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Divanillin-based epoxy precursors as DGEBA substitutes for bio-based epoxy thermosets

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Bio-based epoxy monomers from divanillyl alcohol were successfully synthesized and fully characterized. Diglycidylether of divanillyl alcohol (DiGEDVA), triglycidylether of divanillyl alcohol (TriGEDVA) and tetraglycidyl of divanillyl alcohol (TetraGEDVA) were cured with cyclo-aliphatic diamine (IPDA) a common diamine hardener. Main properties of these vanillin-based epoxy resins were determined by DSC, TGA, DMA, tensile tests and compared to DGEBA-based reference. These bio-based systems displayed phase transition T_{α} from 140 to 200 °C and exhibited thermal degradation comparable to the DGEBA-based network with high char residue. Such bio-based aromatic monomers are promising substitutes to the DGEBA and can be used in high performance epoxy resin applications as bio-based aromatic polyglycidylethers.

Introduction

Structural adhesives are an important class of materials in aerospace industry, notably. They advantageously replace mechanical joining because of their excellent mechanical performances, good thermal properties and weight saving.¹ Among them, epoxy adhesives represent an important family and are mostly derived from bisphenol-A (BPA),² a reprotoxic substance, subjected to strong regulation.^{3–8} Developing substitutes to BPA is thus a real challenge to tackle. In addition to health care issues, the need for renewable building-blocks becomes today crucial.⁹ Subsequently, the design of effective bio-based substitutes to diglycidylether of bisphenol-A (DGEBA) is a challenge both for environmental and healthcare concerns.

Vegetable oils are one of the most important classes of renewable sources due to their abundant availability and rather low price.^{10,11} However, their aliphatic structures do not generally allow the achievement of high performance epoxy materials.^{12,13} The design of bio-based epoxy thermosets from synthons exhibiting a more rigid skeleton, such as rosin, glucose derivatives or cardanol was recently reported.^{14–18} Despite the good potential of these bio-sourced materials, their thermal and thermo-mechanical properties are generally lower than the ones of classical DGEBA-based epoxy network. The search for bio-based aromatic and rigid synthons is thus a hot topic in this field. Indeed, aromatic bio-based synthons from tannins and lignin are promising candidates as BPA-substitutes for the design of epoxy thermosets.^{19–22} However, these renewable resources suffer from their variable and complex structures together with their difficulty to process. In this way, the development for well-defined bio-based aromatic synthons, available in large quantities and easily processable is of prime importance.

In this way, vanillin is a very interesting candidate because

it is one of the non-hazardous aromatic compounds industrially available from biomass.²³ Since 1962, the Borregaard's biorefinery has developed the lignin-to-vanillin process at an industrial scale.²⁴ Today, lignin-derived vanillin represents 15 % of the overall vanillin production.^{25,26} Therefore, vanillin and derivatives have grown a strong interest as bio-based building blocks for renewable polymers and notably epoxy thermosets.^{27–36} Recently, we have developed an efficient C-C coupling of phenolic molecules through enzymatic catalysis leading to a large palette of bis-phenolic structures, such as divanillin.^{36–38} In comparison to already existing structures, such bio-sourced bisphenols have a huge potential for epoxy thermosets as the two phenol rings are linked through the 5 and 5' positions without any spacer.

Herein, novel divanillin-based epoxy synthons were thus prepared and used as monomer precursors of epoxy thermosets. The curing was performed with isophorone diamine (IPDA), which is liquid at room temperature and exhibits a good reactivity towards epoxy functions. Thermal and thermo-mechanical properties of the resulting bio-based epoxy thermosets were investigated and compared to the DGEBA-based reference.

Results and discussion

Synthesis of divanillin-based epoxy monomers

The synthesis of divanillin by selective enzymatic oxidative coupling, followed by the reduction of aldehyde moieties to prepare divanillyl alcohol (DVA) with high yield (85 %) and purity was already reported in previous papers (**Scheme 1**).^{36,39} The direct glycidylation of DVA was then performed as described in **Scheme 2**. In addition to the two phenol functions, DVA exhibits two benzylic alcohols, which can be also derivatized into epoxy groups thus yielding to pluriglycidylethers (GEDVA) of DVA. Several works describe the synthesis of epoxy compounds from phenolic substrates in the presence of epichlorohydrin, a phase-transfer catalyst (PTC) and a base.^{40–42} Usually, a large excess of epichlorohydrin is used to prevent the formation of oligomers. Moreover, additional solvents are not necessary during the synthesis as

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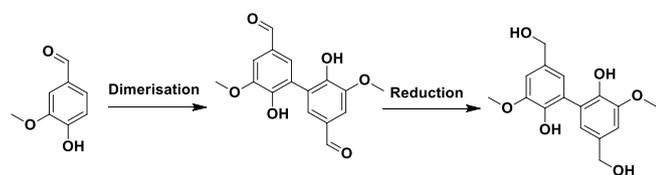
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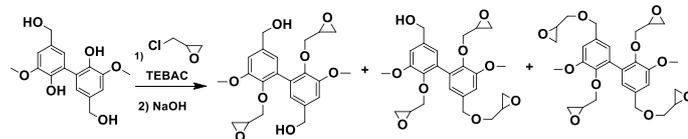
Electronic Supplementary Information (ESI) available: ¹H NMR, ¹³C NMR, DSC thermograms, DMA and tensile test traces.

See DOI: 10.1039/x0xx00000x

epichlorohydrin acts as a reactive solvent. The synthetic pathway adapted for DVA takes place in two steps. First, the PTC eases the nucleophilic substitution of epichlorohydrin with phenol by assisting the phenolate ion into the organic phase. The nucleophilic substitution directly leads to the synthesis of epoxy moieties, but a ring-opening mechanism occurs also yielding “open-epoxy” intermediates. The second step thus consists in adding a base at room temperature in order to close the epoxy ring intermediates. At this stage, the base is also needed to catalyze the glycidylation of the benzyl alcohol moieties. Following this synthetic route, different DVA-based epoxy monomers were prepared: diglycidylether of divanillyl alcohol (DiGEDVA), triglycidylether of divanillyl alcohol (TriGEDVA) and tetraglycidylether of divanillyl alcohol (TetraGEDVA) (Scheme 2). These latter compounds are generally obtained as a mixture at different ratios, which is fractionated by flash chromatography. Nevertheless, two key parameters have been identified to control this reaction, i.e. the sodium hydroxide content and the second step reaction duration. In this way, by tuning these two parameters, the reaction is more oriented towards one type of GEDVA. The kinetics of glycidylation reaction was followed by HPLC with respect to the equivalent number of NaOH per OH group (benzyl alcohol + phenol) as shown on the Figure 1. For a ratio NaOH/OH equal to 10, TetraGEDVA is mainly obtained (80 % yield). In contrast, at lower NaOH/OH ratios, DiGEDVA is mainly obtained (80 % yield). Subsequently, it is rather convenient to selectively obtain a majority of DiGEDVA or TetraGEDVA with very good yields. GEDVA monomers were then fully characterized by HRMS and NMR spectroscopy (Figure 2 and Figures SI-S10). The glycidylation of phenols was confirmed by the presence of signals of epoxy moieties at 2.36, 2.60, 2.95, 3.74 and 3.88 ppm.



Scheme 1 Synthesis of divanillyl alcohol from vanillin



Scheme 2 Structure of bio-based epoxy monomers from DVA, from left to right: diglycidylether of divanillyl alcohol (DiGEDVA), triglycidylether of divanillyl alcohol (TriGEDVA) and tetraglycidylether of divanillyl alcohol (TetraGEDVA)

Glycidylation of benzyl alcohols of TriGEDVA and TetraGEDVA was confirmed by the characteristics signals of epoxy moieties at 2.55, 2.73, 3.14, 3.28, and 3.70 ppm and by the gradual decrease of the benzyl alcohol signal at 5.16 ppm. In addition, TriGEDVA NMR spectrum shows a duplication of aromatic and methylene signals at 6.71 and 4.47 ppm respectively, reflecting a loss in the symmetry of the molecule. GEDVA monomers were also characterized by FTIR (Figure S15). Indeed, benzylic

alcohol signal at 3400 cm^{-1} gradually disappears with the formation of epoxide functions. In the case of TetraGEDVA, this specific band has vanished, while for the DiGEDVA, the band is still visible. The C-H and C=C aromatic ring stretching are also visible at 2920 cm^{-1} and 1600 cm^{-1} , respectively.

The processability of epoxy prepolymers is a key parameter in the handling of such substrates at the industrial scale. The thermal and physical properties of GEDVA monomers were thus determined and compared to DGEBA (Table 1). DGEBA monomer is a solid, which can be melted into very low viscosity liquid at a temperature above 45°C . It can thus be homogeneously mixed with various curing agents. The viscosity of GEDVA monomers is thus very dependent on the number of epoxy groups carried by the substrate. This feature can be explained by the presence of two free benzylic alcohol moieties in DiGEDVA compound, which can undergo hydrogen bonds and thus increase the viscosity. As DiGEDVA exhibits a $T_g = 16^\circ\text{C}$ and a viscosity of $1300\text{ Pa}\cdot\text{s}$ at 40°C , it is thus a highly viscous material at RT that is difficult to blend with any hardener.

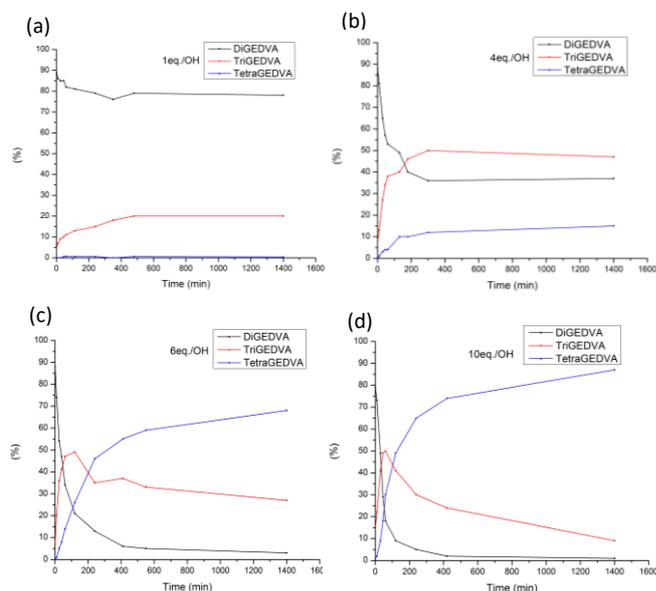


Figure 1 Variation with time of DiGEDVA, TriGEDVA and TetraGEDVA with respect to NaOH eq./OH; 1 NaOH eq./OH (a), 4 NaOH eq./OH (b), 6 NaOH eq./OH (c), 10 NaOH eq./OH (d)

Table 1 Thermal and physical properties of DGEBA and GEDVA monomers

Properties	DGEBA	DiGEDVA	TriGEDVA	TetraGEDVA
Melting point ($^\circ\text{C}$)	45	-	-	-
Glass transition ($^\circ\text{C}$)	-18	16	-6	-15
Viscosity ($\text{Pa}\cdot\text{s}$) ^a	1	1300	60	2
EEW th.	170	209	158	132
EEW exp.	171	232	164	129

^aat 40°C

In contrast, TetraGEDVA is much easier to handle as it exhibits a $T_g = -15^\circ\text{C}$ and a viscosity of $2\text{ Pa}\cdot\text{s}$ at 40°C and TriGEDVA exhibits thermal and mechanical properties in between those of Di- and TetraGEDVA. In addition to the fact that is possible to recover pure Di, Tri or TetraGEDVA after separation step, the use of mixtures of these polyfunctional structures will

enable to control the processing of these prepolymers. Moreover, the thermomechanical properties of these different blends cured with IPDA were also investigated and the formulation of mixture of GEDVA monomers proved to be an efficient way to tune the average properties of the epoxy thermosets (see **Figure S18** and **Figure S19**).

