Aromatics from Lignocellulosic Biomass: A Platform for High-Performance Thermosets

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Abstract: Renewable and sustainable thermosets with thermomechanical properties that are equivalent to, or better than, those of petroleum-derived commercial incumbents are desirable to mitigate environmental and human health impacts. Current bio-derivable or biobased thermosets typically are aliphatic/cycloaliphatic and lack the robust structural features necessary to generate materials competitive with those made from conventional aromatics such as bisphenol A. Lignocellulosic biomass (LCB) is the most abundant, renewable feedstock for the production of platform aromatic chemicals (*e.g.*, phenolics from lignin, furanics from cellulosics) which are ideal as sustainable, biobased alternatives to petroleum-derived constituents for high-performance applications. This Perspective provides an overview of LCB-derivable aromatic monomers, including epoxies, cyanate esters, vinyl esters, benzoxazines, and cyclic carbonates, and it benchmarks the corresponding materials against commercially available thermosets. Furthermore, green synthesis approaches to minimize environmental impacts, robust processing methods to increase versatility, structure-property relationships to guide materials design, and life-cycle management strategies to improve the recyclability of thermosets are discussed, along with additional avenues to advance the commercial relevance of biobased thermosets. For instance, the positive impacts of the inherent functionality in biobased monomers on toxicity and environmental considerations, as well as opportunities to leverage the synergies between experimental and computational activities, are highlighted.

Keywords: biobased, aromatic, lignin, furanic, thermoset, recycling, biomass, life-cycle management

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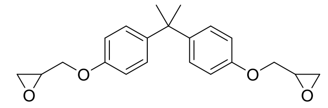
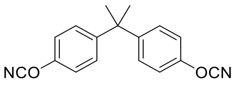
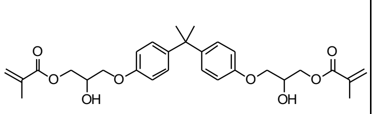
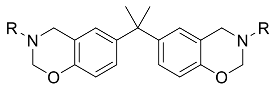
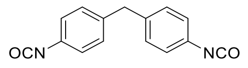
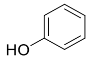
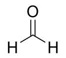
Introduction

Thermosetting polymers (thermosets) are crosslinked networks that are dimensionally stable under various conditions such as elevated temperature, physical stress, and chemical exposure.[1] This stability makes them ideal for diverse applications, including coatings, adhesives, electronic materials, automotive parts, and aerospace parts, among others.[1-5] Commercially available thermosets are most commonly derived from epoxy, cyanate ester, vinyl ester, benzoxazine, and isocyanate monomers.[1-3] These monomers, representative thermochemical properties of the corresponding thermosets (*e.g.,* glass transition temperature (T_g), degradation temperature at 5% weight loss ($T_{d5\%}$), and storage modulus (E')), and some of the benefits and challenges associated with each are summarized in Table 1. The corresponding materials are high-performance with respect to service temperature and modulus, enabling many of the technologies used in everyday life. However, commercial thermosets typically are petroleum-based, employ toxic precursors, and are not recyclable.[5-8]

Table 1. Summary of some common commercial thermosets, representative properties, and key characteristics.

Conventional monomer example	**Thermoset class**	**Curing chemistry example**	**Thermo-mechanical properties***	**Key characteristics**
 Bisphenol A (BPA) diglycidyl ether	Epoxy	Ring-opening polymerization (ROP) of epoxy groups with multifunctional nucleophilic or electrophilic species	T_g = ~100-180 ºC $T_{d5\%}$ = ~300-400 ºC E' = ~2-3 GPa	**Pros** • Widely tunable thermomechanical properties • Excellent adhesion on various substrates • Highest market share of all thermosets **Cons** • Most are BPA-derived (90%)
 BPA cyanate ester	Cyanate ester	Cyclo-trimerization reaction to form cyanurate ring	T_g = ~250-300 ºC $T_{d5\%}$ = ~400-450 ºC E' = ~2.5-3 GPa	**Pros** • Low water uptake • Electrical resistance • Flame-retardant **Cons** • Long curing times
 BPA glycidyl dimethacrylate (epoxy vinyl ester)	Vinyl ester	Free-radical, chain-growth, co-polymerization between styrene and vinyl ester monomers	T_g = ~140-155 ºC $T_{d5\%}$ = ~250-300 ºC E' = ~2.5-3 GPa	**Pros** • Less expensive and easier to process than epoxies • Combines properties of epoxies and unsaturated polyesters **Cons** • Needs reactive diluents such as styrene

 BPA benzoxazine	Poly-benzoxazine	ROP of benzoxazine monomer	T_g = ~160-250 ºC $T_{d5\%}$ = ~200-350 ºC E' = ~1.5-2.5 GPa	**Pros** • Combines properties of epoxies and phenolic resins • Flame-retardant • Minimal shrinkage during curing **Cons** • High curing temperatures
 Bisphenol F (BPF) diisocyanate or 4,4'-Methylene diphenyl diisocyanate (MDI)	Polyurethane (PU)	Nucleophilic addition polymerization of isocyanates and polyols	T_g = ~0-100 ºC $T_{d5\%}$ = ~250 ºC E' = ~1 GPa	**Pros** • Widely tunable thermomechanical properties • Excellent adhesion on many substrates **Cons** • Isocyanates are hazardous
 Phenol  Formaldehyde	Phenol-formaldehyde (PF)	Polycondensation of phenols and formaldehyde	T_g = ~100-200 ºC $T_{d5\%}$ = ~350 ºC E' = ~1.5-3 GPa	**Pros** • Low cost • Good electric and chemical resistance • Flame-retardant **Cons** • Volatile and toxic formaldehyde • Shrinkage upon curing

*The thermomechanical properties are highly dependent on the structure of curing agent and thermoset monomer with the phenol-, or BPA-, or BPF-based versions listed being some of the most common.

Aromatics, such as BPA, are the precursors of choice for high-performance engineering materials owing to their rigidity, hydrophobicity, and thermal stability.[2, 7] However, BPA and other commercial bisphenols exhibit estrogenic activity and are suspected human endocrine disruptors.[9-12] Many other petroleum-based monomers/chemicals employed in the production of thermoset resins, such as phenol, formaldehyde, styrene, and many isocyanates, are volatile and toxic, carcinogenic, mutagenic, or reprotoxic.[13-16] In the case of bisphenols, estrogenic activity arises from the phenolic hydroxy groups binding with estrogen receptors and mimicking the estrogen hormone, estradiol.[12, 17] The binding affinity and efficacy are significantly reduced by bulky substituents on bisphenol molecules,[12, 18] but many BPA alternatives still exhibit some degree of estrogenic activity.[17-19] Humans can be exposed to bisphenols from many sources. Leaching from bisphenol-derived plastics is of particular concern in food contact materials (FCMs)[20-22] because bisphenols are considered contributing factors in numerous health conditions, including diabetes,[23, 24] obesity,[25] reproductive disorders,[26, 27] breast cancer,[28] birth defects,[29, 30] chronic respiratory diseases,[31] and cardiovascular disease.[32] Thus, several countries have banned BPA-containing products for FCMs,[33] and safer and more sustainable alternatives to bisphenols are needed for FCMs and, more generally, thermosets.

Apart from the potential health hazards posed by the production and use of these materials or their precursors, there are growing concerns about the long-term environmental impacts of plastic production and waste generation.[34-36] At the beginning of the polymer life cycle, the use of petrochemicals contributes to ecological harm from fossil fuel extraction and greenhouse gas emissions, and at the end of the polymer life cycle, ~150 million tons of plastic waste are discarded annually,[37, 38] with only ~9% being recycled.[6] Furthermore, current recycling strategies generally are limited to thermoplastics because of the permanent crosslinks in thermosets,[5, 39] meaning that most thermoset plastic waste is landfilled or incinerated. Hence, there is a significant need to produce next-generation materials that are sustainably sourced, have minimal potential health impacts, perform at least as well as conventional materials, and minimize waste generation through careful design and robust life-cycle management strategies.

Biomass feedstocks can play a major role in the shift toward more sustainable materials, and the renewable polymer market is growing rapidly, expanding from an annual production of ~3.5 million tons (1.5% of the total polymer output) in 2011 to ~12 million tons (3% of the total polymer output) in 2020.[40] Numerous studies have focused on the development of less/non-toxic renewable thermoset resins derived from renewable sources such as plant oils,[41, 42] fatty acids,[43, 44] and rosins.[45-47] Epoxidized soybean oil, an industrially available platform chemical, is one prominent example and is used in renewable epoxy resins.[42, 48-52] However, most of the available biobased platform chemicals/resources (plant oils, fatty acids, and rosins) are aliphatic or cycloaliphatic in nature, and the materials prepared from these precursors have comparatively lower T_g, thermal stability, and E' than those of many conventional thermosets.[53] Because of this limitation, renewable aromatics are necessary to produce sustainable materials with thermomechanical properties that meet or exceed those of conventional, high-performance, aromatic-based thermosets.

Lignocellulosic biomass (LCB) is the most abundant potential source of renewable aromatic chemicals.[6, 7, 54] It does not compete with food resources or require new crops, unlike other common sources that are limited in scale and/or used as food, such as plant oils, tannins, and vanilla bean pods.[55-57] LCB is around 15-30% lignin by weight, with 40-60% cellulose and 10-40% hemicellulose as the remainder.[2, 6, 58] Lignin is an amorphous, aromatic polymer that consists of three types of phenylpropanoid units, *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), linked together by numerous bond types, with the β-O-4 linkage being the most common.[2, 54, 59-64] The relative content of these three units, and the linkages between them, vary with the source of biomass and its processing history (*e.g.,* pulping).[59, 64, 65] Approximately 70 million tons of lignin are separated from biomass annually as a byproduct of pulping processes, and more than 98% of the separated lignin is burned for chemical and energy recovery.[66] Several pulp mills have begun isolating lignin from their byproduct streams,[7, 54] and bulk lignin has applications in asphalt and concrete binders, dust suppressants, and tire fillers.[6, 67] However, the use of lignin in polymer composites, most commonly derived from epoxy resins, presents several challenges, including polymer structural variation with plant type,[68] unpleasant odors,[68] dark colors,[68, 69] and limited reactivity.[70] This structural heterogeneity can lead to inconsistent material properties, and the color and odor of bulk lignin limit use to lower-value applications. Additionally, the low reactivity of bulk lignin arises from the inaccessibility of reactive phenolic hydroxy and other groups.[70] The phenolic hydroxy groups are mostly etherified, and the *ortho* and *para* positions of phenolic moieties typically are occupied, leading to reduced crosslink density and limited control over the thermomechanical properties of the resulting materials.[70] In contrast to lignin, cellulose and hemicellulose (together considered cellulosics) are semi-crystalline polysaccharides composed of glucose and other sugars, respectively.[6, 71, 72] Cellulosics are limited with respect to available functional groups, but they are not hindered by color and odor.[6] Most of the cellulose separated from biomass can be used in paper or personal care products; however, cellulose also has found applications as a reinforcement/filler in biocomposites, as food packaging (*e.g.,* cellophane), and in other materials.[73, 74] The abundance and large-scale availability of LCB and its components make it a reliable, scalable, and cost-effective feedstock, but conversion to monomers is extremely desirable for the production of high-performance and high-value thermosets.[2, 6, 7, 54, 65]

Depolymerization of the LCB components to their respective monomers (*i.e.*, phenolic compounds [lignin] and sugars [cellulosics]) can overcome the aforementioned challenges through increased functionality, consistency, and value.[75, 76] Lignin can be depolymerized by catalytic,[62, 77-79] enzymatic,[80] or pyrolytic[81-83] pathways to yield mixtures of bio-phenols that correspond to the H, G, and S phenylpropanoid units. Several functional groups may be present in these bio-phenols depending on the depolymerization strategy, including aliphatic/aromatic hydroxy, methoxy, aldehyde, carboxylic acid, alkyl, allyl, and alkenyl groups, and many of these chemical handles can be leveraged to generate safer, renewable thermosets.[2, 6, 7, 54, 84, 85] Cellulosics similarly can be depolymerized to sugars and further converted into platform furanics, such as hydroxymethylfurfural (HMF), through continued acid-catalyzed dehydration.[6, 71, 72] Together, lignin-derived phenolics and cellulosic-derived furanics can significantly improve the properties of renewable thermosets, and moreover, their inherent functionalities can be leveraged to generate performance-advantaged materials (*i.e.,* polymers with improved properties relative to those of the incumbent) that can be recycled or further modified for unique applications.

