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Incorporation of lignin into adhesives: a review

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Adhesives are essential in various industries; however, petroleum-based resins raise concerns about environmental and health impacts. Lignin, a renewable biopolymer, offers a sustainable alternative due to its functional groups, which enable its integration into adhesives. Lignin-based resins reduce dependence on fossil resources, lower costs, and improve sustainability. However, challenges such as low reactivity, structural heterogeneity, and performance limitations hinder their commercialization. This review comprehensively discusses the fabrication of lignin-derived adhesives. Modification strategies, such as hydroxymethylation, depolymerization, and phenolation, improve lignin's reactivity, with the best performance observed when using enhancers including urea, melamine, polyethyleneimine (PEI), and furfural. Lignin-phenol formaldehyde (LPF) and lignin–polyurethane (LPU), which increase water resistance while maintaining bonding strength, are closest to commercialization due to their lower production costs. Lignin-epoxy (LEP) and lignin–tannin adhesives exhibit strong mechanical properties but require further optimization. Lignin–phenol–formaldehyde (LPF) adhesives are among the most commercially available, with companies such as Latvijas Finieris incorporating bio-based lignin in plywood production while maintaining performance. Similarly, the properties of lignin–polyurethane (LPU) adhesives have improved significantly for commercialization, with efforts focused on replacing 80%–100% of phenols to improve sustainability and performance. Research on lignin-melamine, lignin-PEI, and lignin–furfural adhesives remains limited, although they hold potential for improving durability and processing. The most promising approach to enhancing adhesive performance is to utilize urea, melamine, PEI, and furfural as additives to improve the adhesion and curing efficiency of lignin-based adhesives. Despite advancements, lignin-based adhesives continue to face challenges in terms of strength, durability, water resistance, and processing efficiency. Many require costly enhancers to achieve good performance, increasing production costs. Issues such as brittleness and high modification costs limit their widespread adoption. Market reluctance and the lack of standardized formulations further complicate the commercialization process. Future research should focus on cost-effective processing, performance enhancement, and the development of formaldehyde-free formulations. Standardizing lignin modification techniques and expanding applications in construction, automotive, and packaging industries will be crucial for making lignin-based adhesives a viable commercial alternative.

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1. This work critically reviews the state of the art in incorporating lignin into adhesives for sustainable adhesive fabrication. The green material, *i.e.*, lignin-derived adhesive, is a viable pathway to replace synthetic adhesives.
2. This work discusses how incorporating lignin derivatives into adhesive formulations enables the manufacture of various functional adhesives for different applications, some of which are currently under consideration for commercialization.
3. In future work, the formulation can be further optimized to incorporate more lignin derivatives, resulting in improved performance for broader applications.

Introduction

Adhesives play a vital role as auxiliary materials in various industries. The main function of an adhesive is to join two surfaces and resist separation under shear.[1] The adhesion of surfaces can be carried out through physical, chemical, and/or mechanical bonding processes. Typically, physical bonds are

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weak as they rely on intermolecular forces, whereas mechanical bonds form when the adhesive penetrates surface pores, cracks, or rough areas, creating an effective mechanical interlock. Chemical bonds are also strong, but they can be challenging to form due to the need for specific chemical interactions.[2] Chemical bonds are essential for many applications in packaging, transportation, construction, manufacturing, healthcare, and renewable energy sectors.[3] In 2020, the global adhesive market was reported to be around 58 billion USD.[3]

Historically, adhesives were derived from natural resources, including animal bones, plants, and minerals.[4] In the early 1900s, synthetic adhesives were developed and implemented industrially.[4] These synthetic adhesives permitted significantly stronger adhesive bonds, leading to an extended service life and increased water and heat resistance.[4,5] Some of the first synthetic adhesives were made from formaldehyde, such as phenol-formaldehyde, urea-formaldehyde, and melamine–formaldehyde adhesives, which are primarily used to bond plywood. The first truly synthetic adhesive was phenol formaldehyde, used in extreme environments, such as waterproofing plywood on boats.[4] As research progressed, acrylates were introduced, which paved the way for the subsequent emergence of polyurethanes. This option significantly broadened the spectrum of adhesive applications.[4] The creation of epoxy adhesives soon followed the path that has been merited for the most significant milestone in adhesive development.[4]

However, these synthetic adhesives use petroleum derivatives such as phenol, formaldehyde, and polyether polyols as feedstock for their synthesis.[5,6] Thus, with the growing demand for petroleum, increasing prices, foreseen supply shortages, and environmental and health concerns, more environmentally friendly alternatives have been investigated. Biobased adhesives have gained significant attention over the years in an effort to reduce our dependence on petroleum. Biobased adhesives have been synthesized using tannin, furfural, soy proteins, and polyethylenimine.[7–10] Despite their popularity, biobased adhesives possess inferior mechanical strength and water resistance to synthetic adhesives. Therefore, the incentives for generating biobased adhesives with improved characteristics are high.

In addition to the synthetic and bio-based resin systems discussed herein, minor categories of lignin-based adhesives—such as lignosulfonate binders and binderless fiberboard adhesives relying on lignin's intrinsic bonding ability—have been reported. However, these remain less developed and less widely studied.[11–13]

The objective of this literature review is to provide a comprehensive analysis of lignin-based adhesives, compiling all known methods of incorporating lignin into adhesive formulations. The novelty of this review lies in its comprehensive analysis of both synthetic and bio-based resin adhesives, consolidating key findings into a single resource. Unlike previous studies that focused solely on synthetic resins,[14] phenolic-based adhesives,[5] or formaldehyde-based systems,[15] this review provides a broader perspective, covering various adhesive formulations. While some prior work includes both synthetic and bio-based resins,[3] they lack extensive quantitative comparisons, detailed property assessments, and mechanistic explanations. Although review articles are available on the topic of lignin and adhesives, they mostly focus on specific resin types or general lignin chemistry. This review is distinct in emphasizing lignin–synthetic hybrid adhesives, providing side-by-side comparisons of adhesive properties, synthesis pathways, and both advantages and shortcomings. By positioning these findings within a green chemistry context, this article offers a unique, consolidated perspective that complements and extends previous reviews.[3,5,7,14–20]

Lignin derivatization

Lignin is the second-largest renewable source, following cellulose, and stands as the primary source of aromatic compounds on Earth.[21,22] Lignin is a three-dimensional, amorphous, highly branched, high-molecular weight macromolecule. It is currently produced as a by-product of the pulp and paper industry, where it is burned as a fuel for energy recovery.[23] Its structure primarily depends on its delignification process and the type of source (*e.g.*, softwood, hardwood, or non-wood).[23,24] Although its chemical structure is complex and undefined, the lignin polymer primarily consists of three phenylpropanoid monomeric building blocks: the syringyl (S), guaiacyl (G), and *para*-hydroxyphenyl (H) monomers (Fig. 1).[23,25] Softwood species are predominately composed of G monomers, while hardwoods mainly consist of S.[23] Lignin also contains various functional groups, *i.e.*, aliphatic and phenolic hydroxy, carboxy, methoxy groups, and some terminal aldehyde groups, as well as aryl, alkyl, ester, and ether linkages.[23,24] The most common linkages include C–O (ether) (*e.g.*, β-O-4, α-O-4, and 4-O-5) and C–C (*e.g.*, β–β, β-5, and β-1). The most common linkage in lignin is the ether (β-O-4) linkage, which represents approximately 50% and 60% of the total linkages in softwood and hardwood, respectively.[3,26] Lignin can be classified as native or technical. Native lignin refers to lignin that exists in plants in its original structure, while technical lignin refers to lignin that has been extracted and isolated from biomass (delignified).[3]

Recent advances in large-scale lignin production have created a reliable and increasingly high-purity feedstock for lignin-based adhesive development. Industrial processes such

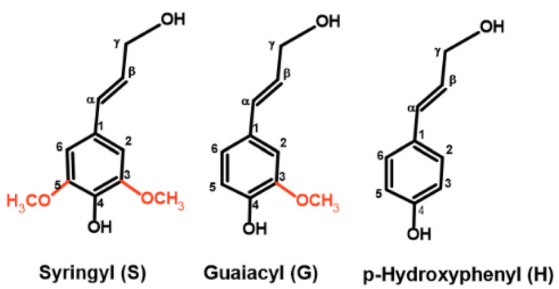

Fig. 1 Lignin monomers.

as kraft pulping, lignosulfonate recovery, soda pulping, and emerging organosolv technologies—enabled by platforms like LignoBoost™ and LignoForce™—now supply tens of thousands to over 50 million tonnes of technical lignin annually.[27] While kraft lignin dominates global output, biorefineries are producing organosolv and soda lignins with uniform structures and high phenolic hydroxyl content, well-suited for resin synthesis. Major producers including Stora Enso, Domtar, West Fraser, and Borregaard have established commercial-scale facilities, ensuring consistent quality and scalable supply chains that can meet both pilot- and industrial-scale adhesive manufacturing demands. This expanded availability reduces raw material costs, improves formulation consistency, and supports the transition of lignin-based adhesives from research to commercial applications.[27]

Most studies focus primarily on technical lignin, which includes kraft, hydrolysis, soda, organosolv, lignosulfonate, and pyrolytic lignin.[3,23] The composition, molecular weight, and functionality of lignin depend on the delignification process.[3] The physical and chemical properties of technical lignin may vary significantly within the same species. However, the main issues with lignin are its low reactivity, large intrinsic steric hindrance, and complex heterogeneous structure.[5,28,29] The low reactivity of lignin is due to the polyphenols having fewer *ortho*- and *para*-reactive sites.[30] The *ortho* positions of lignin can be occupied by one or two methoxy groups, inherently contributing to its steric hindrance. If these methoxy groups were to be removed, the number of free reactive phenolic hydroxy groups would naturally increase, thereby enhancing the reactivity of lignin.[30]

The reactivity of lignin can be improved through various modifications. The most common modifications for improving the reactivity of lignin are demethylation, depolymerization, phenolation, hydroxymethylation, and glyoxalation.[31–37] The mechanism for the modification is illustrated in Fig. 2. Demethylation involves the removal of the methoxy group from the aromatic structure of lignin. The demethylation is usually conducted using hydroiodic acid, iodocyclohexane, 1-dodecanethiol, or sodium sulfite at a relatively high temperature (130 °C).[34,38] Depolymerization consists of the degradation of the complex lignin compound into value-added products made of smaller molecules.[39,40] The depolymerization of lignin has been conducted by various methods including hydrothermal conversion, pyrolysis, enzymatic degradation, photocatalytic degradation, electrochemical degradation, ionic liquid degradation, and microwave irradiation oxidation.[39,40] Typically, depolymerization is conducted at elevated pressures and temperatures. Phenolation involves the grafting of a phenol group to the aliphatic chain of lignin.[41] It is typically conducted by reacting lignin with phenol under acidic conditions.[41] Generally, it is seen that the amount of phenol incorporated into the lignin structure is dependent on the amount of aliphatic hydroxy.[42] Hydroxymethylation consists of grafting a hydroxymethyl group onto the lignin structure using formaldehyde.[37] It allows for condensation and crosslinking to occur between lignin and phenol. Glyoxalation involves grafting a glyoxal group onto lignin using glyoxal under a nitrogen atmosphere.[43]

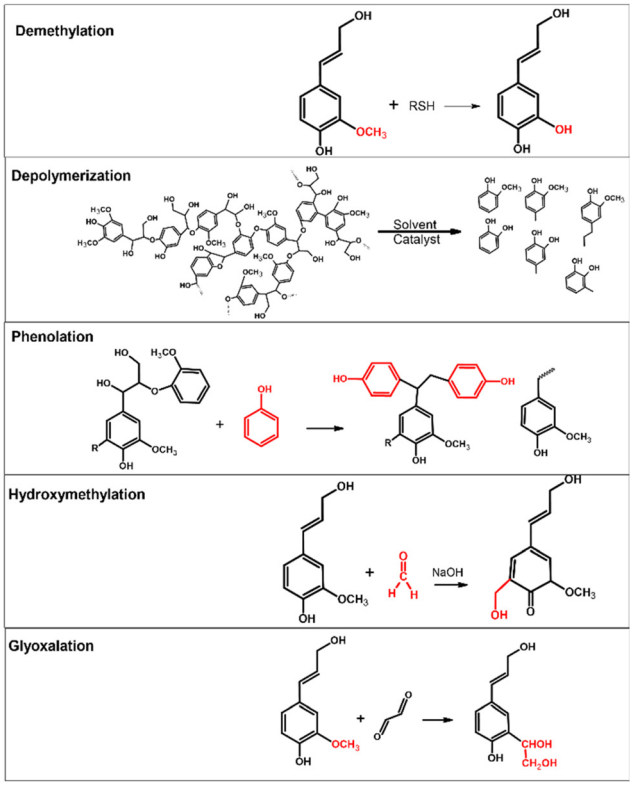

Fig. 2 Mechanism of lignin modifications.

Glyoxal is a natural aldehyde and, therefore, can replace formaldehyde in adhesive systems.[44] The impact of lignin types on their modifications was studied for adhesive applications.[45,46] Hydroxymethylation was conducted on sodium lignosulfonate, kraft lignin, and organosol lignin.[45] It was observed that sodium lignosulfonate demonstrated the most promising potential for phenol formaldehyde (PF) resins despite containing the most impurities, while the purest, organosolv lignin, exhibited the lowest compatibility.[45] This difference in performance is associated with the increased number of reactive hydroxy sites in sodium lignosulfonate compared to organosolv lignin.[45] Phenolation was performed on corncob lignin, poplar lignin, hydrothermally treated poplar lignin, kraft lignin, and wheat straw alkali lignin, where it was seen that corncob demonstrated the highest conversion, which was associated with its increased reactivity compared to the other lignin types.[46] It was observed that the lignin with the highest number of reactive sites resulted in the highest reaction conversion.

Synthetic adhesives

Lignin–phenol–formaldehyde adhesives (LPFAs)

Phenol-formaldehyde (PF) adhesives are thermosetting polymers produced when phenol reacts with formaldehyde in the presence of a basic catalyst.[29] With the total worldwide con-

sumption of PF adhesives estimated to be approximately 3.5–4 million tonnes per year, PF adhesives play an important role in several industry applications.[29] PF adhesives are widely used for engineering wood products such as particle board, plywood, oriented strand boards (OSBs), wafer board, headboard, and laminated veneer lumber.[29,47] Additionally, PF resins can be used for other applications such as moldings, electrical insulators, brake linings, and brake pads. Due to the unique network-crosslinked structure of this polymer, it exhibits excellent heating resistance and bonding strength, as well as good aging and weather resistance and satisfactory chemical stability.[29] The properties of PF resins can be seen in Table 1. The bonding strength is the most critical performance parameter. This is because the primary function of LPFA adhesives in plywood and particleboard applications is to ensure strong, durable adhesion under hot pressing and subsequent service conditions.

PF resins have several shortcomings; they can be brittle, limiting their use in flexible applications.[48] As a feedstock, phenol and formaldehyde are highly toxic and non-renewable petrochemical derivatives.[29,49] As a result, research has leaned toward finding more sustainable and healthy alternatives.[49] During production and curing, they release formaldehyde, posing health and environmental risks.[48] It should be mentioned that the maximum allowable free formaldehyde content is 0.3%, according to GB/T-14074.[49] The synthesis and curing processes require precise control, complicating manufacturing. As thermosetting plastics, PF resins do not melt or degrade easily, making recycling challenging and impacting the environment.[48] Additionally, they require high pressing pressures for applications such as wood impregnation, which can limit their commercial use.[48]

To generate sustainable PF resins, the incorporation of lignin into PF resins has been studied in the past. The mechanism of lignin-PF resin fabrication is illustrated in Fig. 3. Typically, hydroxymethylation is the first step in the reaction, with phenol undergoing this process at a faster rate than lignin.[5] Initially, phenol reacts with formaldehyde at its more reactive *para* position, forming *para*-hydroxymethyl phenol (a), as shown in Fig. 3. As the reaction progresses, additional formaldehyde is introduced in stages and hydroxymethylation occurs at the *ortho* position, also leading to the formation of

Table 1 Properties of synthetic adhesives

Properties	PF[61]	UF[62]	MF[63]	Epoxy[64]	Polyurethane[65]
Density, kg m^{-3}	1360	147–1520	1500	860–2600	1050–1250
Water absorption, wt% day^{-1}	0.2	0.5	0.1	0.03–1.20	1.0
Ultimate tensile strength, MPa	—	30	36–90	5–97	29–49
Young's modulus, GPa	—	9	7.6–10	0.0207–215	—
Rockwell hardness	—	—	115–125	—	—
Elongation at break, %	—	—	—	—	10–21
Thermal conductivity, W m^{-1} K^{-1}	0.25	0.30–0.42	0.167	0.1–1.20	0.21
Specific heat capacity, J kg^{-1} K^{-1}	—	1200	1674	—	1800
Coefficient of thermal expansion, 1 $°C^{-1}$	1.6×10^{-5}	2.2×10^{-5}–9.6×10^{-5}	2.2×10^{-5}	1.6×10^{-5}–1.75×10^{-4}	10^{-4}–2×10^{-4}
Relative permittivity (@1 MHz)	5.0–6.5	—	—	—	—
Electrical resistivity, Ω cm	1012	—	—	—	—
Dielectric field strength, kV cm^{-1}	120–160	120–160	110–160	3.20–6.60	
Electrical resistance, Ω cm	—	—	—	—	10^{12}
Refractive index (589 nm)	—	1.55	—	1.48–1.54	–

