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Biobased epoxy thermosets from vanillin-derived oligomers

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ABSTRACT

Novel vanillin-derived epoxy oligomers were prepared and crosslinked to yield biobased epoxy thermosets. This work directly continues the efforts engaged by our team to use vanillin as a renewable building block for polymer chemistry as it is an industrially available, non-toxic, wood-derived compound. The oligomers were synthesized by adapting and optimizing an industrial strategy currently in use, consisting in the chain-extension of a diepoxy monomer in excess by the poly(addition) of a diphenol. The length of the oligomers prepared was controlled by the stoichiometry of the reactants, and well-predicted by Carothers' equation. A ^{1}H NMR titration method was implemented to determine the epoxide indexes of the oligomers, which were very close to the ones calculated. The thermal properties of the oligomers were investigated and their T_g increased with the chain length, in accordance with the Flory–Fox equation. Thermosets were prepared by crosslinking these biobased epoxy oligomers with a common industrial amine hardener. The materials obtained displayed good thermo-mechanical properties that were tunable with the chain length of the oligomer employed. The current strategy used in industry was found to be applicable to renewable resources-based epoxy resins.

1. Introduction

In a context of environmental concerns and predicted scarcity of petrobased resources, the use of renewable resources is an ecological and economical necessity. The polymer industry has its role to play in this transition and the biosourcing of polymers is currently a hot topic for both academic and industrial research in this field.

Great efforts have been made toward this goal during the last decade [1]. These efforts were successful in some areas like the development of polymers based on plant oils [2], which is already an industrial reality. The field of (poly)saccharides is also currently under intense investigation [1], either for a direct use like cellulose or starch, or indirectly to prepare from this resource all-purpose building-blocks [3]. This approach led to the development around these building-blocks of platforms of monomers and compounds usable in polymer chemistry like in the case of isosorbide for instance [4].

However, aliphatic monomers give polymers with low T_g – especially long fatty acids from plant oils – which is not suitable for applications with demanding thermo-mechanical properties. Also, polymers from poly(saccharides) have a tendency to take up water, which might also limit the potential applications. Thus, the development of a sourcing of aromatic intermediates from renewable resources is a key challenge, especially since the petro-based raw materials tend to shift from oil to shale gas, which limits aromatic availability. This is especially true for thermosetting materials as the presence of aromatic rings, very stable moieties, brings the thermo-mechanical performances required for this kind of polymers in their industrial applications. Moreover, thermosetting materials, being cross-linked, cannot be recycled and thus need a renewable carbon content as high as possible. Regarding

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the importance of this topic, the past few years have seen an increasing contribution from the scientific community, mostly at the academic level [5].

Epoxy polymers especially have been investigated [6] as they are used in many industrial fields such as aerospace, automotive and construction and through diverse applications such as adhesives, coatings and composite matrices. Currently, 75% of the epoxy polymers worldwide are based on Bisphenol A, a reprotoxic compound [7] that is under close monitoring and the use of which might be restricted in certain applications in the future. The use of renewable aromatics to prepare new, biobased epoxy polymers could thus have the double positive effect of Bisphenol A replacement and renewable resources use.

As mentioned, research and process development for the use of renewable aromatics are only at the starting point in this area, and epoxy thermosets are no exception. The only biobased epoxy prepolymers industrially available are based on cardanol. However, this abundant biobased phenol extracted from the cashew nutshell present a C_{15} aliphatic chain, which decreases the thermo-mechanical properties of the final material [8]. Recently, a handful of reports could be found in the literature on the subject of biobased aromatics for high-performance epoxy polymers. Some authors started directly from the raw resources such as lignin [9,10] or tannins [11,12]. This approach, however, suffers from several drawbacks such as structure complexity of the resource, issues with processability due to reactivity, high molecular weights and insolubility and composition variability depending on the species or the time of year.

Another strategy found in the literature consists in synthesizing aromatic epoxy monomers from various biobased aromatic molecules such as furans [13,14], 4-hydroxybenzoic acid [15], cinnamic acid [16], catechin [11,17], gallic acid [18], eugenol [19], vanillic acid [20] and vanillin [21–23]. Among them, vanillin and derivatives are especially interesting as vanillin is the only monoaromatic compound currently industrially produced from lignin [24]. In a previous paper [25], our team investigated the functionalization of vanillin and its derivatives at different oxidation states. These molecules formed a platform of potential biobased difunctional monomers, including epoxy monomers. Biobased thermosets were then synthesized from these vanillin-derived aromatic epoxy monomers [26]. The epoxy materials prepared exhibited excellent thermo-mechanical properties; however they were only based on monomeric units. Usually, industrial epoxy resins are not purely monomeric but oligomeric. This strategy holds numerous advantages such as control of the properties through the degree of polymerization of the oligomer used or an easier handling by avoiding crystallinity of pure monomers [27].

In this study, we decided to go one step further and apply this established industrial method to biobased epoxy thermosets. The strategy of this work is summed up in Scheme 1. This strategy necessitated the syntheses of methoxyhydroquinone **2** and diglycidyl ether of methoxyhydroquinone **3** from vanillin **1**. These syntheses were previously described by our team [25]. We then adapted and optimized an industrial method to obtain oligomers **4** from the reaction between **2** and **3**. With this method, oligomers with varying degrees of polymerization were prepared. We also developed a ^{1}H NMR titration protocol to measure the epoxide index of these oligomers. Finally, they were cross-linked with isophorone diamine, a common industrial hardener, to obtain vanillin-based thermosetting polymers with tunable properties.

2. Experimental

2.1. Materials and methods

TriEthylBenzylAmmonium Chloride (TEBAC) (99%), triphenylbutylphosphonium bromide (99%), methoxyhydroquinone (>98%), IsoPhoroneDiAmine (IPDA) (>99%), sodium hydroxide (>98%), 1,3,5-trioxane (>99%), trifluoroacetic acid (99%) and all solvents used (>99%) were purchased from Sigma–Aldrich. Epichlorohydrin (>99%) was purchased from Fluka. All reactants were used as received.

