Chapter

THERMOSETTING MATERIALS FROM EUGENOL DERIVATIVES

Dailyn Guzmán,[1,2]* Angels Serra,[1,2] and Xavier Ramis[3]

1. CTQC (EURECAT-UTQ) Marcel·li Domingo s/n Edif. N5, 43007 Tarragona (Spain)
2. Department of Analytical and Organic Chemistry Marcel·li Domingo s/n Edif. N4, 43007 Tarragona (Spain)
3. Thermodynamics Laboratory, ETSEIB, Universitat Politècnica de Catalunya, Avda. Diagonal 647, 08028 Barcelona (Spain)

ABSTRACT

Green chemistry explores safer ways to prepare new materials from renewable resources. Thermosets are generally prepared from a mixture of monomers, with at least one of them having three or more reactive functions. This allows the formation of a covalent three-dimensional network that gives the material some characteristics such as infusibility and insolubility, which are necessary for many applications such as coatings, adhesives, structural compounds, etc. Thermosetting materials are widely used in sectors of the electrical and electronics industry, in aeronautics and in construction, among others.

If we consider biomass resources, eugenol is highly attractive as a raw material since it is easy to obtain and has a great natural abundance, which reduces its cost. It has a versatile structure that allows its easy modification to reach the convenient functionality for the preparation of the polymer network through various procedures. The structure of eugenol is quite rigid and compact, with a phenolic group and an allyl group that can later be transformed, and its structure allows a dimerization that generates bis-eugenol.

Many researchers have started from eugenol to prepare adhesives by thiol-ene reactions or coatings by thiol-epoxy processes or even by homopolymerization of acrylic derivatives. Bisbenzoxazines or bismaleimides have also been prepared and polymerized, which have allowed obtaining a wide range of thermosetting materials.

Finally, and even more important, eugenol can be used in food industry at low concentrations and, therefore, it is safe as a starting material for the preparation of green and non-toxic thermosets to be in contact with food or beverages.

In the present chapter, a revision of the eugenol based thermosetting materials will be presented. This will include not only their preparation, but also some important characteristics and applications.

* Corresponding Author address
Email: dailyn.guzman@ctqc.org

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INTRODUCTION

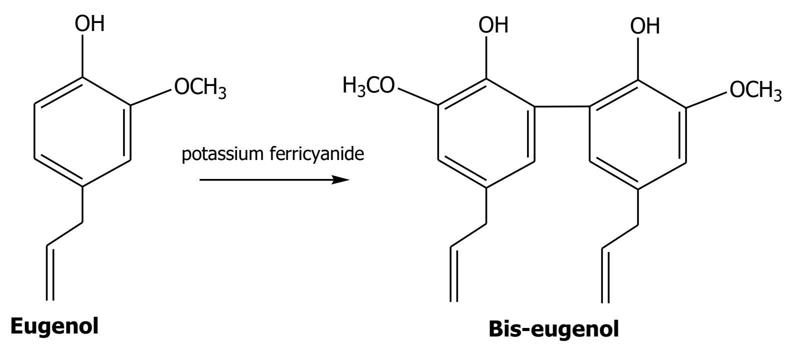
Thermosets are one of the highest consumption materials in the polymeric industry sector due to their excellent thermal and mechanical properties [1]. These materials are obtained through an irreversible polymerization process [2] and their most common applications include: resins, adhesives, coatings, inks, paints and composite materials [3,4,5].

Thermosetting materials are generally prepared from non-renewable sources [6,7]. However, in recent years the aim of preparing materials from renewable resources to preserve the environment from the aggressions coming from industrial processes and minimize dependence on petroleum has lead research in several new ways or strategies [8]. There is a wide range of natural products that are used in industrial applications to partially replace, and to some extent totally, petroleum based polymers. Polymers designed under this strategy can compete or even surpass existing materials by adding better properties involving the respect for the environment [9-13].

Many investigations have focused on obtaining thermosets from different renewable sources used as raw materials [14-18]. Eugenol is highly attractive as a starting material for the development of new functional materials favourable towards the environment.

Eugenol is the main compound of clove oil [19], it offers a great natural abundance and low cost [20]. It is also considered safe for application in food industry [21] and that's the reason why it can be used as starting monomer to prepare environmentally friendly thermosetting materials. One the most relevant characteristics of the compound is that it has a rigid, compact and very versatile structure that allows obtaining materials with excellent characteristics for the application in advanced technologies with higher requirements.

Bis-eugenol is the most important eugenol derivative in medical applications [22,23]. This compound is present in nature, but in low concentrations [24]. The best known procedure to prepare bis-eugenol consists in the eugenol's oxidative coupling performed under mild conditions, by treating it with an aqueous mixture of potassium ferricyanide in a basic medium at room temperature [25], shown in Scheme 1. The dimerization of eugenol allows the obtaining of a compound with a similar structure as commercial bisphenol A epoxy resin (DGEBA) and for this reason it could be employed as a green alternative to petrochemical materials.