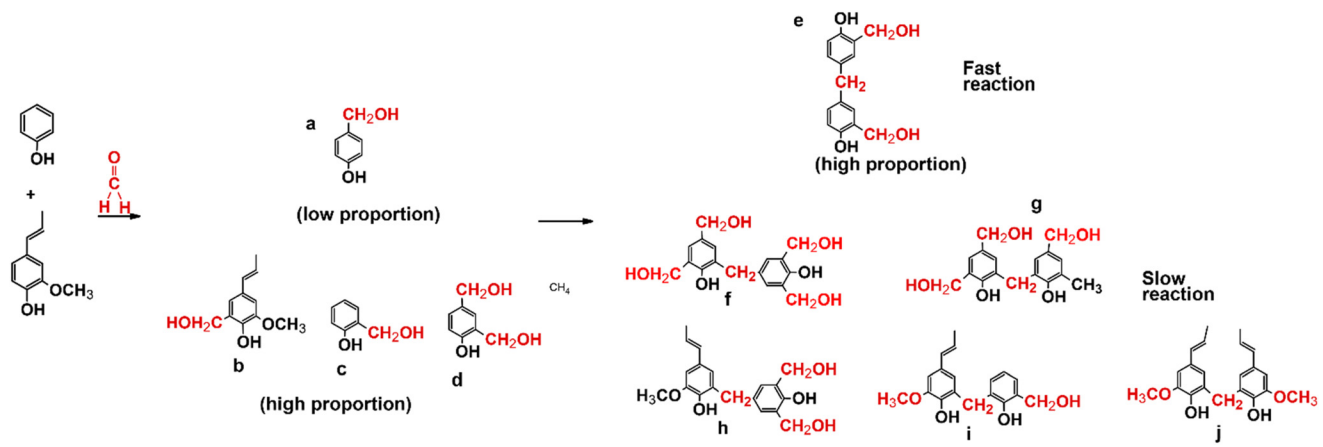

Fig. 3 Most probable mechanisms for lignin-phenol-formaldehyde resin,[5] (a) phenol-formaldehyde reaction, (b–d) lignin-formaldehyde reaction, (e–j) final products of lignin-phenol-formaldehyde reactions.

ortho and *ortho-para*-hydroxymethyl phenols (c & d, respectively, in Fig. 3).[5] Following this step, lignin undergoes hydroxymethylation, but at a slower rate than that of phenol (b in Fig. 3). In the next stage, *ortho-para*-hydroxymethyl phenol undergoes condensation, forming a dimer linked by a methylene bond (e in Fig. 3). Additionally, condensation occurs at unsubstituted active sites on the benzene rings of hydroxymethylated phenol and phenol (f & g), hydroxymethylated lignin and phenol (h & i), and hydroxymethylated lignin and lignin (j), producing prepolymers (Fig. 3).[5] As polycondensation progresses, particularly in the later stages, methylol groups from different prepolymers begin to react, forming a crosslinked network structure. This ultimately results in a lignin-based phenol-formaldehyde (PF) adhesive, which is interconnected by both methylene and methylene ether bonds (not shown in Fig. 3).[5] Lignin-PF adhesives have demonstrated a bonding strength ranging from 0.6 to 15.2 MPa, with free formaldehyde content from 0.089 to 1%.

Similarly, lignin–phenol–formaldehyde adhesives (LPFAs) share the same applications as PF adhesives, including engineered wood products, moldings, electrical insulators, and friction materials such as brake linings and pads.

Due to its similarity in molecular structure to phenol, lignin has been investigated as a promising alternative since the 1990s.[50,51] However, this has proved challenging due to the heterogeneous molecular weight, complex structure, and low reactivity, which result in lignin-PF adhesives with lower performance when compared to PF adhesives.[29] This low reactivity is a result of the methoxy groups that occupy the *meta* position of lignin and prevent it from crosslinking in the PF adhesive reaction. This lower reactivity is why the addition of lignin generally decreases the bonding strength of the adhesive, resulting in higher free formaldehyde and phenol emissions.[3] Due to the decrease in bonding strength and the increase in toxic emissions, the amount of lignin that can be substituted in the adhesives has been limited.

Some modifications such as hydroxymethylation, phenolation, demethylation, and depolymerization have been made to improve the reactivity of lignin. Demethylation and depolymerization are the most intensively researched, as shown in Table 2. Generally, it is observed that the bonding strength of lignin-based PF adhesives increases with lignin modification.[52,53] However, the modified LPFAs are not as strong as the PF adhesives due to the fact that the reactivity of lignin is inherently weaker than that of phenol.[53]

The effect of temperature on lignin modification was examined (A4, A5, A6, A9, A16 in Table 2). For depolymerization, it is observed that the amount of phenolic content/bio-oil decreases with the elevation in temperature (A4, A5 in Table 2). This is because, as the temperature is elevated, the bio-oil is further broken down into gases. There is no clear trend for the effect of temperature on lignin demethylation. At an optimum temperature of 170 °C, Di *et al.* observed a 58% increase in bonding strength with 40 wt% lignin (A5 in Table 2). The demethylation of wheat straw alkali lignin using iodocyclohexane (ICH) was reported to exhibit an increase and then a decrease in conversion as the temperature was elevated from 130 to 155 °C. At an optimum temperature of 145 °C, a 10% decrease in bonding strength was observed with 40 wt% lignin (A6 in Table 2). Meanwhile, the demethylation of alkali lignin using sodium sulfite and NaOH was reported to result in a decrease in conversion when the temperature was increased from 80 to 100 °C (A9 in Table 2). At 80 °C, the bonding strength decreased by 14% with 50 wt% lignin (A9 in Table 2). The variation in the optimum reaction temperature required by each modification for resin production is attributed to the different reagents used and their underlying mechanisms. The demethylation of ICH is generally conducted through a nucleophilic attack, whereas demethylation using sodium sulfite and NaOH is achieved through a combination of nucleophilic attack and hydrolysis. The presence of hydrolysis allows for a reduced reaction temperature.[54]

The effect of lignin fractionation on the modification efficiency has also been examined (A3, A13 in Table 2). For example, kraft lignin was separated into three fractions: ethyl acetate, acetate/petroleum ether, and ether-soluble fractions, and then phenolated with phenol. Interestingly, the ether-soluble fraction, which contained the highest number of carboxylic, aromatic, and aliphatic hydroxy reactive sites, produced resins with the highest bonding strength and lowest free formaldehyde emissions, comparable to those of PF adhesives (A13 in Table 2). In the same vein, the bio-oil and oligomer products of the base catalytic depolymerization of lignin were incorporated to produce LPFAs. It was seen that not only did the LPFA using the oligomers outperform the LPFA using oil, but it also performed better than the commercial PF adhesive (A3 in Table 2). Li *et al.* conducted the demethylation of soda lignin using a variety of sulfur-containing reagents. It was found that Na_2SO_3 was the most effective sulfur-containing reagent for the demethylation of lignin in PF resin applications (A10 in Table 2). Lignin nanoparticles have also been recently explored for PF adhesives, showing promising results in improving their bonding strength (A18, A19, and A20 in Table 2).

For the optimal performance of lignin-based resins, depolymerized or nanoparticles from kraft or organosolv lignin can be employed in conjunction with resin and urea synthesis (F/P molar ratio 1.3–2.0; NaOH/P molar ratio 0.2–0.5) to scavenge residual formaldehyde. Hot pressing at 130–150 °C under 1–3 MPa for 3–7 min with an adhesive spread of 50–150 g m^{-2}, particularly when using sulfur-assisted or lignin nanoparticles, results in the highest bonding strength and the lowest formaldehyde emissions.

The main shortcomings of LPFAs are (1) increased formaldehyde emissions and typically decreased bonding strength, which is the result of the addition of lignin with a low reactivity when compared to phenol,[55] (2) increased viscosity of resin, which is due to the larger molecular weight of lignin compared to phenol,[55] and (3) the inconsistent quality of lignin incorporated in LPFAs due to the varied quality and properties of lignin.[21]

Recent advancements including hydroxymethylation, phenolation, demethylation, and depolymerization have been

Table 2 Studies on lignin-PF adhesives

Modification	Lignin type	Reagent	Conditions	Lignin Substitution, %	Resin synthesis, F/P[d] (mol/mol), NaOH/P[d] (mol/mol)	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Free formaldehyde content, %	Symbol	Ref.
Unmodified	White birch bark, white spruce bark	—	—	25, 50	F/P[d]: 1.8	250 g m^{-2}	WBB-LPF-50: 1.33, WSB-LPF-50: 1.78	−39	0.54[a]	A1	66
					NaOH/P 0.35	150 °C, 3 MPa, 4 min		−46	0.45[a]		
					• 84 °C, 180 min						
	Bagasse	ClO_2, acetic acid	55 °C	15	F/P[d]: 1.37	250–300 g m^{-2}	LPF: 0.13[b]	−43	—	A2	67
					KOH/P: 0.06	130 °C, 1 MPa, 7 min		7			
					• 70 °C, 60 min + KOH						
Depolymerization	Kraft	Base-catalysed, catalytic	320 °C, 25 MPa, 10 min	50, 60, 70	Preferred resin method (commercial)	200 g m^{-2}	DLPF-oligo-70: 15.2	11	N/A	A3	68
						120 °C, 0.8 MPa, 20 min	DLPF-oil-70: 11.6	−15	0.9		
	Organosolv	Base-catalyzed, catalytic hydrothermal	340 °C, 5 MPa, 2 h	50, 75	F/P[d]: 1.3	250 g m^{-2}	LPF-50: 2.3	28	1.0	A4	69
					NaOH/P[d]: 0.54	140 °C, 17 MPa, 4 min	DLPF-50: 2.0	11	0.5		
					• 80 °C, 120 min + NaOH						
					• 80 °C, 120 min, +F (dropwise)						
	Wheat straw	Microwave alkali catalysis	130–170 °C, 10–40 min	20–100	F/P[d]: 1.5	140 g m^{-2}	LPF-40: 1.3	8	1.0	A5	70
					NaOH/P[d]: 0.26	150 °C, 1 MPa, 5 min	DLPF-40: 1.9	58	0.9		
					• 90 °C, 90 min + NaOH						
					• 60 °C, 60 min + 80%F						
					• 80 °C, 90 min + 20%F						
Demethylation	Wheat straw alkali	Iodocyclo-hexane	145 °C, 3 h	40	F/P[d]: 5.28	125 g m^{-2}	LPF: 1.13	−56	0.65	A6	55
					NaOH/P: 0.43	150 °C, 1 MPa, 6 min	DLPF: 2.28	−10	0.22		
					• 50 °C, 15 min + NaOH						
					• 90 °C, 120/210 min + F (dropwise)						
	Wheat straw soda	Sulfur	225 °C, 10 min	50, 60, 65	F/P[d]: 3.6	125 g m^{-2}	DLPF-50: 1.52	—	—	A7	50
					NaOH/P[d]: 0.35	145 °C, 1 MPa, 3.5 min	DLPF-60: 1.35				
					• 60 °C, 15 min + NaOH		DLPF-65: 1.09				
					• 95 °C, 45 min + 80%F						
					• 70 °C + 20%F						
					• 95 °C, 90 min						

Table 2 *(Contd.)*

Modification	Lignin type	Reagent	Conditions	Lignin Substitution, %	Resin synthesis, F/P[d] (mol/mol), NaOH/P[d] (mol/mol)	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Free formaldehyde content, %	Symbol	Ref.
	Alkali	HI or HBr	135 °C, 12 h	50	F/P[d]: 2.2 NaOH/P[d]: 0.79 • 60 °C, 30 min + 67% • 70 °C, 30 min + 17%F • 90 °C, 60 min + 16%F (NaOH added at each step)	150 g m^{-2} 130 °C, 1.2 MPa, 7 min	DLPF-HI: 0.9 DLPF-Br: 0.6	−40 −60	0.47[a] 0.49[a]	A8	53
	Alkali	Na_2SO_3 with NaOH	80 °C, 1 h	50	F/P[d]: 2.2 • 85 °C, 50 min • 85 °C, 60 min + 33%F • 85 °C, 50 min + 66%F (NaOH added at each step)	125–150 g m^{-2} 130 °C, 1.2 MPa, 5 min	DLPF: 1.07	−14	0.31[a]	A9	71
Demethylation	Soda	S, NaSH, Na_2SO_3, or mercaptan	90 °C, 1 h	30	F/P[d]: 2.2 NaOH/P: 0.58 • 87 °C, 50 min + 38%F • 87 °C, 60 min + 31%F • 87 °C, 50 min + 31%F • 87 °C, 30 min + urea (NaOH added at each step)	250–300 g m^{-2} 130 °C, 1 MPa, 7 min	DLPF-Na_2SO_3: 1.14 Na_2SO_3 was the most effective sulfur-containing reagent	−9%	0.56	A10	28
	Alkali	Urea, NaOH	Room temp, 16 h	10–60	F/P[d]: 2 NaOH/P: 0.2 • 85 °C, 60 min + 66%F • 85 °C, 50 min + 33%F (NaOH added at each step)	180 g m^{-2} 180 °C, 1.2 MPa, 4.5 min	DLPF-20: 1.6 DLPF-60: 1.2	33 0	0.12 0.28	A11	49
	Kraft	Na_2SO_3 with NaOH	80 °C, 2 h	10–70	F/P[d]: 0.5 • NaOH/P: 0.35 90 °C, 90 min + F + NaOH	250–280 g m^{-2} 130 °C, 1.2 MPa, 15 min	DLPF-30: 2.43 DLPF-50: 2.18 DLPF-70: 1.34	70 52 −6	0.09 0.19 0.27	A12	30

Table 2 *(Contd.)*

Modification	Lignin type	Reagent	Conditions	Lignin Substitution, %	Resin synthesis, F/P[d] (mol/mol), NaOH/P[d] (mol/mol)	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Free formaldehyde content, %	Symbol	Ref.
Phenolation	Organosolv	Phenol	110 °C, 2.5 h	40	F/P[d]: 5.49 • NaOH/P: 0.24 • 80 °C, 60 min + 50%F • 80 °C, 90 min + 50%F • 60 °C, 30 min (NaOH added at each step)	50 g m^{-2} 150 °C, 1.5 MPa, 6 min	PLFP:1.36[c]	−9	0.31	A13	72
	Kraft, hydrolysis, wheat straw alkali	Phenol	90 °C, 1 h	—	—	—	—	—	—	A14	46
Hydroxymethylation	Softwood Kraft	*para*-Formaldehyde	80–120 °C, 15–240 min	—	—	—	—	—	—	A15	73
	Kraft, sodium lignosulfonate organosolv	*para*-Formaldehyde	50 °C, 45 min	—	—	—	—	—	—	A16	45
	Cornstalk	H_2O and NaOH	60–80 °C, 210 min	—	—	—	—	—	—	A17	74
Nanoparticles/ macroparticles	Alkali	HCl	pH 2	10–60	F/P[d]: 1.8 NaOH/P: 0.37 • 65 °C, 40 min + 67% (F + NaOH) 85 °C, 240 min + 33% (F + NaOH) + Urea	—	LPF-40: 1.11 NLPF-30: 1.59 NLPF-40: 1.30 NLPF-50: 1.10	14 64 34 13	3.20 0.12 0.28 0.53	A18	75
	Hydrolysis	HCl	35 °C, 240 min	5, 10	—	80 °C, 72 h 100 °C, 1 h	NLPF-5: 9.58 MLPF-5: 10.92 NLPF-10: 8.10 MLFP-10: 5.90	10 26 −7 −32	—	A19	76
	Alkali		50–95 °C, 240 min	—	—	—	—	—	—	A20	77

[a] mg L^{-1}. [b] Molding. [c] Wet strength. [d] F: formaldehyde, P: phenol

explored to enhance the lignin reactivity and improve the adhesive performance. However, these strategies introduce additional challenges such as higher production costs, multi-step processing, and environmental concerns associated with the use of harsh chemicals or solvents. Moreover, modified lignin still exhibits batch-to-batch variability, and the resulting LPFAs often fail to completely match the mechanical strength and durability of conventional PF adhesives, limiting large-scale industrial applications.

Lignin-urea-formaldehyde adhesive (LUFA)

The most common type of thermoset adhesive is urea formaldehyde adhesive (UFA).[56] Urea formaldehyde (UF) resins are synthesized *via* the polycondensation of urea formaldehyde and other modifiers.[57] The mechanism for lignin-UF resins can be seen in Fig. 4. The synthesis of lignin-UF resin mainly consists of two stages. First, in the hydroxymethylation stage, an addition reaction occurs in which both urea and lignin react with formaldehyde, resulting in the formation of hydroxymethyl urea and hydroxymethylated lignin.[15] Second, in the condensation stage, linear or branched oligomers are formed through the condensation of hydroxymethyl urea under acidic conditions.[15]

UF adhesives are most commonly used in the manufacturing of wood-based composites such as medium-density fiberboard (MDF), particleboard, and plywood.[58] Additionally, UF resins can be used in a variety of applications such as abrasives, foams, impregnated paper laminates, textiles, molded compounds, coatings, and slow-release fertilizers.[56,57,59] Approximately 11 million tons of UFAs are produced annually.[60] In 2022, UF adhesives accounted for nearly 80% of the total world demand for thermoset adhesives.[56]

UF resins have been widely utilized in the industry due to their low-cost raw materials, excellent thermal stability, resistance to microorganisms and abrasion, high hardness, strong mechanical properties, superior adhesion to wood, low curing temperature, aqueous solubility, and colorless glue line.[57,58,60,78] The properties of UF resins are presented in Table 1. The literature reports bonding strength values ranging from 0.03 MPa to 4.84 MPa, with free formaldehyde levels in cured wood products ranging from 0.0017% to 0.0093%.[56,60,79] This is slightly higher than the international standard (EN ISO 12460-5:2015) of 0.008%.

