Solvent-fractionated alkaline lignins: from analysis and structure-property correlations to functional materials

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Challenges of the using the most abundant acromatic bioresource-Technical Lignin

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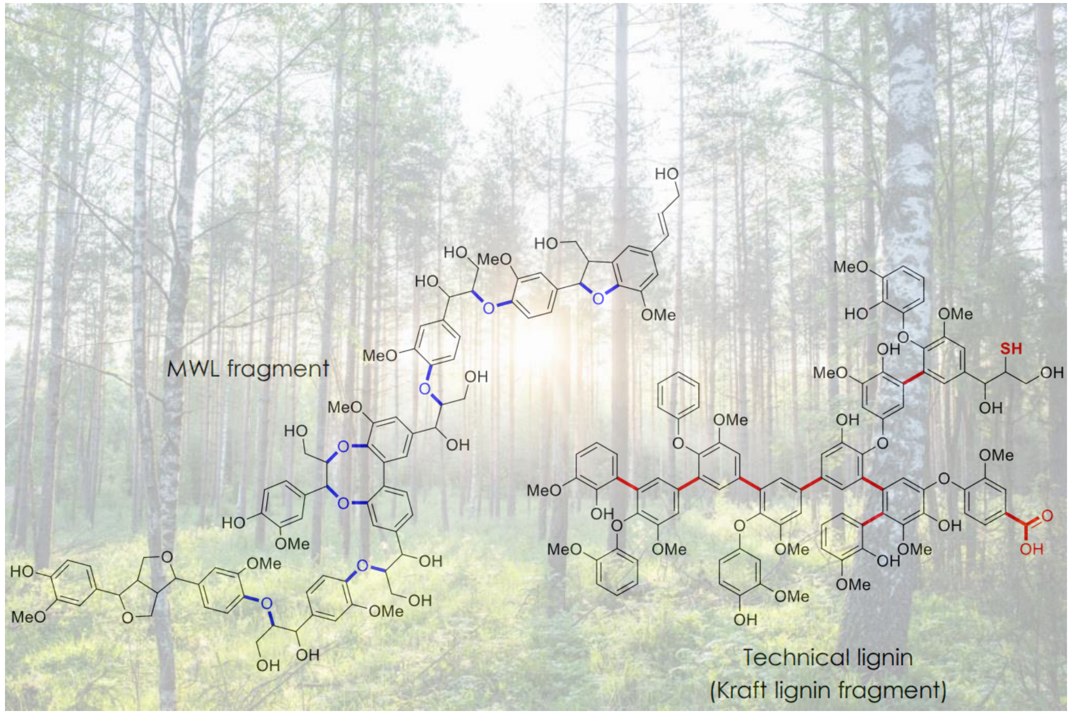
- **Inherent variability** (softwood/hardwood/grass)
- **Lignin is not valued in the pulping and biorefinery process** (condensed lignin structure and low reactivity)
- **Often altered structure compared to native lignin**
- ***Heterogeneity*** in molecular weight distribution, types of functional groups (mainly phenolic-OH, aliphatic-OH, and COOH), and reactive sites



Molecular fragments of spruce milled wood lignin and Kraft lignin

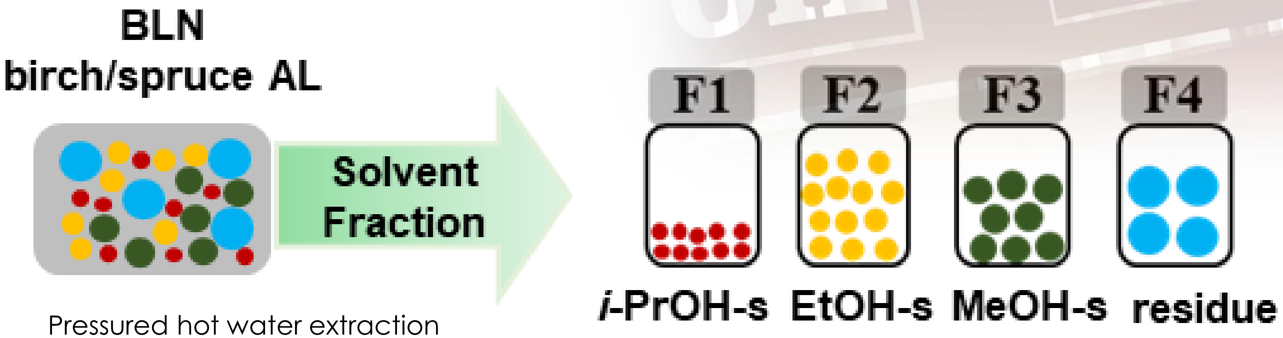
Crestini et al. Biomacromolecules 2011, 12, 11, 3928-3935 Crestini et al. Green Chem., 2017,19, 4104-4121
Website: https://ligniox.eu/objectives/

How do we treat technical lignin? -Refining or fractionation

- **Refine/Fractionate lignin to a set of products with consistent specifications**

'pure lignin'

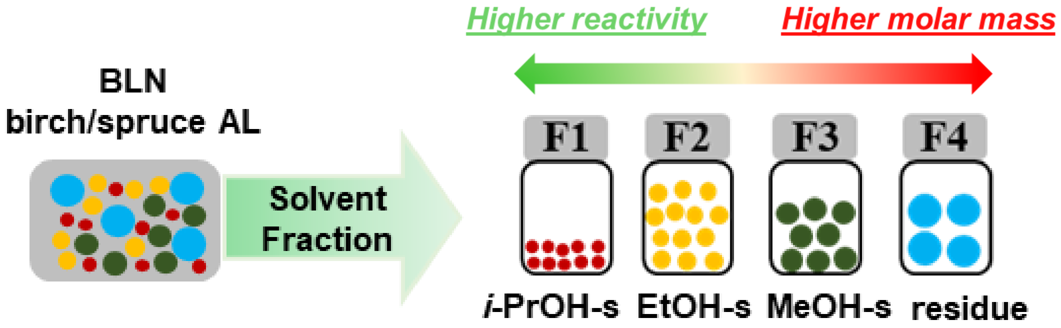
- **Trace carbohydrate**
- **Trace extractives**



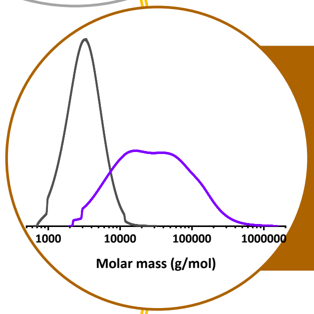
Pressured hot water extraction
+Mild alkali pulped process

Wang L, Lagerquist L, Zhang Y, et al. Tailored Thermosetting Wood Adhesive Based on Well-Defined Hardwood Lignin Fractions. *ACS Sustainable Chemistry and Engineering*. 2020;8(35):13517-13526. doi:10.1021/acssuschemeng.0c05408

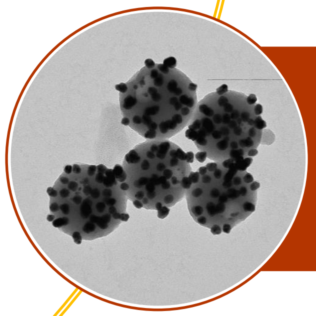
Valorize lignin as polymeric material



Lignin-containing phenolic resin (lignin-structure-property-performance)



Laccase-induced lignin polymerization (lignin-structure-property-performance)

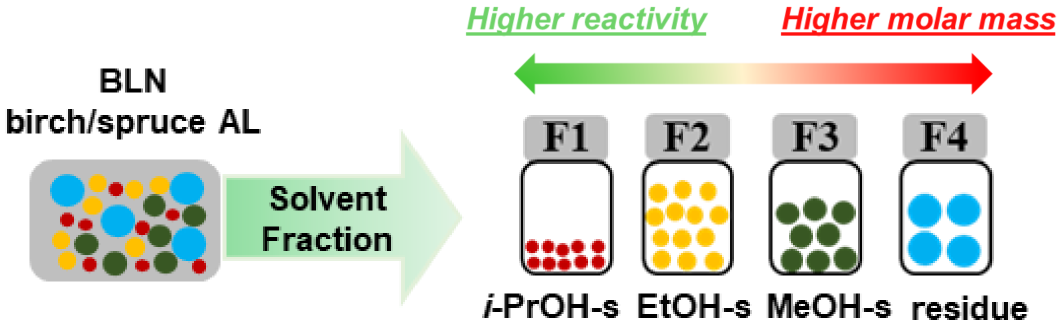


Lignin nanosphere supported Ag nanoparticle

Wang L, Lagerquist L, Zhang Y, et al. Tailored Thermosetting Wood Adhesive Based on Well-Defined Hardwood Lignin Fractions. *ACS Sustainable Chemistry and Engineering*. 2020;8(35):13517-13526. doi:10.1021/acssuschemeng.0c05408

Wang L, Tan L, Hu L, et al. On Laccase-catalyzed Polymerization of Biorefinery Lignin Fractions and Alignment of Lignin Nanoparticles on the Nanocellulose Surface *via* One-pot Water-Phase Synthesis. *ACS Sustainable Chemistry and Engineering*. 2021. doi: 10.1021/acssuschemeng.1c01576

Valorize lignin as polymeric material



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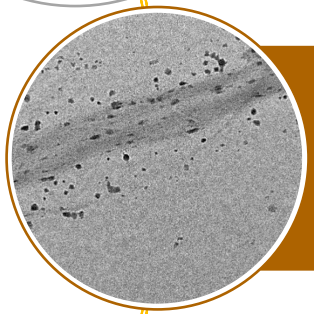
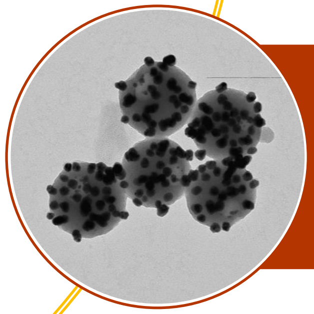


In situ alignment of laccase-polymerized lignin on cellulose fiber surface



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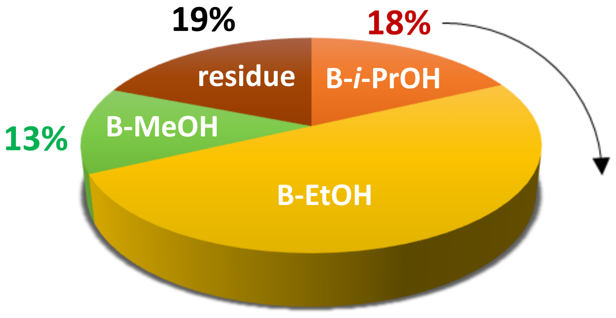
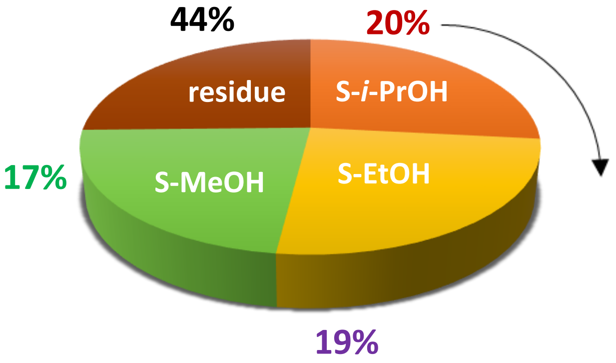
Structural features of lignin fraction in molar mass distribution

