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Anne-Sophie Mora, Russell Tayouo, Bernard Boutevin, Ghislain David, Sylvain Caillol.
Vanillin-derived amines for bio-based thermosets. *Green Chemistry*, 2018, 20, pp.4075-4084.
10.1039/C8GC02006J . hal-01863524

HAL Id: hal-01863524

<https://hal.science/hal-01863524>

Submitted on 24 Sep 2022

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Vanillin-derived amines for bio-based thermosets

Anne-Sophie Mora, Russell Tayouo, Bernard Boutevin, Ghislain David, Sylvain Caillol*

In the scope of fully bio-based materials development, the access to bio-based aromatic amine monomers is one of the main industrial challenges over the coming years. In this paper, new bio-based amine monomers derived from vanillin were prepared by direct amination of epoxy monomer with aqueous ammonia. These synthesized amines exhibited high reactivity due to the presence of secondary OH groups. Then these amines were added to epoxies to form thermosets by cross-linking reaction. After curing, the thermal and mechanical behaviors of the synthesized networks were determined and compared to a petroleum-based reference system with DGEBA as epoxy.

Introduction

The beginning of epoxy thermosets commercialization dates back to the late 1940s and these materials are now widely used in various applications (global epoxy resins market was 2.5 Mt in 2014).¹ Because of their high thermo-mechanical properties and chemical resistance conferred by their aromatic moieties, thermosets are invaluable in industry. However, they are cross-linked polymers and thus in most cases cannot be recycled, except if one of the compounds can be hydrolyzed.^{2,3} Consequently, in order to decrease the carbon footprint, the recent interest in the use of renewable raw materials to prepare thermosetting polymers is increasing and the number of contributions to this subject is growing rapidly.^{4,5}

Currently, 75 % of the worldwide epoxy polymers are derived from diglycidyl ether of bisphenol A (DGEBA).⁶ Aromatic moieties of DGEBA (**1**, **Figure 1**) induce excellent thermal and mechanical properties to the epoxy thermosets. However, DGEBA is petroleum-based and derived from bis(4-hydroxyphenylene)-2,2-propane (bisphenol A, BPA). Unfortunately, BPA is a recognized endocrine disruptor which can have important consequences on the human health.⁷⁻⁹ Consequently, many studies recently led to new bio-based or less toxic BPA and DGEBA substituents.¹⁰⁻¹³ Some research groups have synthesized aromatic epoxy monomers derived from lignin,^{14,15} cardanol,¹⁶⁻¹⁹ tannins,^{20,21} and eugenol.^{22,23} However, much of the research has been focused on more available biomass, such as sugars,²⁴ oils,²⁵⁻²⁷ and isosorbide.²⁸ Nevertheless, these renewable resources generally led to poorer network properties than those of DGEBA-based networks, due to the absence of aromatic groups. Indeed, there are three main natural phenolic sources available, cashew nutshell liquid, tannins, and lignin, which limits the range of possibilities.

Another way to bring aromaticity to the final network is the amine structure. In fact, epoxy networks are cross-linked systems obtained by the reaction between a diepoxy monomer and a diamine hardener. However, aromatic amines are often dangerous and exhibit a very low reactivity. Benzylic amines such as m-xylylenediamine (MXDA) are also used in the industry because of their high reactivity while retaining aromatic moieties, conferring high thermo-mechanical properties and chemical resistance to the final epoxy network.

Moreover, most of the current amines are issued from petrochemical resources and only a few amines are derived

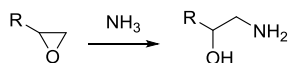
from biomass. Hence, our team carried out an important clarification on the synthesis of bio-based amines.²⁹ This review reports that the only natural amines available are chitosan and amino acids. Even if chitosan is cheap, non-toxic, water soluble, and available in industry,³⁰ our works demonstrated limited thermal properties in water-based epoxy-amine thermosets.³¹ Concerning amino acids, lysine is a promising compound for industry because of its low price and availability (global production of 3,100 t/year). Furthermore, lysine possesses a backbone with two amine functions. A recent patent of Pioneer Surgical Technology illustrates the potential of lysine by using poly(lysine) in the formulation of dental cement.³² Another patent describes the method of obtaining the lysinol, by hydrogenating lysine, followed by the synthesis of lysinol-epoxy thermosets.³³

In addition to natural amines, synthetic pathways exist for obtaining bio-based amines by chemical functionalization of molecules originating from biomass. For instance, functionalization methods of vegetal oil, i.e. unsaturated fatty acids (or ester derivatives), such as olefin metathesis and radical additions, etc. are described.³⁴ Bio-based amines are also of interest to the industry. An inexpensive industrial way is the modification of sugars and derived polyols by amination methods, such as a polycondensation reaction between at least two identical or different bio-based monomers,³⁵ by hydrogenating aliphatic α,ω -dinitriles³⁶ or again by an enzymatic process.³⁷ In addition, many bio-based primary amines can be achieved from molecules originating from biomass such as terpenes,³⁸⁻⁴⁰ lignin,^{12,41} and cardanol^{42,43} derived from cashew oil or vegetable oil.^{44,45} In addition, these syntheses are limited by catalysts utilization requiring a purification step, or by a reductive amination step. Furthermore, some toxic reactants can be used which is not appropriate within an environmentally friendly context.

Therefore, access to bio-based and non-harmful amine monomers containing aromatic groups is one of the main industrial challenges over the coming years.

In this context, we aimed at developing a simple and inexpensive method to synthesize bio-based amines, in accordance with green chemistry principles.⁴⁶ The direct amination of alcohols and aldehydes with ammonia has been widely used for the synthesis of amines.⁴⁷⁻⁴⁹ Furthermore, this method has also been used on epoxy compounds (**Scheme 1**). In the literature, the direct epoxy amination method is described with three ammoniac derivatives: dry ammoniac (NH_3), aqueous ammonia solution $\text{NH}_3 \cdot \text{H}_2\text{O}$ (NH_4OH), and

ammonium acetate (NH₄OAc). This method was used to synthesize building blocks for the preparation of biologically active compounds,⁵⁰ dental materials,⁵¹ insecticidal agents,⁵² and as chiral ligands for asymmetric catalysis.⁵³ However, this method was never used for synthesizing polymer intermediates.