However, UFAs have their limitations such as high formaldehyde emissions and poor water resistance.[80] Additionally, the modifiers, *e.g.*, glycerol diglycidyl ether (GDE), PMDI, and melamine, that are used to enhance their performance are expensive.[78] To address these limitations, researchers have studied the incorporation of lignin in UFA adhesives to improve their environmental impacts. Lignin can be used to improve UFA's water resistance, formaldehyde emission, and thermal stability while maintaining its mechanical properties when compared to UFA.[58,60,79,81,82] LUFAs share the same applications as UF adhesives, including MDF, particleboard, plywood, abrasives, foams, impregnated paper laminates, textiles, molded compounds, and coatings. However, the low reactivity of lignin limits its direct utilization. Some modifications used to improve the reactivity of lignin in LUFAs are glyoxalation, depolymerization, phenolation, sulfonation, and ionic-liquid treatment (Table 3).

The use of various modifiers including epoxy (B5 in Table 3), glycerol diglycidyl ether (GDE) (B7 in Table 3), pMDI (B8 in Table 3), and malleated lignin-based polyacids (B9 in Table 3) has been demonstrated to enhance the LUFA performance. For example, a malleated lignin-based polyacid catalyst (MA-HL) was synthesized to enhance the water resistance and bonding strength of UFA (B9 in Table 3). The lignin-based catalyst was compared with commercial catalysts such as ammonium chloride (NH_4Cl) and isophthalic acid (IPA). When a 1% MA-HL catalyst was used, the lignin-based polyacid resin exhibited the lowest shear strength and the longest curing time.[57] It should be noted that the formaldehyde emission decreased with the use of the lignin-based polyacid catalyst, suggesting that the remaining active sites of lignin were potentially reacted with formaldehyde.[57] When the catalyst dosage was increased to 5% MA-HL, a bonding strength of 1.74 MPa was achieved, which was higher than that of LUFA using a commercial catalyst at 1%. Additionally, its water resistance increased when compared to the commercial catalyst NH_4Cl (B9 in Table 3).[57] In another study, the glyoxalation and ionic liquid treatment of lignin were compared to observe how these modifications affect the performance of LUFAs (B3 in Table 3). The ionic liquid-treated LUFA exhibited an extended gel time and increased shear strength compared to the glyoxalated LUFA.[80] This is because lignin contained more acetate anion and imidazolium cation reactive sites than glyoxalation after ionic liquid treatment.[80] Both modified LUFA samples had a slightly lower shear strength than that of the UFA sample. Additionally, the phenolation of kraft lignin has been conducted to investigate its effect on formaldehyde emissions and the bonding strength of particleboard (B11 in Table 3). Interestingly, the bonding strength of LUFA using 20% pheno-

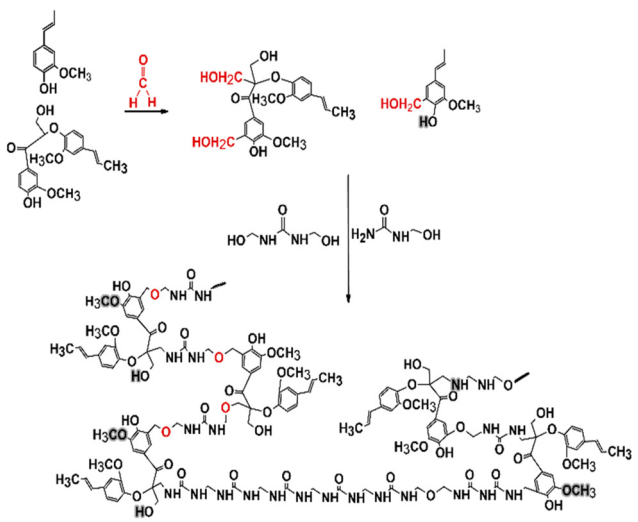

Fig. 4 Most probable mechanism for lignin-urea-formaldehyde resin.[15]

Table 3 Studies on lignin-UF adhesives

Modification	Lignin type	Reagent	Conditions	Lignin Substitution, %	Application	Resin synthesis	Hot Press Conditions	Bonding Strength, MPa	Bonding strength percent difference, %	Free formaldehyde content[a], mg per 100 g	Symbol	Ref.
Unmodified	Magnesium, sodium lignosulfonates	—	—	10, 20, 30, 50, 75, 100	Resin – particleboard	Purchased UF resin	200 °C, 2.5 MPa, 10 min	Mg-LUF-10: 0.16 Na-LUF-10: 0.14 Mg-LUF-100: 0.06 Na-LUF-100: 0.03	−7 −15 −65 −83	2.4 2.0 0.8 1.7	B1	60
	Alkali bagasse and molasses	—	—	5, 10, 13, 15	Resin – particleboard	Purchased UF resin	190 °C, 2.26 MPa, 7 min	B-LUF-10: 4.84 M-LU-10: 4.20 B-LUF-13: 4.23 M-LU-13: 4.52	7 −7 −6 0	3.1 — — 3.3	B2	79
	Sodium lignosulfonates	—	—	20	Resin – plywood	F/U[e]: 2.0 > 1.5 > 1.1 • 80 °C, 30 min, (F/U = 2) • pH 4–4.5 (H_3PO_4), then 85–90 °C • pH 6–6.5 (NaOH) + Urea (F/U = 1.5) • Urea (F/U = 1.1), pH > 7	180 g m^{-2} 120–125 °C, 1.2 MPa, 60 s mm^{-1}	0.88[d]	−2	0.12[b]	B3	57
Glyoxalation	Bagasse soda black liquor	Glyoxal, NaOH (30%)	58 °C, 8 h	10, 15, 20	Resin – plywood	Purchased UF resin	250 g m^{-2} 120 °C, 1 MPa, 5 min	GLUF-10: 1.89 GLUF-15: 1.56 GLUF-20: 1.32	−2 −19 −32	3.4 3.2 3.2	B4	80
	Bagasse soda black liquor	Glyoxal, NaOH (30%)	58 °C, 8 h	15 + epoxy	Resin – plywood	• 40 °C, 30 min + urea • 75 °C, 120 min • GL + CH_2O_2 (pH 4–4.5), 75 °C, 60 min	310 g m^{-2} 180 °C, 6 MPa, 5 min	GLUF + 5% epoxy: 1.7	295	No formaldehyde used	B5	82
	Bagasse soda black liquor	Glyoxal, NaOH (30%)	58 °C, 8 h	10, 15, 20	Resin – plywood	F/U[e]: 1.3 • 90 °C, 60 min, F + NaOH + Urea (65 wt%) • 90 °C, 90 min, +lignin (20 wt% of urea) • 40 °C + remained of urea	250 g m^{-2} 120 °C, 1 MPa, 5 min	GLUF-10: 1.78 GLUF-15: 1.51 GLUF-20: 1.29	−7 −21 −33	3.4 3.2 3.2	B6	58
	Kraft	Glyoxal, NaOH (33%)	60 °C, 3 h	62 + glycerol diglycidyl ether (GDE) extender	Resin – particleboard	• GL + urea + dialdehyde, 25 °C, 90–120 min • 5 wt% GDE	220 °C • 2.8 MPa, 3 min • 1.2 MPa, 4 min • 0.58 MPa, 3 min	0.81	—	No formaldehyde used	B7	93

Table 3 *(Contd.)*

Modification	Lignin type	Reagent	Conditions	Lignin Substitution, %	Application	Resin synthesis	Hot Press Conditions	Bonding Strength, MPa	Bonding strength percent difference, %	Free formaldehyde content[a], mg per 100 g	Symbol	Ref.
Ionic liquid	Bagasse soda black liquor	1-Ethyl-3-methylimidazolium acetate	120 °C, 30 min	15 + 6% pMDI isocyanate	Resin – plywood	F/U: 1.3 • Urea + F + NaOH 40 °C, 30 min • 90 °C over 30 min, hold 60 min • pH 5–5.5 with CH_2O_2 • Add IL, 90 °C, 90 min • Add final urea, 40 °C • + pMDI	250 g m^{-2} 120 °C, 1 MPa, 5 min	ILUF-6PMDI: 2.2	40	2.9	B8	94
	Bagasse soda black liquor	1-Ethyl-3-methylimidazolium acetate	120 °C, 30 min	10, 15, 20	Resin – plywood	F/U[e]: 1.3 • Urea + F + NaOH 40 °C, 30 min • 90 °C over 30 min, hold 60 min • pH 5–5.5 with CH_2O_2 • Add IL, 90 °C, 90 min • Add final urea, 40 °C	250 g m^{-2} 120 °C, 1 MPa, 5 min	ILUF-10: 1.89 ILUF-15: 1.56 ILUF-20: 1.32	−2 −19 −32	3.7 3.5 3.0	B4	78
Hydroxymethylation	3-Methoxy-4-hydroxyphenyl-propane	Form-aldehyde	90 °C, 1 h	1, 3, 5 used as a polyacid catalyst	Resin – medium density fiberboards, plywood	F/(urea + melamine): 1 • F + 33% (U + M) • 33% (U + M) • 33% (U + M)	280 g m^{-2} • 0.8 MPa, 1 h • 125 °C, 0.2 MPa, 60 s mm^{-1}	HLUF-1: 1.33 HLUF-3: 1.42 HLUF-5: 1.72	29 37 67	0.42[b] 0.21[b] 0.19[b]	B9	37
Depolymerization	Alkali	NaOH/urea	−16 °C, 24 h	50	Resin – plywood	F/P[f]: 1.2 • P + lignin + NaOH +33% F, 85 °C, 50 min • +33% F, 85 °C, 60 min • +33% F, 85 °C, 50 min • U + NaOH 80 °C, 15 min	125–150 g m^{-2} • 25 °C, 0.8 MPa, 30 min • 130 °C, 1.2 MPa, 5 min	1.06	−14	0.38[b]	B10	95
Phenolation	Kraft	Phenol with oxalic acid catalyst	130 °C, 50 min	10, 15, 20	Resin – particleboard	F/U[e]: 1.3 • Urea + lignin + NaOH + F, 40 °C, 30 min • Increase 90 °C, 30 min ramp + 60 min • pH 5–5.5 with CH_2O_2, then neutralize with NaOH • Add lignin, 90 °C, 90 min • Add final urea, 40 °C	• 180 °C, 2.5 MPa, 5 min • 25 °C, 2.5 MPa, 5 min	PLUF-10: 1.88 PLUF-15: 1.84 PLUF-20: 1.76	−2 −4 −8	3.2 2.9 2.7	B11	33

Table 3 *(Contd.)*

Modification	Lignin type	Reagent	Conditions	Lignin Substitution, %	Application	Resin synthesis	Hot Press Conditions	Bonding Strength, MPa	Bonding strength percent difference, %	Free formaldehyde content[a], mg per 100 g	Symbol	Ref.
Sulfonation	Kraft	Purchased modified lignin	—	5, 10, 15, 20, 30	—	• Purchased UF resin	—	—	—	—	B12	59
Demethylation	Alkali	Urea, NaOH	Room temp., 16 h	10–60	Resin – plywood	F/P[f]: 2 NaOH/P: 0.2 • 85 °C, 60 min + 66% F • 85 °C, 50 min + 33% F • (NaOH added at each step)	180 g m^{-2} 180 °C, 1.2 MPa, 4.5 min	DLPF-20: 1.6 DLPF-60: 1.2	33 0	0.95[c] 0.62[c]	B13	49
Nanoparticles	Softwood kraft (demethylated)	Sodium sulfite, NaOH	95 °C, 3 h	1, 3, 7	Resin – medium-density fiberboards	F/U[e]: 1.12 • F + NaOH, 45 °C • Add urea 89 °C, 50 min • pH 5–5.5 with CH_2O_2 • Add 2nd urea, 50 °C • Add lignin nanoparticles	185 °C, 3.4 MPa, 5 min	NLUF-1: 0.55 NLUF-3: 0.53 NLUF-7: 0.48	−2 −5 −14	9.3 6.9 2.9	B14	56
	Kraft (maleated)	1-Ethyl-3-methylimidazolium acetate	80 °C, 3 h	10, 20, 30	Resin – plywood	F/U[e]: 1.3 • F + NaOH, • Add Urea. 40 °C, 30 min • Increase 90 °C, 30 min ramp + 60 min • pH 5–5.5 with CH_2O_2, then neutralize with NaOH • Add NL, 90 °C, 90 min • Add final urea, 40 °C	300 g m^{-2} 120 °C, 1 MPa, 5 min	NLUF-10: 1.43 NLUF-20: 1.59 NLUF-30: 1.72 MNLUF-10: 1.74 MNLUF-20: 1.86 MNLUF-30: 2.14	−26 −18 −11 −10 −4 10	2.9 2.8 2.8 2.7 2.5 2.4	B15	96

[a] Free formaldehyde content of cured plywood. [b] mg L^{-1}. [c] mg m^{-3}. [d] Wet strength. [e] F/U – formaldehyde/urea (mol/mol). [f] F/P – formaldehyde/phenol (mol/mol).

lated lignin was comparable to that of raw UFA. There was no observable change in performance when the lignin substitution increased from 10% to 20%, while the bonding strength of LUFA made from unmodified KL decreased with the increase in substitution.[33] Regardless, the formaldehyde emissions decreased with the addition of both modified and unmodified lignin.[33] In the same vein, the incorporation of modified lignin nanoparticles into LUFA has been investigated (B14, B15 in Table 3). Interestingly, demethylated lignin-based nanoparticles improved the bonding strength and reduced the free formaldehyde content of LUFAs (B14 in Table 3). In contrast, when the substitution of maleated lignin nanoparticles increased from 10% to 30%, the bonding strength increased, and the amount of free formaldehyde decreased, surpassing the performance of the UFA (B15 in Table 3). Additionally, urea can be used to improve PF resin performance by creating a PF-UF resin mixture (B10, B13 in Table 3). The incorporation of urea resulted in bonding strength and free formaldehyde content comparable to raw PF resin. Demethylated lignin was used to produce a lignin-PF adhesive with 60% demethylated lignin (B13 in Table 3). The modified lignin-PF adhesive (LPFA) had bonding strength and free formaldehyde content comparable with those of commercial adhesives.[49] The low free formaldehyde content at high substitutions was attributed to the addition of urea, which was used to produce urea-formaldehyde adhesives, thereby improving the bonding strength and consuming free formaldehyde.[49] It should also be noted that, as the substitution of lignin increased, so did its viscosity. In this case, a large volume of water was required to reduce viscosity, thereby improving spreadability and allowing for more lignin to be substituted. The best-performing LUF adhesives employed glyoxalated bagasse soda black liquor lignin with epoxy (B5), achieving 1.7 MPa and a 295% increase in bonding strength while eliminating formaldehyde. Hydroxymethylated lignin (B9) minimized free formaldehyde to 0.19 mg per 100 g, and the ionic liquid with pMDI (B8) provided 2.2 MPa with 40% improvement, balancing performance and scalability.

Modified lignin urea-formaldehyde adhesives, while beneficial in certain aspects, have several shortcomings compared to UF adhesives. These include lower bonding strength due to lignin's less reactive nature, longer curing times, and reduced water resistance, which can limit their application in moisture-prone environments. Additionally, the variability in lignin's chemical structure can lead to inconsistencies in adhesive performance. Although lignin can help reduce formaldehyde content, modified lignin UF adhesives may still emit formaldehyde, albeit at lower levels. Another challenge arises from the processing and scalability of these adhesives, as incorporating lignin often increases resin viscosity, complicates resin handling, and may require higher curing temperatures or longer press times. Furthermore, chemical modifications such as glyoxalation, phenolation, or depolymerization are frequently required to enhance lignin reactivity, which contributes to the costs and complexity of production. These technical and economic challenges continue to hinder the widespread industrial adoption of LUFAs despite their environmental advantages.

Lignin-melamine–formaldehyde adhesives (LMFAs)

Another type of formaldehyde-based adhesive is a melamine–formaldehyde adhesive, which is synthesized by reacting melamine with formaldehyde. Melamine formaldehyde (MF) resins are used in various applications including laminates, tableware, automotive coatings, insulation foam, textile finishes, paper treatment, and adhesives for wood products such as plywood, particleboard, and fiberboards.[3,83–88] Melamine–formaldehyde resins are valued for their durability, thermal and flame resistance, water resistance, and excellent electrical insulation. Their adhesives offer strong bonding, easy curing, and high resistance to heat, water, abrasion, and aging, making them superior to urea-formaldehyde adhesives in strength and stability for demanding applications.[3,89] Compared to urea-formaldehyde adhesives, melamine–formaldehyde adhesives contain higher strength and heat stability properties. Incorporating lignin into MF resins (LMFA) has been proposed mainly for sustainable wood composites and construction materials, where high thermal and water resistance is essential, while also reducing the reliance on petrochemical feedstocks. The properties of MF resins are presented in Table 1. The main shortcomings of MF resin include high brittleness and poor flexibility, which make it prone to cracking under stress, thereby limiting its use in applications that require elasticity. Additionally, it exhibits low storage stability and emits formaldehyde, which raises health and environmental concerns.