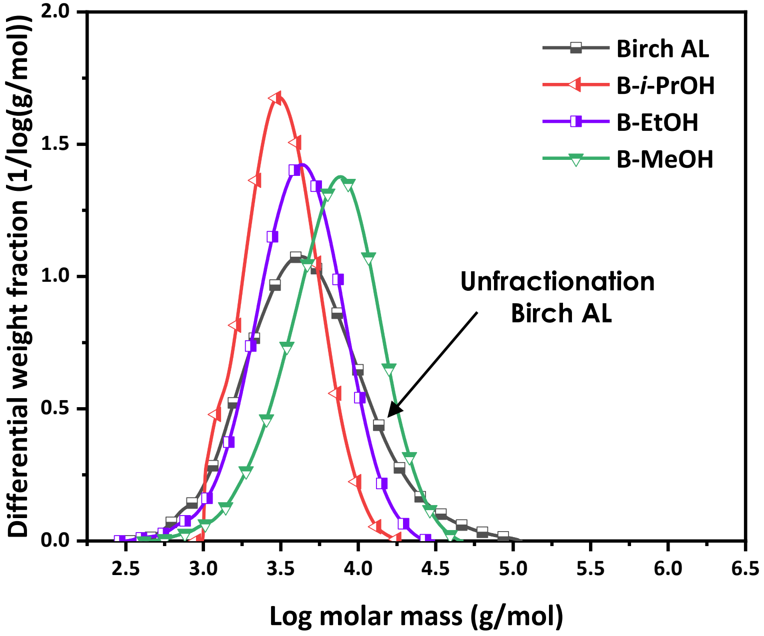
- **Narrow molar mass dispersity of lignin fractions was obtained after solvent fractionation**

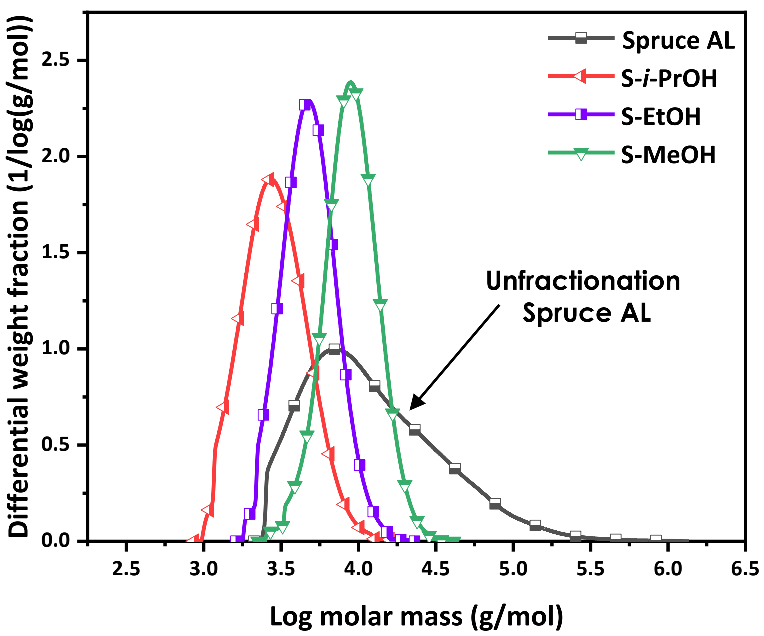
birch lignin fractions



spruce lignin fractions

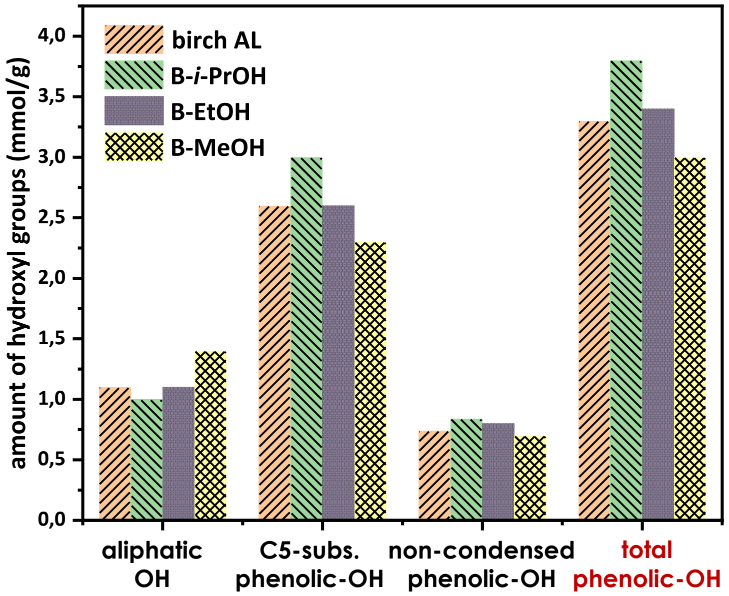


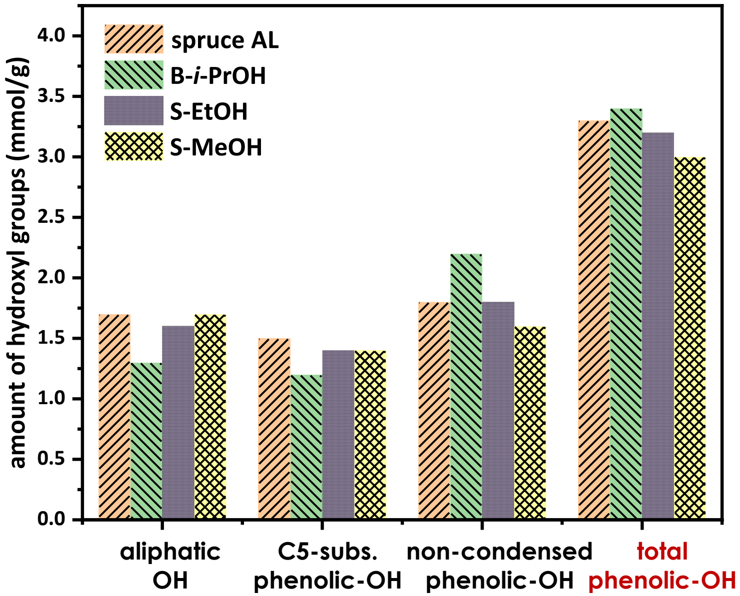


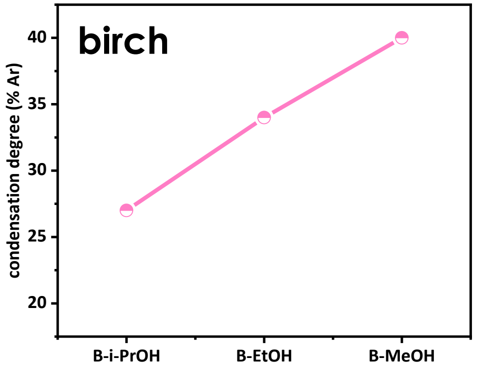


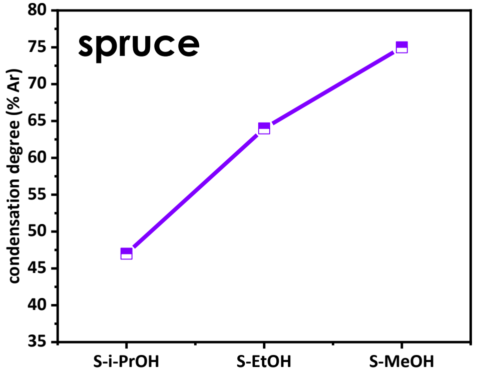
Hydroxyl group distribution and condensation degree of lignin fractions

- *i*-PrOH-soluble lignin fraction has low molar mass and high phenolic-OH groups
- Condensation degree at aromatic ring increased along the fractionation sequence



