Bio-sourced alternatives to diglycidyl ether of bisphenol A in epoxy–amine thermosets

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Biosourced alternatives to diglycidylether of bisphenol A in epoxy-amine thermosets: a focus on materials properties and endocrine activity

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Abstract

Since 1940s, bisphenol A (BPA) has been used in plastic industry reaching production of 10 million tons in 2022. More than 30 % of the produced BPA is used in the production of epoxy resins. Decades of research has now provided enough evidence that (BPA) has endocrine disrupting activity. Hence, it is an urgent matter to replace the use of BPA in production of epoxy resins. In the past years, considerable effort have been put into finding alternatives to the toxic BPA. However, the diglycidylether bisphenol A (DGEBA) does not only exhibits high polymerization reactivity, but the presence of aromatic rings confers interesting thermos-mechanical resistance to epoxy networks therefrom. Hence, this properties are also expected from potential alternatives to BPA. In this review, first the elements leading to toxicity of BPA is explained and then a thorough account of possible bio-sourced aromatic alternatives to BPA are gathered. The reported synthetic routes to each of these alternatives and their toxicity are described. Also, their use in synthesis of epoxy resins and how the new alternatives influence the mechanical properties are discussed. This is a concise summary of the structure-property and structure-toxicity relationship for possible bio-sourced substitutes of BPA in synthesis of epoxy resins.

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40 ## Introduction
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42 Epoxy thermosetting resins are an important class of plastics that are used in a wide range of fields such as paints,
43 coatings, composites, electronics, adhesives, construction, wind turbines, etc. The global epoxy resin market size is
44 estimated to worth 11.26 billion dollars by 2026, and it was valued at 7.6 billion dollars in 2019.[1] The main
45 application segments of epoxies are paints and coatings, for over 40 % of the total market. The most used epoxy
46 monomer is diglycidylether of bisphenol A (DGEBA), followed by diglycidylether of bisphenol F (DGEBF). The
47 majority of epoxy resins are derived from fossil resources.
48 The shift toward the use of bioresources for polymer synthesis could be a major move in the reduction of fossil
49 carbon dissemination into the environment. For example, in the field of packaging, more than 80 billion kg are
50 annually produced and originate from fossil resources.[2] A recent analysis of patent literature shows that there is a
51 growing interest in sustainability in industry. More specifically, the use of bioresources for the production of
52 chemicals, process optimisation that minimize waste or emissions are some of the main source of innovations.[3] In
53 addition with tackling the global challenges for a more sustainable use and production of plastics, the use of
54 bioresources is also a source of innovation, thanks to the diversity of monomer design from naturally available
55 building blocks.[4]
56 Polymer scientists have long been working on biobased epoxy monomers for synthesis of epoxy networks. The use
57 of biobased starting materials is an effective way to reduce the carbon footprint, and it allows to valorise organic
58 wastes, as well as investigating new structures for thermosetting epoxies. The use of biobased materials in itself
59 does not specifically prevent the use of toxic or hazardous compounds, but following the green chemistry principles
60 usually includes the seek for low impacts either on the environment than on health. Epoxy monomers can be
61 obtained from the oxidation of unsaturated compounds (epoxidation of carbon-carbon double bonds), or via the
62 addition of a glycidyl moiety, for example using epichlorohydrin. When converting a double bond to an epoxide
63 moiety, the reaction does not imply the introduction of carbon into the monomer, it is usually carbon neutral
64 (considering only the atoms introduced, and ignoring any use of solvent, catalyst or waste generation). However, the
65 introduction of a glycidyl moiety will involve the addition of carbon into the monomer. But this step does not
66 necessarily involve the introduction of fossil carbon, since commercially available biobased epichlorohydrin can be
67 utilized to target 100 % biobased epoxy monomers. For example, the synthesis of DGEBA using petrosourced BPA
68 and biobased epichlorohydrin will lead to nearly 30 % of carbon originating from renewable resources. Several
69 manufacturers are already selling epoxy formulations that contain a high biobased carbon percentage.[5] Academic
70 scientists however have conceived a wider range of epoxy monomers obtained from biobased compounds, and
71 several reviews have already focused on these monomers. For instance, in 2014, Auvergne *et al.* published an
72 important review on biobased thermosetting epoxy resins, which covered the whole available literature on biobased
73 epoxy monomers.[6] Since then, other groups also worked on gathering new data from literature, either for a general
74 purpose[7–11], or for specific applications such as aerospace industry.[12] With a focus on specific starting materials,
75 such as furanics or aromatics, other reviews have gathered valuable information on reported structures. Ng *et al.*
76 focused their work on aromatic compounds[13], Wan *et al.* worked on phenols[14], Caillol *et al.* on eugenol[15], while a
77 very recent paper by Eid *et al.* highlights the progress made in furanic monomers.[16,17] The use of specific biomass
78 types for synthesis of monomers is also investigated, and especially aromatic-containing biomass such as lignin is an
79 important area of research.[18–21] Since BPA is not only used as an epoxy precursor, some work of interest on the
80 generation of potential for substitutes for any application can feed the research on thermosetting epoxy resins, for
81 instance, Liguori *et al.* provided a very complete overview of potential substitutes, focusing on their synthesis.[22]
82 Synthetic tools to obtain functional monomers from biobased furans and phenols have also been reviewed recently
83 by Decostanzi *et al..*[23] Finally, it is worth mentioning that in the case of epoxy-amine networks, it is also important
84 to consider the origin of the amine, and especially, the availability of biobased amine is still low.[24,25]
85 In this review, available structures that could replace bisphenol A, or more specifically, DGEBA in the synthesis of
86 epoxy-amine resins are summarized. For this purpose, the initial focus would be on potentially biosourced
87 compounds, and then on phenolic or furanic derivatives, that would be the most relevant structures to replace
88 DGEBA in the synthesis of thermosets. For each compound, the thermoset properties using amine hardeners are
89 discussed and compared with the same network obtained using DGEBA. Further, the available data on their
90 endocrine disruption are compared with the know hazards of BPA.
91 BPA is used as a monomer in the synthesis of polycarbonate thermoplastics and as monomer precursor in epoxy
92 resins.[26] Thus, environmental BPA contamination mainly comes from leaching from the polymers under specific
93 conditions, depending on the stability of the material. For example, the release of BPA from polycarbonates occurs
94 due to hydrolysis under acidic conditions and upon heating.[27] Similarly, BPA is released from epoxy resins when

95 heated above 100 °C (often during sterilization step).[28,29,30] BPA contamination has also been detected from dental
96 sealants,[31] in house dust and air,[32] as well as in textile.[33]

97 Endocrine activity assays
98
99 The toxicity of BPA is due to its similar activity to 17β-oestradiol hormone, a human oestrogen α receptor.[34] This
100 activity is due to the chemical structure of BPA mimicking 17β-oestradiol (Figure 1). Several factors control this
101 similar activity. First is the presence of the two hydroxyl groups ensuring the efficient interaction between the
102 receptor and the potential agonist. The second factor is the size of the receptor and the compound. In order to have a
103 binding inside the receptor's binding site, the compound has to fit inside the receptor pocket. The size of the
104 receptor pocket is 440 Å, while the size of 17β-oestradiol is 245 Å, allowing an adequate fitting. Apart from these
105 factors the distance between the hydroxyl groups as well as the hydrophobic nature of the middle part of the
106 molecule (for example, the two methyl units in BPA) also influence the interactions between the compound and the
107 receptor (Figure 2).[35,36]
108
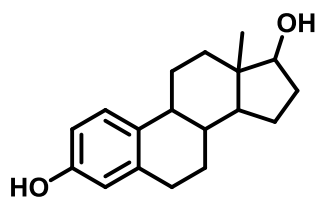
109

110   Figure 1 - Chemical structure of 17β-oestradiol
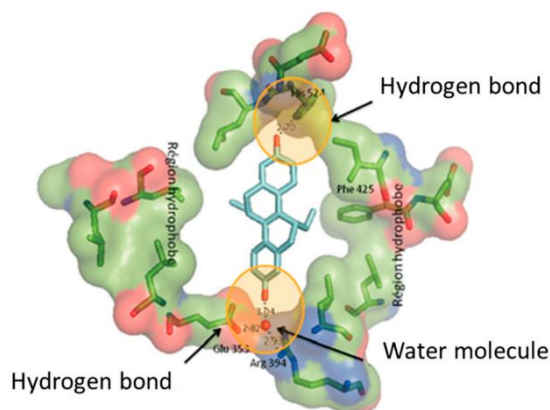
111

112   Figure 2 - X-ray structure of the pocket of ERα, reproduced from Ng et al.[13]

113

114 evaluation of endocrine disruption is not only due to the oestrogen receptor α,[34] but also to other biochemical
115 mechanisms that have influence on the oestrogen binding.[37] The entire steroid metabolism have an effect on the
116 oestrogen binding, since oestradiol belongs to the class of steroids. Hence, any effect on the steroid metabolism
117 could have an effect on the binding in ERα.[38]
118
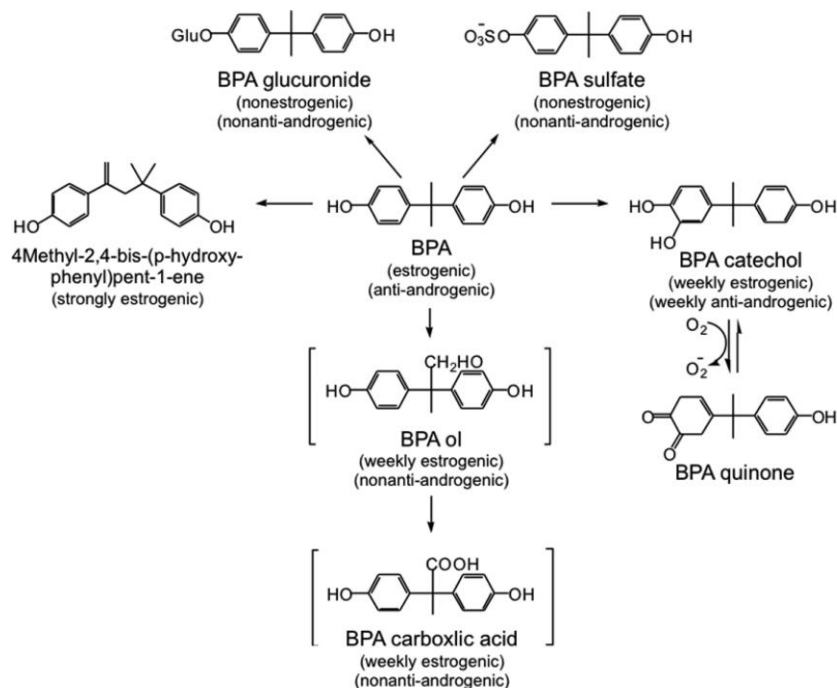
Figure 3 - Postulated metabolitic pathway of Bisphenol A, reproduced from Chen et al.[39]

Usually, regarding *in vitro* or *in vivo* bioassays, the compound activity is compared with the activity of the natural hormone, in order to determine a coefficient of activity. In addition, as a control, the activity of the tested compound is also compared to the vehicle, which is the vector used to drive the compound to the receptor. For instance, the vehicle is the solvent in which the compound is solubilised for *in vitro* testing, or the type of food in which the compound is included for *in vivo* experiments.

152 Abbreviations

153

Abbreviation	Full term
17βE2 / E2	Human oestradiol
AR	Androgen receptor
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetric analysis
E'	Young's modulus
EA	Oestrogen affinity
EC_{50}	Lower concentration efficacy
ED	Endocrine Disruptor
EEW	Epoxy equivalent weight
EFSA	European Food and Safety Authority
Erα / hERα	Human oestrogen receptor alpha
HRC	Heat release capacity
LOI	Limiting oxygen index
_m_CPBA	_meta_-chloroperbenzoic acid
PXR	Steroid receptor
REE	Relative oestrogen efficacy
% RME2	Normalized EA
SVHC	Substance of very high concern
T_{α}	Alpha transition temperature
$T_{d5\%}$	Temperature of 5 % degradation
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TMA	Thermomechanical analysis
TRβ	Thyroid receptor beta

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156   Amine hardener structures
157

Name(s)	Abbreviation(s)	Structure
4,4'-methylenedianiline or 4,4'-diaminodiphenylmethane	DDM (or MDA)	
Amicure	PACM	
isophorone diamine	IPDA	
4,4'-diaminodiphenylsulfone	44DDS	
3,3'-diaminodiphenylsuflone	33DDS	
dicyandiamide	DICY	
triethylenetetramine	TETA	
diethylenetriamine	DETA	
decanediamine	DA10	
difurfurylamine A	DIFFA	
Jeffamine D400 or D230	D400/D230	MW=230 or 400
hexamethylenediamine	HMDA	
Polyetheramine EDR-148	EDR-148	
Polyetheramine EDR-192	EDR-192	
diethyltoluenediamine	Epikure W	
methylenedifurfuryldiamine	DFDA	
ethylidenedifurfuryldiamine	DFDA-Me	

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159   Phenols
160
161   I.   Vanillin


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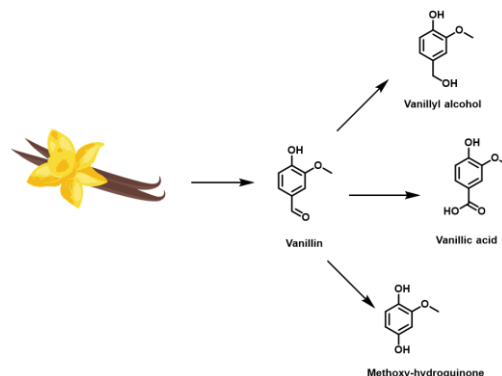
Figure 4 - Chemical structure of vanillin and some simple vanillin derivatives used as epoxy monomer precursors

Vanillin (Figure 4) is a natural monophenol, bearing a methoxy moiety and an aldehyde. It is one of the main components of natural vanilla aroma, and it has been produced on a large scale from fossil resources mainly for food industry. Vanillin is also synthesized from bioresources on an industrial scale.[40] As a food additive, its toxicological profile is thus positive, and it has led researcher to study different chemical modification of the compound for the synthesis of epoxy monomers.[41] Vanillin derivatives has been widely used in the literature for the synthesis of epoxy monomers.

Vanillin in itself does not seem to have an impact on the endocrine system. A recent article by Ji *et al.* has evaluated the activity of vanillin on different receptors, such as ERα, androgen receptor, thyroid receptor and retinoic X receptor β.[42] Vanillin did not show any activity against these receptors, for all the concentrations tested.

    1.   Vanillyl alcohol
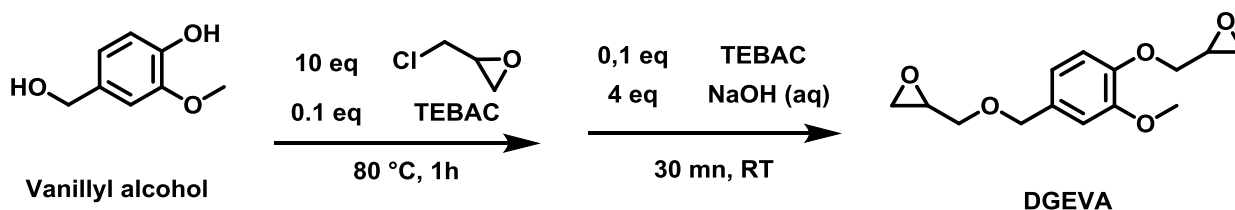
Figure 5 – Synthesis procedure for DGEVA by Fache *et al.*[41]

Vanillyl alcohol (VA) is a vanillin derivative that can be obtained from the reduction of the aldehyde. VA is commercially available since it is used as a flavouring.[43] This aromatic compound contains a methoxy moiety, a phenolic hydroxyl and a primary alcohol, the two latter being the reactive sites for glycidylation. Diglycidylether of vanillyl alcohol (DGEVA, Figure 5) has been synthesized first by Fache *et al.* as part of a series of monomers obtained from vanillin.[41] Since then, several groups used DGEVA in order to elaborate thermosets, with different hardeners, and some thermomechanical properties are reported in

Table **1**. Fache *et al.* studied the curing behaviour of DGEVA with IPDA, and they obtained lower T_g (97 °C) than with DGEBA (166 °C).[44] This can be explained by the fact that there is less aromatics in DGEVA compared to DGEBA, and that DGEVA contains a methylene, that can induce more mobility of the chains. The calculated crosslink density is also lower for DGEVA (0.7 mmol·m^{-3} vs 1.4 mmol·m^{-3} for DGEBA). Degradation under nitrogen is a one step process for both DGEBA and DGEVA-IPDA thermosets, and the DTG peak corresponding to the degradation happens for both materials around 360 °C, but DGEVA produces more char yield (19 % vs 10 % for DGEBA).

195   Table 1 - Thermomechanical properties of DGEVA cured with different amines, from the literature

Amine Hardener	T_g or T_α (°C)		E'_{glassy} (GPa)		$T_{d5\%}$ (°C)		Char yield (%)	
	DGEBA	DGEVA	DGEBA	DGEVA	DGEBA	DGEVA	DGEBA	DGEVA
IPDA	166	97	-	-	-	-	10	19
PACM	190	100	-	-	-	-	2	7
DICY	146	93	-	-	342	289	13	23
DDM	154	111 / 124	2.3	2.8	-	-	-	-
TETA	142	71 & 109*	4	3.7	-	-	-	16
DETA	100	90	2	3.5	305	247	8	7
44DDS	238	108	-	-	-	-	14	7
DFDA	109	81	2.4	3.7	330	304	23	46

196   * two relaxations are observed by DMA

197   Hernandez *et al.* used a dicyclohexyl diamine (Amicure), with DGEVA and other vanillin-based epoxides.[45] The
198   thermosets were compared with DGEBA and DGEBF. DGEVA thermoset displays a T_g around 100 °C, compared to
199   the DGEBA system (190 °C). The glass transition temperature of DGEVA cured with IPDA and PACM is thus very
200   close, which is not surprising considering the two amines are based on cyclohexyl moieties, however, the storage
201   moduli are higher for DGEVA and DGEBA cured with PACM than with IPDA. Finally, the degradation of
202   DGEVA-PACM occurs at a lower temperature than with DGEBA, under nitrogen. The char yield is higher for
203   DGEVA thermoset (7 %) than for DGEBA (2 %), following the same trend than DGEVA-IPDA.
204   Ng *et al.* used DGEVA with dicyandiamide (DICY) for the elaboration of coatings.[46] They used oligo-DGEBA and
205   pure DGEBA for comparison. The cure temperature of the neat mixture of amine and epoxide is 220 °C for both
206   DGEBA types and 210 °C for DGEVA, which are very close. Glass transition temperatures determined for DGEBA
207   material are 146 °C and 93 °C for DGEVA, which is following the same trend than discussed before. The $T_{d5\%}$ under
208   nitrogen is 342 °C for DGEBA, and 289 °C for DGEVA, which is slightly lower. However, the char yield is higher
209   for DGEVA (23 %) than for DGEBA (13 %). The adhesion properties of the corresponding coatings performed well
210   with or without adhesion promoter, with an ISO 2409 classification of 0 or 1 on a 5-scale (the lower the value, the
211   higher is the adhesion). Reinforcement of a glass plate was also evaluated by measuring the break strength, and it is
212   higher for DGEVA formulation than for pure DGEBA, but very similar to oligomerized DGEBA.
213   Tian *et al.* used DGEVA with the addition of an eugenol-based diepoxide for the elaboration of shape-memory
214   polymers.[47] They used DDM as the curing agent. They obtained T_gs between 111 and 124 °C (respectively from
215   DSC and DMA as *tan δ* peak), as compared to DGEBA/DDM system that reaches 154 °C (from *tan δ* in the work of
216   Wan *et al.*[48]). The storage modulus at 25-30 °C is 2.8 GPa for DGEVA thermoset, that is higher than for DGEBA-
217   DDM material (2.3 GPa). In overall, formulation with the eugenol-based monomers have shown effective shape
218   memory properties, especially using DGEVA as a hard segment, for the induction of phase separation, as evidenced
219   by AFM.
220   Wang *et al.* prepared epoxy composites using DGEVA/TETA as the matrix and lignin-containing cellulose nano-
221   fibres. They obtained for the neat resin two exothermic signals, with maxima at 113 °C and 167 °C. The two peaks
222   are attributed respectively to the reaction of primary and secondary amines. In the DGEBA/TETA system, only one
223   peak is observed for stoichiometric compositions, with a maximum at 98 °C.[49,50] This two-stage curing behaviour
224   could be attributed to diffusion differences between DGEBA et DGEVA systems, since stoichiometric ratios were
225   applied with DGEVA. A study of TETA/DGEVA ratios *vs* T_g of materials should be of interest. Mechanical
226   properties of cured DGEVA were reported, especially using DMA. Two relaxations were found for DGEVA, with
227   T_α of 71 °C and 109 °C, revealing an inhomogeneous network, probably due to two types of crosslinking brought by
228   the amine containing both primary and secondary NH. The storage modulus at 30 °C was found to be 3.7 GPa.
229   DGEBA cured with TETA presents also two *tan δ* peaks, but with a maximum contribution of the second peak,
230   which maximum is 142 °C, and the storage modulus at 40 °C is around 4 GPa.[49] Degradation behaviour of
231   DGEVA/TETA has been investigated under nitrogen, and a two-step degradation pathway was found, with a
232   maximum of degradation at 309 °C and a char yield of 16 %. The DGEBA system presents a single-stage

233 degradation with a DTG peak at 372 °C, which shows a better thermal stability.[51] Char yield was not reported for
234 this material, but is believed to be lower than for DGEVA according to the trend observed.
235 Gnanasekar *et al.* synthesized a phosphorylated epoxy monomer using vanillin as the precursor.[52] In order to assess
236 the effect of the phosphorylation, they also used DGEVA as a phosphorus-free control. The study was also focused
237 on the use of polyurethane as a toughening agent in the synthesis of epoxy thermosets. DGEVA and the
238 phosphorylated monomer were cured with DETA. DGEVA/DETA properties could then be compared with
239 DGEBA. DMA tests showed a glassy modulus at 30 °C for DGEVA/DETA to be around 3.5 GPa, compared to 2
240 GPa for the DGEBA network as reported in the literature.[53] The tan δ peak of the DGEVA/DETA network appears
241 around 90 °C, which is slightly lower than that of DGEBA (100 °C). Thermal stability under nitrogen was also
242 assessed. The $T_{d5\%}$ of DGEVA/DETA was 247 °C and char yield at 600 °C is 7 %, compared to DGEBA/DETA
243 with a $T_{d5\%}$ of 305 °C and a char yield of 8 %. The lower thermal stability could be attributed to the presence of the
244 methoxy moiety, consistently with the other reports from literature. However, the lower char yield is unexpected
245 compare to the other DGEVA networks. However, it is worth mentioning that the low char yield was expected due
246 to the aliphatic structure of the hardener.
247 In a different work, Gnanasekar *et al.* used phosphorylated vanillin-based epoxy monomer, with modified graphene
248 oxide as the filler.[54] They also used DGEVA as a phosphorus-free control. The authors report the use of 4,4'-DDS as
249 the hardener, without describing the curing procedure. They determined the glass transition temperature of
250 DGEBA/44DDS using DSC at 108 °C. As a comparison, DGEBA/44DDS network has a T_g of 238 °C.[55] Thermal
251 stability under nitrogen was also assessed, and the DGEVA/44DDS showed a $T_{d10\%}$ of 251 °C, which is lower than
252 $T_{d5\%}$ for DGEBA/44DDS thermosets reported (> 300 °C). Char yield at 600 °C was 7 %, which is lower than when
253 DGEBA is used (approx. 14 %). The global lower performances of DGEVA cured with 44DDS can be attributed to
254 the lower aromatic density, and the presence of a methylene moiety in the structure of the epoxy monomer.
255 Mauck *et al.* used a diamine based on furfurylamine with DGEVA in order to get epoxy thermosets.[56] The
256 methylenedifurfurylamine (DFDA) was used to harden several epoxy monomers derived from biophenols. The
257 authors determined the EEW of their synthesized DGEVA at 133 g·eq⁻¹, slightly lower than the DGEBA used for
258 comparison (190 g·eq⁻¹). Thermomechanical properties were evaluated for cured networks. DMA showed that the
259 DGEVA/DFDA has a T_α of 81 °C compared to 109 °C for DGEBA/DFDA network. The Young's modulus at 25 °C
260 is 3.7 GPa for DGEVA compared to 2.4 GPa for DGEBA. It is consistent with all other articles discussed herein,
261 DGEVA giving lower T_g values and higher stiffness. As expected, the crosslinking density is higher for DGEVA,
262 which is composed on one aromatic ring compared to DGEBA, respectively 3.82 mmol·m⁻³ *vs* 2.62 mmol·m⁻³.
263 Regarding thermal stability under inert atmosphere (Ar), DGEVA thermoset degrades earlier than DGEBA, as
264 shown by the $T_{d5\%}$, namely 304 °C for DGEVA/DFDA compared to 330 °C for DGEBA/DFDA. However, char
265 yield at 600 °C is higher with DGEVA (42 % *vs* 23 % for DGEBA).
266 Mora *et al.* synthesized new aromatic-containing amines and cured DGEVA and DGEBA for comparisons.[57] They
267 reported lower thermal stability for all DGEVA-based thermosets ($T_{d5\%}$) but higher char yields. Glass transitions
268 temperatures and T_α were also lowered with DGEVA compared to DGEBA. They also reported the synthesis of
269 nearly full vanillin-based epoxy networks, using an aminated DGEVA as the curing agent with DGEVA, and with
270 DGEBA for comparison.[58] This resulted in lower decomposition temperatures as well as T_g / T_α but higher char yield
271 for DGEVA. As demonstrated by Noè *et al.*, DGEVA could also be used in photopolymerisation process. However,
272 in such case conversion gets limited by a fast vitrification of the forming coating.[59] Epoxy thermosets based on
273 DGEVA could also be used in manufacturing of composites with cellulose nano-fibres as the filler[60] as well as glass
274 coatings for food contact material.[46]
275
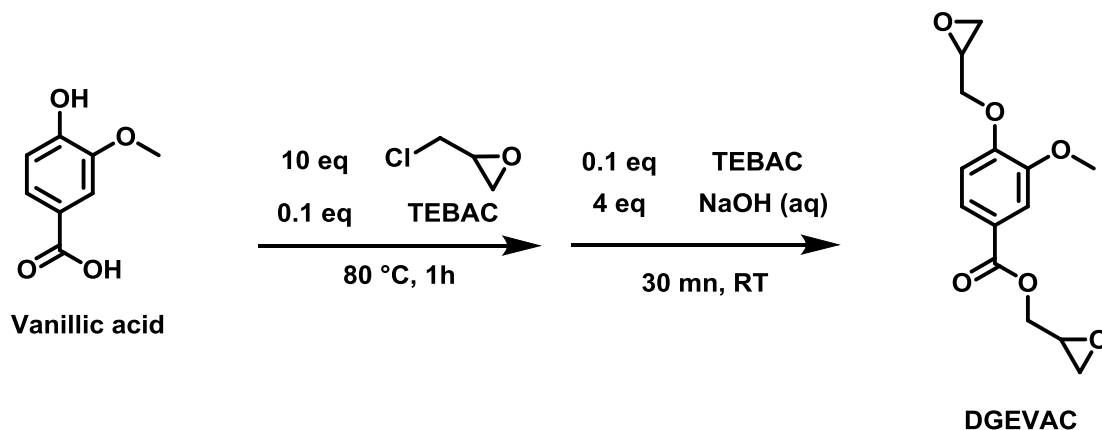
2. Vanillic acid