Similar to other resins, incorporating lignin into the resin has benefits. The mechanisms for the lignin-melamine formaldehyde resin reaction are illustrated in Fig. 5. Lignin is first activated *via* hydroxymethylation with formaldehyde present in the system. The source of formaldehyde is primarily free formaldehyde. Next, due to the abundance of active sites in

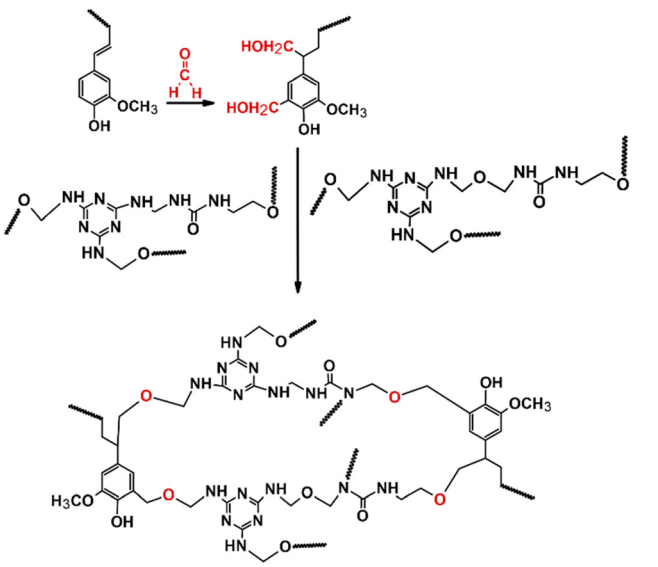

Fig. 5 Most probable mechanism for lignin-melamine–formaldehyde resin.[90]

lignin, the resulting structures of the product would be relatively complex, ultimately leading to the formation of a three-dimensional crosslinked network of resin.[90] It should be noted that lignin units that would not participate in the reaction could act as fillers, integrating into the MUF structure *via* electrostatic absorption.[90] Although there is still a lot to be explored, in the literature, lignin-MF adhesives (LMFA) have demonstrated a bonding strength of 1.34 MPa, with a free formaldehyde content of 0.06%. However, lignin-melamine–formaldehyde adhesives (LMFA) have a high production cost due to the high cost of melamine,[91] because the price of melamine is about 70–50% more expensive than phenol.[91]

Although it has not been researched as extensively as the LPFA and LUFA, lignin has been used to make lignin-melamine–formaldehyde adhesives (LMFAs) (C1 in Table 4) and lignin-melamine-urea-formaldehyde adhesives (LMUFAs) (C2 in Table 4), as seen in Table 4. For example, tosylated lignin was reacted with formaldehyde to develop an LMFA (C1 in Table 4). The LMFA demonstrated good thermal stability; however, the elevated curing temperature of the resin (around 200 °C) is a drawback.[92] In another work, hydroxymethylated alkali lignin was mixed with urea and formaldehyde, producing an LMUFA (C2 in Table 4).

In this work, the gel time and bonding strength increased while decreasing the emission of free formaldehyde.[90] This decrease in formaldehyde emissions suggested that hydroxymethylated lignin could potentially be used as a formaldehyde scavenger. When the substitution of lignin was too high (*e.g.*, 8 wt%), it deteriorated the resin's performance. This could be a result of unreacted active sites of lignin's benzene ring reacting with formaldehyde, which affected the urea-formaldehyde and melamine–formaldehyde reactions. It is also a result of the steric hindrance created by the lignin's complex structure.[90] In practice, the best performance of LMFA (C1) and LMUFA (C2) adhesives is achieved using hydroxymethylated lignin at moderate substitution levels (typically 4–6 wt%), which balances formaldehyde scavenging with bonding strength. This approach offers improved thermal stability and reduced formaldehyde emissions, making it the most suitable route for industrial wood adhesive applications. The most critical performance parameter is bonding strength, as these adhesives are primarily intended for wood applications where mechanical integrity is essential. Thermal stability is also important, particularly for high-temperature curing resins like C1, but the affinity to achieve strong, durable bonds (up to 1.34 MPa for C2) ultimately determines practical applicability. Additionally, LMFA development faces challenges, such as the poor reactivity of lignin's aromatic structure, difficulty in achieving uniform dispersion within the resin, and the resulting trade-off between formaldehyde reduction and bonding performance.

Lignin-epoxy adhesives (LEAs)

Epoxy adhesives consist of a three-dimensional network of a thermoset polymer, which is produced by reacting an epoxide resin with a curing agent *via* self-homo-polymerization.[32] Furthermore, its epoxide terminal groups can be easily modi-

Table 4 Studies on lignin-MF adhesives

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis, F/U[a] (mol/mol) NaOH/P[b] (mol/mol)	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Free formaldehyde content, %	Symbol	Ref.
Tosylation	Kraft	Tosyl chloride with triethylamine catalyst	25 °C, 24 h	100	Resin	Copolymer • Lignin + melamine in DMSO, 100 °C, 6 h resin • Copolymer + THF, 65 °C • Add F, pH 9.0, 1 h • Cool down solution	—	—	—	—	C1	92
Hydroxymethylation	Alkali	Formaldehyde + urea	90 °C, 1 hr	2, 4, 6, 8	Resin – plywood	F/U[a]: 1.12 • F + NaOH, 50 °C, pH 9.0 • Add U, M, lignin, 90 °C •pH 5.0–5.2, 60 min • pH 8.7–8.9, add M • pH to 9.0, 45 °C •Add U, 10 min • pH 8.0–8.5, 25 °C	160 g m^{-2} 130 °C, 1.5 MPa, 5 min	HLMF-2: 1.01 HLMF-4: 1.25 HLMF-6: 1.34 HLMF-8: 1.16	18 37 47 27	0.08 0.06 0.06 0.07	C2	90

[a] F/U – formaldehyde/urea (mol/mol). [b] NaOH/P – sodium hydroxide/phenol (mol/mol).

fied using a variety of reagents (such as amines, anhydrides, and other acids, alcohols, and esters) to obtain different properties.[16]

In 2022, global epoxy resin consumption was estimated to be approximately 3.6 million tons. It is estimated to grow up to 5 million by 2030.[97] Epoxies are incredibly versatile, resulting in various applications such as adhesives, plywood, furniture manufacturing, sealants, high-performance composites, electronic component packaging, electronic laminates, electric insulators, and flooring.[16,32,98–100] This wide range in applications is a result of their excellent strength, adhesion ability, thermal and dimensional stability, and chemical, solvent, and corrosion resistance.[32,99,101] Similarly, lignin–epoxy (LEP) adhesives share many of these applications, particularly in wood composites, coatings, and high–performance structural materials. The properties of epoxy resin can be seen in Table 1. Epoxies contain a high degree of crosslinking that can lead to increased brittleness.[100] Additionally, bisphenol-A (BPA) and epichlorohydrin (ECH) are the raw materials for epoxy synthesis. BPA has been proven to be an environmental hormone and an endocrine disruptor that negatively affects human health.[102] Prolonged exposure to BPA may induce reproductive, developmental, and metabolic disorders.[102] Currently, the most common commercial epoxy adhesive is a diglycidyl ether of bisphenol A (DGEBA), which is synthesized by mixing bisphenol A (BPA) and epichlorohydrin (ECH), and it consists of about 90% of the worldwide epoxy adhesive market.[16,102]

The mechanism for lignin-epoxy resins is illustrated in Fig. 6. First, lignin undergoes epoxidation using epichlorohydrin under alkaline conditions (NaOH/KOH) with tetrabutylammonium bromide (TBAB) as a catalyst, forming a reactive epoxy resin. In the second step, the epoxy groups react with a diamine hardener, resulting in crosslinking *via* amine-epoxide reactions. This curing process yields a stable, three-dimensional network, resulting in a lignin-based epoxy-cured material with enhanced structural properties.[16] In the literature, lignin-epoxy adhesives (LEA) have demonstrated a bonding strength ranging from 2.7 MPa to 99.4 MPa. Despite its use in pristine form, lignin modifications such as depolymerization, demethylation, phenolation, and amination have proven to improve its molecular weight and reactive sites for epoxy resin (Table 5). For example, the impact of demethylated, phenolated, and demethylated-phenolated lignin has been compared on LEA performance (D4 in Table 5). The demethylated LEA exhibited a 19% decrease in flexural and impact strength, whereas the phenolate LEA showed a 5% increase in these properties.[101] With the demethylated-phenolated lignin, the flexural and impact strength increased by 10%, surpassing demethylated and phenolated LEAs.[101] Demethylated lignin was used to produce a lignin epoxy adhesive (LEA) at different lignin substitution levels (10–35 wt%) (D5 in Table 5). LEA with 30 wt% lignin substitution exhibited a 148% increase in bonding strength compared to commercial epoxy adhesives. In another study, depolymerized lignin was separated into water-soluble, ammonia–water–ethanol-soluble, and ethylenediamine-ethanol-soluble fractions (D10 in Table 5). The bonding strength increased by 49% for the use of water-soluble fraction in resin, 49% for the ammonia water–ethanol soluble fraction, and 42% for the ethylenediamine-ethanol soluble fraction at 2 wt% dosage.[103] Depolymerized lignin was also used to make 100% lignin-substituted LEA using oligomer products with and without epoxied cardanol glycidyl ether (ECGE) (D7 in Table 5). Without the ECGE, the bonding strength of the depolymerized LEA decreased by 19%, while the addition of the ECGE increased the bonding strength by 4% compared to a commercial epoxy.[104]

Lignin has also been investigated as a curing agent for epoxy adhesives (D3, D13 in Table 5). Demethylated and esterified organosolv lignin has been used as a curing agent for commercial epoxy adhesive, E-51 (D3 in Table 5).[105] Aminated lignin has also been used as a curing agent for commercial epoxy (D13 in Table 5).

Lignin nanoparticles have also been explored in epoxy resins (D14, D15, and D16 in Table 5). The incorporation of nanoparticles shows promising performance with up to 50 wt% lignin substitution.[109,110] Lignin–epoxy adhesives perform best when lignin is demethylated or depolymerized and used at moderate substitution levels (10–30%), with stepwise curing at elevated temperatures ensuring complete crosslinking and optimal bonding performance. For lignin–epoxy adhesives, the bonding strength is the most critical parameter because the primary goal is to achieve strong bonding between substrates while maintaining sufficient thermal and chemical stability. Water resistance is typically secondary but necessary for durable performance.

For shortcomings, the mechanical properties of lignin-incorporated resins may still not match those of fully synthetic adhesives, and depending on the type of modification, water resistance may be affected. Moreover, the variability in lignin's structure between biomass sources can lead to inconsistent resin performance, and achieving uniform reactivity remains a challenge. Scaling up these resins is also limited by their high production costs and, in some cases, the elevated curing temperatures required for optimal performance. Additionally, some LEAs still require the use of BPA, which is harmful to human life.[113,114] These technical and economic barriers collectively hinder the large-scale commercialization of lignin-based adhesives despite ongoing research advancements.

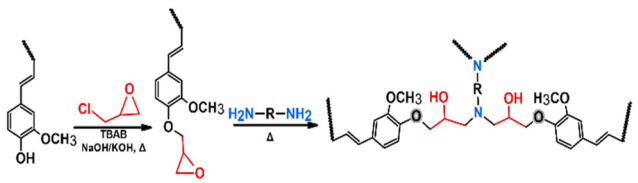

Fig. 6 Most probable mechanism for lignin-epoxy resins.[16]

Lignin-polyurethane adhesives (LPUAs)

Polyurethanes are commonly used plastics synthesized by reacting petroleum-derived polyols with di- or tri-

Table 5 Studies on lignin-epoxy adhesives

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis,	Curing conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Raw	13 commercial lignin	—	—	9	Resin – mold	• Lignin + DMF, 25 °C, 10 min • TBAB + ECH, 60 °C, 3 h • TBAB + NaOH (dropwise), 25 °C, 8 h	• Add GX-3090, 130 °C, 2 h • 150 °C, 1 h	—	—	D1	106
	Kraft	—	—			• Lignin, ECH, NaOH, 50 °C, 5 h	• Add Jeffamine D2000, 50 °C, 1 h • 100 °C, 2 h • 150 °C, 2 h	LEP: 66	14	D2	107
Demethylation	Organosolv + esterification	HBr	110 °C, 24 h	5, 10, 20, 30 + 1% DMAP	Resin – mold	• Purchased E51	• Add lignin curing agent+ DMAP, 80 °C, 1 h • 150 °C, 3 h • 190 °C, 2 h	DLEP-5: 39.19 DLEP-10: 71.54 DLEP-20: 55.43 DLEP-30: 35.26	—	D3	105
	Alkali	HI	120 °C, 20 h	10	Resin – mold	• Lignin + phenol + H_2SO_3 + Formaldehyde, 65 °C, 2 h • TBAB + ECH, 65 °C, 3 h • NaOH, 65 °C, 3 h	• Add MNA, 85 °C, 10 min • 85 °C, 4 h • 120 °C, 4 h • 160 °C, 4 h	DLEP: 98.38[a] DPLEP: 134.12[a]	−19 10	D4	101
	Unspecified	HBr	120 °C, 3 h	10, 20, 30, 35	Resin – mold	• Lignin + DMF, 25 °C, 1 h • NaOH + ECH (E-44), 80 °C, 3 h	• Add E-44 + T-31, 80 °C, 4 h	DLEP-10: 36.78 DLEP-20: 55.43 DLEP-30: 62.50 DLEP-35: 39.96	46 105 148 59	D5	32
	Enzymatic hydrolysis	1-Dodecanethiol	—	2, 5, 10, 15 + E-51	Resin – mold	• Lignin + ECH, 25 °C • NaOH, 80 °C, 30 min	• Add polyamine 593, 60 °C, 2 h • 80 °C, 3 h • 120 °C, 1 h	DLEP-2: 52.20 DLEP-5: 55.52 DLEP-10: 41.19 DLEP-15: 29.94	19 27 −6 −32	D6	99

Table 5 *(Contd.)*

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis,	Curing conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Depolymerization	Alkali	Partial-reductive	275 °C, 4.5 MPa, 4/8/12 h	8	Resin – mold	• Lignin + ECH + TEBCA, 110 °C, 5 h • Cooled to 50 °C • Add NaOH, 60 °C, 5 h	• Add MeTHPA + DMBA, 90 °C • 120 °C, 4 h • 160 °C, 1 h • 180 °C, 4 h	DLEP: 60 DLEP + ECGE: 77	−19 4	D7	104
	Organosolv	Reductive	350 °C, 1 h	33	Resin	• Lignin + ECH + TBAB, 80 °C, 1 h • Add NaOH, 55 °C, 8 h	—	—	—	D8	108
	Alkali	Hydrolysis	250 °C, 1.5 h	—-	Resin – mold	• BPA + ECH, 50 °C • Add Lignin, 30 min • 90 °C, 1 h	• Add EDA, 100 °C, 4 h	DLEP: 2.66	—	D9	98
	Dealkalized	Hot compressed ethanol-H_2O	260 °C, 30 min	.5, 1, 1.5, 2	Resin – mold	• E44, 120 °C, 1 h • Add Lignin, 30 min • 80 °C, 2 h • Cooled to 50 °C	• Add polyamide 651, 25 °C	WDLEP-1.5: 91.25 ADLEP-1.5: 96.88 EDLEP-1.5: 99.37 WDLEP-2: 88.13 ADLEP-2: 92.50 EDLEP-2: 92.50	47 57 61 42 49 49	D10	103
	Rice husks + silica	Hydrothermal	250 °C, 1.5 h	15, 20, 25, 30, 35, 40	Resin – mold	• BPA + ECH, 50 °C • Add Lignin, 90 °C 30 min • 90 °C, 1 h	• Add EDA, 100 °C, 4 h	DLEP-35 + S: 3.98 DLEP-40 + S: 2.52	83 16	D11	100
	Reed magnesium bisulfite	Hydrolysis	160 °C, 3 h	17	Resin – mold	• Lignin + ECH + NaOH, 90 °C 30 min	• Add E-57 + T-31	DPLEP-17: 10.42	228	D12	102
Phenolation	Alkali	Phenol	110 °C, 1 h	10	Resin – mold	• Lignin + phenol + H_2SO_3 + Formaldehyde, 65 °C, 2 h • TBAB + ECH, 65 °C, 3 h • NaOH, 65 °C, 3 h	• Add MNA, 85 °C, 10 min • 85 °C, 4 h • 120 °C, 4 h • 160 °C, 4 h	PLEP: 127.5[a]	5	D4	101
Amination	Kraft	Nano-alumina, $CO(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$, hydrazine hydrate	140 °C, 4 h	10, 13, 16	Resin – mold	• Purchased	• Add lignin curing agent + DMF • 125 °C, 2 h • 150 °C, 1 h	ALEP-13: 86.91	—	D13	92

Table 5 *(Contd.)*

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis,	Curing conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Nanoparticles	Kraft	Ethanol, THF, deionized water	25 °C, 15 min	33, 50, 67, 100	Resin – plywood	• ECH, 43 °C • Add Lignin, 1 ml min^{-1}, 11 min	• 300 g m^{-2}, 145 °C, 5 min, 1.1 MPa	LNEP-33: 10.28 LNEP-50: 11.26 LNEP-67: 8.97 LNEP-100: 3.96	9 19 −5 −58	D14	109
	Dealkalized	Glycerol triglycidyl ether (GTE), NaOH	100 °C, 30 min	40, 50, 60	Resin – plywood	• Mix GTE, lignin, and NaOH, 100 °C, 30 min	• 140 °C, 3 min, 0.3 MPa • 140 °C, 7 min, 0.5 MPa	LNEP-40: 12.18 LNEP-50: 14.62 LNEP-60: 12.93	43 71 52	D15	110
	Alkali	Ethylene glycol (EG)	35 °C, 1 h, pH 3 (3 drops per min) HCl, H_2SO_3	15	Resin – mold	• Lignin + EPI, 25 °C, 30 min • Add BPA, 80 °C, 2 h • Add NaOH, 80 °C, 3 h • Add NaOH, 80 °C, 2 h • 25 °C, 2 h	—	LNEP-15: 44.80	—	D16	111

[a] Flexural strength.