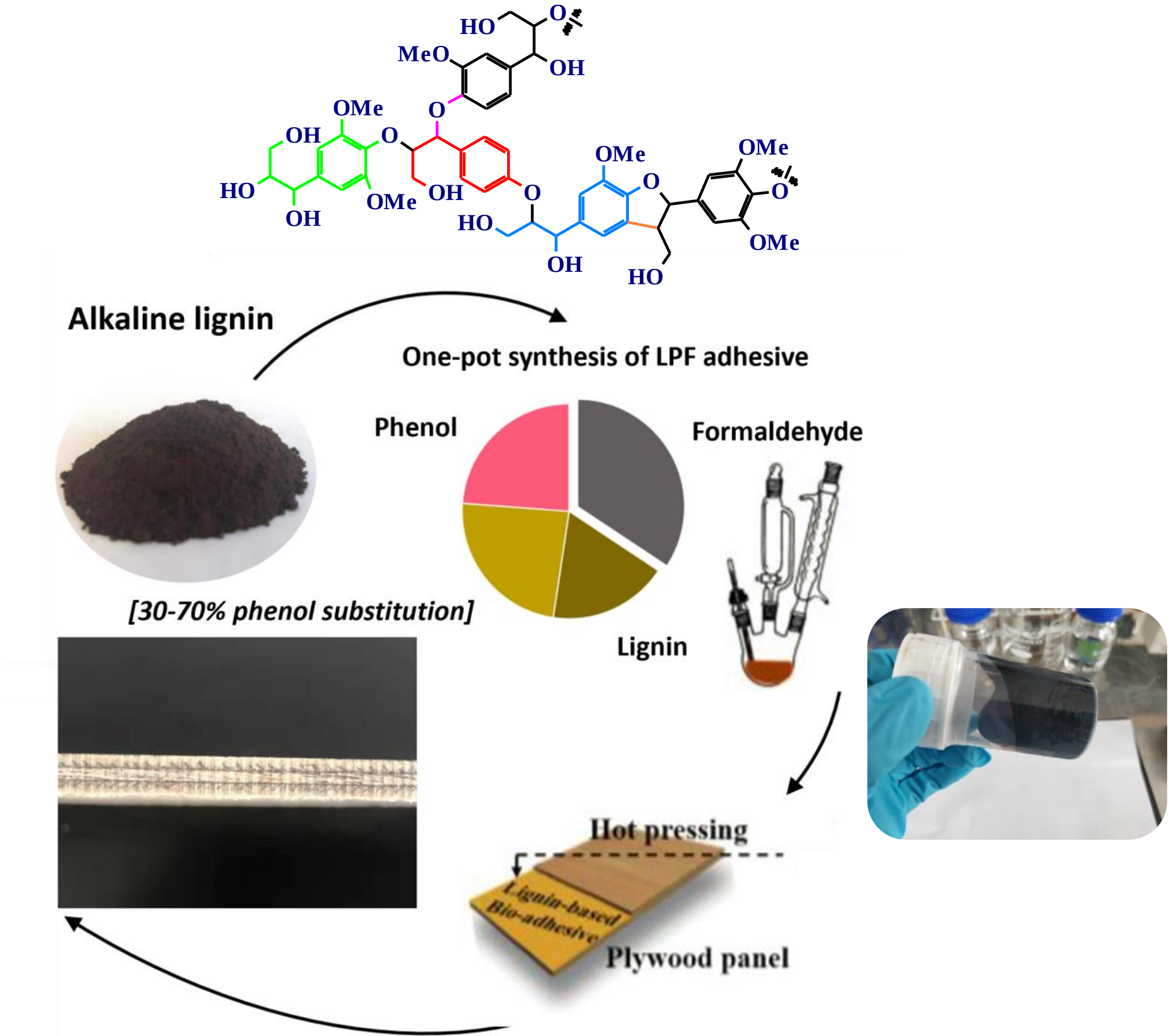


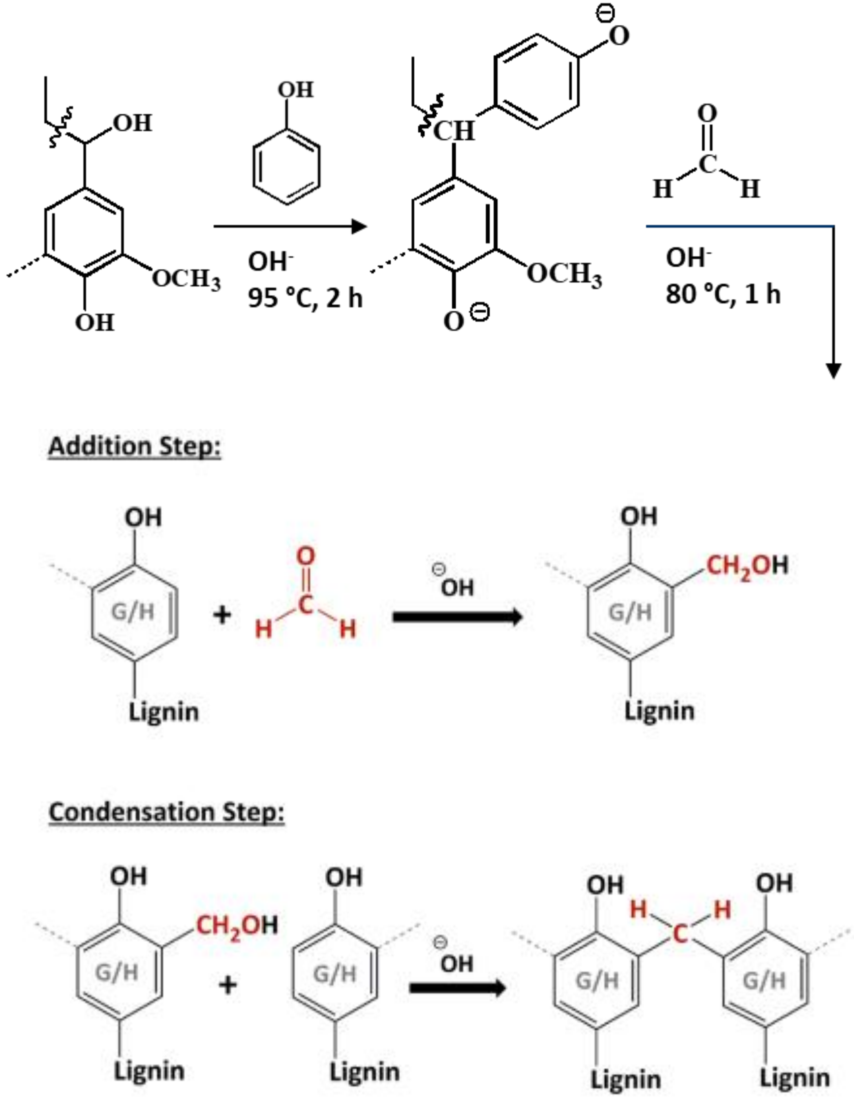




C5-subs. Phenolic-OH: C5-condensed G unit and S unit with free phenolic-OH)
non-condensed Phenolic-OH: G units with free phenolic-OH

One-pot synthesis of lignin-containing phenolic resins





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Wet bonding strength test
-Wood failure performance of plywood

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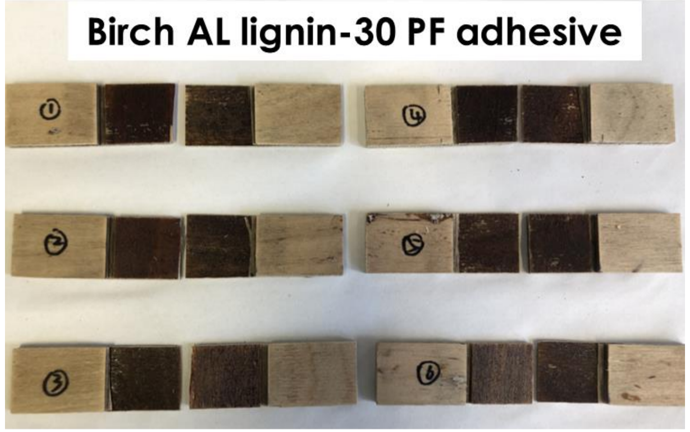
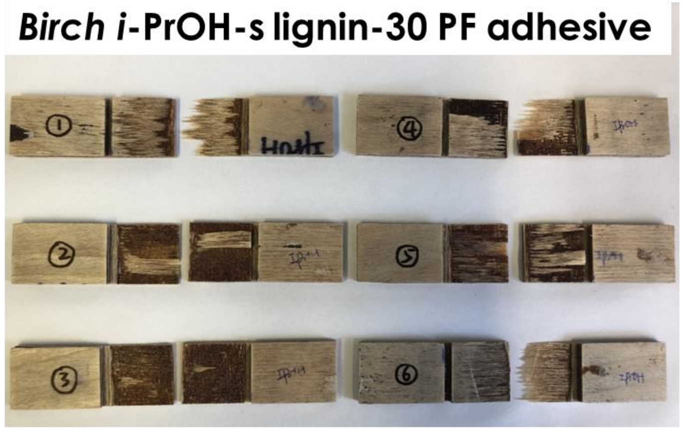
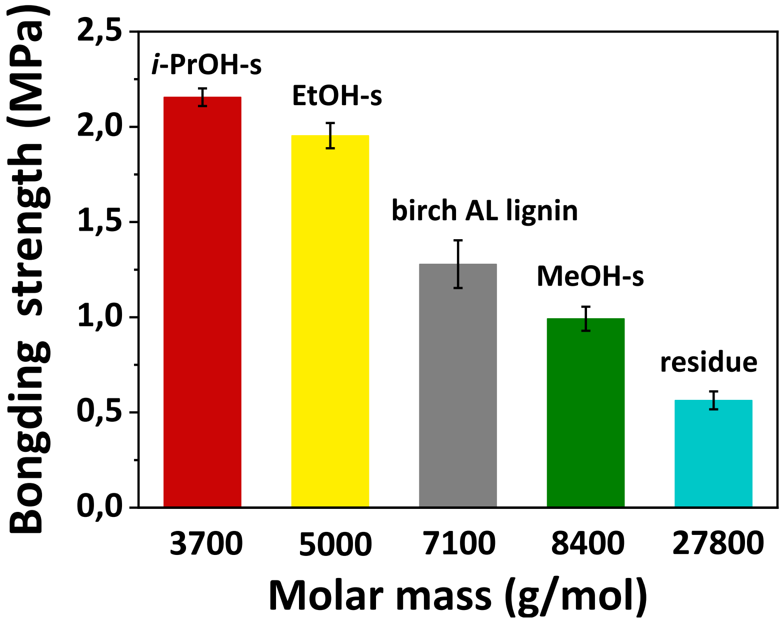




Cohesive failure
Low bonding strength

Wood failure
High bonding strength



*30% phenol substitution by lignin

Molar mass of lignin is a key factor in the production of a high-performance phenol replacement lignin to be used in phenolic resins

Increase lignin content in lignin-containing phenol-formaldehyde adhesives

- The larger the amount of phenol we attempt to replace with lignin, the more difficult it gets
- The *i*-PrOH-soluble fraction from spruce lignin fractions exhibited lower wet bonding strength than its counterpart from birch

plywoods	M_W and $Đ_M$ of lignins (g/mol)	wet bonding strength (MPa)
BAL-PF-30	7200 (2.8)	1.28 (0.13)
BAL-*i*-PrOH-PF-30	3700 (1.4)	2.16 (0.05)
BAL-EtOH-PF-30	4900 (1.5)	1.95 (0.07)
BAL-MeOH-PF-30	6200 (1.6)	1.00 (0.06)
BAL-*i*-PrOH-PF-50	3700 (1.4)	1.62 (0.13)
BAL-*i*-PrOH-PF-70	3700 (1.4)	1.01 (0.13)
SAL-*i*-PrOH-PF-30	3200 (1.2)	1.94 (0.27)
SAL-*i*-PrOH-PF-50	3200 (1.2)	1.44 (0.11)
SAL-*i*-PrOH-PF-70	3200 (1.2)	0.85 (0.20)

