Eugenol's journey to high-performance and fire-retardant biobased thermosets

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Eugenol, biobased polymers, fire-retardant, thermoset

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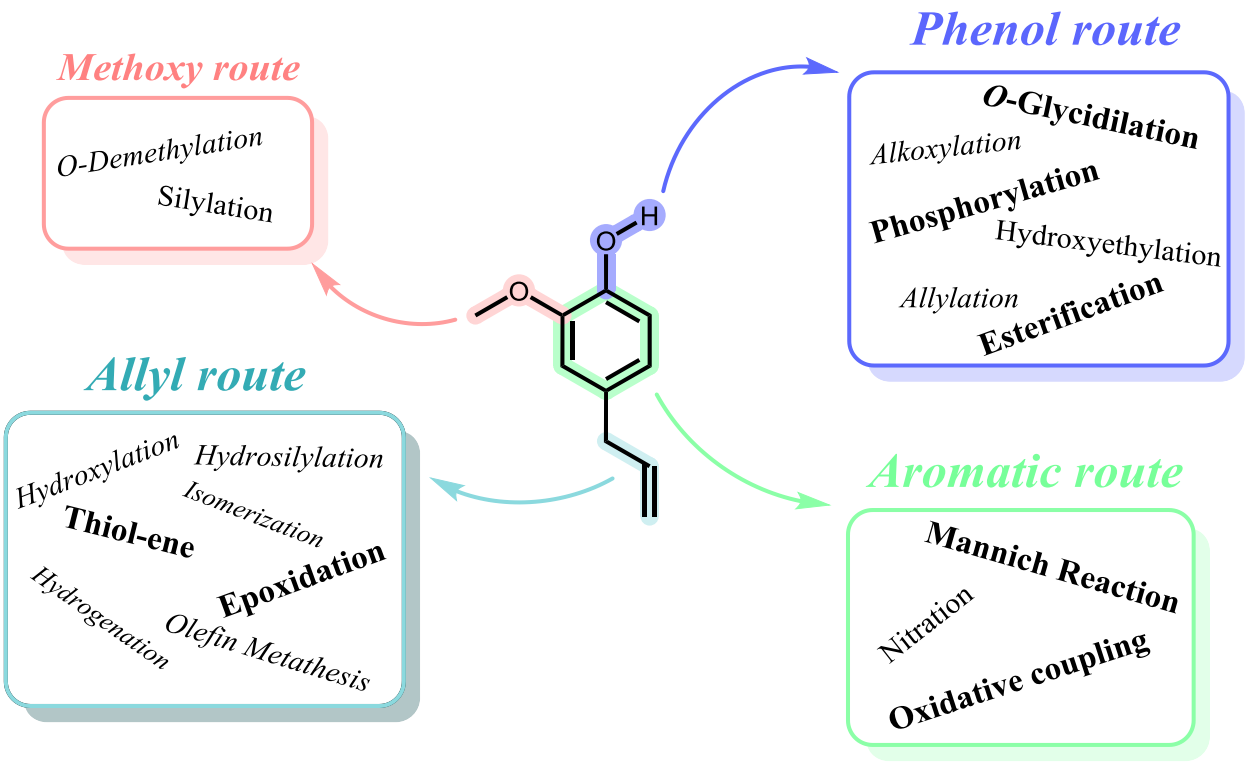
Introduction

Thermosets correspond to 10% of global polymer production 400 Mt/y. [1] Most of them present outstanding properties which are essential for designing high-performance composites (wind turbine blades, aeronautics, etc.). Among precursors, bisphenol A, bismaleimide (BMI) or phenol-formaldehyde are well suited to produce chemically crosslinked networks used as matrices for composites. Their rigid chemical structures, *i.e.* high aromatic content and/or fused cycles, results in materials with glass transition temperature (T_g) exceeding 100 °C. These precursors are petroleum-based and often pose risks to human health, leading to intensive research in the past decades for sustainable and safer alternatives. [2] However, common bio-based thermosets from vegetable oils [3] or cashew nut shell liquid derivatives [4] often lack the high T_g required for high-performance applications. Building blocks based on furanic (5-hydroxymethylfurfural, furfural) and aromatic (eugenol, vanillin) groups bear potential as precursors for high T_g polymers. [2, 5 ,6]