isocyanates.[3,14] The worldwide consumption of PU resins was estimated to be nearly 25.8 million tons in 2022, with predicted growth to 31.3 million tons by 2030.[115] PU resins are used in a wide variety of applications such as insulation materials, automotive parts, coatings, adhesives, elastomers, foams, fibers, appliances, and biocompatible materials for medical devices and the construction industry.[6,17,116–119] Its wide range of applications is attributed to its excellent tensile and compressive strength, thermal stability, insulation properties, fatigue durability, and resistance to abrasion, as well as chemical and water resistance.[3,113] Additionally, PU can be formulated to be rigid or flexible. The mechanical properties of traditional polyurethane adhesives can be controlled by the degree of crosslinking.[14] Similarly, lignin-based polyurethane (LPU) adhesives exhibit the same broad application potential as conventional PU, benefiting from the combination of high mechanical performance, thermal and chemical resistance, and tunable flexibility or rigidity. Incorporating lignin provides a more sustainable adhesive option without compromising these functional applications. The properties of PU resins can be seen in Table 1. Some of the drawbacks of PU resins include their sensitivity to moisture, which can lead to incomplete curing, susceptibility to UV degradation, limited resistance to extreme temperatures, and resistance to strong acids or bases.[120,121] Additionally, the high production costs, poor biodegradability, and environmental pollution are associated with polyurethane production.[3,14,31,120,121] Alternatively, safer and more environmentally friendly alternatives such as lignin should be investigated. Lignin contains phenolic and aliphatic hydroxy groups and can act as polyols, which can potentially react with isocyanate to produce a lignin–polyurethane adhesive (LPUA).[3] The mechanism for lignin-PU resins can be seen in Fig. 7. In the first step, lignin's hydroxy (–OH) groups react with the isocyanate (–N═C═O) groups of toluene diisocyanate (TDI), forming urethane (–NH–COO–) linkages and a lignin-TDI intermediate.[112] In the second step, additional TDI reacts with remaining hydroxy (–OH) or newly formed amine (–NH) groups, creating more urethane (–NH–COO–) and urea (–NH–CO–NH–) bonds.[112] This results in a highly crosslinked, three-dimensional polyurethane network with lignin as a bio-based structural component. In the literature, lignin-PU (LPU) resins have exhibited bonding strengths and compressive strengths ranging from 4.4 MPa to 91.2 MPa and 0.09 MPa to 0.92 MPa (E2, E4, E5, E10 in Table 6). The properties of the LPUA can be altered by adjusting the molecular weight of lignin.[3] However, the substitution of lignin is currently limited due to lignin's poor solubility in polyol systems, high molecular weight, and low hydroxy group content, which can decrease LPUA's strength.[31] Additionally, the lower nucleophilicity of phenols with respect to aliphatic alcohols diminishes their reactivity with isocyanate monomers.[14]

Similar to the incorporation of lignin in formaldehyde-containing resins, modifications have been conducted to improve lignin's performance in polyurethane, such as demethylation, depolymerization, and oxypropylation (Table 6). Demethylation and depolymerization were performed to

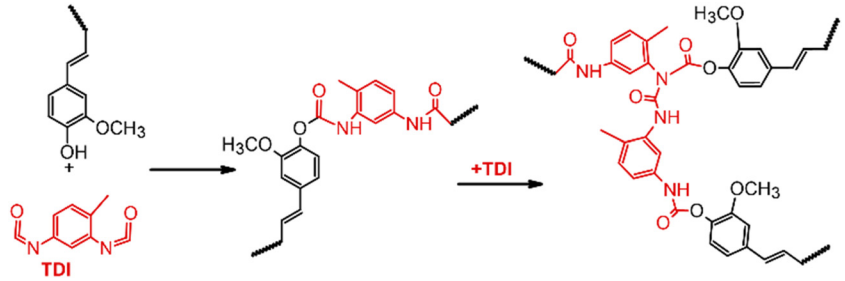

Fig. 7 Most probable mechanism for lignin–polyurethane resins.[112]

decrease the molecular weight of lignin while increasing its solubility and hydroxy content. Oxypropylation, on the other hand, increased the aliphatic hydroxy content. For example, the demethylation of lignin was conducted to produce a lignin-PU adhesive (LPUA) (E10 in Table 6). It was observed that the LPUA showed an increase in glass transition temperature, bonding strength, Young's modulus, and elongation at break compared to PU.[112] The bonding strength increased by 66% and 39% with a lignin substitution of 20% and 25%, respectively.[112] This improvement is attributed to the following reasons: (1) demethylation converts unreactive methoxy into hydroxy; (2) demethylation would produce more reactive sites in the *ortho* position, which could react with TDI; (3) more reactive sites would result in an increased crosslink density and rigidity in polyurethane adhesives; and (4) lignin copolymerizes with PU, forming a large number of covalent bonds, rather than acting as a filler.[112]

In a similar study, Xu *et al.* developed a heat-resistant, UV-curable polyurethane/polysiloxane pressure-sensitive adhesive by grafting 6-bromo-1-hexene onto demethylated bamboo lignin (E7 in Table 6). LPUAs were produced with the modified lignin at different lignin substitutions. It was seen that the lap shear strength increased with the substitution of lignin. With 40% lignin substitution, the bonding strength increased by 321%.[125]

A bio-based PUA was developed using depolymerized lignin *via* a solvolysis reaction in acid catalysis in the presence of diethylene glycol (DEG) (E2 in Table 6). All of the depolymerized lignin-incorporated resins exhibited lower bonding strength than their unmodified lignin counterparts. This decrease in performance was attributed to the unreacted DEG from the glycolysis product, which induced a plasticizing effect on the resulting crosslinked polymeric structure of the LPUA adhesive.[123] Moreover, a lignin-PU foam adhesive was developed using depolymerized lignin or a combination of both depolymerized and oxypropylated (50/50) kraft lignin (E6 in Table 6). It was observed that, with 50% depolymerized lignin substitution, the compression strength increased by 113%. However, when a combination of 50% depolymerized lignin and 50% oxypropylated lignin was used, a 409% increase in compression strength was observed.[117] The significant improvement in performance with oxypropylation was attributed to the fact that oxypropylation converts all phenolic hydroxy groups to aliphatic hydroxy groups, which transform lignin into a highly branched and functional polyol.[117] Lignin nanoparticles have also been investigated for PU resins (E12, E13, E14 in Table 6). No clear trend was identified. Typically, the optimum amount of lignin nanoparticles is seen to be 5 wt% in this application. Wu *et al.* produced an LPU film with a 222% increase in tensile strength when 5 wt% of lignin was substituted (E12 in Table 6). For lignin-based polyurethane adhesives, the critical performance parameter depends on the application. Foam LPUs prioritize water resistance and thermal stability to maintain insulation properties. Resin LPUs rely on the adhesion strength for structural bonding, while film LPUs emphasize flexibility and mechanical durability to prevent brittleness.

The best practices for LPU adhesives depend on lignin type and application. Resin LPUs perform best with stepwise lignin–isocyanate mixing under moderate heat (115–195 °C). Foam LPUs require short, high-shear mixing and ambient curing with post-curing at 80 °C. The films of LPUs achieve better adhesion using ultrasonic lignin dispersion in suitable solvents (DMF or GVL). Overall, stepwise mixing and controlled curing maximize bonding performance.

While modified lignin-based polyurethane (LPU) resins would offer several environmental and performance benefits, they have some shortcomings. For example, the quality of lignin can vary, leading to inconsistencies in the final resin properties.[130] Lignin's lower reactivity compared to traditional polyols can affect the resin's curing and mechanical properties.[18] The modification process to improve reactivity and compatibility with isocyanates can be complex and costly.[18] Limited solubility in common solvents poses formulation challenges. Additionally, these resins can sometimes exhibit brittleness, limiting their use in flexible applications.[124] Beyond these intrinsic material issues, the heterogeneity of lignin structure, variability between biomass sources, and the challenge of achieving consistent crosslinking make industrial reproducibility difficult. Balancing water resistance, adhesion strength, and mechanical durability while keeping production cost-effective remains a critical hurdle for scaling LPU adhesives.

Lignin-polyethyleneimine adhesives (LPEIAs)

Marine adhesive proteins (MAPs) are strong and water-resistant adhesives produced by marine mussels to stick to rocks

Table 6 Studies on lignin–polyurethane adhesives

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis	Curing conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Depolymerization	Pinus radiata	Hydrogenolysis, enzymatic mild acidolysis	3.45 MPa, 195 °C, 2–24 h	—	Resin	—	—	—	—	E1	122
	Broadleaf sawdust	Solvolysis	160 °C, 4 h	20	Resin	A: lignin + PETOL 46–3 MB B: PETOL 250–2 + MDI • Mix A + B	—	4.4	−31	E2	123
	Corncob	Hydrolysis	280 °C, 15 min	—	Resin	—	—	—	—	E3	116
	Sodium lignosulfonate	Hydrolysis	170 °C, 2 h	20, 30	Foam	• Mix lignin, polyols, water, catalyst, and surfactant	• 25 °C, 24 h	DLPU-20: 0.90[a]	−44	E4	124
						• Add PMDI curing agent, 10–15 s	• 80 °C, 72 h	DLPU-30: 0.84[a]	−48		
	Hydrolysis	Hydrothermal	250 °C, 1 h, 2–3 Mpa	30, 50	Foam	• Mix polyols, lignin, glycerol, acetone, catalyst, surfactant, and water for 60 s.	• Add pMDI, 25 °C, 24–48 h	DLPU-30: 0.16[a]	−69	E5	6
								DLPU-50: 0.09[a]	−83		
	Kraft	Hydrolysis	250 °C, 2 h	50	Foam	• Mix polyols, lignin, glycerol, acetone, catalyst, surfactant, and water for 12 s.	• Add pMDI, 25 °C, 24–48 h	0.216[a]	113	E6	6
Demethylation	Bamboo	HBr	115 °C, 20 h	10, 20, 30, 40	Resin	• Mix PGG, PDMS, DBTDL, and IPDI, 50 °C, 1 h • Add HEMA, 50 °C, 2 h • Add lignin + photoinitiator, 25 °C, 30 min	• 70 °C, 10 min • UV (108 mJ cm^{-2}), 60 s	DLPU-40: 0.082	321	E7	125
	Softwood	HBr	115 °C, 20 h	34	Foam	• Mix lignin with TDI, 75 °C, 5 min • Add PEG 200, 75 °C, mix 5 min	• 75 °C, 2 h	0.34[a]	942	E8	118
	Organosolv	Indium triflate + microwave radiation	275 °C, 4 h	—	Resin	—	—	—	—	E9	126
	Acetic acid	HBr	125 °C, 20 h	10, 15, 20, 25	Resin	• Mix lignin with TDI, 25 °C, 5 min	• Add PEG, 25 °C, 2 h	DLPU-20: 91.21 DLPU-25: 76.35	66 39	E10	112

Table 6 *(Contd.)*

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis	Curing conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Oxypropylation	Demethylated kraft	Propylene oxide	150 °C, until pressure stabilizes	50, 100	Foam	• Mix polyols, lignin, glycerol, acetone, catalyst, surfactant, and water, 12 s	• Add pMDI, 25 °C, 24–48 h	DLPU-50: 0.22[a]	113	E6	6
								ODLPU-50: 0.52[a]	409		
	Kraft	Propylene oxide	150 °C, until pressure stabilizes	10, 30, 60, 100	Resin	• Mix polyols, lignin, catalyst, and surfactant, 1 min	• Add MDI and blowing agent, 25 °C, 48 h	OLPU-30: 0.11[a]	10	E11	119
								OLPU-60: 0.10[a]	0		
								OLPU-100: 0.14[a]	40		
Nanoparticles	Kraft	γ-Valerolactone (GVL)	Ultrasonic, 30 min	0.5, 1, 3, 5, 10	Film	• Polyol + IPDI, 85 °C, 1 h • Add 1,4-butanediol, 3 h • Add triethylamine, 60 °C, 30 min	• Add lignin, mix 2 h • 120 °C, 2 h	NLPU-0.5: 19.87	7	E12	127
								NLPU-1: 29.30	58		
								NLPU-3: 48.80	163		
								NLPU-5: 59.67	222		
								NLPU-10: 53.42	188		
	Bamboo acetic acid	DMF	Ultrasonic, 1 h	5, 10, 15	Film	• Polyol, DMF, DBTDL, DMF, 60 °C, 4 h • Add lignin + DMF, 80 °C, 8 h	• Air dry 60 °C, 8 h • Vacuum oven, 80 °C, 8 h	NLPU-5: 55.24	13	E13	128
								NLPU-10: 50.58	3		
								NLPU-15: 47.35	−3		
	Enzymatic hydrolysis	DMF/H_2O	5 h	0.5, 1, 2, 5	Films	• Polyol, DMPA, 80 °C • Add IPDI + catalyst + acetone, 3 h • Add 1,4-butanediol, 40 min • 40 °C, add neutralizing agent	• 25 °C until dry	NLPU-0.5: 14.33	−33	E14	129
								NLPU-1: 14.83	−31		
								NLPU-2: 22.84	7		
								NLPU-5: 29.65	38		

[a] Compression strength.

and other substances in the seawater in order to withstand the impact of turbulent tides and waves.[131] MAPs are prime examples of formaldehyde-free and renewable adhesives. MAPs are composed of two key functional groups: an amino and a catechol group.[3] Various reactions between the amino and catechol groups solidify and crosslink MAPs, forming a very strong and highly water-resistant adhesive.[131] However, MAPs are not readily available in the market.

Polyethyleneimine (PEI) is a synthetic version of MAP, which is created through the acid-catalyzed polymerization of aziridine.[132] PEI is a water-soluble polyamine whose molecular chain possesses a great quantity of primary, secondary, and tertiary amines, which have strong protophilic properties and can form strong hydrogen bonds with proton donors.[133] Polyethyleneimine (PEI) resin is used as an adhesive for polyvinyl chloride (PVC) solutions and epoxy resin crosslinkers.[134] It also functions as a laminate anchor coating agent for paper, cloth, oriented polypropylene (OPP) film, and polyethylene terephthalate (PET) film, as well as a heavy metal chelating agent, a metal plating additive, a foam retainer in fire extinguishers, an ink adhesion enhancer, and a coagulant in water treatment.[134] Polyethyleneimine (PEI) has high reactivity with cellulose, making it useful in paper and textile applications.[133] Its molecular weight variability allows control over ductility, rigidity, and thermal stability while also enabling formaldehyde-free formulations.[135] The cationic nature enhances adhesion to negatively charged surfaces, and its water solubility ensures easy processing.[131] Once cured, PEI resin exhibits good strength and excellent water resistance for durable applications.[136] PEI resin has limitations, including sensitivity to hydrolysis, leading to reduced durability under humid conditions.[131] It has limited thermal stability, brittleness after curing, and high chemical reactivity, which can cause unwanted side reactions.[131,135] Its high viscosity complicates processing, while its relatively high cost may limit widespread use.[131,135] Aesthetic concerns, like yellowing, and health risks, such as skin and respiratory irritation, require careful handling.[131,135] Environmental concerns arise from production and disposal, and compatibility issues may restrict adhesion to certain surfaces.[131,135] Additionally, PEI may degrade during storage over time, and has limited long-term water resistance compared to synthetic resin adhesives.[135]

Lignin, which contains phenolic hydroxy groups, can be expected to produce an environmentally friendly adhesive that mimics MAP when blended with PEI.[3] The mechanism of the lignin-PEI adhesive (LPEIA) is illustrated in Fig. 8. It is worth noting that the mechanism between lignin and PEI is not yet fully understood. Initially, lignin undergoes demethylation, exposing catechol moieties that are prone to oxidation at elevated temperatures (140 °C).[137] This oxidation leads to the formation of quinones, which then react with PEI's amino groups to form Schiff bases.[137] Additionally, Michael's addition reactions between quinones and PEI further contribute to crosslinking.[137] Strong hydrogen bonding also occurs between PEI, lignin, and wood hydroxy groups, enhancing adhesion.[137] These reactions collectively form a highly cross-linked, water-resistant adhesive network. Lignin-polyethyleneimine adhesives (LPEIA) share the same applications as conventional PEI adhesives.

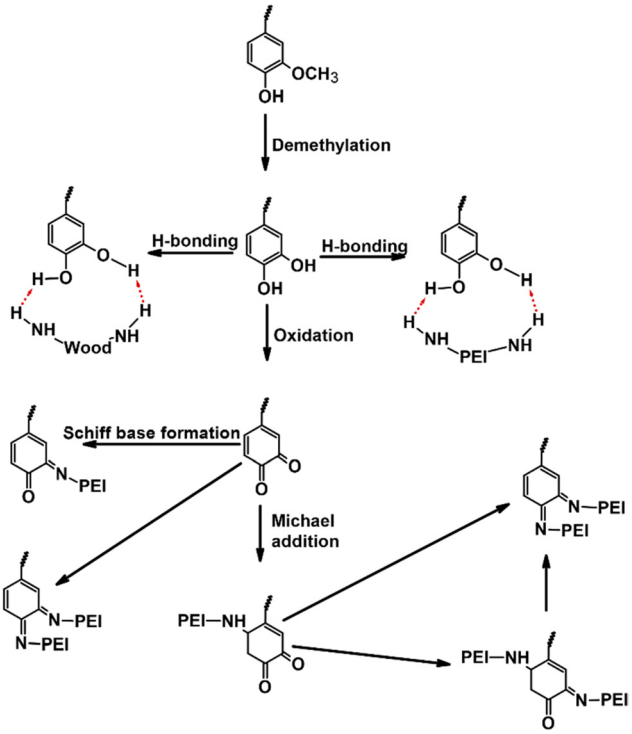

Fig. 8 Most probable mechanism for lignin-polyethyleneimine resins.[137]

To improve the reactivity of lignin, several modifications have been incorporated when producing lignin-PEI adhesive (LPEIA), including demethylation, oxidation, and reduction.[35,131,136,138] A summary of LPEI adhesives is presented in Table 7. A lignin-PEI adhesive (LPEIA) was developed using poplar wood lignocellulose with a glutaraldehyde enhancer, achieving a lignin content of 95 wt% (F1 in Table 7). The enhancer significantly improved bonding strength by 2957%, compared to a 986% increase with neat lignin-PEI adhesives.[133] Demethylated brown-rot fungus lignin was used to develop an LPEIA (F4 in Table 7). The reduction of demethylated lignin increased the bonding strength of the adhesive by 180%.[138] The optimum $NaBH_4$ dosage was found to be 1 wt%. The reduction time was found to significantly affect the bonding strength, with extended reactions being preferred.

