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Anne-Sophie Mora, Russell Tayouo, Bernard Boutevin, Ghislain David, Sylvain Caillol. Synthesis of biobased reactive hydroxyl amines by amination reaction of cardanol-based epoxy monomers. *European Polymer Journal*, 2019, 118, pp.429-436. 10.1016/j.eurpolymj.2019.06.020 . hal-02159911

HAL Id: hal-02159911

<https://hal.science/hal-02159911>

Submitted on 7 May 2020

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Synthesis of biobased reactive hydroxyl amines by amination reaction of cardanol-based epoxy monomers

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Keywords: cardanol; epoxide; amine; thermoset; reactivity

Abbreviations: DGEBA, diglycidyl ether of bisphenol A, BPA, bisphenol A, CMR, Carcinogenic, Mutagenic and/or Reprotoxic, DHAVA, dihydroxyaminopropane of vanillyl alcohol, DGEVA, diglycidyl ether of vanillyl alcohol, EEW, epoxy equivalent weight, ECH, epichlorohydrin, NMR, nuclear magnetic resonance, ppm, parts per million, TGA, thermogravimetric analysis, DSC, differential scanning calorimetry, DMA, dynamic mechanical analysis, AHEW or HEW, amine hydrogen equivalent weight, CNSL, cashew nut shell liquid, EC, epoxidized cardanol.

Abstract

Most of the current amines are issued from petrochemical resources and only a few of them are derived from biomass. Hence, there are increasing expectations for bio-based amines, particularly for aromatic ones. We have designed and synthesized new bio-based amines containing aromatic moieties from cardanol, an aromatic non-edible co-product from agri-food industry of cashew nut. We used green amination reaction of epoxy monomers with ammonia under microwave irradiations, from two commercial epoxidized cardanol monomers with different epoxy functions: NC-514 and GX-2551 (Cashew, nutshell liq., polymer with epichlorohydrin). We studied the efficiency of our amination route onto both glycidyl and epoxy functions at the middle of the chain and the reactivity of synthesized amines toward ring opening of epoxy function. The synthesized bio-based amines were further evaluated as curing agents for epoxy resins. The thermo-mechanical properties of final bio-based thermosets synthesized therefrom are almost similar ($T_g = 51$ °C, $T_d5\% = 332$ °C and $T_\alpha = 64$ °C for T-NC thermoset, $T_g = 58$ °C, $T_d5\% = 340$ °C and $T_\alpha = 78$ °C for T-GX thermoset). Moreover, another aim of this study was to

reduce the viscosity of hardeners compared to DHAVA hardener (400 000 mPa.s at 50 °C), which was synthesized in previous work. Lower viscosities were observed in the case of cardanol-based hardener (362 000 and 33 000 mPa.s at 50 °C for respectively NC-A and GX-A hardener).

1. Introduction

The epoxy-amine networks are widely used in a broad range of industrial domains such as composites, adhesives, paints and coatings due of their high thermal and mechanical properties.¹ The research concerning the reduction of the carbon footprint of these materials is growing rapidly with the increasing development of bio-based aromatic epoxy monomers from tannins,^{2,3} lignin,^{4, 5} eugenol,^{6, 7} plant oils^{8,9} and cardanol.¹⁰ More recently, the interest for bio-based amines is also increasing with the synthesis of amines from lignocellulose,^{11, 12} chitin,¹³ amino acids,¹⁴ fatty acids and oils¹⁵. However, only a few bio-based amines were still reported and their syntheses often require some toxic reactants or hard reaction conditions.^{16, 17} For instance, direct alcohol or phenol amination with NH₃ in gas phase is a common process to obtain amines, but it requires a high temperature (around 400 °C) or/and pressure, H₂ or a catalyst.^{18,19,20} Similarly, reductive amination of carbonyl functions is a route to synthesize amines from vegetable oils with similar drawbacks.^{21,22} In an eco-friendly context, we have recently reported an easy and cheap method to synthesize primary amines from glycidyl monomers, in accordance with green chemistry principles,²³ using aqueous ammonia solution which is a non-toxic reactant, in mild conditions.²⁴ Hence, dihydroxyaminopropane of vanillyl alcohol (DHAVA, Figure 2), a new bio-based amine hardener for epoxy curing, was synthesized from diglycidyl ether of vanillyl alcohol (DGEVA). However, despite the good thermo-mechanical properties of the DHAVA-based thermoset, we faced two main drawbacks for further industrial applications. First, the viscosity of the β-hydroxylamine DHAVA was very high due to hydrogen bonds, which may be formed between methoxy and hydroxyl moieties. The short backbone structure of DHAVA also induces a decreased mobility and therefore a higher viscosity. Moreover, the initial epoxy monomer was not commercial and needed to be synthesized. Therefore, we were interested in the use of commercial bio-based epoxy monomers with a longer backbone, exhibiting long alkyl chain in order to overcome both viscosity and supplying issues. In this view, we turned to cardanol derivative, which is cashew Nut Shell Liquid (CNSL) oil.

Cardanol is a fast-growing renewable resource, which is commercially available as epoxidized monomer, and with a great potential in the epoxy thermoset field.²⁵ In fact, cardanol is a non-edible co-product from the agri-food cashew nut industry, with natural phenolic function, bearing long unsaturated aliphatic chain. Cardanol is a mixture of m-[(Z)-8-Pentadecenyl]phenol, m-[(Z)-8,11-Pentadecenyl]phenol and m-[(Z)-8,11,14-Pentadecenyl]phenol. Epoxidized cardanol is widely used as reactant in various applications of epoxy thermoset industry, such as coatings,²⁶ high-performance thermosetting resins,²⁷ epoxy foams,²⁸ flame retardant thermoset.^{29, 30} To the best of our knowledge, only a few amines were

synthesized from cardanol such as phenalkamine, the most commonly developed curing agent from cardanol which is synthesized by Mannich reaction between cardanol, formaldehyde and diamines.³¹ Moreover, thiol-ene chemistry allowed synthesizing a cardanol-based amine containing aromatic moieties.³² Indeed, first, cardanol was allylated with allyl bromide and then, all the unsaturations of the cardanol (allyl and alkyl) were functionalized with cysteamine. Nevertheless, these syntheses require toxic reactants. Therefore, we have chosen to adapt our previously developed amination method to obtain new cardanol-based β -hydroxylamines. Moreover, cardanol stands out as a possible green precursor for β -hydroxylamine hardener of lower viscosity than previously developed DHAVA due to its long unsaturated aliphatic chain.