Among natural compounds, the peculiar chemical structure of eugenol holds a strong potential to prepare suitable thermosets for high performance composite applications. Eugenol is a non-edible natural phenol, which can lead to monomers with relatively similar structures to many petroleum-derived monomers. Eugenol does not have the plasticizing aliphatic chain(s) of cardanol and vegetable oils but only a short allylic moiety directly grafted on the *para*-position of the phenolic ring Thus, higher thermo-mechanical properties are achievable with eugenol while keeping potential chemical modification on the alkene function. [3, 4] Several reviews dealing with eugenol-based polymers appeared in the last years. The main focus was put on the possibilities of functionalization offered by eugenol to obtain high T_g thermoset for the manufacture composites, coatings or target fire-retardancy. [7, 8, 9, 10, 11, 12] This review aims at emphasizing the growing potential of eugenol for high-performance applications (construction, automotive, aeronautics, …). Starting with a survey of the functionalization routes of eugenol (methoxy, phenol, allyl, aromatic) we will summarize the different pathways to prepare eugenol-based precursors with constrained structures (biphenyls, Alder-ene, benzoxazines). Finally, fire-retardant polymers achievable by the introduction of specific spacers between eugenol molecules are presented (silicones, phosphates, cyclophosphazenes).

Functionalization routes eugenol

Nowadays, 6 kt/y of oil are extracted from the clove tree world-wide. [13] Eugenol represents 70 to 90 w.% of clove-oil and can be recovered in good yields. Eugenol can also be synthesized from lignin derivatives, which opens the way to massive production. It is already used to synthesize part of the 50 kt/y of vanillin.[7, 8] The cosmetic and pharmaceutic industry are major consumers of eugenol for its intrinsic wide range of biological activities and anti-oxidant properties (among others). [7, 14 , 15] An array of other applications is possible using eugenol's functionalization routes (methoxy, hydroxyl, aromatic, allyl, Scheme 1). [7, 9, 10, 11] Their chemistries can be exploited, alone or together, to graft chemical functions and introduce spacers. Another of the advantages of eugenol is its low oxygen concentration, which limits the reduction reactions which must often be carried out on natural derivatives.



Scheme 1. Eugenol's reactive sites

Transformation of the methoxy group has been limited but it can be converted to a hydroxyl function by either oxidative *O*-Demethylation or sillylation followed by hydrolysis. [7, 16] This modification allows to introduce another hydroxyl, either for direct polymerization or for further functionalization *via* the phenol route.

The phenol route is of significant interest for the production of monomers. Phenolic hydroxyls can be (hydroxy)alkoxylated yielding more reactive aliphatic alcohols which can be employed for rigid poly(urethane) foams. [7, 17] Esterification with anhydrides or acyls is a way to graft functional groups or dimerise/trimerise eugenol with rigid or flexible spacers to tune the T_g of the resulting materials. [18] Phosphorylation with phosphorous oxychloride yields a eugenol trimer. The introduction of phosphorylated moieties is a strong asset when fire-retardant properties are targeted (*vide infra*). [12, 19,20]

O-Glydicylation can be employed to introduce an epoxy ring, a convenient function for the manufacture of thermosetting resins (about 8% of the thermosets are epoxies). [11, 21] O-Glycidylation involves epichlorohydrin. Although it can be bio-based, this compound is both carcinogenic and toxic, thus greener paths for *O*-Glycidylation are desirable. [22, 23] Hydroxyl