This increase in bonding strength is most probably due to the reduction of *ortho*-quinones into catechol moieties, which then further react with the amino groups of the PEI in a manner similar to MAP.[138] Peng *et al.* developed a lignin-PEI adhesive using oxidized wheat straw lignin (F5 in Table 7). When the PEI content exceeded the lignin content, the bonding strength and modulus of elasticity were higher, but water resistance was lower than ratios with more lignin than PEI.[136] The optimum amount was found to be 50 wt% lignin,

Table 7 Studies on lignin-PEI adhesives

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis, F/P, mol/mol	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Raw	Poplar wood lignocellulose	—	—	95 + glutaraldehyde	Resin – adhesive	• Mix PEI + water • Add lignin • Add glutaraldehyde	180 °C, 2.5 MPa, 10 min	LPEI: 0.76 LPEI-Glu: 2.14	986 2957	F1	133
	Kraft	—	—	33, 50, 67, 75, 80	Resin – plywood	Mix PEI + lignin, 10–180 min	100 °C, 120 °C, **140 °C**, 160 °C, 1.91 MPa, 2, 4,6, 8, **9**,12 min	LPEI-33: 3.41 LPEI-50: 3.39 LPEI-67: 4.85 LPEI-75: 3.50 LPEI-80: 3.28	209 208 340 217 197	F2	135
Demethylation	Demethylated kraft (purchased)	—	—	20, 33, 50, 67, 80	Resin – plywood	• Mix lignin + water + NaOH (pH 10) • Add PEI + water, 10 min	41.6 g m^{-2}, 100 °C, **120 °C**, 140 °C, 1.91 MPa, 3, **5**, 12 min	LPEI-20: 3.84 LPEI-33: 4.55 LPEI-50: 7.06 LPEI-67: 5.59 LPEI-80: 2.45	36 61 150 98 −13	F3	131
	Brown rot fungus	Brown rot fungus, NaBH4	70 °C, 2 h, 25 °C, 1 h	17	Resin – plywood	Mix lignin + PEI, 25 °C, 60 min	120 °C, 1.9 MPa, 5 min	4.98 + PEI	−11	F4	138
Oxidization	Wheat straw soda	Sodium periodate	25 °C, 1 h	20, 25, 33, 50, 67, 75, 80, 100	Resin – particleboard	Mix lignin + NaOH + PEI, 1 h	130 °C, 140 °C, 150 °C, 160 °C, 170 °C, **180 °C**, 190 °C, 4, 7, 10, **13**, 16 min, 5 MPa	LPEI-20: 0.82 LPEI-25: 0.99 LPEI-33: 1.20 LPEI-100: 0.80	371 468 587 361	F5	136
	Lignosulfonate	Sodium periodate	60 °C, 0.5 h	50, 75, 83, 87.5, 90	Resin – Fiberboard	Mix lignin + water + PEI, 30 min	150 °C, 160 °C, **170 °C**, 180 °C, 190 °C, 3, 5, **7**, 11 min, 4–10 MPa (until the thickness is 5 mm)	LPEI-50: 0.83 LPEI-75: 0.72 LPEI-83: 1.02 LPEI-87.5: 1.19 LPEI-90: 0.59	—	F6	35
Nanoparticles	Hardwood soda (hydrolyzed and ammoxidized)	—	—	50	Resin – wood plastic composite (polypropylene)	Mix lignin, water, NaOH, and PEI, 15 min	Extrusion, 175 °C, 5 min, mold cure, 120 °C, 60 MPa	NLPEI-H: 38.5 NLPEI-A: 39.8	47 52	F7	139

in which the bonding strength and water resistance increased compared to lignin and PEI systems alone. This suggests that oxidized lignin and PEI were able to create a tight crosslinking between wood shavings, forming a three-dimensional network polymer with a physicochemical reaction.[136] The effect of temperature and time on the curing process has been examined in the literature (F2, F3, F5, F6 in Table 7). The strength of lignin-PEI adhesives increased with temperature, but the optimal range varied depending on the material and adhesive type. While higher temperatures enhanced bonding, excessive heat led to adhesive degradation and a reduction in strength. Similarly, longer curing durations improved the strength, but over-curing offered no additional benefits and might even cause degradation.[35,131,135,136] Identifying the right balance of temperature and curing time is crucial for maximizing the adhesive performance. In another study, LPEIA was developed by incorporating 33–80 wt% kraft lignin, and the optimal performance was observed at 67 wt% lignin, where the bonding strength increased by 340% (F2). In this case, increasing the curing temperature and time improved performance; however, excessive conditions led to adhesive degradation. In another study, oxidized ammonium lignosulfonate and polyethyleneimine (PEI) were used to produce a binder for fiberboards (F6 in Table 7). In this case, a mole ratio of 7/1 lignin/PEI produced the adhesive with the highest bonding strength.[35] The bonding strength and water resistance increased by 200% and 34%, respectively, with the incorporation of oxidized lignin.[35] Increasing the hot-pressing temperature to 170 °C and extending the time to 7 minutes enhanced mechanical performance, but further increases led to degradation. Hydrolyzed and ammoxidized lignin was used to formulate an LPEIA, which exhibited an increase in bonding strength of 51% and a decrease in wettability.[139] Lignin nanoparticles have also been incorporated into LPEIAs (F7 in Table 7). Best practices for LPEIA synthesis emphasize using chemically modified lignin, such as demethylated or oxidized types, to enhance the adhesion and bonding strength. Moderate lignin substitution levels (20–67%) generally provide optimal performance, as excessive loading can reduce durability. High-temperature hot pressing (≥140 °C) combined with crosslinkers or nanoparticle reinforcement further improves water resistance and mechanical properties, ensuring more reliable adhesive performance. For LPEI adhesives, the most critical property is adhesion strength, as it directly determines their suitability for wood, fiberboard, and laminate applications. Thermal stability is also important due to the high curing temperatures required (up to 140–190 °C), but the bonding strength ultimately dictates performance and usability. Water solubility primarily aids processing but is secondary to achieving strong and durable adhesion.

Lignin-PEI adhesives face several challenges, including a slow reaction rate at room temperature, which requires prolonged mixing times and high curing demands of 140 °C for up to 9 minutes, thereby increasing energy costs.[131] Their performance depends on the quality of lignin, with variations in source and purity affecting adhesion.[131] Limited long-term data raise concerns about stability, while high-quality lignin extraction remains costly.[131,135] The incorporation of lignin can reduce the reactivity of PEI, sometimes resulting in lower crosslink density and diminished mechanical strength compared to conventional PEI adhesives. Processing complexities include precise pH control, potential odour issues, and scalability challenges.[131,135] Additionally, the high viscosity and partial water solubility of lignin–PEI blends can complicate mixing and application in industrial settings. Adhesive properties vary based on formulation, with potential limitations in thermal resistance, elasticity, and durability.[135] Brittleness after curing and reduced long-term water resistance further restrict flexible or moisture-exposed applications. Additionally, limited shelf life and aesthetic concerns, such as odour and cured colour, may affect the usability of lignin-incorporated LPEIA.[131,135] Collectively, these factors highlight the need for the optimization of lignin modification techniques, processing conditions, and curing strategies to achieve consistent, high-performance LPEIA suitable for commercial adoption.

Bio-based adhesives

Lignin-tannin adhesive (LTA)

Tannins are naturally occurring polyphenols that are extracted from the bark, roots, fruits, and leaves of several plants. Until the mid-2000s, tannins were used to replace phenol in PF adhesives due to their polyphenolic structure. Tannins have demonstrated higher reactivity with formaldehyde compared to phenol.[140] Tannin adhesives are usually synthesized using various hardeners such as paraformaldehyde, glyoxal, and hexamine.[140] The worldwide consumption of tannin was 1.4 million tons in 2020, with an estimated growth to 2 million by 2027.[141]

Tannin resins are widely used in plywood, particle boards, wood composites, and laminating veneer, as well as for wood preservation and impregnated resins.[142,143] They also play a role in finger joints and have applications beyond wood, including use on steel, fiber, and paper.[142,143] Additionally, they are utilized for mercury(II) absorption and uranium recovery, demonstrating their versatility in both industrial and environmental applications.[144,145] These resins are environmentally friendly and offer antibacterial, antiviral, and UV-resistant properties. They also exhibit high tensile strength, excellent deformation properties, good thermal stability, and strong adhesion, making them highly durable and versatile.[146,147] Additionally, condensed tannins, or proanthocyanidines, are repeating units of flavan-3-ol, consisting of A and B type rings, which are attributed to their adhesive and antioxidant properties.[140] In the literature, tannin resins have been reported to have a bonding strength ranging from 0.31 MPa to 63.16 MPa (F3, F7 in Table 8).

While tannin resins offer several environmental and performance benefits, they have some shortcomings. Tannin resins do not possess the bonding strength and water resistance demonstrated by synthetic adhesives.[137] The quality of

Table 8 Studies on lignin–tannin adhesives

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis	Curing conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Glyoxalation	Organosolv	Glyoxal	65 °C, 8 h	10, 20, 30, 40, 50	Resin – particleboard	• Lignin, water, NaOH, pH 12–12.5, 65 °C, 30 min • Add glyoxal, 65 °C, 8 h • Mix with tannin/ hexamine solution (pH 10)	195 °C, 0.36 kPa	GLT-10: 0.81 GLT-20: 0.77 GLT-30: 0.75 GLT-40: 0.72 GLT-50: 0.45	16 10 7 3 −36	G1	151
	Hardwood & softwood kraft	Glyoxal	—	40	Resin – particleboard	• Tannin, water, NaOH, pH 10.4 • Add hexamine and lignin	195 °C, 2.75 MPa, 7.5 min	3436 [a]	—	G2	19
	Wood, acetic acid, wheat straw	Glyoxal	58 °C, 8 h	55, 60	Resin – particleboard	• Lignin, tannin, pH 11.5–12 • Add pMDI	195 °C, 2.5 MPa, 7.5 min	GLT-55: 0.36 GLT-60: 0.	—	G3	158
	Organosolv	Glyoxal	58 °C, 8 h	40, 50	Resin – particleboard	• Tannin + NaOH, pH 10 • Add hexamine and lignin	195 °C, 3.5 MPa, 7.5 min	GLT-40: 0.33 GLT-50: 0.41	—	G4	159
	Organosolv	Glyoxal	58 °C, 8 h	40, 50	Resin – particleboard	• Tannin + hexamine, lignin	195 °C, 7.5 min total • 3.43 MPa • 1.18 MPa • 0.69 MPa	GLT-40: 0.43 GLT-50: 0.39	—	G5	36
	Organosolv	Glyoxal	75 °C, 8 h	40, 100	Resin	Tannin + hexamine, lignin	100 °C, 150 °C, 200 °C	—	—	G6	140
	Oil palm empty fruit bunch	Glyoxal	60 °C, 8 h	40 + 10–20% PEI	Resin – plywood	• Tannin + NaOH, pH 10 • Add hexamine, lignin • Add PEI	250 g m^{-2}, 140 °C, 17.2 MPa, 7 min	GLT: 31.06 GLT-PEI-10: 35.63 GLT-PEI-16: 47.43 GLT-PEI-20: 63.16	—	G7	137
	Sodium lignosulfonate, aluminum lignosulfonate	Glyoxal	58 °C, 8 h	40, 50, 60, 80	Resin–wood joints	• Tannin + NaOH, pH 10 • Add hexamine, lignin	—	GLT-40: 2497[a] GLT-50: 2294[a] GLT-60: 2264[a] GLT-80: 1905[a]	—	G8	8
Glycidolated	Kraft, organosolv	Glycidol	—	20, 40, 50, 60, 80, 100	Resin – plywood	• Lignin + Tannin + NaOH, pH 11–12 • Add hexamine	150 °C, 1.2 MPa, 15 min	GLT-KL-50: 8.49 GLT-OL-50: 5.35	−31 −56	G9	150
Oxypropylated	Kraft, organosolv	Propylene oxide	—	20, 40, 50, 60, 80, 100	Resin – plywood	• Lignin + Tannin + NaOH, pH 11–12 • Add hexamine	150 °C, 1.2 MPa, 15 min	OLT-KL-50: 4.46 OLT-OL-50: 5.43	−64 −56	G9	150

[a] Modulus of elasticity (MOE).

tannin can vary, leading to inconsistencies in the final resin properties. Tannins exhibit lower reactivity than synthetic resins, which affects their curing and mechanical properties.[146] The modification processes to improve reactivity and compatibility can be complex and costly. Additionally, tannins have limited solubility in common solvents and can sometimes exhibit brittleness, limiting their use in flexible applications.[146] Despite being renewable, the chemical processes used to modify tannins can involve hazardous substances and generate waste.[146] In the literature, lignin was used in tannin-based resins. Lignin–tannin adhesives share the same applications as tannin resins, including wood composites, laminates, finger joints, and environmental uses, while providing strong adhesion, durability, and eco-friendly properties. The mechanism for lignin–tannin resins can be seen in Fig. 9. In the first step, tannin reacts with hexamine, forming a tannin-hexamine complex where amine (–NH) groups are introduced (Fig. 9a), enhancing its reactivity. In the second step, lignin is modified using glyoxal, introducing hydroxy (–OH) groups to increase its reactivity (Fig. 9b). Finally, the tannin-hexamine complex reacts with glyoxal-modified lignin *via* the condensation of glyoxal's aldehyde groups with hexamine's amine groups, forming stable linkages. Moreover, the concurrent reactions of aldehyde groups with phenolic hydroxyls in lignin and tannins generate additional cross-links.[140] This structure improves adhesive strength and durability through covalent and hydrogen bonding.

Many efforts have been made to prepare lignin–tannin adhesives in order to improve their performance. A summary of all the LTAs is provided in Table 8. Typically, lignin is activated through glyoxalation before mixing with tannin and a hardener (G1, G2, G3, G4, G5, G6, G7, and G8 in Table 8). Glyoxal is used because it is a naturally occurring aldehyde derived from biological processes and lipid oxidation.[36,140] In one study, a formaldehyde-free adhesive was synthesized using glyoxalated lignin, glyoxalated tannin, or a combination of both (G6 in Table 8). It was observed that the adhesive prepared with both glyoxalated tannin and glyoxalated lignin exhibited improved thermal stability compared to the control samples (raw lignin and raw tannin).[140] This was attributed to extended crosslinking resulting from the improved reactivity of the modified lignin and tannin. In one study, Faris *et al.* developed a lignin–tannin adhesive modified with polyethyleneimine (PEI) (G7 in Table 8), observing that increasing the PEI content (0–12% w/w) led to an increase in solid content and tensile strength from 31% and 32 MPa to 57% and 62 MPa, respectively.[137] Water resistance was also improved with higher PEI levels, likely due to enhanced reactions between the amino groups in PEI and the catechol moieties in lignin and tannin, resulting in increased crosslinking and, consequently, greater tensile strength and water resistance.[137] Sarazin *et al.* produced a lignin–tannin adhesive (LTA) using oxypropylated, glycidolated, or unmodified kraft and organosolv lignin (G9 in Table 8). The bonding strength of oxypropylated, unmodified, and water-soluble kraft lignin samples was all very similar and significantly higher than that of glycidolated kraft lignin and all of the organosolv samples.[148] Various low-toxicity alternatives were produced using unmodified lignin at varying substitutions. No change in bonding strength was observed with lignin substitution beyond 10%. For samples with more than 10% lignin, the bonding strength threshold of 10 N m^{-2} was not reached.[148] However, all samples, including those exceeding 10% lignin, remained within 10% of this threshold, suggesting that optimization could potentially achieve the required threshold. For the best practice of lignin–tannin adhesives, the use of glyoxalated lignin (organosolv or kraft) blended with tannin under alkaline pH 10–12 with hexamine as a hardener is exploited at moderate lignin substitution (10–40%). For higher performance, adding a small PEI as a co-crosslinker (10–20%) markedly boosts the bonding strength (G1, G2, G7, and G8 in Table 8). For LTAs, the bonding strength is the most critical parameter, as it dictates the structural reliability of plywood, particleboard, and composite applications. While water resistance and thermal stability contribute to durability, insufficient bonding strength directly limits performance and usability. Adhesives such as GLT-PEI-20 achieved bonding strengths up to 63.16 MPa, demonstrating their structural potential (G7 in Table 8).

Modified lignin tannin resins, while offering environmental benefits and potential cost savings, face several challenges. They often exhibit low reactivity, leading to longer curing times and reduced efficiency.[150] High viscosity can complicate processing and handling.[36] The mechanical properties of these resins may not always match those of traditional resins.[151] Lignin–tannin adhesives also face challenges such as variability in lignin quality, slow curing without formaldehyde, and limited long-term durability data. Processing requires controlled pH and precise formulation to achieve consistent bonding, while scaling up remains hindered by cost and performance variability. Variability in lignin sources and extraction processes can also result in inconsistencies in resin quality and performance. Additionally, if formaldehyde is used in resin synthesis, concerns may arise about formaldehyde emissions.

