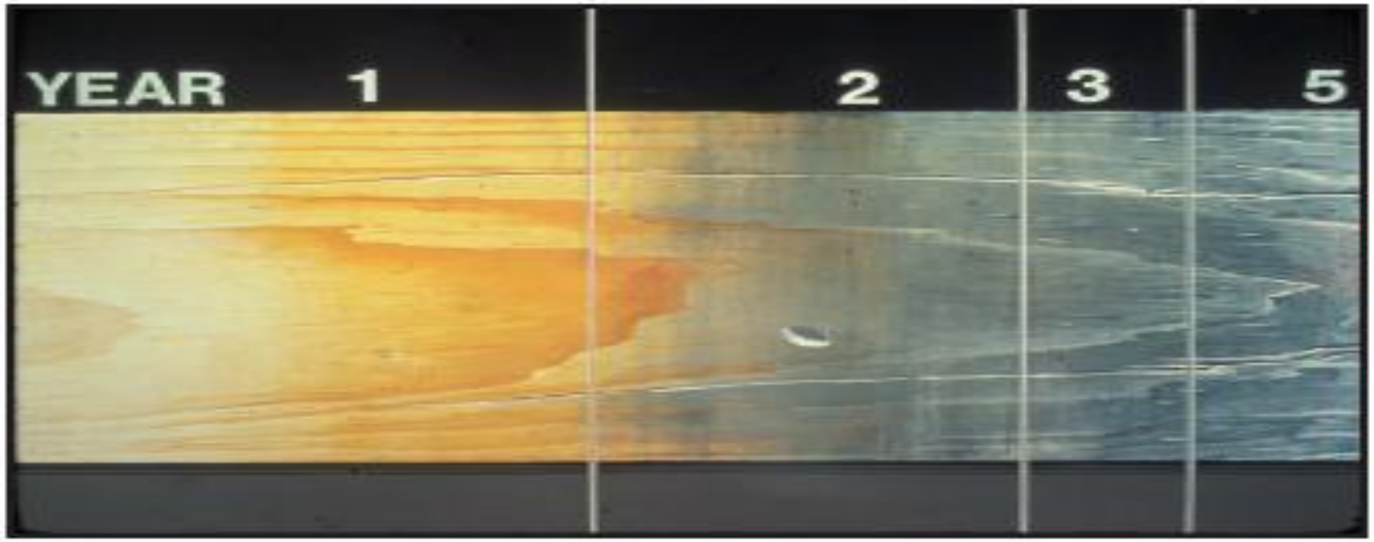


Biobased UV-Stabilizer

Weathering of Wood

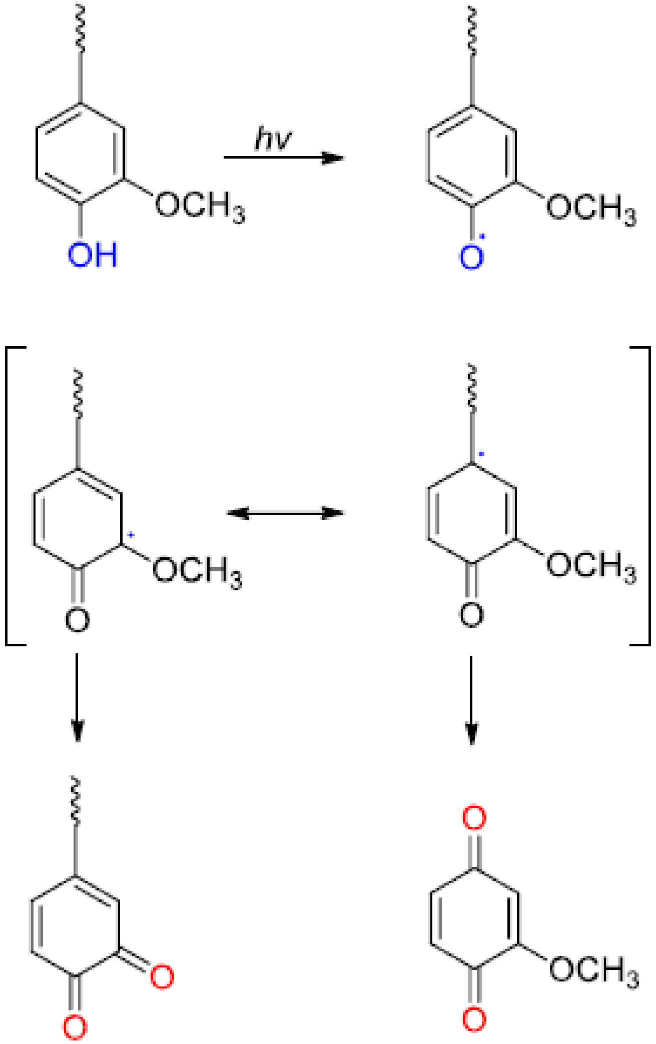
- Discoloration
- Roughening
- Checking of wood
- Mildew growth
- Delamination of fibers

