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Perspective

Lignin-Based Covalent Adaptable Network Polymers—When Bio-Based Thermosets Meet Recyclable by Design

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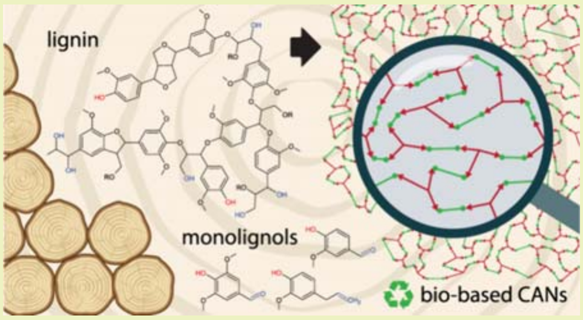

ABSTRACT: Covalent adaptable networks (CANs) play an important role in polymer chemistry, as they provide an innovative link between thermoplastics and thermosets. The breakthrough idea behind CANs is to at least partially replace irreversible crosslinks in classic thermoset polymers with dynamic covalent bonds that allow for reversible polymer character and recyclability. Besides, CANs also offer other popular features such as self-healing, weldability, configurability, and shape memory. Most CANs are still petroleum-based, yet shifting toward more sustainable approaches is of the utmost interest. Considering this and the high abundance of lignocellulosic biomass, this perspective focuses on all the research found on lignin-based CANs, including both those starting from fractionated lignin and from lignin-based monomers. This is clearly a new branch within bio-based CANs that holds great potential in various industries. Additionally, some examples of thermoset polymers derived from the same lignin building blocks are given to showcase important chemical transformations that can be used for CANs design in the future. Although CAN design has been extended to many different types of bonds, imines and disulfides largely prevail in the current literature. Lastly, a SWOT (strengths, weaknesses, opportunities, and threats) analysis is presented, considering the performance, competition, opportunities, and drawbacks of lignin-derived CANs.

KEYWORDS: *Dynamic Covalent Bonds, Bio-Based Polymers, Lignin, Vanillin, Eugenol, Syringaldehyde*

INTRODUCTION

The type of molecular interaction defines the properties of matter. In the context of polymers, thermosets and thermoplastics are distinguished. In thermoplastics, the polymer chains are associated via weak intermolecular interactions, for instance, van der Waals forces, which endow them with certain properties, such as moldability at an elevated temperature. Thermosets, on the other hand, are polymers in which the polymeric chains are held together by irreversible (covalent) bonds, hence conferring them more resistance to solvents and corrosive environments.[1] Due to the strong crosslinking between the polymer chains, which is ensured by reactive functional groups on the monomer units, thermosets also display better mechanical properties and thermal stability compared to thermoplastics.[2] They do not melt or dissolve even under harsh conditions[3] and are prone to irreversible damage by high stress. Therefore, thermosets typically cannot be reprocessed or recycled, and after their useful life, disposal accompanied by consequential environmental pollution is usually the only option.

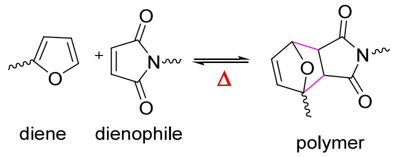

Figure 1. Primordial example of the CAN concept. Diels−Alder linkage is cleaved and reformed upon thermal change (bold red).[8] Reversible bonds are highlighted in bold purple.

Despite the general belief that thermosets are not recyclable, there have been some attempts in this regard. Mechanical, thermal, chemical, and high-voltage fragmentation are commonly used to recycle thermosets.[4,5] Among the chemical recycling methods, a fiber-matrix separation method applied to carbon fiber reinforced thermosets with two different media (water and a water/ethanol mixture) under sub- and supercritical conditions has been reported.[6] More modern and forefront recycling methods also exist, such as sono-chemical transformation. Specifically, an epoxy−amine thermoset embedded with Diels−Alder (DA) bonds has been successfully

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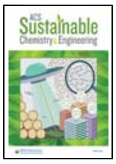

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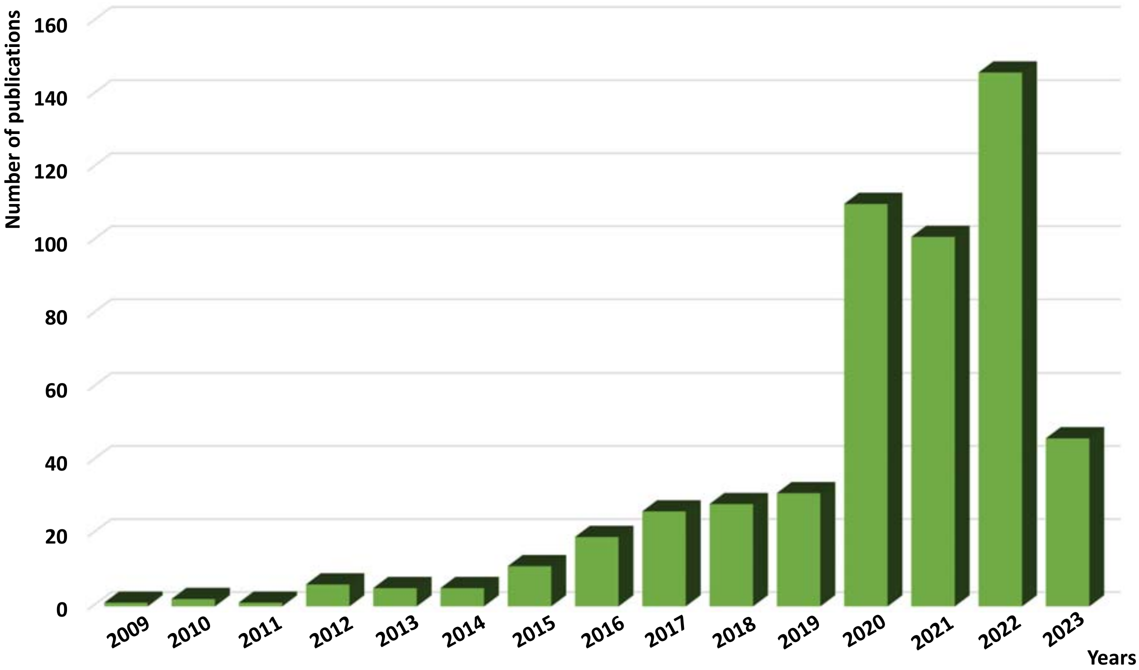

Figure 2. Number of articles published per year (2009−2023) using "covalent adaptable networks" as a keyword in Web of Science. Data assessed April 23, 2023.[42]

transformed into the soluble polymers by means of sonochemistry.[7] However, these approaches are not straightforward nor widely applicable for the different types of thermosets; thus, a more practical solution is still sought after.

The concept of covalent adaptable networks (CANs) was developed in 2002.[8] Authors described this subclass of thermosets as an organic polymeric material that can repeatedly be mended or "remended" under mild conditions. Herein, a thermally reversible DA cycloaddition of a multifuran diene and multimaleimide dienophile was used to prepare the thermoset (Figure 1). It was observed through solid state NMR that at temperatures above 120 °C, approximately 30% of linkages disconnected and then reconnected again upon cooling.

It is now well established that dynamic covalent bonds are the key to CANs. This particular type of reversible bonds possesses an intermediate bond dissociation energy, which allows chemical reactions to proceed reversibly and give the thermodynamically most stable product under the selected conditions.[9] Among the wide variety of reversible chemical linkages, the most common are reversible radical interactions, acylhydrazone bonds,[10] boronate ester complexes,[11] DA bonds,[8] diselenide bonds,[12] disulfide bonds,[13] and imine (Schiff base) bonds.[14] This broad range of bonds makes the so-formed networks more responsive to different types of stimuli, such as light, temperature, chemicals and/or pH.[3] When these are incorporated into resins forming the matrix material, they allow us to tune the properties of new and reprocessable thermosets for target applications.

Classical thermosets describe a generic family of polymers including, for example, unsaturated polyesters, vinyl esters, epoxy, and polyurethane resins,[15] typical representatives of CANs encompass epoxy-,[16] polyester-,[17] polyurethane-,[18] polyacrylate-[19] and phenolic-based resins. Among the most common monomer units used in CAN design are (i) bisphenol A diglycidyl ether (BADGE)[20] and diglycidyl ether of bisphenol F (DGEBF),[21] which are used to prepare epoxy-based CANs; (ii) diols[22] and dicarboxylic acids,[23] which are employed to produce polyester-based CANs; (iii) hexamethylene diisocyanate (HDI)[24] and toluene diisocyanate (TDI) that are usually selected for the formation of polyurethane-based CANs; (iv) methyl methacrylate (MMA)[25] and butyl acrylate (BA), which are commonly chosen to formulate acrylate-based CANs; and (v) phenol and formaldehyde[26] are preferred to develop phenol-based CANs. Despite their varying compositions, all of these materials are petroleum-based, which is no longer acceptable, given the current environmental crisis. Not only are they nonrenewable but also their extraction and processing pose detrimental effects on the environment, causing air, soil, and water pollution, habitat destruction, and climate change. In this sense, it became imperative to switch to renewable resources as raw materials for the preparation of bio-based CANs.

To render the canonic thermosets more sustainable, considerable efforts have been dedicated toward designing bio-based CANs from renewable resources, especially in the past decade. The targeted feedstocks are vegetable oils,[27,28] natural rubbers,[29] sugars,[30] lignin,[31,32] and lignin derivatives.[33,34] The increasing interest into the advanced CAN materials is evidenced by several excellent reviews on the topic,[2,14,18,35−41] while the number of publications involving CANs has also raised significantly, especially in the past few years. Considering the period from 2009 to 2023 (updated on April 2023), 538 results were generated on Web of Science using the keyword "covalent adaptable networks" (Figure 2).[42] However, the keywords "bio-based covalent adaptable networks", "lignin-based covalent adaptable networks", and "lignin-based thermosets" only afforded a few hits, namely 3,[43] 1,[44] and 37,[45] respectively, which demonstrates the paucity of research dealing with bio-based and lignin-based CANs, which is addressed in this review paper. Note also that the last keyword investigated does not guarantee reprocessable thermosets, and in fact, several papers included consider the preparation and/or application of traditional thermosets.

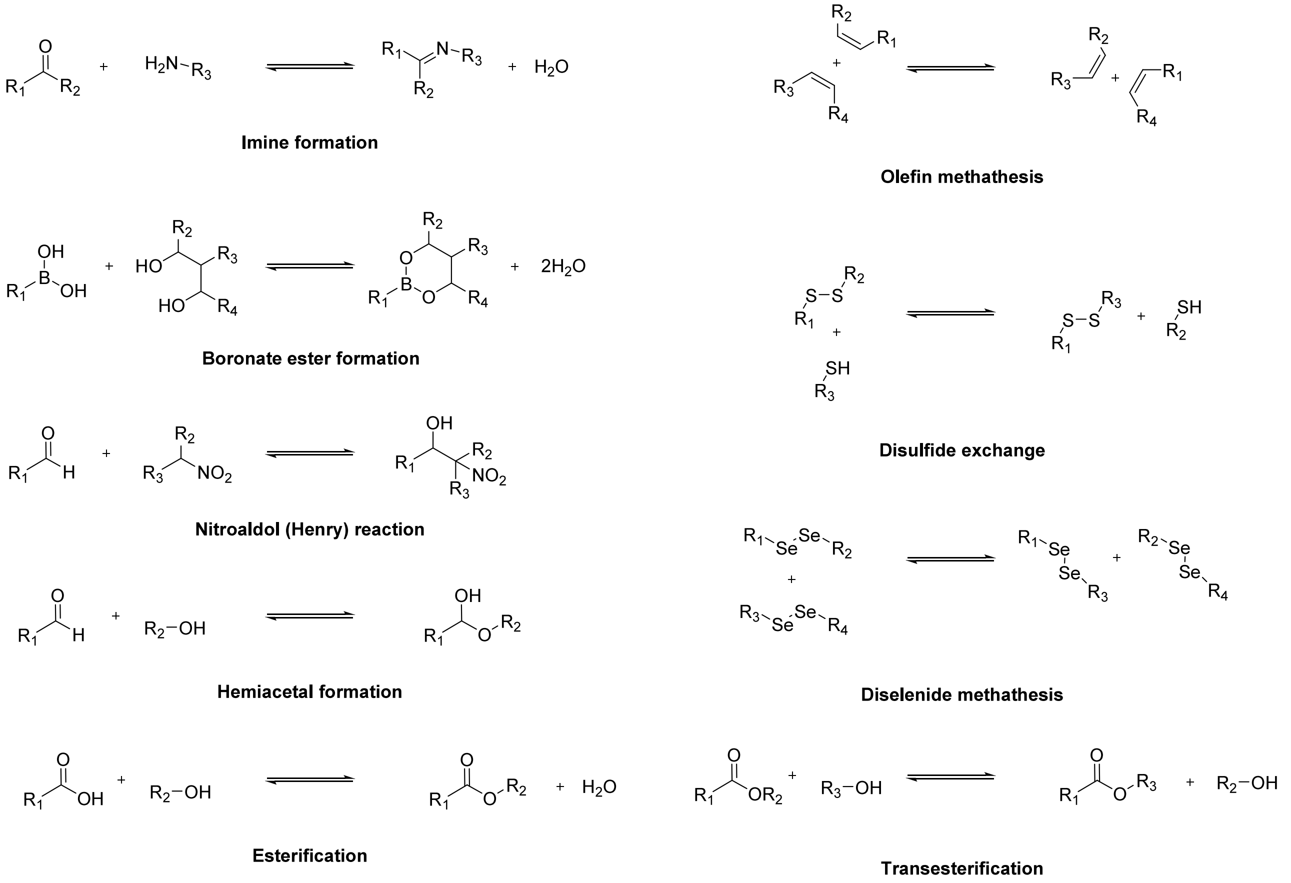

Figure 3. Common representative examples of dynamic covalent reactions.[46−48]

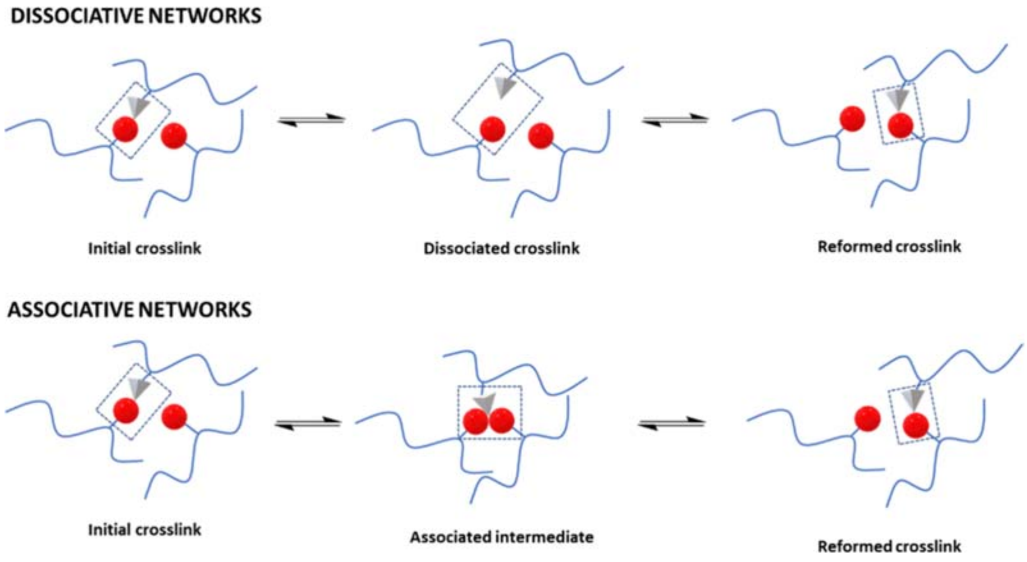

Figure 4. Schematic representation of dissociative and associative types of CANs. In dissociative CANs the degree of connectivity decreases with temperature, whereas in the associative type a constant fixed network is the hallmark even during bond exchange.

In summary, traditional thermosetting polymers are polymers that undergo irreversible crosslinking, making them rigid and difficult to recycle or reshape after curing. In contrast, CAN-based polymers are polymers with dynamic and reversible covalent bonding, which allow them to be reshaped, repaired, and/or reprocessed multiple times upon a stimulus without significant degradation of properties. Most CANs are still petroleum-based, yet shifting toward more sustainable approaches are of the utmost interest. Considering this and the high abundance of lignocellulosic biomass, some authors have focused on lignin-based CANs, where the polymeric material incorporates lignin to create sustainable and eco-friendly materials while reducing the environmental impact and the dependence on fossil derivatives.

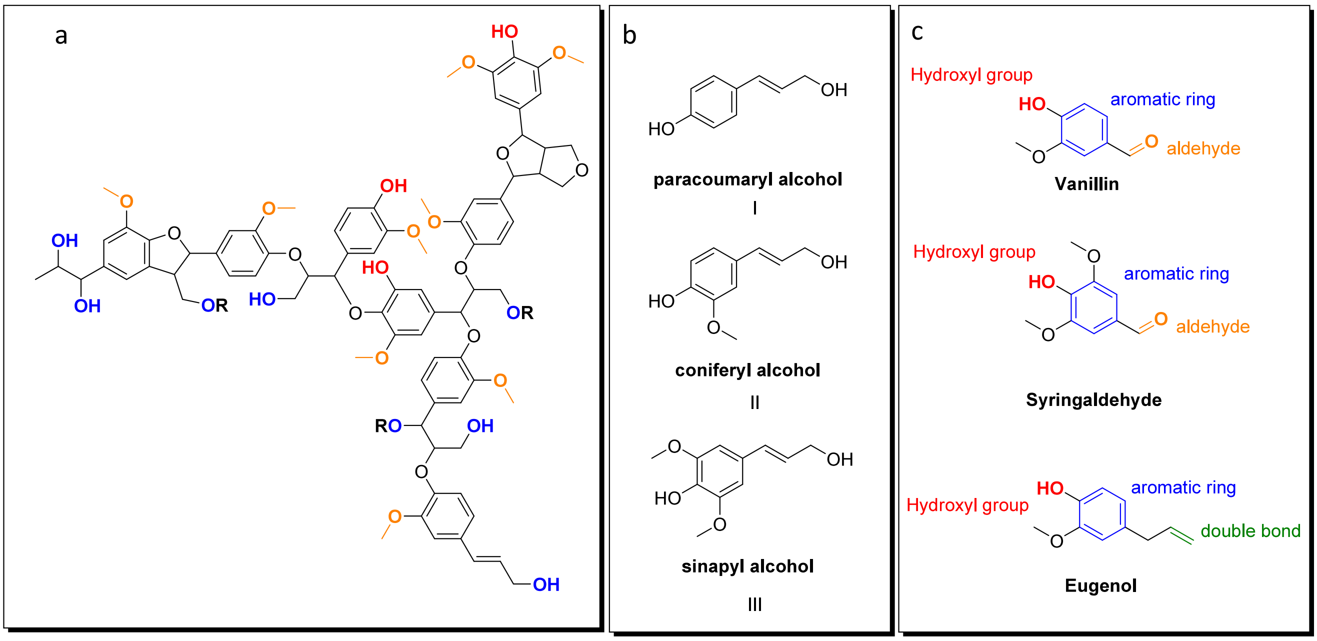

Figure 5. (a) Simplified structure of organosolv lignin. Alcoholic groups are marked in bold blue, phenolic in bold red, and methoxy in bold orange. (b) Three main aromatic alcohols (monolignols) that form lignin by oxidative polymerization: paracoumaryl alcohol (I), coniferyl alcohol (II), and sinapyl alcohol (III). (c) Structure of vanillin, syringaldehyde, and eugenol with respective reactive sites.