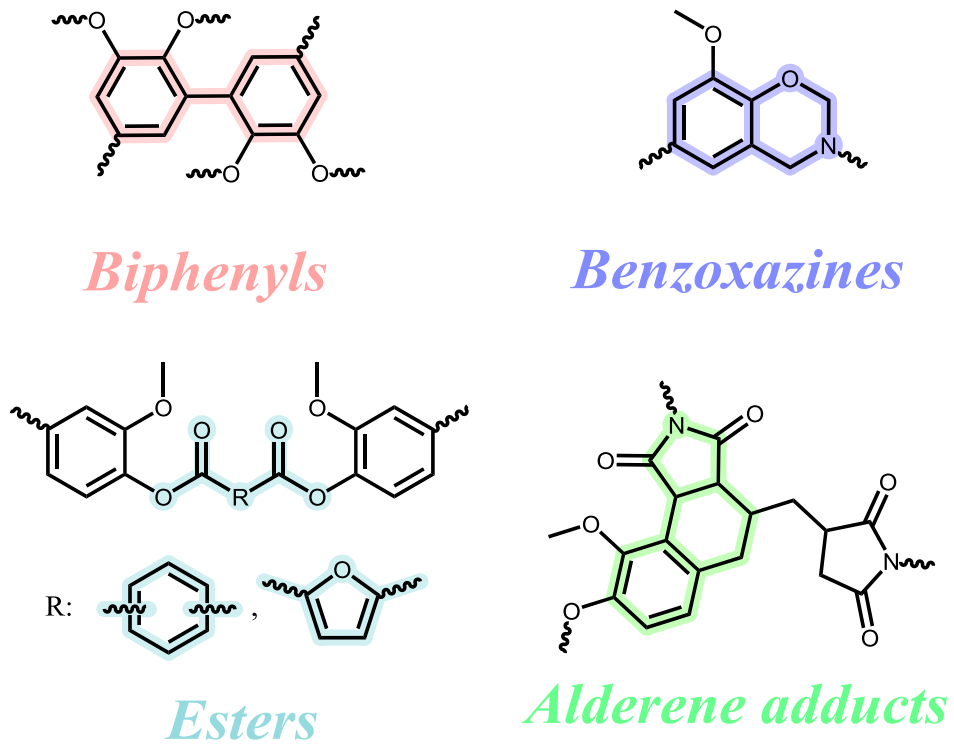
group can undergo Willamson etherification or Tsuji-Trost allylation to give allyl functions. [2, 7, 24] A major interest of allyl functions is their ability to undergo thiol-ene click reactions either in a thermally (composite matrices) or photo-initiated process (coatings, 3D printing). As one allyl group is already present on eugenol, the addition of another one is convenient to access pluri-functionality. [7, 25]

Thiol-ene click reaction is one of the most advantageous routes to functionalize allylic moieties. [26] It is suitable to introduce either flexible or rigid spacers between eugenol dimers. This leads to a broad range of achievable properties. Hydrosillylation is a valuable way to obtain silicones with thermal resistance and potential anti-bacterial properties. [27, 28, 29] Epoxy functions can be obtained using oxidants such as *m*-CPBA or ozone. [30] The enzyme-catalyzed epoxidation with hydrogen peroxide was never performed on eugenol. It would be worth investigating. [31] Phenol oxidative-coupling is a mean to reach dimers with biphenyl moieties, *i.e.*, higher T_g and better fire-resistance. [7, 24, 30, 32, 33] Benzoxazine derivatives can be obtained through Mannich-like reactions (*via* intramolecular cyclisation) . [7, 34, 35] All these examples are suited for thermally and/or mechanically demanding applications through the input of rigid and/or fire-resistant spacers.

High-performance thermosets from Eugenol

Eugenol's aromatic ring provides intrinsic rigidity to the resulting polymers. For instance, diglycidyl [8 ,11, 12, 36] and triglycidyl eugenol [10, 11, 12] yield thermosets with T_g between 103 °C and 155 °C. A series of patents claimed the functionalization of eugenol with triglycidyl [37], dicarbonate [38] and acrylic [39] groups as well as eugenol-based amine curing agents. [40, 41] They were submitted in the last two years, showcasing the interest in eugenol. Authors limited their approach to monoeugenol systems. The performance of eugenol-based polymers can be further improved through advanced chemical modification (fused cycles, dimerization).

Light can be shed on four eugenol-derived structures for high-performance thermosets (Scheme 2). Biphenyl structures from oxidative coupling were reported as poly(urethanes) hard segments [7], di and tetra allyl eugenol [7, 11] as well as di and tetra glycidyl eugenol. [11, 12, 30] Such systems without spacers allowed to reach T_g as high as 216 °C (tetraglycidyl eugenol).