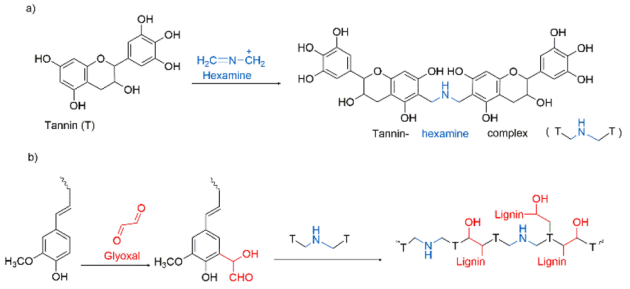

Fig. 9 Most probable mechanism for lignin–tannin resins, (a) tannin and (b) lignin upgrading.[140,148,149]

Lignin-soy protein adhesives (LSPAs)

Soy protein adhesives are another group of interesting alternative adhesives investigated for the industry. Typically, it is for-

mulated using a soy protein isolate and a crosslinking resin. During the period spanning from the 1930s to the 1960s, soy proteins were widely used in the wood product industry.[152] Soy protein (SP) is an agricultural biomass resource consisting of complex macromolecules composed of 20 different amino acids with different side chains.[3] These side chains contain functional groups that dictate the amino acid's hydrophobic and hydrophilic nature and offer reaction sites for interactions with wood or crosslinking agents.[3] The worldwide soy production was estimated to be 350 million metric tons in 2022.[153]

Soy protein adhesives are widely used in interior decorative plywood, engineered wood flooring, particleboard, fiberboards, and laminates, offering a sustainable alternative to synthetic adhesives. Beyond wood products, they are also applied in heat-resistant paper coatings, packaging, soundproof flooring, and fiberglass insulation.[20,154] Lignin–soy protein adhesives (LSPAs) have the same applications as soy protein adhesives (SPAs). Soy protein isolate (SPI) is a by-product of the soybean oil industry, making it an ideal feedstock as it is renewable, inexpensive, and highly abundant in nature, with good biodegradability, heat resistance, and ease of modification.[155,156] However, its high viscosity, poor mechanical properties, and water resistance are the primary obstacles that hinder the use of soy protein-based materials.[3,152,155–157]

This is attributed to the weak intermolecular interactions, the presence of numerous hydrophilic groups (such as –COOH, –NH2, and –OH), and molecular entanglement within the polymer chain.[156,157] Furthermore, the presence of soy proteins and polysaccharides makes it susceptible to the attack by mold, bacteria, and fungi, which cause mildew and affect its shelf life and performance.[157] One method of modifying soy protein adhesive systems involves incorporating lignin due to its hydrophobic nature. Additionally, modifying lignin by increasing its phenolic and aliphatic hydroxy contents can enhance its reactivity. These hydroxy groups interact with the amine of the soy proteins to form a dense network structure, which improves the bonding strength, water resistance, and bio-durability of the adhesives.[3,156] The mechanism for lignin-soy protein adhesive (LSPA) is illustrated in Fig. 10. First, lignin undergoes carboxymethylation *via* a reaction with sodium chloroacetate in the presence of sodium hydroxide (NaOH), introducing carboxy (–COOH) groups to enhance its reactivity. The modified lignin then interacts with soy protein through covalent bonding between carboxy (–COOH) and amine ($–NH_2$) groups, as well as hydrogen bonding.[157] This crosslinked structure enhances the mechanical properties and water resistance of the resulting lignin-soy protein resin. In the literature, the bonding strength of lignin-soy protein adhesives (LSPA) ranges from 0.41 MPa to 12.7 MPa (H10 and H13 in Table 9). Various modification methods have been employed to enhance the reactivity of lignin, including demethylation, depolymerization, depolymerization by laccase, amination, and carboxymethylation (Table 9). In one study, a soy protein adhesive was produced using kraft lignin (KL) that was first enzymatically demethylated and then reduced with $NaBH_4$ (H10). The demethylated lignin-soy protein adhesive showed no improvement over unmodified lignin; however, when reduced demethylated lignin was used, the bonding strength increased by 500%.[160] Another type of soy protein adhesive was produced using aminated and aminated depolymerized lignin (H13 in Table 9). While amination significantly improved bonding strength (by 31%), further depolymerization pretreatment prior to the amination reaction led to only a slight 2% increase.[9] After three water-soaking and drying cycles, the shear stress of the lignin-amine adhesive reached 5.0 MPa, surpassing that of the phenol-formaldehyde adhesive.[9] A lignin-soy protein adhesive (LSPA) using depolymerized lignin (H7 in Table 9) exhibited varying bonding performance depending on the depolymerization conditions. For example, the bonding strength increased by 13% at 170 °C with 50 wt% lignin substitution, whereas using raw lignin at the same substitution level resulted in a 14% decrease.[152] This is because the bonding strength increased as the depolymerization temperature increased from 140 °C to 170 °C, but declined at higher temperatures due to the decomposition of oligomers. The use of enhancers in lignin-soybean systems has also been reported in the literature (H1, H4, H5, H10, H11, H15, and H16 in Table 9). Typically, the incorporation of enhancers improves the performance of LSPAs. For example, an LSPA was developed using kraft lignin and various coadjutant polymers (H5). A 47% increase in bonding strength was observed with 20 wt% lignin substitution and cellulose nanofibers (CNFs).[157] Cao *et al.* developed a soy protein adhesive modified with dopamine-functionalized hexagonal boron nitride (PDA-BN) and carboxymethylated lignin (CML) (H16 in Table 9). With a 10 wt% lignin substitution, the bonding strength increased by 64%. Additionally, the incorporation of CML and PDA-BN increased resistance to water, flame, and mildew.[157]

The incorporation of SP adhesives with PF resins has been reported in the literature (H3, H4 in Table 9), where an increase in bonding strength was observed. For example, J. Luo *et al.* formulated an LPF resin with soy protein and corncob lignin, achieving a 200% boost in bonding strength relative to SPA.[161] The incorporation of SP adhesives with epoxy resins has also been observed in the literature (H14, H15 in Table 9). The bonding strength increases with the incorporation of epoxy. For example, S. Chen *et al.* observed a 364% increase in bonding strength compared to SPA with the incorporation of epoxy (H14 in Table 9). The best performance for

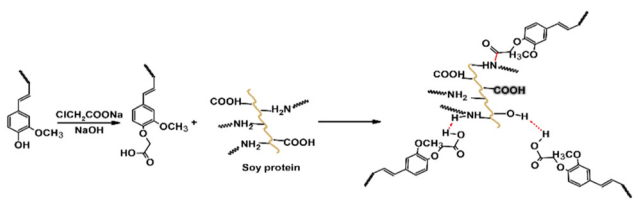

Fig. 10 Most probable mechanism for lignin-soy protein resin.[155]

Table 9 Studies on lignin-soy protein adhesives

Modification	Lignin Type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Raw	Kraft	—	—	1, 2 + 0.5, 1 PAE	Resin – plywood	SP + lignin + PAE + water, mix 30 min	150 °C, 2 MPa, 10 min	LSP-1: 5.7 LSP-2: 4.9 LSP-2-PAE-0.5: 5.8 LSP-2-PAE-1: 5.0	8 −8 9 −6	H1	162
	Kraft	—	—	20, 40, 50	Resin – plywood	SP + lignin + water, pH 4.5, mix 2 h	170 °C, 2 MPa, 10 min	LSP-20: 6.4 LSP-40: 5.5 LSP-50: 5.6	19 2 4	H2	163
	Corncob	—	—	5, 10, 15, 20, 25 + PF resin (5–25)	Resin – plywood	LPF • Lignin + phenol + F + NaOH, 80 °C, 1 h • F + NaOH, 80 °C, 1 h • F + NaOH, 80 °C, 1 h SP • Mix SP + water + LPF	180 g m^{-2} 135 °C, 1.2 MPa, 70 s mm^{-1}	LSP-5: 0.78[a] LSP-10: 1.05[a] LSP-15: 0.91[a]	123 200 160	H3	161
	Softwood	—	—	10 + PEA	Resin – plywood	LPF • Lignin + phenol + F + NaOH, 80 °C, 1 h • F + NaOH, 80 °C, 1 h SP • Mix SP + water + LPF + PAE	200 g m^{-2} 130 °C, 0.8 MPa, 90 s mm^{-1}	LSP: 1.32 LSP-PAE: 1.63	35 66	H4	164
	Kraft	—	—	20 + coadjutant polymer	Resin – plywood	• Mix NaOH + acetonitrile, 21 °C • Add coadjutant polymer, then SP, then lignin	155 g m^{-2} 171 °C, 2.4 MPa, 10 min	LSP: 7.64 LSP-CNF: 12.27	−9 47	H5	165
	Sorghum	—	—	10, 20, 30, 40, 50	Resin – plywood	SP + lignin, 25 °C, 2 h	170 °C, 2 MPa, 10 min	LSP-10: 5.70 LSP-20: 6.40 LSP-30: 6.12 LSP-50: 5.84	−8 4 −1 −6	H6	166

Table 9 *(Contd.)*

Modification	Lignin Type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Depolymerization	Kraft	Base-catalyzed	140–200 °C, 100–150psi, 3 h	33	Resin – plywood	SP + lignin, 50 °C, 1 h	• 25 °C, 0.235 MPa, 2 min • 120 °C, 0.101 MPa, 30 min	1.46	13	H7	152
	Alkali	Ultrasound-induced oxidation	50 °C, 16 h, 20 kHz, 480 W. 1 h	20	Resin – plywood	• Mix SP + water + lignin, pH 7.2, 1 h • Ad PEGDE, 85 °C, 30 min	215–237 g m^{-2}, 150 °C, 1.03 MPa, 10 min	DLSP-O: 2.39 DLSP-UO: 2.45	42 46	H8	167
Demethylation	Kraft	Laccase enzyme	25 °C, 24 h	1	Resin – plywood	• SP + lignin + water, HCl, pH 4.5, 2 h • 21 °C	150 °C, 1.03 MPa, 10 min	5.8	−16	H9	168
	Hardwood kraft	Laccase enzyme + reduction	25 °C, 3 h	50	Resin – plywood	• SP (chitosan or PEI) + lignin + sodium acetate, ABTS, laccase, 25 °C, 3 h	120 °C, 2 MPa, 15 min	DLSP: 0.41 DLSP-R: 1.81	−84 −31	H10	160
	Alkali	1-Dodecanethiol	130 °C, 1.5 h	1, 2, 3, 4 + Cu additive	Resin – plywood	• Mix SP + lignin + water, 25 °C, 15 min	180 g m^{-2} 120 °C, 1 MPa, 6 min	DLSP-1: 1.77 DLSP-2: 1.91 DLSP-3: 1.88 DLSP-4: 1.84 DLSP-2-Cu: 1.90	5 13 11 9 12	H11	156
Amination	Enzymatic hydrolysis	$NaBH_4$	25 °C, 20 min	14, 23, 32, 42	Resin – plywood	• Mix SP + lignin + water + ESO	200 g m^{-2} 130 °C, 1 MPa, 6 min	ALSP-23: 0.94[a] ALSP-32: 1.07[a] ALSP-42: 0.99[a]	77 102 87	H12	155
	Depolymerized hydrolysis	$NaBH_4$	25 °C, 20 min	1	Resin – plywood	• Mix SP + water + NaOH, 60 °C, 2 h • Add lignin, 30 min	120 °C, 1 MPa, 5 min	ALSP: 9.02 ADLSP: 7.02	31 2	H13	9
Epoxy	Enzymatic hydrolysis	EGDE	30 °C, 4 h	41	Resin – plywood	• Mix SP + water + lignin, 25 °C, 20 min	200 g m^{-2} 120 °C, 1 MPa, 7 min	1.02[a]	364	H14	10
	Enzymatic hydrolysis	EGDE	30 °C, 4 h	41 + preservatives	Resin – plywood	• Mix SP + water + lignin, 25 °C, 20 min	200 g m^{-2} 120 °C, 1 MPa, 7 min	EPLSP: 1.02[a] EPLSP-P: 0.86[a]	364 291	H15	169

Table 9 *(Contd.)*

Modification	Lignin Type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Symbol	Ref.
Carboxy-methylation + hexagonal boron nitride functionalized	Kraft	Sodium chloroacetate	40 °C, 4 h	5, 10, 15	Resin – plywood	• Mix lignin + water, ultrasonic, 2 h, 200 W • Add SP + CAL, 5 min • Add TGA, 10 min	200 g m^{-2}	SPI-BN: 1.76	40	H16	157
							120 °C, 1 MPa, 6 min	CLSP-5-BN: 1.75	39		
								CLSP-10-BN: 2.07	64		
								CLSP-15-BN: 1.45	15		

[a] Wet strength.

amination-modified lignin-soy protein adhesives is achieved with 14–42% lignin, $NaBH_4$ treatment, and hot pressing at 130 °C/1 MPa for 6 min, providing up to 1.07 MPa bonding strength with improved wet adhesion (H11 in Table 9). Epoxy-modified systems (41% lignin, EGDE at 30 °C/4 h) pressed at 120 °C/1 MPa for 7 min yield 1.02 MPa strength with 364% higher wet resistance, making epoxy the preferred option for moisture-resistant applications (H15 in Table 9).

Although modified lignin soy protein adhesives offer several benefits, they also have some shortcomings that can limit their applications. These adhesives often exhibit weaker bonding strength and lower water resistance compared to synthetic adhesives, making them less suitable for high-strength and moisture-prone environments.[114] Additionally, they can be susceptible to mildew under humid conditions, affecting their durability and longevity.[114] The modification process to enhance their properties can be complex and costly, making it infeasible for all manufacturers. Their processing can be complicated by pH sensitivity and the need for precise denaturation control of soy protein to achieve optimal adhesion. Additionally, prolonged curing times and limited shelf life remain barriers to large-scale industrial adoption. Furthermore, their thermal stability is generally lower than that of some synthetic adhesives, limiting their use in high-temperature applications.[114] These shortcomings highlight the need for ongoing research and development to improve the performance of bio-based adhesives and expand their range of applications.

Lignin-furfural adhesives (LFAs)

Furfural-based resins are polymers derived primarily from furfural. Furfural is a naturally occurring compound produced *via* sugar dehydration and present in various agricultural byproducts. Hemicellulose, a key component of biomass, can be transformed into different furan-based chemicals, including furfural and furfuryl alcohol.[170] Due to its high reactivity, furfural exhibits similar reactions to other aldehydes and aromatic compounds.[3,171] The global market of furfural was estimated to be 365 thousand metric tons in 2022, with an estimated growth to 505 thousand metric tons by 2023.[172] Furfural resins are widely used in both the materials and food industries. They serve as lubricating oils, binders in abrasive wheels, and wood adhesives.[173,174] Additionally, they are integral in the production of PF resins, binders for refractory materials, rubber adhesion, moisture-cure adhesives, coatings, and laminates.[175–178]

Furfural resins are renowned for their exceptional resistance to acids and alkalis, making them well-suited for applications that require chemical durability.[179] They also exhibit good thermal stability, with continuous use at temperatures up to 120 °C, and some grades can withstand up to 150 °C.[180] With its unsaturated double bond, oxygen ether bond, diene, and aldehyde functional groups, furfural possesses high chemical activity along with excellent heat and water resistance.[181] Additionally, these resins are characterized by low flammability and minimal smoke emission, enhancing safety in various

industrial applications.[180] They also offer good bonding strength, making them effective in adhesive and composite applications.[182]

Furfural-based resins have several shortcomings that impact their usability. These resins can become brittle after curing, compromising their performance in flexible applications. Health hazards are also a concern, as furfural can irritate the skin and mucous membranes, potentially causing dermatitis or eczema.[183] Additionally, furfural is classified as a Category 3 carcinogen.[184] Environmental issues also arise from the production and use of furfural resins, particularly regarding waste management and emissions.[185] Furthermore, processing challenges exist, as furfural resins can degrade under prolonged acidic conditions, reducing the yield and efficiency during production.[186]

In theory, lignin could serve as a substitute for phenol, while furfural could replace formaldehyde. The mechanism for lignin–furfural resins is illustrated in Fig. 11. Under acidic conditions, lignin undergoes activation as electron density increases at the C2 and C6 positions due to inductive and resonance effects, rendering these sites highly reactive to electrophilic substitution.[7] In the next step, furfural, acting as an electrophile, reacts with these activated positions, leading to condensation and crosslinking.[7] This results in the formation of a lignin–furfural resin, although competing depolymerization and repolymerization reactions may also occur.[7] It is important to note that the lignin–furfural mechanism is not yet fully understood and requires further research. Lignin–furfural adhesives have gained attention for plywood and laminate applications, offering chemical durability and thermal stability comparable to conventional resins. In the literature, lignin furfural adhesives (LFA) have demonstrated bonding strengths ranging from 0.24 MPa to 153 MPa (H7, H8 in Table 10).

Various types of lignin have been investigated in the development of lignin–furfural adhesives (LFA), including enzymatic hydrolysis, hydrolysis, softwood kraft, bagasse, sugar maple, and plasticized lignin, which are all summarized in Table 10. The incorporation of furfural into PF resins has been examined by various researchers (I3, I4, I5, I8 in Table 10).

