WASHINGTON STATE UNIVERSITY

Mechanochemical Modification of Lignin and Application of the Modified Lignin for Polymer Materials

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Significance

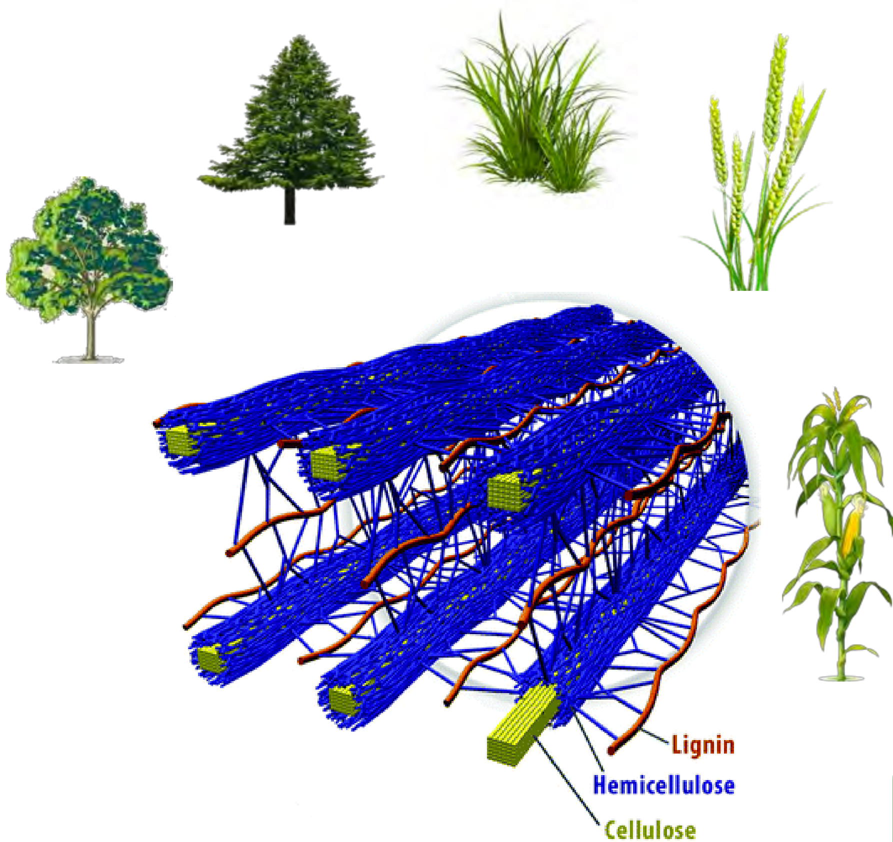
Petroleum-based products have big issues

A shift to biobased products

Lignocellulosic biomass

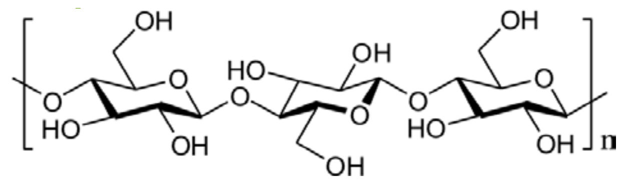
- ✧ most abundant renewable resource
- ✧ annual yield: 200 billion tons

Lignocellulosic Biomass

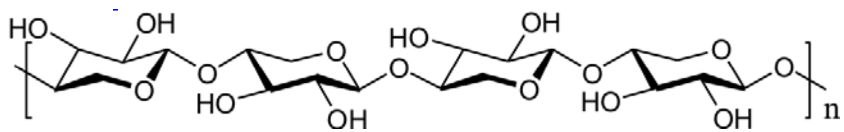


A Brandt, J Gräsvik, JP Hallett, T Welton. Green chem., 2013, 15, 550-583.