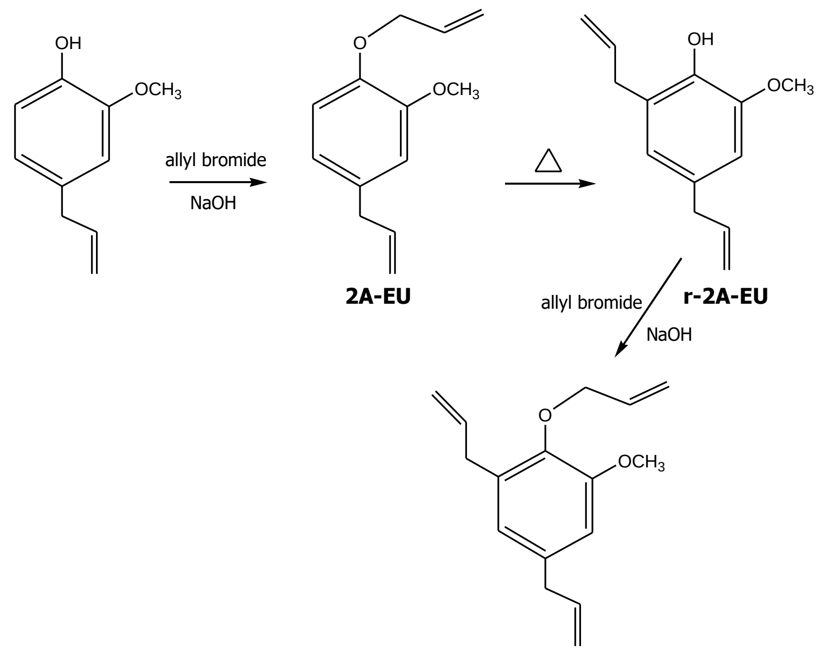


Scheme 1. Synthesis of bis-eugenol.

The versatile chemical structure of eugenol allows the introduction of different functional groups into the structure to obtain new species that can be used for preparing thermosetting materials with a great range of characteristics and properties. The main derivatives from eugenol are the following: allyl, epoxy, acrylate, benzoxazine and bismaleimide, each one of them further described in this chapter.

THERMOSETS FROM ALLYL EUGENOL DERIVATIVES

The allylic compounds take an important position in adhesive industry. Allyl derivatives from eugenol can be prepared with different degrees of functionality following simple synthetic procedures. Yoshimura et al. [26] reported the synthesis of triallyl eugenol derivative, by using diallyl eugenol as starting material, prepared by the allylation of eugenol's phenolic group (see Scheme 2). This derivative is submit to the Claisen rearrangement generating a new phenolic group that can be subjected to an allylation in order to obtain the triallyl derivative. This procedure allows increasing eugenol's functionality degree. For tetrafunctional derivatives, the use of bis-eugenol is necessary [27]. All derivatives can be used as starting material to prepare green thiols by following the synthetic procedure consisting of a photochemical thiol-ene addition of thioacetic acid and further saponification [28]. They can also be used for the preparation of epoxy derivatives employing different synthetic routes [29].



3A-EU

Scheme 2. Synthetic procedure used in the preparation of the diallyl (2A-EU) and triallyl derivative (3A-EU).

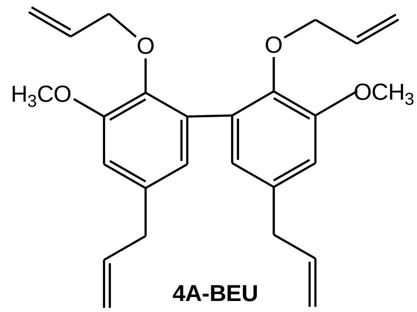
Thermosets of allylic derivatives can be prepared by photopolymerization. In recent years, thiol-ene reactions have acquired a considerable importance in the technological and scientific field of curing by UV irradiation, so to avoid the limitations of conventional photopolymerizations.

The thiol-ene process is a type of click reaction, which are characterized for being selective and stereospecific, and therefore it allows a more controllable photopolymerization process leading to a homogeneous polymer network [30].

For the preparation of thermosets by thiol-ene reaction the presence of a radical photoinitiator is sometimes required. The most used photoinitiator for this purpose is 2,2-dimethoxy-2-phenylacetophenone (DMPA) [31], but in the particular case of eugenol, its use is not advisable since the reaction does not proceed even when high proportions of this photoinitiator are added. Benzophenone has also been used, but the best choice to carry out a succesful photopolymerization of eugenol is a mixture of Irgacure 184/Irgacure 819 photoinitiators [26].

In different studies we confirmed that the efficiency of the photocuring process is affected by the stability of the allyl eugenol radicals, the nature of the thiols and stability in photochemical processes [32,33]. We do not advise the use of allyl derivatives of eugenol for photopolymerization reactions because the radicals formed during the process have an inadequate stability which leads to secondary reactions. Due to the low reactivity of the allyl eugenol derivatives during photopolymerization, the thiyl radicals formed during the process will react with each other [32].

In the photocuring of tetrallyl biseugenol, the formed allyl radical is more stable than the radical from triallyl eugenol because the chemical structure of tetrallyl contains an additional allyl ether which reduces the problems inherent to allyl radicals directly linked to the aromatic ring (Scheme 3)[33].

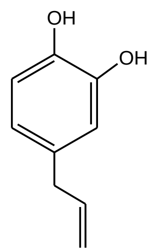


4A-BEU

Scheme 3. Chemical structure of allyl derivative from bis-eugenol (4A-BEU).

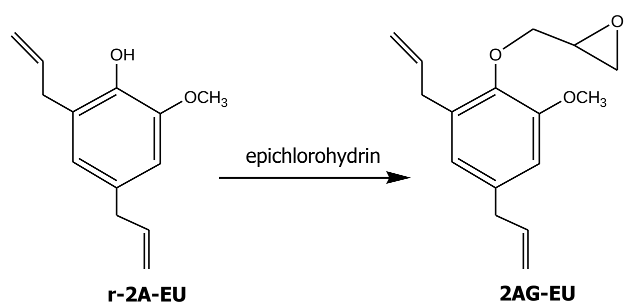
The materials prepared by thiol-ene showed poor mechanical properties in contrast to other thermosetting materials. The results obtained lead to the conclusion that the application of materials derived from allyl eugenol by curing with thiol-ene is very limited due to its low thermomechanical characteristics. The structure and functionality of the thiol crosslinker generally have a significant influence on the thermomechanical properties of the materials, but the adaptation of the properties of these materials is negatively affected by the incomplete reaction and the appearance of unwanted side reactions that occur in the eugenol monomers, therefore their application is quite restricted.