Table 1. Main Features of the Pulping Processes

Pulping process	Reaction conditions	Advantages	Disadvantages
Soda pulping	NaOH at temperatures up to 170 °C.[62]	Sulfur-free; Performed at industrial scale.[66]	Condensation reactions hinder further lignin valorization.[62]
Kraft pulping	NaOH and Na_2S at temperatures around 170 °C.[62]	Reduced reaction times, more efficient waste recovery;[67] Wider employability of woods;[68] Performed at industrial scale.	Smell of hydrogen sulfide and other thiols.
Sulfite pulping	Sodium, ammonium, or magnesium sulfite or bisulfite salts at temperatures between 140 and 170 °C.[62]	Highest pulp yields;[69] Reduced Environmental Impact;[69] Performed at industrial scale.	Sulfurous acid is hazardous for health;[69] Expensive technique due to chemicals and energy consumption;[69]
Organosolv	Organic solvents such as methanol, ethanol, acetone glycols, esters, organic acids.[62,68]	High level of delignification;[70] Relatively easy solvent recovery;[70] Wide applicability to both woody and nonwoody biomass;[70] More sustainable approach.	High energy requirements;[71] Use of flammable solvents and potential for explosion;[71] Performed at a pilot scale.

Numerous everyday items made from fossil fuels contain components that are detrimental to consumers and are not sustainable. Novel biopolymer solutions are therefore receiving increased attention, but they are either difficult to produce or lack essential properties, such as mechanical rigidity and age resistance. Another frequent issue is that the cost of such materials is a barrier to industries that want to switch to greener materials. In the woody cell wall of plants, lignin serves as a crucial, multifunctional antiaging and strengthening element at an alluring price.

Hence, this attracted our attention to highlight the underexplored topic of lignin-based CANs, identify research gaps, and emphasize the most important challenges to be addressed in the future.

■ REVERSIBLE BONDS: THE KEY PLAYERS IN COVALENT ADAPTABLE NETWORKS

Reversible bonds, as the name evokes, are bonds that can break and reform under appropriate conditions as opposed to the irreversible bonds, which do not reform easily after they have been broken due to the huge energy change accompanying bond cleavage. Furthermore, dynamic covalent bonds are the type of reversible bonds that enable the molecular structure to respond chemically to an external stimulus (i.e., heat, light, or solvent) and reform without the introduction of external energy or original reactants. The most common reactions involved in the formation of dynamic covalent bonds are listed in Figure 3.

Dynamic bonds can be of a dissociative or associative nature. Associative chemistry mostly relies on the kinetic control, whereas dissociative networks depend on thermodynamics.[38] The differences between the two types of dynamic bonds are listed in Figure 4.

In the case of CANs, loss in network connectivity following the dissociative mechanism of bond-breaking and bond-forming reaction sequence results in a decrease in crosslinking density.[49] On the other hand, associative CANs displays more fixed crosslinking density during the bond exchange, with simultaneous breakage and reformation of dynamic bonds. Polymers possessing the associative type of dynamic crosslinks are usually referred to as vitrimers,[50] the name being inspired by the viscosity-temperature relationship that resembles vitreous silica, following the Arrhenius-like dependence.[51] This concept has been comprehensively overviewed by several authors[41,52] while putting high focus on bio-based vitrimers. Typical examples of dissociative networks are given by the Diels−Alder reaction[49] and boronic ester formation,[53] whereas associative networks chemistry can be well represented by transesterification[51] and imine transamination.[53] Despite this general classification, some authors have demonstrated dissociative CANs to exhibit vitrimer-like properties.[54]

■ LIGNIN: AN UNDEREXPLORED BYPRODUCT

Lignocellulosic biomass, including agricultural and forest residues, is an abundant and renewable source of carbohydrates (cellulose and hemicellulose) and lignin. Lignocellulosic biomass accounts for 50% of the world's total available biomass.[55] Cellulose, the most abundant biopolymer on Earth,[56] can be used in many fields such as papermaking, clothing, cosmetics, and pharmacy,[57] while lignin as the most abundant natural aromatic polymer on the planet is typically considered a low value byproduct from the pulp and paper industry. Nonetheless, lignin has gained attention as a potential feedstock for the production of biofuels and other valuable chemicals. Due to its complex structure and chemical bonds involved, lignin is highly resistant to degradation, hence evidencing the difficulty in processing it and, in turn, explaining why it is still a poorly valorized residue. Yet, it is a unique renewable source of aromatic compounds, such as vanillin or eugenol, that are crucial to replace the respective petroleum-based counterparts. Therefore, in recent years, research has focused on affordable methods to transform lignin into value-added products including biofuels, biomaterials, and biochemicals, reinforcing and developing the idea of fully integrated biorefineries[58] contributing to a circular and green bioeconomy.[59]

Lignin is a complex polymer composed of aromatic monomers, whose synthesis starts in the cytoplasm of the plant cell and is followed by the transport of the three monolignols to the cell wall, where they are oxidized and polymerized to form lignin[60] (Figure 5a and b). The exact composition of lignin varies between plant species and even within different parts of the same plant. Nevertheless, it is generally composed of three main units: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S),[61] which are arranged in a highly crosslinked and three-dimensional network, providing structural support to the plant. Vanillin, syringaldehyde, and eugenol (Figure 5c) are compounds that are related to these units and will be discussed more deeply in the next paragraphs. Considering the general structure of lignin, it is the presence of hydroxyl and carbonyl groups that allow using lignin for the development of reprocessable thermosets and triggers the design of lignin-based CANs. The degree of crosslinking and the ratio of these units can, however, affect lignin properties, such as its solubility and reactivity.[57]

Lignin valorization starts with isolation from the lignocellulosic biomass. In order to obtain lignin in high yields, biomass is first delignified (pulping process), obtaining a solid fraction rich in cellulose and a liquid one mainly containing lignin and hemicellulose.[62] There are various pulping methods available, among which soda, kraft, sulfite and organosolv pulping are the most notable,[62] affecting the solubility and reactivity of produced lignins. In general, kraft pulping, where sodium hydroxide (NaOH) and sodium sulfide (Na_2S) are used to enhance delignification,[62] is strongly preferred over the other processes due to the ability of employing various types of wood and the high-quality fibers generated. Consequently, kraft lignin is a kind of industrial lignin, which accounts for about 85% of the total lignin production in the world.[63] However, kraft lignin is of very limited solubility and is only partly soluble in alkaline solutions.[64] In sulfite pulping, on the other hand, sulfite or bisulfite salts are employed which modify the aliphatic chains of lignin monomers and create lignosulfonates that are water-soluble, which is a huge advantage.[62] Finally, organosolv pulping is a more recent approach that utilizes organic solvents such as methanol or ethanol but also acetone, glycols, esters, and organic acids[65] for the solvolysis in presence or absence of acids, which act as catalysts (Brønsted, e.g., H_3PO_4, H_2SO_4, AcOH, CF_3SO_3H; or Lewis acids such as $FeCl_2$, $ZnCl_2$).[62] Consequently, organosolv lignin is soluble in ethanol, methanol, phenol, and dioxane.[64] A summary of the most common pulping processes as well as the main advantages and disadvantages can be found in Table 1.

In order to improve solubility of the lignocellulosic biomass, which is often problematic, a pretreatment step is typically applied that can be mechanical, chemical, physicochemical or biological.[72] However, other attractive alternatives have also been proposed, such as the use of neoteric solvents like ionic liquids (ILs) and deep eutectic solvents (DES). These have been used for lignin isolation due to their low vapor pressure, high thermal and chemical stability, high solvation capacity, low melting point, tailor-made characteristics as well as greener and recyclable character.[73,74] The benefit of using ILs is represented by the effective fractionation of various biomass components with high purity owing to selective dissolution of carbohydrates or lignin fractions.[75−77] Depending on the IL used as well as the biomass, IL is able to solubilize up to ∼50 wt % of the lignin[77] and allows for the extraction of up to ∼97 wt % of the lignin present in the lignocellulosic biomass.[76] Similarly, lignin yields and purity obtained by using DES ranged from 15 to 95% and 94%, respectively.[72] In addition to pure lignin isolation in high yields,[75−77] both ILs and DES have also shown outstanding performance in lignin depolymerization.[75,78−80] Over the past decade, many greener and more sustainable approaches have been developed for lignocellulose treatment; however, more research is still needed to put them along with the four lignins in Table 1.

Moreover, fractionation of lignin into homogeneous fractions is effective in reducing lignin heterogeneity. Lignin fractionation methods have been elaborated and their industrial potential discussed elsewhere.[81] Upon lignin breakdown, three main monolignols can be produced, namely coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol, which can be further processed and transformed into value-added chemicals of wide applicability, such as vanillin, eugenol, and syringaldehyde (Figure 5c). Vanillin, an aldehyde-containing phenol, is produced by tens of thousands of tons annually. It is used as a fragrance and a flavoring agent in food as well as in cosmetics and as a starting

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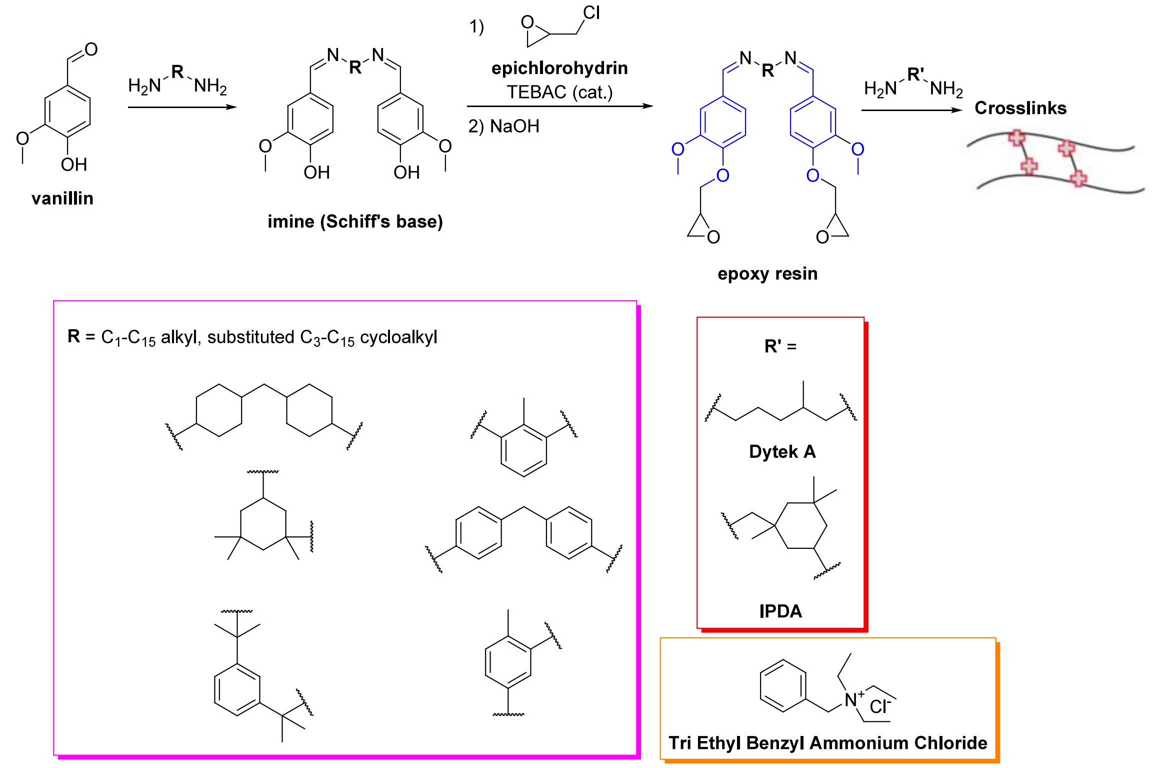
Table 2. Vanillin-Based CANs, Their Mechanical Properties, and Possible Applications

Tensile strength (MPa)	T_g (°C)	Dynamic bond/main chemistry involved	Amines used for formation of imines	Additional comments	Possible applications	Ref
na[a]	na[a]	Imine	Aliphatic and aromatic diamine	The epoxy derivative was cured with several diamines	—	96
80.3 (DDM-based)	183.0 °C (DDM-based) 214 °C (*p*-phenylenediamine-based)	Diimine reduced to diphosphonate intermediates	DDM[b] and *p*-phenylenediamine	Phosphorus-containing resin Curing agent: DDM	Flame retardants	34
(47.4 ± 2.5)−(57.1 ± 6.0)	48.0−64.0	Imine	Diethylenetriamine and tris(2-aminoethyl) amine	Butane linker between two vanillin monomers	Self-healing and chemically recyclable polymer materials	97
84.1 (no free CHO groups available for the dialdehyde)	75.0−89.0	Imine	Diethylene triamine	Vanillin dialdehyde (derived from 1,2-dibromoethane) and trifunctionalized aldehyde (phosphorus oxychloride-based)	—	98
34.6 ± 1.4	288.0 ± 2	Imine/disulfide bonds	Hexyl isocyanate	Dual dynamic covalent bonds of a Schiff base made from cystine exhibited self-healing and recyclability in crosslinked polyurethanes	Coatings, adhesives, foams, and elastomers	99
13−21	31.1 ± 0.4 (diamine-derived) 25.2 ± 0.3 (triamine-derived) Curing agent: BAPO	Imine	2,2′-(Ethylenedioxy)bis(ethylamine) or trimethylolpropane tris[poly(propylene glycol), amine terminated]	Methacrylation step (with methacrylic anhydride) was followed by the formation of imine	—	100
60.8	170.1	Imine	4-Amino-4*H*,1,2,4-triazole	Curing agent: bio-based 5,5′-methylenedifurfurylamine	Flame retardants	101
57.9 ± 0.9 (virgin) 56.3 ± 0.8 (recycled)	98.4	Imine	Polyetheramine D-230	Curing agent: Polyetheramine D-230	Flame retardants	102
62	70.0	Imine	4-Aminophenol	Curing agent: glycerol triglycidyl ether	Fully recycled carbon fiber reinforced composites	103
37.4 ± 4.1 (for the epoxy vitrimer with crosslinked density of 296.8 mol/m^3)	66.0	Imine	4,4′-Methylenedianiline	Curing agent: epoxidized soybean oil	Uncompetitive due to the costly and complex fabrication and purification of epoxy monomers	28

[a] Not available. [b] Abbreviations: BAPO: phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, CHO: aldehyde group, DDM: 4,4-diaminodiphenylmethane, Polyetheramine: Polyoxypropylenediamine.

Scheme 1. Chemical Synthesis of Vanillin-Based Epoxy Resins[96a]



[a] Different steps are discussed in the text. In the purple box are the amines used for the formation of a Schiff base, whereas some of the used curing agents are shown in the red box. Tri ethyl benzyl ammonium chloride catalyst is depicted in orange box. Red crosses indicate crosslinks formed between the epoxides by curing agents.

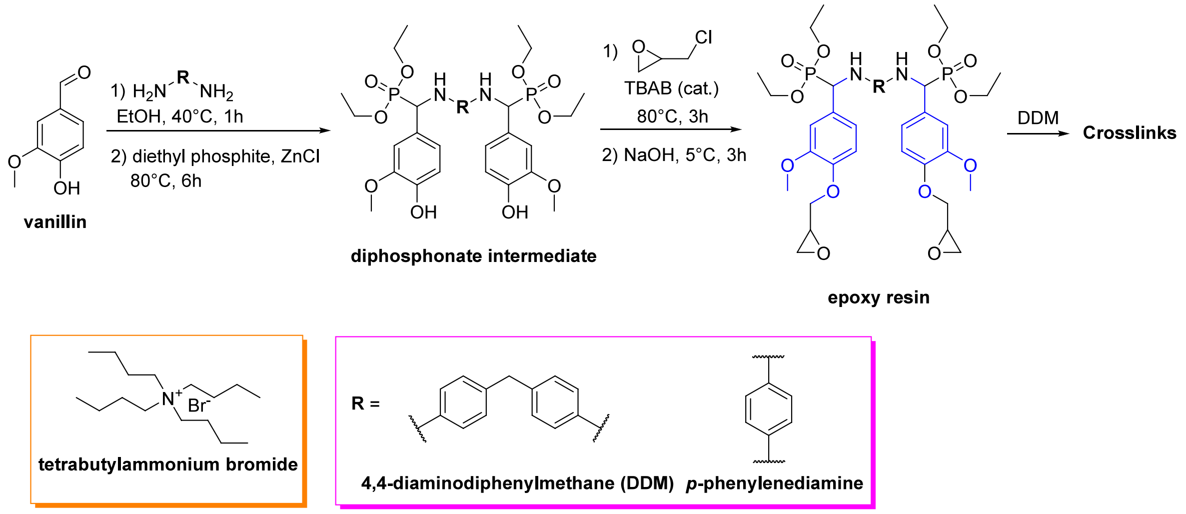
material for pharmaceuticals. Nowadays, naturally occurring vanillin and its production from depolymerization of lignin, which accounts for only 15% of the world production of vanillin,[82] cannot meet the rising world demand.[83] Nevertheless, its production from lignin is gaining increasing attention, as it is imperative to develop sustainable and renewable alternatives to petroleum-based flavoring compounds. Eugenol, on the other hand, is an allylic compound typically obtained from clove oil but also from lignin depolymerization.[84] Syringaldehyde is found in fruits, nuts, and plants that synthesize lignin and related compounds.[85]

■ LIGNIN-BASED CANS

Vanillin, eugenol, and syringaldehyde are all methoxyphenols that can be derived from the breakdown of lignin. Vanillin and syringaldehyde can be derived from the sinapyl units, whereas eugenol is related to the guaiacyl unit. Syringaldehyde is formed through the oxidation of sinapyl alcohol, while vanillin is formed through the oxidation of syringaldehyde. Eugenol, on the other hand, is produced by the methylation of coniferyl alcohol, which forms G-type units in lignin. The three lignin-derived aromatic monomers possess different reactive sites that can be exploited to obtain CAN resins. They all share phenolic and methoxy functionalities, while vanillin and syringaldehyde characterize themselves as phenolic aldehydes and eugenol has an alkene moiety attached. The phenolic, carbonyl, and allyl functional groups on the aromatic ring account for monomer's reactivity (*e.g.*, formation of reversible bonds and crosslinked modifications), whereas the methoxy group is generally inert and is usually left untouched. The respective reactive sites are listed in Figure 5c. In particular, the phenolic hydroxyl group can undergo O-glycidylation,[86] allylation,[87] alkoxylation,[88] hydroxyethylation,[89] and esterification.[90] The aromatic ring can undergo modifications such as oxidative coupling[91] and nitration,[92] while the double bond in eugenol can participate in several reactions, such as epoxidation,[93] thiol–ene reactions,[94] hydrogenation, and hydroxylation.[95] Last but not least, aldehydes are usually exploited for the formation of dynamic imine bonds given their electrophilic nature. Overall, lignin's unique chemical structure confers it high reactivity while also allowing it to break and reform covalent bonds under specific conditions, enabling the CAN polymer to be depolymerized into its constituent monomers or oligomers. This depolymerization process further contributes to the CAN possibility of recycling and reshaping the material.

