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Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin

Chahinez Aouf [a,b,c,*], Hélène Nouailhas [d], Maxence Fache [e], Sylvain Caillol [e], Bernard Boutevin [e], Hélène Fulcrand [a,b,c]

[a] INRA, UMR1083 Sciences Pour l'Oenologie, F-34060 Montpellier, France
[b] Montpellier SupAgro, UMR1083 Sciences Pour l'Oenologie, F-34060 Montpellier, France
[c] Université Montpellier I, UMR1083 Sciences Pour l'Oenologie, F-34060 Montpellier, France
[d] Innobat, Cap Alpha, Avenue de l'Europe, 34830 Clapiers, France
[e] Institut Charles Gerhardt, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 05, France

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ABSTRACT

Novel biobased epoxy thermoset was synthesized from gallic acid, a phenolic acid encountered in various plants, both in its simple form and as a part of gallotannins. The functionalization of gallic acid was carried out using a two-step synthesis involving the allylation of OH groups followed by the epoxidation of resulting double bonds. The performance of two oxygen transfer agents (*meta*-chloroperbenzoic acid (*m*CPBA) and methyl(trifluoromethyl) dioxirane generated in situ from 1,1,1-trifluoroacetone and oxone) was evaluated in the epoxidation of the allylic double bonds. The glycidyl derivative of gallic acid (GEGA) obtained from *m*CPBA epoxidation was cured in epoxy polymer formulation with isophorone diamine (IPDA). The thermal and mechanical preliminary analyses showed that this new epoxy network based on GEGA displayed interesting properties compared to the epoxy polymer formulated with commercial diglycidyl ether of bisphenol A (DGEBA). A higher glass-transition temperature of GEGA/IPDA epoxy resin indicates a higher crosslinking density of this network.

1. Introduction

Epoxy resins constitute a major class of thermosetting resins and are extensively used as coatings, electronic materials, adhesives. Owing to their outstanding mechanical and electrical properties, chemical resistance, adhesion, and minimal shrinkage after curing [1], they are used in structural applications as well. Most of these thermosets are industrially manufactured from bisphenol A (BPA), a compound that was initially synthesized as a chemical oestrogen [2]. The aromatic ring of BPA is particularly suitable since it confers a good thermal resistance to epoxy resins. But this endocrine disruptor can mimic the body's own hormones and may lead to several negative health effects [3–6] including alterations in both immune and reproductive systems along with a modification in brain chemistry [7]. The negative impact of BPA on human health and environment necessarily implies to focus the researches for the substitution of BPA especially since some countries, such as Canada or France, have recently banned the use of BPA in food contact materials. Therefore, there is an increasing interest of chemical industry for non-harmful aromatic compounds allowing the synthesis of epoxy thermosets without BPA.

Moreover, with the limitation and high costs of fossil resources, renewable resources keep being in common

* Corresponding author at: Montpellier SupAgro, UMR1083 Sciences Pour l'Oenologie, F-34060 Montpellier, France. Tel.: +33 499612454; fax: +33 499612857.
E-mail addresses: aouf@supagro.inra.fr, Chahinez.Aouf@supagro.inra.fr (C. Aouf).

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interest of both academic and industrial laboratories at the time. Hence, biomass is a potential source of biopolyphenols which could lead to the production of heat resistant cross-linked epoxy thermosets and overcome petroleum-based BPA. Natural polyphenols which are very abundant in forest/agricultural biomass or residues [8] are structurally similar to materials already employed for this purpose.

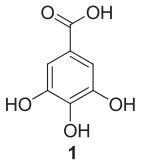
Some studies have reported the use of natural polyphenols in thermosetting applications. Lignins co-produced during papermaking were formulated with epoxy networks and cross-linked by direct heating [9–12]. Research works at IBM reported the incorporation of lignin into epoxy polymers used in the fabrication of printed wiring boards for the microelectronics industry [13]. However, none of these works aim at functionalizing directly lignin to epoxy reactants, probably because of the poor solubility of this polymer in organic solvents.

The other terrestrial source of phenolic compounds is tannins. These biopolyphenols exhibit a wide structural diversity and have generally more than two phenolic hydroxyl groups, but this is not a drawback in the perspective of cross-linked epoxy thermosets, which constitute the main applications.

In our previous research, one of the building blocks of polymeric condensed tannins, namely catechin, was reacted with epichlorohydrin in alkaline medium to give the expected tetraglycidylether of catechin along with a benzodioxane derivative. The formation of this cyclic by-product is directly related to the catechol ring (B ring) within the catechin structure. Indeed, the oxirane ring introduced in the first substitution step undergoes an intramolecular nucleophilic attack from the second phenolate anion located in *ortho* position to yield the benzodioxane-type derivative. In fact, catechin derivatives with three methyloxirane functions on average were actually obtained [14].

In 1985 Haruo Tomita et al., disclosed in their invention the use of gallic acid (a phenolic acid occurring free or as a part of gallotanins in different plants) as a phenolic source in the epoxy thermosets production [15].

In this patent, gallic acid **1** (Scheme 1) was reacted with epichlorohydrin in the presence of a phase transfer catalyst and in the substantial absence of water, thereby causing addition reaction of epichlorohydrin to carboxyl group and at least one phenolic hydroxyl group to occur. Surprisingly, the vicinity of the phenolic hydroxyl groups in the gallic acid structure does not allow the formation of by-products (or they have not been described in the patent). Thus, the chemical reactivity is dependent in a very subtle way on the chemical structure of a given component.



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Scheme 1. The gallic acid chemical structure.

Gallic acid **1** contains three phenolic hydroxyl groups and one carboxylic group which can be exploited in order to obtain new biobased epoxy thermoset with improved thermal and mechanical properties.

Therefore, to overcome the incomplete functionalization of the phenolic hydroxyl groups of gallic acid by epichlorohydrin, we investigated another route to gallic acid glycidylation based on a two-step chemical synthesis: the alkaline assisted allylation of hydroxyl groups followed by the epoxidation of the resulting double bonds. Two oxygen transfer agents were compared in the epoxydation of the allylic double bonds: *meta*-chloroperbenzoic acid (*m*CPBA) and methyl(trifluoromethyl) dioxirane generated in situ from 1,1,1,-trifluoroacetone and oxone. The efficiency of each reagent to produce the full glycilated derivative of gallic acid was evaluated.