Donovan et al [34] prepared adhesives by mixing a mono allyl phenolic compound from eugenol (4-allylpyrocatechol, Scheme 4) with commercial pentaerythritol triallyl ether, and pentaerythritol tetra(3-mercaptopropionate) as the thiol. The mentioned materials were prepared by a thiol-ene reaction. The results show that high values of concentrations of the allyl derivative from eugenol into the thiol-ene system increase the adhesion to materials such as glass, aluminium, marble and steel because the versatile structure of eugenol allows the inclusion of two hydroxyl groups, which improve the adhesion and the allyl group responsible for system compatibility.



Scheme 4. Chemical structure of 4-allylpyrocatechol

Our research group prepared an allyl glycidyl compound from eugenol, which was used for the preparation of different materials by thiol-ene/thiol-epoxy dual curing. Glycidyl derivative can be prepared by reacting a diallyl phenolic compound (r2A-EU) (obtained by a Claisen rearrangement, see scheme 2) with epichlorohydrin in excess in the presence of a quaternary ammonium salt.



Scheme 5. Synthetic procedure used in the preparation of glycidyl derivative from eugenol (2AG-EU)

The different materials were prepared by curing the allyl glycidyl derivative (2AG-EU) with thiols as curing agents. This dual system was based on a two step curing in which the first reaction was activated by UV light for the curing of the allyl groups with thiol employing a photoinitiator (thiol-ene reaction), and subsequently the glycidyl group reacted with thiols in a second process initiated by thermal stimuli in the presence of amines as catalysts (thiol-epoxy reaction). As a result, the materials obtained showed better final properties than the materials obtained from the triallyl eugenol.

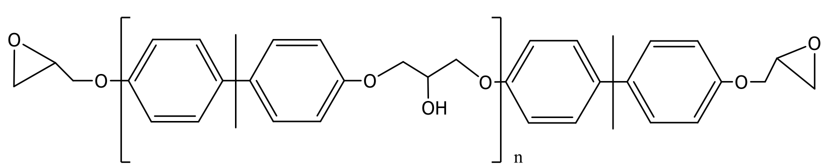
The incorporation of other functional groups into the structure of allyl derivative from eugenol allowed obtaining materials with better thermal and thermomechanical characteristics than the ones obtained by the photocuring of the triallyl eugenol compound [32].

THERMOSETS FROM EPOXY EUGENOL DERIVATIVES

Thermosetting materials prepared from epoxy resins have a great demand in the polymer global market, with applications ranging from coatings [4,5], adhesives [2], electrical and electronic components [35] to the aeronautical industry [36].

The epoxy resins are prepolymers characterized by having at least two epoxy groups capable of reacting during the polymerization process (curing process). The thermosetting materials are prepared through reaction between epoxy resins and different curing agents allowing the manufacture of materials with excellent thermomechanical, chemical and thermal properties [37]. The curing process can be started by external stimuli such as ultraviolet light or heat, depending on the type of formulation (epoxy resin/curing agent).

The commercial epoxy resin with the wider range of applications is the diglycidyl ether of bisphenol A (DGEBA) (Scheme 6). This resin is prepared by reaction of bisphenol A with epichlorohydrine in NaOH [2]. Nevertheless, the excessive exposure to this compound causes serious damage to health [38] and for this particular reason continuous research has recently focused on replacing this commercial resin with another obtained from renewable resources [39].

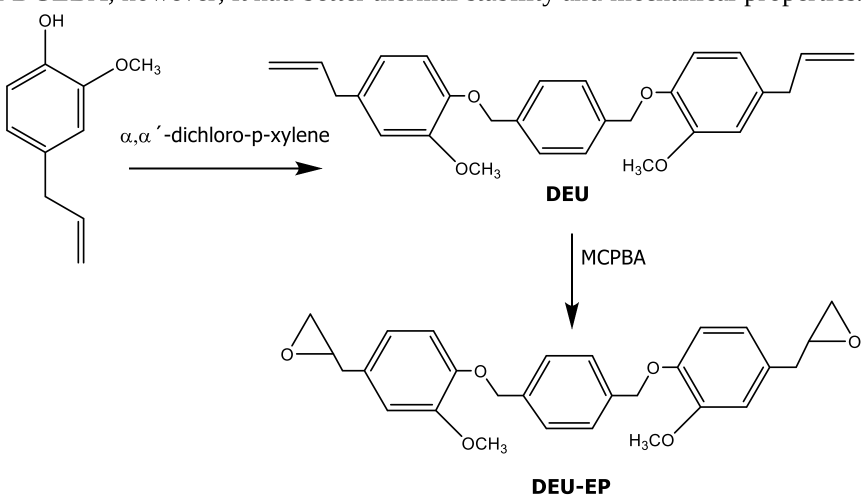


Scheme 6. Chemical structure of a commercial epoxy resin (DGEBA).

Eugenol has been used in many occasions as starting material for the preparation of epoxy monomers because it has a versatile structure with two functional groups such as hydroxyl and allyl that allows its total epoxidation, in addition to that, this monomer is also environment-friendly and safe for health.

Wan et al. synthesized an epoxy derivative of eugenol (DEU-EP) with a chemical structure similar to DGEBA [40]. The epoxy monomer was prepared in two stages as represented in Scheme 7. In a first reaction, an intermediate compound (DEU) was synthesized from the reaction between eugenol and α,α´-dichloro-p-xylene in a basic medium at room temperature for 3 hours and then at 60°C for 3 days. The allyl groups present in the obtained compound allowed to carry out the epoxidation reaction using m-chloroperbenzoic acid (MCPBA), at temperatures of 0°C during the addition of the oxidizing agent and then at room temperature for 7 days.

The epoxy thermoset from the DEU-EP monomer was obtained using 4,4'-diamino diphenyl methane as the curing agent. The results revealed that the new material had a glass transition temperature (Tg) 40°C lower than the material based on DGEBA, however, it had better thermal stability and mechanical properties.

