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ARTICLE

Epoxy thermosets from model mixtures of the lignin-to-vanillin process

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Epoxy thermosets were prepared from mixtures of phenolics modelling the product stream of the lignin-to-vanillin process. Vanillin is one of the only mono-aromatic compound produced on an industrial scale from lignin. This process leads to mixtures of phenolic compounds. Isolation of pure vanillin is costly both economically and environmentally. The present work demonstrates that these purification steps are not necessary in order to prepare high-performance epoxy thermosets from biomass. Model mixtures of depolymerization products of lignins from both softwood and hardwood were prepared. These mixtures were subjected in a first step to a Dakin oxidation in order to increase their phenolic functionality. In a second step, they were glycidylated to obtain mixtures of epoxy monomers. Each of the component of the mixtures was individually subjected to the same reactions to provide further insights on their reactivity. Epoxy thermosets were conveniently prepared from these epoxy monomers mixtures. These potentially bio-based epoxy thermosets displayed outstanding thermo-mechanical properties while avoiding environmentally damaging purification steps. Thus, their production could advantageously be integrated in a biorefinery as high added-value product from lignin processing.

Introduction

Using resources from biomass as raw materials for chemical production instead of crude oil is a more sustainable approach and thus a challenge we have to face right now. The polymer industry is a very large end-user of chemicals, and thus using renewable resources to prepare polymers is a burning issue. Recent years have seen a rising awareness of the polymer community on this topic.¹ This is especially relevant for thermosetting polymers² as they are cross-linked and thus cannot be recycled. However, thermosets are irreplaceable in industry because of their good thermo-mechanical properties. Their cross-linked nature is not the sole reason of these high performances. In many cases, it is also because they are based on aromatic monomers, which bring stability and rigidity. Epoxy polymers is one of the most used class of thermosets in many applications (coatings, adhesives, composites etc.) for their excellent adhesion properties, chemical and heat resistance, and good mechanical properties among others. Therefore, epoxy polymers from renewable resources are currently a hot topic.^{3,4} A monomer intended for the substitution of petro-based epoxy polymers must thus be: 1) Derived from renewable resources; 2) Aromatic to keep the level of performance; 3) Based on a feedstock available at an industrial scale.

Lignin is a phenolic macromolecule that accounts for

roughly 15–30% of the dry weight of ligno-cellulosic biomass.⁵ It is thus the second most abundant biopolymer and the biggest natural source of aromatics⁶. Lignin is a random, three-dimensional network composed of three types of phenylpropanoid units⁷: p-hydroxyphenyl (H) unit, guaiacyl (G) unit, and syringyl (S) unit. These units originate from the three monolignols depicted in Figure 1A:

Insert Figure 1, single column

As explained in the literature⁸, lignins from softwood (pines, spruces, fir, etc.) are mainly composed of G units and of a small proportion of H units and are thus called G lignins. Lignins from hardwood (birch, eucalyptus, beech, poplar, etc.) contain both S and G units, with a very small proportion of H units, and are called GS lignins. Lignins from some crop plants or palm trees, comprise all three units, although with the predominance of H type, and are called HGS lignins. These units are variously linked together and the β -O-4 linkages (Figure 1B) are the most frequent, with around 50% of the linkages.⁸

Lignin in itself is a fascinating renewable polymer that is envisaged or used in multiple applications.⁹ However its use is also limited by some issues. Its chemical structure is very variable and depends on many parameters (type of plant or wood, extraction process, etc.).¹⁰ Its structure is also complex due to the many different types of chemical linkages,^{10, 11} which makes precise characterization and reaction mechanism understanding challenging.⁷ Finally, this biopolymer is also difficult to process. To overcome these limitations, lignin

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depolymerization to produce biobased aromatics seems to be a promising approach. However, even if under intense investigation, this approach is not a mature technology yet.¹¹

One of the only aromatics produced from lignin on an industrial scale is vanillin.^{12, 13} Vanillin is one of the most important commercial flavors and 85% of the vanillin is derived from petroleum, mainly from guaiacol as a raw material. The dominant process is depicted in Scheme 1.¹⁴

Insert Scheme 1, single column

However, vanillin-from-lignin processes are also in use, accounting for 15% of the overall production.¹⁵ Borregaard, the second largest producer worldwide, operates a plant based on this technology. Recently, a resurgence of interest for vanillin-from-lignin routes undeniably took place.⁸ The only lignin-based process industrially implemented for vanillin production is the alkaline oxidation of lignosulphonates.¹⁶ An aqueous solution of lignin is treated with oxidants, at alkaline pH, and high temperatures and pressures. The dominant reaction is the cleavage of β -O-4 bonds. The parameters influencing this process are numerous: nature of the oxidant, catalysts, lignin type, temperature, pressure, pH, etc. Extensive details concerning these conditions can be found in literature, from early patents¹⁷⁻²² to more recent works.^{8, 14-16, 23-29} The cleavage of a guaiacyl unit (G, Figure 1) leads to the vanillate ion, which gives vanillin **1** after protonation. As mentioned earlier, G units are predominant in lignins from softwoods (G lignins). However, in the case of lignins from hardwoods (GS lignins), syringyl units (S, Figure 1) are also present and their cleavage leads to the formation of syringaldehyde **2** along with vanillin **1**.⁸ Depending on the species, various amounts of p-hydroxyphenyl units (H, Figure 1) can also be found in the lignin, which leads to p-hydroxybenzaldehyde **3**. These aldehyde products are submitted to a harsh oxidative and alkaline environment. Their oxidation to the corresponding vanillic acid **4** and syringic acid **5** is an unavoidable side-reaction of the process. Other important by-products are acetovanillone **6** from G units and acetosyringone **7** from S units. The formation of **6** was explained by Tarabanko et al.³⁰

Insert Table 1, single column References³¹⁻³⁶ relate to Table 1

The oxidative depolymerization of lignin gives a complex mixture of products. Those depicted in Table 1 are the major low molecular weight ones. Typical yields of these products for G and GS lignins are also summarized in Table 1. The reaction mixture also contains high molecular weight lignin fragments. The processes employed for the downstream treatment are not the primary focus of this study and more details are available in the literature.^{8, 14, 15, 37, 38} One must note, however, that vanillin isolation and purification are difficult to achieve due to the similar structures of the other phenolics obtained. The bisulfitation method is one of the most selective processes. Briefly it consists of mixing the crude vanillin solution with a solution of NaHSO₃ (sodium hydrogen sulfite,

or sodium bisulfite) to prepare a “vanillin bisulfite complex”^{8, 39}, i.e. sodium vanillyl- α -hydroxysulfonate as depicted in Scheme 2.

Insert Scheme 2, single column

The hydrosulfite anion reacts selectively with the aldehyde moiety. The derivatives produced have a good solubility in water, as opposed to the starting aldehydes and to the other products from the crude mixture.¹⁷ The aqueous phase must be further acidified to recover aldehydes and SO₂.¹⁷ Apart from the technical difficulties of this method, the major drawbacks of the bisulfitation are the use of a large amount of acidic solution and the loss of vanillin during precipitation of high molecular weight compounds⁸, drawbacks that are costly both economically and environmentally.

Also, this method is selective towards aldehydes, which means that p-hydroxybenzaldehyde and syringaldehyde⁴⁰ are extracted along with vanillin. This is especially relevant in the case of GS and HGS lignins as these compounds are major products of the depolymerization reaction. Vanillin is difficult to isolate from these compounds, as pointed out by numerous works.^{8, 29-31, 37} This leads to further purification steps, impacting even more the environmental and economic efficiency of the whole process⁸

Despite these difficulties, vanillin is one of the only mono-aromatic compounds readily available from biomass. Precedent works demonstrated the potential of the use of vanillin to prepare renewable polymers,^{13, 41} especially epoxy thermosets.⁴²⁻⁴⁴ Why not use the unrefined mixture of phenolics available from lignin-to-vanillin processes (Table 1) to prepare epoxy polymers?

By-passing the difficult purification steps would hold many advantages - both economic and environmental - such as reduced use of acids and solvents, reduced energy consumption, increased productivity, etc. Moreover, more biomass would be transformed into commercializable products instead of being burned for energy. Also, instead of using only G lignins from softwoods to maximize the yield in vanillin, lignins from all woods would be a potential feedstock. Working on mixtures instead of pure compounds to prepare polymers would also allow a drastic production cost – and thus selling price – decrease.

The intention of this work is to prove that such a strategy is viable by using model mixtures of phenolics as starting materials and, from these mixtures, prepare and characterize epoxy polymers. Mixtures of phenolics modelling the products obtained from G and GS lignins alkaline oxidative depolymerization were thus prepared after a careful review of the literature, as presented in Table 1. These mixtures are referred to as “model mixtures of G- (or GS-) type phenolics” throughout the rest of this work. In a first step, they were subjected to a green Dakin oxidation⁴³ in order to increase their phenolic functionality. The second step was the glycidylation of the various phenolics present in the mixtures to prepare epoxy monomers. Each product of each step of the reaction was individually prepared and characterized by ¹H

NMR to elucidate the composition of the mixtures at each step. The epoxy mixtures prepared were hardened with a common industrial amine hardener, isophorone diamine. The properties of the potentially biobased epoxy thermosets obtained were investigated to demonstrate the potential of this approach.