Figure 6 - Reaction scheme for the synthesis of DGEVAC according to Fache *et al.*[41]

Vanillic acid is the oxidized form of vanillin, where the aldehyde is transformed into a carboxylic acid. This compound gives the flavour of natural vanilla, and is also an artificial flavouring. Diglycidylether of vanillic acid (DGEVAC, Figure 6) is a diepoxy readily obtained from the reaction between vanillic acid and epichlorohydrin. The nucleophilic substitution of the phenolate and the carboxylate can occur at the same time.[41] Another way to obtain this compound is the one pot allylation of the same moieties, followed by epoxidation *via* the use of *m*CPBA, or through an enzymatic process.[61]

Fache *et al.* cured DGEVAC with IPDA, and they obtained a glass transition temperature of 152 °C and a T_α of 166 °C, these values are slightly lower compared to those reported for DGEBA-IPDA (T_g of 166 °C and T_α of 182°C).[44] The presence of the ester linkage on the aromatic ring could bring rigidity, compared to the above-mentioned DGEVA that contains a methylene instead. It is noteworthy that the T_g values are very close, even if the epoxy monomers have very different structure (two aromatic rings for DGEBA compared to only one for DGEBA). Usually, the T_g value increases linearly with the number of aromatic rings in the monomer. It can be observed that rigid structures like ester linkages can be as effective as aromatic density to improve the T_g of the epoxy thermosets. This behaviour is not correlated to the crosslinking density that has been calculated to be 1.4 mmol·m^{-3} for both DGEVAC and DGEBA materials. In addition, the storage modulus of DGEVAC thermoset was measured at 2.1 GPa, as compared to 1.9 GPa for DGEVA. Thermal stability under nitrogen is however lower for DGEVAC compared to DGEBA. DGEVAC/IPDA degrades in two step, measured at 315 and 370 °C compared to the unique decomposition temperature of DGEVA system, with a peak at 360 °C. This two-step degradation behaviour can be attributed to the earlier rupture of the ester bond. The char yield of DGEVAC thermoset follows the trend observed with DGEVA, since it is higher than for DGEBA (14 % for DGEVAC and 10 % for DGEBA).
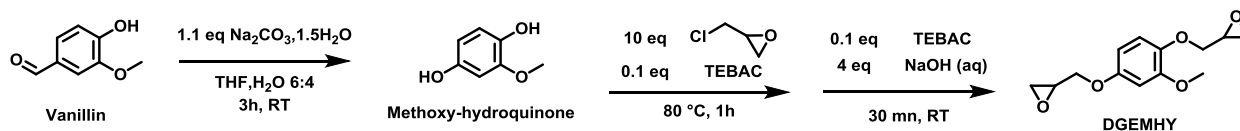
No more investigation has been performed on epoxy-amine thermosets with DGEVAC. However, there are examples on the epoxy-anhydride thermosets, such as the use of methylhexahydrophthalic anhydride and the hydrolytic degradation.[62,63] DGEVAC has also been used with nadic methyl anhydride as the curing agent.[64]

3. Methoxy-hydroquinone



Figure 7 - Reaction scheme for the synthesis of DGEMHY starting from vanillin according to Fache *et al.*[41]

Methydroxyquinone is a commercially available compound, but it can also be obtained from the Dakin oxidation of vanillin, using sodium percarbonate as the oxidizing agent. The aldehyde from vanillin is oxidized into a phenol in mild conditions. The diglycidylether of methoxyhydroquinone (DGEMHY) can be obtained through the glycidylation of both phenolic moieties (Figure 7). It was first prepared by Fache *et al.*[41] and the curing reaction with IPDA was extensively studied.[44] T_g and T_α values of 132 °C and 154 °C were reported. DGEBA with the same

curing agent gave higher transition temperatures. The calculated crosslinking density was similar to the DGEBA system (1.4 mmol·m^{-3}) and in the DGEMHY system (1.3 mmol·m^{-3}). The degradation of the thermoset under nitrogen atmosphere resulted in a single step weight loss with a peak at 338 °C, lower than in the case of DGEBA (360 °C). However, the char yield obtained was 20 % at 600 °C compared to 10 % with DGEBA.

Curing of DGEMHY has also been performed with other amines: DA10 is decanediamine, an aliphatic biobased amine obtained from castor oil, vanillylamine is a vanillin-derived amine and BFAA is bisfurfurylamine A, a potentially biobased diamine.[65] DGEMHY cured with the biobased amines shows lower T_g values than DGEBA-based thermosets. The aliphatic amine DA10 gave a T_g of 74 °C with DGEMHY (98 °C with DGEBA), vanillylamine gave nearly the same T_g with DGEMHY (64 °C) and DGEBA (67°C) and BFAA lead to a T_g of 111 °C with DGEBA and 85°C with DGEMHY. The aromatic content seems to be the most influential contributor to the T_g values of these epoxy thermosets, leading to higher values with DGEBA. The higher decrease regarding DA10 and BFAA with DGEMHY could be due to the presence of the methylene moieties in both amine and epoxy monomers. The lower T_g values were obtained for DGEBA and DGEMHY cured with vanillylamine, which could be due to the lower functionality of the amine.

The commercially available DGEBA mainly contains two epoxide moieties, (or as oligomers) with different epoxide contents and chain lengths. DGEMHY has been also studied in its oligomerized form.[66] Fache and co-workers performed a catalytic oligomerization by using triphenylbutylphosphonium bromide, using methoxyhydroquinone with an excess of DGEMHY. Then, the crosslinking of the oligomers was obtained using IPDA as the hardener. A decrease in the T_g and T_α of the cured samples were observed with the increase of the repeating units. This is due to the higher chain length between two crosslinking nodes. However, the effect of the chain length was counter balanced by the higher aromatic density in the oligomers, which rather limited the increase of the T_g and T_α values.
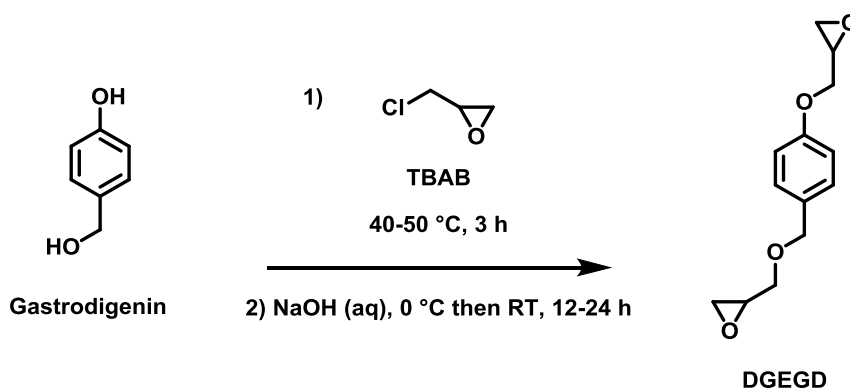
4. Gastrodigenin

Figure 8 - Synthesis of DGEGD by Hernandez *et al.*[45]

Gastrodigenin is a monophenolic compound that can be found in *Gastrodia elata*, a flower from the Orchidaceae family. This compound is one of the main active ingredients of this plant, and has shown some analgesic effects.[67] The structure of this molecule consist in a phenol bearing a methylenol in para position. The glycidylation of this compound leads to a diepoxy monomer, as shown in Figure 8. Hernandez *et al.* prepared DGEGD monomer with an EEW of 119 g·eq^{-1} and used PACM as the hardener.[45] Dynamic mechanical analysis of the DGEGD revealed a T_α of 132 °C, which is lower than with DGEBA (158 °C). The storage modulus of the DGEGD thermoset at 25 °C is 2.29 GPa, which is very close to DGEBA (2.37 GPa). Regarding thermal stability under nitrogen, the DGEGD networks degrades earlier than DGEBA. More specifically, the $T_{d5\%}$ of DGEGD/PACM is 337 °C, and DGEBA/PACM is 379 °C. This may be due to the presence of the methylene in DGEGD, which could induce a lower thermal stability. However, char yield is lower with DGEBA (2 % at 650 °C) compared to 4 % with DGEGD. Mauck *et al.* have used DFDA as hardener.[56] With this furan-based diamine, they obtained a T_α of 84 °C for DGEGD/DFDA compared to 109 °C with DGEBA. The storage moduli however are close, namely 2.29 GPa for DGEGD and 2.44 GPa for DGEBA. It has to be noted that the crosslinking density for DGEGD/DFDA is 4.97 compared to 2.62 for DGEBA/DFDA. It may be due to the lower molecular weight of DGEGD compared to DGEBA. The presence of a methylene and a single aromatic ring in gastrodigenin, may explain the lower T_g but due to the higher crosslinking density, a comparable storage modulus. The thermal stability under argon reveals an earlier degradation of DGEGD/DFDA with a $T_{d5\%}$ of 297 °C compared to 330 °C with DGEBA. However, the char yield in those systems is higher with DGEGD (40 % at 600 °C) compared to DGEBA (23 %). Gastrodigenin has

357 been identified as a bisphenol F (BPF) metabolite. BPF has a well-known endocrine activity. In the work of Fic et
358 al., gastrodigenin has been evaluated among other compounds, but has shown no deleterious activity.[68] The
359 XenoScreen XL YES/YAS assay used in this report is a yeast based in vitro method to assess the activity of
360 compounds both on the ERα receptor and the human androgen receptor.
361

362   5. Bisvanillyls
363

364
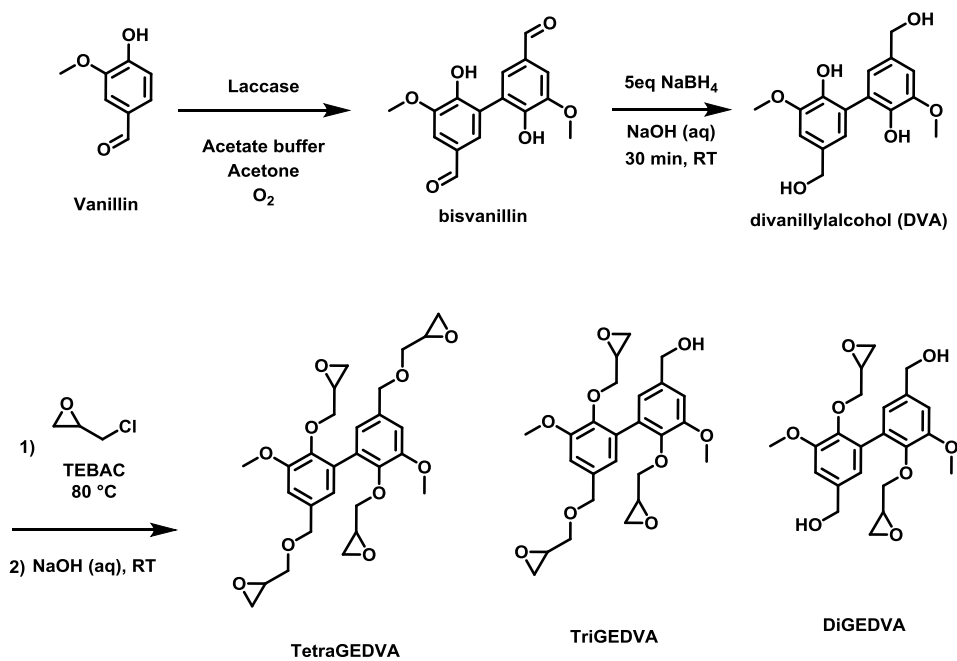
Figure 9 - Synthesis of bisvanillyl based epoxy monomers according to Savonnet *et al.*[69]

366 The oxidative coupling of phenolics by enzymatic processes leads to the formation of diphenolic compounds that
367 can help access to difunctional aromatic monomers.[70] The coupling of vanillin, and the reduction of the aldehyde
368 moieties lead to a bisaromatic compound bearing two phenolic hydroxyls and two hydroxymethyl moieties. Thus, a
369 tetra-functional epoxy monomer can be afforded after glycidylation. Savonnet *et al.* performed the synthesis of
370 tetrafunctional monomer, but also obtained tri and difunctional monomers, by adjusting the ratios of epichlorohydrin
371 in the glycidylation reaction of divanillylalcool (Figure 9).[69] Purification allowed the study of these different
372 monomers, especially upon curing with IPDA.
373 The three monomers are DiGEDVA (diglycidylether of divallinylalcool), where the two hydroxymethyl moieties are
374 reacted with epichlorohydrin, TriGEDVA with one phenolic moiety reacted, and then the TetraGEDVA, fully
375 reacted. Interestingly, the viscosity at 40 °C shows that the tetrafunctional monomer has the lower viscosity.
376 TetraGEDVA has a viscosity of 2 Pa·s, compared to DGEBA with 1 Pa·s. The TriGEDVA has a viscosity of 60
377 Pa·s, and the DiGEDVA has a viscosity of 1300 Pa·s. This increase in viscosity is due to the number of free
378 hydroxyl groups (1 for TriGEDVA and 2 for DiGEDVA). Free phenols or hydroxyls can provide hydrogen bonding
379 to the system, and thus increase the viscosity or the crystallinity.
380 The crosslinked networks with IPDA give different T_g values, DiGEDVA has the lowest one at 138 °C, TriGEDVA
381 intermediate one at 163 °C and TetraGEDVA the higher one at 198 °C. The functionality of the epoxy monomer can
382 help to tune the T_g, especially because DGEBA gives usually a high T_g, such as 152 °C with IPDA, as studied by the
383 authors. DMA was also performed, and properties such as the α transition temperatures, the Young's moduli and the
384 crosslinking densities were measured. The T_α followed indeed the same trend than T_g measured by DSC. The
385 GEDVA epoxy monomers have $T_\alpha s$ of respectively 140, 177 and 200 °C with increasing functionality, as compared
386 with DGEBA/IPDA with a T_α of 155 °C. In overall, the Young's moduli on the glassy state are higher than for
387 DGEBA, in the range 1.9-2.4 GPa, with the higher for TriGEDVA. On the rubbery state, higher moduli are also
388 measured for the GEDVAs, ranging between 35 and 210 MPa, with values increasing from mono to tetrafunctional.
389 Interestingly, DGEBA/IPDA give a modulus 35 MPa, similar to DiGEDVA. Crosslinking densities are similar
390 between DGEBA and DiGEDVA networks (namely 9.2 and 9.5 kmol·m^{-3}). For the higher functionalities,
391 crosslinking density increases accordingly, with 25 kmol·m^{-3} for TriGEDVA and 49 kmol·m^{-3} for TetraGEDVA.

The higher crosslinking densities of tri and tetra epoxy monomers mainly explain the higher mechanical properties observed. Tensile tests performed revealed that GEDVA monomers lead to higher Young's moduli, with increasing value when functionality also increases. However, elongation at break is lower in all cases than the DGEBA network. The rigidity of the monomers with a single carbon-carbon bond attaching the two aromatic rings seems to be detrimental to the elasticity of the network. Thus, DGEBA/IPDA displays an elongation at break of 6.3 % whereas DGEVAS network are between 3.3 and 4.7 %.

The thermal stability under air and under inert atmosphere showed that degradation of GEDVA networks happens at lower temperature than with DGEBA. The presence of the methoxy moieties usually leads to lower degradation temperatures. The $T_{d5\%}$ is similar for all networks under air and under nitrogen, in the range 273-292 °C for GEDVAs and around 330 °C for DGEBA. There is no residue at 600 °C under air for all the networks. Under inert atmosphere, the char yield at 700 °C is around 10 % for DGEBA/IPDA, whereas it increases for GEDVAS. Tri and TetraGEDVA have a char yield around 30 % whereas it is 40 % for DiGEDVA. This is simply explained by the free hydroxymethyl moieties in DiGEDVA. It is known that hydroxymethyl moieties can undergo a novolac-type condensation that could possibly happen during the degradation of the network, finally increasing the char formation.

It is worth mentioning that a biobased amine was also prepared from the difunctional vanillin derivative, and it was used as the hardener in fully vanillin-based epoxy-amine thermosets.[71] This amine was also used to crosslink DGEBA, and quite elevated T_g was obtained (176 °C), however lower than DGEVA/44DDS (204 °C).

6. Spiro-divanillin
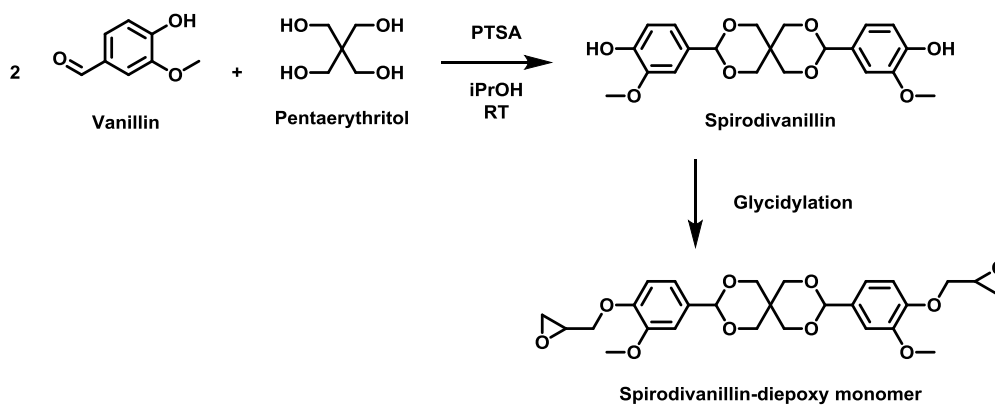
Figure 10 - Synthesis of spirodivanillin according to Mankar *et al.*.[72] Glycidylation conditions were not reported.

Vanillin and other aromatic aldehydes derivatives were also used in order to synthesize rigid structures using a spiroacetal linker, based on pentaerythritol, a tetra-hydroxyl compound (Figure 10).[72] Different bisphenolic structures were synthesized by Ochi *et al.* in order to analyse the contribution of methoxy moieties in epoxy thermosets using mechanical and dielectric analyses.[73,74] The monomers cured with DDM show slightly less crosslinking densities than DGEBA, and present alpha transitions very close to the DGEBA-DDM system (around 160 °C). The presence of methoxy moieties have shown to improve impact strength of the materials. However, no more study has been reported in the literature about degradation behaviour or other properties.
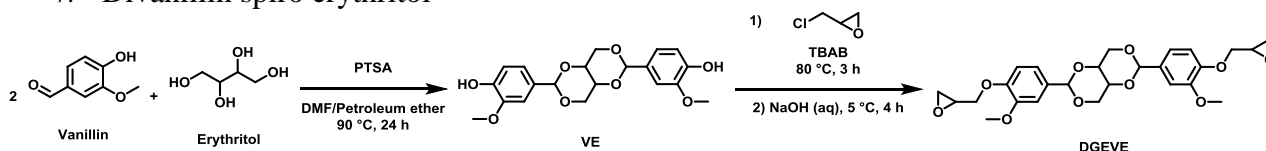
7. Divanillin spiro erythritol

Figure 11 - Synthesis of DGEVE from vanillin and erythritol, according to Yuan *et al.*[75]

15

429 A bisphenol based on vanillin and the sugar substitute erythritol was synthesized by Yuan *et al.*.[75] The glycidylation
430 leads to a diepoxy monomer (DGEVE, Figure 11), which was then cured with DDS and compared with DGEBA-
431 based thermoset. The high melting temperature of the monomer (245 °C), led the team to heat the formulation at
432 250 °C prior to a curing step at 180 °C, but the DGEBA-based mixture had the same curing scheme for comparison.
433 Dynamic mechanical analysis revealed an alpha transition temperature of 184 °C which is close to the
434 DGEBA/DDS formulation (208 °C). This high transition temperatures reveals a very rigid behaviour of the spiro
435 acetal containing monomer. The rubbery plateau is lower for the newly synthesized monomer (11 MPa for the
436 DGEVE monomer and 23 MPa for DGEBA). However, on the glassy plateau, from the published curves, we can
437 observe that the modulus at 0 °C is about 1.5 GPa for DGEBA epoxy, compared to 3 GPa for the methoxy-
438 containing network. The degradation behaviour showed that methoxy-containing material degrades at lower
439 temperature than DGEBA. For instance, under inert atmosphere, the $T_{d5\%}$ of DGEBA/DDS is 394 °C whereas it is
440 343 °C for the DGEVE/DDS network. The char yield is higher with the methoxy-containing network since it nearly
441 triples (34.4 % for DGEVE vs 11.7 % for DGEBA, at 700 °C).
442 Tensile strength measurements were also performed on both networks. It can be remarked that DGEBA/DDS has a
443 higher elongation at break (7.1 %) than DGEVE/DDS (3.1 %). However, the tensile modulus is higher for DGEVE
444 (3.3 GPa) than for DGEBA network (1.8 GPa). The tensile strength is similar (71-83 MPa). The DGEVE monomer
445 gives a higher hardness to the system, due to the rigid spiro acetal structure. However, the lower elongation at break
446 shows a higher brittleness of the network.
447 Degradation in aqueous conditions have also been monitored. Indeed, the linker based on acetal moieties can be
448 easily cleaved in acidic conditions. Epoxy film samples were immersed in a mixture of polar organic solvent and
449 water with different mineral acids. Then the time was measured to the point where no observable material was
450 remained. Hydrochloric acid showed the lowest degradation time compared to sulphuric and phosphoric acid.
451 Regarding the organic co-solvent it was observed that degradation was accelerated when the most polar solvent was
452 used. Degradation time was between 55 and 160 minutes depending on the organic solvent used with 0.1 M HCl at
453 50 °C. Degradation was also monitored by NMR spectroscopy, and it was observed that the degradation occurred
454 through acidic cleavage of the acetal moiety, leading to regeneration of the aldehyde. The aging of the epoxy resin
455 was also studied using a Xenon test chamber, at a temperature of 60 °C and a humidity of 95 %. Under such
456 conditions the T_g of the material did not change significantly after 15 days.
457
458 ## 8. Bisguaiacol F and other guaiacyls and syringyls

459
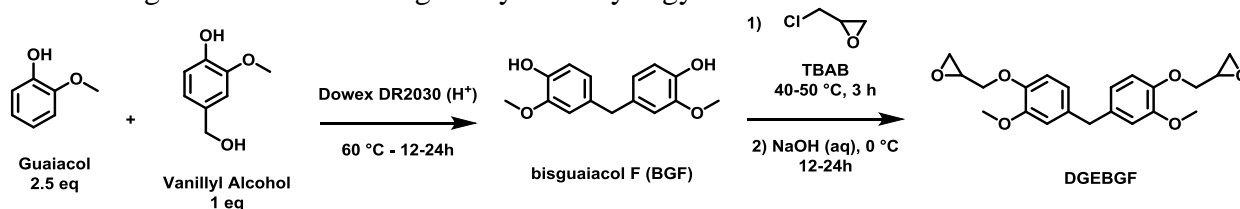
460 Figure 12 - Synthetic scheme of DGEBF synthesis according to Hernandez *et al.*[45]

461
462 Coupling of phenolics is an interesting way to access bisphenolic compounds, with a structure close to BPA.[23] The
463 properties of their epoxide derivatives are expected to be close to DGEBA. Hernandez *et al.* prepared a bisphenol
464 from vanillyl alcohol and guaiacol, another lignin derivative (Figure 12).[45] Reaction was conducted in acidic
465 medium, and purification by column chromatography afforded the desired isomer. After glycidylation, the EEW was
466 determined to be 193 g·eq^{-1}, a value close to the DGEBA used for comparison (190 g·eq^{-1}). The bisguaiacol was
467 cured with PACM, and compared with DGEBA/PACM system. Dynamic mechanical analysis was performed on the
468 networks, and it was observed that DGEBGF gave the higher *E'* (3.35 GPa) compared to DGEBA (2.37 GPa).
469 However, the *tan δ* of the DGEBA network displayed a peak maximum at 158 °C, whereas DGEBGF displayed a
470 peak at 111 °C. DSC confirmed the trend with a measured T_g of 149 °C for DGEBA network and 104 °C for
471 DGEBGF. It was observed that the presence of the methoxy moieties in DGEBGF gave higher loss modulus on the
472 glassy plateau, but that the packing of the network was less efficient due to the same methoxy moieties. This could
473 explain both the higher loss modulus and the lower T_g in comparison with DGEBA, which does not bear any
474 methoxy. Degradation under nitrogen atmosphere revealed that the DGEBA network started to degrade at a higher
475 temperature than DGEBGF, however the char yield was lower (2.3 % compared to 5.6 % for DGEBGF). The
476 bisguaiacol-based epoxy showed the same trend than all the other vanillin-based monomers, resulting in lower T_g
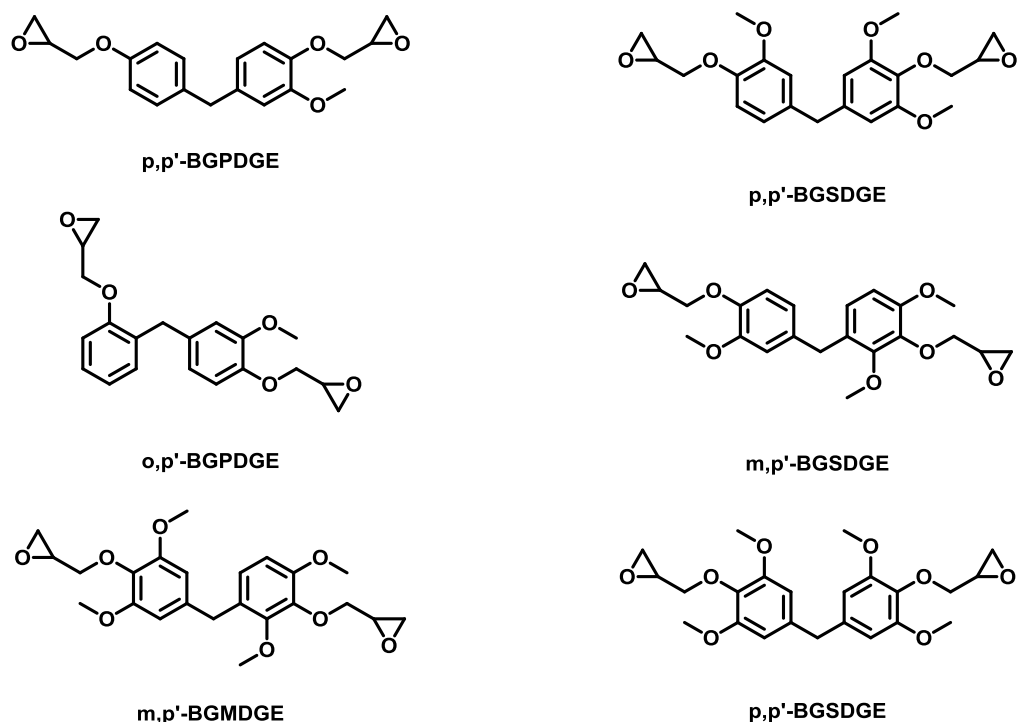477 but higher thermal stabilities.
478

p,p'-BGPDGE

p,p'-BGSDGE

o,p'-BGPDGE

m,p'-BGSDGE

m,p'-BGMDGE

p,p'-BGSDGE

Figure 13 - Bisphenolic epoxy monomers synthesized by Nicastro *et al.*[76]

In a more recent paper, Nicastro *et al.* synthesized several bisphenols based on vanillic alcohol or syringyl alcohol, condensed with other phenols,[76] using a similar protocol than Hernandez *et al.*.[45] The condensation on the aromatic ring could happen at different position (ortho, meta, para), depending on the phenol, and the authors obtained mixtures, some of them were purified to obtain pure isomers. Thermomechanical properties evaluated by DMA of the pure isomers and the glycidylated mixtures of isomers (shown in Figure 13) are summarized in Table 2. All the thermosets were prepared using MDA as the hardener. All the thermosets displayed alpha transition temperatures lower than the DGEBA/MDA system, but it should be noted that most of the prepared monomers have higher EEW than DGEBA. A higher oligomerization degree could lower the crosslinking density. It has also been shown that at the rubbery state, the storage modulus decreased as the number of methoxy moieties increased.