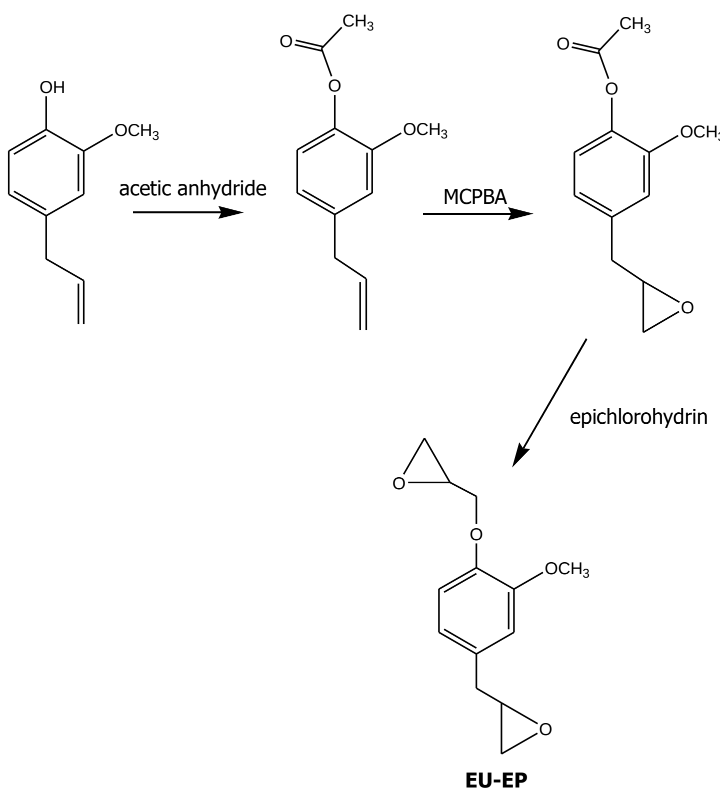


Scheme 7. Synthesis of the rigid diepoxy monomer from eugenol (DEU-EP).

The synthesis of another diepoxy derivative of eugenol was reported by Qin et al. [41]. The synthetic procedure was based on the combination of three different reactions. The first reaction is the acetylation, used to protect the hydroxyl group, for which acetic anhydride was added at 85°C for 30 min. The obtained acetyl eugenol derivative was epoxidized by reaction with MCPBA at room temperature.

This acetyl epoxy eugenol was reacted with an excess of epichlorohydrin in a basic medium to carry out the deacetylation of the phenolic group and its subsequent glycidation at 85°C for 4h (Scheme 8).

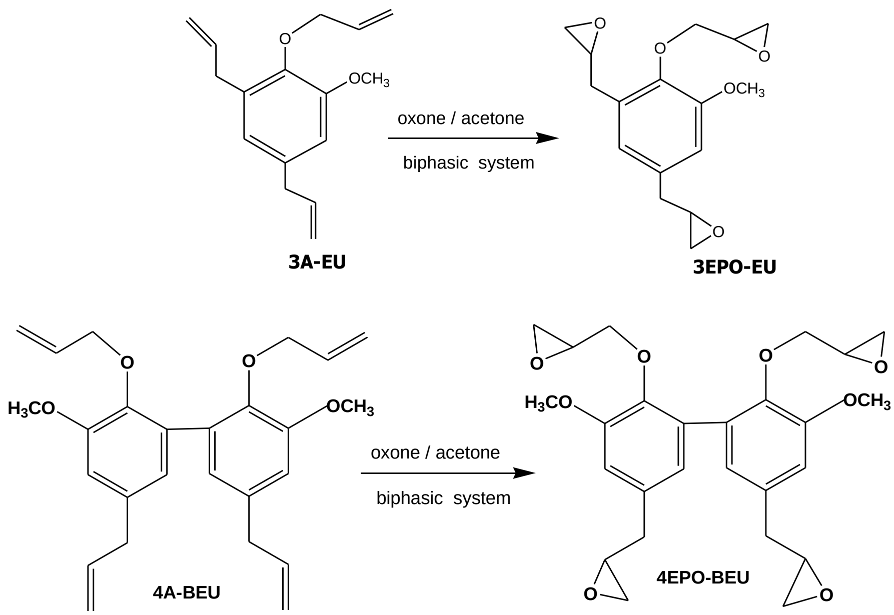
Different thermosetting materials were prepared from the EU-EP, using two different curing agents such as methyl tetrahydrophthalic anhydride (MTHPA) or with anhydride derived from rosine (MPA) in the presence of an imidazole as the catalyst. The materials obtained using MPA showed thermal and thermomechanical properties similar to commercial petrol derived epoxy thermosets.



Scheme 8. The synthetic procedure for the preparation of diepoxy monomer from eugenol (EU-EP).

In a previous study, our group synthetized two new epoxy monomers tri (3EPO-EU) [28] and tetra functional (4EPO-BEU) [33[33]] derived from eugenol and bis-eugenol respectively. For the synthesis of epoxy monomers, oxone was used as an oxidizing agent instead of MCPBA, following the concept of green chemistry since oxone offers many more advantages, is cheap, involves easy purification processes and, most importantly, does not require the use of chlorinated solvents.

The use of oxone (potassium peroxomonosulphate) as an oxidizing agent requires the presence of acetone, since it allows the formation of a dioxirane, the one responsible for carrying out the epoxidation reaction of the allylic compounds (Scheme 9) [42]. The synthesis of the epoxy compounds was carried out by reacting the allylic derivatives with the oxidizing agent in a biphasic water/ethyl acetate system in a basic medium, using a phase transfer catalyst. The reaction remained under vigorous stirring at room temperature for 3-5 days.



Scheme 9. Synthetic procedure to access triepoxy monomer (3EPO-EU) from eugenol and the tetraepoxy monomer (4EPO-BEU) from bis-eugenol.

The materials were prepared employing thiols of different functionalities as curing agents with different basic catalysts because the use of thiols in the curing of epoxy monomers is very attractive from the industrial point of view for the preparation of adhesives, high performance coatings and composite materials [43].