Figure —Surface changes on typical softwood during the natural weathering process.



JCT CoatingsTech

Photo-Degradation of Lignin

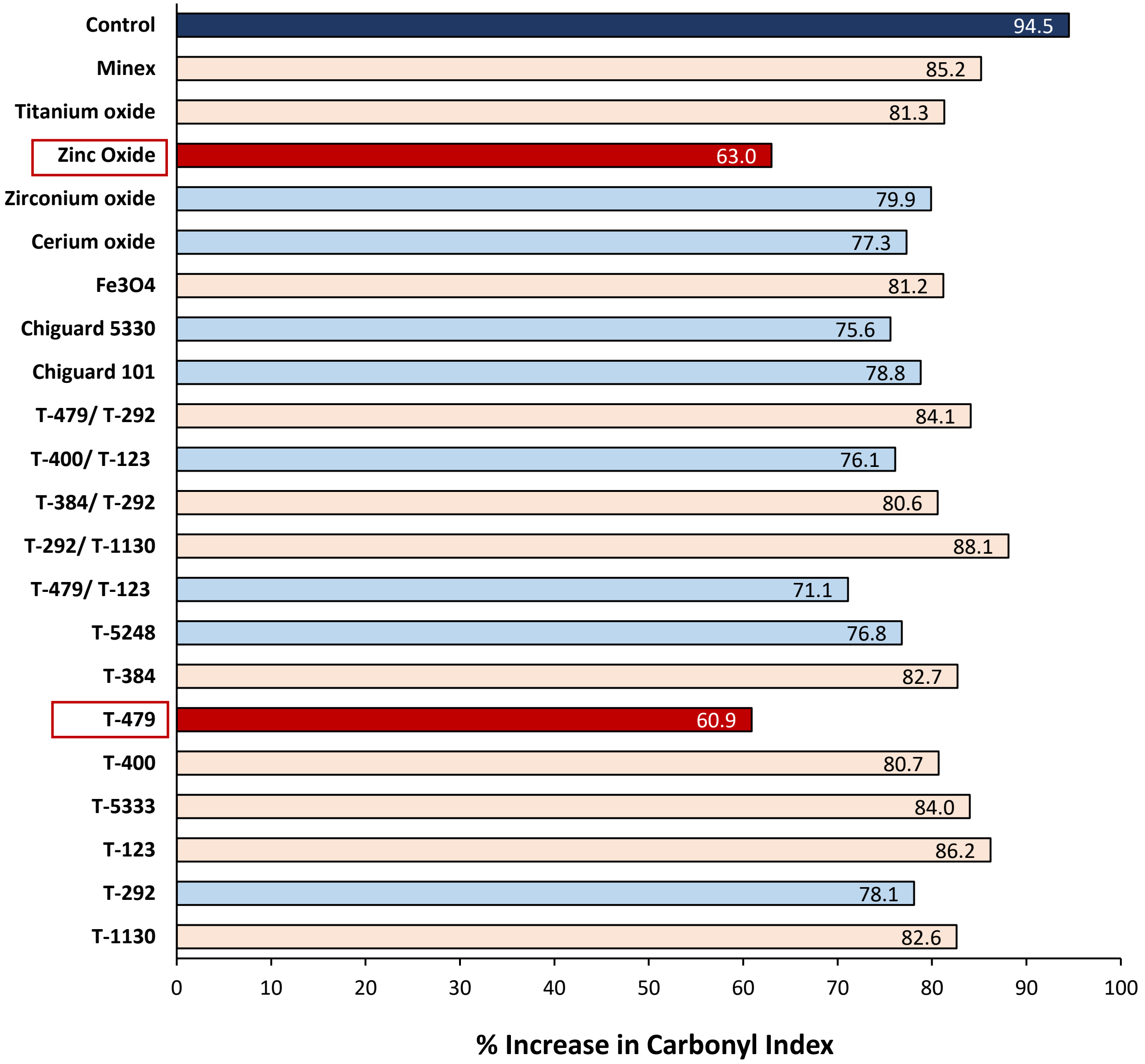


Absorption coefficient of wood components:

