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Eugenol, a developing asset in biobased epoxy resins

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Keywords: Eugenol; epoxide; thermoset.

Abbreviations:

bisphenol A (**BPA**), bisphenol F (**BPF**), metachloroperbenzoïc acid (**m-CPBA**), Steric exclusion chromatography (**SEC**), nuclear magnetic resonance (**NMR**), Dichloromethane (**DCM**), Acetic anhydride (**Ac₂O**) Mono glycidyl silyl etherated eugenol (**GSE**), diglycidylether of bisphenol A (**DGEBA**), hexahydrophthalic anhydride (**HHPA**), Methylhexahydrophthalic anhydride (**MHHPA**), 2,4,6-tris(diMethylaminomethyl)phenol (**DMP**), diglycidylether diphenolates n-pentyle (**DGEDP-Pe**), eugenol mono-glycidyl ether (**GE**), 2-ethyl-4-methylimidazole (**EMID**), diepoxidized isoeugenol (**Iso-eug**), diepoxidized eugenol (**Eug**), maleopimaric acid (**MPA**), isophoronediamine (**IPDA**), diglycidyl benzyl bis-eugenol (**DEU-EP**), diglycidyl butyl bis-eugenol (**Eu-EP**), 3,3'-Diaminodiphenylsulfone (**33DDS**), N,N-Dimethylacetamide (**DMAc**), N,N-diméthylpyridin-4-amine (**DMAP**), 4,4'-methylenedianiline (**DDM**), m-xylylenediamine (**MXDA**), hexachlorocyclotriphosphazene (**HCP**), Matrix Assisted Laser Desorption Ionisation/Time Of Flight (**Maldi-TOF**), hexachlorocyclotriphosphazene (**HCP**).

Abstract

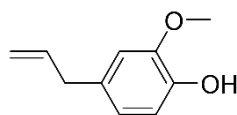
The synthesis of polymers from renewable resources is largely investigated in a context of sustainable development. Polyepoxide networks, widely used in many applications, constitute a major class of thermosetting polymers synthesized from bisphenol A (BPA), a substance identified as chemical estrogen. Moreover, epichlorohydrin used to graft a glycidyl ether group onto BPA to yield diglycidyl ether of BPA (DGEBA) is very toxic. This review proposes to demonstrate that eugenol represents an asset in the development of sustainable epoxy thermosets, by giving a general approach of the researches on the use of eugenol and its isomers for the synthesis of epoxidized precursors. The syntheses of precursors with hetero atoms (nitrogen, phosphorus or silicon) used in specific applications in electrochemistry or as flame-retardants is compared to DGEBA materials.

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I INTRODUCTION

The substitution of bisphenol A in resins and in particular in epoxy resins is the subject of numerous studies that we have reviewed recently¹. For epoxy resins, most of these works have replaced BPA with compounds from renewable resources, and in particular from natural phenols, such as tannins^{2,3,4} lignin derivatives (such as vanillin^{5,6}) or ferulic acid^{7,8}, cardanol^{9,10} and others¹¹. However, eugenol, another natural phenol is gaining increasing interest, not only due to its sourcing, but also due to its structure and the properties conferred to polymers. **(Scheme 1)**.



Scheme 1 : Chemical structure of Eugenol

There is a growing and recent interest in the literature concerning the use of eugenol or its isomer, isoeugenol, for the preparation of monomers and polymers such as cyanates esters¹², benzoxazines^{13,14}, polyesters¹⁵, methacrylates¹⁶ but also using specific reactions such as thiol-ene coupling¹⁷ and Alder-ene¹⁸.

Eugenol is a natural product, highly present in cloves (bp = 254 °C; mp = -9 °C). It is generally extracted with water, thanks to its azeotrope, at a temperature slightly below 100 °C. Natural clove-based eugenol constitutes a limited resource but different routes allow interesting production. First, a biosynthesis starts from tyrosine and leads to eugenol after deamination and various oxidations. Eugenol can also be obtained by Claisen rearrangement from gaiacol with allyl chloride^{19,20}. More interestingly, the depolymerization of lignin is a very promising strategy for the production of eugenol²¹. Hence, depolymerization by ionic liquids is widely studied^{22,23}.

In 2001 it was estimated that approximately 2,000 tons of oil was produced annually with a gross market value of US\$30–70 million per year especially for its aromatic ingredient and fragrance and antibacterial agent applications²⁴.

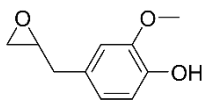
Eugenol, and its isomer, isoeugenol, are thus natural very interesting compounds for the synthesis of materials. Despite a growing number of works in this field, no review has reported the use of eugenol and isoeugenol in epoxy resins. Cloves have been used for a very long time as flavoring substances, antimicrobial and antiseptic additives in fragrances and cosmetics, skin protection agents and even in food and in pharmaceutical and dental products. However, studies show that at high concentration problems of toxicity, cytotoxicity and genotoxicity appear. A recent article²⁵ showed that this subject is controversial, and concluded that the studies are insufficient and should be carried on.

Hence, our review aims at presenting a comprehensive approach of the research on the synthesis of eugenol-based epoxidized precursors, the polymers obtained thereof and promising physico-chemical characteristics of the final products. Various monomers were reported, mono epoxy reactive diluents, di- or multifunctional glycidyl monomers and grafted ones. These compounds are often compared alone, or in mixture to diglycidyl ether of BPA in order to evaluate the contributions of the eugenol-based structures. Finally, resins carrying hetero-atoms (nitrogen, phosphorus or silicon) and their specific applications in electrochemistry or as flame retardants have also been described.

II Mono-epoxidized Eugenol

II.1 Epoxidation of allyl function

- Recently Sun et al.²⁶ have carried out epoxidation reaction of double bond of eugenol with metachloroperbenzoic acid (m-CPBA) as oxidant with a yield of 80% **(Scheme 2)**.

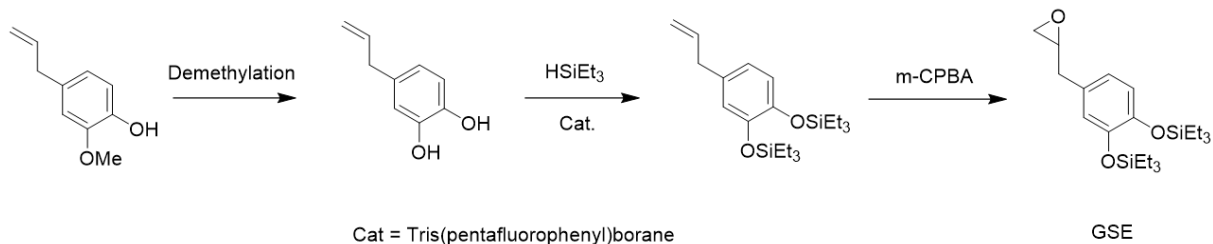


Scheme 2 : Chemical structure of epoxy Eugenol

Epoxy eugenol was then converted into a solid material named molecular glass material by a thermochemical oligomerization at 170 °C during 12 h. This oligomerization reaction was monitored by SEC and H^1 NMR analyses. The SEC showed new signals corresponding to higher molecular weight compared to both epoxidized and pristine eugenol. NMR analysis showed the appearance of the signal of a proton in alpha of phenoxy group, which demonstrated that oligomerization was due to the epoxy ring opening reaction by the phenol. This molecular glass material presented a stable amorphous solid state at room temperature and a typical glass transition temperature at 70 °C. An excellent flowability upon heating to 75 °C and a rapid solidification from the molten state could be interestingly achieved within a narrow temperature range. These properties made the eugenol molecular glass an ideal candidate material for the design of self-healing multiphases. Then eugenol-derived molecular glass and the epoxidized soybean oil matrix (ratio 1:2) have been cross linked to obtain a self-healing material with good mechanical properties. Hence, the self-healing ability was attributed to the multi-phased structure of this material.

