Synthesis, Curing, and Properties of an Epoxy Resin Derived from Gallic Acid

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An aromatic epoxy monomer, formed by glycidylation of gallic acid, was crosslinked by adopting different curing agents to obtain bio-based, crosslinked resins with suitable engineering properties. Specifically, tri- and tetra-glycidyl ether of gallic acid (GEGA) were obtained using a two-step synthesis. These bio-based monomers were cured in the following three epoxy formulations: a stiff cycloaliphatic primary amine, isophorone diamine, and a flexible polypropylene oxide amine (Jeffamine D-230). Next, the homopolymerization of GEGA was studied using an ionic initiator, N,N-dimethylbenzylamine, and a complex curing mechanism highlighted by calorimetric and mass spectra analysis. Calorimetric and rheological measurements were used to compare the curing behavior of the studied GEGA-based formulations. Mechanical properties of the gallic acid-based epoxy resins were comparable with those of standard epoxy resin formulations, based on di-glycidyl ether of bisphenol A. Thermogravimetric analysis of cured samples showed a relevant char content at high temperatures.

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INTRODUCTION

Epoxy resins are widely used in many applications, such as coatings, adhesives, laminates, electronic materials, and composite matrices. The wide variety of epoxy resins includes different grades of high performance thermosetting polymers, which are categorized by mechanical strength, adhesive properties, and corrosion resistance (May 1988; Mohan 2013). In most resin formulations the main component is diglycidyl ether of bisphenol A (DGEBA), due to the presence of aromatic rings that support thermal resistance, stiffness, and strength in epoxy resins. However, many studies have shown that bisphenol A (BPA) is harmful to human health because it is a hormonally active agent that exhibits an estrogen-like property dangerous to humans and wildlife (vom Saal and Hughes 2005; Okada *et al.* 2008; vom Saal and Myers 2008; Flint *et al.* 2012).

Many research efforts have focused on replacing BPA in epoxy resins. Renewable resource based polymers, including materials derived from starch, cellulose, vegetable oil, and natural occurring phenols, have demonstrated their potential to replace petrochemical products. In particular, natural polyphenols, which are abundant in biomass, are structurally similar to many building blocks of thermosetting resins. These natural polyphenols could potentially be a resource for epoxy and benzoxazine resins, contributing to properties comparable to oil based bisphenols (Maffezzoli *et al.* 2004; Calò *et al.* 2007; Benyahya *et*

al. 2014; Chen *et al* 2015; Niedermann *et al.* 2015). This includes lignins co-produced during papermaking, which are formulated with epoxy networks and cross-linked by direct heating (Hofman and Glasser 1994). Tannins are another source of natural polyphenols, exhibiting wide structural diversity and generally having more than two phenolic hydroxyl groups. Flavonoids such as resorcinol, catechol, and catechin can be glycosylated by epichlorohydrin to prepare aromatic-based epoxy resins (Nouailhas *et al* 2011). Gallic acid is a phenolic acid that occurs freely or as a part of gallotannins in different plants. These structures contain three phenolic hydroxyl groups and one carboxylic moiety, which can be used to obtain new bio-based epoxy thermosetting resins. Aouf *et al.* (2013) synthesized gallic acid-based epoxy resins that were then cured with a diamine to yield a cross-linked material. The thermal properties of the resulting epoxy network were compared with standard BPA-based epoxy resins. In another recent study, an epoxy resin based on gallic acid and a formaldehyde resin were synthesized as matrix of a glass fiber composite material (Chen *et al.* 2015). Additionally, Hou *et al.* (2016) prepared bio-based epoxy resins from renewable gallic acid; the resulting bio-based nanocomposite and glass fiber-reinforced composite was formulated with succinic anhydride as a curing agent.

In this study, gallic acid glycidylation was performed by slightly modifying the two-step chemical synthesis reported by Aouf *et al.* (2013). Tri- and tetra-glycidyl ethers of gallic acid were obtained, and their chemical structures were characterized. These bio-based epoxides were used to formulate three different model systems as curing agents, a stiff cycloaliphatic primary amine, isophorone diamine (IPDA), and a flexible polypropylene oxide amine, Jeffamine D-230 (DPG). These renewable epoxides were homopolymerized using N,N-dimethylbenzylamine (BDMA) as an ionic initiator (Dell'Erba and Williams 2006). The thermal, rheological, and mechanical properties of the gallic acid-based epoxy resins were characterized and compared with standard DGEBA-based formulations. The results showed that the GEGA structure is suitable to replace BPA-based epoxy resins.

EXPERIMENTAL

Materials

Gallic acid (GA, 97.5%), allyl bromide (C_3H_5Br, 99%), potassium carbonate (K_2CO_3, $\geq$ 99%), triethylamine (Et_3N, $\geq$ 99%), 3-chloroperoxybenzoic acid (MCPBA, 70%), anhydrous magnesium sulfate ($MgSO_4$, $\geq$ 99.5%), sodium bicarbonate ($NaHCO_3$, $\geq$ 99.7%), sodium thiosulfate ($Na_2S_2O_3$, $\geq$ 98%), acetonitrile (CH_3CN, 99.8%), chloroform ($CHCl_3$, $\geq$ 99%), and dichloromethane (CH_2Cl_2, $\geq$ 99.8%) were provided by Fluka (Munich, Germany) or Sigma-Aldrich (Milan, Italy) and were used as received. All reactions were monitored by thin layer chromatography (TLC). TLC was performed on silica gel 60 F254. Tetrahydrofuran (THF; $\geq$ 99%, Sigma-Aldrich) was used as a solvent for swelling measurements.

Two curing agents and an ionic initiator were evaluated: isophorone diamine (IPDA; $\geq$ 99%, Sigma-Aldrich); poly(propylene glycol) bis(2-aminopropyl ether) amine (DPG; $\geq$ 95%, trade name Jeffamine D230 (JD230), Huntsman, Everberg, Belgium); and N,N-dimethylbenzylamine tertiary amine (BDMA; $\geq$ 99%, Sigma-Aldrich). The IPDA and JD230 amine equivalent weight (AEW) were 42.5 and 57.5, respectively.

For comparison purposes, a commercial diglycidyl ether of bisphenol A (DGEBA), Epikote 828 (Hexion, Solbiate Olona, Italy) characterized by an epoxy equivalent weight

(EEW) of 185 to 192 was used with IPDA and DPG.