One of the great advantages of thiol-epoxy click reactions in the curing of epoxy resins is that the cross-linking forms a homogeneous network, compared to a homopolymerization process [44].

In the thiol-epoxy curing process, the reactivity of the epoxy/thiol/catalyst formulation will depend on the chemical nature of the starting compounds and their degree of functionality. The thermosetting materials were prepared from formulations with stoichiometric amounts of epoxy/SH groups (1:1). Two of the thiols used came from natural sources such as hexathiol from squalene (6SH-SQ) and trithiol from eugenol (3SH-EU), while pentaeritol tetrakis thiol (3-mercaptopropionate) is commercially available (PETMP). The curing of triepoxy monomer was catalysed by 4-(N,N-dimethylamino)pyridine (DMAP). In some cases it was necessary to use a diluting agent to give more flexibility to the structure and thus avoid topological problems [29].

The triepoxy monomer of eugenol (3EPO-EU) has a simple structure that allows a faster and cleaner curing process than in the case of the tetra-epoxy derivative of bis-eugenol. When thiols with a high functionality were used to cure 4EPO-BEU, such as 6SH-SQ, topological problems were generated during the curing process, decreasing the reactivity of the thiol. Although the thiol-epoxy reactions are highly selective, the topological constrains of the thiol in the attack to the epoxy groups makes them available to participate in the homopolymerization reaction catalyzed by 1-MI, which is employed in the thiol-epoxy process [33].

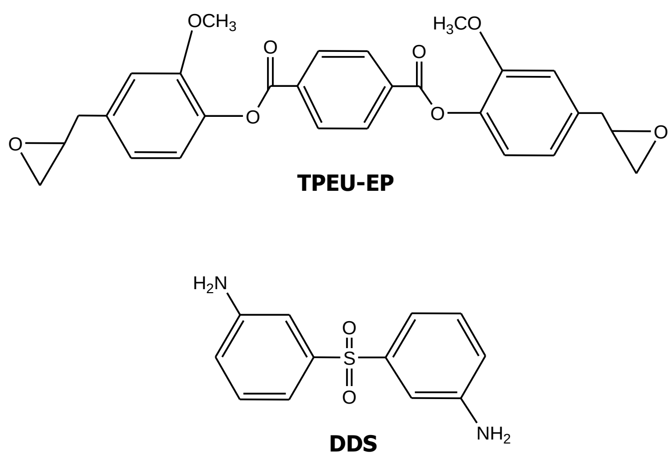
The materials prepared from epoxy derivatives of eugenol present excellent thermal stability due to the presence of aromatic rings in their structure. In general, all materials showed good characteristics. The increase in the functionality of the epoxy monomer allows to obtain materials with better thermal, thermomechanical and mechanical properties, as well as a greater hardness.

When comparing the final properties of the thermoset prepared from the tetra-epoxy derivative of bis-eugenol with that obtained from DGEBA, cured by thiol-epoxy processes [45] we can confirm that the bis-eugenol derivative is a good alternative to replace the commercial resin derived from oil. Generally, epoxy monomers derived from eugenol can be used to obtain environmentally friendly, safe for health thermosets with good final properties, and in addition, the use of thiols from a natural origin with different chemical structures allows to obtain a wide diversity of resulting characteristics increasing the range of the potential applications.

The epoxy eugenol monomers, also have been widely used as a starting material for the preparation of flame-resistant materials. This stated property usually boosts with the increase of aromatic rings and/or the incorporation of certain chemical elements such as phosphorus, nitrogen or sulphur.

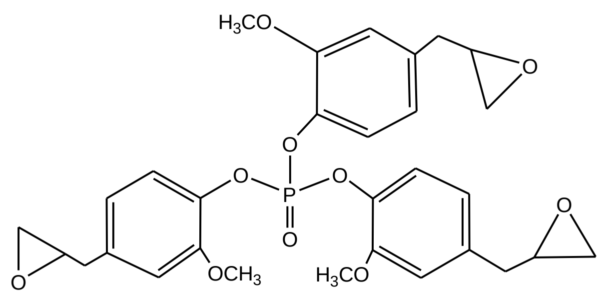
Wan et al [46] prepared a new epoxide compound from eugenol which like the previous cases was obtained from the epoxidation of double bonds. The synthetic procedure consists of two steps. In the first step, an intermediate diene was prepared from the reaction of eugenol with terephthaloyl chloride in a basic medium at temperatures under 10°C for two hours, then at room temperature for an additional 4 hours. The epoxide derivative TPEU-EP was prepared from the reaction of the intermediate compound with MCPBA at 0°C, then left to react for 4 days at room temperature.

For the preparation of thermosets from TPEU-EP, 3,3´-diaminodiphenylsulfone (DDS) was used as a curing agent in stoichiometric proportions (Scheme 10). The thermosets showed a high thermal resistance, better mechanical properties and better flame retardancy compared to the thermoset prepared from the DGEBA. It can be used as a substitute for commercial resin in applications such as powder coatings.



Scheme 10. Chemical structures of the epoxide derivative TPEU-EP and curing agent DDS.

In another study, an epoxy monomer derived from eugenol was synthesized by an intermediate allyl compound prepared from the reaction of eugenol with phosphorus oxychloride in the presence of triethylamine (Scheme 11). The reaction was maintained at 0°C for 30 minutes and then at room temperature for 16 hours. The triepoxide synthesis was performed from the epoxidation of the intermediate compound with MCPBA at 0°C for 3 minutes and then at room temperature for 24 hours.



TEEP

Scheme 11. Chemical structure of the epoxide derivative TEEP.

The epoxy compound was cured with two different amines 2,2'-(ethane-1,2-diylbis (oxy)) bis (ethan-1-amine) known as JEFFAMINE® EDR-148 and m-xylylenediamine (MXDA). The materials obtained showed final properties similar to those prepared from DGEBA, however they showed high char yield after degradation, which suggests that they could be used as flame resistant materials [47].