According to the standard test method, the EEW (Epoxy Equivalent Weight) of GEDVA monomers was determined and compared with DGEBA reference.⁴³ The experimental EEW values, gathered in Table 1, were found slightly higher than theoretical values. This difference in between theoretical and experimental data can be explained by the presence of by-products or oligomers in the sample.⁴⁴ Indeed, size exclusion chromatography were performed on GEDVA monomers (see **Figure S16**) and SEC traces revealed the presence of higher molecular mass molecule, especially for the DiGEDVA monomer.

Synthesis and characterizations of epoxy thermosets by DSC

The reactivity of GEDVA monomers towards the formation of epoxy thermosets was investigated in the presence of isophorone diamine (IPDA), used as curing agent. The control of the stoichiometry ratio, r , in between epoxy and N-H moieties is a key parameter to obtain an optimal curing, leading to thermosets with controlled properties. This quotient is defined as given in Equation 1:

Equation 1

$$r = \frac{f_{epoxy} * n_{epoxy}}{f_{hardener} * n_{hardener}}$$

Usually the stoichiometric a ratio epoxy/N-H of 1 leads to epoxy thermosets with the highest thermomechanical properties.⁴⁵ This value will be used in the following of the study. The reaction between GEDVA monomers (DiGEDVA, TriGEDVA, TetraGEDVA) and IPDA was performed in DSC capsules and compared with DGEBA system. The polyaddition reaction between an epoxide group and a primary amine occurs in two stages, by successive reaction of each N-H linkage with one epoxy equivalent. It has been reported in the literature,^{44,46–48} that primary amines react faster than secondary amines. This feature can be experimentally checked

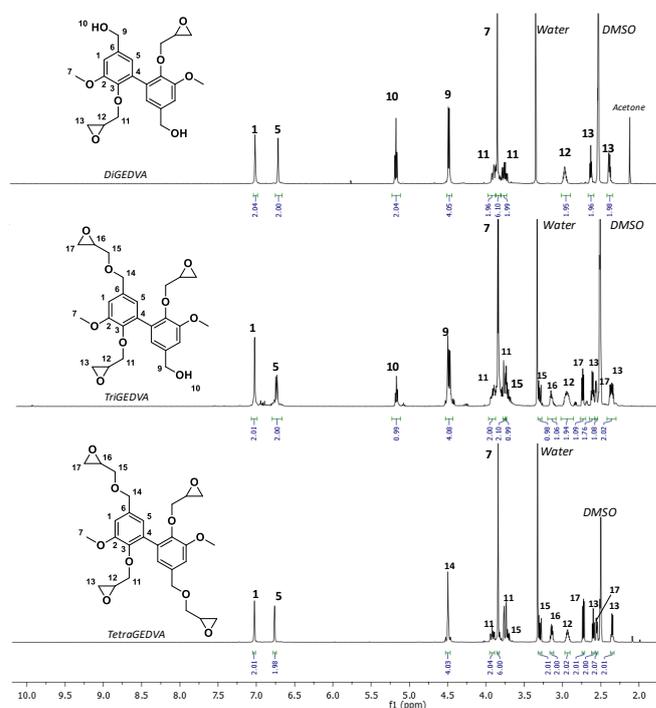


Figure 2 ¹H NMR spectra of DiGEDVA, TriGEDVA and TetraGEDVA in DMSO-*d*₆

by DSC, in the case of tetraGEDVA cured with IPDA, where a first exothermic peak is observed at 100 °C followed by a second one at 140 °C, which corresponds to the difference of reactivity between primary and secondary amino moieties of IPDA (**Figure 3** and **Figure S17**). It is worth noting that the high viscosity of the DiGEDVA monomer made more difficult the mixing process with IPDA. By consequent, the ratio epoxy/amine may have been distorted by the inhomogeneity of the mixture.

Different thermodynamical parameters with respect to the curing reactions between GEDVA and IPDA are summarized in **Table 2**.

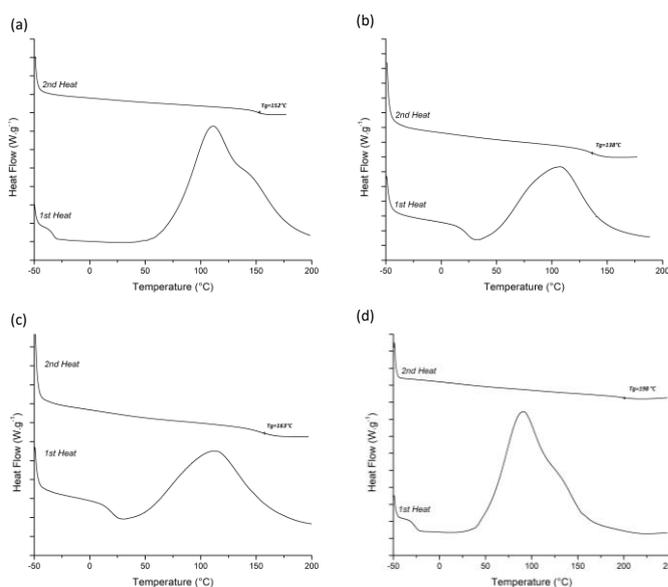


Figure 3 DSC thermograms of (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA cured with IPDA for $r = 1$

Table 2 Thermal properties of epoxy thermosets cured with IPDA

Epoxy prepolymer/IPDA	T _{onset} (°C)	T _{Exo.} (°C)	ΔH (J.g ⁻¹)	ΔH (kJ.mol ⁻¹)	T _g (°C)
DGEBA	73	111	430	91	152
DiGEDVA	47	107	180	45	138
TriGEDVA	40	84	324	65	163
TetraGEDVA	50	92	426	75	198

All the so-formed GEDVA-based thermosets exhibit lower onset temperatures than the DGEBA-based system, demonstrating a high reactivity of these GEDVA monomers towards amino group. In terms of energy released during the curing, TetraGEDVA exhibits an enthalpy of reaction similar to the DGEBA reference. In contrast, DiGEDVA and TriGEDVA exhibit lower total heat reaction. This result could be explained by the fact that reaction with IPDA may have already started during the mixing process. This hypothesis is verified on the **Figure 3b** and **3c**, where a glass transition temperature higher than the one determined for the monomer is visible during the first heat. This observation confirmed that the curing reaction has already started by forming an early network before to run the DSC analysis.

At the second heating ramp, the so-formed epoxy networks exhibited T_g ranging from 138 to 198 °C as a function of the GEDVA monomer. TriGEDVA and TetraGEDVA networks displayed higher T_g than the DGEBA-based system.

Characterization of epoxy thermosets by DMA and mechanical analysis

In order to evaluate the mechanical properties of these GEDVA-based thermosets, curing reactions were then performed on larger quantities (2g) in moulds enabling tensile tests. The thermomechanical features of the epoxy networks were then determined by dynamic mechanical analysis (DMA) using three-point bending geometry. Data are gathered in **Table 3**. From DMA, the maximum of tan delta called alpha transition (T_α) corresponding to the transition from a glassy to a rubbery state could be determined and the cross-linking density (ν) could be also estimated from Equation 2, according to rubber-like elasticity theory.⁴⁹

Equation 2

$$\nu = \frac{E'(T_{\alpha+30})}{\phi \cdot R \cdot T_{\alpha+30}}$$

with T_α the maximum of tan delta, E' the storage modulus of the network at T_α + 30 K, φ the front factor approximately equal to 1 in Flory theory⁵⁰ and R = 8.314 J.mol⁻¹.K⁻¹ the gas constant. GEDVA-based epoxy thermosets exhibit T_α values ranging from 140 to 200 °C, values mainly influenced by the number of reactive epoxy groups. Indeed, the cross-linking density of TetraGEDVA-based network is almost five times and two times higher than DiGEDVA-based and TriGEDVA-based networks, respectively.

Table 3 Thermomechanical properties of epoxy networks formed after curing with IPDA for r = 1

Epoxy prepolymer/IPDA	T _α (°C)	E' (GPa)	E'(T _{α+30}) (GPa)	ν (10 ³ mol.m ⁻³)
DGEBA	155	1.7	0.035	9.2
DiGEDVA	140	1.9	0.035	9.5
TriGEDVA	177	2.4	0.10	25
TetraGEDVA	200	2.1	0.21	49

As expected, segments of highly cross-linked epoxy networks have a reduced mobility thus leading to higher T_α. In comparison with DGEBA-based thermoset, TetraGEDVA, TriGEDVA showed much higher T_g and T_α values. The cross-linking density also increase with the functionality of the epoxy used from 9.2 to 45 10³ mol.m³. **Figure 4** compares the profile of DMA curves obtained for epoxy networks formed after curing of DGEBA and GEDVA with IPDA, respectively. It is worth noting that the intensity of tan delta peak of Di, Tri and TetraGEDVA systems decrease from 1 to 0.2 respectively. This feature could be attributed to the increasing cross-linked density of networks formed upon the curing with IPDA. Indeed, tan delta is the ratio between loss and storage modulus, representing the way in which a material absorbs and disperses energy. In that purpose, a low cross-linked material will have the ability to dissipate more energy by deformation and thus will exhibit a higher tan delta value than a more cross-linked and rigid network. In addition, DGEBA/IPDA and TetraGEDVA/IPDA systems exhibited a broad tan delta, which could also be explained by the heterogeneity of the networks thus formed.⁵¹

Tensile tests were also performed on GEDVA- and DGEBA-based thermosets. Results are summarised in **Table 4** and tensile traces are available in ESI. DGEBA-based thermoset exhibits a Young's modulus of 1300 MPa and an elongation at break of 6%. In the cases of GEDVA-based thermosets, Young modulus range from 1400 to 1900 MPa and elongation at break from 4% to 5%. In contrast, DGEBA-based thermoset shows a slightly higher elongation at break. The presence of the spacer between the two phenolic rings allows more flexibility to the networks in comparison with the GEDVA-based thermosets.