GEGA formulations with primary amines were prepared using a stoichiometric ratio, *i.e*., considering a reactive amine hydrogen for each epoxy group. An amount of 3% by weight of BDMA was used for homopolymerization of GEGA. All components of the epoxy formulations were liquid at room temperature; the reactive mixtures were prepared by mechanical stirring.

Measurements

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Varian Inova 400 MHz spectrometer (Palo Alto, U.S.A.) using $CDCl_3$ (deuterochloroform) as the solvent. The sample temperature was stabilized at 25 °C.

Gas chromatography-mass spectrometry (GC-MS) spectra were recorded on a Shimadzu GLC 17-A gas-chromatograph (Milan, Italy) linked to a Shimadzu GLC/MS QP5050A selective mass detector (capillary column: HP-5 MS, 30 m).

High-resolution mass spectra (ESI-TOF) were recorded on a Shimadzu LCMS-IT-TOF instrument, using the following settings: mass range, 200 to 2000 m/z; electrospray ion source in positive-ion mode; nebulizer gas, nitrogen at 1.5 L/min; dry gas, nitrogen at 102 MPa and 250 °C; collision gas, argon.

To evaluate the rheological behavior of GEGA-based formulations, isothermal experiments at room temperature were carried out using a strain-controlled rheometer (ARES, Rheometrics Scientific, Bristol, UK). The process was repeated twice to assess the reproducibility of the results. The rheological analyses were performed in steady shear mode at shear rates ranging from 0.1 to 100 s^{-1}, a frequency of 1 Hz, and a strain amplitude of 5%. Moreover, for the all GEGA-based formulations, the occurrence of the gelation event was evaluated measuring the complex viscosity dependence on the temperature, according to ASTM D4473 (1995).

The reactive behavior and glass transition of all formulations were characterized by differential scanning calorimetry, using a Mettler Toledo DSC 823 (Novate Milanese, Italy). All samples were prepared in sealed aluminium pans, and non-isothermal scans were performed at 10 °C/min from 25 to 300 °C under nitrogen atmosphere (50 mL/min). Small sample weights (3 to 5 mg) were tested to minimize the temperature gradient within the sample during the test.

Thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851, according to the ASTM E1131 standard (1998). The samples (15 to 20 mg) were prepared in aluminium pans and heated from 25 to 1000 °C at 10°C/min, under nitrogen flow of 50 mL/min.

Mechanical tensile properties were investigated according to ASTM D638 (2000), using a MTS Insight 10 dynamometer (Eden Prairie, USA.) equipped with a 10 kN capacity load cell. The tensile test was carried out with a testing speed of 5 mm/min. Five specimens were tested for each formulation.

The soluble fraction in the cured resins was measured using tetrahydrofuran (THF) as solvent. For all formulations analysed, a cured thin squared sample, with side length of 18 mm, was immersed in THF until weight stabilization, *i.e*., for 48 h. The samples were extracted from the solvent, oven-dried at 60 °C for 72 h, and weighed (W_{d0}). The soluble fraction was measured according to Eq. 1,

$$\text{Soluble fraction } = \frac{W_d - W_{d0}}{W_d} \qquad (1)$$

where W_d is the mass of the dry sample before solvent absorption. Accounting for the results of non-isothermal DSC scans and thermogravimetric analysis, all epoxy formulations were cured at 120 °C for 1 h and post-cured at 150 °C for 1 h.

RESULTS AND DISCUSSION

Glycidylation of Gallic Acid

Gallic acid glycidylation was based on a two-step chemical synthesis (Aouf *et al.* 2013): 1) the alkaline assisted allylation of hydroxyl groups, leading to the corresponding tetra-allylated gallic acid (AGA), and 2) the epoxidation of the resulting double bonds to produce a mixture of GEGA, as shown in Fig. 1.
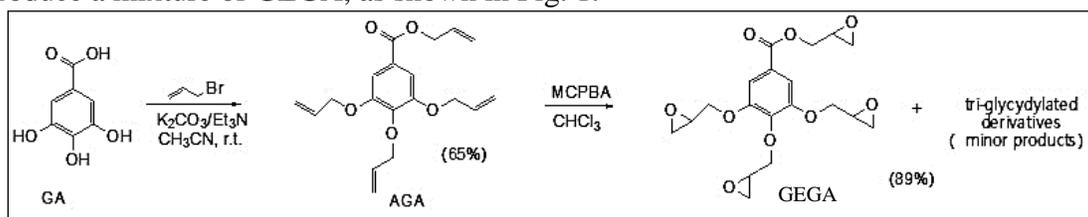
**Fig. 1.** Two-steps synthetic route of allyl 3,4,5-tris(allyloxy)benzoate (GEGA)

The first step of allylation was optimized by replacing the dimethylformamide solvent with acetonitrile and adding triethylamine as an additive, which enhanced the reaction rate. In the second step, tetra-allyl phenolic compound intermediate (AGA) was epoxidized with the common oxidizing agent m-chloroperbenzoic acid (MCPBA) to produce tetra-glycidyl gallic acid (GEGA) as the main product, together with minor amounts of tri-glycidylated regioisomers in a 7:3 ratio, in 89% of overall yield.

The first step of gallic acid allylation is detailed below. In a 1 L two-necked flask, equipped with a magnetic bar and a dropping funnel, 15 g (0.086 mol) of gallic acid (GA, 97.5%) was dissolved into 500 mL of CH_3CN. The resulting solution was stirred for 30 min at 0 °C. While maintaining the temperature at 0 °C, 72 g of K_2CO_3 (0.521 mol) was added with vigorous stirring for 3 min. Next, 68 mL (0.786 mol) of allyl bromide (C_3H_5Br) was added dropwise over the course of an hour, followed by the dropwise addition of 15 mL (0.107 mol) of triethylamine. The resulting mixture was left to react at room temperature for 15 h. The reaction mixture was filtered, and the liquid was evaporated under a vacuum at 80 °C to remove solvent and excess allyl bromide. The residue was purified by silica gel chromatography (hexane/ethyl acetate: 96/4) to give allyl 3,4,5-tris(allyloxy)benzoate (AGA), a pale yellow oil (65% yield).