Cellulose 40-45%
- Crystalline
- Linear polysaccharide of

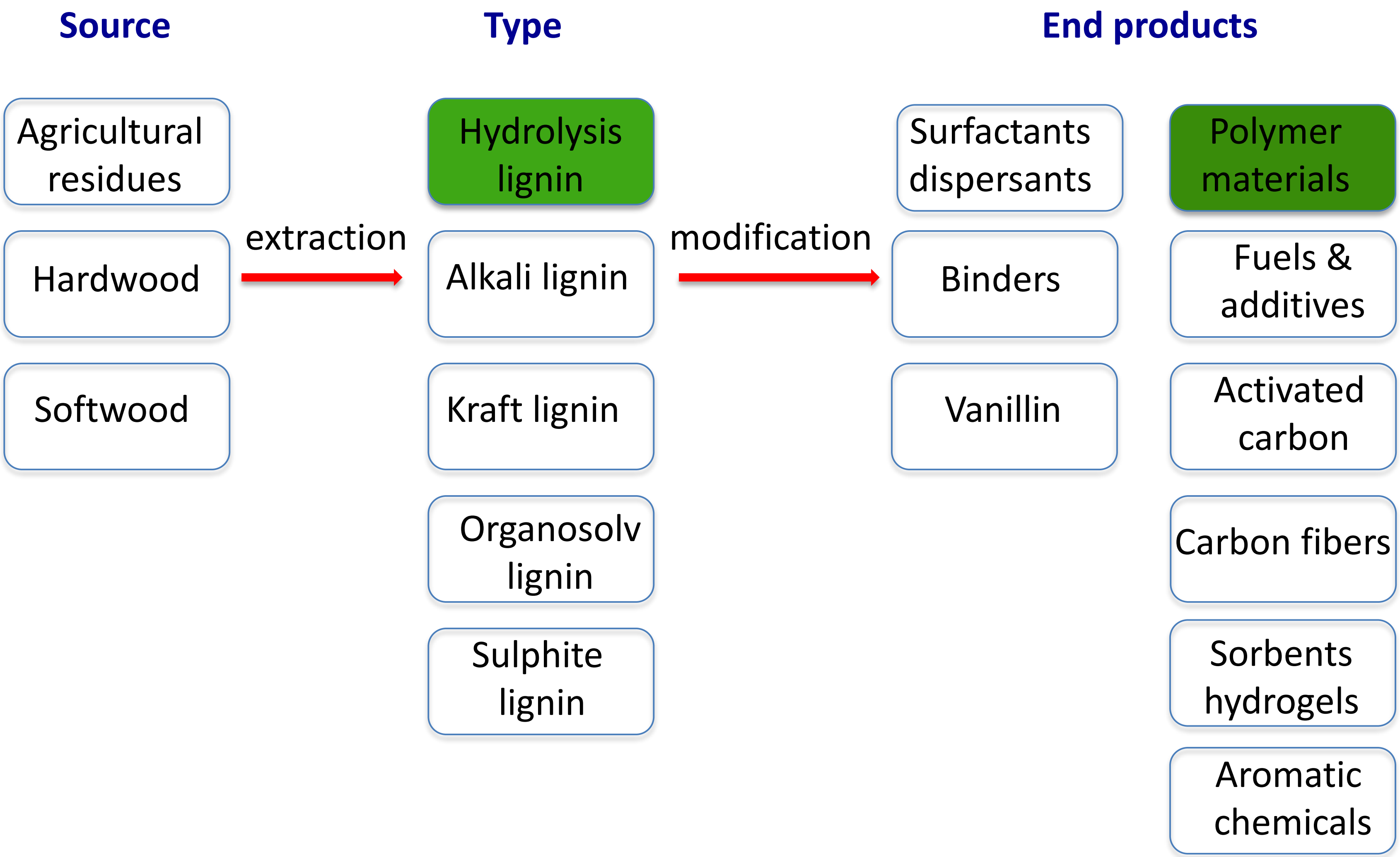


Hemicellulose 25-35%
- Amorphous
- Branched polysaccharide of

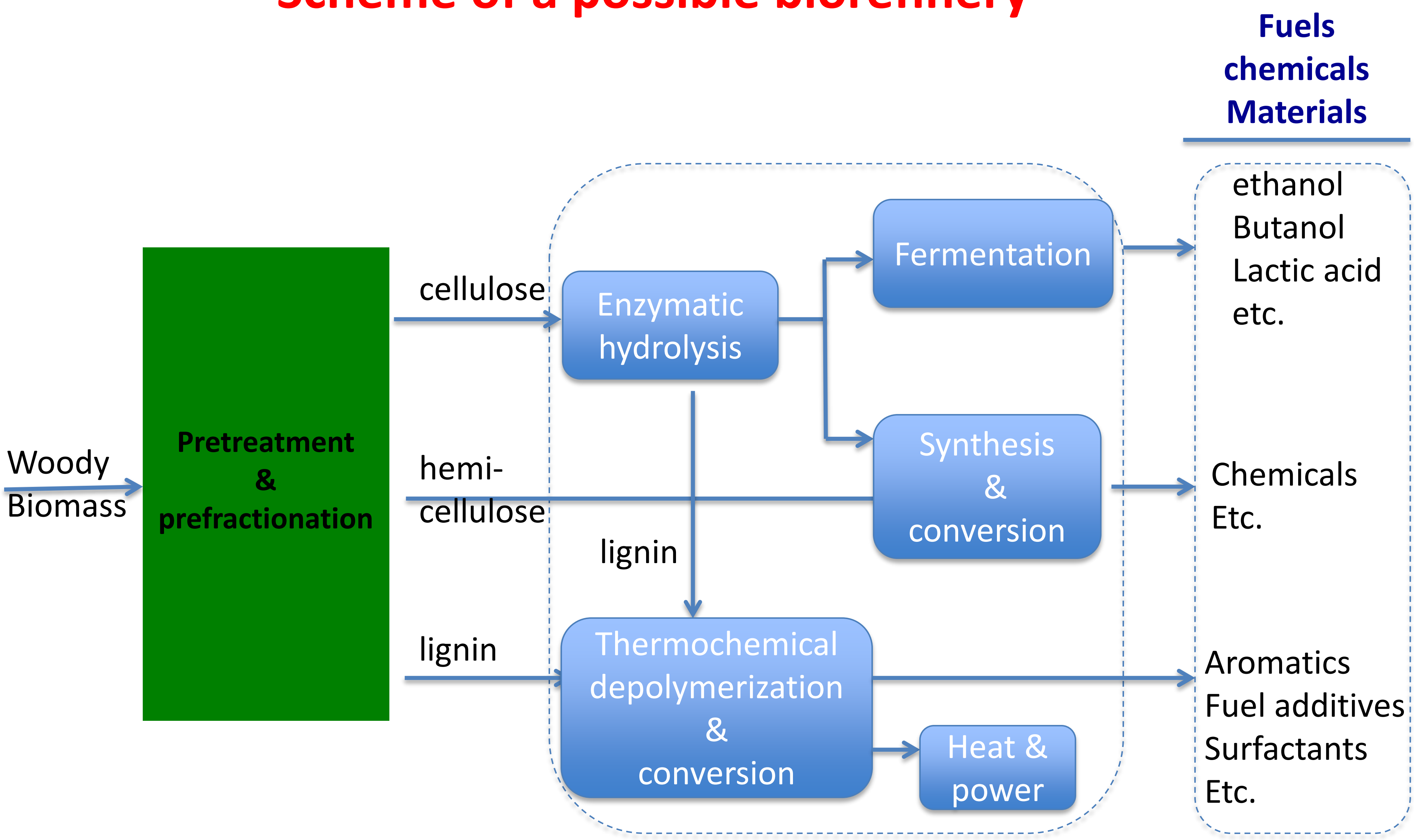


Lignin 10-30%
- Amorphous
- Highly branched aromatic polymer
- Phenylpropanols

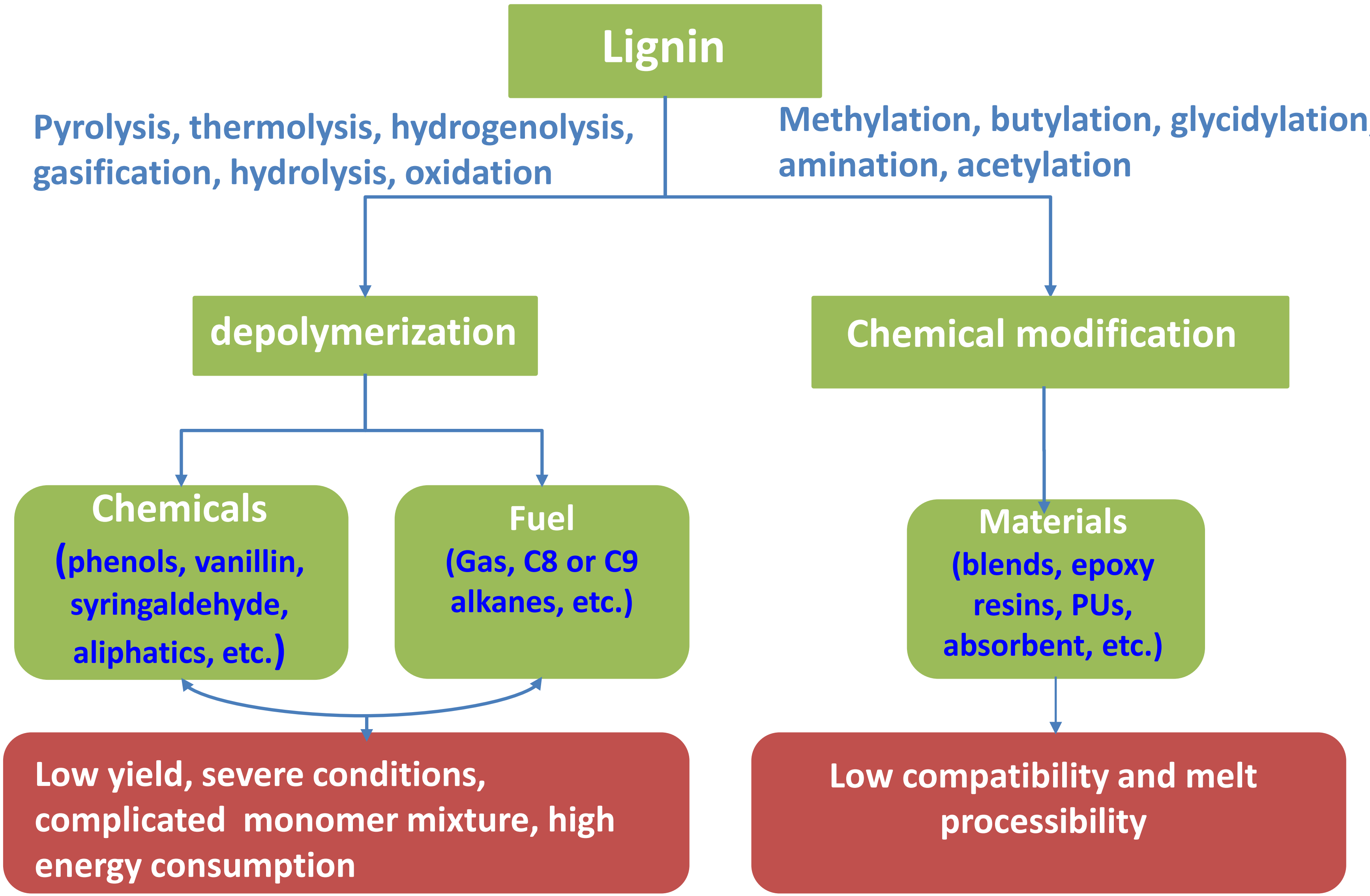
Sources, types and potential products and applications of lignin