Hydroxyl group distribution and condensation degree of lignin fractions

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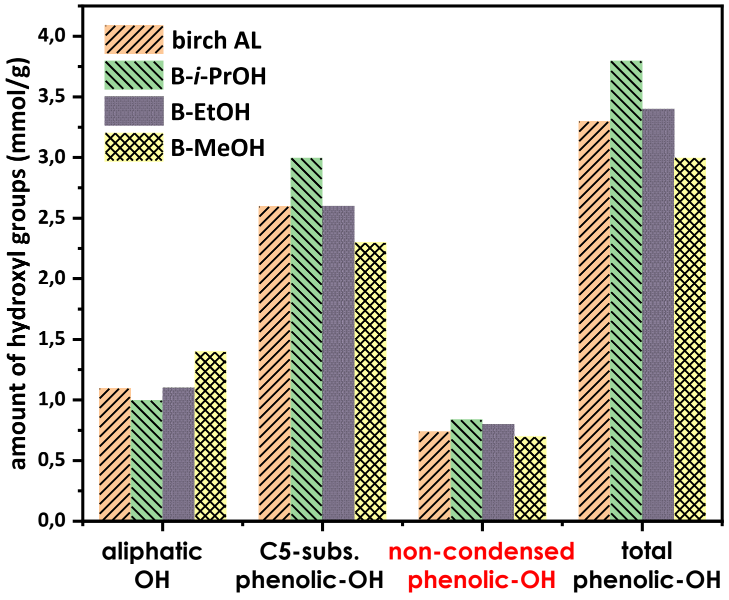
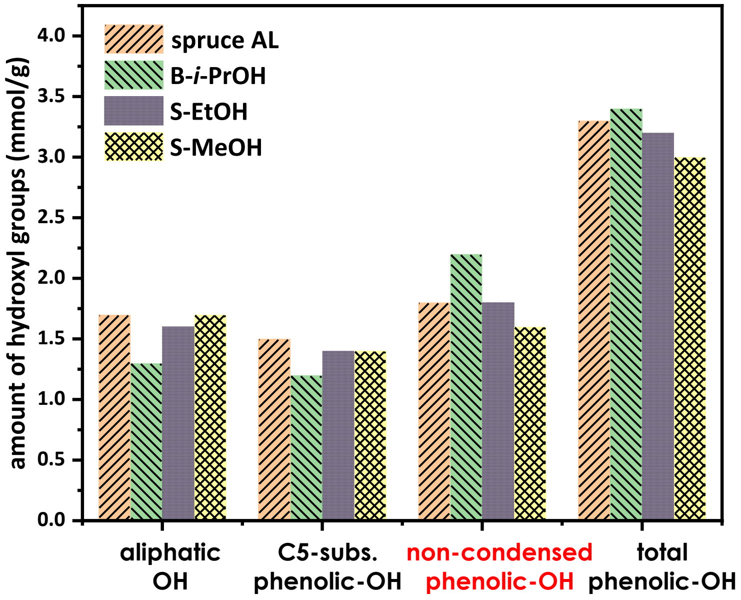
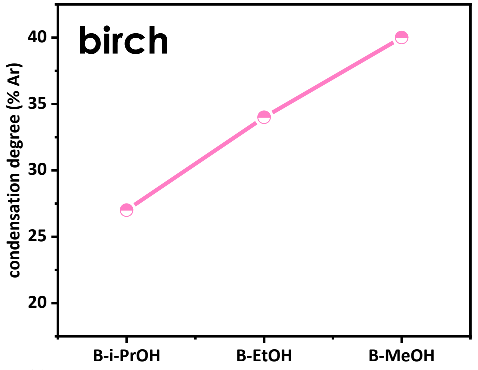
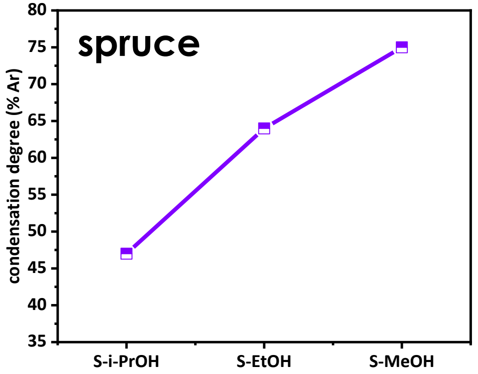
- Condensation degree at aromatic ring increased along the fractionation sequence





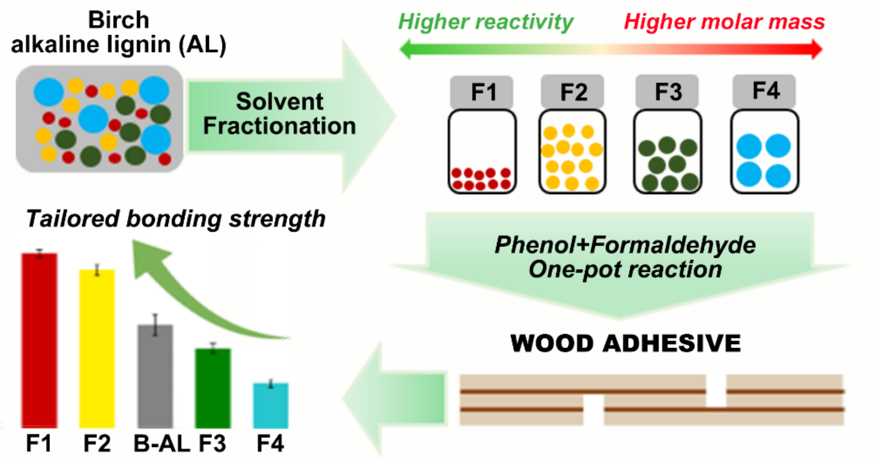




C5-subs. Phenolic-OH: C5-condensed G unit and S unit with free phenolic-OH)
non-condensed Phenolic-OH: G units with free phenolic-OH

Short summary and outlook

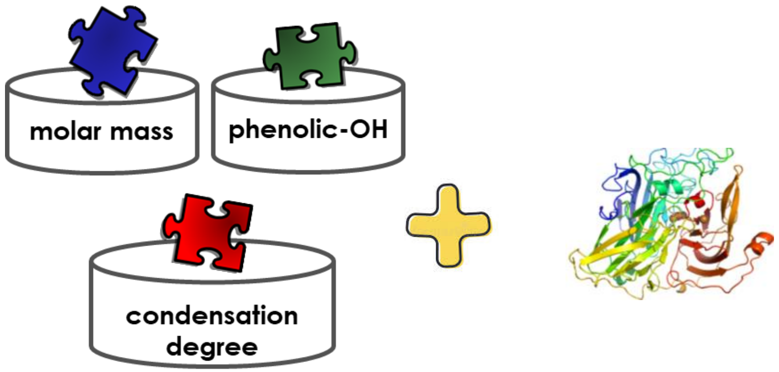
- Valorize **technical hardwood alkaline lignin** in the lignin-containing phenol-formaldehyde adhesive field
- We should limit the lignin-structure-performance correlations to **experimental scope**
- Encourage to put more effort into **optimizing the lignin extraction process** to produce purer lignin with even lower molar mass in the future



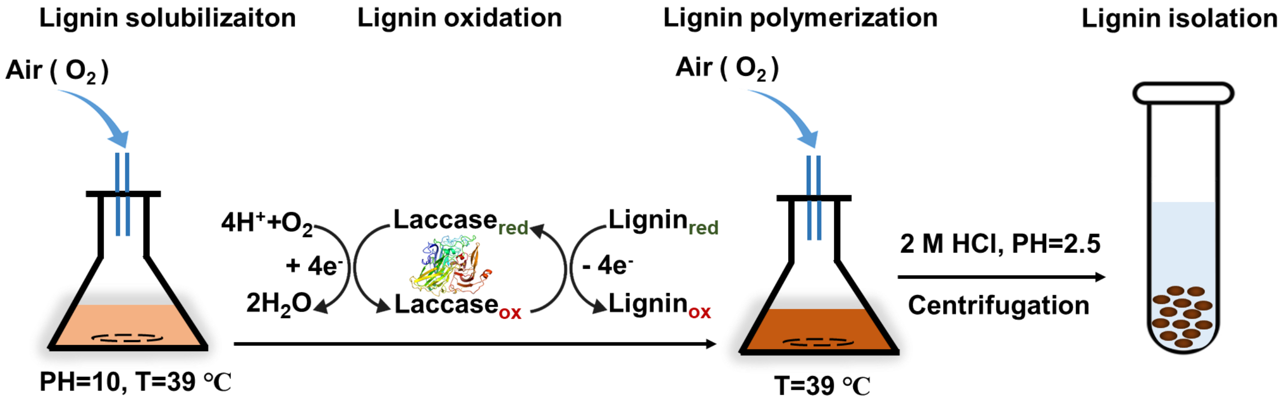
https://www.ch-bioforce.com/molar-mass-of-lignin-the-key-factor-in-the-production-of-a-high-performance-phenol-replacement-new-study/

Laccase-induced lignin polymerization

- Bacteria-derived alkaliphilic laccase-address lignin solubility challenge
- Investigate the correlations between lignin structural characteristics and alkaliphilic laccase-assisted lignin oxidation/polymerization performance



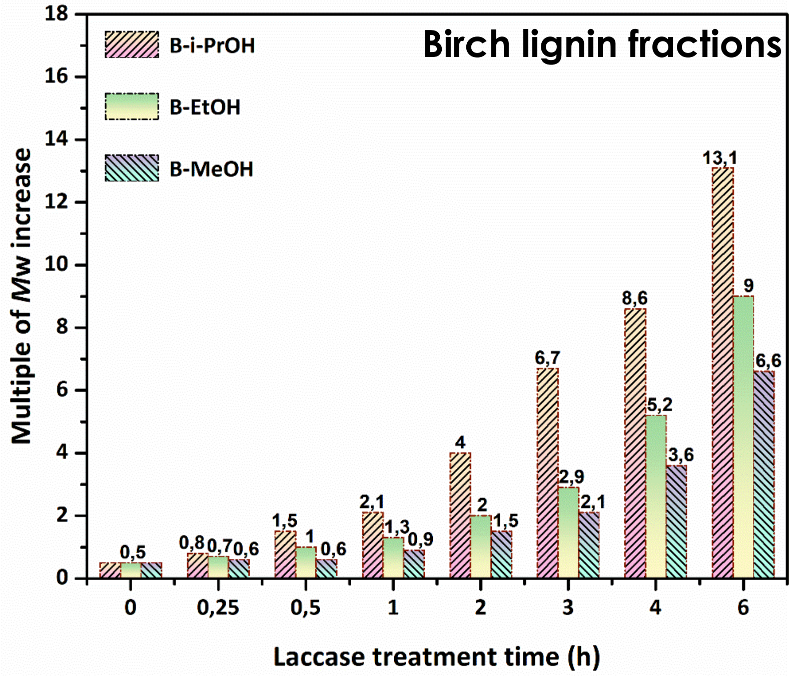
Lignin fractions with molar-mass-dependent differences

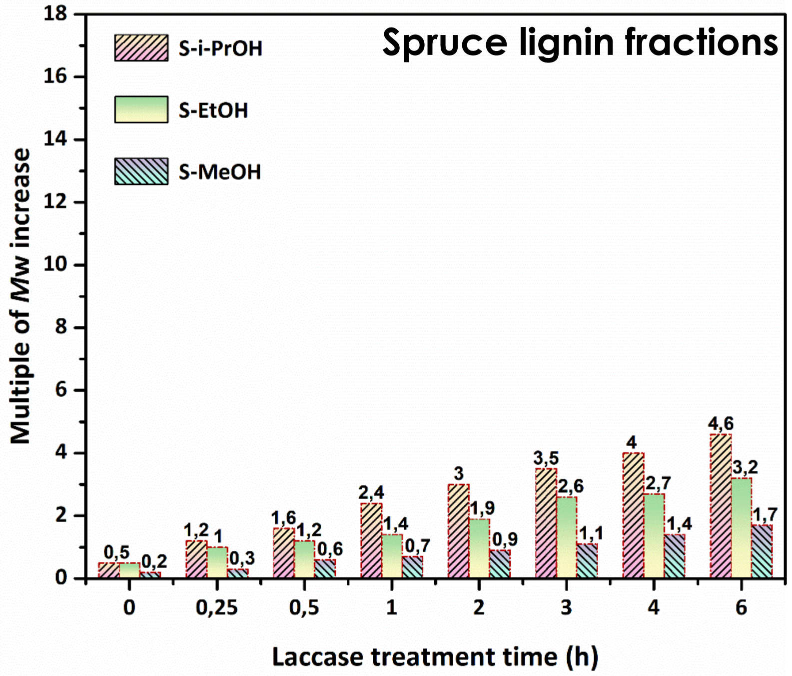


Laccase-catalyzed polymerization of lignin in an alkaline aqueous solution

Fractionation-dependent lignin polymerization kinetics

- Alkaline lignin fractions with low molar mass and low condensation degree as well as high content of phenolic-OH groups, reached higher polymerization degree
- Polymerization (GPC/RI/MALS) in spruce lignin fractions is much less pronounced than in birch