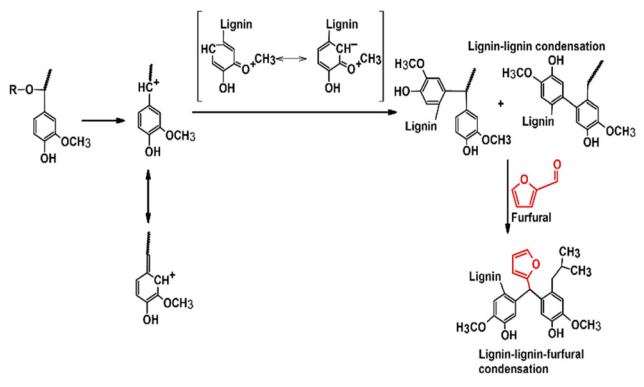

Fig. 11 Most probable mechanism for lignin–furfural resin.[7]

Typically, it is seen that the bonding strength decreases with the incorporation of furfural. For example, a lignin-PF resin was synthesized using kraft lignin with various amounts of furfural (I4 in Table 10). As more furfural (0–30 wt%) was added to the system, the bonding strength decreased, while the free formaldehyde content increased.[181] The optimum amount of furfural in the lignin–furfural PF resin was found to be 15 wt%.[181] Oxidized lignin was used to develop a lignin-PF resin (I8). A 7% increase in bonding strength was achieved with 15 wt% lignin.[67] A lignin–furfural adhesive (LFA) was developed using phenolated depolymerized hydrolysis lignin (I6 in Table 10). With 50 wt% lignin, the bonding strength decreased by 18% and the resin required higher curing temperatures and longer times.[171] The thermal stability also increased, being stable until 315 °C (in air or N_2) when compared to phenol furfural adhesives.[171] In another study, lignin modified using a low-transition-temperature mixture (LTTM) was employed to synthesize a lignin–phenol–furfural resin (I7 in Table 10). When the substitution of lignin was 50 wt%, the bonding strength decreased by 17%.[182] At this substitution level, the bonding strength was much greater than the Chinese National Standards (0.7 MPa). However, the free aldehyde emission of 0.39% was slightly higher than the 0.30% of the Chinese National Standards.[182] For lignin–furfural adhesives, the best practice so far relies on unmodified lignin with moderate substitution levels (10–30%) and hot-pressing at 140–160 °C under 1–3 MPa for 3–7 min (Table 10). The most critical performance parameter is bonding strength, as mechanical integrity dictates suitability for wood. Thermal stability is generally sufficient for moderate curing temperatures (140–160 °C), whereas water resistance remains secondary since excessive lignin substitution often reduces adhesion.

Key challenges include achieving consistent molecular weight distribution, improving water and thermal resistance, and mitigating brittleness without compromising the bio-based content. Modified lignin–furfural resins exhibit inferior mechanical properties compared to conventional phenol-formaldehyde resins, limiting their use in demanding applications.[7] The curing process increases brittleness, reducing flexibility and durability. Additionally, the high molecular weight and low reactivity of lignin would lead to longer curing times and higher temperatures during synthesis.[7] While lignin and furfuryl alcohol are sustainable, second-generation products from agricultural or paper industries, these raw materials are not ideal for resin fabrication compared to specialized polymers derived from synthetic routes, which are specifically engineered to meet specific performance criteria.[187]

Best sustainable lignin-incorporated adhesives and future directions

The best formulations, demonstrating the highest improvement in performance, were achieved for LPFAs with alkali lignin nanoparticles, which resulted in a 64% increase in bonding strength (1.59 MPa) at 30 wt% lignin with a urea enhancer (A18 in Table 2). LUFAs with glyoxalated Bagasse

Table 10 Studies on lignin–furfural adhesives

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Free formaldehyde content[a], %	Symbol	Ref.
Raw	Plasticized	—	—	20, 30	Resin	FF/MA: 50 • Add mix lignin + FF + MA, 110 °C, 30 min	160 °C, 1.2 MPa, 2 h	—	—	—	I1	187
	Softwood kraft	—	—	30	Resin	Lignin + FF + water + acid, 50 °C, 60 min	—	—	—	—	I2	170
	Sugar cane bagasse	Sodium periodate	25 °C, 25 min	100	Resin – mold	• Phenol + F + NaOH, 70 °C, 1 h • Add resorcinol and lignin, 50 °C, 30 min	• 75 °C, 2.5 ton, 1 h • 85 °C, 5 ton, 30 min • 95 °C, 7.5 ton, 30 min • 105 °C, 7.5 ton, 30 min • 115 °C, 10 ton, 30 min	153	−31	—	I3	188
	Kraft	—	—	50 + 5, 10, 15, 20, 30 furfural substitution	Resin – plywood	F/P: 1.6 • 80 °C, 180 min + NaOH • 90 °C, 50 min, 70%F • 40 min, 30%F + FF	250 g m^{-2} 140 °C, 17 MPa, 4 min	LFF-10: 1.19 LFF-15: 1.30 LFF-20: 1.11 LFF-30: 1.01	−6 2 −13 −20	0.21 0.24 0.47 0.71	I4	181
	Sugar maple acid hydrolyzed	—	—	5, 8, 16 furfural substitution	Resin – adhesive reinforced glass fibers	• 0, 5, 8, 16% FF • 90 °C, 60 min	250 g m^{-2} 150/180 °C, 3 MPa, 4 min	LFF-5: 9.96[b] LFF-8: 9.35[b] LFF-16: 7.33[b]	−11 −16 −34	—	I5	7
Depolymerization	Hydrolysis (phenolated)	Patent pending	150–250 °C, 30–120 min, <250 psig	50 + additive	Resin	Mix lignin + FF + glucose + water + catalyst	—	89	-18	—	I6	171
Low transition temperature mixtures	Enzymatic hydrolysis	Oxalic acid, choline chloride	100 °C, 6 h	20, 40, 50, 60, 80	Resin – plywood	FF/P: 0.8 • Mix P + NaOH, 45 °C • Add furfural + urea, 135 °C, 2 h	—	LTLFF-20: 2.05 LTLFF-40: 1.92 LTLFF-50: 1.84 LTLFF-60: 1.64 LTLFF-80: 0.98	−7 −13 −17 −26 −56	0.30[a] 0.33[a] 0.39[a] 0.45[a] 0.53[a]	I7	182

Table 10 *(Contd.)*

Modification	Lignin type	Reagent	Conditions	Lignin substitution, %	Application	Resin synthesis	Hot press conditions	Bonding strength, MPa	Bonding strength percent difference, %	Free formaldehyde content[a], %	Symbol	Ref.
Oxidation	Bagasse	ClO_2, acetic acid	55 °C	15	Resin – mold	F/P: 1.37 KOH/P: 0.06 • Mix P + F + KOH 70 °C, 60 min • Mix lignin + FF	250–300 g m^{-2} 130 °C, 1 MPa, 7 min	OLFF: 0.24	7	—	I8	67

[a] Free aldehyde content. [b] *N*/(m g).

soda black liquor lignin saw a remarkable 295% increase (1.7 MPa) at 15 wt% lignin, using an epoxy enhancer, which eliminated formaldehyde (B5 in Table 3). LMFAs with hydroxymethylated alkali lignin were improved by 47% (1.34 MPa) at 6 wt% lignin with a urea enhancer (C2 in Table 4). LSPAs with depolymerized reed magnesium bisulfite lignin showed a significant 228% increase (10.42 MPa) at 17 wt% lignin with T-31 as an enhancer (D12 in Table 5). LPUA foams with demethylated softwood lignin saw an outstanding 942% increase in compression strength (0.34 MPa) with 34 wt% lignin and PEG 200 as an enhancer (E8 in Table 6). LPEIA with poplar wood lignocellulose achieved the highest relative improvement, with a 2957% increase (2.14 MPa) using 95 wt% lignocellulose and glutaraldehyde as an enhancer (F1 in Table 7). LTA with glyoxalated organosolv lignin showed a moderate 16% increase (0.81 MPa) at 10 wt% lignin (G1 in Table 8). LSPA with epoxidized enzymatic hydrolysis lignin experienced a strong 364% increase (1.02 MPa) at 41 wt% lignin (H15 in Table 9). LFA with oxidized bagasse lignin exhibited a limited 7% increase (0.24 MPa) at 15 wt% lignin, utilizing a PF resin prepolymer enhancer (I8 in Table 10). While these formulations exhibit the most substantial improvements in performance, a key downside is that all rely on expensive enhancers to achieve these results.

Despite progress in lignin-incorporated resins, they still face challenges. Future advancements in lignin-based adhesives should prioritize reducing formaldehyde emissions, enhancing water resistance, and increasing lignin content to improve the sustainability of resins. Phenol-, urea-, and melamine–formaldehyde adhesives must minimize formaldehyde content while maintaining cost-effectiveness and performance, and epoxy and polyurethane variants should replace petroleum-based components with sustainable alternatives for polyols and curing agents. Tannin and soy protein adhesives require improved curing efficiency and durability, whereas furfural and polyethyleneimine adhesives need optimized processing and scalability for broader applications. Enhancing the bonding strength, thermal stability, and overall adhesive performance is crucial for lignin-based systems to compete with conventional adhesives. Additionally, integrating circular economy principles by utilizing lignin from waste streams, developing formaldehyde-free formulations, and expanding applications into the automotive, construction, and packaging industries will drive commercialization and environmental benefits. Lignin-based adhesives show strong potential across various formulations. Lignin–phenol–formaldehyde adhesives lead in research due to their ability to replace phenol while maintaining strong bonding properties. Lignin-epoxy and lignin–polyurethane adhesives offer excellent mechanical strength and versatility, with ongoing research optimizing curing and reactivity (Tables 5 and 6). Lignin-polyethyleneimine adhesives demonstrate high bonding strength for wood applications. Additionally, soy proteins, PEI, and furfural can be used as enhancers to improve adhesion in synthetic adhesives, such as LPF, LPU, and LEP. Lignin–tannin adhesives stand out for being fully bio-based with strong

adhesive properties. Continued advancements focus on improving performance, sustainability, and scalability to enhance commercial viability. Lignin–phenol–formaldehyde (LPF) adhesives are among the most commercially available, with companies like Latvijas Finieris incorporating bio-based lignin from Stora Enso to reduce reliance on fossil-based phenols in plywood production while maintaining performance and lowering carbon footprints[189] Similarly, the properties of lignin–polyurethane (LPU) adhesives have improved, facilitating their broader commercialization, with efforts focused on improving sustainability and performance.[190]

Despite their promise, lignin-based adhesives still face challenges in reactivity, chemical heterogeneity, and performance, often struggling to match the strength, durability, and water resistance of synthetic alternatives. Issues such as odor, color, and formaldehyde emissions further limit their adoption, while high extraction and modification costs make scalability challenging. Market acceptance remains a hurdle as industries hesitate to transition from traditional adhesives. Additionally, a lack of standardized curing and resin synthesis procedures in the literature makes it difficult to compare formulations, even within the same adhesive type, further complicating research and development efforts.

Conclusion

Lignin shows promising potential for use as a feedstock in industrial adhesive systems. Not only does the application of this biomass precursor reduce production costs, decrease environmental pollution, and decrease our dependency on petroleum, but it also reduces lignin waste. Unfortunately, the use of lignin is not yet practical due to its low reactivity and complex heterogeneous structure. Various modifications can enhance the reactivity of lignin. Among the most common methods are demethylation, depolymerization, phenolation, hydroxymethylation, and glyoxalation. The best-performing adhesive was reported to use enhancers. Alkali lignin nanoparticles in a PF resin adhesive with a urea enhancer (30 wt% lignin) increased tensile strength by 64% (1.59 MPa) while maintaining a free formaldehyde content of only 0.12%, well below the Chinese standard of 0.3% (A18). Similarly, hydroxymethylated lignin in a UF resin adhesive with a melamine enhancer (5 wt% lignin) acted as a polyacid catalyst, enhancing the bonding strength by 67% (from 1.72 MPa) while reducing free formaldehyde emissions compared to commercial resin catalysts (B9). Although less researched, hydroxymethylated alkali lignin in an MF resin adhesive with a urea enhancer (6 wt% lignin) resulted in a 47% increase in bonding strength (1.34 MPa) with minimal formaldehyde emissions (0.06%) (C2). In epoxy resin systems, depolymerized lignin (reed magnesium bisulfite) with an E-57 resin enhancer (15 wt% lignin) improved bonding strength by 228% (10.42 MPa) compared to commercial epoxy resins (D12). In PU resin foam applications, demethylated softwood lignin with a PEG 200 enhancer (34 wt% lignin) resulted in a remarkable 942% increase in compression strength (0.34 MPa) (E8). In tannin resin adhesives, glyoxalated lignin (oil palm empty fruit bunch) with a PEI enhancer (40 wt% lignin, 20 wt% PEI) achieved a 103% increase in bonding strength (63.16 MPa) over formulations without PEI (F7). Epoxidized enzymatic hydrolysis lignin in a soy protein resin adhesive (41 wt% lignin) boosted the wet bonding strength by 364% (1.02 MPa), though the addition of a preservative reduced this increase to 291% (0.86 MPa) (G14). Oxidized bagasse lignin in a furfural-PF resin mold (15 wt% lignin) provided a modest 7% improvement in bonding strength (0.24 MPa) (H8). Finally, a poplar wood lignocellulose PEI resin adhesive with a glutaraldehyde enhancer (95 wt% lignin) exhibited the most dramatic increase, with the bonding strength improved by 2957% (from 0.72 to 2.14 MPa) (I1). These findings highlight the diverse applications of lignin-based resin materials, demonstrating their potential as sustainable, high-performance alternatives in adhesive and composite resin formulations. However, challenges in reactivity, consistency, and performance often result in falling short of synthetic alternatives in terms of strength, durability, and water resistance. Additionally, factors such as odor, color, and formaldehyde emissions hinder widespread adoption, while high processing costs limit scalability. Market reluctance to shift from conventional adhesives further slows progress. Continued research and innovation in lignin modification, cost-effective processing, and performance optimization will be essential for bridging the gap between lignin-based and synthetic resin adhesives, paving the way for wider industrial adoption.

Author contributions

Juan Paez: conceptualization, literature search, writing – original draft preparation. Pedram Fatehi: supervision, writing – review & editing.

Conflicts of interest

The authors declare no financial and non-financial conflicts of interest.

Abbreviations

PF	Phenol-formaldehyde
LPF	Lignin–phenol–formaldehyde
LPFA	Lignin-phenol formaldehyde adhesive
UF	Urea-formaldehyde
UFA	Urea-formaldehyde adhesive
LUF	Lignin-urea-formaldehyde
LUFA	Lignin-urea formaldehyde adhesive
GDE	glycerol diglycidyl ether
MA-HL	Maleated lignin-based polyacid catalyst
MF	Melamine–formaldehyde
MUF	Melamine-urea-formaldehyde

LMF	Lignin-melamine–formaldehyde
LMFA	Lignin-melamine formaldehyde adhesive
LEA	Lignin-epoxy adhesive
BPA	Bisphenol-A
ECH	Epichlorohydrin
DGEBA	Diglycidyl ether of bisphenol A
TBAB	Tetrabutylammonium bromide
PU	Polyurethane
LPU	Lignin–polyurethane
LPUA	Lignin–polyurethane adhesive
TDI	Toluene diisocyanate
DEG	diethylene glycol
PEI	Polyethyleneimine
LPEIA	Lignin-polyethyleneimine adhesive
MAP	Marine adhesive protein
PVC	for polyvinyl chloride
OPP	oriented polypropylene
PET	polyethylene terephthalate
LTA	Lignin–tannin adhesive
SP	Soy protein
LSPA	Lignin-soy protein adhesive
KL	Kraft lignin
CNF	Cellulose nanofiber
PDA-BN	Dopamine-functionalized hexagonal boron nitride
LFA	Lignin-furfural adhesive
F/P	Formaldehyde/phenol, mol mol^{-1}
F/U	Formaldehyde/Urea, mol mol^{-1}
FF/MA	Furfural/malic acid, mol mol^{-1}
FF/P	Furfural/phenol, mol mol^{-1}
NaOH/P	Sodium hydroxide/phenol
WBB-LPF	White birch bark lignin–phenol–formaldehyde
WSB-LPF	White spruce bark lignin–phenol–formaldehyde
LPF	Lignin–phenol–formaldehyde
PLPF	Phenolated lignin–phenol–formaldehyde
NLPF	Lignin nanoparticle-phenol-formaldehyde
MLPF	Lignin macroparticle-phenol-formaldehyde
B-LUF	Alkali bagasse lignin-urea-formaldehyde
M-LUF	Alkali molasses lignin-urea-formaldehyde
LUF	Lignin-urea-formaldehyde
GLUF	Glyoxalated lignin-urea-formaldehyde
ILUF	Ionic liquid modified lignin-urea-formaldehyde
HLUF	Hydroxymethylated lignin-urea-formaldehyde
DLUF	Demethylated/depolymerized lignin-urea-formaldehyde
PLUF	Phenolated lignin-urea-formaldehyde
NLUF	Lignin nanoparticles-urea-formaldehyde
TLMF	Tosylated lignin-melamine–formaldehyde
HLMF	Hydroxymethylated lignin-melamine–formaldehyde
LEP	Lignin-epoxy
WDLEP	Water-soluble lignin-epoxy
ADLEP	Ammonia water/ethanol soluble lignin-epoxy
EDLEP	Ethylenediamine/ethanol soluble lignin-epoxy
DLEP	Demethylated/depolymerized lignin-epoxy
PLEP	Phenolated lignin-epoxy
ALEP	Aminated lignin-epoxy
NLEP	Lignin nanoparticles-epoxy
DLPU	Demethylated/depolymerized lignin–polyurethane
OLPU	Oxypropylated lignin–polyurethane
NLPU	Lignin nanoparticles-polyurethane
LPEI	Lignin-polyethylenimine
DLPEI	Demethylated/depolymerized lignin-Polyethylenimine
OLPEI	Oxidized lignin-polyethylenimine
NLPEI	Lignin nanoparticles-polyethylenimine
GLT	Glyoxalated/glycidolated lignin–tannin
OLT	Oxypropylated lignin–tannin
LSP	Lignin-soy protein
DLSP	Demethylated/depolymerized lignin-soy protein
DLSP-R	Reduced-demethylated lignin-soy protein
ALSP	Phenolated lignin-soy protein
EPLSP	Lignin nanoparticles-soy protein
CLSP	Carboxymethylated + hexagonal boron nitride functionalized lignin-soy protein
LFF	Lignin-furfural
DLFF	Demethylated/depolymerized lignin–furfural
LTLFF	Low transition temperature mixture modified lignin–furfural
OLFF	Oxidized lignin–furfural
LTTM	Low-temperature transition mixture

Data availability

No primary research results, software or code has been included and no new data were generated or analysed as part of this review.

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