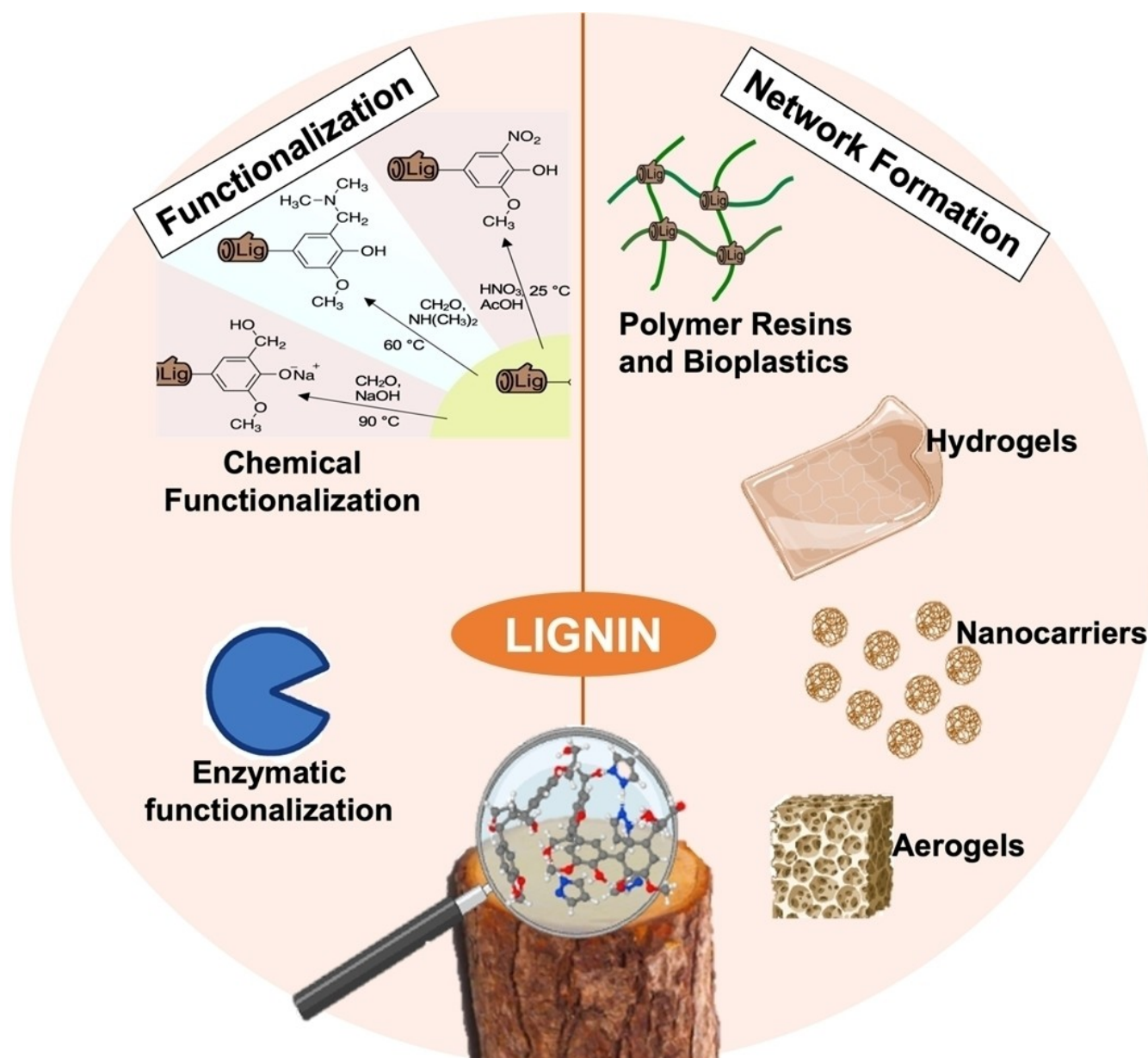


Lignin Valorization

Lignin Upconversion by Functionalization and Network Formation

Sanjam Chandna, Carmen A. Olivares M., Egor Baranovskii, Gunnar Engelmann, Alexander Böker, C. Christoph Tzschucke, and Rainer Haag*



Abstract: Lignin, a complex and abundant biopolymer derived from plant cell walls, has emerged as a promising feedstock for sustainable material development. Due to the high abundance of phenylpropanoid units, aromatic rings, and hydroxyl groups, lignin is an ideal candidate for being explored in various material applications. Therefore, the demand on lignin valorization for development of value-added products is significantly increasing. This mini-review provides an overview of lignin upconversion, focusing on its functionalization through chemical and enzymatic routes, and its application in lignin-based polymer resins, hydrogels, and nanomaterials. The functionalization of lignin molecules with various chemical groups offers tailored properties and increased compatibility with other materials, expanding its potential applications. Additionally, the formation of lignin-based networks, either through cross-linking or blending with polymers, generates novel materials with improved mechanical, thermal, and barrier properties. However, challenges remain in optimizing functionalization techniques, preserving the innate complexity of lignin, and achieving scalability for industrial implementation. As lignin's potential continues to be unlocked, it is poised to contribute significantly to the shift towards more eco-friendly and resource-efficient industries.