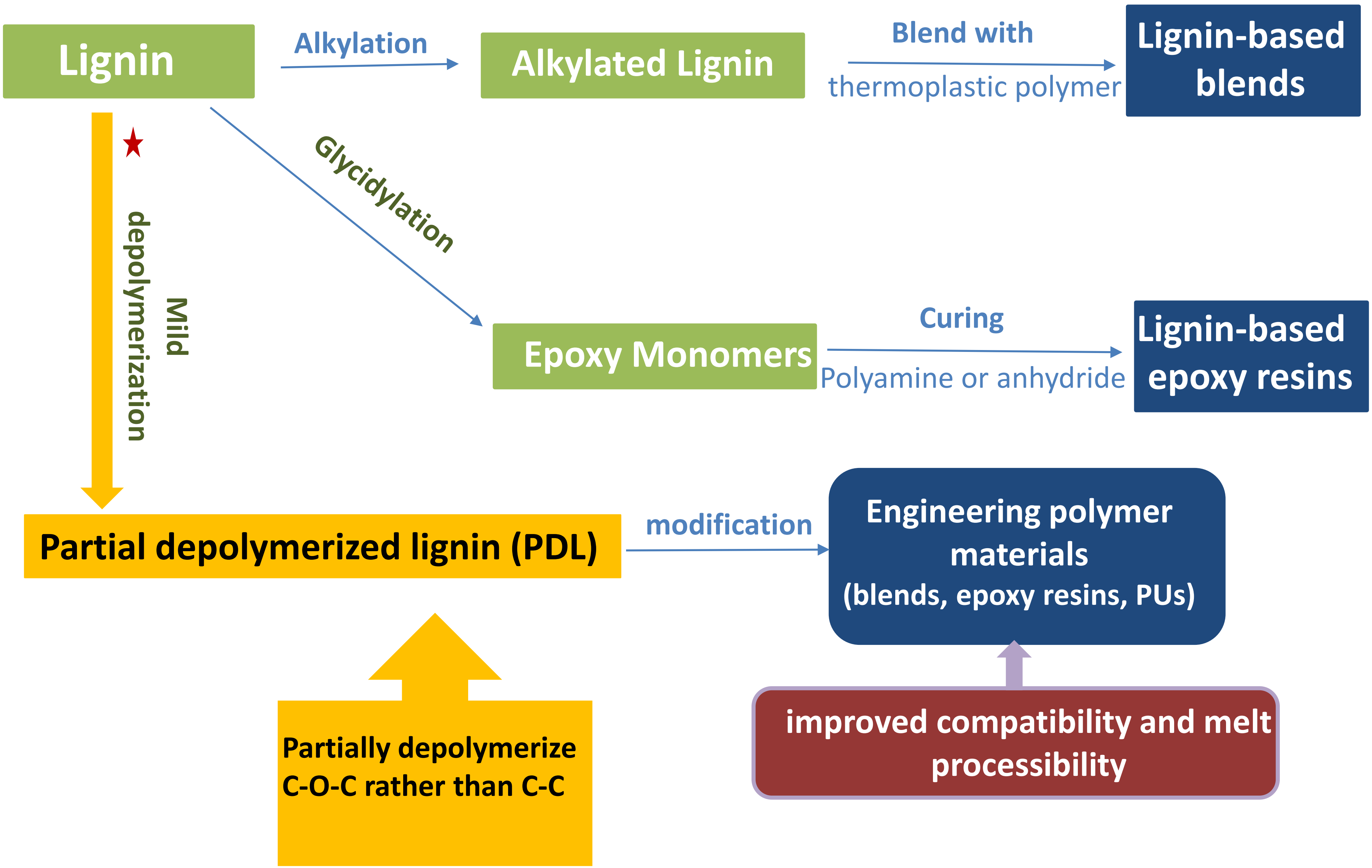
Scheme of a possible biorefinery



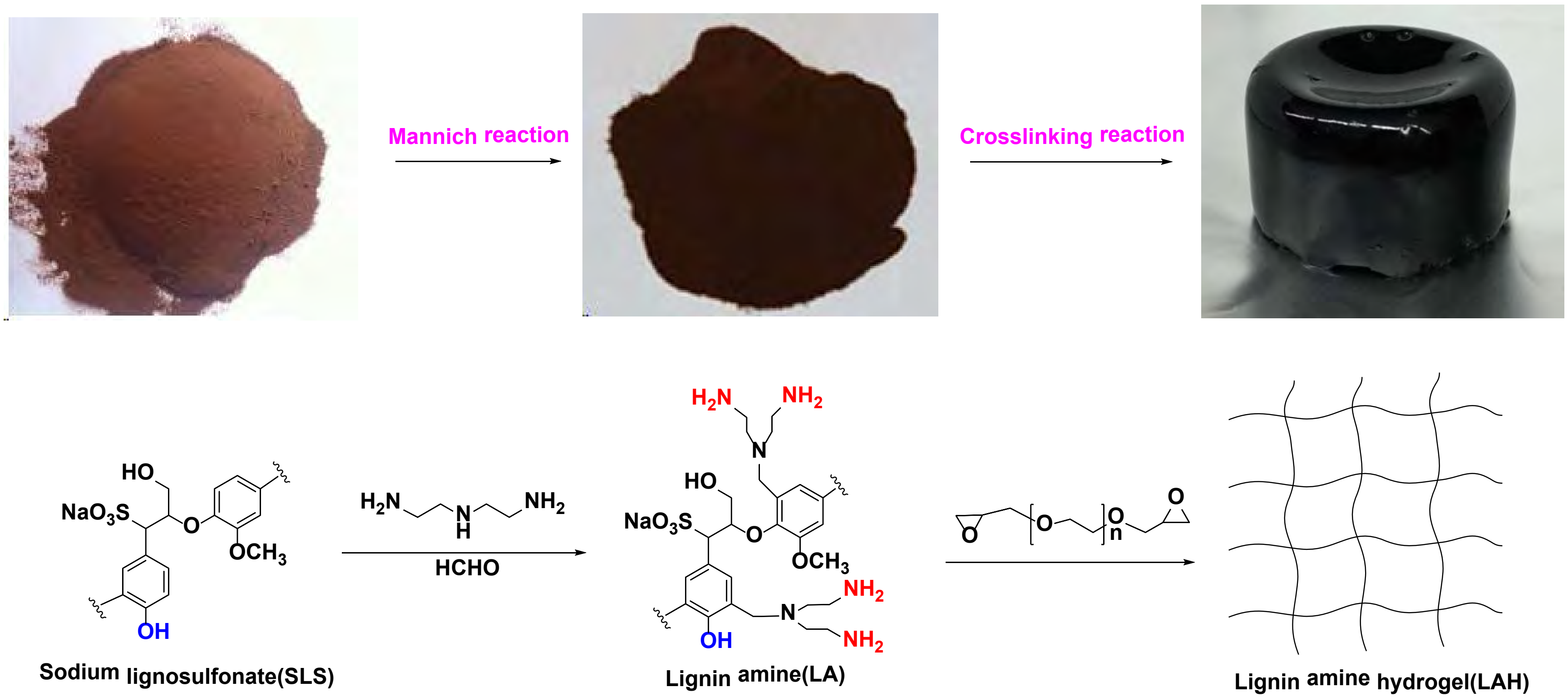
Conversion of Lignin to bioproducts



Use of lignin for materials - Methods

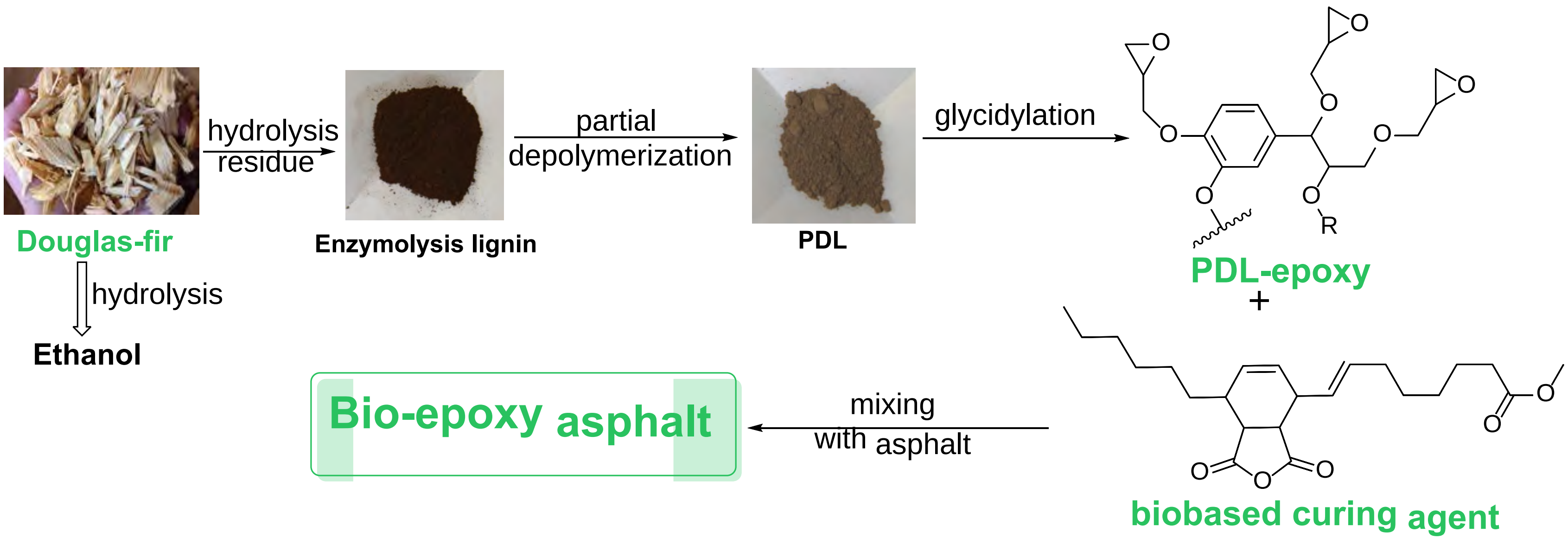


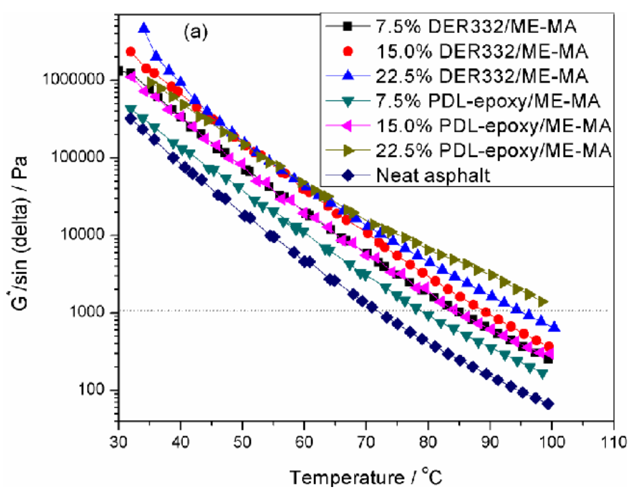
Hydrogel made from lignosulfonate



Xiaoxu Teng, Junna Xin, Hui Xu, Jinwen Zhang (submitted)