Scheme 2. Promising hard segments for Eugenol-based polymers

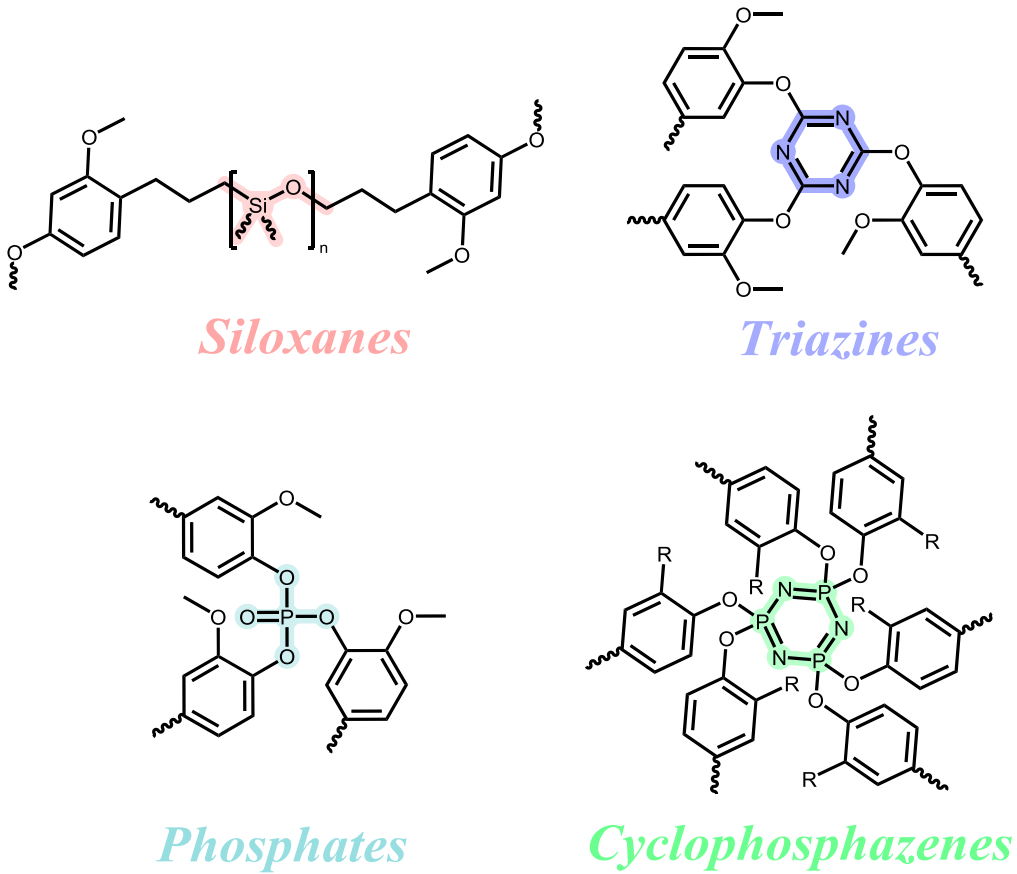
Esterification can be employed to dimerise eugenol with the acyl derivatives of furandicarboxylic acid [42, 43] isophtalic acid and benzene-1,3,5-tricarboxylic acid yielding respectively dimers and trimers. [18] Similarly to biseugenol systems, thermosets from esterified eugenol exhibit T_g between 153 and 208 °C.

Poly(benzoxazines) synthesized through cationic ring-opening polymerization of benzoxazines are a recent class of thermoset with attractive thermal and mechanical properties. [2, 5] The occupied *ortho*-position of eugenol is preventing the occurrence of chain-growth limiting the development of fully eugenol-based benzoxazines. Examples of copolymerization [7] using eugenol-based monomers and furfurylamine (T_α = 162 °C) [34] or *n*-octadecaneamine/furfurylamine [35] are promising as attested by similar patented systems involving eugenol-based benzoxazines. [44, 45]