This Perspective provides an overview of LCB-derived aromatic precursors for thermoset applications. Green synthesis strategies, advanced processing methods, and life-cycle management approaches are highlighted to demonstrate the unique performance and sustainability characteristics of bio-derivable thermosets. Structure-property and structure-activity relationships also are discussed in the context of maximizing performance and safety. For comparative purposes, bio-derivable and biobased materials are benchmarked against appropriate commercial thermosets with emphasis on suitability for potential applications. The remainder of this Perspective is divided into two major sections: lignin-derived phenolic building blocks and cellulosic-derived furanic building blocks. Each section is subdivided into the key functional handles that are used to generate thermosets from each precursor. The impact of these functionalities on materials synthesis and performance is described, and the properties of the bio-derivable materials are compared to those of commercial analogues. Reprocessable and recyclable materials with reversible chemistries also are examined to emphasize a holistic approach to life-cycle management that accounts for the beginning (*i.e.,* feedstock choice), middle (*i.e.,* processing), and end (*i.e.,* recycling or disposal) of the polymer life cycle. Finally, some future opportunities for the development of safer, higher-performance, biobased thermosets are provided. Figure 1 serves as an illustrative summary of major topics that are highlighted in this Perspective.

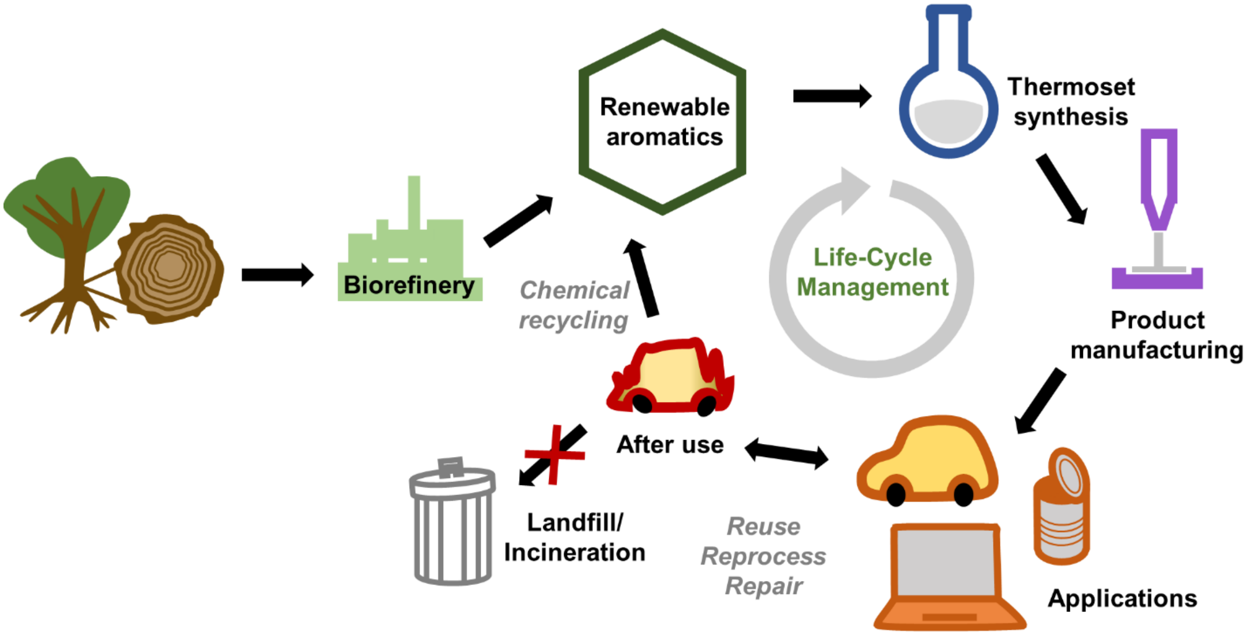


Figure 1: Key aspects of LCB-derived thermosets. The generation of renewable aromatic chemicals, monomer and thermoset synthesis, material processing, product applications/performance, recyclability and life-cycle management are all crucial in the development of next-generation, sustainable materials.

Lignin: biobased phenolics

Lignin depolymerization can produce well-defined, aromatic molecules/monomers, such as methoxyphenols (guaiacol, syringol), alkylmethoxyphenols (methyl to propyl guaiacols/syringols), aldehydes (vanillin, syringaldehyde), catechols, and substituted phenols.[6, 7, 54, 86-88] These compounds possess several inherent functional handles that are important in the generation of high performance renewable materials as shown in Figure 2. Additionally, these moieties can be leveraged to tune the thermomechanical properties of the resultant thermosets and impart unique and useful features such as reversible bond formation, self-catalyzed curing, or reduced estrogen receptor binding.

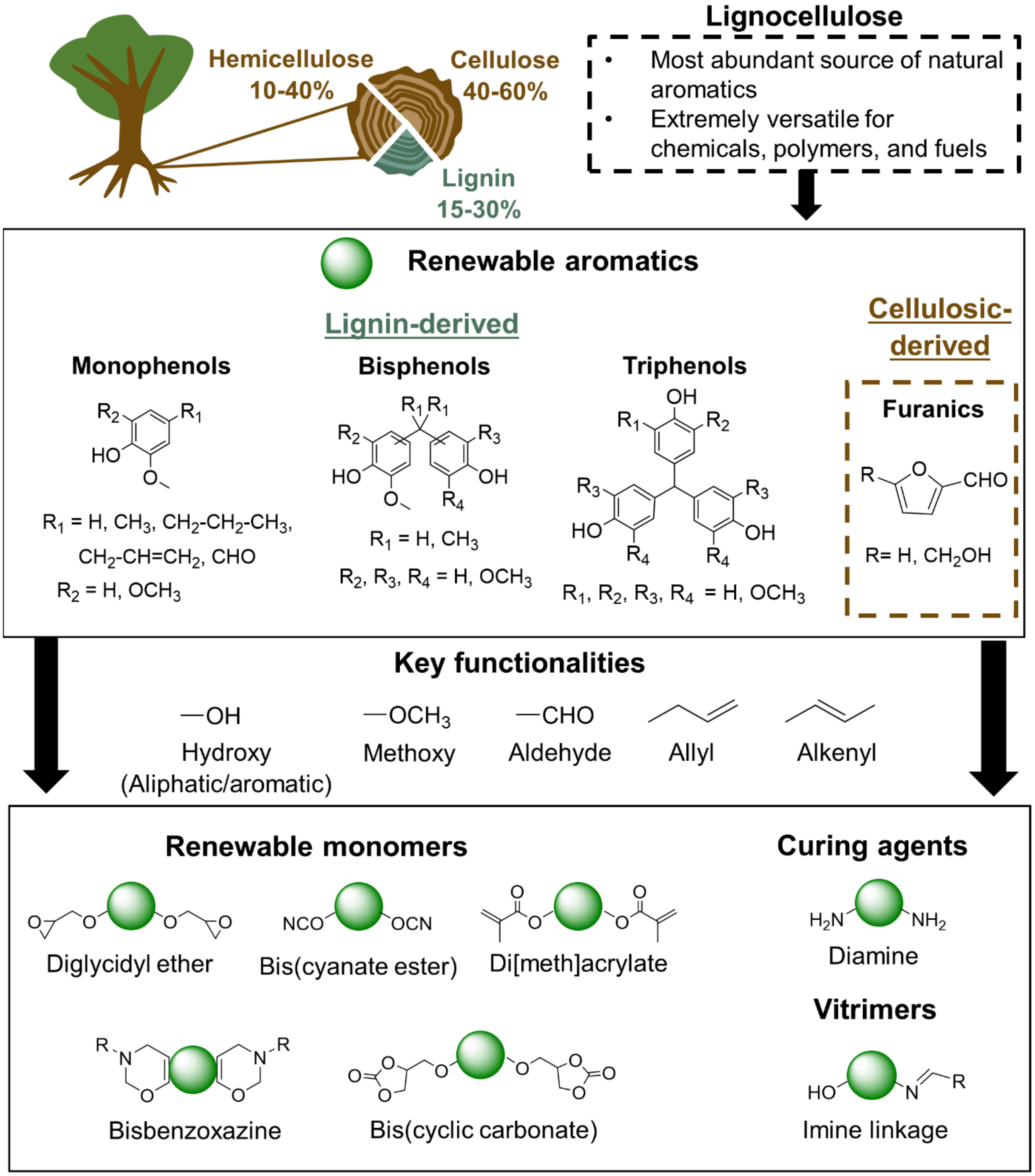


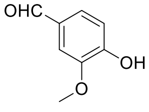
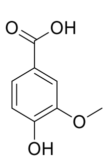
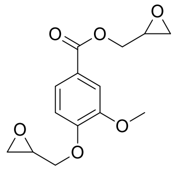
Figure 2: Overview of LCB-derivable building blocks for thermoset applications, along with key characteristics and functionalities, and general structures of monomers and curing agents.

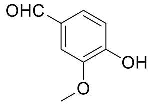
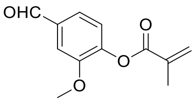
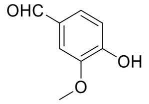
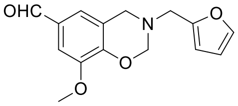
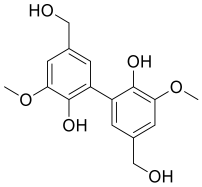
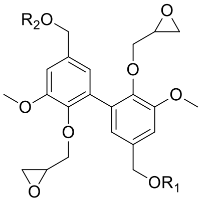
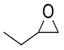
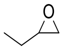
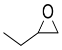
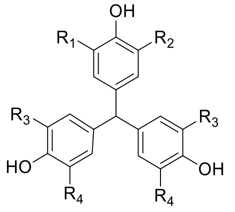
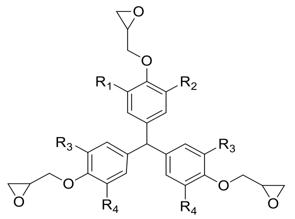
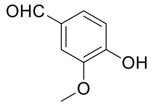
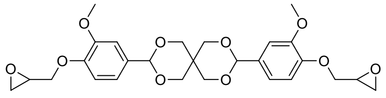
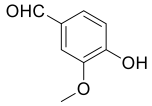
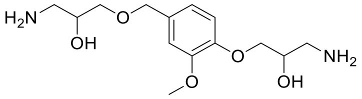
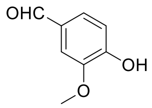
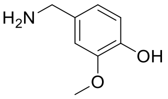
Monophenolic compounds also can be converted into biobased bisphenols (*e.g.,* bisguaiacols, biseugenol, divanillin) that closely resemble conventional bisphenols such as BPA and BPF.[89-91] The monophenols can be coupled either by direct aromatic substitution,[89, 90] aldehyde/ketone coupling,[92] or 'click' chemistry.[93] The bisphenol compounds impart more structural rigidity than monophenols, and materials with equivalent or better thermomechanical properties relative to commercial bisphenol-based polymers are achievable.