Table 2 - Thermomechanical properties of epoxy thermosets from bisphenols and MDA

Epoxy monomer	E'_{30} (GPa)	E'_{200} (MPa)	T_{α} (°C)
p,p'-BGPDGE	2.5	46	151
o,p'-BGPDGE	2.8	22	141
p,p'-BGSDGE	2.7	33	134
m,p'-BGSDGE	2.4	28	129
p,p'-BGMDGE	2.5	26	141
m,p'-BGMDGE	2.0	15	119
DGEBA	2.5	46	167

Koelewijn *et al.* worked on the synthesis method of bisguaiacol F isomers in order to obtain polycarbonates via copolymerisation of BGF.[77] They also conducted in vitro experiments to assess the human oestrogen receptor α activity of BGF, using two of the BGF isomers, namely 4,4'-BGF et 3-4'-BGF. Comparison was also made with 4-4'-BPF and 4,4'-BPA, and the natural hormone oestradiol. It was shown that BPA and BPF fully activated hERα in a dose-dependent manner, whereas the dose-response curves were only partial for the BGF isomers. The relative oestrogenic efficacy (REE) is an indication of the efficacy of the receptor activation compared to the one of the hormones (that has a REE of 100 %). REE for BPA and BPF were respectively 96 and 126 % showing a similar

17

interaction between the bisphenols and the oestrogen receptor, whereas it was only 48 and 37 % for BGF isomers. The para-para orientation of 4,4'-BGF showed a higher activity compared to the 3-4' isomer, which confirmed that the para-para orientation is an important criterion. The lower concentration needed for a given effect, called EC_{50} was $1.3 \cdot 10^{-11}$ M for the 17β-E2 compared to $6.6 \cdot 10^{-7}$ M for BPA and as high as 9.4 and $8.7 \cdot 10^{-5}$ M for 4,4' and 3,4' isomers respectively. This means that a higher amount of BGF is required to activate the receptor. Overall, BGF isomers showed 426-457 times lower affinity than BPA. These results are promising, as they are consistent with previous reports using other evaluation methods.[78]

Peng *et al.* also performed in vitro testing on bisguaiacol F isomers.[79] Since the synthesis of bisguaiacol could generate isomer mixtures, they determined the ratios of isomers that were obtained from the condensation of vanillyl alcohol and guaiacol, and used these mixtures for the in vitro testing. The two in vitro assays chosen were MCF-7 cell proliferation assay and VM7Luc4E2 TA test. E2 and BPA were used as positive controls. Both assays gave consistent results. Three mixtures testes contained ratios of 3,4-BGF and 4,4-BGF (4,4-BGF being the major one), and one mixture contained the three isomers, with a majority of 2,4-BGF. The results showed that when the mixtures contained a high proportion of 4,4-BGF, or when it contained 2,4-BGF, an increase in the proliferation rate was observed in the MCF-7 assay, indicating an oestrogen affinity. However, the proliferation rate was lower than that of BPA. The mixtures containing higher proportions of 3,4-BGF did not induce MCF-7 cell proliferation. The VM7Luc4E2 test also showed that the high 3,4-BGF containing mixtures had non-detectable EA. The other BGF mixtures did show some EA, but with lower EC_{50} values. These results suggest that high 4,4-BGF concentration and 2,4-BGF containing mixtures are moderately active on the oestrogen receptor, but still less active than BPA.

BPA   BPF   *p,p'*-BGP   *o,p'*-BGP

p,p'-BGS   *m,p'*-BGS   *p,p'*-BGM   *m,p'*-BGM

p,p'-BGF   *m,p'*-BGF   *o,p'*-BGF
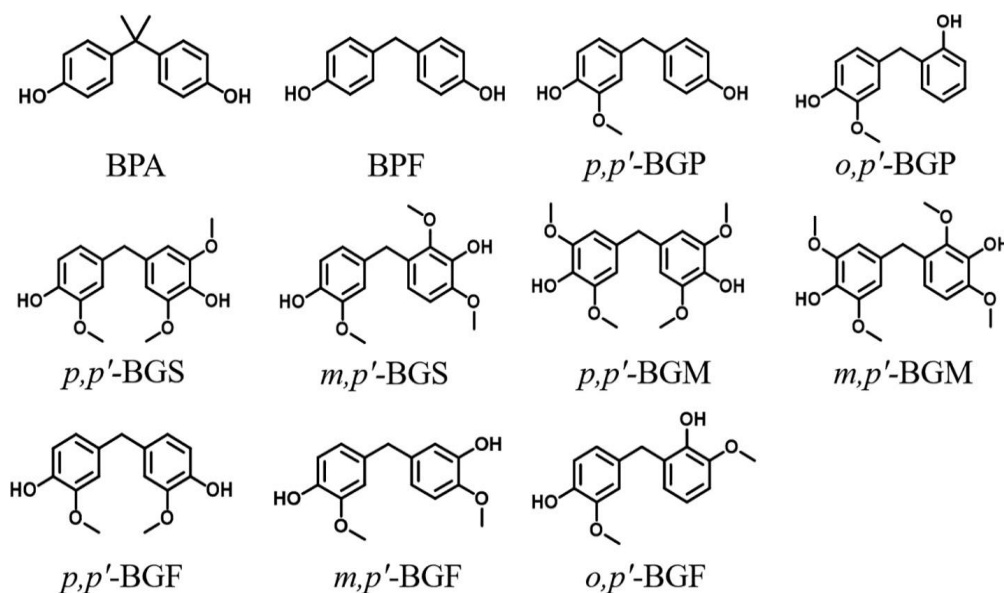
Figure 14 - Bisphenols and bisguaiacols used in ERα affinity tests

in a different report, Peng *et al.* tried to determine the influence of methoxy groups on the oestrogen affinity of bisphenols, especially at relevant environmental concentrations.[80] They synthesized a total of 9 bisphenols bearing different numbers of methoxy moieties, with different phenol orientations (Figure 14). They also performed a comparison of oestrogen activity with BPA and BPF. The assays conducted were first the determination of the oestrogen affinity, especially the lower concentration at which an effect is observed. Secondly, they tried to assess the effect of environmental concentrations of bisphenols on the viability of human cell lines (MCF-7 cells and VM7Luc4E2). Their work showed that the presence of only one methoxy on the bisphenol, drastically reduced the EA. No bisguaiacol had a detectable EA at concentrations lower than 10^{-7} M. At relevant environmental concentrations of bisphenols, the two in vitro assays of cell proliferation were consistent. At this concentration, for all bisguaiacols, the % RME2 that illustrates the normalized EA was lower than for BPA or BPF, in at least one cell line. The only exception was for one meta-para isomer which would require further investigations.

Amitrano *et al.* designed a study using molecular docking in order to study the influence of methoxy groups on the calculated binding affinity of bisphenols with the ERα receptor.[81] The authors evaluated several structures that could be derived from lignin, bisphenols bearing one or two methoxies on each aromatic ring. The influence of the bridging unit between the phenols was also studied, and the orientation of methoxy substitution on the ring. Their results suggest that methoxies do have an influence on the interaction between the bisphenols and the receptor via steric hindrance. However, the effect was especially significant when at least two methoxies were attached to one of

540   the phenols, when there was no substitution on the bridging methylene. The authors also suggest that bulky
541   substituents on the bridging unit have also an influence on the affinity with the receptor, likely due to the steric
542   hindrance, especially when the phenols were substituted. Both methoxy substitution on the phenol and bulky groups
543   on the bridging unit are the key parameters to possibly prevent interaction with ERα. The substitution orientation
544   (*ortho, meta, para*) do not have a significant influence for bulky monomers, *i.e.* containing 2 methoxies on one
545   phenol ring. However, when containing one methoxy on each phenol ring, the results were consistent with the
546   reported in vitro tests by Peng and co-workers.[79]
547   Some guaiacyl and synringyl bisphenolic compounds were evaluated by Hong *et al.* with intention to predict the
548   oestrogen activity of a set of compounds using an *in silico* model, based on available data from the literature.[82] In
549   this work, p,p'-BGF, p,p'-BGS (from Figure 14), and another bisguaiacol having one methoxy group on one of the
550   ortho position, with a dimethyl-substituted bridging unit *i.e.* Bisguaiacol A (also reported in Amitrano *et al.*[81]) were
551   evaluated and their biding affinity predicted. From this three monomers, p,p'-BGS and bisguaiacol A were predicted
552   as non-binder to the receptor. Bisguaiacol F (p,p'-BGF) was predicted to be binder to the receptor, but with a
553   moderate confidence (probability to be binder is lower than 80 %). The quantitative binding affinity calculated for
554   this latter bisphenol was slightly lower than BPA. This result is in accordance with the reported in vitro data
555   described before. If bisguaiacol F do show an activity in vitro, as described *e.g.* in Koelewijn *et al.*, the real-life
556   concentration needed would be higher than for BPA, thus the ED potential would be lower.[77]

557
558   9.   Cyclopentanone bisvanillin
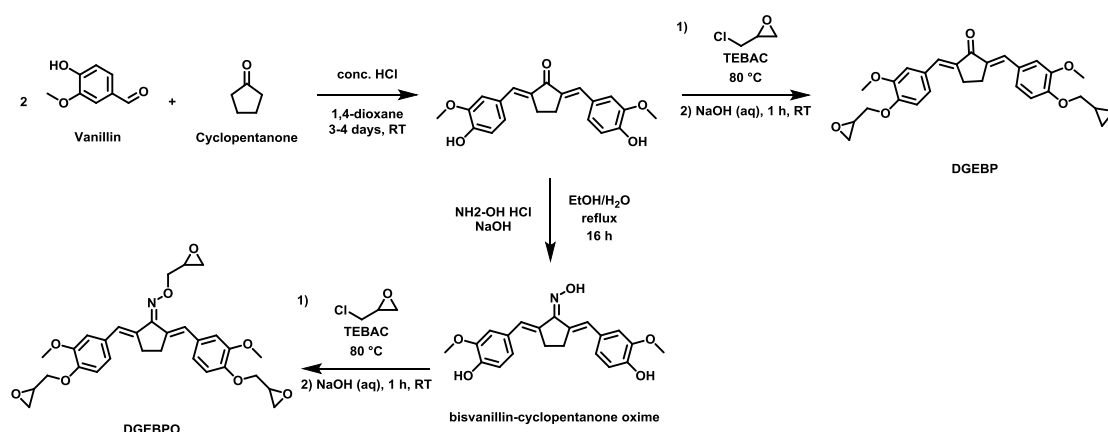559

561   Figure 15 - Synthesis of DGEBPO and DGEBP from vanillin, according to Mogheiseh *et al.*[83]

562   Shibata and Ohkita synthesized a divanillin-based monomer by an aldol condensation between two equivalents of
563   vanillin and cyclopentanone (Figure 15), and used phenolic hardeners in order to generate epoxy-phenol
564   thermosets.[84] More recently, Mogheiseh *et al.* used this divanillin-based monomer, and synthesized a slightly
565   modified epoxy-phenol.[83] They formed an oxime by the reaction of the ketone with hydroxylamine. The compound
566   containing two vanillin moieties and the oxime could be glycidylated, adding three glycidylether moieties. They
567   used several hardeners, some containing hydroxyls, among them the biobased decanediamine (DA10). The fully
568   cured material with the amine was characterized using infrared spectroscopy, gel content, mechanical and thermal
569   properties. The glass transition temperature of the system DGEBPO/DA10was 102 °C and the alpha transition
570   measured by DMA was 109 °C. For comparison, DGEBA/DA10 thermoset has a T_g of 98 °C and $T_α$ of 97 °C
571   according to Ménard.[85] The thermoset based on DGEBPO displayed a storage modulus of 1.7 GPa compared to 1.0
572   GPa for DGEBA/DA10, due to the more rigid structure of DGEBPO that is brought by the cyclopentenedione link
573   between the two aromatic rings, and the higher epoxy functionality. The same trend is observed at the rubbery state
574   with a modulus of 93.0 MPa for DGEBPO based material, compared with 23.2 MPa for DGEBA/DA10. In terms of
575   thermal stability under inert atmosphere, the $T_{d5\%}$ of DGEBPO material was 313 °C, which is slightly lower than
576   DGEBA/DA10 (337 °C). This trend is often observed with methoxy-containing monomers such as vanillin-based
577   compounds. Char yield at 700 °C was determined for the cured materials and DGEBPO, displaying 2.5 % compared
578   to 5.2 % for DGEBA/DA10. Usually, it was observed that vanillin-based epoxies give higher char yields, and this
579   result could be explained by a lower contribution to char formation of the cyclopentenedione link between the
580   aromatics, even if the higher functionality of the monomer could lead to a better stability as compared to the
581   difunctional DGEBA.
582

II.   Syringaldehyde
       Syringaresinol
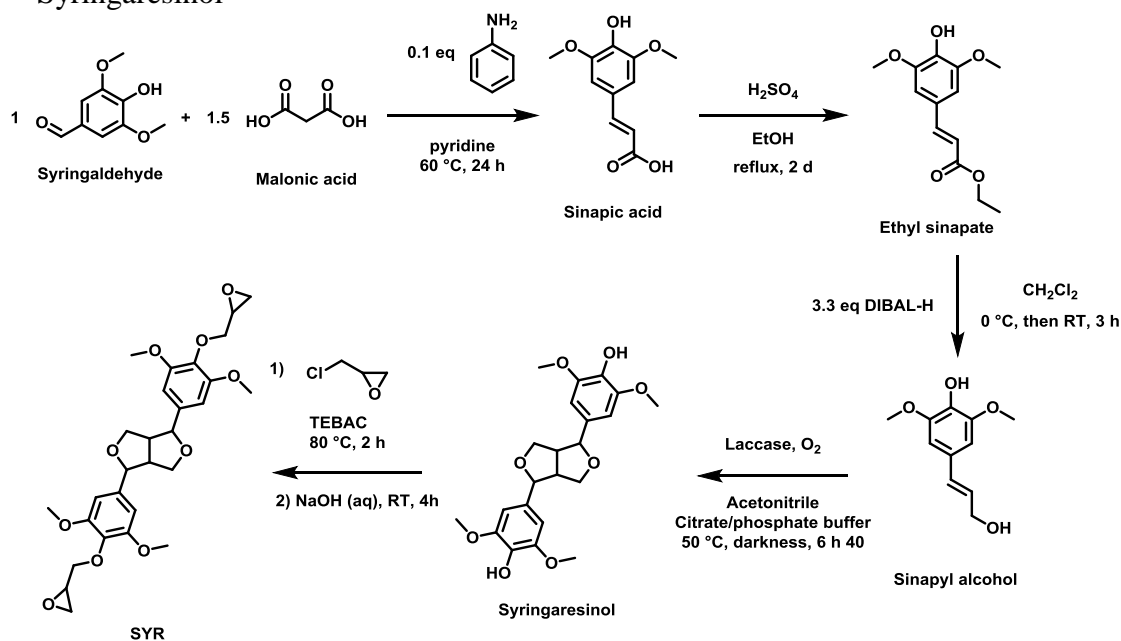
Figure 16 – Synthesis of epoxy monomer of Syringaresinol from Syringaldehyde according to Janvier *et al.*[86]

Syryngaresinol is a natural polyphenol found in some plants, but in very low yields. However, researchers have developed several catalytic and biocatalytic processes to afford multigram scale of this antioxidant.[87] Access to large quantities of this natural molecule has led to its use as an epoxy precursor, after glycidylation (Figure 16). Janvier *et al.* performed the synthesis of this diepoxide, and then studied the network properties with different hardeners such asDA10, IPDA and DIFFA.[86] The IPDA/SYR network displayed a T_g of 126 °C, which is slightly lower than DGEBA. The α transition temperature of the SYR network was 157 °C (as compared to 166 °C for DGEBA/IPDA. The glassy modulus (measured at 50 °C) of SYR/IPDA was 758 MPa while with DGEBA the value was 783 MPa. The moduli and transition temperatures were similar to each-other, indicating that even if the crosslinking density was expected to be lower for the SYR network (due to a higher molecular weight between the crosslinks), the rigidity brought by the bicyclic linkage counterbalanced the effect on the network. At the rubbery plateau, the DGEBA network displayed a modulus of 16 MPa, compared to 12 MPa for the SYR network. The presence of a higher density of aromatics in DGEBA lead to a higher modulus.

When cured with DA10, the SYR network displayed a T_g of 73 °C, compared to the DGEBA network reported by Ménard *et al.* with a T_g of 98 °C.[88] However, regarding the α transition, the reported DA10/DGEBA value was 97 °C whereas for the SYR network, the $T_α$ was 102 °C. The similar values displayed under mechanical investigations lead to the conclusion that the SYR based networks display excellent mechanical properties compared with DGEBA. At the glassy plateau, the values were not comparable for DGEBA and SYR networks since the measurements were not performed at the same temperature (at 50 °C reported by Janvier *et al.* and at 0 °C reported by Ménard *et al.*). At the rubbery state, the SYR-DA10 material had a modulus of 14 MPa compared to the reported 23.2 MPa for DGEBA. The lower value obtained is probably due to the lower crosslinking density.

Finally, the last hardener used is DIFFA, which lead to a T_g of 102 °C and a $T_α$ of 108 °C, whereas the DGEBA/DIFFA network had a T_g of 92 °C and a $T_α$ of 110 °C. These very similar values, show promising results for this epoxy monomer as a substitute for DGEBA. Regarding the rubbery modulus, the SYR network displayed a value of 10 MPa compared to 23.2 MPa for DGEBA. The rigidity brought by the bicyclic linkage does not prevent free rotation once the α transition happened. The global thermal stability of the networks was lower for SYR compared with DGEBA (over 300 °C for DGEBA, and slightly under for SYR, with a difference of approximately 30 °C). The char formation was higher for SYR networks, attaining 29.4 % for DIFFA/SYR at 700 °C.

Syringaresinol and its glycidylated derivative were evaluated by Janvier *et al.* against ERα and compared with BPA, DGEBA, E2 and an isosorbide-based bisferulate described later in this review.[86] The activity relatively to the human hormone were plotted for all the compounds tested, at 10^{-8} M. It was shown that the new epoxy monomers and the corresponding diols did not show any oestrogenic activity, since they display the activity corresponding to the vehicle (Figure 17). In addition, no dose-response was observed in the concentration range 10^{-13} to 10^{-5} M.
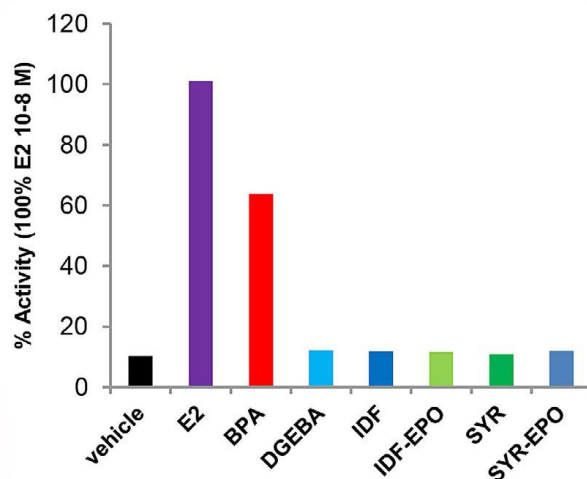
Figure 17 - In vitro evaluation of relative activity of syringaresinol diol (SYR) and diepoxy (SYR-EPO) against HERα by Janvier *et al.*[86] Comparison were made with BPA, DGEBA. IDF and IDF-EPO are isosorbide-based compounds.
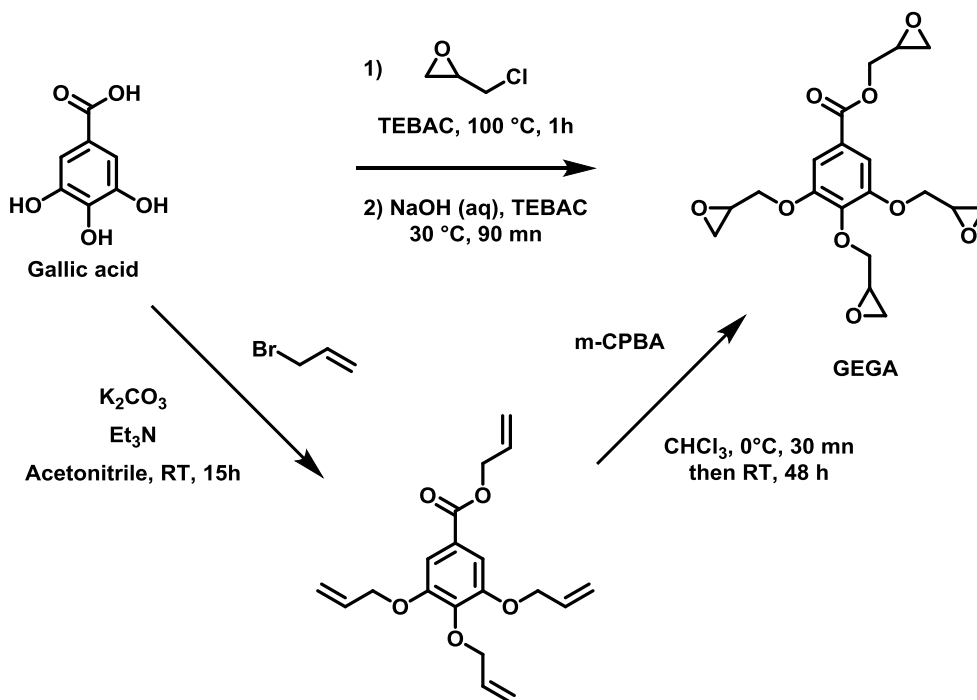
III.   Gallic acid

Figure 18 - Synthethic patwhays for the synthesis of GEGA, from Tarzia *et al.* and Aouf *et al.*[89,90]

Glycidylether of gallic acid was prepared by allylation of the carboxylic acid and the subsequent epoxidation of the allylic double bonds (Figure 18).[90] Aouf *et al.* performed the oxidation using two methods, the first using *m*CPBA and the second one using Oxone in milder conditions. However, the Oxone method gave lower yield of the tetra-epoxide compared with the *m*CPBA method. GEGA was cured with IPDA using a mixture of the trifunctional and tetrafunctional monomers, with a mean of 3.8 epoxy per monomer. The thermoset properties were compared with the DGEBA/IPDA system. Dynamic mechanical analysis showed a T_α of 233 °C for GEGA, much higher than for DGEBA (160 °C). This higher transition can be explained by the higher crosslinking density of GEGA, due to a higher functionality and the lower molecular weight compared to DGEBA. The temperature of 5 % degradation of the material under inert atmosphere ($T_{d5\%}$) is 300 °C for GEGA and 350 °C for DGEBA. The lower thermal stability of GEGA is probably due to the presence of the ester bond. However, the char yield at 600 °C was 23 % for GEGA

637 and 8 % for DGEBA. The higher crosslinking and aromatic density brought by GEGA lead to a higher stability and
638 char formation at high temperature, compared to DGEBA.
639 In the work of Tarzia *et al.*, curing of GEGA was performed using IPDA and Jeffamine D230, which is a
640 polypropylene-oxide based diamine.[89] They observed by DSC comparable curing exotherms with both amines
641 (488 J·g^{-1} with Jeffamine and 531 J·g^{-1} with IPDA). They also observed similar peak temperatures (respectively 94
642 and 90 °C). The glass transition temperature after curing at 150 °C was also measured by DSC. The IPDA system
643 displayed a T_g of 145 °C and the one with Jeffamine was 83 °C. In comparison, from Duchet and Pascault[91], the
644 DGEBA/IPDA system displayed a T_g of 156 °C, and the DGEBA cured with Jeffamine D230 had a T_g of 80 °C. In
645 the work of Tarzia *et al.*, the glass transition temperatures of GEGA thermosets are very similar to DGEBA
646 thermosets. Compared with the work of Aouf *et al.* it can be observed that the reported values for IPDA/GEGA
647 were slightly different. Indeed, as a comparison with T_g, the alpha transition of IPDA/GEGA from Aouf *et al.* is 233
648 °C.[89,92] However, in the work of Tarzia *et al.*, the reporting curing procedure at 150 °C was different than the
649 procedure from Aouf *et al.* which was 30 minutes at 90 °C and then 2 hours at 200 °C. Due to the high functionality
650 of GEGA one could expect that with the same amine, GEGA would lead to higher glass transition temperatures or
651 T_α than with DGEBA. It could be deducted that the differences were due to an incomplete curing process from
652 Tarzia *et al.* since the ratio between trifunctional and tetrafunctional GEGA was reported to be the same. This is also
653 confirmed by the fact that Tarzia *et al.* observed some residual enthalpy in the 2nd heating ramp in DSC. Thus,
654 thermosets obtained from GEGA could have similar transitions than with DGEBA only if the thermoset was not
655 fully cured. Regarding the degradation of the cured thermosets, in the work of Tarzia *et al.* the char yield reported
656 for IPDA/GEGA was 18 % at 600 °C, which was lower than the one reported by Aouf *et al.*, confirming the
657 incomplete curing process. Regarding tensile tests, DGEBA systems gave lower tensile modulus than GEGA
658 systems. The tensile strength for epoxides cured with IPDA was higher with GEGA than with DGEBA. The
659 opposite trend was observed for both epoxides cured with Jeffamine. It seems that the DGEBA systems can be
660 subjected to more plastic deformation than GEGA systems. This is confirmed by the global higher percentage of
661 elongation at break. The GEGA systems were more brittle due to the crosslinking density.
662 In a study screening 253 industrial chemicals, gallic acid was evaluated for its activity against androgen receptor.
663 The results indicated that this compound does not have any activity against the AR.[93] Unexpectedly, some studies
664 report a protective effect of gallic acid on the toxicity induced by BPA. For example, a recent study by Trivedi *et al.*
665 showed in vitro that the addition of gallic acid reduced the toxicity induced by BPA, especially on red blood
666 corpuscle.[94]

668 IV.   Protocatechuic acid
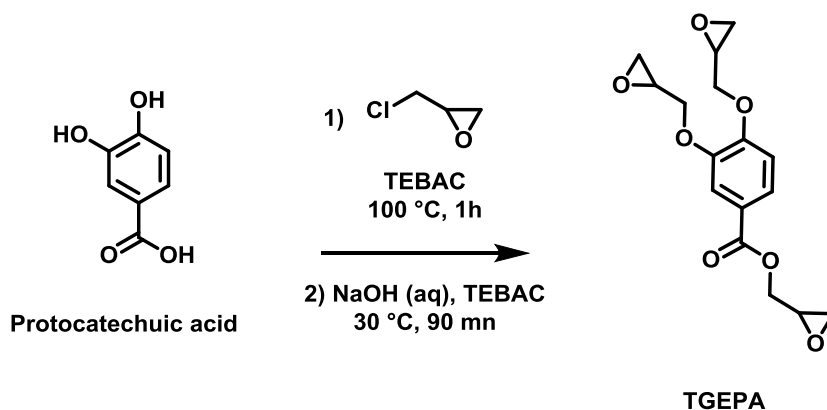
Figure 19 - Synthesis of TGEPA from protocatechuic acid, according to Aouf *et al.*[90]

673 Protocatechuic acid is a catechol bearing a carboxylic acid moiety. It is a natural polyphenol found in seeds such as
674 chia, canola or sunflower, or in fruits and berries such as mangosteen.[95] It has also been demonstrated that
675 protocatechuic acid can be obtained from glucose, via microbial fermentation.[96,97] The glycidylation reaction of
676 protocatechuic acid was first performed by Aouf *et al.* in a paper describing the effect of different substituents of
677 natural phenols on the reaction of glycidylation.[90] No thermosetting polymers were prepared from this study, but
678 recently, Chen *et al.* prepared crosslinked networks with DDM as the hardener.[98] It has to be noted that the
679 trifunctional epoxy monomer can also be obtained by allylation and subsequent oxidation of the double bonds.[99]

680 Chen *et al.* performed non-isothermal curing kinetics using Kissinger's method in order to assess the activation
681 energies of the TGEPA/DDM system. Using five different heating rates, the authors measured an E_α of 54 kJ·mol^{-1}
682 compared to 57 kJ·mol^{-1} for DGEBA/DDM system, reported before with the same method.[100] The slightly more
683 favourable activation energy was attributed to the presence of the ester moiety that could activate one of the glycidyl
684 residue. The alpha transition determined by DMA for TGEPA/DDM was not observed by the tan δ peak before
685 250 °C, which is quite higher than DGEBA/DDM, which T_α was measured at 189 °C. The storage modulus of the
686 TGEPA network was higher than DGEBA (respectively 1.9 GPa *vs* 1.6 GPa) at room temperature, and it is
687 explained by the rigid structure of the monomer compared to DGEBA. It has also to be noted that the single
688 aromatic ring of the new monomer prepared by the authors could also lead to a higher aromatic density in the
689 network, and thus, a higher rigidity. The very high T_g was also confirmed by the measurement of coefficient of
690 thermal expansion, determined by thermal dilatometry. Using this method, T_g was measured to be 176 °C for
691 DGEBA/DDM compared to 221 °C for TGEPA/DDM, which is coherent with previous characterizations. Finally,
692 regarding thermal stability under nitrogen atmosphere, the $T_{d5\%}$ of TGEPA network was 321 °C, lower than for
693 DGEBA (364 °C), as often observed with monomers containing esters. However, the char yield measured at 1000
694 °C was 16 % for the DGEBA network, compared to 28 % for TGEPA network, showing a better charring ability,
695 probably due to the high aromatic density of the network. 3,4-dihydroxybenzoic acid (protocatechuic acid) is
696 considered as a human metabolite resulting from the exposure to parabens.[101] Parabens are well known preservatives
697 that are also suspected of endocrine disruption. However, so far they have not been evaluated as endocrine
698 disruptors.