1. General Introduction and Scope

Today's synthetic plastic materials ($350 \cdot 10^6$ t/a) have non-degradable backbones and are predominantly composed of petrochemicals, leading to the accumulation of plastics in the environment.^[1a] The key problems generated by the use of plastics are insufficient recollection and slow degradability. The durability of plastics is of great importance in various areas, such as building materials.^[1a] Here, sustainability can only work through improved material design or value conservation of existing material flows. The plastic materials of the future must originate from sustainable and long-term available resources by using biogenic resources. The complete life cycle of plastic materials, including additives/monomers/oligomers must be analyzed and evaluated for specific applications to carry out a sustainable resource assessment. For plastic waste that escapes recycling, environmental degradation is the only solution. Lignin is the most abundant natural phenolic polymer with a complex cross-linked and highly branched structure.^[1b] The specific lignin structure depends on the source (e.g., hardwood or softwood).^[1c] Before any modification, lignin is referred to as native lignin and is found as part of lignocellulosic biomass ($15\text{--}20 \cdot 10^9$ t/a). In nature, the three most common precursors of lignin are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol and the ratio of the monomers depends on the source of lignin.^[2] The linkages among the monomers are mainly carbon-carbon and ether linkages. The most common ether linkage found in the structure of lignin is β -aryl ether ($\beta\text{-O-}4'$).^[1] A general structure of lignin (along with the various subunits) is

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depicted in Figure 1. The term technical lignin refers to the lignin extracted from biomass including lignin as industrial by-product.^[1a] The major industrial processes to extract lignin are kraft (treatment with sodium hydroxide and sodium hydrosulfide), sulfite (treatment with a metal sulfite and sulfur dioxide with calcium, magnesium, or sodium as counter ions), soda (treatment with sodium hydroxide, often using anthraquinone as a catalyst) and organosolv process (treatment with organic solvents).^[1] All these isolation/solubilization processes occur at elevated temperatures at $120\text{--}190^\circ\text{C}$.

Being the major by-product of the paper industries (approximately 100 Million t/a), valorization of lignin through the development of novel high-value side products, is a key aspiration of various industries.^[4] However, lignin is currently used for energy generation by combustion or simply composted. Currently, lignin-based materials have not been sufficiently scaled, however, they can be considered as non-fossil alternatives for some thermosets, such as phenolic resins.^[5]

This minireview describes the great potential of polyphenolic lignin for upconversion into valuable chemicals and formation of polymer networks. We focus mainly on the chemical and enzymatic functionalization of lignin and the material development through the formation of hard and

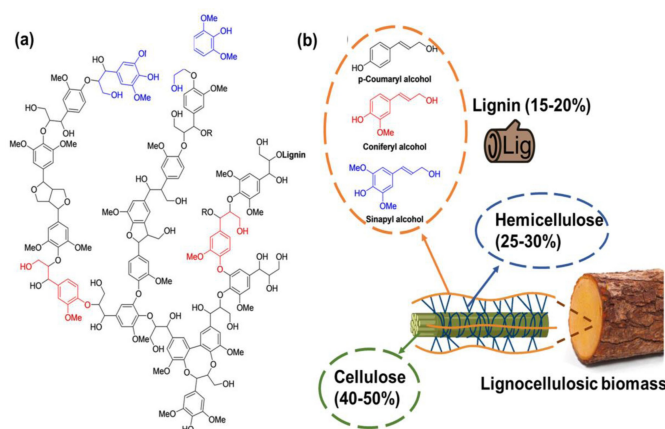


Figure 1. Lignin idealized chemical structure along with various subunits of lignocellulosic biomass.^[3]



Rainer Haag, is Professor of Organic and Macromolecular Chemistry at Freie Universität Berlin. Since 2021, he is spokesperson of the Collaborative Research Center 1449 "Dynamic Hydrogels at Biological Interfaces" and the research facility "Supra-FAB". His research focuses on biodegradable and multivalent macromolecules, supramolecular architectures, nanotransporters for drug delivery, and sustainable polymer syntheses. In start-up-oriented teaching, he won the 2014 teaching award at Freie Universität Berlin with his project "Translation of Project Ideas." Together with the company Dendropharm, he received the Innovation Award Berlin-Brandenburg in 2016. Since 2019, he has been an elected member of the German Academy of Science and Engineering (acatech). In 2022, he was awarded the ERC Advanced Grant. His scientific achievements are documented by >630 peer-reviewed publications and 45 patent applications.



Christoph Tzschucke, is Professor of Organic Chemistry and Catalysis at Freie Universität Berlin since 2009. He studied Chemistry at Albert-Ludwigs-Universität Freiburg and the University of Wisconsin-Madison. He obtained his doctoral degree working with Prof. Willi Bannwarth on the recycling of perfluoroalkyl-tagged palladium-catalysts. As post-doctoral researcher he worked with Prof. John F. Hartwig at Yale University and with Steven V. Ley at Cambridge University. His research interests include transition metal catalyzed C–H activation and C–C cross-coupling reactions, metal complexes as therapeutic agents and cross-linkers in polymer networks, and sustainable re-use of polymeric materials.



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His scientific output consists of more than 175 peer-reviewed papers as well as and 16 patent applications. The main research interests of his group include integration of biological functions into polymer materials and guided self-assembly of colloidal and polymer systems.



Gunnar Engelmänn studied chemistry at the Humboldt University in Berlin and graduated in 1990 with a topic on drug design. He received his PhD in 1995 in the field of electrically conductive polymers. From 1996 to 1998, he studied business administration at the Technische Fachhochschule Berlin (TFH) and graduated with an associate degree in economics. In 1999, he moved to the Fraunhofer Institute for Applied Polymer Research (IAP) in Teltow-Potsdam. His research interests include the chemical modification of biopolymers for their application in thermoplastic composites. After a research stay in England (Wilton) in 2002, he worked on the modification and application of nanoparticles in the field of material development. In addition, aromatic biopolymers such as lignin are used for the preparation of biobased thermosets and composites. Furthermore, microencapsulation is being adapted from a sustainability perspective to successfully address the new challenges for such particulate systems.



Sanjam Chandna, is a post-doctoral scientist in the field of polymer science and biochemistry at Freie Universität Berlin, Germany. She is a member of the Collaborative Research Center 1449 "Dynamic Hydrogels at Biological Interfaces". She obtained her Ph.D. from Panjab University, Chandigarh, India and subsequently received a Rising Star Fellowship from the Freie Universität Berlin for her post-doctoral research in 2021. Her research focuses on lignin valorization, functional material synthesis, nanocarriers and green chemistry. She works on multiple research projects focused on lignin upconversion for diverse applications including sustainable hydrogels for multivalent virus binding, 3D printing and lignin-based flocculants for environmental remediation.



