lignoCOST

Reactive Lignin Materials for High Performance Composites-Modification Methods and Characterization

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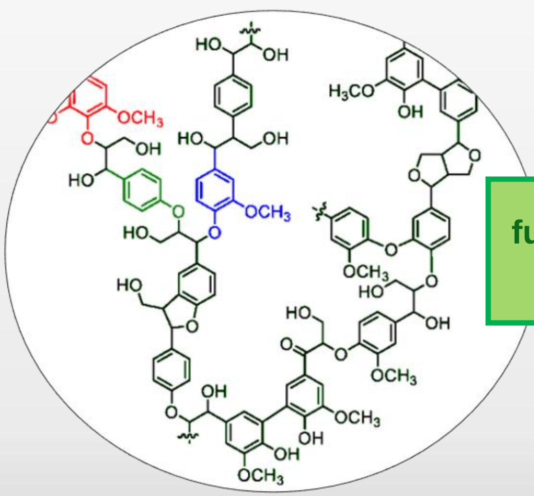


functionalization/ modification

High performance materials

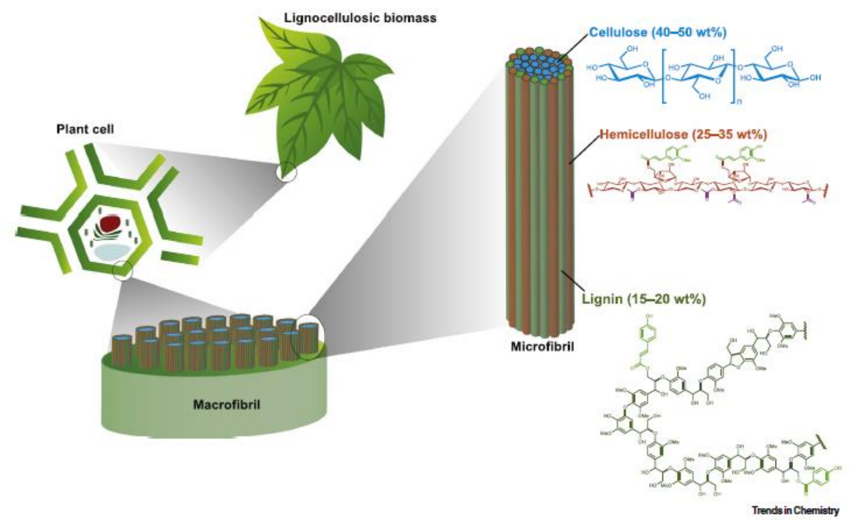
Reactive monomers for resin synthesis

Reactive fillers for composites

Composites for waster remediation

Lignin: An attractive feedstock for renewable reactive monomers production

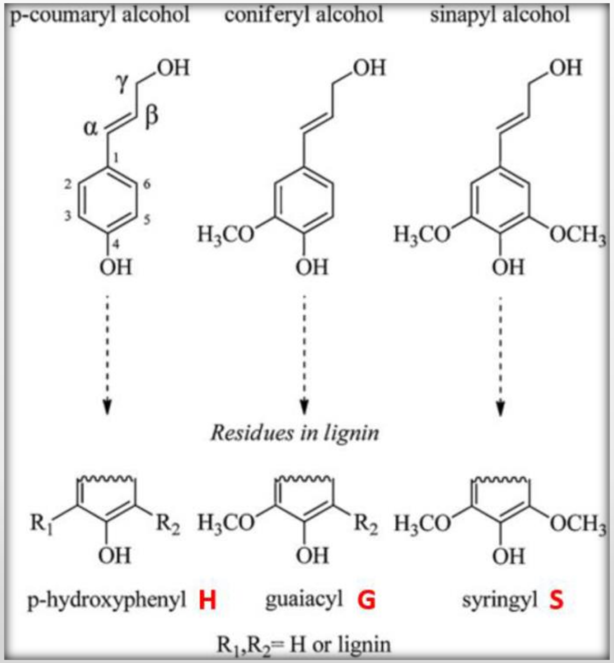
- Lignin is the major constituent of the lignocellulosic biomass
- Substance with a **binding** properties that causes the **compactness** of wood cell structure
- Lignin is the **largest natural source** of aromatic molecules
- **Low-cost**, and **eco-friendly** material



Lignin: An attractive feedstock for renewable reactive monomers production

- An increasing attention is being given to lignin valorization into new chemicals and materials

- Lignin aromatic and phenolic functionalities are important in chemicals and materials production such as polymers, resins and coatings production

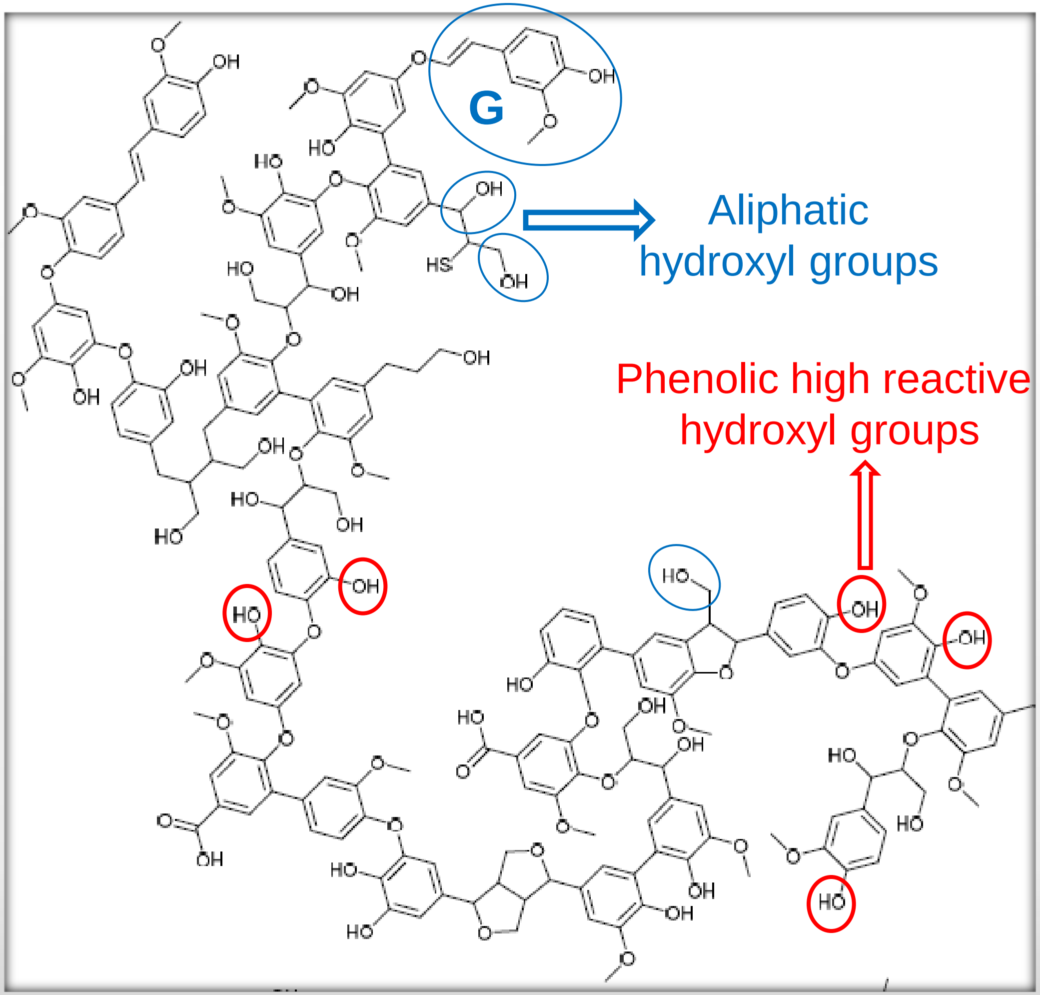


Aromatic functionalities originates from:

- Randomly branched three main polyphenols (H, G, S)

- Monomer composition (H, G, S) content depend on across different types of plant species

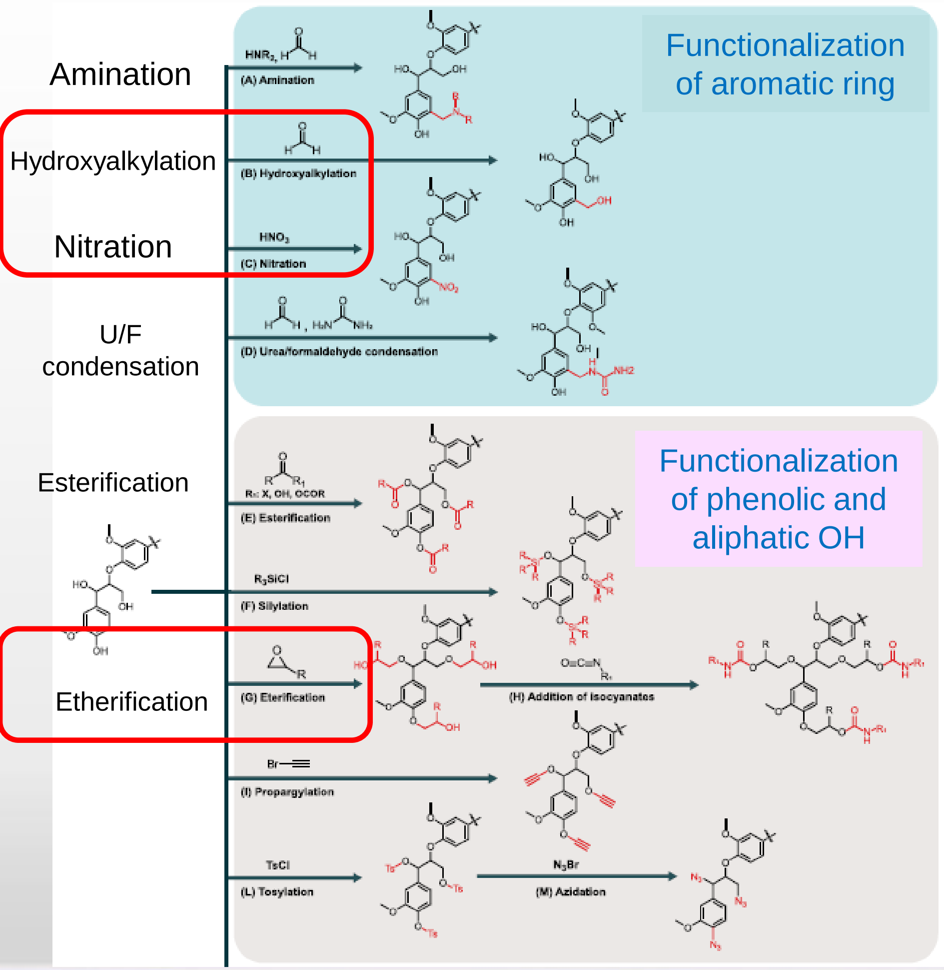
Lignin: An attractive feedstock for renewable reactive monomers production