The second step of AGA epoxidation proceeded as follows. A 2 L two-necked flask equipped with a dropping funnel and a mechanic stirrer was charged with a solution of 50 g of AGA (0.151 mol) in 700 mL of $CHCl_3$. Next, 172.5 g (0.700 mol) of MCPBA (70%) was slowly added at 0 °C over a period of 30 min. The mixture was warmed to room temperature and stirred for 48 h. The reaction was diluted with 300 mL of CH_2Cl_2 and washed with an aqueous solution of 30% $Na_2S_2O_3$ (3 x 200 mL) to remove the excess oxidant (MCPBA), and then washed with a saturated aqueous solution of $NaHCO_3$ (3 x 200 mL) to neutralize MCBA by-product. The product was then washed with 100 mL of distilled water. The organic layer was dried over Na_2SO_4, filtered, and evaporated under a vacuum.

Chemical Characterization

Reaction products were identified by comparison of their GC-MS and ^{1}H-NMR spectra with those reported in the literature and the NIST database. The ^{1}H-NMR spectrum of the reaction product in the first step (Fig. 2) confirmed the formation of tetrallylated gallic acid (AGA), as shown by the following signals: δ = 4.62 (dt, J = 5.08, 1.3 Hz, 6H), 4.79 (dt, J = 5.66, 1.33 Hz, 2H), 5.18 (dq, J = 10.35, 1.17 Hz, 1H), 5.29 (dq, J = 10.54 Hz, 2H), 5.33 (dq, J = 17.18, 1.37 Hz, 2H), 5.39 (dq, J = 16.20, 1.36 Hz, 1H), 5.43 (dq, J = 17.37, 1.56 Hz, 2H), 6.06 (m, 4H), 7.31 (s, 2H) (Aouf *et al.* 2013). MS data (EI) mz (%): 330 (1), 302 (9), 261 (100), 219 (24), 175 (10), 145 (11), 133 (15), 119 (11), 105 (13), 91 (17).
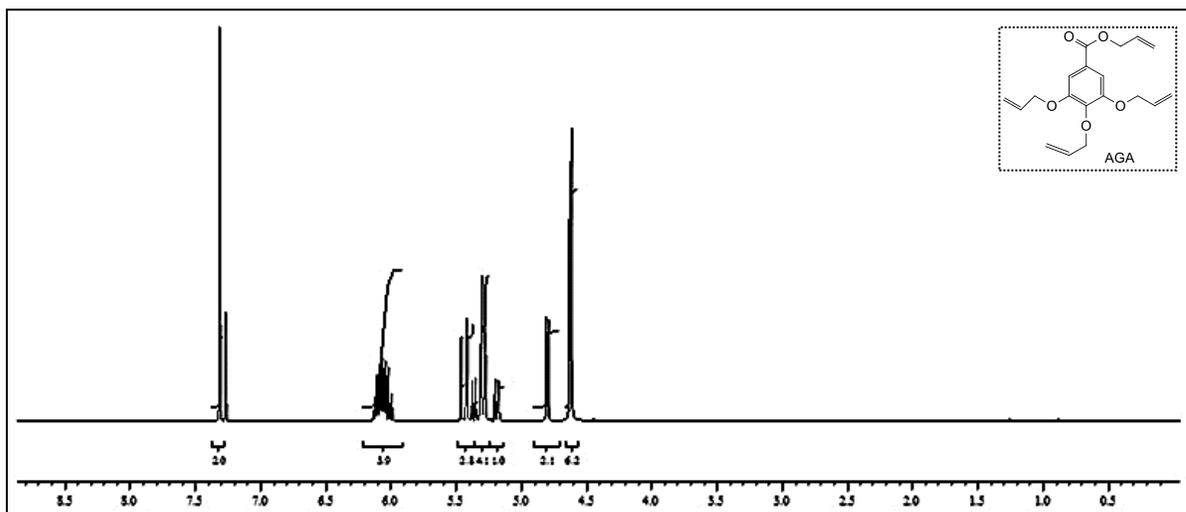
Fig. 2. ^{1}H NMR spectrum of allyl 3,4,5-tris(allyloxy)benzoate (AGA)

The exact composition of the reaction mixture after the epoxidation step was determined using both GC-MS and ^{1}H NMR analyses. The GC-MS chromatogram (Fig. 3a) shows the formation of four epoxidation compounds: GEGA (the most abundant product (75%)), two regioisomeric derivatives of tri-epoxide (TGA, in 23% of overall abundance), and a small amount of only one regioisomer of di-epoxide (DGA, 2%). Neither mono-epoxide derivatives nor the starting reagent, AGA, were detected.
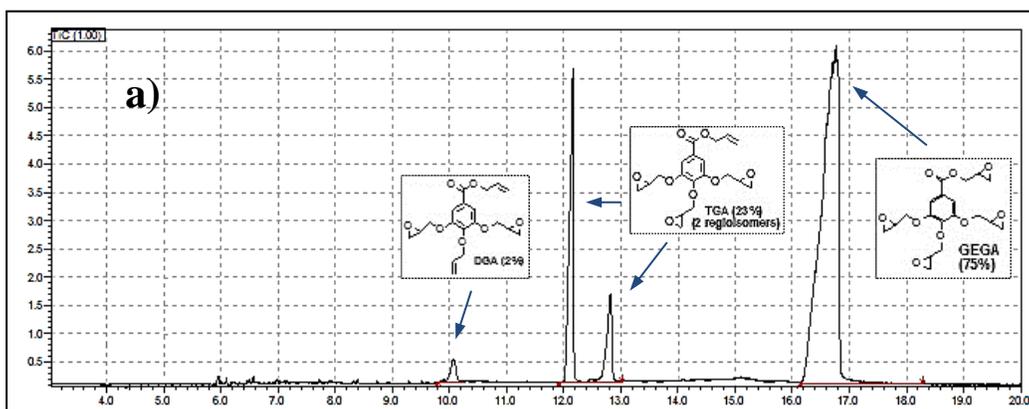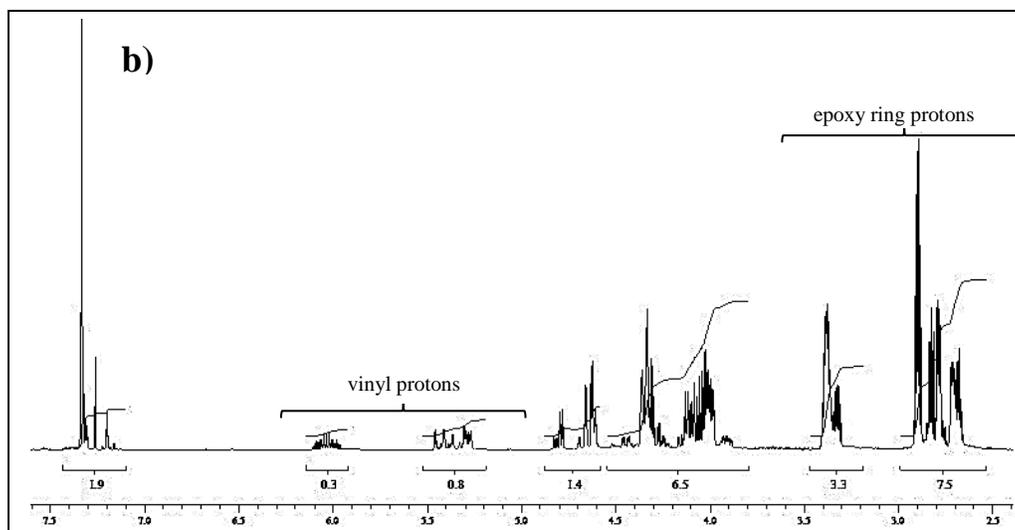
Fig. 3. a) GC-MS chromatogram displaying composition of GA epoxides (determined based on peak areas) and b) ^{1}H NMR images of the epoxidation products of AGA