Scheme 1 : Epoxy ring-opening with ammonia.

The ring-opening reaction of the epoxides was carried out on vinyl,⁵⁴ aromatic and aliphatic⁵⁵ mono epoxy monomers, aromatic mono glycidyl ether monomers,⁵⁶ and aromatic or aliphatic diglycidyl ether,⁵⁷ including DGEBA ($n = 0$).⁵¹ In the curing agent industry, it is well known that the epoxy amine reactions between epoxy prepolymers such as DGEBA and polyamines such as DETA, TETA, etc. yield amine adducts which can be crosslinked with epoxy prepolymers to form epoxy resins.^{58,59} In order to enhance reaction rates and reduce by-products, reaction were carried out in solvent media (methanol, dioxane, and THF), and by using microwave irradiation meaning best yield and selectivity results. The use of aqueous ammonia solution NH₃·H₂O (NH₄OH) and ammonium acetate (NH₄OAc) allows obtaining primary amines, unlike dry ammoniac NH₃, which leads to tertiary amines. In our work, the easiest and cheapest method to achieve primary amines is targeted, *i.e.* by using aqueous ammonia solution, a liquid and inexpensive product.

Our work proposes a previously unexplored way to develop bio-based amines for epoxy networks. These amines should contain aromatic groups and have a reactivity comparable to an aliphatic amine. To reach new bio-based diamines, we tried to take advantage of new, recently developed monomers to substitute DGEBA. To this end, we have decided to promote diglycidyl ethers derived from vanillin previously developed in our team.¹¹ It is a way to promote lignin as renewable resource because vanillin could be produced from the depolymerization of lignin.⁶⁰ These molecules are diglycidyl ether of methoxyhydroquinone (DGEMHY, **2**) and diglycidyl ether of vanillyl alcohol (DGEVA, **3**).

As a first step, we have tested the amination methodology applied to DGEBA (**1**) as a reference system, following the protocol described by Xu *et al.*⁵¹ After this first approach, we have chosen to apply this methodology to lignin derivatives (**2** and **3**) for the purpose of synthesizing new bio-based primary diamines. Amine reactivity in cross-linking reactions and thermo-mechanical properties of epoxy networks have been studied in a second part.

Experimental

Materials and methods

Diglycidyl ether of bisphenol A (DGEBA, **1**), aqueous ammonia solution (25 % NH₃ basis), 2-methyltetrahydrofuran (purity ≥ 99.5 %), 2-amino-1-butanol (purity ≥ 97.0 %) and butylamine (purity ≥ 99.5 %) were purchased from Sigma-Aldrich. 1-amino-2-butanol (purity ≥ 98.0 %) and 1,4-dioxane were purchased respectively from TCI and Honeywell. Diglycidyl

ether of methoxyhydroquinone (DGEMHY, **2**) and diglycidyl ether of vanillyl alcohol (DGEVA, **3**) have been previously synthesized in the laboratory following the methodology described by Fache *et al.*⁹ Epotec YD 128® (Aditya Birla Chemicals (Thailand) Ltd., Epoxy Division) is described as an unmodified, medium viscosity (10 000 – 12 000 cPs at 25 °C), general-purpose DGEBA.

Epoxy equivalent weight (EEW) is the weight of resin in grams which contains one equivalent of epoxy groups in moles. For Epotec YD 128, the EEW is 185 to 194 g.eq⁻¹. Each molecule has two epoxy groups (Fig. 1), so the average molecular weight of Epotec YD 128 ranges from 370 to 388 g.mol⁻¹. The epoxy group content (EGC) is the number of epoxy groups per mass unit and is equal to 1/EEW. The EGC is between 5.155 × 10⁻³ and 5.405 × 10⁻³ mol.g⁻¹.

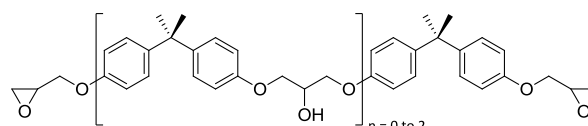


Figure 1 : Structural formula of Epotec YD 128 epoxy prepolymers.

Characterization techniques

¹H and ¹³C (APT mode) NMR spectra were recorded on a 400 MHz Bruker Aspect Spectrometer at 23 °C. Deuterated solvents used are given for each molecule. Chemical shifts are in ppm.

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 6700 FTIR spectrometer with “diamond ATR” equipment in transmittance and with a band accuracy of 4 cm⁻¹. 32 scans were performed in the range of 4000-650 cm⁻¹ and with a resolution of 4. OMNIC software was used.

MS measurements were performed on a Waters Synapt G2-S High Resolution Mass Spectrometer (HRMS) equipped with an ESI ionization source.

Thermogravimetric analysis (TGA) was carried out with an F1-Libra analyzer from NETZSCH. Data were collected using a 20 °C.min⁻¹ ramp between 20 and 600 °C. All experiments were run under a stream of nitrogen. The initial weight of each sample tested was between 9 and 10 mg. The moisture and volatile content, the percentage of residue at 600 °C, and the degradation temperature (T_d) were determined.

Differential scanning calorimetry (DSC) measurements were carried out using a Netzsch DSC 200 F3 calibrated with indium standard. Samples (*ca* 15 mg) were placed in an aluminium cell and cooled to -100 °C. Heating thermograms were recorded from -100 to 200 or 250 °C (until end reaction) at 10 °C.min⁻¹. The values of glass transition temperatures were measured.