Silica gel chromatography was performed on a Grace Davison Reveleris Flash Chromatography device.

MS measurement was performed on a Waters Synapt G2-S High Resolution Mass Spectrometer (HRMS) equipped with an electrospray ionization source.

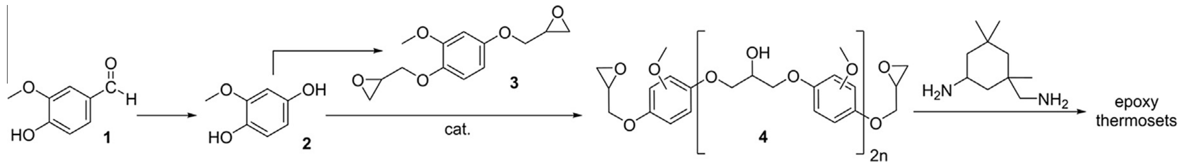
2.2. Synthesis of diglycidyl ether of methoxyhydroquinone 3

A round-bottomed flask was filled with methoxyhydroquinone (**2**, 1.0 eq.), TEBAC (0.1 eq.) and epichlorohydrin (10 eq.). The mixture was stirred for 1 h and a half after reaching 80 °C and was then cooled down to room temperature. An aqueous solution of TEBAC (0.1 eq.) and NaOH (4 eq., 5 mol L^{-1}) was then added and the mixture was stirred 30 min at room temperature. Ethyl acetate and deionized water were added and the two-phase mixture was stirred for a few minutes. The aqueous phase was extracted three times with ethyl acetate. Organic phases were combined, rinsed twice with brine, dried on anhydrous $MgSO_4$and filtered. Ethyl acetate and epichlorohydrin excess were removed on rotary evaporator.

Purification was achieved by silica gel flash chromatography using a gradient of cyclohexane/ethyl acetate mixtures as eluent. The proportion of ethyl acetate was automatically and gradually increased from 0% to 100% to separate all fractions.

2.3. Oligomerization reaction

The optimal experimental conditions for the preparation of oligomers **4** from **2** and **3** were determined by DSC. Mixtures of **2** and **3** (1/1) and catalyst (from 0 to 10 w.‰ of the total mass) were placed in sample pans to investigate the effects of the catalyst amount. The time needed to reach the completion of the reaction was also determined. Once the experimental conditions were set, glass vessels were filled with **2** (1.0 eq.), **3** (from 1.1 to 2.0 eq.) and triphenylbutylphosphonium bromide (5 w.‰ of the total weight). The mixtures were placed in an oil bath and magnetically stirred for 2 h at 125 °C.



Scheme 1. Strategy employed to prepare epoxy thermosets from vanillin.

2.4. Polymerization of oligomers with IPDA

Epoxy polymers were prepared from the oligomers **4** synthesized by cross-linking them with IsoPhoroneDiAmine (IPDA). The Epoxide Index (EI, number of moles of epoxy groups per gram) of each oligomer was first determined by ^{1}H NMR (see Section 2.6). A mass of oligomer corresponding to 1.0 eq. of epoxide groups was first heated at 130 °C in a rectangular silicone mold during approximately 15 min to obtain a free-flowing liquid. The appropriate amount of IPDA (2.0 eq.) was added to each oligomer, and the mixtures were thoroughly hand-stirred with a pre-heated stirring rod to obtain homogeneous liquid mixtures. The mixtures were cured for 1 h and 45 min at 130 °C and left to cool down to room temperature. The polymers were then post-cured at 150 °C for 1 h.

2.5. DSC analyses

Differential scanning (DSC) analyses were carried out on a Netzsch DSC200 calorimeter. Cell constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as the purge gas. Samples were placed in aluminum pans.

For the determination of the oligomerization reaction parameters, the thermal properties of the reaction were recorded between −40 °C and 250 °C. The thermal properties of the oligomers **4** themselves were recorded between −40 °C and 125 °C, the amine-hardened epoxy materials between −20 °C and 170 °C. In each case, the heating rate was 10 °C min^{-1} and the thermal history of the samples was erased with a first heating ramp. The T_g was measured at the second ramp at the inflexion point and given at ± 2 °C.

2.6. NMR analyses

^{1}H and ^{13}C (APT mode) NMR spectra were recorded on a 400 MHz Brucker Spectrometer at room temperature. The ^{1}H NMR spectrum of the oligomer prepared with a ratio of **3**–**2** of 1.85/1 is available as an example in Fig. 1.

The Epoxide Index (EI, number of moles of epoxide groups per gram) of the oligomers **4** was measured by ^{1}H NMR. The method consisted in solubilizing a known mass of the oligomers (14.44 mg in this example) and of an internal standard (1,3,5-trioxane – 6 equivalent H – 0.64 mg–7.1 mmol) in DMSO-d6. The number of moles of epoxide groups per gram of oligomer was determined by comparing the integration of the standard (6 H) with the integration of the epoxide group (2 H) as shown in Fig. 1. The average number of repeating units was also measured by ^{1}H NMR, comparing epoxide groups integrations (4 H per molecule) with aromatic integrations ($3(2n + 1)$ H per molecule).

2.7. DMA analyses

Dynamic Mechanical Analyses (DMA) were carried out on a Metravib DMA 25. The DMA samples had a rectangular geometry (length: 10 mm, width: 20 mm, thickness: 2.5 mm). Uniaxial stretching of samples was performed while heating at a rate of 2 °C/min from 30 °C to 150 °C, keeping frequency at 1 Hz. In order to perform measurements in the linear viscoelastic region, deformation was kept at 0.001%. The storage modulus (E'), loss modulus (E'') and $\tan\delta$ curves as a function of temperature were recorded and analyzed using the software Dynatest 6.8. E' is the elastic response of the material and is related to the mechanical energy stored per cycle upon deformation. E'' is the viscous response and is related to the dissipated energy per cycle when the sample is deformed. The loss factor δ is defined as $\tan\delta = E''/E'$, δ being the angle between the in-phase and out-of-phase components of the modulus in the cyclic motion. The temperature T_α of the α relaxation process, was determined as the temperature at the peak maximum of the $\tan\delta$ curve.