The ^{1}H NMR spectrum of the mixture (Fig. 3b) corroborates the presence of products deriving from the partial epoxidation (TGA and DGA), evidenced by the signals of vinyl protons at 5.4 and 6.0 ppm. Based on integrals of vinyl and epoxy rings protons, the latter being in the range 2.5-3.5 ppm, the ratio between tetra-epoxide (GEGA) and partially epoxidation products is 7:3 (Aouf *et al.* 2013). The mixture of epoxides was obtained in an 89% overall yield (yellow oil). NMR signals of reaction products (Fig. 3b): $\delta = 2.55 - 2.92$ (m, 7.5 H, epoxy ring CH_2), 3.29 – 3.42 (m, 3.3 H, epoxy ring CH), 3.88 – 4.84 (m, 7.9 H, epoxy and allyl CH_2O), 5.25 – 5.47 (m, 0.8 H, vinyl CH_2), 6.03 (m, 0.3 H, vinyl CH), and 7.15-7.35 (br s, 1.9 H) ppm. MS data of epoxide products [(EI) mz (%), (Fig. 3a)]: 3,4,5-tri-glycidylether glycidyl benzoate (GECA, RT 16.8 min) 394 (M[+], 17), 321 (10), 247 (9), 191 (6), 153 (7), 107 (8), 57 (100); tri-glycidylated regioisomer (RT 12.1 min) 378 (M[+], 29), 348 (3), 321 (5), 265 (3), 107 (6), 57 (100); tri-glycidylated regioisomer (RT 12.8 min) 378 (M[+], 23), 321 (5), 305 (6), 247 (13), 191 (5), 119 (10), 91 (18), 77 (23), 57 (100); di-glycidylated epoxide (RT 10.1 min) 362 (9), 321 (49), 219 (7), 175 (4), 119 (10).

EEW determination of the mixture of GA epoxides was based on percentages of GEGA, TGA and DGA in the epoxide products mixture evaluated by both 1H NMR and GC-MS analyses. ^{1}HNMR led to EEW=104.07 g/equiv and GC-MS to EEW=105.70 g/equiv. Both values were found to be very close to that obtained by Aouf *et al.* (2013) of 103 g/equiv.

Calorimetric Analysis

Non-isothermal DSC analyses were performed to investigate polymerization behavior of GEGA-based epoxy formulations (Fig. 4). The heat of the reaction, ΔH, and the peak temperature, T_{peak}, are summarized in Table 1.

A single exothermic peak, corresponding to the polymerization reaction, was observed for GEGA/IPDA and GEGA/DPG (Fig. 4). This peak suggests the occurrence of the well-known opening mechanism of the epoxide ring by primary and secondary amine groups (Fig. 5) (Horie *et al.* 1970; Finzel *et al.* 1995). For both formulations, reactions began at room temperature, showing a reaction peak at about 90 °C.
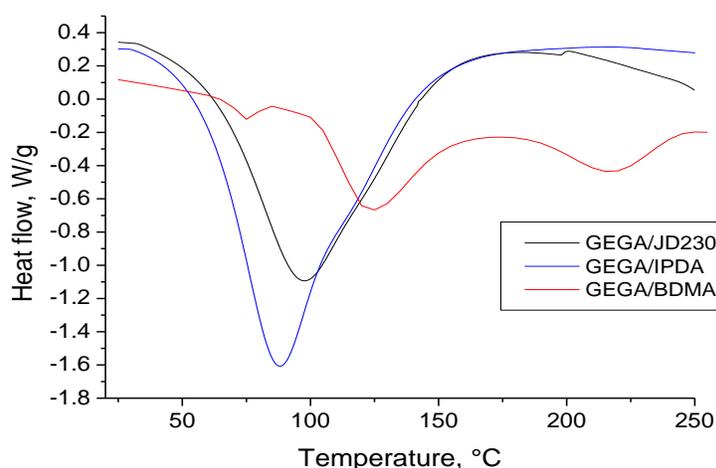
Fig. 4. DSC thermograms of the GEGA-based formulations (endo-up)

Table 1. DSC Analysis for GEGA-based Formulations

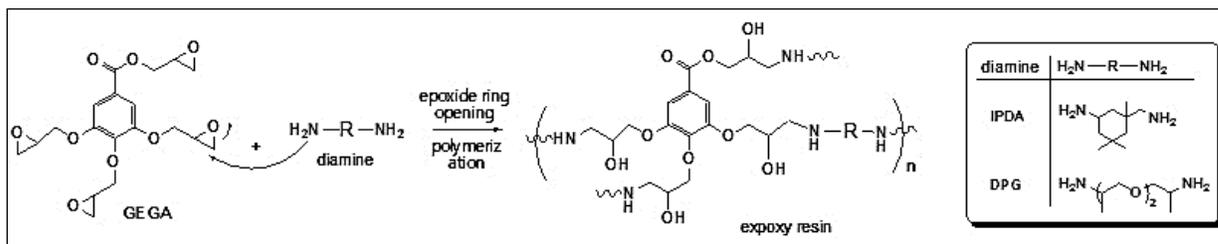|	ΔH (J/g)	ΔH (kJ/mol)	T_{peak} (°C)	T_g (°C) 2nd DSC scan	T_g (°C) Cured at 150 °C
GEGA/IPDA	531	55.7	90	158	145
GEGA/DPG	488	51.1	94	98	83
GEGA/BDMA	12/182/90	29.8	76/124/218	136	127
For GEGA/BDMA sample, the data associated with the three peaks of Fig. 4 are reported					