Reaction was carried out in a Discover SP Microwave apparatus from CEM. Dynamic method was used with maximal pressure and power fixed to 17 bar and 200 W under air atmosphere.

Dynamic mechanical analyses (DMA) were carried out on a Metravib DMA 25 with Dynatest 6.8 software. Uniaxial stretching of samples was performed while heating at a rate of 3 °C.min⁻¹ from $T_g - 80$ °C to $T_g + 80$ °C, keeping the frequency at 1 Hz and a fixed strain corresponding to elastic domain of the network samples. This elastic domain was determined by

the application of a variable stress to the material at a constant temperature ($T_g + 30$ °C). For the second test, the dynamical strain value was chosen based on this elastic domain.

Swelling index were measured with three samples of around 15 mg each were respectively placed in THF for 24 h. The swelling index (SI) was calculated according to equations (1): where m_1 is the mass of the material after swelling in THF and m_2 is the initial mass of the material.

Gel content were measured after SI measurements, the three samples were dried in a ventilated oven at 70 °C for 24 h. The gel content (GC) was calculated according to equations (2): where m_3 is the mass of the material after drying and m_2 is the initial mass of the material.

$$(1) SI = \frac{m_1 - m_2}{2} \quad (2) GC = \frac{m_3}{m_2} \times 100$$

Synthesis of dihydroxyaminopropane of bisphenol A (4)

A 10 ml microwave flask was charged with diglycidyl ether of bisphenol A (DGEBA, 1.0 eq.) in 2-MeTHF (2.7 ml) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25 % solution, 2.7 ml) was then added. The mixture was stirred for 1 h after reaching 85 °C. The solution was then cooled down to room temperature. The solvent and residual $\text{NH}_3 \cdot \text{H}_2\text{O}$ were removed on a rotary evaporator and a freeze dryer was used to remove any traces of water. A white solid was obtained (> 99 %).

IR, ^1H NMR and ESMS were described in the literature (Supporting Information).⁵¹

^{13}C NMR (101 MHz, MeOD, ppm) δ : 158.1 (2xO-Cq_{Ar}), 144.7 (2xCq_{Ar}), 128.8 (4xCH_{Ar}), 115.0 (4xCH_{Ar}), 72.0 (2xHO-CH), 71.4 (2xO-CH₂), 45.4 (2xH₂N-CH₂), 42.6 (Cq), 31.5 (2xCH₃).

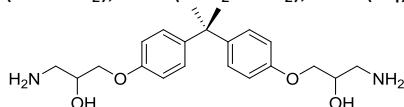


Figure 2 : Dihydroxyaminopropane of bisphenol A (DHABA, 4).

Synthesis of dihydroxyaminopropane of methoxy hydroquinone (5)

A 10 ml microwave flask was charged with diglycidyl ether of methoxyhydroquinone (DGEMHY, 1.0 eq.) in 2-MeTHF (2.7 ml) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25 % solution, 2.7 ml) was then added. The mixture was stirred for 1 h after reaching 85 °C. The solution was then cooled down to room temperature. The solvent and residual $\text{NH}_3 \cdot \text{H}_2\text{O}$ were removed on a rotary evaporator and a freeze dryer was used to remove any traces of water. A yellow solid was obtained (> 99 %).

IR (neat, ν , cm^{-1}): 3357-3299 (O-H and $\text{N}_{\text{primary}}\text{-H}$), 2919, 2865, 1595 ($\delta\text{N-H}$), 1507-1421 ($\text{C}=\text{C}_{\text{aromatic}}$), 1281, 1260, 1220, 1163, 1136, 1023, 934, 829, 789.

^1H NMR (400 MHz, MeOD, ppm) δ : 6.89 (d, 1H, $J = 8.8$ Hz, H_{Ar}), 6.63 (d, 1H, $J = 2.7$ Hz, H_{Ar}), 6.46 (dd, 1H, $J = 8.8$ and 2.7 Hz, H_{Ar}), 4.08 – 3.83 (m, 10H, 2xHO-CH, 2xO-CH₂ and O-CH₃), 2.90-2.71 (m, 4H, 2xH₂N-CH_a, 2xH₂N-CH_b).

^{13}C NMR (101 MHz, MeOD, ppm) δ : 155.8 (O-Cq_{Ar}), 152.1 (O-Cq_{Ar}), 144.0 (O-Cq_{Ar}), 116.9 (CH_{Ar}), 105.9 (CH_{Ar}), 102.2 (CH_{Ar}), 74.0 (2xO-CH₂), 71.9 (2xHO-CH), 56.4 (O-CH₃), 45.3 (2xH₂N-CH₂).

HRMS (m/z , ES+, [$\text{M}+\text{H}^+$]): $\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_5$; Calculated 287.1607; found 287.1608.

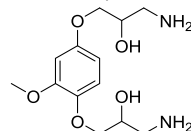


Figure 3 : Dihydroxyaminopropane of methoxyhydroquinone (DHAMHY, 5)

Synthesis of dihydroxyaminopropane of vanillyl alcohol (6)

A 10 ml microwave flask was charged with diglycidyl ether of vanillyl alcohol (DGEVA, 1.0 eq.) in 2-MeTHF (2.7 ml) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25 % solution, 2.7 ml) was then added. The mixture was stirred for 1 h after reaching 85 °C. The solution was then cooled down to room temperature. The solvent and residual $\text{NH}_3 \cdot \text{H}_2\text{O}$ were removed on a rotary evaporator and a freeze dryer was used to remove any traces of water. A yellow liquid with high viscosity was obtained (> 99 %).

IR (neat, ν , cm^{-1}): 3358-3299 (O-H and $\text{N}_{\text{primary}}\text{-H}$), 2907, 2860, 1591 ($\delta\text{N-H}$), 1512-1419 ($\text{C}=\text{C}_{\text{aromatic}}$), 1260, 1230, 1159, 1135, 1093, 1026, 927, 853, 799.