The same mono-epoxidized eugenol has been used with diepoxy resorcinol by Renard et al.²⁷ in photopolymerisation reaction catalyzed by iodonium salt in order to obtain epoxy co-network materials. The authors studied the presence of phenol as antioxidant. The results showed that the presence of eugenol in the co-network led to an increase of mechanical flexibility and promising antibacterial properties with a reduction of the bacterial adherence by more than 90%.

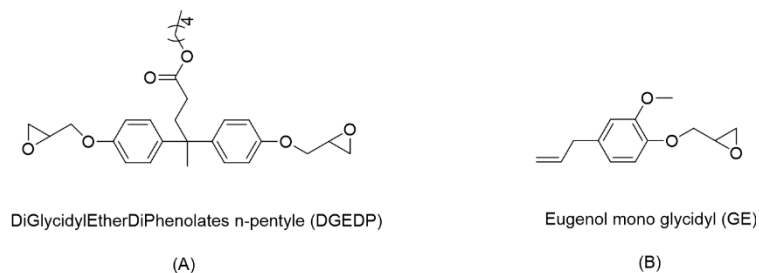
- Mono glycidyl silyl etherated eugenol (GSE) was synthesized as reactive epoxy diluent (**Scheme 3**) by Zhao et al.²⁸ who used it in epoxy/ anhydride curing system (DGEBA/cis-1,2-cyclohexanedicarboxylic anhydride (HHPA)) catalyzed by 2,4,6-tris(dimethylaminomethyl)phenol (DMP). The viscosity decreased from 25 to 0.5 Pa.s with 30 wt.% of reactive diluent whereas the glass transition temperature decreased by 30 °C with only 15 wt.% of reactive diluent. The effects of GSE on the thermo-mechanical properties and thermal stability of EP/HHPA/GSE systems indicated that it could effectively improve the toughness and thermal decomposition temperature of the epoxy system.



Scheme 3 : Synthesis of mono glycidyl silyl etherated eugenol²⁸

II.2 Epoxidation of phenol

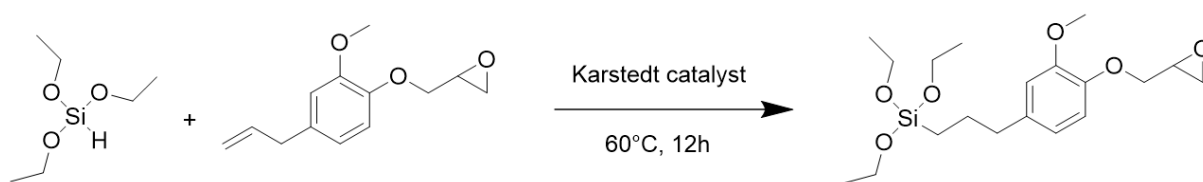
In order to replace BPA in epoxy thermosets for composite matrix, Maiorana et al.²⁹ have synthesized a new bio-based epoxy monomer, the diglycidylether diphenolates n-pentyle (DGEDP-Pe) (**Scheme 4 A**). The materials elaborated with this new epoxy presented good thermal and mechanical properties. However, this monomer exhibited a higher viscosity than DGEBA, and low viscosity epoxy monomers are required in order to allow suitable conditions to infuse continuous fibers and prepare composites with fillers. Therefore in a second study³⁰ the authors interestingly synthesized a mono glycidyl ether of eugenol (GE) (**Scheme 4 B**) as a reactive diluent for their DGEDP-Pe.



Scheme 4 : A) diglycidyl diphenolates n-pentyle²⁹; B) mono glycidyl ether of eugenol (GE)³⁰

The glycidylation reaction was performed with an excess of epichlorohydrin (7.5eq) under alkaline conditions (NaOH, 1.1 eq) and under homogenous conditions with 2-propanol at reflux. The resulting product was obtained with yields ranging from 85% to 90%. Dimeric co-products were observed but were not able to be quantified. As GE viscosity was very low (25 mPa.s), it presented an outstanding potential for composites preparation. The glassy modulus of cured GE/DGEDP-Pe epoxy resins remained between 2,000 and 3,000 MPa. The glass transition temperature decreased linearly with increasing amounts of GE. However careful attention should be given to the usage temperature of the composites as the glass transition temperatures of DGEDP-Pe/GE mixtures with 15 wt.% GE were significantly lower (70 °C) than those based on bisphenol A (90 °C).

A very recent study³¹ concerns the functionalization of silica "powder" by a new reactive silane containing eugenol group. The synthesis of additive was made by hydrosilylation by triethoxysilane by eugenol mono glycidyl (**Scheme 5**).

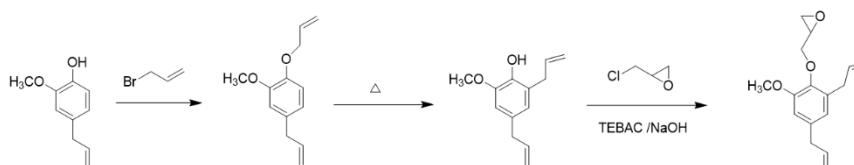


Scheme 5 : Synthesis of silicone additive graft mono glycidyl eugenol³¹

The use of the modified nano-SiO₂ particles in nano-composites with DGEBA as matrix showed excellent results and improved both thermal and mechanical properties. Only 4.0 wt% modified-nano-SiO₂-DGEBA/IPDA used in the system showed higher glassy storage modulus (+12°C), better thermal, flexural properties, and toughness. These great results were due to strong interfacial interaction leading to a better dispersion and compatibility of modified than unmodified nano-SiO₂ particles.

Additionally, a dual-curable monomer, diallyl glycidyl eugenol, has been prepared by Serra et al.³². Diallyl glycidyl eugenol was synthesized in a three-step procedure (**Scheme 6**), with allylation reaction followed by Claisen rearrangement and a terminal glycidylation of the phenol obtained with epichlorohydrin in basic medium. Then, this monomer was cured with polythiols combining a photoinduced radical thiol-ene reaction followed by a thermally activated thiol-epoxy reaction.

Compare to the only use of polythiol and thiol-ene reaction, the contribution of thermal thiol-epoxy reactions improved both thermal and thermomechanical characteristics of the thermosets in comparison to purely photocrosslinked materials.