Results and discussion

Dakin oxidation of individual compounds

The general strategy of this study is to prepare two mixtures of phenolics modelling the products obtained from the depolymerization of, on the one hand, G lignins from softwoods, and, on the other hand, GS lignins from hardwoods. These starting mixtures comprise phenolic aldehydes, acids, and ketones (Table 1). Phenolic acids can give diepoxy monomers but not aldehydes and ketones. Thus, these compounds were subjected in a first step to a Dakin oxidation, which is an oxidative decarboxylation leading to diphenolic compounds in this case.

The reaction proceeds via the mechanism shown in Scheme 3:

Insert Scheme 3, single column

Sodium percarbonate dissociates in solution into carbonate anions and H_2O_2 , which in turn can form a hydroperoxide anion. The reaction starts with a nucleophilic addition of this hydroperoxide anion to the carbonyl. The aromatic ring undergoes a [1,2]-aryl migration, which liberates a hydroxide anion. This hydroxide attacks the intermediate phenyl ester formed, cleaving the ester bond and liberating formic acid in the case of aldehydes and acetic acid in the case of ketones.

The protocol used⁴⁵ is very efficient and the handling simple. Moreover, the oxidation reagent used, sodium percarbonate, has major advantages: it is inexpensive, large-scale available as it is extensively used in the detergent industry as a bleaching agent, easier to handle than a classic H_2O_2 solution and, finally, respects sustainable development principles due to its safety and environmental innocuity.

Each carbonyl-containing component of the starting mixtures was first individually reacted in order to understand their reactivity and to determine the mixtures composition after this first step. The results are summarized in Table 2. Hydroquinone **8** was obtained from p-hydroxybenzaldehyde **3**. Methoxyhydroquinone **9** was obtained from vanillin **1** and acetovanillone **6**. 3,5-Dimethoxyhydroquinone **10** as well as the by-product 3,5-dimethoxyquinone **11** were obtained from syringaldehyde **2** and acetosyringone **7**. The presence of **11** was attributed to the tendency of **10** to auto-oxidize.⁴⁶ The chemical shifts of this by-product were consistent with the literature.⁴⁷

Insert Table 2, single column

It is worthy to note that the oxidation of ketones gave lower yields than aldehydes, most likely due to a slower reaction rate induced by steric hindrance.⁴⁸

Dakin oxidation of the mixtures

The starting mixtures (Figure 2) were prepared based on depolymerization yields determined from the literature survey presented in Table 1. Vanillin accounts for 72.6% of the total amount of G-type phenolics. Compared to the hypothetical use of vanillin alone, the use of the whole mixture represents an improvement of 138% of the amount of substance actually used. In the case of GS-type phenolics, the improvement is even higher (193%). The resulting mixtures compositions after the first step of Dakin oxidation were determined by ^1H NMR analysis, using the characteristic signals of each product that were found from the individual reactions. These compositions are also summarized in Figure 2:

Insert Figure 2, double column, color

Dakin oxidation of the mixture of G-type phenolics

Concerning the model mixture of G-type phenolics, all products **8**, **9**, **10**, and **11** individually prepared (Table 2) were identified in the resulting oxidized mixture. There were no residual aldehyde signals from **1**, **2**, and **3**. The vanillic acid **4** content was unchanged compared to the starting mixture, indicating that it did not react in these conditions. The proportions of products **10** and **11**, arising from syringaldehyde **2**, were different from what was observed in the individual reaction. Indeed, **2** alone gave 90% of **10** and 5% of **11** (and 5% of unreacted **2**). In the mixture, however, **2** gave 74% of **10** and 26% of **11**. This difference was attributed to the tendency of **10** to oxidize easily and even auto-oxidize⁴⁶ to **11**. A difference in the conversion of **6** between the reaction of the compound alone and in the mixture can also be observed. In the case of the individual reaction, the conversion of **6** to **9** was 69%, whereas in the case of the mixture it was only 8%. This difference was attributed to the fact that ketones are less reactive than aldehydes towards the Dakin oxidation.⁴⁸ In the mixture, the aldehyde compounds would thus react first, lowering the H_2O_2 concentration to low levels. This concentration drop would affect the reaction rate of acetovanillone **6**, giving lower conversions than in the individual reaction. Besides, the rate of oxidation of **10** to **11** might also be higher than the oxidation rate of **6**. H_2O_2 would be consumed by **10** instead of **6**, leading to a higher proportion of **11** and a lower conversion of **6** than in individual reactions, which is what is observed experimentally. As all the products and their proportions were identified, a mean molecular mass of the model mixture of G-type phenolics ($\bar{M}(\text{G1})$) could be calculated and was found to be 144.7 g.mol^{-1} . The isolated molar yield of this reaction was found to be 99%. The mean hydroxyl functionality (phenol + acid moieties, $\bar{f}(\text{G1})$) of this mixture was found to be 1.87. $\bar{f}(\text{G1})$ is lower than 2 because of the formation of **11** ($f = 0$) and of the low conversion of **6**.

Dakin oxidation of the mixture of GS-type phenolics

Concerning the model mixture of GS-type phenolics, all products **8**, **9**, **10**, and **11** individually prepared (Table 2) were also identified in the resulting oxidized mixture. However, in this case, residual aldehyde signals from **1**, **2**, and **3** were detected. Contrary to the previous mixture, the conversion of aldehyde compounds was not total. The content of carboxylic acids **4** and **5** was unchanged, which was consistent with the previous mixture and confirmed their non-reactivity towards Dakin oxidation. The proportions of products **10** and **11**, arising from syringaldehyde **2**, were 89% of **10** and 10% of **11** (and 1% of unreacted **2**). Once again, the amount of **11** formed is higher than in the individual reaction (5%), which was attributed to the auto-oxidation of **10**. Ketone products **6** and **7** did not undergo the Dakin oxidation in the mixture, even though they were converted respectively to **9** and **10** with 91% and 69% conversion in the case of individual reactions. This is consistent with the model mixture of G-type phenolics, in which the conversion of the ketone **6** was also very low, and was attributed to the same phenomenon, *i.e.* a lower reactivity of ketones than aldehydes towards the Dakin oxidation. The mean molecular mass of the model mixture of GS-type phenolics ($\bar{M}(\text{GS1})$) was found to be 165.1 g.mol⁻¹ and the isolated molar yield of this reaction was 94%. The mean hydroxyl functionality of this mixture ($\bar{f}(\text{GS1})$) was found to be 1.75. $\bar{f}(\text{GS1})$ is lower than $\bar{f}(\text{G1})$ because unreacted aldehyde and ketone compounds ($f = 1$), as well as compound **11** ($f = 0$), account for a more important part of the resulting mixture.

Glycidylation of individual compounds

As in the case of the previously described Dakin oxidation, all compounds taking part to the glycidylation reaction were first individually reacted and the products characterized by ¹H NMR analysis. The general procedure for the glycidylation was the same in each case.

Aouf et al. proved that aromatic hydroxyl and acid functions readily react with epichlorohydrin in the absence of a solvent.⁴⁹ We adapted this method for the synthesis of compounds **12** to **21** (Table 3). The reaction mechanism is depicted below in Scheme 4:

Insert Scheme 4, single column

In a first step, a phase transfer catalyst (triethylbenzylammonium chloride – TEBAC) is used to allow the phenolate ion to exist in organic solution. In a second step, this phenolate ion reacts with epichlorohydrin via two possible mechanisms, namely S_N2 and ring opening. S_N2 gives the expected glycidylated product and ring opening leads to a chlorinated intermediate. In a third step, this chlorinated intermediate is closed by an intramolecular S_N2 reaction in the presence of an aqueous solution of NaOH. These reactions do not require organic solvents since epichlorohydrin is used as a reactive solvent. Also, epichlorohydrin is an industrially-produced biobased compound via the Epicerol® process from Solvay.

Overall, all phenolics were readily converted to (di)epoxide products (Table 3). It is worthy to note, however, that products **15** and **16** from aromatic acids were obtained in slightly lower conversions. This might be due to the fact that aromatic acid moieties are less nucleophilic than phenolic moieties, and thus less reactive towards the glycidylation reaction. The phenolic moieties of the syringyl series (products **14**, **16**, **18**, **21**) were somewhat harder to functionalize. This was attributed to the steric hindrance of the two adjacent methoxy groups. 4% of **11** were detected, as well as 14% of the side-product **22** and 2% of another unidentified side-product **A**. As mentioned, compound **10** has a tendency to auto-oxidation to give **11**. The expected products from **10** during this glycidylation step are thus **21** and **11**. After the glycidylation step of **10**, the remaining amount of **11** was low but the amount of **22** was quite high. Thus **22** was hypothesized to evolve from the reaction of **11** with epichlorohydrin. In order to confirm this hypothesis, pure **11** was also subjected individually to the glycidylation step and did indeed afford **22** in a 93% yield.