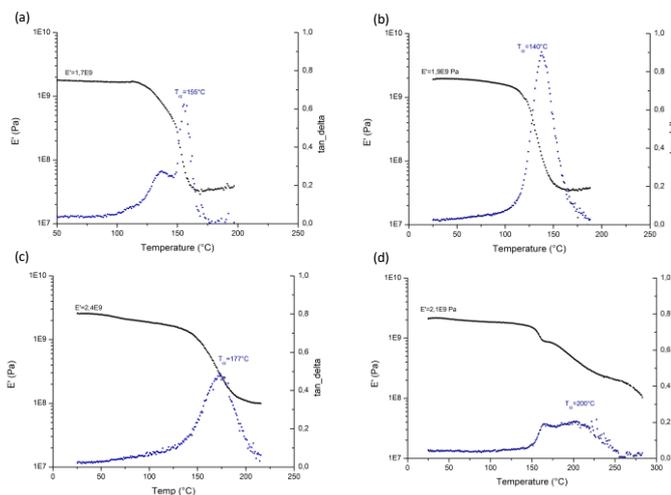


Figure 4 DMA traces of epoxy networks formed after curing with IPDA (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA

Table 4 Mechanical properties of epoxy networks formed after curing with IPDA for $r = 1$

Epoxy prepolymer/IPDA	Young's modulus (MPa)	Elongation at break (%)
DGEBA	1350 ± 100	6,3 ± 1,1
DiGEDVA	1450 ± 200	3,6 ± 1
TriGEDVA	1550 ± 150	4,7 ± 0,5
TetraGEDVA	1900 ± 20	4,5 ± 1

Thermal stability of epoxy thermosets

The thermal degradation behaviors of these networks were investigated by thermogravimetric analysis (TGA). From the two degradation temperatures weight loss $T_{d5\%}$ and $T_{d30\%}$, it is possible to calculate the statistic heat-resistant index (T_s) as follows:⁵²

Equation 3

$$T_s = 0.49 \cdot (T_{d5\%} + 0.6 \cdot (T_{d30\%} - T_{d5\%}))$$

The statistic heat-resistant index (T_s) gives an indication of the thermal stability of an epoxy thermoset. The thermal decomposition behaviours under air of the GEDVA- and DGEBA-based epoxy/IPDA networks are given in **Table 5** and **Figure 5**. First, the thermal degradation under air of all the GEDVA-based networks occurs in two stages, a first 40% weight loss at around 275 °C and a second 60 % weight loss around at 500 °C. The thermal degradation of DGEBA-based networks starts at around 330 °C with about 70 wt% loss followed by a second 30 wt% loss at 500 °C. The values of statistic heat-resistance index for the GEDVA-based networks are 20 °C lower than the ones of DGEBA-based network. The faster heat degradation of GEDVA-based system in comparison to DGEBA may be explained by the degradation of methoxy groups linked to the aromatic rings.^{19,53}

The thermal degradation of these networks was also investigated under nitrogen (**Table 5**). The traces showed a single step of degradation process, which starts at around 275 °C and 350 °C for GEDVA-based and DGEBA-based

networks, respectively. Interestingly, the residual mass at 700 °C ranges from 24 to 32 % in the case of GEDVA-based networks while DGEBA-based network has a residual mass at 700 °C of 8 %. Some authors reported that the char formation is related to the cross-linking density of the networks.⁵⁴ These values are in agreement with the results obtained with TetraGEDVA and TriGEDVA, which exhibit a high cross-linking density. However, DiGEDVA-based system exhibited the highest char content, whereas its network density is equivalent to

Table 5 Thermal degradation of epoxy resins cured with IPDA under air and N2

Epoxy prepolymer /IPDA	$T_{d5\%}$ (°C)		$T_{d30\%}$ (°C)		T_s		Char ₆₀₀ (%)	
	Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂
DGEBA	336	349	364	366	172	176	1.1	8
DiGEDVA	273	275	337	334	153	152	0.5	32
TriGEDVA	292	296	335	333	156	155	0.9	28
TetraGEDVA	275	276	316	313	147	146	1.1	24

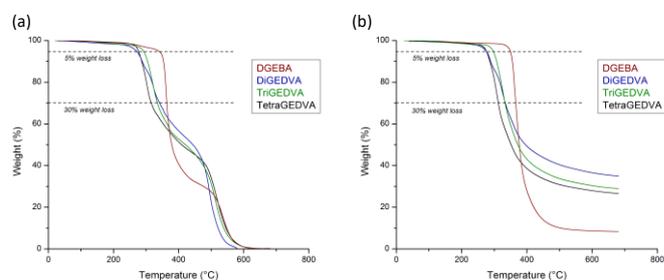


Figure 5 TGA thermograms of epoxy monomers cured with IPDA under (a) Air and (b) N₂

DGEBA-based system (**Figure 5**). The capacity of the free benzyl alcohols on the DiGEDVA structure could react at high temperature, leading to a network density increase and thus higher char yield. High char residue value is a good indication of flame retardancy properties of the materials.⁵⁵ As a consequence, flaming tests have been performed on GEDVA-based samples. In direct contact with flame, DGEBA-based thermoset specimens burn and the combustion spreads rapidly to the rest of the sample. Contrarily, the combustion is rapidly stopped by the direct formation of a char layer at the surface of GEDVA-based thermosets.

Conclusion

New bio-based epoxy monomers derived from divinyl alcohol (DVA) were successfully synthesized and characterized. The degree of glycidylation of DVA could be easily tuned leading to GEDVA substrates with two, DiGEDVA, three, TriGEDVA or four, TetraGEDVA, epoxy functions. These GEDVA were then cured with IPDA and this reaction compared with a DGEBA-based reference. The bio-based epoxy thermosets so-formed displayed remarkable properties with respect to T_g and T_α values which range from 140 to 200 °C. In terms of mechanical properties, GEDVA-based systems exhibits similar Young modulus values to the DGEBA-based thermoset, but

lower elongation at break. Thermal stability of GEDVA-based networks also exhibited similar values to the DGEBA-based reference, but a much higher char residue, which is a promising feature in terms of additional flame retardancy properties. In conclusion, these divanillin-based epoxy substrates were found valuable and realistic alternatives to DGEBA towards high performance epoxy resin applications.

Experimental

Materials and methods

Laccase from *Trametes versicolor*, benzyltriethylammonium chloride (99%), diglycidylether of bisphenol-A (D.E.R.™ 332), tetraethylammonium bromide (98%), hydrochloric acid (37.5%) and potassium hydrogen phthalate (99%) were purchased from Sigma-Aldrich. Epichlorohydrin (99%) and isophorone diamine (97%) were purchased from TCI. Vanillin (99%), perchloric acid solution and sodium borohydride (99%) were purchased from Acros. Sodium hydroxide was purchased from Fisher. All products and solvents (reagent grade) were used as received, unless mentioned explicitly.

Instrumentations

All NMR experiments were performed at 298 K on a Bruker Avance 400 spectrometer operating at 400 MHz, in deuterated solvent (DMSO).

Flash chromatography was performed on a Grace Reveleris apparatus, employing silica cartridges from Grace and a dichloromethane/methanol gradient solvent equipped with ELSD and UV detectors at 254 and 280 nm.

Mass spectroscopy analyses were performed by the Centre d'Etudes Structurales et d'Analyses des Molécules (CESAMO) in Bordeaux. The measurements were carried out on a TOF mass spectrometer AccuTOF GCv using an FD emitter with an emitter voltage of 10kV. One to two microliters solution of the compound is deposited on a 13mm emitter wire.

High-performance liquid chromatography (HPLC) was performed using a Spectra system instrument fitted with a Phenomenex Luna 5 μ C18 100A column and compounds were detected with SpectraSYSTEM UV2000 from Thermo Separation Products. These analyses were performed with acetonitrile/water.

Differential Scanning Calorimetry (DSC) measurements were performed on DSC Q100 (TA Instruments). The sample was heated from -50 °C to 220 °C at a rate of 10 °C.min⁻¹. Consecutive cooling and second heating run were also performed at 10 °C.min⁻¹. The glass transition temperatures and melting points were calculated from the second heating run.

Dynamic Mechanical Analysis (DMA) measurements were performed on DMA-RSA3 system from TA instruments. The three point bending sample (width = 2 mm; thickness = 2 mm

and length of fixed section = 10 mm) was heated from 25 °C to 220 °C at a heating rate of 5 °C.min⁻¹. The measurements were performed in a 3-point bending mode at a frequency of 1 Hz, an initial static force of 0.5 N and a strain sweep of 0.01%.

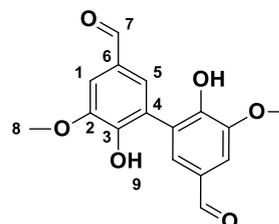
Thermogravimetric analyses (TGA) were performed on TGA-Q50 system from TA instruments at a heating rate of 10 °C.min⁻¹ under air atmosphere.

Tensile test were performed on MTS QTest 25 system. The measurements were performed on standardized dog-bone samples (width = 2 mm; thickness = 2 mm and length of fixed section = 12 mm) using a 500 N load cell and a crosshead speed of 1 mm min⁻¹.

Rheological properties were assessed on Anton Paar MCR 301 stress controlled rheometer. Temperature was controlled on the bottom plate by Peltier effect. The geometry used for the measurement was a plate-plate (25mm).

Procedure for dimerization of vanillin

Divanillin. A solution of vanillin (1.5 g) in acetone (20 mL) was added to NaOAc buffer (180 mL, 0.1 M, pH 5.0). The solution was saturated in O₂ for 5 min. Laccase from *Trametes versicolor* (20 U, 12.4 mg) was added and the reaction was stirred at room temperature for 24 h. The precipitate was filtered off and the product dried overnight at 80 °C under vacuum. Yield: 90%.

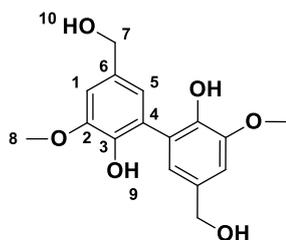


¹H NMR (400 MHz, DMSO, δ (ppm)): δ 9.81 (s, H₇), 7.43 (s, H₁, H₅), 3.93 (s, H₈).