The glycidylated product was then cured with commercial 3-aminomethyl-3,5,5-trimethyl cyclohexylamine (Isophorone diamine: IPDA) to estimate its capacity to yield a cross-linked material. The thermal properties of the resulting epoxy network were compared to the standard diglycidyl ether of bisphenol A (DGEBA) epoxy polymer.

2. Experimental

2.1. General

Gallic acid (97.5%), allyl bromide (99.0%), isophorone diamine (IPDA, $\geqslant$99.0%), *meta*-chloroperbenzoic acid (*m*CPBA, $\leqslant$77.0%), Trifluoroacetone (97.0%), Oxone™ monosulfate compound, sodium bicarbonate ($\geqslant$99.5%), CH_3CN (99.8%), DMF (99.8%) and CH_2Cl_2 (99.8%) were purchased from Sigma–Aldrich. The conventional petroleum-based epoxy monomer used was a diglycidyl ether of bisphenol A (DGEBA) supplied by Aditya Birla Chemicals (Epotec), with an Epoxide Equivalent Weight (EEW) of 182 g/equiv. The IPDA Amine Equivalent Weight (AEW) is 42 g/equiv.

All the reactions were monitored by thin layer chromatography (TLC). TLC was performed on silica gel 60 F254. ^1H and ^{13}C NMR spectra were recorded in DMSO-*d*6, $CDCl_3$ and Acetone-*d*6 solutions at 500 MHZ using a VARIAN Unity-Inova spectrometer. Chemical shifts are reported in ppm relative to DMSO-*d*6 [signals for residual DMSO-*H*6 in the DMSO-*d*6: 2.50 for ^1H NMR and 39.4 for ^{13}C NMR], $CDCl_3$ [signals for residual $CHCl_3$ in the $CDCl_3$: 7.26 for ^1H NMR and 77.0 for ^{13}C NMR] and Acetone-*d*6 [signals for residual Acetone-*H*6 in the Acetone-*d*6: 2.05 for ^1H NMR and 30.83 for ^{13}C NMR]. ESI-MS analyses in positive mode were performed using a Brucker Daltonics Ion trap mass spectrophotometer (Bremen, Germany).

2.2. Allylation of gallic acid

A 100 mL two-necked flask equipped with a septum cap and a magnetic stirring bar was charged with 30 mL of DMF and 0.68 g (4 mmol) of gallic acid. The solution was cooled with an ice bath and potassium carbonate (2.21 g, 16 mmol) was added. After three minutes, allyl bromide (1.4 mL, 16 mmol) was added dropwise by a syringe. The solution was stirred for 30 min at 0 °C and then at room

temperature during 48 h. Fifty millilitres of water was added and the aqueous phase was extracted with 3×50 mL of ethyl acetate. The organic phase was washed with 50 mL of brine then dried with $MgSO_4$ and vacuum concentrated.

The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate: 90/10) to give **2** (pale yellow oil, 1.06 g, 3.2 mmol, 80% yield).

*2.2.1. Allyl 3,4,5-tris(allyloxy)benzoate **2***

^{1}H NMR (500 MHz, DMSO-d6) δ = 4.54 (d, J = 5.68 Hz, 2H), 4.63 (d, J = 4.92 Hz, 4H), 4.78 (d, J = 5.29 Hz, 2H), 5.16 (d, J = 10.60 Hz, 1H), 5.26 (d, J = 10.5 Hz, 2H), 5.30 (d, J = 15.20 Hz, 1H), 5.34 (d, J = 17.20 Hz, 1H), 5.37 (d, J = 10.60 Hz, 1H), 5.43 (d, J = 17.04 Hz, 2H), 6.03 (m, 4H), 7.25 (s, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-d6) δ = 65.02, 69.04 (2C), 73.05, 107.88 (2C), 117.08 (2C), 117.30, 117.70, 124.44, 132.52, 133.30 (2C), 134.25, 141.01, 151.80 (2C), 164.75 ppm. [$C_{19}H_{22}0_5$+H^+]: 331.1.

2.3. Epoxidation of allylated gallic acid 2 with meta-chloroperoxybenzoic acid (mCPBA)

A 100 mL two-necked flask equipped with dropping funnel and magnetic stirring bar was charged with a solution of 0.33 g of **2** (1 mmol) in 10 mL of CH_2Cl_2. The *meta*-chloroperoxybenzoic acid $\geqslant$70% (wt/wt) (2.95 g, 12 mmol) was dissolved in 40 mL of CH_2Cl_2 and added slowly at 0 °C over 5 min. The solution was stirred at 0 °C for 1 h and then at room temperature overnight.

After this time, 100 mL of 10% (wt/v) of Na_2SO_3 aqueous solution was added followed by 100 mL of saturated aqueous solution of $NaHCO_3$ and 100 mL of H_2O. The aqueous phase was extracted with 2×50 mL of CH_2Cl_2. The organic phase was dried with $MgSO_4$ and vacuum concentrated.

The crude product obtained was purified by silica gel chromatography (petroleum ether/ethyl acetate 50/50) to give a mixture of the triglycidyl ether of gallic acid **3** and the tetraglycidyl ether of gallic acid **4**:

*2.3.1. Product with three epoxy groups **3**: yellow oil, 0.064 g, 0.17 mmol, 17% yield*

^{1}H NMR (500 MHz, DMSO-d6) δ = 2.76 (m, 3H); 2.84 (dd, J = 9.28, 4.40 Hz, 3H), 3.90 (m, 3H), 4.08 (dd, J = 6.34, 12.37 Hz, 1H); 4.26 (m, 3H); 4.44 (d, J = 11.40 Hz, 2H); 4.66 (d, J = 5.05 Hz, 1H); 4.80 (d, J = 5.29 Hz, 1H); 5.28 (dd, J = 5.10, 10.58 Hz, 1H); 5.41 (dd, J = 5.06, 18.31 Hz, 1H), 6.06 (m, 1H); 7.27 (s, 1H); 7.30 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d6) δ = 43.64, 43.84, 44.11, 49.30, 49.97, 50.46, 65.75, 69.50, 70.33, 74.30, 108.60, 108.64, 118.17, 125.09, 133.60, 141.78, 151.98, 152.13, 165.21 ppm. [$C_{19}H_{22}0_8$+H^+]: 379.1