699

700 ## V.   Ferulic acid

701

702 Ferulic acid is a phenolic compound that can be found in bagasse, wheat and rice brans or beetroot pulp. It is
703 composed of an aromatic phenolic ring bearing a methoxy moiety in ortho position, and an α,β-unsaturated
704 carboxylic acid in para position. This compound that can be extracted from non-edible agricultural waste.[88]

705

706 ### 1.   Bisferulates with alkyl ester linker

707

708 Maiorana *et al.* synthesized an ester of ferulic acid by an acidic esterification with ethanol. The obtained ester was
709 subsequently reduced in the same pot, using Pd/C and dihydrogen at ambient temperature and pressure. This ester
710 was then used as a starting material for transesterification reactions using a lipase in order to obtain di or
711 trifunctional derivatives with different linkages. The diols utilized were ethanediol, propanediol, butanediol and
712 hexanediol (all linear) as shown in Figure 20.[102] Ménard *et al.* used the same method using isosorbide, butanediol
713 and butanediamine to obtain bisferulates, and glycerol was used to obtain a trifunctional compound.[88] The
714 corresponding esters or amides were then subjected to glycidylation, in order to obtain the corresponding epoxy
715 monomers. Thermosets were prepared with different amines, and compared with DGEBA systems in each case.
716 Three amines were used as hardeners, namely IPDA (cycloaliphatic), DA10 (aliphatic) and difurfurylamine A
717 (DIFFA) obtained from the condensation of furfurylamine with acetone.

718
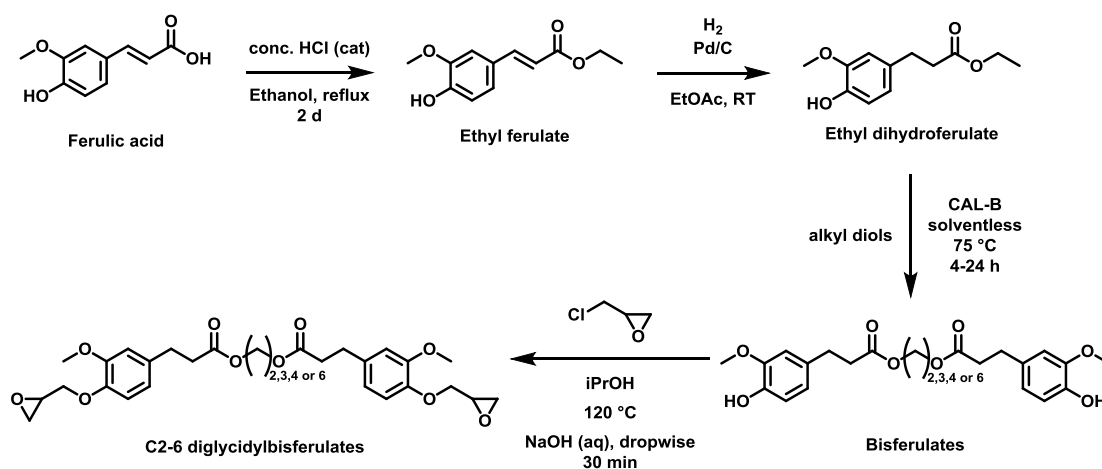
720 Figure 20 - Reaction scheme for the synthesis of alkyl bisferulates derived epoxy monomers according to
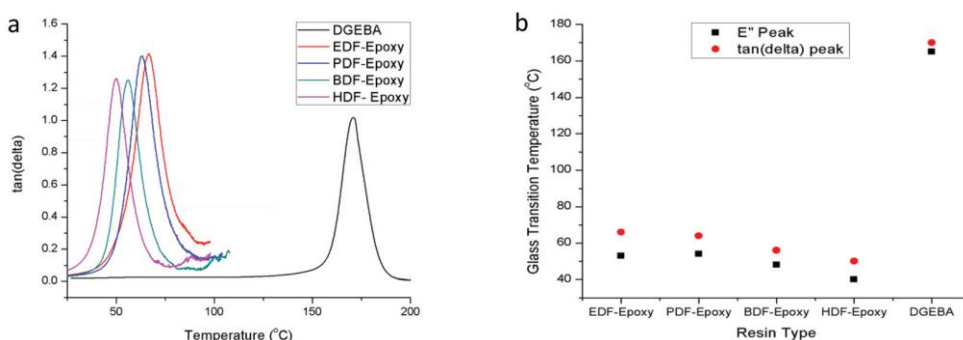721 Maiorana *et al.*[102]

722

Regarding bisferulates synthesized from linear diols, Maiorana *et al.* used IPDA as the hardener. They were able to compare the epoxy-amine networks properties as a function of diol size, and with DGEBA also for comparison. They compared the viscosity of the epoxies at 25 °C, and calculated the flow activation energy. They showed that the temperature dependence of the viscosity for the bisferulates were similar to DGEBA. A linear correlation was observed for the storage moduli at 25 °C when it was plotted against the diol length. The storage moduli were reduced as the length of the linker increased. This is mainly due to the increased chain mobility in the thermoset. The glassy moduli of the bisferulates based networks were in the range 2300-3500 MPa, while the value for DGEBA network is 2640 MPa (close to the C4 bisferulate (Figure 21)).

731

732
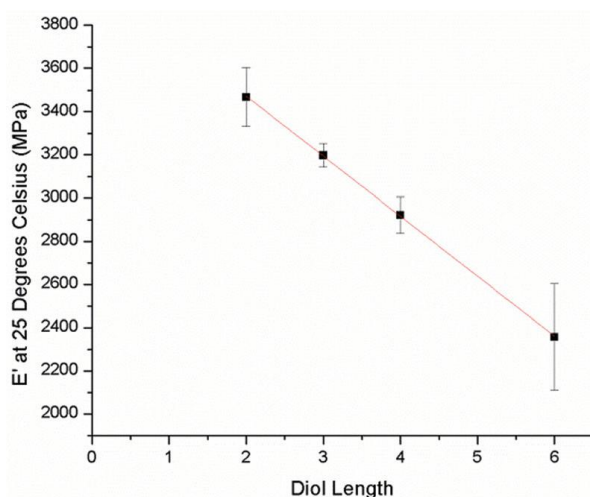
Figure 21 - Young's modulus of bisferulates/IPDA thermosets as a function of the diol spacer length, from Maiorana *et al.*[102]

Regarding the α transition of the networks and the loss moduli peaks, a slight decrease was observed as the linker length increased (Figure 22). This is consistent with the increase in chain mobility as the number of carbons in the linker increased. However, for all the bisferulates diepoxies, the transitions were observed at lower temperatures, in the range 40-70 °C as compared to DGEBA (higher transition around 170 °C).

739

740

Figure 22 - a) tan δ peaks of alkyl bisferulates based thermosets with IPDA, b) E" peaks and tan δ peak temperatures plotted against the different epoxy structures. EDF = C2, PDF = C3, BDF = C4 and HDF = C6, reproduced from Maiorana *et al.*[102]

744

The degradation behaviour of all the thermosets was also investigated under nitrogen. It was observed that longer linkers resulted in higher $T_{d5\%}$, with an increase from 300 to 331 °C for C2 to C6 diols. The onset of degradation was slightly higher for DGEBA network, however in the same range of temperature. Similar thermal resistance indicates similar thermal stability and suitability of the thermoset for same type of applications. It can also be noted that the char yields were higher for bisferulates (shorter chains gave higher char yields). As mentioned previously, the

methoxy-containing monomers are more prone to increase the char formation. However, the increase in alkyl carbon content decreases the char formation, mainly due to the lower density of the aromatics and the crosslinking.

The hydrolytic degradation of the networks was studied in alkaline conditions at 60 °C), providing interesting information regarding the possible chemical recycling of the thermosets, and also the possible leaching of the compounds. The cured samples were immersed in an alkaline media at 60 °C and their weight was monitored as a function of time (Figure 23). This figure shows that the DGEBA does not degrade even after 50h, whereas the degradation kinetics for ester containing materials have a linear correlation with the linker size. Shorter alkyl chains degrade faster since the hydrophilicity of shorter chains are higher as confirmed by contact angle measurements.
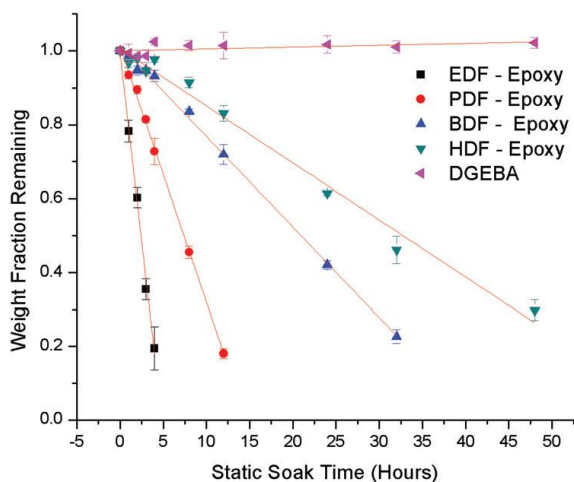
Figure 23 - Solid fraction as a function of soaking time in alkaline medium for alkyl bisferulate based thermosets, reproduced from Maiorana *et al.*[102]

The C4 linker containing epoxide was also cured with DA10 and DIFFA by Ménard and co-workers.[88] It could be observed that the use of aliphatic hardeners with the C4 monomer gave a slightly less stable material with $T_{d5\%}$ of 314 °C for IPDA and DA10, compared to the use of DGEBA as the epoxide (respectively 331 and 337 °C). With DIFFA however, the thermal stabilities were comparable with DGEBA (306 °C for the bisferulate and 301 °C for DGEBA). It seems that the crosslinking density of the DGEBA-DIFFA is responsible for the lower thermal stability. Char yields were higher with all the hardeners with bisferulates, the highest values were obtained with DIFFA as the hardener for all the networks. The glass transition temperatures for all networks based on the C4 bisferulates were nearly one third of the ones obtained with DGEBA, for all hardeners (due to lower crosslinking densities). DMA measurements showed that the alpha transitions followed a similar trend. The glassy modulus of C4 bisferulate was the same as the DGEBA when DA10 was used as the hardener. The elastic modulus of bisferulate network with DA10 however was half of the value obtained for DGEBA (10.8 MPa *vs* 23.2 MPa). It seems that the rigidity of the monomers is comparable at $T < T_g$, whereas at $T > T_g$, the molecular motion is responsible (for bisferulate), probably due to the lower crosslinking density, and the presence of a linear alkyl chain (inducing free rotations). For the networks obtained with DIFFA, the glassy modulus is higher for DGEBA (2.1 GPa) than for the bisferulate (1.75 GPa), probably due to the higher aromatic density with DGEBA. Over the glass transition temperature, similar trends with DA10 was observed.

Maiorana *et al.* performed screening of the EA of the n-alkyl bisferulates before glycidylation. Comparison between EA was performed using the natural oestrogen, BPA, BPS and DGEBA (Figure 24).[102] The assay conducted was a measure of the activity of the ERα. While BPA and BPS showed 60 % activity compared to the hormone E2, the n-alkyl bisferulates did not show a significant activity compared to DGEBA or the vehicle. No dose-response effect was measured in the studied concentration range.
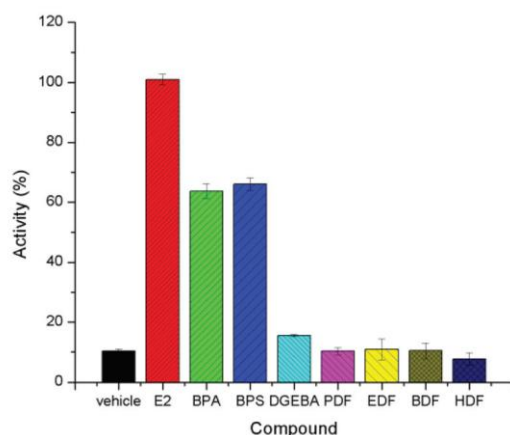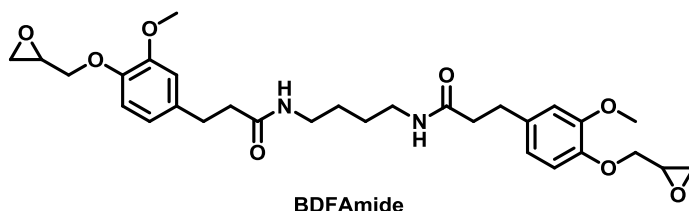
783

784 Figure 24 - In vitro activity comparison of alkyl bisferulates, from Maiorana *et al.*[102]

785

786 2. Bisferulate with amido linker

787

BDFAmide

788

789 Figure 25 - Structure of the BDFAmide synthesized by Ménard *et al.*[88]

790 In the work of Ménard *et al.*, butanediamine was used as a linker for the synthesis of a bisferulate, which
791 glycidylation affords a diepoxy monomer (Figure 25). After curing with DA10, IPDA and DIFFA, properties of the
792 networks were evaluated against DGEBA systems. With DA10, the $T_{d5\%}$ are respectively 297 °C for the bisferulate
793 and 337 °C for DGEBA, which shows a better stability for the network that did not contain amide bonds. It was also
794 observed that the stability of the ester-containing network was higher, which was unexpected since amide bond is
795 considered thermally more stable. Char yield of the BDFAmide network was 18.2 % compared to 5.2 % for
796 DGEBA. The T_g of the amide containing thermoset was 69 °C, which was lower than for DGEBA (98 °C). This can
797 be due to a lower crosslinking density. It was also observed that the amide containing network has a higher T_g than
798 the ester pendant (33 °C), probably due to the hydrogen-bonding ability of the amide moiety. Mechanical properties
799 of the material were not evaluated due to the high melting point of the monomer. The measured T_g was 75 °C, half
800 the value of DGEBA network. The IPDA/BDFAmide system lead to a $T_{d5\%}$ of 282 °C (lower than DGEBA at 331
801 °C). The char yield was 18.2 %, higher than that of DGEBA (10.2 %). It can be noted that the char yield for IPDA-
802 cured amide bisferulate was similar to DA10-cured network. The cycloaliphatic or linear aliphatic amine did not
803 seem to have an influence on the char formation. The low thermal stability could most probably be due to
804 incomplete curing.
805 Finally, the use of furfurylic diamine DIFFA led to a $T_{d5\%}$ of 271 °C versus 301 °C for DGEBA, and a char yield of
806 23.7 % (14.8 % with DGEBA). The use of a furan-containing hardener increased the char yield globally, but it
807 decreased the thermal stability as compared to the aliphatic amines (char formation is promoted by aromatic
808 containing moieties, such as DIFFA). The T_g of 74 °C was similar to IPDA and DA10. The presence of furan rings
809 should increase the rigidity; however, the crosslink density was decreased dueto the structure of the DIFFA.

810

811   3.   Bisferulate with isosorbide linker
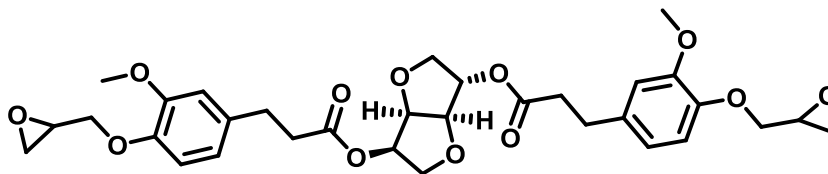
812

813   Figure 26 - Structure of the isosorbide-based bisferulate epoxy monomer by Ménard *et al.*[88]

814

815   The bisferulate based on isosorbide linker synthesized by Ménard *et al.* also provided insight into the properties of
816   bisferulate-based epoxides (Figure 26).[88] With all three hardeners, isosorbide-bisferulate networks had lower
817   thermal stabilities (lower $T_{d5\%}$) compared to DGEBA, but higher char yield due to the presence of the methoxy
818   moiety. Glass transition temperature and alpha transition temperatures were also lower than DGEBA. Comparing
819   with the other bisferulates, the T_g was lower than the amide linker, but higher than the linear ester linker (C4). But
820   the glassy moduli with DA10 and IPDA were lower for DGEBA networks. The bicyclic linker provided significant
821   higher rigidity to the networks, although the effect was counterbalanced by the crosslinking density when DIFFA
822   was used, resulting in similar modulus (around 2.0 GPa). At $T > T_g$, the elastic modulus was lower for all the
823   networks with the bisferulate than with DGEBA. Even if the bicyclic structure of isosorbide linker conferred an
824   important rigidity, it seems that at high temperature, it does not impact the mobility of the chains in order to the
825   elastic modulus high (also confirmed by the relatively low alpha transitions temperatures).
826   The endocrine activity of the bisferulate and its glycidylether derivative was assessed.[86] The activity of the
827   bisferulates at 10^{-8} M was comparable to the one of the vehicle, meaning that the diol and the epoxy monomer did
828   not show any specific activity. In addition, no dose-response activity was observed in a concentration range between
829   10^{-13} and 10^{-5} M.

830
831   4.   Trifunctional ferulic ester epoxy monomer

832
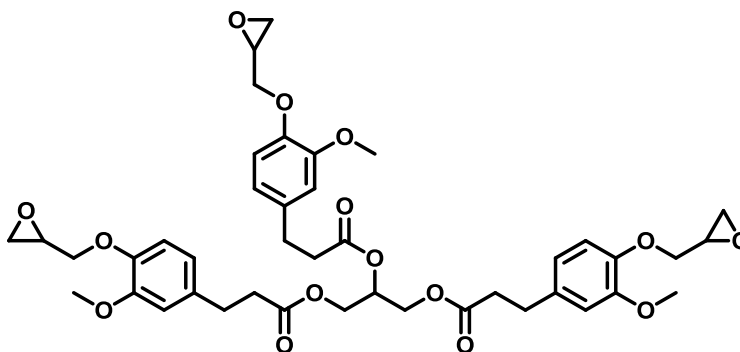
GTF

833

834   Figure 27 - Structure of the trifunctional ferulate ester (GTF) epoxy monomer synthesized by Ménard *et*
835   *al.*[88]

836   Using glycerol as the linker between ferulate residues, Ménard *et al.* also provided data about the behaviour of a
837   trifunctional monomer in different networks (Figure 27).[88] The glycerol-based triferulate GTF gave lower thermal
838   stabilities than for DGEBA for all hardeners, but higher char yields. The higher crosslinking and aromatic density
839   did not increase the thermal stability, mainly due to the presence of the fragile ester linkages, but as expected the
840   higher aromatic density did improve the char formation. Glass transition and α transitions were also lower with the
841   glycerol-based monomer than with DGEBA with all the hardeners, namely 58 °C for DIFFA, 54 °C for DA10 and
842   73 °C for IPDA (glass transition) compared with respectively 92, 98 and 150 °C for DGEBA. The same trend was
843   observed for T_α. Mechanical properties revealed different trends. With IPDA as the hardener, DGEBA and GTF had
844   the same glassy modulus (1.7 GPa) and the elastic modulus was lower for GTF (16.4 MPa vs 21.0 MPa for
845   DGEBA). With DA10, the glassy modulus was higher for GTF (2.4 GPa vs 1.0 GPa) whereas the elastic modulus
846   was almost the same (around 23-24 MPa). With DIFFA, the glassy modulus was 1.7 GPa for GTF while with

847 DGEBA it was 2.1 GPa. The elastic modulus was very low for GTF (7.9 MPa), while it was 21.2 MPa for DGEBA.
848 It seems that in the case of DIFFA, increasing the crosslinking density improves the rigidity at the glassy plateau,
849 but not too beneficial for temperatures above T_α.
850
851   5.   Bisferulate ester with side-chain containing linker
852
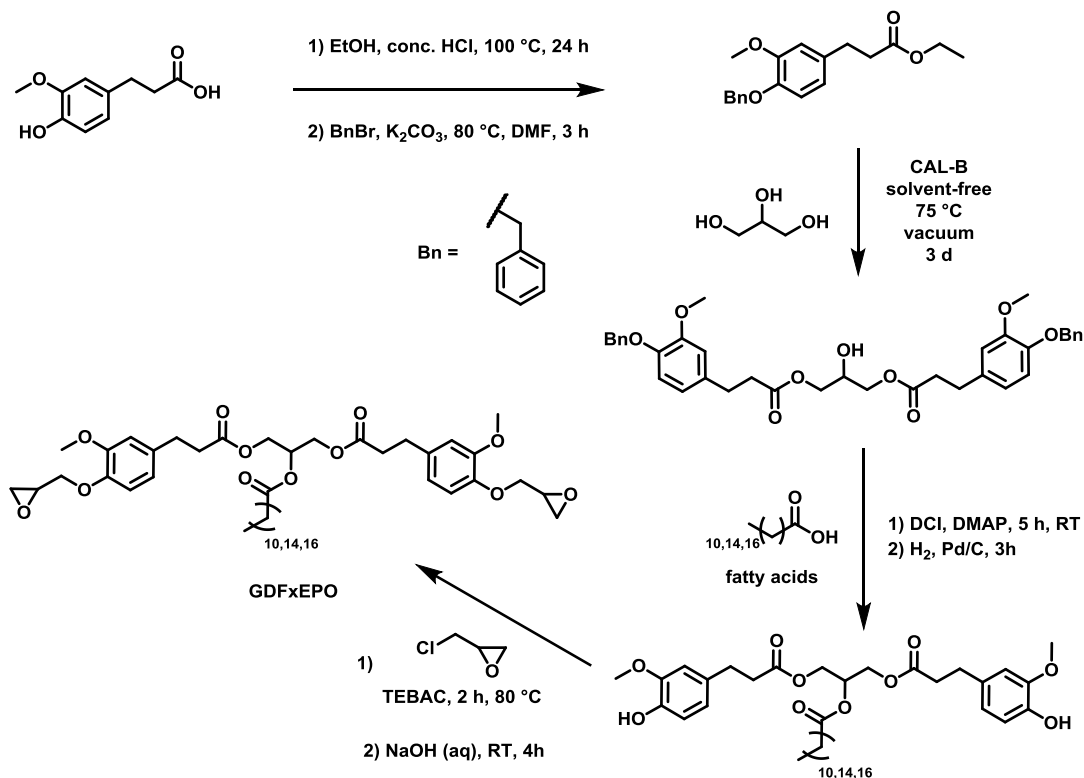
854   Figure 28 - Synthetic pathway for GDFxEPO monomers, by Hollande *et al.*[103]

855

856 Ferulic acid was also used to synthesize other diepoxides, based on a glycerol linker, but with the addition of a fatty
857 ester chain. The variation of the length of this fatty acid residue allowed Hollande *et al.* to study the influence of
858 hydrophobic properties on the degradation in acidic aqueous environment, and on the endocrine receptor activities
859 of the bisphenols (which is discussed later in this review).[103] All the monomers were denoted GDFxEPO with x
860 corresponding to the number of carbon of the fatty side chain (Figure 28). The monomers cured with DA10 led to T_g
861 between 3 and 5 °C. As a comparison, the C4 bisferulate by Ménard *et al.* led to a T_g of 33 °C, and DGEBA/DA10
862 of 98 °C.[88] The addition of a fatty acid side-chain led to a dramatic decrease of the T_g, as the side-chain acts as a
863 plasticizer. The same trend was observed with the other hardeners: DIFFA cured GDFxEPOs led to T_g between 11
864 and 16 °C as compared to 32 °C for the C4 bisferulate and 92 °C for the DGEBA. For the IPDA-based networks, the
865 T_g of the GDFxEPOs were between 18 and 23 °C, 51 °C for the C4 bisferulate and 150 °C for DGEBA. For all the
866 GDFxEPO, the char yields obtained range between 7 and 17 %, the highest obtained for DIFFA cured monomers.
867 These values were very close to the char yields obtained with DGEBA. Usually, the presence of the methoxy on
868 phenols tend to increase the char yields, but the presence of the fatty acid esters lower the aromatic density in the
869 networks, decreasing the char formation. Thus, the decrease in alkyl content increases the char in ferulic acid based
870 monomers with phenolic methoxy groups, it. The opposite phenomena is observed for DGEBA networks, since
871 there is no phenolic methoxy or long alkyl chains present in the structure. However, regarding degradation
872 temperatures (especially $T_{d5\%}$), it was observed that for the GDFxEPOs, temperatures of 280 to 310 °C were
873 measured (300-330 °C for DGEBA). The fatty chains-containing bisferulates had slightly lower thermal stabilities
874 compared to the same networks with DGEBA. In overall, the plasticizing effect of the alkyl chains led to similar
875 thermal stabilities, with lower T_g values as compared to DGEBA networks.
876 Regarding the wettability and degradation in aqueous acidic conditions, all the thermosets were evaluated by
877 measuring the contact angle, and the weight loss during incubation in 3 M HCl aqueous solution at 60 °C, up to