Fig. 5. Scheme of polymerization reaction in GEGA/IPDA and GEGA/DPG formulations through the epoxide ring opening (single exothermic peaks in Fig. 4)

No relevant differences in the reaction rate were observed, while the heat of reaction was slightly higher for the formulation cured with IPDA than that with DPG (531 J/g for IPDA *vs*. 488 J/g for GEGA/DPG). The observed behavior is associated with the higher molecular weight of DPG, corresponding to a lower content of reactive groups, per unit weight. Table 1 also reports the heat of reaction per mole, obtained using an average value of EEW= 104.89 g/equiv. The molar heat of reaction obtained for amine cured GEGA is only slightly higher than those found in the literature for amine addition to tetra- and di-epoxides, usually between 45 and 50 kJ/mol (Apicella *et al.* 1984; Nunez *et al.* 1999; Swier *et al.* 2004). The slight difference in peak temperatures could be explained by the lower steric hindrance of the cyclic amine compared with polyether. The DSC signal of the GEGA/BDMA formulation shows three different exothermic peaks, with enthalpy of reaction, in order of appearance, of 12, 182, and 90 J/g, respectively.

To gain insight into the reaction mechanism, high-resolution mass spectra analyses were carried out on the reactive mixture, which was heated to 85 °C, *i.e.*, the temperature was measured at the end of the first exothermic event, for 3 min. After heating, the blend was still liquid and soluble in methanol; therefore, it can be analysed by the ESI-TOF technique. The resulting spectrum showed the presence of three initiator species, at m/z ratios of 498, 514, and 530, formed by a reaction between tertiary amine and epoxides precursors, *i.e.*, di-, tri-, and tetra-glycidyl ether of gallic acid, respectively (Fig. 6a).
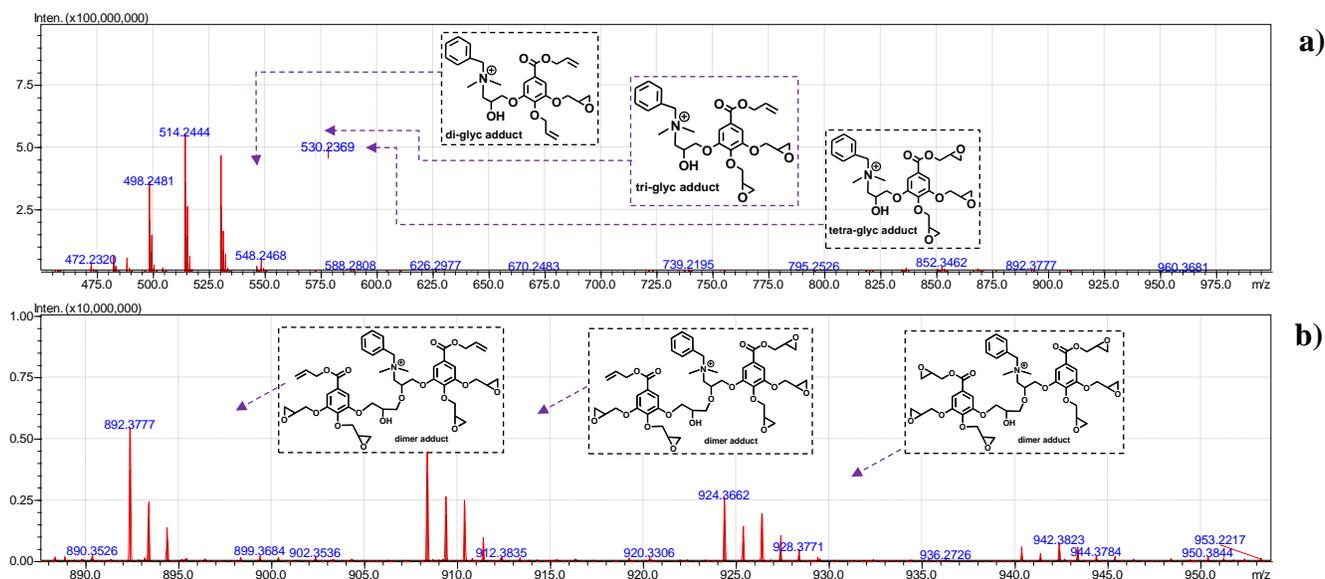
Fig. 6. a) HR-MS of initiator adducts formed in the first step of homo-polymerization of the GEGA/BDMA formulation (first exothermic peak in Fig. 4). b) Expanded range of ESI-TOF spectrum (880-950 *m/z* ratio) showing dimers adducts of homo-polymerization reaction

Moreover, in the *m/z* range 850-950, three dimers in small amounts (at 892, 908, and 924 m/z), consisting of two molecules of epoxide, joined by an ether bond, were identified (Fig. 6b). Therefore, the first peak is associated with the formation of cationic initiators.

The second and the third exothermic DSC peaks, shown by the GEGA/BDMA curve in Fig. 4, are associated with the next steps of reaction between the structures described above and the remaining epoxy groups. Specifically, the third peak, characterized by a heat of reaction of about half of that associated with the second peak, was attributed to the epoxy groups with higher steric hindrance. This reasonably includes the fourth unreacted epoxy group of GEGA, which requires higher reaction temperatures. In correspondence with the third peak, the DSC signal for both amine hardened samples (more evident for DPG/GEGA) presents a deviation, probably due to the onset of degradation.

