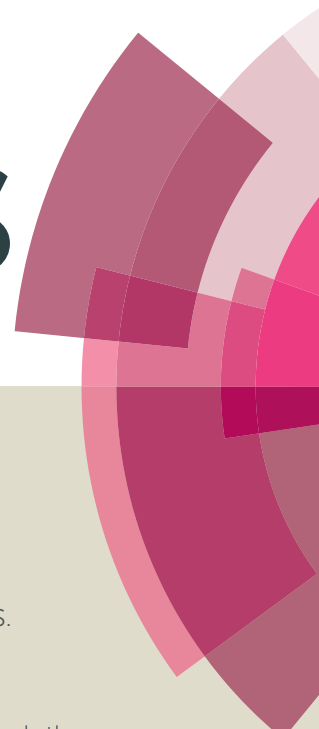


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Diglycidylether of *iso*-eugenol: A suitable lignin-derived synthon for epoxy thermoset applications

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A novel lignin-based synthon, diglycidylether of *iso*-eugenol (DGE-*iso*Eu) is used as a prepolymer for the preparation of thermosetting resins. DGE-*iso*Eu is synthesized in a two-step procedure with a satisfactory yield from bio-based *iso*-Eugenol (*iso*Eu, 2-Methoxy-4-(1-propenyl)phenol) catalytically fragmented from lignin in an organosolv process. DGE-*iso*Eu was fully characterized by NMR, MS and FTIR. Curing of DGE-*iso*Eu monomer has been then investigated in the presence of several carboxylic acid derivatives hardeners. Thermal and mechanical properties of each material were recorded showing in particular high T_g and instantaneous modulus values in the range of 78–120 °C and 4.6–5.5 GPa, respectively. The lignin derived new materials gives very attractive thermo-mechanical properties comparable to that of common BPA-containing epoxy resins.

1. Introduction

Until the 2000s, bisphenol-A (BPA) played a significant role in the field of polymers and was widely used as basic building block for the preparation of polycarbonates, polysulfones, polyesters, polyimides, and epoxy resins.¹ Thereafter, toxicological studies have suspected the potential risks for health in the use of BPA-based materials, which was later classified as an endocrine-disrupting chemical.^{2,3} As many applications involving BPA concern the areas of food and health, the quest of non-toxic alternatives to BPA has become a major focus and has attracted great interest among the communities of chemists and polymerists.⁴ Thus, in the sector of epoxy resins, the replacement of a diglycidylether of bisphenol A (DGEBA) by bio-based synthons is strongly considered.⁵ Beyond the toxicological aspects, and from an environmental and energy perspective, this involves the replacement of petroleum-based building-blocks by monomers from renewable resources.

During the last decade, advances in the catalytic conversion of biomass have led to a wide range of useful platform molecules.⁶

This approach is also widespread in the field of polymers.^{7,8} In the specific domain of biobased epoxy thermosets, the state of art was recently and concomitantly reviewed by David *et al.*, and by Matharu and Ding, highlighting the potential of polyphenols, tannins, cardanol, vegetable oils, starch, sugar, and terpenes employed as precursors for the synthesis of epoxy monomers.^{9,10} Aromatic molecules extracted during the fragmentation of the biomass, in particular from the lignin, can be also considered as appropriate candidates.^{11,12,13} Indeed, the thermomechanical properties recorded for some of these building blocks (revealed by high T_g values), and mainly derived from vanillin, are very competitive to DGEBA-based thermosets.^{14,15,16} However, with the objective of future industrial developments, accessibility and availability of raw materials are key criteria. The lignin which is produced in abundant amounts (an estimated 50 million tonnes of lignin are annually produced worldwide by the pulp and paper industry) well fits with these conditions and constitutes a remarkable pool of high-added value aromatic molecules.¹⁷ In this context, the Samec's research group (Stockholm) recently reported a tandem organosolv and palladium-catalyzed depolymerisation process to fractionate lignocellulosic biomass into cellulose, hemicellulose and an *iso*-eugenol rich of lignin.¹⁸ This innovative process provides access to bio-based *iso*-eugenol which is a precursor for the synthesis of vanillin.¹⁹

In our ongoing studies on the chemical modification of biobased building-blocks for material applications,^{20,21} we herein report the chemical transformation of *iso*-eugenol isolated from lignin into a diglycidylether derivative (DGE-*iso*Eu) and its use as a prepolymer in