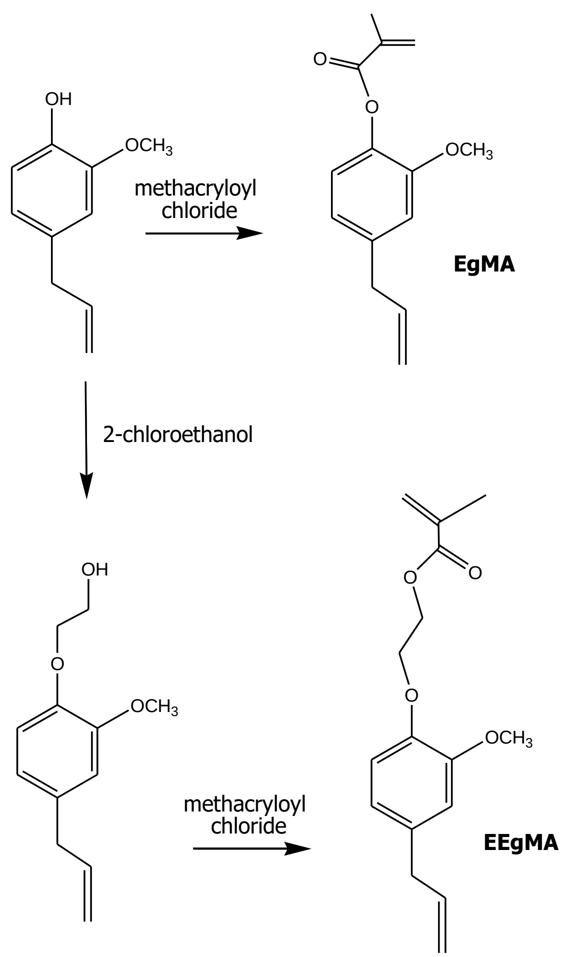
Other applications that have been reported for these materials could consist of them being used as intelligent coatings capable of self-healing [48], having shape memory [49] as well as being used as diluting agents in some polymeric systems [50].

THERMOSETS FROM ACRYLIC EUGENOL DERIVATIVES

The thermosets from commercial acrylates are extensively used for the preparation of dental cements [51]. Acrylic monomers derived from natural resources have also been reported as good diluents for vinyl ester resins, replacing styrene which has been reported as a carcinogen. The use of diluents in these systems allows the extension of the polymer chain and the decrease in viscosity and thus avoid problems in the manufacture of parts by molding liquids [52].

The structural versatility of eugenol allows the preparation of acrylates by different synthetic procedures. Rojo et al [53] reported two new acrylic derivatives from eugenol for dental applications (Scheme 12). On the one hand the synthesis of eugenyl methacrylate (EgMA) was carried out using stoichiometric quantities of eugenol and triethylamine in the presence of an excess of methacryloyl chloride.

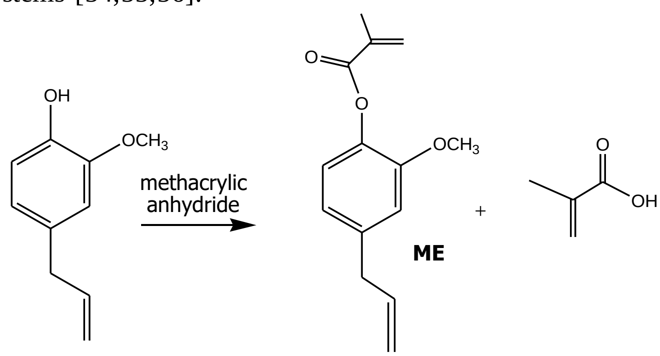
The reaction was maintained under a nitrogen atmosphere at room temperature for 48 h. On the other hand, the synthesis of ethoxyeugenyl methacrylate (EEgMA) was performed in two steps. The first step an intermediate compound was prepared by reacting eugenol with 2-chloroethanol in presence of KOH solution containing 0.5% KI as cocatalyst. The reaction was maintained at reflux temperature under inert atmosphere for 24 hours. After that, the second step consisted of reacting the intermediate compound with an excess of methacryloyl chloride following the same conditions used in the synthesis of the EgMA compound.



Scheme 12. Synthesis of the different methacrylates derivatives from eugenol.

Thermosetting materials were created by homopolymerization of the eugenol (metha)acrylates and also by copolymerization with ethyl methacrylate. These polymers showed better thermal properties and better antibacterial activity compared to the commercial ethyl methacrylate polymer.

Another synthetic procedure for the preparation of acrylic monomer derived from eugenol (ME) describes the reaction between eugenol and methacrylic anhydride in the presence of DMAP as represented in Scheme 13. The reaction is maintained under an inert atmosphere at 45° C for 24 hours. This synthetic route has been reported by several authors who used acrylic monomers as a diluent agent in different systems [54,55,56].



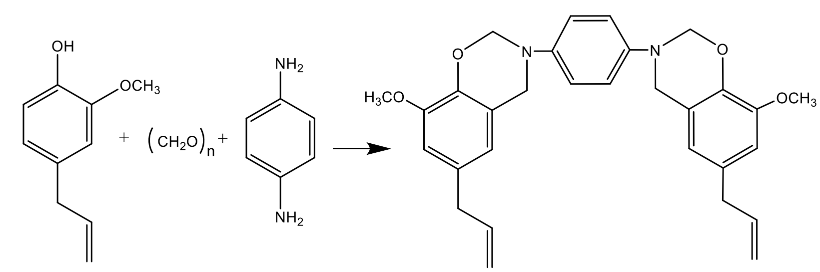
Scheme 13. Synthetic procedure for the preparation of methacrylate from eugenol.

The acrylic monomers derived from eugenol are suitable for totally replacing commercial compounds used as diluents for vinyl ester resins, without compromising their final properties [54,55]. They have also been employed as reactive diluents of commercial epoxidized soybean oil resin that allow to obtain thermosetting materials from renewable resources with better properties than when styrene is used as diluent [56].

