Collège Doctoral du Languedoc-Roussillon

THÈSE

Pour obtenir le grade de

Docteur

Délivré par **l'Ecole Nationale Supérieure de Chimie de Montpellier**

Préparée au sein de l'école doctorale
Sciences Chimiques Balard (ED459)
Et de l'unité de recherche
ICGM-IAM (UMR 5253)

Spécialité : **Chimie et Physico-Chimie des Matériaux**

Présentée par **Maxence Fache**

Fonctionnalisation et polymérisation de dérivés phénoliques naturels: Vers des matériaux aromatiques biosourcés

Sera soutenue le 20 Novembre 2015 devant le jury composé de :

M. J.-P. PASCAULT, Professeur émérite, INSA Lyon	Rapporteur
M. H. CRAMAIL, Professeur, LCPO	Rapporteur
M. F. ALLAIS, Professeur, AgroParisTech	Examinateur
M. P. LACROIX-DESMAZES, Directeur de recherche, CNRS	Président du jury
M. B. BOUTEVIN, Professeur émérite, ENSCM	Examinateur
M. S. CAILLOL, Chargé de recherche, CNRS	Directeur de thèse

ENSCM CHIMIE Montpellier

Acknowledgments

This Ph.D. work has been performed within the Ingénierie et Architectures Macromoléculaires (IAM) team of the Institut Charles Gerhardt de Montpellier (ICGM) located in Montpellier, France. It has been financed by the French Ministry of Research, which is gratefully acknowledged.

M. Jean-Jacques Robin and M. Patrick Lacroix-Desmazes, who welcomed me in the IAM team and allowed me to take on this project, are also gratefully acknowledged.

I thank M. Henri Cramail and M. Jean-Pierre Pascault for accepting to be examiners of this thesis. I hope they will enjoy reading it as much as I enjoyed writing it.

I also thank M Florent Allais, M. Patrick Lacroix-Desmazes, and M. Bernard Boutevin for accepting to review and judge this manuscript.

I wish to express all my gratitude and admiration to Sylvain Caillol, director of this PhD, who always found time to expertly guide me, advise me, and answer my questions despite his rather full timetable.

My gratitude and admiration also go to Bernard Boutevin. What I know about polymers comes mostly from his encyclopedic knowledge of this field. His ideas and pieces of advice were very precious to me.

Rémi Auvergne, who co-supervised this work, is also warmly thanked for his advice and the time taken correcting my work.

Claire Negrell deserves special thanks for being always ready to lend a helpful hand and make everything run smoothly, she is the mother of this lab.

Of course, I also thank every other permanent member of the IAM team.

I thank all the PhD students and post-docs for the great moments I lived in this lab and outside. I am proud to call you guys my friends, even if most of you are nuts!

Finally, I want to thank from the bottom of my heart my family, my friends, and my love, without their support this manuscript would not exist. They all know my feelings towards them.

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General Introduction

Using resources from biomass as raw materials for chemical production instead of crude oil is a challenge we have to face right now. A resource that can renew itself and recycle CO_2 on a decade timescale is of course more sustainable than fossil resources, *i.e.* petroleum, natural gas and coal, formed over several hundred million of years. These resources are not renewable on our time scale and their extraction is slowing down as the demand increases, which makes them less and less available.

From a socio-economic standpoint, oil-drilling will lead to major problems. Drilling the remaining reserves will prove more and more technically challenging and thus costly. Indeed, future wells will attain unprecedented depths or be located in inhospitable environments like deep sea or the arctic. Their location might also lead to geopolitical conflicts.[1] Price volatility and supply insecurity will surely be a consequence. On the contrary, renewable resources will provide security of domestic feedstock supplies, leading to price stability and competitiveness. It will also promote regional development and reduce the dependency on petrochemical exportations, hopefully diminishing the political and economical tensions ensuing.

When it comes to the predicted scarcity of non-renewable resources, the primary issue is energy, considering that more than 90% of these resources are used as fuels. Alternative energy sources are vigorously debated, intensively investigated, and slowly implemented. However, non-renewable resources are also raw materials for the vast majority of organic chemicals and polymers. Finding alternative solutions from the biomass feedstock is thus an equally important challenge. In this context, the concept of bio-refinery started gaining importance. Similarly to the crude oil refinery, the idea is to (bio)chemically turn each component of the feedstock into a variety of useful products.

The industrial production and scientific research at the end of the 19^{th} century were actually turned towards the exploitation of biomass. Many products based on renewable resources that were developed then are still industrially relevant today (cellulose acetate, natural rubber, etc.). After the Second World War, the petro-chemical industry entered a golden age with the improvements made in terms of petroleum refining. The new availability of various petro-based chemicals in large amounts has seen the development of the polymer industry – a very large end-user of these chemicals – with optimized processes specifically designed for this feedstock. Now is the time to do the same with renewable chemicals.

Recent years have seen a rising awareness of the polymer community on this topic.[2] This effort has been driven by environmental concerns, but also by the absolute necessity of being economically relevant. Polymers from renewable resources have been a very active area of research and many strategies have been developed to design them with performances high enough and cost low enough that they could be introduced on the market.

Regardless of the strategy employed, some successful replacements of petro-based polymers in various applications are already a reality. One can cite the packaging field, in which bio-based Poly Lactic Acid (PLA), PolyEthylene Terephthalate (PET), and PE are already in use. Polymers based on vegetables oils, especially PolyAmides (PA) are also already an industrial reality. Even if it seems clear that the seeds of a successful industrial production of bio-based polymer have already been planted, one can note that the bio-sourcing of thermoplastics is more advanced than for thermosets. However, thermosets are

irreplaceable in industry because of their good thermo-mechanical properties and chemical resistance. Using a renewable feedstock to prepare thermosetting polymers is especially relevant since they are cross-linked and usually cannot be recycled, contrary to thermoplastics.
This work will thus deal with the design of thermosets from renewable resources. In the current context, many parameters have to be taken into account, such as the availability of the natural resource, its price, toxicity, and performance, the regulatory context, etc. This necessitates a reasoned approach that could be summed up by the two following questions: What type of thermoset? From what renewable resource? The answers to these questions are the starting point of this Ph.D. work.
"What type of thermoset?" is a rather large question in the sense that all polymers would be more sustainable if based on bio-resources. However, epoxy polymers are one of the major classes of thermosets and are irreplaceable in many industrial fields such as electronics, aerospace, packaging, construction etc. Currently, 75% of the epoxy polymers worldwide are prepared from the DiGlycidyl Ether of Bisphenol A (DGEBA)[3], himself based on bisphenol A, a reprotoxic compound[4] under close monitoring worldwide. The use of bisphenol A-based polymers in food-contact applications has even been prohibited in France in 2015. The bio-sourcing of epoxy thermosets could thus have the double positive effect of bisphenol A replacement and renewable resources use.
"From which renewable resource?" is the question that comes next, bearing in mind the target of epoxy thermosets. Often, thermosets are used in applications requiring good thermo-mechanical properties. Therefore, they are often based on aromatic monomers, the stability and rigidity of this group conferring good performances to the polymer. Epoxy thermosets are no exception, as bisphenol A and thus DGEBA are both aromatics. In order to design bio-based epoxy thermosets as good as industrial standards, the use of renewable aromatics seem to be a valid approach.

At this point of the reflection, a careful literature analysis on both matters, *i.e.* epoxy thermosets and bio-based aromatics, has to be carried out. This literature review constitutes the **Chapter 1** of this thesis. It comprises an overview on epoxy thermosets, especially epoxy-amine thermosets, and a description of the different sources of renewable aromatics available and of their use in epoxy thermosets. This chapter also explains the choice of vanillin as the starting renewable resource as well as its use to prepare renewable polymers in a published review article.
The **Chapter 2** consists in a published work, in which the potential of vanillin as a bio-based aromatic building-block for the preparation of various monomers is further explored. The monomers synthesized bear functionalities enabling the preparation of many types of polymers, thermosets and thermoplastics alike.
Among the monomers prepared, epoxy monomers are further investigated in **Chapter 3**. In this published article, vanillin-based epoxy thermosets are prepared, characterized and their structure-property relationships investigated. A comparison to the current bisphenol A-based industrial reference is also performed.
This comparison to existing systems is pursued in **Chapter 4**. The strategy of oligomerization industrially used for DGEBA in order to modulate thermo-mechanical properties of the final material is applied to vanillin-derived monomers. These published results demonstrate the feasibility of applying well-established industrial strategies to bio-based systems.

Chapter 5 explores the possibility of using other renewable compounds of interest to further improve the versatility of epoxy polymers. More precisely, the syntheses of a tri-functional bio-based epoxy monomer and of bio-based amine hardeners are described in this submitted article. Epoxy polymers were also prepared, their properties investigated and linked to the structure of the monomers used.

Previous chapters explore the vanillin-to-polymers, downstream process. The **Chapter 6** intends to shorten the path from biomass to epoxy thermosets by investigating the upstream, lignin-to-vanillin process. This process leads to mixtures of phenolic compounds, from which isolation of pure vanillin is costly both economically and environmentally. This published work demonstrates that these purification steps are not necessary in order to prepare high-performance epoxy thermosets from biomass.

Chapter 1: Literature analysis

1. Introduction

Thermosets are characterized by the fact that they are formed from a mixture of co-monomers that can react among themselves by an external action such as heating or UV irradiation. The necessary condition to generate a thermosetting polymer is that one or more of the monomers has more than two reactive sites per molecule.[5] The reaction, once completed, leads to a tridimensional cross-linked network impossible to reshape. This explains that contrary to thermoplastics, thermosetting polymers generally cannot be recycled and have to be incinerated at their end of life. Using renewable resources for their synthesis is thus an especially relevant challenge as well as a burning issue.

The first part of this chapter consists of a brief introduction aiming at explaining the structure and scope of this literature analysis.

Among thermosets, epoxy polymers are an important target as they are extensively used in many fields while being based on bisphenol A, a reprotoxic compound[4]. Substitution of bisphenol A-based by bio-based epoxy polymers could thus have a double positive effect. The second part of this chapter deals with epoxy polymers in general, with an emphasis on previously-reported bio-based epoxy polymers.

Often, thermosetting polymers in general and epoxy thermosets in particular are based on aromatic compounds such as bisphenol A, especially in thermo-mechanically demanding application. Indeed, the aromatic ring brings stability and rigidity to the network. Thus, in order to prepare renewable thermosets, bio-based aromatics are needed. In nature, aromatics are found as phenolic compounds and their different sources are summed up in the third part of this chapter.

Vanillin is especially discussed as it is the only molecular phenolic compound that is available from wood at an industrial scale. The different sourcing of this compound are discussed in the fourth part, with an emphasis on the method employing lignin as a raw materials.

Recently, the use of vanillin to prepare renewable polymers has been intensively investigated. A published review is presented in the fifth part of this chapter to take into account these recent developments in the literature.

Conclusions drawn from this study are summed up in the sixth part, as well as the axes of research opened by this literature analysis and references are given in the seventh part.

2. Epoxy thermosets

Epoxy thermosets are an important class of industrial polymers. These include a broad range of different polymers obtained by reaction of epoxy monomers with co-monomers (hardeners) and/or initiators[5]. This overview will mainly focus on epoxy monomers or pre-polymers, their synthesis and their reaction with hardeners.

2.1. Generalities and industry overview

2.1.1 Generalities

When it comes to epoxy monomers and polymers, the term epoxy resins is loosely used to include epoxy monomers, oligomers, pre-polymers, uncured epoxy formulations or cross-linked epoxy thermosets. By strict definition[3] and in the rest of this work, epoxy resins will only refer to uncross-linked monomers, oligomers, or pre-polymers containing epoxy groups. The epoxy group, also known as oxirane, refers to the three-membered ring constituted of one oxygen atom and two carbon atoms, substituted or not. These epoxy functions are highly reactive and can undergo a large variety of addition and (homo)polymerization reactions[5]. The vast majority of industrially important epoxy resins are bi- or multifunctional epoxides. These pre-polymers are reacted with a co-monomer[5], also referred to as a cross-linking agent, hardener or curing agent, to form cross-linked thermosets.

The global demand on epoxy resin was estimated at roughly US$ 18.6 billion in 2013.[6] The market value will reach US$ 25.8 billion by 2018 and increase to US$ 33.6 billion by 2022 in the forecast, following the annual growth rate of 6.8% in the coming years.[6] In terms of market volume, the epoxy market accounted for 2 million tons in 2010 and is projected to reach 3 million tons by 2017.[7]

Industrially, epoxy formulations meet the needs of a large variety of applications as shown in **Figure 1**. They are found for instance in metal can coatings, automotive paint primers, printed circuit boards, semiconductor encapsulants, adhesives, and aerospace composites.[3]

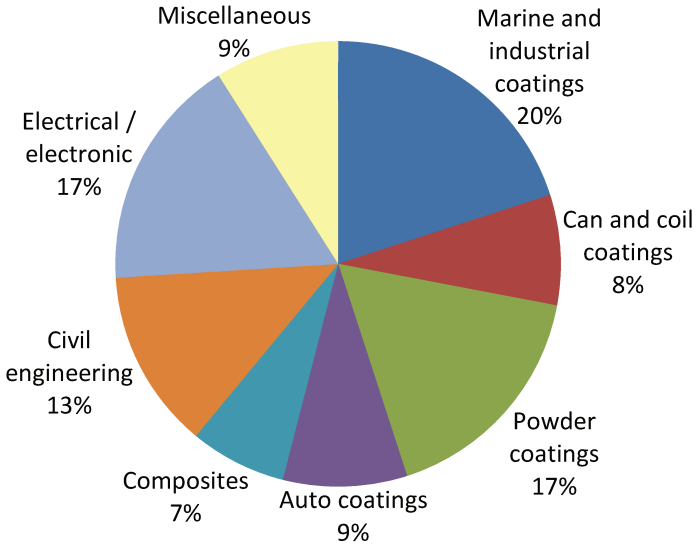
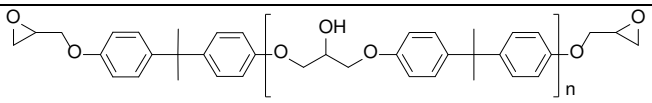
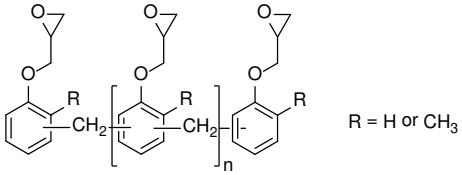
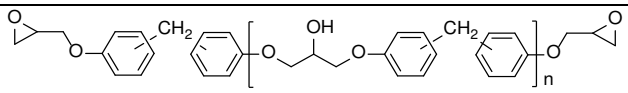
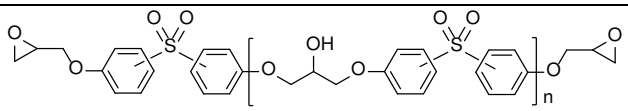
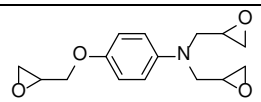
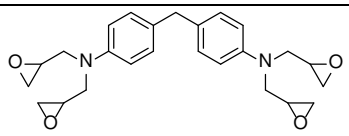
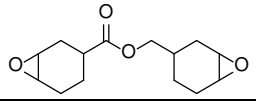
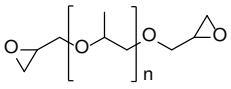
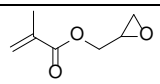
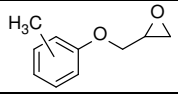
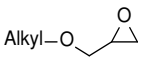


Figure 1 : Percentage of the total volume of epoxy polymers used in their different applications

Epoxy thermosets usually display outstanding properties in terms of mechanical strength and toughness, chemical and corrosion resistance, durability, adhesion, and electrical insulation[8]. Additionally, they are compatible with a great number of materials and their formulation and curing are also advantageous as they present no volatile emissions and low shrinkage upon cure[8].

Many different epoxy resins are commercially available; some of the most important commercial ones are shown in **Table 1**.[3, 5, 9] The three leading producers of epoxy resins are Hexion (formerly Shell's Epoxy Resins and Resolution Performance Products), Dow and Huntsman. Together they account for approximately 75% of the world's capacity[9].

Table 1 Examples of the most important epoxy resins available commercially and of some manufacturers.

Examples of manufacturers and commercial names	Name	Formula
Dow Chemical (D.E.R., D.E.N.) Hunstman (Araldite) Mitsubichi Chemical (jER) Thai Epoxy (Epotec) Hexion (Momentive Specialty Chemicals) (Epikote, Epon) Kukdo (YD)	DiGlycidyl Ether of Bisphenol A (DGEBA or BADGE)	
	R = H : Epoxy Phenol Novolac (EPN) R = CH_3 : Epoxy Cresol Novolac (ECN)	 R = H or CH_3
	DiGlycidyl Ether of Bisphenol F (DGEBF or BFDGE)	
	DiGlycidyl Ether of Bisphenol S (DGEBS or BSDGE)	
	TriGlycidyl ether of Para-AminoPhenol (TGPAP)	
	TetraGlycidyl ether of Methylene DiAniline (TGMDA)	
	3,4-Epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ECC)	
	Polypropylene glycol diglycidyl ether	
	Glycidyl MethAcrylate (GMA)	
	Cresol Glycidyl Ether (CGE)	
	Alkyl glycidyl ethers of C_8-C_{10} (Epoxide 7) Alkyl glycidyl ethers of C_{12}-C_{14} (Epoxide 8)	 Alkyl = C_8-C_{10} or C_{12}-C_{14} Alkyl chain

The most widely used epoxides are the DGEBA derivatives (**Table 1**) with more than 75% of market volume.[3] This market dominance of bisphenol A-based epoxy resins is a result of a combination of their relatively low cost and adequate-to-superior performance in many applications.

Epoxy thermosets are widely used in industry because of their versatility. Indeed, the final material properties can be modulated by the chemical structure of the epoxides employed in the formulation, by their length, and by the overall functionality of the epoxy resin.[3] Epoxides can be mono-, bi-, or multi-functional. Mono-functional epoxides are used mostly as reactive diluents and/or viscosity modifiers.[9] The nature of the cross-linker employed also has a great influence on the properties[3] and cure temperatures and kinetics; it can be adapted to specific needs. In order to facilitate processing and/or to modify the cross-linked polymer properties, other constituents may be included in the compositions: fillers, solvents, diluents, plasticizers, catalysts, accelerators, and toughenners.[3] In fact an optimal epoxy thermoset is designed for a specific application by tuning and optimizing the following criteria[3]:

- Selection of the proper combination of epoxy resin(s) and curing agent(s)
- Ratio of epoxy to curing agent
- Selection of catalyst/accelerator
- Curing and post-curing conditions
- Addition of formulation modifiers mentioned above

2.1.2 Synthesis

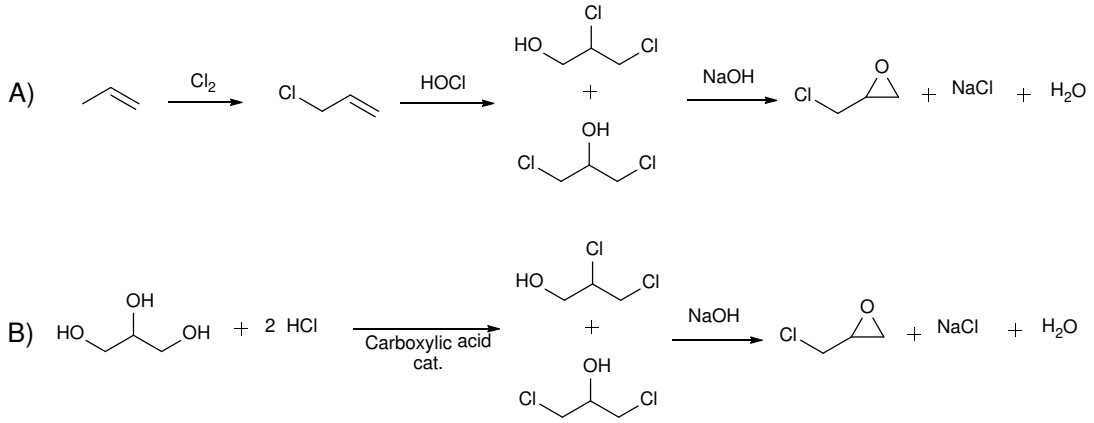
The first method to prepare epoxy-bearing compounds is the oxidation of C=C double bonds (**Scheme 1A**). It is usually achieved by the Prilezhaev reaction, that requires hydroperoxides, especially peracids[10]. They can be formed from the reaction of H_2O_2 with a carboxylic acid. The peracid is able to oxidize the double bond by a mechanism known as the “butterfly mechanism”[10]. Substrates include double bonds of unsaturated aliphatic or cycloaliphatic compounds[5] like limonene or triglycerides. Terminal alkenes are more difficult to oxidize than in-chain alkenes.[11] However, in-chain, di-substituted oxirane rings are less reactive than their terminal counterpart because of the steric hindrance induced by substituents.[12] Other peroxides, less environmentally-friendly, have thus to be used to prepare terminal epoxy, such as the meta-ChloroPerBenzoic Acid (m-CPBA). The hazardous nature of these techniques and the potential to hydrolyze the epoxide preclude their use on a large scale.[13]

It is also worth mentioning that the oxidation of allyl ethers to glycidyl ethers is usually not discussed in papers dealing with the preparation of epoxy compounds from alkenes. When mentioned, this reaction was found to give poor conversion.[14] Glycidyl ethers are interesting epoxy monomers and research on oxidation catalysts is underway[15], but this topic will not be further discussed here as it is outside the scope of this study.

Epoxides can also be formed by the reaction of hydroxyl-containing compounds with epichlorohydrin. Actually, this chemical is produced in such large volumes that other industrial epoxides are prepared from it, as depicted in **Scheme 1B**, which explains that so many of them are glycidyl ethers.

Scheme 1 : Main methods of preparation of epoxy resins

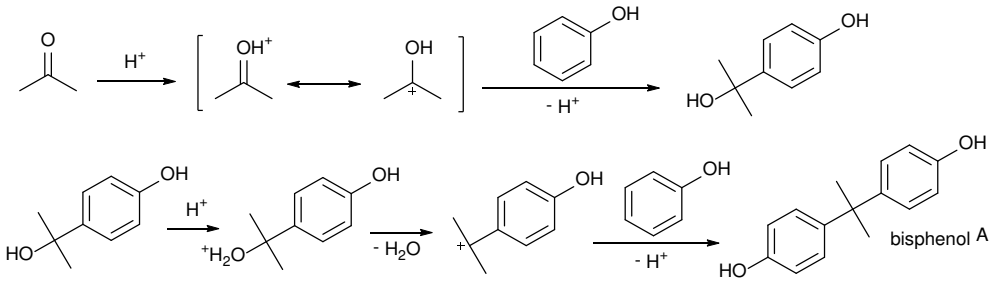
Epichlorohydrin is a liquid, highly reactive, toxic compound bearing an oxirane ring and produced in large quantities. The conventional process for epichlorohydrin production is the chlorination of propylene, followed by the chlorohydrination of the allyl chloride obtained[9] (**Scheme 2A**). The last step is the cyclization of the chlorohydrin formed in a basic medium.



Scheme 2 : Epichlorohydrin synthesis methods

However, Solvay or Dow Chemicals commercialize epichlorohydrin prepared from the chlorination of bio-based glycerol[16], a by-product of bio-fuels production (**Scheme 2B**). Epichlorohydrin, may it be petro- or bio-based, is a category 1B (presumed) carcinogenic compound according to EU regulations, as well as a category 2 reprotoxic and a category 1B skin corrosive compound.

The majority of industrial epoxy monomers and oligomers are prepared by a glycidylation reaction between epichlorohydrin and hydroxyl-containing compounds. These compounds are usually phenolics, as shown in Table 1. The phenol used for the preparation of more than 75% of the total volume of epoxy resins[3] is bisphenol A. Bisphenol A is an inexpensive, solid compound prepared from the condensation reaction of two phenol molecules with acetone under acid catalysis[17] (**Scheme 3**).



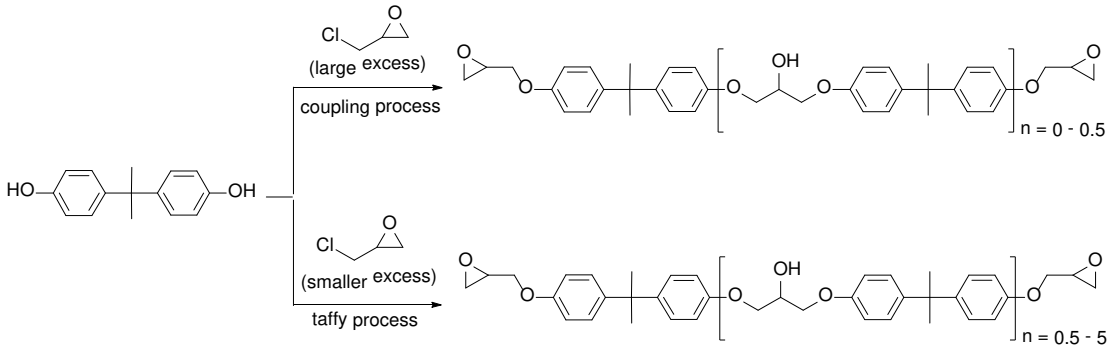
Scheme 3 : Bisphenol A formation mechanism from phenol and acetone

Bisphenol A is used in large-volume applications such as epoxy or polycarbonate polymers synthesis. It is prepared from phenol and acetone, two large-scale available compounds produced from cumene oxidation, which makes bisphenol A inexpensive. Another reason why this compound is so widely used for the synthesis of epoxy monomers is its ideal structure. Indeed, aromatic rings bring the rigidity and thermal resistance needed for epoxy polymers[7], and phenolic hydroxyls are easily reacted with epichlorohydrin to afford glycidyl ethers.

The example of bisphenol A-based epoxy pre-polymers will be developed in the rest of this paragraph, as it is the most representative. Typical monomers or pre-polymers (“resins”) are commercially available with n values lying in the range of 0.03 – 35. At room temperature, DGEBA monomer or pre-polymers

are crystalline solids for n values close to zero (the melting point of pure DGEBA is 43°C[3] and its T_g is -17°C[18]), liquids for n values up to n = 0.5, and amorphous solids (glass transition temperature, T_g in the range of 40 – 90 °C) for higher n values.[5].

The glycidylation reaction with epichlorohydrin is used to prepare low molecular weight epoxy pre-polymers. Two types of processes exist to prepare these pre-polymers of varying length (**Scheme 4**): the "coupling" and "taffy" processes.[9]

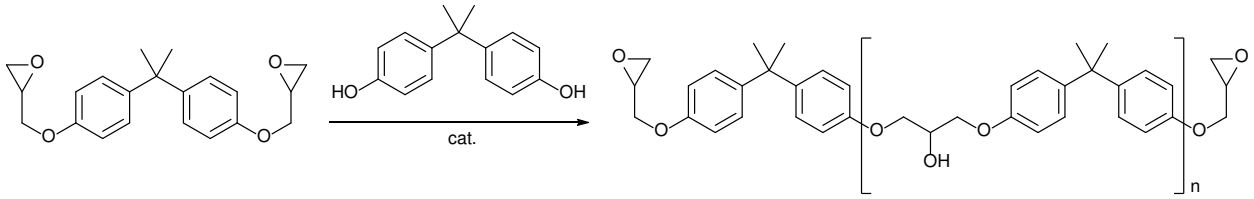


Scheme 4 : DGEBA pre-polymers syntheses from the « coupling » and « taffy » processes

The "coupling" process is used to prepare Liquid Epoxy Resins (LER), i.e. with low n value (of the order of 0.2).[9] The mechanism proceeds in two steps. The first one is the coupling of bisphenol A with epichlorohydrin to form a chlorohydrin intermediate, and the second one the closing of the oxirane ring by dehydrochlorination to afford the glycidyl ether.[19] The catalyst used can either be a base (typically $NaOH_{(aq)}$) or a phase-transfer catalyst (quaternary ammonium salts for instance).[9] More details on the mechanisms specific to each catalyst can be found in **Chapter 2**.To obtain a purely monomeric compound, epichlorohydrin is used in large excess: five equivalents of epichlorohydrin per phenolic hydroxyl give mostly the monomeric DGEBA.[9]

In the "taffy" process, lowering the excess of epichlorohydrin allows a control over the average chain length. This process is usually limited to the preparation of pre-polymers with up to about 5 repeating units.[9] Higher molecular weight species synthesis suffers from practical limitations of handling and agitation as the crude mixture consists of an alkaline brine solution and of an insoluble polymer.[9]

Higher molar mass epoxy pre-polymers are prepared by the "advancement" process. It consists of a chain-extension of an epoxy monomer or of a low molecular weight oligomer by its (poly)addition reaction with a diphenol as shown in **Scheme 5**[3]:



Scheme 5 : DGEBA chain-extension reaction

The reaction is performed at relatively high temperatures (150-190°C) in presence of a catalyst.[3] This catalyst can be an inorganic base, a tertiary amine, an ammonium salt, or (the ones usually preferred) an aryl- or alkylphosphonium salt.[3] The diglycidyl ether is usually introduced in excess to perform chain-extension while keeping epoxy chain-ends. The extent of reaction and thus the average chain length is

controlled by the ratio of the reactants, as in every step-growth polymerization reaction. The lower the excess of diepoxy to diphenol, the higher the molecular weight of the pre-polymers.[3] These epoxy compounds are then formulated and cross-linked with a hardener to give epoxy thermosets.

2.2. The cross-linking of epoxy thermosets

2.2.1 Curing agents

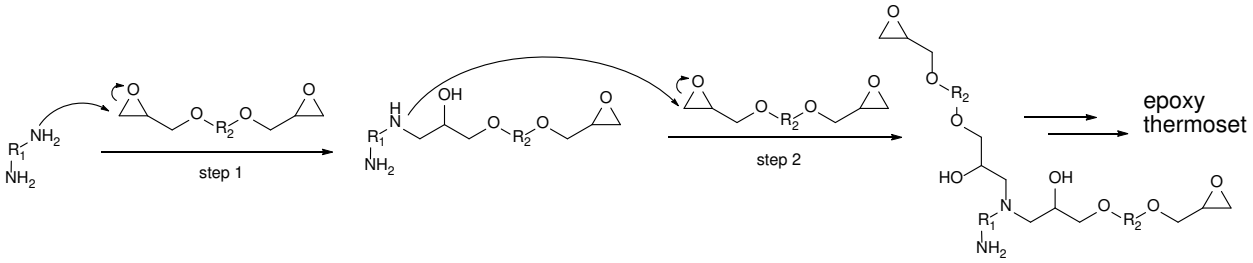
Many types of curing agents are available for epoxy resins due to their high reactivity. Indeed, the oxirane ring has highly strained bond angles, and the C-C and C-O bonds are highly polarized. The electron-deficient carbon can undergo nucleophilic reactions, whereas the electron-rich oxygen can react with electrophiles.[20] Selecting the proper curing agent is dependent on the requirements of the application process, pot life, cure conditions, and desired ultimate properties of the material. Curing agents are either catalytic or co-reactive.

A catalytic curing agent functions as an initiator for epoxy chain-growth polymerization.[5] They are usually Lewis acids (for instance, boron trihalides), or Lewis bases (for instance, tertiary amines)[5] and will not be discussed further here as this work is mainly centered on epoxy thermosets prepared with co-reactive hardeners.

A co-reactive curing agent acts as a co-monomer. The most common are amines, acids, and anhydrides and their mechanism of action will be described in the following sections. Other hardeners like phenolics, mercaptans, phenolic-, melamine-, and urea-formaldehyde resins, isocyanates, or cyanate esters[9] are also in use but will not be detailed here.