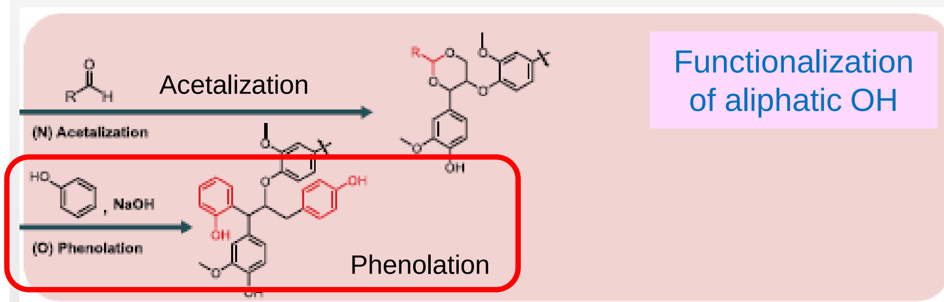
- The functional groups present in lignin make it a very reactive compound
- Functionalization possibilities mainly come from the reactivity of the aromatic rings of guaiacol and syringol units, as well as in the aliphatic hydroxyl groups present along the lignin backbone.
- chemical modification of lignin introduces new functional groups and makes the noncovalent interactions more favourable during the blending process

Lignin: An attractive feedstock for renewable reactive monomers production

- Lignin functionalization have created new opportunities for the production of controlled lignin structures and the incorporation of these structures into materials

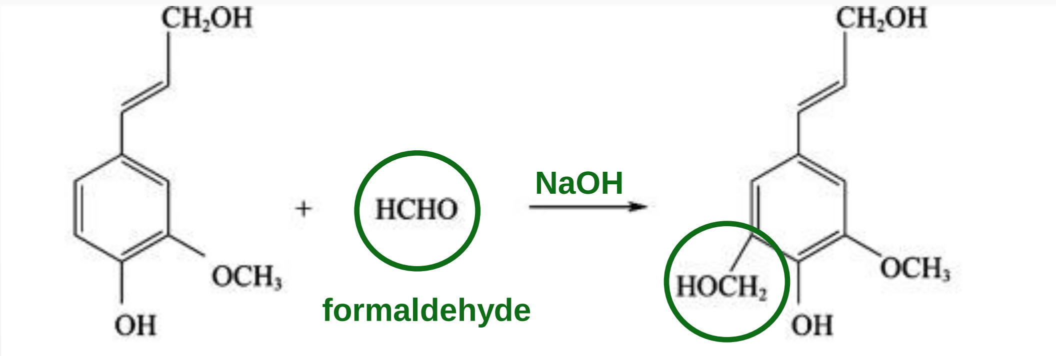


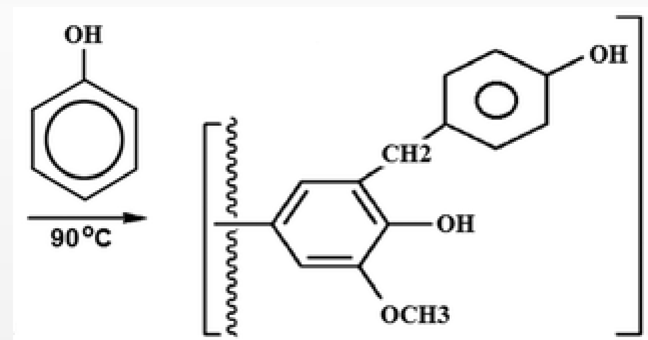
Possible Chemical Modifications of the Lignin Backbone



Functionalization of the Lignin aromatic rings: Hydroxyalkylation of phenolic units

- Hydroxyalkylation of phenolic units using formaldehyde in the presence of a strong base such as NaOH

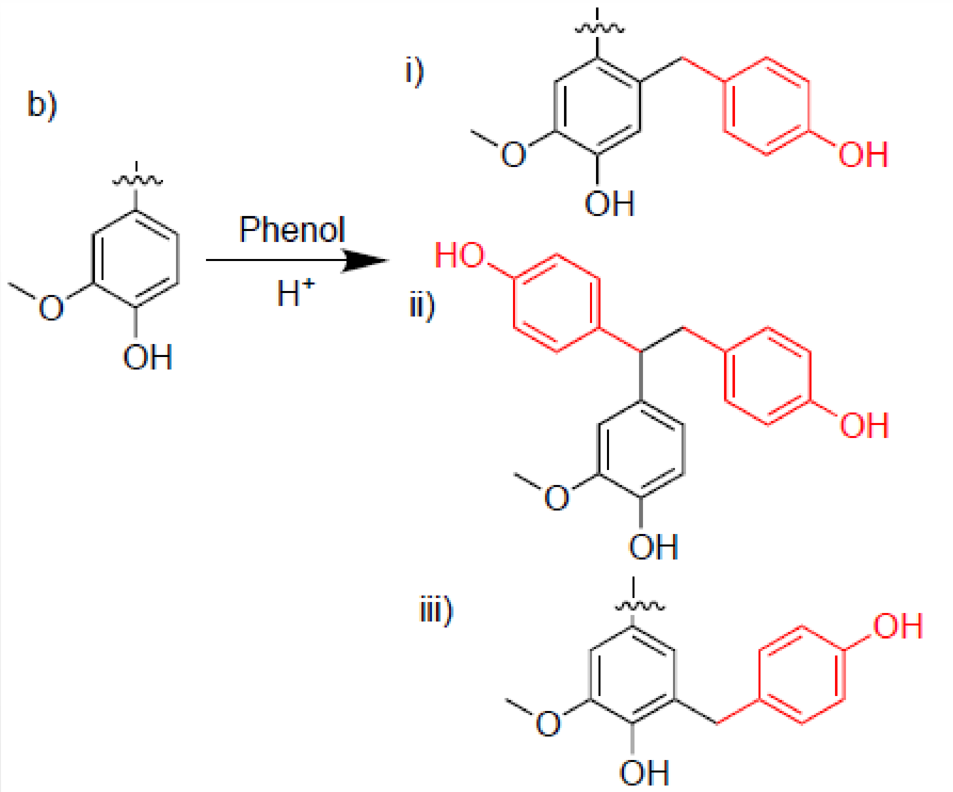




Hydroxymethylated lignin

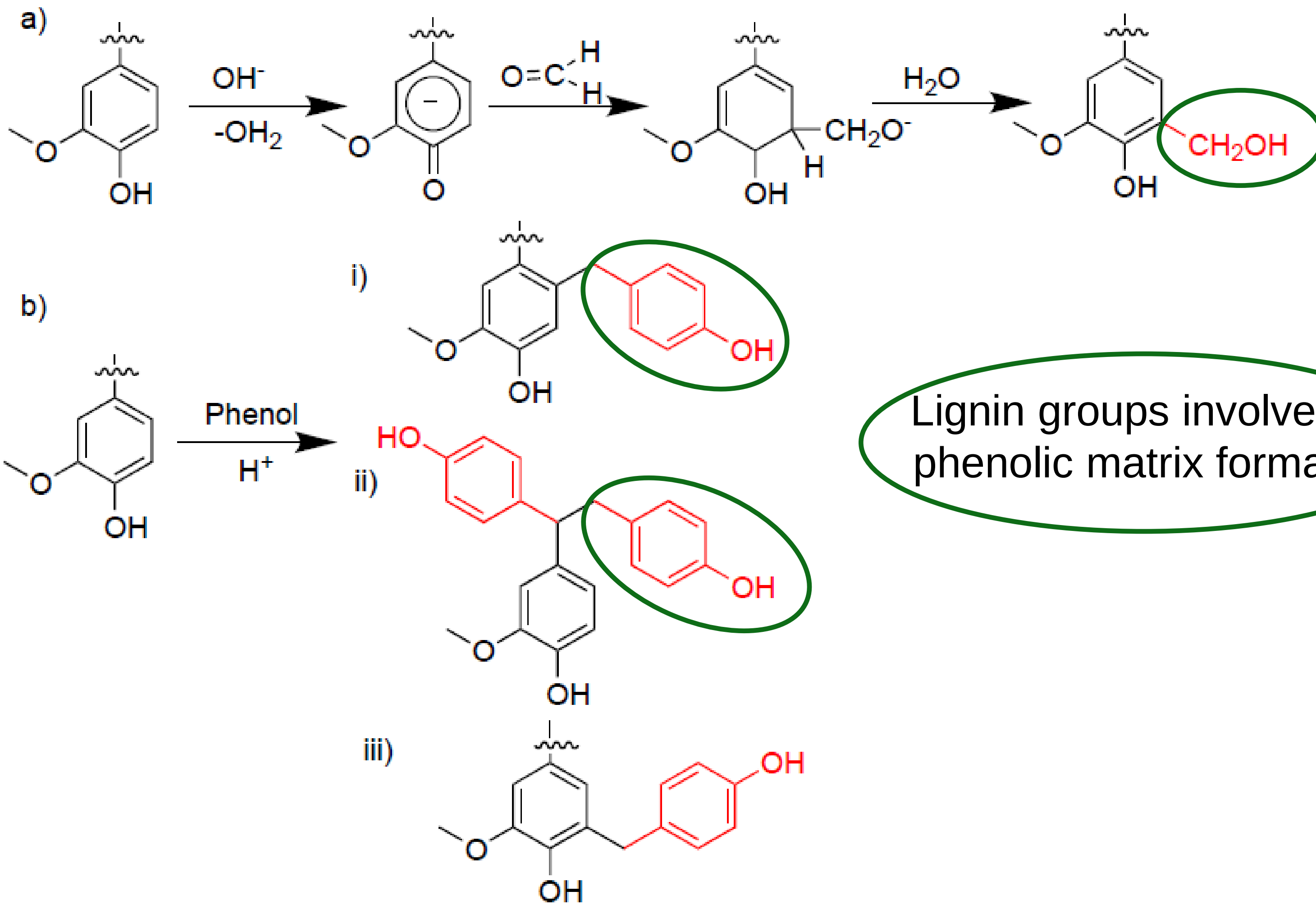
- The goal of lignin hydroxyalkylation is to obtain lignin which has the same function as phenol and to substitute some of this petrol-based and toxic chemical to produce lignin-phenol-formaldehyde (LPF) resins for use as adhesives in the preparation of plywood

Functionalization of the Lignin aliphatic OH: Phenolation



- The phenolation procedure involves treating lignin with phenol under acidic conditions in organic solvents
- Reaction leading to the condensation of phenol with lignin side chains and aromatic rings

Generalized scheme of lignin based phenolic resin synthesis

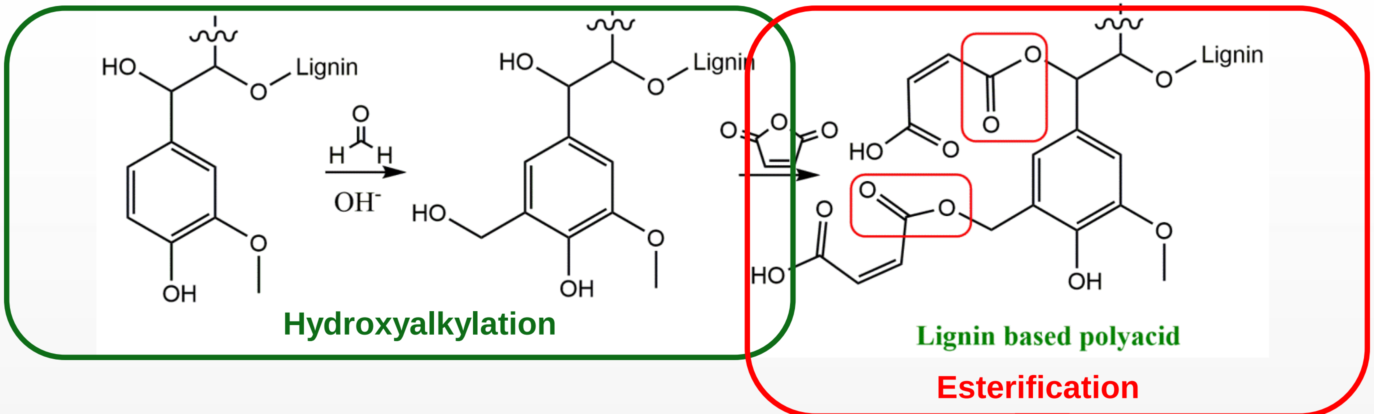


Lignin groups involved in phenolic matrix formation

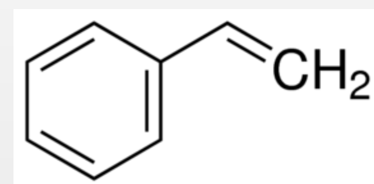
Functionalization of the hydroxymethylated lignin: Synthesis of lignin-based polyacids