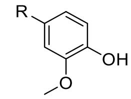
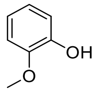
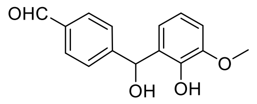
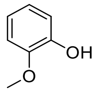
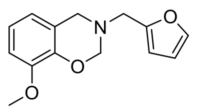
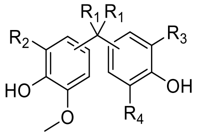
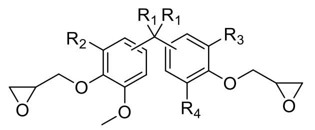
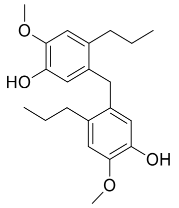
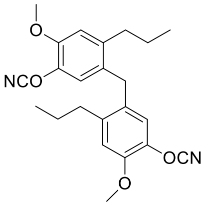
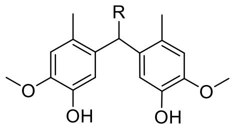
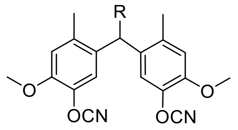
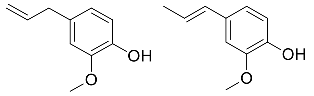
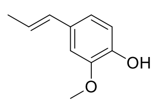
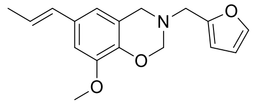
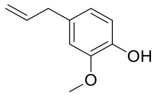
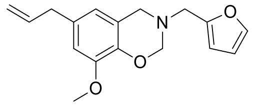
Triphenols are more rigid in comparison to mono/bisphenolic compounds, and the increased tunability and functionality can be leveraged to design robust materials with higher crosslink densities and potentially reduced toxicities.[94] Triphenols are synthesized *via* condensation of phenolic aldehydes, such as 4-hydroxybenzaldehyde, vanillin, or syringaldehyde, with two molecules of phenolics, such as phenol, catechol, guaiacol, or syringol.[94] The lignin-derivable aldehyde compounds serve as bridging elements to obviate the need for petroleum-based bridging groups (*e.g.,* formaldehyde, acetone) and also provide additional reactive sites for materials synthesis.[94]

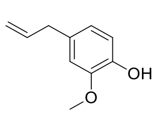
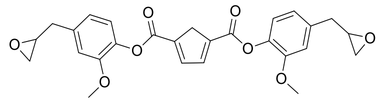
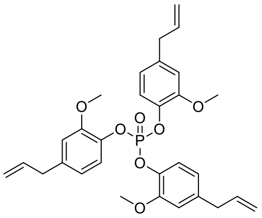
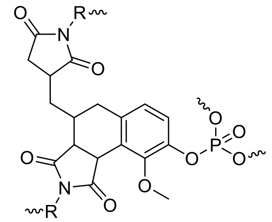
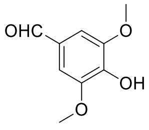
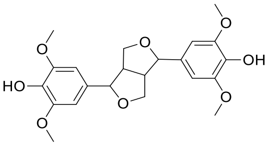
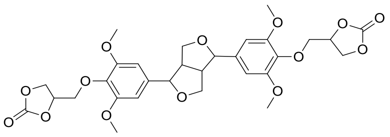
The remainder of this section highlights the applications of mono/bis/triphenolic precursors in thermoset materials and is divided into three main subsections: (1) vanillin and its derivatives, (2) guaiacols and alkyl guaiacols, and (3) allyl and alkenyl guaiacols. Key structure-property relationships are discussed in the context of designing new monomers and curing agents/hardeners that could offer improved performance, safety, and sustainability versus conventional thermosets for various applications. The chemical structures and characteristics of select bio-derivable monomers/thermosets are summarized in Table 2.

Table 2. Summary of various bio-derivable phenolic building blocks and thermomechanical properties of the resultant thermosets.

No.	Bio-derivable aromatic	Monomer	Thermoset class	Characteristics	Ref.
	 **Vanillin**				
1	 Vanillic acid	 Diglycidyl ether of vanillic acid (DGEVAC)	Epoxy (cured with isophorone diamine [IPDA])	T_g = 152 ºC Peak degradation temperature (T_p) = 370 ºC E' = 2.1 GPa @30 ºC	95

2	 Vanillin	 Vanillin methacrylate	Vinyl ester (cured with glycerol dimethacrylate)	T_g = 155 ºC Degradation temperature at 50% weight loss ($T_{d50\%}$) = 405 ºC E' = 3.6 GPa @25 ºC	15
3	 Vanillin	 Vanillin-furfurylamine benzoxazine	Polybenzoxazine	T_g = 270 ºC $T_{d5\%}$ = 351 ºC	96
4	 Divanillyl alcohol (DVA)	 (1) R_1 = H, R_2 = H Diglycidyl ether of divanillyl alcohol (DiGEDVA) (2) R_1 = , R_2 = H Triglycidyl ether of divanillyl alcohol (TriGEDVA) (3) R_1 = , R_2 =  Tetraglycidyl ether of divanillyl alcohol (TetraGEDVA)	Epoxy (cured with IPDA)	(1) T_g = 138 ºC $T_{d5\%}$ = 275 ºC E' = 1.9 GPa @25 ºC (2) T_g = 163 ºC $T_{d5\%}$ = 296 ºC E' = 2.4 GPa @25 ºC (3) T_g = 198 ºC $T_{d5\%}$ = 276 ºC E' = 2.1 GPa @25 ºC	91
5	 R_1, R_2, R_3, R_4 = H, OCH_3 Triphenol	 Triglycidyl ether of triphenol	Epoxy (cured with diethylenetriamine [DETA])	T_g = 118-132 ºC $T_{d5\%}$ = 184-257 ºC E' = 2.2-2.7 GPa @30 ºC	94
6	 Vanillin	 Diglycidyl ether of 4,4′-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methoxyphenol)	Epoxy (cured with IPDA)	T_g = 164 ºC E' = 9.1 MPa @220 ºC	97
7	 Vanillin	 Dihydroxyaminopropane of vanillyl alcohol	Epoxy (used with diglycidyl ether of BPA [DGEBA])	T_g = 72 ºC $T_{d5\%}$ = 320 ºC	98
8	 Vanillin	 Vanillylamine	Epoxy (used with DGEBA)	T_g = 67 ºC (T_p) = 230 ºC	99

	 R = H, CH_3, C_3H_7 **Alkyl guaiacols**				
9	 Guaiacol	 Guaiacol-terephthalaldehyde (TPA) adduct	PF	T_g = 164 ºC Degradation temperature at 10% weight loss ($T_{d10\%}$) = 345 ºC E' = 1.6 GPa @50-100 ºC	100
10	 Guaiacol	 Guaiacol-furfurylamine benzoxazine	Polybenzoxazine	T_g = 148 ºC $T_{d5\%}$ = 352 ºC	101
11	 R_1 = H R_2, R_3, R_4 = H, OCH_3 Bisguaiacols	 Diglycidyl ether of bisguaiacols	Epoxy (cured with 4,4′-methylenedianiline [MDA])	T_g = 111-151 ºC $T_{d5\%}$ = 344-368 ºC E' = 2-3.2 GPa @30 ºC	90
12	 *m,m'*-bis(4-*n*-propylguaiacol)	 *m,m'*-bis(4-*n*-propylguaiacol) cyanate ester	Cyanate ester	T_g = 193 ºC $T_{d5\%}$ = 389 ºC	92
13	 R = H, CH_3, CH_2CH_3 Biscreosols	 Biscreosol cyanate ester	Cyanate ester	T_g = 219-248 ºC $T_{d5\%}$ = 329-360 ºC	102
	 **Eugenol** **Isoeugenol**				
14	 Isoeugenol	 Isoeugenol-furfurylamine benzoxazine	Polybenzoxazine	T_g = 164 ºC $T_{d5\%}$ = 375 ºC	103
15	 Eugenol	 Eugenol-furfurylamine benzoxazine	Polybenzoxazine	T_g = 162 ºC $T_{d5\%}$ = 338 ºC	103

16	 Eugenol	 Diglycidyl ether of bis(4-allyl-2-methoxyphenyl) furan-2,5-dicarboxylate	Epoxy (self-cured)	T_g = 161 ºC $T_{d5\%}$ = 350 ºC	104
17	 Trieugenylphosphate (TEP)	 (1) R = Ph TEP-*N,N'*-1,3-phenylene bismaleimide (PhBMI) adduct (2) R = $[Si(CH_3)_2O]_n$ TEP-polydimethylsiloxane bismaleimide (SiBMI) adduct	Bismaleimide (BMI)	(1) T_g = 247 ºC $T_{d5\%}$ = 359 ºC E' = 1.49 GPa @ Room temperature (RT) (2) T_g = -113 ºC $T_{d5\%}$ = 381 ºC E' = 4.4 MPa @RT	105
	 **Syringaldehyde**				
18	 Syringaresinol (SYR)	 Cyclic carbonate of SYR	Non-isocyanate PU (NIPU)	T_g = 62 ºC $T_{d5\%}$ = 225 ºC	106

Vanillin and its derivatives

Vanillin is used widely as a flavor and fragrance ingredient, specialty chemical intermediate, and pharmaceutical precursor, with a production rate of ~20,000 tons/yr.[53, 107] Solvay dominates the vanillin market and supplies ~85% of the world's vanillin from a petroleum-based catechol-guaiacol process.[108] Wood-based vanillin, which accounts for ~3,000 tons annually (~10% of the world's supply), is produced predominantly by Borregaard LignoTech through an oxidative biorefinery approach using lignosulfonates.[109, 110, 111] Thus, lignin is a major feedstock for industrial scale, sustainable vanillin production.[53] In its native state, the hydroxy and aldehyde functionalities in vanillin are advantageous for the development of renewable monomers and curing agents for high-performance thermosets,[99, 112, 113] and the aldehyde group can form reversible chemical bonds through imine exchange to prepare biobased vitrimers.[8] Therefore, vanillin has significant potential for materials applications. The following subsection highlights the use of vanillin and its derivative monomers for epoxy, vinyl ester, and benzoxazine resins, along with as critical components in hardeners and vitrimers.

Vanillin-derived monomers

Vanillin and its derivatives serve as a platform for designing biobased epoxy thermosets with tunable thermomechanical properties, and some of these vanillin derivatives can compete in terms of thermomechanical/performance properties with conventional BPA-based epoxy systems.[95, 112] For example, DGEVAC cured with IPDA (Table 2, 1) exhibited equivalent thermomechanical properties (T_g ~152 ºC, $T_{d5\%}$ ~370 ºC, E' ~2.1 GPa at 30 ºC) to those of a DGEBA/IPDA thermoset (T_g ~166 ºC, $T_{d5\%}$ ~360 ºC, E' ~1.9 GPa at 30 ºC). This similarity in behavior was attributed to the conjugated ester group in DGEVAC that restricted the rotation of the polymer backbone in a manner akin to the isopropylene bridge in BPA.[95] In addition to the comparable properties, vanillic acid is expected to be safer than BPA because it is a food additive and was granted 'generally recognized as safe' (GRAS) status by the U.S. Food and Drug Administration.[114] In essence, this example highlights that potentially safer, lignin-derived compounds can be used in thermosets with equivalent performance properties versus commercially available systems.

Biobased vinyl ester resins from vanillin also can offer application-relevant thermomechanical properties with little waste generation. For example, Wool and co-workers reported a two-step, one-pot approach for the synthesis of vanillin-derived vinyl esters (Table 2, 2).[15] In the first step, vanillin was reacted with methacrylic anhydride to yield the desired mono-functional monomer (vanillin methacrylate); methacrylic acid was the byproduct. The methacrylic acid subsequently was consumed by reaction with glycidyl methacrylate to generate a crosslinker, glycerol dimethacrylate.[15] The monomer mixture was thermally polymerized to produce a vanillin–glycerol dimethacrylate resin without the need for any reactive diluents (*e.g.*, styrene) or formation of any byproducts.[15] The thermomechanical properties of the lignin-derivable vinyl ester resin (T_g ~155 ºC, E' ~ 3.6 GPa at 25 ºC) were comparable to those of a commercial vinyl ester resin (VE828) with 45 wt% styrene as the reactive diluent (T_g ~145 ºC, E' ~2.7 GPa at 35 ºC).[15] Additionally, the low viscosity and photopolymerizability of this potentially biobased resin are compatible with additive manufacturing techniques as reported by Stanzione and co-workers.[115] In that case, stereolithography (SLA) was used to fabricate materials with thermal (T_g

~153 ºC) and mechanical (E' ~3.8 GPa at 25 ºC) characteristics that were equivalent to analogous resins cured *via* thermal techniques.[115] These vanillin-based vinyl esters are appealing because of their atom-efficient synthesis, photopolymerizability, low viscosity, and thermomechanical properties. Efforts toward expanding this approach by substituting more rigid di- and tri-glycidyl ethers of biobased bisphenols or triphenols for the glycidyl methacrylate could further increase the T_gs and moduli of the resulting materials making them suitable for higher-temperature applications while maintaining atom efficiency.