¹³C NMR (400 MHz, DMSO, δ (ppm)): δ 191.62 (s, C₇), 150.88 (s, C₃), 148.61 (s, C₂), 128.64 (s, C₆), 128.21 (s, C₄), 125.02 (s, C₅), 109.6 (s, C₁), 56.25 (C₈).

Procedure for reduction of divanillin

Divanillyl alcohol. 20 mmol of divanillin (\approx 6 g) were dissolved in 100 mL of NaOH (0.5M). The flask was put in an ice bath and 3.6 g of sodium borohydride (100 mmol) were added slowly. Then, the mixture was stirred at room temperature for 30 min. The solution was acidified with HCl to pH 7. The precipitate was filtered off and the product dried overnight at 80 °C under vacuum. Yield: 90%.

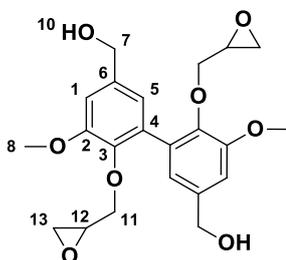


^1H NMR (400 MHz, DMSO, δ (ppm)): δ 8.22 (s, H₉), 6.88 (s, H₅), 6.67 (s, H₁), 5.01 (t, H₁₀), 4.41 (d, H₇), 3.82 (s, H₈).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 147.94 (s, C₃), 142.77 (s, C₂), 133.08 (s, C₆), 125.92 (s, C₄), 121.83 (s, C₅), 109.50 (s, C₁), 63.38 (s, C₇), 56.25 (s, C₈).

Procedure for glycidylation of divanillyl alcohol

Diglycidylether of divanillin. 3 g of divanillyl alcohol (10 mmol) were dissolved in 15 mL of epichlorohydrin (0,2 mol). 0,3 g of tetrabutylammonium chloride (TEBAC) (0.95 mmol) were added and the solution was stirred at 80 °C for 1 h 30. 8 mL of a solution of NaOH (5M) (40 mmol) were added and the solution was stirred at room temperature for 1 h. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent (95/5). Yield: 80%.



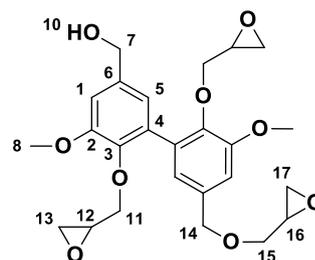
^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.0 (s, H₅), 6.71 (s, H₁), 5.16 (t, H₁₀), 4.47 (d, H₇), 3.88 (m, H₁₁), 3.83 (s, H₈), 3.74 (m, H_{11b}), 2.95 (m, H₁₂), 2.6 (t, H₁₃), 2.36 (t, H_{13b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.33 (s, C₃), 144.47 (s, C₂), 138.26 (s, C₆), 132.59 (s, C₄), 120.86 (s, C₅), 110.79 (s, C₁), 74.22 (s, C₁₁), 63.14 (s, C₇), 56.18 (s, C₈), 50.53 (s, C₁₂), 43.97 (s, C₁₃).

HRMS (m/z, ES+, [M+Na⁺]): calculated: 441.1519; found: 441.1505.

Triglycidylether of divanillyl alcohol. 3 g of divanillyl alcohol (10 mmol) were dissolved in 15 mL of epichlorohydrin (0,2 mol). 0,3 g of tetrabutylammonium chloride (TEBAC) (0.95 mmol) were added and the solution was stirred at 80 °C for 1 h 30. 8 mL of a solution of NaOH (5M) (40 mmol) were added and the solution was stirred at room temperature for 4 h 30. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Further

purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent (95/5).

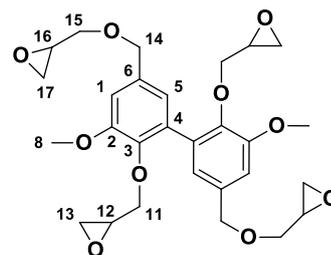


^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.01 (s, H₅), 6.75 (s, H₁), 5.18 (t, H₁₀), 4.47 (d, H₇ H₁₄), 3.92 (m, H₁₁), 3.84 (s, H₈), 3.76 (m, H_{11b}), 3.69 (m, H₁₅), 3.29 (m, H_{15b}), 3.14 (m, H₁₆), 2.97 (m, H₁₂), 2.72 (m, H₁₇), 2.6 (m, H₁₃), 2.5 (m, H_{17b}), 2.36 (m, H_{13b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.02 (s, C₃), δ 151.89 (s, C₃), 144.38 (s, C₂'), 143.68 (s, C₂), 138.12 (s, C₆'), 133.39 (s, C₆), 132.06 (s, C₄'), 131.76 (s, C₄), 121.78 (s, C₅'), 120.26 (s, C₅), 111.55 (s, C₁'), 110.46 (s, C₁), 73.85 (s, C₁₄), 71.81 (s, C₁₅), 70.79 (s, C₁₁), 62.67 (s, C₇), 55.90 (s, C₈), 50.42 (s, C₁₂), 50.16 (s, C₁₆), 43.42 (s, C₁₃ C₁₇).

HRMS (m/z, ES+, [M+Na⁺]): calculated: 497.1782; found: 497.1770.

Tetraglycidylether of divanillyl alcohol. 3 g of divanillyl alcohol (10 mmol) were dissolved in 15 mL of epichlorohydrin (0,2 mol). 0,3 g of tetrabutylammonium chloride (TEBAC) (0.95 mmol) were added and the solution was stirred at 80 °C for 1 h 30. 16 mL of a solution of NaOH (10M) (160 mmol) were added and the solution was stirred at room temperature for 24 h. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent. Yield: 80%.



^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.02 (s, H₅), 6.76 (s, H₁), 4.50 (s, H₁₄), 3.92 (m, H₁₁), 3.86 (s, H₈), 3.76 (m, H_{11b}), 3.70 (m, H₁₅), 3.28 (m, H_{15b}), 3.14 (m, H₁₆), 2.97 (m, H₁₂), 2.73 (m, H₁₇), 2.60 (m, H₁₃), 2.55 (m, H_{17b}), 2.35 (m, H_{13b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.10 (s, C₃), 144.51 (s, C₂), 133.51 (s, C₆), 131.81 (s, C₄), 121.83 (s, C₅), 111.52 (s, C₁), 73.77 (s, C₁₄), 71.90 (s, C₁₅), 63.14 (s, C₁₁), 55.79 (s, C₈), 50.30 (s, C₁₂), 50.03 (s, C₁₆), 43.44 (s, C₁₃ C₁₇).

HRMS (m/z, ES+, [M+Na⁺]): calculated: 553.2044; found: 553.2064.

Procedure for tensile testing samples preparation

Epoxy prepolymers were mixed vigorously with stoichiometric amount of IPDA. The mixture was poured into a silicon mould. Samples were degased at room temperature or with a minimum of heat under vacuum. Silicon mould was then heated in an oven during 1h at 100 °C followed by 1h 140°C. The full conversion were checked by DSC analysis prior to further mechanical test.

Procedure for flaming test

Cured samples of epoxy thermosets were putted in direct contact with flame from a blowtorch during 3 seconds. This procedure was repeated until the combustion of the sample starts.

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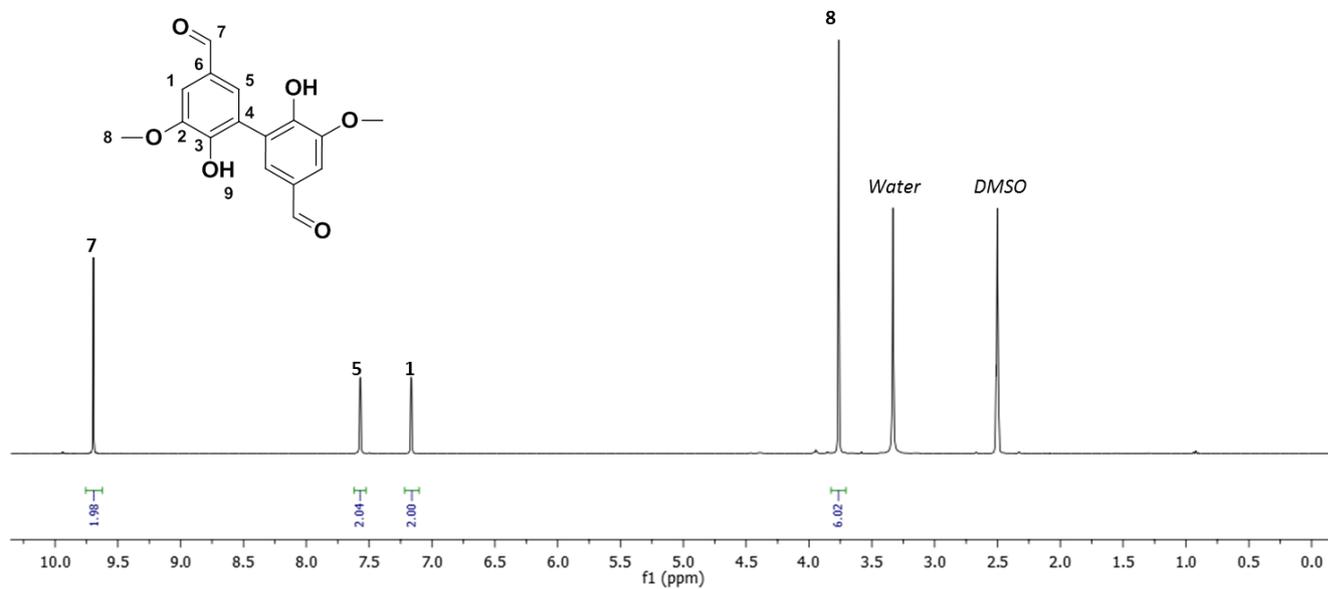
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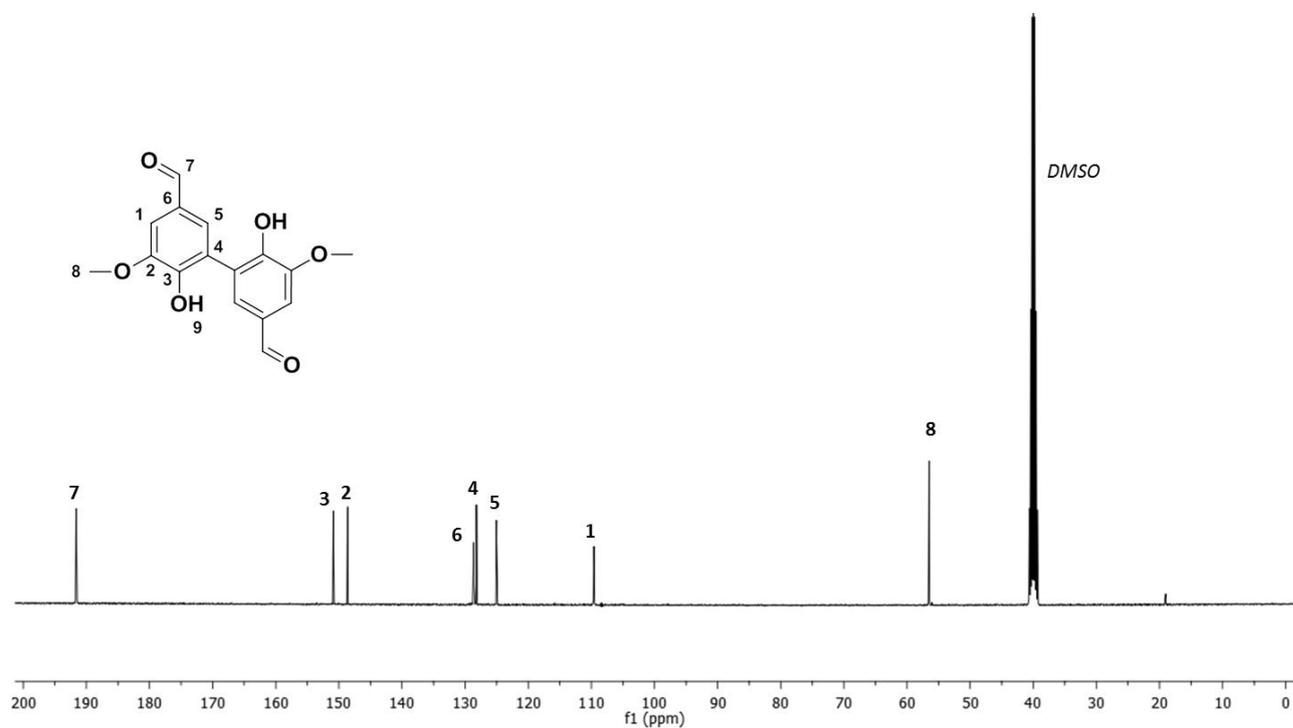
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Electronic Supplementary Information