1. **Lignin: 80-95%**
2. Carbohydrates: 5-20%
3. Extractives: 2%

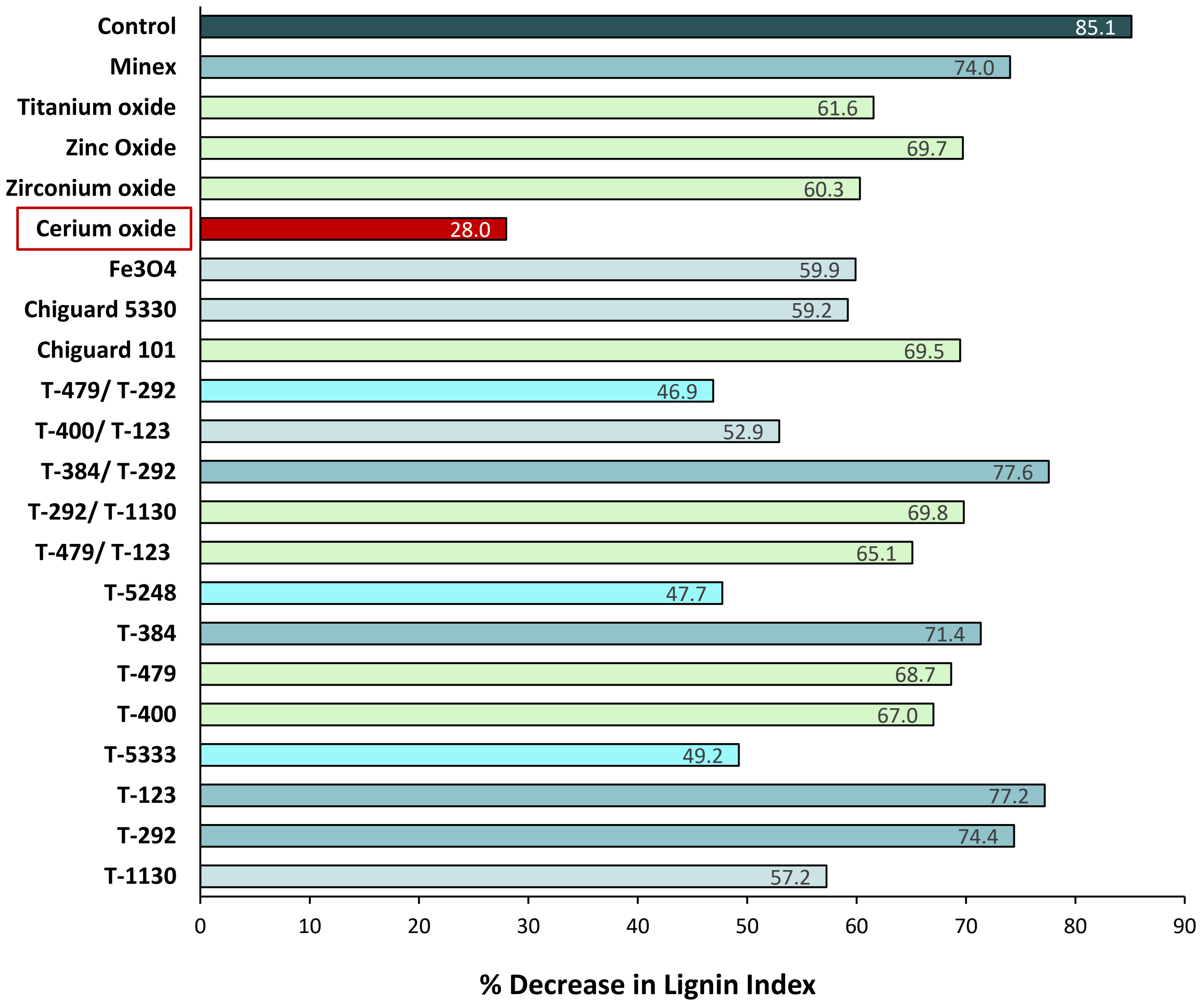
Formation of phenoxy radicals that can be readily oxidized to yellow ortho and para-quinones.