Neda *et al.* suggested an approach where di and tetraallylbiseugenol react with bismaleimide to yield a thermoset with a T_{α} > 357 °C and a $T_{5\%}$ > 475 °C (inert atm). [24] In this line, Alder-ene chemistry, *i.e.* a ene-reaction and Diels-Alder reaction followed by rearomatization, leads to highly constrained structures composed of fused cycles. Alder-ene chemistry was employed with eugenol [46], eugenyl-phosphate [47,], eugenol/hydroxymetyleugenol [48], eugenol-silsesquioxane [49] and eugenol-siloxane-resveratrol. [50] Theses Alder-ene systems with their fused aromatic, imide and alkyl cycles allow T_g between 250 and 380 °C. Alder-ene systems are, to the best of our knowledge, the eugenol-based systems with the highest T_g that were reported so far. In the case of eugenol-phosphate, fire retardancy is achievable on top of its high T_g. [47] The following section aims to further highlight promising eugenol precursors bearing potential for materials with resistance to thermal and thermo-oxidative degradation.

Flame retardancy from eugenol-based compounds

The global flame retardant market size was valued at USD 8.63 billion in 2022 and is anticipated to grow at a compound annual growth rate (CAGR) of 7.1% from 2023 to 2030. [51] Forty percent of the market share of flame retardants (FRs) is held by halogenated compounds. [52] Despite being highly efficient FRs, they are also considered as both hazardous and toxic chemicals. [53] Greener alternatives include silicon and organophosphorus derivatives. [52, 53] Though chemical functionalization, eugenol can become an intrinsically fire-retardant thermoset precursor. Flourishing eugenol-based structures suited for these purposes are presented in Scheme 3.



Scheme 3. Promising Eugenol-based segments bearing fire/heat resistance.

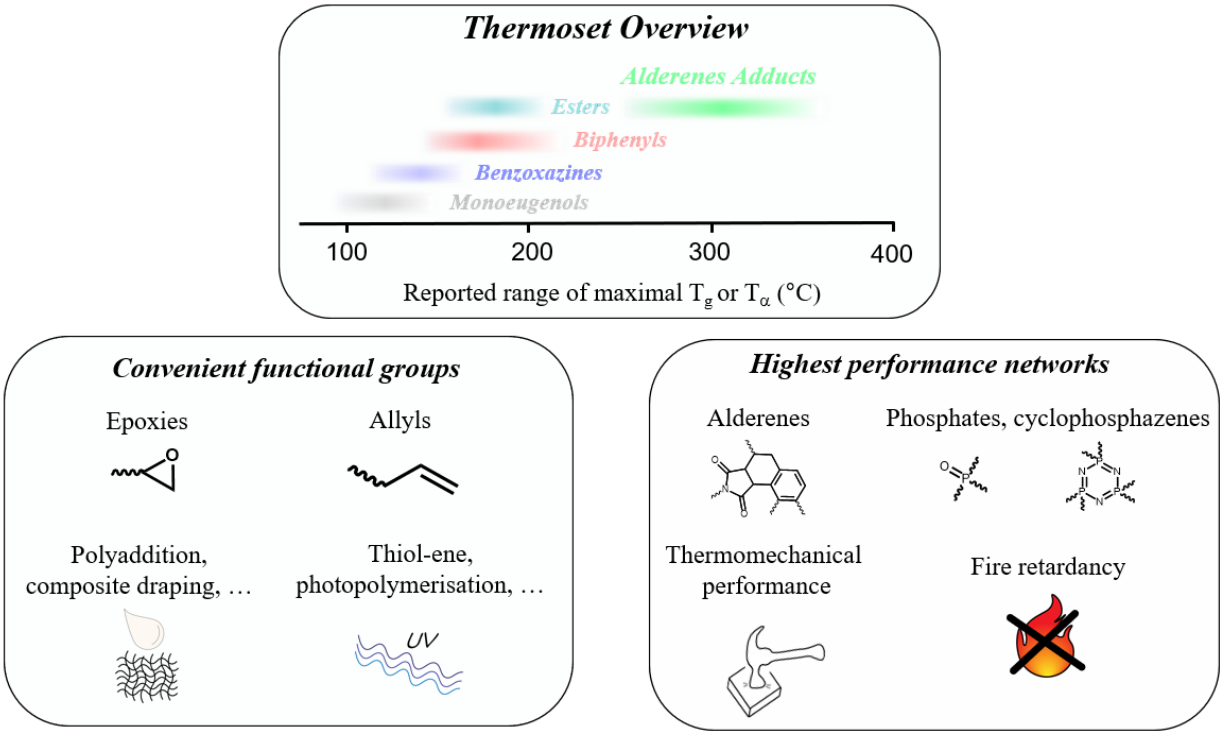
Hydrosillylation was used to introduce silicon-based spacers between eugenyl moieties. Even at low concentrations (≤ 3%), hydrosillylated eugenol enhanced the properties of waterborne poly(urethanes) [27]. When eugenol was employed in higher proportions in silicones, it improved their char yield and reduced their rate of thermal degradation. [28, 29] Systems comprising eugenol-silicon spacers [54], eugenol-polysiloxane-carbonate systems [55, 56], and eugenol grafted siloxane [57] have been patented since 2022, underscoring the growing interest in these innovative polymers. The downside of silicon spacers is their flexibility, when high T_g materials are targeted.