Insert Table 3, double column**Glycidylation of the mixtures**

After characterizing each individual glycidylation product, the mixtures obtained from the Dakin oxidation reactions were subjected to the same glycidylation step. The resulting mixtures compositions after this second step were determined by ¹H NMR analysis, using the characteristic signals of each product that were found from the individual reactions. These compositions are summarized in Figure 3.

Insert Figure 3, double column, color**Glycidylation of the mixture of G-type phenolics**

Concerning the model mixture of G-type phenolics, compounds **4**, **6**, **8**, and **9** were fully converted to their glycidylation products **15**, **17**, **19**, and **20** respectively. Compound **10** was converted to **21**, however, as in the case of the individual reaction, this conversion was only partial. The side-product **22**, detected in the individual reaction, was also present in the resulting mixture. The signals of compound **11**, which were present in the mixture after the first oxidation step, disappeared. This confirmed that, as first shown in an individual reaction, **22** comes from **11**. All the products and their proportions were identified, apart from **A**, which ¹H NMR signal was very low. A mean molecular mass of the glycidylated mixture of G-type phenolics ($\bar{M}(\text{G2})$) could thus be estimated, without taking into account **A**, and was found to be 248.9 g.mol⁻¹. The isolated molar yield of this step was 93% and the mean epoxy functionality of this mixture, $\bar{f}(\text{G2})$, was found to be 1.87. As in the case of $\bar{f}(\text{G1})$, $\bar{f}(\text{G2})$ is lower than 2 because of the presence of **17** ($f = 1$).

Glycidylation of the mixture of GS-type phenolics

Concerning the model mixture of GS-type phenolics, the same results as previously were observed. Indeed, compounds **1** to **9** were fully converted to their glycidylation products, *i.e.* products **12** to **20**. It is worthy to note that this glycidylation method was effective for both aromatic acids and phenolic functions and was not impacted by the type of substituent. Indeed, all phenolic acids, ketones, aldehydes and diphenolic compounds were readily converted. The only exception was compound **10**, which was also the major constituent of this mixture. As previously, compound **10** was only partially converted to **21**. As in the case of the individual reaction of **10**, the side-products **22** and **A** were detected. They were present in fairly large amounts. However, contrary to the individual reaction, the product **11** was not present. A possible explanation for these results would be that **10** is simultaneously converted to **21** and **11**. **11** itself is then quite rapidly converted to **22** and **A**, which would explain its disappearance. A significant amount of the unidentified side-product **A** was present in the mixture (estimated to 10.3%, see Figure 3), which impacts the calculation of a mean molecular mass. Nevertheless, the mean molecular mass ($\overline{M}(\text{GS2})$) was estimated without taking into account **A**, and was found to be 263.2 g.mol⁻¹. In the individual reaction, no epoxy signal was detected for **A**, which means that the epoxy functionality of **A**, $f(\text{A}) = 0$. The mean epoxy functionality of the mixture of GS phenolics $\overline{f}(\text{GS2})$, was thus calculated and found to be 1.45. $\overline{f}(\text{GS2})$ is lower than 2 because of the presence of **17** ($f = 1$), and **22** and **A** ($f = 0$).

¹H NMR epoxy titration

In order to formulate epoxy thermosets with optimal properties, the Epoxide Index (EI, number of moles of epoxide groups per gram, eq.g⁻¹) must be known. This value can be calculated from the mean functionality of the mixtures. However, it was only estimated in the case of the mixture of G-type phenolics and could not be determined for the mixture of GS-type phenolics. In a previous paper⁴⁴, our team reported the successful use of a ¹H NMR titration method for the determination of the EI. This method was employed in this work in order to determine the EI of the mixtures of G-type (EI(G)) and GS-type (EI(GS)) phenolics. The titration involved the dissolution of a known mass of the mixture and of an internal standard (1,3,5-trimethoxybenzene, TMB) in acetone-d₆. The ¹H NMR signal from the 3 equivalent aromatic H of the TMB did not overlap with any of the signals of the mixtures. The number of moles of epoxide groups per gram of mixture could thus be determined by comparing the integrations of the standard (3 aromatic H) with the integration of a signal accounting for all the oxirane rings. This signal was the sum of the characteristic multiplets formed by the -CH- of the different oxirane rings. It was situated between 3.15 and 3.40 ppm, depending on the components of the mixture. Results are summarized in Table 4.

The Epoxide Equivalent Weight (EEW) is a value commonly used in industry and represents the mass of mixture accounting for 1 mole of epoxide groups. It is linked to the EI,

mean molecular mass $\overline{M}$ and mean functionality $\overline{f}$ as shown in Equation 1:

$$EEW = \frac{1}{EI} = \frac{\overline{M}}{\overline{f}}$$

In both cases of G-type and GS-type phenolics the estimations made from the mixture compositions were consistent with the EEW measures by NMR titration, as shown in Table 4.

Insert Table 4, single column

EEW(GS) is higher than EEW(G) because of the lower mean functionality of the epoxy monomers mixture. Indeed, there are more mono-functional glycidylation products in the mixture from GS-type phenolics than in the mixture from G-type phenolics as shown in Figure 3.

Epoxy thermosets preparation

Epoxy thermosets were then prepared from the glycidylated mixtures. The epoxy monomers constituting the mixtures were cross-linked with a diamine. The amine hardener used was isophorone diamine (IPDA), a cycloaliphatic hardener commonly used in industry. The general reaction of epoxy curing by amine hardeners proceeds as shown in Scheme 5:

Insert Scheme 5, single column

As it can be seen, each of the two active H of an amine function can react with an epoxy group. IPDA being a diamine, it can potentially react with 4 epoxy groups. The mixtures were formulated accordingly, based on the number of epoxy groups per gram of mixture (IE) determined by titration. The glycidylated mixture of G-type phenolics was pasty and partially crystallized. The glycidylated mixture of GS-type phenolics was a highly viscous liquid, uncrystallized. In order to obtain free-flowing liquids, the epoxy mixtures were pre-heated at 70°C for 15 minutes. They were then weighed accurately and the appropriate amount of IPDA was added. The mixtures were thoroughly hand-stirred and did not display any problems of miscibility. After curing (110°C, 1 hour), brown, homogeneous glassy materials were obtained. A post-cure (150°C, 1 hour) was performed in order to ensure complete reaction of all epoxy and amine functions. The synthesis of homogeneous epoxy polymers confirms the validity of preparing epoxy polymers starting from phenolic products of lignin depolymerization.

DSC analyses

The thermal properties of the polymers prepared were investigated by DSC analyses. The thermograms obtained at 20°C.min⁻¹ are displayed in Figure 4:

Insert Figure 4, single column

In both cases, no residual exothermicity was detected, which confirms the complete curing of the materials. The only transition detected in each case was an endothermic second-order transition, which was assigned to the glass transition of the thermosets. The glass transition temperatures of the polymers prepared from the model mixtures of G-type monomers ($T_g(G)$) and of GS-type monomers ($T_g(GS)$) were respectively 113°C and 99°C at the inflexion point. These high T_g were attributed to the fact that the epoxy monomers composing the mixtures are all aromatic. Also, $T_g(G) > T_g(GS)$. This result was expected since there are more non- or mono-functional epoxy monomers in the glycidylated mixture from GS-type phenolics than in the mixture from G-type phenolics. Thus, $EI(G) > EI(GS)$, which means that the mixture of glycidylated G-type phenolics has more epoxy groups per mass unit than the one of GS-type. As the thermosets are fully cured with the same hardener, this translates in more cross-link points per mass unit for the epoxy polymer from the mixture of G-type monomers than for the polymer from the mixture of GS-type monomers. A more cross-linked material means shorter, stiffer segments in-between the cross-link points. This also means that the material needs more energy to coordinate large-scale motions (glass transition), thus the higher T_g . The heat capacity change between the glassy and rubbery states of the epoxy polymers prepared from the mixtures of G-type monomers ($\Delta C_p(G)$) and of GS-type monomers ($\Delta C_p(GS)$) were respectively 0.473 J.g⁻¹.K⁻¹ and 0.408 J.g⁻¹.K⁻¹. These values are close; however, one would expect a lower ΔC_p for the more cross-linked material, which has less degrees of freedom, is more "locked", and has thus a lower capacity to store or dissipate heat. It is not the case here. This fact is explained by the structural and composition differences between the two mixtures. Indeed, different monomers will not contribute to the heat capacity of the polymer in the same manner. Overall, using model mixtures of phenolic lignin depolymerization products to prepare potentially biobased, high- T_g epoxy polymers is a valid approach.