2.2.2 Amine hardeners

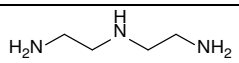
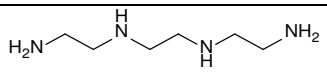
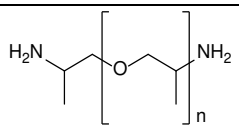
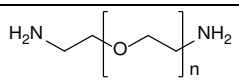
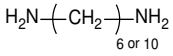
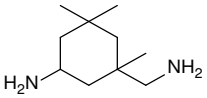
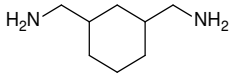
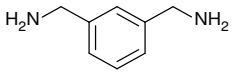
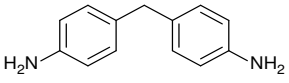
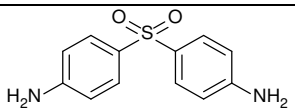
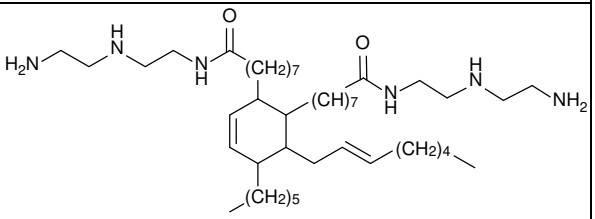
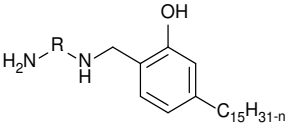
Amines are the most used of epoxy resin curing agents.[3] Primary amines can react in a two-step fashion with epoxides to form a cross-linked polymer as shown in **Scheme 6**. The first step leads to a secondary amine that can also react with one epoxy group. In the case of an aromatic amine, the secondary amine formed reacts 2 to 5 times slower than the primary amine.[20]



Scheme 6 : Synthesis of epoxy thermosets by epoxy-amine reaction

Many different amine hardeners are available commercially. Some of the main ones are summarized in **Table 2**:

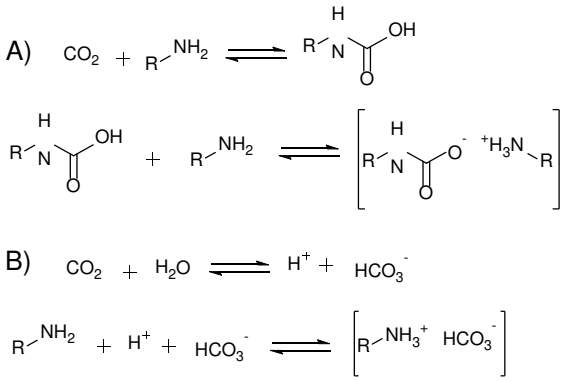
Table 2 : Examples of the most important amine hardeners available commercially and of some manufacturers.

Examples of manufacturers and commercial names	Name	Formula
Huntsman (Jeffamine) Dow Chemicals (D.E.R.) Hexion (Epon) BASF (Versamid, Baxxodur) Evonik (Vestamin, Vestamid) Croda (Priamine) Mitsui Chemicals	DiEthyleneTriAmine (DETA)	
	TriEthyleneTetrAmine (TETA)	
	PolyPropylene Glycol diamine	
	PolyEthylene Glycol diamine	
	1,6-hexanediamine or 1,10 decanediamine	
	IsoPhoroneDiAmine (IPDA)	
	1,3-bis(aminomethyl)-cyclohexane (1,3-BAC)	
	Meta-XylyleneDiAmine (MXDA)	
	Methylene DiAniline (MDA) or Diamino Diphenyl Methane (DDM)	
	DiaminoDiphenylSulphone (DDS)	
	Poly(amidoamines) (Example from dimer fatty acid and DETA)	
	Phenalkamine	

The reactivity of amines towards epoxides depends on their structure. The order of reactivity usually observed is the following: aliphatic > cycloaliphatic > aromatic.[20]

The hydroxyls formed during the process are also able to react with epoxy groups, but their rate of reaction is much lower, making this reaction marginal unless epoxy groups are introduced in excess.[20] The tertiary amines catalyze this reaction by abstracting the hydrogen of the hydroxyls.[3] Amine curing rate can also be enhanced by adding hydroxyl-containing accelerators such as phenolics[21], aryl alcohols or poly-functional alcohols. These compounds form tri-molecular complexes by hydrogen bonding with the oxygen of the epoxy group[20], making the oxirane carbons more electrophilic. Amines react then faster. Hydroxyls are formed during the polymerization reaction upon oxirane ring-opening, making this reaction self-catalyzed.[20]

Amine cross-linked systems are resistant to saponification but less so to oxidation.[3] Aliphatic amines display such a good reactivity that room temperature curing is possible[22], making them suitable for applications such as adhesives or coatings. However, they also display a high peak exotherm and are strongly irritant.[22] One drawback of amine hardeners, especially low molecular weight aliphatic primary amines, is their tendency to undergo carbonation reactions in presence of atmospheric carbon dioxide. Industrially, this reaction is referenced as “blushing”[8]. In fact this phenomenon consists in two reactions[23]. The first one (**Scheme 7A**) is the reaction of one equivalent of carbon dioxide to two equivalent of amine to form an ammonium carbamate. The second one is the addition to an amine of one equivalent of hydrogen carbonate, formed from CO_2 in presence of water, to afford ammonium hydrogen carbonate (**Scheme 7B**).



Scheme 7 : Carbonation reactions of primary amines

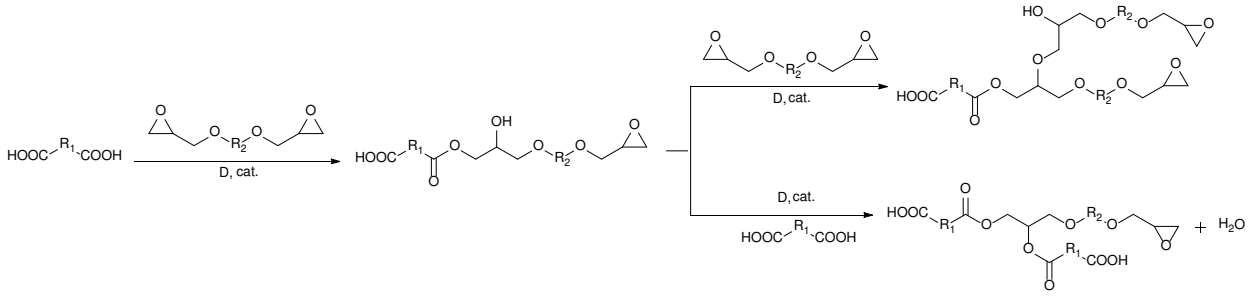
Aromatic amines give thermosets with high thermal and chemical resistance and they have a longer pot-life with reduced exotherm[22], but some of them are toxic[24], and they require high temperatures or catalysts[22]. Indeed, the reaction of amines onto epoxides is a nucleophilic attack; sterically hindered reactants are less reactive. The polymers prepared from them can also have color stability problems.

Many other amine hardeners exist such as amidoamines (prepared by the reaction of an excess of (poly)amine onto a carboxylic acid), amine adducts (excess of a poly(amine) onto an epoxy-containing compound), phenalkamines (prepared via a Mannich reaction, see **Section 3.1.2.2**), ketimines, dicyandiamide (2-cyanoguanidine) etc. All these species possess a real industrial relevance but detailing their respective mode of action, advantages and drawback would be a lengthy task out of the scope of this work. For more information, the reader is referred to the relevant literature.[3, 8, 22]

2.2.3 Acid hardeners

Carboxylic acid hardeners are usually produced by reaction of an excess of an anhydride or a multi-functional acid on a poly-alcohol.[3] By changing the nature of the reactants, the properties of the acid-terminated hardener can be changed (MW, viscosity, mechanical properties of the final material etc.).[3] Thus, they are especially well-suited to coatings, in which their properties are easily adapted to the application. They are also relatively cheap. Acid hardeners have been growing rapidly in powder coatings formulations with epoxy resins.[9] This is driven in part by the versatility and cost efficiency of acid–epoxy powder coatings. Emerging markets for these powder coatings include automotive and wood coatings.[9]

The mechanism of epoxy-acid curing is described in **Scheme 8**[20]:



Scheme 8 : Synthesis of epoxy thermosets by epoxy-acid reaction

The ester moieties formed can also be the subject of trans-esterification reactions with free hydroxyls.[20] This reaction was recently cleverly used to prepare epoxy thermosets that, despite being cross-linked, could be re-processed owing to the mobility brought by these exchange trans-esterification reactions.[25]

One drawback of acid hardeners is their rather low reactivity, which implies high curing temperatures[26] (> 100°C) and/or the systematic use of catalysts. Compounds such as tertiary amines and phosphonium salts catalyze these reactions.[9] Upon esterification of hydroxyl and acid moiety water is produced. This condensation by-product must be eliminated during the curing process to avoid coating defects.[9]

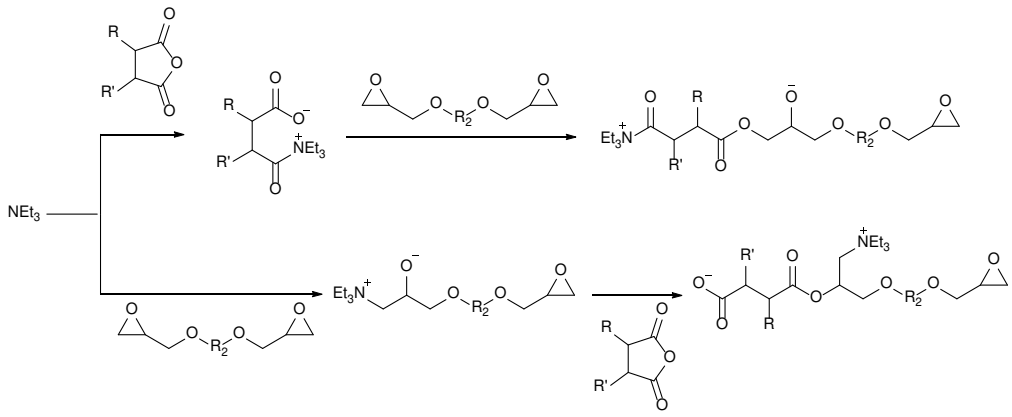
2.2.4 Anhydride hardeners

Anhydrides are the second most important class of epoxy hardeners. They are in fact cyclic anhydrides and have been successfully replacing more toxic aromatic amines in composites. They are very scarcely used in coatings but account for 70% of the volume of curing agents used in structural composite applications.[9] Their excellent dielectric properties also make them suitable for Printed Circuit Board (PCB) laminates.[9] Maleic, phthalic, and hexahydrophthalic anhydrides are for instance used for electrical or high-temperature applications.[22] They are also resistant to oxidation, but less so to moisture, especially in the presence of basic components.[3] As carboxylic acid-terminated polyesters, anhydrides are used in heat-cured applications only because of their slow curing at temperatures below 200°C.[3]

Anhydrides require thus the use of Lewis acid or base catalysts that will play the role of initiators. Indeed, contrary to amines or acids, the polymerization reaction with anhydride hardeners takes place through a chain-growth mechanism instead of a step-growth mechanism.[20] Commonly used initiators include tertiary amines (ex. benzyldimethylamine[22]), imidazole, or ammonium salts for anionic chain

polymerization, and boron trifluoride complexes, complex aromatic salts of Lewis acids such as diaryl iodonium, triarylsulfonium, or arene diazonium for cationic chain polymerization.[5]

A post-cure is often needed to reach the excellent thermo-mechanical properties generally displayed by epoxy-anhydride polymers.[3] On major advantage of epoxy–anhydride systems is their low exothermic heat of reaction, which enables large reaction masses.[9] The first steps of the curing process (initiation) are illustrated in **Scheme 9** with the example of triethylamine as catalyst[5, 27]:



Scheme 9 : Initiation step of epoxy thermoset synthesis by the epoxy-anhydride reaction

The next steps (propagation) consist either in the reaction between a carboxylate and an epoxy group (slow) or between an alkoxide and an anhydride (fast)[20]. The overall curing mechanism is thus a chain-growth co-polymerization. The rate difference between these reactions explains the alternating sequence.[28, 29] In case of an excess of epoxy, etherification can also be observed by reaction of an alkoxide onto an epoxy group (homopolymerization).[9]

2.3. Current industrial challenges for epoxy polymers

2.3.1 Bisphenol A substitution

Many vastly different properties are needed for epoxy thermosets, which depend upon the application. These properties can be tuned by the choice of hardener, but also by the choice of epoxy pre-polymer. Still, as mentioned, 75% of the epoxy pre-polymers are based on one single molecule: BisPhenol A (BPA). Interestingly, bisphenol A was first studied as a synthetic estrogen and since then is a well-known endocrine disruptor.[30] Many debates took and are taking place on how exactly it affects our health (infertility, diabetes, cancer, obesity, etc.).

Regulations on the use of this compound have been issued in many instances. The most notable ones include the European regulation N°321/2011 prohibiting the use of BPA for the fabrication of baby feeding bottles, and in all food-contact applications for infants in Denmark (2010, Belgium, Sweden (2012), and France (2013). In a January 2015 report, the European Food Safety Authority (EFSA) comprehensively re-evaluated BPA exposure and toxicity and concluded that “BPA poses no health risk to consumers of any age group at current exposure levels”.[31] However, these new data and refined methodologies have led EFSA’s experts to considerably reduce the safe level of BPA from 50 to 4 micrograms per kilogram of body weight per day.[31] Also, the Risk Assessment Committee of the European Chemical Agency (ECHA) issued a favorable opinion for the change of BPA labelling from reprotoxic category 2 (suspected) to category 1B (probable).[4] The official text is to be published in

November 2015. Also, France adopted the 1st of January 2015 a regulation prohibiting all BPA-containing food-contact packaging. The envisaged substitutes for BPA are BisPhenol F (BPF) and BisPhenol S (BPS). However, concerns over these compounds are the same than for BPA: they are also endocrine disruptors, as concluded from a recent literature review on the topic.[32]

Thus, this topic is a burning issue and there is a growing need for bisphenol A substitutes. From an industrial point of view, it is definitely a challenge, but could also be considered as an opportunity. Indeed, new monomers will be needed to substitute, for instance, DGEBA in epoxy polymers. These new monomers should be designed while bearing the green chemistry principles in mind. For instance why not prepare substitutes of bisphenol A-based epoxides that would also be based on renewable resources and kill, so to say, two birds with one stone? Of course, the safety, price, and performance would also be part of the equation.

2.3.2 Commercial bio-based epoxy resins

Reducing the dependence to fossil chemicals by implementing industrial bio-based solutions is currently the other great challenge for epoxy polymers. Some solutions are already commercial like Vikoflex from Arkema[33], based on epoxidized vegetable oils, some products of the Denacol series from Nagase ChemTex, based on glycidylated sorbitol, glycerol, or isosorbide[34]. Products from specific renewable resources are usually destined to be mixed with other epoxy monomers or pre-polymers in order to meet the needs of the application envisaged. Solutions from less well-defined raw materials are also available. Sicomin proposes the products Greenpoxy, especially adapted to laminate applications. The company claims that more than 50% of the product is derived from renewable resources.[35, 36] Tannin, lignin, and vegetable oils are cited as the starting materials. Another example of a bio-based epoxy solution is the product Super Sap from Entropy Resins. The product disclaimer mentions a 50% reduction of the greenhouse gas emissions. The raw materials are “co-products or from waste streams of other industrial processes, such as wood pulp and bio-fuels production”[35, 37]. Another good example of an epoxy pre-polymer based on renewable resources is the EpoBioX product.[35] The technical datasheet is available from Amroy Europe Oy. EpoBioX is designed for the composite industry, especially for windmill blades. The data sheet mentions more than 70% of renewable carbon and a product constituted for example of epoxidized pine oil waste. One can note that most of the products available are based on aliphatic or cyclo-aliphatic structures.

A great deal of research was and still is performed on the use of renewable resources to prepare epoxy polymers. Comprehensive works reviewing this subject are available in the literature[7, 38-42]. Many of these works also deal with aliphatic or cyclo-aliphatic structures. As mentioned in the introduction, the approach of this work is centered on the use of aromatics, more particularly phenolics, from natural resources in order to take advantage of the rigidity and thermal stability of the benzenic ring and impart good thermo-mechanical to the epoxy polymers. Also, as mentioned in the literature[43], phenolic epoxides are usually preferred due to their inherent thermal stability and moisture resistance. Therefore the next section is dedicated to (poly)phenolics from renewable resources and their use in epoxy polymers.

3. Phenolics from renewable resources

The three major classes of phenolics from renewable resources are tannins, lignin and Cashew NutShell Liquid (CNSL)[44]. There is a striking paradox between the enormous amount of (poly)phenolic materials found in Nature and their relatively under-developed industrial use for the preparation of bio-based epoxy polymers – or polymers in general – compared to aliphatic resources like vegetable oil. In terms of research, a respectable amount of work has been accomplished and this section deals with these three types of phenolics and their use in the field of epoxy thermosets.

3.1. Cashew NutShell Liquid

3.1.1 Description and sourcing

The liquid contained within the shell of the cashew nut is called "Cashew Nut Shell Liquid" (CNSL) and is a by-product of the cashew industry. Cashew nuts themselves grow on trees, Anacardium occidentale, native from Brazil and abundantly available in many parts of the world such as Brazil, India, and South-East Asia.[45] CNSL is constituted of long-chain hydrocarbon phenols and constitutes 18 – 27% of the total raw nut weight.[46]

Natural CNSL contains mainly four components as shown in **Figure 2**[47]: anacardic acid (74-77%), cardanol (1-9%), cardol (15-20%), and 2-methyl cardol (1-3%). They are all phenols with a long hydrocarbon side-chain at the metaposition. The components of CNSL are themselves mixtures of four compounds differing in the side chain unsaturation, namely saturated (5 – 8%), mono-ene (48 – 49%), di-ene (16 – 17%) and tri-ene (29 – 30%).[46]

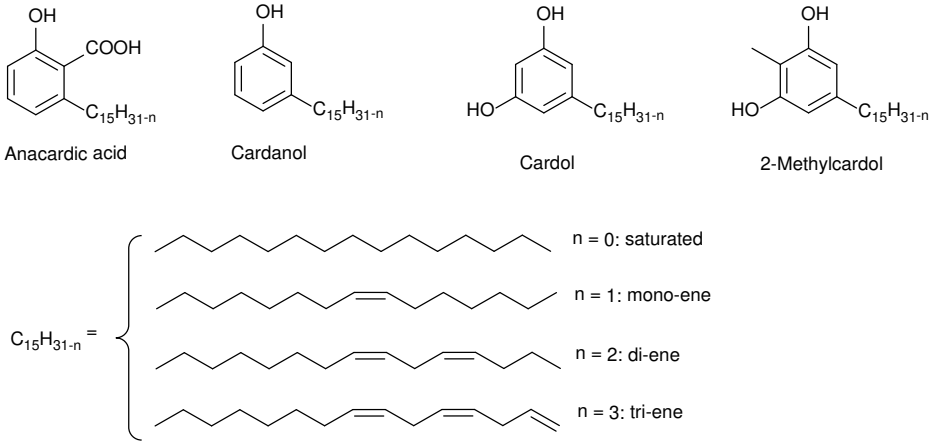


Figure 2 : CNSL different constituents

Commercial-grade CNSL contains hardly any anacardic acid because during the process, it is converted to cardanol by decarboxylation upon heating.[47] Cardanol itself is obtained by distillation of CNSL.[45] Additionally, CNSL or cardanol can also be readily hydrogenated to give the corresponding saturated hydrocarbon chains.[45] Commercial suppliers of CNSL include Cardolite Corporation, world leader in developing and manufacturing products from CNSL, Palmer International in North America and several companies in India and Brazil mostly.[45] The potential of CNSL is about 450 000 tonnes per year.[46] In terms of actual production, India is the first manufacturer with a production capacity over 20,000 tonnes

per year and around 10,000 tonnes per year exported.[48] The CNSL international price is around US$300/ton, and cardanol is worth US$ 3000/ton in the world market.[49]

3.1.2 Uses in epoxy thermosets

3.1.2.1 As epoxy resins

Cardanol, through its interesting structure, offers different possibilities as a chemical building-block for monomer and polymer synthesis and its use has been the subject of many investigations.[45] As an example, cardanol-based novolac resin, which structure is depicted in **Figure 3A**, can be prepared from the condensation reaction between cardanol and formaldehyde. They can serve as pre-polymers for the synthesis of phenol-formaldehyde-type thermosets.

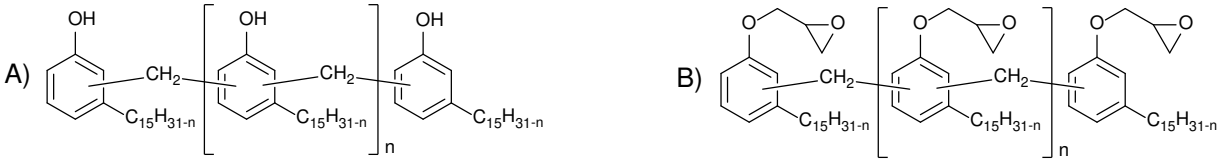


Figure 3 : Cardanol-based novolac resin and cardanol-based epoxy novolac pre-polymer

These novolac resins, reacted with epichlorohydrin, lead to the formation of epoxy novolac pre-polymers as shown in **Figure 3B**. These products are commercialized by Cardolite under the name NC-547.[50]
Other ways to prepare epoxides from cardanol can be found in the literature, for instance by simple glycidylation of the phenolic hydroxyl, one can obtain a reactive diluent bringing flexibility and water resistance. This product is already commercial, for instance from Cardolite under the name NC-513.[50]
In order to obtain an epoxy functionality higher than 1, various methods are described in the literature, all taking advantage of the C=C double bond(s) along the alkyl chain. A first method consists in the phenolation of these unsaturations and subsequent glycidylation of the phenolic hydroxyls (example of structure **Figure 4A**). The product obtained is commercially available under the name NC-514 from Cardolite.[50] This product has been employed in a number of studies dealing with bio-based epoxy polymers[51-53]. However, this commercial product has been demonstrated to not have the structure proposed by the supplier, but to be partially oligomerized.[54, 55]

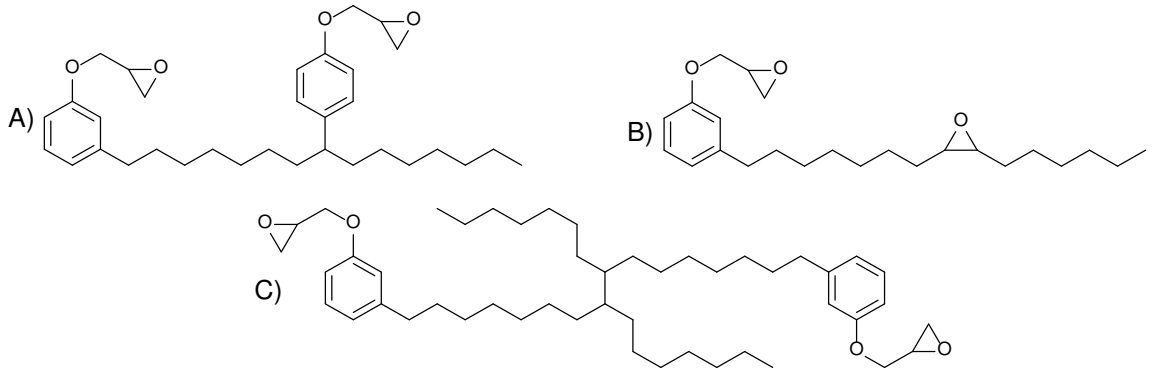


Figure 4 : Structures of different epoxy pre-polymers prepared from cardanol

Another method consists of the glycidylation of the phenolic hydroxyl, followed by the oxidation of the unsaturations along the cardanol chain[56, 57]. Like in the case of vegetable oils, peracids can be used to perform this reaction and alkyl-substituted oxirane rings are then formed. The epoxy groups borne by

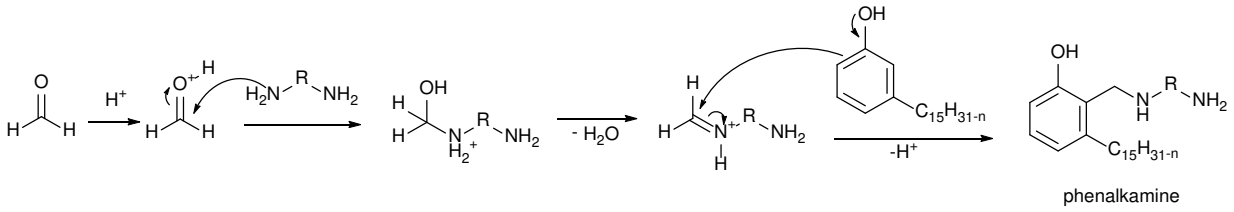
the monomer formed (example of structure **Figure 4B**) are different and thus will not have the same reactivity. In one of these studies[57], the authors mixed this pre-polymer with various amounts of DGEBA and studied the properties of the thermosets obtained after curing with the phthalic anhydride (hardener)/trimethylamine (catalyst) system.

The synthesis of a pre-polymer from mono-glycidylated cardanol was also reported[58], (example of structure **Figure 4C**). The authors reported an increase of molecular weight and a decrease of the amount of unsaturations when the mono-glycidylated cardanol was subjected to a high temperature (160°C) under air (oxidative conditions). The oligomerization did not occur under nitrogen. They concluded that the oligomerization reaction proceeded through auto-oxidation of the side-chain unsaturations.

It must be emphasized that CNSL-based epoxy resins give in every case thermosets with low Tg compared to the traditional DGEBA. This is due to the long alkyl chains that bring flexibility to the network.

3.1.2.2 As hardeners

The main epoxy thermosets curing agents from CNSL are phenalkamines. Phenalkamines are the product of a Mannich reaction between cardanol, formaldehyde, and a multi-functional amine.[59] The reaction scheme is depicted in **Scheme 10**:



Scheme 10 : Mannich reaction on cardanol

As mentioned, phenolic hydroxyls are catalysts for the epoxy-amine reaction. Cardanol-based phenalkamines inherently possess a phenol and thus display fast curing properties, even below 0°C.[60] The aromatic ring ensures a good chemical resistance. They also have a good surface appearance and non-blushing properties.[60] The aliphatic side-chain of cardanol brings hydrophobicity, thus the good water resistance displayed by these phenalkamines, which can be applied under wet or humid conditions even on a wet or damp surface.[61] However, phenalkamines suffer from the disadvantage that the cured epoxy products are very dark in color. Furthermore, the phenol hydroxyl in phenalkamines will be oxidized by air, and the formation of quinonoid chromophoric groups causes bad color stability.[61]

It is worthy to note that an interesting amine hardener completely different from phenalkamines has been prepared from cardanol.[62] The phenolic hydroxyl was functionalized with allyl bromide in a first step. In a second step, a thiol-ene reaction was performed to graft cysteamine molecules onto the unsaturations of the allyl phenol and of the side-chain, leading to the structure depicted in Figure 5:

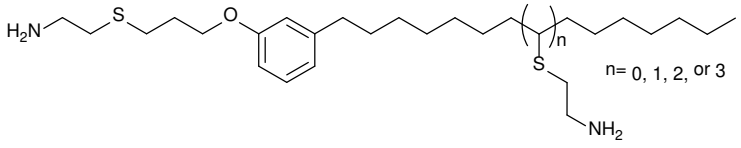


Figure 5 : Preparation of a cardanol-based amine hardener *via* allylation followed by thiol-ene reaction with cysteamine

CNSL and cardanol have already found applications as bio-based raw materials for epoxy thermosets. Phenalkamines from a variety of different amines are commercial products available from Cardolite, although it is worth mentioning that the formulated curing agents sold as phenalkamines include also free amines. They suit perfectly certain applications, for instance in on-site marine coatings and concrete deck applications.[3] Their excellent water resistance and fast cure properties are the main reasons why. However, in some other applications, these cross-linkers are not suitable. For instance, in demanding thermo-mechanical applications, like structural composites, the final material does not display a Tg sufficiently high.[63] Aromatic rings bring this rigidity and stability, and even if cardanol bears a phenolic moiety, these properties are out-balanced by the long alkyl chain. Their color and poor color stability is also a problem in many applications.

Besides these structural drawbacks, a non-negligible part of the CNSL-based products for epoxy formulations, like phenalkamines or cardanol-based epoxy novolacs, are prepared by condensation with formaldehyde. Formaldehyde is a category 1B carcinogenic and category 2 mutagenic compound according to European regulations, and formaldehyde-free polymers are currently being actively investigated in the context of green chemistry.

Thus, even if cardanol is close to ideal as a raw material in some low Tg applications, other phenolics from renewable resources have to be used to unlock the whole spectrum of properties - especially high glass transition temperatures - for bio-based epoxy thermosets.

3.2. Tannins

3.2.1 Description and sourcing

Tannins are polyphenolic compounds, non-hazardous, and are able to bind and precipitate proteins.[64] The term “tannins” originates from the use of theses compounds for the tanning of animal hides into leather. Indeed the tannin-rich bark of oak, chestnut, mimosa, or quebracho trees have traditionally been used for leather tannin.[65] Tannins are abundant in many different plant species and contrary to lignins, tannins are mainly situated in the soft tissues of the plant such as such as leaves, needles, bark, seeds, and fruits.[66] They are thought to play a role in the defense mechanisms of the plant against insects or fungi.[67] Tannins can be classified in four broad families, differing by their macromolecular structures[66, 67]. The hydrolysable tannins have a molecular weight of a few thousands grams per mole and their structure consist mainly in a D-glucose core esterified by gallic acid or ellagic acid molecules (**Figure 6A**).[44] Condensed tannins, also named proanthocyanidins, are biopolymers with a higher molecular weight than hydrolysable tannins. They are built on a variable number of flavan-3-ol subunits (**Figure 6B**), mostly (-)-epicatechin and (+)-catechin.[66] Complex tannins comprise both esterified gallic/ellagic acids and a flavan-3-ol unit condensed on the core sugar.[64] Phlorotannins are somewhat different. They are found in brown algae in which, among many other roles, they act as structural components of cell walls.[68] They are oligomers arising from the condensation of phloroglucinol (1,3,5-trihydroxybenzene) molecules[67], as exemplified by the eckol structure (**Figure 6C**).

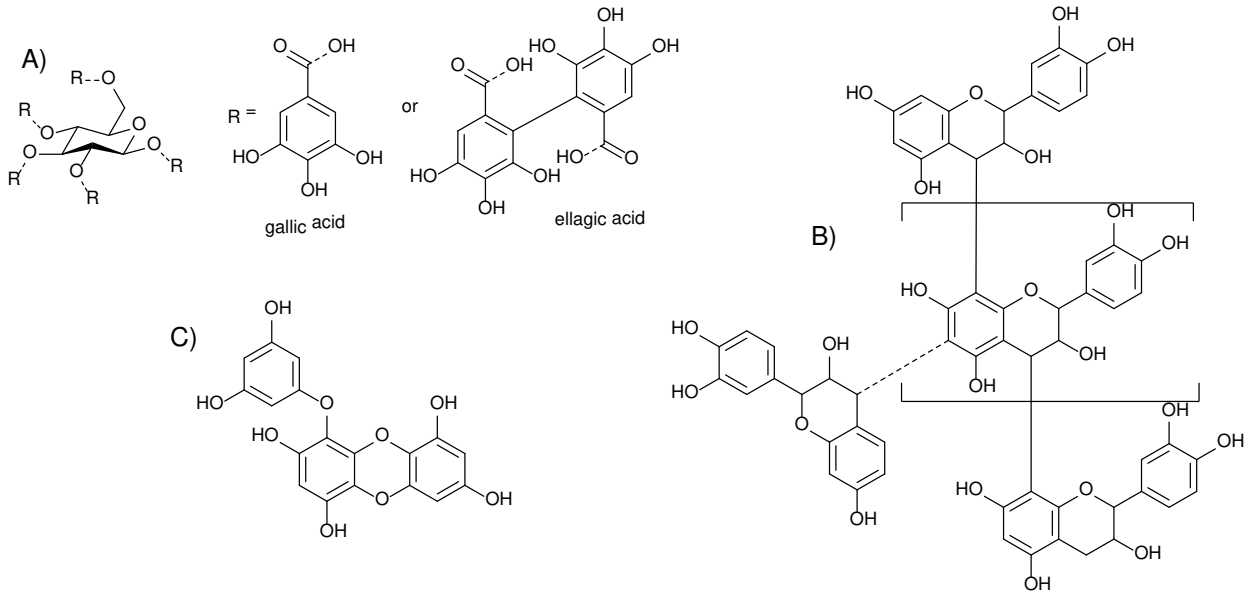


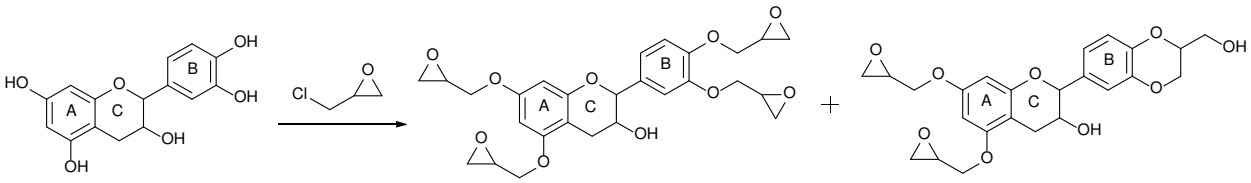
Figure 6 : Typical structures of hydrolysable- (A), condensed- (B) and phloro-tannins (C)

The most abundant polyphenols are the condensed tannins, found in virtually all families of plants, and comprising up to 50% of the dry weight of leaves. They account for more than 90% of the total world production of commercial tannins (2.10^5 tons per year).[44] Extraction yields vary a lot depending on the method[69] and the species. Commercial tannin price varies between 0.7 and 1.5 € kg^{-1}.[67]

3.2.2 Uses in epoxy thermosets

3.2.2.1 As pre-polymer

Only few teams tried to prepare epoxy pre-polymers from tannins. Still, a handful of reports are available in the literature and the use of tannins for the preparation of epoxy pre-polymers was even patented.[70] Aouf et al. thoroughly investigated the reaction of epichlorohydrin with various phenolic structures in order to understand the reactivity of tannins towards glycidylation.[19] One of their major finding is that an aromatic ring substituted with two phenolic hydroxyls in the ortho position did not fully undergo the glycidylation of both phenols, but also formed benzodioxane structures from an internal cyclization of epichlorohydrin (**Scheme 11**), which gave an amount of epoxy groups lower than expected. Catechin is a good model compound for condensed tannins (**Figure 6B**). The same team also studied catechin glycidylation[71, 72] and detected the formation of the same benzodioxane structure on the B ring of catechin as depicted in **Scheme 11**.