*2.3.2. 3,4,5-triglycidylether glycidyl benzoate **4**: yellow oil, 0.23 g, 0.6 mmol, 60% yield*

^{1}H NMR (500 MHz, CDCl3) δ = 2.72 (m, 2H), 2.80 (m, 2H), 2.84 (t, J = 4.58 Hz, 1H), 2.92 (q, J = 4.88 Hz, 3H), 3.34 (dd, J = 5.80, 3.05 Hz, 1H), 3.40 (bs., 3H), 4.03 (m, 2H), 4.07 (dd, J = 12.05, 6.87 Hz, 1H), 4.13 (dd, J = 12.36, 6.56 Hz, 1H), 4.36 (m, 3H), 4.66 (dd, J = 12.21, 2.75 Hz, 1H), 7.36 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 43.00, 43.06, 43.43, 48.62, 49.27 (2C), 49.75, 65.10, 69.70 (2C), 73.64, 108.04 (2C), 124.16, 141.18, 151.45 (2C), 164.51 ppm. [$C_{19}H_{22}0_9$+H^+]: 395.1.

2.4. Epoxidation of allylated gallic acid 2 with methyl(trifluoromethyl)dioxirane

Trifluoroacetone (0.67 mL, 7.6 mmol) was added to a stirred solution of allylated gallic acid **2** (0.33 g, 1 mmol) in 10 mL of 50% aqueous acetonitrile. A homogeneous mixture of Oxone™ (4.18 g, 6.8 mmol) and $NaHCO_3$ (1.18 g, 14 mmol) was added to the reaction mixture in one portion at room temperature. The reaction was monitored by TLC and the resulting suspension was treated with water (30 mL) after 17 h. The reaction mixture was extracted with ethyl acetate (3×25 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous $MgSO_4$, and evaporated to give the crude epoxide. The purification over silica gel chromatography using the same eluting system as mentioned above gave a mixture of the triglycidyl ether of gallic acid **3** and the tetraglycidyl ether of gallic acid **4**. Overall yield: 75%.

*Product with three epoxy groups **3***: yellow oil, 0.114 g, 0.30 mmol, 30% yield and *3,4,5-triglycidylether glycidyl benzoate **4**:* yellow oil, 0.175 g, 0.44 mmol, 45% yield.

2.5. Curing of the epoxy resins

The mixture of triglycidyl derivative **3** and tetraglycidyl derivative **4** of gallic acid (GEGA) obtained from *m*CPBA epoxidation was tested in epoxy resin formulation and compared to the pure commercial diglycidyl ether of bisphenol A (DGEBA). Resins were cured with the same cycloaliphatic amine, isophorone diamine (IPDA). All the reaction systems were prepared in a 1:1 M ratio of epoxy group to active H of amine in the curing agent to obtain the optimal crosslink architecture of cured epoxy materials. DGEBA (1.00 g; EEW = 182 g/equiv) was mixed vigorously and rapidly at room temperature to IPDA (0.231 g; AEW = 42 g/equiv) to form a homogeneous system. The mixture obtained was cured for 30 min at 90 °C and additional 2 h at 200 °C to get the DGEBA/IPDA epoxy resin.

The GEGA/IPDA epoxy resin was formulated in the same conditions by mixing GEGA (1.00 g; EEW = 103 g/equiv) to IPDA (0.408 g; AEW = 42 g/equiv). The EEW determination of GEGA was based on percentages of compounds **3** and **4** in the mixture evaluated by ^{1}H NMR analysis.

2.6. Swelling measurements

Swelling measurements of the networks were carried out using tetrahydrofuran (THF) as solvent. The swelling percentage was calculated from the differences in weight between dried and swollen networks. Bar samples (3 mm^3) of the cured epoxy polymers were cut, weighed, and immersed in THF for 24 h. The swollen bars were then blotted between sheets of paper and finally weighed. The swelling percentage was calculated as follows:

$$\text{Swelling } (\%) = (W_s - W_d)/W_d \times 100$$

where W_s and W_d are the weights of the swollen bar and the dry bar, respectively. Swollen bars were put in an oven at 60 °C for 24 h to dry them. Then, the bars were weighed again (W_{do}):

$$\text{Soluble part } (\%) = 100 - [(W_{do}/W_d) \times 100]$$

2.7. Thermal analysis

Thermogravimetric analyses (TGA) of the two epoxy networks were performed on a Perkin Elmer TGA6 instrument. The initial weight of each sample tested was about 5 mg. Each sample was heated from 20 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Degradation temperatures at 5% (T_{d5}) and 30% (T_{d30}) weight loss and the char yield at 600 °C ($Char_{600}$) were then recorded for the two cured resins.

2.8. DMA analysis

DMA assays were conducted in dynamic-mechanical thermal equipment (Metravib DMA 25). The DMA samples had a rectangular geometry (length: 10 mm, width: 2.5 mm, thickness: 0.5 mm). Uniaxial stretching of samples were performed while heating at a rate of 3 °C/min from 30 to 300 °C, keeping frequency at 1 Hz (viscoelastic region) and strain at 0.1%.

The storage modulus (E'), loss modulus (E'') and $\tan\delta$ curves as a function of temperature were recorded and analysed using the software Dynatest 6.8. E' is related to the mechanical energy stored per cycle when the sample is subjected to a deformation and it is the elastic response of the material. E'' is the viscous response and it is related to the dissipated energy as heat per cycle when the sample is deformed. Loss factor is defined as $\tan\delta = E''/E'$, δ being the angle between the in-phase and out-of-phase components of the modulus in the cyclic motion. Temperatures of the relaxation processes associated with glass transition temperatures were determined through the inflexion point of the storage modulus E' curve as well as the maximum peak in both the loss modulus E'' and $\tan\delta$ curves [16–17].

3. Results and discussion

Epichlorohydrin is widely used in the synthesis of epoxy thermosets as well in academic laboratories as in industry [18–19].