TGA analyses

TGA analysis was performed on both epoxy thermosets. Results are shown in Figure 5:

Insert Figure 5, single column

Characteristic parameters of thermal degradation include the onset of degradation temperature (T_{onset} , °C), the maximum degradation rate temperature (T_{max} , °C, corresponding to the peak of the mass loss derivative curve), and the amount of residual char at 600°C ($Char_{600}$). Their values are summarized in Table 5:

Insert Table 5, single column

Both polymers displayed a one-step mass loss under N₂ and an onset of degradation at 254°C and 289 for respectively GS-type phenolics and G-type phenolics-based polymers. These results are consistent with epoxy thermosets prepared from

glycidylated natural lignins and a phenol novolac hardener, for which temperatures in the range of 266-293°C have been reported.⁵⁰ T_{onset} and T_{max} are higher in the case of the epoxy polymer prepared from the mixture of G-type monomers, which means it is more thermally stable. Once again, this result can be explained by the fact that $EI(G) > EI(GS)$, which induces a more cross-linked network in the case of the polymer based on the mixture of G-type monomers. A higher degree of crosslinking implies more bonds to break per mass unit in order to observe a mass loss, and thus a higher T_{onset} . It is worthy to note that the derivative curves of the mass loss (Figure 5) both present a single peak. However, these peaks present multiple shoulders, accounting for multiple degradation events. In the case of the polymer prepared from the mixture of GS-type monomers, the peak is broader and more shoulders are visible, which means that more degradation events take place over a broader range of temperature. This phenomenon was attributed to the fact that the mixture of GS-type monomers is composed of more different compounds (Figure 3). These different epoxy monomers each account for one degradation event in the polymer, at temperatures varying slightly with their structures. $Char_{600}$ is around 20% in both cases, which is high and desirable in terms of fire retardation properties. Interestingly, the polymers prepared displayed intumescent properties, as shown in Figure 6. Intumescent materials have especially good fire retardation properties as foamed char residue acts as a shield between the flame and the polymer, limiting heat, combusive, and fuel transfers⁵¹.

Insert Figure 6, single column, color

Therefore, preparing epoxy thermosets from aromatic lignin depolymerization products is also a valid approach in terms of thermal stability and fire retardation, which are generally issues with biobased materials.

DMA analyses

The thermo-mechanical properties of the epoxy thermosets prepared were investigated by DMA. The storage moduli E' and $\tan \delta$ of the polymers are shown in Figure 7:

Insert Figure 7, single column

The storage moduli $E'(G)$ and $E'(GS)$ at 25°C are both close to 3.3 GPa, which is a high value characteristic of thermosets in general and of high-performance epoxy thermosets in particular. These storage moduli display a sharp decrease of more than two decades upon heating, showing the glass transition of the polymers under mechanical stress, the frequency applied being 1 Hz. This phenomenon is also known as the α relaxation process, corresponding to the relaxation of the networks starting to coordinate large-scale motions. The temperature $T_\alpha(G)$ and $T_\alpha(GS)$ were determined as the temperatures at the peak maximum of the $\tan \delta$ curves. T_α is commonly associated with the glass transition temperature T_g , which is measured by DSC under no mechanical stress. Here,

$T_g(G) = 117^\circ\text{C}$ and $T_g(GS) = 113^\circ\text{C}$. These values are high compared to existing lignin-based systems. For example, in a study involving oxypropylated lignin-based epoxy pre-polymers, the team of Glasser⁵² obtained T_g values between 80 and 130°C . The authors chose to perform the lignin oxypropylation prior to glycidylation in order to overcome the low solubility of lignin as well as the low and non-uniform reactivity of the hydroxyls.⁵² The polypropylene oxide chains lower the T_g of the final epoxy thermosets, even though these were hardened with an aromatic diamine, known to give higher T_g thermosets than the IPDA we used⁵³. $T_g(G) > T_g(GS)$, which is consistent with the T_g results and is explained by the same considerations: the mixture of G-type epoxy monomers has a higher mean functionality than its GS-type counterpart, the polymer therefrom is thus more cross-linked, and the glass transition occurs at a higher temperature. The non-functional compound like **22** can also act as plasticizers of the network. Another indication that the epoxy thermoset from the mixture of G-type monomers is more cross-linked is the value of $E'(G)$ in the rubber region (above T_g), which is well above $E'(GS)$. Indeed, the more cross-linked the thermoset, the higher E' in the rubber region. The broadness of the $\tan \delta$ peak is a good indication of the homogeneity of a material: the more homogeneous the sample, the sharper the $\tan \delta$ peak. Here, the polymer from the mixture of GS-type monomers displays a broader $\tan \delta$ peak, which confirms its less homogeneous nature compared to its G-type counterpart. This result is consistent with the conclusions drawn from DSC and TGA and is explained in the same manner: the mixture of GS-type monomers is composed of more different compounds, with also different epoxy functionalities; they each take part to the glass transition at slightly different temperatures and thus broaden the $\tan \delta$ curve.

Experimental

Materials and methods

Vanillin (99%) was purchased from ABCR. Syringaldehyde ($\geq 98\%$), 4-hydroxybenzaldehyde (98%), syringic acid ($\geq 95\%$), acetovanillone (98%), acetosyringone (97%), sodium percarbonate $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ (available H_2O_2 20–30%), epichlorohydrin ($\geq 99\%$), triethylbenzylammonium chloride (TEBAC, 99%), sodium hydroxide (99%), 1,3,5-trimethoxybenzene ($\geq 99\%$) and all solvents used ($\geq 99.5\%$) were purchased from Sigma-Aldrich. Isophorone diamine (IPDA, $\geq 99\%$) was purchased from Evonik under the brand name Vestamin[®] IPD. Vanillic acid (99%) was graciously provided by Specific Polymers. All reagents were used as received. ^1H NMR spectra were recorded on a 400 MHz Bruker Aspect Spectrometer at 25°C in acetone- d_6 . Chemical shifts are given in ppm.

Dakin oxidation reactions

A two-necked round-bottomed flask was charged, in the case of individual reactions, with a solution of **1**, **2**, **3**, **6**, or **7** (0.25 mol.L^{-1} , 1.0 eq.) in THF. In the case of model mixtures of G-

and GS-type phenolics (see Figure 2); the total amount of aldehyde and ketone compounds was considered as 1.0 eq. A solution of sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$, 1.1 eq.) in deionized water (40% vol.) was then added. The reaction was conducted overnight at 25°C under N_2 and vigorous stirring. Portions of an HCl solution (0.1 mol L^{-1}) were added to the mixture under vigorous stirring until $\text{pH} = 1$ to quench the reaction. THF was evaporated under reduced pressure and the aqueous phase was immediately extracted thrice with ethyl acetate. The organic phases were collected, washed thrice with a saturated solution of NaCl adjusted at $\text{pH} = 1$ with HCl, and dried on anhydrous Na_2SO_4 . Ethyl acetate was then removed under reduced pressure.

Glycidylation reactions

A two-necked round-bottomed flask was charged, in the case of individual reactions, with compound **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, or **10** (1.0 eq.) and TEBAC (0.05 eq. per hydroxyl and acid functions). In the case of model mixtures of G- and GS-type phenolics, the total amount of acid and hydroxyl functions was considered as 1.0 eq. and was calculated from the compositions determined by ^1H NMR (see Figure 2). In this case, TEBAC was also added in a 0.05 eq. per acid and hydroxyl function. Epichlorohydrin (5.0 eq. per acid and hydroxyl functions) was added and the mixture was stirred for 3 hours after reaching 90°C . The solution was then cooled down to room temperature and excess epichlorohydrin was evaporated to dryness at 55°C under reduced pressure. An aqueous solution of NaOH (1.1 eq., 15 %w.) was added and the mixture was vigorously hand-shaken and stirred for 30 minutes at 30°C . Ethyl acetate and deionized water were then added. The mixture was extracted thrice with ethyl acetate. Organic layers were combined, rinsed thrice with brine and dried on anhydrous Na_2SO_4 . Ethyl acetate was removed on a rotary evaporator.

Formulation and polymerization

The number of moles of epoxy groups per gram of mixture was determined using a ^1H NMR titration method (see Results and Discussion) successfully employed by our team in a previous paper⁴⁴. The mixtures of G- and GS-type epoxy monomers were preheated at 70°C in order to obtain free-flowing liquids. Appropriate amounts of the epoxy monomers mixture and IPDA were then added in a silicon mold. The amount of epoxy groups introduced was considered as 2.0 eq. IPDA was introduced in a stoichiometric amount, *i.e.* 1.0 eq. of amine group for 2.0 eq. of epoxy group. The mixtures were thoroughly hand-stirred with a pre-heated stirring rod to obtain a homogeneous liquid mixture. They were then poured in aluminum foil molds and cured at 110°C for 1 hour. The materials formed were then cooled down to room temperature and post cured at 150°C for 1 hour.