Effect of Various Additives in Increasing Carbonyl Index



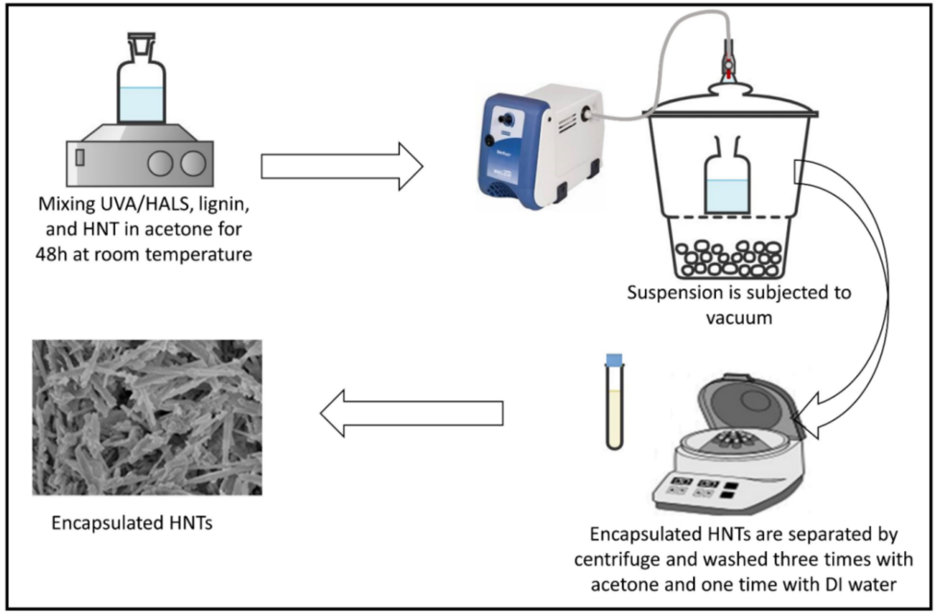
- Decrease in carbonyl index (%) ($\frac{A\ 1735}{A2921}$) of various samples after 35 days of UV irradiation (lower numbers are better),
- Bars with the same color are not significantly different (α=0.05).
- Zinc Oxide and T-479 were the best.