A second DSC scan was performed to evaluate the maximum glass transition temperature (T_g) of the GEGA-based formulations (Table 1). The results of the calorimetric characterization are summarized in Table 1. Higher glass transition temperatures are associated with a higher degree of crosslinking and stiffness of the tridimensional epoxy network. The lower glass transition temperature of GEGA/DPG was explained by the linear, flexible backbone of DPG. Conversely, the epoxy network based on IPDA exhibited

a higher crosslinking density and lower flexibility due to the presence of the IPDA ring, which is much smaller and less flexible than DPG. GEGA/IPDA shows a T_g almost equal to that reported in the literature (Duchet and Pascault 2003), *i.e.* $T_g = 156°C$. On the other hand, GEGA induced a T_g higher than the value obtained by Duchet and Pascault (2003) using DGEBA when DPG was used. This can be directly related to the higher number of epoxy groups of GEGA.

Rheological Measurements

The rheological isothermal experiments at room temperature showed Newtonian behavior for the GEGA precursor, with a measured viscosity value of 2 Pa·s. According to the ASTM D4473 standard (1995), the temperature corresponding to a modulus of the complex viscosity $|\eta^*|$ value of 100 Pa·s is considered the dynamic gel temperature. The complex viscosity as a function of temperature for the three epoxy systems is reported in Fig. 7. The results obtained for all formulations indicated the occurrence of the gelation event at temperatures of 73 °C, 92 °C, and 114 °C for GEGA/IPDA, GEGA/DPG, and GEGA/BDMA epoxy mixtures, respectively. Considering that curing with IPDA and DPG follows a similar mechanism, this result further highlights the higher reactivity of IPDA-based formulation.
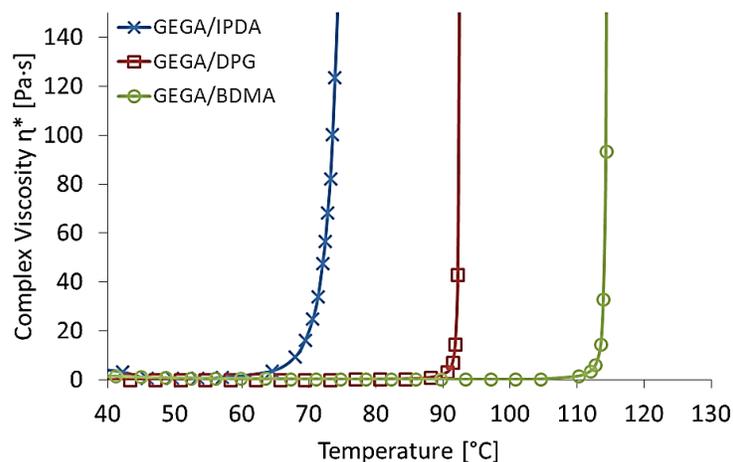

Fig. 7. Gel time curves for the GEGA-based formulations

Swelling Properties

The swelling results calculated for the three epoxy formulations that were analysed are listed in Table Table 2.

Table 2. Values of Swelling Measurements for the GEGA-based Formulations

	Soluble Fraction (%)
GEGA/IPDA	1.47
GEGA/DPG	1.42
GEGA/BDMA	1.05

The soluble fraction, as defined in Eq. 1, provides information about the amount of the sol fraction in the epoxy polymer. The results show that only a small amount of polymer, ranging from 1.05 % to 1.47 %, remained soluble and not bonded to the

crosslinked network. This soluble fraction was the lowest when ionic polymerization on neat GEGA was performed.

Thermogravimetric Analysis

Thermogravimetric studies were carried out to investigate the thermal stability and charring behavior of the cured samples. The onset degradation temperatures and the residual mass at 600 °C, summarized in Table 3, were obtained from the TGA thermograms reported in Fig. 8. There was only one-step of degradation for all samples. The results show a negligible weight loss up to 250 °C for systems with primary amines, while Fig. 4 suggests that the degradation of DPG/GEGA, not including weight losses, started below 250 °C. The beginning (T_{onset}) and final (T_{endset}) degradation temperatures of systems cured with both amines are similar. However, the homopolymerized GEGA shows a higher onset of degradation temperatures, meaning better thermal stability, which was also observed by DSC analysis. As the temperature increased, the polymer decomposed rapidly at a temperature level of about 250 °C. At higher temperatures, no additional mass loss was observed, resulting in a remaining residual char. At 600 °C, a char of 16%, 18%, and 30% was measured for systems with DPG, IPDA, and the epoxy resin with tertiary amine, respectively.
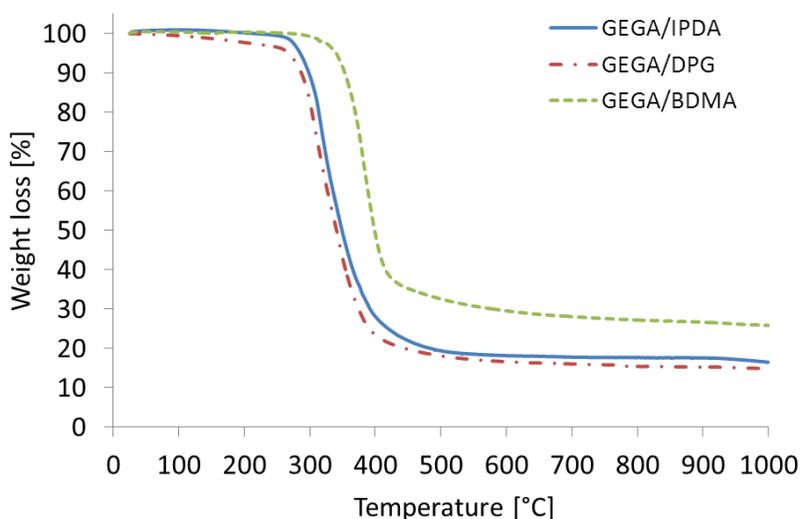

Fig. 8. Thermogravimetric analysis of GEGA-based epoxy resins

Table 3. TGA Analysis

	T_{onset} (°C)	T_{endset} (°C)	Char at 600°C (%)
GEGA/IPDA	292	370	18.1
GEGA/DPG	284	365	16.6
GEGA/BDMA	353	411	29.5

The initial thermal decomposition temperature was primarily determined by the basic elemental composition of the network. When amines are the crosslinking agent, the structure consists of connections between epoxy and amine molecules and the difference of the thermal lability of the amine, *i.e.*, short or long chain, aliphatic or aromatic structure. The tertiary amine, instead, acts as an ionic initiator, leading to a crosslinked structure

made of ether bonds linking aromatic rings. This structure appears to be much more stable than the previously mentioned amine crosslinked epoxies. These structures also display a higher amount of char, due to the very high aromatic content of the GEGA/BDMA system, which favors carbonization similar to other aromatic polymers. In addition to the high carbon/hydrogen content, the arrangement of the epoxy rings is important, since the smaller the distance between them, the greater the charring capacity (Dyakonov *et al.* 1996). Furthermore, the slight difference between the char residue of the two systems crosslinked with amines can be attributed to the chemical nature of DPG, a linear amine with a long chain keeping GEGA aromatic rings distant from each other, compared to the structure of GEGA/IPDA where the amine backbone is shorter.