Epoxy thermosets analyses

Differential Scanning Calorimetry (DSC) analyses were carried out using a Netzsch DSC200F3 calorimeter. Constant calibration was performed using n-Octane, indium, tin, and

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zinc standards. Nitrogen was used as the purge gas. The thermal properties were recorded at 20 °C.min⁻¹ between 20 and 200 °C. Glass transition temperatures (T_g) were determined as the inflexion point of the heat capacity jump. Thermo-Gravimetric Analyses (TGA) were performed on a Q50 device from TA Instrument. The samples were heated in an aluminum crucible from 25°C to 600°C under a nitrogen flow (60 mL/min). The experiments were carried out at a heating rate of 10°C/min.

Dynamic Mechanical Analyses (DMA) were carried out on a Metravib DMA 25. The samples had a rectangular geometry (length: 10 mm, width: 5 mm, thickness: 1 mm). Uniaxial stretching of samples was performed while heating at a rate of 2°C/min from 25°C to 200°C, keeping frequency at 1 Hz. In order to perform measurements in the linear viscoelastic region, deformation was kept at 1.10⁻⁵ %.

Conclusions

Vanillin is the only molecular aromatic industrially available from lignin. The process of vanillin production from lignin depolymerization gives mixtures of phenolics that are both economically and environmentally costly to purify. Our approach aims at using model mixtures of lignin depolymerization products to by-pass this purification. Mixtures of phenolics modelling the products obtained from G and GS lignins depolymerization were prepared with compositions as realistic as possible. In a first step, these mixtures and each of their individual components were subjected to a Dakin oxidation in order to increase their phenolic functionality. In a second step, the mixtures and their individual components were glycidylated to obtain mixtures of epoxy monomers. Epoxy thermosets were prepared from these epoxy monomers mixtures and their thermo-mechanical properties were investigated. In this work, potentially biobased and bisphenol A-free epoxy thermosets with remarkably good thermo-mechanical properties were prepared. This work exemplifies the strategy of preparing polymers having good properties and that are based on mixtures of lignin depolymerization products instead of single pure compounds, which paves the way to cheaper lignin-based polymers. This approach is also valuable in a biorefinery context as it unlocks a potential stream of high added-value products (the mixtures of monomers), complementary to the production of lignin and vanillin. Also, the final properties of the materials can be tuned by varying the composition of the starting mixture, which is possible through fine process adjustment or simply by varying the feedstock. Biomass variability becomes an industrial asset for fine product tuning instead of a drawback. In future works, real mixtures of products from lignin-to-vanillin processes should be used to prepare epoxy polymers. Intumescent properties of the materials prepared should also be further investigated. Finally, the potential of this approach should be further investigated for other polymers than epoxy polymers.

Acknowledgements

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Table of captions

Figure 1: Lignin monolignols (A) and a β -O-4 linkage (B)

Figure 2: Composition of the model mixtures of G- and GS-type phenolics before and after Dakin oxidation

Figure 3: Composition of the model mixtures of G- and GS-type phenolics before and after glycidylation

Figure 4: DSC thermograms of the epoxy thermosets prepared from model mixtures of G- and GS-type monomers

Figure 5: TGA thermograms under N₂ and their derivatives of the epoxy thermosets prepared from model mixtures of G- and GS-type monomers

Figure 6: Epoxy polymers from model mixtures of G- and GS-type monomers after TGA

Figure 7: DMA analyses of the epoxy thermosets prepared from model mixtures of G- and GS-type monomers

Scheme 1: Outlines of the main petrochemical synthesis of vanillin

Scheme 2: Reaction of vanillin with sodium bisulfite to form the "vanillin bisulfite complex", sodium vanillyl- α -hydroxysulfonate

Scheme 3: Mechanism of the Dakin oxidation

Scheme 4: Phenol glycidylation mechanism under solvent-free conditions

Scheme 5: Synthesis of cross-linked thermosets by epoxy/amine reaction

Table 1: Main products of the alkaline oxidative depolymerization of lignin in the cases of softwoods and hardwoods.

Table 2: Dakin oxidation products from the aldehyde and ketone components of the starting mixtures

Table 3: Glycidylation products from each individual component of the oxidized mixtures.

Table 4: Epoxide Index and Epoxide Equivalent Weight of the glycidylated mixtures.

Table 5: Thermal degradation characteristic parameters under N₂ of the epoxy thermosets prepared from model mixtures of G- and GS-type monomers

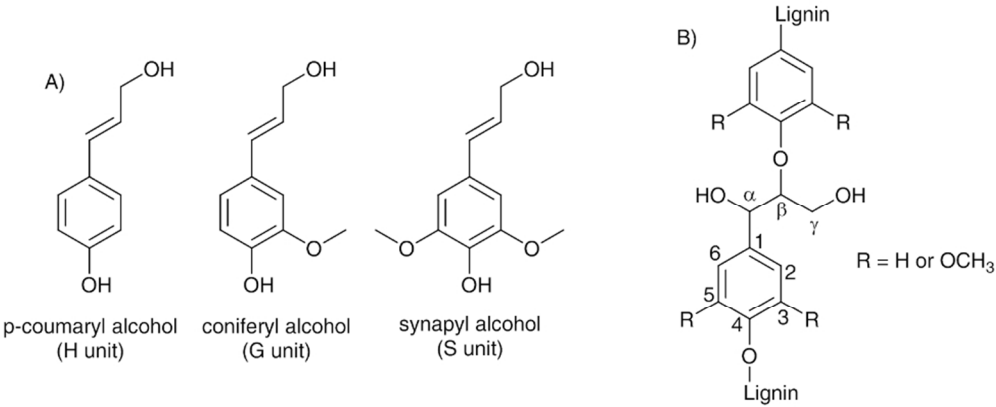


Figure 1
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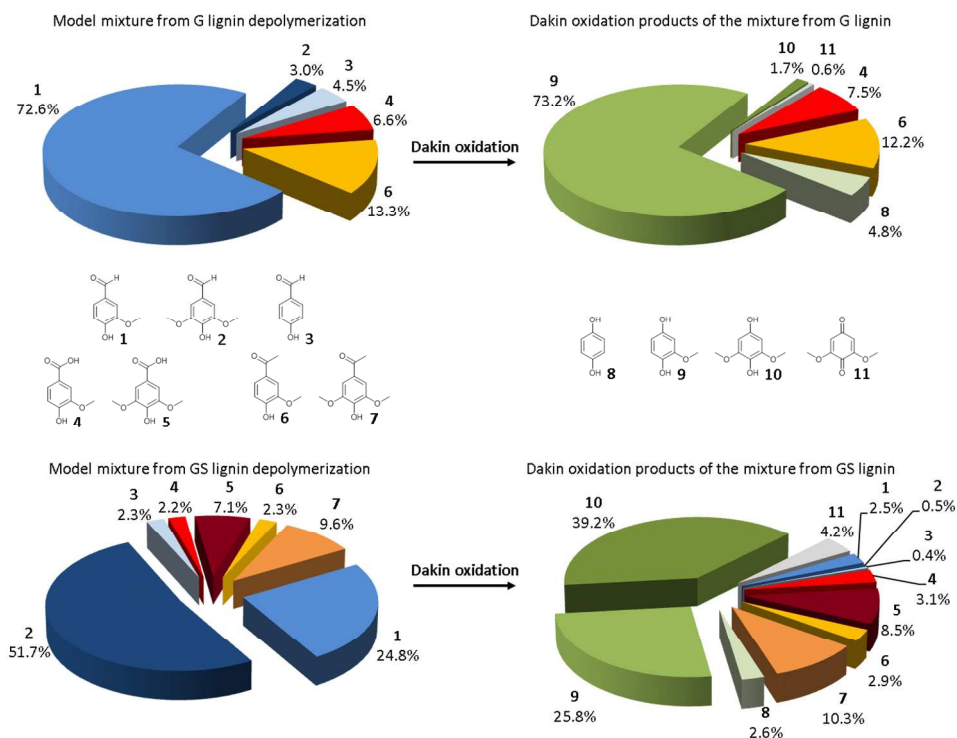