Lignin-derived epoxy modified asphalt



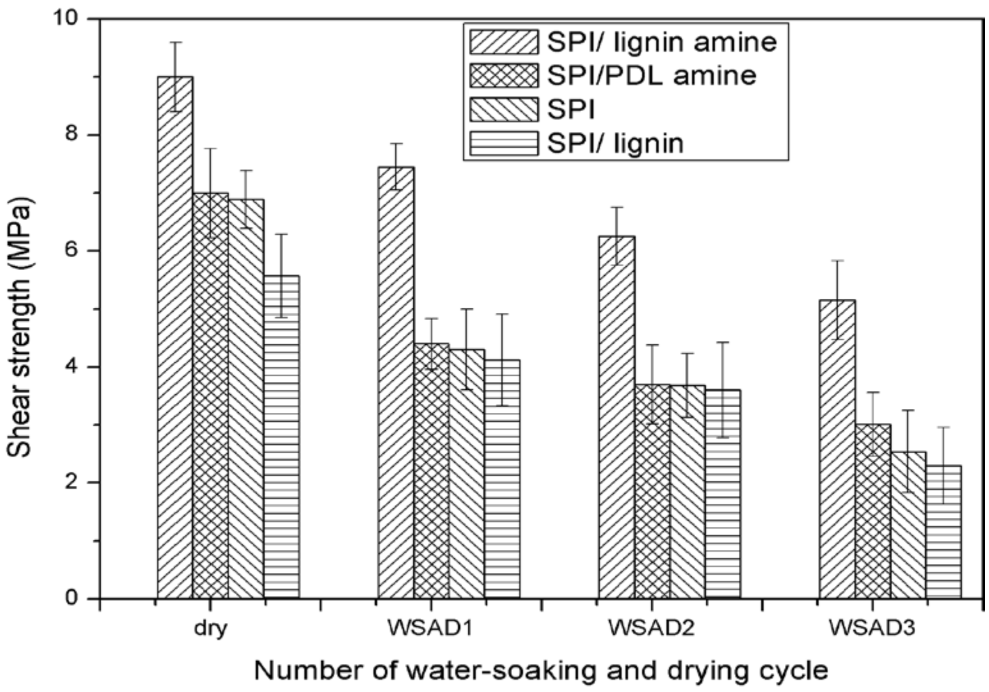


ACS Sustainable Chemistry and Engineering 2016

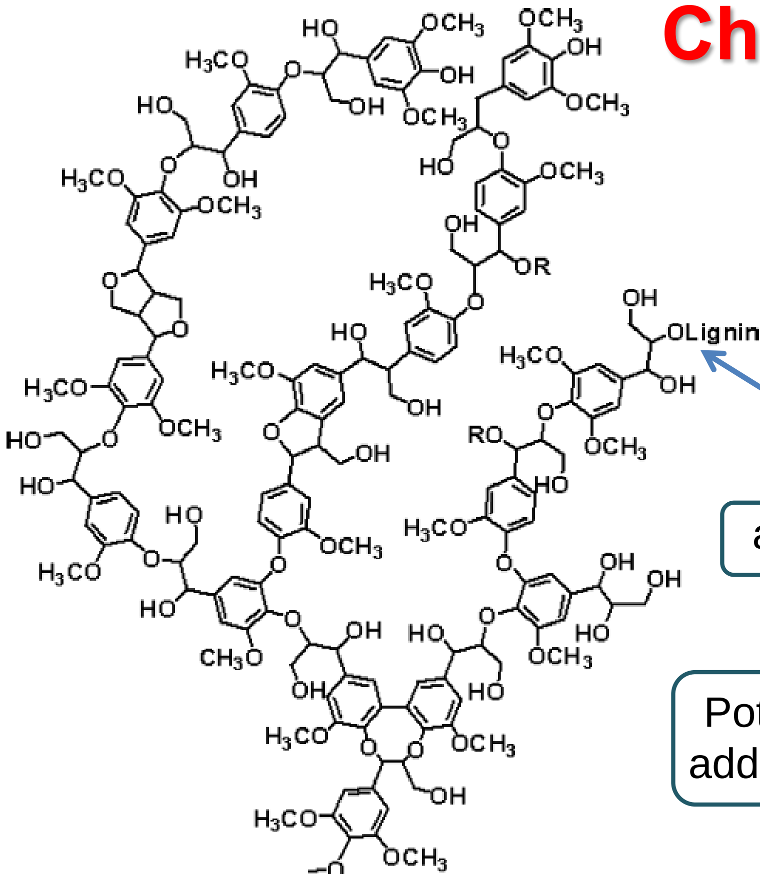
Lignin modified soy protein adhesives for wood composites

Lignin amine

Soy protein adhesive



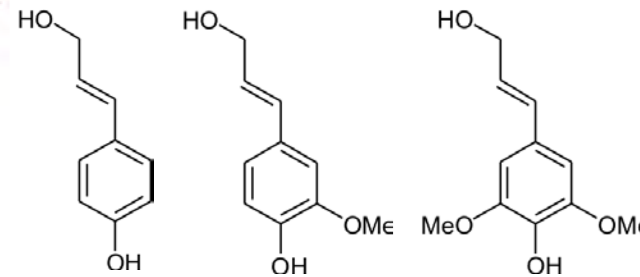
Challenges of lignin modification



https://www.e-education.psu.edu/egee439/node/665

abundant hydroxyls

Potential feedstock: value-added chemical compounds



coumaryl alcohol *coniferyl alcohol* *syringyl alcohol*

Highly branched structure
Strong intramolecular force
Low solubility in solvents

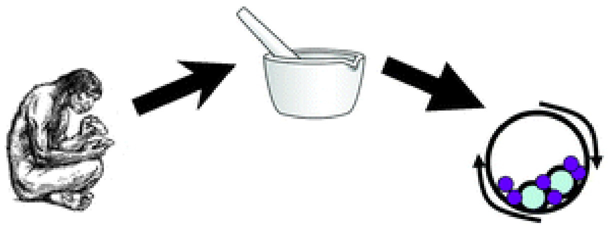
Low accessibility of hydroxyls (OH)

Low reaction efficiency and conversion

Need a simple and green method for lignin modification

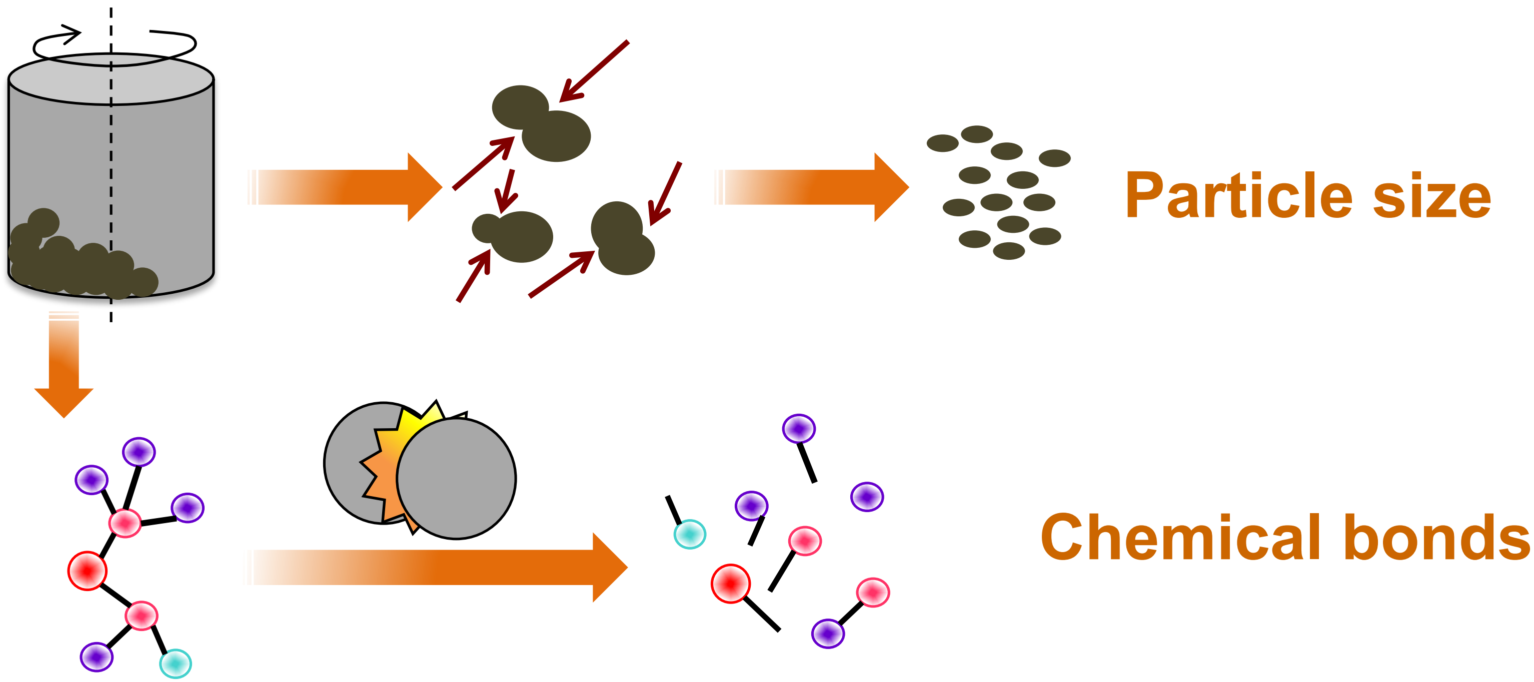
Mechanochemistry

History

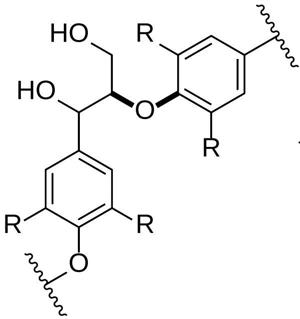


Merits

- ✧ Initiate reaction in the absence of solvent
- ✧ Reduce by-products and toxic wastes
- ✧ Reduce reaction time (energy savings)



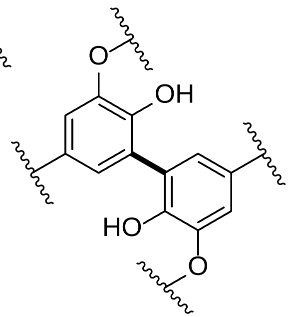
Major linkages in lignin



A

46% (SW)
60% (HW)