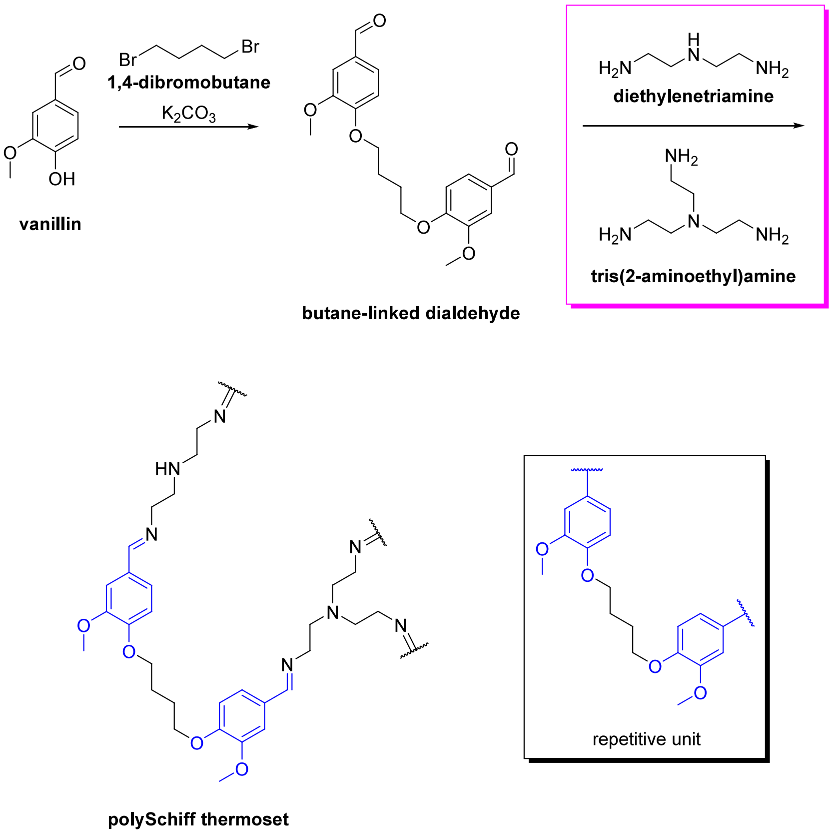
In this paper, lignocellulosic biomass is considered as a feedstock for bio-based CANs. Besides lignin-derived monomers such as vanillin, eugenol, and syringaldehyde, polymeric lignin isolates and lignin fractions are also explored as sources of lignin-based CANs. In general, the focus is on the underlying chemistry, which is discussed in parallel with the resulting mechanical and other relevant physicochemical properties of so-produced CANs that are largely scattered in literature. Among the most important mechanical properties are tensile strength (the resistance of a material to breaking under tension) and tensile modulus (a mechanical property that measures its stiffness) but also elongation at break, which measures the extent to which a material can deform before it breaks under the tensile stress. Moreover, glass transition temperatures (T_g) is another important property of thermosets describing the transition

Scheme 2. Chemical Synthesis of Phosphorous-Containing, Vanillin-Based Epoxy Resins[34a]



[a] Vanillin core is highlighted in blue. In the purple box are the amines used for the formation of a Schiff base, while 4,4-diaminodiphenylmethane (DDM) is also used for curing. Tetrabutylammonium bromide catalyst is shown in the orange box.

Scheme 3. Chemical Synthesis of Vanillin-Based polySchiff Thermosets[a]



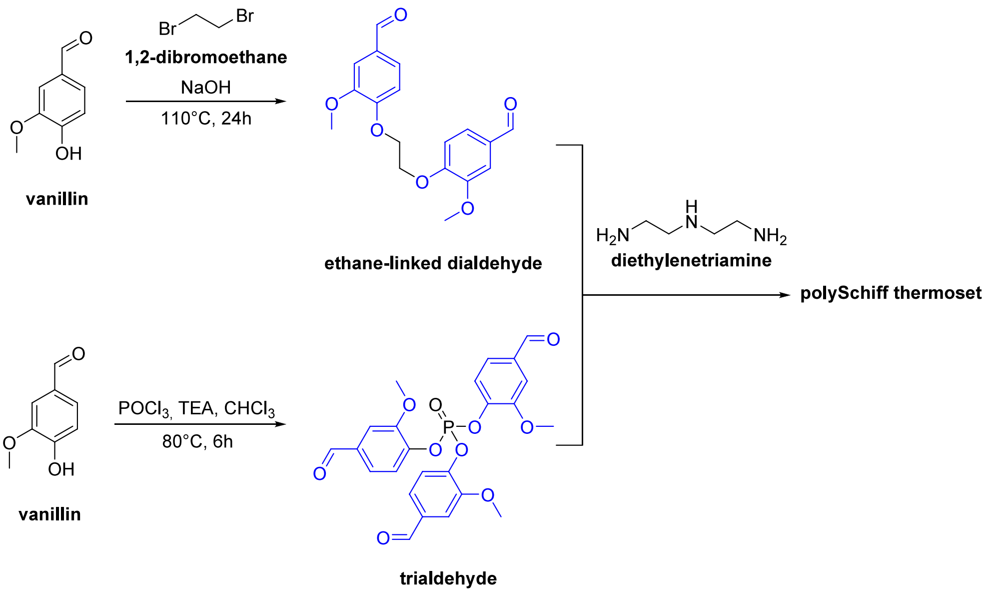
[a] Vanillin core is highlighted in blue. In the purple box are the amines used for the formation of a Schiff base. The repetitive unit contained in the thermoset is displayed in the gray box.

temperature at which a polymer transforms from a hard, glassy material to a soft, rubbery material. When considering the use of CANs as flame retardants, the limit oxygen index (LOI) is also considered, which refers to the minimum concentration of oxygen in a nitrogen/oxygen mixture that is needed to support the flaming. Later, a future outlook is given with the further inclusion of possible applications for specific CANs.

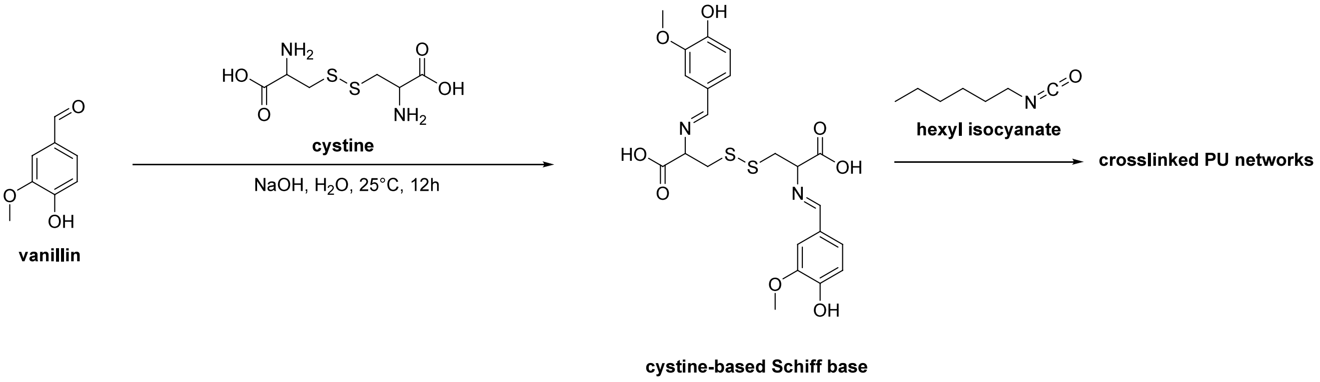
■ LIGNIN BUILDING BLOCKS-BASED CANS

Vanillin-Derived CANs. The majority of vanillin-based CAN monomers reported in the existing literature possess an

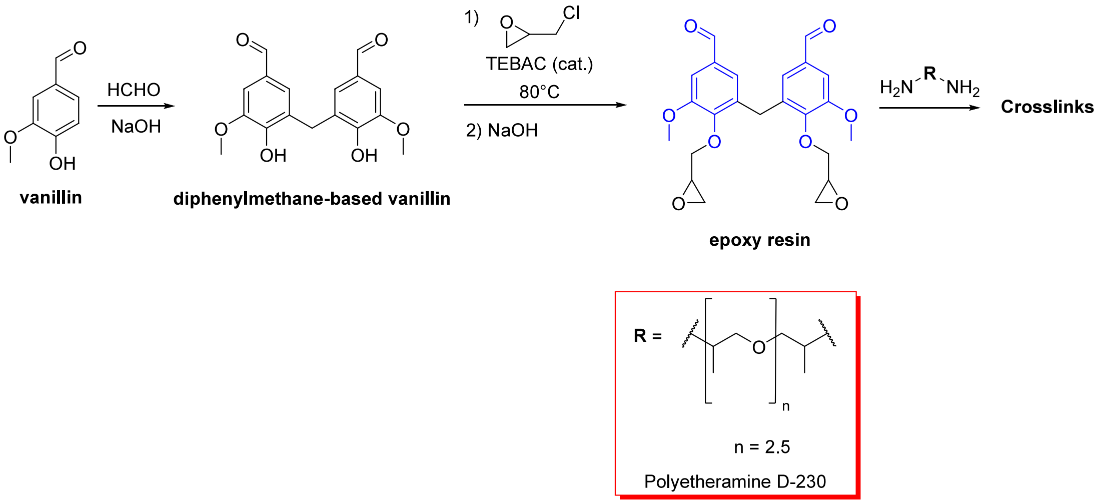
Scheme 4. Chemical Synthesis of Vanillin-Based polySchiff Thermosets via Mixing Dialdehyde and Phosphorous-Containing Trifunctionalized Aldehyde in the Presence of Diethylenetriamine as a Curing Agent[98]



Scheme 5. Chemical Synthesis of Crosslinked Polyurethane Networks from the Disulfide Bond-Containing Schiff Base Obtained from Cystine and Vanillin[99]

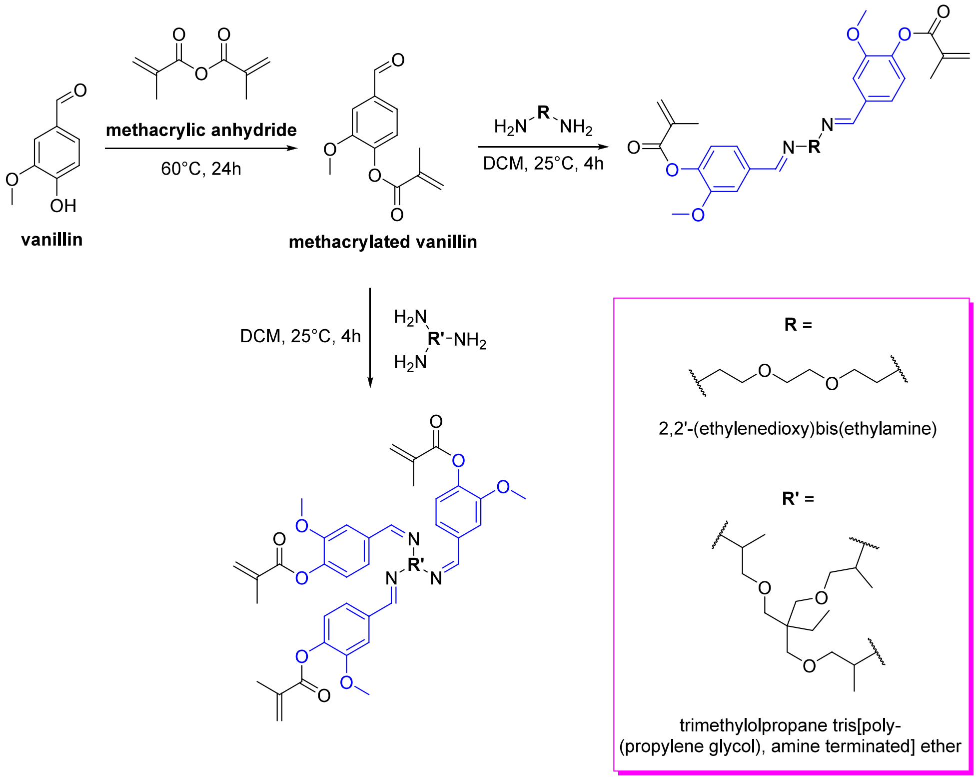


Scheme 6. Chemical Synthesis of Diphenylmethane-Based Epoxy Resin[33a]



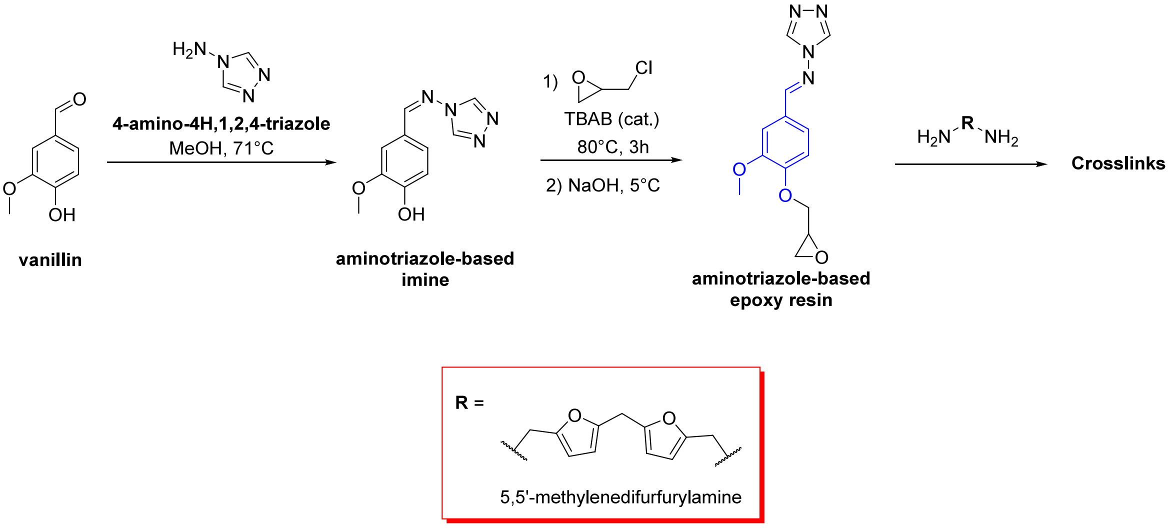
[a]Vanillin core is highlighted in blue. The curing agent Polyetheramine D-230 is shown in the red box.

Scheme 7. Chemical Synthesis of Vanillin-Based Vinyl Ester (Methacrylate) Resins[a]



[a]In the purple box are the amines used for the formation of a Schiff base.[100] Vanillin core is highlighted in blue.

Scheme 8. Chemical Synthesis of 4-Amino-4*H*,1,2,4-triazole-Based Epoxy Resin[101a]

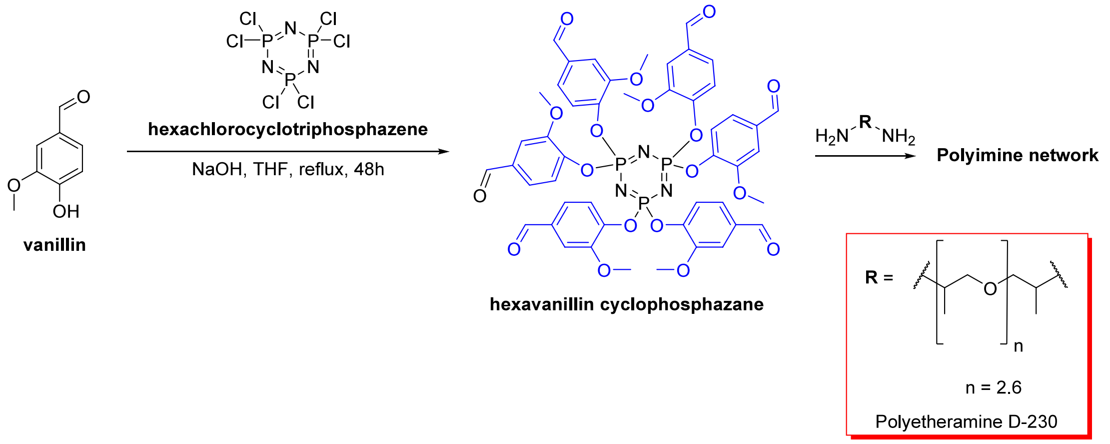


[a]Vanillin core is highlighted in blue. The bio-based curing agent 5,5′-methylenedifurfurylamine is shown in the red box.

imine, which is typically formed in a reaction between an aldehyde and a primary amine, and an epoxy functional group that is generally added to the phenolic group via alkylation. Alternative to epoxidation that allows for fast curing upon the addition of polyamines, acrylate ester groups can be introduced to the scaffold, serving on one hand for UV curing and, on the other hand, as an additional dynamic bond in the network. Polyurethanes possessing the dynamic imine bonds have also been reported, and some other modifications on the vanillin scaffold (*e.g.* oxidation or reduction) are also reviewed as a source of inspiration for the reader. The chemistry involved together with the mechanical and other relevant properties, and possible applications of the existing vanillin-based CANs are summarized in Table 2 and further discussed below.