Carmen A. Olivares M. obtained her Bachelor's degree in Chemical Engineering at the Instituto Universitario Politécnico "Santiago Mariño" in Venezuela with Summa Cum Laude honors. She worked with lignin-based polymeric materials from coconut fibers for her Bachelor's thesis research. Then, she completed her M.Sc. program in Polymer Science at the Freie Universität Berlin, Technische Universität Berlin, Humboldt Universität zu Berlin, and Universität Potsdam in Germany. Her Master's thesis research was focused on bioselective membrane functionalization. She has additionally worked with sustainable copolymers and lignin depolymerization. Her research interests include lignin-based materials, surface functionalization, and sustainable polymers.



Egor Baranovskii obtained his Bachelor's degree in Chemistry in 2021 at St. Petersburg State University, Russia with distinction. Working in the fields of organic, inorganic and analytical chemistry, he did his thesis in the field of polymer chemistry, which was related to synthesis and functionalization of polysiloxane materials for optoelectronics. Currently he is obtaining his Master's degree in Polymer Science at Freie Universität Berlin, Technische Universität Berlin, Humboldt Universität zu Berlin, and Universität Potsdam in Germany. After successfully finishing an internship at BASF SE, he started his Master's thesis devoted to mechanochemical conversion of lignin for its valorization with the focus on 3D printing.

soft polymer networks. The field of lignin upconversion shows rapid development in a broad range of areas, from simple functional lignin bioplastics to new polyphenol-based resins for 3D printing, as well as lignin-based hydrogels for biomedical applications.^[6] The current potential of lignin applications goes far beyond this minireview and includes its use in plant protection, its conversion into biofuels (which can be used as a substitute for fossil fuels), and its degradation into phenolic or oligophenolic building blocks (such as vanilline type aromatic systems by simple electrochemical conversion)^[7] and for 3D printing applications.^[6c]

2. Lignin Functionalization

2.1. Chemical functionalization of lignin

The main active sites of technical lignin apart from aromatic rings are hydroxyl groups.^[1a] The properties of lignin (e.g., solubility in organic solvents) can be enhanced by modifying the functional groups of the active sites.^[1b] In this manner, new chemically active sites can be introduced to the aromatic rings of lignin by hydroxymethylation, aminomethylation, nitration, sulfomethylation, and sulfonation (Figure 2).^[1b,8]

Hydroxymethylation is one of the most common chemical modifications of lignin. Lignin is treated with formaldehyde under alkaline conditions to obtain lignin-phenol-formaldehyde (LPF) resin adhesives for plywood production.^[8-9] Amino groups can be introduced to the lignin structure by aminomethylation.^[8] The simplest method in

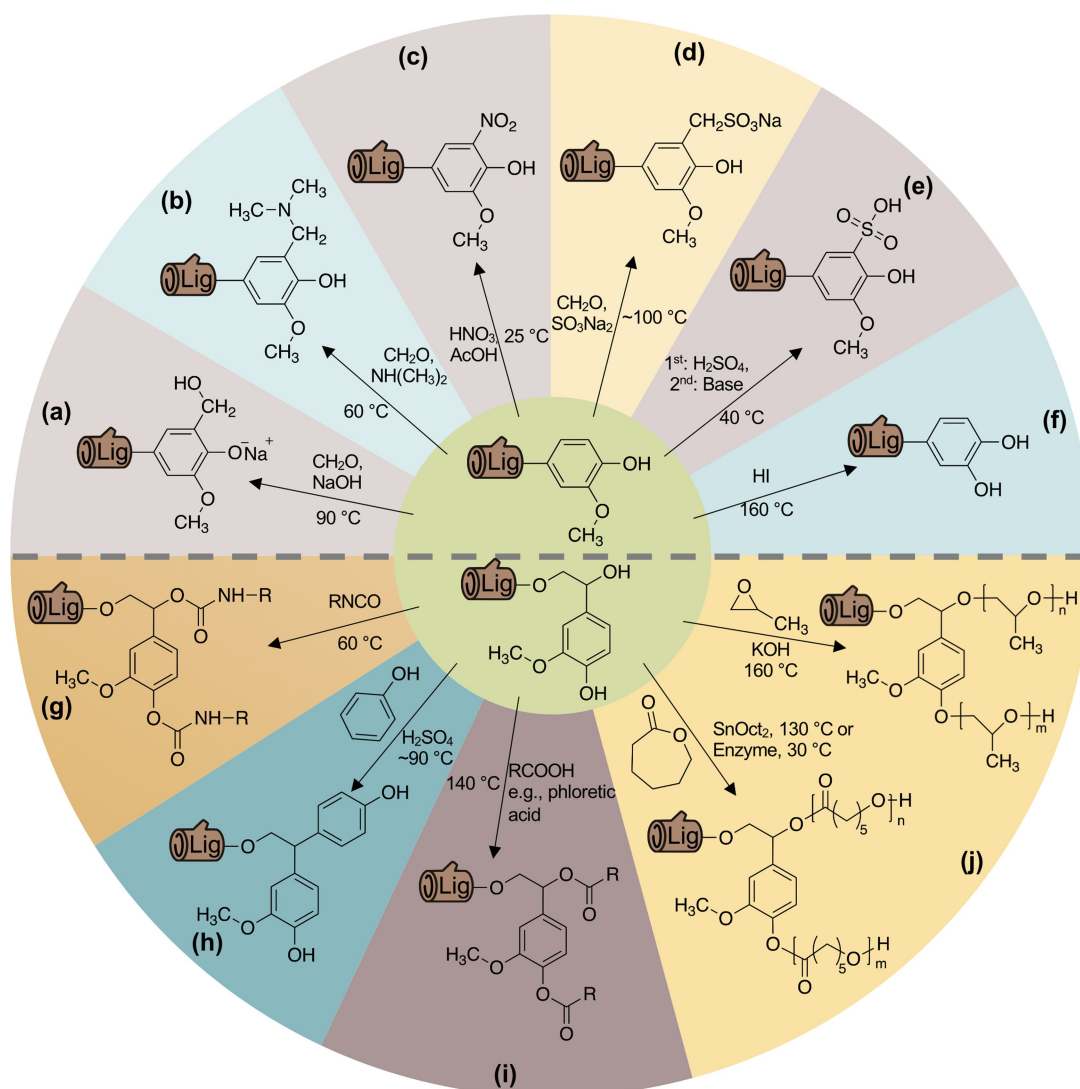


Figure 2. Lignin chemical modification approaches. Upper section: modification strategies of the aromatic ring, (a) hydroxymethylation, (b) aminomethylation, (c) nitration, (d) sulfomethylation, (e) sulfonation, (f) demethylation. Lower section: modification strategies for the hydroxyl groups, (g) urethanization, (h) phenolation, (i) esterification, (j) ring opening polymerization.