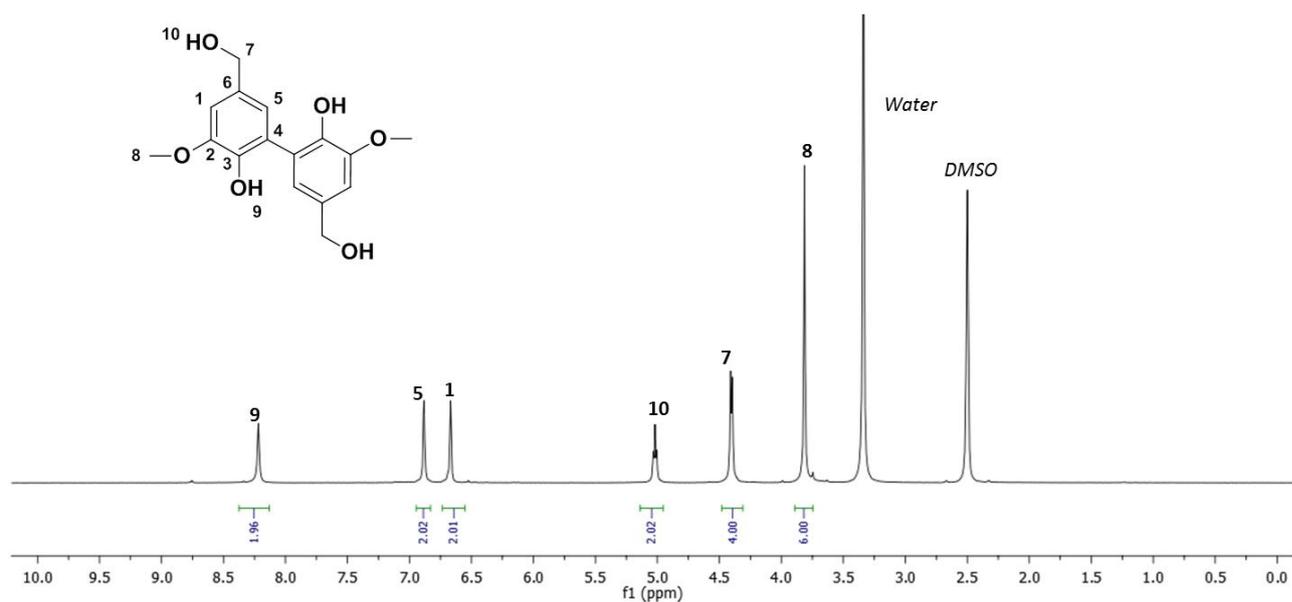
S1 - ^1H NMR spectrum of divanillin (DMSO- d_6).



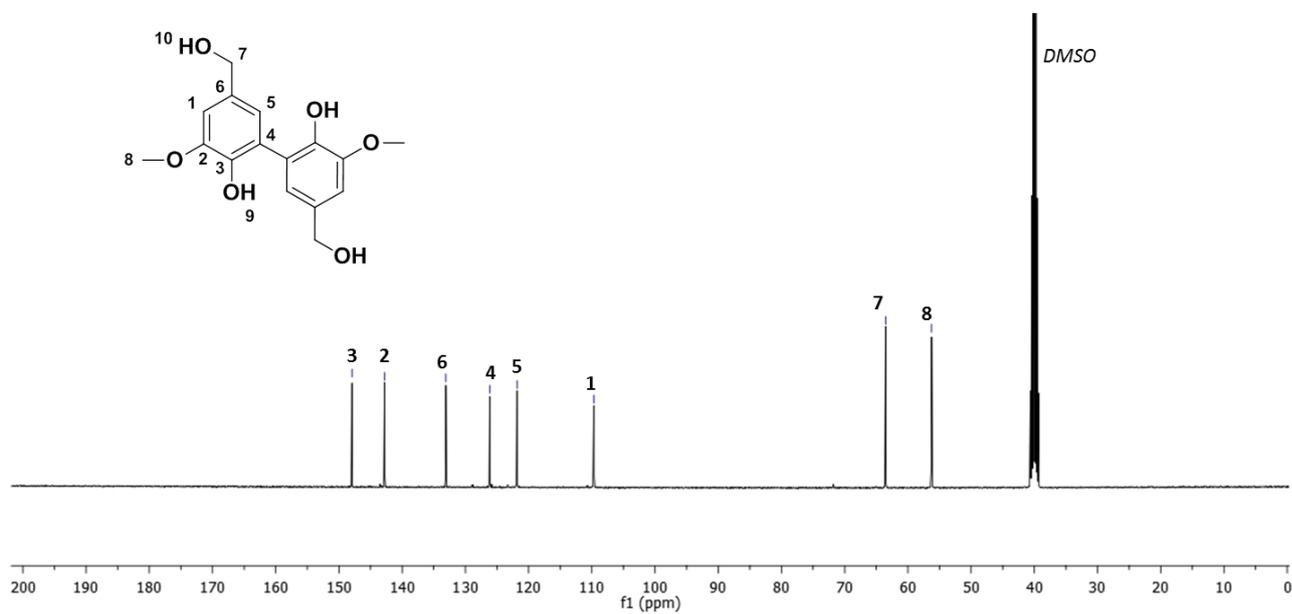
S2 - ^{13}C NMR spectrum of divanillin (DMSO- d_6).



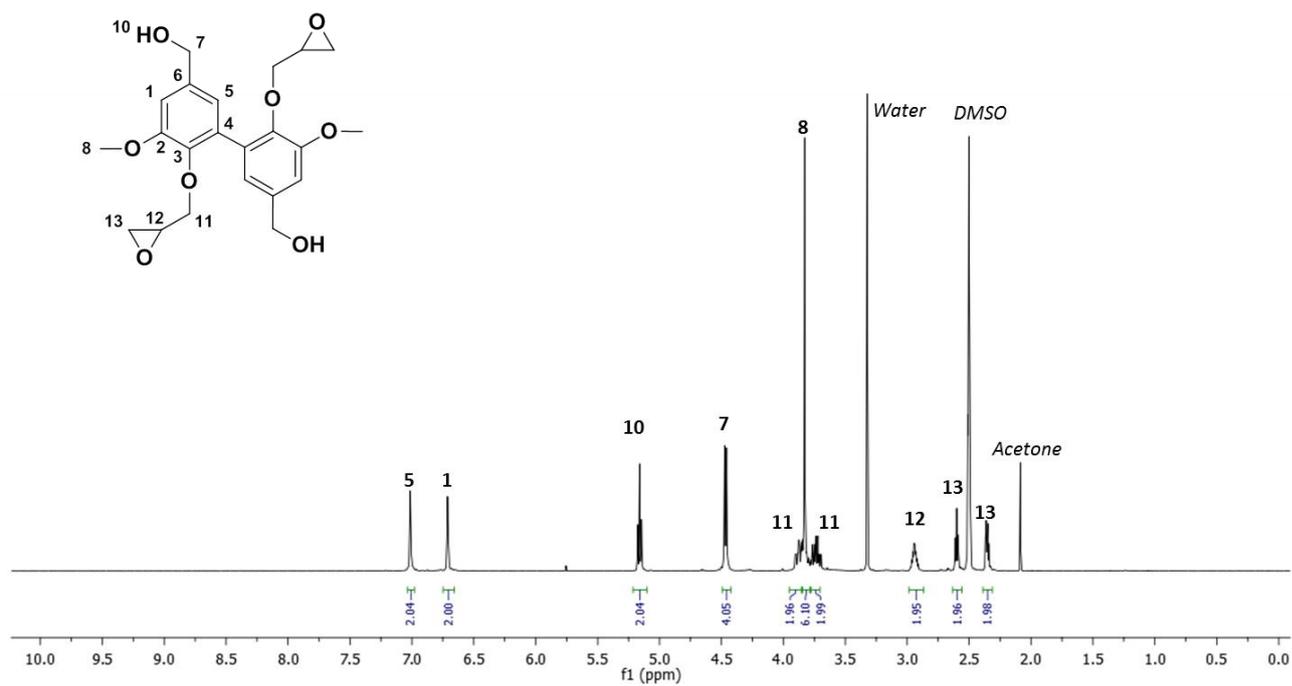
S3 - ^1H NMR spectrum of divanillyl alcohol (DMSO- d_6).