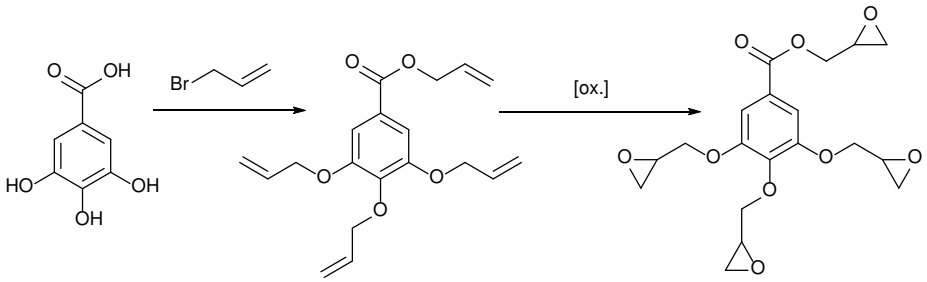


Scheme 11 : Catechin glycidylation products

Authors used the mixture of epoxy monomers prepared as a partial replacement of DGEBA to prepare an epoxy polymer by reaction with an amine hardener.[71] Thermo-mechanical characteristics were comparable to the purely DGEBA-based materials. In another contribution, the epoxy pre-polymer was

fully based on catechin and cross-linked with IsoPhoroneDiAmine (IPDA), which gave thermosets with a high Tα of 179°C.[72]

Concerning hydrolysable tannins, a good model compound is gallic acid (**Figure 6A**). Direct glycidylation with epichlorohydrin and a phase-transfer catalyst, a protocol described in a 1983 patent[73], afforded good results when re-done with better characterization of the products.[71] The addition occurs on both the carboxylic acid group and at least one phenol group. However, all hydroxyls could not be glycidylated and the average epoxy functionality was close to 2.[7] The formation of benzodioxane products was not detected in this case. To obtain an epoxy monomer of higher functionality, another glycidylation method was used. This method consists of the tetra-allylation of gallic acid followed by the oxidation of the allyl groups as shown in **Scheme 12:**



Scheme 12 : Synthesis of tetra-glycidyl ether of gallic acid by allylation followed by oxidation

This oxidation can be performed by using lipases as biocatalysts[74] or with usual organic peroxide such as m-CPBA.[75] In this last work, epoxy polymers were prepared by cross-linking the poly-functional, gallic acid-based epoxy monomer synthesized with IPDA. Its high functionality afforded a thermoset with a high Tα of 233°C. These works based on model compounds bring useful information on whether the preparation of epoxy pre-polymers from tannins is a viable approach or not. Other works dealt with the preparation of epoxy pre-polymers from real tannins. Epoxy pre-polymers were prepared from green tea tannins[72], mainly composed of epigallocatechin gallate, from tara tannins extract[76], or from beetle-infested pine bark.[77] In all cases the thermosets prepared displayed good thermo-mechanical properties, comparable to petroleum-based epoxy polymers. Tannins can even impart specific additional properties to epoxy thermosets, highly desirable from an applicative point of view. For instance, the use of hydrolysable tannin-epoxy resins with good thermal and electrical properties was patented as semi-conductor encapsulants. The advantage brought by hydrolysable tannins consists in an easy acid- or alkali-mediated decomposition of the epoxy thermoset, which allows the recovery of the semi-conductor.[78] Another example is the use of polyglycidyl ether of gallic acid, prepared by the same method as shown in **Scheme 12**, that enhanced the dispersion properties of graphene sheet in a DGEBA matrix.[79] This better dispersion impacted positively many properties of the composite and suppressed the need for chemical modification of graphene, which made this composite more environmentally-friendly.

3.2.2.2 As hardener

Tannins are poly-phenolic compounds and as such can be used to cross-link epoxy resins. Shibata et al. published various works in which they prepared various epoxy composites from bio-based resources.[80-82] More precisely, the hardener they used was tannic acid (**Figure 7A**), reacted for 3 hours at 160°C.

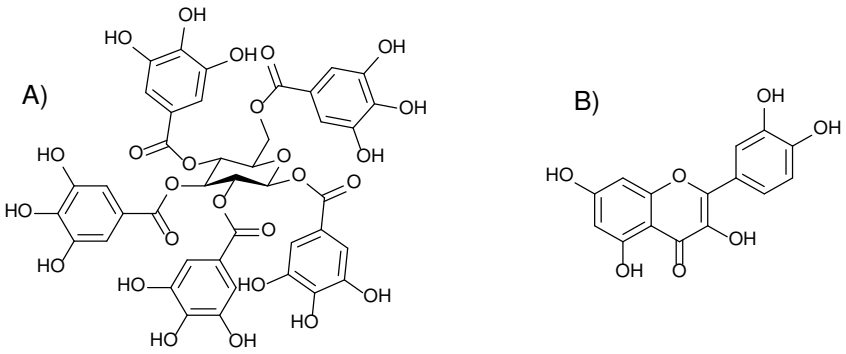


Figure 7 : Structures of tannic acid (A) and quercetin (B)

The authors obtained the highest Tg with a hydroxyl-to-epoxy ratio of 1.4, which shows that not all the phenols react, most likely due to steric hindrance. Nevertheless, cross-linked materials with relatively high Tα and excellent mechanical properties were obtained. These good properties were also due to a good compatibility between the matrix and the reinforcement in the final composite. Wood flour and micro-fibrillated cellulose were used as particle reinforcements and tannic acid is believed to increase the matrix-particle compatibility through unreacted phenolics and weak interactions. In an another interesting work, the same team also used quercetin (**Figure 7B**), which structure is close to catechin, as a hardener to cross-link sorbitol poly(glycidyl ether). This thermoset was used as a matrix for the preparation of fully bio-based composites with wood flour.[82] The authors compared the properties of the matrix cured with quercetin with one cross-linked with a petro-based phenol Novolac and showed that the fully bio-based materials displayed comparable thermal and mechanical properties.

Concerning real condensed tannin, some contradictory information is available in the literature. On the one hand, Aouf et al. mention, in a contribution dealing with condensed tannin depolymerization, that the synthesis of epoxy pre-polymers from real depolymerized condensed tannins was not successful.[83] On the other hand, Soto et al. concluded that condensed tannins indeed react with epoxy resins.[84] However, they also mention that the reaction rate is dependent of the experimental conditions, and of the epoxy pre-polymer used. Finally, powdered epoxy thermosets hardened with tannins were used as chelating polymers for the removal of metals in aqueous solutions.[85]

The approach is based on the chelating properties towards metal ions of the unreacted tannin phenolic hydroxyls. The authors studied the influence of different parameters and found good chelating properties. Unfortunately, the synthesis is poorly described and neither the type of tannin used nor the epoxy resin nature is known.

3.2.3 Problems associated

Tannins are the second most abundant source of natural aromatics. However, they suffer from some drawbacks mainly linked to their very nature. Indeed, tannins chemical structures are usually complex and thus difficult to characterize.[86] Moreover, a plethora of different structures co-exist[66], which adds even more to the complexity. The raw material can vary in nature, composition, and properties depending on the nature of the plant, the part harvested (leaves, bark etc.), the extraction method etc.[67] The extraction itself is a very complex process and the yield can be poor if the process conditions are not finely tuned[87]. All of these drawbacks make tannins commercial availability more limited than

what could be expected from their natural abundance. Finally, they are usually solids, which is not ideal for an application in epoxy polymers.

Glycidylated tannins are also usually solids or highly viscous materials, which limits their processability. They can also be tricky to synthesize and characterize owing to their complex structures, potential side-reactions[71], or even non-reactivity towards glycidylation, especially for condensed tannins.[83] All these issues could be circumvented by process optimization. However, tannin products with constant properties, which would be a necessary condition for their commercialization, are still far away because of the variability in both chemical structures and feedstock, and limited availability.

3.3. Lignin

3.3.1 Description and sourcing

Lignin is a phenolic macromolecule that accounts for roughly 15–30% of the dry weight of lingo-cellulosic biomass.[88] It is thus the second most abundant biopolymer in Nature and the biggest source of renewable aromatics.[89] Lignin binds cellulose micro-fibrils to hemicellulose and is thus responsible for the structural integrity and stiffness of the plant.[90] As such, it is a by-product of the pulp and paper industry[91], pulping being the extraction and separation of cellulose fibers from other components of the wood. Large volumes of lignin are thus produced industrially[91].

Lignin is a random, three-dimensional network composed of three types of phenylpropane units[92]: p-hydroxyphenyl (H) unit, guaiacyl (G) unit, and syringyl (S) unit. These units originate from the three monolignols depicted in **Figure 8A**:

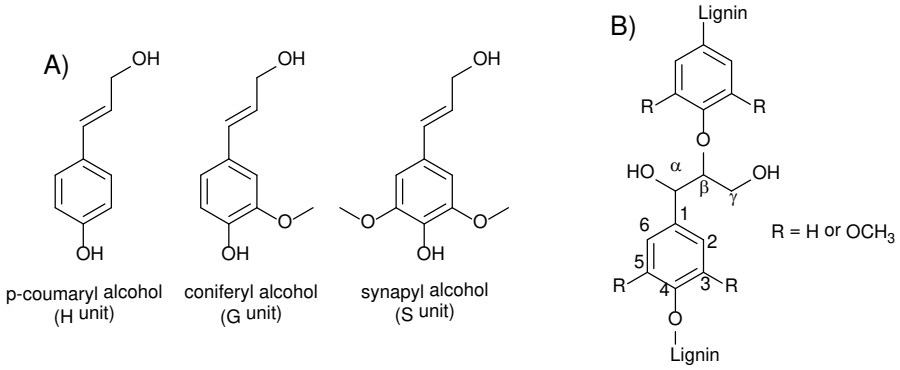


Figure 8 : Lignin monolignols (A) and a β-O-4 linkage (B)

The lignin structure depends on the nature of the wood, or plant, considered. Indeed, the type of bonds present in the lignin structure, as well as their relative proportions, can vary. The most frequent type of bond encountered is the the β-O-4 linkage shown in **Figure 8B**, with around 50% of the bonds.[91]

The same variability is observed concerning the relative proportions of H, G, and S units in the lignin. This last parameter can generally be linked to the nature of the wood. These units are variously linked together and the β-O-4 linkages (**Figure 8B**) are the most frequent, with around 50% of the linkages.[90, 91] Indeed, 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 low amounts of H units, and are called GS lignins. Lignins that include significant amounts of H units are called HGS lignins. Plants like sugar cane, bamboo, grass,

palm trees, or banana plants produce such lignins. The relative frequency of the different units is summed up in **Table 3**, adapted from[90, 93, 94]

Table 3 : Amount of H, G, and S in the different lignin types

Type of lignin	H unit	G unit	S unit
G lignin	<5%	>95%	/
GS lignin	0-8%	14-50%	46-84%
HGS lignin	5-51%	33-80%	9-55%

An example of a possible structure of G lignin is depicted in **Figure 9**.[90] This structure also displays other possible linkages than β-O-4.

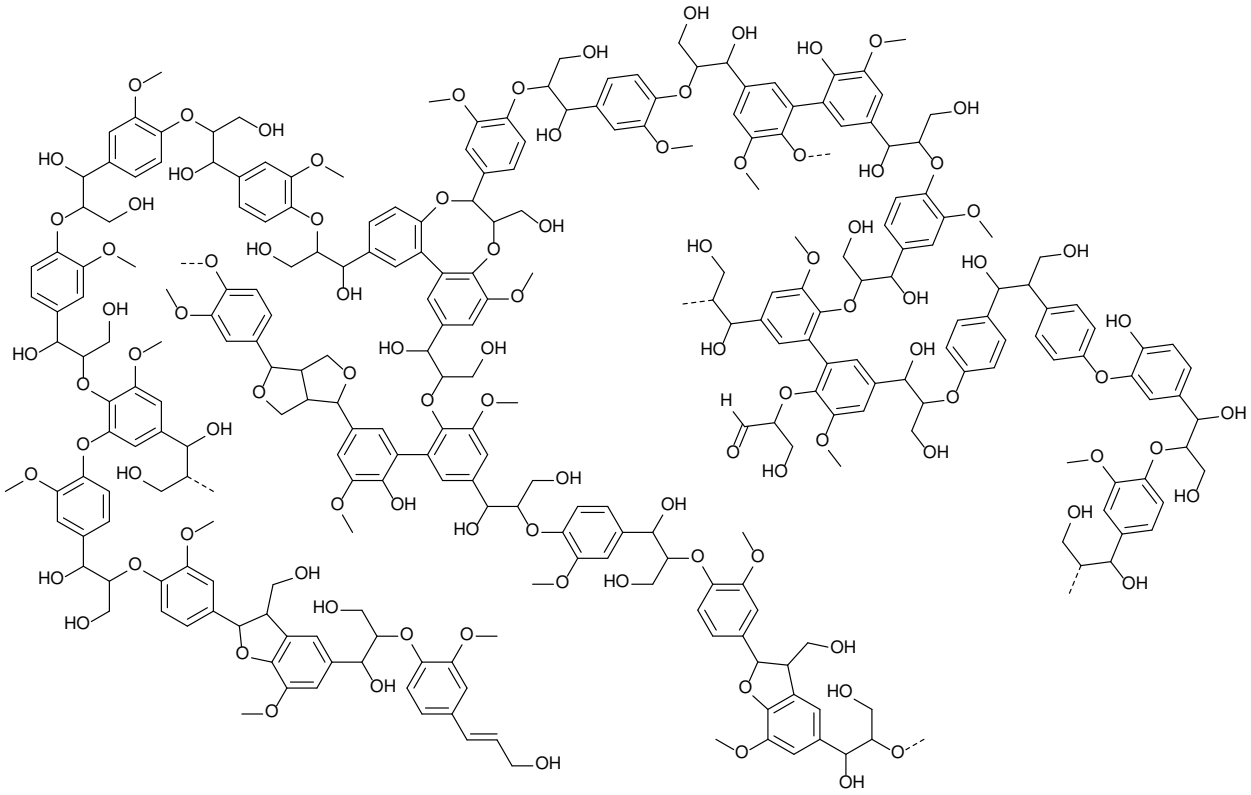


Figure 9 : Possible structure of G lignin

Industrial lignins usually have different structures from the native lignins present in wood. Indeed, during the extraction and separation processes the wood is submitted to in order to produce pulp and paper, lignins are modified. For instance, the acid sulfite pulping of wood is a process used for cellulose fiber production. Lignins obtained by this process are called lignosulfonates. Their production is approximately 1 million tonnes per year worldwide with the major producer being Borregaard Lignotech (Norway) with production facilities in 6 different countries.[95] Major uses are found as concrete water reducers, dispersants in various applications, or animal feed binders.[96] Sulfite pulping consists in chemically breaking down the lignin and hemicellulose fractions of wood to smaller (Mw = 20kDa-50kDa[97]) and water-soluble fragments while maintaining the integrity of cellulose fibers. In this process, sulfites (SO_3^{2-}), or bisulfites (HSO_3^-) are the pulping agents, depending on the pH. The main reaction in β-O-4 linkages of lignin during sulfite pulping is the introduction of sulfonic groups in the α position as shown in **Figure 10**.[98]

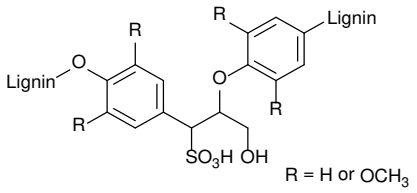


Figure 10 : Sulfonated α position in β-O-4 linkages of lignosulfonates

The oxygen borne by the Cα is protonated and then attacked by the nucleophilic HSO_3^-, leading to the formation of the lignosulfonate fragment shown in **Figure 10**, which is water-soluble and thus separated from cellulose fibres. The initial sulfonation in the α-position may be followed by sulfidolytic cleavage of the β-O-4 bond, but the extent of the reaction is lower than in Kraft pulping.

Since the 1940's, the Kraft process surpassed the acid sulphite process for the manufacture of pulp and paper. The pulping is carried out in this case in a strong alkaline solution composed mainly of OH^- and HS^- ions, removing around 90% of the initial lignin.[91] Kraft lignins present molecular weights in the range of 1-3kDa, which is lower than lignosulfonates.[91] This difference is due to the fact that the main reaction involved in Kraft pulping is the cleavage of β-O-4 linkages[99], leading to lower molecular weight lignins. The Kraft process nowadays accounts for approximately 80% of the pulp produced worldwide[97], which represents a potential production of Kraft lignin of 50 million tonnes per year.[100] However, the commercial production of Kraft lignin is much lower – around 100,000 tonnes per year[95]– due to the fact that the black liquor, the lignin-rich by-product of the Kraft pulping process, is usually burned to provide energy for the process and to recover the cooking chemicals[97], which is necessary to the economic viability of the process. Uses of Kraft lignins include asphalt emulsions, lead-acid storage batteries and products for cement and concrete industries.

New sulfur-free processes for lignin extraction and isolation are emerging, mostly by solvolysis. These processes lead to Organosolv lignins, which are high-purity, low molecular weight lignins that are soluble in organic solvents and closer to the native structure of lignin found in plants[89]. Thus, these lignins show great promises for chemical functionalization or as a source of bio-based chemicals. The most common Organosolv processes are based on an ethanol/water mixture (Lignol, Alcell), methanol/water mixture (Organocell), acetic acid/water mixture (Acetosolv, Acetocell), formic acid/water mixture (Chempolis), or acetic acid/formic acid/water mixture (CIMV).[89]

Overall, approximately 1–2% of lignin is isolated from pulping liquors and used for specialty products.[101] Regardless of the process used for its production, lignin is a fascinating renewable polymer that is envisaged or used in multiple applications, either as obtained or after chemical modification. The next section deals with the use of lignin in epoxy thermosets.

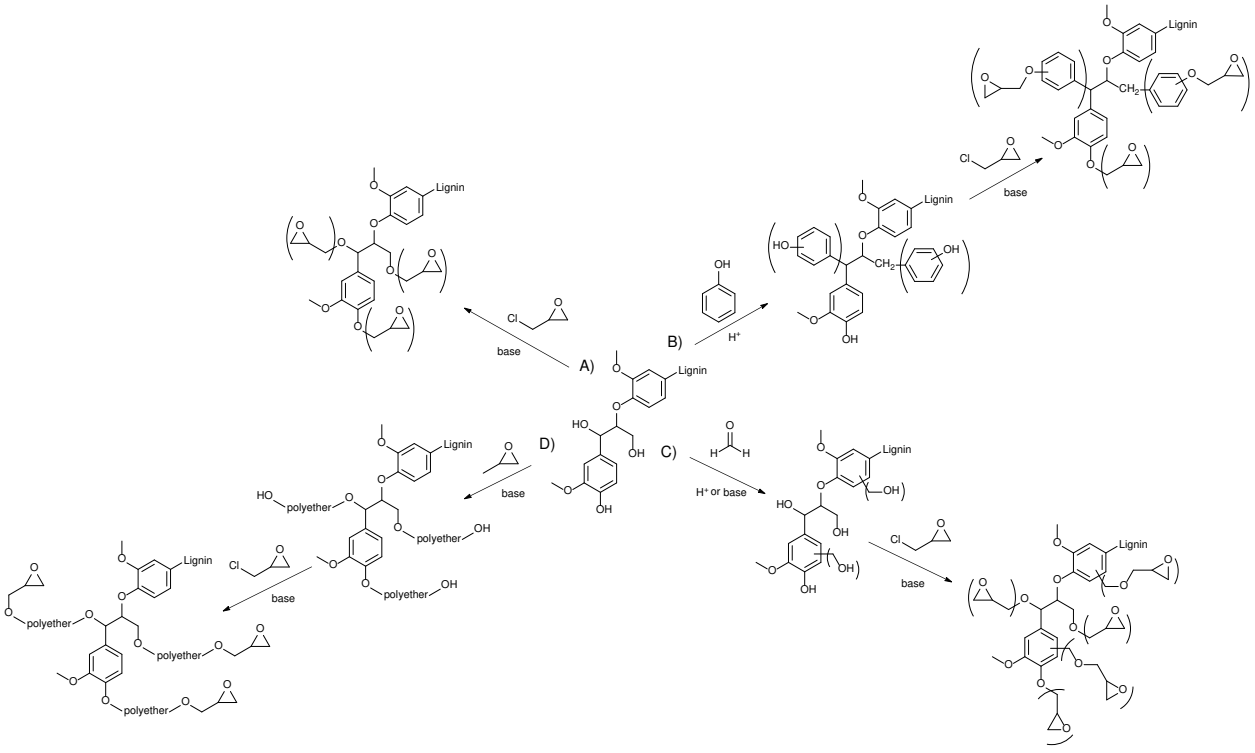
3.3.2 Uses in epoxy thermosets

The potential of lignin as a raw material for different applications has been evaluated in a US government report.[102] Among the promising applications cited, the use of lignin – modified or unmodified – as hardener for epoxy thermosets, or the functionalization of lignin to an epoxy pre-polymer are mentioned.

3.3.2.1 As pre-polymer

The idea of functionalizing lignin to introduce epoxy groups and thus obtain an epoxy pre-polymer is not new. Indeed, such a concept was already patented as early as 1976.[103] The method employed in this case consisted in a direct reaction of the free lignin hydroxyls with epichlorohydrin (**Scheme 13A**). Such a method is extensively used in the literature, including in recent works[104, 105], and is relevant because it is a one-step procedure. In the latter work cited, it also led to materials with an improved adhesive shear strength compared to a petro-based epoxy polymer. However, extensive functionalization can prove difficult[106], especially on the secondary aliphatic hydroxyls borne by lignin.

Therefore, many other functionalization methods have been employed to introduce epoxy functions onto lignin.[107] For instance, lignin can be submitted to a phenolation reaction under acidic catalysis in order to increase the phenolic hydroxyl content, which are prone to react in a second step with epichlorohydrin to afford the phenolated lignin epoxy pre-polymer (**Scheme 13B**).[108] Another common strategy is the preparation of a phenolic resin by reaction of lignin with formaldehyde (or glyoxal). Methylol moieties are introduced onto the lignin, which increase the overall hydroxyl content and thus the amount of epoxy groups introduced in the second step of glycidylation with epichlorohydrin (**Scheme 13C**).[109]



Scheme 13 : Examples of lignin functionalization to epoxy pre-polymers

Lignin can also be functionalized by –OH-terminated ethers prior to glycidylation. The goal of this reaction is to graft accessible, primary aliphatic hydroxyls, which can then be glycidylated easily. These ethers can be introduced by a grafting *onto* method like the acid-catalyzed etherification of lignin hydroxyls with alcohols.[110] Ether dangling chains can also be obtained by a grafting *from* method, like the oxypropylation of lignin hydroxyls (**Scheme 13D**).[111]

Other methods have been developed to prepare epoxy pre-polymers from lignin, but this topic will not be further developed here. More information is available in the following reviews.[89, 112]

3.3.2.2 As hardener

Lignin can also act as a hardener for the preparation of epoxy thermosets. Due to its high amount of free hydroxyls, lignin can be used directly to cross-link epoxy resins. All hydroxyls are not equally as reactive towards epoxy groups, but phenolic hydroxyls, the most reactive ones, are present in various amounts on the lignin structure. This approach is quite well-known in the literature and a good example is the integration of high amounts of lignin in an epoxy formulation to prepare laminates to be used as printed wiring boards in the electronic industry.[43] Authors mention that polymers with a 50%w. lignin content were formulated on a pilot scale and used to prepare pre-impregnated composites. They also mention that the properties of the materials obtained exceeded the standards used in this field. Preparing epoxy thermosets with lignin as hardener is thus a valid approach, and the renewable carbon content can be increased even more by using an epoxy pre-polymer also based on lignin.[104]

However, the same problem than with lignin-based epoxy pre-polymers can be encountered. More precisely, the reaction of lignin hydroxyls is difficult, especially secondary aliphatic hydroxyls. Cross-linking epoxy resins can thus necessitate a high lignin loading and/or a high curing temperature, which in turn can be detrimental to the processability or final properties. Thus, here again, lignin modification or functionalization was investigated. In literature examples of anhydride-grafted[113] , acid-grafted[114], or amine-grafted lignins are available. The grafting of amine functions onto lignin was performed either via a Mannich reaction[115, 116] (see **Section 3.1.2.2**), or by a two-step procedure consisting of the glycidylation of lignin with epichlorohydrin followed by the opening of epoxy groups with an excess of a diamine.[117] In the case of the Mannich reaction, it was proven that a prior phenolation of the lignin greatly increased the amount of amine introduced.[116] The ozonization of lignin is a different strategy in the sense that nothing is grafted onto the lignin. During this reaction, the lignin aromatic rings are cleaved to give two conjugated carboxylic acids. These groups are able to react with epoxides[118], forming thermosets.

As in the case of lignin-based epoxy pre-polymers, the reader is directed to the two excellent reviews[89, 112] already cited for more information.

3.3.3 Problems associated

As briefly shown here, the literature abounds with reports dealing with the use of lignin in the field of epoxy thermosets. It is also true with other types of polymers such as phenolic resins, polyurethanes etc.[89, 101, 119, 120] Yet, the old industrial saying that goes “You can make anything out of lignin… except money” remains widely true. The reasons behind this lack of industrial development, despite the enormous research effort consented on lignin, are multiple[121] as summarized in **Figure 11**. A transversal issue, encountered at every step of the process, is that precise characterization and reaction mechanism understanding are challenging due to the heterogeneous nature of lignin.

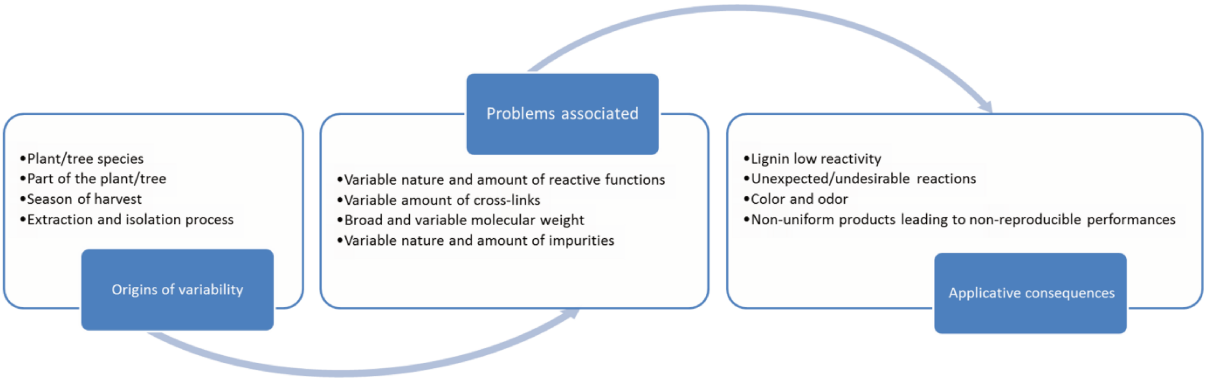


Figure 11 : Problems associated with lignin

To overcome these limitations, lignin depolymerization to produce bio-based aromatics or low molecular weight oligomers seems to be a promising approach. However, even if under intense investigation, this approach is not a mature technology yet.[122] Indeed, as mentioned in the US government report already cited[102], the production of aromatics from lignin is identified as a promising technology, but with technical challenges still to be answered. More precisely, the authors identify two strategies to produce aromatics from lignin depolymerization. The first one is a non-selective, aggressive depolymerization leading to the production of Benzene Toluene, and Xylenes (BTX), for which further process already exist as they are currently important petro-based intermediates. The second approach would be the development of selective depolymerization methods that would lead to “a plethora of complex aromatics that are difficult to make via conventional petrochemical routes”, many of them being phenolics with higher added-value than BTX. Both these strategies are described as long term, the second one being even longer term as highly selective lignin bond scission will be more difficult to implement than a non-selective method. Also, maybe the greatest challenge will be to change the way the chemical industry is used to work. Indeed, petroleum provided single, pure-molecule raw materials, and using mixtures of products, as would arise from lignin and maybe more generally from biorefineries, will be a challenge[102]. Simply put, “there is a vast difference between a valuable mixture of chemicals and a mixture of valuable chemicals”.[123] For now, strategies employing bio-based single molecules have the best potential for industrialization.

4. Vanillin sourcing

The resources described in the previous section, CNSL, tannins, and lignin, are the major sources of (poly)phenols available. However, each has drawbacks, limiting their use in epoxy thermosets and for the time being, a single pure molecule isolated from these feedstocks seems a more viable option. Vanillin is the only pure mono-aromatic phenol currently produced at an industrial scale from lignin[102]. Indeed, 15% of the worldwide vanillin production comes from wood.[97] Thus, vanillin will be discussed in the next section.