However, it was established in our previous work that epichlorohydrin reacts with the *ortho* phenolic OH groups of catechin to yield a benzodioxane-type substitution in addition to the double glycidylation [14]. Moreover, the functionalization of gallic acid with epichlorohydrin led to a non-controlled glycidylation as mentioned by Tomita et al. [15] (the carboxylic group and at least one of the phenolic groups).

Thus, in order to control the functionalization of gallic acid, another route involving the O-allylation of hydroxyl groups followed by the epoxidation of the resulting double bonds was investigated. The epoxidation was carried out using two different reagents *meta*-chloroperbenzoic acid *m*CPBA and trifluoroacetone with oxone.

3.1. The gallic acid allylation

The aprotic solvent DMF was chosen to limit the phenolates solvation and then facilitate the O-allylation reaction.

Several allylation tests were carried out to study the reactivity of gallic acid **1** towards allyl bromide. These allylation tests are summarised in Table 1.

The allylation products were identified by ESI-MS.

The reaction of gallic acid **1** with 4 equiv of allyl bromide and 4 equiv of potassium carbonate during 48 h at room temperature allowed the complete-allylation of gallic acid to yield the tetra-allylated product **2** in 80% yield after silica gel purification (Scheme 2).

^{1}H NMR spectrum of compound **2** (Fig. 1) shows the disappearance of signals around 9 ppm associated with the protons of phenolic OH. The proton integrations in the region of 5.16–6.08 ppm indicate the presence of four allylic double bonds, and the eight protons located at 4.54–4.78 ppm correspond to the $\underline{CH_2}$–O protons (Ha, Hd and Hh).

3.2. The epoxydation of the tetra-allylated gallic acid 2 with mCPBA

Tetra-allylated gallic acid product **2** was first reacted with 7 equiv of *meta*-chloroperbenzoic acid (*m*-CPBA) to afford products with one and two epoxy groups. To obtain mainly the tetra-glycidylated derivative, the reaction requires 12 equiv of peracid. Under these conditions, product **4** with four epoxy group was isolated in 60% yield with the minor formation of product **3** which corresponds to the triepoxidized derivative of tetra-allylated gallic acid **2** (Scheme 3).

The formation of tetra-glycidylated derivative **4** is confirmed by the total disappearance of the allylic double bond proton (Fig. 2) in the 5–6 ppm spectral region and by the shielding of $\underline{CH_2}$–O protons of glycidyl groups at 3.01–4.68 ppm. The oxirane ring protons appeared at 2.70–3.40 ppm.

^{1}H NMR spectrum of compound **3** (Fig. 3) shows three different signals at 4.57–4.80 ppm which correspond to $\underline{CH_2}$–O protons of glycidyl groups. These different signals indicate the presence of a mixture of three regioisomers each bearing three glycidyl groups. The residual allylic group appears at 5.26–6.09 ppm spectral range.

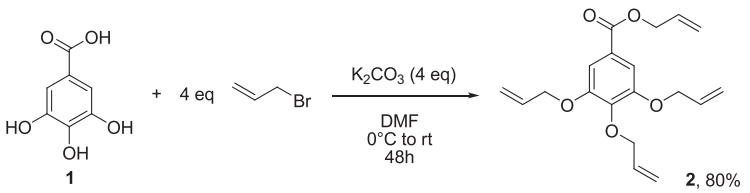
3.3. The epoxydation of the tetra-allylated gallic acid 2 with methyl(trifluoromethyl)dioxirane

The total epoxidation of tetraallylated gallic acid **2** required the use of excessive amount of *m*CPBA (3 equiv per allylic double bond) along with the production of *meta*-chlorobenzoic acid which is difficult to eliminate. Under these limiting conditions, it seems more convenient to epoxidize the double bonds by in situ generated dioxirane. As dioxiranes are electrophilic in nature, epoxidation of electron deficient alkenes like allylic doubles bonds using in situ generated dioxiranes is usually very slow, when

Table 1
The gallic acid allylation.

	Reactants (mol equiv)			Reaction products[a] (yield%)				Time of reaction (h)	Total yield%
	Gallic acid	Br	K_2CO_3	Mono-allylated	Di-allylated	Tri-allylated	Tetra-allylated		
Entry 1	1	1	0.8	None	32	None	None	2.25	32
Entry 2	1	5	5	None	None	21	30	48	51
Entry 3	1	4	4	None	None	None	80	48	80

[a] Number of allyl functions per gallic acid molecule.



Scheme 2. Allylation of gallic acid **1**.

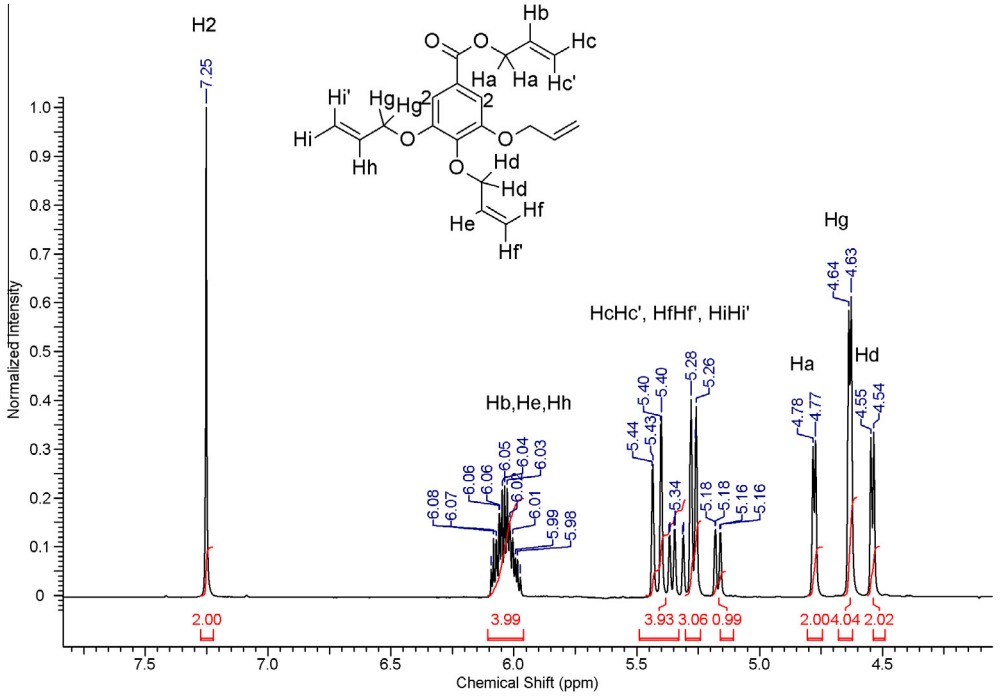
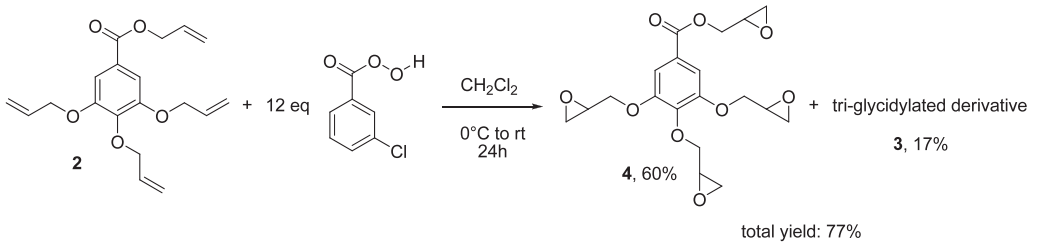