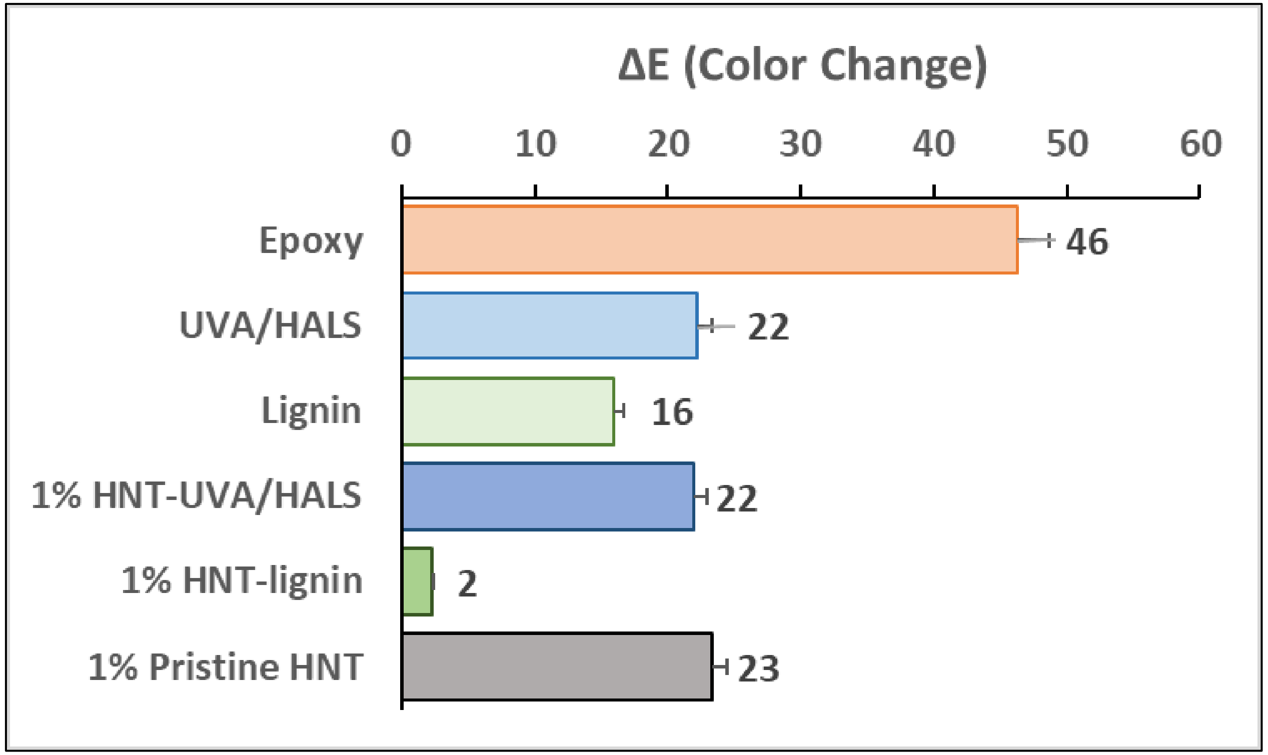
Effect of Various Additives In Reducing Lignin Index



- Decrease in lignin index (%) ($\frac{A\ 1508}{A2921}$) of various samples after 35 days of UV irradiation (lower numbers are better),
- Bars with the same color are not significantly different (α=0.05)
- Cerium Oxide was the best.

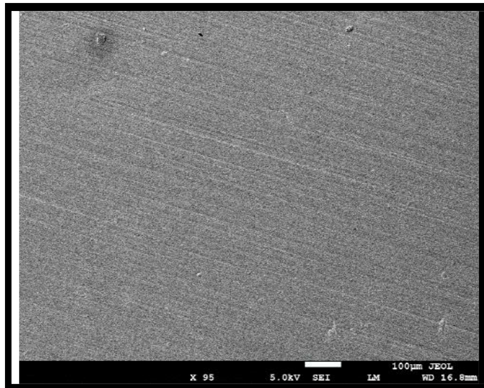
SEM Images of Epoxy Resins Before and After UV