Lignin-derived aldehyde compounds, such as 4-hydroxybenzaldehyde, vanillin, and syringaldehyde, also have potential to replace toxic and volatile formaldehyde in conventional PF resins and reduce volatile emissions during curing.[16, 100] Furthermore, difunctional aromatic aldehydes, which are interesting candidates for formaldehyde substitution because of their aromaticity, can be obtained from various lignin aldehydes listed above.[16] For instance, 4,4'-oxydibenzaldehyde and 4-(4-formylphenoxy)-3-methoxybenzaldehyde can be produced from 4-hydroxybenzaldehyde and vanillin, respectively.[16] The substitution of these compounds for formaldehyde resulted in PF thermosets with higher thermal stability ($T_{d10\%}$ >440 ºC) and higher char yield (~60-70% at 900 ºC) in comparison to conventional PF materials ($T_{d10\%}$ ~400 ºC and char yield ~60% at 900 ºC).[16] Additionally, methoxyphenols can be substituted for conventional phenols to yield potentially biobased PF resins.[100] For example, a guaiacol/TPA thermoset (Table 2, 9) exhibited T_g ~164 ºC, $T_{d10\%}$ ~345 ºC, and char yield ~60% at 900 ºC.[100] Although these bio-derivable PF resins can remove some of the hazards associated with conventional PF resins, they do not address all of the shortcomings of PF thermosets, such as shrinkage upon curing and the need for a polymerization catalyst.[101, 116-118]

Polybenzoxazines overcome some of the challenges with PF resins, and the aldehyde functionality of vanillin is advantageous for the synthesis of biobased polybenzoxazines with widely tunable molecular design for use in many thermoset applications.[116-118] In general, polybenzoxazines exhibit reduced shrinkage upon curing and lower moisture absorption relative to PF resins and do not require a polymerization catalyst. Together, the increased sustainability, versatility, and performance of biobased polybenzoxazines make them excellent substitutes for conventional PF resins in thermoset applications, such as flame-retardant materials, structural composites, adhesives, and other applications.[96, 101, 103, 118] One of the major challenges with conventional benzoxazines is the requirement for high curing temperatures (~250 ºC). For biobased systems, the aldehyde group of vanillin can be leveraged to design benzoxazine resins with lower curing temperatures and higher crosslink densities versus their commercial counterparts, such as poly(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine) (P-a).[119] For instance, bio-derivable benzoxazine monomers were synthesized by Varma and co-workers *via* a Mannich condensation reaction of vanillin, furfurylamine, and paraformaldehyde using a solventless approach (Table 2, 3).[96] The aldehyde moieties of vanillin served two purposes in the ROP of the benzoxazine monomer. First, a fraction of the aldehyde groups was oxidized to carboxylic acids that self-catalyzed the ROP reaction, after which the remaining aldehyde groups participated in the ROP. Together, these features resulted in a lower curing temperature and an increased crosslink density relative to commercial analogues.[120] The curing temperature was 170-200 ºC, which was ~40-50 ºC lower than the curing temperature of the petroleum-based P-a.[96] Additionally, the increased crosslink density resulted in vanillin-based polybenzoxazines with superior thermal properties and a better char yield (T_g ~270 ºC, char yield ~65% at 800 ºC) than either P-a (T_g ~111 ºC, char yield ~44% at 800 ºC)[119] or poly(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine-6-carboxylic acid) (T_g ~124 ºC, char yield ~43% at 800 ºC).[96] The high char yield indicates that this bio-derivable polybenzoxazine has potential as a flame-retardant coating, and the reduced curing temperature could significantly lower energy costs associated with the manufacture and use of polybenzoxazines. Further study of the structure-property relationships among this class of materials could be leveraged to develop high-performance, biobased thermosets with faster curing kinetics and higher char yields suitable for coatings and electronic materials. Additionally, tuning the carboxylic acid and aldehyde content in these resins could provide control over curing rate and crosslink density, and these biobased monomers could be mixed with conventional benzoxazines to reduce fabrication costs and increase performance.

Vanillin-derived bisphenols

Biobased bisphenols prepared from vanillin are promising building blocks for thermoset applications. For example, Savonnet *et al.* reported a divanillin compound, DVA, for use as an alternative to BPA in epoxy thermosets (Table 2, 4). The DVA was prepared by selective enzymatic oxidative coupling of vanillin followed by reduction of the aldehyde groups to alcohols;[91] then it was glycidylated with epichlorohydrin to yield a mixture of DiGEDVA, TriGEDVA, and TetraGEDVA.[91] These products were separated by flash column chromatography and cured with IPDA. The T_g and E' of the resulting thermosets increased with the number of epoxy groups because the additional epoxy moieties resulted in higher crosslink densities. The thermomechanical properties of cured TriGEDVA/IPDA (T_g ~163 ºC, E' ~2.4 GPa at 25 ºC) and TetraGEDVA/IPDA (T_g ~198 ºC, E' ~2.1 GPa at 25 ºC) resins were higher than those of a DGEBA/IPDA thermoset (T_g ~152 ºC, E' ~1.7 GPa at 25 ºC).[91, 121] The GEDVA-based thermosets did exhibit lower thermal stability ($T_{d5\%}$ ~275-296 ºC) than the DGEBA-based materials ($T_{d5\%}$ ~349 ºC)[91] likely because of the electron-donating methoxy groups along with increased oxygen content in the polymer backbone that accelerated the decomposition process in the lignin-derived thermosets.[89, 122] However, the thermal stability still is sufficient for most applications, such as coatings, adhesives, automotive parts, and electrical casings.[121, 123] Typical upper service temperatures of commercial epoxy resins are ~180 ºC,[123] and GEDVA resins are stable ~100 ºC above this limit. Altogether, the potential of highly selective biological/enzymatic synthetic routes for biobased monomer production offers another strategy to leverage the aldehyde groups of vanillin to generate performance-advantaged materials. Future efforts could focus on toxicity evaluation as the bridging structure and substituent groups of DVA are significantly different than those of conventional bisphenols and may result in reduced estrogenic activity.

Vanillin-derived triphenols

The increased functionality of lignin-derivable triphenols can be used to design robust materials with high crosslink densities.[94] Abu-Omar and co-workers synthesized triphenols by the condensation of bio-derivable aldehyde monomers with two molecules of lignin-derivable phenolics (Table 2, 5).[94] Triphenols with different methoxy contents, ranging from 0-4 methoxy groups, were converted into epoxy networks by glycidylation with epichlorohydrin, followed by curing with DETA.[94] The T_gs and E's at 30 ºC of these thermosets were in the range of 118-132 ºC and 2.2−2.7 GPa, respectively.[94] These values were higher than those of an equivalent BPA-based epoxy network (T_g ~100 ºC, E' ~2.0 GPa at 30 ºC),[94] owing to the greater functionality of the rigid triphenols. Although the thermal stabilities of the triphenol-based materials were lower ($T_{d5\%}$ ranged from 184-257 ºC) than that of the BPA-based system ($T_{d5\%}$ ~305 ºC) and showed a downward trend with an increase in the number of methoxy groups, the triphenol architecture provides opportunities to use various bio-phenols and their inherent functionalities to design renewable materials that can compete with or outperform BPA depending on the application. Expanding on this concept, a triphenol based on 3,4-dihydroxybenzaldehyde and catechol could be used to fabricate materials with high crosslink densities and high thermal stabilities. The six hydroxy groups per molecule likely would result in higher crosslink densities, T_gs, and E's, and the lack of electron-donating methoxy groups could result in a thermal stability closer to that of BPA. Thus, there is potential to generate a broader range of phenolic compounds with different functional groups that enable the fabrication of high-performance materials for high-temperature applications like structural coatings, adhesives, and composite parts for the aerospace and automotive industries.

Vanillin-derived, recyclable, reprocessable, and degradable thermosets

Renewably sourced materials address the sustainability challenges at the beginning of the polymer life cycle; however, conventional thermosets, both biobased and petroleum-based, are not reusable or recyclable. Fortunately, recent advances in polymer chemistry have enabled the fabrication of covalent adaptable networks (CANs) and the incorporation of degradable linkages to produce materials that, like conventional thermosets, are dimensionally stable under most thermal, mechanical, or chemical stress but are reprocessable, repairable, weldable, or degradable under external stimuli, such as heat, ultraviolet light, pH, *etc.*[5, 124-126] CANs also could address some of the sustainability challenges around waste management by increasing the useful lifetime of next-generation thermoset materials and enabling facile recycling.[127] For example, imine-based vitrimers, a subset of CANs often applied in self-healing hydrogels, leverage reversible bonds formed through an associative, dynamic exchange reaction mechanism between aldehydes and amines.[128-130] Several types of reversible chemistries are shown in Figure 3, including associative (*e.g.,* imine exchange,[8] transesterification,[39, 131] disulfide exchange,[52, 132] transcarbamoylation[133, 134]) and dissociative (*e.g.,* Diels-Alder (DA),[6, 135] cyclic carbonate aminolysis[133, 134]) reactions for CANs and degradable linkages (*e.g.,* spiro acetals[97]) for thermosets that selectively break down.

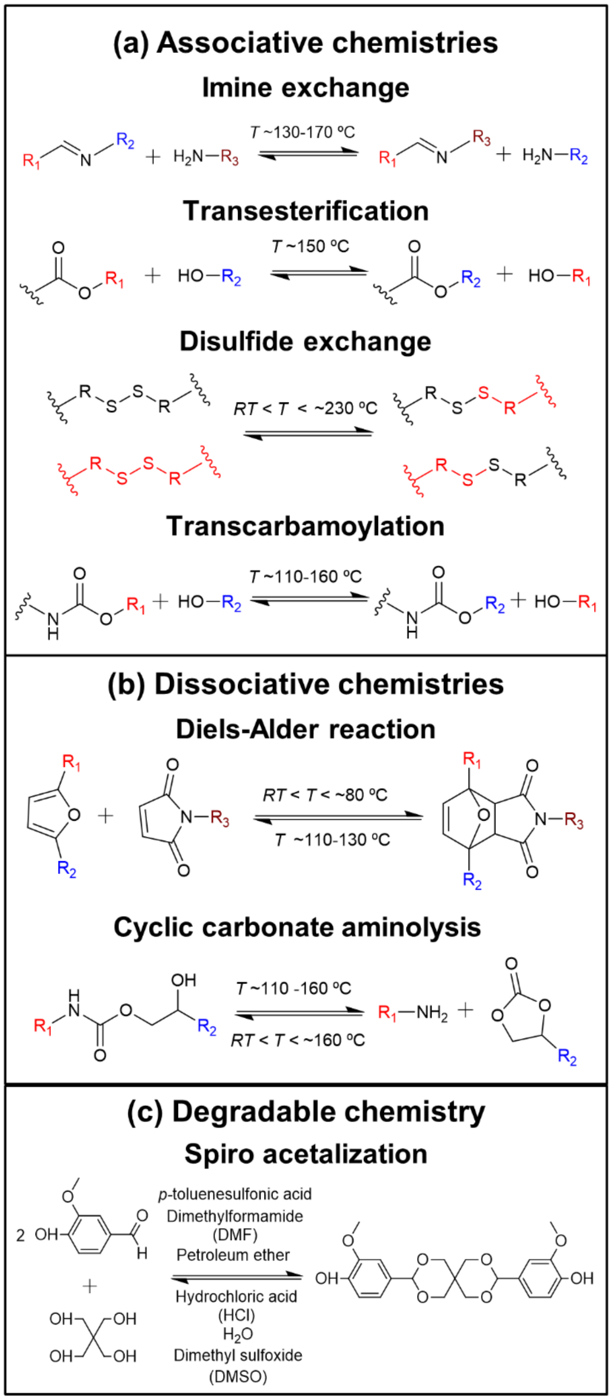


Figure 3: Several strategies for the incorporation of reversible or degradable chemistries into bio-derivable thermosets for increased recyclability.

Next-generation, vanillin-derived, epoxy vitrimers with full retention of mechanical properties, such as Young's modulus, tensile strength, and elongation at break, after recycling can be fabricated by leveraging imine chemistry. For example, Yu *et al.* cured the monoglycidyl ether of vanillin with IPDA to form a network (T_g~121 ºC, E'~2.3 GPa) with irreversible epoxy linkages at the glycidyl functionality and reversible imine bonds at the aldehyde group.[136] Although the T_g of this bio-derivable thermoset was relatively low versus a conventional BPA-based system (T_g ~160 ºC), application of these materials as pressure-sensitive adhesives and paper coatings is still possible.[137] These vitrimers were reprocessed (*i.e.,* remolded) at 130 ºC and recycled (*i.e.,* fully dissolved) by immersion in an HCl solution at 70 ºC.[136] Importantly, the reprocessed vitrimers exhibited negligible changes in mechanical properties when compared to the original network, after three cycles. Using a different approach, Zhao *et al.* first prepared a vanillin-based bisphenol (VAN-AP) with an imine bridge by reacting vanillin and aminophenol.[8] The VAN-AP was glycidylated and cured with a Jeffamine hardener to form a vitrimer (T_g~71 ºC, E'~2.0 GPa at 30 ºC).[8] The thermoset was chemically degraded by acid hydrolysis (0.25 mol/L HCl in DMF at 60 ºC) through dynamic exchange reactions,[8] and the acid and DMF then were evaporated. The resultant viscous gel was re-crosslinked by curing at 120 ºC, and the glassy moduli and T_gs of the virgin and recycled thermosets were comparable, suggesting good recyclability (Figure 4a).[8] These vitrimers also exhibited resistance to numerous solvents, including benzene, toluene, tetrahydrofuran, ethanol, DMF, DMSO, and H_2O (Figure 4b).[8] Future research on the design of larger imine-linked monomers with additional functionality (*e.g.,* a triamine reacted with three vanillin molecules) could result in materials with higher crosslink density and thermomechanical properties that are close to those of BPA-based resins. Furthermore, the extension of imine-linked bis/triphenols to other conventional thermosets, such as vinyl esters, could enable the development of more sustainable materials without sacrificing performance.