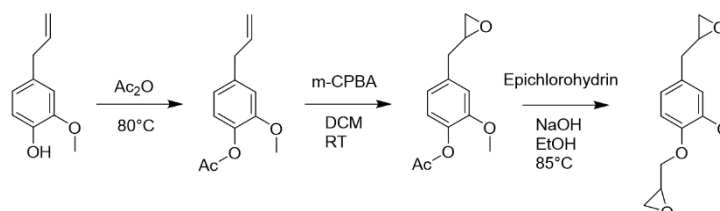


Scheme 6 : Synthesis of diallylglycidyl of eugenol³²

III Multipoxidized eugenol

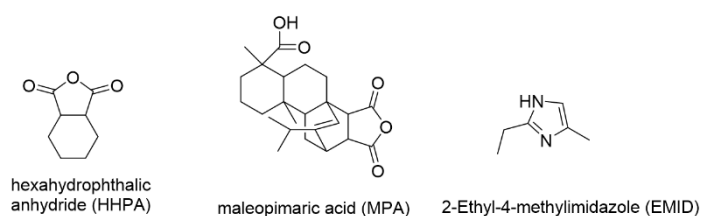
III.1 Diepoxidized eugenol or 2-[3-methoxy-4-(oxirane-2-ylmethoxy)benzyl]oxirane

Diepoxidized eugenol is the simplest diepoxy derivative of eugenol. In 2014, Zhang et al.³³ have prepared diepoxidized eugenol in three steps (**Scheme 7**) with first a phenol protection with acetate, followed by epoxidation of allyl functions and final glycidylation reaction. The authors noted that the procedure with the glycidylation reaction as first step did not succeed.



Scheme 7: Synthesis of 2-[3-methoxy-4-(oxirane-2-ylmethoxy)benzyl]oxirane³³

Diepoxidized eugenol was then cured with either hexahydrophthalic anhydride or a rosin-derived anhydride in presence of 2-ethyl-4-methylimidazole (EMID) as catalyst (**Scheme 8**).

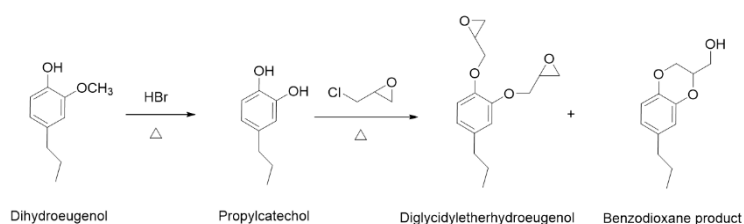


Scheme 8: chemical structure of anhydride agents and catalyst used by Zhang et al.³³

A classical effect on reactivity was observed with the decrease of the curing temperature and total conversion of curing reactions in the presence of 2-ethyl-4-methylimidazole as catalyst. Furthermore, whatever the epoxy, based on eugenol or on bisphenol A, the results of dynamic mechanical properties and thermal stability were similar.

In 2017, Plasseraud et al.³⁴ have completed this work in order to elaborate biobased epoxy formulations for composite processing including natural fibers. Hence, they compared diepoxidized eugenol to commercial epoxy resin formulated with six different anhydride hardeners. The mechanical performances of their eugenol-based materials were very close to those of the materials based on standard commercial formulations. Moreover, the authors reported the crystal structure³⁵ and the melting point (115 °C) of the diglycidyl ether of eugenol previously prepared by Zhang et al.³³.

The following study was not performed on eugenol, but on dihydroeugenol (2-methoxy-4-propylphenol). However, it is worth mentioning it since this study also presented an interesting diglycidyl ether of 2-methoxy-4-propylphenol³⁶ (**Scheme 9**).



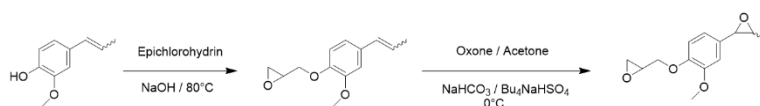
Scheme 9 : Synthesis of diglycidylether of dihydroeugenol³⁶

The synthesis of diglycidylether of dihydroeugenol was done in two steps, with a first reaction of demethylation followed by glycidylation reaction. During glycidylation reaction of the ortho-positions of the two phenolic hydroxyl groups, the formation of a side reaction, that our team already reported on tannin epoxidation^[2], occurred, leading to benzodioxane side-product (60 wt.%) and reducing average functionality (< 2) of products mixture.

Then, the authors elaborated biobased epoxy thermosets from nano-montmorillonite (0 to 12 wt.%) and diglycidylether of dihydroeugenol /diethylenediamine as resin. The formulations were cured at 95 °C during 2 h. The nanocomposite materials exhibited improved storage modulus and thermal stability which represents alternatives to petrosourced epoxy thermosets.

III.2 Diepoxidized isoeugenol

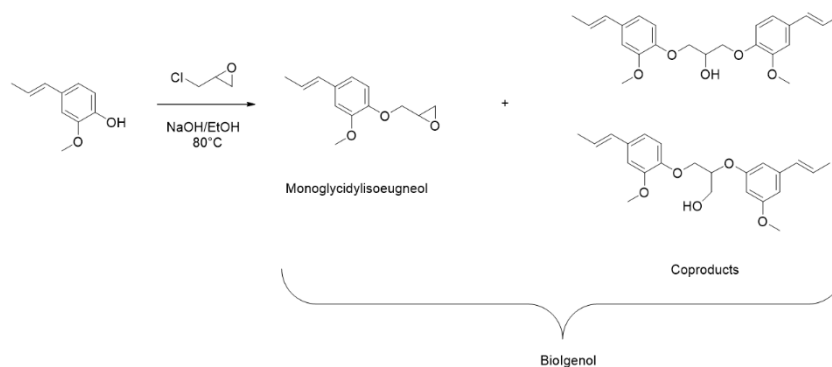
During the same period Plasseraud et al.³⁷ worked on the synthesis of diepoxidized isoeugenol and thermosetting epoxy materials thereof. Epoxidation reaction was performed in a two-steps process, with a first glycidylation reaction with epichlorohydrin followed by epoxidation reaction with oxone (**Scheme 10**). After the first step, the intermediate was purified by column chromatography to yield the intermediate as a white solid (70% yield). The following epoxidation reaction occurred with a 90% yield.