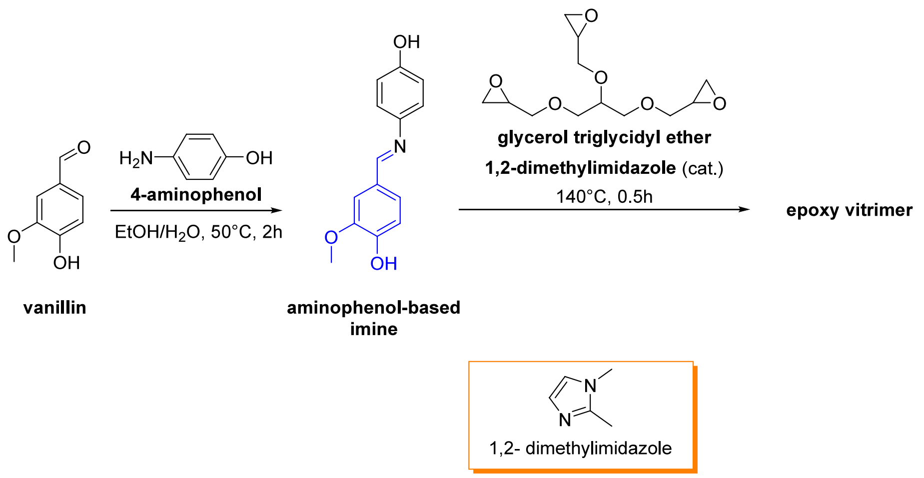
A group of generic imine-containing vanillin-based epoxy resins is reported. Several diamines (aliphatic and aromatic) have been used to first form a Schiff base starting from the aldehyde contained in vanillin.[96] A general strategy to form such

Scheme 9. Chemical Synthesis of Hexavanillin Cyclophosphazane-Based Polyimine Network Used in the Preparation of Carbon Fiber Reinforced Polymer Composites[102a]



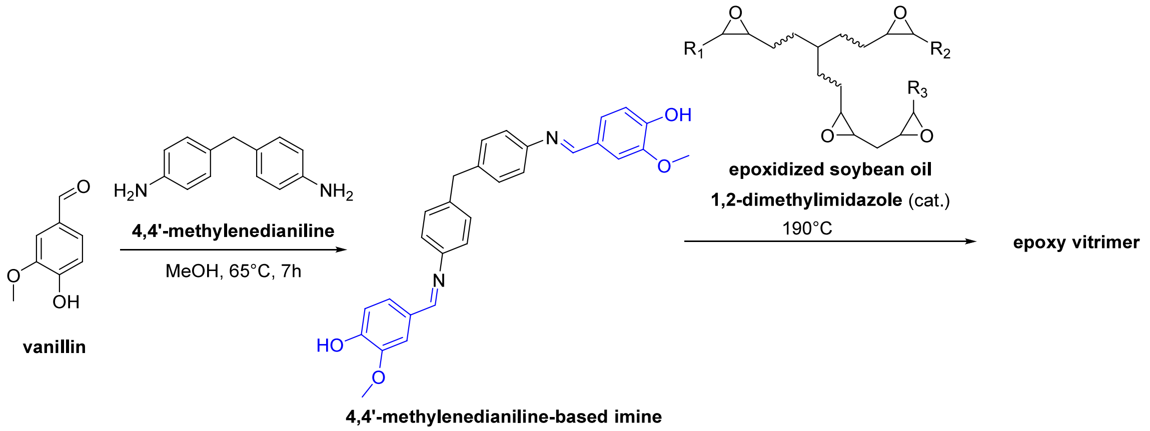
[a]Vanillin core is highlighted in blue. The curing agent Polyetheramine D-230 is shown in the red box.

Scheme 10. Chemical Synthesis of a Bio-Based Vitrimer Obtained from Vanillin and 4-Aminophenol and Subsequent Treatment with Glycerol triglycidyl ether[103a]



[a]Vanillin core is highlighted in blue. Structure of 1,2-dimethylimidazole is given in the orange box.

Scheme 11. Chemical Synthesis of a Bio-Based Vitrimer Obtained from the Epoxidized Soybean Oil[28a]



[a]Vanillin core is highlighted in blue.

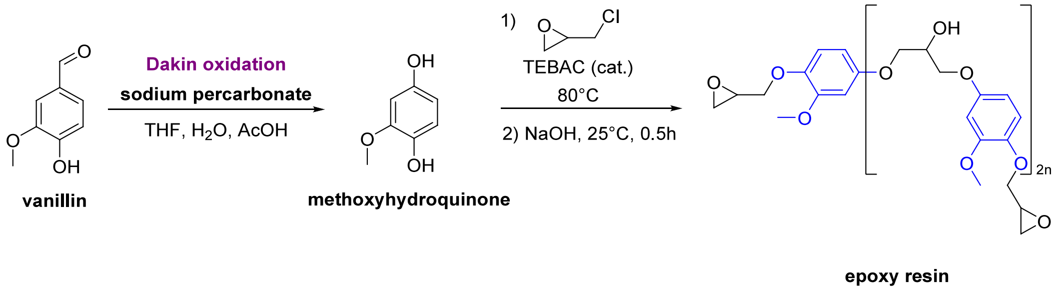
resins involves the initial reaction of vanillin with diamine. The resulting imine is then subjected to epichlorohydrin and a phase-transfer catalyst (*e.g.*, tri ethyl benzyl ammonium chloride, TEBAC) followed by the NaOH treatment. Lastly, the epoxy

Table 3. Vanillin-Based Polymers That Are Not Based on CANs, Their Mechanical Properties, and Possible Applications

Building block used	Tensile strength (MPa)	T_g (°C)	Source of dynamic bond/main chemistry involved	Additional comments	Possible applications	Ref
Vanillin	14.9 ± 1.9 30.6 ± 1.7 (different samples)	na[a]	Oxidation of vanillin to methoxyhydroquinone	Curing agent: EpikureF205 based on isophorone diamine; An inorganic accelerator (calcium nitrate) has been added	Composite industries	105
Vanillin	na[a]	149.0 (cured with 1,6-diaminohexane)	Hydrovanilloin-based polymer	Curing agents: 1,2-diaminoethane, 1,4-diaminobutane, 1,6-diaminohexane, and IPDA;[b] Hydrovanilloin:epichlorohydrin 1:2 mol ratio gave a hard thermoplastic; Large excess of epichlorohydrin yielded a curable thermoset	Metal ion separation in aqueous medium and water purification	106
Vanillyl alcohol	32.9 ± 3.96	na[a]	—	Curing agent: TETA;[b] Vanillin-based epoxy resin was further reinforced by LCNFs[b]	Thermally resistant nanocomposites	107

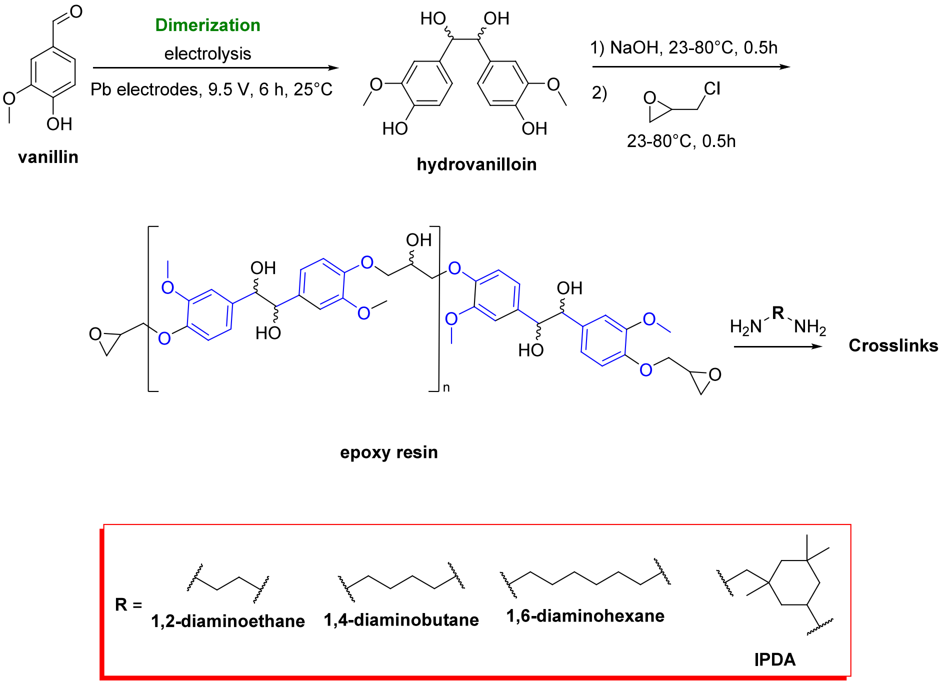
[a] Not available. [b] Abbreviations IPDA: isophorone diamine, LCNFs: lignin-containing cellulose nanofibrils, MXDA: meta-xylenediamine, TETA: triethylenetetramine.

Scheme 12. Chemical Synthesis of Vanillin-Based Epoxy Resins via Dakin Oxidation and Epoxidation[a]



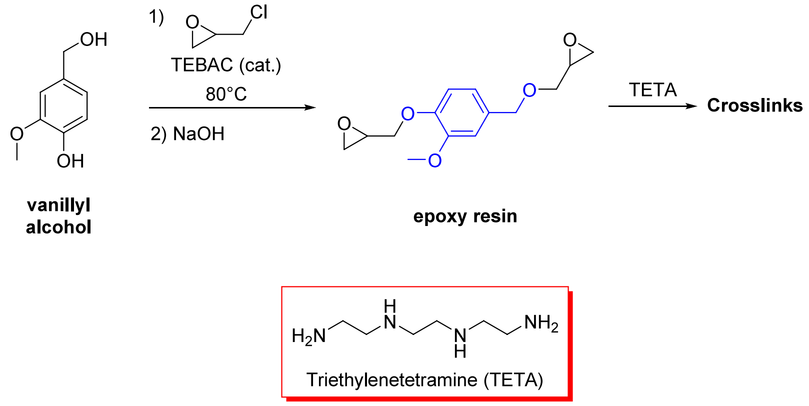
[a] Vanillin core is highlighted in blue.

Scheme 13. Chemical Synthesis of Hydrovanilloin–Diglycidyl ether phenoxy Resins[a]



[a] The dimerization step is marked in green.[106] Vanillin core is highlighted in blue. Curing agents are shown in the red box.

Scheme 14. Chemical Synthesis of Vanillyl Alcohol-Derived Epoxy Resins[107a]



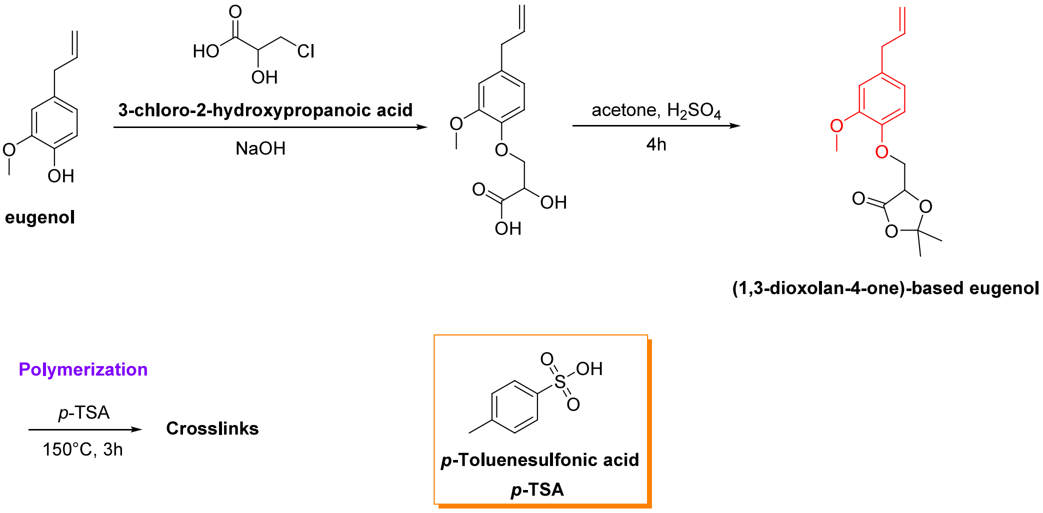
[a]Vanillin core is highlighted in blue. The curing agent TETA is shown in the red box.

Table 4. Eugenol-Based CANs, Their Mechanical Properties, and Possible Applications and Eugenol-Based Polymers That Are Not Based on CANs

Tensile strength (MPa)	T_g (°C)	Dynamic bond/main chemistry involved	Amines used for formation of imines	Additional comments	Possible applications	Ref
Eugenol-Based CANs, Their Mechanical Properties, and Possible Applications						
70.8 ± 0.7	125.0	Dynamic ester bonds (transesterification exchange)	—	Polymerization starting from 1,3-dioxolan-4-one monomers was carried out using *p*-TSA[b] at 150 °C	—	110
38.8 ± 1.2	53.03	Disulfide bonds	—	Curing agent: 4-aminophenyl disulfide; Silicone modified eugenol polymer	Composites	111
Eugenol-Based Polymers That Are Not Based on CANs						
na[a]	84.0 (cured with MXDA) 62.0 (cured with 2,2′-(ethylenedioxy)bis(ethylamine))	Phosphorus-containing polymers	—	Curing agents: 2,2′-(ethylenedioxy)bis(ethylamine) or MXDA;[b] Trieugenylphosphate core was prepared by dropwise additions of phosphorus oxychloride	Flame retardants	112
85 ± 11	60.0	Cysteamine-based	—	Eco-friendly thermoset based on dicysteamine-allyl eugenol	Flame retardants	113

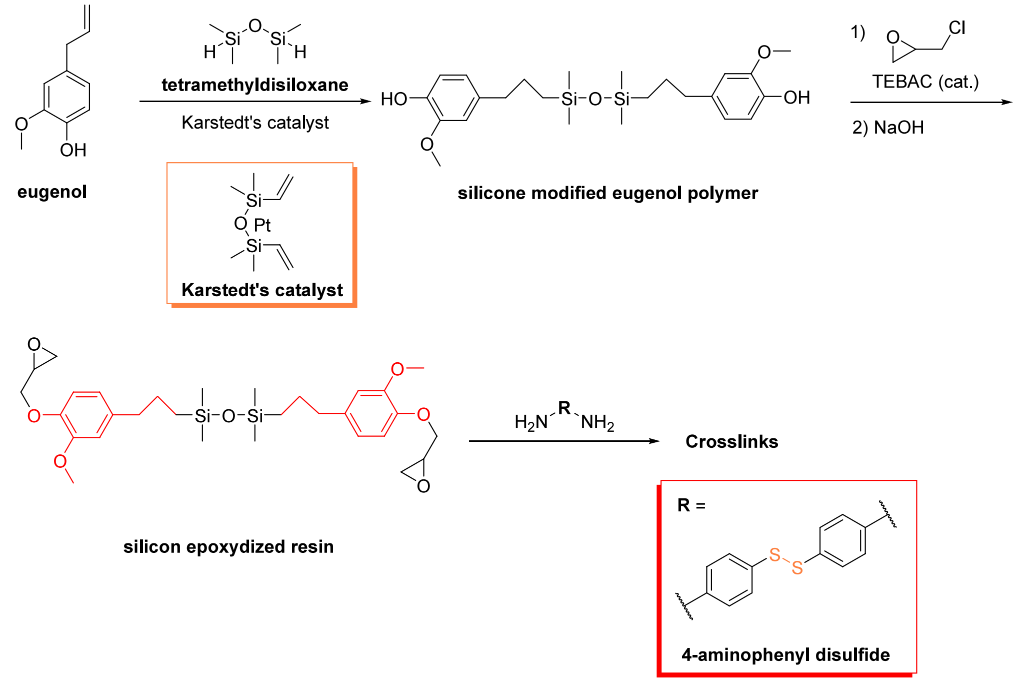
[a]Not available. [b]Abbreviations: MXDA: meta-xylenediamine, *p*-TSA: *p*-toluenesulfonic acid.

Scheme 15. Chemical Synthesis of Functionalized Eugenol, 1,3-Dioxolan-4-one-Based Thermosets[110a]



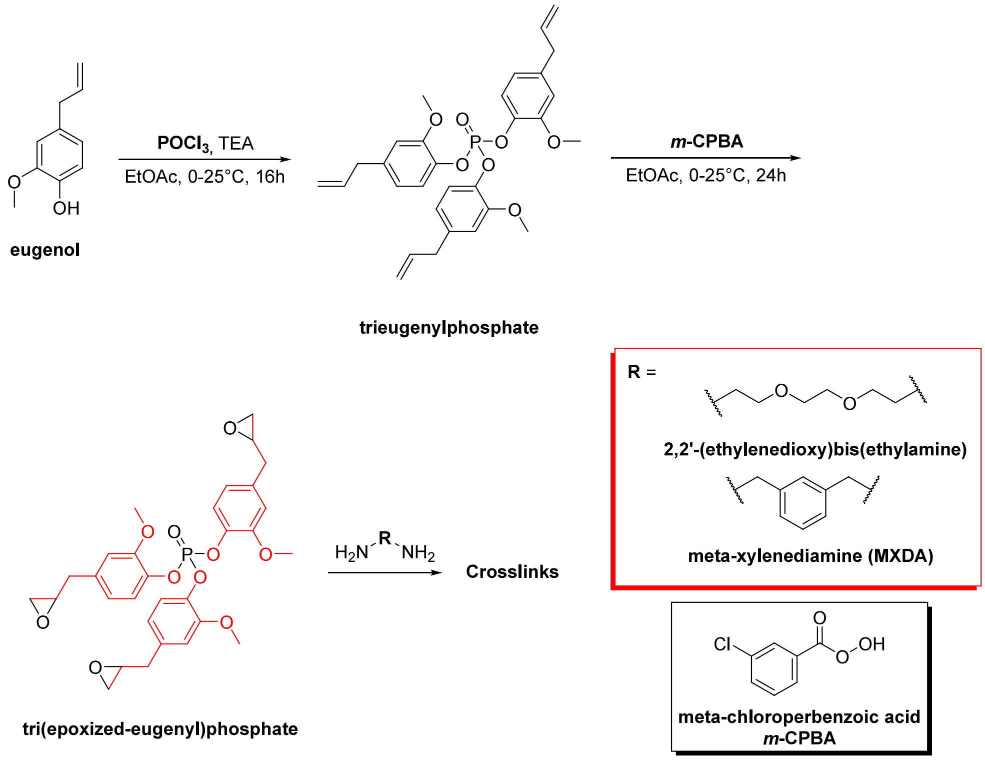
[a]Eugenol core is marked in red. Catalyst *p*-toluenesulfonic acid is shown in the orange box.

derivative is cured with a diamine [*e.g.*, 2-methylpentane-1,5-diamine (Dytek A), isophorone diamine (IPDA)] to afford a crosslinked polymer (Scheme 1). For the Schiff base formation, a reaction in solution is preferred, but greener methods (*e.g.*, grinding) have also been described.[96] In the case of solution chemistry, solvents such as methanol, ethanol, propanol, Scheme 16. Chemical Synthesis of Silicon-Containing Eugenol-Based Epoxy Resins Based on the Disulfide Bond Exchange[111a]



[a]Eugenol core is highlighted in red. Karstedt's catalyst is shown in the orange box. Curing agent is shown in the red box. Disulfide bond highlighted in orange.