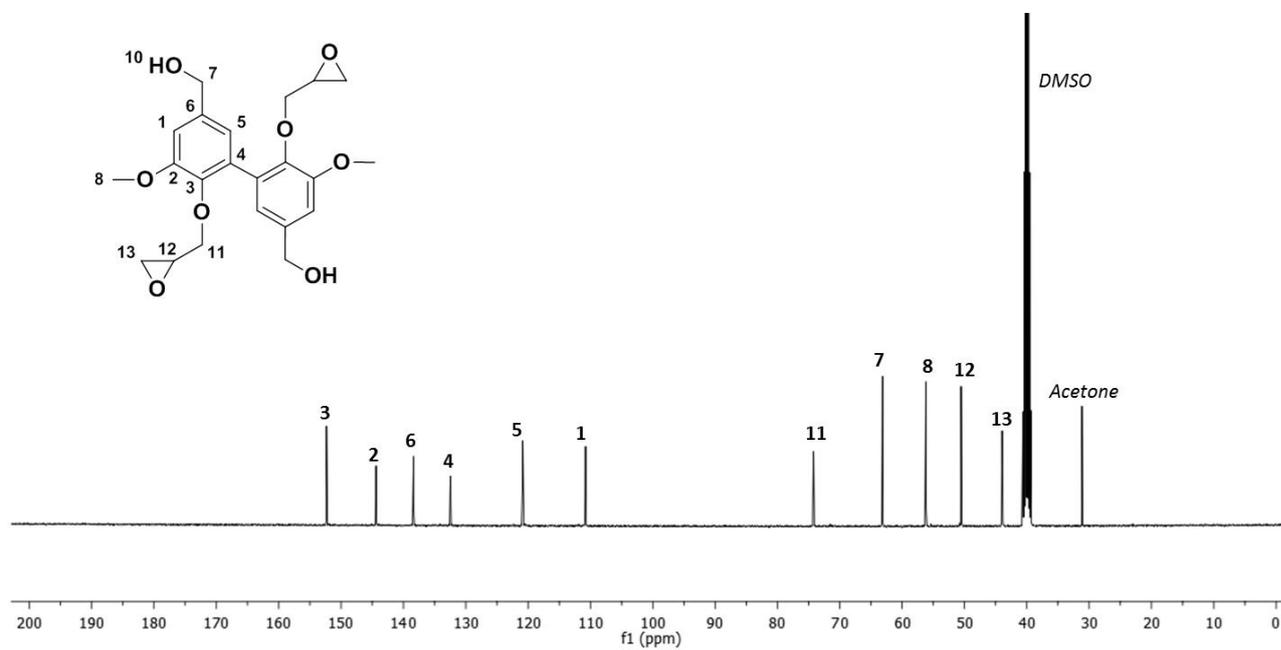
S4 - ^{13}C NMR spectrum of divanillyl alcohol (DMSO- d_6).



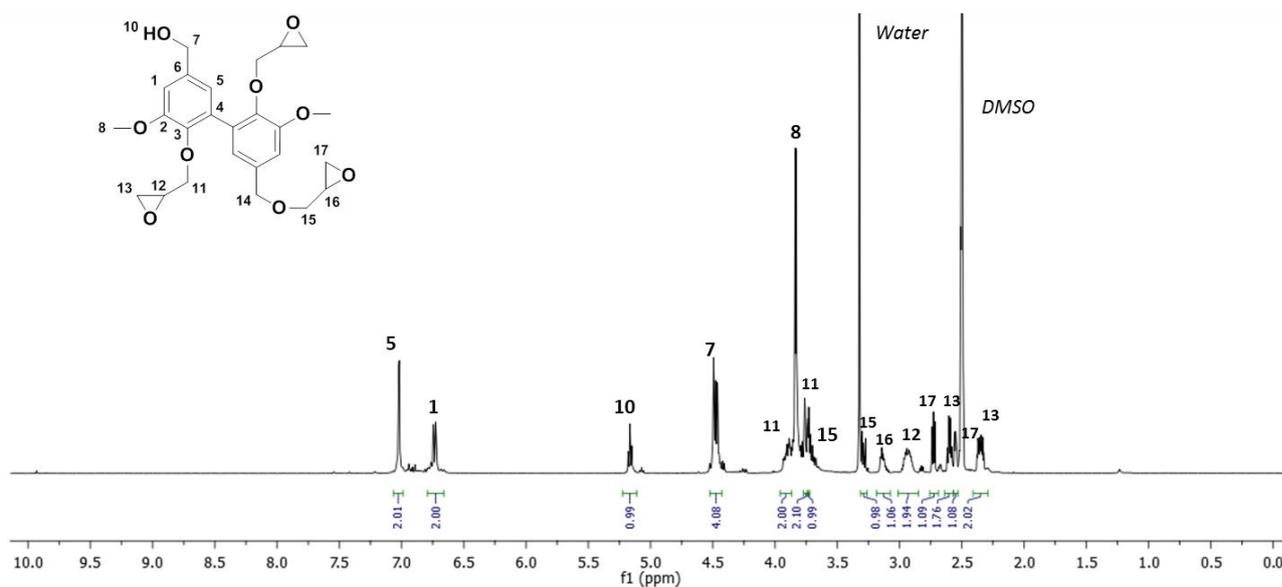
S5 - ^1H NMR spectrum of diglycidyl ether of divanillyl alcohol (DMSO- d_6).



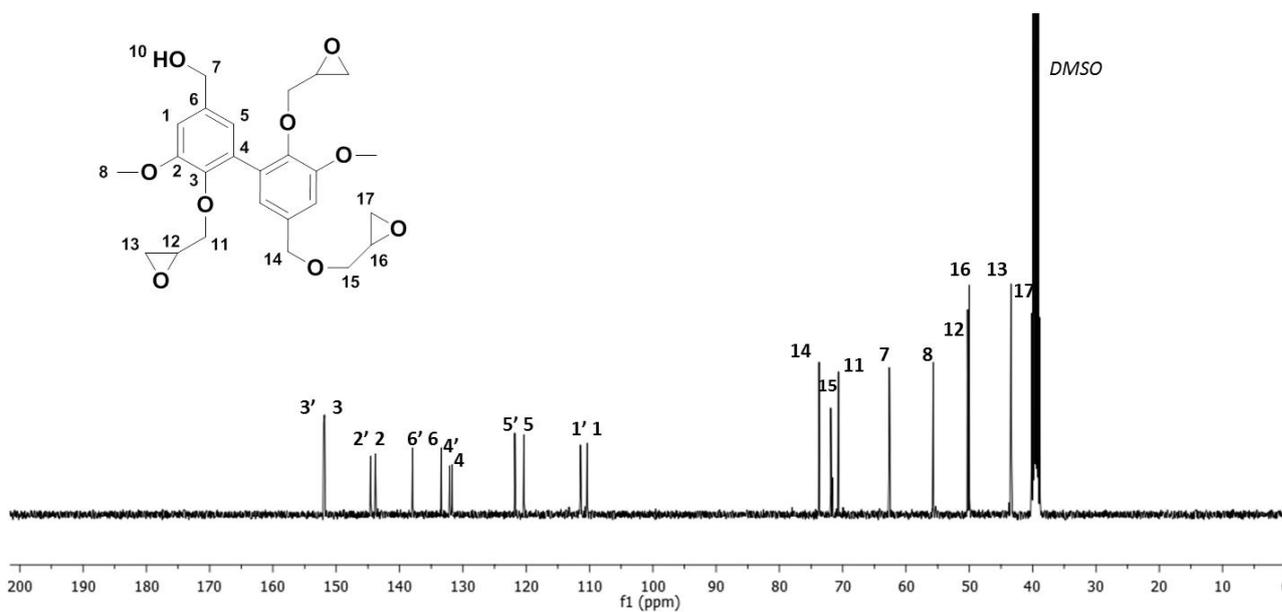
S6 - ^{13}C NMR spectrum of diglycidyl ether of divanillyl alcohol (DMSO- d_6).



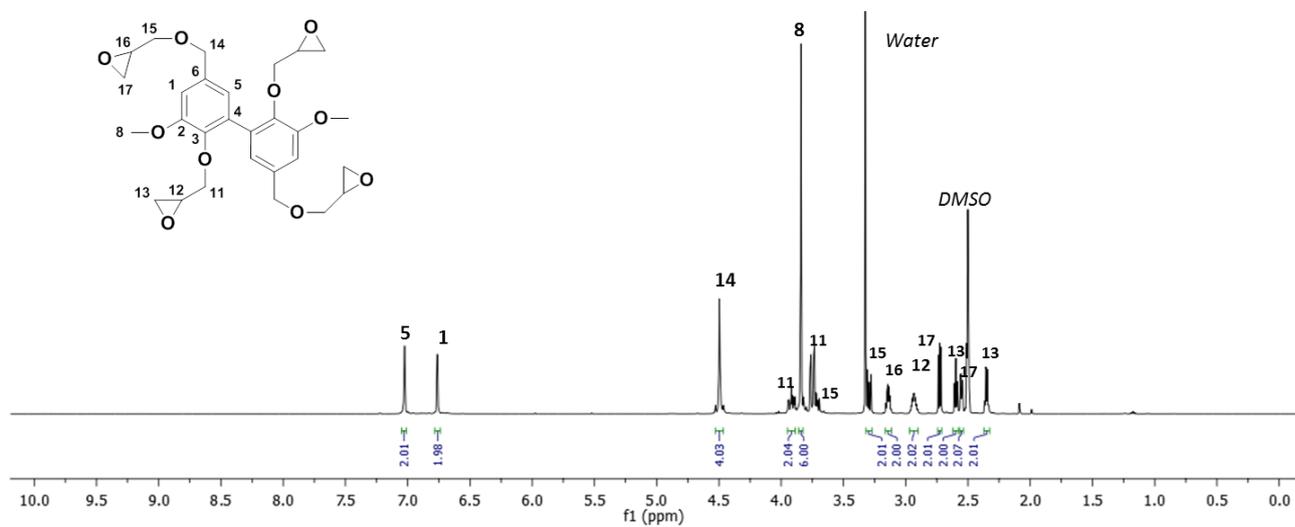
S7 - ^1H NMR spectrum of triglycidyl ether of divanillyl alcohol (DMSO- d_6).