^1H NMR (400 MHz, MeOD, ppm) δ : 7.06 – 6.77 (m, 3H, 3xH_{Ar}), 4.47 (s, 2H, O-CH₂), 4.12 – 3.73 (m, 7H, 2xHO-CH, O-CH₂ and O-CH₃), 3.44 (d, 2H, O-CH₂), 2.89 – 2.59 (m, 4H, 2xH₂N-CH₂).

^{13}C NMR (101 MHz, MeOD) δ 150.8 (O-Cq_{Ar}), 149.3 (O-Cq_{Ar}), 133.1 (Cq_{Ar}), 121.8 (CH_{Ar}), 114.7 (CH_{Ar}), 113.1 (CH_{Ar}), 74.1 (O-CH₂), 73.5 (O-CH₂), 73.0 (O-CH₂), 72.3 (HO-CH), 71.8 (HO-CH), 56.5 (O-CH₃), 45.6 (H₂N-CH₂), 45.4 (H₂N-CH₂).

HRMS (m/z , ES+, [$\text{M}+\text{H}^+$]): $\text{C}_{14}\text{H}_{25}\text{N}_2\text{O}_5$; Calculated 301.1763; found 301.1764.

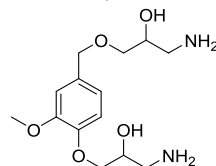
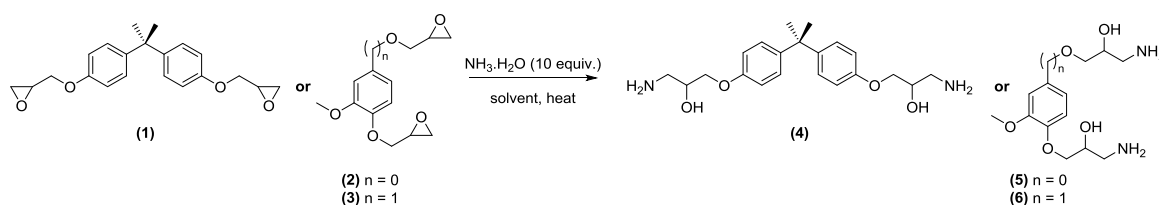


Figure 4 : Dihydroxyaminopropane of vanillyl alcohol (DHAVA, 6)



Scheme 2. DHABA (4), DHAMHY (5) and DHAVA (6) synthesis.

Methodology for synthesis of epoxy thermosets

All materials were prepared in various ratios by calculation of the function equivalent using Epotec YD 128® as epoxy

prepolymer (EEW is 185–194 g.eq⁻¹). The mixtures were homogenized by stirring. Then, they were cured at 70 °C for 2 h (to free air bubbles) and 4 h at 105 °C. The synthesized amine (6) contains two primary amine functions. Each of them can react twice with an epoxide, N(NH₂). Consequently, the number of active hydrogens per primary amine is equal to 2. Therefore, for a theoretical molar ratio of 1:2 between amine groups and epoxy groups, the necessary amount of hardener for 100 g of epoxy prepolymer is calculated according to equations (3) and (4):

$$(1) AHEW = \frac{M_{amine}}{n_{fonction NH}} \quad (2) m_{hardener} = \frac{100 \times HEW}{EEW}$$

Equation (4) may be adjusted by multiplying the amount by the desired ratio of amine/epoxy.

Results and discussion

Synthesis of amine monomers

The main goal of this work is to synthesize and investigate the properties of potentially bio-based amines for use as hardeners. To this end, two epoxy vanillin derivatives and DGEBA, as petro-based reference, were used as building blocks for amination (Scheme 2). Diglycidyl ether of methoxyhydroquinone (2) and diglycidyl ether of vanillyl alcohol (3) are obtained by the glycidylation of ethers of methoxyhydroquinone and vanillic alcohol through environmentally friendly reactions.⁴¹ These two molecules have almost similar structures besides one CH₂ hinge.

DGEBA amination was carried out first as a reference according to Xu *et al.*⁵¹ (Table 1, entry 1). In order to improve this methodology, the conditions were changed according to a “green” pathway while maintaining quantitative reactions. First, dioxane was substituted with 2-MeTHF, a bio-based and nontoxic solvent⁶¹ (Entry 2). Conversion and isolated yield were still quantitative. Moreover, there was no purification step and just an evaporation was necessary to remove excess aqueous ammonia. One test was carried out without solvent (Entry 3) but cross-linking was observed. This result indicated that the presence of solvent is required to limit the reaction between newly formed amines and epoxy building blocks. In fact, these amines can react with epoxy building blocks to produce random three-dimensional networks. The heating time can be reduced by increasing the temperature (Entry 4) and even more by using microwave irradiations (Entry 5). The use of dioxane allows a decrease in the reaction time to 30 min while maintaining complete conversion (Entries 6 and 9). Then, this route was applied to both DGEMHY and DGEVA and these reactions showed full conversions and isolated yields (Entries 7-10).

Table 1. Amination reaction of DGEBA (1), DGEMHY (2) and DGEVA (3).

Entry	Reactant	Heating [b]	solvent	T [°C]	Time	Conv. [%] ^[a]
1	(1)	Sealed flask	dioxane	100	2h30	> 99

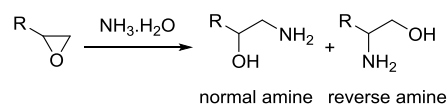
2	(1)	Sealed flask	2-MeTHF	85	2h30	> 99
3	(1)	Sealed flask	-	50	2h30	Cross-linking
4	(1)	Sealed flask	dioxane	110	1h30	> 99
5	(1)	MW	dioxane	110	30 min	> 99
6	(1)	MW	2-MeTHF	85	1h	> 99
					30 min	57
7	(2)	MW	dioxane	110	1h	> 99
8	(2)	MW	2-MeTHF	85	1h	> 99
9	(3)	MW	dioxane	110	1h	> 99
					30 min	> 99
10	(3)	MW	2-MeTHF	85	1h	> 99

[a] Conversions of epoxy were determined by ¹H NMR
[b] MW = microwaves

Another part of this work was to investigate the competition between the formation of normal and reverse amines (Scheme 3). Two possibilities of epoxy ring-opening exist depending on the attack on carbon atom (-CH₂ or -CHR).