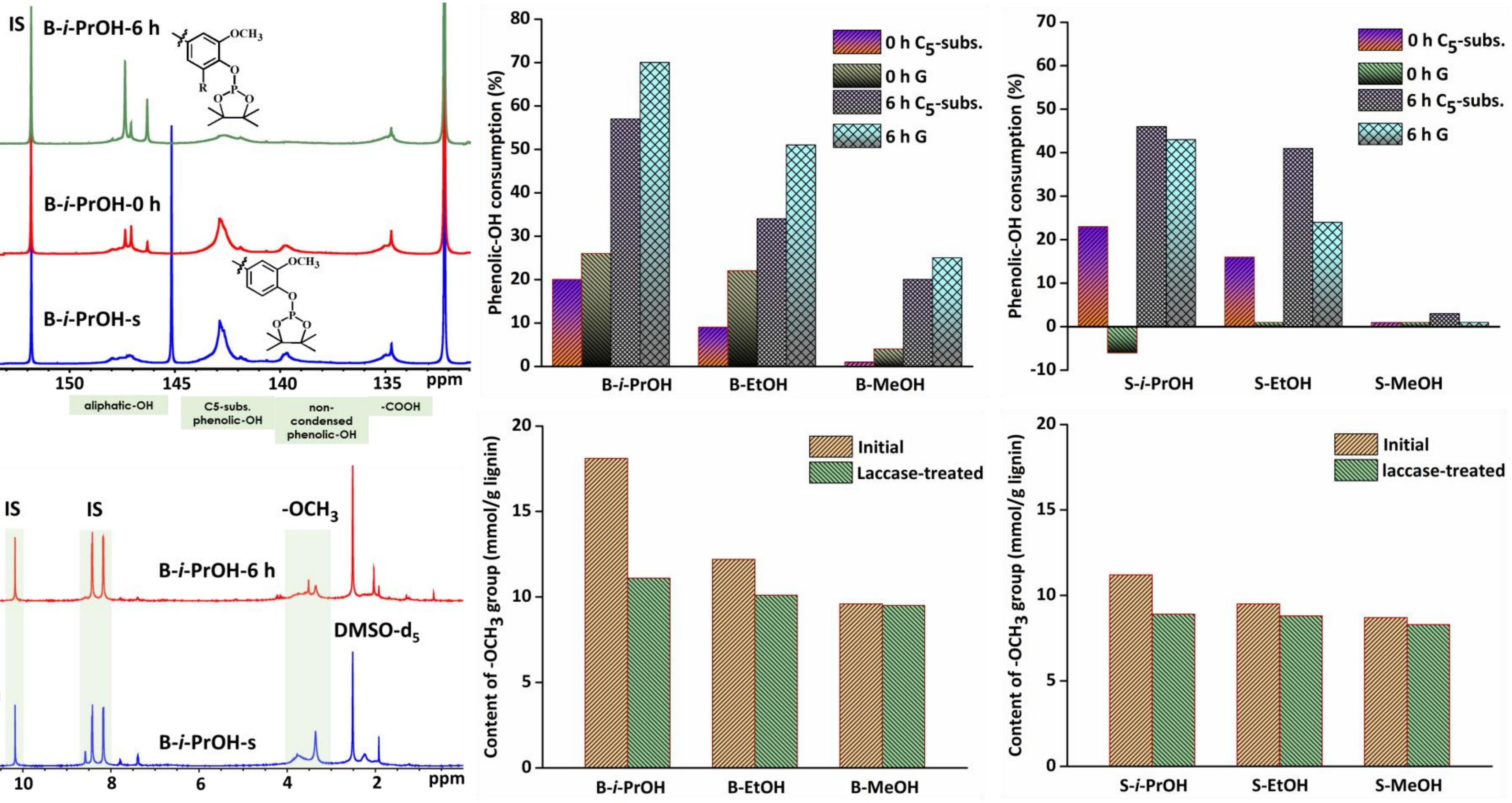


Evolution of the molar mass increase fold in laccase-polymerized lignin as a function of laccase incubation time

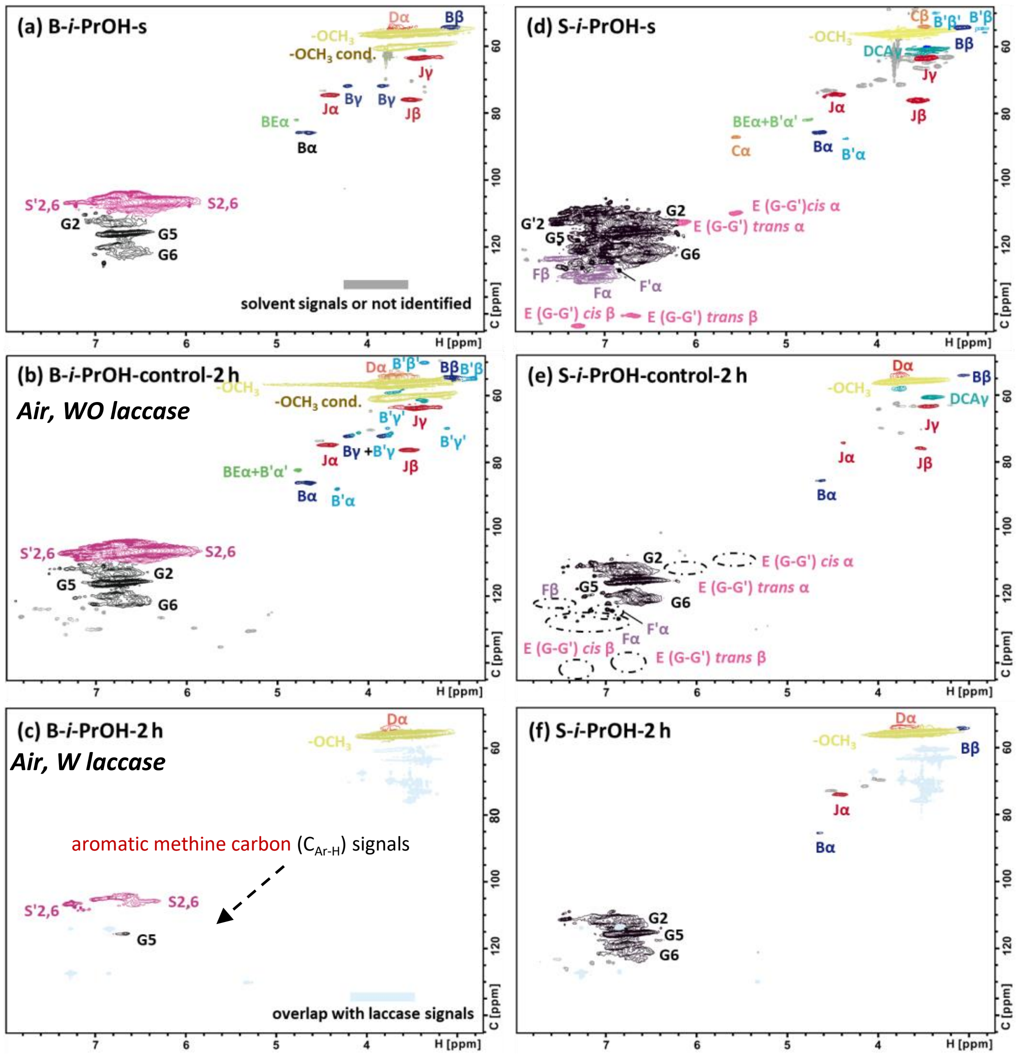
Structural modifications of lignin-Laccase-induced oxidation and demethylation

Phenolic-OH consumption
- Phenoxy radical
- Oxidation

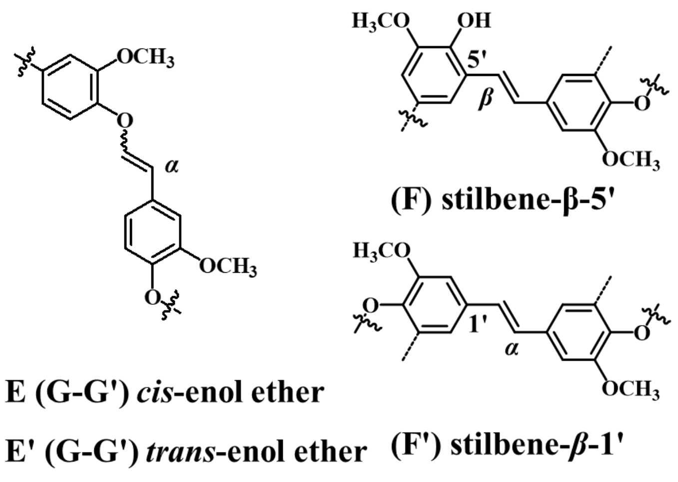
$-OCH_3$ decreased
- Oxidative demethylation



Structural modifications of lignin-Laccase-induced aromatic condensation

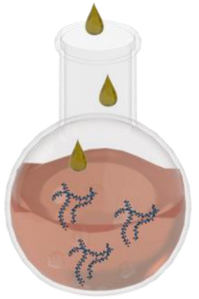


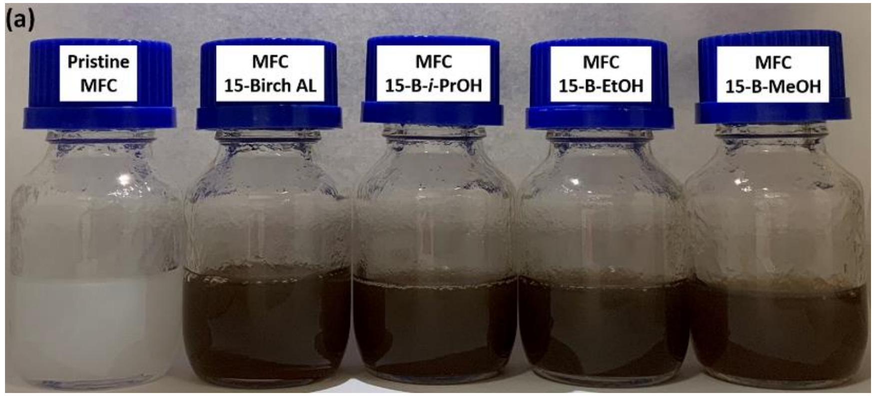
Aryl-vinyl moieties in spruce lignin fractions