this regard is the Mannich reaction involving different types of amines and formaldehyde under alkaline, neutral or acidic conditions.^[1b] For example, lignin can be treated with dimethylamine, formaldehyde, and acetic acid in aqueous solution to incorporate amino groups to the structure.^[1b,10] The resulting materials have potential applications as cationic surfactants.^[8,10]

Nitration is another way to incorporate nitrogen in the lignin structure by using nitrating agents in non-aqueous solvents (e.g., acetic anhydride, acetic acid, sulfuric acid).^[1b,11] Nitrolignin can be potentially applied as a precursor for electrocatalysts for oxygen reduction reactions.^[12] Finally, sulfur moieties can be incorporated to the lignin structure by sulfomethylation and sulfonation.^[1b] Sulfomethylation enables the addition of methylene sulfonate groups to the aromatic ring involving formaldehyde and an alkali metal sulfite salt in water under alkaline conditions. In this reaction, formaldehyde introduces the hydroxymethyl group in the lignin followed by the sulfite substitution of its hydroxyl group. As a result, methylene sulfonate groups are formed (Figure 2d).^[1b,11,13] This modification has been performed to develop adsorption removal materials for cationic dyes.^[14] Alternatively, direct sulfonation enables the addition of sulfonate groups to the lignin structure by treatment with sulfuric acid or sodium sulfite. The sulfating agent forms a covalent bond carbon-sulfur with the aromatic rings of the lignin structure as shown in Figure 2, section (e).^[13] Sodium sulfite supports lignin degradation in the sulfite process leading to the formation of aliphatic C–S-bonds. The resulting lignosulfonates have several applications including dispersants for concrete and binders.^[15] Additionally, the aromatic methoxy groups in lignin can be converted to phenolic hydroxyl groups by demethylation. There are different demethylation agents including hydroiodic acid (HI) and iodocyclohexane (ICH) that contribute to the increase of the phenolic hydroxyl content in the lignin structure. Demethylated lignin has exhibited enhanced reactivity and it has been investigated as a potential precursor of lignin-based resins and adhesives.^[16]

The hydroxyl groups of the lignin structure can be modified by different methods as shown in the lower section of Figure 2. In this context, esterification involves the reaction between the hydroxyl groups of lignin and an activated acid (e.g., acid anhydride or acid chloride) with a catalyst (e.g., pyridine or imidazole). Different esterification approaches involve distinct reaction conditions.^[1b,8,16a] For instance phloretic acid is a phenolic acid, and this approach combines the advantages of esterification with phenolation as the number of phenolic groups in lignin increases.^[17] Phenolation is a modification approach, which activates the aliphatic hydroxyls to increase the number of phenol groups in the structure of lignin by C–C-bond formation. Conventionally, lignin is treated with phenol in organic solvents (e.g., methanol or ethanol) under acidic conditions.^[1b,16a] Normally, sulfuric acid is used as catalyst in this process and the reactivity is increased as aromatic hydroxyl groups are more reactive than aliphatic hydroxyl groups in lignin.^[11]

Alternatively, urethane bonds can be incorporated into the lignin structure by the reaction between the hydroxyl groups of lignin and isocyanates, such as 4,4'-diphenyl methane diisocyanate (MDI).^[1b,18] The process is known as urethanization and leads to the synthesis of lignin-based polyurethanes.^[1b] Finally, the hydroxyl groups of lignin can react with cyclic monomers such as propylene oxide or ϵ -caprolactone via ring-opening polymerization (ROP) as shown in Figure 2.^[1b,16a] The specific ROP reaction between propylene oxide and lignin is called oxypropylation. This reaction is usually performed at 160 °C using potassium hydroxide as catalyst to form liquid polyols with comparable properties to the conventional polyols (which are used to produce polyurethane rigid foams).^[19]

2.2. Enzymatic functionalization of lignin

Technical lignin can be functionalized by enzyme-mediated modifications to obtain high-value materials such as lignin-based polymers, fillers, and coatings under milder conditions (e.g., lower temperatures) compared to the conventional chemical lignin modification strategies.^[20] For instance, in the ROP reaction of lignin with ϵ -caprolactone shown in Figure 2, the difference in temperature between enzymatic catalysis and the chemical approach is ≈ 100 °C. In the conventional system with tin(II) 2-ethylhexanoate as a catalyst, the reaction occurs at 130 °C.^[21a] Meanwhile, the same reaction catalyzed by enzymes (e.g., *C. antarctica* lipase B, one of the most widely studied enzymes for this reaction) usually occurs at 30 °C.^[22b]

Different enzymes participate in lignin modification processes including laccases, peroxidases, hydrolases, and some lipases.^[20a,22a] Laccases are particularly promising as they require relatively simple co-substrates (e.g., molecular oxygen) compared to other enzymes.^[20a] They have a wide substrate range including phenols and polyphenols (e.g., lignin), polyamines, aryl diamines, and inorganic ions. Laccases are found in many natural systems including plants, fungi, insects, and bacteria.^[20b]