It is expected that the selectivity of this reaction will be in favor of normal amines. In fact, SN₂ attack is favored because of the high basic pH of aqueous ammonia solution (pH = 13). Steric hindrance should become the controlling factor and aqueous ammonia should attack only the primary end of the epoxide. However, syn- and anti-attacks can occur and diastereoisomers can be formed despite the configuration.

In the literature, Favretto *et al.*⁵⁵ have studied the selectivity of (*R*)-styrene oxide ring-opening with ammonium hydroxide without solvent under MW irradiations. Under these conditions, a selectivity of 75:25 in favor of normal amine was obtained. They observed that the selectivity can be enhanced by increasing the amount of dioxane added to homogenize the system (selectivity of 91:9 in favor of normal amine with 68 % of dioxane). Swanstein *et al.*⁵⁶ have studied the selectivity of aromatic mono glycidyl ethers amination. Under the conditions used by Favretto *et al.*, they observed the formation of 93-95 % of the normal amines. For DGEBA amination, Xu *et al.* have not described the formation of reverse amines as a side product in their works. This is why the selectivity of epoxy amination was investigated in this study. ¹H NMR spectra were performed to determine the presence of side products for each case.



Scheme 3 : Competition between normal and reverse amine formation.

First, ¹H NMR spectra of two references (1-amino-2-butanol and 2-amino-1-butanol) were compared to those of DHAMHY and DHAVA in order to confirm the presence of reverse amine side products (Figure 5). It should be noted that

the α -CH signal of the amine groups *a* of 2-amino-1-butanol (as reference for reverse amine side product), shows a ddd signal around 3.5 ppm and a low intensity multiplet *b* around 2.7 ppm for the α -CH₂ of the hydroxyl functions. In contrast, the 1-amino-2-butanol corresponding to the normal amine reference shows a ddd signal around 2.6 ppm, which corresponds to the α -CH₂ of the amine groups *d*. The α -CH of the hydroxyl functions *c* was assigned to the low intensity multiplet around 3.4 ppm.

The positions of the α -CH₂ amine or α -CH hydroxyl signals present in the DHAMHY and DHAVA spectra were coincident with the appearance of 1-amino-2-butanol normal amine reference. There was a shift between the signals due to the presence of an oxygen heteroatom in the DHAMHY and DHAVA structures that was not in the reference spectra.

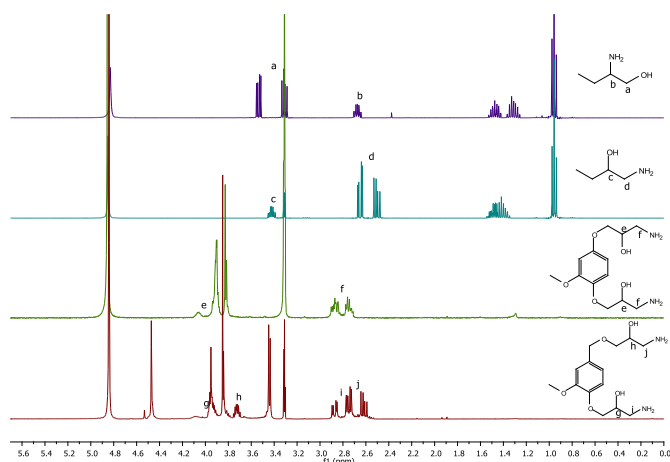


Figure 5 : ¹H NMR spectrum of DHAMHY, DHAVA and two references recorded in MeOD.

A ¹H NMR spectrum of DHAMHY is displayed in **Figure 6**. This spectrum shows the typical multiplet at 2.81 ppm and multiplet at 4.06 ppm, assigned respectively, to the α -CH₂ of the amine groups and α -CH of the hydroxyl functions. The complex signal (multiplet) at 3.91 ppm was assigned to the O-CH₂ protons of the opened epoxy group (designated as 11 and 3 in the spectrum). The typical singlet corresponding to the O-CH₃ of the methoxy group was split into two signals at 3.82 and 3.83 ppm because of the presence of the diastereoisomer induced by anti- and syn- attacks of amine on the epoxy. This result showed that unfavorable syn- attack took place. It is induced by the steric hindrance on the epoxy end. This diastereoisomer presence can be supported by looking at the aromatic proton signals at 6.89, 6.63 and 6.46 ppm. The -CH signal designated as 5 was coupled with -CH designated as 6 and was clearly identified at 6.89 ppm with a typical doublet (³J = 8.8 Hz), while the -CH 6 (6.46 ppm) was coupled with -CH 5 and -CH 8 with a typical doublet of doublet (³J = 8.8 Hz and ⁴J = 2.7 Hz). The last signal is -CH 8 which was at 6.63 ppm with a typical doublet (⁴J = 2.7 Hz). These three signals definitively confirm the presence of diastereoisomers.

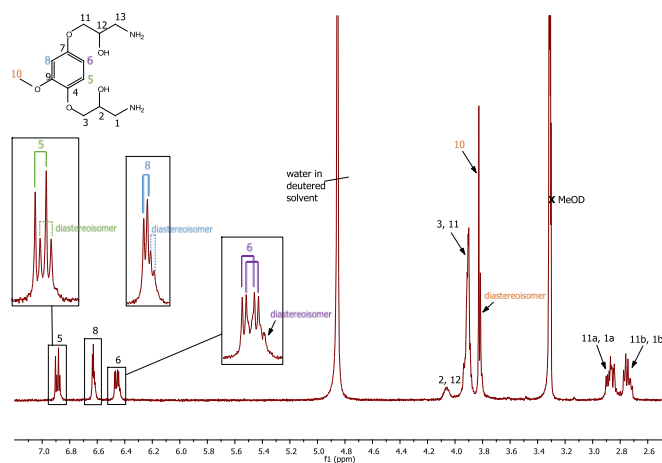


Figure 6 : ¹H NMR spectrum of DHAMHY synthesized by DGMHY amination recorded in MeOD.