Scheme 10 : Synthesis of diepoxidized isoeugenol³⁷

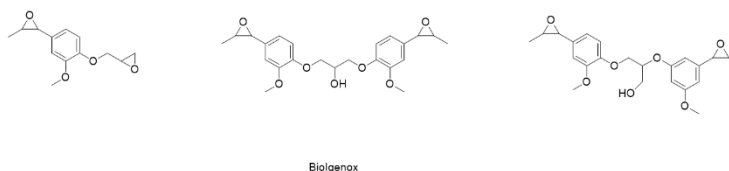
The authors compared diepoxidized isoeugenol (Iso-eug) to diepoxidized eugenol (Eug) in various formulations with maleopimaric acid (MPA) and 1,2-cyclohexanedicarboxylic anhydride (HHPA) as hardeners (1 :0,8 molar ratio), 2-ethyl-4-methylimidazole as catalyst, that were cured at 150 °C during 1 h. The authors have noted that the values of the reaction enthalpies related to the polymerization of hardener used with isoeugenol were lower than those of diepoxidized eugenol. As the enthalpies polymerization correspond to both value of the reaction enthalpy and the progress of the reaction, the authors did not compare the epoxy reactivity which could vary with the position of epoxy function on eugenol and epoxidized isoeugenol. The Tg value of the Iso-eug/HHPA formulation was 120 °C, slightly higher than that of Eug/HHPA (114 °C) whereas the Tg value of Iso-eug/MPA (93 °C) was much lower than that of Eug / MPA (155 °C). The authors explained these results by a lower extent of the polymerization reaction. Overall, the thermo-mechanical properties were slightly lower than those of diepoxidized eugenol-based materials, but remained suitable for thermosetting material applications.

To enhance attractiveness of diepoxidized isoeugenol as precursor of biosourced epoxy resin the same authors proposed recently³⁸ an improvement of this previous bio-based epoxy resin in order to make its scale-up possible. Extensive characterization allowed the authors to identify all side-products formed during the first step of the reaction (**Scheme 11**). The mechanism occurred through the addition of phenate on the two carbons of glycidyl function formed during the reaction leading to co-products. This mechanism has never been described in literature. The whole mixture of three (co)products was named Biolgenol.



Scheme 11 : Formation of monoepoxidized isoeugenol and coproducts during the reaction of glycidylation of isoeugenol³⁸

After epoxidation reaction with oxone catalyst, a mixture of diepoxidized isoeugenol named Biolgenox was obtained (**Scheme 12**) with 55 – 85 wt.% of diepoxidized monoisoeugenol.



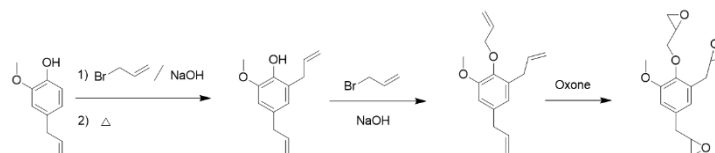
Scheme 12 : Synthesis of Biolgenox by epoxidation reaction of Biolgenol³⁸

Thermal and mechanical properties were studied in order to determine the optimal conditions and stoichiometry to obtain materials with the best properties. Biolgenox was formulated with either camphoric or 1,2-cyclohexanedicarboxylic anhydride as hardeners (1:0.9 molar ratio), 2-ethyl-4-methylimidazole as catalyst and were cured at 150 °C during 2 h. The mechanical properties of Biolgenox-based materials were similar to those from petrosourced DGEBA resin. Hence, the works of Plasseraud et al. demonstrated the possibility to synthesize a biobased epoxy matrix (Biolgenox) without chromatography purification step, making possible its scale up as a promising solution for the replacement of DGEBA.

III.3 Triepoxidized eugenol

The synthesis of triepoxidized eugenol was based on the works of Shibata et al³⁹ who were the first to synthesize the triallyleugenol by coupling allylation reaction and Claisen rearrangement. Then, the authors used their triallyleugenol to elaborate materials by thiol-ene photopolymerization with polythiols.

As reported in paragraph II.2 Serra et al³² used coupling of allylation reaction and Claisen rearrangement to elaborate, after glycidylation reaction, a dual (thermal and UV) cure monomer. Serra et al recently published two articles on the synthesis and use of polyepoxy eugenol^{17,40}. From the polyallyl eugenol synthesized by Shibata, the epoxidation of double bonds with the oxone as oxidant allowed to obtain a triepoxidized eugenol (**Scheme 13**).



Scheme 13 : Synthesis of triepoxidized eugenol by allylation, Claisen transposition and epoxidation reactions⁴⁰

The authors cured triepoxidized eugenol with three different polythiols by thiol-epoxy click reaction in the presence of a base as catalyst. To reduce the steric and topological constrains, the authors added 1,6-hexanediol diglycidylether as

reactive diluent. The Tg values of obtained thermosets were between 47 and 103 °C and the materials displayed good thermo-mechanical performances (Young's modulus and stress at break).

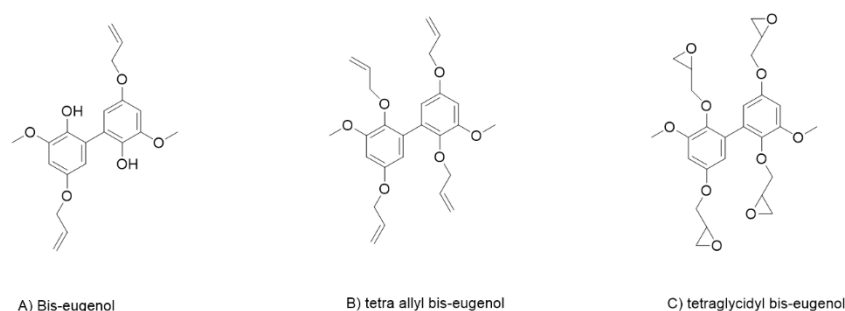
The authors used the triepoxidized eugenol in thermosetting formulations with either Jeffamine D400 or isophorone diamine (IPDA) and compared them to a DGEBA equivalent formulation, even if DGEBA is a difunctional monomer. Thermoset materials from triepoxidized eugenol logically presented higher glass transition temperatures than DGEBA-based materials. The degradation temperatures of eugenol-based materials were above 300 °C, slightly lower than those from DGEBA, but with slower degradation rates. The mechanical properties of these materials perfectly reflected their functionalities: higher modulus and stress and lower elongation for the triepoxidized eugenol-based materials.

IV Eugenol dimer

Lots of works have been done on the synthesis of eugenol dimer (named bis-eugenol) in order to develop an epoxy resin for thermosetting materials.

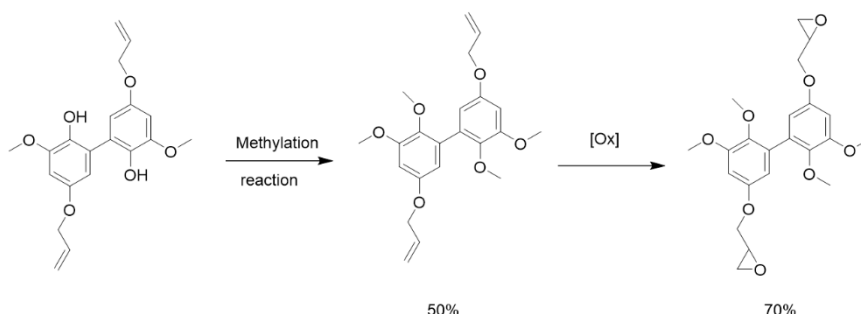
IV.1 Di(or multifunctional) epoxidized of bis-eugenol without spacer

Bis-eugenol (**Scheme 14 A**) was prepared by oxidative dehydrodimerization of eugenol using iron(III) chloride or potassium ferricyanide^{41,42}. After allylation, Serra et al.⁴³ used tetra allyl bis-eugenol (**Scheme 14 B**) in order to synthesize tetraglycidyl bis-eugenol (**Scheme 14 C**) by epoxidation reactions with oxone.