Two different di-epoxidized cardanol are commercialized: cardanol NC-514 and cardanol GX-2551 (Cashew, nutshell liq., polymer with epichlorohydrin) showing both different epoxy equivalent weight (EEW) values and different reactivity regarding to nucleophiles (Figure 1). Cardanol NC-514 is well known in the literature,^{26, 33-35} and accurately described recently by Jaillet *et al.* as a mixture of polymer structures with closed and opened epoxy rings, induced by phenol addition and oligomerization.³⁶ It is indeed obtained by the phenolation of unsaturations, and then, by the incorporation of epoxy units in the phenol substrate by means of the epichlorohydrin (ECH) addition. Cardanol GX-2551 is a new industrial epoxidized cardanol, which was never reported so far, to the best of our knowledge. The GX-2551 synthesis involves adding ECH to introduce epoxy functions into the cardanol structure, followed by the epoxidation of the unsaturations. NC-514 is highly reactive towards nucleophiles, due to its two terminal epoxy moieties, but it requires the use of phenol, which is carcinogenic. In contrast, the synthesis of the GX-2551 does not require any phenol, intern epoxies are present and they are well known to exhibit a lower reactivity compare to terminal ones.³⁷ Furthermore, the long aliphatic chain of GX-2551 contains either β -unsaturated intern epoxy or intern epoxy with saturated chain as substituent. It is reported in the literature that allyl epoxy functions (similar to β -unsaturated intern epoxy functions found in the epoxidized cardanol) are more reactive to ammonia than alkyl intern epoxy due of inductive effect.³⁸ Hence, the higher are the inductive or mesomeric effects, the higher is the reactivity of epoxy groups (allyl < vinyl < aromatic).³⁹ To the best of our knowledge, this amination method was never applied so far to long aliphatic chain carrying unsaturations.

In this work, the amination reaction of each epoxidized cardanol (NC-514 and GX-2551) was performed using the ammonium hydroxide solution as reagent in order to obtain new fully bio-based

amines derived from cardanol, expecting lower viscosity than previously synthesized DHAVA hardener. The amination of intern epoxy was studied for the first time. The reactivity of each epoxy function toward ammonia was studied. The obtained amines were then used as curing agents for the production of bio-based epoxy thermosets. The optimal ratios were determined by DSC analyses for each thermoset. Then, bulk thermosets were synthesized and their thermo-mechanical properties were determined and compared.

2. Experimental section

Materials and methods

Aqueous ammonia solution (25% NH₃ basis) and 2-methyltetrahydrofuran (purity $\geq 99.5\%$) were purchased from Sigma-Aldrich. 1,4-dioxane was purchased from Honeywell. Epotec YD 128[®] (Aditya Birla Chemicals (Thailand) Ltd., Epoxy Division) is a general-purpose DGEBA described as an unmodified compound with a medium viscosity (EEW = 185-194 g.eq⁻¹). Cardanol and epoxy monomers Cardolite GX-2551 and Cardolite NC-514 were supplied from Cardolite Corporation and used as received. Cardanol is a mixture of m-[(Z)-8-Pentadecenyl]phenol, m-[(Z)-8,11-Pentadecenyl]phenol and m-[(Z)-8,11,14-Pentadecenyl]phenol. Epoxy cardanols are polymers of cardanol and epichlorohydrin. For each epoxy cardanol, we used EEW given by Cardolite. The same GX-2551 and NC-514 cardanol batches were used during the study. Cardolite GX-2551 is di-functional epoxy resin based on cashew nutshell liquid with a low viscosity (EEW = 165-200 g.eq⁻¹). Cardolite NC-514 is a di-functional glycidyl ether epoxy resin with a medium viscosity (EEW = 350-500 g.eq⁻¹). Deuterated solvents were obtained from Sigma Aldrich for NMR study.

Characterization techniques

¹H and ¹³C NMR analyses were recorded in deuterated solvents on a 400 MHz Bruker Aspect NMR spectrometer (temperature of 23 °C). The chemical shifts are in parts per million (ppm) relative to tetramethylsilane.

Thermogravimetric Analyses (TGA) were recorded with a Netzsch F1-Libra analyzer at a heating rate of 20 °C.min⁻¹ between 25 and 600 °C (under a stream of nitrogen). 9-10 mg of each sample was placed in an alumina crucible and heated. The analyses allow to determine the moisture and volatile content, the percentage of residue at 600 °C, and the degradation temperature (T_d).

Differential scanning calorimetry (DSC) measurements were performed using a NETZSCH DSC200F3 calorimeter F3 calibrated with indium standard under nitrogen atmosphere. Approximately 10 mg of

each sample was placed in pierced aluminum crucible. The thermal properties were recorded from -100 °C to 120 °C at 20 °C.min⁻¹ and the glass transition temperature (T_g) values were measured on a second heating ramp.

Dynamic Mechanical Analyses (DMA) were carried out on 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 $T_g + 100$ °C, keeping constant frequency of 1 Hz with a fixed strain (corresponding to the elastic domain of the network samples). The elastic domain of each sample was previously determined by the application of a variable stress to the material at a fixed temperature ($>T_g + 30$ °C). The dynamic strain applied was chosen on this elastic domain for the second test.