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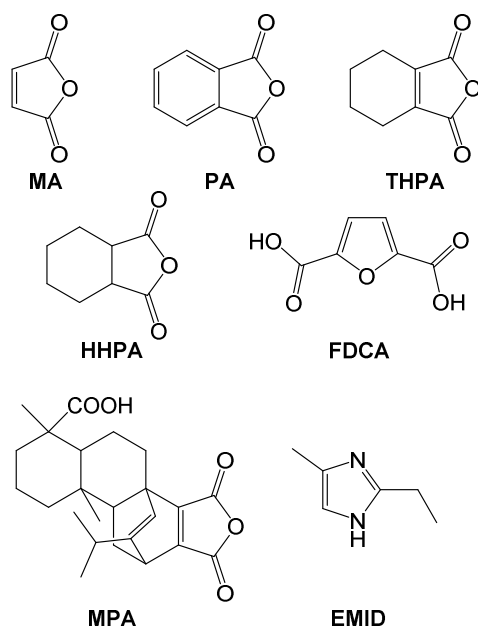
the preparation of epoxy thermosets together with several acid derivatives hardeners. Although amines are the most used hardeners, this family of curing agents was preferentially selected because they also can be efficiently prepared from biorenewable resources.²² DGE-isoEu was fully characterized by nuclear magnetic resonance (NMR), mass spectrometry (MS) and Fourier transform infrared spectroscopy (FT-IR). The polymerization and the resulting materials were monitored and analysed by differential scanning calorimetry (DSC), thermogravimetric analyses (TGA), and nanoindentation. Finally, the curing properties of DGE-isoEu, directly derived from lignin, are compared to those of diglycidylether of eugenol (DGE-Eu), derived from clove, and recently reported by Zhang *et al.*²³

2. Materials and methods

2.1. Materials

2.1.1. Synthesis of DGE-isoEu. 2-Methoxy-4-(1-propenyl)phenol (isoEu) was prepared according to published procedures.¹⁸ Epichlorohydrine (> 99% purity), Bu₄NHSO₄ (97% purity), and Oxone were purchased from Sigma-Aldrich and were used without any further purification. NaHCO₃ (Analytical grade) was obtained from Fisher Scientific.

2.1.2. Thermosetting polymerization. Maleic anhydride (MA, 99% purity), phthalic anhydride (PA, 99% purity), 3,4,5,6-tetrahydrophthalic anhydride (THPA, 95% purity), 1,2-cyclohexanedicarboxylic anhydride (HHPA, 95% purity), 2,5-furandicarboxylic acid (FDCA, 97% purity), and 2-ethyl-4-methylimidazole (EMID, 95% purity) were purchased from Sigma-Aldrich and were used without any further purification. Maleopimaric acid (MPA) was prepared according to a published procedure.²³ Molecules are described in Scheme 1.



Scheme 1. Molecular representations of reagents used for the resin manufacturing process (hardeners: MA, PA, THPA, HHPA, FDCA, MPA; catalyst: EMID).

2.2. Methods

2.2.1. Synthesis of diglycidylether of iso-eugenol (DGE-isoEu).

A solution of NaOH (4.5 mL, 14 M, 63 mmol) was slowly added to iso-eugenol (10 g, 61 mmol) and epichlorohydrin (19 mL, 242 mmol) and heated to 80 °C. After three hours, the reaction mixture was cooled down and the product was extracted with toluene (70 mL), washed with water (20 mL) and brine (20 mL), dried with MgSO₄, filtered. After evaporation the resulting yellowish oil was purified by column chromatography to yield the intermediate as a white solid (9.35 g, 42 mmol) in 70% yield. This intermediate (0.30 g, 1.3 mmol) was dissolved in 5 mL water and 5 mL dichloromethane (DCM) and cooled to 0 °C. NaHCO₃ (0.57 g, 6.7 mmol), Bu₄NHSO₄ (23 mg, 0.068 mmol), acetone (1 mL, 1.3 mmol), and Oxone (aq) (10 mL, 0.4 M, 4 mmol) were slowly added. The reaction mixture was let to reach room temperature and stirred for 3 hours. The reaction was worked-up by adding DCM (5 mL), the organic phase was washed with water 10 mL and brine 10 mL, dried using MgSO₄, filtered, and the solvents were evaporated to yield the product (280 mg, 1.2 mmol) as a transparent oil in 92% yield.

¹H NMR (400 MHz, CDCl₃) δ 6.87 (m, 1H, Ar), 6.81 (m, 1H, Ar), 6.73 (m, 1H, Ar), 4.21 (dd, *J* = 11.4 and 3.5 Hz, 1H, CH₂O), 4.00 (dd, *J* = 11.4 and 5.6 Hz, 1H, CH₂O), 3.84 (s, 3H, Me), 3.51 (d, *J* = 2.1 Hz, 1H, CH(O)CHMe), 3.35 (m, 1H), 2.99 (qd, *J* = 5.1 and 2.1 Hz, 1H, CH(O)CHMe), 2.86 (dd, *J* = 4.9 and 4.2 Hz, 1H), 2.70 (dd, *J* = 4.9 and 2.7 Hz, 1H), 1.41 (d, *J* = 5.1 Hz, 3H, Me); cis isomer (incomplete): 3.85 (s, 3H, Me), 3.28 (m, 1H), 1.07 (d, *J* = 5.5 Hz, 3H, Me); ¹³C(¹H) NMR (100 MHz, CDCl₃) δ 149.8, 147.8, 131.4, 118.2, 114.0, 108.6, 70.3, 59.4, 58.8, 55.8, 50.1, 44.8, 17.7; MS (EI) (*m/z*) (rel. intensity): 236 (M⁺, 45%), 207 (18%), 193 (55%), 151 (14%), 137 (100%), 122 (10%), 107 (8%), 91 (10%), 77 (10%); IR (neat, cm⁻¹): ν_{max} 3000, 2964, 2930, 1609, 1593, 1515, 1461, 1417, 1378, 1352, 1319, 1269, 1247, 1229, 1195, 1162, 1137, 1081, 1022, 971, 928, 912, 862, 840, 803, 757, 720.