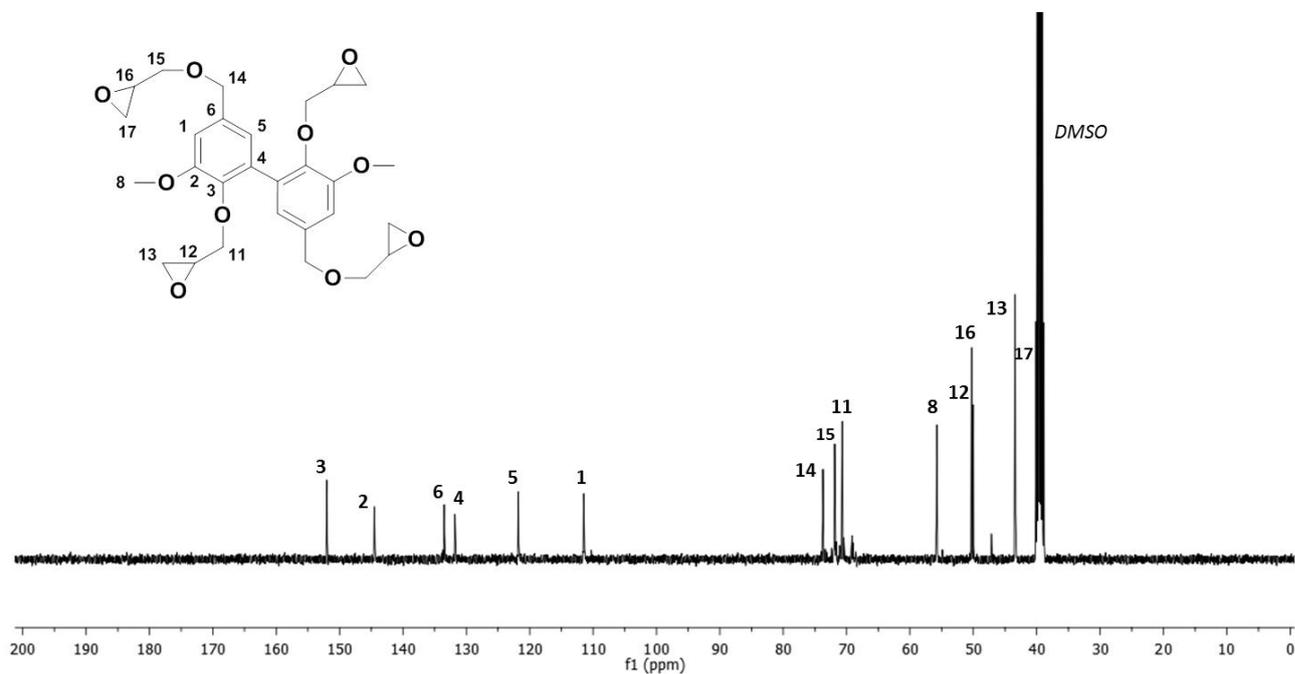
S8 - ^{13}C NMR spectrum of triglycidyl ether of divanillyl alcohol (DMSO- d_6).



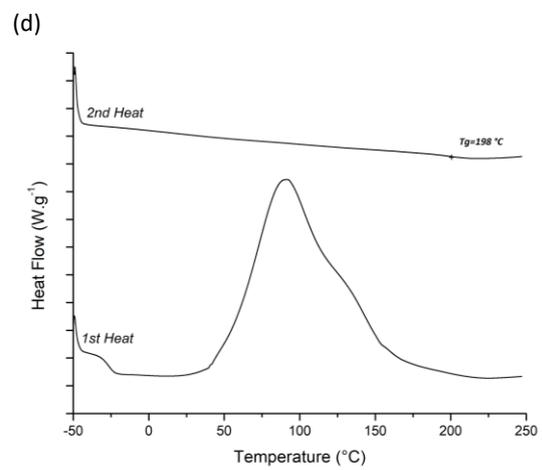
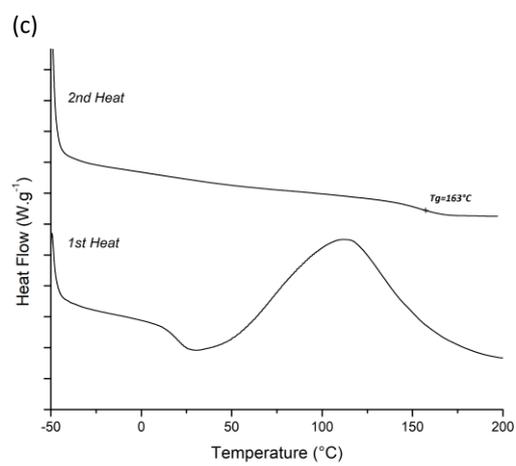
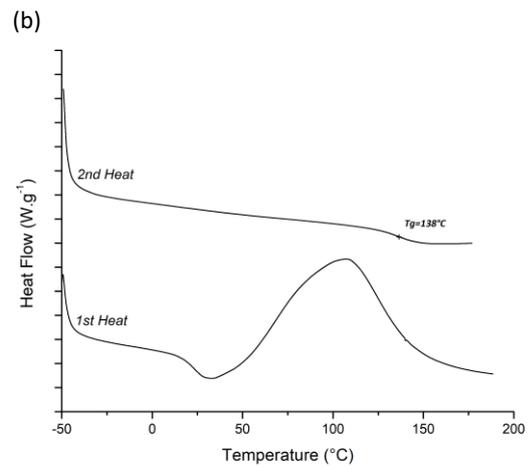
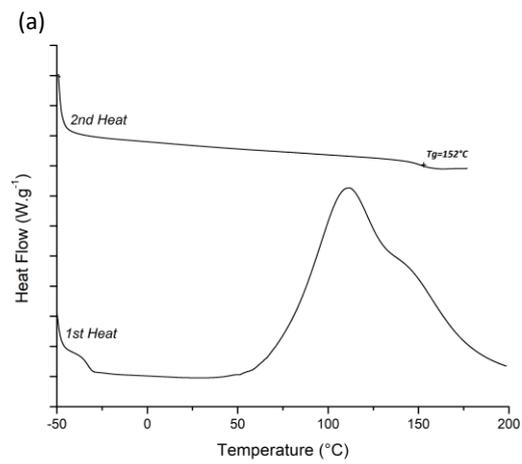
S9 - ^1H NMR spectrum of tetraglycidyl ether of divanillyl alcohol (DMSO- d_6).



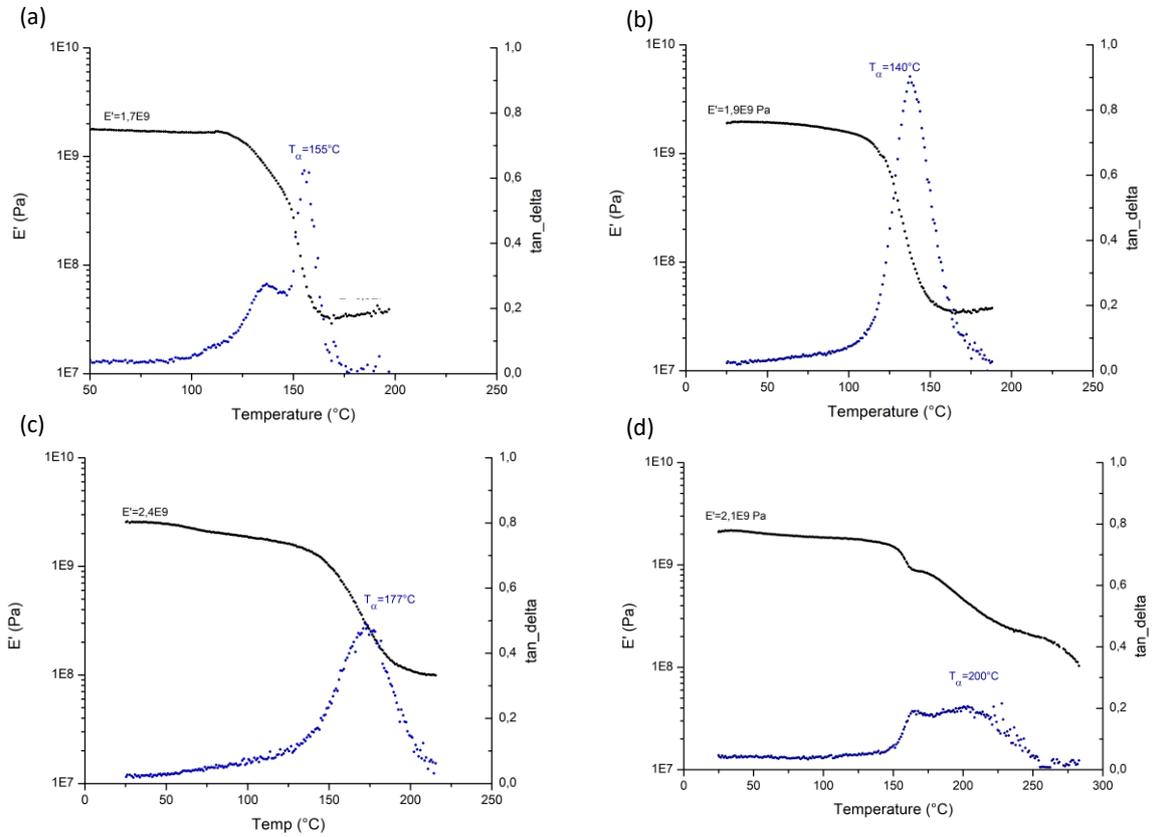
S10 - ^{13}C NMR spectrum of tetraglycidyl ether of divanillyl alcohol (DMSO- d_6).



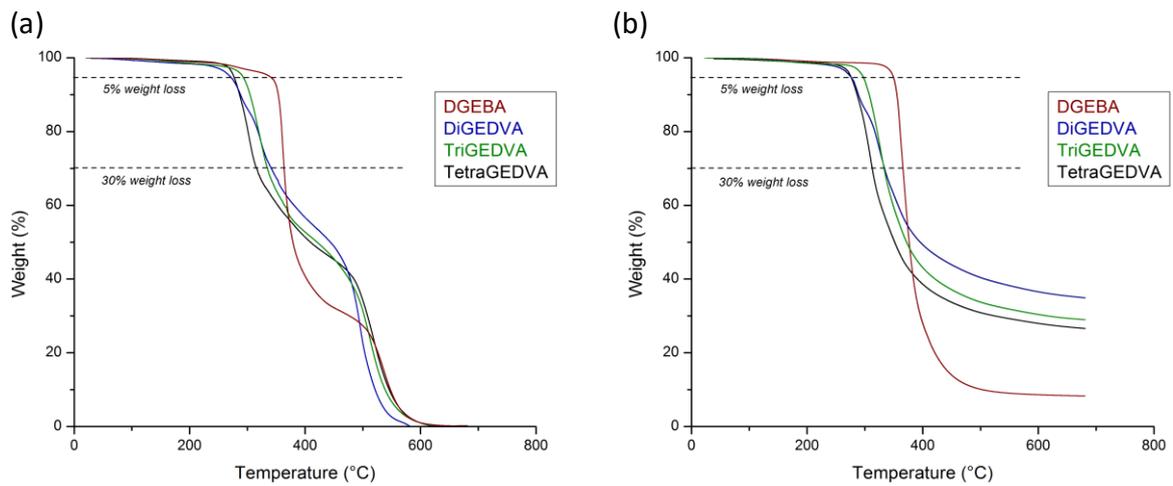
S11 - DSC Thermograms of (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA cured with IPDA for $r = 1$