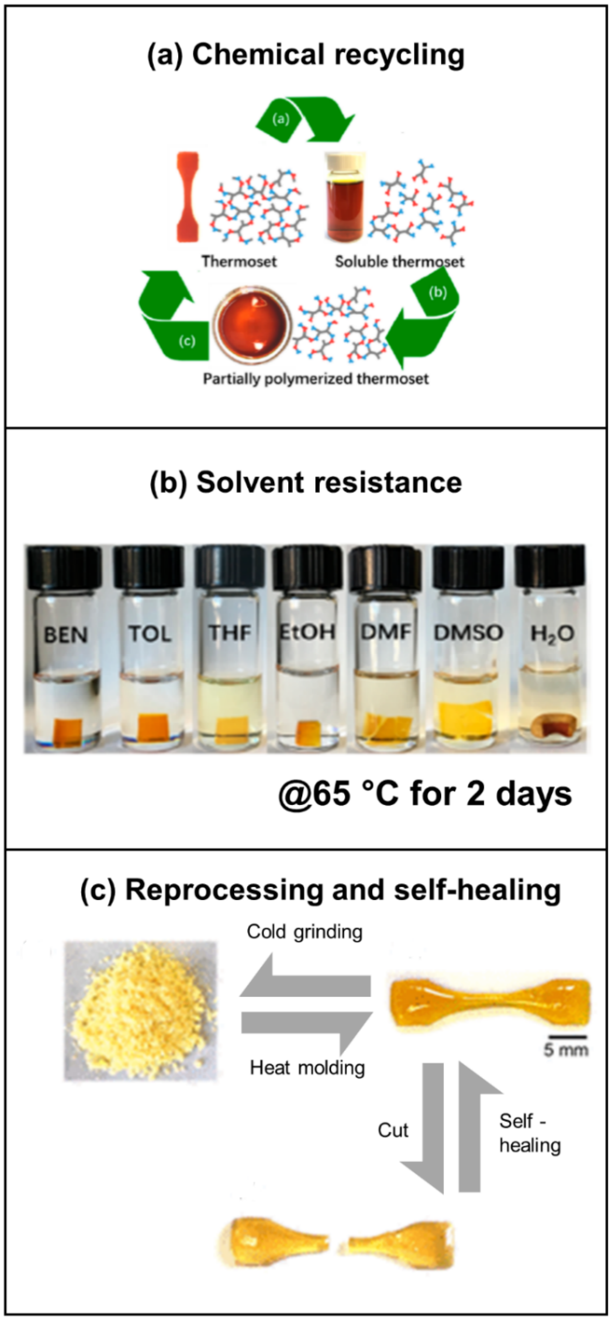


Figure 4: (a) Chemical recycling process of cured, vanillin-derived, epoxy vitrimers. Adapted with permission from (Ref. 8). Copyright (2018) American Chemical Society. **(b)** Solvent resistance of vanillin-derived vitrimers in different solvents such as benzene (BEN), toluene (TOL), tetrahydrofuran (THF), ethanol (EtOH), DMF, DMSO, and H_2O. Adapted with permission from (Ref. 8). Copyright (2018) American Chemical Society. **(c)** Reprocessing and self-healing of catechol-based epoxy vitrimers. Adapted with permission from (Ref. 88). Copyright (2019) American Chemical Society.

The aldehyde groups in vanillin also can facilitate the synthesis of degradable thermosets with spiro diacetal triggers.[97] In one study, vanillin was reacted with pentaerythritol, and the spiro diacetal compound was glycidylated (Table 2, 6).[97] This epoxy monomer was cured with IPDA, and the thermoset had nearly equivalent thermochemical properties (T_g ~164 ºC, tensile strength ~85 MPa, tensile modulus ~3.1 GPa) to a BPA-derived epoxy thermoset (T_g ~157 ºC, tensile strength ~87 MPa, tensile modulus ~2.7 GPa), owing to the rigid nature of the divanillin compound.[97] Furthermore, the bio-derivable network could be de-crosslinked in acidic media (such as 0.1-1 M HCl) through the conversion of the acetal linkage to the original aldehyde groups.[97] In another study, this aldehyde-based resin was reinforced with carbon fibers to produce high-performance composite materials with equivalent or better mechanical performance (tensile strength ~730 MPa, tensile modulus ~40 GPa) versus a BPA-based composite (tensile strength ~660 MPa, tensile modulus ~40 GPa).[97] The carbon fiber reinforced composites were soluble in acidic media, and the carbon fibers were fully recoverable and reusable.[97] Fully recyclable composites, such as those described above, provide a snapshot of some of the exciting developments enabled by triggerable and reversible chemistries.

Guaiacols and alkyl guaiacols

Guaiacols

Guaiacol is one of the simplest bio-phenols derived from lignin and has the potential to be employed as a biobased alternative to phenol benzoxazines in polymer applications such as flame-retardant materials, structural adhesives, and composites for electronic appliances.[138, 139] For instance, a bio-derivable benzoxazine monomer, 3-furfury-8-methoxy-3,4-dihydro-2H-1,3-benzoxazine (Bzf), was prepared by reacting guaiacol and paraformaldehyde with furfurylamine (Table 2, 10).[101] The guaiacol-based polybenzoxazine (polyBzf) thermoset exhibited equivalent thermal properties (T_g ~148 ºC and $T_{d5\%}$ ~352 ºC)[101] to those of a commercially available, BPF-based polymer (T_g ~144-155 ºC and degradation temperature at 7% weight loss, $T_{d7\%}$ ~350 ºC),[138, 139] and the char yield of the polyBzf at 800 ºC was 56%, which was comparable to values from various petroleum-based polybenzoxazines (~35-75%).[101, 118] The high T_g, thermal stability, and char yield of the polyBzf material was attributed to the participation of the furanic ring in the ROP *via* electrophilic aromatic substitution, which accelerated the copolymerization curing process and led to an increase in crosslink density.[101] The effect of the furanic group on crosslink density was similar to that of the aldehyde unit in the above-mentioned vanillin-based polybenzoxazines; except the furanic groups likely self-catalyzed the curing process because acid groups were not formed. Substitution of furfurylamine with amines containing both furan rings and carboxylic acid groups also could result in benzoxazine resins with reduced curing temperatures and higher crosslink densities.

Bisguaiacols

Renewable bisguaiacols have drawn attention as potential alternatives to commercial bisphenols because they are structurally similar with the exception of the methoxy substituents on the phenyl rings.[90, 140] Guaiacols easily can be converted into bisguaiacols *via* acid-catalyzed direct aromatic substitution[89, 90] or aldehyde condensation reactions.[19] Using the former approach, Nicastro *et al.*[90] and Hernandez *et al.*[89] reported lignin-derivable bisguaiacol compounds as potential alternatives to BPA for epoxy networks.[90] Bisguaiacols were produced by directly coupling substituted hydroxybenzyl alcohols (*e.g.,* vanillyl alcohol, syringyl alcohol) and substituted phenols (*e.g.,* guaiacol, syringol).[90] This synthetic strategy eliminated the use of hazardous bridging elements, such as formaldehyde and acetone, in favor of potentially biobased reagents. Glycidylated bisguaiacols were cured with a model diamine, MDA (Table 2, 11).[90] The MDA-cured bisguaiacol epoxy resins had T_gs above 100 ºC, $T_{d5\%}$s above 300 ºC, and E's above 2.0 GPa at 30 ºC.[90] The thermomechanical properties of these bisguaiacol-based epoxies were similar to those of cured diglycidyl ether of BPF (T_g ~138 ºC, $T_{d5\%}$ ~375 ºC, E'~2.4 GPa at 30 ºC), but they were slightly lower than those of cured DGEBA (T_g ~167 ºC, $T_{d5\%}$ ~381 ºC, E'~2.5 GPa at 30 ºC).[90] This trend likely was a result of the bisguaiacol bridging structure being identical to that of BPF, which is less sterically hindered than the isopropylene bridge of BPA. The number of methoxy groups and regioisomer (*p-p, o-p*, and *m-p* adducts*)* content also affected the thermomechanical properties.[90] The T_g decreased with an increase in the number of methoxy groups,[90] and the T_gs of materials prepared from pure isomers were higher than those of thermosets made from mixtures of regioisomers; both effects presumably were attributed to chain packing and free volume considerations.[90] Moreover, the methoxy groups are electron donors and contributed to the reduced thermal stability of the phenoxy-glycidyl, oxygen-carbon bond in comparison to conventional bisphenol-based resins,[90] yet the thermal stability was still above 300 ºC in all cases, which is suitable for most applications.

Abu-Omar and co-workers recently reported a catechol-based bisguaiacol for the synthesis of recyclable epoxy thermosets with tunable properties.[88] The bisphenol was prepared *via* the direct aromatic substitution of vanillyl alcohol and 4-methylcatechol, and glycidylation resulted in a mixture of single- and tri-epoxide compounds.[88] The thermal properties (T_g ~11-23 ºC, $T_{d5\%}$ ~300-354 ºC) of the corresponding resins were tuned by varying the epoxy content of the two catechol glycidylation products and curing with fatty acids.[88] Additionally, these thermosets were thermally reprocessable through transesterification reactions between the fatty acids and the hydroxy groups produced in the ROP of the epoxy groups,[131] and the polymers were cut and then self-healed with >92% efficiency by heating to 100 ºC without the application of high pressure (Figure 4c).[88] The facile self-healing highlights the utility of dynamic transesterification reactions,[131] and unlike imine exchange, the transesterification reactions were not constrained to epoxy monomers with aldehyde groups. Additionally, the T_gs and E's of these bio-derivable thermosets were similar to those of vegetable oil-derived epoxy resins owing to the flexible fatty acid hardeners, making them suitable for applications like self-adhesive tapes, pressure-sensitive adhesives, and paper coatings.[137] Overall, these transesterification reactions enable the development of materials that self-heal under mild conditions, wherein the temperature at which transesterification occurs increases with the stiffness of the material.[141]

Apart from epoxy resins, bisguaiacols also can be used in biobased cyanate ester resins. This class of materials offers numerous advantages over epoxy resins, such as higher T_gs, reduced water uptake, and excellent electrical and flame-retardant properties due to the cyanurate linkages.[92, 102] These properties make them potential candidates for marine and aerospace applications.[102] As one salient example, Sels and co-workers demonstrated the utility of alkyl-substituted guaiacols in the design of high-performance cyanate ester resins.[92] The bisphenol, *m,m'*-bis(4-*n*-propylguaiacol), was synthesized by the reaction of two molecules of softwood-derived 4-*n*-propylguaiacol with formaldehyde in an acid-catalyzed condensation reaction.[92] The *m,m'*-bis(4-propylguaiacol) then was reacted with cyanogen bromide to produce the cyanate ester resin (Table 2, 12).[92] The methylene bridge and the propyl chains imparted structural flexibility to this thermoset, and the T_g (~193 ºC)[92] was in the same range as that of commercially available bisphenol E- and bisphenol

M-based resins (~170-350 ºC), typically used as adhesives for circuit boards and other electronics applications.[142] Additionally, the water uptake of the lignin-based (~1.2%) and BPA-derived materials (~1-3%) were equivalent.[92] Overall, these resins can serve as alternatives to relatively low-T_g bisphenol-based materials, but additional strategies are needed to match the thermomechanical properties of commercial BPA-counterparts such as the incorporation of isopropylene bridging structures or catechol moieties to increase rigidity or crosslink density, respectively.