2.2.2. Curing of the epoxy monomers. A comparable protocol as previously depicted by Zhang *et al.* was repeated for each sample of this study.²³ DGE-isoEu prepolymer and curing agents (MA, PA, THPA, HHPA, FDCA, MPA) in a 1:0.8 molar ratio were first ground in a mortar at room temperature until an homogeneous mixture is obtained. EMID used as catalyst (ratio 0.08 eq or 0.12 eq with respect to curing agent (see details in table 1) was then added and intimately ground. The 1:0.8 molar ratio instead of a 1:1 was used to take into account the possible reaction involving hydroxyl groups formed and epoxy functions, leading to polyether.

A few milligrams of this homogeneous mixture was placed in a DSC pan in order to study polymerisation reaction. The remaining mixture was transferred in an aluminium pan and cured in an oven at 150 °C during 1h.

Table 1. Epoxy thermoset formulations.

Hardeners	Molar ratio (DGE-isoEu/curing agent/catalyst)
MPA	1/0.8/0.12
HHPA	1/0.8/0.08
THPA	1/0.8/0.08
PA	1/0.8/0.08
MA	1/0.8/0.08
FDCA	1/0.8/0.08

2.3. Characterization techniques

2.3.1. Fourier transform infrared spectroscopy (FT-IR). FT-IR spectra were recorded on a Bruker Vector 22 fitted with a Specac MKII Golden Gate Diamond Attenuated Total reflectance (ATR) device equipped with ZnSe lenses in the 4000–500 cm^{-1} wavenumber range (twelve scans at a spectral resolution of 4 cm^{-1}).

2.3.2. Nuclear magnetic resonance (NMR). NMR spectra were recorded on a Varian UNITY spectrometer (^1H at 399.5 MHz, ^{13}C at 100.6 MHz). Chemical shifts are referenced indirectly to tetramethylsilane *via* the residual solvent signals (^1H : CHCl_3 at 7.26 ppm, $^{13}\text{C}\{^1\text{H}\}$: CDCl_3 at 77.0 ppm).

2.3.3. Mass spectrometry (MS). EI-MS analysis was run on an Agilent Technologies spectrometer 5975 Series MSD with a 7820A GC system.

2.3.4. Differential scanning calorimetry (DSC). DSC analyses were carried out using TA MDSC 2920 under nitrogen flow (60 mL min^{-1}) with a sample mass of 10 ± 3 mg. To study curing reaction, samples were heated from -20 $^\circ\text{C}$ to 180 $^\circ\text{C}$ at a heating rate of 5 $^\circ\text{C min}^{-1}$. To determine glass transition temperatures (T_g), the cured resin was heated from -20 $^\circ\text{C}$ to 180 $^\circ\text{C}$ at a heating rate of 20 $^\circ\text{C min}^{-1}$.

2.3.5. Thermogravimetric analyses (TGA). Thermogravimetric analyses were performed on a TA Instruments TGA Q600 thermoanalyzer using aluminum pans. Samples (5–10 mg) were heated from room temperature to 800 $^\circ\text{C}$ at a rate of 20 $^\circ\text{C min}^{-1}$ under air flow (100 mL min^{-1}). Weight loss percentages were determined using the TA Universal Analysis 2000 software accompanying the instrument.

2.3.6. Nanoindentation mechanical property analysis. Nanoindentation tests were realized with an Anton Paar Ultra-nanoindenter. All the tests were performed using a Berkovich tip calibrated in fused silica. Before carrying out the test, the samples were polished with SiC paper, alumina particles until 0.03 μm and then Colloidal Silica. Multicycle nanoindentations were carried out in order to measure instantaneous indentation modulus (E_i) and hardness (H). Corresponding load profiles as a function of time are shown in Figure 1a. Each indentation includes 15 cycles. Three

indentations are performed on each sample. Next, nanoindentations exhibiting a holding of 1200 seconds at a maximum force of 500 μN have been also performed in order to determine values of relaxed indentation modulus (E_R) (Figure 1b).