Fig. 1. ^{1}H NMR spectrum of **2** in *d*6-DMSO.



Scheme 3. Epoxidation of **2** by *m*-CPBA.

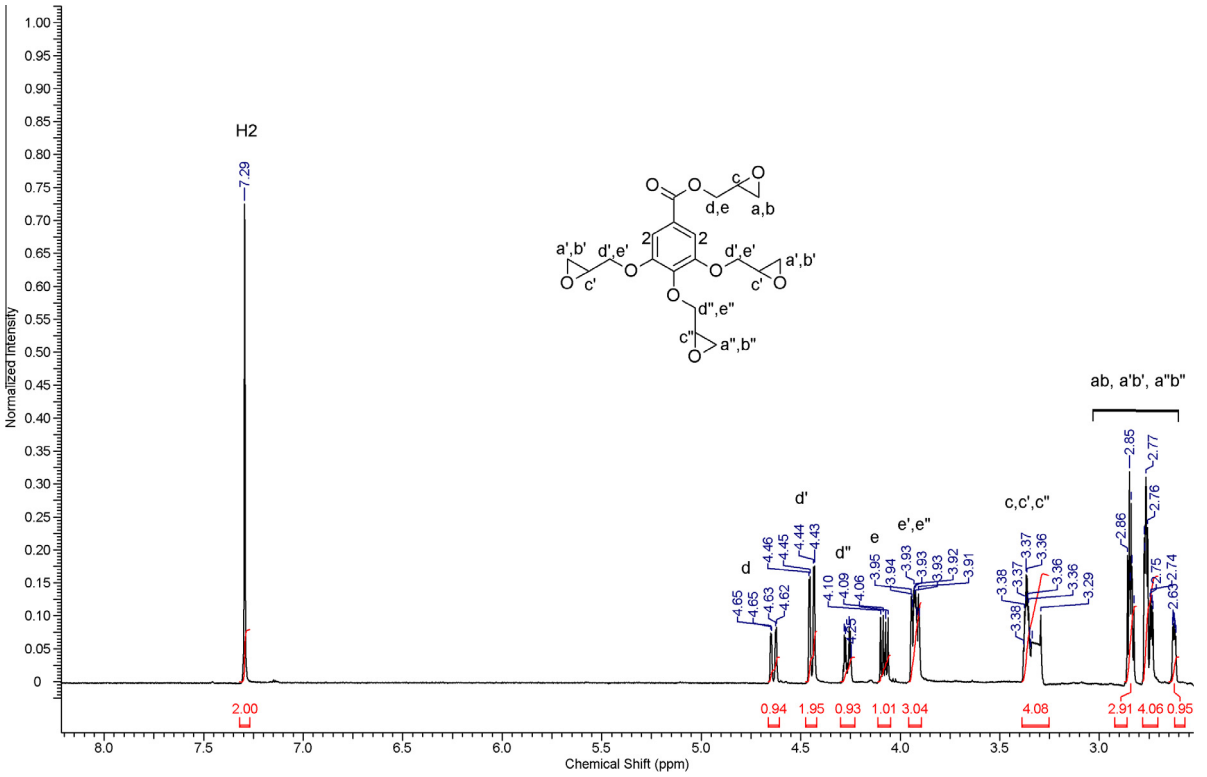


Fig. 2. ^{1}H NMR spectrum of **4** in $CDCl_3$.

normal ketones such as acetone, 2-butanone and hexanones are used [20–22].

Yang et al. [23] described the enhanced rate of epoxidation by in situ generated methyl(trifluoromethyl) dioxirane from 1,1,1-trifluoroacetone and Oxone™, where the high electronegativity of fluorine makes it a stronger epoxidizing agent.

Then, this less hazardous alternative was employed for the epoxidation of tetraallylated gallic acid **2**. The reaction took place at room temperature in 50% aqueous solution of acetonitrile in the presence of $NaHCO_3$ as a buffer. The methyl(trifluoromethyl)dioxirane generated in situ from 1,1,1-trifluoroacetone and of Oxone™ acted as oxygen transfer agent to yield the mixture of epoxidized compounds **3** and **4** within 17 h (Scheme 4).

To find the best reaction conditions, the epoxidation of tetraallylated gallic acid **2** was initially studied under different conditions. The use of 1.9 equiv of 1,1,1-trifluoroacetone with 1.7 equiv of oxone per double bond were found to be optimum for this epoxidation reaction.

Compared to the reaction with *m*CPBA (17% of **3** and 60% of **4**), these experimental conditions led to a lower rate of tetraglycidylether of gallic acid **4** (45%) and a higher rate of triglycidylether of gallic acid **3** (30%), the overall epoxidation yield remaining quasi-unchanged.

Contrary to the epichlorohydrin reaction, the two-step functionalization – allylation, epoxidation – allows a better control of the epoxidation reaction and a much higher rate of glycidylation of gallic acid, with a mixture of tri-and tetra-glycidylether derivatives.