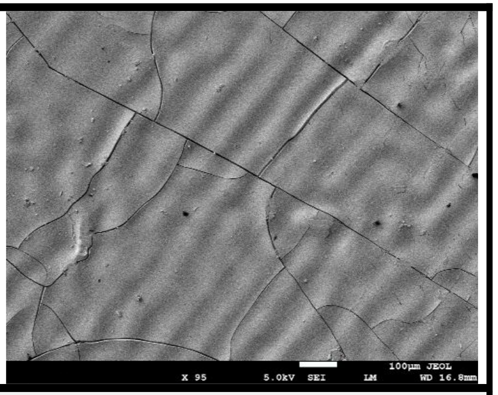


Epoxy resins containing 1% HNT-lignin had the lowest color change (best performance)

SEM Images of Epoxy Before & After UV-Exposure

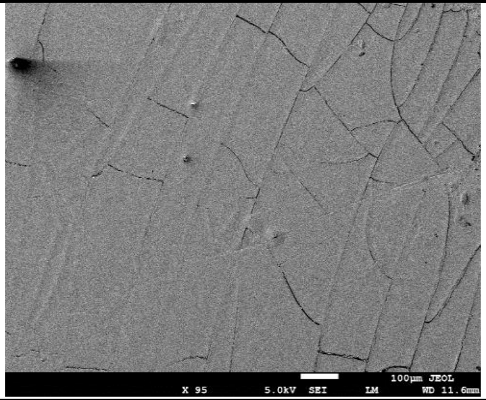


Pure epoxy-before

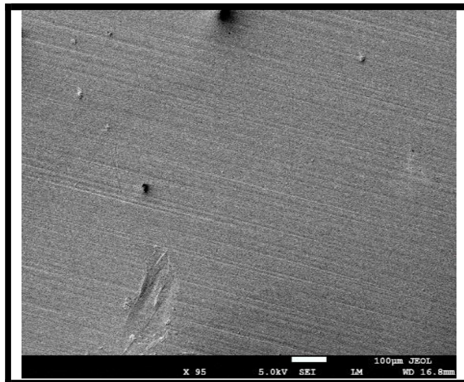


Pure epoxy-after 35 days

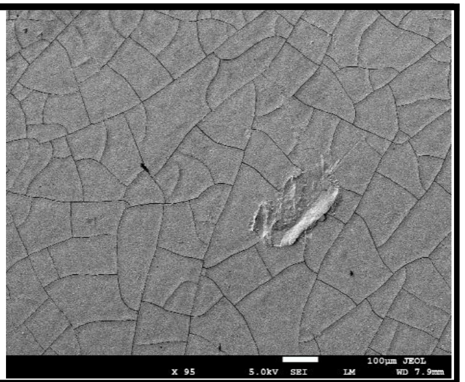
Epoxy with mixture of UVA/HALS-before



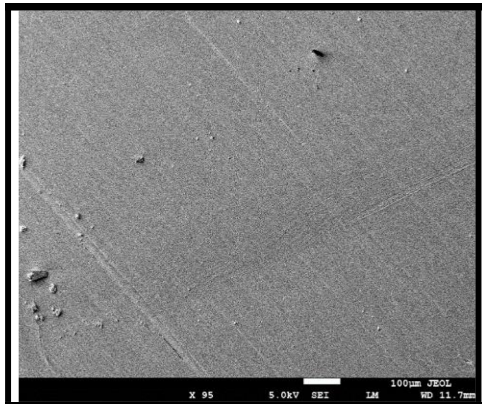
Epoxy with mixture of UVA/HALS-after 35 days