I step

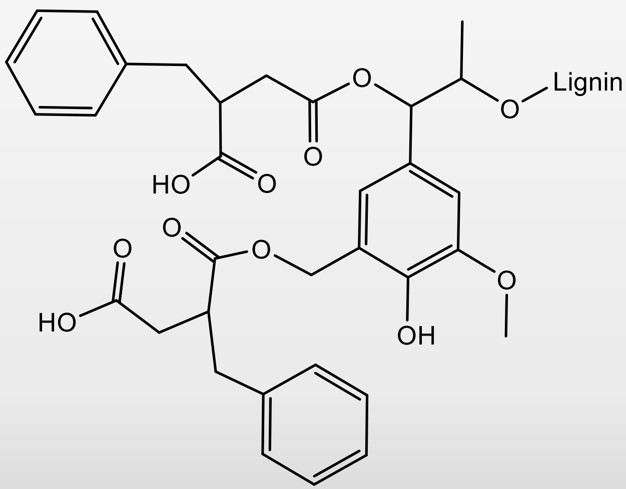
II step



Monomer for polyester resin production



Styrene (vinyl monomer)



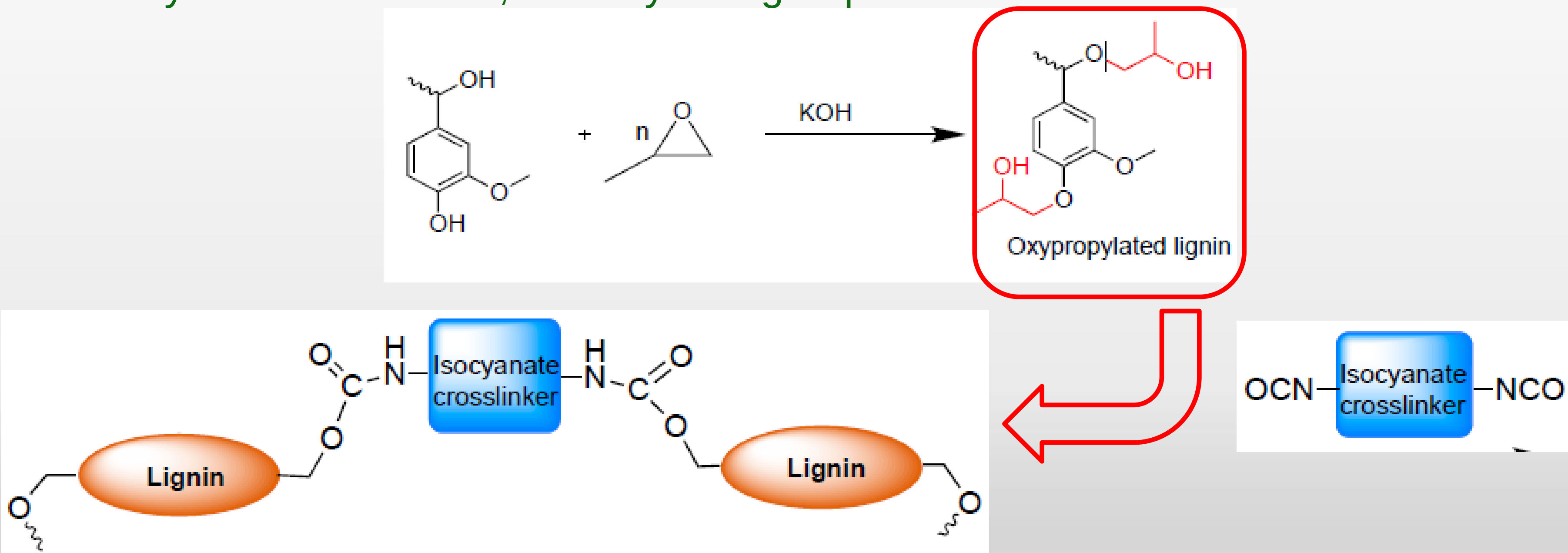
Cross-linked lignin based polyester resin

Functionalization of the Lignin aromatic rings: Etherification of phenolic and aliphatic OH

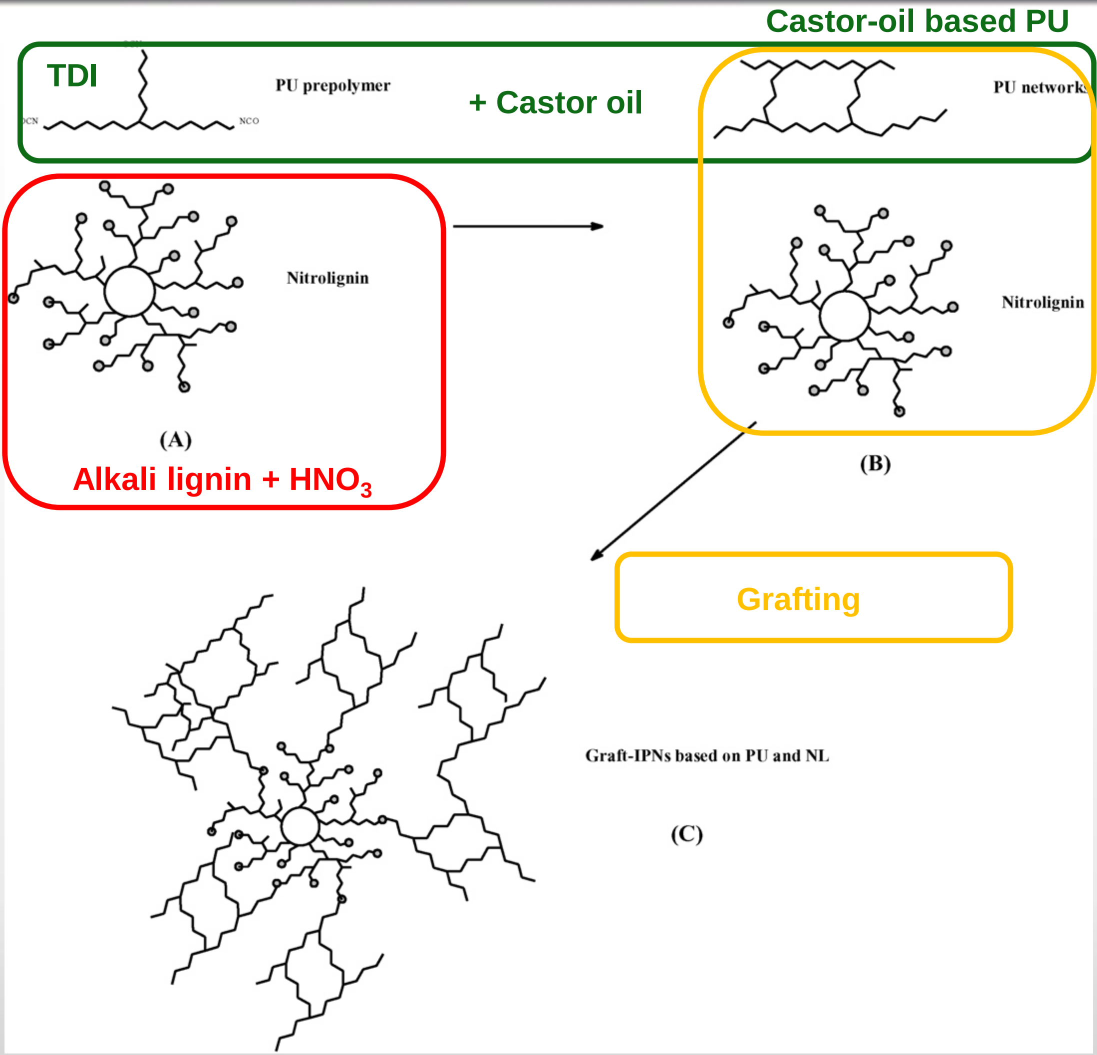
- An important set of reactions also includes the etherification of hydroxyl groups to synthesize long-chain polyethers

- Oxypropylation has been recognized as an especially productive method for the liquefaction of lignin

- Consequently, the phenolic moieties in lignin do not anciently react with isocyanate monomers, but alkyl OH groups do!