878 50 h. It was observed that, for all hardeners used, the water contact angle increased as the length of the fatty chain
879 increased. All the contact angles were measured between 60 and 90°, showing poor affinity with water. Hydrolytic
880 degradation was however faster for the shorter fatty acid chains. Complete degradation was observed for GDFxEPO
881 with x=10 after 50 h. No comparison with DGEBA was performed. And under alkaline conditions, barely any
882 degradation was observed for DGEBA/IPDA .[102]
883 The work of Hollande *et al.* also focused on the determination of oestrogenic affinity of the prepared bisferulates.[103]
884 Two other hormone receptors were also tested, namely PXR, a steroid receptor and AR, an androgen receptor. The
885 concentrations tested were in the range 10^{-14} to 10^{-5} M. At these concentrations, an oestrogen receptor activity was
886 recorded for the E2 hormone, and for BPA. No significant activity was observed for the GDFx (Figure 29). At
887 higher concentration, 10^{-5} M, no abnormal receptor activity was measured for all the GDFx as well as other
888 receptors (PXR and AR). Also no antagonist activity of the GDFx was recorded for all the receptors.
889
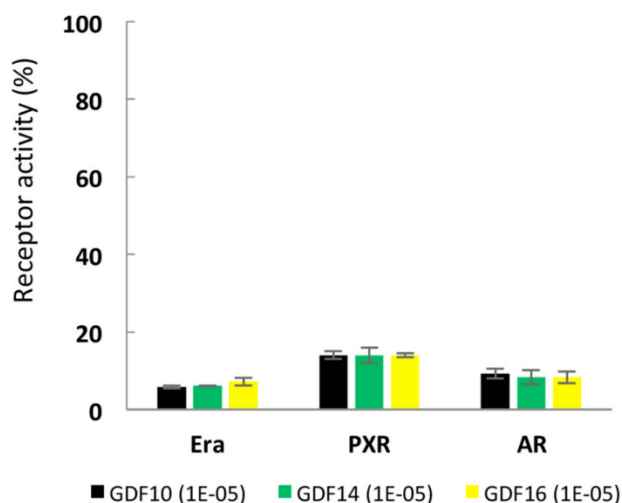
890

891 Figure 29 – *In vitro* activity of the GDFxEPO diols against several hormone receptors by Hollande *et al.*[103]

892 VI.   Resorcinol
893
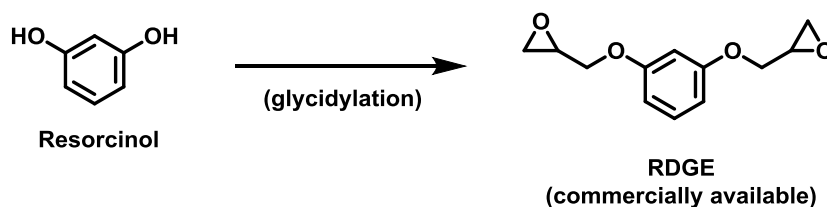
894

895 Figure 30 – Structures of Resorcinol and its diglycidylether derivative

896 Diglycidylether of resorcinol (RDGE, Figure 30) is a diepoxy monomer that has been widely reported in the
897 literature. It is composed of a monoaromatic phenolic compound, bearing two substituted phenolic hydroxyls,
898 leading to the diepoxide. This monomer has found a large range of applications, and appears in several patents. The
899 specific position of the two phenolic moieties of resorcinol gives high reactivity to the monomer. However,
900 resorcinol, that is the parent compound of the diglycidylether of resorcinol, has only been evaluated since 2016 as
901 regards to endocrinal disruption activity. It seems that resorcinol may have an effect on thyroid.[104] Recently, the
902 French health agency ANSES (Agence nationale de sécurité sanitaire alimentation, environnement, santé), has
903 recommended its classification as a SVHC for its endocrine disruption properties.[105] Since March 2022the EU
904 regulation commission has added RDGE to the list of carcinogenic and mutagenic substances.[106]
905 Resorcinol based diepoxy monomer and its homopolymer, are used in all kinds of applications given the existence
906 of more than 1200 patents and 350 research journal articles. Among these articles, only a few of them give
907 qualitative data about thermosetting epoxy, cured with standard amine hardeners. For example, Mattar *et al.* used
908 HMDA and obtained thermosets with a T_g of 80 °C and a T_α of 110 °C.[107] The modulus at the glassy plateau was 2.5
909 GPa, and at the rubbery plateau, it was 20.52 MPa. The presence of the aromatic ring inside the network led to

910   relatively high transition temperatures. As a comparison, DGEBA/HMDA network showed an alpha transition at
911   118 °C and the E' at the rubbery state was 27.4 MPa.[108] The close values between DGEBA and resorcinol
912   diglycidylether showed that the higher crosslink density with the resorcinol gave close thermomechanical properties
913   to DGEBA thermoset, even if less aromatics were in the monomer structure. In a study evaluating the effect of the
914   geometry of the monomer in epoxy-amine networks, Riad *et al.* prepared several thermosets using resorcinol
915   diepoxy, cured with several aniline derivatives.[109] They obtained high T_g with monoaromatic diamines, between 129
916   and 148 °C. They also obtained a glass transition temperature of 175 °C with a diamine containing two benzene
917   rings in its structure. The rigidity of this latter hardener, and the higher aromatic density of the obtained network
918   leads to higher T_g. As mentioned earlier resorcinol and its derivatives are not recommended and are considered as
919   endocrine disruptor.
920
921   VII.   Phloroglucinol
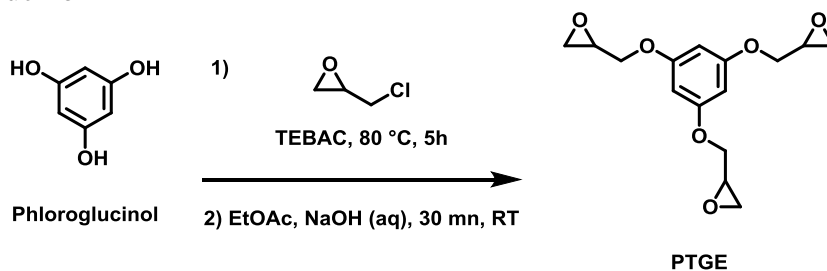
Figure 31 - Synthesis of PTGE according to Ménard *et al.*[85]

924   Phloroglucinol is a biobased phenolic compound bearing 3 phenolic hydroxyls. The structure of phloroglucinol can
925   be found in tannins.[110] This phenolic compound is also a widely used drug, especially for the symptomatic treatment
926   of abdominal pain.[111] The glycidylation reaction leads to a triepoxy monomer (Figure 31), containing generally
927   oligomers, due to the high reactivity of the phenol. More than 70 patents mention the use of PTGE (phloroglucinol
928   triglycidyletherin fiber-reinforced composites for medical prosthesis, binder for cork composites, anti-fouling
929   membranes and adhesives.
930   Ménard *et al.* used PTGE cured with several amine hardeners, and compared the thermomechanical properties with
931   and without the addition of a flame retardant.[85] The three curing agent used were DA10, DIFFA and IPDA. The
932   glass transition temperature of PTGE/IPDA network was 177 °C, compared to 157 °C for DGEBA/IPDA. This can
933   be explained by the higher functionality of the epoxy monomer, leading to higher T_g via limiting the chain mobility
934   in the network. Thus, despite the lower number of aromatic rings in the epoxy monomer compared to DGEBA, the
935   T_g value is higher. Similar trend was observed when the two other curing agents were used. The PTGE/DIFFA
936   network has a T_g of 134 °C, whereas the DGEBA/DIFFA network has a T_g of 92 °C, and the PTGE/DA10 network
937   has a T_g of 137 °C, compared to 98 °C for DGEBA/DA10.[88] The thermal stability of PTGE/IPDA was however
938   lower under nitrogen, with a $T_{d10\%}$ of 306 °C compared to 369 °C for DGEBA/IPDA. The lower aromatic content of
939   the monomer may explain the reported lower stability. Char formation was higher for PTGE networks compared to
940   DGEBA. The higher crosslinking density seems to be beneficial for the char formation using this epoxy monomer. It
941   can also be noted that without any fire-retardant additives, the PTGE networks display lower heat release rate.
942   However, the lower thermal stability of all the networks lead to fuel gas emissions at temperatures lower than for
943   DGEBA/IPDA thermoset (around 300 °C versus nearly 400 °C for DGEBA/IPDA). Phloroglucinol is known to
944   have an effect on human health since it is widely used as an anti-abdominal pain medication.[111] However, some
945   studies suggest the phloroglucinol to be potentially disruptor of thyroid receptors.[112] More studies are required to
946   verify the effect of this compound on the endocrine system.
947

948 ## VIII.   Diphenolic acid
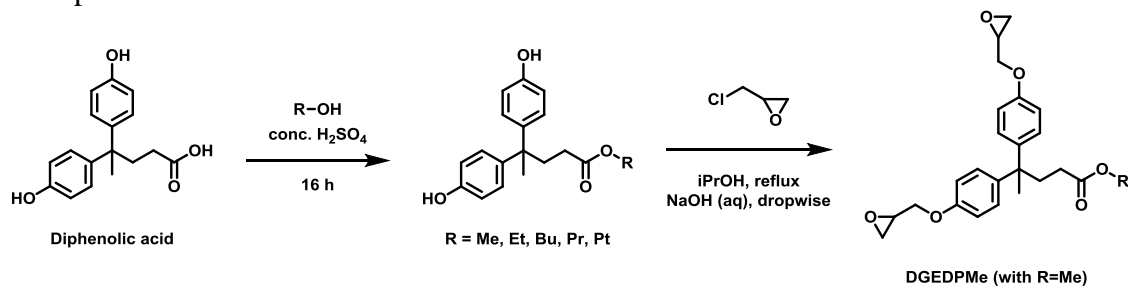
949

950   Figure 32 – Synthesis of diphenolic acid ester based epoxy monomers according to Maiorana *et al.*[113]

951   Levulinic acid is a biobased compound that can be obtained from cellulose. It is a linear carboxylic acid containing a
952   methyl ester moiety. The condensation of two equivalents of phenol with the ester leads to a diphenolic compound
953   that is very similar to BPA, but instead of having two methyl moieties between the aromatic rings, the linker is
954   composed of a methyl and a carboxylic acid terminated alkyl chain. After esterification, Maiorana *et al.* obtained
955   several monomers with different length of side chain esters (Figure 32).[113] The glycidylation of these different
956   diphenols led to several monomers noted DGEDPMe for methyl, DGEDPEt for ethyl, and two others with butyl
957   (Bu) and pentyl (Pt) side chains. The viscosities of the pure monomers were measured and compared to DGEBA, at
958   25 °C. All the monomers displayed higher viscosities (12 to 792 Pa·s), compared to DGEBA (4 Pa·s). The methyl
959   ester monomer had the highest viscosity (792 Pa·s), with several orders of magnitude above all the other esters (12
960   to 63 Pa·s), probably due to a higher oligomerisation degree, evidenced by a higher deviation of the EEW compared
961   to the other esters. It was also mentioned that from ethyl ester, viscosity decreases with the increased chain length.
962   All the monomers were cured with IPDA and compared with DGEBA. The glass transition temperatures (from the
963   peak of loss modulus) decreased as the alkyl chain increased, from 158 °C (DGEDPMe) to 86 °C (DGEDPPt), and
964   were lower than for DGEBA (165 °C). Storage moduli were measured at 25 °C. For the methyl ester, this was
965   higher than for DGEBA (2640 MPa for DGEBA and 3278 MPa for DGEDPMe). For all the other monomers, the
966   storage moduli were lower, and decreased with the increase in the chain length. Tensile properties were also
967   measured. Higher tensile strength were measured for the esters between Me and Bu, and it was similar between Pt
968   and DGEBA thermosets. Strain at break was higher with Et and Pt (respectively 9.3 and 11 %), lower for Me (4.6
969   %) and similar with Bu (8.3 %), compared to DGEBA/IPDA (8.7 %). From these mechanical properties, it can be
970   seen that the presence of the methyl ester does not act as a plasticizer, contrary to longer alkyl chains, as it is shown
971   by storage moduli and T_g decreasing with the increase in the ester length. The different behaviour of the methyl ester
972   derivative was mainly due to the presence of triglycidylated products. During the synthesis of the monomer, the
973   formation of a carboxylate resulted in addition of some epichlorohydrin on the carboxylate residue in addition to the
974   phenols. The presence of trifunctional epoxide monomer, led to an increase of the mechanical properties. This can
975   also explain the lower elongation at break, due to a more tightly crosslinked network, hence the brittleness. The
976   thermal stabilities of the networks were also assessed. The $T_{d10\%}$ were measured. These were similar for all the
977   esters, ranging from 361 to 363 °C, and slightly lower than for DGEBA (378 °C). Char yields were similar for all
978   the materials considered, between 10 and 13 %. These results show that the mechanical properties are very similar
979   for all the esters, and very close to DGEBA in the case of the methyl ester.
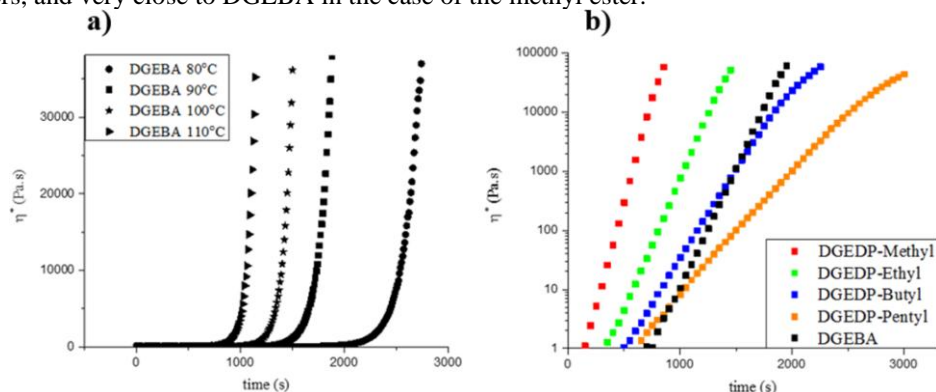

980

981   Figure 33 - Evolution of the complex viscosity as a function of cure time for (a) DGEBA at different
982   temperatures (y-axis linear scale). (b) DGEBA and DGEDP epoxies studied herein at 90 °C cure
983   temperature (y-axis log scale). Reproduced from Patel *et al.*[114]

984　Chemorheology of IPDA/DGEDP esters was also studied, and compared with DGEBA, in the work of Patel *et al.*,
985　as depicted in Figure 33.[114] Complex viscosities of formulations at 90 °C were determined, and it was shown that the
986　viscosity of the Me and Et esters increased faster than all the other formulations, including DGEBA. The induction
987　time in the rise of viscosity was longer for Bu and Pt, but lower than for DGEBA. However, once the viscosity
988　started to rise for DGEBA, the rate of the increase was faster for DGEBA than for the Pt and Bu esters. Moreover, a
989　slower rate of viscosity increase was observed for the pentyl ester. These data in addition with the kinetic studies,
990　lead to the conclusion than the pentyl ester monomer could be a good substitute for DGEBA for infusion moulding
991　applications, whereas the high reactivity of the methyl ester monomer (also containing trifunctional monomers)
992　could be interesting for adhesive applications, for which a fast reaction time is required. McMaster *et al.* cured *t*hese
993　monomers with IPDA, in addition to a propyl ester monomer, and evaluated their dielectric properties.[115]
994　Interestingly, they found that the propyl ester has a high dielectric constant (5.26 at 0.05 Hz), higher than the Bu and
995　Et esters, and especially higher than DGEBA. The DGEDPMe has higher dielectric constants, but as already
996　mentioned earlier, the thermomechanical properties are less consistent. The thermomechanical properties of the
997　DGEDPPr were also measured, with a T_g of 129 °C, strain at break of 8.3 % and tensile strength of 58 MPa. These
998　epoxy thermosets could be used as structural capacitors. Gao *et al.* studied the DGEDPMe cured with DDM.[116] They
999　measured a T_g of 153 °C for DGEDPMe/DDM, compared to 164 °C for DGEBA/DDM. The thermal stabilities of
1000　the thermosets were also quite similar under air, especially with the measure of the temperature at the onset of
1001　degradation which was 315 °C for DGEBA and 310 °C for DGEDPMe. The residual weight at 700 °C was slightly
1002　higher for DGEDPMe (2.7 % compared to 0.1 % for DGEBA). Impact strength, tensile strength and elongation at
1003　break were also very similar between both epoxy networks. Regarding flame retardant properties, the heat release
1004　rate peak was lower for DGEDPMe (520 kW·m⁻²) compared to DGEBA (711 kW·m⁻²), but the total heat release was
1005　similar, as well as smoke emission parameters (such as average smoke production rate, total smoke release or
1006　average CO production rate) were determined. Up to now the diphenolic acid based epoxy monomers have mainly
1007　been used in composites with different type of fillers such as cellulose nanocrystals.[117] Some reports have described
1008　the endocrine activity of the diphenolic acid derivatives, with R=H. Some research articles have concluded that
1009　diphenolic acid did not present any activity over several receptors, such as oestrogen receptor or androgen
1010　receptor.[118] However, some others *in silico* research suggest that diphenolic acid could be a weak ERα agonist.[119]
1011　More studies are required to assess the complete toxicological profile of this bisphenol. None of the ester derivatives
1012　have been evaluated for potential endocrine activity.
1013
1014　IX.　Triphenols
1015
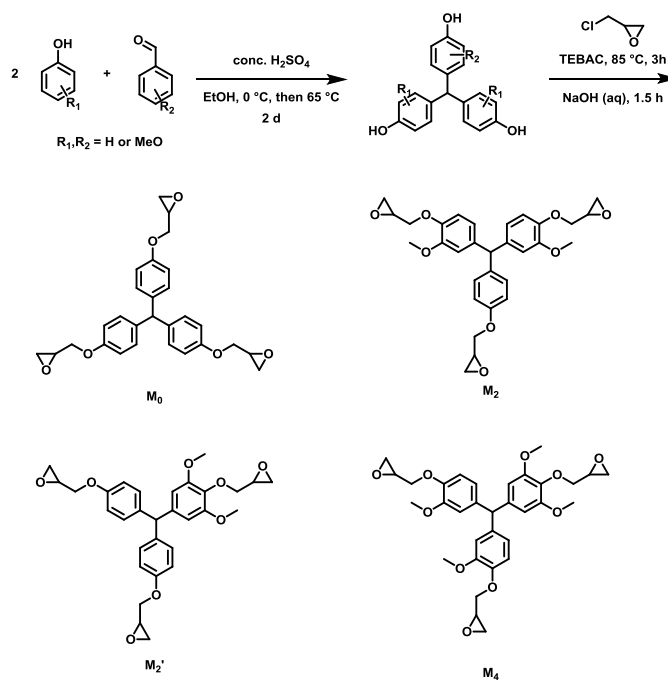
1017　Figure 34 - Synthetic scheme and structures for the obtention of triphenol epoxy monomers from Zhao *et*
1018　*al.*[53]

Zhao *et al.* used the condensation of aromatic aldehydes on phenols in order to obtain several triphenols, bearing methoxies (Figure 34).[53] From all the synthesized triphenol, they used four of them for glycidylation reactions, and obtained triepoxy monomers. Curing was performed with DETA, and thermomechanical properties were measured. All the formulations presented low temperature reactivity, as monitored by DSC. For all the monomers, the curing exotherm started around 40 °C with a peak around 80 °C. The obtained networks were characterized using DMA and TGA (Table 3.

Table 3 - Thermal and mechanical properties of thermosets studied by Zhao *et al.*[53]

| Epoxy monomer	T_α (°C)	E_{30}' (MPa)	$T_{d5\%}$ (°C)	Char yield (%)
M_0	132	2745	257	20
M_2	125	2598	206	17
M_2'	120	2249	218	18
M_4	118	2477	184	14
DGEBA	100	2042	305	8

All the results were compared to DGEBA thermoset, using the same amine hardener. As expected, alpha transitions temperatures were higher compared with DGEBA. Indeed, the higher rigidity of the monomers, due to their structures and aromatic densities, led to higher transition temperatures. Plus, the use of trifunctional monomers usually give higher transition temperatures and higher glassy moduli, due to a high crosslink density. The presence of methoxies lowered the values of transition and Young moduli. Thermal stability was also affected by the presence of the methoxy moieties. As expected, increasing the methoxy content, reduced the thermal stability. BPA-based thermoset in the absence of such methoxies, degrade at higher temperatures. Char yield however was higher for the triphenolic monomer based epoxies. The increase in char yields could be attributed to the increase in the aromatic density (compared to DGEBA). Surprisingly, the increase in methoxy functionality did not lead to an increase in char yield. In this case, the reduction of char yield with increasing methoxy content could be attributed to a lower crosslinking density. The steric hindrance brought by the methoxy groups may have a higher effect on the network structure, leading to reduced mechanical properties, compared to the doping effect on the char yield, as char formation is also highly dependent on the crosslinking density.

Tensile tests of these thermosets, and all the triphenol-based networks displayed similar maximum stress (74.9−80.0 MPa), and elongation at break of 2.55−2.68 %. As a comparison, DGEBA/DETA network showed a maximum stress of 62.2 MPa and elongation at break of 3.56 %. The triphenol networks showed a higher rigidity and a higher brittleness, due to the crosslinking density. The only evaluated compound, M_0 (under commercial name of Tactix 742.[120]) did not show any strong activity on the receptor in competitive binding assay against ERα.[121] . None of the other triphenol compounds have been evaluated so far. The work of Hong *et al.* predicts the binding affinity of a triphenol compound where the three phenols bear a methoxy group on the ortho position.[82] The compound has been predicted to be an ERα binder, with a moderate prediction confidence. However, the model could not calculate the quantitative affinity, since the monomer did not fit the receptor in the molecular docking calculations. The authors thus concluded that it is unlikely that this monomer would have a real affinity for the receptor.
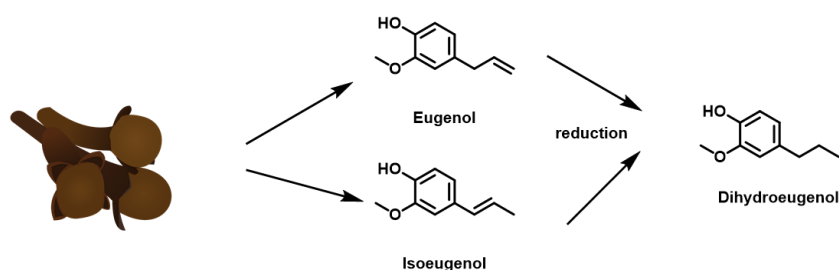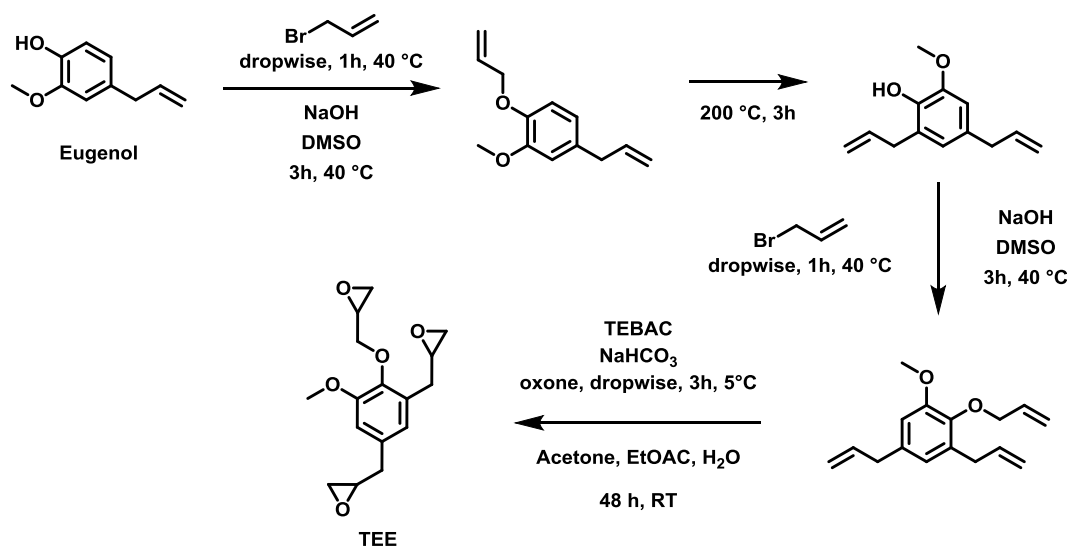
X.   Eugenol

Figure 35 - Structure of eugenol and isoeugenol from cloves, and their reduction to dihydroeugenol. These structures are epoxy monomer precursors.

Eugenol is a natural phenol, one of the main constituents of clove oil. Its structure is a phenol bearing a methoxy moiety and an allyl moiety (Figure 35). It can also be obtained from the enzymatic hydrolysis of lignocellulose. It is used in perfumes, as food additive as well as in pharmaceutics.[122] Eugenol can be easily modified to obtain diepoxy monomers, and its derivatives have been used as a starting compound, for the synthesis of thermoset polymers.

Endocrine activity of eugenol has been assessed especially in the context of the use of essential oils that have gained a growing interest in the past years. Howes *et al.* looked at the activity of eugenol on the oestrogen and androgen receptors, using enzymatic tests(modified enzymes expressing the human receptors).[123] In this work, eugenol did not show any activity against the androgen receptor. However, it did show an activity on the oestrogen receptor, but at high concentration compared to the E2 hormone. It also showed an activity towards a competitive displacement bioassay, at high concentration (10^4 to 10^5 higher than 17 β-oestradiol). Overall, eugenol showed an anti-oestrogenic activity.

1. Tri-epoxy-eugenol

Figure 36 - Synthesis of TEE from Guzman *et al.*[124] and Yoshimura *et al.*[125]

A triepoxy can be obtained from eugenol, by a multi-step process, as depicted in Figure 36.[124,125] First, eugenol is reacted with allyl bromide, leading to the allylation of the phenol moiety. Then, a Claisen rearrangement can be performed via a thermal activation. The allyl moiety grafted onto the phenol is rearranged into an allyl moiety, but on the ortho position of the aromatic ring. The further allylation of the now free phenolic moiety leads to a triallyl monomer, since eugenol is naturally bearing an allyl moiety on para position. The oxidation of the three allyl moieties leads to a triepoxy monomer (triepoxy eugenol (TEE)). Santiago *et al.* used this trifunctional monomer in order to make thermosets, with IPDA and Jeffamine D400 as the hardeners.[126] The results were also compared with the corresponding DGEBA networks.