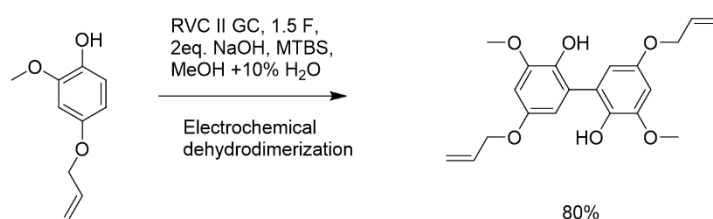
Scheme 14 : Chemical structure of bis-eugenol (A)^{41,42}, tetra allyl bis-eugenol (B)⁴³ and tetraglycidyl bis-eugenol (C)⁴³

An enzymatic approach was reported by Llevot et al.⁴⁴, giving the bis-eugenol in good yields (>85%). The laccase-catalyzed dimerization relied on oxygen as a terminal oxidant and required the addition of relatively expensive purified enzymes. The authors have prepared the diglycidyl bis-eugenol⁴⁵ by methylation reaction of bis-eugenol with iodomethane, under basic conditions followed by an epoxidation in presence of m-CPBA (**Scheme 15**).



Scheme 15 : Synthesis of diglycidyl bis-eugenol⁴⁵

Waldnogl et al.⁴⁶ have developed an electrochemical dehydrodimerization of eugenol in order to obtain bis-eugenol (**Scheme 16**). After the eugenol coupling, the authors synthesized the diglycidyl and the tetraglycidyl bis-eugenol by methylation or allylation reaction followed by epoxidation reaction with oxone.



Scheme 16 : Synthesis of bis-eugenol by electrochemical dehydrodimerization⁴⁶

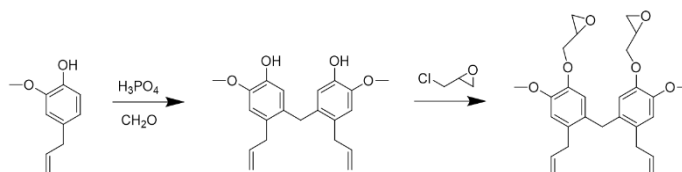
Waldnogl⁴⁶ compared materials elaborated with synthesized di- and tetra-glycidyl eugenol or DGEBA and formulated with methyl hexahydrophthalic anhydride (MHHPA) and 2-ethyl-4-methylimidazole (EMID) as catalyst. Materials from DGEBA and diglycidyl bis-eugenol exhibited similar glass transition temperatures (T_g) (153 °C) and, as expected, a higher T_g was obtained with the tetra glycidyl (216 °C). The analysis of thermal stability showed a better stability for DGEBA-based materials with a degradation temperature corresponding to 5 wt.% loss (T_{5%}) was 359 °C. The T_{5%} of tetraglycidyl bis-eugenol and diglycidyl bis-eugenol based materials were lower, respectively 330 °C and 269 °C.

Serra et al.⁴³ cured respectively tetra allyl bis-eugenol by photochemical thiol-ene reaction with polythiol and irgacure as catalyst and tetraglycidyl of bis-eugenol by thiol epoxy thermal curing with organic basis. The materials prepared by the thiol-epoxy thermal curing exhibited better thermal and mechanical properties than those cured by photochemical thiol-ene reaction.

IV.2 Di(or multifunctional) epoxidized of bis-eugenol with spacer

IV.2.a Spacer "methylene" via carbon-carbon bond

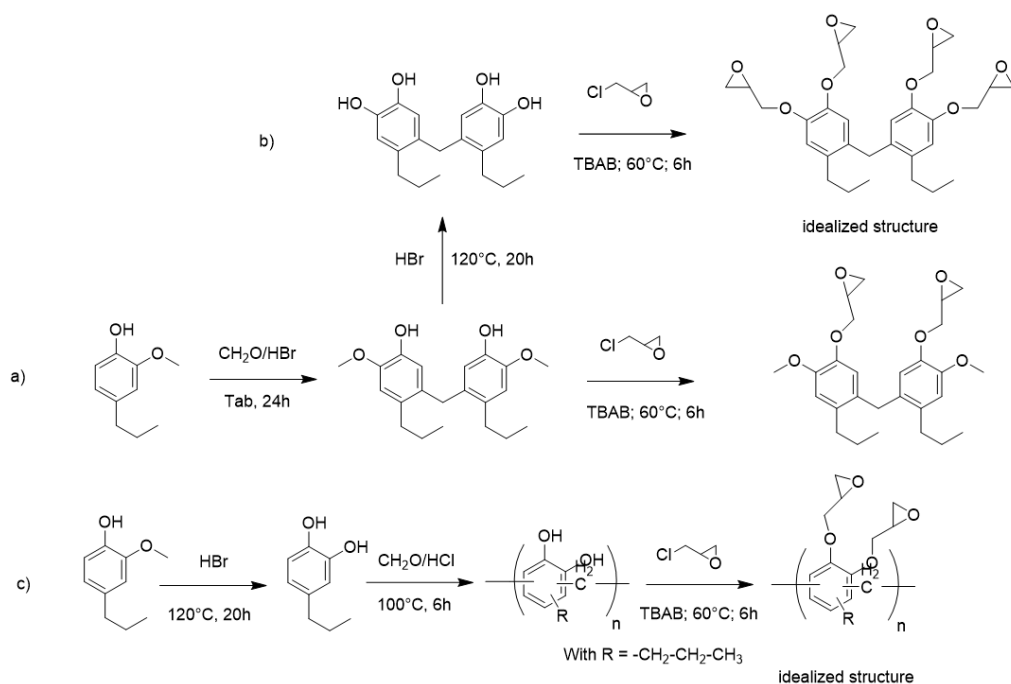
Zhao et al.⁴⁷ have carried out dimerization of eugenol with phosphoric acid and formaldehyde to followed by glycidylation reaction with epichlorohydrin leading to a diglycidyl ether of bis-eugenol (**Scheme 17**).



Scheme 17 : Synthesis of diglycidyl monomer of bis-eugenol with methyl spacer⁴⁷

The estrogenic activity test performed by the authors revealed that the eugenol-based bisphenol precursor of diglycidyl monomer presented a lower estrogenic activity than commercial bisphenols (BPA and BPF). Furthermore, the thermo-mechanical properties (thermal stability, glass transition temperature, storage modulus) and hydrophobic properties were comparable to those from conventional epoxy thermosets.

As presented in paragraph III.1, Omar et Al.⁴⁸ have worked on dihydroeugenol (2-methoxy-4-propylphenol). The authors presented (**Scheme 18**) the synthesis of di-, tetra- and poly-glycidyl starting from dihydroeugenol. Firstly, diglycidyl was obtained by coupling eugenol with HBr (at room Temperature during 24 h) followed by epoxidation with epichlorohydrin (a). Secondly, after coupling the authors proceeded to the demethylation in order to obtain the tetraphenol and subsequently the tetraglycidyl (b). Finally, the authors used acidic oligomerization reaction of dihydroeugenol with formal at 100 °C during 6 h. This novolac type oligomers have been demethylated and epoxidized with epichlorohydrin (c).