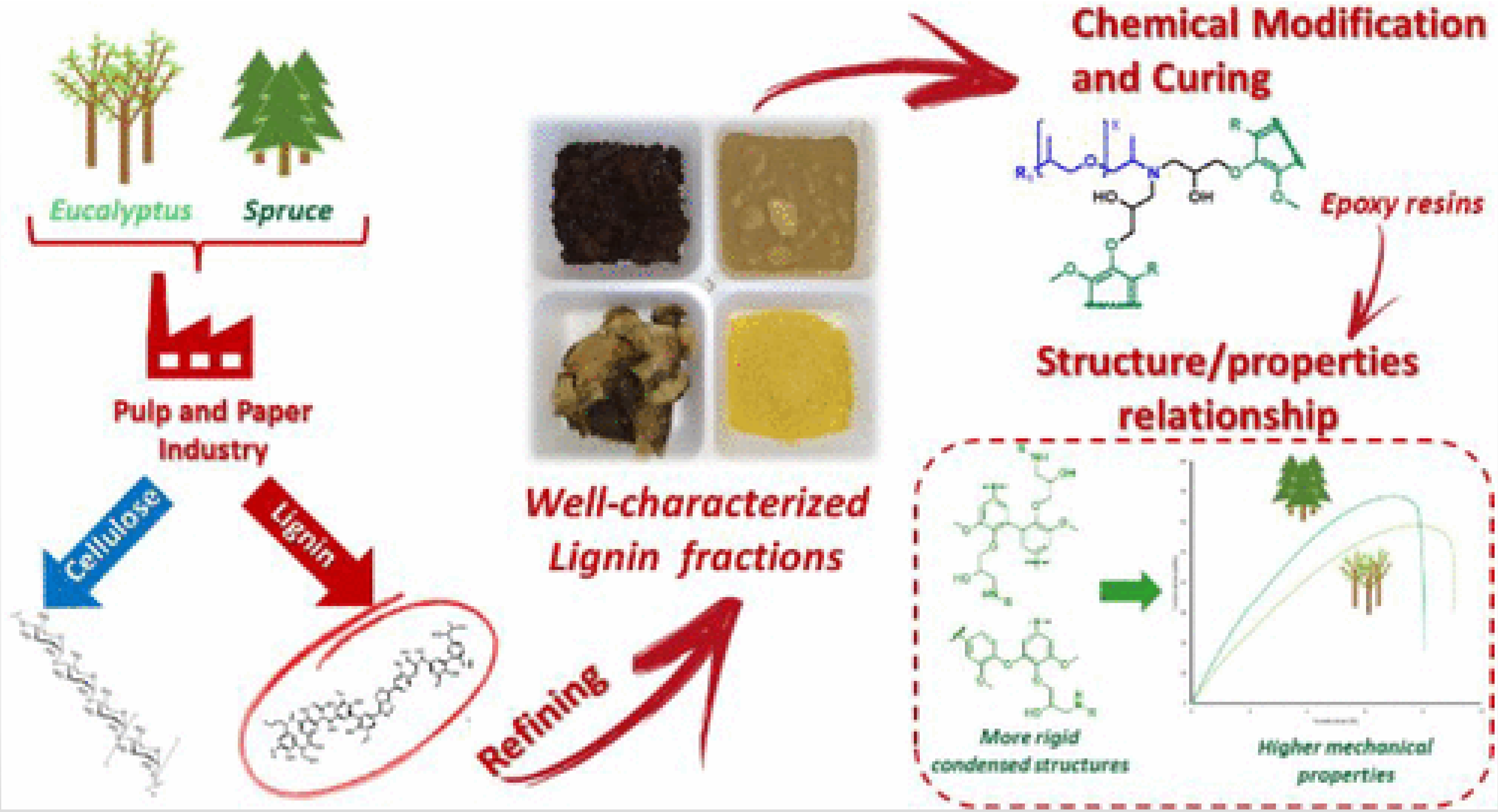


Functionalization of the Lignin aromatic rings: Nitration and synthesis of nitro-lignin based PU



- Graft-interpenetrating polymer network is synthesized from castor-oil based PU and nitro-lignin
- Molar ratio of reactants affects morphology and mechanical properties
- With an increase of NCO/OH molar ratio the T_g and tensile strength increase to

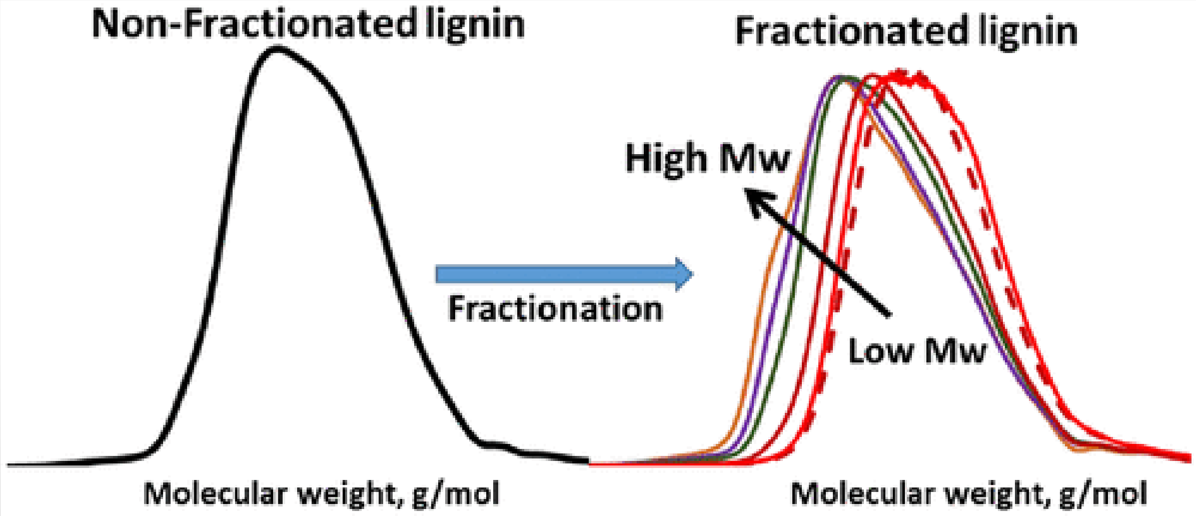
Functionalization of the Lignin for epoxy resin synthesis



Source: Gioia et.al., *Lignin-Based Epoxy Resins: Unravelling the Relationship between Structure and Material Properties, Biomacromolecules 2020, 21, 5, 1920–1928*

Functionalization of the Lignin for epoxy resin synthesis

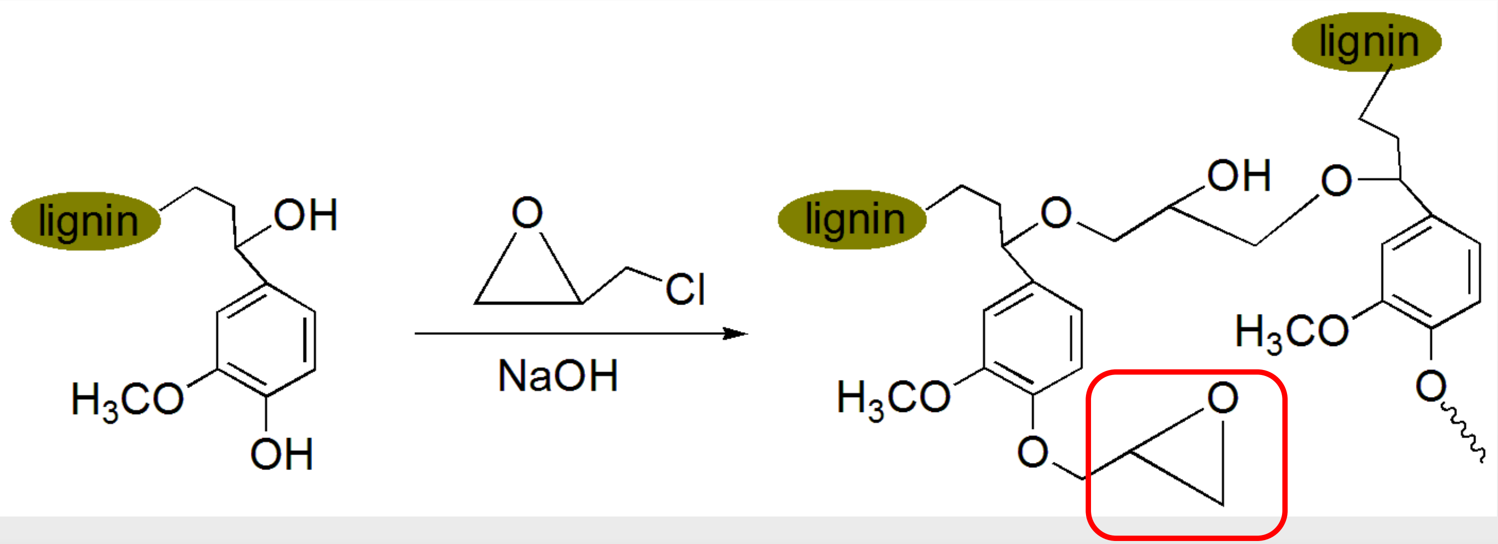
- Technical lignins from different sources, obtained from the Kraft process, can be used
- After Kraft process, technical lignin should be refined by solvent fractionation
- Properties of the final thermoset resins depend on lignin fraction molar mass and molecular structure



- Preparation of lignin with lower structural complexity and polydispersity
- Lignin fractionation is one of the primary solutions to engineer lignin into a value-added material.

Functionalization of the Lignin for epoxy resin synthesis

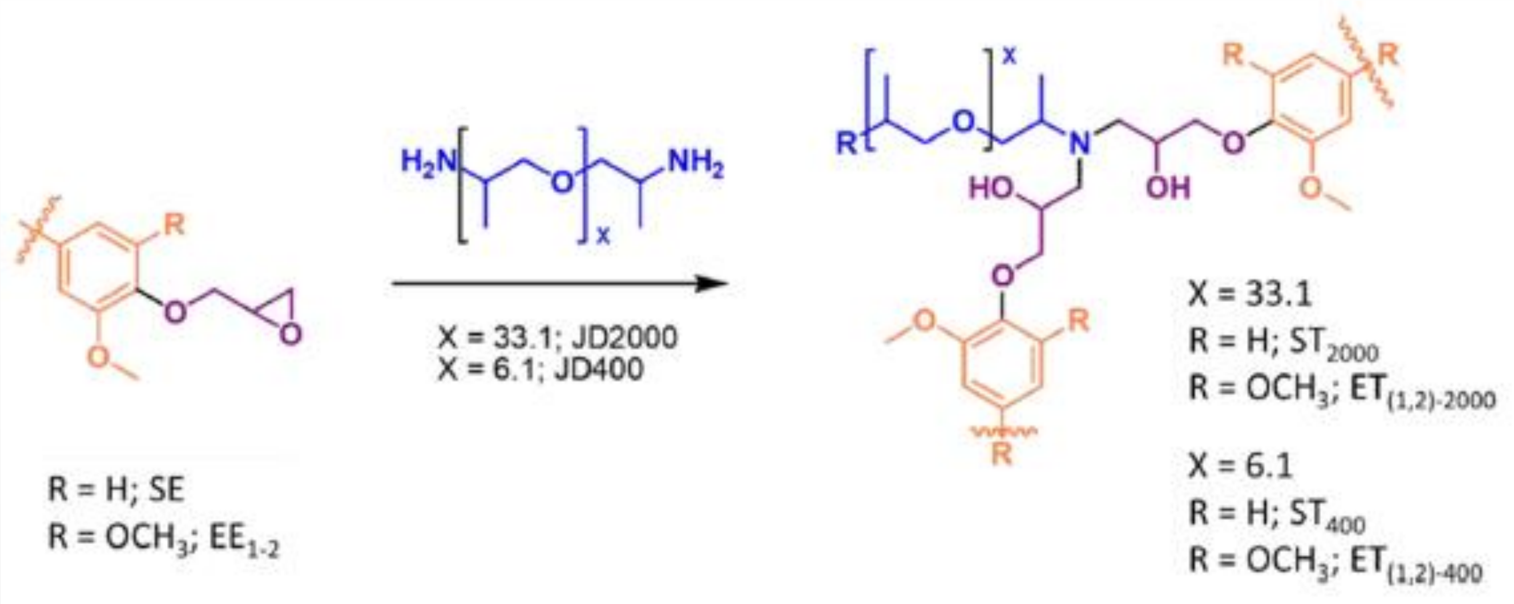
- Oxirane moieties can be selectively introduced to the refined lignin fractions
- The epoxidation modification of lignin was typically performed under the mild condition (Scheme) in 10 wt% NaOH aqueous solution using the epichlorohydrin and catalyst



The epoxy value of modified lignin affect its reactivity and cross linking

Functionalization of the Lignin for epoxy resin synthesis

- The resulting lignin epoxides can be subsequently cross-linked with commercially available polyether diamines