The reaction process is affected by different factors including temperature, pH, solvent, laccase origin, dosage, and redox potential along with the concentration, origin, and previous treatments of lignin.^[20] For example, for optimum catalytic activity of laccase, its origin and temperature are interdependent. Bacterial laccases are often more thermostable than fungal laccases. Most laccase-mediated lignin polymerization reactions are performed at room temperature or 37 °C.^[20b,23] Thermostable enzymes have gained interest as industrial processes often involve more elevated temperatures. For example, the *Trametes hirsuta* laccase mediated polymerization of lignosulfonates with 1 % w/w alginate to obtain fertilizer slow-release granules has been investigated in a temperature range from 23 °C to 60 °C. As a result, the rate of oxidation increased as the temperature increased.^[24]

Enzyme-mediated transformations make it possible to graft other molecules including acrylic, phenolic, nitrogen-containing compounds, inorganic silanes, and cellulose thiols

into the lignin structure by the formation of covalent bonds.^[20] A pioneering study reported using a laccase extracted from the fungal species *T. hirsuta* to graft different fluorophenols onto the lignin structure. The hydrophobicity of the resulting material increased 65.5 % after grafting 4-[4-(Trifluoromethyl) phenoxy] phenol.^[23] One of the most prominent patented examples for covalent modification by laccase catalysis is a sulfonated lignin-carbohydrate complex known as Ecohelix. The material has an enhanced thermal stability compared to the initial sulfonated lignin. This improvement enables potential high-value applications such as polymeric films.^[20b,25]

3. Lignin-based Cross-Linked Materials

3.1. Lignin-based polymer resins

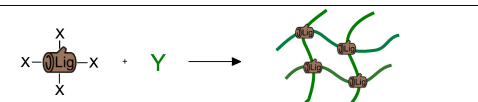


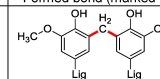








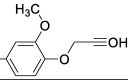
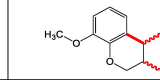
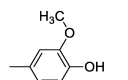
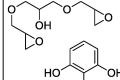
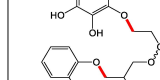
Based on the high number of reactive sites and a broad range of potential functionalization reactions, lignin can be used to enhance the properties of the existing materials or create new ones. Current state-of-the-art approaches to synthesize lignin-based polymer resins can be separated into two main categories: conventional resin synthesis using “raw” or functionalized lignin to substitute one of the main components of a material (e.g., in polyurethanes, epoxy or phenol-formaldehyde resins), and unconventional resin synthesis with formulations developed specifically for lignin.^[5] The latter group includes resins based on different cross-linking techniques, such as reactions between epoxide and hydroxyl or carboxyl groups, esterification reactions or even thiol-ene/yne click chemistry.^[26] Apart from the well-known applications of conventional resins, those for unconventional lignin-based materials include adhesives, flame retardants, 3D-printing resins, or food packaging.^[5,6c,26–27]

Polymeric lignin-based materials are not only comparable in properties to conventional ones, but also surpass them in some cases. Lignin improves mechanical and thermal properties when added to a formulation, however, high lignin content can also have adverse effects and reduce material performance. The issues with complicated processing and functionalization of lignin due to its heterogeneous nature are still the major challenges to be surmounted for its commercial use. Despite that, lignin-based polymer resins are still prominent materials to be used both in well-known and emerging fields, such as adhesives,^[28] flame retardants, 3D-printing resins, food packaging, supercapacitor electrode materials,^[29] bio-based road materials,^[30] foams,^[31] etc.^[5,6c,26–27] The main types of cross-linking reactions utilized in lignin-based resin formulations are explained in table 1.

3.1.1. Conventional resin synthesis

Lignin is a promising alternative to Bisphenol A in epoxy resin formulations, which already allows to obtain materials with characteristics superior or equivalent to commercially available products with lignin content above 50 % w/w. The structure-property relationships are crucial for material

Table 1: Various types of cross-linking reactions utilized in lignin-based resin formulations.

				
X	Y	Procedure	Formed bond (marked red)	Ref
		1M NaOH; -OH:CH ₂ O = 1:2; Cured at 85 °C		[5]
-OH	OCN-NCO	Solution casting from THF with different fractions of a secondary polyol with 1.5% dibutyltin dilaurate	Lig-O-C-N	[21a]
	H ₂ N-NH ₂	Blended with different amounts of BADGE; Cured at 40-120 °C	Lig-O-CH ₂ -NH	[21b]
	HO-OH	5 wt.% DMAP, DMF; Cured at 190 °C	Lig-O-C-O	[21c]
		5 mol.% Zn(acac) ₂ ; Cured at 120-160 °C	Lig-O-CH ₂ -O-C-O	[22c]
	HS-SH	Mixed in EtOAc; Cured at 120 °C	Lig-CH ₂ -S	[37]
-OH		2-methylimidazole, DMF; Cured at 150 °C	Lig-O-CH ₂ -O	[38a]
		Mixed in EtOH at 80 °C; Cured at 120-150 °C	Lig-O-CH ₂ -O	[36]
	—	Cured under 4 MPa at 190-250 °C		[38b]
		Mixing in acetone; Evaporation; Cured at 80-120 °C		[39]

development, but are rarely reported in the field of lignin-based materials. To address this question, oxirane moieties were introduced in softwood and hardwood lignins followed by cross-linking with commercially available polyetheramines.^[32] Properties of epoxy resins with lignin content of more than 60 % w/w were highly dependent on lignin structure, in both cases having glass transition temperatures T_g and tensile strengths in the same range as a commercial epoxy resin and strain to failure of 8 % which was twice as high as for commercial resin.