As mentioned above, different bridging groups for biobased bisphenols provide additional control over the thermomechanical properties of thermosets. Three examples of possible biobased biscreosols were prepared by the condensation of creosol (4-methyl-2-methoxyphenol) with formaldehyde, acetaldehyde, or propionaldehyde by Meylemans *et al.*[102, 143] The bisphenols were converted into cyanate ester resins by reaction with cyanogen bromide, and the cured resins (Table 2, 13) exhibited T_g*s* ranging from 219-248 ºC (in the range of analogous BPE-based systems – T_g ~170-350 ºC),[142] with the T_gs decreasing as a function of increasing alkyl chain length in the bridge.[102] The products also displayed good thermal stability (>330 ºC) along with the possible recovery of the starting phenolics at ~390-400 ºC *via* pyrolysis.[102] Future research directed towards the incorporation of more complex bridging elements, such as ketones or aromatic aldehydes, could make these bio-derivable systems competitive with their conventional BPA-based counterparts in terms of raising T_g to ~300 ºC.

The toxicity of renewable monomers is as important as the performance of biobased thermosets in the context of replacing incumbent materials. As mentioned previously, the estrogenic activity of commercial bisphenols, such as BPA and its analogues, arises from hydrogen bonding between the phenolic hydroxy groups and the estrogen receptor.[17] The bulky methoxy groups in bio-derivable bisphenol and triphenol alternatives can hinder this estrogen binding and significantly reduce endocrine disruption potential (Figure 5a).[12, 19] Peng *et al.* confirmed the role of methoxy substituents on estrogen activity using two *in vitro* assays: MCF-7 cell proliferation and VM7Luc4E2 transactivation.[18] Similarly, Sels and co-workers performed toxicity studies on alkyl-substituted bisguaiacols *via* MCF-7 cell proliferation and ERE-βGlob-Luc-SVNeo (MELN) assays (Figure 5b).[19, 92] The BGF isomers displayed a significantly reduced potency (~450x lower affinity than BPA) and efficacy (~50% of BPA's maximum induction).[19] Thus, bisguaiacols could be more sustainable and potentially less-toxic alternatives to conventional bisphenols. These toxicity studies could be expanded to include a larger slate of renewable compounds, including monophenols, other bisphenols, and triphenols, to elucidate structure-activity relationships that could be leveraged to design even safer monomers for thermoset materials.

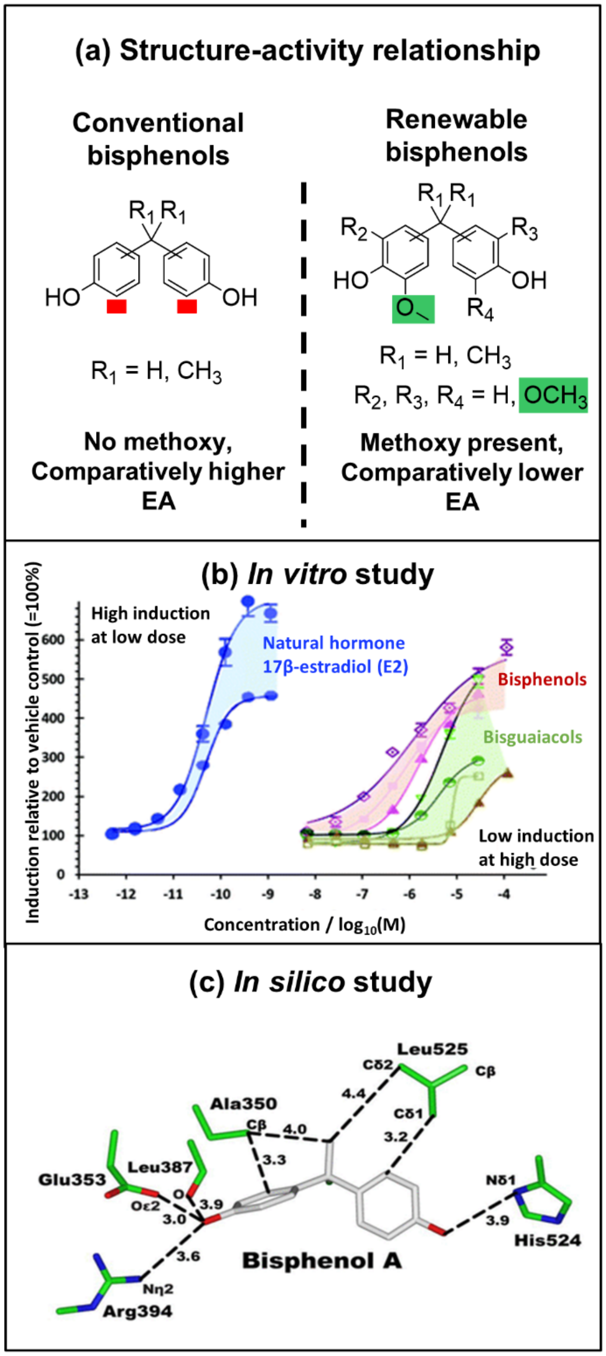


Figure 5: Toxicity studies: estrogen activity (EA). **(a)** Structure-activity relationship, indicating methoxy groups in renewable aromatics play an important role in estrogen-receptor binding. **(b)**

In vitro study of the estrogenic activity of bis(4-alkylguaiacol)s using MCF-7 cells human breast cancer cell line (MELN assay). Three zones of sigmoidal responsiveness are indicated for reference estradiol (blue), commercial bisphenols (magenta), and renewable bisphenols [bisguaiacols (green)]. Adapted from Ref. 92 with permission from the Royal Society of Chemistry. **(c)** Molecular docking approach to investigate the estrogen binding affinity of BPA. "This article was published in The Journal of Steroid Biochemistry and Molecular Biology, 184, Michael E. Baker and Richard Lathe, The promiscuous receptor: Evolution of physiological estrogens and response to phytochemicals and endocrine disruptors, 29-37, Copyright Elsevier (2018)."

Allyl and Alkenyl functionalities

Eugenol and Isoeugenol

Eugenol is an allyl-substituted guaiacol found in essential oils, mainly clove oil, which can be produced from lignocellulosic biomass *via* catalytic depolymerization.[144, 145] The hydroxy and allyl groups are useful handles for functionalization and polymerization. For example, Amarnath *et al.* reported polybenzoxazines from eugenol, isoeugenol, paraformaldehyde, and furfurylamine with thermal properties (T_g, $T_{d5\%}$, char yield) comparable to, or better than, those of commercially available phenol- or BPA-based polybenzoxazines.[103] The allyl and alkenyl functional groups reacted with the iminium ion intermediate in the ROP, leading to a high crosslink density, and the extended conjugation along the alkenyl chain in the isoeugenol-based benzoxazines was more reactive than the allyl group of eugenol and favored ROP.[103] Additionally, the isoeugenol-based system (Table 2, 14) formed shorter methyl-substituted alkyl chains as opposed to the longer unsubstituted chains in the eugenol-based material (Table 2, 15). The differences in crosslinking behavior and alkyl chain structure resulted in the isoeugenol-based material having similar T_g and char yield and a higher thermal stability (T_g ~164 ºC, $T_{d5\%}$ ~375 ºC, char yield ~60% at 700 ºC) in comparison to the eugenol-derived polymer (T_g ~162 ºC, $T_{d5\%}$ ~338 ºC, char yield ~52% at 700 ºC).[103] The thermal performance of these bio-derivable systems was equivalent to, or better than, that of a commercially available BPA-based benzoxazine thermoset (T_g ~161 ºC, $T_{d5\%}$ ~313 ºC),[138, 146] and the char yield also was comparable to those of petroleum-based polybenzoxazines (35-75%).[118] Based on the above similarities in properties, biobased materials are potential alternatives to commercial BPA-based benzoxazine resins for structural adhesives, coatings, and laminates.[146]

Bisphenols from eugenol

The allyl functional group of eugenol and allyl syringol can be leveraged to eliminate toxic epichlorohydrin from epoxy thermoset synthesis through the formation of a self-curing epoxy network. For instance, Chen *et al.* synthesized four bio-derivable monomers through esterification of the phenolic hydroxy groups of eugenol with diacid chlorides (succinyl, adipoyl, suberoyl, and 2,5-difuroyl chlorides).[104] The allyl group on each was subsequently oxidized to an epoxide group by reacting the esterified compounds with 3-chloroperoxybenzoic acid in ethyl acetate.[104] The monomers were self-cured through a 4-dimethylpyridine catalyzed reaction of the active esters and epoxides.[104] The epoxy thermosets exhibited tunable thermomechanical properties (T_g ~92-161 ºC, $T_{d5\%}$ ~350-392 ºC, rubbery modulus ~29-52 MPa) depending on the structure of the acid chloride.[104] Importantly, the epoxy thermoset derived from 2,5-difuroyl chloride (the only aromatic of these acid chlorides) exhibited equivalent thermal properties (T_g ~161 ºC, $T_{d5\%}$ ~350 ºC)[104] (Table 2, 16) to those of a BPA-derived analogue (T_g ~160 ºC, $T_{d5\%}$ ~300-400 ºC).[90] By eliminating epichlorohydrin, these self-curing epoxy resins potentially are greener alternatives to conventional epoxies, especially if the acid chlorides and 3-chloroperoxybenzoic acid can be replaced by anhydrides or carboxylic acids and other oxidizing agents, respectively.[15, 147, 148]

Biobased acrylic polymers also are garnering significant interest for the fabrication of materials using additive manufacturing because of their photopolymerizability.[93, 149] For example, Reineke and co-workers prepared high-performance phenolic acrylate resins *via* an efficient and scalable thiol-ene click reaction followed by acrylation with acryloyl chloride.[93] Guaiacyl acrylate was used as a reactive diluent, and vanillyl alcohol dimethacrylate was incorporated as a crosslinker.[93] This approach leveraged the aromatic nature of lignin-derivable phenolics to generate materials that were competitive with BPA-based vinyl ester resins in terms of their thermomechanical properties (T_g ~107-130 ºC, E' ~2.5-3.4 GPa at 25 ºC versus T_g ~145 ºC, E' ~2.7 GPa at 35 ºC).[15, 93] These eugenol-based resins were similar to the abovementioned vanillin-derived 3D-printing resins reported by Stanzione and co-workers[115] and further demonstrate the potential utility of biobased phenolics for high-performance and efficient additive manufacturing applications.[93, 115]

Triphenols from eugenol

The eugenol-based trifunctional monomer, TEP, has been used to synthesize high-performance BMI thermosets with tunable thermomechanical properties using Alder-ene chemistry (Table 2, 17).[105] TEP was prepared by reacting eugenol with phosphorus oxychloride, a reaction that could be carried out in water for improved sustainability.[150] Thermosets with tunable thermal properties were obtained by curing TEP with two different BMIs, PhBMI and SiBMI. The thermosets exhibited relatively high thermal stability ($T_{d5\%}$ >350 ºC).[105] Furthermore, the PhBMI-based thermoset had a higher T_g and char yield (T_g ~247 ºC, char yield ~60% at 800 ºC) than the SiBMI-based analogue (T_g ~ -113 ºC, char yield ~20% at 800 ºC) partly because of its more rigid, aromatic structure.[105] Thus, BMI thermosets with widely tunable thermomechanical properties can be produced using lignin-based aromatics.

TEP also can be used to generate reprocessable networks with disulfide linkages that rearrange at elevated temperatures through disulfide metathesis reactions.[132] For instance, Ocando *et al.* used this approach to create a partially biobased thermoset by curing epoxidized TEP with 4-aminophenyl disulfide. The network reorganization was conducted above the T_g of the thermoset (~230 ºC) without the need for a catalyst.[132] The thermoset was found to be reshapeable, recyclable, and self-healable.[132, 151] Disulfide linkages are useful for the generation of recyclable thermosets, and the design of biobased monomers with disulfide linkages, *e.g.,* bisphenols coupled with disulfide bridges rather than curing agents with disulfide bonds, could lead to new opportunities in recyclable polymers.