The glycidyl ether derivative of gallic acid (GEGA) composed of the mixture of **3** and **4** was formulated with isophorone diamine (IPDA) as curing agent. The network based on the formulation of diglycidyl ether of bisphenol A (DGEBA) with the same hardener was used as reference. All the reaction systems were prepared in a 1:1 M ratio of epoxy group based on NMR data to H active of amine in the curing agent to obtain optimal crosslinking architecture of cured epoxy materials. Thus, the DGEBA/IPDA equimolar mixture cured at 90 °C for 30 min and additional 2 h at 200 °C yielded the DGEBA/IPDA epoxy resin while the presence of 3.8 epoxy groups in GEGA required the use of 1.9 M equivalent of IPDA to get the GEGA/IPDA epoxy resin in the same curing conditions.

Tests on swelling properties, thermal stability and dynamic mechanical properties of GEGA/IPDA resin were performed and compared to the reference DGEBA/IPDA one.

3.4. Swelling properties

The swelling experiments were performed to investigate the actual degree of crosslinking. The soluble part allowed the quantification of the molecules which are not implicated in the cured resin network. Lower crosslinking density usually results in greater distances between network nodes and then a greater solvent absorption. Results obtained for the various cured epoxy polymers are displayed in Table 2.

No significant difference was found between the two epoxy networks. The degree of swelling was slightly lower for GEGA/

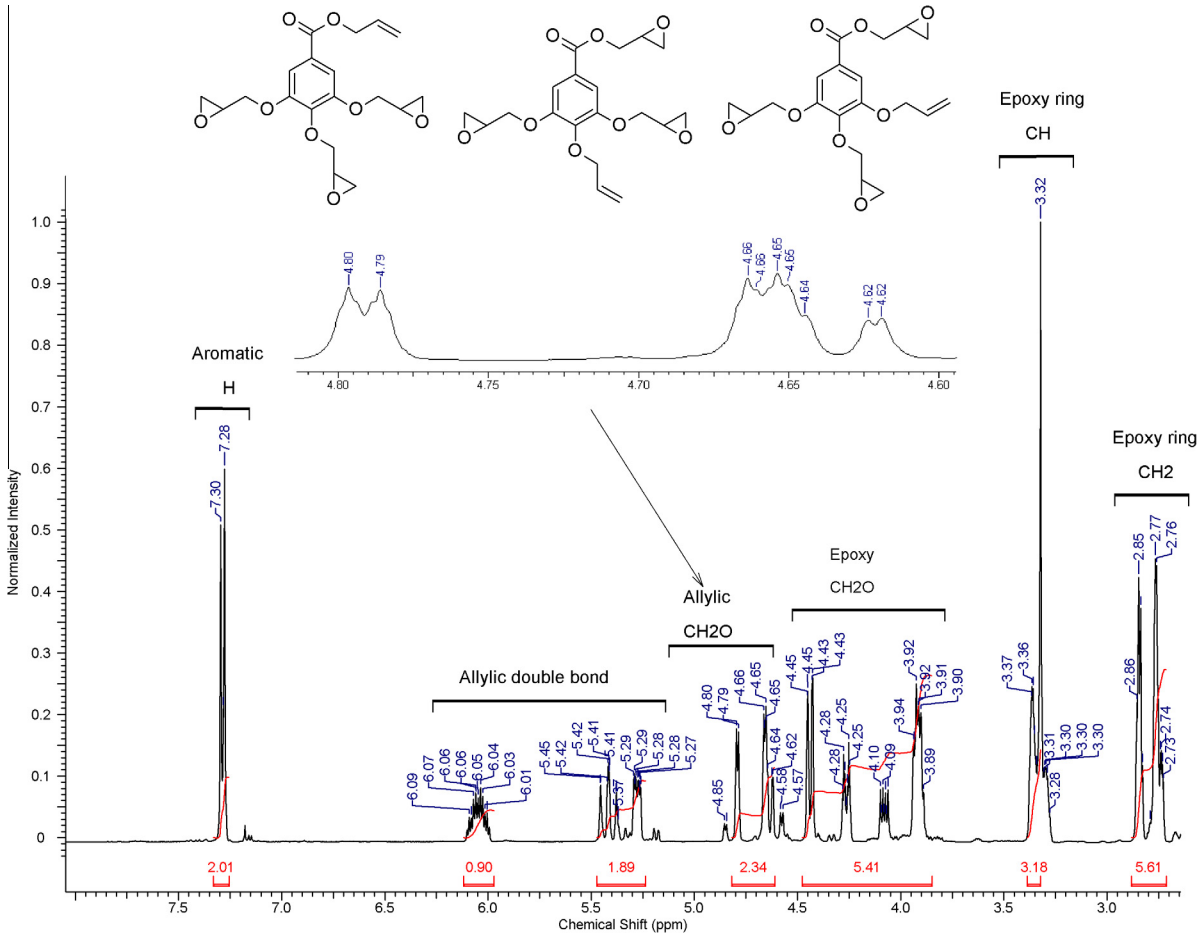
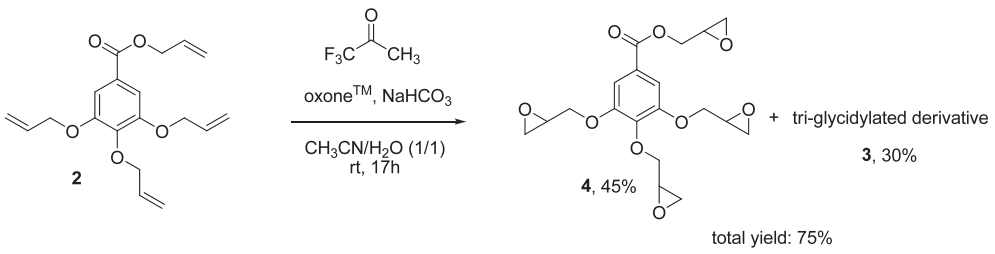


Fig. 3. ^{1}H NMR spectrum of **3** in DMSO-*d*6.



Scheme 4. Epoxidation of **2** by methyl(trifluoromethyl)dioxirane.

IPDA because it has larger molar epoxy content (all the polymer reaction sites were fully reacted through an epoxy reaction with the amine) than the DGEBA resin. Both epoxy networks have a same soluble part value equal to 1% which is within experimental error. This indicates that all components of the GEGA product do participate to the network.