Glass transition and α relaxation are commonly used as synonyms as they are related to the same molecular phenomenon: the appearance of coordinated large-scale motions in the network (or of the chains present in the amorphous regions for thermoplastics). However, T_g is measured by DSC under no mechanical stress and T_α by DMA under mechanical stress at a given frequency. T_g and T_α values can thus be quite different depending on the frequency used for mechanical stress.

3. Results and discussion

3.1. Synthesis of diglycidyl ether of methoxyhydroquinone *3*

In a previous paper, our team described an environmentally friendly synthesis of methoxyhydroquinone **2** starting from vanillin **1**, and its subsequent glycidylation to prepare the diglycidyl ether of methoxyhydroquinone **3** as shown in Scheme 1 [25]. Briefly, this glycidylation step was performed using TriEthylBenzylAmmonium Chloride (TEBAC) as a phase transfer catalyst to allow the phenolate ion to exist in organic solution. Then, this phenolate ion reacts with epichlorohydrin via two possible mechanisms (S_N2 and ring opening). S_N2 gives the expected product whereas the ring opening gives an intermediate, which is closed in a second step by intramolecular reaction in presence of an aqueous solution of NaOH and phase transfer catalyst.

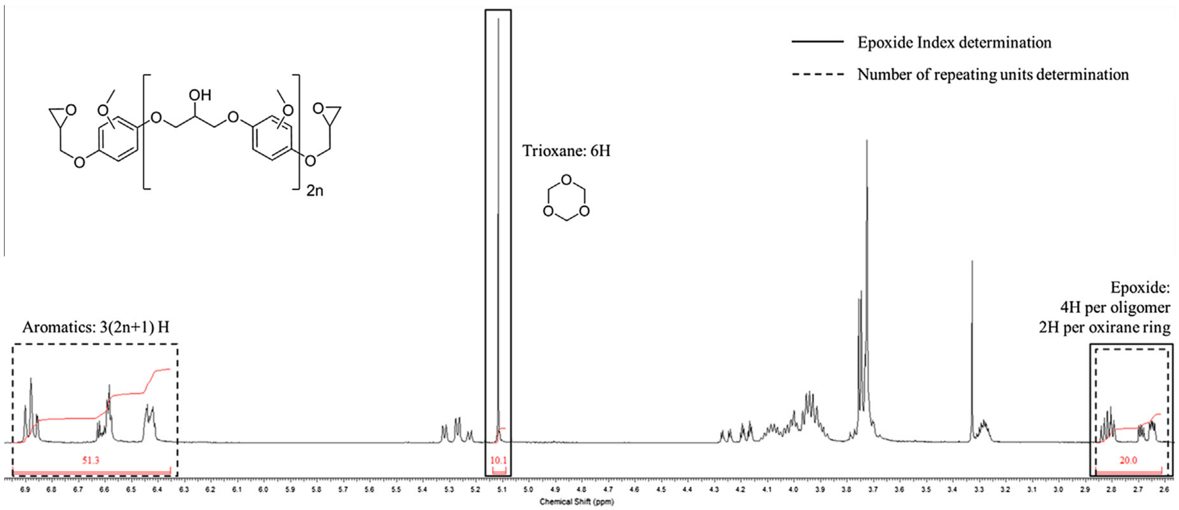


Fig. 1. ^{1}H NMR determination of epoxide index and number of repeating units of the oligomers prepared.

The product was characterized by ^{1}H and ^{13}C NMR as shown in Fig. 2.

Diglycidyl ether of methoxyhydroquinone (80%; white solid, m.p. 87 °C).

^{1}H NMR (400.1 MHz, acetone-d6, ppm) δ: 2.66 (m, 2H, H_{10a}, H_{13a}); 2.81 (m, 2H, H_{10b}, H_{13b}); 3.27 (m, 2H, H_9, H_{12}); 3.81 (m, 2H, H_{8a}, H_{11a}); 3.81 (s, 3H, H_7); 4.23 (m, 2H, H_{8b}, H_{11b}); 6.43 (dd, $^3J_{H6H5}$ = 8.8 Hz, $^4J_{H6H2}$ = 2.8 Hz, 1H, H_6); 6.63 (d, $^4J_{H2H6}$ = 2.8 Hz, 1H, H_2); 6.88 (d, $^3J_{H5H6}$ = 8.8 Hz, 1H, H_5).

^{13}C NMR (100.6 MHz, acetone-d6, ppm) δ: 44.91 (s, C_{10}, C_{13}); 51.16 (s, C_{12}); 51.32 (s, C_9); 56.63 (s, C_7); 71.09 (s, C_{11}); 72.89(s, C_8); 102.57 (s, C_2); 105.90 (s, C_6); 117.37 (s, C_5); 144.29 (s, C_4); 152.51 (s, C_3); 155.66 (s, C_1).

HRMS (m/z, ES+, $[M + H^+]$): $C_{13}H_{17}O_5$; Calculated 253.1079; found 253.1076.