Lignin-derived curing agents

Amines are important crosslinking agents for high-performance materials due to their nucleophilic characteristics, which enable ambient temperature reactions with epoxy resins.[152, 153] Current commercial amines generally are petroleum-derived, and biobased amines are desirable because of the toxicity and volatility associated with many petroleum-based amines.[152] Numerous bio-derived aliphatic amines have been reported, primarily from bio-sources such as vegetable oils and their derivatives, chitosan, and amino acids,[152] but biobased aromatic versions are essential to realize the same thermomechanical performance enabled by existing commercial aromatic amines.[154] For instance, the dihydroxyaminopropane of methoxyhydroquinone and the dihydroxyaminopropane of vanillyl alcohol were obtained through direct amination of epoxy monomers with aqueous ammonia, and vanillylamine was synthesized *via* reductive amination of vanillin (Table 2, 7).[98] Although networks synthesized with these amines exhibited somewhat lower T_gs and T_ps in comparison to thermosets prepared with common commercial amines, these synthetic strategies serve as a framework for the development of lignin-derivable aromatic amines that can compete with curing agents such as IPDA. For example, IPDA is tetrafunctional, whereas vanillylamine is trifunctional,[99] and the thermal properties of a DGEBA/vanillylamine thermoset (T_g ~67 ºC and T_p ~230 ºC) (Table 2, 8) were lower than those of DGEBA/IPDA (T_g ~166 °C, T_p ~300 ºC) because of reduced crosslink density.[99] Applying the amination methods above to synthesize biobased aromatic amines with more functional groups per molecule could bridge the gap in thermal properties. For instance, lignin-derived bisphenolic/triphenolic precursors could be used to prepare curing agents with additional amine groups and higher rigidity to enhance the thermomechanical properties of the resulting materials.

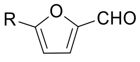
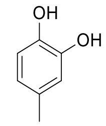
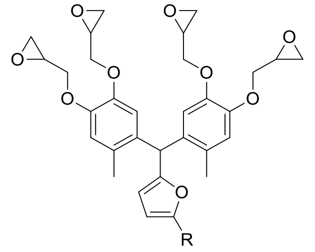
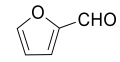
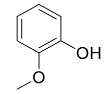
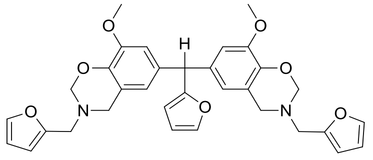
Taken together, the diversity in chemical structures along with the inherent functionalities of biobased phenolics can be leveraged to fabricate thermosets with equivalent or better properties than incumbent materials, while also potentially reducing hazard profiles. Additionally, some of the inherent functionality of bioderived building blocks, particularly aldehydes, enable the realization of materials with reversible linkages. This combination of renewable sourcing, green fabrication techniques, and vitrimer chemistries could be critical for robust life-cycle management in next-generation materials.

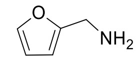
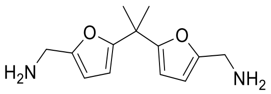
Cellulosics (Furanics)

Cellulose is the most abundant natural polymer, and hemicellulose is the third most prevalent macromolecule, behind lignin.[6] The high abundance and straightforward depolymerization of cellulosics present many opportunities for the production of renewable platform chemicals for polymer applications. Cellulosics also are versatile, as both aromatic and non-aromatic monomers can be obtained from depolymerization. For example, isosorbide, a chiral diol with a unique bicyclic ring structure, has been studied extensively in biobased polymers, including as an alternative to BPA,[46, 155-157] and dilactones are being investigated for thermoset applications.[158] The reader is directed to a review by Klemm *et al.*[159] for additional information on other non-aromatic, cellulosic-derived building blocks. The remainder of this section will focus on aromatic furans because of their unique reactivity that enables the synthesis of high-T_g compounds with utility as monomers, aminic curing agents, and reprocessable thermosets.

Furans are the most promising aromatic chemicals from cellulosics. They are versatile building blocks for renewable polymer development because they possess numerous functional handles that easily can be converted into amines, diols, acrylates, and epoxies.[160, 161] The two most common furanic chemicals are HMF and furfuryl alcohol, which are produced through continued dehydration of cellulose- and hemicellulose-derived monosaccharides, respectively.[160, 162, 163] Recently, another furanic compound, furandicarboxylic acid (FDCA), has been recognized as a valuable precursor for biobased alternatives to polyesters like poly(ethylene terephthalate) (PET).[164] In particular, poly(2,5-ethylene furandicarboxylate) (PEF) is gaining commercial traction because of its improved barrier properties in comparison to PET.[164] The remainder of this section highlights how furanic building blocks (as shown in Table 3) can be used to design monomers, curing agents, and vitrimers for thermosets.

Table 3. Summary of various bio-derivable furanic building blocks and thermomechanical properties of the resultant thermosets.

No.	Bio-derivable aromatic	Monomer	Thermoset class	Characteristics	Ref.
1	 (1) R = H Furfural (2) R = CH_2OH HMF  4-methylcatechol	 (1) R = H Tetraglycidyl ether of 4-methylcatechol-furfural (2) R = CH_2OH Tetraglycidyl ether of 4-methylcatechol-HMF	Epoxy (cured with DETA)	(1) T_g = 100 ºC $T_{d5\%}$ = 174 ºC E' = 6.6 GPa @45 ºC (2) T_g = 110 ºC $T_{d5\%}$ = 214 ºC E' = 9.6 GPa @45 ºC	75
2	 Furfural  Guaiacol	 6,6′-(furan-2-ylmethylene)bis(3-(furan-2-ylmethyl)-8-methoxy-3,4-dihydro-2H-benzo[e][1,3]oxazine)	Polybenzoxazine	T_g = 287 ºC $T_{d5\%}$ = 340 ºC	165

3	 Furfurylamine	 Bisfurfurylamine A	Epoxy (used with DGEBA)	T_g = 111 ºC T_p = 340 ºC	99

Furanic-derived monomers

Bisphenol-furan adducts have utility in high-performance epoxy thermosets. For instance, 4-methylcatechol was coupled using HMF or furfural to yield a compound with four hydroxy groups that subsequently was glycidylated and then cured with DETA (Table 3, 1).[75] The HMF-based thermoset (T_g ~110 ºC, E' ~9.6 GPa at 45 ºC) exhibited a similar T_g and a higher modulus relative to the furfural-based material (T_g ~100 ºC, E' ~6.6 GPa at 45 ºC), as the additional hydroxymethyl group in HMF resulted in a higher crosslink density and increased hydrogen bonding.[75] The moduli of both furan-based thermosets were much higher than that of a conventional BPA-derived epoxy thermoset (E' ~2.6 GPa at 45 ºC).[75] This mechanical behavior was attributed to the rigidity of the furan moieties, and the additional reactivity resulted in higher char yields for both furanic thermosets (~27-35%) versus for the BPA-derived thermoset (~10%).[75] Similarly, bio-derivable polybenzoxazines with superior properties to BPA-based analogues were synthesized from a benzoxazine monomer with three furan moieties (Table 3, 2).[165] The tri-functional benzoxazine monomer was obtained *via* the reaction of guaiacol, furfural, furfurylamine, and paraformaldehyde in two steps.[165] The corresponding polybenzoxazines exhibited increased thermal properties (T_g ~287 ºC, $T_{d5\%}$ ~340 ºC) and equivalent char yield (~60%) relative to those of several petroleum-based analogues (T_g ~160-250 ºC, $T_{d5\%}$ ~200-350 ºC, char yield ~30-75%), owing to the rigidity of the bulky monomer.[165] These hybrid furan-bisphenol compounds are synergistic, combining the reactivity of furans with the rigidity and size of bisphenols, and can be used to achieve significantly higher thermal transitions in comparison to many petroleum-derived analogues. Their bulky structure also may reduce binding to estrogen receptors, resulting in reduced estrogenic activity relative to conventional bisphenols. Toxicity studies could be conducted on these monomers to better understand the role of furanic moieties on endocrine disruption potential.

Furanic-derived curing agents

The various functional handles of furanic compounds, such as aldehyde, hydroxy, and carboxylic acid groups, can be converted into amine functionalities. For instance, the reductive amination of the hydroxy group of furfuryl alcohol yields furfurylamine, a common, commercially available, aromatic amine that has been used in thermoset synthesis.[160, 166] Further derivatization of furfurylamine results in more complex compounds with additional functionality or enhanced rigidity. As an example, difurfuryl diamines (Table 3, 3) that resemble conventional aromatic diamines have been prepared from the acid-catalyzed coupling of furfurylamine using formaldehyde.[167] Similarly, HMF was converted into diamines, such as 2,5-bis(aminomethyl)furan, through a 2,5-diformylfuran intermediate.[168] The introduction of rigid furanic moieties in curing processes can offer significant performance advantages, and further development of this class of compounds, including combinations of furanic precursors with other aromatic amines, could enable the synthesis of thermosets with thermomechanical properties similar to those of resins cured with commercial amines like IPDA (cycloaliphatic) and MDA (aromatic).

Furanic-derived reprocessable thermosets

DA reactions between polymers with pendent furan groups and bismaleimides have gained popularity in recyclable thermosets.[135, 169-171] The thermo-reversibility of furan-bismaleimide adducts without the need for a catalyst or the formation of byproducts is particularly promising for materials applications due to the versatility of DA reactions.[169-172] As one example, Luo *et al.* synthesized an aromatic polyamide with furan moieties from a furan-containing diacid and crosslinked the material with BMI at 60 ºC to form a dissociative CAN.[135] The crosslinking reaction was reversible at 130 ºC, and the thermoset exhibited good recyclability with the tensile strength maintaining ~80% of its original value in the recycled sample.[135] Similarly, polystyrene-*co*-poly(2-vinylfuran)s were reacted with BMI to produce DA adducts at room temperature, and the materials were recyclable in ~1 min by heating to 150 ºC.[173] DA chemistry could be applied to other furan-containing systems, such as the amine-containing curing agents discussed above, along with other systems like vinyl ester resins, to improve the recyclability and extend the service life of such materials.

In short, furanics are an interesting class of bio-derivable aromatic compounds that can be used in thermoset polymers and offer increased reactivity in comparison to many of the phenolic compounds discussed in this Perspective. Several materials from furans have been highlighted, such as epoxies and polybenzoxazines, that can compete with or outperform commercial resins in terms of material properties, and furan-derived amines recently have garnered attention as curing agents/hardeners that can replace or complement common cycloaliphatic or aromatic amines, such as IPDA and MDA, in epoxy resins. Finally, the fabrication of dissociative CANs through DA chemistry can enable facile recycling and robust life-cycle management for more sustainable thermosets.

Future opportunities

There are many promising pathways towards the development of biobased aromatic thermosets with commercial potential, but research to improve life-cycle sustainability, thermomechanical properties, and toxicological impacts is of critical importance. Specifically, innovations in biomass processing/depolymerization could improve the efficiency of future biorefineries and reduce the cost of biobased aromatics to enable competition with petrochemicals. Additionally, catalytic or biological pathways to create novel compounds, such as aromatic aminic curing agents, would further expand the range of accessible polymer properties and potentially enable reversible chemistries. The thermomechanical and application-specific (*e.g.,* char yield, water uptake) properties of biobased thermosets also could be improved upon by leveraging structure-property relationships and computational approaches to design higher-performance and potentially safer materials. Together, these advances would result in truly sustainable materials that can outperform conventional thermosets throughout the polymer life cycle.

The future of aromatic thermosets relies on the operation of commercial-scale biorefineries for a stable and cost-effective supply of lignin-derived phenols or cellulosic-based furanics for materials production,[174] especially for precursors like vanillin or eugenol that currently are too expensive to divert to polymer products. The existing chemical processes used to produce biobased aromatics from LCB face many challenges, such as low product yields, complex/expensive separations, and high levels of waste generation.[85] There are several approaches to overcome these challenges. For example, the addition of homogeneous co-catalysts or other additives like formaldehyde can stabilize reactive species and improve lignin monomer yields associated with chemocatalytic depolymerization processes.[175] More robust and less expensive catalysts also can improve biorefinery efficiency to further reduce costs; some potential alternatives to precious metal catalysts are copper,[176, 177] nickel,[178] iron,[179] and cobalt catalysts.[180] Furthermore, process intensification and other novel methods could be used to minimize separations. Zhang *et al.* demonstrated a combined lignin depolymerization and monomer synthesis scheme *via* direct vinylation with calcium carbonate to produce vinyl ether monomers, and microwave- or plasma-assisted depolymerization techniques are an emerging area of research for LCB valorization.[181] In combination with intensification efforts, the synthesis of monomers using biobased mixtures of phenolic precursors would avoid costly separations and increase the economic feasibility of lignocellulosic biorefineries.