Cross-linking density: From rubber elasticity theory,⁴⁰ the uniaxial stretching was studied on the rubbery plateau at $T = T_\alpha + 80$, and at very small deformations. Under these hypotheses, the cross-linking density (ν'), was obtained from Equation (1), where E' is the storage modulus, R is the universal gas constant and T_α is the temperature, in K, of the transition from vitreous to the elastic domain of the material determined at the maximum of the $\tan \delta$ curve. The calculated values are given for information purposes only, and they can only be compared.

$$\text{Equation (1)} \quad \nu' = \frac{E'_{T_\alpha+80}}{3RT_{\alpha+80}}$$

Swelling indices (SI) were measured with three samples which were separately placed in THF for 24 h. The swelling index was calculated according to Equation (2), where m_1 is the mass of the material after swelling in THF during 24 h and m_2 is the initial mass of the material.

$$\text{Equation (2)} \quad SI = \frac{m_1 - m_2}{m_2} \times 100$$

Gel contents (GC) were measured after SI measurements when the three samples were dried in a ventilated oven at 70 °C for 24 h. The gel content was calculated according to Equation (3), where m_3 is the mass of the material after drying and m_2 is the initial mass of the material.

$$\text{Equation (3)} \quad GC = \frac{m_3}{m_2} \times 100$$

Viscosities measurements were performed at 22 °C on the AR-1000 rheometer (TA Instruments). A 20 mm diameter and 4° cone-plan geometry were used. The flow mode was used with a gradient from 1 to 0.01 rad.s⁻¹.

Synthesis of NC-A by amination of NC-514

8.4 mL of 2-MeTHF or 1,4-dioxane were added to 1.4 g (2.5 mmol) of the NC-514 epoxy mixture in a 35 mL microwave flask. Then, 9.6 mL of ammonium hydroxide (25% solution of $\text{NH}_3 \cdot \text{H}_2\text{O}$), were added. The mixture was homogenized using a vortex. The reactor stayed under stirring and microwave irradiations during 2 h at 120 °C. The solution was then cooled down to room temperature. The solvent and residual ammonium hydroxide were removed under reduced pressure. A brown and high viscous compound was obtained (>99%).

Synthesis of GX-A by amination of GX-2551

8.4 mL of 2-MeTHF or 1,4-dioxane were added to 1.0 g (2.8 mmol) of the GX-2551 epoxy mixture in a 35 mL microwave flask. Then, 9.6 mL of ammonium hydroxide (25% solution of $\text{NH}_3 \cdot \text{H}_2\text{O}$), were added. The mixture was homogenized using a vortex. The reactor stayed under stirring and microwave irradiations during 1.5 h at 110 °C. The solution was then cooled down to room temperature. The solvent and residual ammonium hydroxide were removed under reduced pressure. A brown and high viscous compound was obtained (>99%).

Epoxidation of cardanol

Cardanol (5 g, 16.5 mmol), formic acid 60% (1.26 g, 16.5 mmol), p-toluenesulfonic acid (0.280 mg, 1.6 mmol) in toluene (4 mL) was mixed and then heated to 50 °C. Then, a hydrogen peroxide solution (30% (w/w) in H_2O) (6.79 g, 65.9 mmol) was added dropwise. The reaction mixture was stirred at 65 °C for 24 hours. The organic layer was washed successively with saturated sodium bicarbonate, brine and deionized water. The organic layer was dried with anhydrous magnesium sulfate, filtered and then, the solvent was removed under reduced pressure.

Synthesis of 1-Amino-3-phenoxy-2-propanol

2.3 mL of 2-MeTHF were added to 0.3 g (2 mmol) of the 1,2-epoxy-3-phenoxy-propane in a 10 mL microwave flask. Then, 2.7 mL of ammonium hydroxide (25% solution of $\text{NH}_3 \cdot \text{H}_2\text{O}$), were added. The mixture was homogenized using a vortex. The reactor stayed under stirring and microwave irradiations during 1 h at 85 °C. The solution was then cooled down to room temperature. The solvent and residual ammonium hydroxide were removed under reduced pressure. A white solid was obtained (>99%). Described in the literature.⁴¹

Synthesis of epoxy thermosets

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 (4) and (5):

$$(4) AHEW = \frac{M_{amine}}{n_{fonction NH}} \quad (5) m_{hardener} = \frac{100 \times HEW}{EEW}$$

With: AHEW (or HEW) is the amine hydrogen equivalent weight and EEW is the epoxy equivalent weight

An optimal molar ratio can be determined by the adjustment of Equation (5) by multiplying the amount by the desired ratio of amine/epoxy. Then, T_g s were recorded by DSC analysis and the network with the highest T_g corresponds to the optimal molar ratio.

For the synthesis of epoxy thermosets, epoxy prepolymer and amine were mixed with a previously determined optimal molar ratio and the mixtures were cured at 90 °C for 8 h to obtain the final thermosets.

3. Results and discussion

Amination of the two cardanol derivatives

The goal of this study is to synthesize two new cardanol-derived amines. For this purpose, two epoxy cardanol monomers were chosen and the same two batches were used during the study to ensure reproducibility. The first monomer is Cardolite NC-514, obtained by the phenolic condensation of cardanol followed by the incorporation of epoxy units in the phenol substrate by means of the ECH addition. Cardolite NC-514 is a flexible di-functional glycidyl ether epoxy prepolymer with a EEW between 350 and 500 g.eq⁻¹ (determined by nitration by Cardolite, EEW of used batch was 438 g.eq⁻¹). The second monomer is Cardolite GX-2551, obtained by the addition of ECH in order to introduce epoxy functions into the cardanol structure, followed by the direct epoxidation of the unsaturations of alkyl chain (spectra given in *Supporting Information, a. and b. parts*). GX-2551 is also a di-functional epoxy prepolymers with a lower viscosity and EEW between 165 and 200 g.eq⁻¹ (EEW of used batch was 182.5 g.eq⁻¹). NC-514 exhibits a higher reactivity thanks to its glycidyl function, but it is only partially bio-based due to the use of phenol for its synthesis. In contrast, GX-2551 is fully bio-based but presents internepoxies that exhibit a lower reactivity compare to terminal ones.³⁴

NC-514 and GX-2551 aminations were carried out, according to the methodology developed in our previous study (Figure 1).²⁴ The direct amination by aqueous ammonia solution was performed under microwave irradiations allowing to work at higher temperature (120 °C) than conventional heating without losing ammonia solution (boiling point = 35 °C). This methodology allows obtaining quantitative conversion and isolated yield with a low reaction time.