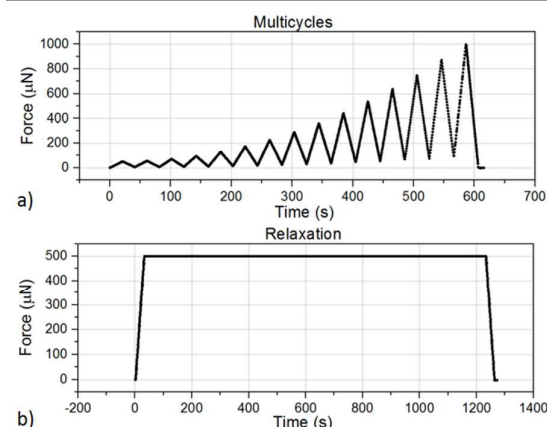
Finally, nanoindentations at constant \dot{h}/h have been also performed in order to determine the strain rate sensitivity (m). Assuming that the material follows a G'Sell–Jonas law²⁴:

$$\sigma = \sigma_0 e^{h_g \varepsilon^u} \dot{\varepsilon}^m$$

where σ_0 is the elastic limit, $\dot{\varepsilon}$ is the strain rate and h_g and u are parameters characteristic of strain hardening. The strain rate sensitivity can be calculated as follow:

$$m = \frac{d \log(F|_h)}{d \log\left(\frac{\dot{h}}{h}\right)}$$

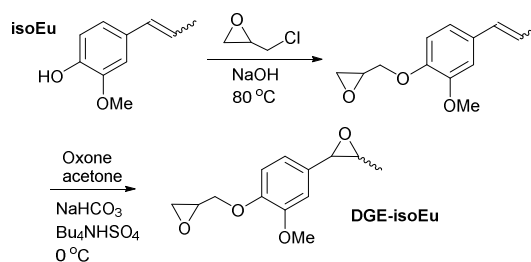
where $F|_h$ is the applied force at a constant penetration depth (here 150 nm). \dot{h}/h between 0.001 s^{-1} and 0.5 s^{-1} have been applied. More details can be found in Gaillard *et al.*²⁵

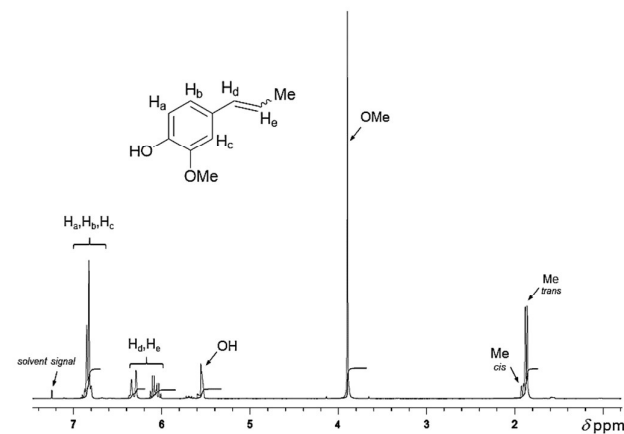
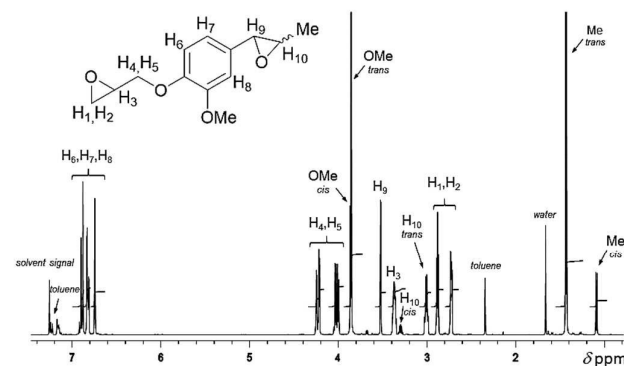
**Fig. 1.** Load/unload profiles of nanoindentation analysis.

3. Results and discussion

3.1. Synthesis of DGE-isoEu

The diglycidylether was prepared from *iso*-eugenol (*iso*Eu) in two reaction steps (Scheme 2). *iso*Eu was treated with epichlorohydrin, in the presence of a mild base to generate the corresponding mono-epoxy *iso*-eugenol. It should be noted that epichlorohydrin can be generated from glycerol.²⁶ This species was then epoxidized using Oxone or alternatively using hydrogen peroxide (tungsten-catalyzed) to generate the product in a 92% yield. DGE-*iso*Eu constitutes an original synthon derived from the lignin. Fully characterized (see section 2.2.1), its ^1H NMR spectrum is depicted in Figure 2b and compared to that of the *iso*Eu precursor (Figure 2a).



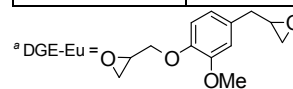
Scheme 2. Chemical transformations of isoEu into DGE-isoEu.**Fig. 2a.** ^1H NMR spectrum (CDCl_3) of isoEu.**Fig. 2b.** ^1H NMR spectrum (CDCl_3) of DGE-isoEu.