THERMOSETS FROM BENZOXAZINE EUGENOL DERIVATIVES

Benzoxazine is a type of phenolic resin used in the preparation of thermosets with excellent thermal and electrical properties and therefore they are very attractive in industrial applications. The polymerization of these monomers is produced by cationic ring-opening of the oxazine with or without added initiator by thermal treatments [57].

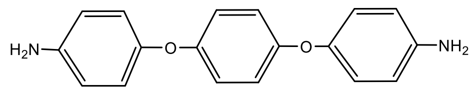
The synthesis of benzoxazines derived from eugenol is very easy to perform. The benzoxazines are prepared by a Mannich condensation of a phenolic compound, in this case eugenol, paraformaldehyde and diamine (Scheme 14) [58].



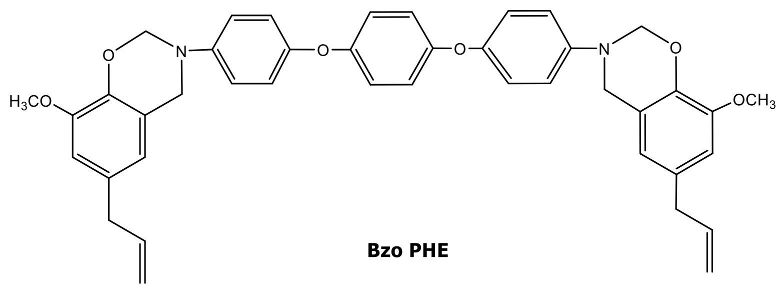
Scheme 14. Synthesis of the bisbenzoxazine monomer from eugenol.

Polybenzoxazines present several drawbacks in processability, brittleness and elevated curing temperatures. To solve these problems, the basic structure of benzoxazine can be modified using diamines with more flexible structures [59]. In addition, the structure of phenol can be modified using a mixture of phenolic compounds [60] or by preparing biseugenol derivatives containing siloxane moieties [61]. The other options that have also been reported include the use of additives such as inorganic-organic hybrid polyhedral oligomeric silsesquioxane (POSS) [62] or carbon nanotubes (CNTs) [63] for the preparation of nanocomposites. The copolymerization of benzoxazine from eugenol with monomers such as bis-maleimide (BMI) has also been reported to improve the final properties of the thermoset [63, 64].

The final properties of polybenzoxazines can also be improved by the preparation of composites that combine bismaleimide for the stabilization of benzoxazine with nanoparticles such as CNTs. Thirukumaran et al. [63] prepared composites from a new benzoxazine eugenol derivative. The new monomer was synthetized by the reaction between eugenol, 1,4-[bis (4-aminophenoxy) benzene] (BAPB, previously synthesized) and paraformaldehyde (Scheme 15).



BAPB



Bzo PHE

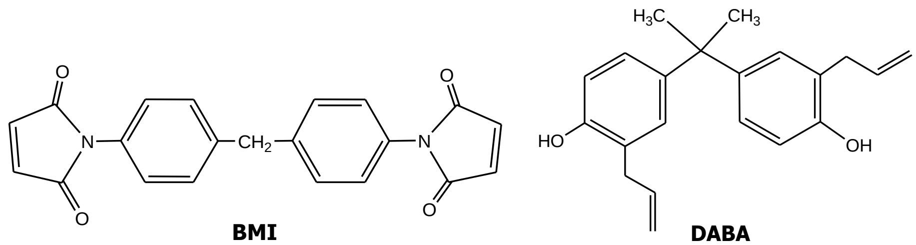
Scheme 15. Chemical structure of the aromatic amine BAPB and benzoxazine monomer Bzo PHE.

The incorporation of the CNTs previously modified with ethylene amine into polymeric matrix improves the electrical, thermal and mechanical properties compared to the polybenzoxazines or the polybenzoxazine/BMI copolymer.

THERMOSETS FROM BISMALEIMIDE EUGENOL DERIVATIVES

Thermosets from bismaleimide have been extensively used for the preparation of composite materials for aeronautics and microelectronic industry. These resins have excellent oxidative, mechanical, electrical and thermal properties. However, these pure resins generate fragile materials with high curing temperatures [65]. For all these reasons it is necessary to modify the chemical structure [66] or incorporate the monomers with functional groups such as epoxy [67], aromatic amine [68], allyl phenols [6971], thiols [72], benzoxazines [64] or cyanates [73,74] for the copolymerization, which allows to improve the final properties of the thermosetting materials. The mechanical and thermal properties of bismaleimide have been improved by the preparation of composites with graphene oxide [75], glass fiber [76], or boron nitride [77].

For industrial applications the bismaleimide is copolymerized with 2,2-diallylbisphenol A (DABA) [70,71] which is a monomer derived from oil (Scheme 16). Nevertheless, it's necessary to replace this commercial monomer with other coming renewable resources. Provided this situation, different allyl compounds from eugenol have been employed for the copolymerization of bismaleimide resin.