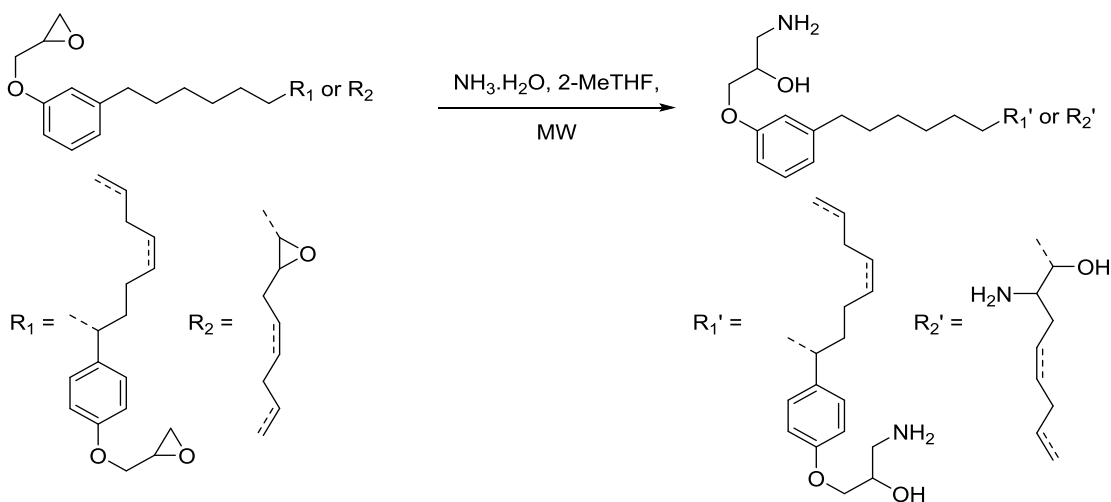


Figure 1: aminations of NC-514 (R_1) and GX-2551 (R_2)

^1H NMR spectrum of NC-A is displayed in Figure 3 (^{13}C DEPT 135 NMR and IR spectra given in *Supporting Information, c. part*). Two typical ABX signals are induced by the formation of non-equivalent protons during the ring opening reaction. The first one at 3.20 ppm ($^3J = 4.6$ Hz and $^2J = 12.2$ Hz), corresponds to the $\alpha\text{-CH}_2$ of the amine groups designated as 3 and 3' in the spectrum. The second one corresponds to the O-CH_2 protons of the opened epoxy group (1 and 1' in the spectrum) at 3.90 ppm ($^3J = 5.6$ Hz and $^2J = 9.1$ Hz). Then, the $\alpha\text{-CH}$ of the hydroxyl function is observed at 4.18 ppm with a typical quintuplet ($^3J = 5.6$ Hz). The signals 1, 1' and 2 are overlapped with oligomers signals (thus, the exact oligomers amount cannot be calculated). The formation of these oligomers can be explained by the autocatalytic effect of β -hydroxylamine on the epoxy-amine reaction due to hydrogen bonding, which was highlighted in our previous work (Figure 2). Due to this autocatalytic effect, the reactivity of β -hydroxylamine toward glycidyl ethers is clearly enhanced.

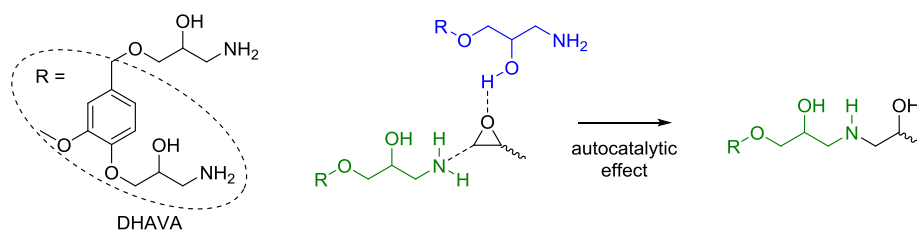


Figure 2: autocatalytic effect of β -hydroxylamine on the epoxy-amine reaction

In order to prove the formation of oligomers during amination reaction by aqueous ammonia, an amine was synthesized from 1,2-epoxy-3-phenoxy-propane in the same conditions and used as model. From NMR (scheme and spectra given in *Supporting Information, d. part*), we can observe that the same signals are obtained, corresponding to dimers and/or trimers. The presence of such oligomers was also confirmed by LC-MS analyse. However, quantitative analysis is complex. Therefore, these results show that some oligomers can be obtained during the amination reaction, competing with the ring opening reaction by aqueous ammonia solution.