3.2. Epoxy thermosets syntheses

Epoxy thermosets were synthesized by heating mixtures of epoxy prepolymer, acid derivatives curing agents and 2-ethyl-4-methylimidazole (EMID) used as a suitable catalyst.²⁷ This study mainly concerns anhydride acid hardeners and was also extended to the bio-sourced 2,5-furandicarboxylic acid.²⁸ The anionic polymerization occurs according a ring-opening mechanism catalysed by EMID. In the past, this mechanism has been studied and described first by Dusek and then by Montero.^{29,30} Depending on the nature of both resin (DGE-Eu or DGE-isoEu) and hardener, the resulting mixture could either be in a powder form or in the form of a waxy paste more or less viscous at room temperature. This obviously makes the mixing operation more or less easy. This practical aspect should be taken in consideration for a potential composite application. The facility of mixing and the consistency of the different formulations at room temperature are reported in table 2. Two DGE-Eu-based mixtures were prepared and inserted for comparison.

Table 2. Implementation of reaction mixtures.

Reaction mixture	Physical aspect of the mixture at room temperature	Facility of mixing
DGE-Eu ^a /MPA	cohesive powder	uneasy
DGE-Eu ^a /HHPA	waxy paste	easy
DGE-isoEu/MPA	cohesive powder/waxy paste	uneasy
DGE-isoEu/HHPA	waxy paste	easy
DGE-isoEu/THPA	waxy paste	uneasy
DGE-isoEu/PA	waxy paste	uneasy
DGE-isoEu/MA	Liquid - strong viscosity increasing due to rapid polymerization	Uneasy (polymerization)
DGE-isoEu/FDCA	powder	uneasy



It should be noted that the formulation DGE-isoEu/MA gives rise to a fast and uncontrolled polymerization as soon as the mixture is ground at room temperature leading to a viscosity increase of the paste. Immediately after mixing and for each formulation, curing reaction was followed by differential scanning calorimetry by heating the sample from $-20\text{ }^\circ\text{C}$ to $180\text{ }^\circ\text{C}$ at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$. In accordance with Zhang *et al.* exothermic peaks related to the polymerization reaction are observed between $50\text{ }^\circ\text{C}$ and $152\text{ }^\circ\text{C}$ depending on the formulation (see table 3).²³ These multiple peaks are probably due to different curing reactions occurring between epoxy and anhydride/acid functions. Indeed each DGE-Eu or DGE-isoEu contains two epoxy functions having different reactivities. It is worth noting that a previous endothermic melting peak of DGE-isoEu is already observed at $45\text{ }^\circ\text{C}$ when this resin is used (see figure 3).

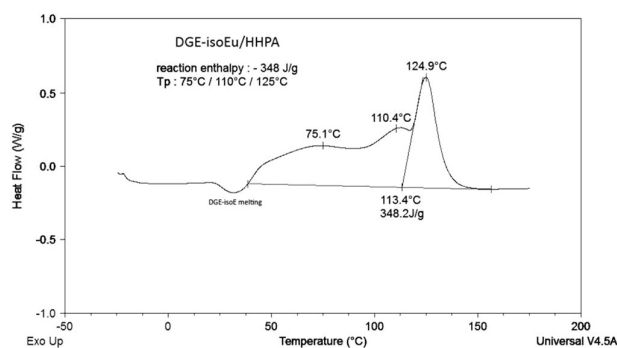


Fig. 3. DSC study of the curing reaction between DGE-isoEu and HHPA.

Table 3. DSC data of the thermosets prepared in this study (° Ref. 23).

Thermosets	T_g (°C)	T polymerization (°C)			ΔH (kJ mol ⁻¹ epoxy)
DGE-Eu/MPA ^a	155	106	127	139	73
DGE-Eu/HHPA ^a	114	119		130	80
DGE-isoEu/MPA	93	53		130	51
DGE-isoEu/HHPA	120	75	110	125	63
DGE-isoEu/THPA	107	95		123	70
DGE-isoEu/PA	120	66	110	132	54
DGE-isoEu/MA	93	58	120	135	36
DGE-isoEu/FDCA	78	53		123	55

Reaction enthalpy was also determined for each polymerization reaction and these values were then expressed by mole of epoxy function in order to take into account the different hardeners molar masses. These data are reported in table 3. Polymerization enthalpies recorded are significantly lower when DGE-isoEu is used instead of DGE-Eu. This could be due to the lower reactivity of the internal epoxy function of the DGE-isoEu. However it is worth noting that polymerization enthalpy measured results from both the value of the reaction enthalpy and the progress of the reaction. Unfortunately the values of the reaction enthalpies related to the polymerization of hardener (HHPA/MPA) with DGE-Eu or DGE-isoEu are not known and could differ according to the position of the epoxy function. Consequently it seems difficult to compare the epoxy reactivity between DGE-isoEu and DGE-Eu only from the polymerization enthalpies measured.