Polyols and phenols used in polyurethane and phenolic resins can be partially or fully substituted by lignin or lignin-derived products. Materials obtained in such way possess higher mechanical strength and better thermal stability. These improvements in most cases correspond to substitution rates of up to 50 %, whereas higher lignin content leads to the opposite result, which limits its use.^[28b,32–33] One of the main challenges in lignin-based resin synthesis is lignin's structural heterogeneity (see Figure 1). An elegant and sustainable solution was described in a recent report, where-in kraft lignin was fractionated by stirring the dispersion of lignin in acetone for 12 h with subsequent filtration.^[5] The acetone-soluble fraction contained more phenolic OH-groups and was used to fully substitute phenol in LPFR formulation. The corresponding resin was tested as a wood

adhesive, resulting in a higher adhesion strength (4.3 MPa) compared to a lab formulated phenol-formaldehyde resin (3.4 MPa), with 100 % wood failure (an important parameter indicating the bonding performance of adhesives). The acetone-insoluble fraction contained more aliphatic OH-groups and was divided in 2 parts, one of which was reacted with MDI to form an isocyanate-terminated prepolymer. Mixing this prepolymer with a second part of acetone-insoluble fraction and an organotin catalyst resulted in a lignin-based polyurethane (LPU) resin, which was then tested as a wood coating. These first results demonstrate lignin's great potential as a substituent for phenols and polyols in a conventional resin formulation.

Lignin-based polymer resins can already be found in the market. The Prefere Resins Company (Erkner, Germany) provide phenolic resins with up to 90 % of phenol replaced by lignin with a quality corresponding to petrochemical-based resins.^[34] Another example is *aerogel-it* start-up from Osnabrück, which offers lignin-based insulating materials.^[35] Compressed lignin aerogel board demonstrated a thermal conductivity of 17 mW/(m·K).

3.1.2. Unconventional resin synthesis

Development of new thermosets from lignin and other bio-resources that can be utilized instead of petroleum-derived materials is a task of high importance. Lignin's complex structure, low reactivity and low solubility in common solvents make it challenging to formulate lignin-based resins without prior modification. One of the possible ways is the introduction of carboxylic groups in lignin structure followed by cross-linking via some reactive functional groups such as epoxides. Lignin has been modified with glycidol and maleic anhydride to introduce multiple carboxylic groups and curing it with citric acid and epoxidized soybean oil.^[36] The obtained fully bio-based thermosets showed relatively high values of tensile strength (33.2 MPa), elongation at break (46.4 %) and T_g (67.6 °C) and were proposed as a sustainable alternative to conventional epoxy thermosets.^[36]

In another study, the ethanol-soluble fraction of Ligno-boost Kraft lignin was allylated and then cured using thermally induced thiol-ene chemistry resulting in a thermoset polymers with relatively high T_g (45–65 °C).^[37] These resins can also be utilized with different thiol cross-linkers to synthesize thermosets with tunable properties, despite lignin's heterogeneity.^[26] Glass transition temperatures above 100 °C, Young's modulus and tensile strength in the range of 4.8 GPa and 68 MPa, respectively, allow the use of these materials in various fields such as adhesive or composite matrices.

Propargylated lignins represent another class of interesting lignin derivatives. Initial work on this topic dealt with the synthesis of such special propargyl ethers and their use as matrix duromers for glass fiber reinforced composites.^[38] DMA studies confirm glass transition temperatures of 350 °C for propargyllignin, which are significantly higher compared to phenolic resins at 220 °C. Flexural strength of the glass-fiber reinforced composites with propargyllignin

reach 432 MPa, whereas for novolac resins values of 356 MPa were found.

The in situ modification of lignin represents an interesting alternative. The conversion of a low molecular weight extract of Kraft lignins can be considered as an example.^[39] The chemical modification of the lignin extract was carried out with an excess of 1,3-glycerol diglycidyl ether. To produce a high-quality thermoset, 1,2,3-trihydroxybenzene, has been used as a co-crosslinking agent. Curing under optimum conditions results in tensile strengths of 80 MPa and elastic moduli of 3.5 GPa. By using cellulose fibers, it is possible to develop fully bio-based composites. The unidirectionally reinforced composites show flexural strengths around 210 MPa and stiffnesses of 12.5 GPa. Thus, the main components of the wood can be reassembled into new materials after their separation from wood.

3.2. Lignin-based bioplastics

Recently, a variety of appealing and substitute materials that can replace synthetic fibres, are increasingly being used as environmentally friendly materials that can simultaneously improve the economy and the environment.^[40] Compared to synthetic fibres (such as polyethylene and polypropylene), lignocellulosic fibres are readily available, biodegradable, renewable, and have low density.^[40] They also cost less than synthetic fibres and offer competitive specific mechanical qualities.^[40] Formulating lignin-based bioplastics can be challenging due to lignin's complex structure and potential compatibility issues with other biopolymers. Lignin is often blended with other biopolymers such as starch, cellulose, proteins, polylactic acid (PLA), or poly hydroxybutyrates^[41] to create composite materials.^[42] The amorphous reassembly of hydrolyzed lignin, cellulose and hemicelluloses (xylan), and hydrolyzed lignin has produced multifunctional bioplastics.^[43] To do this, the biopolymers were dissolved in a solution of trifluoroacetic acid and trifluoroacetic anhydride and combined in various ratios to mimic those of natural woods. After the solvents had completely evaporated, flexible and free-standing films were produced. The physical qualities were easily adjusted by adjusting the xylan and hydrolyzed lignin contents. These bioplastics also shown rapid biodegradation in seawater and can be utilized in various applications including food packaging.

While they offer several advantages in terms of renewability and biodegradability, the development and commercialization of lignin-based bioplastics are still evolving, and researchers continue to explore ways to improve their performance, cost-effectiveness, and versatility for a wide range of applications.

3.3. Lignin-based gels

Being highly abundant and renewable natural resource, lignin has received increasing attention as a potential alternative to synthetic polymers in the development of

three-dimensional fabricated gel structures.^[6b] Owing to its polyphenolic structure and various functional moieties, lignin can be fabricated and modulated to develop hydrogels and aerogels.^[6b,48] The finally developed material depends largely on the desired application. Despite the advantages, lignin-based hydrogels face certain challenges, such as structural diversity depending on the source of extraction and limited solubility in water as well as many common solvents, making its incorporation into hydrogels complex. Nevertheless, last few years have shown tremendous progress in this field, making lignin a promising candidate for the gel synthesis.