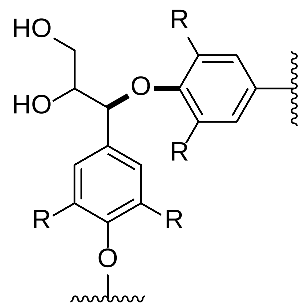
β-O-4



B

9.5-11% (SW)
4.5% (HW)

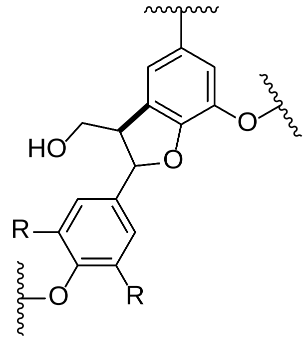
5-5



C

6-8% (SW)
6-8% (HW)

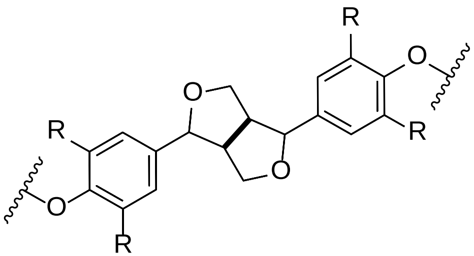
α-O-4



D

9-12% (SW)
6% (HW)

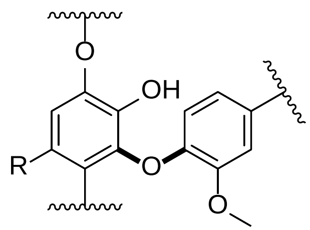
β-5



E

2% (SW)
3% (HW)

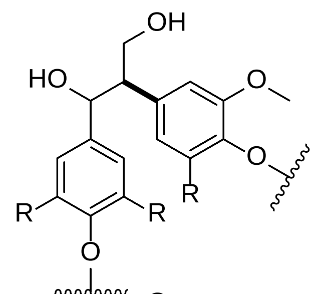
β-β



F

3.5-4% (SW)
6.5% (HW)

4-O-5



G

7% (SW)
7% (HW)

β-1

Mechanochemistry in lignocellulosic biomass

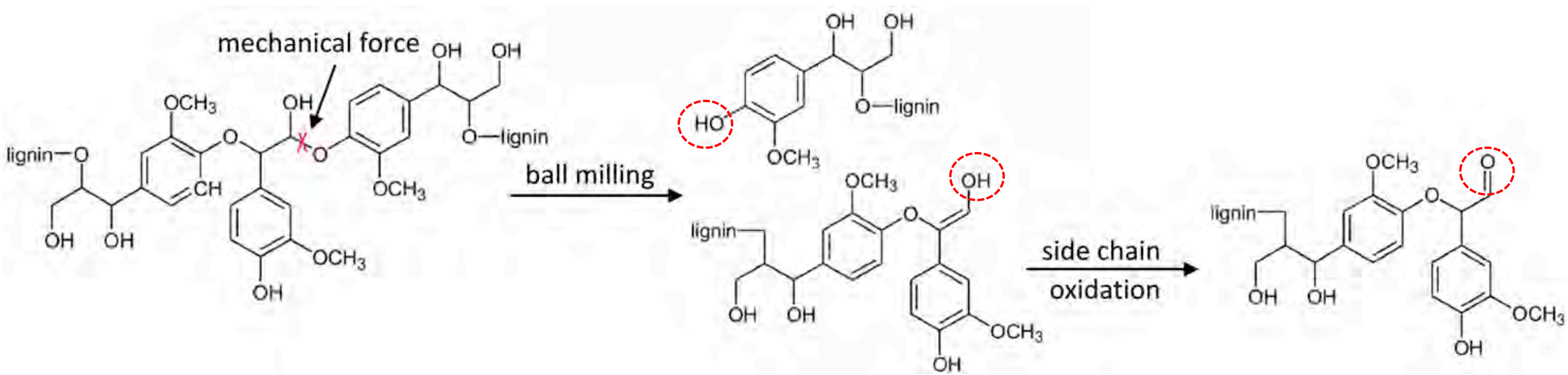
Mechanical energy → Initiate reaction / Structural change

Isolation of lignin from wood and pulp

Free radicals
undergo reaction with
radical scavenger

Ball milling → **Yield** / **Molecular weight** / **Structure**

Cleavage process of β-O-4 linkages in lignin



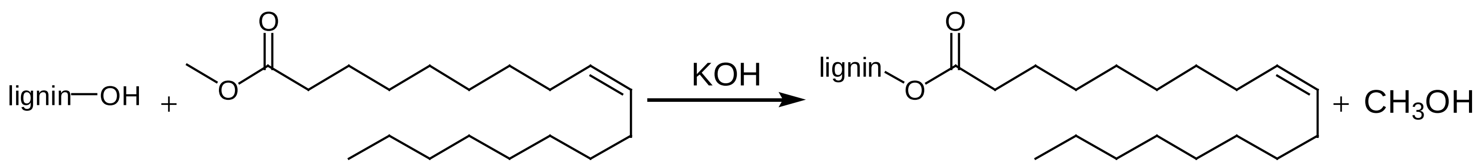
Lignin polymer materials for engineering application

- **Lignin as feedstock for thermoplastics**
  - Mechanochemical modification of lignin

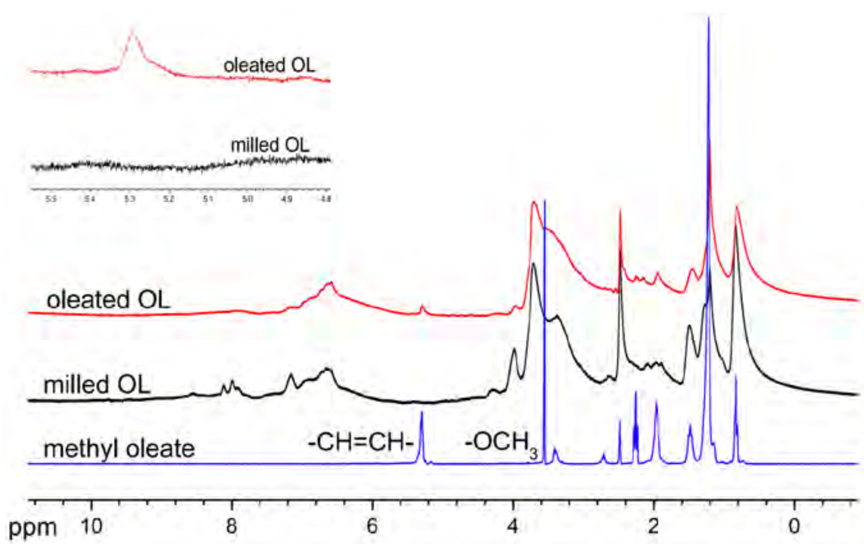
    Transesterification between lignin and fatty oils
  - Modified lignin-based polymer blends
- **Lignin as feedstock for thermosets**
  - Mechanochemical modification of lignin

    Esterification between lignin and anhydrides
  - Modified lignin-derived cured epoxy resins

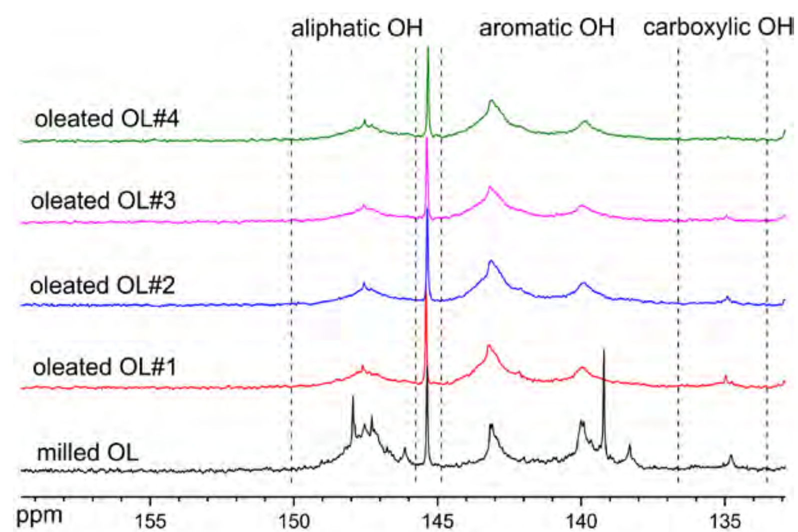
Transesterification between lignin and fatty oils



^{1}H NMR spectra



^{31}P NMR spectra



31 P NMR Spectra of oleated *organoslv lignin (OL)*

Effects of oleation stoichiometry on conversion and hydroxyl value of modified lignin