Polymerization enthalpies are in the range of 50 to 80 kJ mol⁻¹ except for MA. For MA, as the polymerization reaction begins before the DSC analysis, a low value of 36 kJ mol⁻¹ is recorded. Concerning the MPA hardener the same trend was already reported with DGE-Eu.²³ This is partly due to low function (anhydride/acid) density of MPA in connection with its high molar mass. Furthermore in this case the anhydride function carried by a hindered molecule could be less reactive with the internal epoxy group of DGE-isoEu than with the terminal epoxy function of DGE-Eu.

3.3. Characterization of epoxy thermosets

3.3.1. FT-IR analysis. The FT-IR spectra are indicative of the curing reaction. Figure 4 represents the spectra related to the anhydride (HHPA), DGE-isoEu and the resulting polymer (DGE-isoEu/HHPA). The polymerization reaction is highlighted by the appearance of the C=O ester stretching band at 1730 cm⁻¹. At the same time the epoxy bands in the range of 915-800 cm⁻¹, present in

DGE-isoEu spectra, and the anhydride elongation bands at 1856, 1788 cm⁻¹ (C=O) and at 903 cm⁻¹ (C–O–C cyclic anhydride), present in HHPA spectra (a), have disappeared. Concomitantly, according to the proposed mechanism in the presence of labile proton,¹⁴ an O–H elongation band at about 3500 cm⁻¹ resulting from the opening of the epoxy ring appears in the polymer IR spectrum. Comparable IR fingerprints were recorded for the other mixtures reported in Table 1.

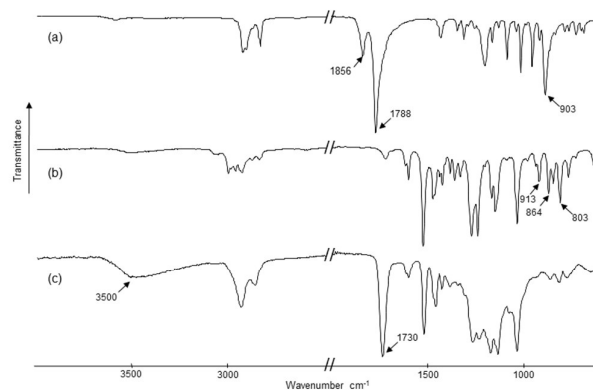


Fig. 4. Infrared spectra (ATR) of (a) HHPA, (b) DGE-isoEu, and (c) DGE-isoEu/HHPA-based thermosets.

3.3.2. Glass transition temperature. Glass transition temperature (reported in table 3) depends on both (i) the chemical structure of the polymer chain and (ii) the architecture of the polymer as the length and the crosslinking rate of the chains. In particular stiff backbones and bulky side-groups are hindrances in the activation of the backbone segmental motion, raising then the glass transition temperature. Thus as expected cured resins obtained from the phthalic anhydride derivatives (DGE-isoEu/HHPA, DGE-isoEu/THPA, DGE-isoEu/PA) give similar high glass transition temperatures ($T_g > 100$ °C). The DSC curve for the DGE-isoEu/HHPA thermoset is shown in Figure 5. It is also noticeable that glass transition temperature obtained with HHPA remains high and similar if DGE-Eu is replaced by DGE-isoEu whereas a lower polymerization enthalpy is recorded in the case of the DGE-isoEu resin. However as previously mentioned in section 3.2 the polymerization enthalpy measured cannot allow concluding on the polymerization conversion. Contrary to HHPA, T_g of DGE-isoEu/MPA is significantly lower than T_g of DGE-Eu/MPA. This could be attributed to a less extent of the polymerization reaction in accordance with polymerization enthalpy measured (see section 3.2).

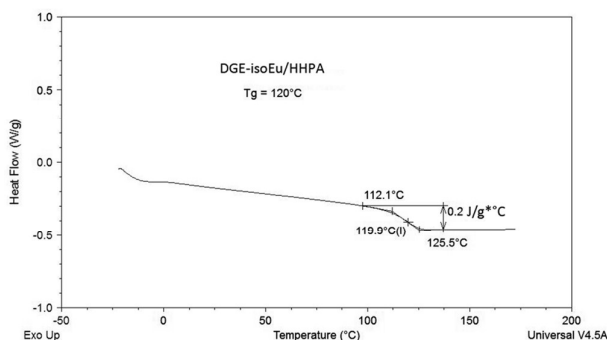
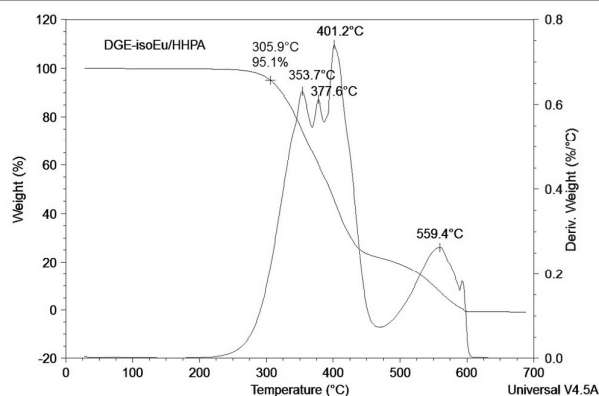


Fig 5. Determination by DSC of the glass transition of DGE-isoEu/HHPA.