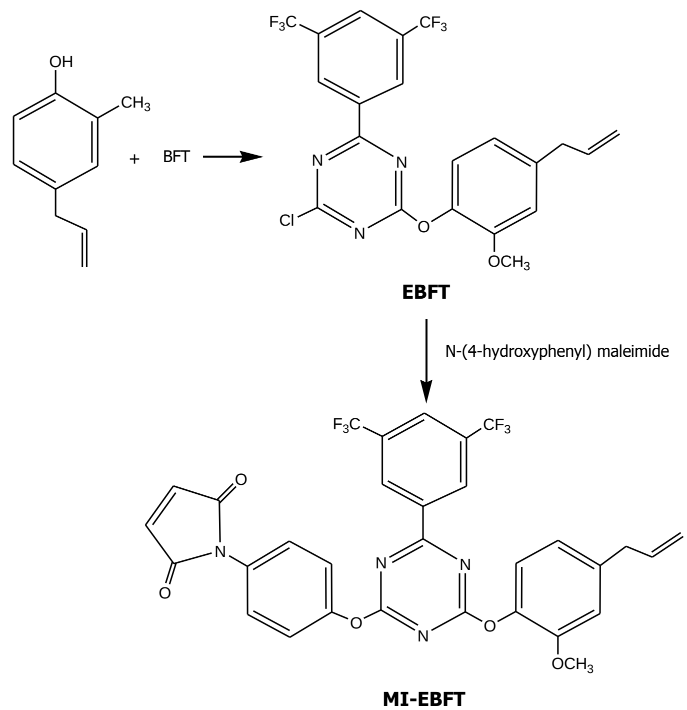
Scheme 16. Chemical structures of 4,4-bismaleimidodiphenylmethane (BMI) and 2,2-diallylbisphenol A (DABA).

Shibata et al. [78] used bis-eugenol and eugenol novolacs (synthesized from the condensation reaction between eugenol and formaldehyde) as starting materials for the copolymerization with bismaleimide resin. In order to achieve that goal, two prepolymer with allyl/maleimide ratios 1:1, 1:2 and 1:3 were prepared and then cured at 250°C for 5 h. The materials obtained showed better final properties than copolymer DABA/BMI.

In a similar study, Neda et al [27] reported the use of a diallyl derivative of eugenol and a tetraallyl derivative of bis-eugenol to prepare different prepolymers to be crosslinked by maleimides. They observed that with the increase of the allyl groups a higher crosslinking is produced and therefore thermosets with improved properties were obtained.

Fang et al. [66] synthesized a new derivative of eugenol having maleimide and allyl functionalities, with trifluoromethyl groups and a triazine ring (Scheme 17). This derivative was prepared in a two-step synthetic procedure. In the first step an intermediate allyl compound (EBFT) was prepared from the reaction of eugenol with BFT (2- (3,5-bis (trifluoromethyl) phenyl) - 4,6-dichloro-1,3,5-triazine), in the presence of N,N-diisopropylethylamine. In the second step the maleimide function (MI-EBFT) was introduced by reacting the compound EBFT with N-(4-hydroxyphenyl) maleimide in a basic medium for 3 h. at room temperature.

The thermosetting materials were obtained by crosslinking through an ene-reaction followed by a Diels-Alder process at 190 ºC. The materials have values of Tg 20°C lower than the commercial bismaleimide and they present better processability before curing. It also shows a lower dielectric constant and a low water-uptake. Thanks to these final characteristics this new monomer is a good candidate to replace commercial bismaleimides in microelectronic applications.

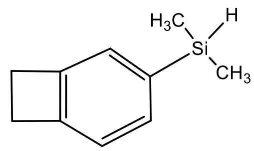


Scheme 17. Synthesis of the allyl-maleimide monomer from eugenol.

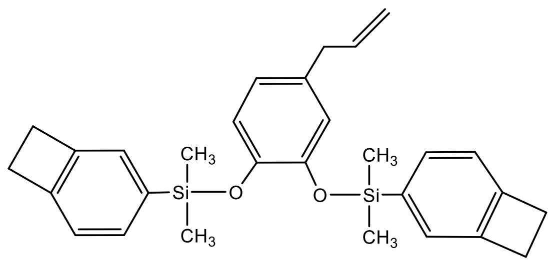
THERMOSETS FROM OTHER EUGENOL DERIVATIVES

Less common eugenol derivatives such as siloxanes [79] or 1,3-dioxolan-4-ones (DOXs) [80] have been used for the preparation of thermosetting materials with different applications.

Chen et al [7979] prepared eco friendly polysiloxanes from eugenol (BCB-Si-E). The synthesis of the siloxane monomer was carried out by the reaction of eugenol and benzocyclobutene organosiloxane (BCB-Si-H) in the presence of small amounts of tris(pentafluorophenyl) borane [B $(C_6F_5)_3$] as a catalyst (Scheme 18).



BCB-SI-H

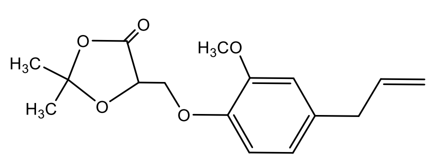


BCB-SI-E

Scheme 18. Chemical structures of BCB-SI-H and siloxane monomer eugenol derivative (BCB-SI-E).

The materials obtained showed excellent thermal properties, a low dielectric constant and a low water-uptake. So they could be used in the micro-industry being good candidates to replace oil-derived polysiloxanes.

Thermosetting materials prepared by curing 1,3-dioxolan-4-ones derivative from eugenol (EuDOX) were reported by Gazzotti et al. [80] (Scheme 19). The monomer was synthesized in two stages. In the first one, an intermediate compound was prepared from the reaction of eugenol with 3-chloro-2-hydroxypropanoic acid in a basic medium at reflux temperature for 2 h, after that, acidification was necessary. In the second step of the synthesis, the intermediate compound reacted with sulfuric acid and the reaction was left at room temperature for 2 hours, then the mixture was treated with a basic solution to increase the pH up to 8.



EuDOX

Scheme 19. Chemical structure of EuDOX monomer.

The monomer was cured in one-pot through the simultaneous polymerization of dioxolane moieties and reaction of eugenol double bonds leading to a crosslinked structure. The thermoset obtained had outstanding mechanical properties and a good thermal stability. Hydrolisis in a microwave-oven in alkaline water or methanol led to the complete degradation of the thermoset producing low molecular weight products. In addition to that, it was observed that these materials presented shape memory and self-healing properties.

In summary, we can state that eugenol is an excellent alternative to prepare thermosets with different properties and applications thanks to its versatile chemical structure. These different eugenol's derivatives can replace a vast variety of commercial monomers, allowing to obtain materials, which can be considered as environment-friendly.

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