3.5. Thermal stability of cured epoxy resins

The thermal decomposition behaviours under air and nitrogen of the GEGA/IPDA and under nitrogen of DGEBA/IPDA cured epoxy resins are shown in Fig. 3, their decomposition temperatures at weight loss of 5% and 30% were listed in Table 2.

Under nitrogen atmosphere, the two studied epoxy resins show a continous single step of degradation process which starts around 300 °C for GEGA/IPDA and at 350 °C for DGEBA/IPDA (Fig. 4).

Thermal decomposition of GEGA/IPDA epoxy resin under air starts also around 300 °C but with two distinct stages of degradation. In the first step, the sample lost about 60% of its weight, and in the second step, it lost about 32% of its weight.

Table 2
Parameters related to Tα, thermal stability, swelling percentage and soluble part of cured epoxy resins.

Samples	Tα (°C)[a]	T_{d5} (°C)[b]	T_{d30} (°C)[c]	Ts[d]	$Char_{600}$ (%)[e]	Swelling (%)	Soluble part (%)
DGEBA/IPDA	160	350	365	176	8	6	1
GEGA/IPDA	233	300	335	157	23	4	1

[a] Alpha transition temperature given by DMA.
[b] Temperature of 5% weight loss under N_2 as given by TGA.
[c] Temperature of 30% weight loss under N_2 as given by TGA.
[d] Statistic heat-resistant index temperature calculated by Eq. **(1)**.
[e] Char yield at 600 °C under N_2 as given by TGA.

$Char_{600}$ value of GEGA/IPDA epoxy resin in air is closed to 8%, which is far below $Char_{600}$ value under nitrogen (23%).

To specify the thermal stability of the cured resins, the statistic heat-resistant index (Ts) was used. It is determined from the temperature of 5% weight loss (T_{d5}) and of 30% weight loss (T_{d30}) of the sample by thermogravimitric analysis (TGA). The statistic heat-resistant temperature (Ts) is calculated by Eq. (1) [24].

$$Ts = 0.49\ [T_{d5} + 0.6\ (T_{d30} - T_{d5})] \quad (1)$$

The value of statistic heat-resistant index (Ts) of the cured GEGA/IPDA material associated with 5% weight loss and 30% weight loss temperatures was lower than that of cured DGEBA/IPDA material. The faster heat degradation of GEGA/IPDA system may be caused by chain scissions of ester bond linkages in the polymer backbone.

However, residual materials of GEGA/IPDA resins at 600 °C under nitrogen represented by the $Char_{600}$ value is higher than that of cured DGEBA resins. This can be attributed to the effect of increased reticulation nodes in the GEGA/IPDA network. Indeed, mechanism of degradation of epoxy polymers is dominated by scission of phenyl ethers to produce phenolic ends. This mechanism was described by Dyakonov et al. [25] who also reported that thermal resistance of epoxy networks was linked to crosslinking density. In their works they showed that epoxy polymers with crosslinking density higher than DGEBA exhibited higher thermal resistance and char formation than DGEBA. In our case, GEGA molecule, with nearly 4 epoxy groups per aromatic ring leads to higher crosslinking density of epoxy resins and lower chain lengths between entanglements compared to DGEBA network. This higher crosslinking density may be responsible for higher thermal char formation.

3.6. DMA analysis of cured epoxy resins

The dynamic mechanical properties of the epoxy networks were investigated using DMA. Figs. 5 and 6 show storage modulus E', loss modulus E'' and loss factor $\tan\delta$ as a function of temperature of DGEBA/IPDA and GEGA/IPDA cured epoxy networks respectively. The transition observed in the high-temperature region corresponds to the α relaxation, associated with the glass transition appearing when the chains in the amorphous regions begin to coordinate large scale motions. The temperature associated with the peak magnitude of loss factor ($\tan\delta$) is defined as Tα, commonly assimilated to the glass transition temperature Tg [26]. The value of Tα is about 160 °C (Fig. 5) for the DGEBA/IPDA system, which is consistent with the literature [27]. Tα value of the GEGA/IPDA system is around 233 °C (Fig. 6).

This value is higher than the DGEBA/IPDA system one, that is mainly due to the higher crosslinking density associated with the higher functionality of GEGA (3.8 epoxy per molecule) compared to DGEBA (about 2 epoxy per molecule). Generally speaking, increasing the crosslinking density affects the loss tangent curve in three different ways. Firstly, the loss tangent peaks shift to

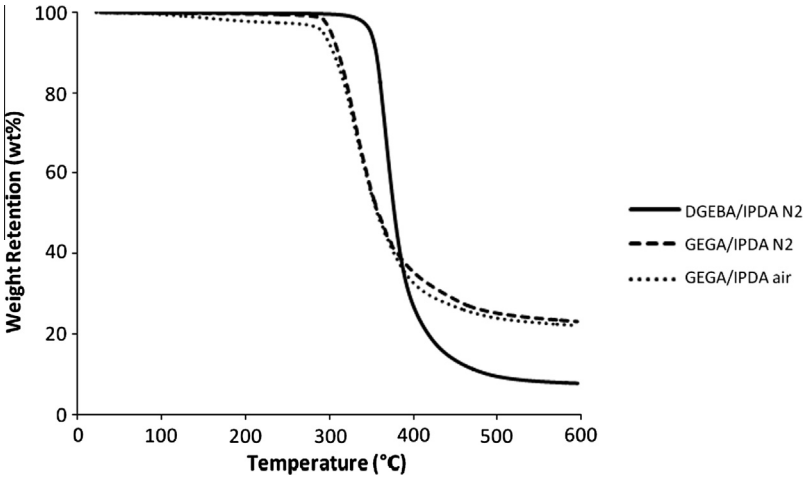


Fig. 4. Thermogravimitric analysis traces of DGEBA/IPDA and GEGA/IPDA cured epoxy resins under air and nitrogen atmosphere.