3.3.3. Thermal degradation. Degradation temperatures of each thermosets corresponding to 5% weight loss and maximum degradation rate are labeled as $T_{5\%}$ and T_{max} (see table 4). Figure 6 shows a typical TGA curve recorded under air atmosphere of the cured resin issued from polymerization of DGE-isoEu with HHPA. The profiles of curves obtained with the different hardeners are very similar. The polymers are thermally stable till about 260 °C indicating their fairly good thermal stability. T_{max} degradation temperatures of cured resins are in the range 322–412 °C and are functions of the nature of the hardeners used.

Table 4. Temperatures of thermal degradation ($T_{5\%}$ and T_{max}) of the resins cured with the different hardeners. (^o Ref. 23).

Thermosets	$T_{5\%}$ (°C)	T_{max} (°C)
DGE-Eu/MPA ^a	317	
DGE-Eu/HHPA ^a	321	
DGE-isoEu/MPA	296	412
DGE-isoEu/HHPA	306	401
DGE-isoEu/THPA	274	396
DGE-isoEu/PA	263	338
DGE-isoEu/MA	310	409
DGE-isoEu/FDCA	277	322

**Fig 6.** Thermal degradation of DGE-isoEu/HHPA studied by TGA.

3.3.4. Nanoindentation measurements. First, multicycle nanoindentations have shown that both indentation modulus (E_i and E_r) and hardness (H) values are homogeneous in depth. Next all the samples, except the MPA, exhibit a strain rate dependence (m). In these cases the size of the residual imprint left at high \dot{h}/h is smaller than the one obtained for low \dot{h}/h , indicating that the

behaviour of the samples is at least visco-plastic. Values of instantaneous (E_i) and relaxed (E_r) modulus are reported in the table 5.

Table 5: Properties measured with nanoindentation technique: Instantaneous (E_i) and relaxed (E_r) modulus, hardness (H) and strain rate sensitivity (m).

Prepolymer		DGE-isoEu					
Curing agent		MA	PA	HHPA	THPA	MPA	
Nano-indentation	E_r (GPa)	Average	4.86	4.47	4.15	4.59	4.52
		Standard deviation	0.04	0.02	0.03	0.09	0.22
	E_i (GPa)	Average	5.54	4.71	4.60	5.18	5.29
		Standard deviation	0.10	0.16	0.08	0.15	0.87
	H (MPa)	Average	395	345	338	342	229
		Standard deviation	6.5	34.0	7.2	10.0	83.0
	m (°)	Average	0.065	0.025	0.026	0.028	0.001
		Standard deviation	0.027	0.008	0.007	0.011	0.047

As expected, values of instantaneous modulus are larger than the relaxed ones. They are ranged from 4.15 GPa to 5.54 GPa. Hardness (H) vary between 230 MPa and 400 MPa. These properties are of the same order of magnitude than common petroleum-based resins. The table 5 shows also the value obtained for the strain rate sensitivity (m). They are in good accordance with typical values encountered for classical polymer materials.³¹ It has been impossible to prepare the surface of the FDCA sample for such nanoindentation experiments.

4. Conclusions

Diglycidylether of *iso*-eugenol was successfully produced from *iso*-eugenol, with a very good yield, according to a two-step process, and then used as a thermosetting epoxy prepolymer. The study of the polymerization conducted in the presence of several acid derivatives based hardeners has highlighted satisfactory thermo-mechanical properties tailored for such material applications. Indeed, and based on their high T_g , elastic modulus E , and hardness values recorded in the presence of HHPA, THPA and PA hardeners, these new bio-based thermoset polymers show promising mechanical properties. Nanoindentation

measurements have also shown that these materials have a good homogeneity. Thus, the diglycidylether of *iso*-eugenol can be considered as a suitable new epoxy prepolymer. Moreover, as *iso*-eugenol is directly prepared from lignin fragmentation by a catalytic process, the availability of diglycidylether of *iso*-eugenol is greatly facilitated, which enhances its attractiveness as precursor of biosourced epoxy resin. Further work is currently underway to achieve fully bio-based epoxy thermosets and to evaluate the potential of these resins for the manufacturing of composites.