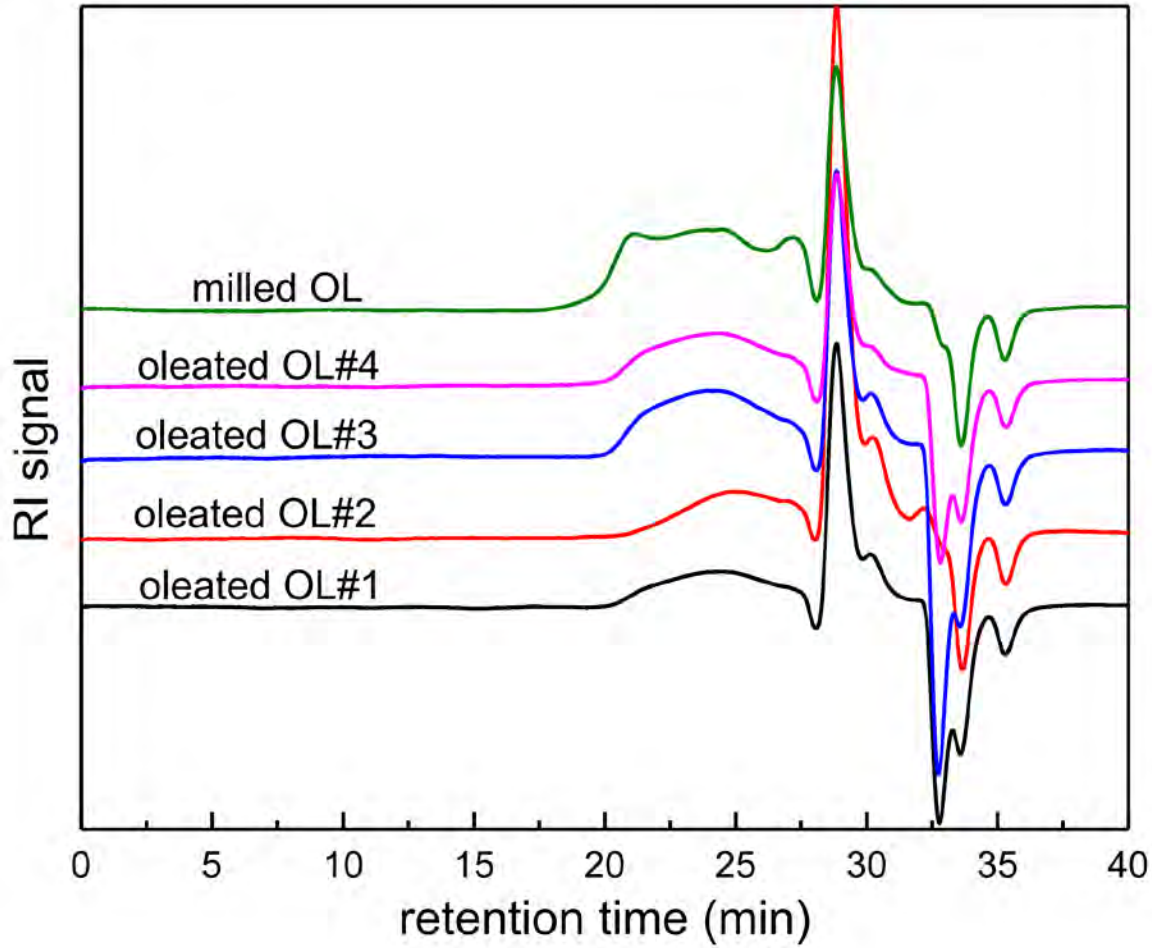
Sample	$n_{L\text{-}OH}:n_{Mo}$ (molar ratio)	Conversion (%)	Hydroxyl value (mmol/g)		
			Aliphatic OH	Aromatic OH	Total
milled OL	/	/	2.35	2.73	5.08
oleated OL#1	1:0.5	25.02	0.70	2.19	2.89
oleated OL#2	1:0.6	25.46	0.64	2.22	2.86
oleated OL#3	1:0.7	24.43	0.59	2.34	2.93
oleated OL#4	1:0.8	22.72	0.72	2.33	3.05

Effects of oleation stoichiometry on particle size and molecular weight

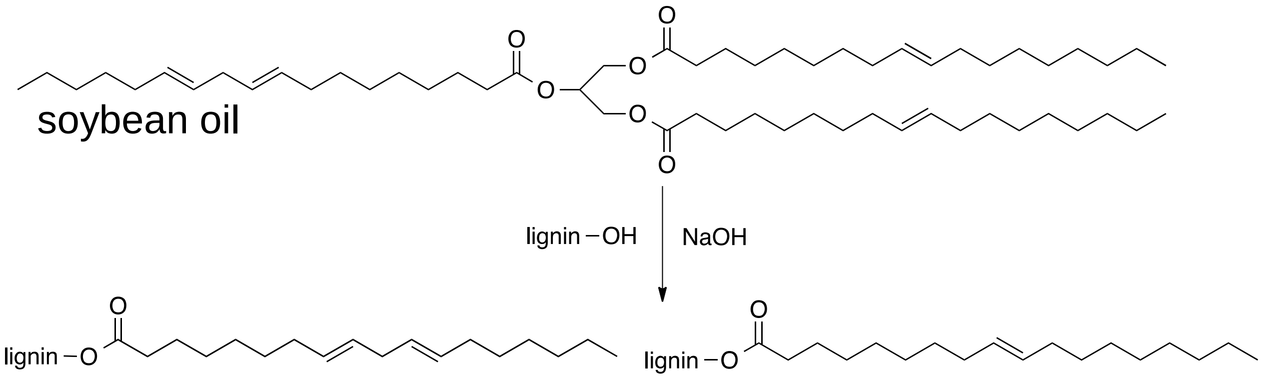
Sample	$n_{L\text{-}OH}/n_{Mo}$ (molar ratio)	Particle size (µm)	Molecular weight		
			M_n	M_w	M_w/M_n
milled OL	/	14.4	2650	8140	3.1
oleated OL#1	1:0.5	3.8	1220	3730	1.8
oleated OL#2	1:0.6	2.0	900	2230	2.4
oleated OL#3	1:0.7	3.2	1320	4090	3.1
oleated OL#4	1:0.8	2.6	1290	4310	3.3