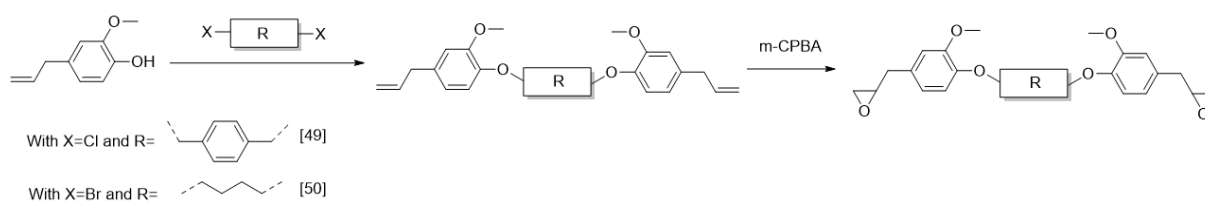
Scheme 18 : Synthesis routes to obtain di and tetra glycidyl monomers (a;b) and polyglycidyl novolac oligomer (c)⁴⁸

Authors have studied the thermal and mechanical properties of cured thermosets, and showed that they strongly depend of many factors such as molecular weight of precursors, position and number of epoxy groups. Therefore, their study highlighted the possibility to improve thermomechanical properties through the variation of crosslinking density from the same biobased precursors.

IV.2.b Spacer aliphatic, cycloaromatic and pseudo aromatic via oxygen-carbon bond

- Ether spacer

Wang et al.⁴⁹ and Zhang et al.⁵⁰ performed similar dimerization reaction of eugenol by nucleophilic substitution reaction of dihalogeno phenylene and butylene, respectively. The obtained dienes monomers were oxidized with *m*-CPBA to obtain eugenol-based diepoxy monomers with aromatic or aliphatic spacers (**Scheme 19**).



Scheme 19 : Synthesis of diglycidyl monomer of bis-eugenol with phenylene⁴⁹ and butylene⁵⁰ spacers

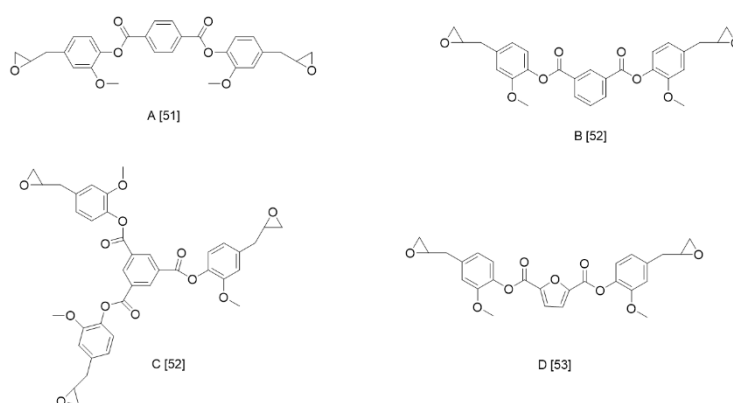
The diglycidyl phenylene bis-eugenol (DEU-EP) was solid at room temperature and its melting point was 124°C . To compare with DGEBA-based materials, the authors formulated both epoxy monomers with methylene dianiline and cured them at 140°C during 5 h. Thanks to differential scanning calorimetry analysis, the authors⁴⁹ determined similar reaction (161 and 166°C) and glass transition temperatures (154 and 144°C), respectively for DGEBA and DEU-EP based materials.

Eugenol-based material exhibited improved mechanical (Young's modulus, hardness) and thermal properties such as a reduced flammability and an increase of char yield.

Concerning the bis-eugenol-based diglycidyl butylene monomer, the purpose of the authors was to elaborate epoxy materials which could be reprocessed, reshaped, and recycled as vitrimers. Hence, they synthesized diglycidyl butylene bis-eugenol (Eu-EP) and formulated it with succinic anhydride at various ratios (1:0.5, 1:0.75, and 1:1) in presence of zinc catalysts. All vitrimers exhibited excellent shape changing, crack healing, and shape memory properties. The authors⁵⁰ studied the stress relaxation rates in function of ratio to evaluate shape changing, crack healing, and physical recycling of the samples. The materials with ratio of 1:0.5 presented better properties than the other ratios.

- Ester spacer

After coupling reaction of eugenol with acyl chlorides derivatives followed by epoxidation reaction with m-CPBA, two types of multifunctional glycidyl eugenol were obtained, aromatic ones, with terephthalic (A)⁵¹, isophthalic (B) and trimesic (C)⁵² groups and a pseudoaromatic one with furanic group⁵³. The terephthalic, isophthalic and furanic eugenol monomers were difunctional whereas trimesic one was trifunctional as shown in **scheme 20**.



Scheme 20 : diglycidyl terephthalic⁵¹ (A), isophthalic⁵² (B), furanic⁵³ (D) monomers of bis-eugenol and triglycidyl trimesic monomer of tris-eugenol⁵² (C)

These eugenol-based multifunctional glycidyl monomers were solid with various melting points, respectively 174 °C for (A), 99 °C for (D) and not determined for (B) and (C).

The diglycidyl monomer (A) was formulated with 3,3'-Diaminodiphenylsulfone (33DDS) and cured at 180 °C for 5 hours. The material obtained was compared to material formulated with DGEBA. The glass transition temperatures were equivalent, 168 °C and 174 °C, respectively. The mechanical and thermal resistance properties were enhanced compared to DGEBA based material.

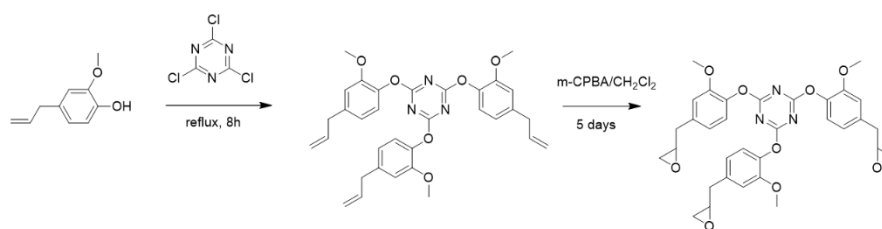
Concerning the multifunctional glycidyl monomers (B) and (C), the authors studied self-curing reaction to elaborate thermoset materials and proposed a mechanism via model study. Regardless of the process by solvent casting (in DMAc with a solid content of 30 wt.%) or melt mixing, (B) and (C) were formulated with 0.5% of DMAP as catalyst and cured at 120 °C, 180 °C, 200 °C, and 220 °C for 2 h at each temperature. The authors elaborated also a standard epoxy thermoset cured with 4,4'-methylene dianiline (DDM) by solvent process. The authors compared their eugenol-based thermosets with DGEBA based materials formulated with 5.2 wt.% of DMAP as catalyst. All materials formulated with (B) and (C) presented better mechanical stabilities with higher T_g (180 °C and 230 °C respectively) than DGEBA material (160 °C). Concerning thermal stability, the self-curing materials presented higher temperature at 5 wt.% of degradation than epoxy/DDM formulation but still slightly lower temperature compare to DGEBA based materials. However all eugenol-based materials exhibited higher char contents than DGEBA based materials. The self-curing materials presented interesting dielectric properties with a much lower dissipation factor compare to those of (B)/DDM, (C)/DDM and DGEBA. Thus, these eugenol-

based multifunctional glycidyl monomers allowed obtaining a self-curing epoxy thermosetting epoxy resin with high Tg and low dissipation factor, suitable for high frequency printed circuit board.