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References

- 1 T. Geens, L. Goeyens and A. Covaci, *Int. J. Hyg. Envir. Heal.* 2011, **214**, 339–347.
- 2 P. Fenichel, N. Chevalier, F. Brucker-Davis, *Ann. Endocrinol.*, 2013, **74**, 211–220.
- 3 J. Michałowicz, *Environ. Toxicol. Phar.* 2014, **37**, 738–758.
- 4 A. M. Nelson and T. E. Long, *Polym. Int.*, 2012, **61**, 1485–1491.
- 5 A. Maiorana, S. Spinella and R. A. Gross, *Biomacromolecules*, 2015, **16**, 1021–1031.
- 6 M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.*, 2014, **114**, 1827–1870.
- 7 M. A. R. Meier, J. O. Metzger and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 1788–1802.
- 8 A. Gandini, T. M. Lacerda, A. J. F. Carvalho and E. Trovatti, *Chem. Rev.* 2016, **116**, 1637–1669.
- 9 R. Auvergne, S. Caillol, G. David, B. Boutevin and J.-P. Pascault, *Chem. Rev.*, 2014, **114**, 1082–1115.
- 10 C. Ding and A. S. Matharu, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2217–2236.
- 11 P. Feng and F. Chen, *BioRes.*, 2012, **7**, 2860–2870.
- 12 T. Koike, *Polym. Eng. Sci.*, 2012, **52**, 701–717.
- 13 A. Llevot, E. Grau, S. Carlotti, S. Grelier and H. Cramail, *Macromol. Rapid Commun.* 2016, **37**, 9–28.
- 14 M. Fache, E. Darroman, V. Besse, R. Auvergne, S. Caillol and B. Boutevin, *Green Chem.*, 2014, **16**, 1987–1998.
- 15 M. Fache, B. Boutevin and S. Caillol, *Eur. Polym. J.* 2015, **68**, 488–502.
- 16 M. Fache, A. Viola, R. Auvergne, B. Boutevin and S. Caillol, *Eur. Polym. J.* 2015, **68**, 526–535.
- 17 A. J. Ragauskas, G. T. Beckham, M. J. Bidy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan and C. E. Wyman, *Science*, 2014, **344**, 709–718.
- 18 M. V. Galkin and J. S. M. Samec, *ChemSusChem*, 2014, **7**, 2154–2158.
- 19 P. Pfeifer, A. Zurawski and T. Roeder, *NiU-Chemie*, 2004, **15**, 34–37.
- 20 A. Mhanna, F. Sadaka, G. Boni, C.-H. Brachais, L. Brachais, J.-P. Couvercelle, L. Plasseraud and L. Lecamp, *J. Am. Oil Chem. Soc.* 2014, **91**, 337–348.
- 21 S. Bigot, M. Daghrir, A. Mhanna, G. Boni, S. Pourchet, L. Lecamp and L. Plasseraud, *Eur. Polym. J.*, 2016, **74**, 26–37.
- 22 C. Robert, F. de Montigny and C. M. Thomas, *ACS Catal.*, 2014, **4**, 3586–3589.
- 23 J. Qin, H. Liu, P. Zhang, M. Wolcott and J. Zhang, *Polym. Int.* 2014, **63**, 760–765.
- 24 C. G'Sell and J. Jonas, *J. Mater. Sci.*, 1979, **14**, 583–591.
- 25 Y. Gaillard, M. Girard, G. Monge, A. Burr, E. Darque Ceretti and E. Felder, *J. Appl. Polym. Sci.*, 2013, **128**, 5, 2713–2719.
- 26 B. M. Bell, J. R. Briggs, R. M. Campbell, S. M. Chambers, P. D. Gaarenstroom, J. G. Hippler, B. D. Hook, K. Kearns, J. M. Kenney, W. J. Kruper, D. J. Schreck, C. N. Theriault and C. P. Wolfe, *Clean*, 2008, **36**, 657–661.
- 27 K. Huang, Z. Liu, J. Zhang, S. Li, M. Li, J. Xia and Y. Zhou, *Eur. Polym. J.*, 2015, **70**, 45–54.
- 28 J. Zhang, J. Li, Y. Tang, Lu Lin and M. Long, *Carbohydr. Polym.*, 2015, **130**, 420–428.
- 29 K. Dusek, *Adv. Polym. Sci.* 1986, **78**, 1–59.
- 30 B. Montero, A. Serra, C. Ramirez and X. Ramis, *Polym. Compos.*, 2013, **34**, 96–108.
- J. L. Bucaille, E. Felder and G. Hochstetter, *J. Mat. Sci.* 2002, **37**, 3999–4011.
- 31 H. Lee, K. Neville, *Handbook of Epoxy Resins*. McGraw-Hill, New York 1967.

Graphical abstract

Diglycidylether of *iso*-eugenol: A suitable lignin-derived synthon for epoxy thermoset applications

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iso-Eugenol (*iso*Eu), catalytically fragmented from lignin, is converted into diglycidylether of *iso*-eugenol (DGE-*iso*Eu) which leads in the presence of anhydride acids based hardeners to new biobased epoxy thermosets.