Scheme 17. Chemical Synthesis of Tri(epoxized-eugenyl)phosphate Thermosets[a]

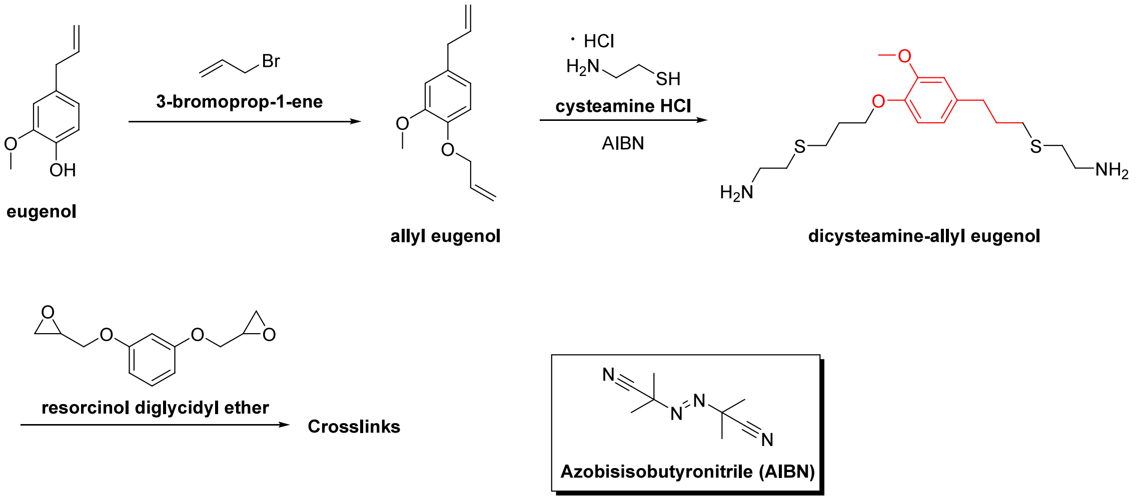


[a]Eugenol core is marked in red. Structure of meta-chloroperbenzoic acid (*m*-CPBA) is given in the grey box. Curing agents are shown in the red box.

chloroform, dichloromethane, acetic acid, diethyl ether, tetrahydrofuran, and water are preferred. These typically dissolve both vanillin and the diamine.

Later, Zhu et al.[34] reported that vanillin, when coupled with diamines and diethyl phosphite and followed by the reaction with epichlorohydrin, yields high-performance flame retardant

Scheme 18. Chemical Synthesis of an Eco-Friendly Thermoset Employing Renewable Resorcinol Diglycidyl ether and Dicysteamine-allyl eugenol[113a]



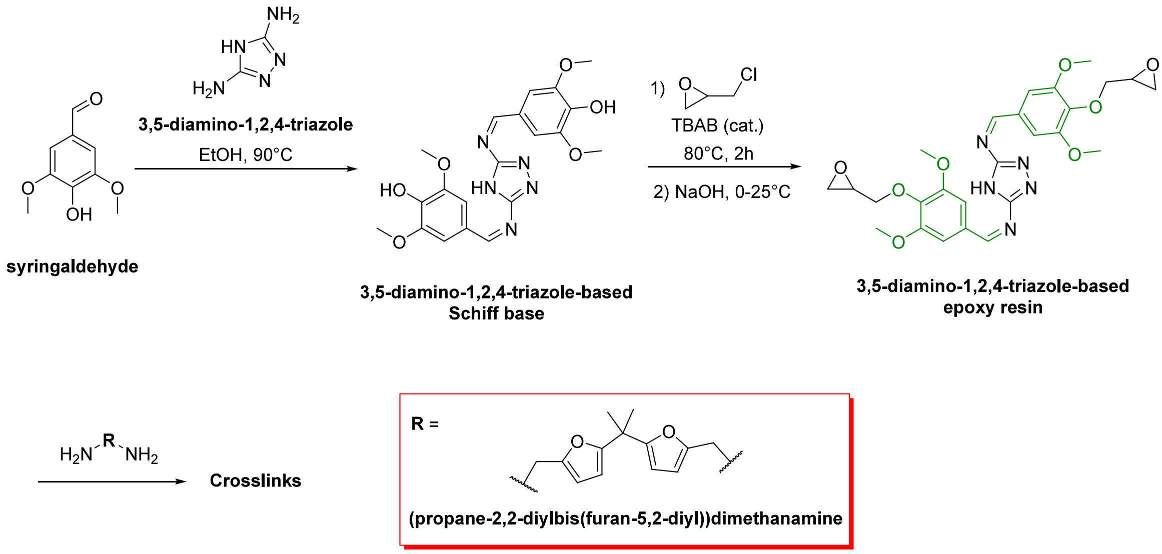
[a]Eugenol core is highlighted in red. Structure of azobisisobutyronitrile (AIBN) is given in the grey box.

Table 5. Syringaldehyde-Based CANs

Building block used	Tensile strength (MPa)	T_g (°C)	Dynamic bond/main chemistry involved	Amines used for formation of imines	Additional comments	Possible applications	Ref
Syringaldehyde	57.4	204	Imine	3,5-Diamino-1,2,4-triazole	Curing agent: (propane-2,2-diylbis(furan-5,2-diyl))dimethanamine derived from furfurylamine; Bio-based epoxy thermoset exhibits antibacterial activities against Gram-positive *S. aureus*[a]	Flame retardants	114

[a]Abbreviations *S. aureus*: *Staphylococcus aureus*.

Scheme 19. Chemical Synthesis of a Bio-Based Epoxy Thermoset from a Syringaldehyde-Derived Epoxy Monomer Cured by a Furan-Derived Amine[114a]



[a]Syringaldehyde core is highlighted in green. Curing agent is shown in the red box.

epoxy resins. Similarly to the steps presented in Scheme 1, the preparation of phosphorus-containing, vanillin-based epoxy resins starts from vanillin and a diamine [*e.g.*, 4,4-diaminodiphenylmethane (DDM) or *p*-phenylenediamine] to form the corresponding Schiff base. The so-formed imine undergoes the attack of diethyl phosphite in the presence of zinc chloride as a catalyst to afford the diphosphonate intermediate, which is last treated with epichlorohydrin and a phase transfer catalyst such as tetrabutylammonium bromide (TBAB) to give the epoxy resin (Scheme 2). For curing, 4,4-diaminodiphenylmethane (DDM) was used.

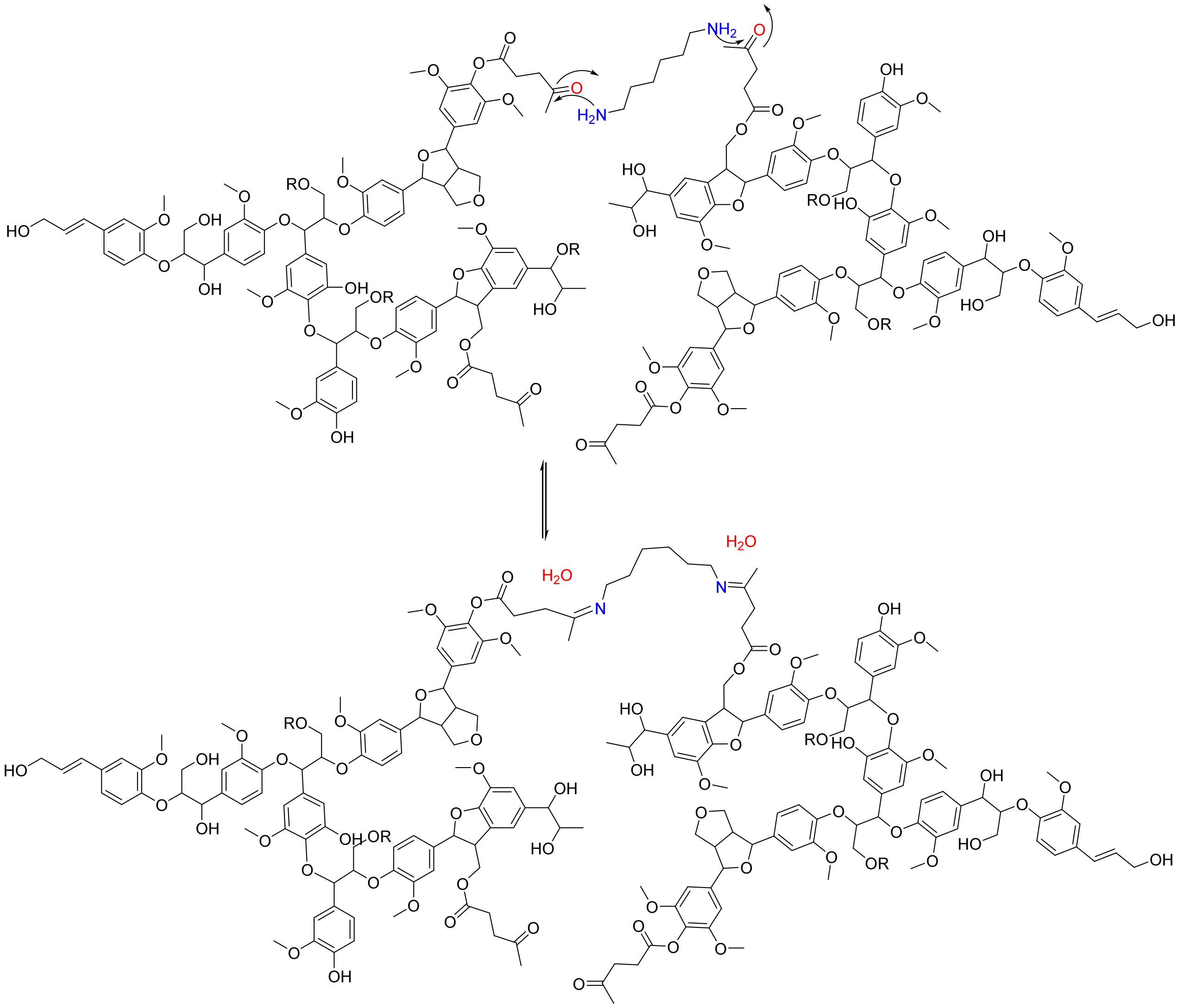


Figure 6. Representative example of imine-bond formation between an organosolv lignin (isolated from woody biomass using an acidified organic solvent reflux for long periods), which is functionalized with levulinic acid, and a diamine, hexamethylenediamine. Nucleophilic nitrogen of hexamethylenediamine are marked in blue, whereas oxygens of the electrophilic ketone are shown in red. In the upper part of the figure, arrows represent the nucleophilic attack of amino groups to the electrophilic ketone moieties and the consequent delocalization of electrons on the electronegative oxygen. In the lower part, the imine bonds are formed due to condensation of the amino groups. Molecules of water generated during the condensation are again represented in red.

Tensile strength and tensile modulus for the DDM-based epoxy resin cured with DDM (~80.3 and ~2114 MPa, respectively) were better than those of Bisphenol A diglycidyl ether epoxy resin DGEBA cured with DDM (~76.4 and ~1893 MPa, respectively). Moreover, the glass transition temperatures (T_g of 183 °C for the DDM-based resin and 214 °C for the *p*-phenylenediamine-based one) were higher than those of DGEBA-DDM with T_g of 166 °C. This is very likely due to the rigid structures of these resins. The values of LOI (31.4% and 32.8%) for the phosphorus-containing vanillin-based epoxy resins were also higher than those for the DGEBA-DDM polymers and endow the material with the desired self-extinguishing properties. Chemical characterization of the newly synthesized resins has been done by NMR and FTIR.[34] In regard to the FTIR analysis, the peaks for O−H (broad peaks ranging from 3200 to 3600 cm^{-1}) accounting for the intermediate imine derivatives disappeared in the corresponding epoxy resins due to phenolic hydroxyl group epoxidation. The broad asymmetric OH-band was, on the other hand, still evident in the DDM-based epoxy resin adducts, which is attributed to the epoxide ring opening. Looking at ^1H NMR, a striking difference was the absence of the phenolic peak in the epoxy resin derivatives compared to that in precursors (diphosphonate intermediates).

Vanillin-based polySchiff thermosets have also been reported to date (Scheme 3).[97] These possessed a butane linker connecting two vanillin monomers. The resulting butane-linked dialdehyde was cured with diethylenetriamine and tris(2-aminoethyl)amine. The tensile strength and elongation at break of such thermosets ranged from 47.43 ± 2.46 to 57.1 ± 6.01 MPa, and from 16.34 ± 2.86 to 13.01 ± 1.51%, respectively.

In a similar fashion, ethane-linked vanillin dialdehyde was employed in a condensation reaction with functionalized vanillin trialdehyde (obtained from phosphorus oxychloride and vanillin)[98] (Scheme 4). Dialdehyde was prepared by mixing vanillin and 1,2-dibromoethane in an alkaline medium (NaOH).

Table 6. Lignin-Based CANs[a]

Tensile strength (MPa)	T_g (°C)	Dynamic bond/main chemistry involved	Amines used for formation of imines	Additional comments	Possible applications	Ref
60.2 ± 2.6 (cured with hexamethylenediamine)	209 (cured with hexamethylenediamine)	Imine	Hexamethylenediamine or 1,12-diaminododecane	Curing agent: hexamethylenediamine or 1,12-diaminododecane	UV protection materials	117
46.8 (epoxy lignin and DGEBA[c] 1:2)	40.7 (epoxy lignin and DGEBA 1:2)	Dynamic ester bonds (transesterification exchange)	—	DEA/PTA[c] (1:1) under the catalysis of zinc acetylacetonate [$(Zn(acac)_2)$] hydrate	—	32
9.7 ± 0.3 (lignin content 20%)	44.0 (lignin content 50%)	Hydroxyl groups that could participate in the exchange reactions with the urethane bond.	—	Lignin isocyanate index[b] of 0.4; PEG[c] 2000 and hexamethylenediisocyanate were used to generate polyurethane network	Smart materials industries. Manipulated materials to respond in a controllable and reversible way as a result of external stimuli.	118

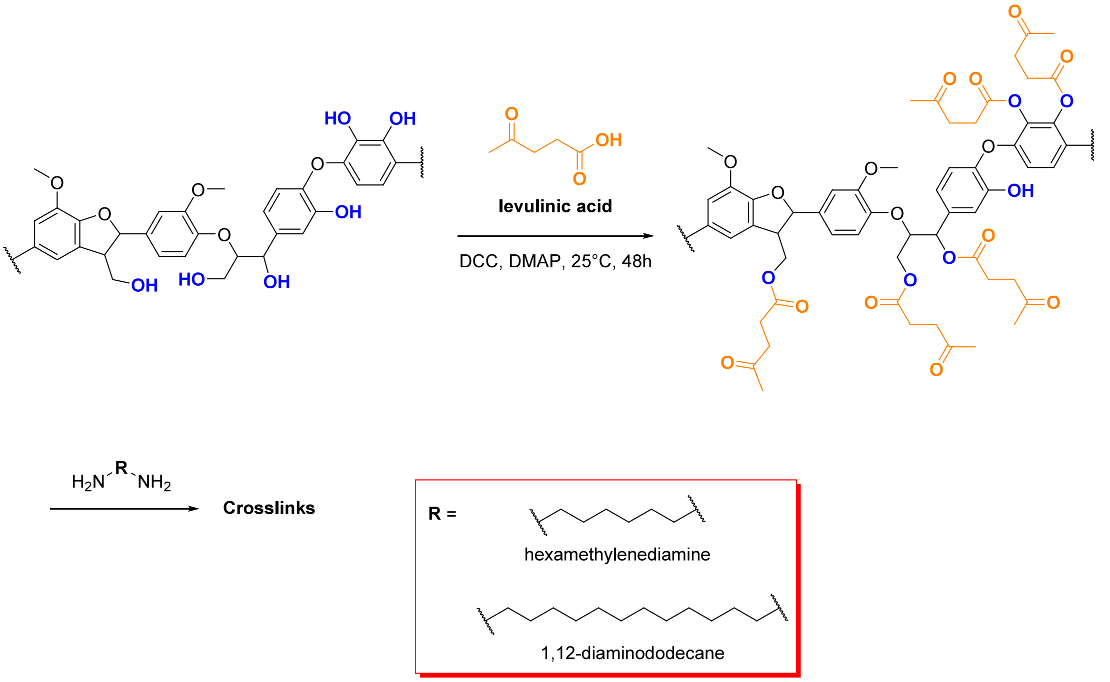
[a] Enzymatically hydrolyzed lignin (EHL) is always used as a starting point. [b] isocyanate index (NCO/OH). [c] Abbreviations DEA: dodecanedioic acid, DGEBA: Bisphenol A diglycidyl ether epoxy resin, PEG: Poly(ethylene glycol), PTA: 1,2,3-propanetricarboxylic acid.