Figure 2
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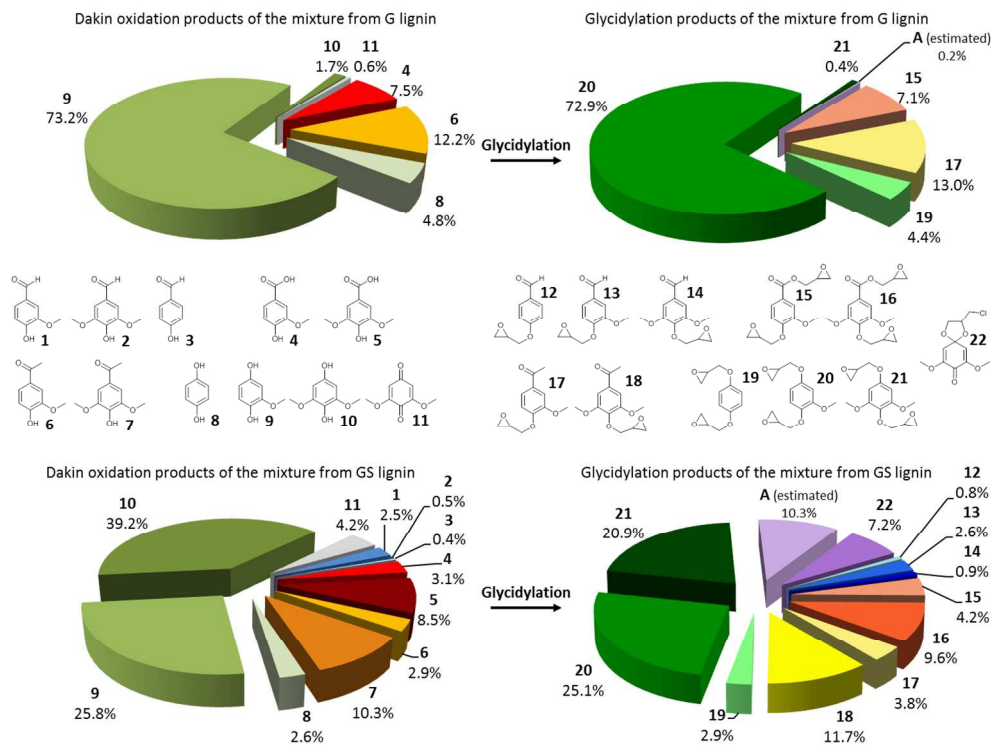


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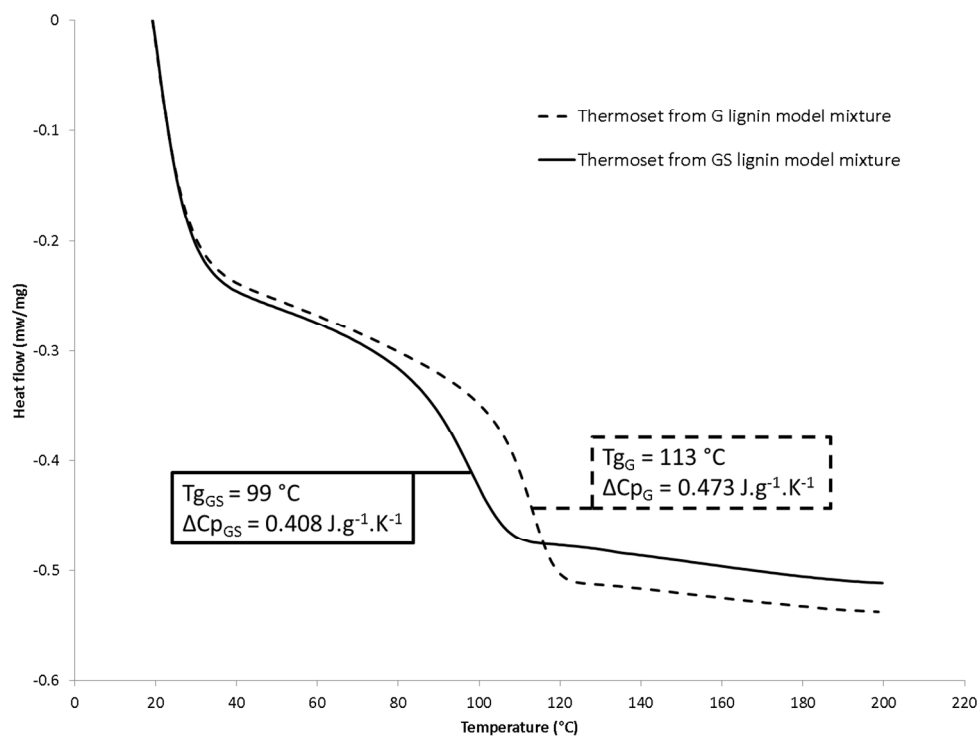


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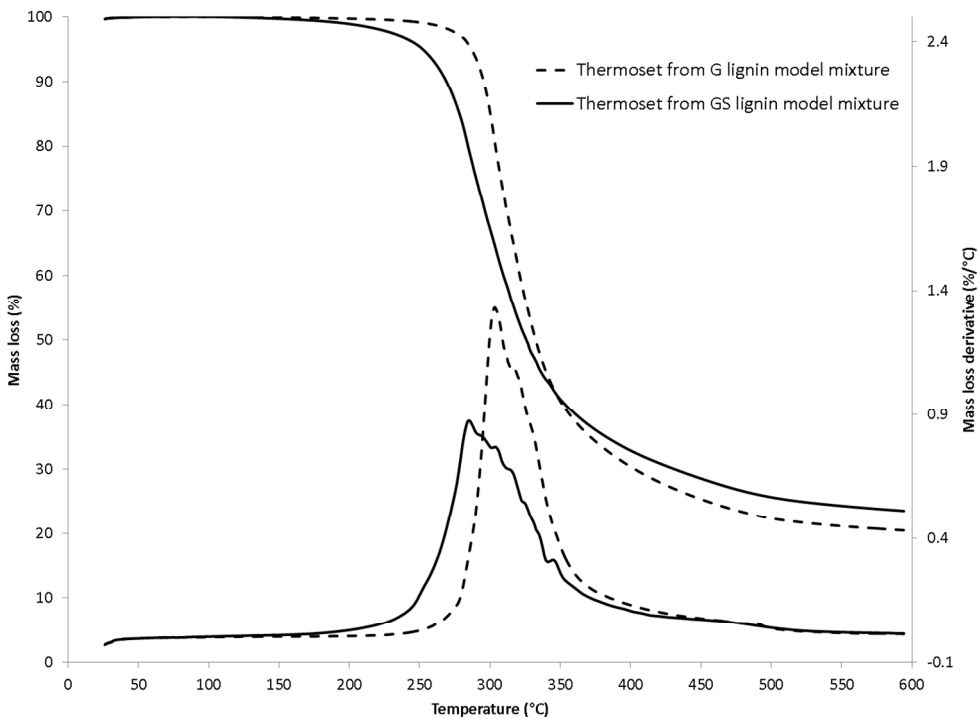


Figure 5
171x128mm (300 x 300 DPI)



Epoxy polymer
from G lignin model mixture
after TGA



Epoxy polymer
from GS lignin model mixture
after TGA

Figure 6
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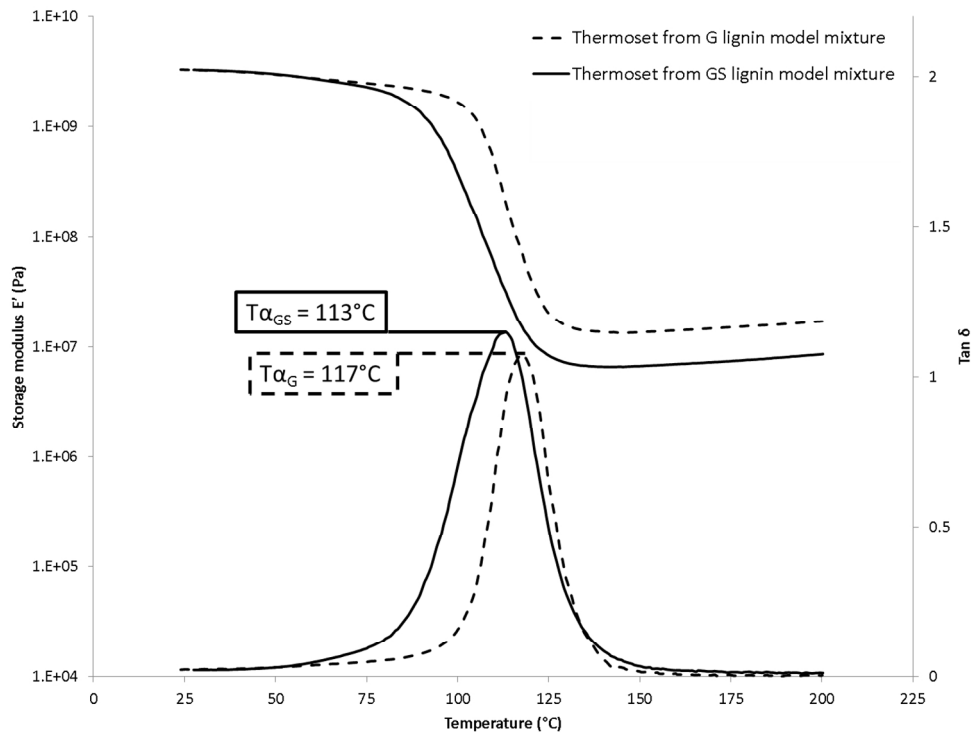
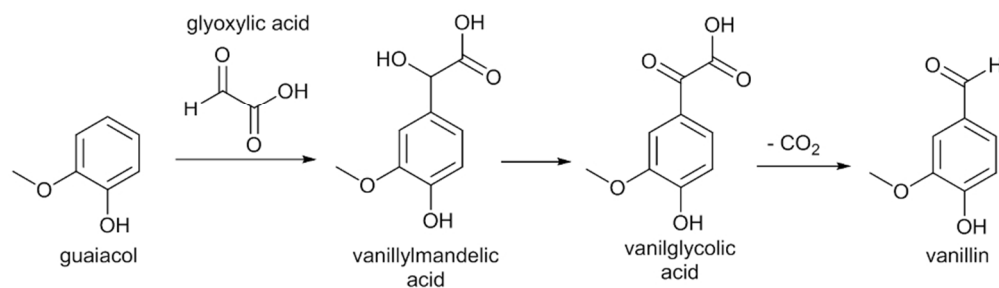
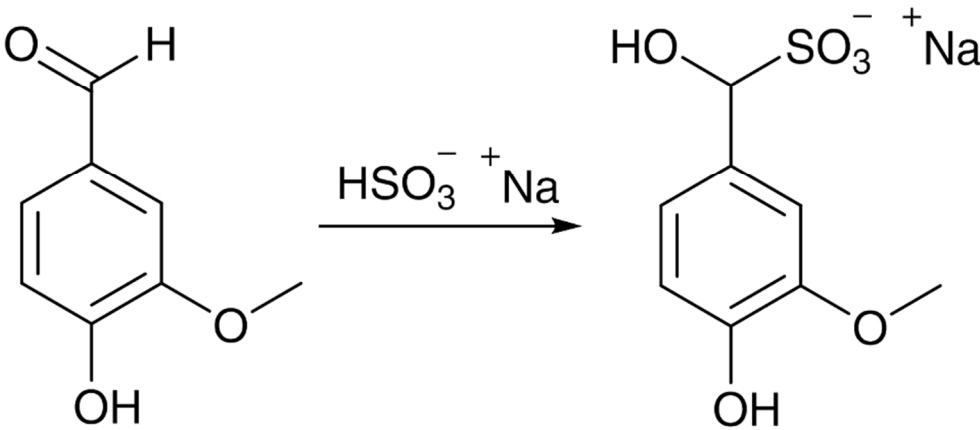