Diglycidyl furanic monomer of bis-eugenol (D) and DGEBA were formulated with methyl hexahydrophthalic anhydride (MHHPA) and cured at 130 °C, 150 °C, 170 °C for 2 h at each temperature. Compared with DGEBA/MHHPA, the furanic material exhibited higher mechanical properties and better flame retardancy with a reduction by 19% of both peak heat release rate and total heat release temperature. However the thermal degradation was inferior by 50 °C.

IV.2.c Spacer with azine function

Wang et al.⁵⁴ synthesized triazine triglycidyl eugenol by reaction between cyanuric chloride and eugenol followed by epoxidation reaction with m-CPBA (Scheme 21).



Scheme 21 : Synthesis of triazine triglycidyl based eugenol⁵⁴

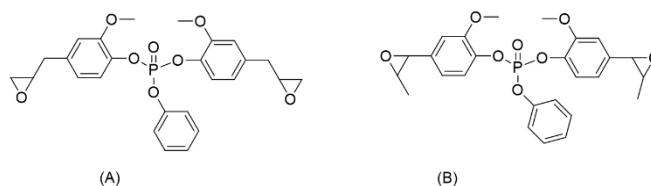
The authors compared materials from triazine triglycidyl eugenol and DGEBA in formulation with 33DDS. They highlighted the ultrahigh Tg, Young's modulus and hardness, outstanding thermomechanical properties, low permittivity and dielectric loss, and reduced flammability of these new eugenol based materials.

IV.2.d Phosphate spacer

Diglycidyl^{55,56} or triglycidyl⁵⁷ phosphates based on eugenol or isoeugenol were presented successively.

- eugenol⁵⁵ or iso-eugenol⁵⁶ based diglycidyl phosphate

Zhao et al.⁵⁵ and Boni et al.⁵⁶ synthesized eugenol (A) or iso-eugenol (B) based diglycidyl phosphates by reaction between dichlorophenylphosphate and eugenol or iso-eugenol followed by epoxidation reaction with m-CPBA or oxone, respectively (Scheme 22). The diglycidyl monomers were formulated with either DDM or anhydrides with imidazole as catalyst.

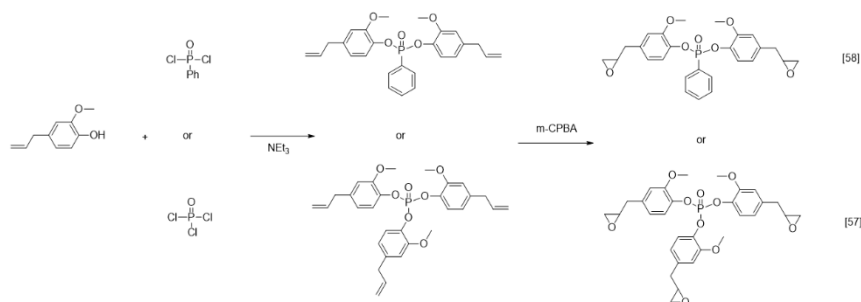


Scheme 22 : eugenol⁵⁵ (A) or iso-eugenol⁵⁶ (B) based diglycidyl phosphates

The materials presented variable Tg, high mechanical performances and superior flame resistance compared to their DGEBA-based equivalents.

- Eugenol-based triglycidyl phosphate⁵⁷ and phosphonate⁵⁸

Caillol et al. synthesized in two steps eugenol-based triglycidyl phosphate and phosphonate by a first reaction between eugenol and phosphorus oxychloride and dichlorophenylphosphine oxide, followed by epoxidation reaction with m-CPBA (Scheme 23).



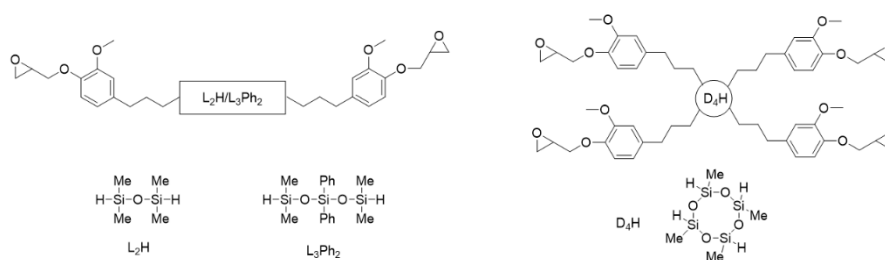
Scheme 23 : Synthesis of eugenol based triglycidyl phosphate⁵⁷ and phosphonate⁵⁸

These synthesized triglycidyl eugenol phosphate and phosphonate were compared to DEGBA in formulations with different amines (m-xylylenediamine (MXDA) or JEFFAMINE[®] EDR-148) with 1 h curing at 150 °C. The objectives of these studies were to elaborate biobased epoxy networks with phosphonate or phosphate functions in order to improve the flame retardant properties. The results showed that the phosphate and phosphonate groups were both equally efficient to promote char and reduce flammability for these materials. The flame inhibition effect was confirmed with a better efficiency for the phosphonate function. For all materials containing phosphorus and eugenol, the same variations were observed, namely a decrease of the degradation temperature of 5 wt.%, of T_g and T_α, of glassy or elastic modulus, and an increase of char content or/and heat release rate (HRR) which confirms the interest of these molecules for flame retardant applications.

Very recently, Wu et al.⁵⁹ and Averous et al.⁶⁰ have used the same phosphorous eugenol-based compound in order to prepare self-healing epoxy network. The concept was based on a reversible disulfide bond present in diamine reactant, the 4,4'-dithiodianiline. The materials were obtained with excellent thermal and mechanical properties and good flame retardancy. These works showed a strong potential for the development of sustainable plastic with high renewable carbon contents (around 70 wt%) and additional properties such as promising reshaping, repairing and recycling capability.

IV.2.e Siloxane spacer

Liu et al.⁶¹ synthesized linear and cyclic siloxane-based multifunctional glycidyl ethers of eugenol (**Scheme 24**) by hydrosilylation reaction of allyl groups of eugenol followed by epoxidation reaction with epichlorohydrin. The ratio eugenol/epichlorohydrin was 1:2.5.