4.1.1 Description and sourcing

4.1.1.1 Brief history

Vanillin (4-hydroxy-3-methoxybenzaldehyde, m.p. 81-83°C, **Figure 12**) is the highest volume aroma chemical produced worldwide.[124]

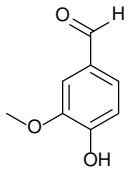


Figure 12 : Vanillin chemical structure

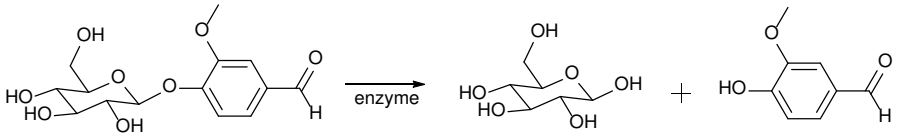
It is the chief constituent of natural vanilla flavoring. As such, it is used as a flavoring and fragrance ingredient in the food or cosmetic industries and the market for vanillin consists mainly of large multinational flavour and fragrance houses (e.g. International Fragrances and Flavors (IFF), Givaudan, Quest, Danisco, Symrise).[125] The manufacture of chocolate and ice-cream are especially demanding in vanillin, as it is used at levels of 0.1% to 0.9% (weight/weight).[124] Thus, the bigger producers of ice cream (such as Unilever) and chocolate (Nestle, Cadbury, Suchard) are huge vanillin buyers.[125] It is also an important intermediate for the synthesis of fine chemicals and pharmaceuticals (for example L-3,4-DihydrOxyPhenylAlanine, L-DOPA).[91] Apart from these major applications, examples of other vanillin uses are as a ripening agent to increase the yield of sucrose in sugarcane, or as a base compound for the preparation of suntans.[124] Interestingly, ethyl vanillin is also used commercially as a vanilla flavoring; and has about 3.5 times the flavor intensity of vanillin itself.[126]

The history of vanillin begins with Cortez, the famous Spanish Conquistador, who is said to have been served a chocolate drink flavored with vanilla by the Aztecs in about 1520. He brought the knowledge of both chocolate and vanilla back to Spain and Europe, where they rapidly became popular.[126] Gobley, in 1858, was the first to isolate and identify the vanillin constituent of the vanilla bean and to confirm that this was the chief flavor component. The vanilla aroma was so popular that in 1875, less than 20 years from its initial isolation, synthetic vanillin prepared from eugenol by its isomerization followed by oxidation became available in France and the United States.[126] Eugenol is the main component (ca. 90%) of clove oil, the essential oil extracted of the clove plant. The production of vanillin from the lignin of waste sulfite liquor began in North America in 1936-1937 based on the works of on the one hand, Sandborn, Salvesen, and Clemens[127] and on the other hand of Hibbert and Tomlinson[128]. This method developed rapidly to become the main production process for synthetic vanillin. Even in the

1970's, when the use of vanillin dramatically shifted from flavor to chemical intermediate[126], this process remained unequalled. The vanillin production of Ontario Pulp and Paper became such a valuable component of their operations that the scale was gradually expanded to 3.4 million kilograms per year by 1981, sufficient to supply 60% of the then current world market[126]. However, almost all the lignin-to-vanillin plants closed at the end of the 1990's due to increased environmental concerns towards the caustic effluents of the process, decreased lignin availability due to the increasing use of the Kraft process for pulping - in which lignin is burnt to produce energy - , and also due to the arising of cheap chemical intermediates from petroleum. Since then, the dominant feedstock for vanillin is petroleum.[126] Through all these years, the production of natural vanilla extract from vanilla beans remained active as this extract contains, apart from vanillin, many other minor flavoring constituent that makes the natural extract unique, and thus much appreciated in some food markets where cost is not the top concern.[126]

4.1.1.2 Current sourcing

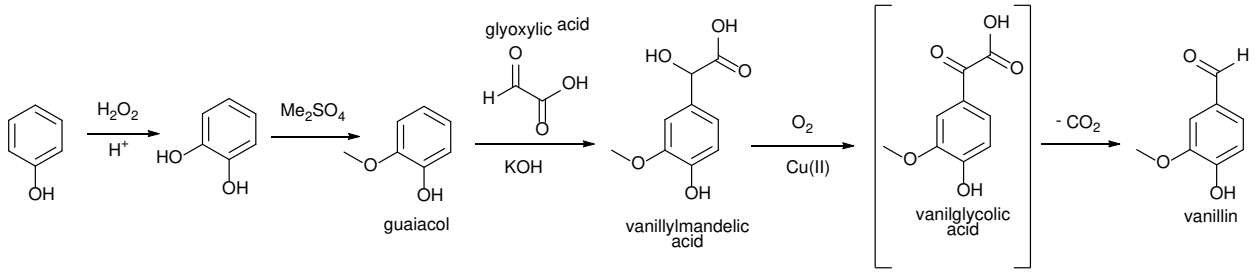
The worldwide production of natural vanilla extract is only 40 to 50 tonnes per year, which represents less than 1% of the total vanillin production.[129] Vanilla beans are harvested from species of the Vanilla orchid, a tropical climbing plant grown in Mexico, Madagascar, Java, Reunion, and Tahiti, and that has to be manually pollinized to attain reasonable yields, which is a very laborious task that discourages the cultivation of these plants at a very large scale.[125] The vanillin in the green bean is found as vanillin glucoside. During the curing process, the vanillin glucoside is enzymatically hydrolyzed to glucose and vanillin as shown in **Scheme 14**.[126]



Scheme 14 : Vanillin glucoside hydrolysis to vanillin and glucose

When vanillin is produced from vanilla beans by this process, the labeling on the consumer product may be indicated as 'natural vanilla flavor', which is a powerful marketing argument.

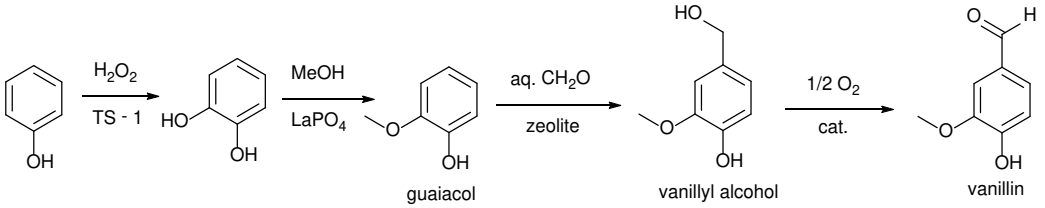
However, synthetic vanillin cannot be labeled as such, but rather as "synthetic" or "artificial" vanilla flavor.[130] Still, 85% of the world supply is produced from petro-based intermediates, especially guaiacol.[91] There are different ways to prepare vanillin from guaiacol; however the most employed is the Riedel process. The first step of this process involves the condensation of glyoxylic acid onto guaiacol to produce vanillylmandelic acid as shown in **Scheme 15**[131]:



Scheme 15 : Riedel route of vanillin production from phenol

The advantage of this reaction is that the glyoxylic acid condensation is highly regioselective towards the para position, which avoids side-products and thus costly separations.[132] The preparation of vanillylmandelic acid has been studied in details and reported to have a yield of 74% based on glyoxylic acid.[133] The low conversion to product based on glyoxylic acid is probably due to Canizzaro reaction of glyoxylic acid in the presence of alkali, leading to the formation of glycolic acid and oxalic acid.[124] In the second step, the vanillylmandelic acid is submitted to an oxidative decarboxylation to form vanillin. This reaction is usually carried out using a copper(II) hydroxide/oxygen system in an aqueous alkaline medium at a temperature of 80 to 130°C.

Rhône Poulenc, now part of the Solvay group, is reported to have developed the process further with the aim to improve the atom efficiency.[132] Their process is reported in **Scheme 16**:



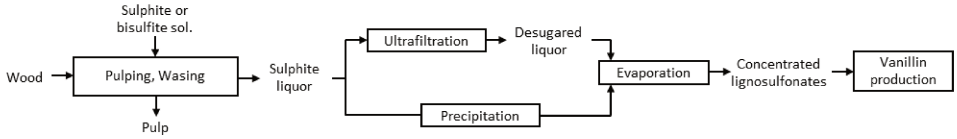
Scheme 16 : Solvay's route of vanillin production from phenol

The labeling regulation subtlety between "artificial" and "natural" vanillin, and the high price and limited availability of vanillin from vanilla beans led to the development of bio-syntheses of vanillin, which could thus be labeled as "natural". Detailed reviews on bio-technological routes to vanillin using different substrates are available.[129, 134, 135] These bio-syntheses are based on feeding native or genetically-modified fungi, yeast, or bacteria with a substrate structurally close to vanillin. The Belgian specialty chemical company Solvay, a leading producer of synthetic vanillin after its purchase of Rhodia, makes "natural" vanillin from a by-product of rice bran oil (or sugar beet pulp) refining, ferulic acid.[129] The process, originally developed by Givaudan and exclusively licensed to Rhodia, involves the fermentation of this substrate by bacteria.[136] Recently, a new enzymatic process for the synthesis of vanillin using D-glucose as the carbon source was reported.[137] The Swiss biotech firm Evolva also begins with sugar to produce vanillin by yeast fermentation. Both Evolva and Solvay are working to scale up their natural vanillin production. Evolva has a partnership with International Flavors & Fragrances to complete development and ready the product for commercialization.[129, 138] This small twist in words between "artificial" and "natural" vanillin provided a financial drive sufficient to lead to huge investments in bio-technologies. However, when made from petrochemical sources, vanillin costs as little as $10 per kg, whereas vanillin made in a way that can be labeled natural can cost hundreds of dollars per kg.[129] The bio-based routes presented are therefore not suitable for a use of vanillin in polymer synthesis, where low price and large volumes are major requirements. The extraction of vanillin from cow dung in sub-critical water, method that won the 2007 Ig Nobel Prize for chemistry, also has a way to go.[139] Petro-based vanillin is of course not desirable as it is a non-renewable feedstock. However, a last production process, in which vanillin is produced from lignin, would be suitable.

4.1.2 Vanillin production from lignin

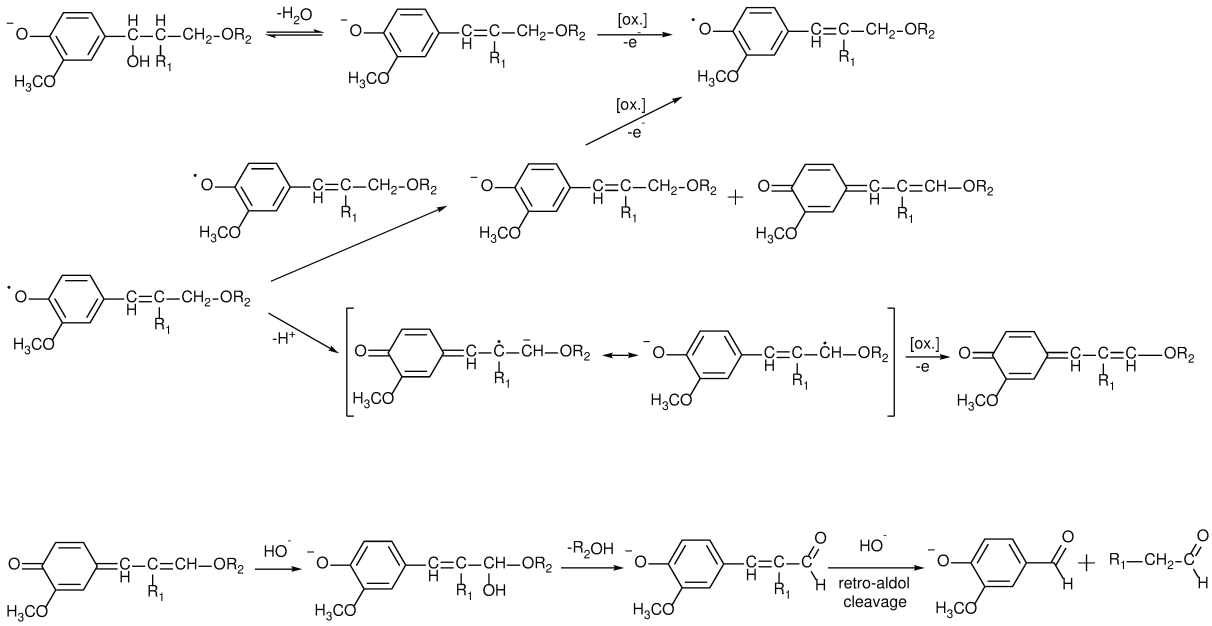
4.1.2.1 Lignin depolymerization

The lignin-to-vanillin process is a rather old mean of producing vanillin, as presented in **Section 4.1.1**. Nowadays, 15% of the overall vanillin production comes from lignin[97], more precisely lignosulphonates, exclusively by the Norwegian company Borregaard that has been running a lignin-to-vanillin plant in Sarpsborg, Norway for more than 50 years. For the last 20 years, they have been the only ones using this process.[129] The process starts with the sulphite pulping of wood, which gives the lignosulfonate-rich sulfite liquor as a by-product. This liquor is further processed as shown in **Scheme 17**.[96]



Scheme 17 : Schematic process for the production of vanillin from wood

The process for vanillin production itself consists of treating an aqueous solution of lignin with oxidants, at alkaline pH, and high temperatures and pressures, in order to depolymerize the lignin and obtain vanillin. Given the complexity and heterogeneity of lignins, establishing a reaction mechanism is extremely challenging. Moreover, there are many parameters influencing the process, which adds even more to the complexity of bringing elementary steps out. Nevertheless, the mechanism shown in **Scheme 18** has been proposed in the literature.[140]



Scheme 18 : Proposed mechanism for lignin depolymerization leading to vanillin

This mechanism of lignin oxidation to vanillin has been and is still the subject of much debates and research[140-144] and is not fully understood yet.

4.1.2.2 Parameters influencing the reaction

The main parameters influencing the alkaline oxidative depolymerization of lignin are summed up in **Table 4**:

Table 4 : Main parameters influencing the alkaline oxidative depolymerization of lignin

Lignin	Lignin natural origin
	Prior processing (pulping process, isolation, pre-treatment etc.)
	Mw, PDI
	Impurities
Reaction conditions	Lignin concentration in feed
	Temperature
	Pressure
	Base nature and concentration
	Oxidant nature and concentration
	Catalyst nature and concentration
	Duration of reaction

Works in which the effect of one or several of these parameters is investigated are numerous. Reviewing them is a tedious task that has already been accomplished in several papers, especially by Rodrigues and his team at the LSRE laboratory in Porto,[91, 97]. Therefore, this section is mostly based on the conclusions drawn by this team, as well as on several other relevant experimental works.

Parameters linked to chemical engineering considerations such as batch or continuous process, shape of reactor and stirring, or catalyst shape and disposition can also potentially play a major role in the yield of the reaction.[125] For instance, in the case of O_2 used as the oxidant, its transfer to the solution is of paramount importance.[97] Most of the experiments reported in literature have been performed in batch. However, from an industrial point of view, the continuous process of lignin oxidation is more attractive due to the large liquor volumes to be treated in a pulp industry, to an easier control of the process to attain constant product characteristics, and to lower overall investments and operating costs.[97]

There is a maximum obtainable vanillin yield from a specific type of lignin. The formation of vanillin or other compounds is strictly related to the available percentage of its precursor in the lignin structure.[97] The oxidation of lignin using alkaline nitrobenzene has been used since the 1940's to elucidate the structure of lignin: the phenolic products from this oxidation are either derived from H, G, or S units. Indeed, nitrobenzene is the oxidant that gives the highest yields.[125] However, nitrobenzene is expensive and its reduction products are harmful and difficult to separate, which is why it has not been accepted as an industrial approach.[145] Other catalysts such as CuO are preferred because they can be easily separated and regenerated.[125] However, CuO gives lower yields than nitrobenzene. Indeed, nitrobenzene is believed to be able oxidize to aldehydes the ketones formed during the reaction, while CuO is not, as nitrobenzene is a stronger oxidant[146] During alkaline CuO oxidation of lignin, vanillin is also slowly converted to vanillic acid.[145] $CuSO_4$ is also a possible catalyst for the oxidation of lignosulfonates to vanillin with O_2. Reaction parameters with this system were finely tuned by statistical experimental design and mathematical modelling to attain good yields.[98] O_2 is an oxidant of choice because of its environmental friendliness, high atom economy, and low price (use of air).[91] O_2 partial pressure and reaction time have to be balanced in order to avoid vanillin degradation and thus increase vanillin yield. A high pO_2 value reduces reaction time but leads to vanillin degradation.[97] A temperature increase can also shorten the reaction times. Overall, short reaction times (30 min - 2 h), high temperatures (130 - 200°C) and severe oxidative conditions seem to work best.[146-148]

The pH is also a crucial parameter for vanillin production. During the lignin oxidation a maximum amount of vanillin is reached from where pH value begins to decrease and, as consequence, the vanillin yield decreases considerably. It is known that at higher alkali concentration (pH > 12) the rate of vanillin degradation is lower. At lower pH values (< 11.5) vanillin losses by oxidation become more significant and a sharp decrease in vanillin yield is observed.[97, 147] High concentrations of alkaline species are thus necessary. Decrease of pH leads to almost complete suppression of vanillin formation. This phenomenon was attributed to the protonation of reaction intermediates, more basic than the phenolics produced, which pKa are much lower (vanillin pKa = 7.4).[148]

Finally, the lignin itself is of course of importance: low molecular weight lignin tends to give better results[98], the presence of residual sugars is highly unfavorable[149], and the less transformations or chemical treatments lignin suffers, the better the phenolic aldehydes yield.[146, 150] This last point is important because the isolation procedure can modify the chemical structure of lignin. More specifically, if lignin separation is performed by acid precipitation, condensation reactions can occur, especially at the position 5 of the aromatic cycle in G units, which leads to bi-aryl structures[150] (**Figure 13**), and decreases the yield of vanillin.[97, 146]

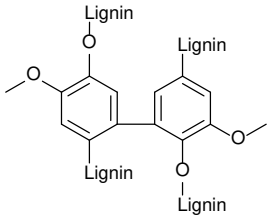


Figure 13 : 5-5' linkage arising from the condensation of two G lignin fragments

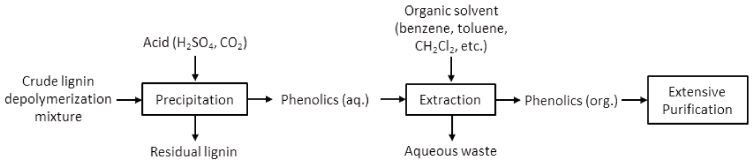
GS lignins tend to give better yields since they comprise more S units, more stable to condensation because of the substitution of the 5 position by a methoxy group.

Alternative methods to obtain vanillin are still actively investigated in the literature.[151-155]

4.1.2.3 Downstream treatment

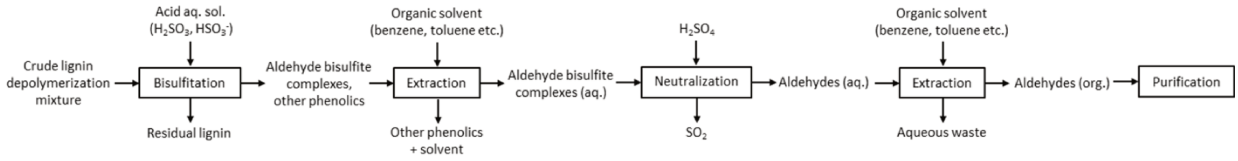
The oxidative depolymerization of lignin gives a complex mixture of products.[91] The major di-functional molecular phenolic compounds obtained for G and GS lignins are detailed in **Chapter 6**. They bear of course aldehyde moieties, but also acid or ketone moieties. Other mono-functional molecular phenolics such as guaiacol or syringol are also present. Given the high pH of the crude mixture, all phenolics are present as phenolates. The reaction mixture also contains side-products such as lactones and lignin fragments of higher molecular weight.[97] They are either unreacted fragments or come from condensation reactions. Given this complex mixture, the downstream treatment of the alkaline oxidative lignin depolymerization reaction is itself a complex topic that was extensively discussed in both patent and academic literature.

The difficulty of isolating pure vanillin from such a mixture is illustrated by the number variety of processes available in the literature. The two major problems are the acidification of the mixture and the residual lignin removal. In one of the oldest process[128] lignin precipitation is performed in acidic conditions and phenolics are then extracted (**Scheme 19**). This process requires huge amounts of acid and solvents and the mixture obtained is still difficult to purify.



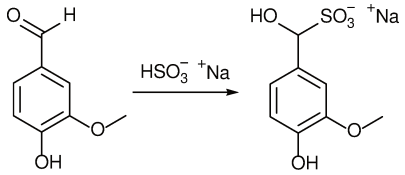
Scheme 19 : Lignin-to-vanillin process involving acidification and an extraction step by organic solvents

A process developed at about the same time [127] (**Scheme 20**) improves the selectivity of the products towards aldehydes.



Scheme 20 : Lignin-to-vanillin process involving bisulfitation and an extraction step by organic solvents

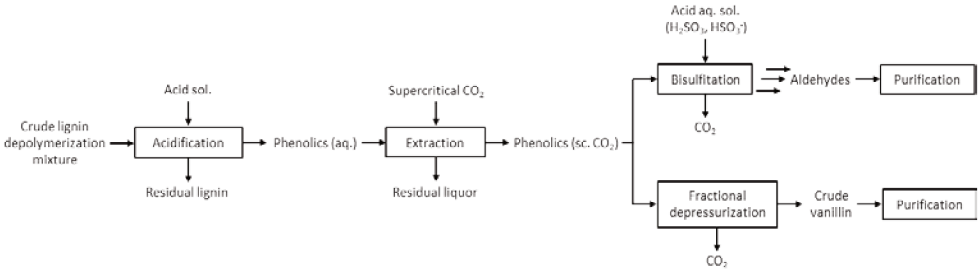
The key step is the bisulfitation of the mixture. Briefly, it consists in mixing the crude lignin depolymerization mixture with a solution of $NaHSO_3$ (sodium hydrogen sulfite, or sodium bisulfite) to prepare from vanillin a "vanillin bisulfite complex"[91, 156], i.e. sodium vanillyl-α-hydroxysulfonate as depicted in **Scheme 21**:



Scheme 21 : Reaction of vanillin with sodium bisulfite to form the "vanillin bisulfite complex"

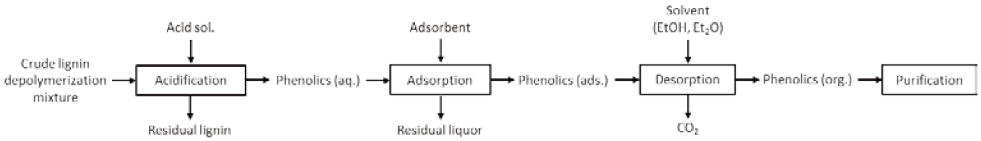
The derivatives produced have a good solubility in water, as opposed to the other products from the crude mixture.[127] The hydrosulfite anion reacts selectively with the aldehyde moiety, which means that p-hydroxybenzaldehyde and syringaldehyde[157] are extracted along with vanillin. Products of high molecular weight precipitate during this step, due to the pH increase of the medium.[127] Once this precipitate has been removed, the aqueous phase must be further acidified to recover aldehydes and SO_2.[127]

One major drawback of these two methods is the use of large amounts of organic solvents such as benzene or toluene. Other processes have been proposed to circumvent this problem. The first one is based on the replacement of these solvents by supercritical CO_2 (**Scheme 22**).[158, 159]



Scheme 22 : Lignin-to-vanillin processes involving an extraction step by supercritical CO_2

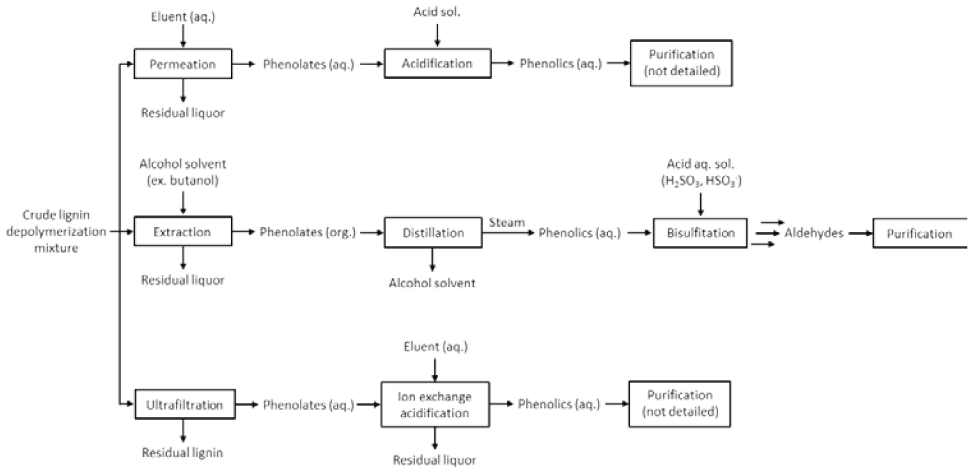
Another way to extract low molecular weight phenolics from the aqueous phase is by adsorbing them. Zeolites[160] as well as a macroporous resin[161] have been proposed as adsorbents (**Scheme 23**).



Scheme 23 : Lignin-to-vanillin process involving an extraction step by adsorption

A major disadvantage of these processes is the requirement of large amounts of acids for neutralization and/or acidification prior to the extraction of vanillin.[162] In order to reduce this amount of acids, a method of neutralization of the crude lignin depolymerization mixture on a cation exchange resin prior to any other step has been proposed.[163]

Another strategy consists of directly isolating the molecular phenolates from the crude mixture and then performing the acidification. The amount of acid necessary and the dilution of the crude liquor is thus greatly reduced.[164] A first method described in the literature is the separation of phenolates from higher molecular weight fragments by elution of the crude lignin depolymerization mixture on a strong cation-exchange resin in the Na^+ form (**Scheme 24**, top path). Indeed, these two types of species do not have the same retention times and can thus be separated[162]. The second method is rather old and consists of extracting the phenolates with an appropriate alcoholic solvent[164, 165], which can then be distilled off (**Scheme 24**, middle path). The last method (**Scheme 24**, bottom path) is more recent and is based on an ultrafiltration step to remove high molecular weight lignin fragments[166] followed by an acidification of the phenolates in the permeate on an ion-exchange resin.[167] This last method has been proposed in an integrated process that can potentially be adapted in a biorefinery.[97] It is worthy to note that the ultrafiltration technology has also been applied to concentrate lignosulfonates in spent sulfite liquor prior to the depolymerization reaction.[168]



Scheme 24 : Lignin-to-vanillin processes involving a direct extraction step of phenolates

The stream of product from all these methods is essentially composed of crude vanillin with varying amounts other phenolics, depending on the process used. Further purification of vanillin to technical grades or food grades is a difficult task. Indeed, the remaining other compounds like acetovanillone or syringaldehyde have very close structures and properties. Separating vanillin from these compounds is thus a difficult task, as pointed out by numerous works.[91, 157, 169]

The methods proposed in these works, multistage crystallization for instance, are all tedious and quite difficult to implement on an industrial scale. Recently, an original method of purification has been proposed. Briefly, it consists of preparing a vanillin-molecularly imprinted polymer and using it to adsorb with a high selectivity vanillin in the stream to be purified.[170]

The amount of research continuously generated on the topic of vanillin production from lignin proves the industrial interest of this technique. The fact that the raw material is bio-based, that petroleum price is on the rise, and the improvements achieved in terms of mechanism understanding, productivity, and waste reduction make this vanillin production path more and more attractive from both a green chemistry and economic point of view. Vanillin, currently being the only molecular phenolic compound manufactured on an industrial scale from biomass, has thus the potential to become a key-intermediate for the synthesis of bio-based polymers. The next section deals with the recent works published on this topic.

5. Vanillin, a key-intermediate of biobased polymers

European Polymer Journal 68 (2015) 488–502

Feature Article

Maxence Fache, Bernard Boutevin, Sylvain Caillol *

Institut Charles Gerhardt, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France

ARTICLE INFO

Article history:
Received 16 October 2014
Received in revised form 20 February 2015
Accepted 7 March 2015
Available online 28 March 2015

Keywords:
Vanillin
Lignin
Biobased
Phenolic
Polymers

ABSTRACT

The use of vanillin for the preparation of renewable polymers is reviewed in this work. The synthesis of polymers from renewable resources is a burning issue that is actively investigated. Vanillin is currently one of the only biobased and aromatic compounds that are industrially available. For this reason, vanillin recently gained much attention from the polymer community. The first part of this work aims at giving an overview of the different existing sources of vanillin, and of their relevance in the context of a potential use in polymer science. The second part of this work sums up the efforts of the scientific community to prepare a wide range of vanillin-based polymers, e.g. phenolic, epoxy and benzoxazine resins, polyesters, acrylate and methacrylate polymers. The interest in the use of vanillin to prepare renewable polymers is recent but the number of contributions on this subject is growing fast.

Contents

1. Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde), a plant metabolite, is the main component of natural vanilla extract and is responsible for its flavoring properties. Natural vanilla is originally extracted from vanilla orchid pods. The composition of natural vanilla extract is complex and contains many more compounds than only vanillin. Also, vanilla orchid growing and harvesting is a costly process. For these reasons, vanillin from natural extract accounts for less than 1% of the total vanillin production

* Corresponding author. Tel.: +33 4 67144327.
E-mail address: sylvain.caillol@enscm.fr (S. Caillol).

http://dx.doi.org/10.1016/j.eurpolymj.2015.03.050
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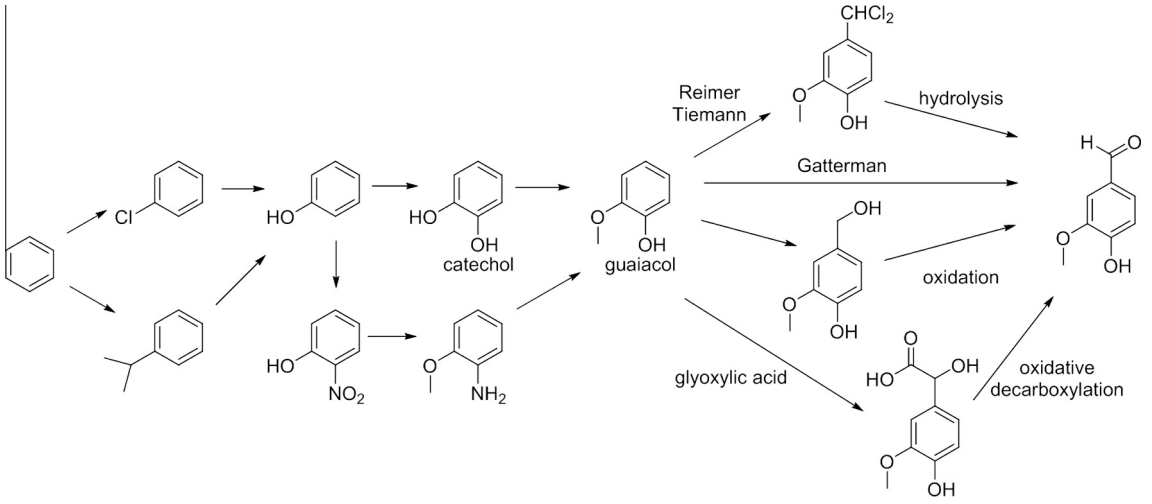


Scheme 1. Outlines of petrochemical synthesis of vanillin adapted from [2].

worldwide [1]. This sourcing is not adapted to an industrial use of vanillin.

As a flavoring and fragrance ingredient, the current global demand for vanillin is estimated to be roughly 20,000 tons per year [1]. To satisfy constantly increasing markets, new chemical routes for the synthesis of vanillin were developed. Today, 85% of the vanillin is produced from the petroleum-based raw material guaiacol [2] (Scheme 1). Solvay-Rhodia dominates the vanillin market using the catechol–guaiacol process.

However, vanillin produced through this process cannot be labeled as "natural vanilla flavor". According to EU regulations, vanillin can be sold as "natural vanilla aroma" only if the base material and the process are natural. This led to the development of other ways of producing vanillin using biotechnology, improving the scientific knowledge and financial investment in this field along the way.

Numerous strategies have been envisaged to produce vanillin by biotechnology processes. Literature reports can be classified in plant-based and microorganism-based approaches. Plant-based strategies [3] consist in growing plant tissues or cells to make use of their biosynthetic pathways for the conversion of various substrates to vanillin. This approach consistently suffers from low and inconsistent yields. Microorganism-based approaches have been extensively reviewed [4–6] and consist in using biotransformation reactions from native or genetically-modified fungi [7,8], yeast [9] or bacteria [10] to produce vanillin (or a derivative in a different oxidation state) from a structurally close substrate. The most available and promising substrates include, ferulic acid extracted from sugar beet pulp [7] or waste of rice bran oil processing [8], glucose [11,12], and even lignin fragments [5]. Separation technologies are maturing [13] and play a key role for the industrial-scale production of vanillin from biotechnologies. Recently, Solvay-Rhodia and Evolva entered a preproduction phase from yeast fermentation of rice bran oil processing waste and glucose respectively [1]. These processes are still emerging technologies producing high-cost vanillin, which is suitable for the aroma and fragrances field for marketing reasons, but not for potential use in renewable resources-based polymers.