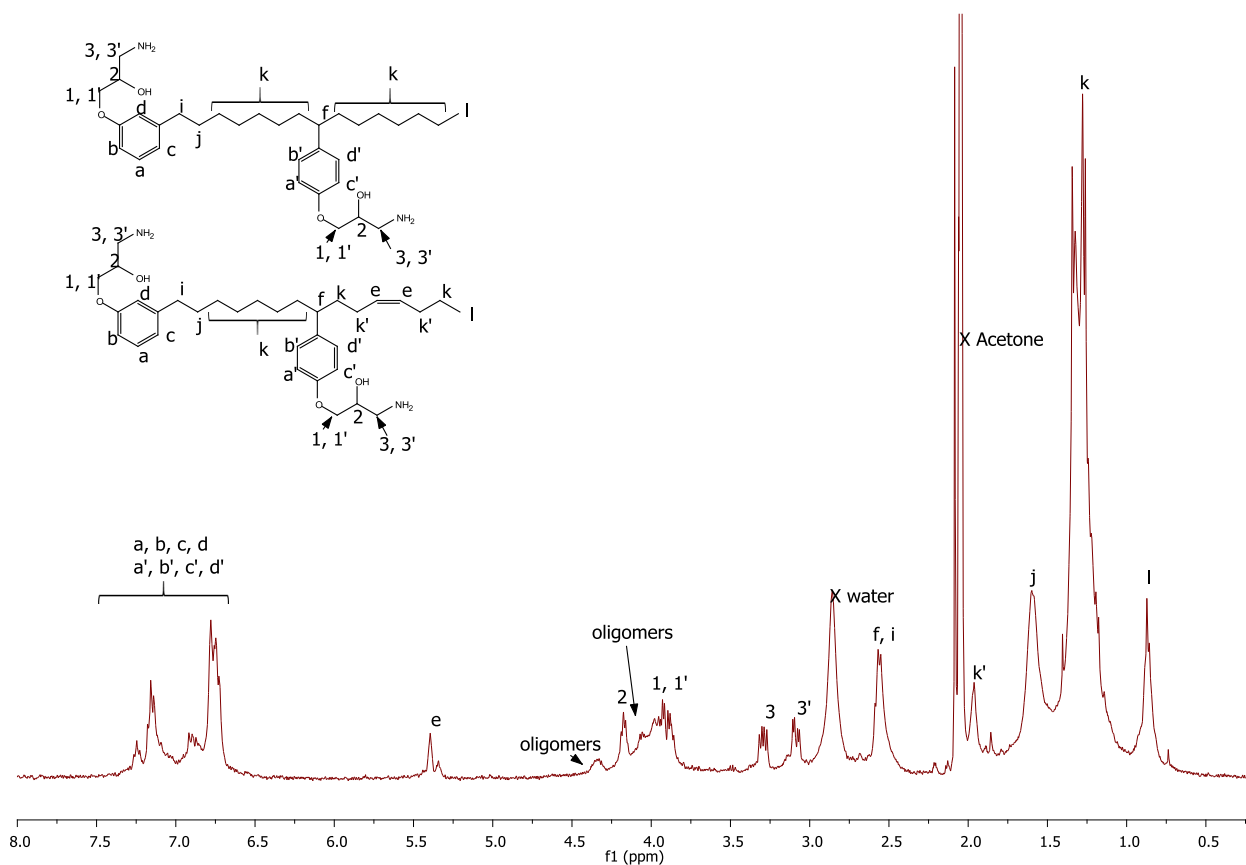


Figure 3: ^1H NMR spectrum of NC-A obtained from NC-514 amination in deuterated acetone.

For the GX-2551, the reactivity of the intern epoxy functions is much lower than the reactivity of terminal ones, but the formation of oligomers is also expected due to the presence of one glycidyl function per molecule. The ^1H NMR spectrum of GX-A (Figure 4) is more difficult to analyze than that of NC-A spectrum because of its two different epoxy functions on the aliphatic chain: one terminal epoxy group and epoxy functions at the middle of the chain (Figure 1, ^{13}C , ^1H - ^{13}C HSQC NMR and IR spectra given in *Supporting Information, e. part*). The amination by ammonia of the first one is favored whereas the intern epoxy function is more difficult to open due to the steric hindrance.

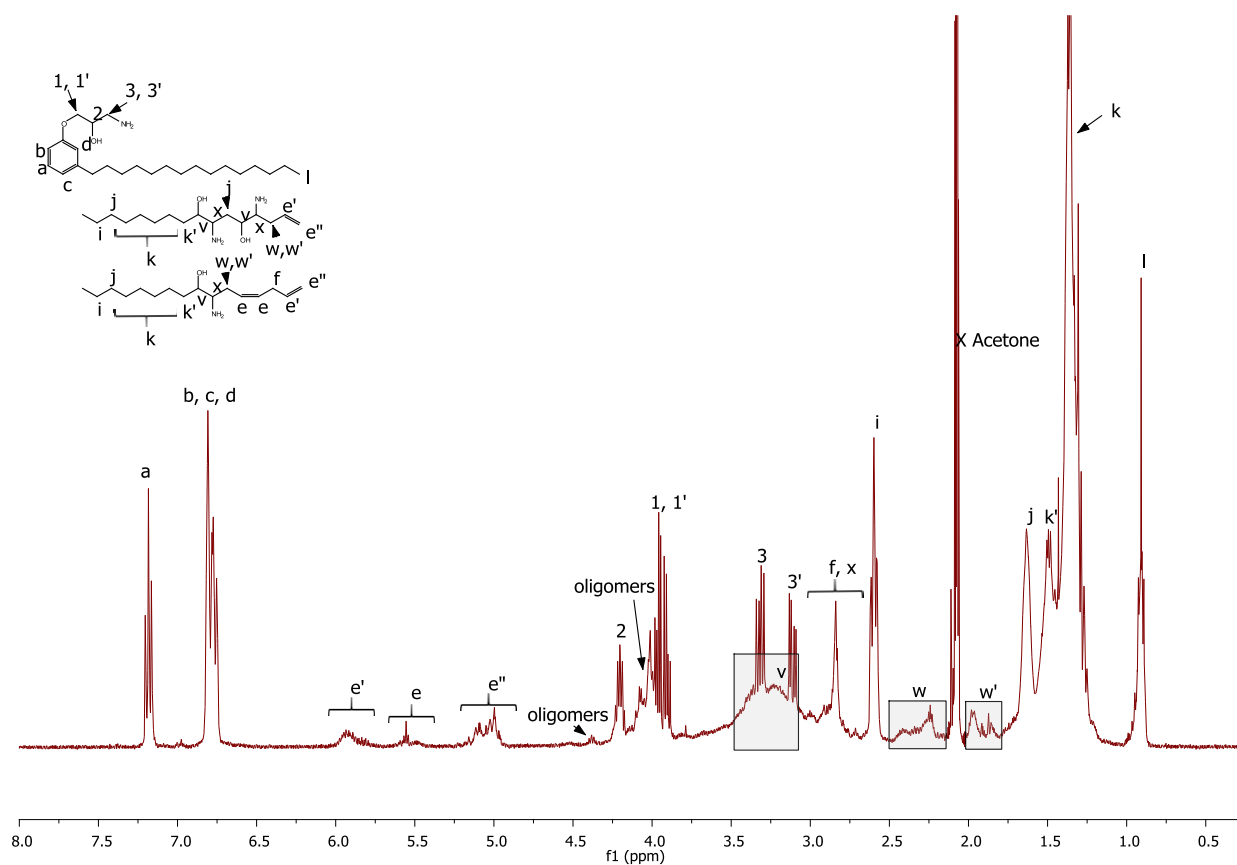
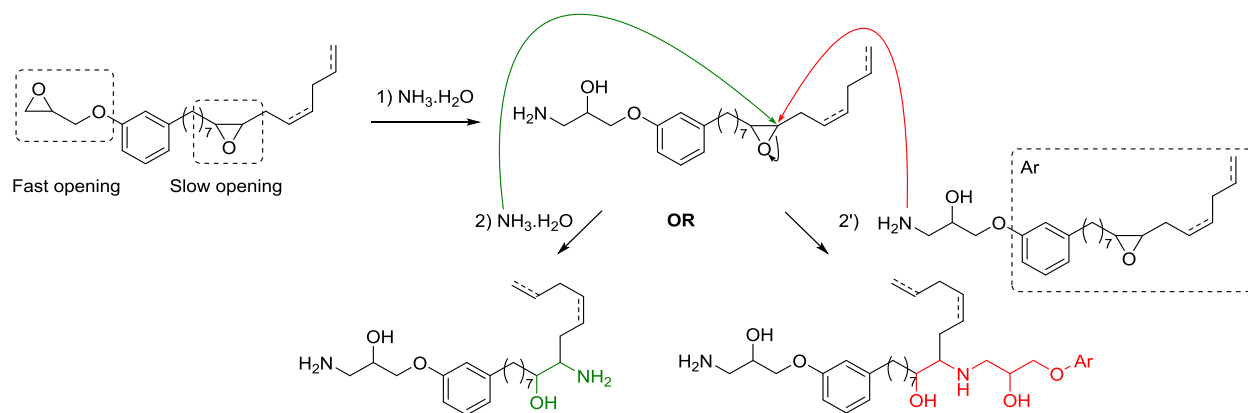