With Jeffamine as hardener, the TEE displayed a T_g of 59 °C, which is slightly higher than with DGEBA (T_g = 50 °C). With IPDA, a more rigid hardener, the T_g of TEE was 174 °C. These high T_g values are mainly because the trifunctional TEE monomer, leading to highly crosslinked networks. This effect is favoured with the rigid diamine IPDA, compared to the use of the polypropylene-based Jeffamine. Dynamic mechanical analysis showed a similar trend. The Young's modulus at the rubbery state were 12 MPa for DGEBA/Jeffamine, 35 MPa for TEE/Jeffamine, 45 MPa for DGEBA and 214 MPa for IPDA. Tensile tests showed that the elongation at break was lower for the TEE networks as compared to DGEBA. The higher crosslinking density resulted in brittle material as the elasticity was reduced.

As observed with methoxy-containing monomers, degradation temperatures of TEE networks were lower than for DGEBA networks, under nitrogen. Using Jeffamine as the hardener, DGEBA network had a $T_{d5\%}$ of 354 °C, whereas the value for the TEE network was 314 °C. The same trend was observed with IPDA, with 348 °C for DGEBA, and 317 °C for TEE. However, the char yield was higher with TEE, thanks to the higher crosslinking density, and the contribution of the methoxy groups to the char formation. The obtained char yield were 7.6 % for DGEBA/Jeffamine and 15.4 % for TEE/Jeffamine, while with IPDA, the DGEBA had a char yield of 9.6 % as compared to 23.5 % when using TEE.

2. Dihydroeugenol diepoxy
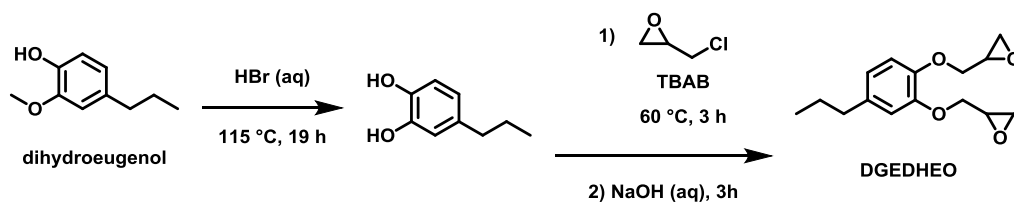
1100

Figure 37 - Synthesis of DGEDHEO from Zhao and Abu-Omar[127]

1102   Dihydroeugenol can be obtained from the hydrogenation of the double bond of eugenol, or *via* a catalytic
1103   depolymerisation of lignin, over a Zn/Pd/C catalyst. Zhao *et al.* used dihydroeugenol, and performed an ortho
1104   demethylation, in order to generate another phenolic hydroxyl, from the methoxy moiety.[127] The glycidylation of
1105   this catechol derivative leads to a diepoxy monomer (Figure 37). The authors studied the curing reaction of the
1106   diepoxy monomer with DETA, used dihydroeugenol or the catechol derivative as catalysts, and prepared composites
1107   using nanoclay. They obtained low temperature curing, with fast kinetics, with a full conversion observed by DSC.
1108   For example, 100 % conversion was obtained in less than 60 minutes. Post curing at 95 °C was however performed
1109   to ensure complete curing. DMA performed on the cured networks revealed a T_α of 40 °C, which is much lower than
1110   the reported data for DGEBA (100 °C). The Young's modulus of the DGEDHEO/DETA was 175 MPa, which is
1111   quite low, compared to the value reported for DGEBA/DETA (2 GPa). The lower transition temperature and lower
1112   modulus could be due to the low aromatic density with a mono-phenolic compound, where the propyl moiety act as
1113   a plasticizer in the network, but also causes steric hindrance. Thermal properties were evaluated by TGA, with a
1114 $T_{d5\%}$ of 190 °C, and a char yield of 3 % at 500 °C under nitrogen. These low values can be explained by the use of an
1115   aliphatic amine, leading to a low aromatic content in the network. As a comparison, DGEBA-DETA thermosets
1116   gave $T_{d5\%}$ of 305 °C and a char yield of 8 %.[53] The epoxy-amine network with DGEDHEO has been used as a
1117   matrix forming material in composites containing nanoclay as filler.[127]

1119   3. Bis-eugenyls with a methylene linker
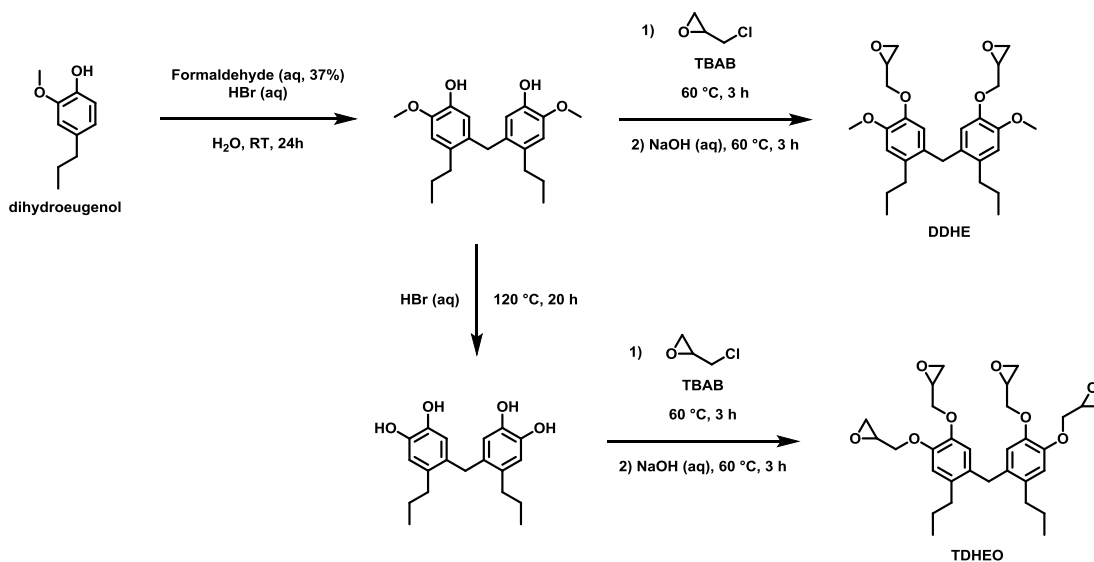
1122   Figure 38 - Synthetic pathway for the synthesis of DDHE and TDHEO monomers from Zhao and Abu-
1123   Omar[128]

1124   In a study, Zhao and Abu-Omar used two dimers obtained from dihydrogeunol.[128] First, dimerization of
1125   dihydroeugenol leads to a bisphenol, which glycidylation results in a diepoxy monomer (DDHE, Figure 388). The
1126   product from o-demethylation of dihydroeugenol, after dimerization, leads to a biscatechol compound, which after
1127   glycidylation results in a tetra-epoxy monomer (TDHEO, Figure 38). Both monomers were cured with DETA. DMA

showed a T_α of 70 °C for the DDHE/DETA network, and of 84 °C for the TDHEO/DETA network. The difference between the alpha transitions of both thermoset can mainly be explained by the higher functionality of the TDHEO network. Compared to DGEBA/DETA (T_α = 100 °C) these transitions are lower.[53] This is explained especially by the effect of the propyl moiety, which can either induce a plasticizing effect, or a steric hindrance in the network. In addition, the Young's moduli at the glassy state were 551 MPa for DDHE compared to 1441 MPa for TDHEO, indicating the important effect of the crosslinking density on the mechanical properties. The calculated crosslinking densities were 1.39 mol·dm^{-3} for DDHE and 3.28 mol·dm^{-3} for TDHEO (2 GPa for the DGEBA/DETA network) which are higher than for both of the eugenol-derived networks. Regarding thermal stability under inert atmosphere, both TDHEO and DDHE thermosets had comparable $T_{d5\%}$, respectively 245 and 235 °C, and between 10 and 11 % char yields. DGEBA/DETA network had a better thermal stability, with a $T_{d5\%}$ of 305 °C and a char yield of 8 %. As evidenced often, the presence of the methoxy moieties lowers the degradation temperatures, but increases the char formation. Koelewijn *et al.* synthesized different bisphenols from lignin derivatives, in order to further synthesize polycarbonates and cyanate ester resins.[129] These bisphenols were mainly guaiacol derivatives, which were coupled in *meta* position. Among all monomers investigated in their work, the m-m'-4-n-propylguaiacol corresponded to the bisphenol based on dihydroeugenol reported by Zhao and Abu-Omar.[128] The different bisphenols were evaluated in vitro, and compared with BPA and the E2 hormone. Results using E2 as the reference showed that the synthesized bisphenol has a lower induction potential (maximum 0.67 relative to E2), and at higher concentrations (around 10^{-6} M compared to 10^{-11} M for E2). These preliminary results should be confirmed by more type of bioassays, as well as in vivo experiments.

4. Bis-eugenyl with aromatic ether spacer
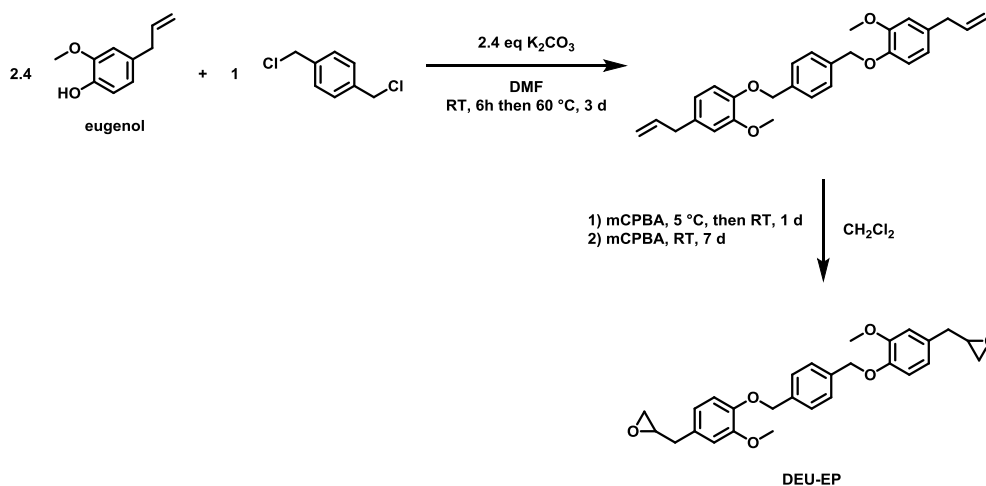
DEU-EP
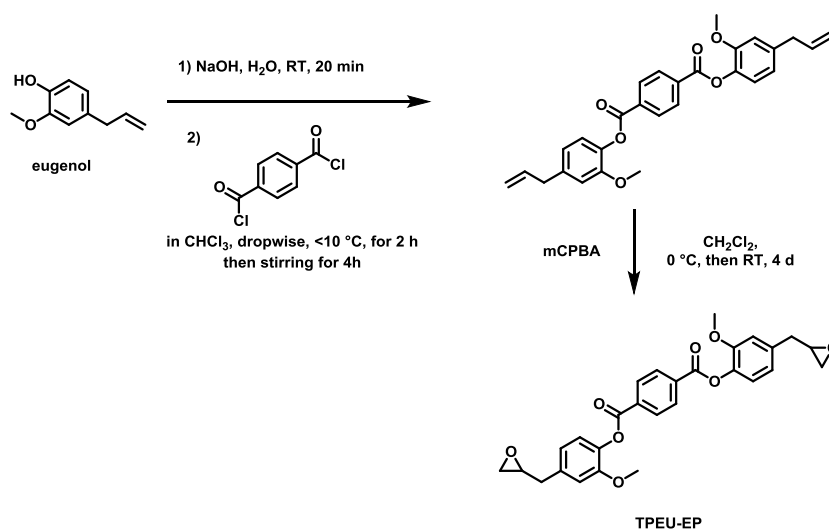
Figure 39 - Synthesis of dieugenyl monomer DEU-EP from Wan *et al.*[48]

A diepoxy monomer was synthesized by Wan *et al.* using a dichloroxylylene, reacted with the phenol.[48] This led to an etherified dieugenyl, containing an additional aromatic cycle. The epoxidation of the allyl bond of eugenol residues was then performed using *m*CPBA, in order to afford the diepoxidized monomer DEU-EP (Figure 39). Curing was performed using diaminodiphenylmethane hardener (DDM) and was compared with the DGEBA/DDM system. The curing was followed by DSC, and the crosslinking took place after successive melting of the hardener, and the diepoxy monomer. The peak maxima of the heat flux rate was nearly at the same temperature, *i.e.* 161 °C with DGEBA and 164 °C with DEU-EP. Isothermal curing kinetics revealed that, even if the total enthalpy of the curing reaction was close in both systems, a longer curing time was necessary to obtain 100 % conversion at 140 °C for eugenol-based monomer. This can be explained by a higher steric hindrance due to the presence of the methoxy moieties from eugenol residues. The mechanical properties were also investigated and compared, with a *tan δ* peak at 154 °C with DGEBA/DDM, and 114 °C with DEU-EP network. Even if the eugenol-based monomer had a higher aromatic density, the crosslink density of the material was lower, as the ether bond of the linker between eugenyls allowed a better motility of the chains, compared to DGEBA network. The crosslinking density was calculated to be 2285 mol·m^{-3} for DGEBA and 1346 mol·m^{-3} for DEU-EP, confirming the hypothesis. However, the storage moduli at the glassy plateau revealed that the dieugenyl epoxy network was more rigid and stiff at 30 °C, with values of 362 MPa for DEU-EP/DDM, and 257 MPa for DGEBA/DDM. At temperatures lower than the T_α the interaction between the polymer chains in the network seem to have a stronger effect, accompanied by the aromatic density.

Regarding the thermal stabilities, a slightly lower thermal stability was observed for the dieugenyl-based network. For the eugenol-based network, the $T_{d5\%}$ under nitrogen was 341 °C (compared to 379 °C for DGEBA). The char yield was higher than with DGEBA (38 % as compared to 18 %). Flammability tests were also performed using a microscale combustion calorimeter, with a total heat release of 16 kJ·g^{-1} for dieugenyl network and 27 kJ·g^{-1} for DGEBA/DDM. The peak temperature of heat release rate was similar, attained at 410 °C for DGEBA, compared to 406 °C for eugenol containing network. However, the peak heat release rate was 447 W·g^{-1} for DGEBA network, compared to 201 W·g^{-1} for the DEU-EP thermoset. In general, the eugenol-based diepoxy network had lower flammability, even if degradation happens at slightly lower temperature. Horizontal burning tests of the eugenol-based network showed that they were able to self-extinguish after burning for 10 seconds. This value for the DGEBA network was above 60 seconds.

5. Bis-eugenyl with aromatic ester spacer

Figure 40 - Synthesis of dieugenyl monomer with aromatic ester spacer from Wan *et al.*[130]

Wan *et al.* used a biseugenyl with an aromatic linker, based on the terephthalic acyl chloride (Figure 40).[130] They used 33DDS in order to obtain epoxy-amine thermosets and compared the results with the DGEBA network with the same hardener. They measured an alpha transition temperature of 168 °C with the dieugenyl monomer, and 174 °C with DGEBA. The storage moduli at 30 °C were 3.5 GPa for TPEU-EP and 2.7 GPa for DGEBA. The higher rigidity of the eugenyl monomer increased the storage modulus, due to the higher aromatic density and the rigidity of the ester bonds. The rubbery modulus however was lower for the dieugenyl (10.59 MPa) compared to DGEBA network (19.53 MPa). This could be due to the influence of the crosslinking density, since it was 900 mol·m^{-3} for TPEU-EP and 1640 mol·m^{-3} for DGEBA. The rigidity brought by the aromatic rings and the ester bonds of the eugenyl monomer had more influence at low temperatures, especially because of the intermolecular interactions, that could be broken at higher temperatures. At the rubbery state, the lower crosslinking density and the breaking of the intermolecular interactions between chains allowed a better molecular motility. Regarding the thermal stability, it was observed that under nitrogen and under air, the eugenyl-based thermoset degraded at lower temperatures compared to DGEBA ($T_{d5\%}$ under nitrogen were respectively 338 °C and 394 °C, and 337 and 387 °C under air). This lower degradation temperature is probably due to the presence of methoxy groups on the eugenyl residues, as well as the thermally labile ester bonds. For the eugenyl-based network the char yield under nitrogen was 32 % (14 % for DGEBA).

Burning behaviors of the thermosets were also investigating, using microscale combustion calorimetry and limiting oxygen index evaluation. The LOI of the DGEBA thermoset was 23.5 compared to 26.8 for the TPEU-EP network, demonstrating a lower flammability with the eugenol. However, even if the total heat release was lower (14.9 kJ·g^{-1} compared to 24.9 kJ·g^{-1} for DGEBA), as well as lower peak heat release rate for eugenyl (123 W·g^{-1} compared to 383 W·g^{-1} for DGEBA). The peak temperature of the heat release was 376 °C for the dieugenyl, compared to 415 °C for DGEBA network. The fact that the eugenyl thermoset degraded at lower temperature could explain the lower peak temperatures. The flammability and the thermal stability of the eugenol containing network were lower compared to DGEBA.

1209
1210   6.   Bis-eugenyls with alkyl ester or furanic ester spacers
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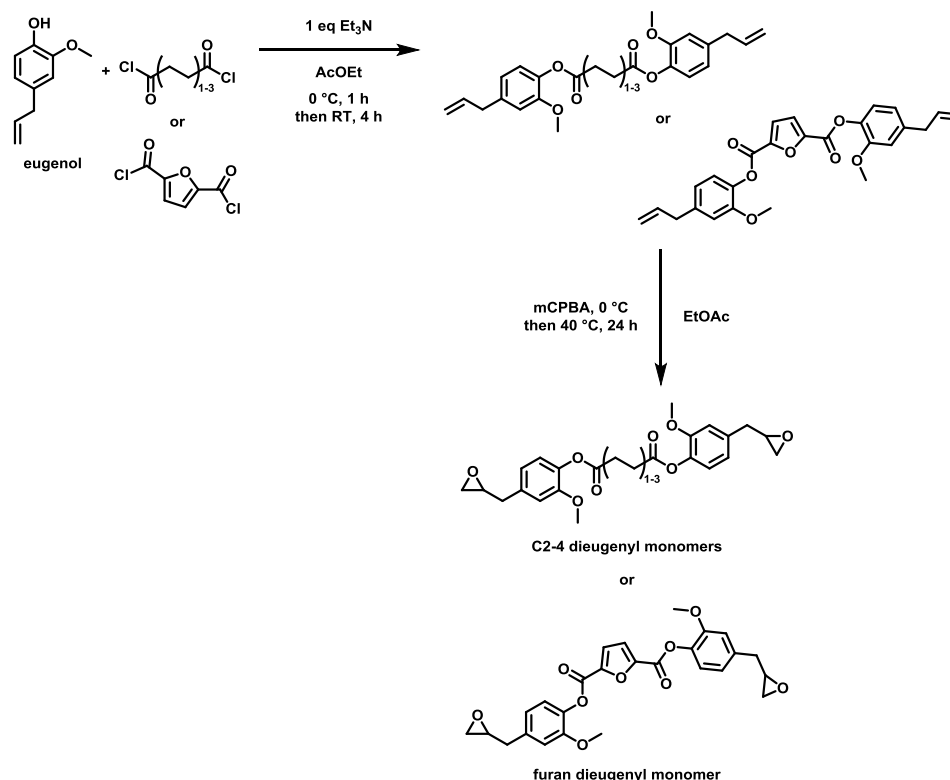
1212
1213   Figure 41 - Structures of dieunyl monomers by Chen *et al.*[131]

1214   Biseugenyls have been synthesized by Chen *et al.*.[131] They synthesized four monomers by reacting two equivalents
1215   of eugenol with diacyl chlorides, in order to obtain dieugenyls with different spacers. The obtained monomers
1216   respectively contained ethyl ester, butyl ester and hexyl ester spacers, and finally a furfuryl ester spacer (Figure 41).
1217   They performed a self-curing reaction, using catalyst, with DDM as the amine hardener. For the amine-cured
1218   networks, they obtained T_g of 118 °C, 99 °C and 91 °C for the monomers containing the C2, C4 and C6 spacers, and
1219   a higher T_g of 169 °C with the furfuryl ester spacer (higher than the 164 °C for DGEBA reported by Gao *et al.*[116]).
1220   Both the furan rings and the ester bonds bring about rigidity to the network. On the contrary, the alkyl spacers
1221   resulted in lower T_g values that were decreased with the increasing length of the alkyl chain. These results are in line
1222   with the DMA results, where T_α of 139 °C, 120 °C and 112 °C were obtained for the C2, C4 and C6 monomers
1223   respectively. These values are lower compared to the values reported by Wan *et al.* for the DGEBA/DDM
1224   system(T_α = 154 °C).[48] The furan-containing monomer had an alpha transition temperature of 181 °C, higher than
1225   DGEBA, probably due to higher rigidity. The rubbery plateau was also measured for the networks. Values of 15 and
1226   21 MPa were obtained for the alkyl containing thermosets, and 36 MPa for the furan-containing network. Regarding
1227   the thermal stability, the $T_{d5\%}$ of the different alkyl containing networks were in the range of 350-368 °C and 341 °C
1228   for the furan containing system. The char yields varied in the range of 20-25 % for the alkyl-containing thermosets,
1229   and 28 % when furan was used. The global thermal stability was thus slightly lower than DGEBA/DDM system,
1230   reported by Wan.[48] Dielectric constants were also measured for all the thermosets, at ambient temperature at1 GHz.
1231   The results were similar for the alkyl containing networks (between 3.03 and 3.08) and 3.10 for the furan-containing
1232   thermoset. Dissipation factors varied between 0.019 and 0.022 for all the evaluated thermosets. Comparing to the
1233   self-cured epoxy networks with diamine cured networks, showed higher dissipation factors when amine hardeners
1234   were used.
1235
1236   7.   Other vinylphenols
1237
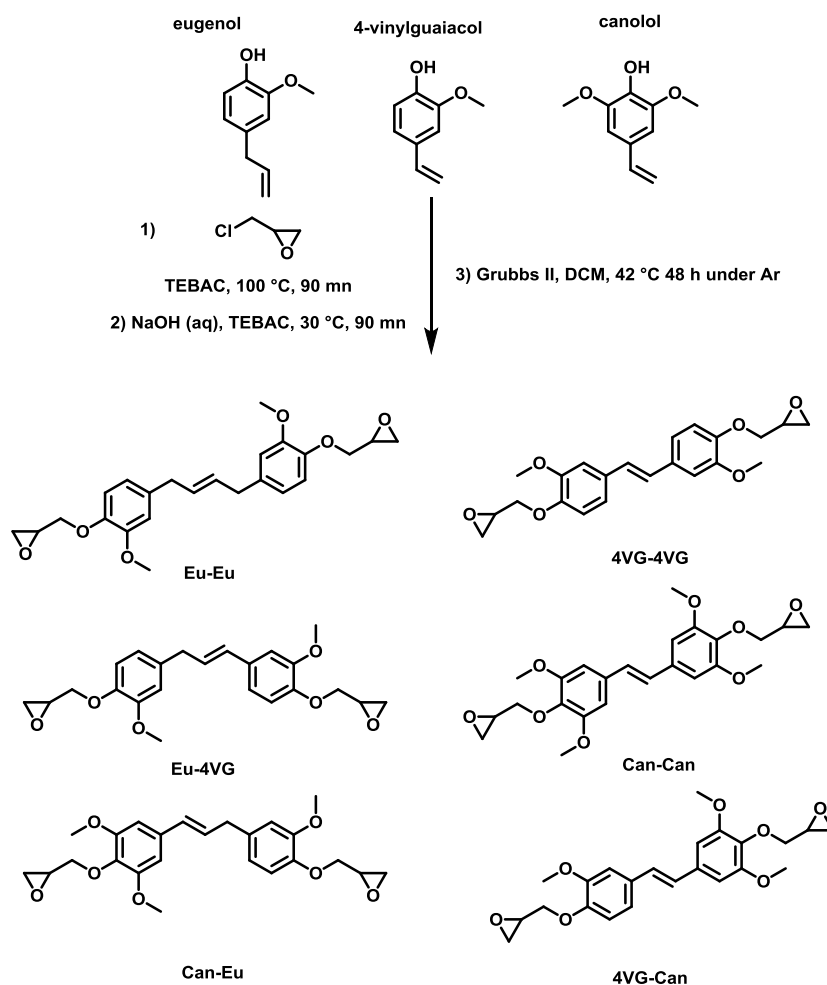
Figure 42 - Reaction pathway for the synthesis of diepoxy monomers from vinylphenols, according to Zago *et al.*[132] Nomenclature of the monomers corresponds to the different starting vinylphenols, eugenol (Eu), 4-vinylguaiacol (4VG) and canolol (Can).

Zago *et al.* designed several epoxy monomers derived from vinylphenols (Figure 42).[132] The first vinylphenol used was eugenol bearing a vinyl moiety, attached to the aromatic ring via a methylene. Two other vinyl phenols were obtained from vanillin and syringaldehyde, using the Knoevenagel–Doebner condensation reaction. The aldehyde was converted into a carbon-carbon double bond, leading to a vinyl moiety directly attached to the aromatic ring. The resulting vinyl phenols, namely 4-vinylguaiacol (from vanillin) and canolol (from syringaldehyde) were glycidylated and finally coupled, by using cross metathesis, in order to obtain diepoxy monomers. However, none of the resulting six diepoxy monomers have so far been used in thermosetting polymers.

These interesting diepoxy monomers were evaluated by computational methods, for their potential ability to bind to the ERα.[132] All the starting monophenols, the glycidylated monophenols, and all the hydrolysed epoxies were evaluated. The molecular docking data revealed that some of the compounds could interact as agonist or antagonist of the receptor. However, when interaction was probable, the dissociation constant calculated, indicated that high concentrations (at least 7 times higher) would be needed to obtain an effective binding (with BPA as the reference). Thus, it is unlikely that these compounds would have an endocrine activity at relevant environmental concentrations. However, these data are only computational, and more investigation would be necessary. In addition, in could also be interesting to generate data for the non glycidylated bisphenols, as often considered regarding BPA and DGEBA.