Green catalysis and atom-efficient approaches to polymer synthesis also play a role in sustainability and life-cycle management. For instance, humin is a recalcitrant polymeric byproduct of cellulose/hemicellulose valorization and has been modified for use as an acid catalyst in the esterification of levulinic acid with *n*-butanol and the hydroxyalkylation of 2-methylfuran and furfural.[182] Humin-derived acid catalysts could be used as renewable alternatives to conventional ion-exchange resins in numerous applications and could be developed further to improve catalytic efficiency and recyclability.[182] Recalcitrant lignin waste similarly could be converted to solid catalysts,[183] or it could be depolymerized further under harsher conditions like catalytic pyrolysis to increase monomer yields. Additionally, enzymatic synthetic strategies are promising for precursor/monomer synthesis because they require lower temperature reactions, reduce organic solvent usage, and minimize the formation of byproducts.[184-186] For example, the laccase-catalyzed oligomerization of ferulic acid-based bisphenols into linear aliphatic-aromatic oligomers with bisguaiacol-type moieties demonstrated the efficiency of enzymatic synthesis in a room temperature, open-to-air aqueous medium.[187] As another related example, aldehyde functionalities derived from aromatic/aliphatic carboxylic acids were converted to amines with ω-transaminase,[188] and these biocatalytic transformations could be used to produce biobased curing agents or other useful molecules that would be difficult or expensive to prepare through conventional synthetic routes.

When practical, hazardous and toxic precursors for thermoset synthesis, such as epichlorohydrin or isocyanates, should be eliminated in favor of renewable and inherently safer compounds. For instance, the allyl functionality in bio-derivable compounds, such as eugenol or allyl syringol, can be leveraged to prepare epoxy monomers through oxidation.[104] While epichlorohydrin is eliminated with this approach, *m*-chloroperoxybenzoic acid typically is used as the oxidizer, and more sustainable oxidizing agents are needed for this approach to be viable.[104] For biobased compounds without allyl groups, greener approaches for allylation are another challenge. Traditionally, allylation is performed using stochiometric amounts of base and allyl halides. Aqueous Tsuji-Trost allylation is an alternative route that could be more sustainable, but it may be desirable to replace the current catalyst, palladium nanoparticles stabilized by poly(vinylpyrrolidone), with less expensive and more environmentally friendly alternatives.[189]

To further improve the sustainability of epoxy resins, diglycidyl ethers can be converted into five-membered, cyclic carbonate moieties that can be cured with di/triamines to yield reversible NIPU thermosets.[106, 190-192] As an example, Janvier *et al.* evaluated SYR for NIPUs.[106] First, SYR was glycidylated, and the epoxy groups were converted into five-membered cyclic carbonates *via* carbonation.[106] The cyclic carbonates then were cured with tris(2-aminoethyl)amine to produce a NIPU thermoset with T_g ~62 ºC and $T_{d5\%}$ ~225 ºC (Table 2, 18). These properties are in the middle of the range of those attainable with conventional PU systems (T_g ~0-100 ºC and $T_{d5\%}$ ~200-300 ºC);[106] and thus NIPUs can be employed in room-temperature coatings applications. However, the reaction of amines with cyclic carbonates generally is slow, leading to long cure times.[106, 193] Similarly, synthesizing high molecular weight, non-crosslinked NIPUs is difficult, and current low molecular weight (~5 kg/mol) NIPUs generally have limited applications, *i.e.,* only adhesives or coatings.[106, 133, 134, 190, 193-196] Efforts to increase the achievable molecular weights in NIPU systems are necessary for widespread implementation, and the broad range of biobased bis(cyclic carbonate)s, such as those from vanillin,[108] creosol,[197] ferulic acid,[198] and FDCA,[199] can play a role in tuning the properties of these materials to better suit the many applications of conventional PUs.

One of the major challenges with thermoset materials is life-cycle management, and renewable sourcing only solves a portion of the problem. Waste generation also must be considered,[36, 200] and the incorporation of reversible chemistries is a very promising strategy to minimize thermoset waste by extending the useful life and increasing the recyclability of thermosets. Imine bond exchange,[8] DA chemistry,[170] cyclic carbonate aminolysis,[133, 190] transcarbamoylation,[133, 134] transesterification[88, 133, 190] and disulfide bond exchange[52, 132] are examples of reactions that could be implemented to improve the availability and versatility of recyclable thermoset materials.[131] Future innovations in recyclable thermosets may target the inclusion of multiple, potentially orthogonal, reversible chemistries to enable selective, yet facile, chemical recycling to monomers (as opposed to only de-crosslinking). This approach could avoid the degradation of polymer chains over multiple reprocessing cycles, which is a common drawback in thermoplastics and many vitrimers with a single type of reversible chemistry, to improve property retention by essentially building a virgin polymer network with every cycle.

The design of biobased thermosets with more robust properties also is essential. Biobased bisphenols tend to have more flexible bridging structures than BPA, and materials derived from the LCB-based compounds typically exhibit reduced thermomechanical performance.[89, 90, 92] Synthetic strategies to generate molecules with bulky bridging groups that are structurally similar to, but safer than, BPA could be a crucial breakthrough in efforts to fully replace BPA and other bisphenols. Several of the functional group present in lignin-phenols could be leveraged to develop these compounds as described in some of the earlier examples herein. Another strategy to improve the thermomechanical properties and renewable content of current resins is the addition of additives or fillers. For example, Abu-Omar and co-workers reported nanoclay-modified, eugenol-based epoxy nanocomposites that exhibited improved storage moduli and thermal stability in comparison to the neat epoxy network.[201]

Computational approaches to investigate the thermomechanical properties of bio-derivable thermosets also should be considered to complement and guide experimental work. For example, recent studies on the calculation of thermomechanical properties (*e.g.,* T_g, modulus) through simulations have shown close agreement with experimental results, especially for T_g values.[202-204] Further refinement of these models by, for example, tuning the intermolecular potential energy model, could increase the accuracy of calculated mechanical properties to enable monomer screening and facile prediction of thermomechanical properties throughout the extensive domain of biobased feestocks.[202] Additionally, *in silico* approaches using software packages, such as AutoDock or AutoDock Vina (Figure 5c),[205] can facilitate faster and more cost-effective analysis of the potential health and environmental hazards for new and existing compounds.[206, 207] The carcinogenicity, mutagenicity, and reproductive toxicity of renewable compounds also are important and should be tested and benchmarked against existing chemicals to evaluate the impact of biobased chemicals on humans, animals, and the environment.[208, 209] By coupling structure-activity[210] and structure-property relationships to understand the key drivers for estrogenic activity and thermomechanical properties, it could be possible to generate safer materials without sacrificing performance.

Finally, advanced manufacturing techniques can augment the sustainability and performance of biobased thermosets. SLA printing and vacuum assisted resin transfer molding (VARTM) are two pertinent examples of such methods. Many lignin-derivable resins are compatible with SLA printing because the monomers are low viscosity and photopolymerizable.[93, 115] Materials that are not compatible with SLA printing could be modified with photopolymerizable groups and mixed with appropriate diluents and photoinitiators. As an example, NIPUs have free hydroxy groups that could be functionalized with photopolymerizable (meth)acrylate groups. Other manufacturing techniques, such as VARTM, build on conventional methods to fabricate materials more quickly and with fewer defects. Dai *et al*. reported eugenol-derived benzoxazine resins suitable for VARTM because of their high stability and low viscosity (less than 1 Pa·s in the range of 60-190 ºC).[211] Although this example demonstrates that the bio-derivable resin is acceptable for VARTM operations, more investigations are needed to define actual processing protocols, and further research into the manufacture of biobased materials using common processing methods, such as compression molding and lay-up techniques (layering dry fibers/fabrics with a resin binder), would increase the commercial relevance of LCB-derived thermosets.

Conclusions

Aromatics from LCB are rich in functionality and can be harnessed to address many of the life-cycle management challenges in thermoset polymers. The broad structural diversity available from biomass depolymerization results in a vast range of accessible material properties, and structure-property and structure-activity relationships can inform design decisions for the development of robust, high-performance materials that are potentially safer than existing thermosets. Reversible chemistries can ameliorate the accumulation of plastic waste by extending the service lifetime of thermoset materials through reprocessing and facile recycling. Finally, advanced fabrication techniques, like SLA printing and VARTM, can leverage the properties of some biobased resins, such as low viscosity relative to conventional resins and photopolymerizability, to fabricate quality materials with fewer defects versus other techniques.

Together, advances in these areas will facilitate the development of next-generation thermosets that are more sustainable and can outperform incumbent materials across the entire polymer life cycle.

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ACKNOWLEDGMENT

J.S.M., R.M.O., L.T.J.K., and T.H.E. are grateful to the National Science Foundation (NSF GCR CMMI 1934887) for financial support during the writing of this manuscript. J.S.M., L.T.J.K., and T.H.E. also thank NSF DMR POL 2004682 and the State of Delaware RAPID funding for financial support during the writing of this manuscript related to green synthesis and furanics, respectively. J.B.N. acknowledges a Delaware Environmental Institute (DENIN) fellowship and NSF EPSCoR (OAI 1757353) for financial support during the writing of this manuscript. T.H.E. also acknowledges the Thomas & Kipp Gutshall Professorship for additional support.

ABBREVIATIONS

BEN: Benzene; BMI: Bismaleimide; BPA: Bisphenol A; BPF: Bisphenol F; Bzf: 3-furfury-8-methoxy-3,4-dihydro-2H-1,3-benzoxazine; CAN: Covalent adaptable network; DA: Diels-Alder; DETA: Diethylenetriamine; DGEBA: Diglycidyl ether of BPA; DGEVAC: Diglycidyl ether of vanillic acid; DiGEDVA: Diglycidyl ether of divanillyl alcohol; DMF: Dimethylformamide; DMSO: Dimethyl sulfoxide; DVA: Divanillyl alcohol; E': Storage modulus; EA: Estrogen activity: EtOH: Ethanol; FCM: Food contact material; FDCA: Furandicarboxylic acid; G: Guaiacyl; GRAS: Generally recognized as safe; H: *p*-hydroxyphenyl; HCl: Hydrochloric acid; HMF: Hydroxymethylfurfural; IPDA: Isophorone diamine; LCB: Lignocellulosic biomass; MDA: 4,4′-methylenedianiline; MDI: 4,4'-Methylene diphenyl diisocyanate; NIPU: Non-isocyanate polyurethane; P-a: Poly(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine); PET: Poly(ethylene terephthalate); PEF: Poly(2,5-ethylene furandicarboxylate); PF: Phenol-formaldehyde; PhBMI: *N,N′*-1,3-phenylene bismaleimide; PolyBzf: Guaiacol-based polybenzoxazine; PU: Polyurethane; ROP: Ring-opening polymerization; RT: Room temperature; S: Syringyl; SiBMI: Polydimethylsiloxane bismaleimide; SLA: Stereolithography; SYR: Syringaresinol; $T_{d5\%}$: Degradation temperature at 5% weight loss; $T_{d7\%}$: Degradation temperature at 7% weight loss; $T_{d10\%}$: Degradation temperature at 10% weight loss; $T_{d50\%}$: Degradation temperature at 50% weight loss; TEP: Trieugenylphosphate; TetraGEDVA: Tetraglycidyl ether of divanillyl alcohol; THF: Tetrahydrofuran; T_g: Glass transition temperature; TPA: Terephthalaldehyde; TriGEDVA: Triglycidyl ether of divanillyl alcohol; TOL: Toluene; VARTM: Vacuum-assisted resin transfer molding.

BIOGRAPHIES

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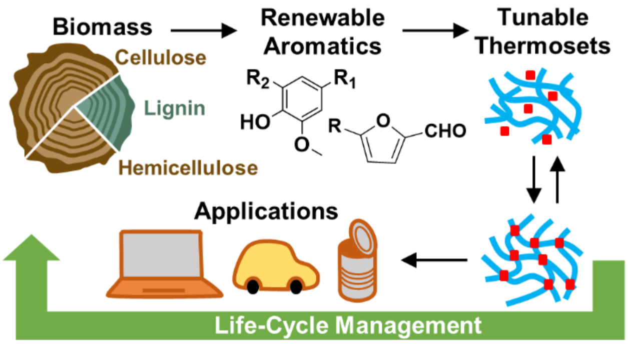
TOC Image



Synopsis

This Perspective provides an overview of aromatic thermosets from lignocellulosic biomass and highlights performance impacts of these materials in addition to future opportunities for the field.