- **Birch lignin fractions**
  -pronounced lignin polymerization at the aromatic ring
- **Spruce lignin fractions**
  -prominent air-induced oxidation of aryl-vinyl moieties

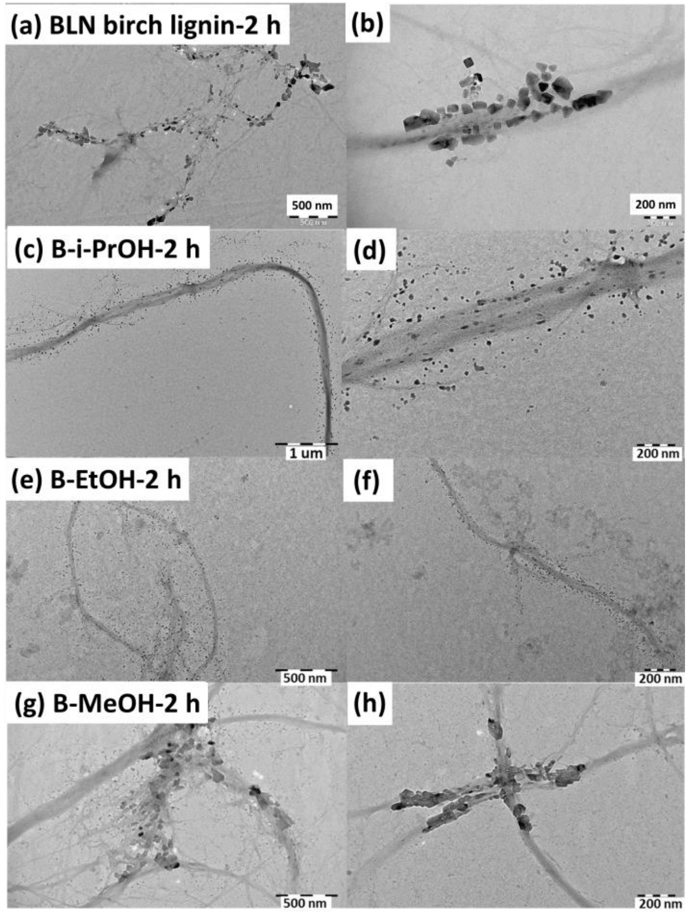
In situ polymerization in fiber suspension at controlled conditions





In situ laccase-polymerized *i*-PrOH-s and EtOH-s birch lignin fractions

- localized and homogeneous coating of lignin nanoparticles along the MFC fiber network

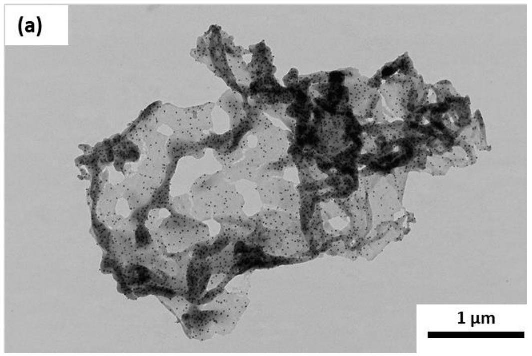


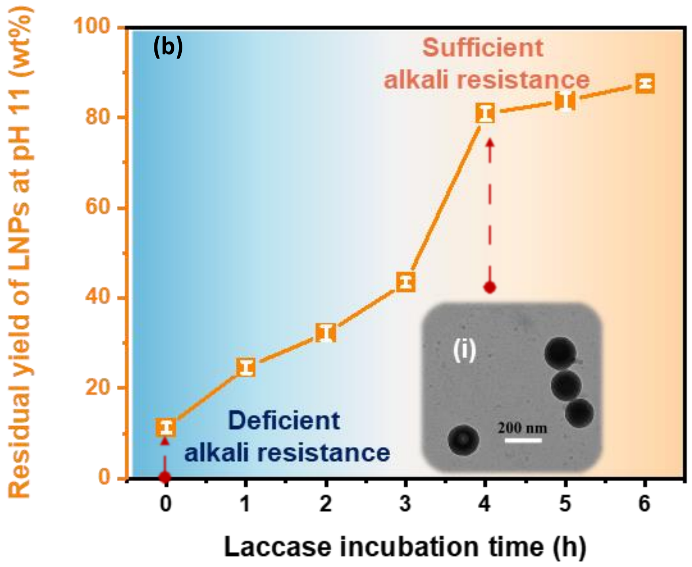
TEM images of spatial confinement of the laccase-polymerized lignin (15%) on micro-fibrillated cellulose (MFC) fibers

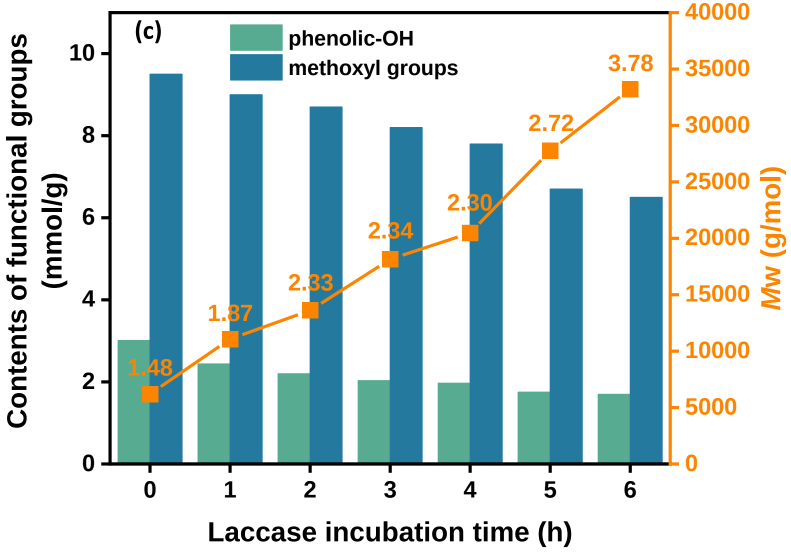
Fabricate functional and robust biopolymer-based nanosphere for *in situ* silver reduction

- **Reduction of silver ions (Ag^+) to Ag^0 nanoparticles from silver ammonia solution (pH 11)**
- **The advantages of lignin nanoparticle (LNP) from laccase-polymerized lignin**
  - ✓ Durable dispersity
  - ✓ Robust interunit carbon-carbon linkages endow the advantages of thermal stability and chemical tolerance (e.g., alkali resistance)
  - ✓ Could retain multi-functional groups (e.g., phenolic-OH and -OCH_3) for redox reaction

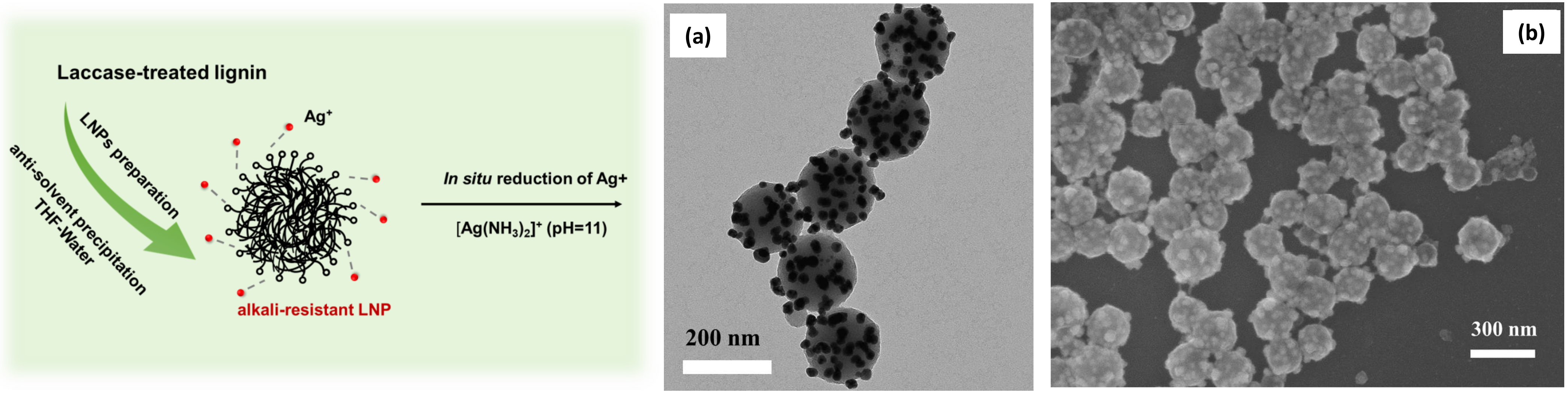
LNP without laccase treatment
LNP-Ag collapsed structure