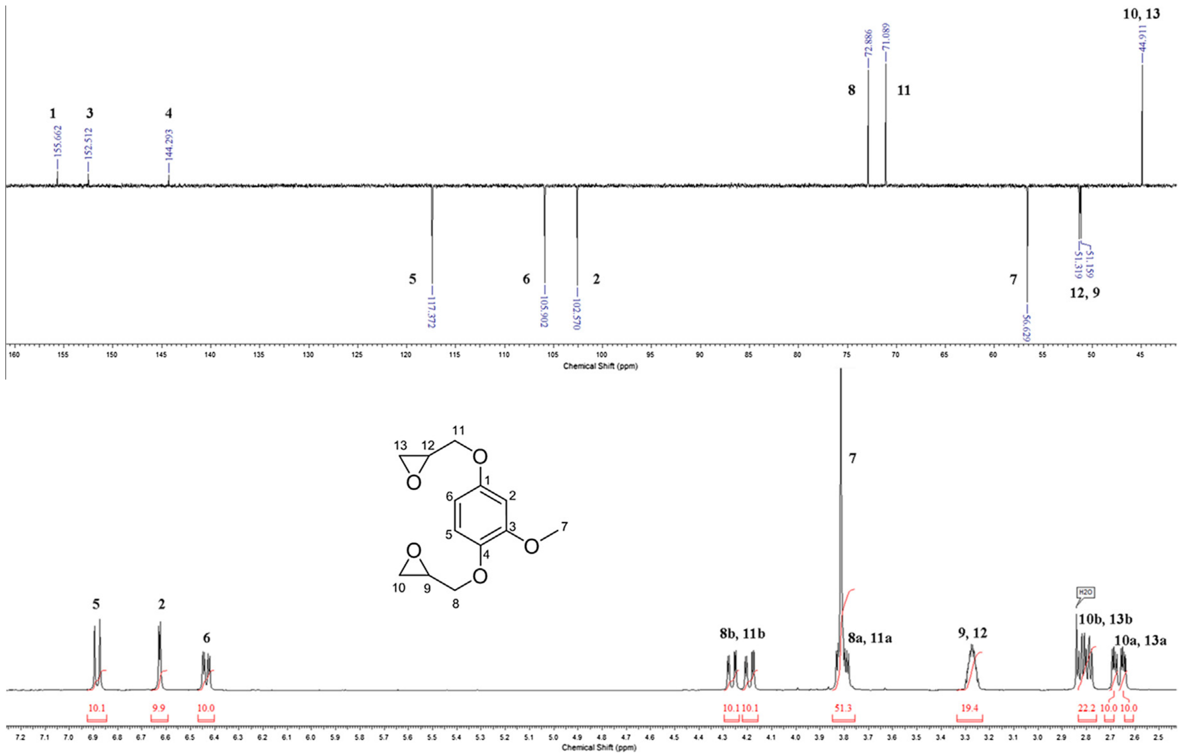


Fig. 2. ^{13}C and ^{1}H NMR characterization of diglycidyl ether of methoxyhydroquinone **3**.

3.2. Oligomerization reaction

Oligomerization of diepoxy monomers could be achieved through two types of processes [27]: the "caustic coupling" (monomer preparation) and "taffy" (low molecular weight oligomers) processes or the "advancement" (with solvent) or "fusion" (without solvent) processes. In both cases, the mechanism is a nucleophilic attack of a phenolate ion onto an oxirane ring leading to its opening as shown in Scheme 2.

In the "taffy" process, oligomers are prepared by a one-step glycidylation reaction between a diphenol and an excess of epichlorohydrin (Scheme 3). The average chain length can be controlled by varying the excess of epichlorohydrin. A large excess is usually employed to prepare either the diglycidyl ether monomer or low molecular weight oligomers.

The "fusion" process consists of a chain extension of a pre-formed diglycidyl ether of a diphenol. The chain length is increased by the (poly)addition reaction of this diphenol. The diglycidyl ether is usually introduced in excess to obtain a diepoxy oligomer (Scheme 4). The extent of reaction and thus the average chain length is controlled by the stoichiometry of the reactants, as in every step-growth polymerization reaction.

The "fusion" process is usually preferred industrially to prepare oligomers. This is due to more simple purification steps. Indeed in the case of the "taffy" process, the removal of the epichlorohydrin excess, of the NaCl formed and of water makes the purification difficult. Also, the "fusion" process offers the possibility to work without solvent and above all, the low chlorine contents of the final products is crucial in some applications. Classic catalysts for this reaction are inorganic bases such as NaOH, KOH or Na_2CO_3. However, they are poorly selective and aryl- or alkyl-phosphonium compounds seem a better alternative already industrially used [27]. We chose to prepare oligomers by this process.

More precisely, we adapted this method for the synthesis of oligomers **4** without any solvent and by using triphenylbutylphosphonium bromide as a catalyst. The optimal experimental conditions were determined by DSC. We first studied the effects of the catalyst amount. DSC thermograms of mixtures of **3** and **2** (1/1) with varying catalyst amounts displayed two peaks on the first heating ramp (10 °C min^{-1}). The first peak was endothermic and was attributed to the melting of the reactants. The second peak was exothermic and was attributed to the oligomerization reaction. On the second heating ramp (10 °C min^{-1}), no exothermic peak was detected, proving that the reaction was complete after the first ramp. However all samples displayed a second order transition, attributed to the glass transition of the oligomers synthesized. A thermogram (1 w.‰ cat.) is available in supplementary information (S01). Fig. 3 shows the variation of the onset and exothermic peak temperatures as a function of the amount of catalyst introduced.

We chose to work in the rest of this study with an amount of catalyst of 5 w.‰. For this catalyst amount, the onset temperature of the reaction is 119 °C. Reactions were performed 6 °C higher, at 125 °C. These parameters were the best compromise between catalyst quantity and reaction temperature. Indeed, doubling the amount of catalyst led only to a minor decrease of the onset and exothermic peak temperatures.

Once these parameters were fixed, the time needed for complete reaction was measured. A mixture of **2**, **3** and 5 w.‰ of catalyst was placed in a sample pan and an isothermal run at 125 °C was performed. The reaction was considered complete when the exothermic peak reached the initial baseline level, after 1 h and 30 min.