Transesterification between lignin and fatty oils in ball milling

GPC curves of oleated OL

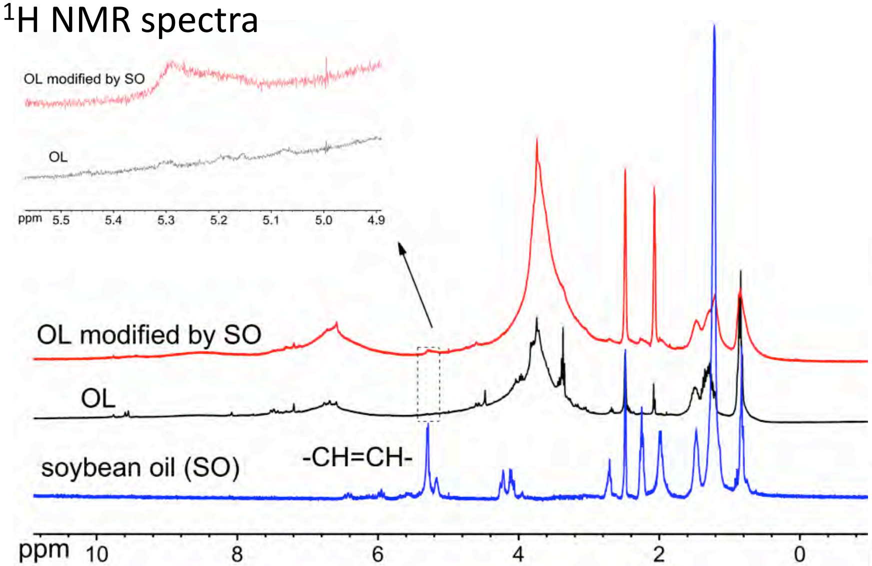


Transesterification between lignin and fatty oils in ball milling

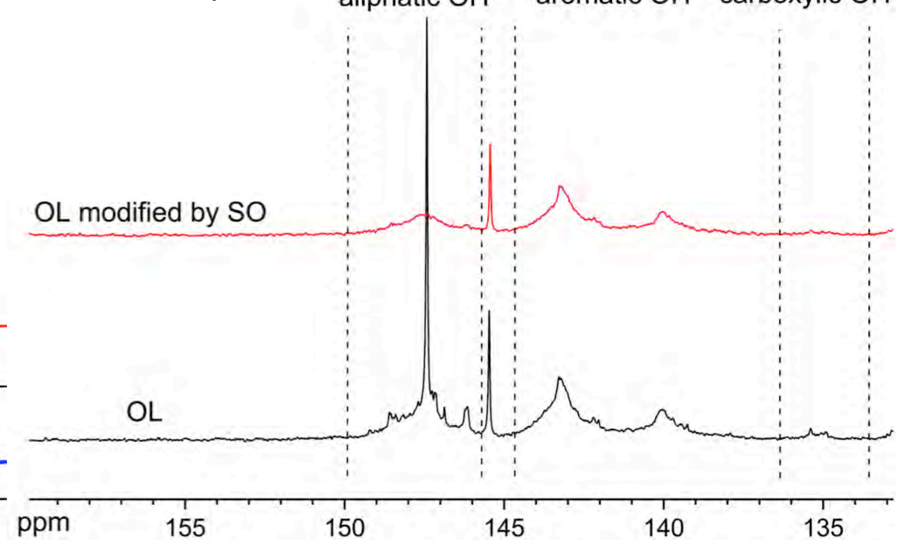


Identification of chemical structure for modified ***organoslv lignin (OL)***

^{1}H NMR spectra



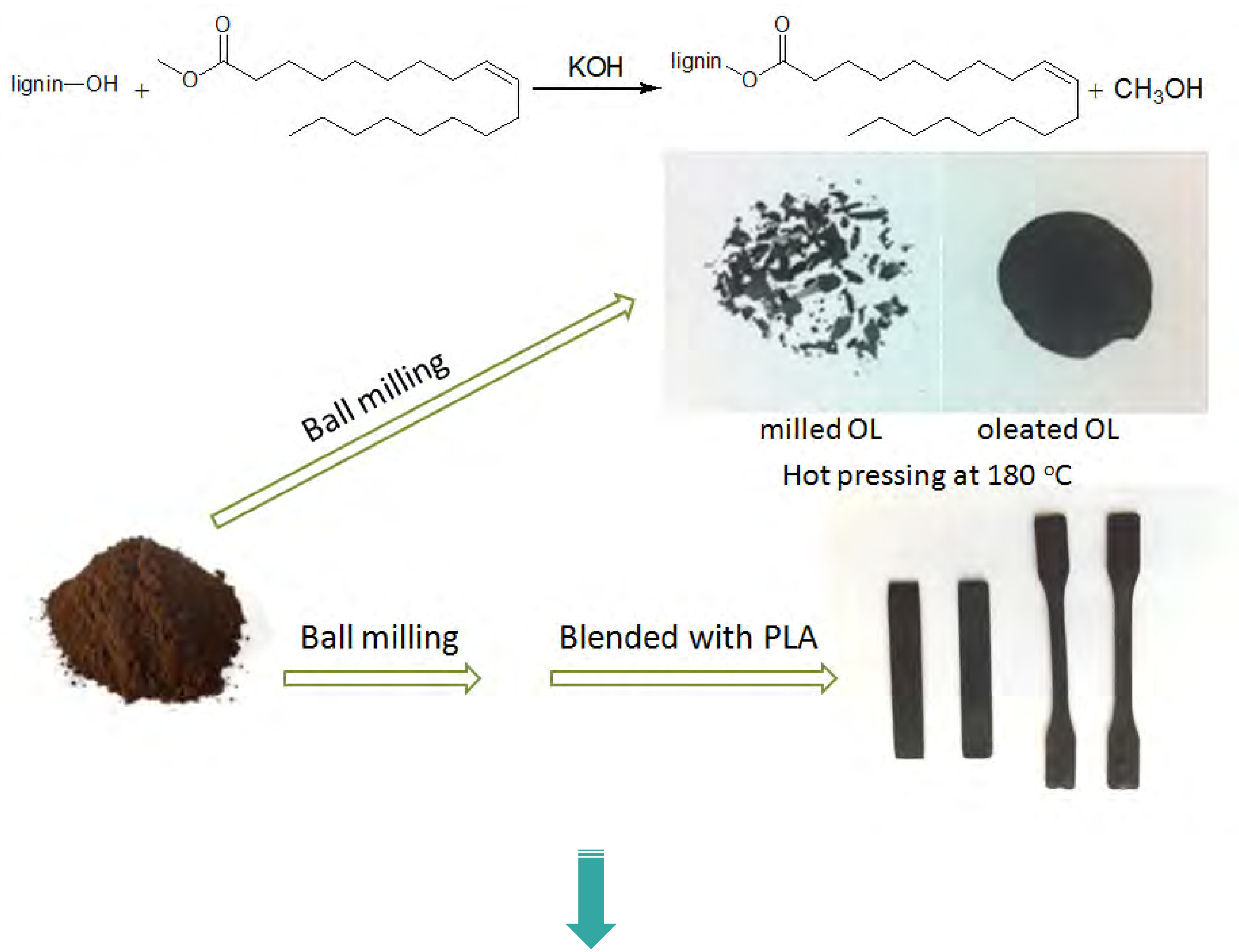
^{31}P NMR spectra



Aliphatic hydroxyls 2.57 mmol/g → 1.04 mmol/g

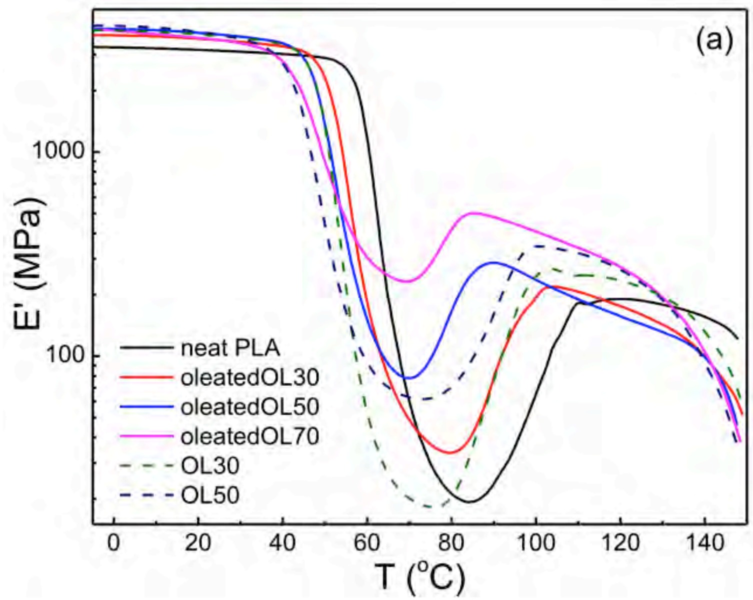
Aromatic hydroxyls 2.60 mmol/g → 2.14 mmol/g

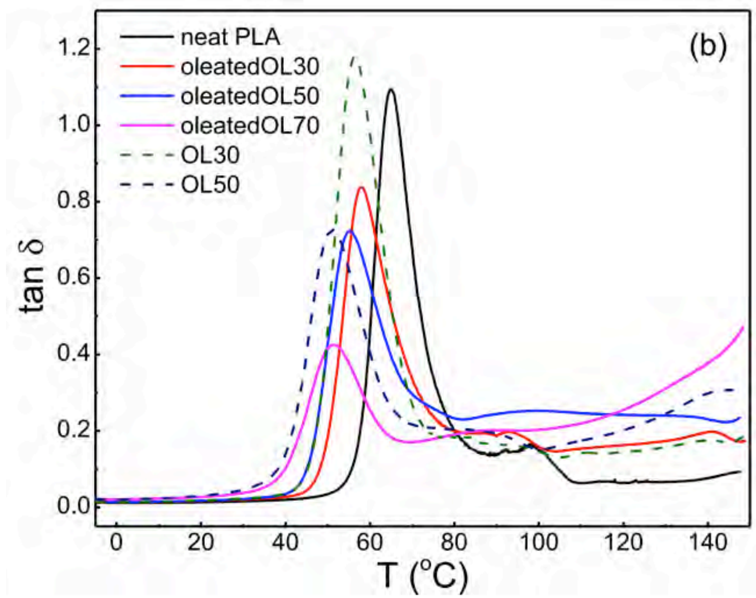
Thermodynamic properties of PLA/lignin blends



Thermoplasticity of lignin is improved after oleation of lignin

DMA curves of (a) storage modulus and (b) tan δ of PLA/lignin blends





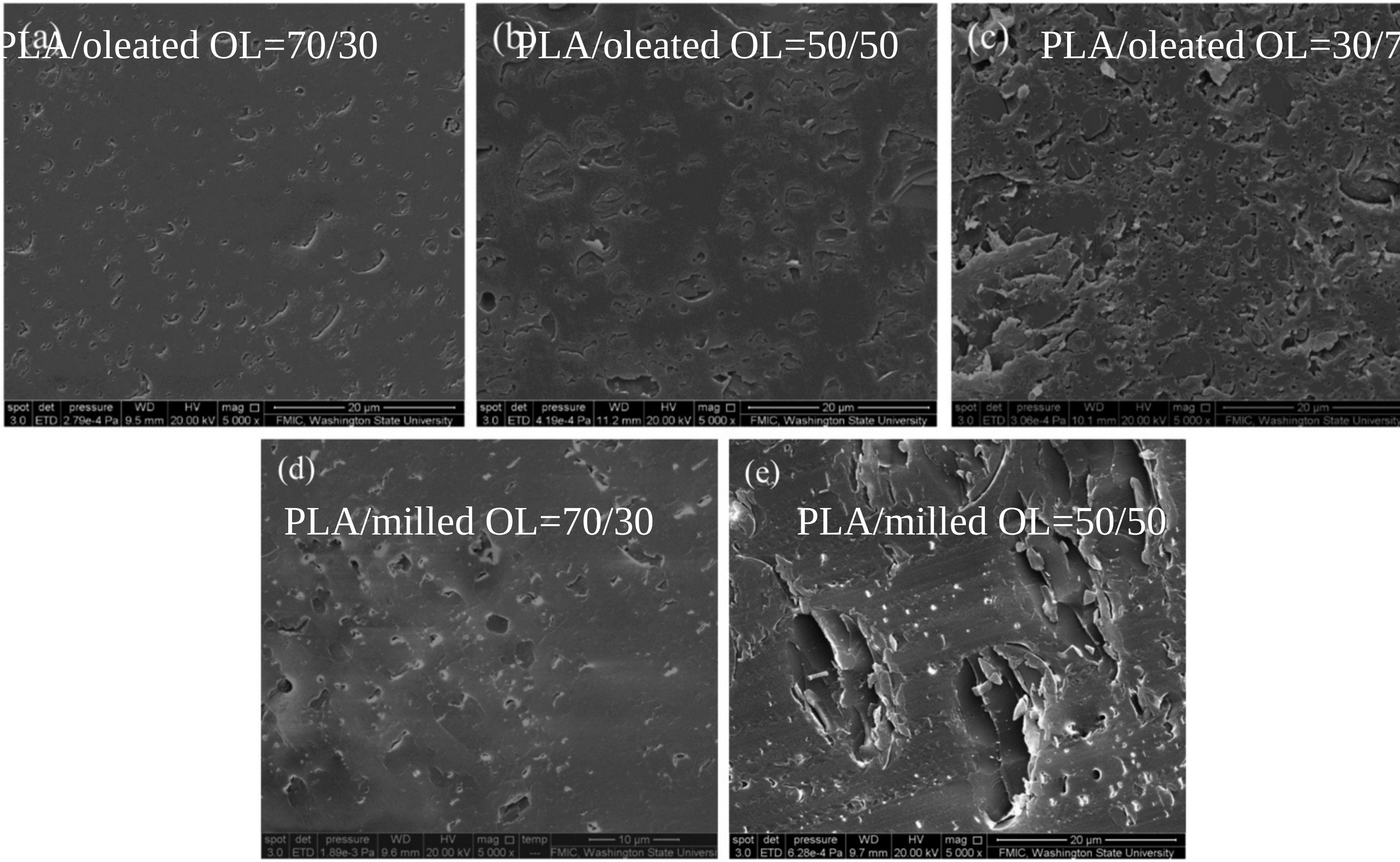
Thermal properties of PLA and its blends