Figure 4: ^1H NMR spectrum of GX-A synthesized by GX-2551 amination in deuterated acetone.

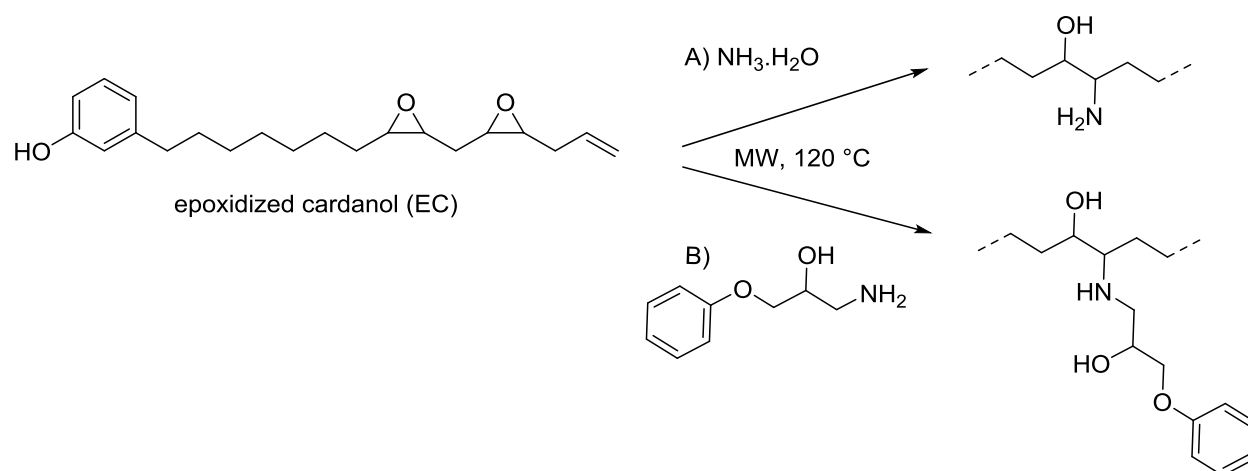
In the ^1H NMR spectrum, all epoxy groups are opened. As for NC-A, amine from the glycidyl group amination was assigned to three signals at 3.21 ppm with ABX signal ($^3J = 4.8$ Hz and $^2J = 12.2$ Hz), designated as 3 and 3' in the spectrum, at 3.93 ppm with ABX signal ($^3J = 4.8$ Hz and $^2J = 9.6$ Hz), designated as 1 and 1', and at 4.20 ppm with a quintuplet ($^3J = 5.4$ Hz), designated as 2. The signal of the α -CH of the amine groups (designated as x), that result from the intern epoxy ring opening was overlapped mainly at 2.84 ppm with an intense multiplet. There was also a low signal between 2.79 to 2.91 ppm corresponding to less favourable amination reaction. For the opening of the intern epoxy ring by the aqueous ammonia solution, the α -CH of the hydroxyl functions (v) was around 3.23 ppm with a broad multiplet appearance because of the two possibilities of ring opening of the intern epoxy function. In fact, the intern epoxy ring can be opened on both sides because of the equivalent steric hindrance induced by the aliphatic chain. Furthermore, the nature of the chain (alkyl, mono or di-alkene) may have an influence on the α -CH signal shift, corresponding to the hydroxyl functions. The broad multiplet is due to a group of overlapping multiplets.

As for NC-A, the formation of oligomers was proved by the overlapping of signals 1, 1' (with a multiplet signal between 3.95 and 4.01 ppm). Two different reactions may lead to these oligomers. First, the opening of the glycidyl by a newly formed β -hydroxylamine, as observed in the synthesis of NC-A. Then, such β -hydroxylamine may successfully open intern epoxy functions thanks to the autocatalytic effect previously described, and to the inductive effect on intern epoxy function provided by the β -unsaturated double bond in the GX-2551 structure (Scheme 1).



Scheme 1: representation of the competition between new β -hydroxylamine and aqueous ammonia solution on intern epoxy functions.

Therefore, the ring opening reaction of intern epoxy ring was investigated with epoxidized cardanol (EC) as model (Scheme 2). First, cardanol was epoxidized with hydrogen peroxide, and then four reactions were carried out in the same conditions for different times: 0.3 g of EC was mixed with 2.3 mL of aqueous ammonia solution and 2.4 mL of dioxane in 10 mL micro-waves flask. Then, the four reactions were sampled respectively at 20 min, 40 min, 1 h and 1.5 h (Figure in *Supporting Information, f. part*). Due to the overlap of the signal of α -CH of epoxy ring (around 3.1 ppm) by the water signal, it was difficult to accurately quantify the ring opening reaction over time. However, the signal of α -CH of epoxy function completely disappeared after 1 h. Then, four reactions were performed between EC and 1-Amino-3-phenoxy-2-propanol as an amine model), corresponding to the aminated glycidyl phenol of GX-A, in the same conditions for different times (20 min, 40 min, 1 h and 1.5 h, Figure in *Supporting Information, g. part*). These reactions did not allow opening epoxy rings despite the presence of β -hydroxylamine and phenol groups of cardanol, which may act as a catalyst for the reaction.⁴² In conclusion, there was no competition between β -hydroxylamine and aqueous ammonia solution on intern epoxy groups and the presence of β -hydroxylamine or phenol moieties as catalyst is not sufficient to allow the ring opening reaction between an intern epoxy function and a β -hydroxylamine.