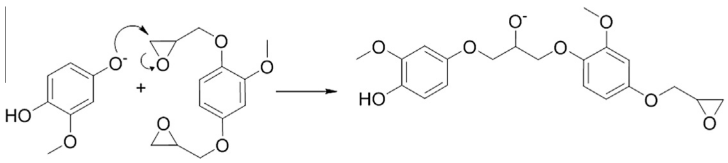
Eight samples of oligomers **4** were prepared using increasing ratios of diepoxy/diphenol (**3**/**2**) from 1.1/1 to 2/1 with the determined conditions (5 w.‰ of catalyst, 125 °C, 1 h 30 min.). Before any analysis, samples were crushed in liquid nitrogen in a mortar and placed in a vacuum desiccator. ^{13}C and ^{1}H NMR spectra of the oligomer prepared with a **3/2** ratio of 1.85/1 is displayed in Fig. 4 as an example.

Oligomers **4** (brown, glassy solids to viscous, see DSC characterization).

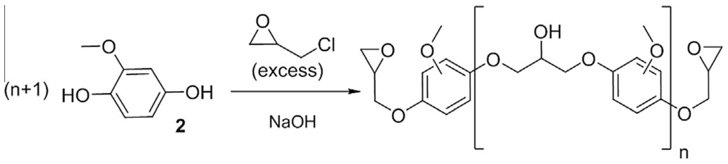
^{1}H NMR (400.1 MHz, DMSO-d6, ppm) δ: 2.67 (m, 2H, H_{10a}, H_{13a}); 2.82 (m, 2H, H_{10b}, H_{13b}); 3.28 (m, 2H, H_9, H_{12}); 3.65–3.80 (m, $2+3(2n+1)$ H, H_{8a}, H_{11a}, H_7, $H_{7'}$); 3.85–4.14 (m, $5(2n)$ H, H_{14}, H_{15}, H_{16}); 4.23 (m, 2H, H_{8b}, H_{11b}); 5.2–6.35 ($3*$d, $2n$ H, H_{17}); 6.43 (m, $(2n+1)$ H, H_6, $H_{6'}$); 6.61 (m, $(2n+1)$ H, H_2, $H_{2'}$); 6.88 (m, $(2n+1)$ H, H_5, $H_{5'}$).

^{13}C NMR (100.6 MHz, DMSO-d6, ppm) δ: 43.66 (s, C_{10}, C_{13}); 49.71–49.83 (s, C_9, C_{12}); 55.54 (m, C_7); 67.64 (m, C_{15}); 69.30–71.30 (m, C_{14}, C_{16}, C_8, C_{11}); 102.57 (m, C_2); 105.90 (m, C_6); 117.37 (m, C_5); 144.29 (m, C_4); 152.51 (m, C_3); 155.66 (m, C_1).

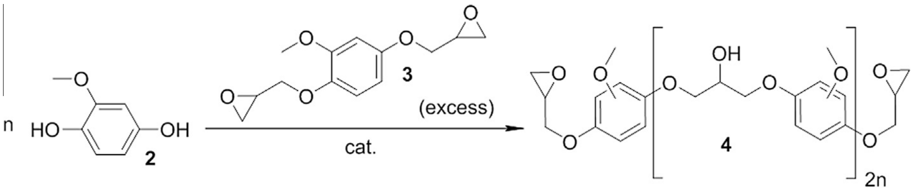
It is worthy to note that compared to the ^{1}H NMR spectrum of pure **3**, signals 14, 15, 16, and 17 have appeared. Signals 14, 15, and 16 were attributed to the glycerol ether repeating unit, which confirmed the oligomerization. Signal 17 was attributed to the proton of the hydroxyl moiety formed upon oxirane ring opening. This attribution was confirmed by the disappearance of this signal upon addition of trifluoroacetic acid.



Scheme 2. Mechanism of the oligomerization reaction.



Scheme 3. Oligomerization by the “taffy” process in the case of methoxyhydroquinone.



Scheme 4. Oligomerization by the “fusion” process in the case of methoxyhydroquinone.

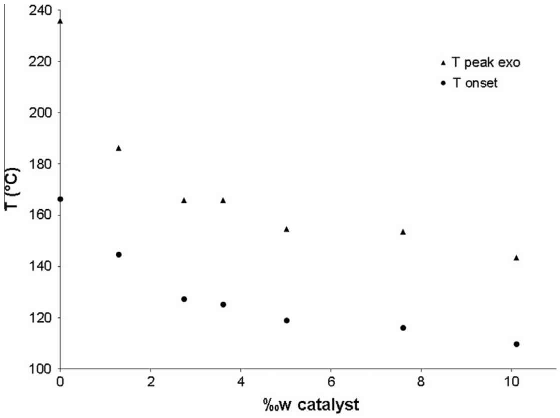


Fig. 3. Onset and exothermic peak temperatures as a function of the amount of catalyst introduced for a 1/1 mixture of **3** and **2**.

3.3. Determination of the degree of polymerization of the oligomers

The number-average value of the degree of polymerization $\bar{X}n$, corresponding to the average number of monomer units in a polymer chain, is given by the modified Carothers' equation [28] (Eq. (1)). In our case of a step-growth polymerization, n diphenol monomers **2** are reacted with an excess of diepoxy monomers **3** (Scheme 4). An oligomer chain will thus contain on average n monomer **2** and $n + 1$ monomer **3**. The average number of monomer units per oligomer chain is thus $\bar{X}n = 2n + 1$ (Eq. (1)). There is $2n$ repeating units plus one diepoxy monomer accounting for the chain-ends (Scheme 4).

$$\bar{X}n = \frac{1+r}{1+r-2rp} = 2n+1 \tag{1}$$

With r the molar ratio of reactants and p the conversion.

We assumed a complete conversion ($p = 1$), as suggested by the return of the exothermic peak to the baseline after 1 h and 30 min. The average number of repeating units was determined experimentally by ^{1}H NMR analysis, by comparing epoxide integrations with aromatic integrations (Fig. 1). Fig. 5 shows the average number of repeating units of oligomers **4** as a function of the **3**/**2** ratio.