Table 7. Lignin-Based Polymers That Are Not CANs

Building block used	Tensile strength (MPa)	T_g (°C)	Source of dynamic bond/main chemistry involved	Additional comments	Possible applications	Ref
Kraft lignin	1.45 (PEG-DCM[c] 600) 4.52 (PEG-DCM 2000)	191 (PEG-DCM 600 cured polymer)	Carboxylic acid groups of PEG-DCM open the epoxides	PEG-DCM used to generate vitrimers	Thermosets with light-controlled remoldability	119
Kraft lignin	68 ± 6 (for the thermoset prepared with 2-ethyl-2-(((3-mercaptopropanoyl)oxy)methyl)propane-1,3-diyl bis(3-mercaptopropanoate)	120 ± 9 (for the thermoset prepared with 2-ethyl-2-(((3-mercaptopropanoyl)oxy)methyl)propane-1,3-diyl bis(3-mercaptopropanoate)	Thiol−ene reactivity	Three thiol crosslinkers were used: 2-ethyl-2-(((3-mercaptopropanoyl)oxy)methyl)propane-1,3-diyl bis(3-mercaptopropanoate), 2,2-bis(((3-mercaptopropanoyl)oxy)methyl)propane-1,3-diyl bis(3-mercaptopropanoate) and dipentaerythritol hexakis-(3-mercaptopropionate)	Thermosetting materials with tunable properties	120
Organosolv lignin	68.62 ± 2.67 (10% carboxylated lignin)	95.91 (10% carboxylated lignin)	Transesterification	Carboxylated lignin addition causes simultaneous reinforcing and toughening of the epoxy resin	—	121
Soda lignin	—	100−105[a] (for monoethanolamine, furfurylamine and stearylamine-derived thermosets)	—	Benzoxazine-containing thermosets; Ring opening-polymerization (ROP) occurs during curing	Fire-resistant thermosets	122
Phenolated lignin[b]	5.312 ± 1 (thermoset heated at 150 °C for 120 min)	<80 °C.	—	azide−alkyne cycloaddition	Fire-retardant thermosets	123

[a] Glass transition (midpoint measured by DSC). [b] Softwood lignin (150 g) and phenol (150 g) were reacted in a closed stainless-steel high-pressure reactor at 275 °C for 1 h. [c] Abbreviations: PEG-DCM: poly(ethylene glycol) bis(carboxymethyl) ether.

Scheme 20. Chemical Synthesis of Polyimine Thermosets Using Enzymatically Hydrolyzed Lignin (EHL) and Levulinic acid[a]



[a]DCC is *N*,*N*′-dicyclohexylcarbodiimide, DMAP is 4-dimethylaminopyridin. Alcoholic groups (phenolic and non-phenolic) are marked in blue. Levulinic acid is marked in orange. Curing agent amines are shown in the red box.

To obtain the trifunctionalized aldehyde, vanillin was mixed with phosphorus oxychloride ($POCl_3$) and triethylamine (TEA) in chloroform as a solvent. Diethylene triamine was used as a cheap polymerization agent to generate the polyimine network. Tensile strength and elongation at break of this polySchiff thermoset (having no free CHO groups on dialdehyde available for further reaction) were 84.1 MPa and 4.5%, respectively.

Functionalized vanillin trialdehyde was used in another work. By mixing phosphorus trifunctionalized with vanillin aldehyde, a polymer obtained from epoxy soybean oil and diethylenetriamine, a thermoset endowed with the highly dynamic nature of hydrogen and imine bonds was afforded. This allows the damaged polymer to self-heal and, as such, it can be recycled multiple times.[104] Another approach to introduce self-healing properties and allow for the recyclability of crosslinked polyurethanes is the introduction of dual-dynamic covalent bonds when polymerizing a disulfide bond-containing Schiff base made from cystine and vanillin with hexyl isocyanate[99] (Scheme 5). Very importantly, polyurethanes crosslinked with the Schiff base showed excellent self-healing and recyclability with lower activation energy for stress relaxation thanks to the synergy of the dynamic metathesis of the imine and disulfide bonds. The synthesized Schiff base containing imine and disulfide bonds was mixed with 1,4-butanediol to ensure miscibility with polyurethane prepolymer (hexyl isocyanate).[99]

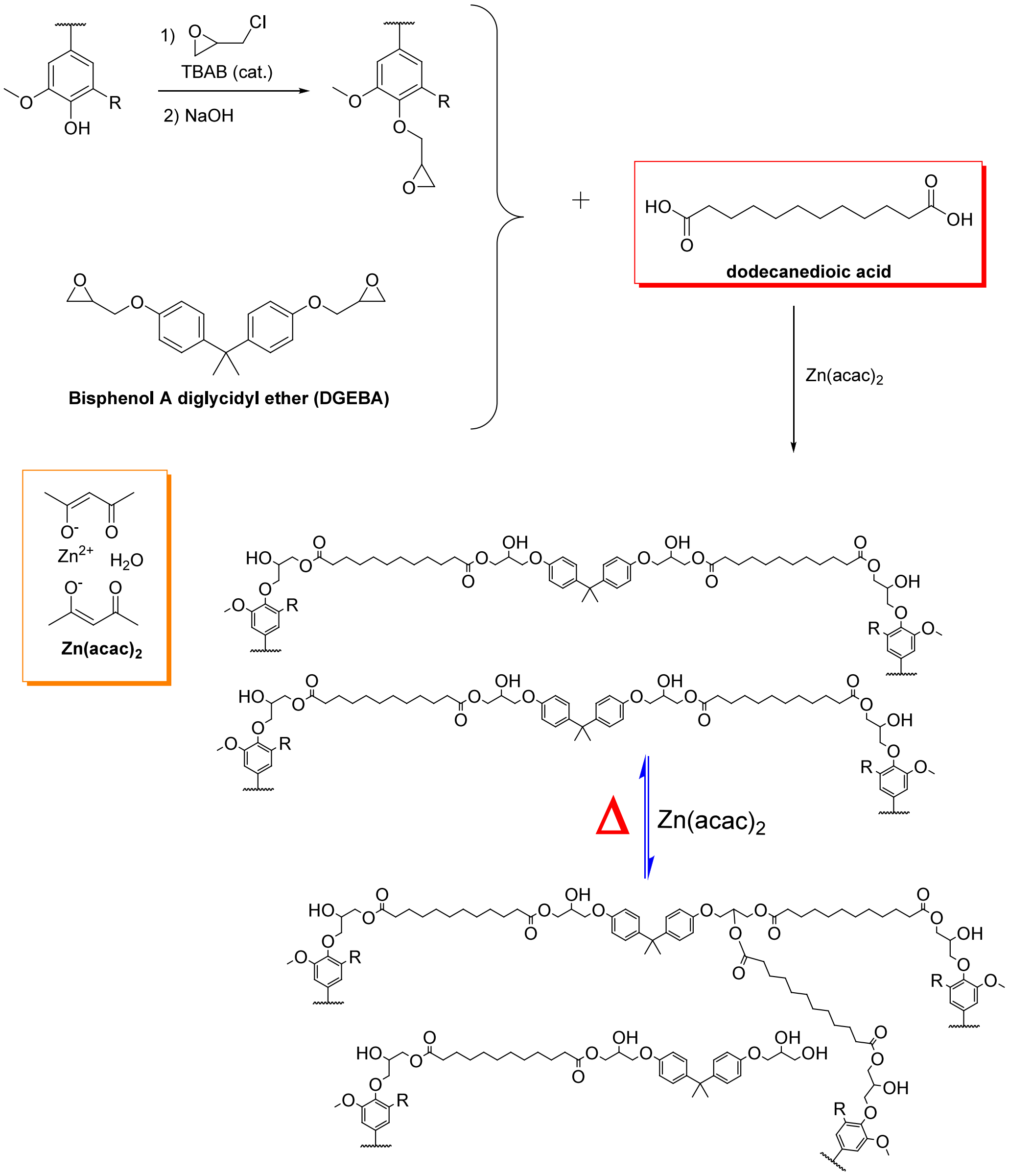
Liu et al.[33] proposed an even different linkage between the two vanillin monomers, *i.e.*, diphenylmethane was used. The diphenylmethane derivative was then treated with epichlorohydrin and a TEBAC catalyst, followed by NaOH addition to form the epoxy resin. The curing agent employed was polyetheramine D-230 (Scheme 6). The so-prepared diphenylmethane-based epoxy resin exhibits higher T_g (106 °C), tensile strength (57.4 MPa) and elongation at break (3.1%) than DGEBA cured with D-230 (98 °C, 45.1 MPa, and 2.4%, respectively). Additionally, it is possible to reprocess and recycle the polyimine network by hot pressing.

Another alternative strategy to make vanillin-based CANs has been reported, involving an initial methacrylation step (using methacrylic anhydride) followed by the formation of imine in dichloromethane. The unsaturated sites of methacrylates are important for further crosslinking, while the aldehyde rapidly reacts with diamines such as 2,2′-(ethylenedioxy)bis(ethylamine) or triamines like trimethylolpropane tris[poly(propylene glycol), amine terminated] ether to afford the vanillin-based vinyl ester resins[100] (Scheme 7). It is worth noting that, in the imine formation step, low temperature and a solvent with poor water miscibility are crucial factors to prevent amine attack on the ester bond, causing aminolysis as a side reaction. The vinyl ester resins can be crosslinked via a fast UV-curing reaction to achieve thermosets. Young's modulus of such thermosets ranged from 470 to 830 MPa, and the tensile stress ranged from 13 to 21 MPa. After the first reprocessing, mechanical properties remained rather similar to the original polymer properties.[100]

An epoxy resin based on vanillin and 4-amino-4*H*,1,2,4-triazole has also been developed (Scheme 8).[101] The so-formed imine was further treated with epichlorohydrin and TBAB to afford a triazole-based epoxy resin, which was cured with bio-based 5,5′-methylenedifurfurylamine (DFA). Glass transition temperature (T_g = 170.1 °C), tensile strength of 60.8 MPa, and elongation at break (2.8%) of the resulting thermoset were better than those of DGEBA-DDM (T_g = 152 °C, tensile strength of 52.1 MPa, and 1.6% elongation at break). Moreover, the LOI value was also higher (38.5% compared with 23.5% for DGEBA/DDM), confirming great flame retardant properties of the epoxy resin.[101]

Another example of a flame retardant thermoset containing phosphor has been reported, in which six vanillin units are linked

Scheme 21. Chemical Synthesis of Vitrimers Endowed with Excellent Self-Healing Properties Using Enzymatically Hydrolyzed Lignin (EHL) and Bisphenol A diglycidyl ether (DGEBA)[a]



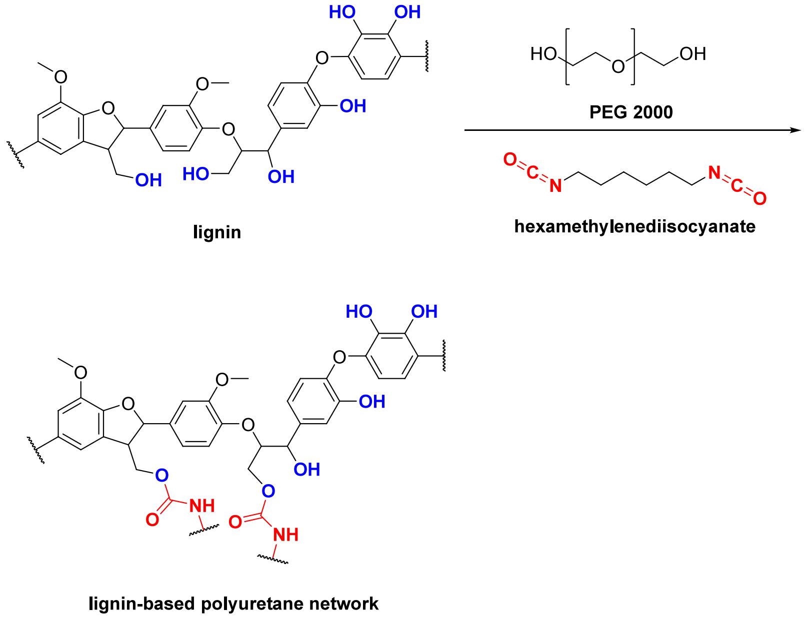
[a]Curing agent, dodecanedioic acid (DEA), is shown in the red box. Structure of zinc acetylacetonate [(Zn(acac)$_2$] hydrate is given in the orange box. Alternatively, 1,2,3-propanetricarboxylic acid (PTA) can also be used for curing. Reversibility of dynamic ester bonds is shown in the lower part of the scheme (blue arrow).

to a central cyclophosphazene (Scheme 9).[102] Vanillin was treated with hexachlorocyclotriphosphazene in the presence of NaOH in THF to afford hexavanillin cyclophosphazane. By incorporating the vanillin-terminated phosphazene monomer into the polyimine binder material, a fully recyclable carbon fiber reinforced composite material with high phosphorus/nitrogen (P/N) content and excellent flame retardancy was designed, exhibiting also high crosslinking density and great mechanical performance.[102]

A completely bio-based epoxy vitrimer with desirable mechanical properties can be synthesized from glycerol triglycidyl ether and an imine-containing hardener (which is also a bio-based compound made of vanillin and 4-aminophenol).[103] The imine is mixed with glycerol triglycidyl ether in the presence of 1,2- dimethylimidazole as a catalyst to afford the epoxy vitrimer (Scheme 10). The presence of two free phenolic groups after the imination step enables the formation of a highly crosslinked network.

A bio-based approach was also applied in the preparation of epoxidized soybean oil (ESO)-derived epoxy thermosets.[28] First, an imine was prepared by treating vanillin with 4,4′-methylenedianiline in methanol at 65 °C. The resulting Schiff base was then treated with epoxidized soybean oil in the presence of 1,2-dimethylimidazole as a catalyst at 190 °C to afford the ESO-vitrimer (Scheme 11). The dynamic Schiff base bonds provide the epoxy vitrimer with excellent mechanical properties and reprocessability, weldability, reconfigurability, and programmability.[28] Among the mechanical properties, an

Scheme 22. Chemical Synthesis of Lignin-Based Polyurethane Networks Using Enzymatically Hydrolyzed Lignin (EHL), PEG 2000, and Hexamethylenediisocyanate[a]



[a]The hydroxyl groups are marked in blue. The carbamate moieties derived from the reaction with hexamethylenediisocyanate are represented in red.

extremely high tensile modulus (1016.7 ± 42.9 MPa) was obtained for the epoxy vitrimer with crosslinked density of 296.8 mol/m^3. The corresponding tensile strength was 37.4 ± 4.1 MPa.

Vanillin-Based Thermosets as an Inspiration for CAN Design. A few examples of vanillin-based polymers that cannot be considered CANs are also described in Table 3. The chemistry behind these reactions involving vanillin and vanillyl alcohol is very interesting and represents a source of inspiration for the reader to develop novel dynamic thermosets by using these transformations. However, mechanical properties of these polymers were not as satisfactory as of those reported in Table 2.

An appealing approach to transform vanillin into an epoxy resin was developed by Naebe et al.[105] It involves the oxidation of vanillin to methoxyhydroquinone via Dakin oxidation mediated by sodium percarbonate.[108] The obtained methoxyhydroquinone is then used in the nucleophilic substitution in the presence of epichlorohydrin and TEBAC as a phase transfer catalyst (Scheme 12).

The curing agent used was EpikureF205 based on the isophorone diamine. Here, calcium nitrate was used as an inorganic accelerator. The addition of an accelerator not only cures the epoxy resins faster, but also improves mechanical properties of the epoxy structure through changing the network architecture. The results of mechanical properties showed that the tensile strength and Izod impact strength (a standardized measure used to determine the impact resistance, or toughness, of a material) were higher than those of DGEBA (specifically, ~3% and ~8% tensile strength and impact Izod strength were reported, respectively).[105]

Another vanillin functionalization leads to hydrovanilloin-based epoxy resins,[106] widening the range of properties that can be afforded. First, hydrovanilloin is synthesized by electrochemical dimerization of vanillin, which is followed by treatment with NaOH and epichlorohydrin to afford the epoxy resin (Scheme 13). The stoichiometry of components turned out critical for the outcome. A hard thermoplastic hydrovanilloin-diglycidyl ether phenoxy resin (T_g = 135 °C), which did not require a curing step, was easily prepared by reacting the disodium salt of hydrovanilloin:epichlorohydrin (1:2 mol ratio) in an aqueous medium at 80 °C. On the other hand, the reaction using an excess of epichlorohydrin with the disodium salt of hydrovanilloin at 80 °C in water gives an oligomer of hydrovanilloin−diglycidyl ether with an average number of 2.1 repeating units, which can be cured with aliphatic diamines: 1,2-diaminoethane, 1,4-diaminobutane, 1,6-diaminohexane, and IPDA to give hard epoxy resins. The long chain aliphatic diamine (*e.g.*, 1,6-diaminohexane) cured hydrovanilloin-based epoxy resin showed similar Shore hardness (a measure of resistance of a material to indentation) (74.6 ± 6.2)[106] to that of long-chain flexible aromatic amine-cured DGEBA epoxy resin (79.6).[109]

Instead of vanillin, vanillyl alcohol has also been employed in the preparation of epoxy resins (Scheme 14) resulting in promising epoxy nanocomposites.[107] Briefly, vanillyl alcohol was treated with epichlorohydrin and TEBAC catalyst, followed by NaOH addition to form the epoxy resin. This was then treated with triethylenetetramine (TETA) as a curing agent to form the crosslinked polymer. TETA was selected to also crosslink with the resin matrix and form different epoxy nanocomposites. Vanillyl alcohol-based epoxy resin was further successfully reinforced by lignin-containing cellulose nanofibrils (LCNFs) at different weight ratios. Despite not resulting in a CAN, this attempt gave excellent mechanical properties: tensile strength and toughness increased by 81% and 185%, respectively, when 1 wt % of LCNFs were added.

Such epoxy resins can be combined with dynamic bond-forming reactants (*e.g.*, vanillin and diamines) to produce CANs with versatile properties.