The residual char content is an important index for evaluating the fire retardant properties of epoxy resins. Several studies have been devoted to improving the fire resistance of epoxy-based formulations by introducing fillers (Dyakonov *et al.* 1996; Puglia *et al.* 2001; Torre *et al.* 2004; Rahatekar *et al.* 2010). To improve fire resistance, the monomer composition can be tailored to increase aromatic content in cured resins. Thus, the high initial degradation temperature and higher char percentage of GEGA-based formulations supports their application in fire resistant resins and composites.

Tensile Mechanical Properties

A maximum curing temperature of 150 °C was adopted to keep all materials above or very close to their maximum glass transition temperature. Although GEGA/BDMA mixtures in DSC experiments presented a very small third reaction peak above 200 °C, which was formerly attributed to the reaction of the epoxy groups characterized by a very high steric hindrance, the specimens for mechanical testing were obtained at 150 °C to limit the crosslinking, favoring more ductile behavior. Furthermore, the DSC signal of GEGA/DPG mixture (Fig. 4) shows a deviation above 200 °C, indicating a possible onset of degradation of polyether chains of DPG. T_g values of samples cured at 150 °C were only slightly lower than those measured after a DSC san up to 250 °C, as reported in Table 1.

Very brittle polymers are typically obtained after the homopolymerization of DGEBA epoxies (Mark 1999). The mechanical properties of GEGA-based formulations are reported in Table 4. All epoxy networks were characterized by an adequately high elastic modulus, showing a brittle fracture without yielding. The epoxy resin based on the more flexible DPG amine gave the highest elongation at break and the greatest strength, hence the highest toughness. The elongation at break of GEGA/IPDA and GEGA/BDMA epoxy mixtures were slightly lower than those obtained when DGEBA epoxy was used (Table 4; Mark 1999). This result was attributed to the molecular structure of GEGA, characterized by a shorter, stiffer backbone (there is a single aromatic ring) and by higher functionality than DGEBA. Similarly, the GEGA/DPG sample exhibited the highest strength, though still lower than that of DGEBA/DPG resin. The elastic moduli were similar for all the investigated systems and higher than DGEBA crosslinked with the same amines (Table 4). This is due to the lower epoxy equivalent of GEGA compared with DGEBA, leading to a higher crosslinking density.

Table 4. Mechanical Properties of GEGA and DGEBA-based Epoxy Resin

	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
GEGA/IPDA	3.6 ± 0.3	43.1 ± 13.1	1.4 ± 0.3
GEGA/DPG	3.5 ± 0.2	70.6 ± 2.9	6.1 ± 0.6
GEGA/BDMA	3.2 ± 0.2	31.2 ± 2.3	1.1 ± 0.1
DGEBA/IPDA	3.1± 0.8	34.1 ± 2.0	1.7± 0.2
DGEBA/DPG	3.0± 0.2	116.4± 7.0	8.6± 0.3

CONCLUSIONS

1. The possibility of replacing Bisphenol A as precursor of epoxy resin with natural phenolic compounds was presented. This specifically included use of a mixture of tri- and tetra-glicydil ether of gallic acid was used. This component was mixed with two primary amines, aliphatic and cycloaliphatic, and a tertiary amine. The primary amines act as crosslinking agents, while the third acted as an ionic initiator for homopolymerization reaction.

2. The chemical structure of the synthesized monomers was characterized, and calorimetric and rheological analyses were performed to characterize the curing behavior of the different formulations.

3. A complex three-step curing process was observed during the homopolymerization of GEGA in the presence of the tertiary amine initiator.

4. GEGA-based epoxy resins were characterized by an elastic modulus slightly higher than that obtained using DGEBA, but they were more brittle, showing a lower strain to break.

5. In all cases, and in particular for homopolymerized GEGA-based network, characterized by a solid residue at 1000 °C of almost 30 wt.%, the high char content represents a very interesting result in view of an application of GEGA in fire resistant systems.

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REFERENCES CITED

Aouf, C., Nouailhas, H., Fache, M., Caillol, S., Boutevin, B., and Fulcrand, H. (2013). "Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin," *European Polymer Journal* 49(6), 1185-1195. DOI: 10.1016/j.eurpolymj.2012.11.025

Apicella, A., Nicolais L., Iannone, M., and Passerini, P. (1984). "Thermokinetics and chemorheology of the cure reactions of tetraglycidyl diamino diphenyl methane-

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diamino diphenyl sulfone epoxy systems," *Journal of Applied Polymer Science* 29, 2083-2096. DOI: 10.1002/app.1984.070290616

ASTM D4473 (1995). "Measuring the cure behavior of thermosetting resins using dynamic mechanical procedures," ASTM International, West Conshohocken, PA.

ASTM D638 (2000). "Standard test method for tensile properties of plastics," ASTM International, West Conshohocken, PA.

ASTM E1131 (1998). "Standard test method for compositional analyses by thermogravimetry," ASTM International, West Conshohocken, PA.