Scheme 2: kinetic study between EC and A) aqueous ammonia solution or B) 1-Amino-3-phenoxy-2-propanol as an amine model

The two new bio-based diamine hardeners were then characterized (Table 1). The HEW of NC-A is almost twice higher than GX-A with respectively 227.5 and 99.8 $\text{g} \cdot \text{eq}^{-1}$, according to the number of epoxy functions for the initial epoxy groups (1.3 per molecule for NC-514 and 1.9 for GX-2551). The two obtained amines show a lower viscosity than that of DHAVA, the previously synthesized amine, due to the long aliphatic chain present in their structures (33 000 mPa.s for GX-A, 362 000 mPa.s for NC-A and 400 000 mPa.s for DHAVA at 50 °C). Moreover, the HEW values of DHAVA and GX-A were close (75.1

against 99.8 g.eq⁻¹ respectively). It is thus interesting to compare their viscosities. GX-A exhibits a viscosity which was almost twelve times lower than DHAVA. The use of commercial epoxidized oil as reagent is thus an interesting pathway to synthesize bio-based amines.

Thermoset syntheses

An easy and inexpensive method to synthesize primary amines was previously developed, in accordance with green chemistry principles. Based on this work, new bio-based amines were interestingly synthesized from cardanol. Hence, cardanol has a unique chemical structure, with an aromatic ring leading to materials with high thermo-mechanical properties and a long aliphatic chain conferring low viscosity during formulation. For this study, diglycidyl ether of bisphenol a (DGEBA) was chosen as epoxy monomer, despite its petro-sourced origin, because of its widespread use in the epoxy polymer industry. Epotec YD 128 was chosen as DGEBA prepolymer due to its liquid form (presence of 15% of oligomers). For each amine, a theoretical HEW was used to determine the optimal amine/epoxy molar ratio. This HEW was calculated from the following equation:

$$(6) HEW_{th} = \frac{EEW \text{ of initial epoxy} + 17}{n_{\text{fonction NH}}}$$

The value of 17 g.mol⁻¹ corresponds to the mass of additional atoms (NH₂ + H)

The difference with the theoretical ratio (2 epoxy for 1 amine) can be explained by several factors such as the use of non-pure DGEBA (Epotec YD 128), or by the method of HEW determination (calculated from commercial data). Therefore, as it was previously explained, oligomers were synthesized during the amination of GX-2551. The determination of the optimal ratio allows to fix the theoretical HEW of GX-A. The compositions of the epoxy-amine mixtures are summarized in Table 1:

Table 1. Composition of epoxy thermosets and characterization of reactants.

Network	Composition amine/epoxy	Optimal ratio	m _{amine} (mg) ^a	EEW _{th} of initial epoxy (g.eq ⁻¹)	Number of epoxy function of initial epoxy (per molecule)	HEW _{th} (g.eq ⁻¹)	Amine viscosity (mPa.s at 50 °C)
T-DH	DHAVA/DGEBA ^b	1.2-2.0	48.2	133.1	2.0	75.1	400 000
T-NC	NC-A/DGEBA	1.2-2.0	136.6	438.0 ^c	1.3	227.5	362 000
T-GX	GX-A/DGEBA	1.4-2.0	76.8	182.5 ^c	1.9	99.8	33 000

^a For 100 mg of epoxy, ^b previously determined results, in the same conditions, ^c EEW given by Cardolite

The optimal molar ratios were determined by the method described in the *experimental section* (DSC values given in *Supporting Information, h. part*). Then, the thermosets with the highest T_g were

synthesized and characterized by DSC, TGA, DMA and their swelling index (SI), gel content (GC) and cross-linking density were determined. All results are summarized in Table 2.

Table 2. Characteristics of synthesized epoxy thermosets.

	$T_d5\%$ (°C)	Char yield ^a (%)	T_g^b (°C)	T_α (°C)	ν' (mol/m ³)	E'_{glassy} (Pa)	E'_{rubbery} (Pa)	SI (%)	GC (%)
T-DH ^c	320	12	63	66	61	$1.4 \cdot 10^9$	$6.4 \cdot 10^5$	134	100
T-NC	332	8	51	64	124	$1.1 \cdot 10^9$	$1.3 \cdot 10^6$	176	93
T-GX	340	12	58	78	318	$1.6 \cdot 10^9$	$3.4 \cdot 10^6$	137	96

^a at 600 °C. ^b mid value. ^c previously determined, in the same conditions

Thermosets were synthesized by curing the epoxy-amine mixture at 90 °C for 8 h according to the corresponding ratios. The DSC analysis of the materials after curing proved that the conversion was complete, since no residual enthalpy was observed in the thermogram. Furthermore, the determination of gel content (GC) allowed confirming the complete conversion with a highly cross-linked material. When the density of cross-links is high, the solvent cannot penetrate into the network to solubilize unreacted molecules and, consequently, the GC value is high. The thermosets exhibited a gel content value lower than 100% due to non-functionalized cardanol chains, as already described in literature.³³

Then, the 5% weight loss ($T_d5\%$) temperature was determined by TGA for each thermoset (data given in *Supporting Information, i. part*). The two thermosets showed similar $T_d5\%$ and char yield at 600 °C. We could have expected a higher thermal stability for T-NC due to the presence of more aromatic moieties in the NC-514 epoxy structure compared to GX-2551. However, we observed a similar stability, which can be explained by the number of epoxy functions (per molecule) of initial GX-2551 which is almost twice higher than NC-514 with respectively 1.9 and 1.3. These values correspond to a lower amount of aromatic moieties than suggested by the theoretical structure of NC-514.