In addition, a ¹H NMR spectrum of DHAVA is displayed in **Figure 7**. This spectrum shows the typical ABX signal, induced by the presence of nonequivalent protons, at 2.68 ppm (³J = 7.5 Hz and ²J = 13.6 Hz), and another at 2.81 ppm (³J = 3.9 Hz and ²J = 13.6 Hz), which was assigned respectively, to the α -CH₂ (14 and 1) of the two amine groups. The shielding of these two signals indicates that the CH₂ which separates the ether chain and the aromatic backbone has an impact on the chemical shift. In fact, shielding of various protons of these alkoxy chains approximately correlates with the distances of their appropriate carbons. Similarly, the shielding corresponding to α -CH of hydroxyl functions (designed ³J = 4.2 Hz and ³J = 5.5 Hz) and the O-CH₂ 12 (³J = 5.4 Hz) was impacted with lower chemical shifts. The typical singlet corresponding to the O-CH₃ (methoxy group) was at 3.85 ppm. As for the previous DHAMHY spectrum, the presence of a diastereoisomer was observed at 3.83 ppm. Again, this diastereoisomer presence can be supported by the appearance of aromatic proton signals at 7.00, 6.93 and 6.88 ppm. The -CH signal designated as 6 was coupled with -CH, designated as 5 and was clearly identified at 6.93 ppm with a typical doublet (³J = 8.16 Hz), while the -CH 6 (6.88 ppm) was coupled with -CH 5 and -CH 8 with a typical doublet of doublet (³J = 8.1 Hz and ⁴J = 1.9 Hz). The last signal is -CH 8 which was at 7.00 ppm with a typical doublet (⁴J = 1.9 Hz). The presence of diastereoisomers is confirmed especially by the -CH 5 signal as shown in the **Figure 7**.

Table 2. Appearance and characterization of DHAMHY and DHAVA

Amine	Appearance	T _{d5%} (°C)	Solubility
DHAMHY	Yellow solid	283	Water, MeOH, CHCl ₃ ,
DHAVA	Yellow liquid	241	CH ₂ Cl ₂ , THF, partially in Acetone

The properties of these two amines were summarized in **Table 2**. DHAVA has the advantage of being a liquid, contrary to DHAMHY. The temperature at 5 % weight loss (T_{5%}) of DHAVA is 241 °C, whereas it is 283 °C for DHAMHY. This can be explained by the presence of methylene groups in the DHAVA structure which decreases the thermal resistance compare to DHAMHY.

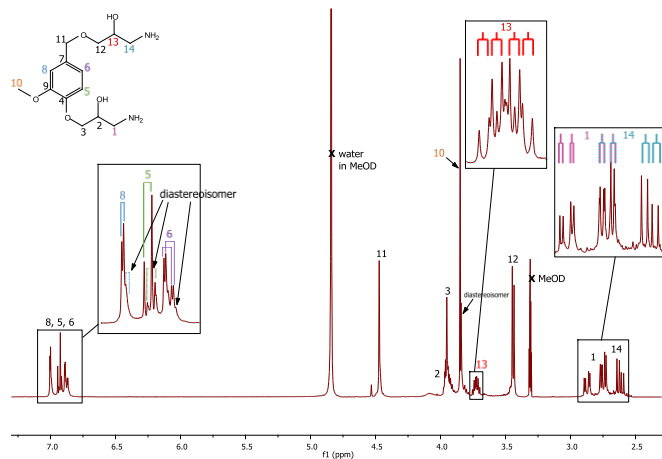
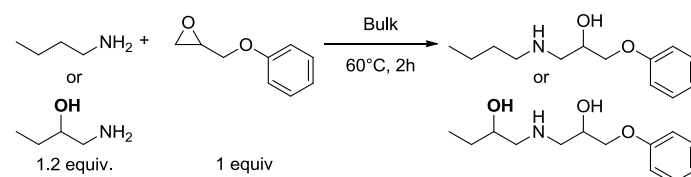


Figure 7 : ^1H NMR spectrum of DHAVA synthesized by DGEVA amination recorded in MeOD.

After the synthesis of these β -hydroxylamines, we studied the influence of the β -hydroxy group on the reaction kinetics of the epoxy amine system. In fact, it is well known that the hydroxyl groups are able to form hydrogen bonds with the oxygen atom of the epoxy group, which is consequently more susceptible to be attacked by the nucleophilic amine.⁶ For instance, the epoxy amine reaction is accelerated by the hydroxyl groups present in the secondary amine reaction products.⁶² Hence, it is expected that the β -hydroxy group of amines **2** and **3** affords good reactivity properties and accelerates the rate of amine curing. In order to prove this, a kinetic study was performed by ^1H NMR analysis.

To determine the differences of kinetic rates between amines and β -hydroxylamines, the model reaction of either butylamine or 1-aminobutan-2-ol (*i.e.* a β -hydroxylamine) with 1,2-epoxy-3-phenoxypropane was monitored in bulk conditions at 60 °C (**Scheme 4**, **Figure 8**). These results clearly confirmed that hydroxylamine is more reactive than its alkyl equivalent. In fact, the 1,2-epoxy-3-phenoxypropane was completely consumed after 20 min with hydroxylamine while only 31 % of epoxy was consumed with butylamine. Butylamine required 2 hours to reach the full consumption of epoxy. At 20 min, the reaction with β -hydroxylamine was approximately 3 times faster, which clearly shows the positive effect of β -hydroxyl groups on amine reactivity.