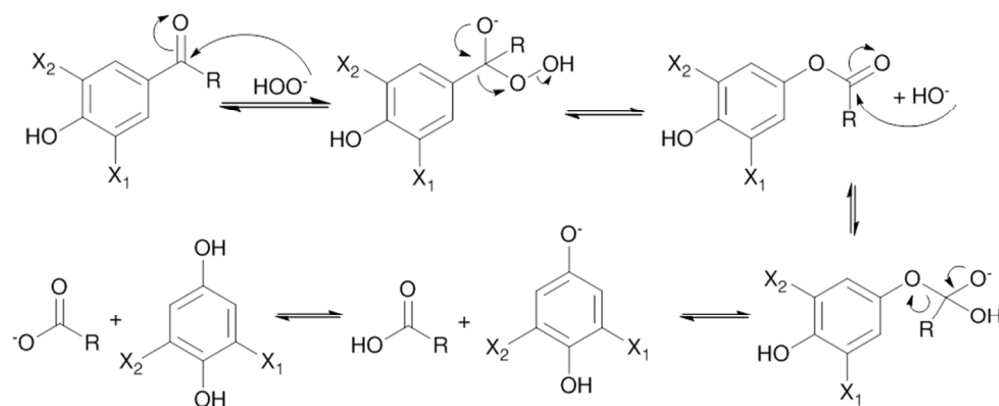
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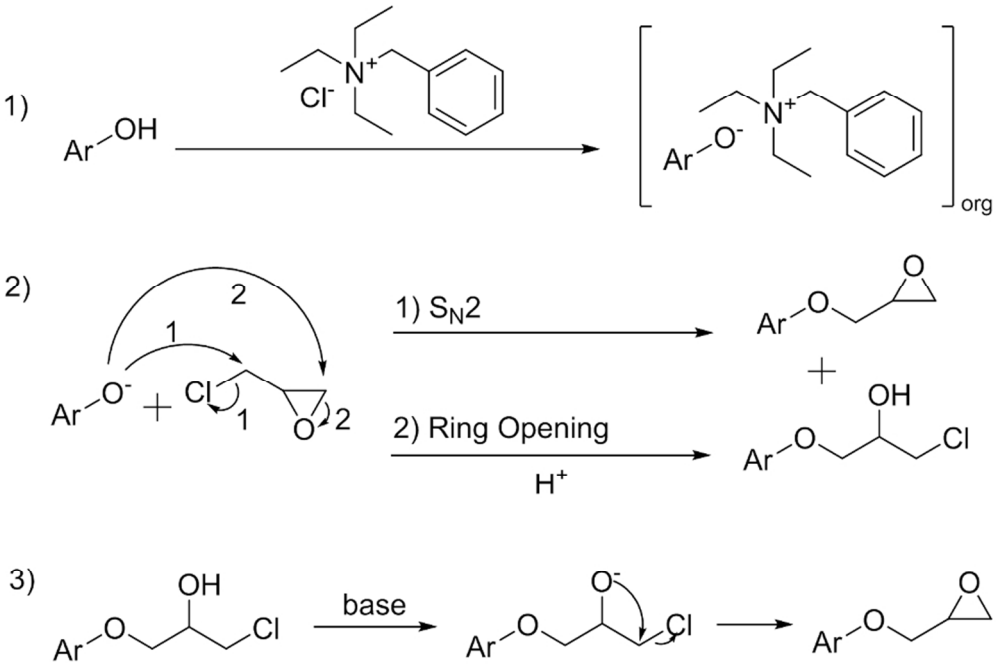
Scheme 1
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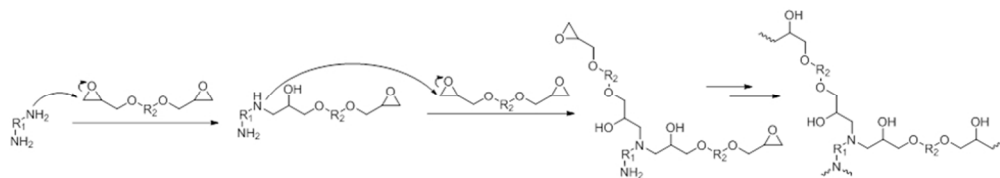
Scheme 2
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 $X_1, X_2 = -\text{H} \text{ or } -\text{OCH}_3$ $\text{R} = -\text{H} \text{ or } -\text{CH}_3$

Scheme 3
82x42mm (300 x 300 DPI)



Scheme 4
82x55mm (300 x 300 DPI)



Scheme 5
82x14mm (300 x 300 DPI)

Table 1: Main products of the alkaline oxidative depolymerization of lignin in the cases of softwoods and hardwoods.

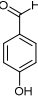
	Compound	Formula	Typical yields in softwoods	Typical yields in hardwoods
aldehydes	vanillin (1)		6-12% 16, 25, 27, 30, 35	1-5% 25, 26, 28, 29, 35, 46-50
	syringaldehyde (2)		0-0.7% 25	4-16% 25, 26, 28, 29, 35, 46-50
	p-hydroxy-benzaldehyde (3)		0-0.5% 25, 31, 35	0-0.5% 25, 26, 35, 46, 48, 49
carboxylic acids	vanillic acid (4)		0.5-1.5% 35	0.2-2.4% 28, 29, 35, 47, 50
	syringic acid (5)		N.D.	0.5-3.9% 28, 29, 35, 47, 50
ketones	acetovanillone (6)		0.6-6.4% 25, 31	0.3-2.6% 25, 26, 29, 46, 48
	acetosyringone (7)		N.D.	1.5-4.2% 25, 26, 29, 46, 48

Table 2: Dakin oxidation products from the aldehyde and ketone components of the starting mixtures

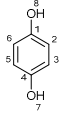
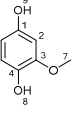
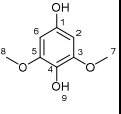
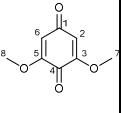
Compound	Formula	Conv.	^1H NMR δ (400.1MHz, acetone-d ₆ , ppm)
hydroquinone (8)		99% from 3	6.66 (s, 4H, H ₂ , H ₃ , H ₅ , H ₆) ; 7.64 (s, 2H, H ₇ , H ₈)
methoxy- hydroquinone (9)		97% from 1 91% from 6	3.77 (s, 3H, H ₇) ; 6.27 (dd, 1H, H ₆) ; 6.46 (d, 1H, H ₂) ; 6.63 (d, 1H, H ₅) ; 6.86 (broad s, 1H, H ₈) ; 7.73 (broad s, 1H, H ₉)
3,5- dimethoxy- hydroquinone (10)		90% from 2 69% from 7	3.75 (s, 6H, H ₇ , H ₈) ; 6.14 (s, 2H, H ₂ , H ₆) ; 6.46 (broad s, 1H, H ₉) ; 7.71 (broad s, 1H, H ₁₀)
3,5- dimethoxy- quinone (11)		5% from 2 4% from 7	3.82 (s, 6H, H ₇ , H ₈) ; 5.90 (s, 2H, H ₂ , H ₆) CDCl ₃ : 3.83 (s, 6H, H ₇ , H ₈) ; 5.86 (s, 2H, H ₂ , H ₆)

Table 3: Glycidylation products from each individual component of the oxidized mixtures.