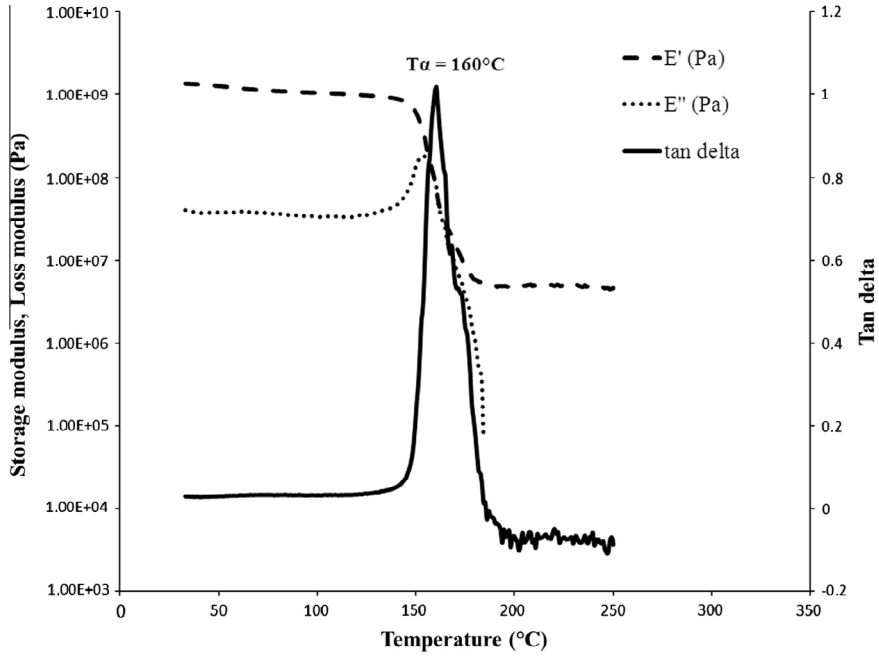


Fig. 5. Storage modulus E', loss modulus E'' and tan δ as a function of temperature for DGEBA/IPDA cured epoxy network.

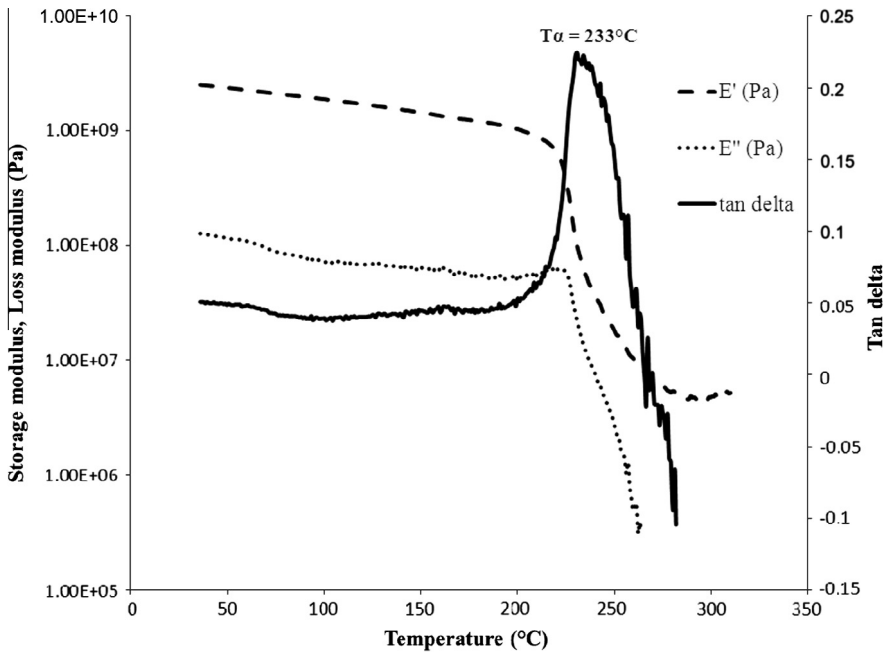


Fig. 6. Storage modulus E', loss modulus E'' and tan δ as a function of temperature for GEGA/IPDA cured epoxy network.

higher temperatures. This occurs because samples with higher crosslinking densities have higher glass-transition temperatures. Secondly, the loss tangent peaks have lower values because samples with higher crosslinking densities have higher elastic moduli relative to their viscous moduli [28]. Thirdly, the loss tangent peaks become broader. The broadening of the loss peak indicates that the relaxation is not a single one and comprises several consecutives ones. Generally, this broadening is attributed to an increase in the distribution of molecular weight between crosslinks [29–30]. Thus, the loss tangent curve of GEGA/IPDA system indicates that this

epoxy network has a higher crosslinking density compared to the DGEBA/IPDA material (Figs. 5 and 6). Moreover, the onset temperature of E' decrease is more pronounced (about 70 °C) for the GEGA/IPDA system indicating that this epoxy network has better mechanical properties at high temperatures compared to the DGEBA/IPDA material (Figs. 5 and 6).

4. Conclusion

This study was focused on the possibility to exploit natural phenolic compounds like gallic acid in the formulation of new biobased epoxy resins. The functionalization of gallic acid involved two steps: the alkaline assisted allylation of the hydroxyls groups followed by the epoxidation of resulting double bonds. If the reaction of gallic acid with allyl bromide easily allowed the quantitative alkylation of gallic acid, the epoxidation of the four resulting double bonds has been more challenging. Indeed, the total oxidation of the allylic double bonds of gallic acid by *m*CPBA required a very large excess of peracid, while the use of trifluoroacetone and oxone as a greener alternative led to a lower conversion into the tetraglycilated derivative.

Contrary to the reaction with epichlorhydrin, this two-step chemical synthesis allowed the functionalization of more than two OH groups of gallic acid. However, it is possible to modify the rate of functionalization by varying the allyl bromide to gallic acid ratio if needed.

Thermal and mechanical tests undertaken on the epoxy networks obtained from the formulation of the glycidyl derivative of gallic acid (GEGA) with IPDA showed a higher crosslinking density, a slightly lower onset of volatilization and a higher char yield than the diglycidyl ether of BPA (DGEBA) network cured in the same conditions. Moreover, the higher Tg and the higher onset temperature of E' decrease indicate that the GEGA/IPDA epoxy network has better mechanical properties at high temperature.

This work demonstrates the feasibility of epoxy thermosets formulation fully based on natural phenolic compound. GEGA, as a crosslinker, appears to be a good candidate to improve mechanical properties of conventional epoxy/amine systems by increasing the Tg.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2012.11.025.

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