In the work of Hong *et al.*, two of the bisphenols synthesized by Zago *et al.* were included for prediction of the ERα binding ability.[82] The bisphenol obtained from cross-coupling of eugenol (Eu-Eu), and the compound obtained from the cross-coupling of 4-vinylguaiacol (4VG-4VG) were evaluated. The 4VG-4VG bisphenol was predicted to be a non-binder to the ERα, with a low prediction confidence. The Eu-Eu bisphenol was predicted to be an oestrogen receptor binder. The quantitative affinity that was calculated indicated a higher binding affinity than BPA. These results are consistent with the work of Zago *et al.*, which showed a potential interaction of this compound both as agonist and antagonist of the receptor.[132] However, the prediction by Hong et al. had a low confidence. In vitro

testing would provide more data to improve the predictions from *in silico* model. But these results suggest that such monomer could not meet the criteria for substitution of BPA. When these results are evaluated regarding the work on guaiacyls or syringyls discussed earlier in this paper, the results are rather consistent, especially regarding the influence of methoxy moieties.[81] The presence of methoxies on the phenolic residues do not provide enough steric hindrance to impede the binding to the receptor. The work of Hong et al. also provides prediction for bisphenols that are similar, but which could be obtained from the double-bond reduction of Eu-Eu and 4VG-4VG. The results show that these to hydrogenated bisphenols are predicted to be binder to the ERα. The absence of the double bond lead to an increased affinity with the receptor. The hydrogenated Eu-Eu is predicted to have a higher affinity than BPA, and the prediction to be binder have a high prediction confidence. The hydrogenated 4VG-4VG has a low prediction to be binder, and the quantitative affinity would be lower than BPA. The authors suggest that this result indicates a planar configuration required for the interaction with the receptor. The natural E2 has a planar configuration, and the influence of the double bond would specifically modify the ability of the bisphenol to adopt the planar configuration. Overall, the nature and the length of the bridging unit in bisphenols is also an important parameter, as previously described.[35,36]
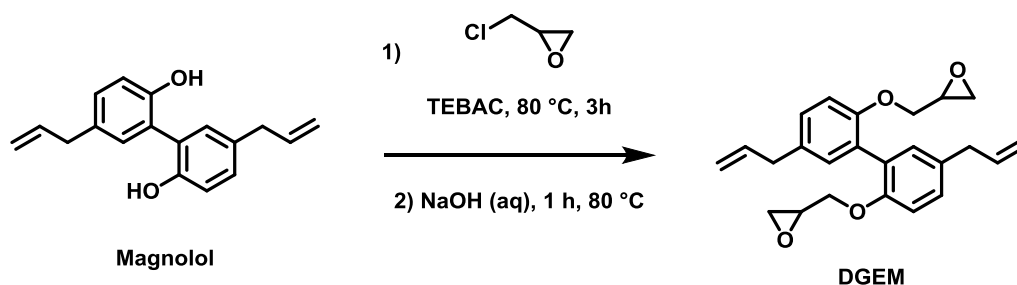
XI. Magnolol


Figure 43 - Synthesis of DGEM according to Qi *et al.*[133]

Magnolol is a natural diphenol, extracted from *Magnoliae officinalis,* bearing two allyl moieties. The glycidylation of the phenolic moieties was performed by Qi *et al.* in order to obtain a diepoxy monomer (Figure 43), that was subsequently cured with 44DDS.[133] The presence of the allyl moieties could provide the possibility of a second crosslinking via thermal polymerization, within the same temperature range used for the epoxy amine polyaddition. The DMA tests revealed an alpha transition at the peak of *tan δ* of 279 °C for DGEM compared to 231 °C for DGEBA/DDS. The Young's modulus of the DGEM at ambient temperature was 3.7 GPa compared to 2.5 GPa for DGEBA. This is mainly explained by a higher crosslinking density of DGEM, due to the further reaction of allyl moieties. The calculated values of crosslinking densities were 3.2 $kmol \cdot m^{-3}$ for DGEM compared to 2.3 $kmol \cdot m^{-3}$ for DGEBA/DDS. Flexural strength of both systems was quite similar, around 106-108 MPa, whereas the flexural modulus of DGEM was 3.5 GPa, compared to 2.5 GPa for DGEBA. This reveals the higher rigidity of the DGEM, resulting from the higher crosslinking density. The thermal stability under nitrogen atmosphere was similar for both thermoset, with a $T_{d5\%}$ of 402 °C for DGEM compared to 399 °C with DGEBA. This is an interesting result, since usually DGEBA displays a higher thermal stability. The char yield was also higher for DGEM than for DGEBA, with a value of 43 % compared to 15 %. These results show that the tetrafunctional monomer from magnolol give outstanding properties to the epoxy networks. These thermosets also had high temperature resistance, with a lower total heat release. DGEM could self-extinguish after 2.3 seconds, increasing to 4 seconds after a second application of flame. Magnolol is a widely studied pharmacological compound. Generally, it has been used in traditional Chinese and Japanese medicine and has been considered as a safe compound, with no reported adverse effects. It has antibacterial, anti-inflammatory and antioxidant activities, among others.[134,135] To the best of our knowledge, no endocrine activity has been reported for this compound.
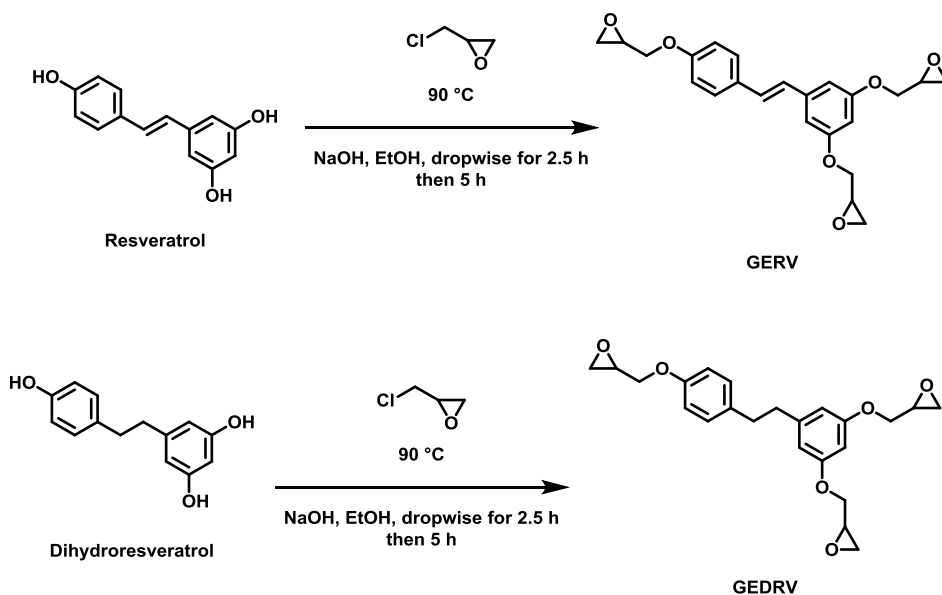
XII.   Resveratrol

Figure 44 - Synthesis of resveratrol based epoxy monomers, according to Garrison *et al*.[136]

Resveratrol is an interesting diphenolic compound that bears three phenolic hydroxyl groups. The glycidylation of those moieties lead to a trifunctional epoxy monomer. Resveratrol can be found in several vegetables, including grapes and more specifically, grape wastes.[137] Garrison *et al.* performed the synthesis of two resveratrol-based monomers, the first compound was made directly from the resveratrol (GERV), and the second from a hydrogenated form of the resveratrol (GEDRV), that originally bears a double bound between the aromatic rings (Figure 44).[136] They used two hardeners, a commercially available (DDM), and a compound prepared from resveratrol, leading to full resveratrol-based epoxy networks. The alpha transition temperature for GERV/DDM was 285 °C, whereas it was 178 °C for the GEDRV/DDM. For comparison, the DGEBA/DDM network displayed a lower T_g of 164 °C.[116] This is mainly explained by the higher crosslinked density from the trifunctional monomers based on resveratrol. Thermal stability was also evaluated, under nitrogen and under air. The $T_{d5\%}$ of both resveratrol-based thermoset under nitrogen were in the range of 355-358 °C which showed no significant difference between saturated and unsaturated monomers. The DGEBA/DDM network under nitrogen displayed a $T_{d5\%}$ of 376 °C, which is slightly higher.[138] The same range of $T_{d5\%}$ was observed under air for DGEBA or resveratrol-based networks. The char yield was superior with the unsaturated epoxy resveratrol epoxy monomer (40.5 % vs 26.1 % for saturated), and significantly lower for DGEBA/DDM network (15 %). The higher crosslinking density in the case of resveratrol-based networks improved the char formation. More recently, Tian *et al.* prepared GERV and used PACM to obtain fully cured networks.[139] In their work, they were able to obtain the monomer with an EEW of 144 g·eq^{-1} compared to 280 g·eq^{-1} by Garrison *et al.*.[136] Tian *et al.* performed DSC using several heating ramps, but did not fit the data with kinetic models in order to assess the activation energies of the curing reactions. Thermomechanical analysis was performed on cured samples, and the GERV/PACM system showed a T_α of 302 °C compared with DGEBA/PACM with a T_α of 149 °C. These results were also in agreement with the DMA analysis, giving a T_α value of above 300 °C for GERV and 161 °C for DGEBA. The glassy moduli for DGEBA and GERV networks were respectively 2, 4 GPa and 1, 9 GPa at 25 °C, indicating a higher rigidity of DGEBA network. At the rubbery state, the E' for DGEBA was 41 MPa (at 200 °C). E' could not be measured for GERV network at 200 °C but at 300 °C the value was 363 MPa. Tensile properties were also evaluated, 78 MPa for GERV network, and 64 MPa for DGEBA. Tensile strain were respectively 4.5 % for GERV and 3.7 % for DGEBA (quite similar values given the standard error). The authors did not comment about the higher Young's modulus of DGEBA compared to GERV. The crosslinking density can be considered higher in GERV since it is a trifunctional monomer. However, it does not seem to imply a higher rigidity as it could have been expected. Thermal stability of the networks was assessed by TGA under nitrogen atmosphere. The reported $T_{d5\%}$ for GERV/PACM was 320 °C and the $T_{d5\%}$ for DGEBA/PACM was 348 °C. This result is in agreement with the work of Garrison *et al.* which showed that resveratrol-based epoxies have lower thermal stability.[136] The authors did not explain the earlier degradation of resveratrol based network, but it could be because of the carbon-carbon double bond between phenol rings, that may be less stable than the isopropylidene in DGEBA. Char yield at 800 °C was however higher in GERV network

1342 (12.4 %) compared to DGEBA (4.2 %), showing that high degrees of crosslinking leads to better thermal stability at
1343 high temperature and a better ability to produce char. Non-isothermal degradation kinetics, using Kissinger's model,
1344 gave activation energy of 182 kJ·mol⁻¹ for GERV and 181 kJ·mol⁻¹ for DGEBA networks. These results show that
1345 there is probably no fundamental difference between the degradation mechanisms of the two thermosets.
1346 Surprisingly, a mixture of DGEBA and GERV cured with PACM showed a significantly higher E_α of degradation
1347 (222 kJ·mol⁻¹). However, the authors did not discuss the reason for obtaining such elevated E_α value. Cone
1348 calorimetry was used to determine the flame retardancy of the networks (LOI determination and SEM analysis of
1349 the pyrolyzed material surfaces). Higher and sharper peak was observed for DGEBA network (2.1 MW·m⁻²
1350 compared to 1.5 MW·m⁻² for GERV). LOI was also higher for DGEBA network (21 % compared to 15.7 % for
1351 GERV). These results along with high char yield indicate a better fire resistance of resveratrol-based thermosets.
1352 SEM images of the pyrolyzed materials showed homogeneous char layer in the case of GERV and an irregular
1353 surface for the DGEBA.

1354 The evaluation of the dielectric permittivity showed that the DGEBA network had a higher permittivity as compared
1355 to GERV. At the range of $10 - 10^7$ Hz, DGEBA/PACM displayed a permittivity of 4.7-4.1 F/m while GERV/PACM
1356 displayed 3.9-3.2 F/m. Generally, resveratrol-based epoxy monomers have very good thermomechanical properties
1357 as well as a fair thermal stability, although lower than that of DGEBA. Resveratrol is a compound that is widely
1358 studied for its pharmacological properties. It has been associated with protective cardiovascular effect in vitro and in
1359 animals. It has also been studied in several clinical trials for its potential effect on cardiovascular diseases, cancer,
1360 neurodegenerative or metabolic diseases. It is also sold as a dietary supplement, for its antioxidant activity.
1361 However, a recent review warns that resveratrol is a phytooestrogen. The review collected evidence regarding the
1362 activity of resveratrol on the ERα in humen.[140] In this work, Qasem concluded that the effect of resveratrol on the
1363 oestrogen receptor is not always reported in studies, since its effect on the endocrine system may arise from repeated
1364 exposure.

1365 In the work of Hong et al., resveratrol and dihydroresveratrol were evaluated for their binding affinity with the ERα,
1366 using *in silico* methods.[82] Resveratrol is considered to be a binder to the receptor, with a calculated affinity that is
1367 lower than BPA, but slightly higher than BPF. This is consistent with the fact that resveratrol is a phytooestrogen,
1368 thus it shows affinity with the oestrogen receptor. However, the calculations for dihydroresveratrol revealed no
1369 binding affinity underlining the effect of the bridging unit between the phenol rings.

XIII. Flavonoids
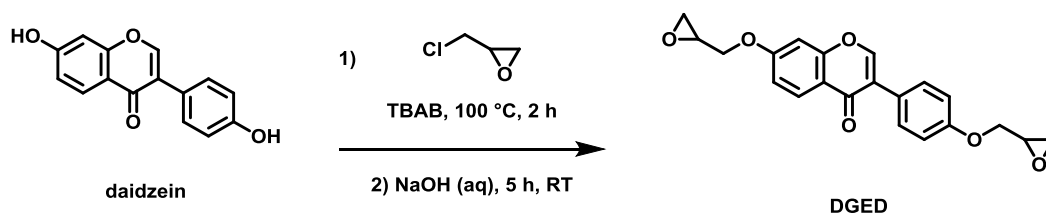
1. Daidzein

Figure 45 - Synthesis of DGED, according to Dai *et al.*[141]

1377 Daidzein is an isoflavone found in soybean biomass.[142] It is used in the food and pharmaceutical industry. The
1378 bisphenolic nature of this compound led to its use as a building block for the synthesis of a diglycidylether. Dai *et*
1379 *al.* performed the synthesis of the monomer (Figure 45), and studied the properties with DDM as the curing agent,
1380 and compared it with DGEBA network.[141] Among the different properties studied, it was found that the DGED had
1381 an alpha transition of 205 °C with DDM, which was higher than the measured for DGEBA/DDM network (172 °C).
1382 The Young's modulus at 25 °C was 2.8 GPa (2.4 GPa for DGEBA). These properties are mainly due to the high
1383 crosslinking density, which was found to be 6.4 mol·m⁻³ for DGED as compared to 3.5 for DGEBA/DDM. Other
1384 mechanical properties were also measured, such as tensile strength and moduli, and also flexural strength and
1385 moduli. In all cases, the thermoset from DGED were superior to DGEBA. Thermal stability under inert atmosphere
1386 was lower, since the $T_{d5\%}$ for DGED was 335 °C, compared with DGEBA network with a $T_{d5\%}$ of 384 °C. The same
1387 trend was observed under oxidative atmosphere. This is mainly due to the presence of the heterocycle in the
1388 structure of daidzein, which may degrade first. However, regarding the char yield at 800 °C, the DGED had a
1389 remarkable superior char formation, 43 % compared to 16 % for DGEBA. The DGED also had low flammability,
1390 with a superior LOI of 31.6 % (compared to 24.5 % for DGEBA), and an ability to self-extinguish within 13

seconds. Daidzein is a phytooestrogen, which means it may have the potential to be agonist or antagonist to the oestrogen receptor.[143] It is well known that the consumption of soybean products may interact with the endocrine system, and daidzein is one of the compounds such a kind of effect. More specifically, daidzein is metabolized into equol that has even more activity. But compared to the natural hormone E2, these activities are lower and happen at higher concentrations (Figure 46).[144] It is also important to note that the mode of exposition between the consumption of soy products and the exposition from the use of epoxy thermosets would be very different. The effect on human health of the ingestion of daidzein and other isoflavones were extensively reviewed by Křížová *et al.*.[143]
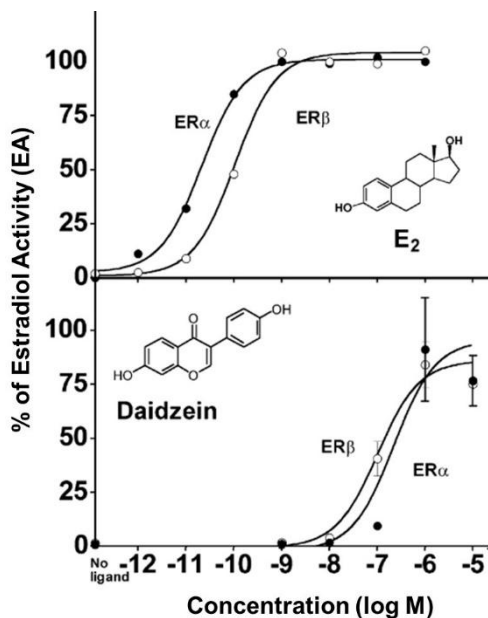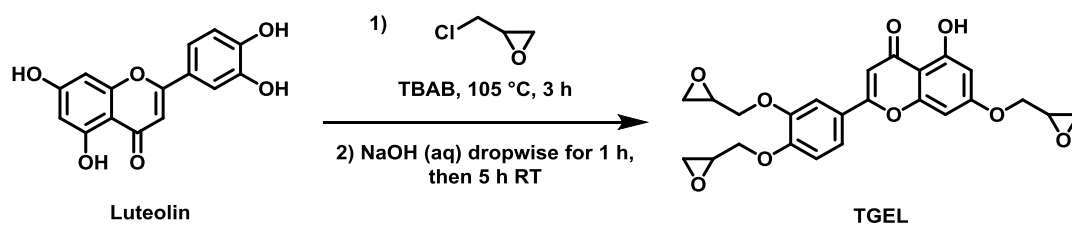

Figure 46 - *In vitro* activity of daidzein and E2, adapted from Muthyala *et al.*[144]

2. Luteolin

Figure 47 - Synthesis of TGEL from Luteolin according to Gao *et al.*[145]

Luteolin is a natural flavonoid that can be found in herbs such as thyme, sage or oregano, in some types of celeries or radicchio, and in lower quantities in beets, Brussel sprouts and lemons.[146] It has shown some anti-microbial activity, anti-inflammatory properties and is considered to have a chemotherapeutic potential.[146] The chemical structure of luteolin is a polyphenol comprising a heterocycle, a resorcinol unit and a pyrocatechol unit. It leads to a compound bearing 4 phenolic hydroxyl moieties (Figure 47). However, only 3 are reactive towards glycidylation since one of the phenolic moieties is blocked by hydrogen-bonding with the carbonyl moiety, as shown by Gao *et al.*.[145] The glycidylation reaction lead to a trifunctional epoxy monomer named diglycidylether of luteolin (DGEL) in the original publication, but that will be referred to as triglycidylether of luteolin (TGEL) in this article. The monomer was subsequently cured with DDS to afford epoxy thermosets. The curing reaction was first assessed by non-isothermal curing kinetics using Ozawa and Kissinger methods, and compared with DGEBA/DDS system. Good correlations were obtained with both methods, and DGEBA/DDS showed a lower activation energy than TGEL/DDS (60.7-65.5 kJ·mol^{-1} for DGEBA/DDS *vs* 64.8-69.0 kJ·mol^{-1} for TGEL/DDS). According to the authors, the lower activation energy was mainly due to the high functionality of the monomer. The thermal stabilities of the

networks were evaluated by TGA under nitrogen and air. In both cases, DGEBA/DDS systems showed a higher $T_{d5\%}$ (393 °C under N_2 and 374 °C under air), compared to TGEL/DDS (379 °C under N_2 and 346 °C under air), due to an early decomposition of the heterocycle in TGEL. Both networks exhibit similar degradation pathways. Under inert atmosphere, DGEBA/DDS and TGEL/DDS show a single main decomposition step. During this step, the weight loss for DGEBA/DDS was higher than in TGEL/DDS, resulting in a low char yields for DGEBA/DDS, at 700 °C (12 % for DGEBA and 44 % for TGEL). Under oxidative atmosphere, the same trend was observed, with two decomposition steps for all networks, but with a first weight loss at lower temperature for TGEL than for DGEBA. The higher functionality and higher aromatic density of TGEL lead to more char yield under nitrogen, and a delayed decomposition of the material. Several mechanical properties were assessed, such as dynamic mechanical and tensile properties. DMA revealed an alpha transition of 314 °C for TGEL/DDS network, which is a high value, compared to DGEBA/DDS with a T_α of 217 °C. The Young's modulus at the glassy plateau at 30 °C were 3.8 GPa for TGEL and 2.7 GPa for DGEBA networks. The high value for TGEL has to be balanced with the fact that a high loss modulus was observed before 100 °C, with a value inferior to 3 GPa at this temperature. The same trend was observed with DGEBA. The rubbery values of Young's modulus were 2.1 GPa for TGEL/DDS and 50 MPa for DGEBA/DDS, illustrating high stiffness of the TGEL. This is in agreement with tensile tests giving lower elongation at break for TGEL (9.5 %) compared to DGEBA (10.8 %), but a higher tensile strength with TGEL compared to DGEBA networks (respectively 69.2 MPa and 57.2 MPa). Surprisingly the crosslinking density of TGEL/DDS network was 1.5 kmol·m^{-3} whereas it was 2.2 kmol·m^{-3} for DGEBA/DDS network. This could be due to the high molecular weight of the epoxy monomer, and to its non-symmetric structure, leading to a lower global crosslinking density. Flame retardant properties were extensively evaluated by Gao et *al.*, using microscale calorimetry, LOI tests, TGA-FTIR and Pyrolysis-GC/MS. MCC revealed a lower total heat release for TGEL/DDS than for the DGEBA network (24.3 kJ·g^{-1} for TGEL vs 29.1 kJ·g^{-1} for DGEBA). The heat release capacity of DGEBA network was four times higher than for TGEL (respectively 399 J·g^{-1}·K^{-1} and 101 J·g^{-1}·K^{-1}). The LOI value of the TGEL network was 32.5 % whereas it was 27.0 % for DGEBA. Raman spectroscopy showed that TGEL network displays a higher graphitization degree after pyrolysis, which is a desirable property when using char-forming material. Decomposition studies showed that DGEBA/DDS could release more aromatic compounds than TGEL/DDS network, indicating that most aromatic compounds stay in the condensed phase. Among all the biological mechanisms of endocrine system, sulfonation of steroids by sulfotransferase enzymes is part of the oestrogenic system. Indeed, the sulfonation of steroids lead to a change in their properties, for instance, oestrogen sulfonates are no longer agonist to the oestrogen receptor.[147] Thus, any activity on these enzymes could affect the endocrine system, and have indirect endocrine disruption potent.

Waring *et al.* evaluated several phytooestrogen or xenooestrogen as inhibitors to sulfonotransferases.[147] The inhibition potent of several flavonoids were tested on SULT 1A1, and luteolin enzymes showed an IC50 of only 3 nM, but did not show any inhibition activity for SULT 1A3 (a sulfotransferase), at submicromolar scale. It had also no effect on the SULT 2A1 activity. These findings were in agreement with a previous study.[148] In the work of Waring *et al.* it was shown that for some enzymes, the inhibition potent of flavonoids is several orders of magnitude superior to the synthetic compounds such as alkylphenols or phthalates.[147] The authors noted that for example supplementation with flavonoids may not be universally beneficial, since the addition of exposition to synthetic endocrine disruptors, naturally occurring flavonoids in diet and supplementation may lead to increased risks of cancer. In another work, Nordeen *et al.* also highlighted luteolin as a multi-functional endocrine disruptor, with a potent progesterone antagonist and oestrogen agonist activity.[149] They assessed the effect of luteolin on the steroid signalling, using T47D cell lines expressing oestrogen and progesterone receptors. The authors also signal out that use of flavonoids supplements could be dangerous for patient with certain type of cancers. Surprisingly, a study described the protective effect of luteolin against bisphenol A toxicity, in drosophila.[150] The protective effect has been partly attributed to the antioxidant properties of luteolin.

XIV. Cardanol and Cardol
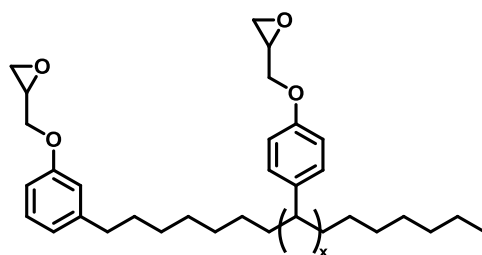
NC-514

Figure 48 – Cardanol-based polyepoxide commercial monomer NC-514 idealized structure, according to Jaillet *et al.*[151]

Cardanol is an interesting natural phenolic compound, extracted from the cashew nutshell oil, which is a by-product of cashew nut production. This vegetable oil has the advantage of providing biobased aromatics, with alkyl chain, allowing the possibility to design new building blocks, especially for polymers.[152] Cardanol based epoxy resins from Cardolite NC-514 (Figure 48), showed interesting properties. In a paper published by Jaillet *et al.*, its networks with IPDA and Jeffamine were studied.[151] The structural characterization led to the conclusion that NC-514 was mainly composed of diepoxy monomers, with a small percentage of unsaturated compounds. The epoxy structure with cardanol was composed of a phenol ring, with a C15 alkyl chain attached on the *meta* position. Natural cardanol has unsaturated bonds, which was reacted with phenol in NC-514. This leads to the attachment of another phenol, as a side-group of the alkyl chain. The phenol substitution led to a low unsaturation degree in the formulation. Both phenolic moieties from the natural cardanol, and the pending phenolic side-groups were then substituted by a glycidyl moiety, leading to a difunctional epoxy resin. In this work the EEW was determined around 363 eq·g^{-1}. Jaillet *et al.*, studied the formulations of NC-514 with diamine hardeners with higher gel content. Network made using NC-514 and IPDA had a T_g of 50 °C (with 90 % gel content). When NC-514/Jeffamine D400 was used the T_g was 15 °C (with 90 % gel content). As a comparison, the DGEBA/IPDA network had a T_g of 158 °C. Regarding the mechanical properties, a T_α of 59 °C was obtained for NC-514/IPDA, and 9 °C for Jeffamine D400/NC-514. DGEBA/IPDA network had a T_α of 158 °C and DGEBA/Jeffamine network had a T_α of around 50 °C as reported by Soares.[153] The presence of long alkyl chain, especially the pending end chain from cardanol after crosslinking, endows plastifying properties that lead to a low glass transition temperatures to the epoxy network. At the glassy state, a Young modulus of 1.2 GPa for NC514/IPDA and 7 MPa with Jeffamine were recorded (compared to 1.4 GPa for DGEBA/IPDA). The use of polyether-based hardener, Jeffamine, led to a sharp decrease in Young's modulus at the glassy state as compared to when cardanol was used. However, at the rubbery state, the difference of Young's modulus was more pronounced for IPDA based networks, with E' of 19.6 MPa for DGEBA and 3.2 for NC-514 (close to the value of NC-514/Jeffamine, of 2.6 MPa). It could be presumed that at the glassy state, the global network is more affected by the presence of rigid moieties (aromatic rings), and the hardener (for IPDA networks). While at the rubbery state, the presence of alkyl chain results in increased mobility and low crosslinking density.
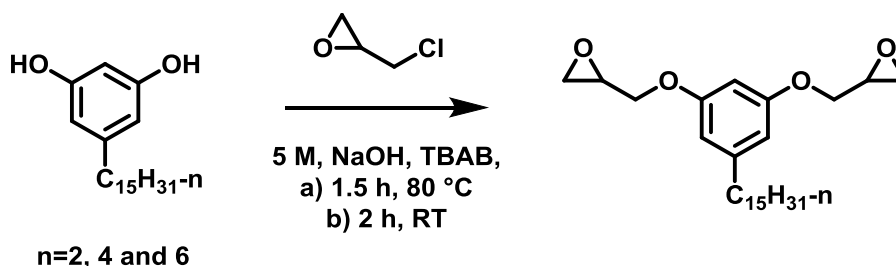
Figure 49 - Synthesis of diglycidylether of cardol by Makwana *et al. [Cite 10.1016/j.eurpolymj.2022.111029]*

Besides cardanol, cashew nutshell liquid also contains cardol, which differs from cardanol mainly by bearing an additional phenolic hydroxyl moiety. Makwana et al. took advantage of this difunctionality by preparing a diepoxy monomer by direct glycidylation of cardol, as shown in Figure 49. [Cite 10.1016/j.eurpolymj.2022.111029] The

diepoxy monomer was used with two amine hardeners, namely DETA and IPDA. Several formulations based on the DGEC (diglycidylether of cardol) in mixture with DGEBA were also performed and cured with IPDA. Pure DGEBA resins were also prepared with both hardeners. Focusing on materials containing pure DGEC as the epoxy monomer, the authors reported an EEW of 215 $g \cdot mmol^{-1}$, and a multi-step curing procedure was adopted. Using non-isothermal DSC, the monitoring of curing reactions revealed that DGEC displayed lower curing exotherms than DGEBA, when cured with both amines. After curing, the crosslinked materials also revealed lower $T_g s$, respectively 63 °C for DGEC-IPDA and 45 °C for DGEC-DETA, compared to 155 and 145 °C for the corresponding formulations using DGEBA. The plastifying effect of the C15 alkyl chain drastically decreases the glass transition temperatures of cardol-based materials. Thermal stability under inert atmosphere of DGEC resins displayed very similar values compared to the DGEBA pendent. Indeed, while DGEC-IPDA and DGEC-DETA show Td5% of 359 and 348 °C, the corresponding DGEBA networks displayed respectively Td5% of 349 and 350 °C. However, char formation of DGEC was significantly lower, respectively 3.4 and 4.8 % with IPDA and DETA, whereas for DGEBA it is 9.3 % and 9.8 % with IPDA and DETA. This again can be explained by the presence of long alkyl chain in cardol, that greatly decreases the aromatic density in the materials compared to DGEBA. Besides the plastifying effect of these alkyl chains revealed by DSC, mechanical properties also confirmed the trend, when determined by DMA and tensile testing. Cardol-based materials prepared with IPDA displayed a T_α of 74 °C (154 °C with DGEBA), a Young's modulus of 0.75 GPa (compared to 2.4 GPa with DGEBA). The tensile strength measured was 23 MPa and the elongation at break was 9.7 % at 1 $mm \cdot min^{-1}$. The same formulation with DGEBA had a tensile strength of 75 MPa and an elongation at break of 3.1 %. Regarding materials prepared with IPDA, the same trend is observed. DGEC materials displayed a T_α of 67 °C (132 °C with DGEBA), a Young's modulus of 0.52 GPa (2.24 GPa with DGEBA). Again, tensile testing revealed a tensile strength of 11.82 MPa (65 MPa with DGEBA) and an elongation at break of 5.1 % (compared with 2.8 % for DGEBA). All those mechanical properties indicate that DGEBA based materials are stiffer than DGEC based one, that display a more elastic behaviour. The authors also analysed the cryo-fracture of samples by scanning electron microscopy, assessing that all materials appear homogenous, indicating that no phase separation occurs during processing.