As expected, the average number of repeating units increases when the **3**/**2** ratio decreases. Moreover, the numbers measured are coherent with the theoretical ones, obtained by the modified Carothers' equation, confirming the hypothesis of a complete conversion. The only formulation somewhat far from the theoretical value is the one with a 1.1/1 **3**/**2** ratio. This formulation gave the highest chain length, leading to a high viscosity. For such a viscosity, in the experimental conditions (magnetic stirring), agitation might not be optimal, leading to incomplete conversion and thus a number of repeating units lower than expected.

3.4. Determination of the epoxide index of the oligomers

The Epoxide Index EI is defined as the number of moles of epoxide groups per gram of oligomer. In our case, we considered difunctional oligomers and the theoretical EI can thus be expressed as a function of $\overline{Mn}$, the number-average molecular mass, as shown in Eq. (2). As stated above, an oligomer chain is constituted on average of $2n$ repeating units plus one diepoxy monomer accounting for the chain-ends (Scheme 4). $\overline{Mn}$ can thus be replaced in Eq. (2):

$$\mathrm{EI} = \frac{2}{\overline{Mn}} = \frac{2}{252 + 196(2n)} \tag{2}$$

The EI was measured by ^{1}H NMR using an internal standard, the 1,3,5-trioxane. Indeed, its signal is a singlet at 5.12 ppm in DMSO-d6, dissociated from the other signals. Known masses of trioxane and of oligomer were introduced and the EI was calculated from the integration values of epoxide and trioxane protons (Fig. 1). Fig. 6 shows the epoxide index of the oligomers **4** as a function of the average number of repeating units.

The EI measured are in agreement with the theory. The small differences could be explained by the possible side reaction on **3** of hydroxyls formed upon epoxy ring-

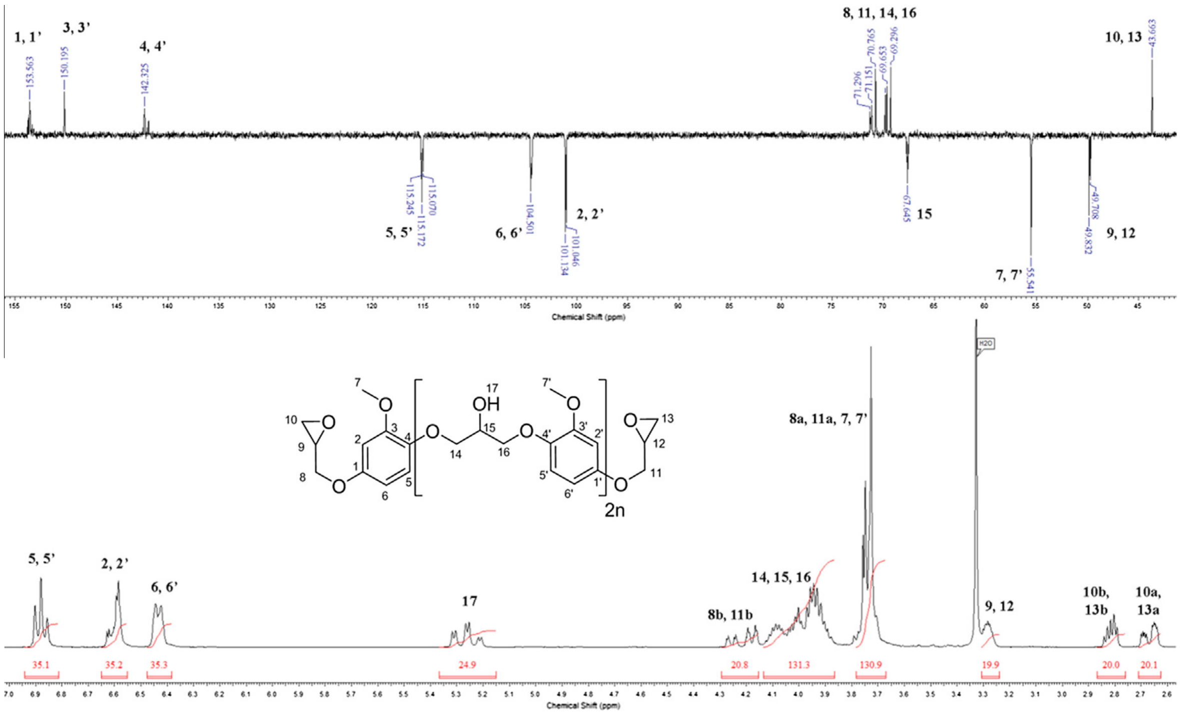


Fig. 4. Oligomers **4** of diglycidyl ether of methoxyhydroquinone.

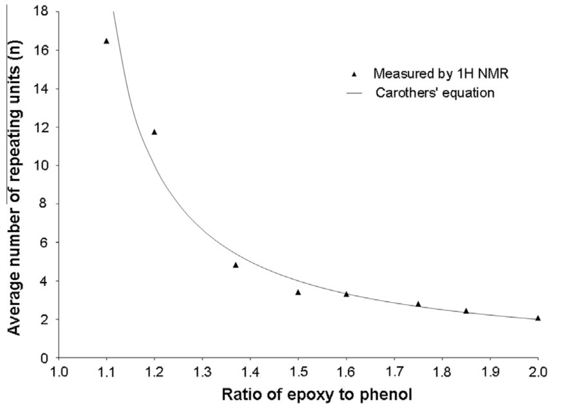


Fig. 5. Experimental and calculated degree of polymerization of oligomers as a function of the reactants ratio.

opening (Scheme 5). Indeed, this addition of an epoxide group would increase the EI.

This method for the determination of the epoxide index proved to be precise, reliable, easy to implement and safe compared to the more classical pH titration techniques in HCl/pyridine mixtures for instance.

3.5. Determination of the T_g of the oligomers by DSC

The oligomers were characterized by DSC. All samples displayed a second order transition, attributed to the glass transition temperature (T_g). Results are summarized in Fig. 7. The T_g values were consistent with qualitative observations: the oligomers with the highest average number of repeating units were solid and those with the smallest were viscous at room temperature.