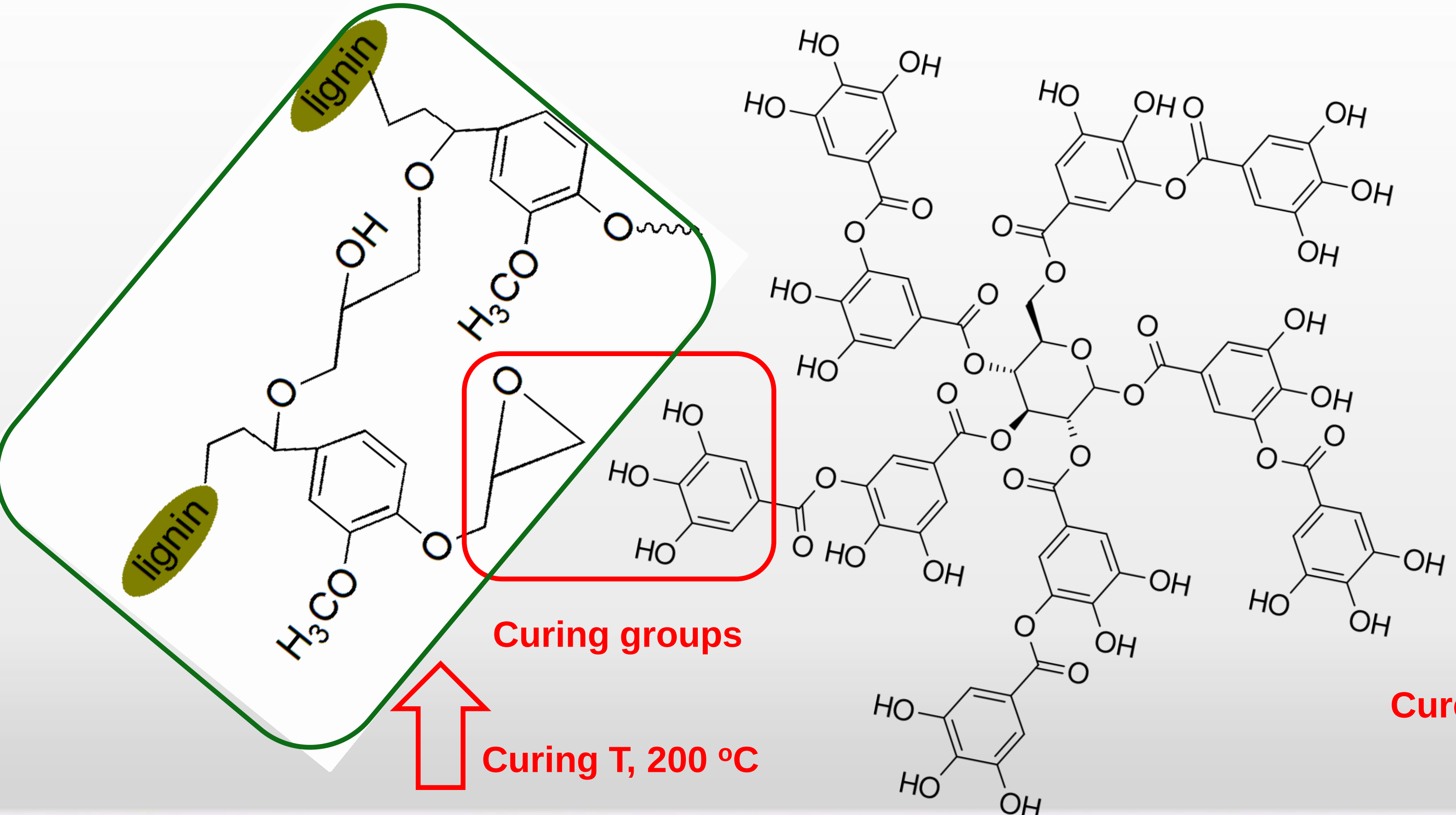


- The epoxy coatings containing lignin show improved anticorrosive effect than pure epoxide

- Improved compatibility and interface bonding of components in lignin based epoxy resin and reduced diffusion channel of water

Functionalization of the Lignin for epoxy resin synthesis

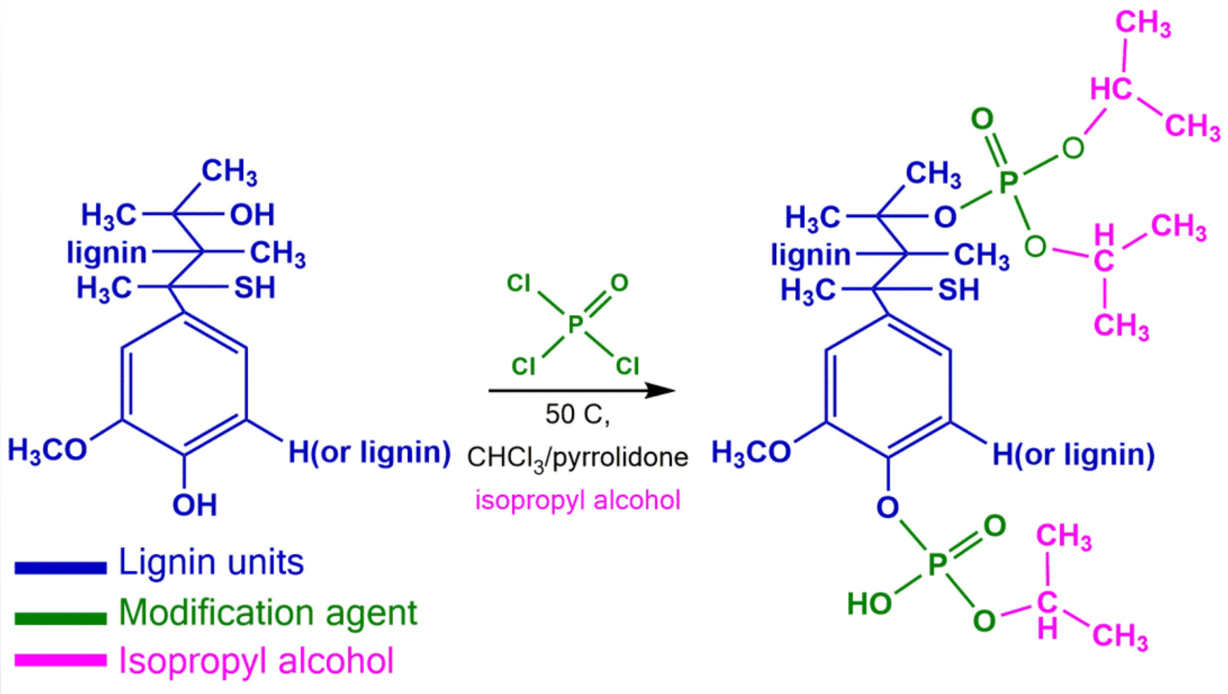
- In our laboratory, we have been using natural hydroxyl contained compounds such as tannic acid and lignin epoxides to obtain fully bio-based epoxy resin



Cured and control samples

Functionalized Lignin for high performance composites: Lignin/polyester composites

- The presence of various functional groups (aliphatic and aromatic OH-groups) makes lignin a suitable substance for functionalization (chemical modification)
- Phosphorylation method for synthesis of phosphorus functionalized lignin



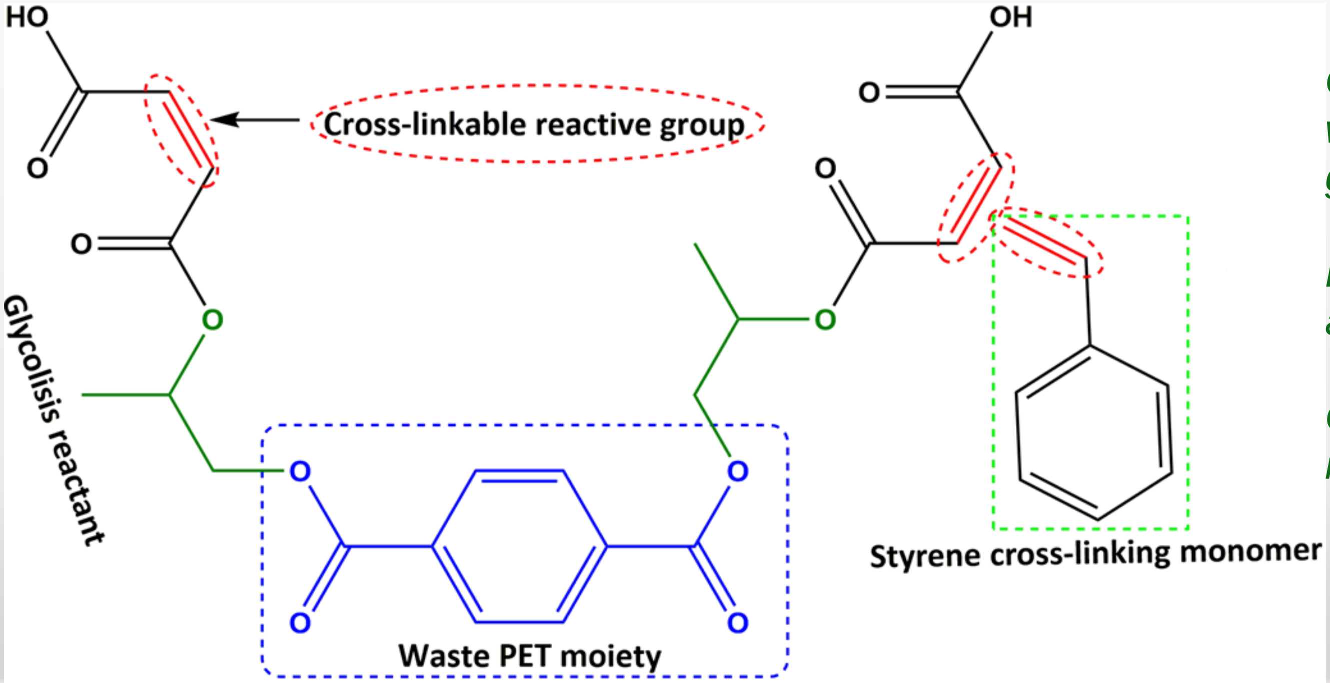
Phosphorous-containing lignin based flame retardants acts as a char promoters

Accumulated char forms protect the layer on the surface reducing the heat transfer

Phosphoric acid, released during thermal decomposition of phosphorous compounds, condenses to polyphosphates and also promotes charring

Functionalized Lignin for high performance composites: Lignin/polyester composites

- Phosphorous-containing lignin is used as a reinforcement in unsaturated polyester resin
- Unsaturated polyester resin based on waste poly(ethlyleneterephthalate) (PET) is synthesized in laboratory of Faculty of Technology and Metallurgy, University of Belgrade