3.3.1. Lignin-based soft hydrogels

Hydrogels are three-dimensional networks of hydrophilic polymer chains that can absorb and retain water, typically up to several hundred times of their dry weight.^[6b,44] In addition to offering mechanical strength, lignin can also improve the biocompatibility of the developed hydrogels, making them more compatible with living tissues. Applications of lignin-based soft hydrogels include wound healing, drug delivery, tissue engineering, and environmental remediation.^[44] They have also been used as scaffolds for tissue engineering and for the removal of heavy metals and dyes from contaminated water.^[45]

Lignin based hydrogels have been significantly researched in the field of biomedical applications. Drug-release systems have been successfully developed using wood (lignin and cellulose)-based hydrogels, wherein paracetamol was used as a standard drug.^[46] The mechanical and swelling properties of these hydrogels were monitored by varying the lignin molecular structure. It was observed that the release rate of paracetamol was improved by 50 % with the presence of lignin as compared to pure cellulose hydrogels, highlighting the potential for lignin valorization. In another study, all-lignin based hydrogels have been synthesized which exhibit fast pH-stimuli-responsive activity.^[44a]

The effect of lignin type and source on the properties of physical lignin hydrogels has been investigated.^[44b] The lignin from the shells of almond and walnut was used to create the hydrogels, which demonstrated strong dye adsorption capacity as well as antifungal qualities. Most notably, the addition of lignin was seen to significantly decrease permeability of dyes (such as methylene blue), while also increasing Young's modulus by as much as 45 % as compared to the PVA-PNIPAm control hydrogels.^[44c] In another study, synthesis and characterization of lignin hydrogels were performed for potential applications as drug eluting antimicrobial coatings for medical materials.^[47] Overall, lignin-based hydrogels have a wide range of potential applications in areas such as drug delivery, tissue engineering, and water treatment.

3.3.2. Lignin-based aerogels

Lignin-based aerogels have received enormous attention in recent years owing to their potential as a sustainable alternative to the traditional aerogels, which are often derived from non-renewable resources. They are typically synthesized by a process known as sol-gel synthesis, which involves the conversion of lignin into a sol, followed by gelation and drying to form the aerogel.^[48] Aerogels are divided into further categories, i.e., cryogels and xerogels. The developed material is highly porous, lightweight, and has a low thermal conductivity, which makes it suitable as an insulator. Due to their biocompatibility and ability to be functionalized with various compounds, lignin-based aerogels find potential applications in the areas of catalysis, adsorption, as well as in biomedical applications such as drug delivery.^[48,57,58]

A fundamental issue with most aerogels is achieving the combination of flame retardancy and excellent mechanical properties. To combat this problem, lignin has been used as a structural reinforcer and char-forming agent to fabricate aerogels by a quick and facile method.^[48] This significantly improved the mechanical strengths of the developed aerogels. It was observed that lignin inclusion enhanced the ability of aerogels to suppress smoke and reducing its fire index simultaneously. Therefore, it provided outstanding fire resistance to the aerogels, which finds enormous applications in the fields of construction and transportation.

In another instance, lignin was utilized as a precursor for the development of a diisocyanate-modified lignin xerogel. For this purpose, a sol-gel process and ambient pressure drying method were utilized and the xerogels exhibited high performance in superhydrophobicity and self-cleaning.^[57] Moreover, another method has been reported for deep eutectic solvent assisted facile synthesis of lignin-based cryogel, through cross-linking lignin with formaldehyde. The developed material is suggested to act as an alternative for the replacement of resorcinol-formaldehyde (RF) based aerogel.^[58] A few examples of the synthetic procedures of lignin gel synthesis and their applications are compiled in the following Table 2.

3.4. Lignin based micro and nanomaterials

Lignin has emerged as a promising class of renewable materials to produce micro and nanomaterials.^[59,60] These lignin-based materials developed through various processing techniques, exhibit unique properties such as biodegradability, high surface area and tunable surface chemistry.^[59-65] The last decade has witnessed a tremendous increase in research for developing innovative techniques to produce lignin nanoparticles, nanofibers, quantum dots, and carbon materials.^[59-65] However, the self-assembly of lignin molecules into nanoparticles can be influenced by factors such as solvent choice, temperature, and pH, requiring careful optimization.

Table 2: Various types of synthesis methods and applications of lignin-based gels.

Components of Lignin Gel	Synthesis procedure	Applications	Ref.
Kraft lignin and poly (ethylene glycol) diglycidyl ether (PEGDGE)	Chemical crosslinking	pH-stimuli-responsiveness for mechanical switching and actuation	[44a]
Lignin, poly(N-isopropylacrylamide) (PNIPAm), poly(vinyl alcohol) (PVA), ammonium persulfate and tetramethylethylenediamine (TME-DA)	Free radical polymerization	T-responsive soft composites	[44c]
Lignin and graphene	Hydrothermal process	Flexible supercapacitors (FSCs)	[49]
Lignin, poly (ethylene glycol) and poly (methyl vinyl ether-co-maleic acid)	Microwave irradiation	Coatings for Drug delivery	[47]
IL-lignin (ionic liquid isolated lignin) and epoxide-terminated poly (ethylene glycol) [ETPEG]	Chemical cross-linking	Food packaging or wound dressings	[50]
Acrylic acid (AA), lignosulfonate (LS) and <i>N,N'</i> -methylene-bis-acrylamide	Free radical polymerization	Superabsorbent	[51]
Lignin and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibrils (TOCNF)	Wet spinning	Conductive-carbon microfibers	[52]
Sodium lignosulfonate and poly (acrylic acid-co-poly(vinyl pyrrolidone))	Ultrasonic method	Drug delivery	[53]
Sodium lignosulfonate (LS), sodium alginate (SA) and phytic acid (PA)	Freeze-thawing	Flame Retardancy and Mechanical Resistance	[48]
Lignin, polyethylene glycol (PEG), polypropylene glycol (PPG), and polydimethylsiloxane (PDMS).	Copolymerization, followed by addition of lignin	Wound healing	[54]
Ag-lignin nanoparticles, pectin and polyacrylic acid	Redox catechol chemistry	Adhesive	[55]
Lignosulfonate and graphene	Hydrothermal process	Adsorbent	[56]