As expected, the T_g increases with the chain length up to a plateau at around 55 °C. This trend is in agreement with the Flory–Fox equation [29] indicating that the T_g depends on $\overline{Mn}$ as described by Eq. (3).

$$T_g = T_g(\infty) - \frac{K}{\overline{Mn}} \tag{3}$$

With $T_g(\infty)$ the value of T_g when $\overline{Mn}$ tends to infinity and K is a constant dependent on the polymer studied. Replacing Eq. (2) in Eq. (3) gives Eq. (4):

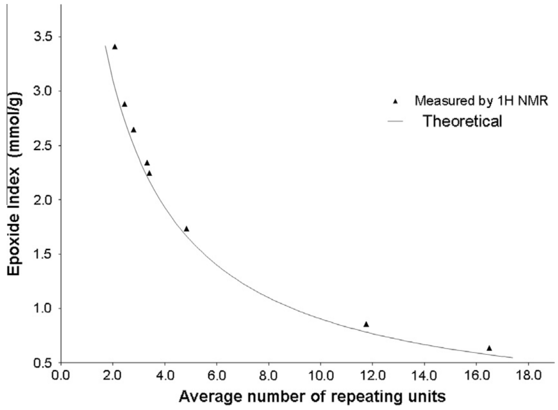
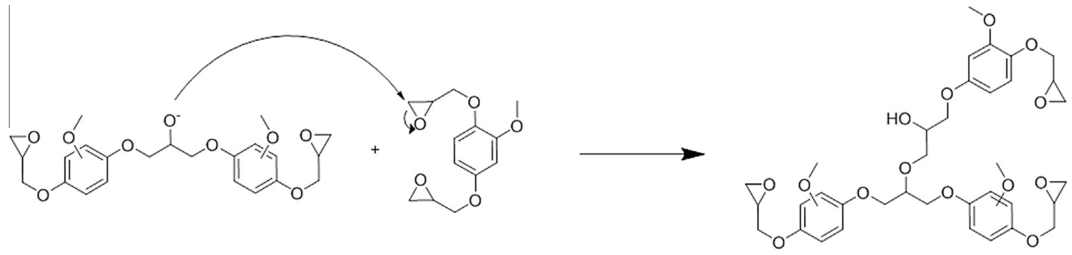


Fig. 6. Epoxide index as a function of the average number of repeating units of the oligomers.



Scheme 5. Possible side reaction of an alcoholate on **3**.

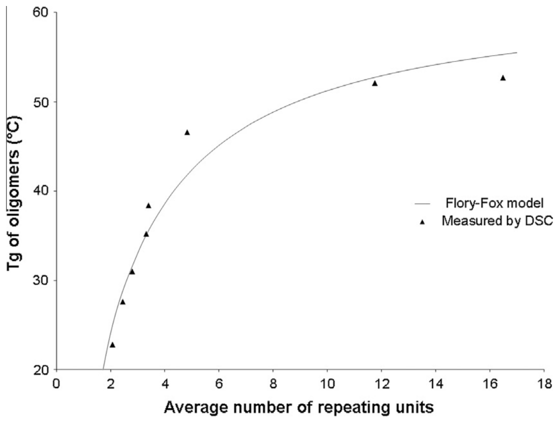


Fig. 7. T_g of the oligomers **4** as a function of the average number of repeating units.

$$T_g = T_g(\infty) - \frac{K}{252 + 196(2n)} \tag{4}$$

The values of $T_g(\infty)$ and K are accessible from the linear regression of $T_g = f(x)$ with $x = 1/(252 + 196(2n))$ and $2n$ the experimental values of the average number of repeating units. In our case, $T_g(\infty) = 62$ °C and $K = 24{,}656$ °C mol g^{-1}. This leads to Eq. (5). One can also calculate $T_g(0)$ corresponding to the theoretical T_g of an oligomer with 0 repeating units, i.e. of only the chain ends (see Scheme 4). In our case $T_g(0) = -35$ °C.

$$T_g = 62 - \frac{24{,}656}{252 + 196(2n)} \tag{5}$$

As shown in Fig. 7, experimental values fit with the Flory–Fox equation. Eq. (5) allows the prediction of the T_g of an oligomer for a given average number of repeating units in our system. As shown above, the number of repeating units can be controlled by the ratio of the reactants. The T_g of the oligomers prepared can thus be controlled and predicted from the diepoxy/diphenol ratio. The T_g values agreed with visual observations: long oligomers are solid and small ones are viscous at room temperature.

From the experimental T_g values of DiGlycidyl Ether of Bisphenol A oligomers found in the literature [30], we applied the same extrapolation than the one previously described and values from $T_g(\infty)$ and $T_g(0)$ were calculated as summed up by Table 1.

The $T_g(\infty)$ value for DGEBA-based oligomers is higher than for oligomers **4**. When $\overline{Mn}$ tends to infinity, the predominant structural effect comes from repeating units. A higher $T_g(\infty)$ means that the repeating unit from the DGEBA-based oligomer is stiffer than the one from **4**. This can be explained by the presence of two aromatic rings separated by only one carbon in the case of the DGEBA-based oligomer instead of only one aromatic ring in the case of the repeating unit of oligomers **4**.

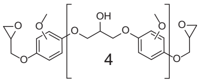
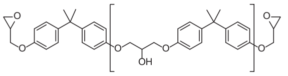
The experimental values of the T_g of the monomers were measured by DSC, on the second heating ramp of either **3** or pure DGEBA (no oligomerization). They are both negative, which is expected in the case of the T_g of molecules. They are also close to $T_g(0)$ values and follow the same trend, i.e. a slightly higher T_g for DGEBA than for **3**. The same structural considerations as the one previously mentioned can explain this result.