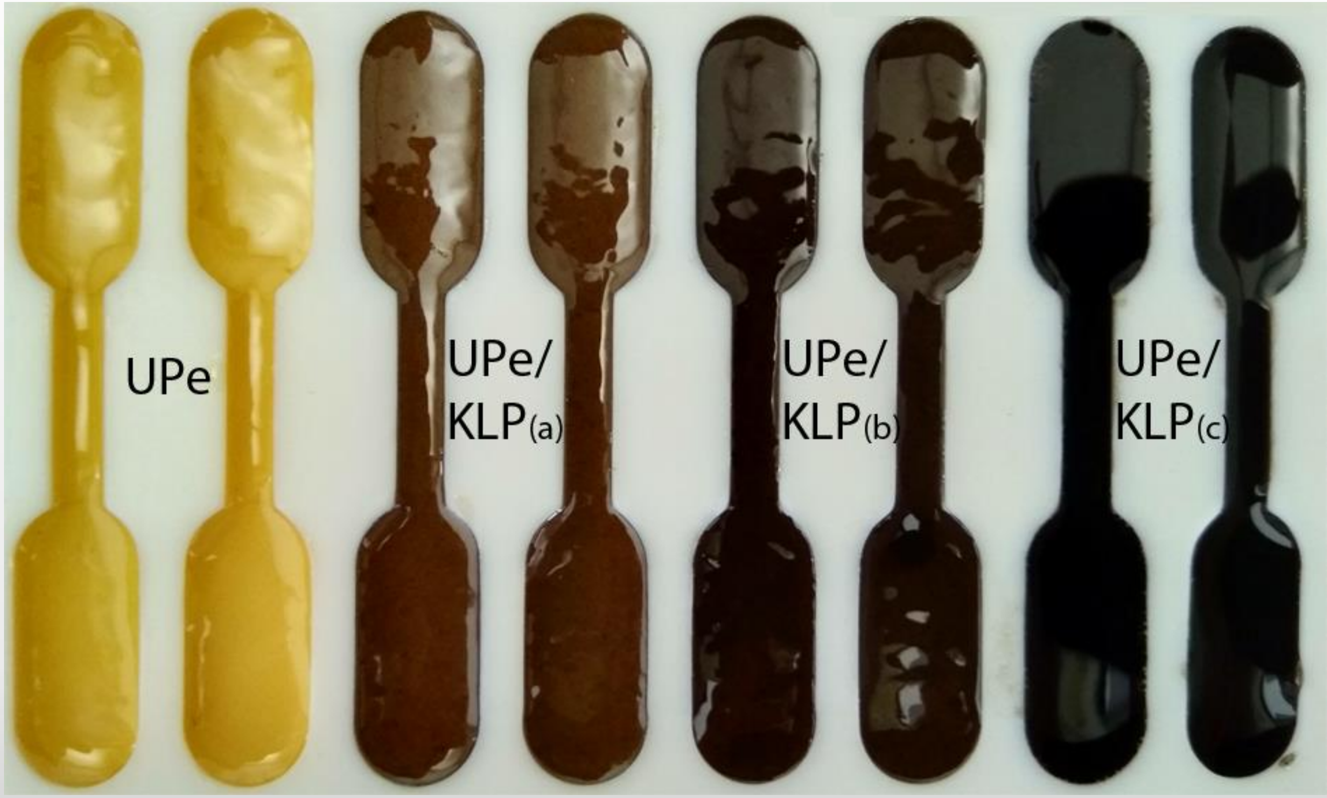
Catalytic depolymerization of waste PET using propylene glycol

Polycondenzation using maleic acid anhydride

Cross-linking with vinyl monomer

Composites preparation (emulsion blending method)

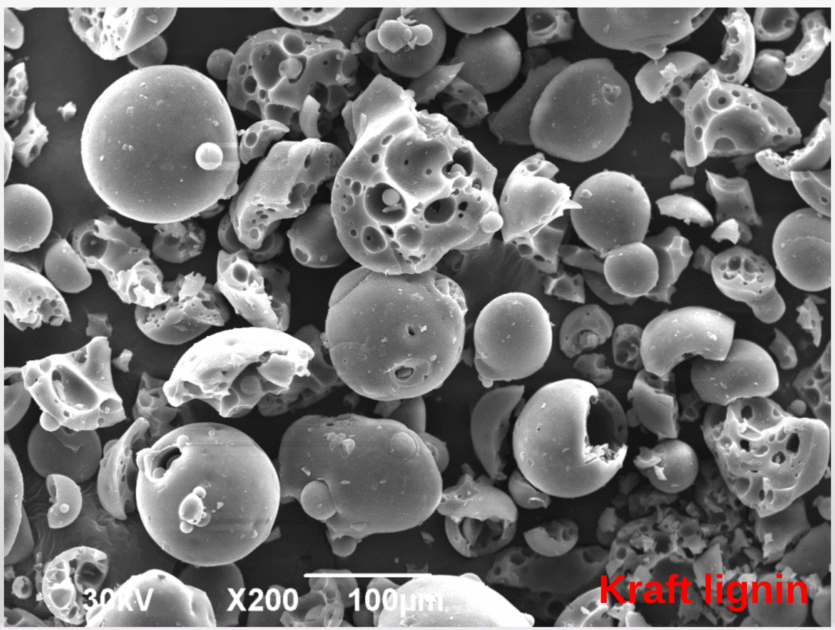
- Unsaturated polyester/phosphorylated lignin based composites (UPe/KLP) with 0.5%, 1.0% and 5.0% of KLP
- An effective and recyclable natural polymer-based composite for high performance thermal-insulation materials

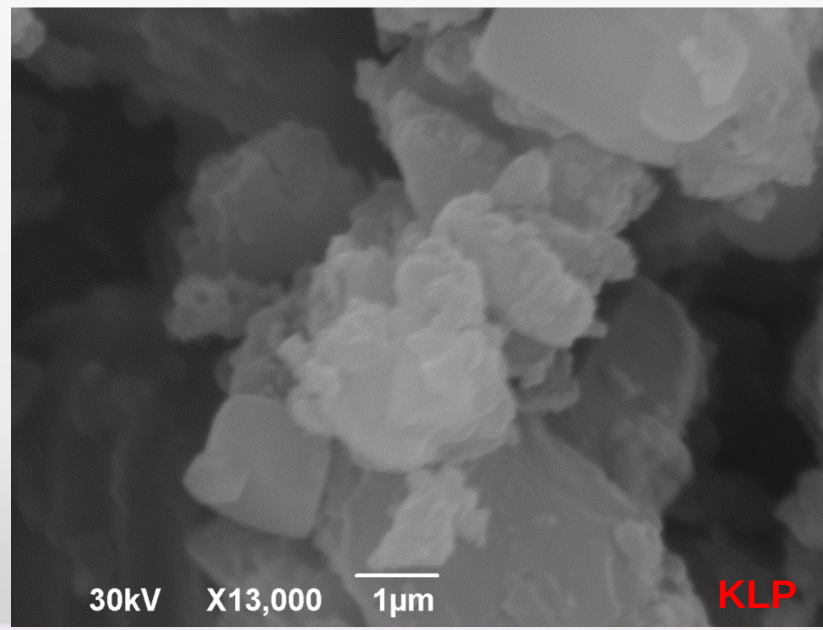


0.5% **1.0%** **5.0%**

Composites preparation (emulsion blending method)

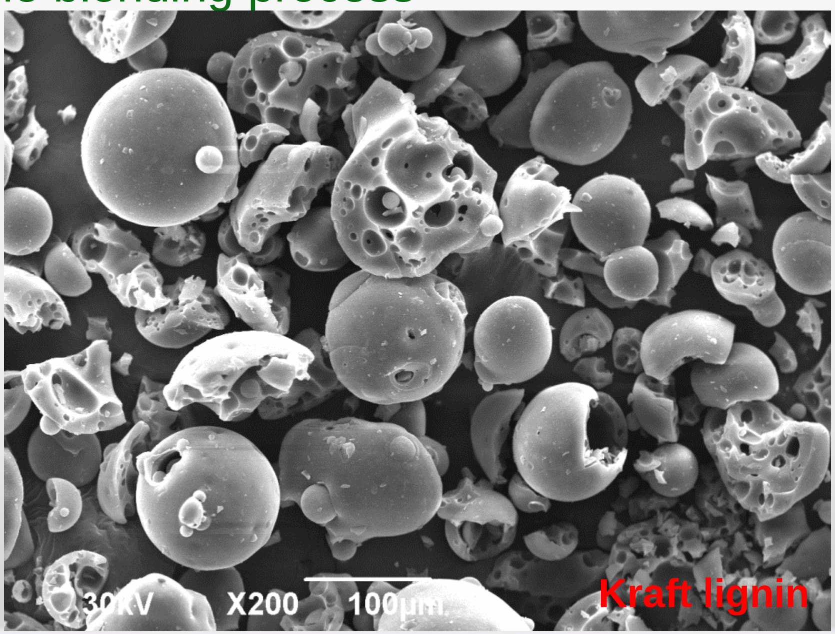
- Chemical modification change morphology of the kraft lignin
- Image of kraft lignin shows a typical morphology for KL powders obtained from Sigma-Aldrich. KL has a rounded or semispherical shape with many open volumes on the rough surface.
- Such morphology might be due to the concentration process of extracting lignin from black liquor. Spherical shape can be thermodynamically more stable compared to other particle shapes.

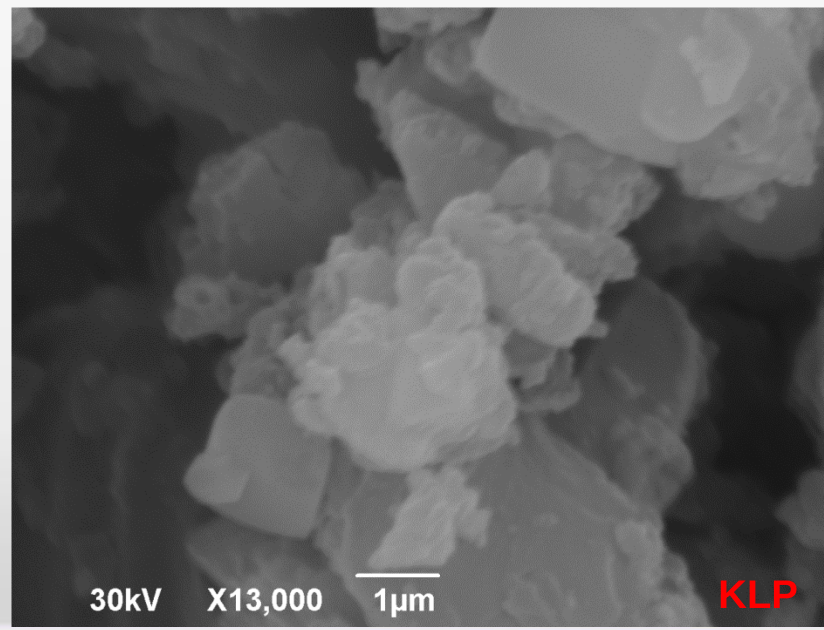




Composites preparation (emulsion blending method)