One last production method might however suit this purpose. The production of vanillin from wood actually accounts for about 15% of the total vanillin production and Borregaard, the second largest vanillin producer worldwide, produces vanillin from lignin [14]. Indeed, chemical depolymerization of lignosulfonate by-products from the paper industry was historically the first industrial synthetic process for vanillin production [15]. However, vanillin-from-lignin plants raised environmental concerns [2]. Recently, this process regained attention thanks to the understanding of lignin depolymerization mechanism [16–18], better yields through process improvement and catalysis [18–22], and better separation and purification techniques [14,23–25].

These advances promoted the lignin-to-vanillin process to one of the most promising in terms of sustainability and economical relevance. Indeed, lignin is the second most available renewable raw material with around 50 million tons per year produced [26]. Vanillin is currently one of the only aromatics industrially available from lignin. The production of other biobased aromatics from lignin depolymerization, although under intense investigation, is not a mature technology yet [27]. The production of vanillin from lignin is not in the scope of this review and more details are available elsewhere [28]. However, the fact that processes to produce vanillin from wood exist, at an industrial scale, and with high sustainability, leads us to consider vanillin as a top-priority renewable building block. Its use for the synthesis of biobased polymers is reviewed in this work.

2. Polymers based on vanillin and derivatives

2.1. Context

The investigation of vanillin as a biobased building block has been very dependent on its sourcing. Indeed,

the early production of vanillin was from biomass – between the 1930s and the 1980s – and works from this period actually deal with the chemistry of vanillin, such as the series of papers from Pearl for example [29]. With the advent of petroleum-based chemistry, the wood-based chemistry fell almost into oblivion. Vanillin production, as a by-product of the paper industry, was one of the only industrial remains in this field. Vanillin requires quite a few reaction steps to be produced from petro-based resources (Scheme 1) and was thus confined to high value-added applications like aroma or pharmaceuticals. Recently, however, the awareness about the predicted scarcity of oil and the necessity of using renewable resources has risen. Lignin chemistry started to be re-investigated with modern analytical tools and processes [26,27]. New opportunities for the future are identified [30], especially the use of lignins in polymer science [31–33]. However, lignins suffer from drawbacks such as complex and variable structures, high molecular weights, and limited processability. Vanillin from lignin, one of the only molecular aromatics largely available from biomass, was thus recently used to prepare renewable polymers and this is the scope of this review.

Using chemicals from biomass is not the only aspect of the development of a "green", sustainable chemistry. Energy efficiency, waste reduction, atom economy, safety toward human health and environment, are also important green chemistry requirements. Using a chemical as a new building-block, as exemplified in this review with vanillin, leads to the development of new reactions, new materials and new processes. This fresh start is an excellent opportunity not to repeat past mistakes by taking into account *from the start* the green chemistry principles. Numerous efforts have been made by the scientific community to integrate this approach to the preparation of vanillin-based polymers.

Strategies to prepare vanillin-based polymers can be classified in three groups. The first one is a direct mono- or difunctionalization of a vanillin derivative, giving a monoaromatic monomer. The second one is the coupling of two vanillin derivatives prior to functionalization, giving a difunctional and diaromatic monomer with the same group on both ends. The third one is the grafting of a vanillin derivative onto a pre-existing polymer. These strategies were employed to prepare a wide range of polymers, either by step-growth or chain-growth polymerization.

2.2. Epoxy polymers

Epoxy polymers are widely employed thermosets, especially in applications with demanding thermo-mechanical conditions such as in the aeronautic or electronic industry. Indeed, epoxy monomers usually have an aromatic structure, which brings stability to the network. Thus, vanillin and its derivatives are excellent candidates for the biosourcing of epoxy polymers. A few teams worked on this topic and used various strategies.

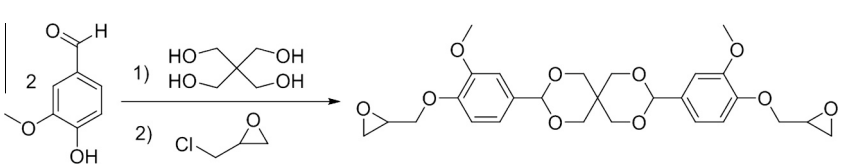
In a review article [34], Koike described an interesting diepoxy monomer based on a coupling strategy as depicted in Scheme 2.

The first step is performed by the acetalization of two vanillin molecules with pentaerythritol. The second step is the glycidylation of the two phenolic hydroxyl groups to obtain a difunctional epoxy monomer. This compound is interesting as the reactants involved in its synthesis are biobased and widely available, and the reactions are well-known and easy to implement. The major drawback of this monomer, however, is the fragility of the acetal group. Indeed acetals are usually employed as protecting groups of carbonyl compounds, as the deprotection is conducted at room temperature in aqueous acidic medium. Nevertheless, Koike reports an epoxide equivalent weight of 270 g/eq, a crosslinking reaction with diaminodiphenylmethane, as well as good impact strength, tensile strength, and elongation of the final material.

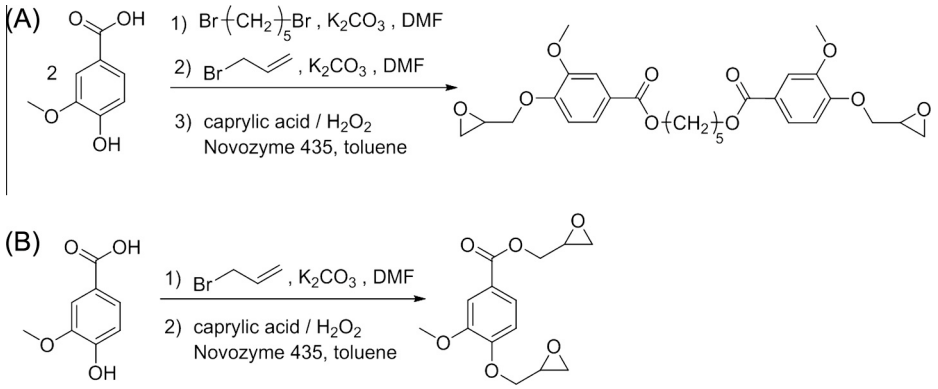
Aouf et al. also used a coupling strategy to prepare a diepoxy monomer from vanillic acid [35] as shown in Scheme 3A.

This diepoxy monomer is based on vanillic acid, which is easily obtained from vanillin and also an available synthon from lignin depolymerization. Ultimately, the epoxidation step is a chemo-enzymatic process (Scheme 3A), a very interesting reaction in terms of sustainability due to the use of a catalytic system (enzyme) and mild condi-tions (40 °C). It led to a mixture of diepoxidized product (66%) and monoepoxidized product. However, the use of DMF as solvent (category 1B reproductive toxicity) in the allylation step is less ideal in terms of safety, and an alter-native solvent could be a possible improvement for this reaction. Also, the presence of ester linkages might limit the thermostability of the final material. The same team also used another strategy by directly functionalizing vanillic acid in a two-step procedure (Scheme 3B) to pre-pare another diepoxy monomer. Once again the diepoxydation was only partial (70%) and the same concerns about the use of allyl bromide and DMF can be raised, even if this enzymatically catalyzed epoxidation reaction is an interesting alternative to the use of epichlorohydrin. These compounds were envisaged as epoxy monomers but polymers were not prepared.

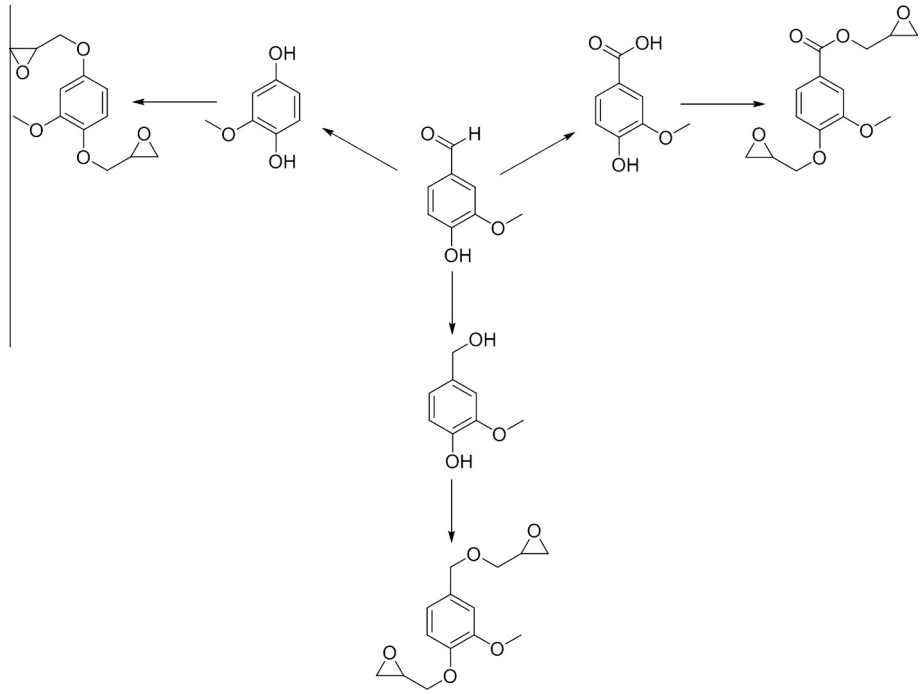
Our team also prepared diepoxy monomers from vanillin derivatives [36]. Scheme 4 shows the three diepoxy monomers prepared from the same direct functionalization strategy.



Scheme 2. Synthesis of diaromatic epoxy monomer from vanillin, pentaerythritol, and epichlorohydrin.



Scheme 3. Chemo-enzymatic synthesis of a epoxy monomers from vanillic acid.



Scheme 4. Diepoxy monomers prepared by direct functionalization of vanillin derivatives.

The three vanillin derivatives chosen were in different oxidation states, either oxidized or reduced. It is worthy to note that methoxyhydroquinone was prepared through a green vanillin oxidation process leading to the loss of one carbon atom. Briefly, vanillin was subjected to a Dakin oxidation with sodium percarbonate as an environmentally-friendly oxidant in a THF/water mixture at room temperature. Sodium percarbonate is a large-scale available chemical commonly used in laundry detergents. It is a good alternative to hydrogen peroxide, which storage and transportation is not desirable for safety reasons. On the contrary, sodium percarbonate is a environmentally-friendly solid compound composed of sodium carbonate and hydrogen peroxide. It is a powerful oxidant, while being cheap, non-toxic, stable upon storing, and easily handled.

Vanillic acid and vanillyl alcohol were purchased as their syntheses (the former by oxidation and the latter by reduction) are conventional reactions, well-described in the literature. Epichlorohydrin was used to perform a one-step glycidylation of these compounds and obtain the three diepoxy monomers shown. It is worthy to note that acid- and amine-functionalized vanillin derivatives were also prepared in the same work. They could potentially be employed as hardeners in epoxy thermosets.

These diepoxy monomers were used to prepared bio-based epoxy thermosets [37]. The polymers, all hardened with the same diamine, displayed excellent thermo-mechanical properties (**Fig. 1**), matching the ones from the current industrial reference, the DiGlycidyl Ether of Bisphenol A (DGEBA). For instance, a T_g of 152 °C was

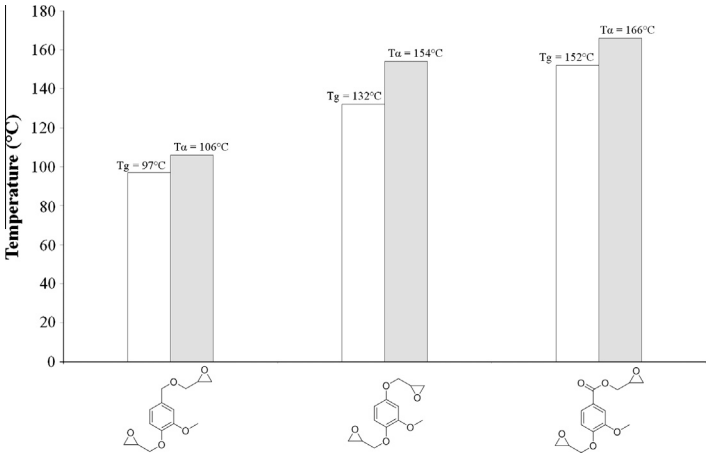
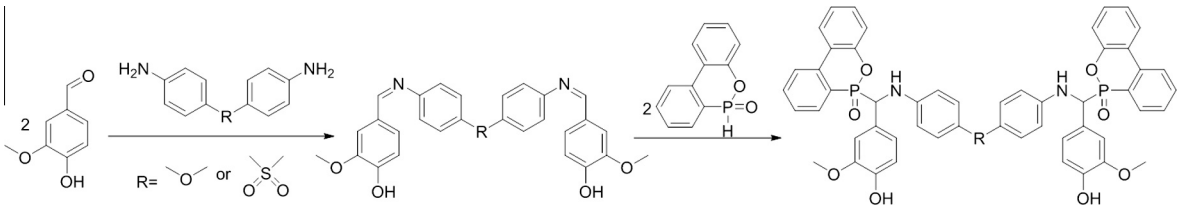


Fig. 1. T_g and T_α from vanillin-based epoxy materials.

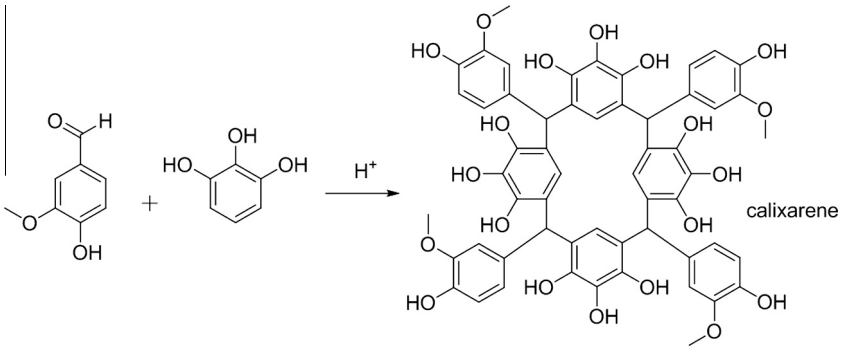


Scheme 5. Synthesis of a vanillin-based, phosphorus-containing, flame-retardant epoxy hardener.

found for the thermoset prepared from the diglycidyl ether of vanillic acid. Moreover, properties could be tuned depending on the starting monomer. They are candidates to the substitution of Bisphenol A in epoxy polymers. Work is underway to prepare oligomers from these diepoxy monomers, using the strategy currently used for the preparation of industrial epoxy resins.

Vanillin can not only be used to prepare epoxy monomers, but also to prepare hardeners for epoxy curing. The study of Gu et al. employed this strategy as they prepared two vanillin derivatives by a coupling strategy to be used as co-curing agents [38]. Additionally, the authors designed these co-curing agents as halogen-free, flame retardants by introducing a common phosphorylated flame-retardant moiety onto them: the 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO). Their synthetic strategy is shown in Scheme 5.

Briefly, the first step consisted in reacting two vanillin molecules with a diamine to form a bis-aldimine with pendant phenols. The DOPO was then grafted on the aldimine liaisons by a Pudovik-like reaction, i.e. the addition of the P-H liaisons on the C=N double bonds. The reaction is straightforward and was conducted as a one-pot procedure. The product is a phosphorus-containing diphenol which was used as a co-hardener during the polymerization of a DGEBA prepolymer with a commercial diamine. The thermal and flame-retardation properties of the thermosets prepared were investigated. The char yield and morphology were improved by the introduction of this vanillin-based co-hardener. The preparation of efficient



Scheme 6. Preparation of a calixarene from vanillin and pyrogallol.

and safe flame-retardant epoxy thermosets is a hot industrial topic in which vanillin could prove useful.

In another study, epoxy polymers were prepared using vanillin in an unexpected way. Indeed, Shimasaki et al.[39] first prepared a calixarene by condensing pyrogallol (also biobased) and vanillin as shown in Scheme 6.

The next step of their work was to prepare a composite with a sorbitol-based epoxy matrix hardened with the calixarene they synthesized from vanillin. They obtained a polymer with a T_α of 148 °C, which is high for biobased epoxy polymers. The next step of their work was to use wood flour as a filler in this epoxy matrix, leading to a fully biobased epoxy composite. One of the major highlight of this work is the preparation of the calixarene used as hardener. This compound was formed by the condensation reaction used to prepare phenolic resins, but in their case, the oligomer formed has a well-defined, polyphenolic cyclic structure. The performance of this compound in other fields might be worth investigating; in catalysis or supramolecular chemistry for its potential host–guest interactions for instance.

2.3. Phenolic resins

Thermosetting phenolic resins were developed as early as the 1900's with the Bakelite resin formed by the condensation of phenol and formaldehyde. Since then, their low price combined with very good thermo-mechanical properties maintained them as an important class of polymers, irreplaceable in some applications. With the current urge to switch from petrobased to renewable resources, there is surprisingly very few studies dealing with the biosourcing of this kind of polymer. Yet, vanillin is a good starting point as it is aromatic, biobased and bears both a phenol and an aldehyde moiety.

Chauhan prepared a terpolymer using the condensation reaction of vanillin and acetophenone with furfural, also a biobased compound [40]. He proposed the following structure (Fig. 2).

Even though the structure of the polymer obtained is likely to be more complex, ^{1}H NMR showed the presence of all three monomers in the final material. Interestingly, the author depicted the vanillin aldehyde moiety as unreacted; although the residual signal of the aldehyde proton in the ^{1}H NMR of the final material is very weak. Further characterization of this polymer revealed a microporous structure and a high thermal stability that could lead to an application in catalysis for example.

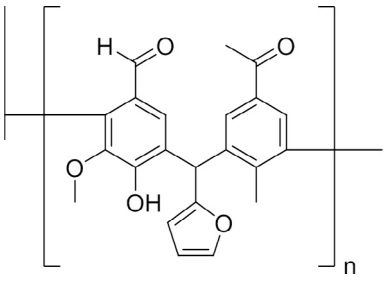


Fig. 2. Proposed structure of a vanillin–furfural–acetophenone terpolymer.

The same author prepared another terpolymer based on the condensation reaction of vanillin oxime and acetophenone with formaldehyde [41]. The oxime group is widely employed for its antimicrobial properties. The preparation of vanillin oxime from vanillin and hydroxylamine is a simple and easy-to-implement reaction with a high yield. The polymer displayed moderate to good antimicrobial activity, depending on the bacteria or fungus tested. The author envisaged the use of this polymer for medical device coating. A drawback of this method is however the use of formaldehyde, a category 1B carcinogenic compound that would advantageously be replaced by a less dangerous, biobased aldehyde.

2.4. (Meth)acrylic polymers

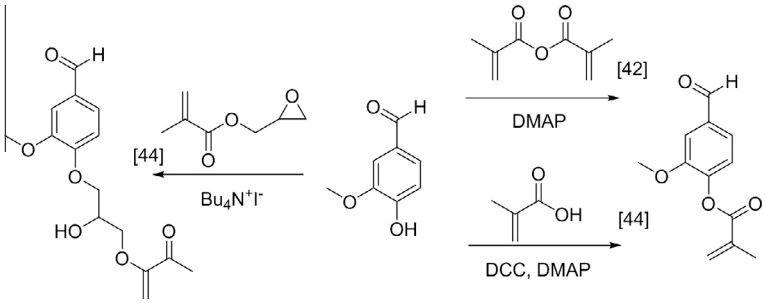
Functionalization with acrylic groups, e.g. acrylate, methacrylate, or acrylamide, is among the most common strategies employed when it comes to the use of chain-growth polymerization. Their polymerization is easily induced by UV or heat in the presence of an appropriate initiator.

A handful of papers report the functionalization of vanillin with methacrylate groups. They are summed up in Scheme 7.

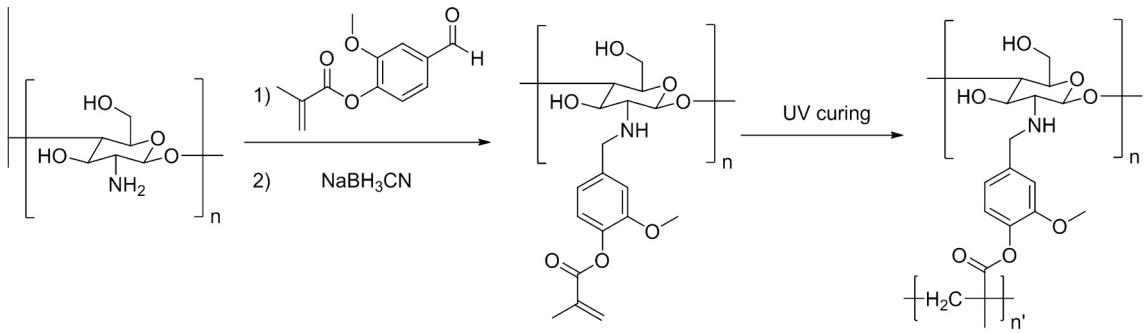
In their work, Stanzione III et al. prepared vanillin methacrylate and polymerized it to obtain a biobased thermoset with glycerol methacrylate as a crosslinker [42]. The reaction was carried out without solvent, which is relevant from a sustainability point of view. Indeed, solvents can be volatile, flammable, and/or harmful substances. Avoiding them is thus beneficial in terms of safety. Also, less waste is generated in the case of solvent-less reactions. The polymer synthesized exhibited a T_α of 155 °C at the tan δ maximum, T_α being the temperature of the α transition, related to the glass transition but under mechanical stress (and thus frequency-dependent). This temperature was taken, as it is common in the literature, as the glass transition temperature (T_g) of the polymer. It is worthy to note that only few biobased polymers are able to reach the thermo-mechanical properties displayed in this work, properties that the authors compared to commercial vinyl ester resins. They envisaged an application as matrix for composites.

Holmberg et al., from the same team, also synthesized by RAFT polymerization [43] homopolymers from vanillin methacrylate with a controlled molecular weight, which exhibited T_g values between 110 ° C and 120 ° C. They also prepared block copolymers of vanillin methacrylate and lauryl methacrylate and showed that this copolymer self-assembled into nanospheres.

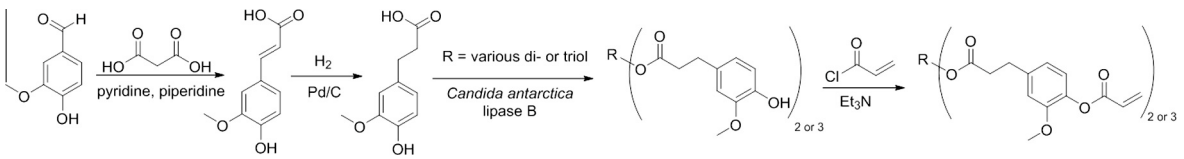
Renbutsu et al. [44] also prepared vanillin methacrylate using a different method: they performed a Steglich esterification (Scheme 7) of the phenolic hydroxyl of vanillin with methacrylic acid. The next step of their work was to functionalize the free amine groups of chitosan by a reductive amination reaction with the aldehyde moiety of vanillin methacrylate. Finally, they crosslinked the system by UV-induced radical polymerization of the methacrylate moieties as shown in Scheme 8.



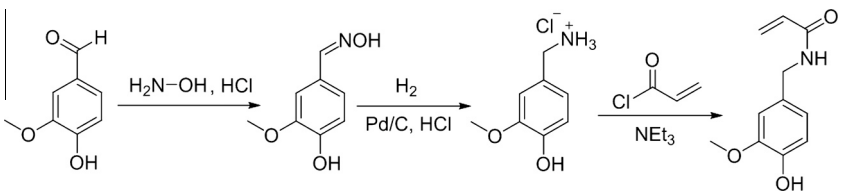
Scheme 7. Vanillin functionalization with acrylate and methacrylate groups.



Scheme 8. Chitosan functionalization with vanillin methacrylate and crosslinking of the system.



Scheme 9. Multi-step procedure to obtain di- or triacrylates from vanillin and various potentially biobased alcohols.



Scheme 10. Synthesis of an acrylamide monomer from vanillin.

The same authors also prepared another methacrylate derivative of vanillin by reacting the phenolic hydroxyl of vanillin with glycidyl methacrylate as shown in Scheme 7. This compound was also used to functionalize chitosan and prepare a crosslinked material, using the strategy depicted in Scheme 8. These crosslinked chitosan derivatives were tested for palladium adsorption and electroless plating with good results in both cases.

Pion et al. used vanillin to prepare acrylates in a multi-step procedure [45] shown in Scheme 9.

The first part of their work is the preparation of ferulic acid from vanillin by a Knoevenagel condensation with malonic acid. Ferulic acid could also be directly obtained from lignin but its production is not industrially developed compared to vanillin. This compound was reduced into dihydroferulic acid, which was then enzymatically esterified with various di- or triols to obtain biobased bis- and trisphenols. These phenols were further functionalized to acrylates to be used as crosslinking agents. Even though the whole procedure might not be industrially viable because of the many steps involved, the intermediates accessed during the synthesis are interesting for the biosourcing of a variety of polymers such as epoxy thermosets or polyesters.

Liu et al. [46] designed an acrylamide monomer from vanillin (Scheme 10). This monomer possesses great potential as it can lead, by radical polymerization, to a vanillin-based polyacrylamide bearing pendant phenolic moieties.

The procedure was performed at room temperature, which is interesting from the energy economy aspect. This monomer was then polymerized to give a polyacrylamide having pendant, covalently bound phenols along the chains acting as antibacterial moieties. The conventional radical polymerization of this monomer proved tricky. Whatever the conditions used (reaction time, initiator concentration and temperature) average molar masses were relatively low ($\leqslant$11,000 g/mol). Authors attributed this phenomenon to the well-known polymerization inhibition effect of phenolic moieties. Branching was also observed, which was attributed to transfer reactions of macroradicals to phenols. The mechanistic aspects of the reaction were investigated by MALDI-TOF. In spite of their low molar masses, one can imagine many applications for this type of innovative polymer. The team focused their work on surface coatings. The authors demonstrated that this polymer with pending phenols exhibited an anti-biofilm activity against *Bacillus subtilis*. As the antibacterial moieties – phenols – are covalently bound to the surface, authors proposed an inhibition of bacterial growth by contact with the surface. Coatings of medical devices could be a potential application.

2.5. Polyesters

The third most-produced polymer worldwide (18%) is Poly(Ethylene Terephthalate) (PET). This fact alone could justify the need of biosourcing polyesters, even if there are many other well-known types of polyester used in a myriad of applications. Numerous strategies exist to obtain biobased polyesters with properties similar to PET, including the direct replacement with bio-PET, which is already an industrial reality, or the use of furan dicarboxylic acid as a substitute to terephthalic acid. Vanillin, being one of the very few biobased aromatic synthon available, has also been used to prepare polyesters.

Mialon et al. used a strategy very similar to the one described above for acrylates in their effort to prepare polyesters from vanillin [47]. More precisely, they used a Perkin reaction to prepare acetylferulic acid, which was then reduced to acetyl dihydroferulic acid. This AB type monomer was then polymerized by a condensation reaction to lead to a vanillin-based renewable polyester as shown in Scheme 11.

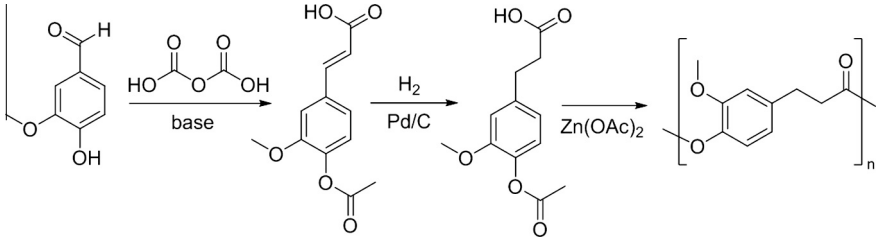
This polymer displayed interesting thermal properties: Its melting temperature is 30 °C lower than PET while both have a T_g around 70 °C. Such properties are critical when it comes to processing and this biobased polymer could thus be envisaged as a PET substitute. This strategy of mimicking PET properties with a polyester derived from renewable resources was also patented [48].

The same team also prepared polyesters from vanillic acid among other hydroxybenzoic acids obtained from wood [49]. They demonstrated that the polymerizations of vanillic acid either by direct esterification or from a transesterification reaction with an AB type monomer – methyl vanillate or O-acetyl vanillic acid – were unsuccessful or only yielded oligomers at best. This might be due to the presence of phenolic hydroxyls, which are less reactive than aliphatic ones. Also, the absence of aliphatic moieties might dramatically increase the viscosity of the mixture during the reaction, limiting the conversion. The authors prepared AB type monomers bearing aliphatic hydroxyls, best suited for direct esterification reaction, and were successful in preparing a series of polyesters (see Scheme 12). They observed a decrease in the T_g with an increasing number of carbons in the alkylene segment. The monomers were prepared by reaction of the phenol group either with chloroalkyls or with oxirane ring-containing compounds like ethylene oxide.

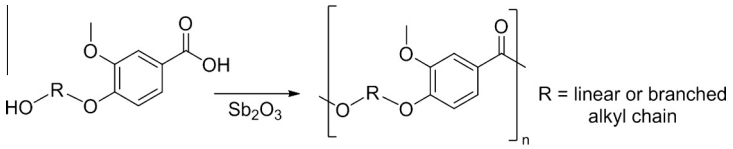
This last reaction had already been discussed in a previous paper by Lange et al. to prepare the AB type monomer from vanillic acid and ethylene oxide, leading to poly(ethylene vanillate) [50]. In the same paper, the authors also mentioned the synthesis of a dibenzoic acid from vanillic acid using a coupling strategy with dibromoethane and the subsequent polymerization of the monomer prepared. They reported a reaction of the phenolic hydroxyls on dibromoethane.

Pang et al. used a similar coupling strategy to prepare the two monomers shown in Fig. 3(A and C) from vanillic acid. Dibromobutane reacted with phenolic hydroxyls of methyl vanillate [51] or vanillic acid [52] to lead to these monomers. Various polyesters were prepared from these two monomers. In the case of the vanillic acid derivative, esterifications with various common alkyl diols [52] were performed. In the case of the methyl vanillate derivative, polymerizations were performed via transesterifications with aliphatic diols prepared via thiol-ene chemistry [51].

The same team also prepared the two asymmetric monomers shown in Fig. 3(B and D) from the same reactants but with another synthetic strategy, i.e. by reacting them with methyl chloroacetate. These monomers were



Scheme 11. Synthesis of an aromatic polyester from vanillin.



Scheme 12. Vanillic acid-based polyesters by esterification of AB type monomers.

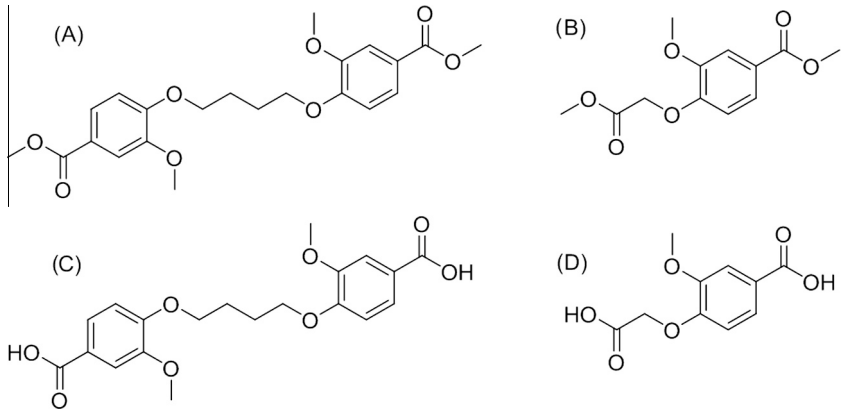
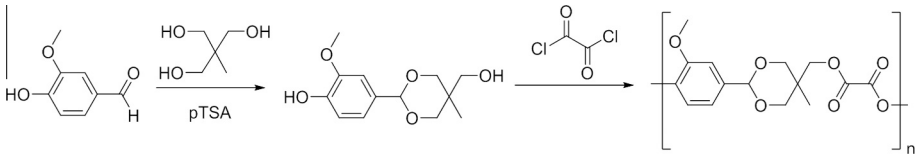


Fig. 3. Di(methyl vanillate) monomers polymerizable by transesterification.