These results show that the synthesized amines by epoxy opening are more reactive than their non-hydroxylated alkyl analogues. The cross-linking time will be much shorter with β -hydroxylamine than with alkylamine.



Scheme 4. Reactions of butylamine or 1-aminobutan-2-ol with 1,2-epoxy-3-phenoxypropane.

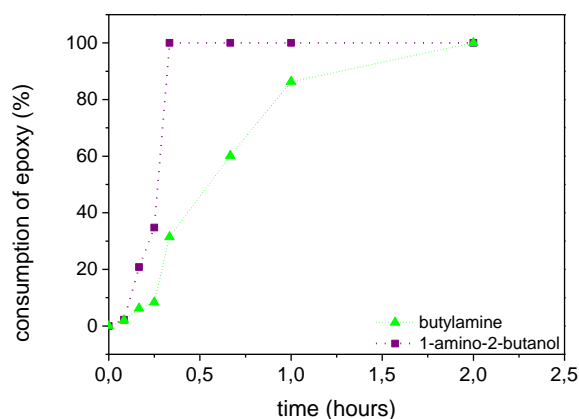


Figure 8 : Curves of conversion of 1,2-epoxy-3-phenoxypropane as a function of time for the epoxy amine reaction at 60 °C without solvent of two different references.

Synthesis of epoxy thermosets

Innovative fully bio-based thermosets were synthesized in this study. This methodology allows to use the same starting material as amine and epoxy compound in a network.

Indeed, the previously synthesized amine DHAVA (**6**) was used as a crosslinking agent in epoxy formulations for this study because of its liquid state. A petroleum-based reference system was studied initially with DGEBA (**1**) as the epoxy because of its common use for epoxy networks. Then, a fully bio-based system was studied with DGEVA (**3**) as the epoxy compound. The thermal behavior of the synthesized networks was investigated using DSC and TGA (under nitrogen atmosphere). Thermal and mechanical analyses of the obtained materials are summarized in **Table 3**. All materials were prepared with the conditions previously described.

First, a kinetic study was performed by DSC between DHAVA and DGEBA, then between m-xylylenediamine (MXDA), a current benzylic hardener with a high reactivity (close to an aliphatic amine), and DGEBA, to compare the reactivity of DHAVA with a current reactive hardener as reference (**Figure 9**). Results showed an onset temperature of 93 °C for the DHAVA-DGEBA network, which was very close to the onset temperature of the reference network ($T_{onset, MXDA} = 86$ °C). In addition, the measured enthalpy of the DHAVA-DGEBA network was lower compared to the reference networks that can be advantageous for industrial applications. This DSC kinetic study consolidates the previous ^1H NMR kinetic study.

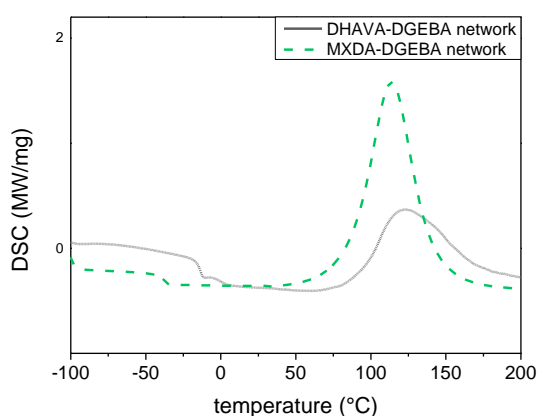


Figure 9 : Kinetic study of polyaddition curing systems.

The cure conditions and the ratio of prepolymer to curing agent have an influence on the properties of the final material. Therefore, the optimal ratio was experimentally determined to achieve the highest T_g . Various epoxy/amine ratios were tested, ranging from 2/0.6 to 2/2.0. Epoxy thermosets were prepared from **6** and Epotec YD 128 (mixture of solid DGEBA monomer (85 %) and oligomers and other hydrolyzed compounds), chosen for their liquid state. Then, their T_g s were measured by DSC (all DSC analyses given in Supporting Information). First of all, no residual releases heat was observed from DSC thermograms of the networks, which confirmed a complete curing. The optimal T_g was obtained for the ratio of epoxy/amine of 2/1.2 at 72 °C. This difference with the theoretical ratio (2/1.0) can be explained by the use of commercial DGEBA (Epotec YD 128), which is a mixture of monomer, oligomers and other undefined compounds. For other ratios, the polymer networks showed unreacted end-groups because of the excess of

either amine or epoxy. The decrease in the T_g may be explained by the presence of these trapped entities inside the polymer structure.

The same methodology was applied to DGEVA (**3**) epoxy monomer to achieve fully bio-based networks. Various epoxy/amine ratios were tested ranging from 2/0.6 to 2/2.0. Epoxy thermosets were prepared and the optimal T_g was obtained for the ratio 2/1.4 at 57 °C. This difference between both T_g s can be explained by the structure of the DHAVA backbone. In fact, the DHAVA/DGEVA system contains more methylene and methoxy groups than the DHAVA/DGEBA system. Furthermore, a recent study has shown that the presence of methoxy groups has a strong impact on the T_g with a drop in T_g of almost 20 °C.⁶³ Moreover, the methylene group of DHAVA enhances the flexibility of the final thermoset, which has a lower T_g . In fact, the methylene group behaves as a spacer between the aromatic ring and hydroxylamine, hence lowering the T_g in cured epoxy-amine systems.