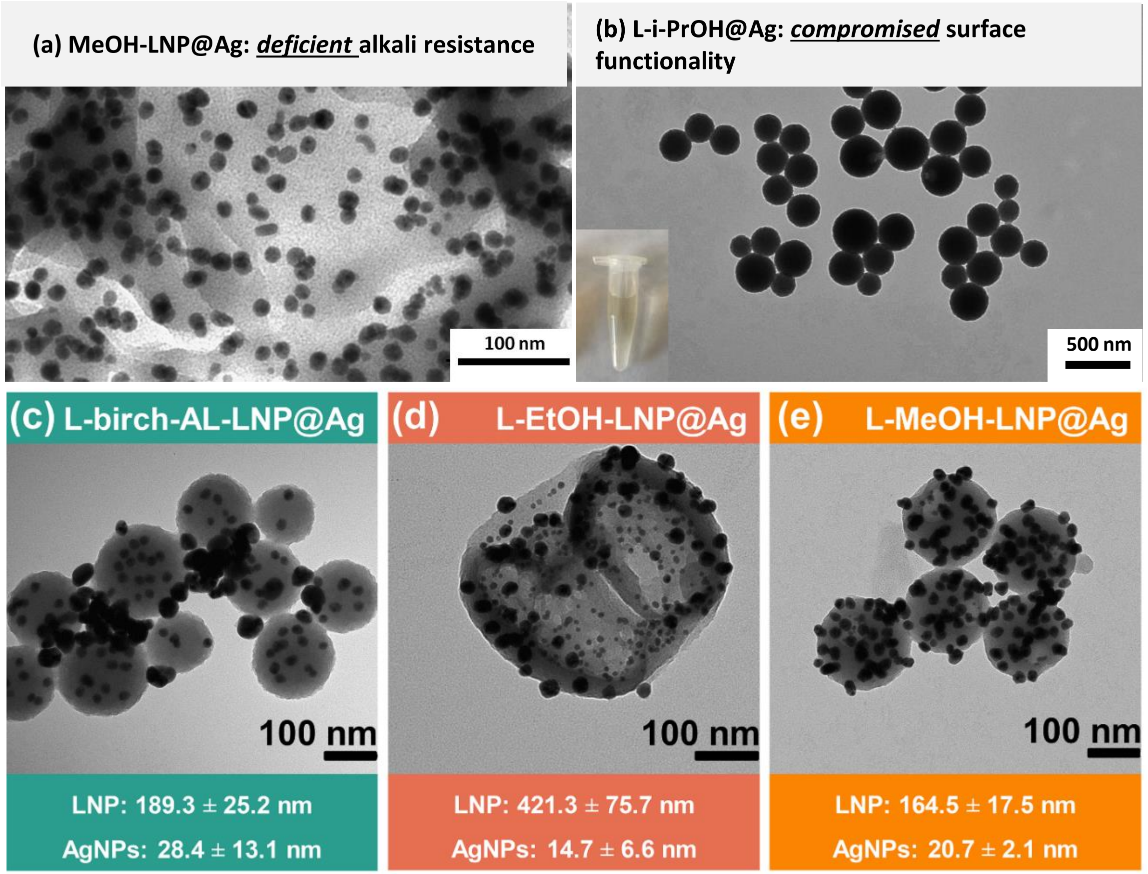


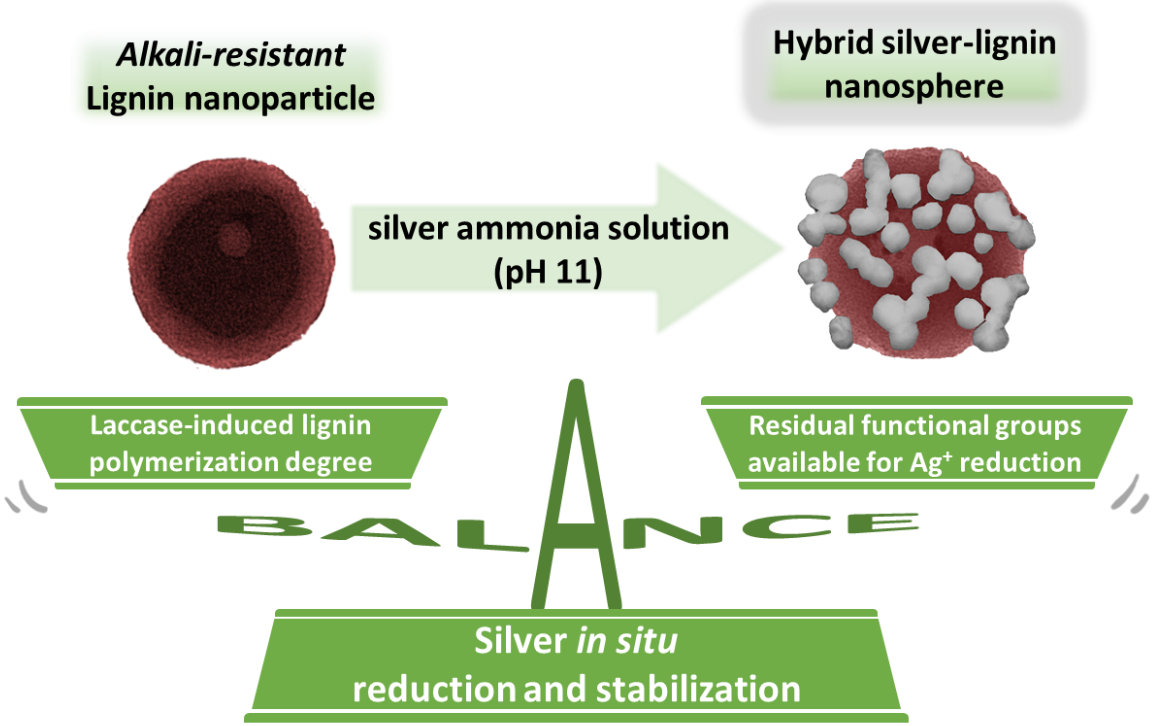


Highlights of silver-lignin nanosphere from laccase-polymerized birch-MeOH-s fraction



- Hierarchical nano-dimensions
- Natural polymer lignin as the nano-carriers and stabilizer of AgNP
- High loading of AgNPs (40 wt%)
- Excellent dispersity in water-phase





Fractionation-dependent lignin polymerization kinetics

Utilization hybrid silver-lignin nanospheres
In custom-designed antimicrobial hydrogel

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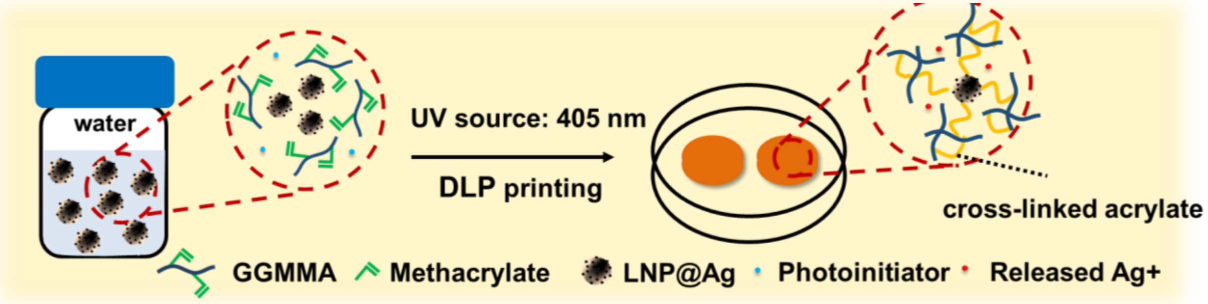
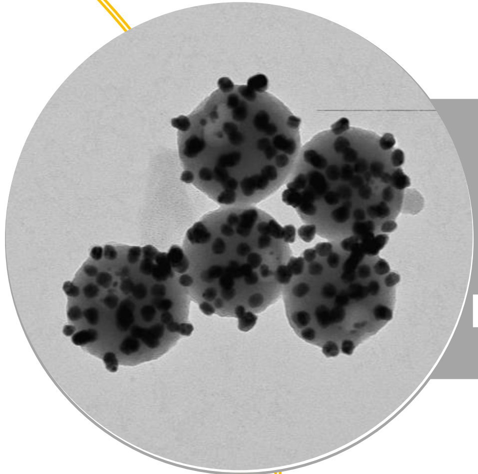
Digital light processing (DLP) 3D-fabricated antimicrobial hydrogel with a sustainable resin of methacrylated woody polysaccharides and hybrid silver-lignin nanospheres†

Luyao Wang,[a] Qingbo Wang,[a] Anna Slita,[b] Oskar Backman,[a] Zahra Gounani,[c] Emil Rosqvist,[d] Jouko Peltonen,[d] Stefan Willför,[a] Chunlin Xu,[a] Jessica M. Rosenholm[b] and Xiaoju Wang *[a,b]





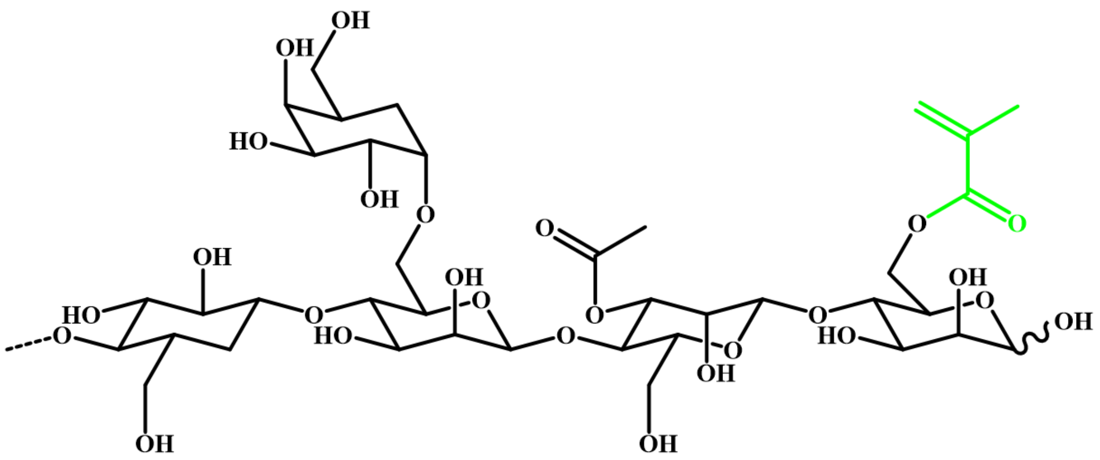
Lignin nanosphere supported Ag nanoparticle (LNP@Ag)

3D-printed antimicrobial hydrogel

Sustainable bio-resin for 3D printing

Åbo Akademi University

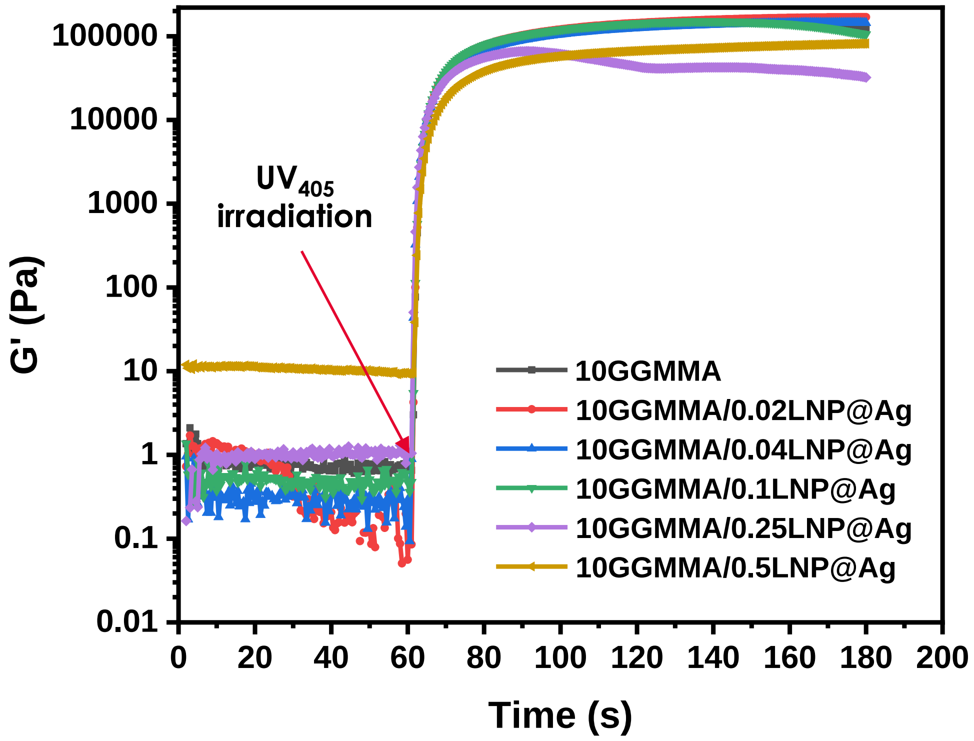
- **Main polymeric matrix-woody heteropolysaccharides**
- ***O*-acetyl-galactoglucomannan (GGM), the major heteropolysaccharides derived from softwood, is modified with photo-reactive methacryloyls to result methacrylated GGMMA**



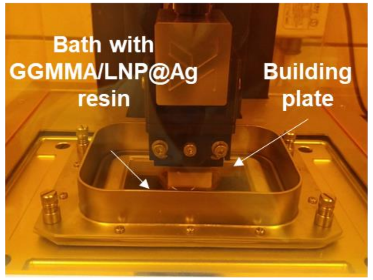
Reference: Xu W, Zhang X, Yang P, Långvik O, Wang X, Zhang Y, Cheng F, Österberg M, Willför S, Xu C. Surface Engineered Biomimetic Inks Based on UV Cross-Linkable Wood Biopolymers for 3D Printing. ACS Appl. Mater. Interfaces, 2019, 11, 13, 12389-12400.