Sample	T_g (℃)[a]	T_g (℃)[b]	T_{cc} (℃)[b]
neat PLA	64.9	57.2	115.8
oleated OL30	58.0	54.4	98.3
OL30	56.1	52.1	101.8
oleated OL50	55.3	49.8	82.8
OL50	51.1	43.7	95.1
Oleated OL70	51.4	44.8	82.9

a: from DMA
b: from DSC

Phase morphology of PLA/lignin blends

SEM micrographs of sliced cross-section surfaces of PLA/lignin blends

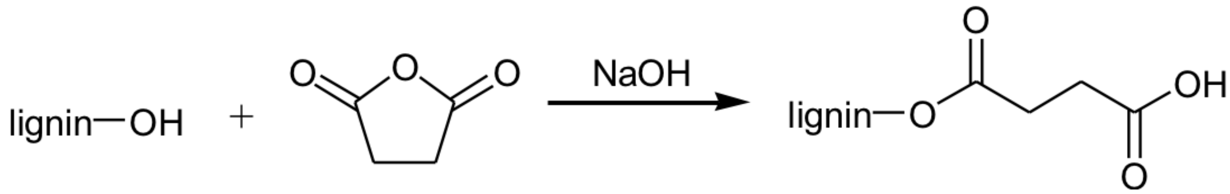


Tensile properties of PLA blends with OL and oleated OL

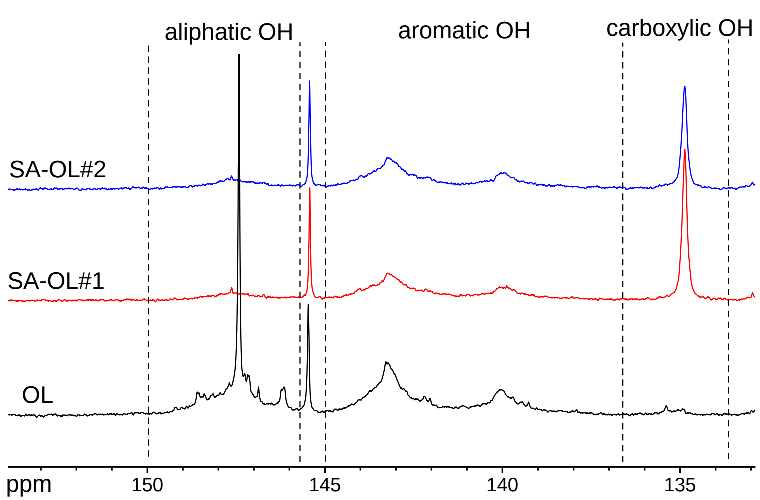
Sample	Elastic modulus GPa	Strength MPa	Elongation @ break %
neat PLA	3.83±0.30	58.30±3.39	1.48±0.12
oleated OL30	3.71±0.16	50.17±1.29	1.40±0.02
milled OL30	3.63±0.41	37.16±2.07	0.94±0.06
oleated OL50	3.62±0.20	30.36±0.97	0.95±0.02
OL50	3.50±0.23	25.83±1.34	0.75±0.13
oleated OL70	3.29±0.13	11.65±1.53	0.60±0.03

Esterification of lignin with various anhydrides in ball milling

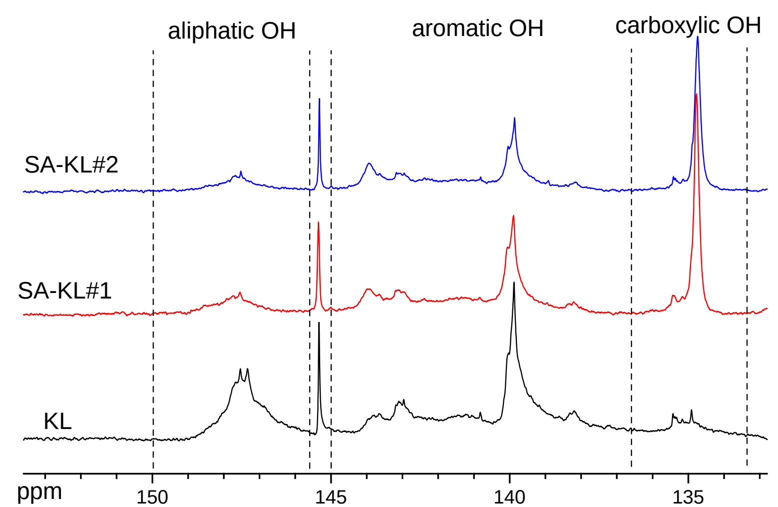
Identification of chemical structure for modified lignin



Organosolv lignin



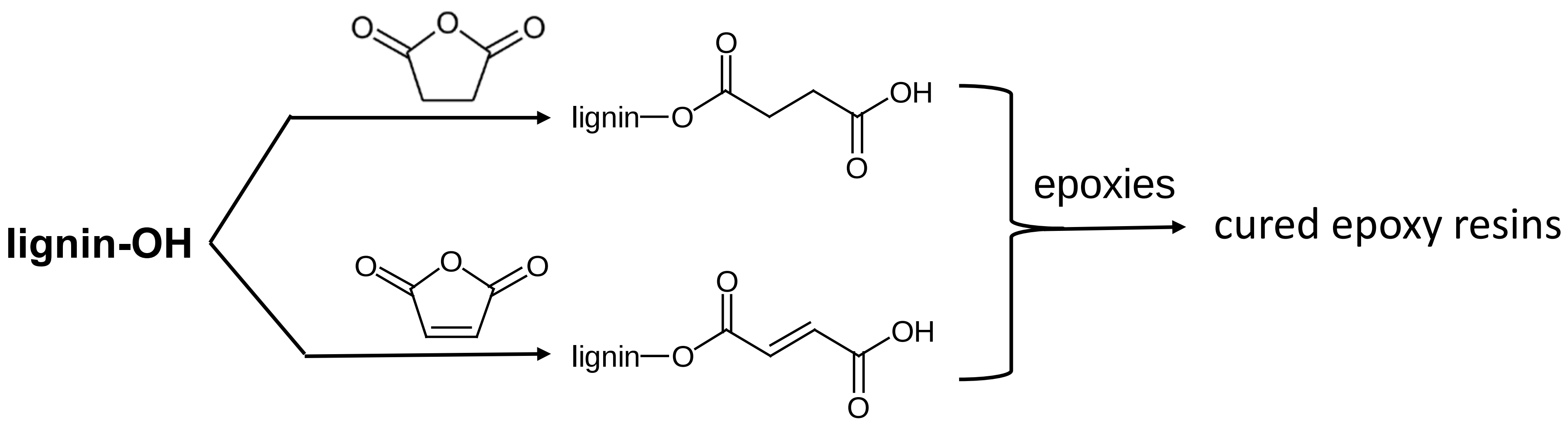
Kraft lignin



^{31}P NMR spectra

Effects of esterification stoichiometry on hydroxyl value of modified lignin

Sample	$n_{L\text{-}OH}$: n_{SA}	Hydroxyl value (mmol/g)		
		Aliphatic OH	Aromatic OH	Carboxylic OH
OL	/	2.57	2.60	0.17
SA-OL#1	1:1	0.24	1.73	1.11
SA-OL#2	1:0.5	0.41	2.02	0.74



Conclusions

- Lignin can be partially depolymerized to yield low MW oligomers by hydrogenolysis under the catalysis of Raney Ni in alkaline solution of mixed dioxane/H_2O solvent or base catalyzed depolymerization in methanol under moderate temperature and pressure
- The resulting PDL can be effectively turned into epoxy monomer by reacting with epicholorhydrin. PDL-epoxy cured with the biobased TMA modified asphalt exhibited improved performance
- Mechanochemical process as a green and solvent-free method can be used for the modification of lignin via transesterification. The compatibility of the modified lignin by methyl oleate with PLA was greatly increased
- The novel strongly swellable hydrogel was successfully prepared from lignosulfonate amine and PEGDEG.

Acknowledgements

Contributors

- Junna Xin
- Jianglei Qin
- Xiaoxu Teng
- Xiaojie Guo
- Ran Li

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