Next, the thermal stability of DHAVA/DGEBA and DHAVA/DGEVA thermosets were determined by TGA (**Figure 10**). The temperature at 5 % weight loss ($T_{5\%}$) of DHAVA/DGEVA is 290 °C, whereas it is approximately 320 °C for the DHAVA/DGEBA thermoset (**Table 3**). This slight difference could be explained by the higher aromaticity of DGEBA, which confers higher thermal stability. In fact, higher energy is required to break aromatic rings than aliphatic bonds because of the conjugation phenomenon of unsaturated C=C bonds.⁶⁴ At 600 °C the residual mass of DHAVA/DGEVA is 22 % against 12 % for DHAVA/DGEBA. This result shows a slightly higher thermal stability over time, which can be due to the absence of the gem dimethyl bridge on DGEVA.

Table 3. Thermal and mechanical characterization of the different epoxy networks.

Network	$T_{d5\%}$ (°C)	Residual mass ^a (%)	T_g (°C)	T_α (°C)	Swelling index (%)	Gel content (%)
DHAVA/DGEBA	320	12	72	66	134	100
DHAVA/DGEVA	290	22	57	57	5	98

^a at 600°C.

The swelling index (SI) and gel content (GC) were measured for the two different thermosets (**Table 3**). The swelling index of the materials is the experimental representation of the distance between crosslinking nodes: the lower the swelling index, the lower the distance and the higher the cross-linking. In our case, DHAVA/DGEVA results have shown a lower swelling index than the DHAVA/DGEBA system. These results indicated a higher cross-linked density of network in the case of DHAVA/DGEVA at ambient temperature (glassy state). However, the T_g of DHAVA/DGEBA was higher than that of DHAVA/DGEVA, which generally indicated a tougher DHAVA/DGEBA network. These results can be explained by the network structures. In fact, DGEBA contains two aromatic functions which lend rigidity to the system, increasing the T_g value. However, DGEBA induces a higher internode distance because of its backbone (gem dimethyl bridge). This distance induces a slacker DHAVA/DGEBA network with a higher swelling index. Additionally, Stanzone and *al.*⁶¹ have recently explained that methoxy moieties may increase stiffness in the bulk polymer networks because of hydrogen bonding. This phenomenon can explain the low swelling index of DHAVA/DGEVA network which contain many methoxy moieties.

The gel content relies on the insoluble parts of the compounds in a solvent (THF was chosen due to its affinity with DHAVA, **Table 2**). A high gel content value means that only few free entities are trapped within the polymer structure. Here, the GC values for the two thermosets are higher than 90 % meaning that they are fully cross-linked networks.

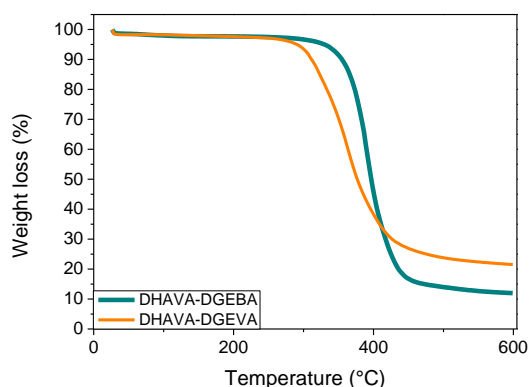


Figure 10 : TGA thermograms of cured resins (20°C.min⁻¹ under nitrogen).

Dynamic mechanical analyses (DMA) were performed on different thermosets formulated with their respective optimal epoxy/amine ratios (**Figure 11**). The curves of the storage modulus (E'), corresponding to the elastic response of the networks, and the $\tan \delta$ curves as a function of temperature for the two different networks respectively, were determined. From these curves, E' in the vitreous and elastic domain were similar for all epoxy materials. The mechanical transition temperature (T_g) was 66 °C for the DHAVA/DGEBA reference system (determined at the maximum of the $\tan \delta$ curves) and DHAVA/DGEVA showed a lower T_g of 57 °C. These results follow the same trend as the T_g values previously determined by DSC.

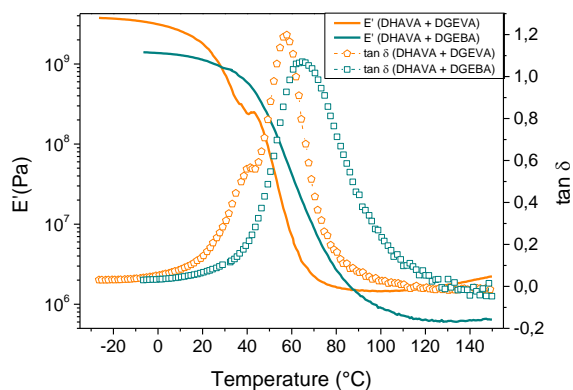


Figure 11 : DMA analysis of cured resins

Conclusion

In conclusion, an amination methodology has been optimized and applied to two bio-based building blocks: DGEMHY and DGEVA derivatives of lignin. Primary amines were selectively synthesized using aqueous ammonia solution which is inexpensive and a non-toxic reactant. Furthermore, 2-methyltetrahydrofuran, a “green” alternative ether solvent compare to dioxane was used for this reaction. These new β -hydroxylamines showed good reactivity

properties and accelerated the rate of amine curing as expected due to hydrogen bonding between the hydroxyl group of amines and the oxygen on the epoxy. A kinetic study on model compounds has demonstrated the autocatalytic effect of amine on the epoxy-amine reaction. One of these amines, DHAVA, has been selected to synthesize two epoxy networks, including one which is fully bio-based. It was cured with DGEVA (bio-based compound) and compared to the petroleum-based epoxy DGEBA. This new bio-based thermoset has shown good thermomechanical properties and high thermal stability, which can be interesting for industrial applications. Therefore, the reactivity of DHAVA was compared to MXDA as current hardener reference and results show very close reactivities. Due to the development of many new bio-based epoxy thermosets over these last few years, this amination methodology can be a real innovation to synthesize bio-based amines. With this methodology, the chemical industry would only need one reactant and aqueous ammonia to obtain bio-based epoxy networks.

Conflicts of interest

There are no conflicts to declare.

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