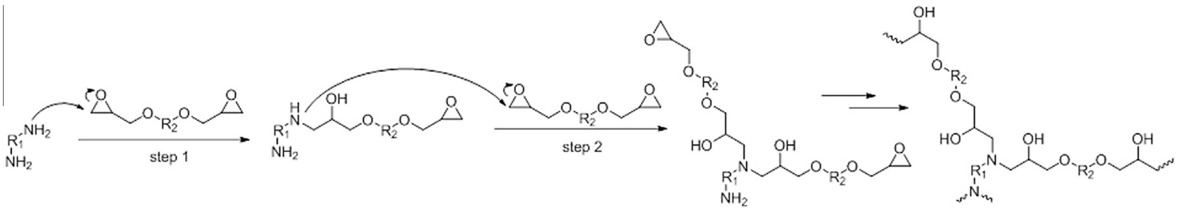
3.6. Synthesis of epoxy materials: polymerization of oligomers with IPDA

Amines are common hardeners for epoxy resins and can react in a two-step fashion to form a cross-linked polymer as shown in Scheme 6.

The difunctional epoxy oligomers prepared were reacted in liquid state (130 °C) with the commercial IsoPhoroneDiAmine (IPDA), as it is a common industrial amine hardener. In a previous paper [26], our team proved that the optimal T_g of a **3**-based material crosslinked with IPDA is attained for an epoxy/amine ratio of 2/1. We used this ratio in our formulations. The minimal temperature to obtain free-flowing liquid oligomers increased with the chain length. A temperature of 130 °C ensured the

Table 1
$T_g(\infty)$ and $T_g(0)$ of the vanillin-based and bisphenol A-based oligomers extrapolated from experimental values and T_g of their monomers.

	$T_g(\infty)$ (°C)	$T_g(0)$ (°C)	T_g of the monomer (°C)
 Oligomers **4**	62	−35	−26
 DGEBA-based oligomers	83	−30	−17



Scheme 6. Synthesis of cross-linked materials by epoxy/amine reaction.

obtention of low viscosity oligomers for an average number of repeating units ⩽5, which was necessary to obtain homogeneous materials. However, the two samples with longer chains were too viscous to obtain a homogeneous mixture with IPDA, even at 130 °C. The materials were post-cured at 150 °C to ensure complete reaction.

3.7. T_g and T_α of the epoxy materials

Fig. 8 shows the T_g and T_α of the materials from oligomer **4** cross-linked with IPDA as a function of the average number of repeating units. DSC and DMA thermograms are available in supplementary information S02 and S03.

The longer the oligomer used, the lower the T_g and T_α of the crosslinked epoxy polymer. This decrease seems to be linear, however the range of chain length studied is not broad enough to be able to extrapolate these results.

The decrease of T_g and T_α with increasing length can be explained by an increase of the distance between two crosslinking points when the oligomer gets longer. This leads to a decrease in the overall crosslink density of the material (number of crosslinking points per volume unit) and thus to a decrease in the transition temperatures.

The magnitude of this decrease is however low. This peculiarity was attributed to the variation of composition of the network. Indeed, the ratio of aromatic cycles from oligomers versus non-aromatic cycles from IPDA increased with the size of the oligomers used. Aromatic cycles are rigid, stable moieties that tend to increase the T_g and T_α of polymers. The introduction of a higher ratio of aromatic cycles versus non-aromatic cycles would thus partly compensate the decrease of crosslink density. These two effects resulted in the trend observed.

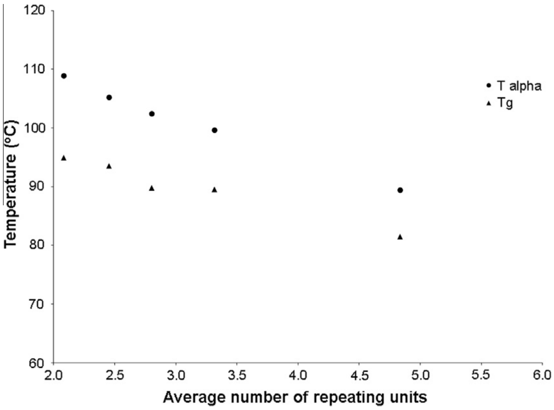


Fig. 8. T_g and T_α of the materials prepared from oligomers **4** as a function of their average number of repeating units.

By using vanillin-based oligomers of varying lengths, the properties of the final biobased thermoset can be controlled, which is the same strategy than the one currently used in industry with petro-based products.

4. Conclusion

In this contribution, novel vanillin-based oligomers and polymers were prepared and their thermal properties investigated. In precedent contributions, our team used vanillin as a biobased aromatic building-block to prepare diepoxy monomers, like the diglycidyl ether of methoxyhydroquinone, and studied their polymerization. However, industrial epoxy resins are usually oligomeric for a better processability or control of the properties. In this study, this established industrial strategy was applied to the vanillin-based diepoxy monomer previously described.

Diglycidyl ether of methoxyhydroquinone was oligomerized by reaction with methoxyhydroquinone. The oligomerization reaction was optimized in terms of catalyst amount and reaction time. Formulations with varying ratios of reactants were prepared and it was found that the length of the oligomers obtained could be predicted from Carothers' equation for step-growth polymerization. A ^{1}H NMR titration method was successfully developed to determine their epoxide index. The thermal properties of these oligomers were also investigated and their T_g increased with their molecular weight to a plateau, following the Flory–Fox model. These oligomers were crosslinked with IPDA, an industrial amine hardener and the thermo-mechanical properties of the materials obtained were measured. The T_g and T_α attained by these novel biobased epoxy thermosets were all comprised between 80 °C and 110 °C. These values are high compared to the majority of the biobased thermosets found in the literature. It was also found that thermo-mechanical properties could be tuned by varying the length of the starting oligomer. This is a common strategy for current petro-based epoxy thermosets and it was applied with success to biobased oligomers.

In future works, further mechanical properties of these biobased thermosets should be tested, such as tensile strength, and polymers other than epoxy thermosets should be prepared from vanillin. Vanillin has the potential to replace oil-derived aromatic monomers in many polymers; this potential should be further investigated.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2015.03.048.

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