3.4.1. Lignin nanocarriers and nanocapsules

There has been a growing interest in lignin utilization as a nanocarrier for various applications, ranging from drug delivery to plant protection.^[59] Lignin-based nanocarriers provide various perks over other nanocarriers, such as biodegradability, biocompatibility and low toxicity.^[59a] Owing to the unique physical and chemical properties of lignin, its surface chemistry can be easily modified to improve its drug-loading capacity and targeting specificity. Various studies have demonstrated the applicability of lignin-based nanocarriers in delivering drugs to cancer cells and other diseased tissues, making them highly promising candidates for future drug delivery applications.

Recent studies have witnessed the potential of the utilization of lignin-based nanocarriers in agricultural applications.^[60] Lignin nanoparticles can be utilized as a carrier for plant growth regulators and pesticides, which can improve their efficacy by reducing their environmental impact. The laboratory studies have initiated a startup (Lignilabs), which focuses on developing novel biobased microcarriers for sustainable plant protection.^[60] In Figure 3, the green arrow indicates the general process of degradation of the host plant by pathogenic fungi by the secretion of wood-decaying enzymes, which eventually leads to further growth of the fungal mycelium and finally, death of the plant.

However, as depicted by the red arrow, a negative feedback loop is initiated by injection of the drug-loaded lignin nanocarriers (NCs), due to the secretion of the lignin-degrading enzymes by fungi release the fungicide from the lignin NCs. The inset shows an exemplary transmission electron microscopy (TEM) image of the synthesized nano-

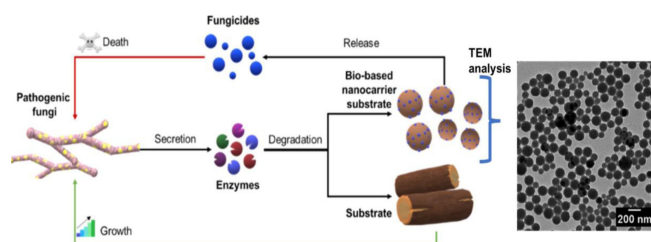


Figure 3. Concept of nanocarrier-mediated drug delivery in plants and exemplary Transmission Electron Microscopy (TEM) image of the cross-linked lignin nanocarriers.^[60]

carriers, which were cross-linked with spermidine. Overall, the use of lignin-based nanocarriers in agriculture can definitely lead to more eco-friendly and sustainable crop production practices. However, further research is needed to optimize the application and formulation of lignin-based nanocarriers for various applications.

Another emerging area is the development of lignin-based cosmetics, which is mostly related to UV protection in sunscreens and the packaging of food materials. These products also provide antimicrobial and antioxidant properties due to the inherent properties of lignin.^[61] Currently, these are developed by incorporating functionalized lignin, raw lignin or lignin-based nanoparticles as active ingredients in a sunscreen cream.^[61b] Recently, lignin-based sunscreens were developed using nanoparticles of partly demethylated kraft lignin (CatLignins) having ample phenolic hydroxyl catechol and auxochrome units.^[62] It was found that the CatLignins outperformed the regular kraft lignin when compared as sunscreen UV absorbers, with high UVB-SPF and UVA-UVB transmittance. Moreover, the conversion of

lignin to nanoparticles significantly enhanced the sunscreen performance.^[62]

3.4.2. Lignin-based carbon fibers (LCFs)

As lignin exhibits a large content of carbon as well as aromatic structural elements, it is an attractive material for the synthesis of carbon fibers.^[63] In recent work, lignin has been subjected to thermo-stabilization and carbonization in air and inert gases, respectively to develop lignin carbon fibers (LCFs).^[64] It was observed that the molecular chains of lignin were cross-linked and there was no softening of the lignin fibers during the stabilization process. The pyrolysis was performed in an inert gas for the removal of volatile hydrocarbons during the carbonization process. The developed processes were even suitable for industrial scale lignin-based carbon fiber production.^[64] The low cost of lignin compared to the typical carbon fiber precursor, polyacrylonitrile (PAN), renders it economically attractive. This is especially interesting as half of the fiber costs are associated with the precursor's synthesis and the spinning process. Here, the possible melt-spinning of LCFs versus the typical solution spinning of PAN yields another cost advantage. Besides advantages, the drawbacks of the use of lignin are the need for additives which allow for a stable spinning process as well as the long times required for carbonization. Moreover, high strengths fibers for use in the automotive - and even more demanding - aerospace industry could only be achieved using PAN as precursor. Therefore, many current studies focus on the improvement of the mechanical properties of LCFs via blending or chemical modification.^[65]

4. Conclusions and Future Perspectives

Although lignin functionalization has been investigated for several decades, the last years have seen a particular acceleration of research. However, only 2 % of lignin residue from paper production is currently valorized to new chemical materials.^[8] We expect that in the near future, lignin-based polymer networks will work their way from niche applications as functional materials into large mainstream material applications, first examples are already on their way.^[39] Such valorization will provide a sustainable source of valuable products and aid in reducing the environmental impact of lignin combustion or disposal. However, many hurdles need to be surmounted for new lignin-based products to achieve their commercialization, such as circularity and stability of the final products. In addition, lignin's highly cross-linked chemically heterogeneous composition will remain a major challenge controlled for functionalization and solubilization efforts. Researchers are actively exploring innovative catalytic processes and biotechnological methods to efficiently break down lignin's complex structure and convert it into high-value products, such as biofuels, biochemicals, and bioplastics. Ultimately, lignin upconversion has the potential to have an important impact on multiple sectors, including basic chemicals, materials, and

agriculture, leading to a more sustainable and circular chemical economy in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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