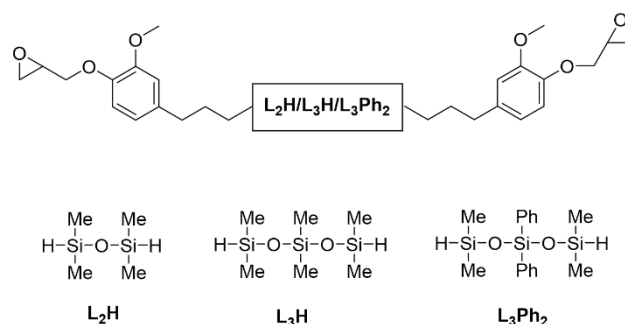


Scheme 24 : Structure of linear siloxane diglycidyl bis-eugenol (L₂H and L₃Ph₂) and cyclic siloxane tetraglycidyl tetrakis-eugenol⁶¹

These siloxane-based multifunctional glycidyl eugenols were formulated with DDM and cured at 80 °C, 120 °C and 160 °C for 2 h at each temperature. The cyclosiloxane-based material exhibited good mechanical properties as well as a low T_g and dielectric constant, respectively 60 °C and 22.7%, lower than those of DGEBA based resin.

The following year, Dubois et al.⁶² studied in details the synthesis of linear siloxane-based diglycidyl bis-eugenol (L₂H, L₃H and L₃Ph₂) (**Scheme 25**). Unlike Liu et al. who have performed hydrosilylation prior epoxidation reaction, Dubois et al.

performed the hydrosilylation reaction of the monoglycidylether of eugenol. Moreover, they optimized the glycidylation of eugenol using optimized eugenol/epichlorohydrin ratio of 1:1 instead of 1:2,5; 1:5; 1:10 and even more in some cases.



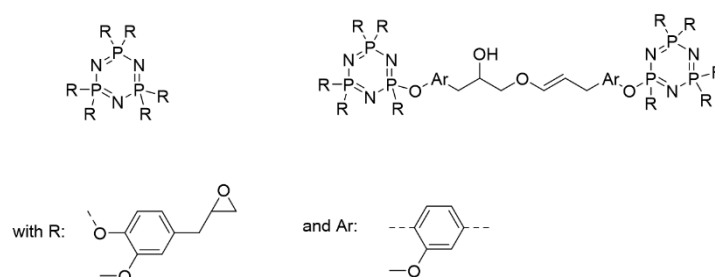
Scheme 25 : structure of linear siloxane diglycidyl bis-eugenol (L_2H , L_3H and L_3Ph_2) synthesized by Dubois et al.⁶²

These glycidyl siloxanes were formulated with DDS and cured at 150 °C, 180 °C and 200 °C for 2 h at each temperature. The presence of short silicon segments decreased the viscosity, facilitating the elaboration of materials. With a dielectric permittivity as low as 3.0, and intrinsic flame retardant properties with LOI values as high as 31, the authors showed clearly a benefic effect of siloxane segments on the dielectric and flame retardant properties of epoxy materials.

It should be noted that dieugenol with siloxane spacers or polysiloxanes grafted onto eugenol have been synthesized through hydrosilylation reactions. These products have been used as additives in DGEBA-based epoxy resins. This work has not been detailed here because it does not fall within the objective of this review.

IV.2.f Phosphazene spacer

In a first study⁶³ Kireev et al. reported the reaction between eugenol (in excess) and hexachlorocyclotriphosphazene (HCP) prior epoxidation with m-CPBA, yielding cyclotriphosphazene-based epoxidized eugenol. Thanks to Maldi-TOF analyses the authors identified high content of dimer co-product (30 wt.%) (**Scheme 26**). The authors explained this side-reaction by the tendency of epoxy groups to enolization.



Scheme 26 : Structure of cyclotriphosphazene based epoxidized eugenol and dimer co-product⁶³

In their second study⁶⁴, the authors synthesized mixtures of chlorocyclophosphazene oligomers $[\text{NPCl}_2]_{3-8}$. After purification via fractional crystallization from *n*-hexane, the authors obtained octachlorocyclotetraphosphazene. After reaction with eugenol followed by epoxidation reaction with m-CPBA, eugenol based cyclophosphazene octaepoxy oligomers and mixtures of eugenol based cyclophosphazene epoxy oligomers were obtained. Thanks to detailed Maldi-TOF analyses, the authors proposed some hypotheses on the nature of side reactions that occurred during epoxidation, coming from uncomplete epoxidation of eugenol, hydrolysis of epoxides, the presence of eugenol/m-CPBA adduct and, as in previous study, the presence of dimer. However both studies did not report the elaboration of any materials.

In their last study⁶⁵, the authors confirmed previous hypotheses concerning side-reactions occurring during synthesis of eugenol based cyclophosphazene epoxy oligomer. To avoid these side-reactions (uncomplete epoxidation, presence of eugenol/m-CPBA adduct and dimerization reaction), the authors studied a new pathway for the synthesis of phosphazene-containing epoxy oligomers without epoxidation of double bonds. Hence, the authors examined the reaction of chlorocyclophosphazenes with large excess of diphenols followed by glycidylation reaction with epichlorohydrin. The main inconvenient of this route was the formation of oligomers which presented higher values of viscosity (150–220 Pa.s at 40 °C) than standard organic epoxides.

These epoxy phosphazenes were formulated and cured with either anhydride or amine. The mechanical, dielectric and adhesive properties of cured epoxy phosphazenes were similar to those of common BPA-based epoxy resins except for fire resistance and even non-combustibility properties which were largely improved.

Recently, Zhao et al. in 2020⁶⁶ used the works of Kireev et al. to synthesize the same hexa-epoxy eugenol cyclotriphosphazene and elaborated materials with Jeffamine D230. The thermo-mechanical and flame retardant properties of these materials were superior to those of BPA-based epoxy materials.

V Conclusion

These numerous works revealed several points that open interesting perspectives to BPA replacement. First, the current state of sourcing shows that only the development of depolymerization of lignin can make it possible to adapt to the tonnages of the resins in which eugenol and its isomers could be incorporated instead of BPA. Moreover, the high performances of materials based on eugenol and its isomers are equivalent to those based on BPA, and sometimes superior in the case of the flame retardant properties. Finally, the use of eugenol allows to avoid epichlorohydrin for epoxidation step, which very important to reduce environmental impacts. Indeed, the epoxidation could easily be carried out only on the allylic group (ex dimers). However, in perspective of this review, more research remains to be done to access the possible industrially substitutes for DGEBA. The first and most important work is a deep study of the toxicity of these monomers because there are still controversies (hemotoxic, allergy, etc). It is also necessary to analyze the other derivative products (adduct, dimers, etc) and their epoxidized derivatives. The second point concerns the epoxidation reaction on the alkene double bond. Indeed, the reagents for eugenol epoxidation are oxone or m-CPBA which are either expensive or toxic. Greener oxidants such as hydrogen peroxide should be deeply studied. Double bond oxidation remains a crucial subject for the development of new epoxy resin without BPA. Eugenol and its isomers should be better envisioned from this point of view.

Conflicts of interest: There are no conflicts to declare

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