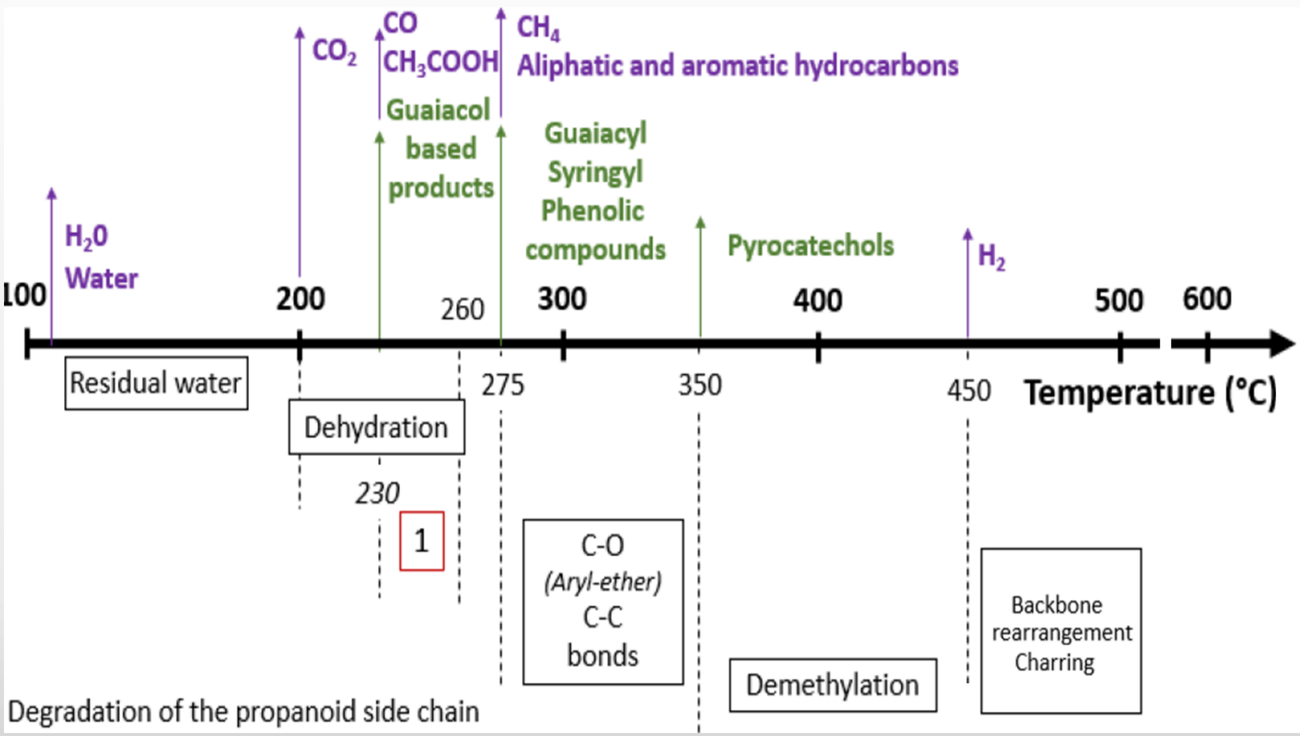
- Morphology for Kraft lignin chemically modified using phosphor oxychloride and isopropyl alcohol is completely different compared with the raw Kraft lignin.
- The structure becomes more amorphous without porous surface
- Compared to the polyester composites with unmodified kraft lignin, the chemical modification of lignin make the noncovalent interactions more favourable during the blending process

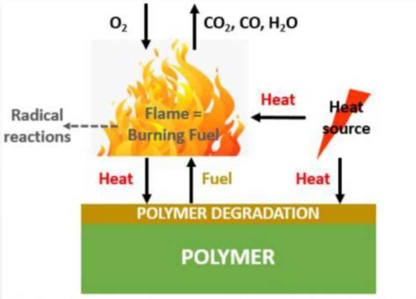




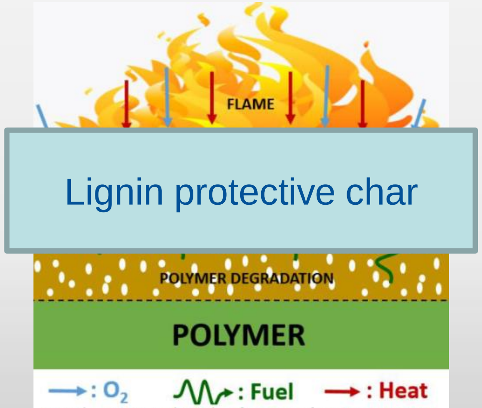
Flame retardancy of modified lignin

- Reduce heat release rate for polymer combustion
- Rearrangement of backbone producing aromatic structure like char



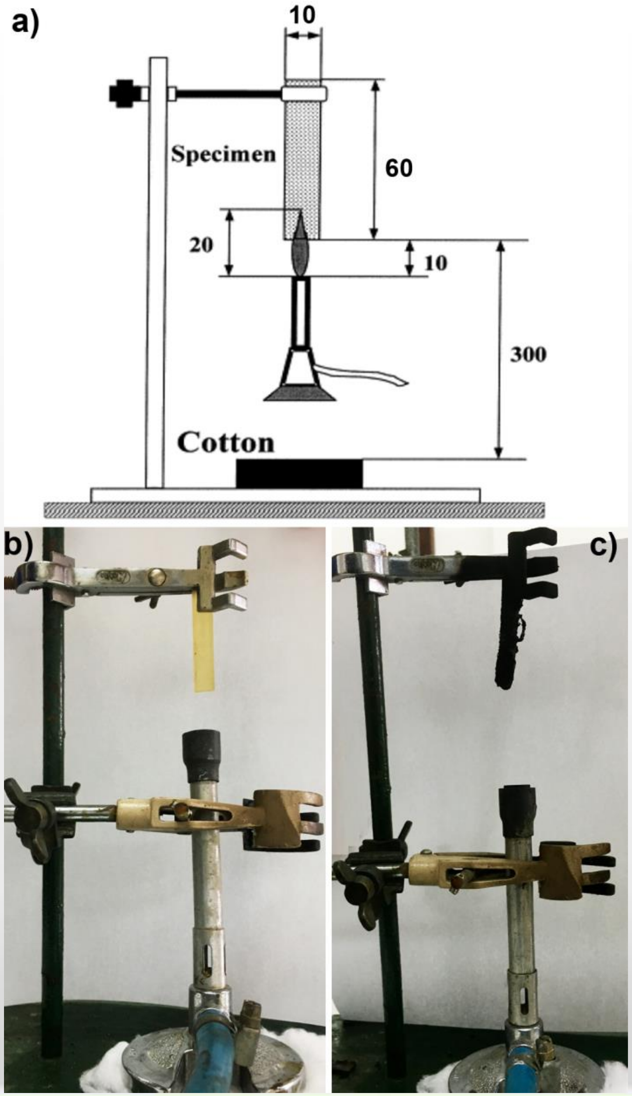


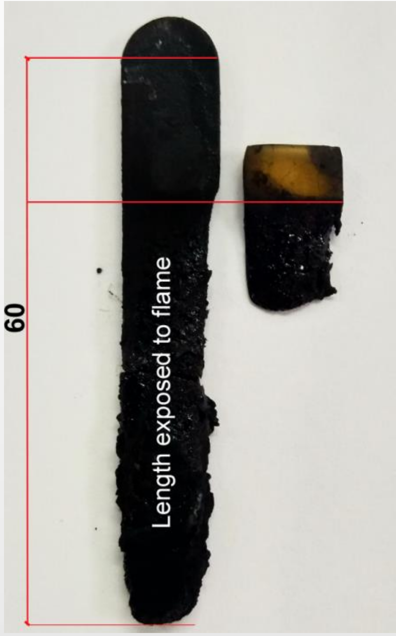
Combustion process and reactions occurring in the flame (R=polymer)



Development and mode of action of an intumescent system

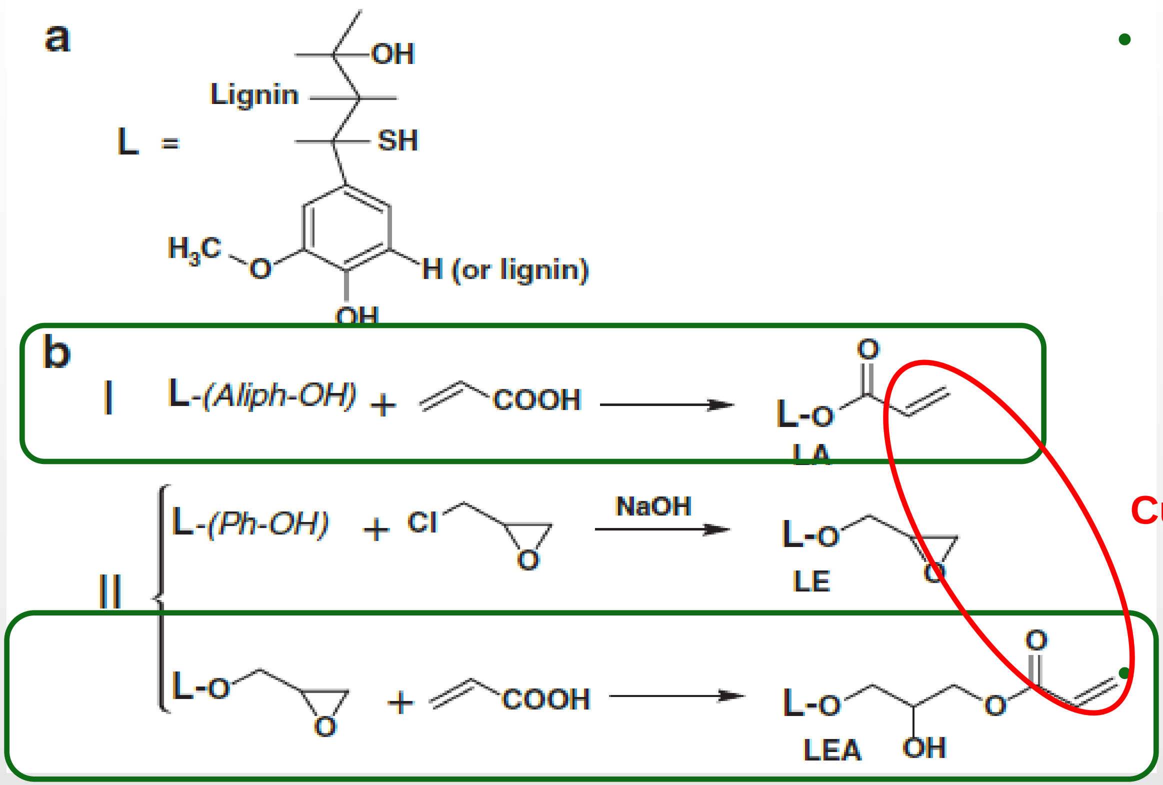
Flame retardancy of modified lignin





- Flame resistant properties were analyzed by UL-94 flammability test
- UPe specimens exhibit bad fire properties, and dropping occurs instantaneously, with the inflamed drops burning the cotton
- The introduction of 5.0% of phosphorylated KL allows an improvement in the fire reaction of UPe blends
- UPe/KLP(c) sample can be classified in V-1 category