Digital light processing printing (DLP)

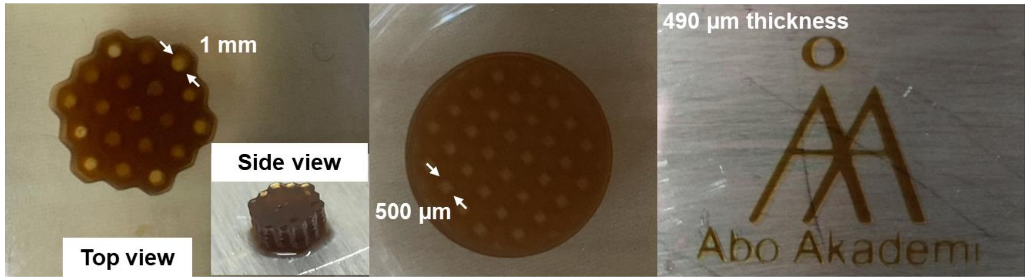
- Bio-resin: Fast-photocurable property
- 3D printing with photo-crosslinkable natural materials



DLP projector

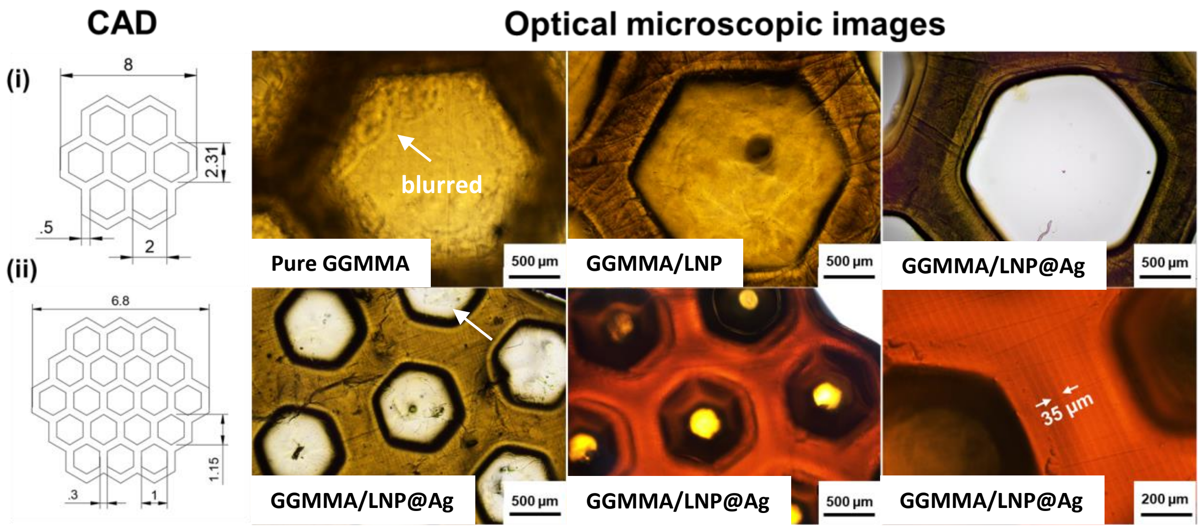


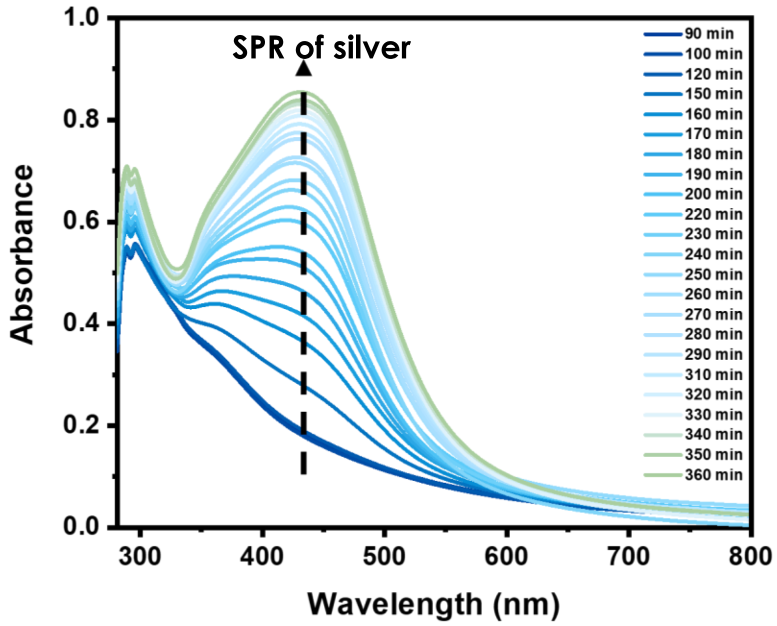
Outputs (e.g., porous architectures)



Pattern fidelity of DLP-printed hydrogel integrated with LNP@Ag

- AgNPs in GGMMA resin served to mitigate excess light penetration into the honeycombs, performing as a "photo-absorber"





- Optically clear GGMMA resin
  -Excessive ''light trespassing'' and excess-crosslinking
- 10GGMMA/0.1LNP@Ag
  -Well-defined projected patterns

- UV-vis absorption spectra of aqueous LNP@Ag dispersion
- Surface plasmon resonance (SPR) absorption peak of metallic Ag at 440 nm

Antimicrobial property of the sustainable hydrogel

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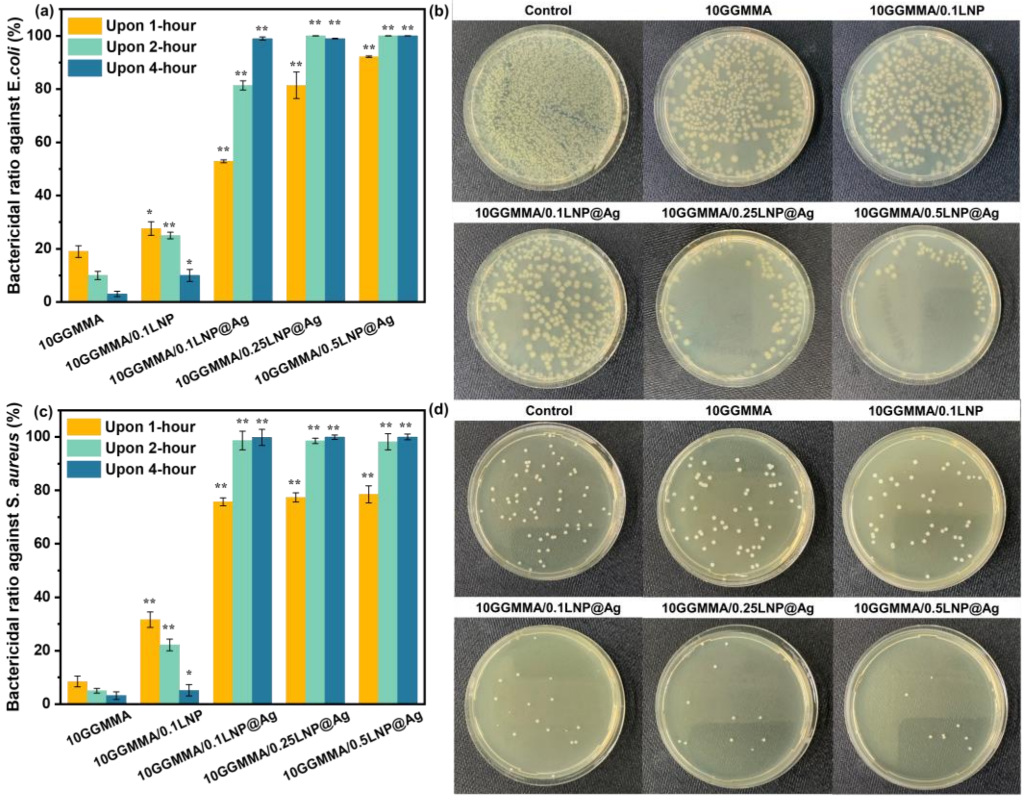
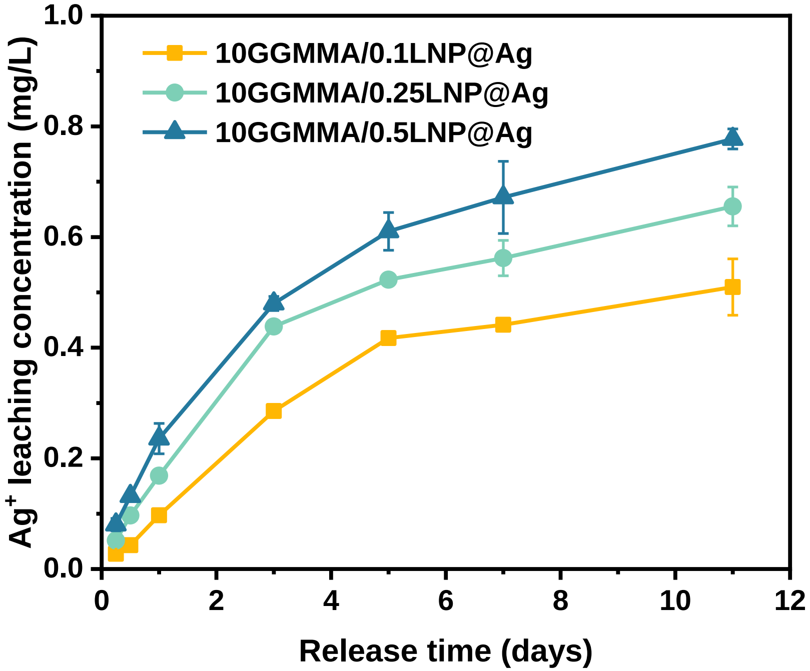
- Strong antibacterial activities against both *Escherichia coli* and *Staphylococcus aureus*
- Sustained leaching of Ag^+ from the embedded AgNPs on LNPs through the hydrogel



Release profile of Ag^+



Summary

- Lignin fractionation: Effective strategy to reduce molecular-weight-dependent heterogeneity for upgraded lignin valorization
- Lignin fractionation in combination with laccase-catalyzed polymerization is a green approach in 'upgrading' lignin
- The structural features of lignin could be tailored by fractionation-dependent laccase-catalyzed polymerization kinetics and yield high-performance lignin nanomaterials

lignoCOST

LigninRESurf

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Thank you for your attention!

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