Scheme 13. Synthesis of an acid- and oxidant-sensitive polyester from vanillin.

reacted with the same diols as previously mentioned. In summary, the authors obtained two series of polyesters, either from the asymmetric monomers or from the ones prepared by a coupling strategy. All these polymers were characterized and authors investigated their crystallinity, molecular weight, transition temperatures, mechanical properties, improving the overall knowledge on biobased polyesters.

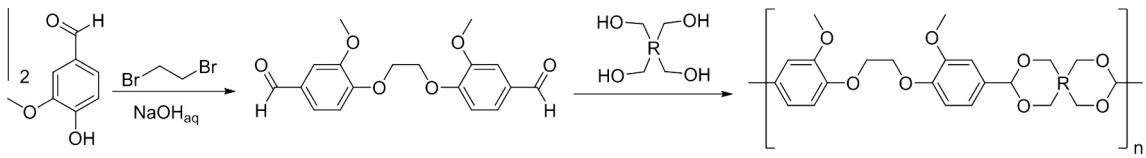
Original polyester microparticles based on vanillin were synthesized by Kwon et al. [53]. Their approach is shown in Scheme 13. In a first step, vanillin was acetalized with trimethylolethane to form a dihydroxyl intermediate that was polymerized in a second step with oxalyl chloride to form a polyester.

The authors designed this polyester to contain vanillin molecules in its backbone that were released in acidic or oxidative conditions by chain cleavage, along with trimethylolethane and CO_2. The free vanillin molecules released had an excellent anti-oxidative and anti-inflammatory activity. These stimulus-responsive polyester microparticles could be used for the controlled release of therapeutics (vanillin here) to treat oxidative stress-associated inflammatory diseases.

2.6. Polyacetal

The contribution of Pemba et al. to the development of polymers from renewable resources also involved the acetalization of vanillin. More precisely, the authors synthesized a polyacetal from dialdehyde and tetraol monomers [54] as displayed in Scheme 14.

The first step of this synthesis involved the preparation of a difunctional monomer from vanillin by a coupling strategy. Two molecules of vanillin reacted on dibromoethane to



Scheme 14. Synthesis of a polyacetal from vanillin.

lead to a dialdehyde monomer. In a second step, this monomer was reacted with a tetrafunctional alcohol – also potentially biobased – to form a polyacetal. Authors investigated the properties of the polymers prepared and reported relatively high T_g for biobased thermoplastic polymers, ranging from 68 °C to 152 °C depending on the structure and molecular weight. The presence of aromatic rings along the backbone might explain this result. The authors also mentioned the rapid hydrolysis of acetal bonds in aqueous acidic media, which can be either a drawback or an advantage depending on the property desired (stability or degradability). When it comes to lowering the carbon footprint of polymers, (bio)degradable and/or easily recyclable polymers are a very promising option.

2.7. Polyaldimines (Schiff base from aldehyde)

The reaction between an aldehyde and an amine leading to a secondary aldimine, better known as a Schiff base, is a well-described reaction. Schiff bases are widely used compounds in many fields such as biochemistry, catalysis as ligands, organic synthesis and polymers. The aldehyde group of the vanillin molecule can undergo such a reaction with an amine. The literature reports many studies where free amines on chitosan chains were functionalized with pendant vanillin molecules as shown in Scheme 15. Amines and aldimines pictured in this scheme might be protonated, depending on the pH conditions used in the studies. This vanillin-modified chitosan has numerous applications.

For instance, Jagadish et al. used this reaction to prepare a vanillin-modified chitosan with a degree of substitution of 63% relative to the amino group. In a second step, they reduced the aldimine bonds with sodium cyanoborohydride. Thus, the authors prepared a N-vanillylamine chitosan polymer [55] and evidenced improved tensile strength, transparency, and water vapor transmission properties compared to native chitosan. Antifungal properties against *Aspergillus flavus* were also assessed. A moderate decrease in biomass proliferation was detected, and also, interestingly, a marked reduction of the aflatoxin produced by the fungus. From these findings, authors proposed the use of this polymer in food packaging applications.

Peng et al. also used the reaction shown in Scheme 15 to synthesize a vanillylimine chitosan polymer. They prepared resveratrol-loaded microspheres [56] from it and assessed the potential of the system for drug delivery applications. The authors mentioned that the formation of these microspheres took place through a chemical crosslinking reaction between chitosan and vanillin. However, as it can be seen in Scheme 15, the Schiff base formation cannot account for a covalent crosslinking as the pendant phenolic hydroxyls groups do not form covalent bonds with the chitosan backbone.

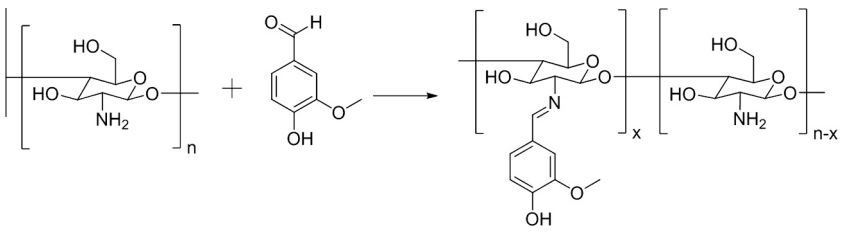
Marin et al. investigated the reaction in more details [57]. They reported the formation of strong gels and attributed this to strong H-bonding instead of covalent crosslinking. Chitosan is only soluble in acidic aqueous medium but the authors obtained very low degrees of substitution in these conditions. This result might be explained by the fact that imine groups are not stable in such conditions: they can be protonated to iminium groups which undergo hydrolysis to give back the starting aldehyde (Stephen reaction). In this case, aldimine bonds are thus reversible and the authors demonstrated that pendant group exchanges took place and called the materials prepared biodynamers. Finally, the authors demonstrated that the solution-to-solid state change process is highly beneficial for imine bond formation and that conversion dramatically increased in a hydrophobic environment.

The same team confirmed by XRD that this crosslinking of vanillin-modified chitosan happened through strong H bonding formation [58], especially at high degree of substitution. They also showed that through this H bonding, vanillin-modified chitosan presented a self-organized lamellar phase in the solid state as displayed in Fig. 4. The antifungal properties of these films on *Candida albicans* strain were investigated and found to be outstanding.

Vanillin-modified chitosan also found applications in water treatment, as a metal ion sorbent. Indeed, imine groups are known for their chelation properties. Cestari et al. studied the thermodynamics of the adsorption of Cu(II) on membranes of vanillin-modified chitosan and were able to fit a Langmuir model to the phenomenon. They concluded that the mechanism followed a monolayer adsorption and that this material was effective to remove low concentrations of Cu(II) from aqueous solutions [59].

Amarasekara et al. also investigated interactions of aldimine groups from vanillin with metal ions, but instead of preparing physically crosslinked materials through H bonding, they prepared covalently crosslinked polymers [60]. They synthesized bisvanillin by an enzyme-catalyzed oxidative coupling of two vanillin molecule (Scheme 16). Then, they used this product as a difunctional aldehyde monomer and polymerized it with various diamines.

The authors used the basic form of the polymer to chelate Fe(II), Cu(II), and Co(II) ions and obtained insoluble materials. Authors confirmed that the metal ions were bound to the imine and phenolic sites. These polymers could be used in water treatment.



Scheme 15. Chitosan functionalization with vanillin by an aldimine bond formation.

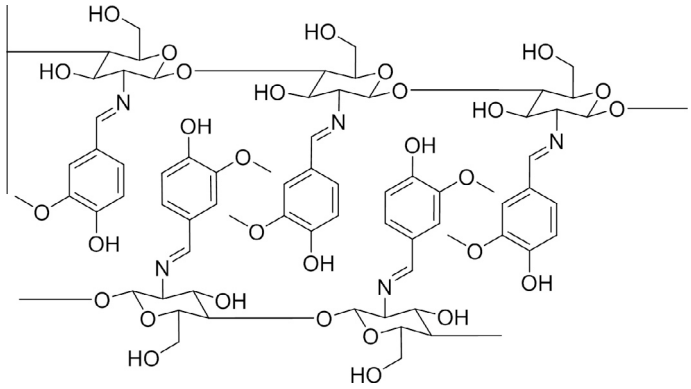
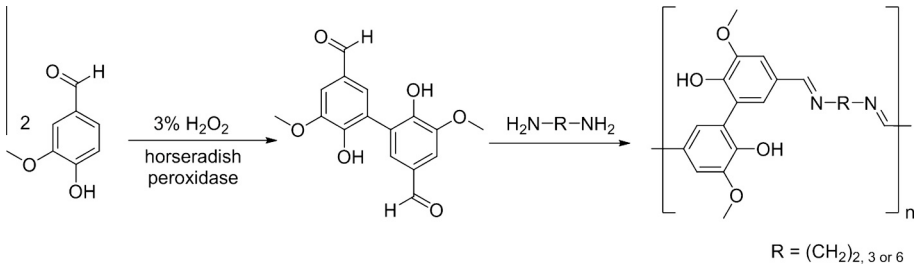
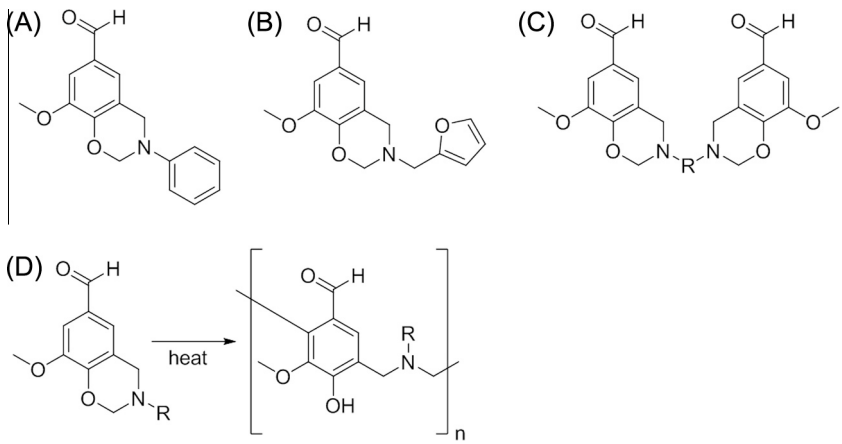


Fig. 4. Lamellar self-organized phase of vanillin-modified chitosan.



Scheme 16. Bisvanillin synthesis and polymerization with diamines to poly(aldimines).



Scheme 17. Benzoxazine monomers based on vanillin and their polymerization.

2.8. Polybenzoxazines

Polybenzoxazines are a relatively new class of high performance thermosetting polymers. They exhibit excellent thermo-mechanical properties and chemical resistance. As for many high performance thermosets, benzoxazine monomers have an aromatic structure. Recently, many contributions reported the synthesis of biobased benzoxazine monomers and polymers. The benzoxazine ring is formed by reacting a phenol, a primary amine and formaldehyde. In some of these works, the phenol used was vanillin.

Van et al., for instance, prepared the monomer displayed in Scheme 17A by reacting vanillin, aniline and paraformaldehyde. The monomer was heated to prepare a thermosetting polymer [61] by ring opening polymerization of the benzoxazine ring as shown in Scheme 17D.

The authors also further functionalized this compound to prepare a surfactant by grafting a Jeffamine hydrophilic tail onto the benzoxazine monomer. The grafting reaction took place between the primary amine of the Jeffamine and the free aldehyde of the benzoxazine to form an aldimine. This surfactant was successfully used in the

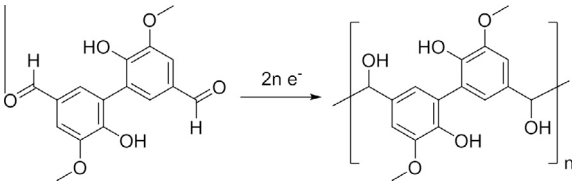
emulsion polymerization of styrene as the hydrophobic benzoxazine part had a strong affinity for (poly)styrene.

The team of Sini et al. also reported the synthesis and polymerization of a benzoxazine monomer based on vanillin. They used the biobased furfurylamine [62] to prepare the monomer depicted in Scheme 17B and increase the content of renewable carbon in their polymer. The same authors also reported the synthesis of bisbenzoxazine monomers from vanillin and various diamines [63] as shown in Scheme 17C. The T_g reported for the polymers based on bisbenzoxazines were above 200 °C and very broad, which might be explained by a very high cross-linking density. In all of these works, the polymers prepared displayed outstanding thermal stability, which supports this hypothesis. However, high polymerization temperatures (around 200 °C) are needed, which is usual for polybenzoxazines but can be a drawback when it comes to their application.

2.9. Polymers from alkenes

The carbon–carbon double bond has always been a valuable tool for polymer chemists, traditionally useful for chain-growth polymerization reactions. Recently however, reactions involving alkenes and leading to polymers by a step-growth mechanism instead of chain-growth were developed. These reactions are Acyclic Diene MEtaThesis (ADMET) and thiol-ene reactions. Both display good control, useful to prepare well-defined architectures, high efficiency, and high functional group tolerance. These characteristics gained importance in the context of green chemistry. ADMET is a transition metal-catalyzed reaction that takes place between two terminal alkenes and that is driven by the release of ethylene (Scheme 18A). Thiol-ene reaction is a well-known example of click chemistry and can be either UV- or heat-induced (Scheme 18B). In their contribution, Firdaus and Meier prepared vanillin-based monomers bearing terminal C=C double bonds suitable for these reactions [64] as shown in Scheme 18C.

These C—C double bonds are introduced either by transesterification with an unsaturated fatty ester or by Williamson etherification with an alkene bromide. The first option might be better from a sustainable chemistry point of view.



Scheme 19. Bisvanillin polymerization by reductive coupling.

2.10. Polymers from reductive coupling of aldehydes

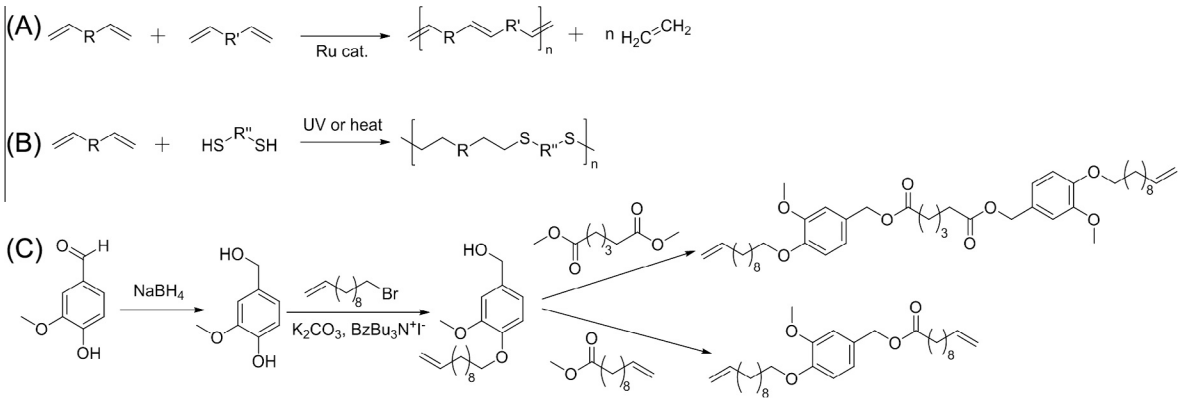
The use of renewable resources is only one aspect among many others that have to be considered to improve chemistry in general. Energy efficiency, atom economy, safety, etc. are examples of green chemistry requirements. To achieve this, new, greener processes are under development. The work of Amarasekara et al. is an example of this research trend.

As mentioned before, they prepared bisvanillin by an enzyme-catalyzed oxidative coupling of two vanillin molecule (Scheme 16). They used an original approach for the step-growth polymerization of this compound: bisvanillin was homopolymerized [65]. Authors used the reductive pinacol coupling of aldehydes to vicinal diols to prepare a polymer entirely based on vanillin as shown in Scheme 19.

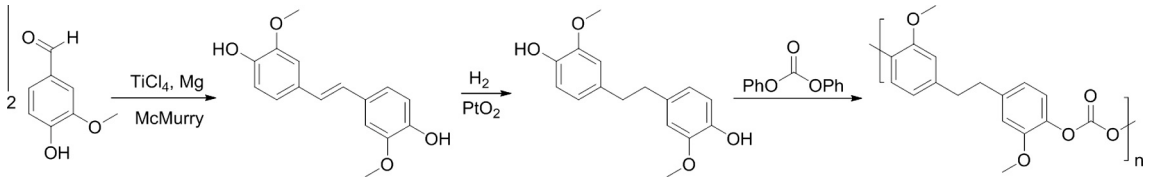
This elegant reaction was performed in an electrochemical cell; the scaling-up to an industrial process will thus require further development. Harvey et al. also used this reductive pinacol coupling of vanillin on a 40 g-scale to prepare hydrovanilloin in a 69% yield [66], which might be a first hint that this process can be used on a larger scale.

Their efforts were directed toward the synthesis of diphenolic monomers. This team also used a harsher reductive coupling reaction, i.e. the McMurry reaction [66], to attain their goal. Instead of obtaining a vicinal diol, the product of this reaction was a diphenolic stilbene, as shown in Scheme 20.

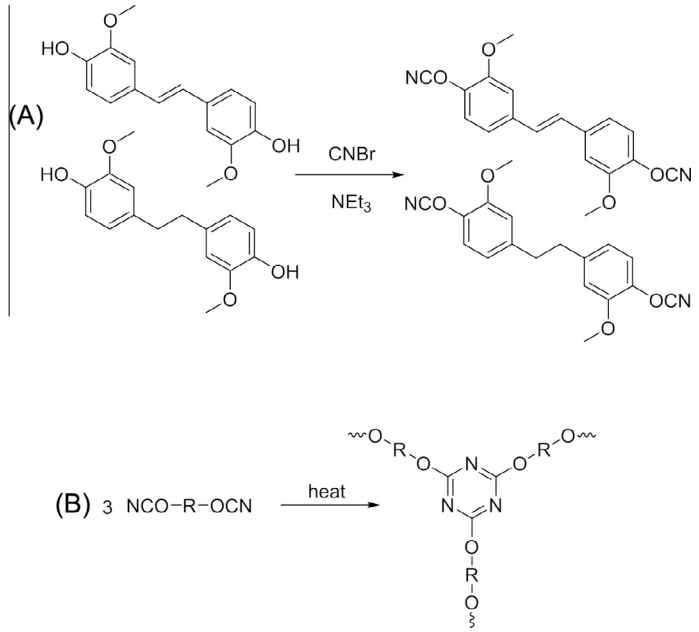
This compound was further reduced by catalytic hydrogenation to the alkyl derivative, which was used as a monomer to prepare a polycarbonate by a transcarbonatation reaction with diphenyl carbonate. The authors investigated the thermal stability of this vanillin-based polycarbonate



Scheme 18. ADMET and thiol-ene polymerization of difunctional terminal alkenes monomers and their synthesis from vanillin.



Scheme 20. Synthesis of two diphenols from a McMurry reductive coupling of vanillin.



Scheme 21. Vanillin-based cyanate esters and their polymerization.

and evidenced an interesting feature of the degradation: the formation of benzodioxolones as a result of the methoxy group ortho to the carbonate.

Both of the diphenol monomers prepared were then modified to cyanate esters (Scheme 21A). Cyanate esters polymerize via a cyclotrimerization reaction (Scheme 21B) to form crosslinked cyanurate thermosets that possess a high thermal stability.

In this study, a high T_α of 202 °C was detected and a high temperature of 335 °C was reached for a 5% weight loss of the polymer. Once again, this work demonstrates the potential of vanillin as a key building block for polymers, here in the case of high performance materials.

3. Conclusion

The use of renewable resources is a burning issue to design a more sustainable chemistry. In polymer science, the use of oils and polysaccharides is already an industrial reality. However, a large number of polymers are based on aromatic monomers. The biosourcing of aromatics is more problematic because the widely available aromatic feedstocks, like lignin, are polymers with complex and variable structures, high molecular weights, and limited processability. Very few molecular aromatic compounds from renewable resources are readily available. Vanillin is one of them. It is also harmless and offers many functionalization possibilities. Considering these advantages, studies on the use of vanillin for renewable polymers are surprisingly recent and rare, although their number is growing fast.

Vanillin can potentially be used to prepare many types of polymers, especially in high-performance thermosets such as epoxy polymers or polybenzoxazines, for which the first results seem very promising. Vanillin also shows potential uses for thermoplastics requiring aromatic monomers such as polyesters. As a consequence of this diversity, vanillin-based polymers, as reported in this review, could be used in a broad range of applications, such as composites, drug delivery, water treatment, flame retardation and antibacterial coatings. It is worthy to note that many research papers were published using vanillin in other contexts than the use of renewable resources, for instance liquid crystalline polymers, even if it was not in the scope of this study.

With the predicted shortcoming of petroleum-based resources and the resurgence of wood-based chemistry, vanillin has the potential to become one of the key building blocks of tomorrow's polymer chemistry. This review underlines the efforts of the scientific community to develop these new, more sustainable polymers from vanillin and shows that the number of contributions on this subject is growing fast.

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Maxence Fache was born in 1988. He obtained his MSc degree in 2012 from the National Graduate School of Chemistry and Chemical Engineering of Montpellier, France, with Polymer Chemistry as major. He is currently in the third year of his PhD program at the University of Montpellier, under the supervision of Dr. Sylvain Caillol. His research interests lie in the field of green chemistry, more precisely on the synthesis of polymers from renewable resources. His PhD works deal mainly with the synthesis of epoxy polymers from vanillin.

Bernard Boutevin was born in 1948. He received his PhD degree in 1974 from the University of Montpellier and joined CNRS. Subsequently he created a Polymer laboratory in Montpellier in 1985. Then he was director of several research units with more than 100 researchers. He was appointed full Professor in 1999. His research interests included the use of fluorine, phosphorous and silicon in monomers and polymers. Recently, he interested in the synthesis of new biobased building blocks and polymers. Now Professor *Emeritus*, he was co-director of more than 200 PhD theses, co-author of more than 250 patents and 1000 articles.

Sylvain Caillol was born in 1974. He received his M. Sc. Degree in Chemistry from the Engineering School of Chemistry of Montpellier in 1998. Then he received his PhD degree in Polymer Science in 2001 from the University of Bordeaux. Subsequently he joined Rhodia group and headed the Polymer Department in the Research Center of Aubervilliers. In 2007 he joined CNRS in the University of Montpellier where he started a new research topic dedicated to the synthesis of biobased building blocks and polymers. He is cofounder and Director of ChemSuD Chair. Co-author of several articles and patents, he won the Innovative Techniques for Environment award.

6. Conclusion

Through this literature analysis, it is clear that epoxy thermosets have been and are of the highest industrial interest. The market is predicted to grow, for a large part due to their use as matrices for composites, which are more and more used as structural lightweight materials. This can be beneficial both economically and environmentally, for instance if used for fuel economy in the transport industry. However, epoxy manufacturers have to face a double problematic. On the one hand, 75% of the epoxy pre-polymers produced worldwide are based on bisphenol A, which is a reprotoxic compound that might be banned in the not-so-distant future. On the other hand, epoxy thermosets are not recyclable because of their cross-linked nature. For this reason, it is of paramount importance to prepare them from renewable resources, while keeping their level of performance and thus their industrial relevance.

These performances are mainly due to their cross-linked nature and to the fact that the epoxy monomers employed are aromatic ethers. Therefore, bio-based aromatics are needed in order to answer both problematics. The literature is rich with examples of CNSL, tannins, or lignin, the three main natural sources of aromatics, used for the synthesis of epoxy thermosets. Unfortunately, all three feedstocks present drawbacks detrimental to high-performance applications. More precisely, CNSL gives epoxy thermosets with too low T_g and the volumes available are not at the levels of tannins or lignin. However, even if available in potentially enormous amounts from biomass, tannins and lignin are highly complex poly(phenols). Their polymeric nature and variability prevent them from being an industrial reality as raw materials for epoxy thermosets. Also, di-functionality is essential to obtain linear structures, and these resources are multi-functional. Vanillin is the only molecular aromatic compound obtained from renewable resources on an industrial scale. As it is one of the major chemical for the aroma and fragrance industries, vanillin is produced from a variety of sources, mainly petroleum (85%), but also from lignin (15%). Vanillin is thus a safe, bio-based, and large-scale available aromatic. Its use for the preparation of renewable polymers is since recently intensely investigated. The rest of this work will deal with the use of vanillin as a bio-based building-block, with a focus on epoxy-amine thermosets.

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Chapter 2: Monomers from vanillin

1. Introduction

The literature analysis performed in the first chapter highlights the problems encountered when dealing with bio-based aromatics. In order to avoid the structural variability of lignins and tannins, variability that the chemical industry is currently not ready to handle, and the problems posed by their polymeric nature, the use of difunctional molecular compounds seems currently the only option. Di-functionality is an essential feature to access linear structures. Vanillin is the only molecular aromatic compound that is available on an industrial scale from biomass. For this reason, many recent works report the use of vanillin to prepare polymers, thermoplastics as well as thermosets. Vanillin has a huge potential to become an important bio-based building-block. The next section is dedicated to exploring this building-block approach.

This strategy is often used for bio-based compounds. The biomass-derived compound is identified as the building-block and first-generation derivatives of interest are prepared from it. These first -generation derivatives can themselves be used as reactants. To avoid multi-step reactions, the process is usually limited to 2 or 3 generations. The reactions used have to be as safe, efficient, and atom-economical as possible in order to fit to the green chemistry principles. The derivatives prepared constitute a platform of compounds, with the building-block at the center of the web.

This section consists of a work already published in which vanillin was used as a starting point to synthesize a platform of monomers bearing various functional groups. The monomers here, many of them prepared and characterized for the first time, include amines, alcohols, carboxylic acids, phenols, cyclic carbonates, allyls, and epoxides. They are usable for the synthesis of a wide range of different polymers.

2. Vanillin, a promising biobased building-block for monomer synthesis

Green Chem., 2014, **16**, 1987

Maxence Fache,[a] Emilie Darroman,[a] Vincent Besse,[b] Rémi Auvergne,[a] Sylvain Caillol*[a] and Bernard Boutevin[a]

Received 23rd December 2013,
Accepted 18th February 2014

DOI: 10.1039/c3gc42613k

www.rsc.org/greenchem

Vanillin was used as a renewable building-block to develop a platform of 22 biobased compounds for polymer chemistry. Vanillin-derived biobased monomers bearing epoxy, cyclic carbonates, allyl, amine, alcohol and carboxylic acid moieties were synthesized. They can be used, among many others, in epoxy, polyester, polyurethanes, and Non-Isocyanate PolyUrethanes (NIPU) polymer synthesis. The epoxy-functionalized compounds were synthesized under solvent-free conditions and are original biobased aromatic epoxy monomers. Cyclic carbonates were prepared through a catalytic reaction between epoxy compounds and CO_2. Thiol–ene reactions allowed the functionalization of allylated compounds with amines, acids and alcohols. The amine-functionalized compounds are, to our knowledge, the first non-aliphatic biobased amine hardeners, usable either in epoxy or NIPU materials.

Introduction

Recent years have witnessed an increasing demand for renewable resource-derived polymers (biobased polymers) owing to increasing environmental concerns and restricted availability of petrochemical resources.[1,2] Some solutions are already industrially available but most of these biobased polymers are aliphatic or cycloaliphatic polymers, for instance derived from cellulose,[1] starch[1] or triglycerides.[3] However, many key commercial chemicals are aromatic compounds, ultimately derived from petrochemical feedstocks.[2]

More recently, great attention was paid to renewable resources-derived thermosetting materials,[4] especially because they are crosslinked polymers and thus cannot be recycled. Also, most of the thermosetting materials contain aromatic monomers, able to confer high mechanical and thermal properties to the network. Moreover, some base chemicals used nowadays have proven harmful and need to be replaced. For instance, bisphenol A is extensively used for the manufacturing of epoxy resins even though it is a reprotoxic substance.[5] Therefore, access to biobased and non-harmful aromatic monomers is one of the main challenges of the years to come.

The three main sources of renewable aromatic compounds available are cashew nutshell liquid, polyphenols and lignin. Even though there have been some very interesting studies based on cardanol[6] or natural flavonoids[7,8] to synthesize promising materials, lignin is the most abundant feedstock.[9] Lignin is an amorphous cross-linked polymer that gives structural integrity to plants, making up 25 to 35% of woody biomass.[10] Thus, depolymerization of lignin is an alluring route to gain access to biobased aromatics needed by the chemical industry. Unfortunately, this route is deceptive. Despite extensive research,[11] there are very few reports on efficient ways of recovering such aromatic products.

The only notable commercial process has been the historical production of vanillin from lignosulfonates contained in the "brown liquor", a by-product of the sulfite pulping paper industry. Even though this process uses cheap and available waste materials, its use declined because of environmental concerns. Nowadays, Solvay dominates the vanillin market using the petroleum-based catechol–guaiacol process. 85% of the vanillin is produced by this method and 15% still from lignin.[12,13]

Most recently, however, lignin-to-vanillin routes regained a lot of interest[12–14] with technical advances in processes[15] as well as waste management. For instance, Borregaard, the second largest vanillin producer in the world and the only one with a vanillin-from-lignin process, employs an ultrafiltration technology, achieving a reduction in waste stream volumes.[16] Therefore, instead of expecting various biobased aromatics from lignin depolymerization, which is not a mature technology, the improvement of lignin-to-vanillin processes and the use of vanillin as a biobased building-block for polymer chemistry seem a better perspective.