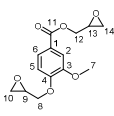
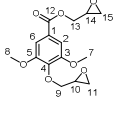
Compound	Formula	Conv.	¹ H NMR δ (400.1MHz, acetone-d ₆ , ppm)
p-Hydroxy-benzaldehyde glycidyl ether (12)		84%	2.75 (dd, 1H, H _{9a}) ; 2.87 (dd, 1H, H _{9b}) ; 3.36 (m, 1H, H ₈) ; 4.01 (dd, 1H, H _{7a}) ; 4.49 (dd, 1H, H _{7b}) ; 7.16 (d, 2H, H ₃ , H ₅) ; 7.88 (d, 2H, H ₂ , H ₆) ; 9.91 (s, 1H, H ₁₀)
Vanillin glycidyl ether (13)		98%	2.75 (dd, 1H, H _{10a}) ; 2.87 (dd, 1H, H _{10b}) ; 3.37 (m, 1H, H ₉) ; 3.91 (s, 3H, H ₇) ; 4.01 (dd, 1H, H _{8a}) ; 4.47 (dd, 1H, H _{8b}) ; 7.18 (d, 1H, H ₅) ; 7.44 (d, 1H, H ₂) ; 7.52 (dd, 1H, H ₆) ; 9.87 (s, 1H, H ₁₁)
Syringaldehyde glycidyl ether (14)		91%	2.59 (dd, 1H, H _{11a}) ; 2.74 (dd, 1H, H _{11b}) ; 3.28 (m, 1H, H ₁₀) ; 3.93 (s, 6H, H ₇ , H ₈) ; 3.97 (dd, 1H, H _{9a}) ; 4.25 (dd, 1H, H _{9b}) ; 7.26 (s, 2H, H ₂ , H ₆) ; 9.90 (s, 1H, H ₁₂)
Vanillic acid diglycidyl ether (15)		91%	2.72 (dd, 1H, H _{10a}) ; 2.74 (dd, 1H, H _{14a}) ; 2.84 (m, 2H, H _{10b} , H _{14b}) ; 3.31 (m, 1H, H ₉) ; 3.36 (m, 1H, H ₁₃) ; 3.89 (s, 3H, H ₇) ; 3.98 (dd, 1H, H _{8a}) ; 4.08 (dd, 1H, H _{12a}) ; 4.43 (dd, 1H, H _{8b}) ; 4.63 (dd, 1H, H _{12b}) ; 7.09 (d, 1H, H ₅) ; 7.56 (d, 1H, H ₂) ; 7.65 (d, 1H, H ₆)
Syringic acid diglycidyl ether (16)		89%	2.59 (dd, 1H, H _{11a}) ; 2.73 (m, 2H, H _{11b} , H _{15a}) ; 2.84 (dd, 1H, H _{15b}) ; 3.27 (m, 1H, H ₁₀) ; 3.31 (m, 1H, H ₁₄) ; 3.90 (s, 6H, H ₇ , H ₈) ; 3.94 (dd, 1H, H _{9a}) ; 4.10 (dd, 1H, H _{13a}) ; 4.21 (dd, 1H, H _{9b}) ; 4.65 (dd, 1H, H _{13b}) ; 7.33 (s, 2H, H ₂ , H ₆)
Acetovanillone glycidyl ether (17)		97%	2.52 (s, 3H, H ₁₂) ; 2.74 (dd, 1H, H _{10a}) ; 2.85 (dd, 1H, H _{10b}) ; 3.36 (m, 1H, H ₉) ; 3.88 (s, 3H, H ₇) ; 3.97 (dd, 1H, H _{8a}) ; 4.43 (dd, 1H, H _{8b}) ; 7.06 (d, 1H, H ₅) ; 7.53 (d, 1H, H ₂) ; 7.61 (dd, 1H, H ₆)
Acetosyringone glycidyl ether (18)		90%	2.57 (s, 3H, H ₁₃) ; 2.59 (dd, 1H, H ₁₁) ; 2.73 (dd, 1H, H _{11b}) ; 3.27 (m, 1H, H ₁₀) ; 3.90 (s, 6H, H ₇ , H ₈) ; 3.93 (dd, 1H, H _{9a}) ; 4.21 (dd, 1H, H _{9b}) ; 7.30 (s, 2H, H ₂ , H ₆)
Hydroquinone diglycidyl ether (19)		>99%	2.68 (dd, 2H, H _{9a} , H _{12a}) ; 2.81 (dd, 2H, H _{9b} , H _{12b}) ; 3.27 (m, 2H, H ₈ , H ₁₁) ; 3.81 (dd, 2H, H _{7a} , H _{10a}) ; 4.25 (dd, 2H, H _{7b} , H _{10b}) ; 6.90 (s, 4H, H ₂ , H ₃ , H ₅ , H ₆)
Methoxy-hydroquinone diglycidyl ether (20)		>99%	2.65 (dd, 2H, H _{10a}) ; 2.68 (dd, 1H, H _{13a}) ; 2.79 (dd, 2H, H _{10b}) ; 2.82 (dd, 1H, H _{13b}) ; 3.27 (m, 2H, H ₉ , H ₁₂) ; 3.81 (m, 2H, H _{8a} , H _{11a}) ; 3.82 (s, 3H, H ₇) ; 4.19 (dd, 2H, H _{8b}) ; 4.26 (dd, 1H, H _{11b}) ; 6.43 (dd, 1H, H ₆) ; 6.63 (d, 1H, H ₂) ; 6.88 (d, 1H, H ₅)
3,5-Dimethoxy-hydroquinone diglycidyl ether (21)		80%	2.53 (dd, 1H, H _{11a}) ; 2.70 (m, 2H, H _{14a} , H _{11b}) ; 2.83 (dd, 1H, H _{14b}) ; 3.23 (m, 1H, H ₁₀) ; 3.28 (m, 1H, H ₁₃) ; 3.77 (dd, 1H, H _{9a}) ; 3.81 (s, 6H, H ₇ , H ₈) ; 3.85 (dd, 1H, H _{12a}) ; 3.98 (dd, 1H, H _{9b}) ; 4.30 (dd, 1H, H _{12b}) ; 6.29 (s, 2H, H ₂ , H ₆)
2-(chloromethyl)-7,9-dimethoxy-1,4-dioxaspiro[4.5]deca-6,9-dien-8-one (22)		14% from 10 93% from 11	3.75-3.79 (m, 2H, H ₁₁) ; 3.78, 3.79 (2*s, 6H, H ₇ , H ₈) ; 4.06 (m, 1H, H ₉) ; 4.48, (m, 1H, H ₉) ; 4.67 (m, 1H, H ₁₀) ; 5.33-5.40 (2*dd, 2H, H ₂ , H ₆)

Table 4: Epoxide Index and Epoxide Equivalent Weight of the glycidylated mixtures.

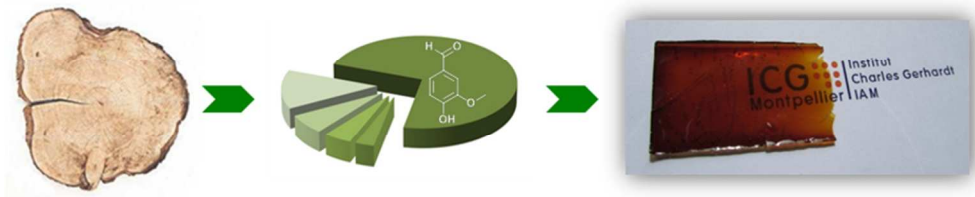
	EI from ^1H NMR titration (eq.g $^{-1}$)	EEW from ^1H NMR titration (g.eq $^{-1}$)	EEW estimated from mixture compositions (g.eq $^{-1}$)
Mixture from G- type phenolics	$8.24 \cdot 10^{-3}$	121	133
Mixture from GS- type phenolics	$5.16 \cdot 10^{-3}$	194	181

Table 5: Thermal degradation characteristic parameters under N2 of the epoxy thermosets prepared from model mixtures of G- and GS-type monomer

	Tonset	Tmax	Char600
Thermoset from model mixture of G-type monomers	289 °C	303°C	20%
Thermoset from model mixture of GS-type monomers	254°C	261°C	23%

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Bio-based epoxy thermosets with good thermo-mechanical properties were prepared from model mixtures of products from the lignin-to-vanillin process.



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