While phenolic compounds extracted from cashew nutshell liquid have a very different structure compared to bisphenol A, it is still interesting to survey literature about endocrine activity. Interestingly, some cardanol derivative has been tested in YES and YAS agonist and antagonist assays. [Cite https://dx.doi.org/10.1016/j.indcrop.2018.12.060] These assays were performed in comparison with phthalates, that are also endocrine disruptors, and widely used as plasticizers. Contrary to the phthalates, epoxidized cardanol derivatives did not show any activity, or non-significant activity. While these tested structures are relatively different than the monomers studied for epoxy amine networks, it is worth mentioning.
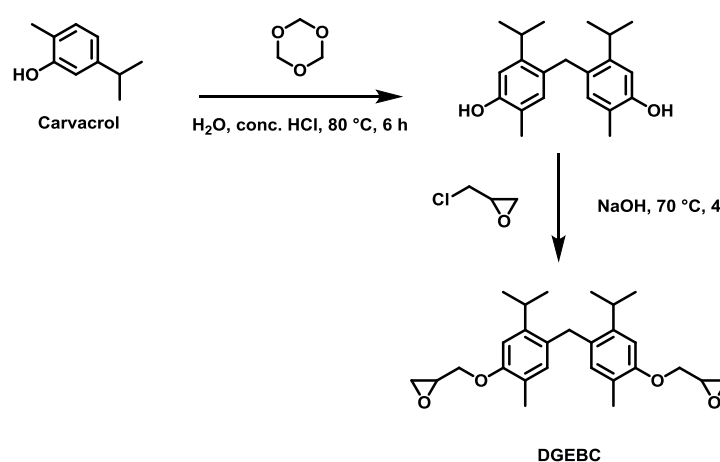
XV.   Carvacrol

Figure 50 - Synthesis of DGEBC from carvacrol

Carvacrol is a terpenoid phenolic compound that is found in oregano oil, or synthesized from cyclic monoterpenes such as *p*-cymene. In 2016, Harvey *et al.* synthesized a bisphenol from carvacrol and a formaldehyde source, trioxane.[154] Garrison and Harvey then used this bisphenol in order to synthesize a diepoxy monomer (diglycidylether of biscarvacrol (DGEBC), Figure 50), and also a diamine.[138] The use of diamine and DDM as hardener with the new

epoxy monomer was studied. For DGEBA/DDM network, T_g was 179 °C whereas it was 161 °C for DGEBC/DDM, as evaluated using DSC measurements. These similar values and the lower values of DGEBC may be due to modest plasticizing effect of the isopropyls. Thermal stability of the cured networks was assessed using TGA both under air and nitrogen. Under nitrogen, $T_{d5\%}$ were 367 and 376 °C for DGEBC and DGEBA cured with DDM. Similar values were obtained when analysis was performed under air. Char yield under nitrogen for DGEBC and DGEBA cured with DDM was 10 - 20 % for DGEBA and less than 10 % with DGEBC. It should be noted that, biscarvacrol contains two isopropyl and two methyl groups on the aromatic rings that degrade at lower temperature thus do not contribute towards char formation.

As discussed earlier Hong *et al.*, evaluated a wide set of potential substitutes of BPA for their binding affinity with ERα using an *in silico* method.[82] This method allowed for the qualitative and quantitative prediction of the binding ability of each compound, as well as the quantitative affinity if considered a binder. The biscarvacrol was part of this set, and it was predicted to be binder. The calculated affinity was 100 times higher than BPA, indicating a strong receptor binder. However, the certitude of the prediction was very low.

Furanics
I. Furan dicarboxylic acid
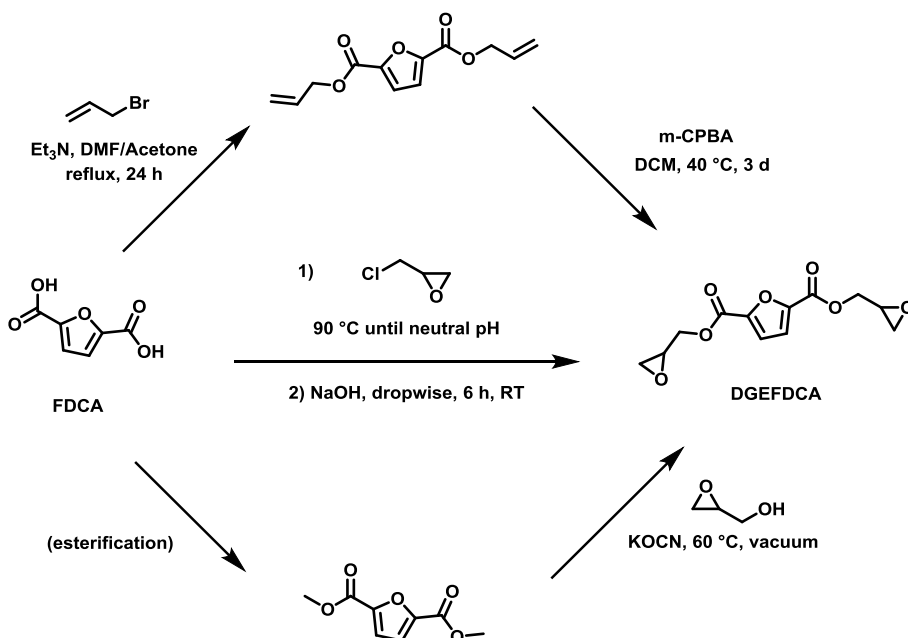
Figure 51 – Several synthesis pathways of DGEFDCA from furandicarboxylic acid

A diepoxy monomer can easily be obtained from furandicarboxylic acid (FDCA). Several synthesis pathways have been reported to date (Figure 50). The first path involves the allylation of both carboxylic acid moieties. The diallyl is then epoxidized with meta-chloroperbenzoic acid to afford the diepoxy monomer.[155] Two other pathways are also available, as reported by Marotta and co-workers.[156] First, the direct glycidylation of the dicarboxylic acid, reacted with epichlorohydrin. Second, transesterification can be performed on the dimethyl ester of the FDCA, with glycidol, using potassium cyanate as a low toxicity catalyst. Several research articles described the properties of networks with DGEFDCA, using different hardeners. Deng *et al.* used two hardeners, an anhydride, and a polyether diamine (commercially known as D230 or Jeffamine D230). This amine is a polypropylene based oligomer of approx. 230 g·mol^{-1}.[155] DGEFDCA cured with D230 led to a T_α of 101 °C, as compared with a DGEBA/D230 network with T_g of 98 °C as determined by Ma and co-workers.[157] When using aromatic amines, such as 33DDS and 44DDS, higher T_g values of 176 °C and 215 °C were obtained. DGEBA/33DDS had a T_g of 184 °C and DGEBA/44DDS of 238 °C.[55] Comparing curing with aromatic amines and polyether amines, the obtained T_g values were very similar to the DGEBA networks. In the recent work of Liu *et al.* the curing of DGEFDCA with DDM showed a higher T_α than the equivalent DGEBA, namely 156 °C for the furan-based network, compared to 124 °C.[158] Indeed, higher crosslink densities were obtained with DGEFDCA (1.9 mol·dm^{-3}) compared to DGEBA/DDM with 0.3 mol·dm^{-3}. The higher molecular weight between crosslinks in the DGEBA thermoset led to a higher chain

mobility in the network. In addition, hydrogen bonding with the furanic ring, increases the rigidity of the network at low temperatures. Higher crosslinking densities with 33DDS and 44DDS were also measured. Mechanical properties of DGEFDCA cured with DDM were also higher than for DGEBA network, with a storage modulus at the rubbery state (22.3 MPa compared to 2.69 MPa for DGEBA). The networks with 33DDS and 44DDS gave similar results both at glassy and rubbery states. Elongation at break, tensile strength and the shore hardness were slightly better for the furanic based network compared to the DGEBA/DDS systems. The rigidity that is brought by the furan moiety seems to be beneficial for the mechanical properties of the cured thermosets. Mechanical properties for networks with D230 were also investigated. The obtained flexural strength was lower for DGEFDCA thermoset, with a strength of 75 MPa, compared with 121 for DGEBA. The flexural moduli was 2.5 GPa for DGEFDCA/D230 and 2.95 GPa for DGEBA/D230.[155] The flexural tests performed on networks with different hardeners demonstrate that DGEFDCA networks are stiffer and more brittle compared to DGEBA networks. The thermal stabilities of the networks were also evaluated under inert atmosphere. For the D230 networks, the $T_{d5\%}$ of DGEFDCA was 267 °C and the char yield 6.8 %, compared to DGEBA/D230 with $T_{d5\%}$ of 366 °C and char yield of 4.4 %. The DDM network led to $T_{d5\%}$ of 326 °C and char yield of 28.1 % for DGEFDCA. Finally, for DDS cured materials, the $T_{d5\%}$ was 324 °C for both 33DDS and 44DDS with DGEFDCA, and respectively 27 and 18 % char yields, compared to 405 and 397 °C for DGEBA/33DDS and DGEBA/44DDS with 20 and 14 % char yields. As discussed earlier, the furan-based thermosets have lower degradation temperatures, but higher char yields. The work of Meng *et al.* also focused on fire resistance behaviour of the thermosets. They reported that the total heat release of DGEFDCA based networks was lower than DGEBA networks. They also showed that the heat release capacities were lower with the furanic epoxide, namely 132 J·g⁻¹·K⁻¹ and 222 J·g⁻¹·K⁻¹ for DGEFDCA/33DDS and DGEFDCA/44DDS respectively (compared to DGEBA/33DDS HRC of 601 J·g⁻¹·K⁻¹ and DGEBA/44DDS HRC of 516 J·g⁻¹·K⁻¹). These results show that furanic based networks have lower flammability, even if they degrade at lower temperature. The work of Sutton *et al.* assessed several endocrine activities of furanic compounds. FDCA was thus evaluated in CALUX bioassays, for the determination of endocrine activity on ERα, an androgen receptor, and also a thyroid receptor.[159] FDCA did not show any activity on sexual hormone receptors, but it did show a repression activity on the thyroid TRβ receptor. The activity obtained with 1 gram of nonylphenol was equivalent to the activity of 1700 grams of FDCA, meaning that the compound could have an activity at a high exposure. However, these in vitro tests are not enough to assess the activity of the compound and more studies are required to get reliable results.

II. 2,5-furfuryldiol
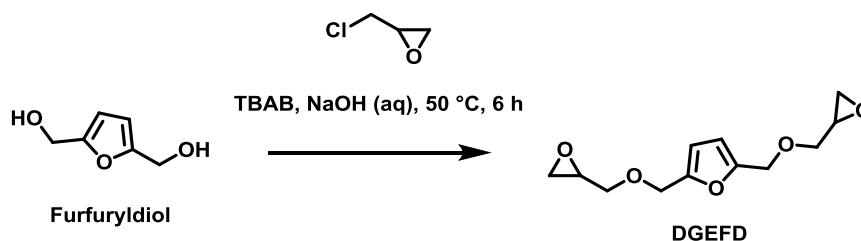
Figure 52 - Synthesis of DGEFD according to Meng *et al.*[160]

Diglycidylether of 2,5-furfuryldiol is a monofuranic diepoxy that has been extensively studied (Figure 52), as a substitute for DGEBA. Several articles reported properties of thermoset with different diamine hardeners, such as PACM[161,162], 4,4'-DDS and 3,3'-DDS[163], polyethers diamines (commercially known as EDR-148 and EDR-192)[160], DDM[164] and some furfurylamine derivatives.[161] These studies suggest that the use of DGEFD give lower T_g values than DGEBA, but with superior mechanical properties such as higher Young's moduli, higher tensile and flexural strength, lower flammability, higher char yield and lower degradation temperatures. The dynamic mechanical properties of these compounds are summarized in Table 4. As can be de-ducted from these data, the higher glass transition temperatures (or alpha transition) from DGEBA thermoset are probably due to the higher aromatic density brought by the bisphenolic moiety. The rigidity of the network (due to aromatics) is not counterbalanced with higher crosslinking density from DGEFD, due to the lower molecular weight of the monomer. Intermolecular interactions such as pi-stacking may also explain the higher T_g with DGEBA, contrary to DGEFD. However, at the glassy state, the Young's moduli were higher for DGEFD, which may be due to the dense packing of the network (crosslinking density) and the intermolecular interactions such as hydrogen bonding brought about by the oxygen of the furan. At the rubbery state, the networks with DDS and DGEFD had higher Young's moduli, most likely due to the packing density of the network, as hydrogen bonding should become very weak at higher temperatures. [163]

Table 4 - Mechanical and thermal properties of DGEFD cured with different amines, and compared with DGEBA

Amine Hardener	T_g or T_α (°C)		E'$_{glassy}$ (GPa)		E'$_{rubbery}$ (MPa)	
	DGEBA	DGEFD	DGEBA	DGEFD	DGEBA	DGEFD
33DDS	184	102	1.9	2.4	17.56	36.15
44DDS	238	114	1.9	2.7	16.02	24.53
DEGA	-	13.5	-	-	-	-
EDR-148	98 / 108 [122]	13	1.34 [122]	-	13.2 [122]	-
EDR-192	-	7.6	-	-	-	-
PACM	176	80	2.37	approx. 2.5	-	-
Epikure W	198	94	-	-	-	-
DFDA	121	62	approx. 2.5	approx. 3.5	-	-
DFDA-Me	128	69	approx. 2.5	approx. 3.5	-	-
DDM	164 [116]	126 / 149	-	2.4	-	17

Regarding the thermal stability of DGEFD thermosets under inert atmosphere, as shown in Table 5 it is clear that the stability of the resins is lower than DGEBA. This is probably due to the presence of the methylene moieties in DGEFD, compared to DGEBA, where the glycidylether is directly attached to the phenol moiety. However, as often observed for thermosets containing furan rings, the char yield is higher in the DGEFD thermosets.

Table 5 - Thermal stability of DGEFD thermosets cured with different amines, and compared with DGEBA

| Amine Hardener	$T_{d5\%}$ (°C)		Char yield (%)	
	DGEBA	DGEFD	DGEBA	DGEFD
33DDS	402	302	20.5	44.1
44DDS	398	255	13.8	42.3
DEGA	-	308	-	21
EDR-148	300 [122]	314	12 [122]	19
EDR-192	-	326	-	15.8
PACM	336	303	0	6
Epikure W	-	-	-	-
DFDA	301	272	<25	40
DFDA-Me	315	303 / 296*	<25	39 / 2*
DDM	376 [138]	296*	15 [138]	4*

* under air

Additional properties were also evaluated. Meng *et al.* characterized mechanical properties via measuring the flexural and tensile strength.[163] They have shown that the DGEFD-based epoxy networks had superior mechanical properties. Both the tensile and flexural strengths were higher for DGEFD than for DGEBA. The shore hardness was also higher in the case of the furan-based epoxy. They reported that the tensile strength of DGEFD cured with 44DDS was comparable to that of polyoxymethylene and Nylon-6. These enhanced mechanical properties were mainly attributed to the hydrogen bonds formed thanks to the heterocycle of DGEFD. The fire resistance of the cured material was also investigated. For example, it was shown than DGEFD cured with both DDS and amine could self-extinguish in 7 seconds. DGEBA-based networks burnt for longer times, where the flame spreading reached 10.2 mm·min^{-1} for DGEBA/44DDS and 8.5 mm·min^{-1} for DGEBA/33DDS. The self-extinction of DGEFD thermoset could be explained by the higher char formation due to the presence of the furan rings. The influence of the amine is also very important. In a different work, using polyetheramines as the curing agents (EDR-148 and EDR-192), it shown that DGEFD thermoset could stay ignited for longer times (> 60 s).[160] The flammability was lowered by using the same curing agent with a monomer bearing 2 furan rings. The ability to self-extinguish may probably be influenced by a ratio of furan rings to the alkylether with better resistance to fire with higher loadings of furan rings. In the case of DGEFD/DDS system, the synergy between aromatic and furanic rings led to low flammability. These results were also confirmed by microscale combustion calorimetry. The DGEFD/DDS systems

showed lower heat release capacities (121 J·g⁻¹·K⁻¹ for 33DDS and 179 J·g⁻¹·K⁻¹ for 44DDS), than for DGEBA (respectively 601 and 516 J·g⁻¹·K⁻¹). The total heat release of the networks with DGEFD were also lower than with DGEBA, precisely 14.9 and 23.6 kJ·g⁻¹ for 33DDS and 44DDS cured materials, compared to 32.3 and 36.4 kJ·g⁻¹ for DGEBA/33DDS and DGEBA/44DDS networks. In the work of Hong *et al.*, [82] one furan-containing molecule was considered. The furfuryldiol was predicted to be non-binder to the oestrogenic receptor α with a good reliability. In a recent paper by Sutton *et al.*, several new furfuryldiols were synthesized and their toxicity was assessed.[159] Especially, endocrine activity for several receptor such as human oestrogen receptor α, androgen receptor and a thyroid receptor, were evaluated,. In all the trials, the CALUX bioassays did not show any activity. For ERα activity, no dose-dependent response was seen. Furfuryldiol did not show any potential *in vitro* endocrine activity.

III. Bisfuran with ether linker
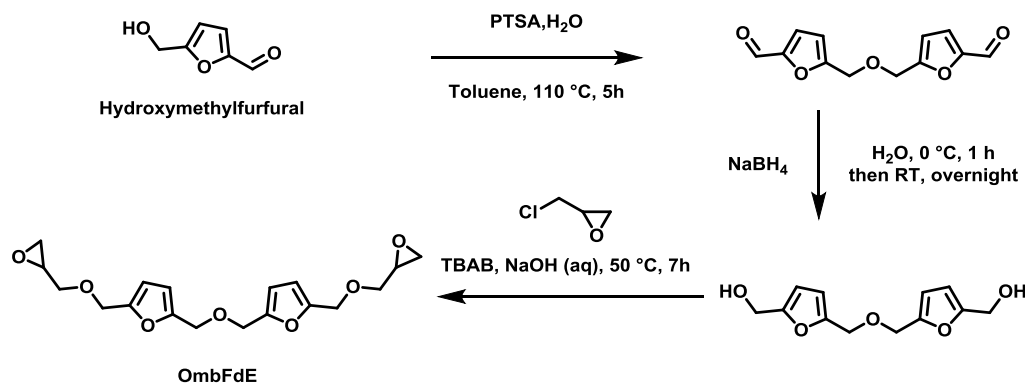
Figure 53 - Synthesis of OmbFdE according to Meng *et al.* from hydroxymethylfurfural[160]

The bisfuranic diepoxy monomer, OmbFdE, was prepared by dimerization of hydroxymethylfurfural (HMF), via a dehydratation reaction.[160] The obtained dialdehyde was then reduced with sodium borohydride to afford the corresponding diol. The glycidylation of the diol led to the formation of the diepoxy monomer (Figure 53). This diepoxy monomer was then cured with different alkylether amines, containing respectively 1 ether linkage (DEGA), 2 ether moieties (also known as EDR-148) and 3 ether moieties (*aka* EDR-192). Thermomechanical properties were measured, and also fire resistancy was investigated. Comparison with DGEBA was not performed, but data of the network with EDR-148 hardener can be found in the article of Faye et al..[122] Glass transition temperatures of EDR-148 network with OmbdFdE was 20.6 °C whereas with DGEBA it was 98 °C as obtained by DSC. The presence of numerous alkyl ether linkages in OmbFdE led to higher segmental mobility inside the networks. This is confirmed by the fact that curing OmbFdE with amine containing increasing number of alkylethers, lowers the T_g (from 25 to 7 °C). The comparison with the above mentioned DGEFD containing two furan rings showed that the higher content of furan rings results in higher T_g values. It seems that even though the use of OmbFdE leads to lower molecular weight between the crosslinks, the T_g would still be higher when two furan rings are present as compared to one in the case of DGEFD.

Examination of the thermal stability and fire resistance, showed that, $T_{d5\%}$ of the cured materials were in the range of 265-291 °C, with the obtained lower temperature for EDR-148 cured monomer. Compared with DGEBA/EDR-148, with a $T_{d5\%}$ of 300 °C, the furanic based monomer showed a lower degradation temperature, as often observed. However, a higher char yield was obtained with OmbFdE, in the range of 18-25 %. This is higher than the case of DGEBA/EDR-148 network with 12 %, and DGEFD with15-21 %. The presence of heterocycles is known to improve the char formation, as evidenced in the case of OmbFdE with 2 furan rings () (compared to one in DGEFD). The presence of these two rings also had an effect on the behaviour of the material in fire. Faster self-extinction was obtained with OmbFdE compared to DGEFD. In addition, the total heat release of OmbFdE/EDR-148 was lower compared to DGEFD (13.7 kJ·g⁻¹ vs 15.6), showing improvement due to the furan loading. In the work of Sutton *et al.*, the endocrine activity of the OmbFdE diol derivative was assessed in vitro, using CALUX testing methods.[159] Several parameters were evaluated such as activity on the ERα, the androgen receptor, and also a thyroid receptor. The diol did not show any activity against the oestrogen α receptor, nor the thyroid receptor. However, a repression effect on the androgen receptor was observed, but at higher concentrations than the corresponding reference, Flutamide (an androgen repressor drug). These *in vitro* results are not sufficient to assess the global impact on human health.

Conclusion and perspectives

As shown in this review, a lot of epoxy monomer precursors could be derived from biomass feedstock, with a wide range of properties. Some of these new materials show promising results for specific applications, and depending on the targeted properties, some may be suitable to replace DGEBA. However, for some, the starting materials have shown some serious toxicity issues, such as resorcinol. Some others are already known to mimic oestradiol (the natural oestrogen hormone). When selecting a potential BPA substituent, one should be aware of the existing tested precursors for their health hazard. Biobased compounds are seen as promising alternative to replace epoxy monomer precursors. Indeed, the wide range of functionalities available in nature is an infinite source of innovation for polymer chemists. The findings gathered here show that many of structures lead to thermoset properties that are close to DGEBA based systems. A balance in material properties have to be found between thermal or mechanical properties, when trying to remove BPA in epoxy resins. It is unlikely that a universal substitute could be found to replace DGEBA. Indeed, most of the time the potential alternatives to BPA lead to lower mechanical properties. Hence, the entire formulation must be replaced, and new hardeners should be envisaged. For example, the use of amido-amines instead of amines could allow to restore some mechanical properties. One of the main issues with BPA is not only that it is harmful, but it is also because its constant presence our daily lives, multiplying the chances of exposure to the substance. The diversity of structures offered by bioresources could help to tackle the challenge of BPA elimination, but if for each application a new monomer is required, the profitability will be difficult to attain for industry, however, biorefining is developing opening new routes to obtain bio-sourced compounds.[165] Substitution of harmful chemicals should not focus only on a single side of the problem. Using biomass feedstock does not truly guarantee a sustainable approach. Hence, the use of low environmental impact biomass should be favoured, such as cardanol. Hence, this non-edible natural phenol is a side-products of the production of cashew nut and is not used. Moreover, if left on the soil after cashew harvesting, it could entail adverse effect to the environment. Its production should attain 1Mt/y in the coming years, making this compound a promising starting substance for the replacement of BPA. This review underlines also that using natural compounds to replace petroleum based BPA could also lead to regrettable substitutions.[166,167] For example of the use of phytooestrogens, such as resveratrol or daidzein should be taken with caution when used for the substitution of BPA. To avoid such issues, the development of easily affordable methods to assess the toxicity of compounds are highly desirable. Many research groups are developing such tests.[168] It is also worth mentioning that bio-refining should be performed also with the evaluation of greenhouse gas emissions, to ensure that fossil resources substitution is environmentally viable. The use of life-cycle analysis or other green metrics is also encouraged to determine the environmental performance of the substitution.[169,170] Collaboration between scientists in different fields, and the access to easy-to-use tools will improve the impact of the research in this field.

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