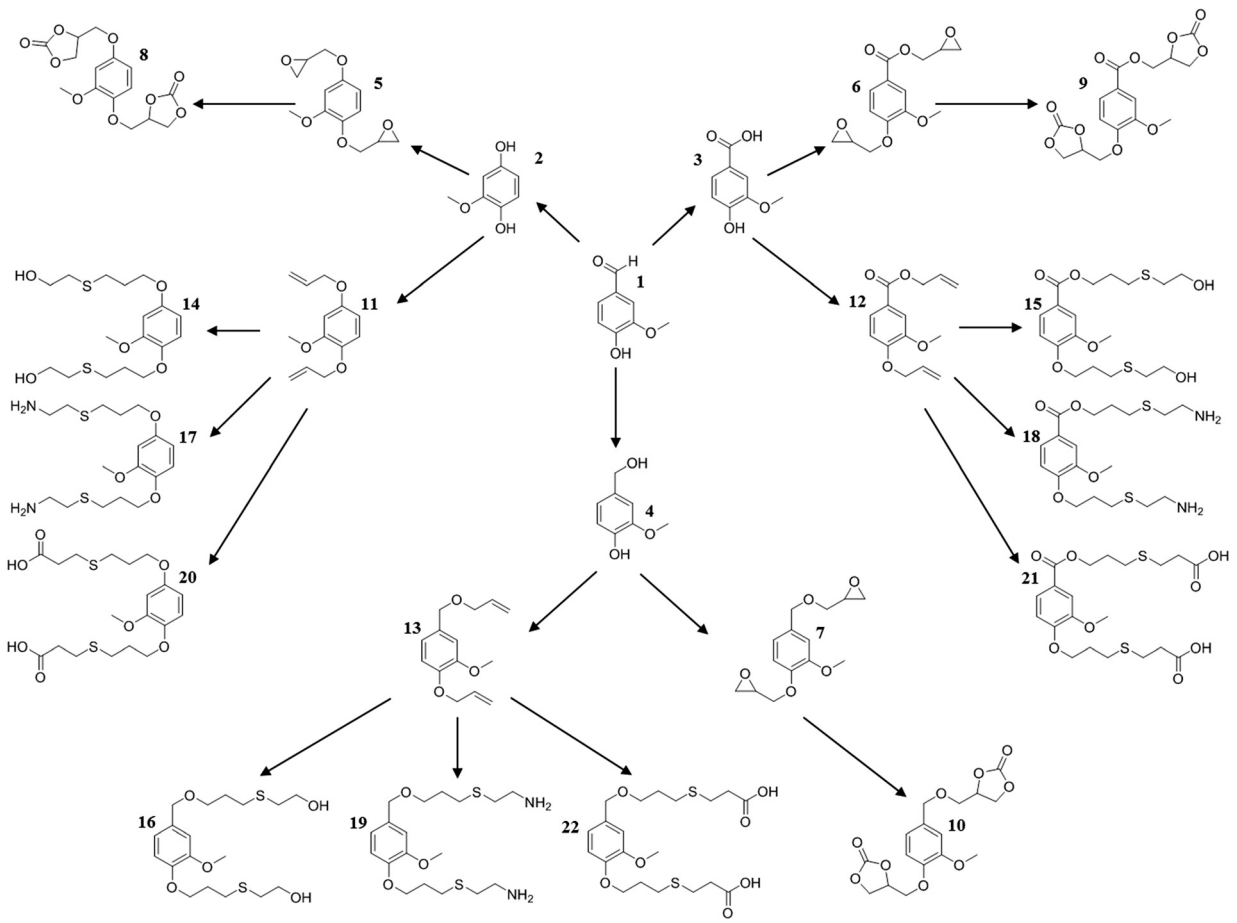
Even though the lignin-derived vanillin is becoming relatively easily accessible, still there are only a handful of reports

[a]*Institut Charles Gerhardt, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France. E-mail: sylvain.caillol@enscm.fr*
[b]*COLAS S.A., 7 place René Clair, 92653 Boulogne-Billancourt, France*

on attempts to utilize vanillin as monomers for biobased polymer synthesis. Amarasekara *et al.* have reported the dimerization and electrochemical reductive polymerization with horseradish peroxidase.[17] The Schiff base synthesized was used for metal ion chelation applications.[18] Schiff bases from vanillin were also prepared by Issam *et al.* and transformed into epoxies in a second step.[19] Concerning epoxy compounds, Aouf *et al.* prepared the allylated vanillic acid and worked on its epoxidation by a chemo-enzymatic process with *Candida antarctica* lipase.[20] Koike described an interesting process allowing the synthesis of an epoxy monomer from vanillin.[21] Other teams reported the synthesis of various biobased polymers from vanillin. Thus, Meier *et al.* reported the synthesis of polymers from vanillin and fatty acids by acyclic diene metathesis (ADMET).[22] Starting from vanillin, Mialon *et al.* synthesized polyesters such as polydihydroferulic acid[23] and polyethylene vanillate.[24] Photoactive liquid crystalline polyesters and polyethers were also prepared from vanillin.[25,26] An original benzoxazine monomer was prepared from vanillin and furfurylamine by Sini *et al.* and then polymerized.[27] Additionally, vanillin was methacrylated and used in the preparation of UV-curable palladium-chelating chitosan derivatives.[28] Vanillin methacrylate also replaced styrene in vinyl-ester resins for composite application.[29] Composites were synthesized directly from vanillin, sorbitol, and pyrogallol with wood flour.[30]

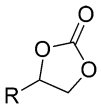
From the few but interesting studies cited, it is clear that vanillin has a huge potential to meet the aforementioned challenge concerning biobased monomers. It is biobased, potentially abundantly available and does not compete with edible resources. Its aromatic structure could provide the desired thermal and mechanical properties to materials and its different substituents led us to consider it to be a versatile biobased platform chemical. Our approach in this work was thus to synthesize from vanillin a wide range of difunctional monomers directly usable in polymer synthesis. These synthesis routes were chosen in order to optimize the yields and with a reduced number of steps, to show the industrial potential of this platform.

We designed this platform with three vanillin derivatives as base chemicals, owing to their different oxidation states. This choice was based on the fact that lignin depolymerization often requires harsh oxidative or reductive conditions.[31] Thus, it is mandatory to consider not only vanillin itself, as it is common in the literature, but also its different oxidative states as potentially available. On the one hand, a vanillin **1** oxidation leads to vanillic acid **3** or even to a methoxyhydroquinone **2** in the case of a decarboxylation (strong oxidative and



Scheme 1 Vanillin platform for polymer synthesis.

Table 1 Functions present in the platform and their use in polymer chemistry

Function of monomers	Compounds	Targeted polymers
	**5, 6, 7**	Epoxy resins
	**8, 9, 10**	PolyHydroxyUrethanes (PHUs); polycarbonates
	**11, 12, 13**	Polymers obtained by radical polymerization
	**14, 15, 16**	PolyUrethanes (PUs), polyesters, polyacrylates, polycarbonates
	**17, 18, 19**	Epoxy resins, PHUs, polyimides, polyureas, polyamides
	**20, 21, 22**	Epoxy resins, polyamides, poly(vinyl-esters), polyesters

alkaline conditions[32]). On the other hand, reduction leads to vanillyl alcohol **4**. Our team functionalized these three molecules, transforming them into a number of original biobased monomers bearing well-known polymerizable functions and thus creating the above-mentioned platform shown in Scheme 1. Many of these compounds were prepared for the first time.

The functions introduced in this platform and the types of polymers in which they could be used are summarized in Table 1.

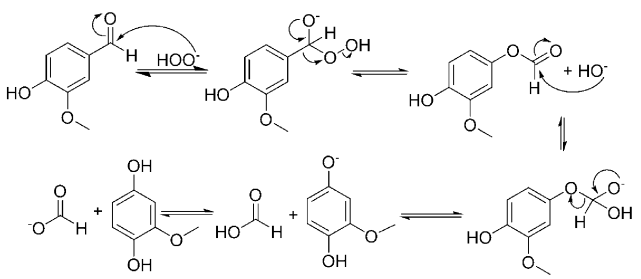
Results and discussion

Platform base chemicals

Among the three platform base chemicals, vanillic acid **3** and vanillyl alcohol **4** are quite common commercial compounds. However, to the best of our knowledge, 2-methoxyhydroquinone **2** is not commercially available. It was thus prepared in 97% yield from vanillin by the Dakin reaction, ultimately leading to one carbon loss. The reaction proceeds *via* the mechanism shown in Scheme 2.

Sodium percarbonate dissociates in solution into H_2O_2 and carbonate anions. As the solution is basic, a hydroperoxide anion can exist. The reaction starts with a nucleophilic addition of this hydroperoxide anion to the aldehyde carbonyl. The final acidification of the mixture is important for two reasons. Firstly, the pH of the solution becomes acidic, and carbonates and hydroperoxide anions no longer exist in solution, thus stopping any further reaction. Secondly, the aqueous phase must be acidic for the phenol form to predominate over the phenolate one in order to perform the extraction efficiently.

The protocol used[32] 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.



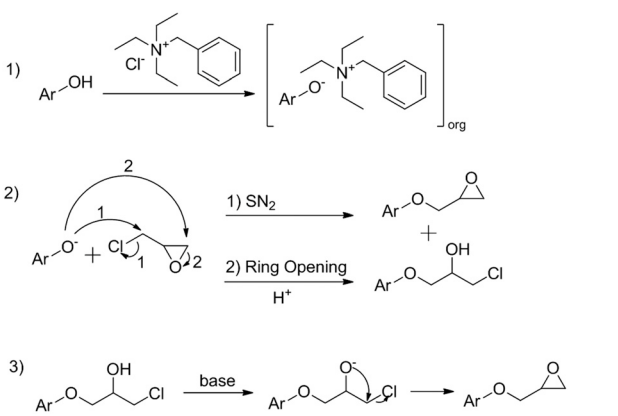
Scheme 2 Mechanism of the vanillin Dakin oxidation.

Glycidylation reactions

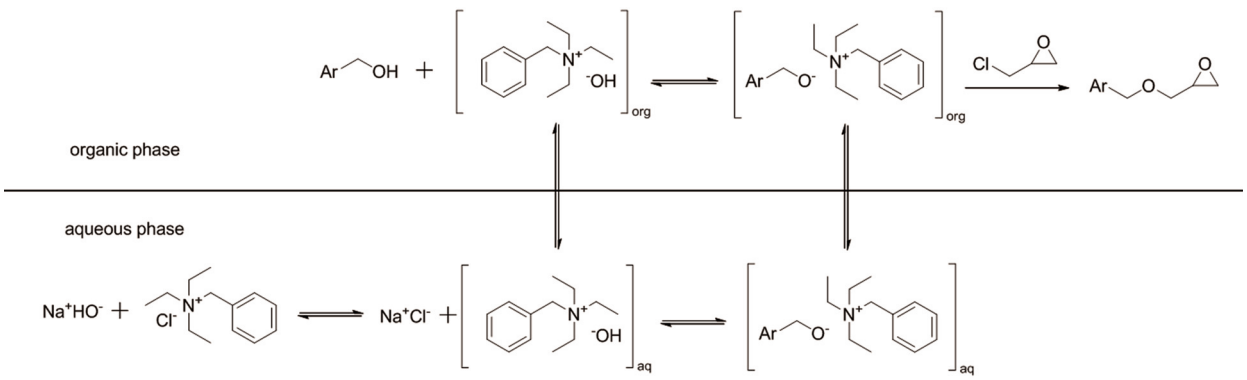
Glycidyl ethers **5**, **6** and **7** were obtained respectively from the three base chemicals **2**, **3**, and **4** in very good yields (≥87%). We are the first, to our knowledge, to synthesize compounds **5** and **7**. In a previous paper, Aouf *et al.* proved that aromatic hydroxyl and acid functions readily react with epichlorohydrin in the absence of a solvent.[33] We adapted this method for the synthesis of **5** and **6**. The reaction mechanism is explained in Scheme 3.

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 SN_2 and ring opening. SN_2 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 SN_2 reaction in the presence of an aqueous solution of NaOH and a phase transfer catalyst.

The synthesis of **7** starting from **4** was attempted with this method. **4** possesses both a phenol and a benzyl alcohol. Glycidylation only occurred on the phenol, and not on the benzyl alcohol. This was explained by the fact that protons from



Scheme 3 Phenol glycidylation mechanism under solvent-free conditions.



Scheme 4 Mechanism of phenol glycidylation by a phase transfer catalysis system.

phenols are more acidic than protons from aliphatic alcohols. Thus, contrary to phenolates, benzyl alcoholates cannot form an ion pair with the phase transfer catalyst to exist in the organic medium. It is worth noting that although this reactivity difference is problematic here, it could be an advantage in another context. In our case, **7** was synthesized using a biphasic phase transfer catalysis system.[34] The mechanism is shown in Scheme 4.

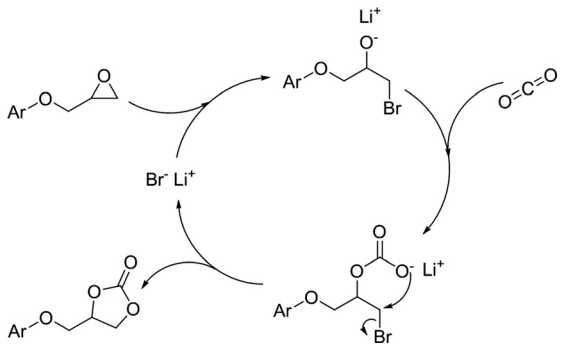
Careful temperature control is mandatory as the reaction is exothermic and any rise of temperature resulted in a colored, crosslinked product.

These reactions do not require organic solvents since epichlorohydrin is used as a reactive solvent. Epichlorohydrin was employed as it is an industrial biobased compound *via* the Epicerol® process from Solvay. Epoxy compounds **5**, **6** and **7** have potential uses in high performance epoxy resins and composites as they are biobased aromatic diglycidyl ethers. Indeed, they are structurally similar to the current petrobased epoxy monomers. They need to be tested as bisphenol A substitutes in terms of safety and material performances.

Carbonation reactions

Cyclic carbonate compounds **8**, **9** and **10** were respectively synthesized from the epoxy compounds **5**, **6**, and **7** previously obtained. Compounds **8** and **10** were obtained quantitatively. In the case of **9**, undetermined side products were detected by ^{1}H NMR, making this synthesis less interesting from an industrial standpoint. However, there is, as far as we know, no other description of compounds **8**, **9** and **10**. These bifunctional cyclic carbonates were obtained by a LiBr-catalyzed CO_2 insertion into the oxirane rings[35] as shown in Scheme 5.

The main advantage of this reaction is the use of CO_2 as reactant. From a sustainable chemistry point of view, two major challenges concern the polyurethane industry. The first one, true for the whole polymer industry, is to switch from petrobased to biobased resources. The second one, more specific to polyurethanes, is to avoid the use of isocyanate compounds since most of them (methylene diisocyanate – MDI, toluene diisocyanate – TDI) are highly toxic or CMR, and are synthesized from phosgene, also highly toxic. Therefore, NIPU (Non-Isocyanate PolyUrethane) systems have received a great deal of interest over the past few years. These systems are actually synthesized by reaction between poly(cyclic carbonates) with polyamines,[35] leading to polyhydroxyurethanes (PHUs). As these systems are shifting from academic studies to industrial use, there is a growing need for bis(cyclic carbonates) monomers and especially aromatic ones in substitution to MDI or TDI for the synthesis of linear polymers. We thus synthesized **8**, **9** and **10** which are biobased, aromatic bis(cyclic carbonates) usable in NIPU systems.



Scheme 5 Cyclic carbonate synthesis from an epoxy compound.

Allylation reactions

Allylated compounds **11**, **12** and **13** were respectively synthesized from base chemicals **2**, **3** and **4**. A method used for the allylation of gallic acid has already been reported by our team.[8] Compounds **11** and **12** were prepared quantitatively using this method. A phenolate (or carboxylate) is first formed by the action of suspended potassium carbonate K_2CO_3. This phenolate (or carboxylate) is then allylated by an easy nucleophilic attack on allyl bromide. As in the case of glycidylation, the benzylic alcohol moiety in **4** is less reactive than phenols or benzoic acids. Compound **4** was thus allylated by using the same phase transfer catalysis system. The mechanism is also the same as the one described in Scheme 4, the only difference being the use of allyl bromide instead of epichlorohydrin. It was found that phase transfer catalysis is a mild and efficient process for the synthesis of **13** (86% yield).

Allyl bromide is not a biobased compound. Since allylated compounds can undergo radical polymerization and thiol–ene click chemistry, compounds **11**, **12** and **13** are therefore essential building blocks to establish our vanillin-based platform for polymer chemistry.

Alcohol functionalization

Alcohol-functionalized compounds **14**, **15** and **16** were obtained in yields ≥90% under solvent-free conditions by thiol–ene "click" addition of mercaptoethanol to allylated compounds **11**, **12** and **13** respectively. This work is the first example, to the best of our knowledge, to report the synthesis of compounds **14**, **15** and **16**.

Click chemistry is a concept now well established and has received a lot of attention lately, especially in the field of sustainable chemistry. Indeed, the click chemistry concepts of efficient, versatile, and safe procedures with high atom economy fit sustainable chemistry principles. Click chemistry reactions are thus increasingly applied to renewable resources.[36]

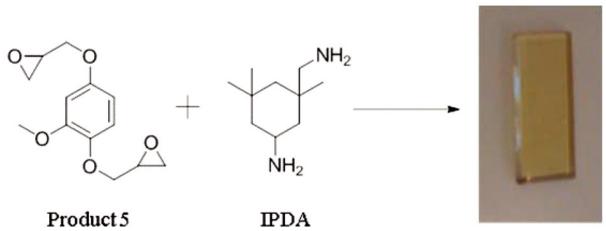
Thiol–ene coupling is considered as a click chemistry reaction and has been extensively used in the polymer field.[37] It consists in the radical addition of a thiol onto a C–C double bond. This coupling was for instance used by our team to synthesize new biobased polyols from vegetable oils. Thiol–ene coupling displays high yields and outstanding functional group tolerance under simple reaction conditions. The reaction can be initiated by either heat or UV irradiation, as in our case.

Molecules **14**, **15** and **16** are alcohol-functionalized biobased compounds bearing an aromatic ring. The aromatic ring provides better thermo-mechanical properties to the material than an aliphatic structure. They also bear primary aliphatic alcohols, making them very reactive. Molecules **14**, **15**, and **16** could therefore bring interesting properties to polyesters or to PU formulations.

Amine functionalization

Amine-functionalized compounds **17**, **18** and **19** were synthesized by thiol–ene addition of cysteamine hydrochloride onto **11**, **12** and **13** respectively in yields ≥88%. Compounds **17**, **18** and **19** are also, as far as we know, described here for the first time. Cysteamine hydrochloride was preferred over cysteamine because the amine moiety catalyzes the formation of disulfide bonds. Interestingly, thiol–ene addition was slower with cysteamine hydrochloride than with mercaptoethanol. Amine-functional compounds were obtained by simple deprotonation of the ammonium in a basic aqueous solution followed by an extraction with an organic solvent.

17, **18** and **19** are of great interest for epoxy thermosets and NIPU manufacturing as they are biobased aromatic compounds bearing two highly reactive primary amines. They can thus react with epoxy and cyclocarbonate moieties. Moreover, hardeners with an aromatic structure will improve thermo-mechanical properties. Concerning epoxy thermosets, good thermo-mechanical properties are one of their characteristic features. As for NIPU systems, tunable properties are needed to fit to the application. These compounds are, to our knowledge, the first non-aliphatic and biobased amine hardeners. They could thus prove very useful from an industrial standpoint.



Scheme 6 Material prepared from **Product 5** and IPDA.

Carboxylic acid functionalization

Acid-functionalized compounds **20**, **21** and **22** were synthesized by thiol–ene addition of 3-mercaptopropionic acid onto **11**, **12** and **13** respectively under solvent-free conditions. To the best of our knowledge, compounds **20**, **21** and **22** are not mentioned in the literature.

In the first place, the reaction was attempted with thioglycolic acid and was much faster but gave rise to unwanted side-products. The literature reports such side-products, especially thioesters, in the case of thioglycolic acid.[38] Thus, the use of 3-mercaptopropionic acid was preferred over thioglycolic acid.

This reaction was slower than the other thiol–ene reactions performed, especially in the case of **11** where only 68% were converted to **20**. **12** and **13** gave good conversions. However, no side-products were detected.

Compounds **20**, **21** and **22** also bear an aromatic ring that may improve the thermo-mechanical properties of materials. They are dicarboxylic acids and can thus be used as epoxy resin hardeners and also as monomers in biobased polyesters.

Example of the material synthesized

Each type of compound is currently evaluated for the synthesis of materials, especially NIPUs and epoxy polymers. These studies will be reported in detail in future articles. However, as an example of the potential use of these compounds, we chose to prepare an epoxy material (Scheme 6) from **Product 5**. The amine hardener chosen was the one most reported in the literature, IsoPhorone DiAmine (IPDA).

Preliminary DSC results indicate a T_g of 117 °C for this material. By improving the formulation and the process, the T_g could reach a value close to the one of the epoxy polymer prepared from DiGlycidylEther of bisphenol A (DGEBA) and IPDA, namely 158 °C.[39] This material is the one most described in the literature and the one most used in industry. However, DGEBA is derived from bisphenol A, a reprotoxic substance,[5] and thus needs to be replaced. The material prepared from **Product 5** is a high-T_g, biobased alternative to the DGEBA–IPDA system that will be investigated in future studies.

Experimental

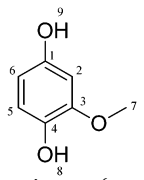
Materials and methods

Vanillin (99%) and vanillic acid (99%) were purchased from ABCR. Vanillyl alcohol (98%), sodium percarbonate $Na_2CO_3{\cdot}1.5H_2O_2$ (available H_2O_2 20–30%), triethylbenzylammonium chloride (TEBAC) (99%), LiBr (99%), mercaptoethanol (>99%), thioglycolic acid (>99%), 3-mercaptopropionic acid (>99%), potassium carbonate K_2CO_3 (>99%), allyl bromide (99%), IPDA (>99%), anhydrous sodium sulfate Na_2SO_4 (99%) and HCl (37.5 wt%) and all solvents used (>99.5%) were purchased from Sigma-Aldrich. Cysteamine hydrochloride (>97%) and epichlorohydrin (>99%) were purchased from Fluka. Sodium hydroxide, NaOH (99%), was purchased from Fisher. All reactives were used as received.

^{1}H and ^{13}C (APT mode) NMR spectra were recorded on a 400 MHz Brucker Aspect Spectrometer at room temperature. Deuterated solvents used are given for each molecule. Chemical shifts are in ppm. Silica gel flash chromatography was performed on a Grace Davison Reveleris device. UV irradiation was performed in a Rayonet RPR-200 UV reactor equipped with a cooling fan and 16 lamps of 35 W each with λ_{max} = 254 nm. A 50 mL Paar autoclave equipped with an overhead stirrer was used for carbonation reactions. MS measurements were performed on a Waters Synapt G2-S High Resolution Mass Spectrometer (HRMS) equipped with an ESI ionization source. DSC analyses were carried out on a NETZSCH DSC200 calorimeter at 20 °C min^{-1}.

Synthesis of methoxyhydroquinone 2 from vanillin 1

A two-necked round-bottomed flask was charged with a solution of vanillin (0.25 mol L^{-1}, 1.0 eq.) in THF. Deionized water (40% vol.) was added. The mixture was degassed with nitrogen. Sodium percarbonate ($Na_2CO_3{\cdot}1.5H_2O_2$, 1.1 eq.) was then added by portions under nitrogen and agitation. The reaction was conducted for 3 hours at room temperature. Portions of a HCl solution (0.1 mol L^{-1}) were added to the mixture under vigorous stirring until pH = 3 to quench the reaction. THF was evaporated and the aqueous phase was extracted with ethyl acetate. The organic phases were collected, washed with brine, dried on anhydrous Na_2SO_4 and ethyl acetate was removed under reduced pressure.



Product 2: methoxyhydroquinone (97%, m.p. 88 °C).

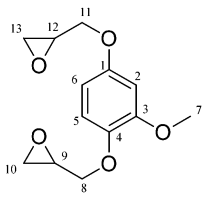
^{1}H NMR (400.1 MHz, acetone-d_6, ppm) δ: 3.77 (s, 3H, H_7); 6.27 (dd, $^3J_{H_6H_5}$ = 8.4 Hz, $^4J_{H_6H_2}$ = 2.6 Hz, 1H, H_6); 6.46 (d, $^4J_{H_2H_6}$ = 2.6 Hz, 1H, H_2); 6.63 (d, $^3J_{H_5H_6}$ = 8.4 Hz, 1H, H_5); 6.86 (broad s, 1H, H_8); 7.73 (broad s, 1H, H_9).

^{13}C NMR (100.6 MHz, acetone-d_6, ppm) δ: 56.38 (s, C_7); 101.40 (s, C_2); 107.64 (s, C_6); 116.13 (s, C_5); 140.71 (s, C_4); 149.07 (s, C_3); 151.82 (s, C_1).

HRMS (m/z, AP+): calculated: 140.0473; found: 140.0473.

Procedures for glycidylation (5, 6, 7)

This protocol was used for the preparation of **5** and **6** from **2** and **3**. A round-bottomed flask was charged with **2** or **3** (1.0 eq.) and TEBAC (0.1 eq.). Epichlorohydrin (10.0 eq.) was added and the mixture was stirred for 1 hour after reaching 80 °C. The solution was then cooled down to room temperature. An aqueous solution of TEBAC (0.1 eq.) and NaOH (4.0 eq., 5.0 mol L^{-1}) was added and the mixture was stirred for 30 minutes at room temperature. Ethyl acetate and deionized water were then added. The mixture was stirred and the aqueous phase was extracted with ethyl acetate. Organic phases were combined, rinsed with brine and dried on anhydrous Na_2SO_4. Ethyl acetate and epichlorohydrin excess were removed using a rotary evaporator. Further purification was achieved by silica gel flash chromatography using a hexane–ethyl acetate gradient as an eluent.

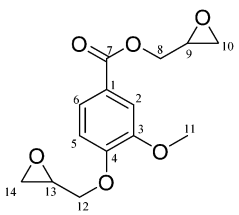


Product 5: 2,2′-(((3-methoxy-1,4-phenylene)bis(oxy))bis(methylene))bis(oxirane) (87%, m.p. 87 °C).

^{1}H NMR (400.1 MHz, acetone-d_6, 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, $^3J_{H_6H_5}$ = 8.8 Hz, $^4J_{H_6H_2}$ = 2.8 Hz, 1H, H_6); 6.63 (d, $^4J_{H_2H_6}$ = 2.8 Hz, 1H, H_2); 6.88 (d, $^3J_{H_5H_6}$ = 8.8 Hz, 1H, H_5).

^{13}C NMR (100.6 MHz, acetone-d_6, 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$^+$]): calculated: 253.1079; found: 253.1076.



Product 6: oxiran-2-ylmethyl 3-methoxy-4-(oxiran-2-ylmethoxy)-benzoate (95%, m.p. 77 °C).

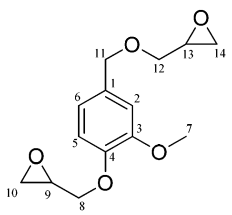
^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 2.72 (m, 1H, H_{14a}); 2.77 (m, 1H, H_{10a}); 2.91 (m, 2H, H_{10b}, H_{14b}); 3.34 (m, 1H, H_{13}); 3.40 (m, 1H, H_9); 3.92 (s, 3H, H_{11}); 4.09 (m, 2H, H_{8a}, H_{12a}); 4.34 (dd,

1H, H_{12b}); 4.64 (m, 1H, H_{8b}); 6.94 (d, $^3J_{H_5H_6}$ = 8.4 Hz, 1H, H_5); 7.57 (d, $^4J_{H_2H_6}$ = 2.0 Hz, 1H, H_2); 7.69 (dd, $^3J_{H_6H_5}$ = 8.4 Hz, $^4J_{H_6H_2}$ = 2.0 Hz, 1H, H_6).

^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 44.68 (s, C_{10}); 44.78 (s, C_{14}); 49.52 (s, C_9); 49.90 (s, C_{13}); 56.04 (s, C_{11}); 65.37 (s, C_8); 69.86 (s, C_{12}); 112.29 (s, C_5); 112.63 (s, C_2); 122.85 (s, C_1); 123.65 (s, C_6); 149.05 (s, C_3); 152.16 (s, C_4); 165;92 (s, C_7).

HRMS (m/z, ES+, [M + H^+]): calculated: 281.1025; found: 281.1025.

For the preparation of **7** from **4**, a phase transfer catalysis system was used. A round-bottomed flask was charged with **4** (1.0 eq.) and TEBAC (0.1 eq.). Epichlorohydrin (10.0 eq.) was added and the mixture was stirred for 4 hours until obtention of a limpid pink solution. This solution was cooled down to 0 °C with an ice bath. A NaOH solution (33 wt%, 15.0 eq.) in deionized water was prepared and poured into the cold mixture under vigorous stirring. The reaction was conducted overnight at room temperature (the ice bath was left to melt over time). Deionized water was added to the mixture to dilute 4 times the NaOH solution. An equal volume of ethyl acetate was added. The mixture was stirred and the aqueous phase was extracted 2 more times with ethyl acetate. Organic phases were combined, rinsed with brine and dried on anhydrous Na_2SO_4. Ethyl acetate and epichlorohydrin excess were removed using a rotary evaporator. Further purification was achieved by silica gel flash chromatography using a hexane–ethyl acetate gradient as an eluent.



Product 7: 2-((3-methoxy-4-((oxiran-2-ylmethoxy)methyl) phenoxy)methyl)oxirane (89%, m.p. 53 °C).

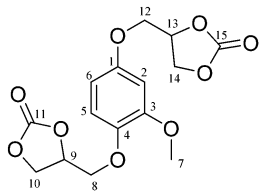
^1H NMR (400.1 MHz, acetone-d_6, ppm) δ: 2.53 (dd, 1H, H_{14a}); 2.69 (m, 2H, H_{10a}, H_{14b}); 2.81 (m, 1H, H_{10b}); 3.10 (m, 1H, H_{13}); 3.30 (m, 2H, H_9, H_{12a}); 3.73 (dd, 1H, H_{12b}); 3.82 (s, 3H, H_7); 3.87 (dd, 1H, H_{8a}); 4.28 (dd, 1H, H_{8b}); 4.47 (d, 2H, H_{11}); 6.86 (dd, $^3J_{H_6H_5}$ = 8.0 Hz, $^4J_{H_6H_2}$ = 1.6 Hz, 1H, H_6); 6.94 (d, $^3J_{H_5H_6}$ = 8.0 Hz, 1H, H_5); 6.98 (d, $^4J_{H_2H_6}$ = 1.6 Hz, 1H, H_2).

^{13}C NMR (100.6 MHz, acetone-d_6, ppm) δ: 44.16 (s, C_{14}); 44.49 (s, C_{10}); 50.76 (s, C_9); 51.28 (s, C_{13}); 56.16 (s, C_7); 71.39 (s, C_8); 71.82 (s, C_{12}); 73.42 (s, C_{11}); 112.91 (s, C_5); 114.76 (s, C_2); 120.99 (s, C_6); 132.93 (s, C_1); 148.86 (s, C_4); 150.75 (s, C_3).

HRMS (m/z, ASAP$^-$, [M$^-$]): calculated: 266.1153; found: 266.1154.

Procedures for carbonation (8, 9, 10)

Epoxy-functionalized compound **8**, **9** or **10** (1.0 eq.) and LiBr (0.05 eq.) were stirred in acetone (35 mL) and introduced into the autoclave. The atmosphere was replaced with CO_2 (P = 12 bar), and then the solution was heated at 80 °C with continuous stirring for 12 hours. The solvent was distilled under vacuum (P = 0.01 bar) at 60 °C. Deionized water was added and the aqueous phase was extracted with ethyl acetate. The organic phase was washed with brine, dried on anhydrous Na_2SO_4 and ethyl acetate was removed using a rotary evaporator.

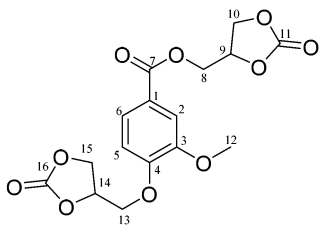


Product 8: 4,4′-(((3-methoxy-1,4-phenylene)bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (100%, m.p. n.d.).

^1H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 3.76 (s, 3H, H_7); 4.16 (m, 4H, H_8, H_{12}); 4.39 (m, 2H, H_{10a}, H_{14a}); 4.61 (q, 2H, H_{10b}, H_{14b}); 5.11 (m, 2H, H_9, H_{13}); 6.47 (dd, $^3J_{H_6H_5}$ = 8.8 Hz, $^4J_{H_6H_2}$ = 2.8 Hz, 1H, H_6); 6.63 (d, $^4J_{H_2H_6}$ = 2.8 Hz, 1H, H_2); 6.93 (d, $^3J_{H_5H_6}$ = 8.8 Hz, 1H, H_5).

^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 55.77 (s, C_7); 65.95 (s, C_{14}); 66.00 (s, C_{10}); 67.91 (s, C_{12}); 69.73 (s, C_8); 74.88 (s, C_{13}); 75.12 (s, C_9); 101.25 (s, C_2); 104.76 (s, C_6); 116.29 (s, C_5); 142.08 (s, C_4); 150.53 (s, C_3); 153.57 (s, C_1); 154.87 (s, C_{11}, C_{15}).

HRMS (m/z, ASAP$^+$, [M + H^+]): calculated: 341.0871; found: 341.0873.

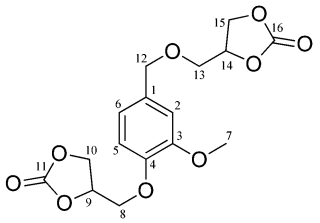


Product 9: (2-oxo-1,3-dioxolan-4-yl)methyl 3-methoxy-4-((2-oxo-1,3-dioxolan-4-yl)methoxy) benzoate (50%, m.p. n.d.).

^1H NMR (400.1 MHz, acetone-d_6, ppm) δ: 3.87 (s, 1H, H_{12}); 4.42 (m, 2H, H_{13a}, H_{13b}); 4.58 (m, 4H, H_{8a}, H_{8b}, H_{10a}, H_{15a}); 4.75 (m, 2H, H_{10b}, H_{15b}); 5.26 (m, 2H, H_9, H_{14}); 7.13 (d, $^3J_{H_5H_6}$ = 8.4 Hz, 1H, H_5); 7.55 (d, $^4J_{H_2H_6}$ = 2.0 Hz, 1H, H_2); 7.62 (dd, $^3J_{H_6H_5}$ = 8.4 Hz, $^4J_{H_6H_2}$ = 2.0 Hz, 1H, H_6).