Benyahya, S., Aouf, C., Caillol, S., Boutevin, B., Pascault, J. P., and Fulcrand, H. (2014). "Functionalized green tea tannins as phenolic prepolymers for bio-based epoxy resins," *Industrial Crops and Products* 53, 296-307. DOI: 10.1016/j.indcrop.2013.12.045

Calò, E., Mele, G., Maffezzoli, A., Mazzetto, S. E., Martina, F., Tarzia, A., and Stifani, C. (2007). "Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites," *Green Chemistry* 9, 754-759. DOI: 10.1039/B617180J

Chen, S., Lv, S., Hou, G., Huo, L., and Gao, J. (2015). "Mechanical and thermal properties of biphenyldiol formaldehyde resin/gallic acid epoxy composites enhanced by graphene oxide," *Journal of Applied Polymer Science* 132(41), app. 42637. DOI: 10.1002/app.42637

Dell'Erba, I. E., and Williams, R. J. J. (2006). "Homopolymerization of epoxy monomers initiated by 4-(dimethylamino)pyridine," *Polymer Engineering and Science* 46(3), 351-359. DOI: 10.1002/pen.20468

Duchet, J., and Pascault, J. P. (2003). "Do epoxy–amine networks become inhomogeneous at the nanometric scale?," *J. Polym. Sci. B Polym. Phys*. 41, 2422-2432. DOI:10.1002/polb.10585

Dyakonov, T., Mann, P. J., Chen, Y., and Stevenson, W. T. K. (1996). "Thermal analysis of some aromatic amine cured model epoxy resin systems - II: Residues of degradation," *Polymer Degradation and Stability* 54, 67-83. DOI: 10.1016/0141-3910(96)00096-1

Finzel, M. C., Delong, J., and Hawley, M. C. (1995). "Effect of stoichiometry and diffusion on an epoxy/amine reaction mechanism," *Journal of Polymer Science Part A: Polymer Chemistry* 33(4), 673-689. DOI: 10.1002/pola.1995.080330409

Flint, S., Markle, T., Thompson, S., and Wallace, E. (2012). "Bisphenol A exposure, effect and policy: A wildlife perspective," *Journal of Environmental Management* 104, 19-34. DOI: 10.1016/j.jenvman.2012.03.021

Hofmann, K., and Glasser, W. (1994). "Engineering plastics from lignin, 23. Network formation of lignin-based epoxy resins," *Macromolecular Chemistry and Physics* 195(1), 65-80. DOI: 10.1002/macp.1994.021950106

Horie, K., Hiura, H., Sawada, M., Mita, I., and Kambe, H. (1970). "Calorimetric investigation of polymerization reactions III. Curing reaction of epoxides with amines," *Journal of Polymer Science Part A: Polymer Chemistry* 8(6), 1357-1372. DOI: 10.1002/pol.1970.150080605

Hou, G., Gao, J., Xie, J., and Li, B. (2016). "Preparation and properties characterization of gallic acid epoxy resin/succinic anhydride bionanocomposites modified by green reduced graphene oxide," *Soft Materials* 14, 27-37. DOI: 10.1080/1539445X.2015.1098704

Maffezzoli, A., Calò, E., Zurlo, S., Mele, G., Tarzia A., and Stifani, C. (2004). "Cardanol

based matrix biocomposites reinforced with natural fibres," *Composites Science and Techonology* 64(6), 839-845. DOI: 10.1016/j.compscitech.2003.09.010

Mark, J. E. (1999). *Polymer Data Handbook*, Oxford Univ. Press, Inc., New York, NY.

May, C. A. (1988). *Epoxy Resin: Chemistry and Technology*, Marcel Dekker, New York.

Mohan, P. A, (2013). "A critical review: The modification, properties and applications of epoxy resins," *Polymer-Plastics Technology and Engineering* 52(2), 107-125. DOI: 10.1080/03602559.2012.727057

Niedermann, P., Szebenyi, G., and Toldy, A. (2015). "Novel high glass temperature sugar-based epoxy resins: Characterization and comparison to mineral oil-based aliphatic and aromatic resins," *Express Polymer Letters* 9(2), 85-94. DOI: 10.3144/expresspolymlett.2015.10

Nouailhas, H., Aouf, C., Le Guerneve, C. L., Caillol, S., Boutevin, B. and Fulcrand, H., (2011). "Synthesis and properties of biobased epoxy resins. Part 1: Glycidylation of flavonoids by epichlorohydrin," *Journal of Polymer Science Part A: Polymer Chemistry* 49(10), 2261-2270. DOI: 10.1002/pola.24659

Nunez, L., Fraga, F., Fraga, L., and Castro, A. (1999). "Kinetic and thermodynamic studies of an epoxy system diglycidyl ether of bisphenol-a/1,2, diamine cyclohexane," *Journal of Applied Polymer Science* 75, 291-305. DOI:10.1002/(SICI)1097-4628(20000110)75:2<291::AID-APP12>3.0.CO;2-A

Okada, H., Tokunaga, T., Liu, X., Takayanagi, S., Matsushima, A., and Shimohigashi, Y. (2008). "Direct evidence revealing structural elements essential for the high binding ability of bisphenol A to human estrogen-related receptor-gamma," *Environmental Health Perspectives* 116(1), 32-38. DOI: 10.1289/ehp.10587

Puglia, D., Manfredi, L. B., Vazquez, A., and Kenny, J. M. (2001). "Thermal degradation and fire resistance of epoxy-amine-phenolic blends," *Polymer Degradation and Stability* 73(3), 521-527. DOI: 10.1016/S0141-3910(01)00157-4

Rahatekar, S. S., Zammarano, M., Matko, S., Koziol, K. K., Windle, A. H., Nyden, M., Kashiwagi, T., and Gilman, J. W. (2010). "Effect of carbon nanotubes and montmorillonite on the flammability of epoxy nanocomposites," *Polymer Degradation and Stability* 95(5), 870-879. DOI: 10.1016/j.polymdegradstab.2010.01.003

Swier, S., Van Assche, G., and Van Mele, B. (2004). "Reaction kinetics modeling and thermal properties of epoxy–amines as measured by modulated-temperature DSC. II. Network-forming DGEBA + MDA," *Journal of Applied Polymer Science* 91, 2814-2833. DOI: 10.1002/app.13467

Torre, L., Lelli G., and Kenny, J. M. (2004). "Cure kinetics of epoxy/anhydride nanocomposite systems with added reactive flame retardants," *Journal of Applied Polymer Science* 94(4), 1676-1689. DOI: 10.1002/app.20162

vom Saal, F. S., and Myers, J. P. (2008). "Bisphenol A and risk of metabolic disorders," *Journal of the American Medical Association* 300(11), 1353-55. DOI: 10.1001/jama.300.11.1353

vom Saal, F. S., and Hughes, C. (2005). "An extensive new literature concerning low-dose effects of bisphenol A shows the need for a new risk assessment," *Environmental Health Perspectives* 113(8), 926-933. DOI: 10.1289/ehp.7713