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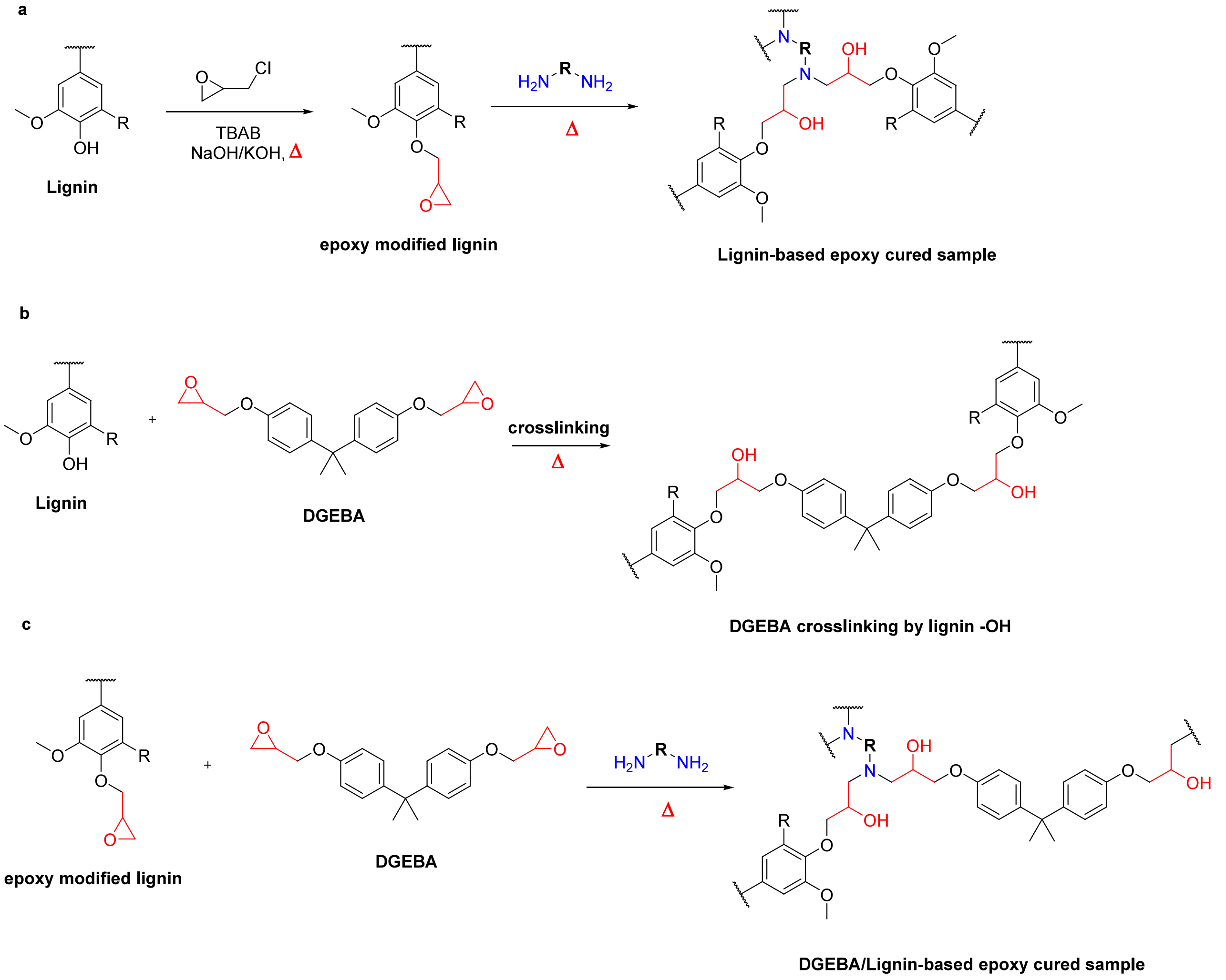
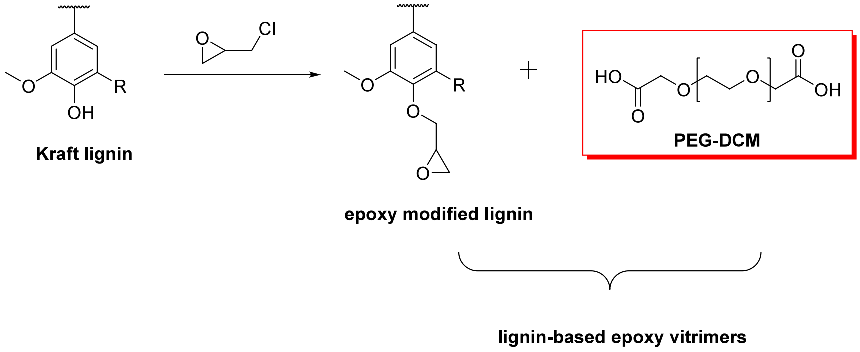
Scheme 23. Summary of Available Strategies to Lignin-Derived Epoxy Thermosets[a]



[a] (a) Lignin epoxidation is followed by curing with a diamine. (b) Crosslinking of DGEBA using lignin (with phenolic hydroxyls) as a curing agent. (c) Amines driving curing reaction between glycidylated lignin and DGEBA.

Scheme 24. Chemical Synthesis of Kraft Lignin-Based Vitrimers[a]

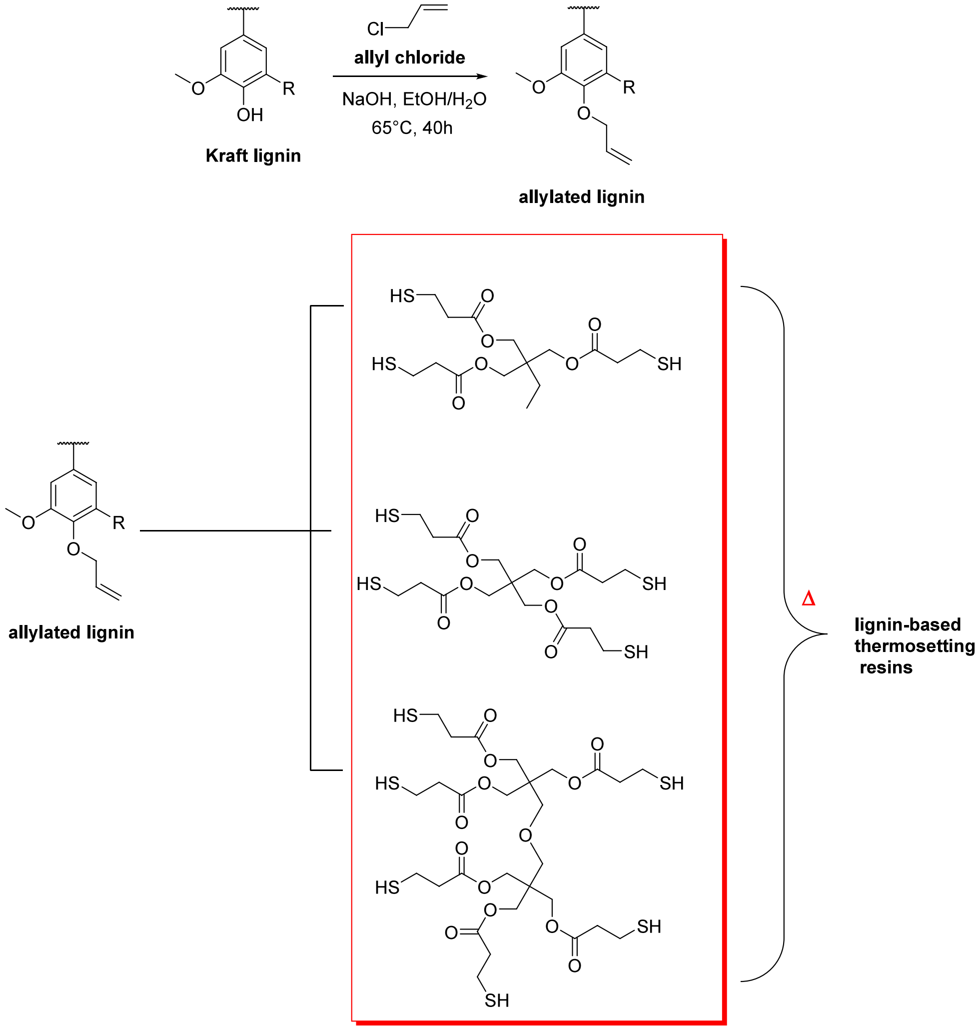


[a] Poly(ethylene glycol) bis(carboxymethyl) ether (PEG-DCM) is used as a curing agent.

Eugenol-Derived CANs. As seen in the case of vanillin, all of the (co)polymers containing eugenol moieties described in literature are produced by first introducing suitable functional groups to the scaffold, allowing for the specific reactivity.[84] The chemistry involved and the mechanical properties of the reported eugenol-based CANs are summarized in Table 4. Also, a couple of examples of eugenol-based polymers that do not contain dynamic bonds but might be useful in the development of CANs in the future are shown in Table 4.

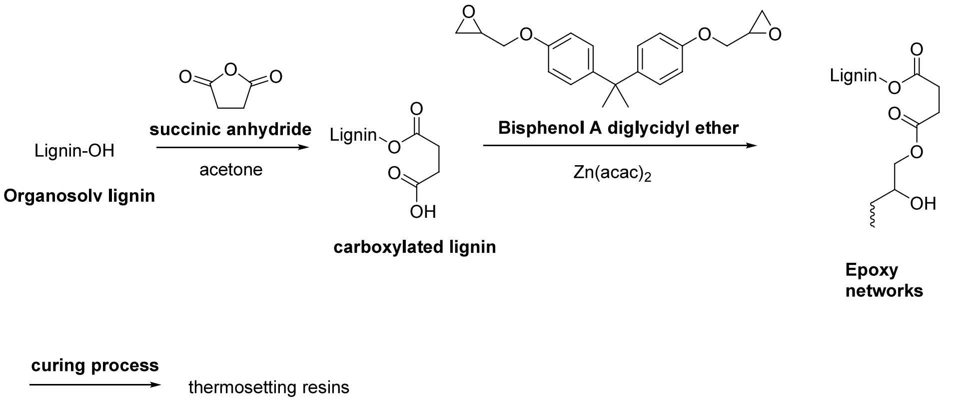
Functionalized eugenol, 1,3-dioxolan-4-one, was reported to produce high-performance thermosets.[110] The synthesis of functionalized eugenol and its polymerization are shown in

Scheme 25. Chemical Synthesis of Thermosetting Resins from the Allylated Kraft Lignin[a]



[a]From top down in the red box: 2-ethyl-2-(((3-mercaptopropanoyl)oxy)methyl)propane-1,3-diyl bis(3-mercaptopropanoate), 2,2-bis(((3-mercaptopropanoyl)oxy)methyl)propane-1,3-diyl bis(3-mercaptopropanoate) and dipentaerythritol hexakis-(3-mercaptopropionate) were used as thiol crosslinkers.

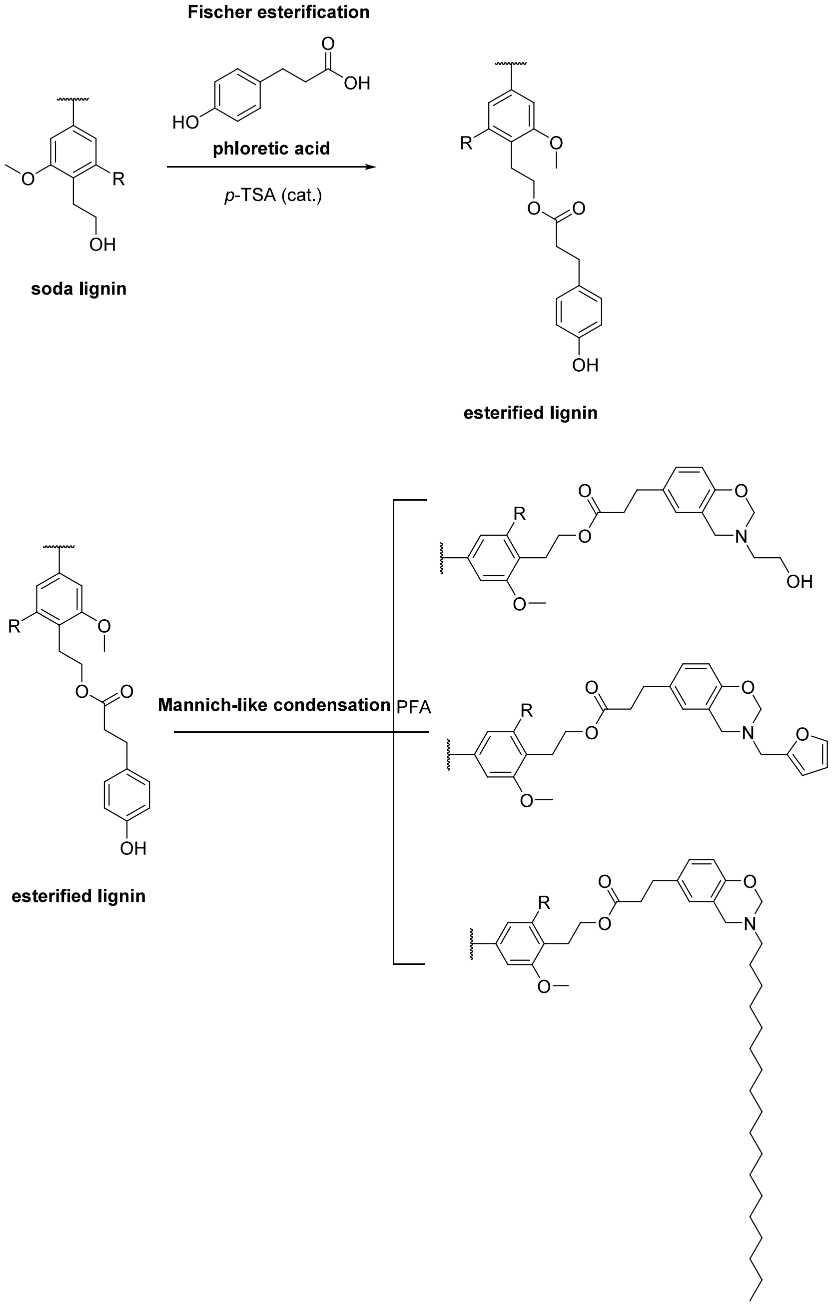
Scheme 26. Chemical Synthesis of Thermosetting Resins from Organosolv Lignin[a]



[a]Carboxylated lignin and Bisphenol A diglycidyl ether were used to prepare the thermosetting resins.

Scheme 15. The proposed structure of the synthesized thermoset is postulated to have ester bonds, free carboxylic and hydroxyl groups (confirmed by broad O−H stretching band in FTIR, centered at 3440 cm^{-1}), and by disappearance of the allyl groups (this was confirmed by the absence of terminal C−H bending characteristic of the allyl group at 1000 cm^{-1}). The

Scheme 27. Chemical Synthesis of Thermosetting Resins from Soda Lignin[a]



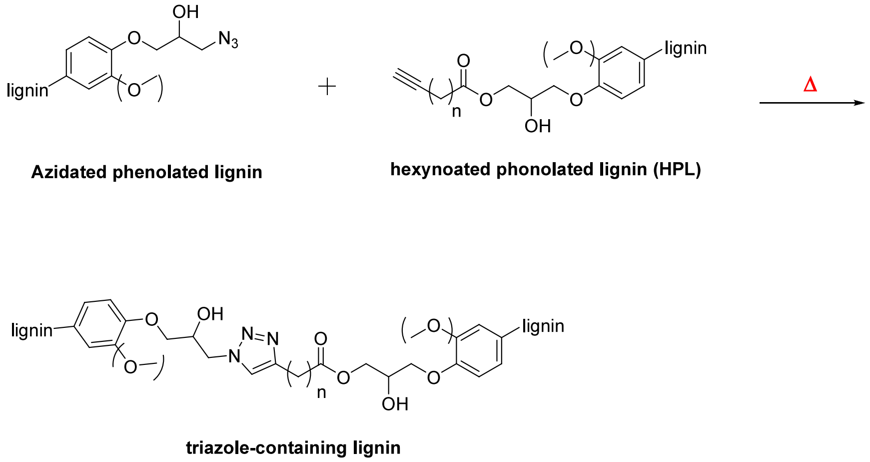
[a] Materials showed fire resistant properties. Amine precursors used in Mannich-like reactions promoted by paraformaldehyde (PFA) were monoethanolamine, furfurylamine, and stearylamine (from top down).

thermoset showed a tensile strength at break of 70.8 ± 0.7 MPa. Also, excellent Young's modulus (8765 ± 19 MPa) and high stiffness were exhibited, probably due to the high aromatic content resulting from eugenol functionalization.[110]

Self-healing silicon-containing eugenol-based epoxy resins based on disulfide bond exchange were also reported.[111] Eugenol was first mixed with tetramethyldisiloxane (TMDS) in THF in the presence of the platinum-based Karstedt catalyst at 70 °C to afford a silicone modified eugenol polymer. Its reaction with epichlorohydrin and TEBAC followed, which resulted in a silicon epoxidized resin. The curing process was carried out by using 4-aminophenyl disulfide (Scheme 16). Reported tensile strength for the cured epoxy resin was 38.8 MPa. The introduction of dynamic disulfide bonds allows the epoxy network to be broken into smaller fragments during the depolymerization, which can be then reorganized and cured back, favoring the healing process.[111]

Eugenol-Based Thermosets as an Inspiration for CAN Design. Similar to the previous section, we summarize in Table 4 a couple of examples of eugenol-based polymers that do not contain dynamic bonds but might be useful in the development of CANs in the future. Interesting epoxy conetworks based on eugenol and possessing promising flame retardant properties have been reported by Caillol et al.[112] (Scheme 17). Despite not

Scheme 28. Chemical Synthesis of Thermosetting Resins Exploiting Azide−Alkyne Cycloaddition



being CANs, the prepared thermosets exhibited excellent char yields (an important measure of fire performance) in the range of 33% and 36% (when cured with MXDA and 2,2′-(ethylenedioxy)bis(ethylamine), respectively), which are considerably higher when compared with the conventional and fossil-based DGEBA thermosets that exhibit 7% and 12% yields at 600 °C (when cured with MXDA and 2,2′-(ethylenedioxy)-bis(ethylamine), respectively).[112]

Another work exploiting the electrophilic nature of the double bond in eugenol has been reported by Langlois et al.[113] Allyl eugenol (formed by the addition of 3-bromoprop-1-ene) was treated with cysteamine hydrochloride and azobis-(isobutyronitrile) (AIBN) to provide dicysteamine-allyl eugenol, which was used for the preparation of an eco-friendly thermoset by mixing it with renewable resorcinol diglycidyl ether (Scheme 18). Flexural strength of the cured epoxy material was 85 ± 11 MPa.[113]

Syringaldehyde-Derived CANs. As per the syringaldehyde-based CANs, it is worth noting a bio-based epoxy thermoset obtained from a syringaldehyde-derived epoxy monomer cured by a furan-derived amine.[114] In detail, a Schiff base was formed between syringaldehyde and 3,5-diamino-1,2,4-triazole in ethanol at 90 °C. Then, the so-formed imine was treated with epichlorohydrin and tetrabutylammonium bromide (TBAB) in refluxing ethanol to give the epoxy resin. The curing process was carried out using (propane-2,2-diylbis(furan-5,2-diyl))dimethanamine derived from furfurylamine (Table 5, Scheme 19). Tensile strength and Young's modulus exhibited by the cured resin were 57.4 and 2600 MPa, respectively.