The glass transition temperature values (T_g) and the alpha transition temperature values (T_α) were recorded by DSC and DMA respectively, from bulk materials. DMA thermograms are presented in Figure 5 with the storage modulus (E') and $\tan \delta$ as a function of the temperature. First, results allow checking the homogeneity of the thermosets with narrow peaks observed for both $\tan \delta$ curves. Then, T_α were determined at the maximum of the $\tan \delta$ curve. Results showed that T_g s and T_α s follow the same trend with a slightly higher value for T-GX ($T_{\alpha(\text{T-NC})} = 64$ °C and $T_{\alpha(\text{T-GX})} = 78$ °C), meaning good thermo-mechanical properties for both. For the storage modulus characterization, results were similar in the vitreous domain with an E'_{glassy} around 1.10^9 Pa, which corresponds to a high level of hardness and stiffness for

thermosetting resins. In the elastic domain, the storage modulus (E'_{rubbery}) allows to give insight on the rigidity of a material and is linked to the cross-linking density (ν'), according to the rubber-elasticity theory.⁴⁰ E'_{rubbery} of each thermoset was within an order of magnitude (10^6 Pa), with a slightly higher value for the T-GX network meaning that this thermoset was more cross-linked and thus more rigid than that of the T-NC thermoset. Furthermore, the swelling index values (SI) were consistent with the cross-linking densities since they were inversely proportional.

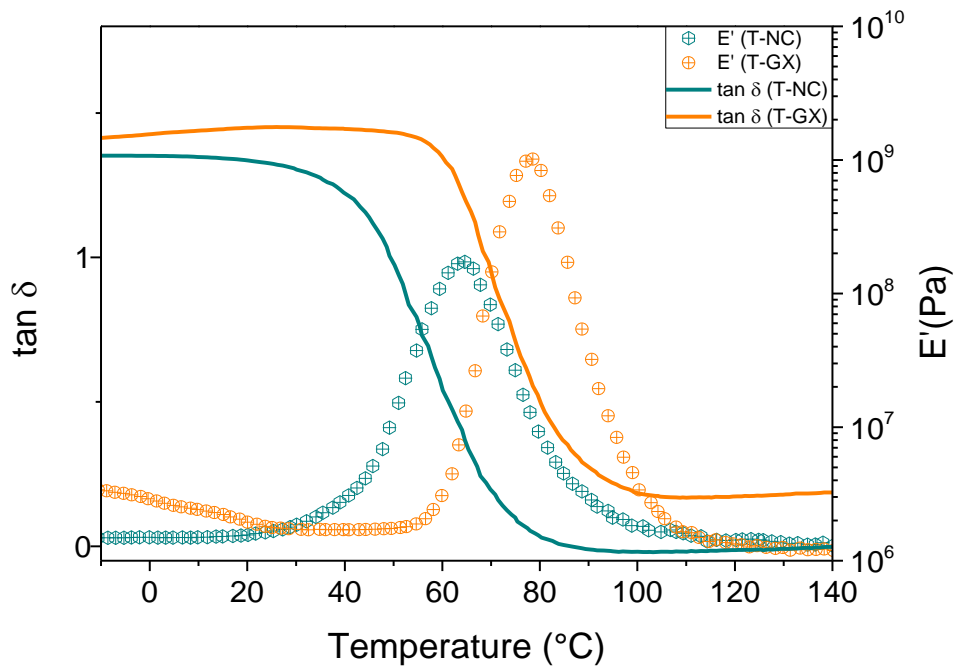


Figure 5: DMA analysis of T-NC and T-GX thermosets

These results were compared to the previously synthesized reference thermoset composed of DHAVA and DGEBA.²⁴ DHAVA has a short backbone structure compare to cardanol, indicating theoretical lower internode distance, and thus higher cross-linking density and higher rigidity resulting in higher E'_{rubbery} value. However, the reference shows lower cross-linking density and lower E'_{rubbery} value than cardanol-based thermosets. It could be explained by the presence of more DGEBA content in reference system due to the lower HEW of amine used, which may lead to an increase of the average internode distance.

4. Conclusions

New bio-based amines were synthesized from both cardanol-based epoxy monomers NC-514 and GX-

2551 by using a green amination route, using aqueous ammonia solution as reactant, under microwave irradiations. Due to the presence of the long aliphatic chain in cardanol structure, lower viscosities were obtained for cardanol-based hardeners compared to the previously synthesized DHAVA hardener, as expected. Moreover, the use of cardanol-derived monomers is very interesting since cardanol is a commercially available non-edible side-product from cashew industry which interestingly contains phenol group and unsaturated alkyl chain.

Generally, when directly linked to aromatic rings amines usually exhibit quite high toxicity. The β -hydroxyl amines obtained in this study still contain aromatic moieties, which are not directly connected to amine groups. Consequently, these amines should be less toxic. Moreover, epoxy monomers exhibit generally a higher toxicity than amines. Indeed cardanol epoxy monomers are non CMR and food contact approved. Therefore the amines synthesized therefrom, owing to a safe route, without toxic solvent nor catalyst, should exhibit a low toxicity profile. However, evaluation of their toxicity will be a necessary step forward for their industrial use.

Then, these amines were used in epoxy thermoset formulations with an optimal epoxy-amine ratio. Both of them exhibited good thermo-mechanical properties and also high thermal stabilities, with almost similar properties ($T_g = 51\text{ }^\circ\text{C}$, $T_d5\% = 332\text{ }^\circ\text{C}$ and $T_\alpha = 64\text{ }^\circ\text{C}$ for T-NC thermoset, $T_g = 58\text{ }^\circ\text{C}$, $T_d5\% = 340\text{ }^\circ\text{C}$ and $T_\alpha = 78\text{ }^\circ\text{C}$ for T-GX thermoset). Moreover, the synthesis of GX-2551 does not require phenol, unlike that of NC-514, leading to a fully bio-based amine. Therefore, the bio-based amine GX-A is very interesting due to its full bio-based origin and the use of non-toxic amination route, which is in agreement with the green chemistry principles with the reduction of the use of hazardous substances.

5. Acknowledgements

We thank the students Antoine Grepinet, Rafael Belem Lavrador and Benjamin Sgro for their help during their training period.

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