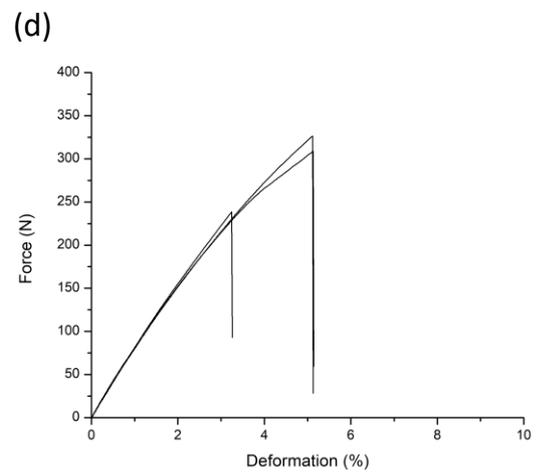
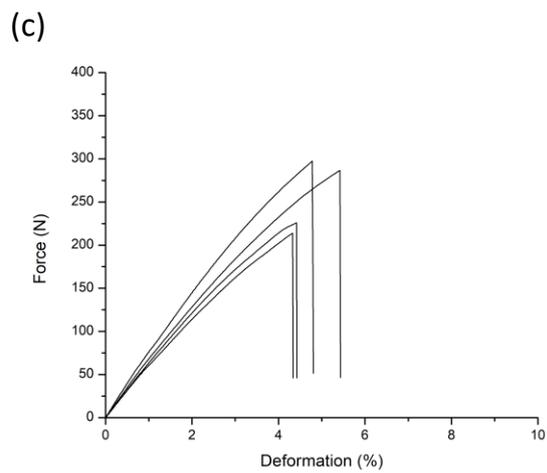
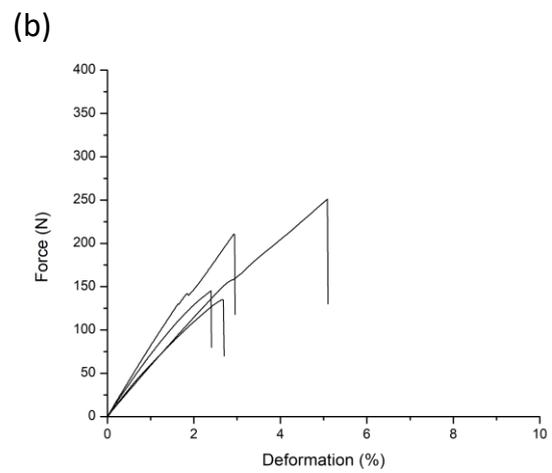
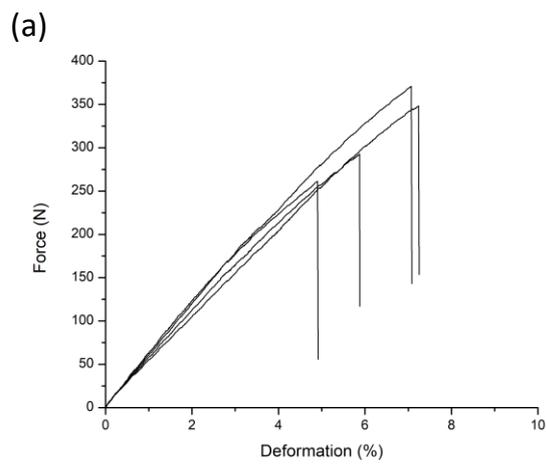
S12 - DMA traces of (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA cured with IPDA for $r = 1$



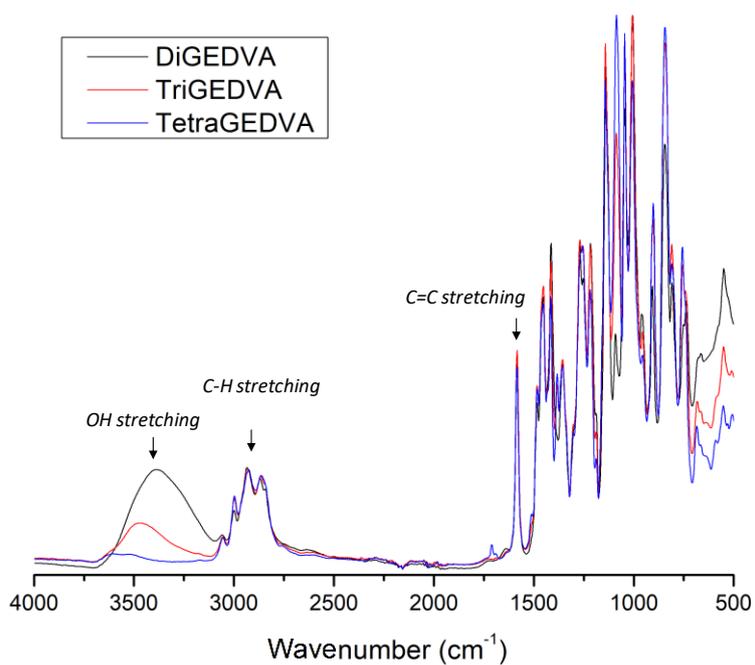
S13 - TGA thermograms of epoxy monomers cured with IPDA under (a) Air (a) and (b) N_2



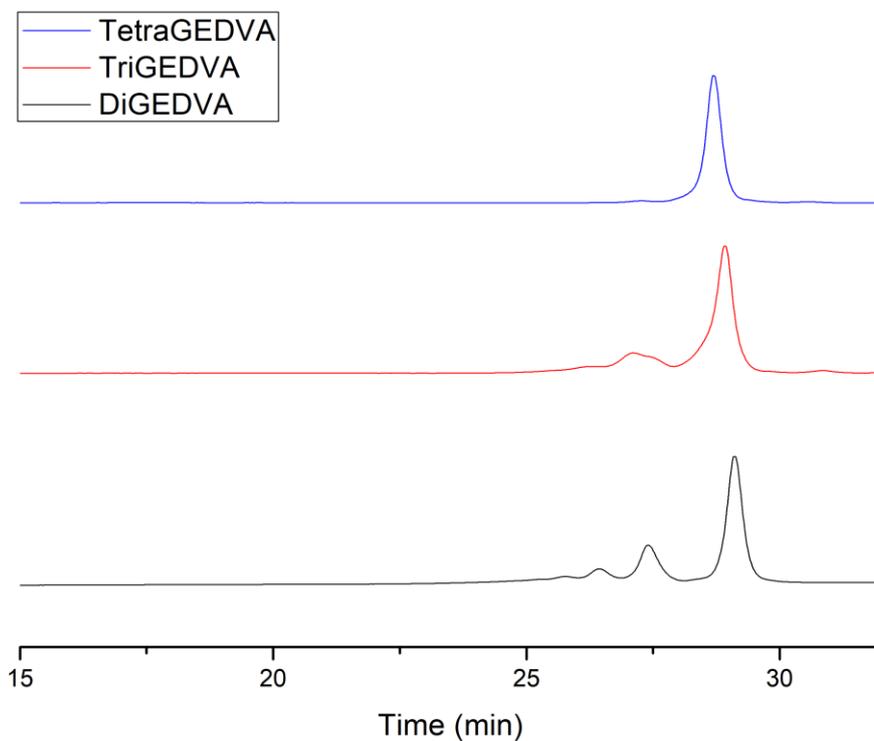
S14 – Tensile test traces of (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA cured with IPDA for $r = 1$



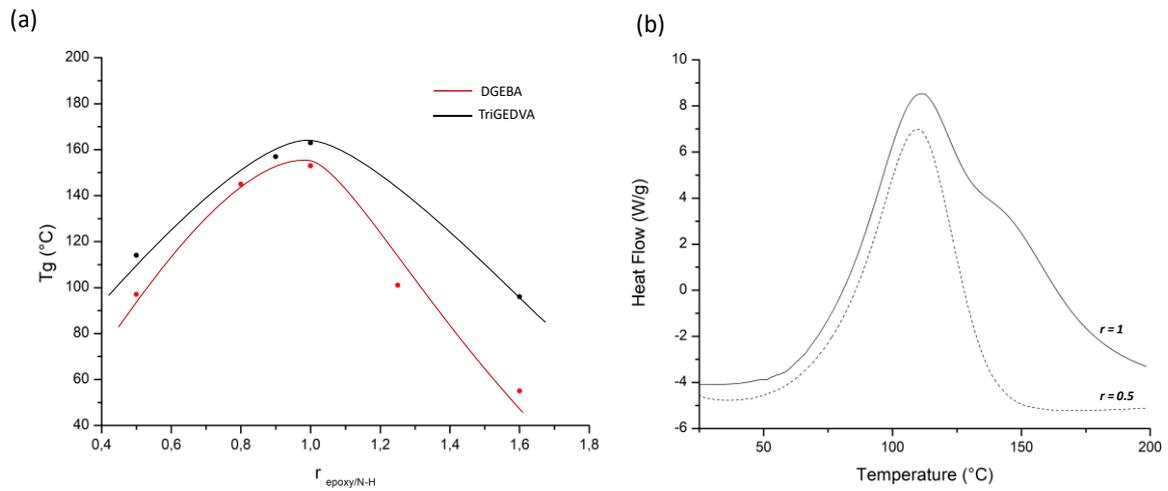
S15 – FTIR spectra of GEDVA monomers



S16 – SEC traces of GEDVA monomers in THF with RI detector and polystyrene calibration



S17 – (a) Glass transition temperature as a function of the epoxy/N-H ratio for DGEBA and TriGEDVA cured with IPDA, (b) DSC thermograms of DGEBA/IPDA for different ratio r



S18 – Thermomechanical properties of epoxy networks cured with IPDA for $r = 1$

Epoxy prepolymer /IPDA	T_g^a (°C)	$T\alpha^b$ (°C)	T_s^c (°C)	Young's modulus ^d (MPa)
DGEBA	152	155	176	1337 ± 102
Di 60%-Tri 20%-Tetra 20%	153	157	155	1489 ± 66
Di 20%-Tri 60%-Tetra 20%	166	171	155	1216 ± 75
Di 20%-Tri 20%-Tetra 60%	187	197	154	1545 ± 110

^adetermined by DSC, ^bdetermined by DMA, ^cdetermined by TGA under air, ^ddetermined by tensile test

S19 – Ternary diagram of (a) T_g determined by DSC, (b) $T\alpha$ determined by DMA and (c) Young's modulus determined by tensile test for different GEDVA-based monomer blends