Lignin-Derived CANs. Lignin, as a high molecular weight polymer, displays enormous challenges in the preparation of functional materials such as unsatisfying compatibility with different matrices. Most often, its poor solubility drives the incompatibility/immiscibility of lignin with other polymers.[115] According to the selected extraction method, different physicochemical properties of isolated lignin, including water solubility, can be achieved. Chemically speaking, the high molecular mass and low reactivity of raw lignin also limit its utilization. Therefore, chemical modification of lignin is often necessary;[32] the presence of alcoholic, phenolic and carbonyl groups in lignin allow for its functionalization (see Figure 6). For example, lignin derived from kraft pulping is generally insoluble in water in neutral and acidic pH ranges. However, copolymerization of Kraft lignin with acrylic acid in an aqueous solution turned into a water-soluble lignin-based copolymer.[116] Despite several challenges facing the functionalization of lignin, some examples of lignin-based CANs have appeared in the literature to date (Table 6). In the next paragraphs, CANs based on lignin will be discussed. Some other examples of lignin-based polymers that are not CANs are again included in Table 7 to follow the short evolution of the application of lignin in thermosets.

Lignin-Based CANs. The following examples employ enzymatically hydrolyzed lignin (EHL), which is obtained from the residue of enzymatic hydrolysis of biomass for the production of bioalcohol or bionatural gas.[124] In the first example, the EHL was first functionalized with levulinic acid in an esterification reaction promoted by *N*,*N*′-dicyclohexyl-carbodiimide/4-dimethylaminopyridin (DCC/DMAP). The resulting free ketone groups are a potential source of several imine bonds after the addition of diamines such as hexamethylenediamine or 1,12-diaminododecane[117] (Scheme 20). Note that the use of levulinic acid is a green approach since it is also produced from lignocellulosic biomass, commercially available, inexpensive, and one of the top 12 value-added chemicals at the moment.[125] Tensile modulus and tensile strength of the thermoset cured with hexamethylenediamine were 2804 ± 154 and 60.2 ± 2.6 MPa, respectively. Glass transition temperature (T_g) was 209 °C.[117]

Another example of EHL-based CANs has been reported by Li et al.[32] In this case, the introduced ester bonds were treated as dynamic bonds. In the first step, epoxy lignin is produced, which is further cured with DGEBA and dodecanedioic acid (DEA) (or 1,2,3-propanetricarboxylic acid (PTA)) under the catalysis of zinc acetylacetonate [$(Zn(acac)_2]$ hydrate (Scheme 21). The prepared vitrimers have excellent self-healing properties, which can be attributed to the highly efficient dynamic trans-esterification reactions in the crosslinked network under external thermal stimulation. The thermoset prepared using the epoxy lignin and DGEBA in the molar ratio by epoxy groups of 1:2 and the curing agents DEA/PTA in the molar ratio by carboxylic acid groups of 1:1 displayed Young's modulus and tensile strength of 1996.6 and 46.8 MPa, respectively.

Lignin has been also exploited in polyurethane networks with CAN properties.[118] Specifically, EHL was treated with poly ethyleneglycol with a molecular weight of 2000 (PEG 2000) and hexamethylenediisocyanate (HDI). The obtained polymer was

Strengths

- Synthetic methods are known (*e.g.*, imines)
- Small molecules-derived polymers are easy for characterization than high MW lignin models

Weaknesses

- Often mechanical properties are not excellent as DGEBA-derived thermosets
- Single monomers (*e.g.*, vanillin) does not have same physico-chemical properties as whole lignin

Opportunities

- Recyclability
- Attractive functionalities such as self-healing, weldability, configurability, shape memory, and intelligent response
- Green, bio-based materials could be implemented

Threats

- Lower performances than fossil-derived thermosets

Figure 7. SWOT analysis of lignin and lignin derivatives-based CANs.

characterized with excess hydroxyl groups that participated in the exchange reactions involving urethane bonds (Scheme 22).

When lignin content was low (<40%), the modulus and tensile strength of thermosets decreased with the increase of the isocyanate index (NCO/OH). In contrast, polymers with 20% lignin content and the isocyanate index of 0.4 exhibited the highest modulus and tensile strength, which were at 373 ± 24 MPa and 9.7 ± 0.3 MPa, respectively.

Lignin-Based Thermosets as an Inspiration for CAN Design. A recently published review[126] has presented very clearly the strategies to make thermoset resins starting from lignin. Among others, lignin-based epoxy resins can be created by direct glycidylation of lignin, and they can be further utilized to create lignin-based epoxy thermosets by curing them alone or in combination with certain amounts of commercial epoxy resins (such as DGEBA). Epoxy curing reactions can be completed using a variety of curing agents, mostly amines and anhydrides, as well as additional types of alcohols and acids. We hereby provide a summary of these strategies (Scheme 23) that can guide the reader in a better understanding of the topic and serves as inspiration for the preparation of novel, applicative thermosets.

Considering the use of lignin in traditional thermosets, kraft, organosolv, and soda lignin have been used (Table 7). In the first example, kraft lignin was reacted with epichlorohydrin, which was also used as a solvent to reduce the viscosity and hydrolyzable chlorine content in the epoxy prepolymer (Scheme 24). Epoxy-modified lignin and poly(ethylene glycol) bis(carboxymethyl) ether (PEG-DCM) were then blended homogeneously and cured at 120 °C for 4 h (or 160 °C for 6 h); the carboxylic acid opened epoxides while hydroxyl groups were generated at the same time.[119] When the molecular weight of PEG-DCM rose from 600 to 2000 Da, the tensile strength increased from 1.45 to 4.52 MPa. Glass transition temperature for PEG-DCM 600 cured polymer was 191 °C, while the sample E-P2000 had no obvious characteristic T_g.

Another example of thermosets prepared from kraft lignin has been published by Johansson et al.[120] In this study, kraft lignin allylation was followed by a curing process with three different thiols (Scheme 25). For the thermoset prepared with 2-ethyl-2-(((3-mercaptopropanoyl)oxy)methyl)propane-1,3-diyl bis(3-mercaptopropanoate), the tensile stress at break and T_g were 68 ± 6 MPa and 120 ± 9 °C, respectively. The T_g increased with higher crosslinking density.

Thermosets with excellent mechanical properties have been also prepared from organosolv lignin.[121] First, lignin treatment with succinic anhydride in acetone gave carboxylated lignin. The so obtained modified lignin was further treated with an epoxy resin (DGEBA) and cured with the addition of $Zn(acac)_2$ as a catalyst, for both curing and dynamic transesterification (Scheme 26). Four different lignin contents were tested: 5, 10, 15, and 20 wt % of carboxylated lignin based on the weight of the epoxy resin. The best tensile strength (68.62 ± 2.67 MPa) was obtained for the thermoset with a 10% carboxylated lignin content. For the same thermoset, the T_g was 95.91 °C.

Lignin-based fire-retardant thermosets have been prepared based on benzoxazine.[122] This time, soda lignin was treated with phloretic acid in a Fischer esterification catalyzed by *p*-toluenesulfonic acid (*p*-TSA). Mannich-like condensation between the esterified lignin, an amine precursor (monoethanolamine, furfurylamine, or stearylamine), and paraformaldehyde (PFA) then took place to afford benzoxazine moiety (Scheme 27). Curing was carried out via a vacuum compression molding manufacturing process. Ring opening-polymerization (ROP) of benzoxazine occurs during the curing. Glass transition midpoint T_g were 105 °C, 100 °C, and 105 °C, respectively, for monoethanolamine, furfurylamine, and stearylamine-derived thermosets.

Fire resistant thermosets exploiting azide−alkyne cycloaddition have also been prepared (Scheme 28).[123] In brief, alkyne-functionalized lignin was reacted with an azide-functionalized lignin to yield a triazole-based lignin. Thermal curing was used to promote the cycloaddition reaction. Tensile strength of 5.312 ± 1 MPa was measured for the thermoset heated to 150 °C for 120 min. All the lignin derivatives exhibit T_g lower than 80 °C.

■ CONCLUSIONS AND FUTURE OUTLOOK

In recent years, scientists have been on a mission to unlock the secrets of lignin—a widely abundant and untapped renewable resource on our planet. This has led to a surge of research into developing cutting-edge technologies that can transform lignin and its building blocks into added-value chemicals that not only benefit the economy but also protect the environment. With its renewable source of aromatic compounds, low cost, and highly branched polymer structure, lignin has emerged as an attractive solution in the quest for sustainable alternatives to petroleum-based chemicals. Furthermore, there is a pressing need to utilize lignin and therefrom obtained bio-based chemicals in existing applications and new technologies, which will be shaping the future. One such examples are CANs.

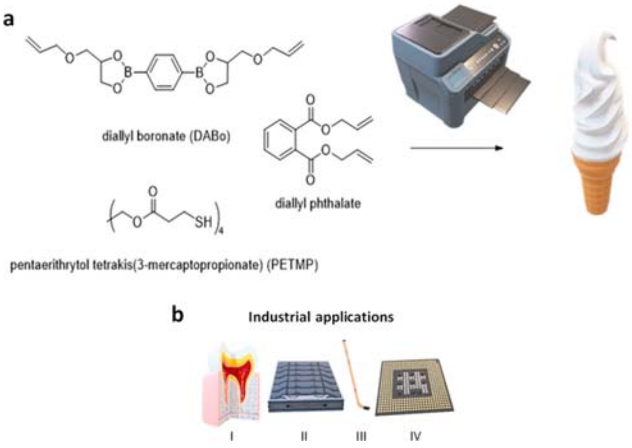


Figure 8. (a) Schematic representation of light-assisted 3D printing of thiol−ene resins based on dynamic boronate esters that can generate complex objects such as an ice cream cone. Monomers [diallyl boronate (DABo), pentaerithrytol tetrakis(3-mercaptopropionate) (PETMP), and diallyl phthalate (DAP)] used to prepare the dynamic bonds are also shown. (b) Some of the industrial applications of CANs: (I) dental restoration, (II) coatings, (III) sports equipment, and (IV) electronics.

The concept of CANs originated in 2002 and since then, it has opened new possibilities in the field of biosustainable chemistry. This concept relies on the reversibility of specific covalent bonds among the polymeric chains that compose classical thermosets. The selected examples in this review show that different CANs based on lignin derivatives such as vanillin, eugenol, and syringaldehyde or even modified forms of lignin (*e.g.*, EHL) can be successfully prepared (Tables 2, 4, 5, and 6). Different types of lignin, namely kraft, organosolv, and soda lignin, have been used to prepare thermosetting materials demonstrating wide applicability of the complex lignin structure.

Although the existing CAN polymers cover a wide range of mechanical and other relevant properties, these data are scattered and inconsistent throughout the literature, which makes them hard to follow. In this paper, we summarize the available information, which hopefully will facilitate targeted research in the field. Moreover, the outstanding factor we observed is the predominance of imine-based lignin-derived CANs in the current literature, for which a plethora of different synthesis pathways exist, still leaving a lot of room for other innovative approaches. Some ideas are even given in this paper by summarizing the most interesting chemical modifications underlying the synthesis of thermosets that can be used in the design of novel CANs (Tables 3, 4, and 7). It should be also stressed, however, that eugenol, given the lack of an aldehydic group in its structure, and exploited lignins give rise to other types of CANs as well (especially dynamic ester bonds and disulfide bonds). Among the three lignin-based CANs reported, all the examples exploited the reactivity of free hydroxyl group, among which one resulted in the synthesis of polyimine network, while in the other two cases, polyesters and polyurethane participate in exchange reactions accounting for the reversibility of the formed bonds.

Typical tensile strength of epoxy thermoset polymers is in the range of 55−130 MPa.[127] Among the examples that contain imine bonds, the tensile strength ranged from as low as 13 MPa to the highest value of 84.1 MPa. This confirms that most of the synthesized CANs are in the desired range. As per the presented thermosets that contain imine bonds, T_g ranged from 25.2 to 288 °C. Classical epoxy thermosets typically behave well below 100 °C, and some special heat-resistant materials can be used up to 200 °C.[128] Interestingly, the highest T_g comes from the example where imine and disulfide bonds act synergistically.[99] A combination of imine and disulfide metathesis also turned out to be crucial for the outstanding self-healing properties and recyclability. In this case, hexyl isocyanate was used as a curing agent, differently from the majority of the presented cases, where a diamine was used instead.

Both aromatic and aliphatic amines have been used to form imine bonds and in the curing process. Aliphatic amines are highly reactive curing agents that, when blended with epoxy molecules, allow one to obtain densely crosslinked networks thanks to the short distance between the active sites. Aromatic amines, on the other hand, react with epoxy resins more slowly.[129] This is easily understandable if we consider the resonance form of an aromatic amine: the lone pair on nitrogen can be delocalized onto the aromatic ring, therefore, reducing its nucleophilicity. Reports of bio-based amines as curing agents are also covered in this paper. For instance, 5,5′-methylenedifurfurylamine[101] and (propane-2,2-diylbis(furan-5,2-diyl))-dimethanamine[114] are derivatives of furfurylamine, which are obtained from renewable feedstocks.[130]

The introduction of other elements than CHNOS, such as phosphorus and silicon, have been explored as well. Phosphorus-containing thermosets exhibit good to excellent flame retardancy and mechanical performance. In particular high phosphorus/nitrogen (P/N) content is imparting these polymer properties.[102] Silicon was used to functionalize the olefin present in eugenol resulting in excellent thermal stability of the final resin.[111]

Among the most complex chemistry reported in this paper is azide−alkyne cycloaddition, which is described in the context of thermoset synthesis from functionalized lignin. Moreover, in the case of vanillin, oxidation of aromatic aldehyde to methoxyhydroquinone via Dakin oxidation represents a way to switch the monomer's reactivity, passing from electrophilic carbon to nucleophilic oxygen. The latter can further undergo nucleophilic attack to epichlorohydrin as presented in the reported example.[105] The dimerization of vanillin by electrolysis[106] is another transformation that generates nucleophilic oxygens. Eugenol, on the other hand, displays an olefinic site which is prone to oxidation[112] and nucleophilic addition by strong nucleophiles (such as cysteamine in ref 113). These transformations altogether represent an innovative starting point for further modifications that allow the preparation of epoxy resins with dynamic covalent bonds.

Overall, lignin-based CANs are promising reprocessable thermosets able to replace their fossil-based counterparts, yet these still need further development. In this sense, we have prepared a SWOT analysis (Figure 7) to summarize the main strengths, weaknesses, opportunities, and threats associated with lignin-based CANs. Lignin's renewable origin, abundance, biocompatibility, biodegradability as well as its plentiful reactive functional groups emerge as the lignin-based CANs straightforward strengths. When considered in more detail, other strengths arise, namely the preparation of lignin-based derivatives uses relatively easy synthetic pathways to form the reversible bonds and the epoxy resins. In turn, this allows the use of simple characterization techniques (by NMR, for example). Additionally, lignin derivatives can offer cost advantages due to their availability as a byproduct from other processes. This can make them an attractive option for manufacturers looking for cost-effective solutions. Weaknesses mainly stem from the fact that monomers (*e.g.*, vanillin) do not possess the same properties as the parent lignin polymer, and consequently, the mechanical properties might not be satisfactory as those reported for DGEBA-derived thermosets. Moreover, lignin derived from different sources and processes exhibits variations in composition, leading to challenges in ensuring consistent quality and performance. This can affect the widespread adoption of lignin derivatives. A lot of opportunities (recyclability is the foremost) are offered by lignin-based CANs, including their use in composite materials. Alongside the technical applications (*e.g.*, flame retardants and responsive smart materials allowing for self-healing), pharmaceutical uses are also possible (thermosets with activity against Gram positive bacteria such as *S. aureus* could lead to a novel class of pharmaceutical active ingredients). Other examples where these materials can be exploited are mostly connected to the coating industry (*e.g.*, coatings and adhesives). In practice, every cured epoxy resin should prevent or slow the development of ignition, and other specific properties can also be targeted by the application of suitable chemistry (*e.g.*, UV-protection). By controlling the type and concentration of dynamic groups, it is possible to tune material's response to different stimuli, enabling CANs a wide range of applications in the fields such as biomedical engineering, soft robotics, and smart materials.[131] Furthermore, CANs have attracted significant interest from the 3D printing industries due to their ability to form strong but still reversible bonds between the printed layers (Figure 8a). In addition to 3D printing, the application of CANs can be expanded to dental restorative resins,[132] composites and coatings,[133] sports equipment,[134] and electronics[134] (Figure 8b). However, more efforts are still needed in order to obtain CANs with properties that match those of robust fossil-based thermosets, being this main threat of lignin-based CANs.

We believe that the broad diversity of chemical modifications presented in this review is only a part of possible transformations that can generate not only functional monomers but also whole polymers suitable for the preparation of thermosets endowed with excellent mechanical and dynamic properties, while keeping their sustainable character. In this paper, we demonstrate that the use of bio-based materials renders polymer science even more intriguing, fostering the transition to a fossil-free society. However, more coordinated research toward the design of novel bio-based CANs would be of great advantage. Additionally, there are a number of other difficulties that require particular attention in the near future. These include the need for effective and affordable lignin extraction techniques and the development of (i) scalable processing processes and (ii) uniform quality standards for lignin-derived goods. Future studies should focus on solving these problems, enhancing lignin modification techniques, and investigating new uses for lignin-based polymers.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AIBN	Azobis(isobutyronitrile)
BA	Butyl acrylate
BADGE	Bisphenol A diglycidyl ether
CANs	Covalent adaptable networks
$CHCl_3$	Chloroform
DA	Diels−Alder
DCC	*N*,*N*′-Dicyclohexylcarbodiimide
DCM	Dichloromethane
DDM	4,4-Diaminodiphenylmethane
DEA	Dodecanedioic acid
DFA	5,5′-Methylenedifurfurylamine
DGEBA	Bisphenol A diglycidyl ether
DGEBF	Diglycidyl ether of bisphenol F
DMAP	4-Dimethylaminopyridin
Dytek A	2-Methylpentane-1,5-diamine
EHL	Enzymatic hydrolysis lignin
EtOAc	Ethyl acetate
EtOH	Ethanol
ESO	Epoxidized soybean oil
HDI	Hexamethylenediisocyanate
IPDA	Isophorone diamine
LCCs	Lignin−carbohydrate complexes
LCNFs	Lignin-containing cellulose nanofibrils
LOI	Limit oxygen index
MMA	Methyl methacrylate
MeOH	Methanol
NaOH	Sodium hydroxide
PFA	Paraformaldehyde
p-TSA	*p*-Toluenesulfonic acid
ROP	Ring-opening polymerization
TBAB	Tetrabutylammonium bromide

TDI	Toluene diisocyanate
TEA	Triethylamine
TEBAC	Tri ethyl benzyl ammonium chloride
TETA	Triethylenetetramine
THF	Tetrahydrofuran
PEG	Polyethylene glycol
$POCl_3$	Phosphorus oxychloride
PTA	1,2,3-Propanetricarboxylic acid
TMDS	Tetramethyldisiloxane
$Zn(acac)_2$	Zinc acetylacetonate

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