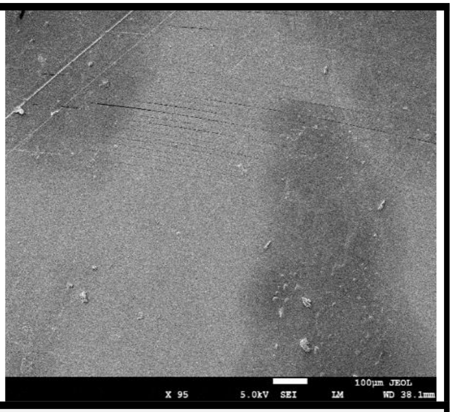
Epoxy with 1% HNT- UVA/HALS-before



Epoxy with 1% HNT- UVA/HALS-after 35 days



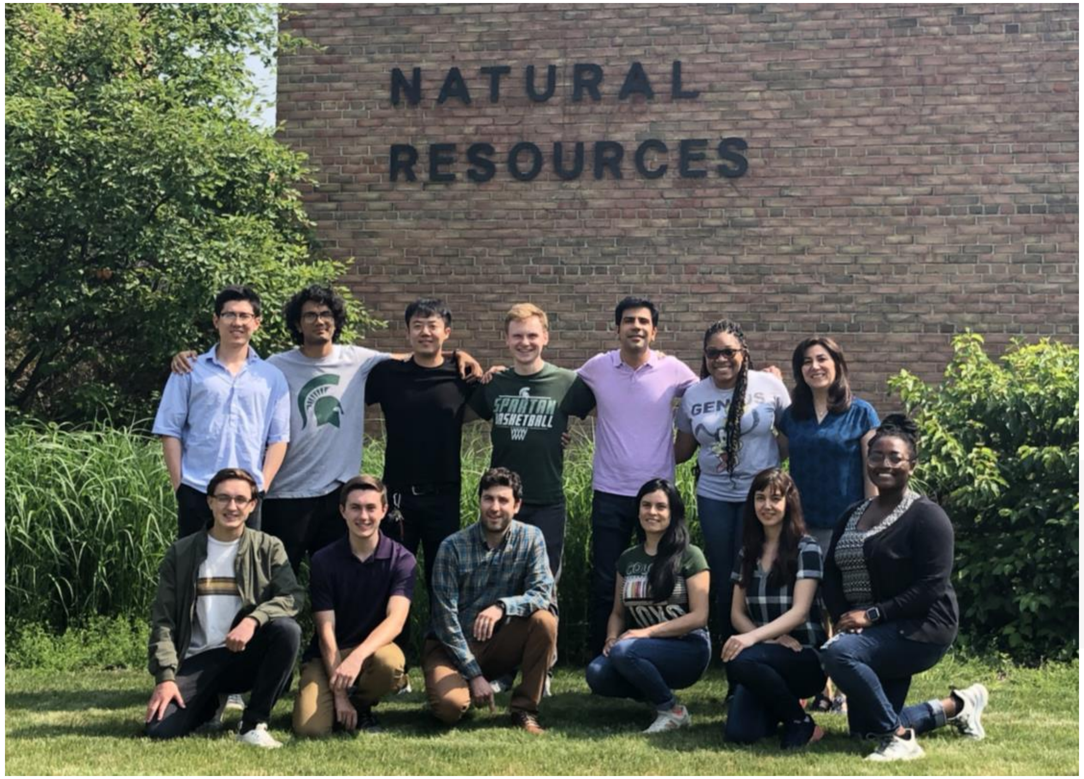
Epoxy with 1% HNT- lignin-before



Epoxy with 1% HNT- lignin-after 35 days

There is no cracks in the epoxy resin containing 1% HNT-encapsulated lignin after UV-Exposure

Acknowledgements



Fortum Bio2X®

POET biorefining

MTRAC AgBio

USDA NIFA

United States Department of Agriculture
National Institute of Food and Agriculture

HEXION™ Responsible Chemistry

Roseburg

ABT

U.S. DEPARTMENT OF ENERGY

ELEMENT5 MODERN TIMBER BUILDINGS

NSF

SHERWIN-WILLIAMS.

epinity

allnex

WBC Wood-Based Composites Center

Henkel

West Fraser

CRIBE centre for research & innovation in the bio-economy

Would you consider using lignin?

Mojgan Nejad, Nejad@msu.edu