If both high T_g and fire-retardancy are desired, phosphorylated eugenol offers a promising alternative. Eugenol was successfully spaced with organophosphorus moieties to enhance the fire retardancy of epoxy [11, 12, 19, 20] and allyl-terminated monomers. [58] While their effectiveness is somewhat limited, nitrogen-based compounds remain as the safest fire-retardants. [52] Eugenol-based triazines were reported in poly(cyanurate) resins [59], as a side-reaction in phthalonitrile resins [60] and in epoxy-terminated triseugenol. [61]

The fire-retardancy of nitrogen compounds synergizes with phosphorylated ones by combining gas-phase and solid-phase actions. [52] Cyclophosphazenes contain both nitrogen and phosphorous. They are emerging as promising fire-retardant moieties. [53] Cyclophosphazene were reported as a spacer for eugenol with up to six left-over allyl functions. These allyl groups can either be used directly in thiol-ene polymerization, [62] self-polymerization [63], or undergo epoxidation [11, 12, 64] or involve series of reactions with the sillyl derivative of 4-vinylbenzocyclobutene. [65] In all these cases, the authors praised the fire-retardancy or thermostability of cyclophosphazene-spaced eugenol. Incorporating fire-retardant spacers reduces the need for potentially leaking fire-retardant additives.

Overall, key structures with high potential can be isolated from the this minireview (Scheme 4). Eugenol compounds functionalized with epoxy or allyl end group offer an ease of manufacturing *via* epoxy-amine and thiol-ene chemistry, for example. In terms of polymer architectures, light can be shed on Alder-enes. Their constrained structures allow high T_g thermosets suitable for high-performance applications. Finally, the introduction of phosphorylated moieties is an advantageous way to increase the fire-resistance of eugenol-based thermosets.

Scheme 4. Overview of the most promising monomer's functional groups and polymer architectures derived from eugenol.



Conclusion

Eugenol, a non-edible natural phenol, is one of the most promising natural phenols whose commercial availability can rapidly increase by deconstruction of lignin. Indeed, it makes it possible to increase renewable carbon content while achieving exceptional properties required in many thermoset polymers, unlike many biosourced compounds. The presence of an *ortho*-methoxy and a *para*-allylic group on a phenolic ring makes eugenol suitable for the synthesis of high-value added thermoset precursors. By itself, eugenol's aromatic group is an asset for both high T_g and fire-retardant materials. When one combines it with the ability of eugenol to form biphenyls, Alder-ene, benzoxazines, phosphates or cyclophosphazenes, precursors to materials with high T_g (> 150 °C) and thermostability can be manufactured. These precursors, especially epoxy and allyl-terminated bear the potential to replace the petroleum-based standards such as bisphenol A, bismaleimide or phenol-formaldehyde. Thus, we can consider that eugenol-based precursors could find their place in mechanically and thermally demanding fields, such as

composites for transport and aeronautics, which is still a pitfall for most derivatives of renewable resources.

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This article combines eugenol-based cyclophophazenes and sillylated benzocyclo- butene to reach high-performance and transparent resins. The resulting polymers exhibit Ta between 111 and 216 °C as well as $T_{5\%}$ above 400 °C (in both inter and oxidative atmospheres)