Reactive Lignin for high performance composites: Lignin/polyester composites



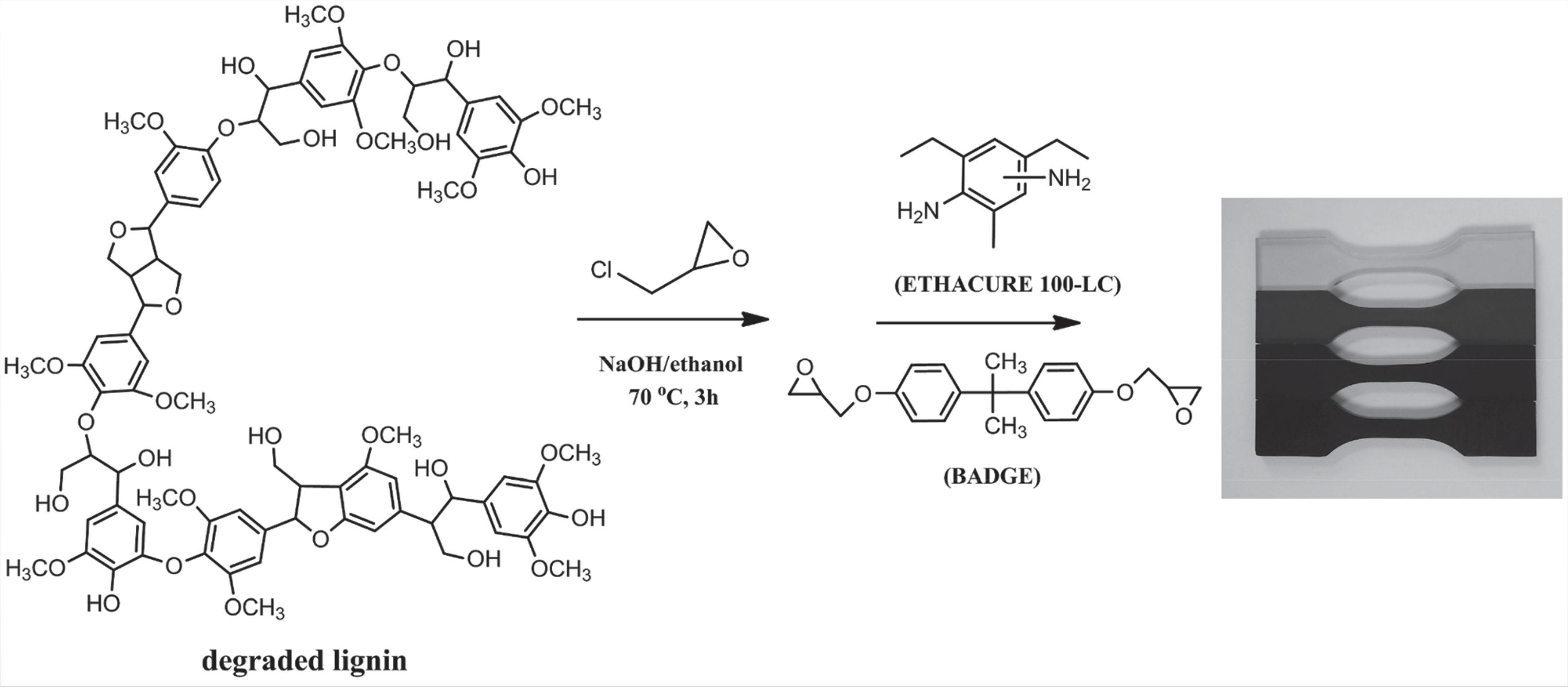
Curing groups

- Reactive lignin obtained by chemical modification with vinyl containing compounds (acrylic acid, methacryloil chloride) are suitable for application in unsaturated polyester composites

- Composites with improved mechanical, dynamic-mechanical and thermal properties

Functionalized Lignin for high performance composites: Lignin/epoxy composites

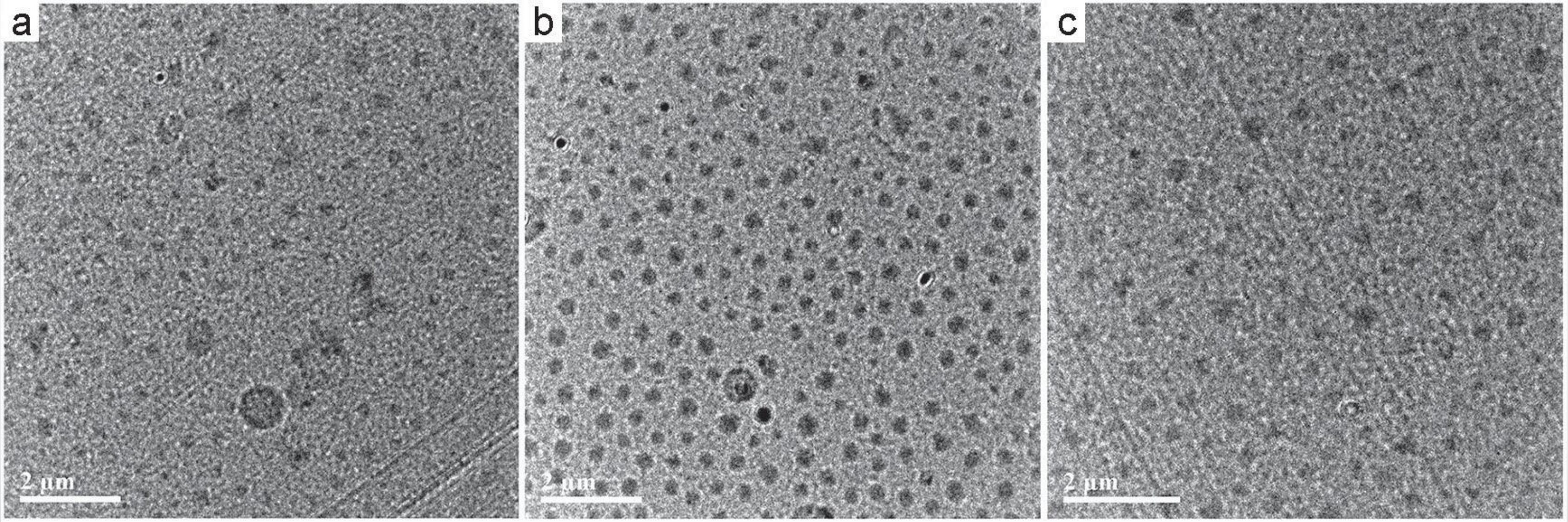
- Lignin epoxy composites is developed through covalent incorporation of depolymerized lignin epoxide into amine-cured epoxy matrix.



Functionalized Lignin for high performance composites: Lignin/epoxy composites

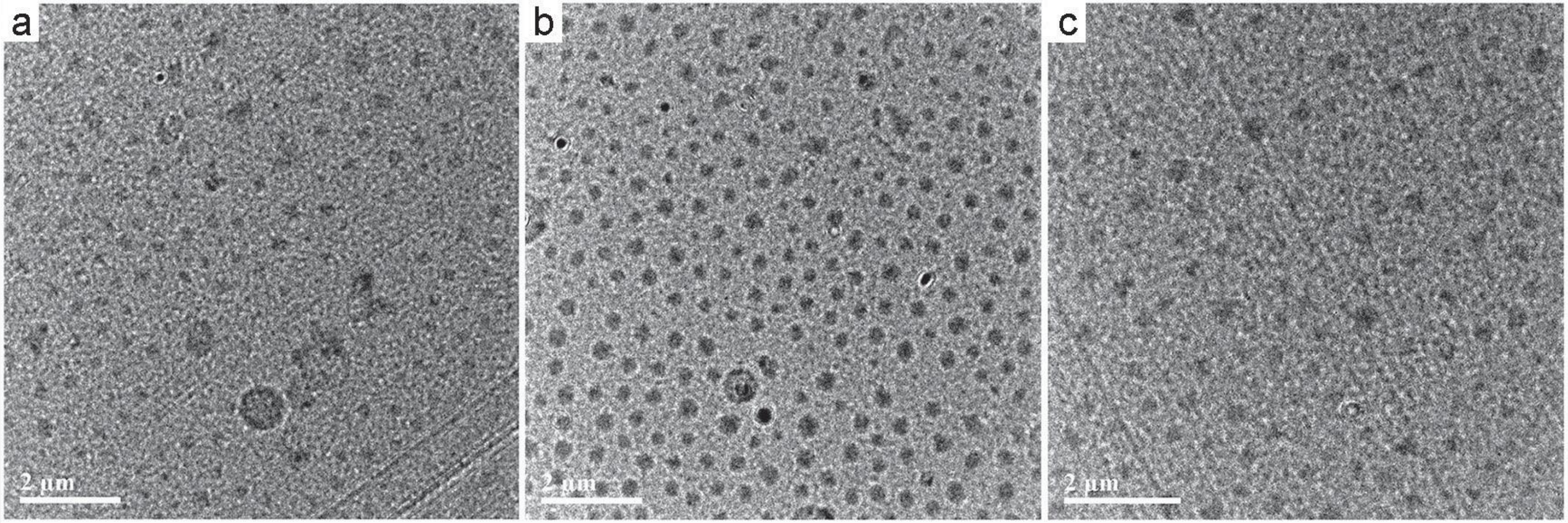
- The partially depolymerized lignin is first epoxidized with epichlorohydrin and the resultant depolymerized lignin epoxide shows decreased solubility in common organic solvents

- When dispersed in epoxy matrix and cured, the depolymerized lignin epoxide is integrated into epoxy networks in the form of submicron aggregates.



TEM images of lignin epoxy composites with 0.5%, 1.0%, and 1.8% of de-lignin–epoxide loadings a-c) after ultracut by microtome.

Functionalized Lignin for high performance composites: Lignin/epoxy composites



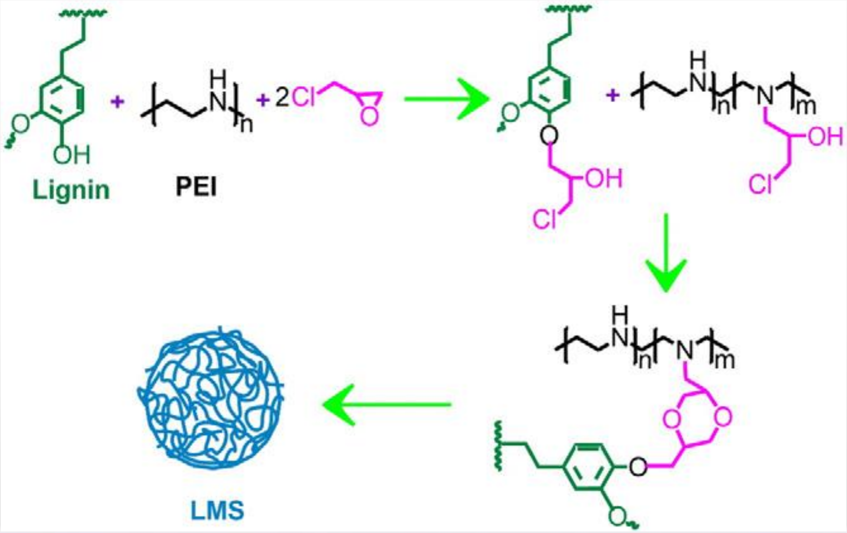
- The homogeneously distributed dark lignin particles with diameters of 300–400 nm could be observed clearly.

- These particles are aggregates of de-lignin–epoxide due to its strong π–π stacking and hydrogen bond interactions, and they should be covalently incorporated into the epoxy matrix through the reaction between exterior epoxy groups of aggregates and amino groups of hardener.

Functionalized Lignin for composites for water remediation

- Effective functionalized lignin-based biosorbents (amino, epoxy, vinyl functional groups, etc.) can be synthesized in one step process through chemical modification with alkyl diamines, hyperbranched poly(ethylene imine), acrylic acid (unsaturated acids) and epichlorohydrin

- Or in two step process through impregnation of amino-modified lignin with hydrous iron oxide forms (goethite, magnetite,…), as well as with iron oxide forms combined with manganese oxide and copper oxide applicable for efficient pollutant removal (or oxyanions: chromate, arsenate, phosphate etc.).



Functionalized Lignin for composites for water remediation

- In laboratory of Department of Organic Chemistry, TMF, the hybrid amino-functionalized lignin microspheres (A-LMS) loaded with magnetite and manganese oxide nanoparticles are developed

- Our study demonstrated that the adsorption process of heavy metals on hybrid amino modified adsorbent was dominated by formation of strong surface complexation with lone pair of nitrogen atom and chelation interaction with oxygen

- Heavy metal oxyanions adsorption occurs spontaneously, followed by both physisorption and chemisorption

Functionalized Lignin for composites for water remediation