^{13}C NMR (100.6 MHz, acetone-d_6, ppm) δ: 56.44 (s, C_{12}); 65.08 (s, C_8); 66.76 (s, C_{10}); 67.29 (s, C_{15}); 69.59 (s, C_{13}); 75.29 (s, C_9); 75.65 (s, C_{14}); 113.76 (s, C_5); 114.32 (s, C_2); 123.87 (s, C_1); 124.23 (s, C_6); 150.45 (s, C_3); 153.27 (s, C_4); 155.62 (s, C_{11}); 155.74 (s, C_{16}); 165.93 (s, C_7).

HRMS (m/z, ES+, [M + Na^+]): calculated: 391.0549; found: 391.0549.



Product 10: 4-((2-methoxy-4-(((2-oxo-1,3-dioxolan-4-yl)methoxy)-methyl)phenoxy)methyl)-1,3-dioxolan-2-one (100%, pale yellow liq.).

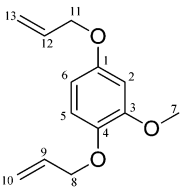
^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 3.62 (dd, 1H, H_{13a}); 3.72 (dd, 1H, H_{13b}); 3.86 (s, 3H, H_7); 4.23 (dd, 2H, H_8); 4.40 (dd, 1H, H_{15a}); 4.60 (t, H_{15b}); 4.54 (s, 2H, H_{12}); 4.61 (d, 1H, H_{10a}); 4.63 (s, 1H, H_{10b}); 4.83 (m, 1H, H_{14}); 5.02 (m, 1H, H_9); 6.82 (dd, $^3J_{H_6H_5}$ = 8.0 Hz, $^4J_{H_6H_2}$ = 1.2 Hz, 1H, H_6); 6.90 (d, $^4J_{H_2H_6}$ = 1.2 Hz, 1H, H_2); 6.91 (d, $^3J_{H_5H_6}$ = 8.0 Hz, 1H, H_5).

^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 55.84 (s, C_7); 66.15 (s, C_{10}); 66.19 (s, C_{19}); 68.67 (s, C_{13}); 69.22 (s, C_8); 73.17 (s, C_{12}); 74.48 (s, C_9); 75.05 (s, C_{14}); 111.78 (s, C_2); 116.13 (s, C_5); 120.14 (s, C_6); 132.27 (s, C_1); 147.10 (s, C_4); 150.36 (s, C_3); 154.76 (s, C_{11}); 154.98 (s, C_{16}).

HRMS (m/z, ES+, [M + Na^+]): calculated: 377.0854; found: 377.0849.

Procedures for allylation (11, 12, 13)

A first protocol was used for the preparation of **11** and **12** from **2** and **3**. A two-necked round-bottomed flask was charged with **2** or **3** (1.0 eq.). Ethanol was added to obtain a 0.5 mol L^{-1} solution. The solution was cooled with an ice bath and K_2CO_3 (4.0 eq.) was added. After 10 minutes, allyl bromide (4.0 eq.) was added dropwise using a syringe. The solution was stirred for 30 minutes at 0 °C and then at room temperature for seven days. Deionized water was added and the aqueous phase was extracted with pentane. The organic phase was washed with brine, dried on anhydrous Na_2SO_4 and pentane was removed using a rotary evaporator. Further purification was achieved by silica gel flash chromatography using a pentane–dichloromethane gradient as an eluent.

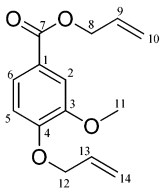


Product 11: 1,4-bis(allyloxy)-3-methoxybenzene (100%, pale yellow liq.).

^{1}H NMR (400.1 MHz, acetone-d_6, ppm) δ: 3.80 (s, 3H, H_7); 4.48 (m, 4H, H_8, H_{11}); 5.20 (m, 2H, H_{10a}, H_{13a}); 5.38 (m, 2H, H_{10b}, H_{13b}); 6.05 (m, 2H, H_9, H_{12}); 6.42 (dd, $^3J_{H_6H_5}$ = 8.6 Hz, $^4J_{H_6H_2}$ = 2.8 Hz, 1H, H_6); 6.60 (d, $^4J_{H_2H_6}$ = 2.8 Hz, 1H, H_2); 6.85 (d, $^3J_{H_5H_6}$ = 8.6 Hz, 1H, H_5).

^{13}C NMR (100.6 MHz, acetone-d_6, ppm) δ: 56.68 (s, C_7); 70.27 (s, C_{11}); 71.98 (s, C_8); 102.73 (s, C_2); 106.03 (s, C_6); 117.24 (s, C_5); 117.57 (s, C_{10}); 117.71 (s, C_{13}); 135.61 (s, C_{12}); 136.02 (s, C_9); 144.09 (s, C_4); 152.56 (s, C_3); 155.41 (s, C_1).

HRMS (m/z, ES+, [M + H^+]): calculated: 221.1178; found: 221.1178.



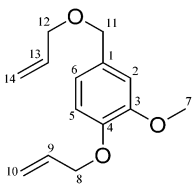
Product 12: allyl 4-(allyloxy)-3-methoxybenzoate (100%, brown liq.).

^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 3.93 (s, 3H, H_{11}); 4.68 (dt, 2H, H_{12}); 4.81 (dt, 2H, H_8); 5.30 (m, 2H, H_{10a}, H_{14a}); 5.42 (m, 2H, H_{10b}, H_{14b}); 6.06 (m, 2H, H_9, H_{13}); 6.89 (d, $^3J_{H_5H_6}$ = 8.4 Hz, 1H, H_5); 7.58 (d, $^4J_{H_2H_6}$ = 2.0 Hz, 1H, H_2); 7.68 (dd, $^3J_{H_6H_5}$ = 8.4 Hz, $^4J_{H_6H_2}$ = 2.0 Hz, 1H, H_6).

^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 56.02 (s, C_{11}); 65.50 (s, C_8); 69.69 (s, C_{12}); 111.95 (s, C_2); 112.40 (s, C_5); 118.04 (s, C_{10}); 118.49 (s, C_{14}); 122.81 (s, C_1); 123.44 (s, C_6); 132.44 (s, C_9); 132.54 (s, C_{13}); 148.95 (s, C_3); 152.04 (s, C_4); 166.01 (s, C_7).

HRMS (m/z, ES+, [M + H^+]): calculated: 249.1126; found: 249.1127.

As in the case of the glycidylation of a benzyl alcohol moiety, a phase transfer catalysis system was used for the preparation of **13** from **4**. A round-bottomed flask was charged with **4** (1.0 eq.) and TEBAC (0.1 eq.). NaOH (5.0 eq.) was dissolved in water to obtain a 20 wt% solution. This solution was poured into the flask and the suspension was stirred for 10 minutes while heating to 50 °C. Allyl bromide (4.0 eq.) was then added to the mixture and the reaction was conducted for 5 hours. Deionized water was added and the mixture was extracted with pentane. The organic phase was washed with brine, dried on anhydrous Na_2SO_4 and pentane was removed using a rotary evaporator. Further purification was achieved by silica gel flash chromatography using a pentane–dichloromethane gradient as an eluent.



Product 13: 4-(allyloxy)-1-((allyloxy)methyl)-3-methoxy benzene (86%, pale yellow liq.).

^{1}H NMR (400.1 MHz, acetone-d_6, ppm) δ: 3.81 (s, 3H, H_7); 3.98 (m, 2H, H_{12}); 4.43 (s, 2H, H_{11}); 4.55 (m, 2H, H_8); 5.11–5.16 (m, 1H, H_{14a}); 5.20–5.25 (m, 1H, H_{10a}); 5.25–5.32 (m, 1H, H_{14b}); 5.38–5.45 (m, 1H, H_{10b}); 5.94 (m, 1H, H_{13}); 6.08 (m, 1H,

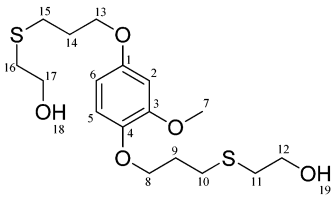
H_9); 6.84 (dd, $^4J_{H_6H_2}$ = 2.0 Hz, $^3J_{H_6H_5}$ = 8.0 Hz, 1H, H_6); 6.91 (dd, $^3J_{H_5H_6}$ = 8.0 Hz, 1H, H_5); 6.96 (dd, $^3J_{H_2H_6}$ = 2.0 Hz, 1H, H_2).

^{13}C NMR (100.6 MHz, acetone-d_6, ppm) δ: 56.7 (s, C_7); 70.9 (s, C_8); 71.9 (s, C_{12}); 73.0 (s, C_{11}); 113.4 (s, C_2); 115.2 (s, C_5); 116.9 (s, C_{14}); 117.8 (s, C_{10}); 121.4 (s, C_6); 133.3 (s, C_1); 135.6 (s, C_9); 136.9 (s, C_{13}); 149.2 (s, C_4); 151.3 (s, C_3).

HRMS (m/z, ASAP$^-$, [M − H$^+$]): calculated: 233.1180; found: 233.1178.

Procedures for alcohol functionalization (14, 15, 16)

Allylated compound **11**, **12** or **13** (1.0 eq.) and mercaptoethanol (6.0 eq.) were mixed without adding any solvent. The solution was irradiated in the UV reactor. The reactions were monitored by ^{1}H NMR.

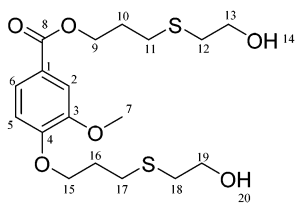


Product 14: 2,2′-((((3-methoxy-1,4-phenylene)bis(oxy))bis(propane-3,1-diyl))bis(sulfanediyl))diethanol (92%, pale yellow liq.).

^{1}H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 1.91 (m, 4H, H_9, H_{14}); 2.57 (dt, 4H, H_{11}, H_{16}); 2.65 (dt, 4H, H_{10}, H_{15}); 3.53 (dt, 4H, H_{12}, H_{17}); 3.74 (s, 3H, H_7); 3.93 (t, 2H, H_8); 3.97 (t, 2H, H_{13}); 4.76 (m, 2H, H_{18}, H_{19}); 6.40 (dd, $^3J_{H_6H_5}$ = 8.8 Hz, $^4J_{H_6H_2}$ = 2.8 Hz, 1H, H_6); 6.56 (d, $^4J_{H_2H_6}$ = 2.8 Hz, 1H, H_2); 6.84 (d, $^3J_{H_5H_6}$ = 8.8 Hz, 1H, H_5).

^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 27.95 (s, C_{10}, C_{15}); 29.12 (s, C_{14}); 29.29 (s, C_9); 33.90 (s, C_{16}, C_{11}); 55.54 (s, C_7); 60.86 (s, C_{12}, C_{17}); 66.33 (s, C_{13}); 67.86 (s, C_8); 101.02 (s, C_2); 104.28 (s, C_6); 115.03 (s, C_5); 142.10 (s, C_4); 150.26 (s, C_3); 153.41 (s, C_1).

HRMS (m/z, ES+, [M + Na$^+$]): calculated: 399.1277; found: 399.1276.

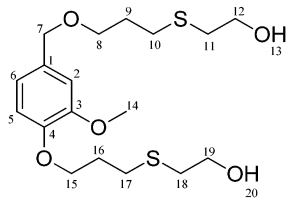


Product 15: 3-((2-hydroxyethyl)thio)propyl-4-(3-((2-hydroxyethyl)thio)propoxy)-3-methoxybenzoate (96%, pale yellow liq.).

^{1}H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 1.97 (m, 4H, H_{10}, H_{16}); 2.58 (2*t, 4H, H_{12}, H_{18}); 2.66 (2*t, 4H, H_{11}, H_{17}); 3.52 (m, 4H, H_{13}, H_{19}); 3.81 (s, 3H, H_7); 4.11 (t, 2H, H_{15}); 4.30 (t, 2H, H_9); 4.87 (broad m, 2H, H_{14}, H_{20}); 7.07 (d, $^3J_{H_5H_6}$ = 8.4 Hz, 1H, H_5); 7.45 (d, $^4J_{H_2H_6}$ = 2.0 Hz, 1H, H_2); 7.57 (dd, $^3J_{H_6H_5}$ = 8.4 Hz, $^4J_{H_6H_2}$ = 2.0 Hz, 1H, H_6).

^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 27.78, 27.97 (2*s, C_{11}, C_{17}); 28.85, 28.54 (2*s, C_{10}, C_{16}); 33.83, 33.89 (2*s, C_{18}, C_{12}); 55.59 (s, C_7); 60.82, 60.87 (2*s, C_{13}, C_{19}); 63.22 (s, C_8); 66.87 (s, C_{15}); 111.95, 112.10 (2*s, C_2, C_5); 121.97 (s, C_1); 123.14 (s, C_6); 148.54 (s, C_3); 152.20 (s, C_4); 165.47 (s, C_7).

HRMS (m/z, ES+, [M + K$^+$]): calculated: 443.0962; found: 443.0964.



Product 16: 2-((3-(4-(3-((2-hydroxyethyl)thio)propoxy)-3-methoxybenzyl)oxy)propyl)thio)ethan-1-ol (100%, pale yellow liq.).

^{1}H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 1.76 (m, 2H, H_9); 1.93 (m, 2H, H_{16}); 2.56 (m, 6H, H_{10}, H_{11}, H_{18}); 2.66 (t, 2H, H_{17}); 3.45 (t, 2H, H_8); 3.52 (m, 4H, H_{12}, H_{19}); 3.75 (s, 3H, H_{14}); 4.00 (t, 2H, H_{15}); 4.36 (s, 2H, H_7); 4.77 (m, 2H, H_{13}, H_{20}); 6.81 (dd, $^3J_{H_6H_5}$ = 8.0 Hz, $^4J_{H_6H_2}$ = 1.2 Hz, 1H, H_6); 6.90 (d, $^4J_{H_2H_6}$ = 1.2 Hz, 1H, H_2); 6.91 (d, $^3J_{H_5H_6}$ = 8.0 Hz, 1H, H_5).

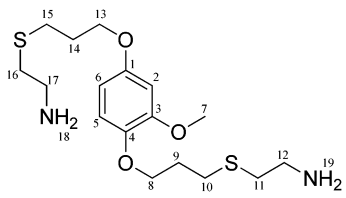
^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 28.08 (s, C_{17}); 28.43 (s, C_{10}); 29.31 (s, C_{16}); 29.84 (s, C_9); 35.25 (s, C_{18}); 35.29 (s, C_{11}); 55.93 (s, C_{14}); 60.30 (s, C_{19}); 60.34 (s, C_{12}); 67.38 (s, C_{15}); 68.34 (s, C_8); 72.89 (s, C_7); 111.65 (s, C_5); 113.27 (s, C_2); 120.32 (s, C_6); 131.36 (s, C_1); 147.80 (s, C_3); 149.56 (s, C_4).

HRMS (m/z, ES+, [M + H$^+$]): calculated: 391.1611; found: 391.1613.

Procedures for amine functionalization (17, 18, 19)

Allylated compound **11**, **12** or **13** (1.0 eq.) and cysteamine hydrochloride (6.0 eq.) were dissolved in a minimum of methanol. The solution was irradiated in the UV reactor. The reactions were monitored by ^{1}H NMR.

When the reaction was complete, the resulting mixture was dissolved in water and K_2CO_3 was added to reach pH = 9. The solution was then extracted with ethyl acetate, dried on anhydrous Na_2SO_4 and ethyl acetate was evaporated under reduced pressure.



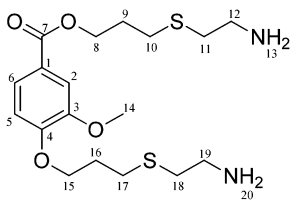
Product 17: 2,2′-((((3-methoxy-1,4-phenylene)bis(oxy))bis(propane-3,1-diyl))bis(sulfanediyl))diethanamine (96%, pale yellow liq.).

^{1}H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 1.90 (m, 4H, H_9, H_{14}); 2.45–2.70 (m, 12H, H_{10}, H_{11}, H_{12}, H_{15}, H_{16}, H_{17}); 3.72 (s, 3H, H_7); 3.94 (m, 4H, H_8, H_{13}); 6.39 (dd, $^3J_{H_6H_5}$ = 8.8 Hz,

$^4J_{H_6H_2}$ = 2.8 Hz, 1H, H_6); 6.54 (d, $^4J_{H_2H_6}$ = 2.8 Hz, 1H, H_2); 6.83 (d, $^3J_{H_5H_6}$ = 8.8 Hz, 1H, H_5).

^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 27.50 (s, C_{15}); 27.52 (s, C_{10}); 29.14 (s, C_{14}); 29.30 (s, C_9); 35.23 (s, C_{16}); 35.25 (s, C_{11}); 41.55 (s, C_{17}); 41.57 (s, C_{12}); 55.56 (s, C_7); 66.34 (s, C_{13}); 67.85 (s, C_8); 101.00 (s, C_2); 104.26 (s, C_6); 114.98 (s, C_5); 142.12 (s, C_4); 150.27 (s, C_3); 153.42 (s, C_1).

HRMS (m/z, ES+, [M + H$^+$]): calculated: 375.1779; found: 375.1776.

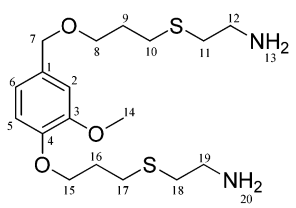


Product 18: 3-((2-aminoethyl)thio)propyl-4-(3-((2aminoethyl) thio) propoxy)-3-methoxybenzoate (93%, pale yellow liq.).

^1H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 1.97 (m, 4H, H_9, H_{16}); 2.52 (2*t, 4H, H_{11}, H_{18}); 2.63 (2*t, 4H, H_{10}, H_{17}); 2.68 (t, 4H, H_{12}, H_{19}); 3.82 (s, 3H, H_{14}); 4.11 (t, 2H, H_{15}); 4.30 (t, 2H, H_8); 7.09 (d, $^3J_{H_5H_6}$ = 8.6 Hz, 1H, H_5); 7.45 (d, $^4J_{H_2H_6}$ = 2.0 Hz, 1H, H_2); 7.58 (dd, $^3J_{H_6H_5}$ = 8.6 Hz, $^4J_{H_6H_2}$ = 2.0 Hz, 1H, H_6).

^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 27.28 (s, C_{10}); 27.47 (s, C_{17}); 28.52 (s, C_9); 28.83 (s, C_{16}); 35.14, 35.16 (2*s, C_{11}, C_{18}); 41.52 (s, C_{12}, C_{19}); 55.59 (s, C_{14}); 63.19 (s, C_{15}); 66.87 (s, C_8); 111.94 (s, C_5); 112.09 (s, C_2); 121.95 (s, C_1); 123.13 (s, C_6); 148.55 (s, C_3); 152.20(s, C_4); 165.44 (s, C_7).

HRMS (m/z, ES+, [M + H$^+$]): calculated: 403.1721; found: 403.1725.



Product 19: 2-((3-((4-(3-((2-aminoethyl)thio)propoxy)-3-methoxybenzyl)oxy)propyl)thio)ethan-1-amine (88%, pale yellow liq.).

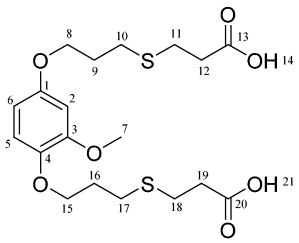
^1H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 1.76 (tt, 2H, H_9); 1.94 (tt, 2H, H_{16}); 2.52 (m, 3H, H_{10}, H_{11}, H_{18}); 2.66 (m, 3H, H_{12}, H_{17}, H_{19}); 3.46 (t, 1H, H_8); 3.75 (s, 3H, H_{14}); 4.01 (t, 1H, H_{15}); 4.36 (s, 2H, H_7); 6.81 (dd, $^3J_{H_6H_5}$ = 8.0 Hz, $^4J_{H_6H_2}$ = 1.2 Hz, 1H, H_6); 6.90 (d, $^4J_{H_2H_6}$ = 1.2 Hz, 1H, H_2); 6.91 (d, $^3J_{H_5H_6}$ = 8.0 Hz, 1H, H_5).

^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 27.41 (s, C_{17}); 27.78 (s, C_{10}); 29.10 (s, C_{16}); 29.57 (s, C_9); 35.19 (s, C_{18}); 35.26 (s, C_{11}); 41.54 (s, C_{12}, C_{19}); 55.49 (s, C_{14}); 66.91 (s, C_{15}); 67.88 (s, C_8); 71.77 (s, C_7); 111.72 (s, C_5); 113.11 (s, C_2); 119.93 (s, C_6); 131.25 (s, C_1); 147.33 (s, C_4); 148.96 (s, C_3).

HRMS (m/z, ES+, [M + H$^+$]): calculated: 389.1932; found: 399.1933.

Procedures for acid functionalization (20, 21, 22)

Allylated compound **11**, **12** or **13** (1.0 eq.) and 3-mercaptopropionic acid (6.0 eq.) were mixed without adding any solvent. The solution was irradiated in the UV reactor. The reactions were monitored by ^{1}H NMR.

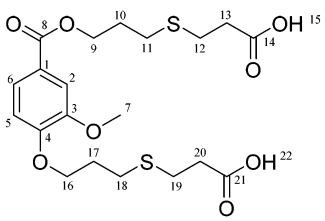


Product 20: 3,3′-((((3-methoxy-1,4-phenylene)bis(oxy))bis-(propane-3,1-diyl))bis(sulfanediyl))dipropionic acid (68%, pale yellow liq.).

^1H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 1.91 (q, 4H, H_9, H_{16}); 2.51 (m, 4H, H_{13}, H_{20}); 6.66 (m, 8H, H_{10}, H_{11}, H_{17}, H_{18}); 3.73 (s, 3H, H_7); 3.93 (t, 2H, H_8); 3.96 (t, 2H, H_{15}); 6.39 (dd, $^3J_{H_6H_5}$ = 8.8 Hz, $^4J_{H_6H_2}$ = 2.8 Hz, 1H, H_6); 6.56 (d, $^4J_{H_2H_6}$ = 2.8 Hz, 1H, H_2); 6.84 (d, $^3J_{H_5H_6}$ = 8.8 Hz, 1H, H_5); 12.28 (broad s, 2H, H_{14}, H_{21}).

^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 26.36, 26.39 (2*s, C_{11}, C_{18}); 27.59, 27.62 (2*s, C_{10}, C_{17}); 28.92, 29.08 (2*s, C_9, C_{16}); 34.45, 34.49 (2*s, C_{12}, C_{19}); 55.55 (s, C_7); 66.33 (s, C_8); 67.85 (s, C_{15}); 101.04 (s, C_2); 104.31 (s, C_6); 115.06 (s, C_5); 142.11 (s, C_4); 150.30 (s, C_3); 153.44 (s, C_1); 172.66 (s, C_{13}, C_{20}).

HRMS (m/z, ES+, [M + H$^+$]): calculated: 433.1357; found: 433.1355.

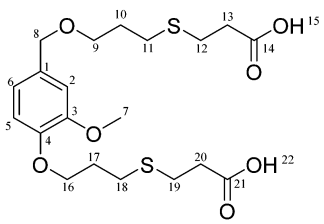


Product 21: 3-((3-((4-(3-((2-carboxyethyl)thio)propoxy)-3-methoxybenzoyl)oxy)propyl)thio)propanoic acid (92%, m.p. 68 °C).

^1H NMR (400.1 MHz, (DMSO-d_6, ppm) δ: 1.97 (m, 4H, H_{10}, H_{17}); 2.51 (m, 4H, H_{13}, H_{20}); 2.67 (m, 8H, H_{11}, H_{12}, H_{18}, H_{20}); 3.81 (s, 3H, H_7); 4.10 (t, 2H, H_{16}); 4.29 (t, 2H, H_9); 7.06 (d, $^3J_{H_5H_6}$ = 8.6 Hz, 1H, H_5); 7.45 (d, $^4J_{H_2H_6}$ = 2.0 Hz, 1H, H_2); 7.58 (dd, $^3J_{H_6H_5}$ = 8.6 Hz, $^4J_{H_6H_2}$ = 2.0 Hz, 1H, H_6).

^{13}C NMR (100.6 MHz, (DMSO-d_6, ppm) δ: 26.31, 26.34 (2*s, C_{12}, C_{19}); 27.39, 27.63 (2*s, C_{11}, C_{18}); 28.34, 28.64 (2*s, C_{10}, C_{17}); 34.42, 34.46 (2*s, C_{13}, C_{20}); 55.60 (s, C_7); 63.22 (s, C_9); 63.8 (s, C_{16}); 111.94, 112.09 (2*s, C_5, C_2); 121.99 (s, C_1); 123.18 (s, C_6); 148.57 (s, C_3); 152.20 (s, C_4); 165.49 (s, C_7); 173.03 (s, C_{14}, C_{21}).

HRMS (m/z, ES+, [M + H$^+$]): calculated: 461.1302; found: 461.1304.



Product 22: 3-((3-((4-(3-((2-carboxyethyl)thio)propoxy)-3-methoxybenzyl)oxy)propyl)thio)propanoic acid (90%, liq.).

^{1}H NMR (400.1 MHz, DMSO-d_6, ppm) δ: 1.76 (quint., 2H, H_{10}); 1.93 (quint., 2H, H_{17}); 2.51 (m, 6H, H_{11}, H_{13}, H_{20}); 2.66 (m, 6H, H_{12}, H_{18}, H_{19}); 3.45 (t, 2H, H_9); 3.75 (s, 3H, H_7); 4.00 (t, 2H, H_{16}); 4.36 (s, 2H, H_8); 6.81 (dd, $^{3}J_{H_6H_5}$ = 8.0 Hz, $^{4}J_{H_6H_2}$ = 2.0 Hz, 1H, H_6); 6.90 (d, $^{4}J_{H_2H_6}$ = 2.0 Hz, 1H, H_2); 6.91 (d, $^{3}J_{H_5H_6}$ = 8.0 Hz, 1H, H_5).

^{13}C NMR (100.6 MHz, DMSO-d_6, ppm) δ: 26.32, 26.42 (2*s, C_{12}, C_{19}); 27.52, 27.91 (2*s, C_{11}, C_{18}); 28.91, 29.39 (2*s, C_{10}, C_{17}); 34.46, 34.51 (s, C_{13}, C_{20}); 55.49 (s, C_7); 66.87 (s, C_{16}); 67.88 (s, C_9); 71.82 (s, C_8); 111.67 (s, C_2); 113.04 (s, C_5); 119.99 (s, C_6); 131.25 (s, C_1); 147.32 (s, C_3); 148.96 (s, C_4); 173.09 (s, C_{14}, C_{21}).

HRMS (m/z, ES+, [M + H^+]): calculated: 447.1505; found: 447.1511.

Material preparation

Epoxy compound **5** (1.20 g, 2.0 eq.) was molten at 100 °C. IPDA (0.81 g, 1.0 eq.) was quickly added and the mixture was vigorously stirred for 1 min at 100 °C. The liquid and homogeneous mixture was then poured into a rectangular silicon mold. The formulation was cured in an oven for 1.5 hours at 100 °C. The polymer obtained was then cooled down to room temperature and post-cured at 160 °C for 1 hour. A DSC analysis was performed and showed a complete reticulation and a T_g of 117 °C.

Conclusions

Vanillin was used as a building block to develop a platform of biobased compounds usable in the polymer field. The lack of biobased aromatic monomers necessary to reach good thermo-mechanical properties was the major identified challenge. Vanillin was chosen as the starting point of the platform as it is one of the few monoaromatic biobased compounds that are abundantly available. Indeed, vanillin is already industrially produced by lignin depolymerization.

Three vanillin derivatives in different oxidation states were chosen as starting materials to take into account differences in lignin depolymerization processes and the possible resulting products. These chemicals were functionalized with epoxy, cyclic carbonates, allyl, amine, alcohol and carboxylic acid moieties. Original biobased monomers useful for epoxy, polyester, PU, and NIPU polymer synthesis were obtained. The epoxy-functionalized compounds could be tested as biobased substitutes for bisphenol A-based epoxy resins. The amine-functionalized compounds are, to our knowledge, the first non-aliphatic biobased amine hardeners, useful either in epoxy or NIPU materials. The cyclic carbonate-functionalized compounds could be useful to tune NIPU properties.

Products from the vanillin-derived methoxyhydroquinone are especially interesting and versatile. Industrialization is possible thanks to clean and straightforward syntheses and there is no fragile bond on the methoxyhydroquinone that could impact polymer properties.

In future studies, compounds from this platform should be used in polymer formulations and thermo-mechanical properties of the corresponding materials should be tested.

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Chapter 3: Epoxy monomers from vanillin

1. Introduction

In the first chapter of this work, the need for bio-based aromatic compounds has been evidenced. Vanillin has been employed to fulfill this role and a platform of bio-based, aromatic monomers bearing various polymerizable functions has been prepared and is presented in the second chapter. The bio-based aromatic epoxy monomers are especially interesting as they could answer two problematics at the same time.

Indeed, as mentioned, Bisphenol A substitution and petroleum-based raw materials substitution are major challenges in the field of epoxy thermosets. These changes are not going to happen unless the level of performance (T_g, thermal stability etc.) of the materials from the substitute proposed is at least equal to current industrial references. In order to reach this level of performance, difunctional aromatic epoxy monomers are needed. Therefore, vanillin-based epoxy monomers seem to be worth investigating.

The next section consists of a published work in which the syntheses of three vanillin-based epoxy monomers are described. These monomers were hardened to give epoxy thermosets, which properties were investigated. A comparison of the thermo-mechanical properties of the thermosets obtained to the DGEBA industrial reference was performed.

2. New vanillin-derived diepoxy monomers for the synthesis of biobased thermosets

European Polymer Journal 67 (2015) 527–538

Maxence Fache, Rémi Auvergne, Bernard Boutevin, Sylvain Caillol *

Institut Charles Gerhardt, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France

ARTICLE INFO

Article history:
Received 29 July 2014
Received in revised form 14 October 2014
Accepted 16 October 2014
Available online 1 November 2014

Keywords:
Biobased thermosets
Vanillin
Epoxy resins
Renewable resources
Renewable resins
Glass transition temperature

ABSTRACT

Biobased epoxy polymers were prepared from vanillin and compared to an industrial bisphenol A-based reference. This work directly continues the efforts engaged by our team to use vanillin as a biobased building block for polymer chemistry as it is an industrially available, non-toxic, renewable compound. Diglycidyl ethers were prepared from vanillin derivatives. These diepoxy monomers were formulated to give polymers that were compared to a bisphenol A-based material as reference of current use. In all cases, IPDA (IsoPhorone DiAmine) was used as it is a common industrial amine hardener. Thermal and mechanical properties of the biobased thermosets prepared were investigated. The influence of the monomer structure on these properties was discussed. The biobased polymers prepared were found to have tunable properties that could reach performances close to the current bisphenol A-based industrial reference. Vanillin-based epoxy polymers can thus be a sustainable alternative in many applications to the current non-renewable epoxy polymers based on bisphenol A.

1. Introduction

During the last couple of decades, the use of renewable resources, especially in the polymer field, is gaining a great interest through scientific and industrial research [1,2]. The main reasons for this surge of interest are undoubtedly the predicted scarcity of fossil resources and the negative environmental impact of petro-based products. Some biobased polymers are already industrially available but most of them are aliphatic or cycloaliphatic polymers, for instance derived from cellulose [1], starch [1] or triglycerides [3]. However, many key monomers are aromatic compounds, ultimately derived from petrochemical feedstocks. This is especially true in the field of 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 crosslinked, cannot be recycled and thus need a renewable carbon content as high as possible. These reasons make the development of biobased aromatic monomers and polymers a top priority issue currently investigated [4,5].

Among thermosetting materials, epoxy polymers are used in many industrial fields such as aerospace, automotive, construction etc. through diverse applications such as adhesives, coatings, composite matrices etc. This is mainly due to their good adhesion to many substrates, good chemical resistance, and excellent thermal and mechanical properties [6]. Currently, 75% of the epoxy polymers worldwide are prepared from the DiGlycidyl Ether of Bisphenol A (DGEBA, **Fig. 1**). However, its manufacturing is based on Bisphenol A (**Fig. 1**), a reprotoxic substance [7] that is under close monitoring and which use might be restricted in certain applications in the future. The biosourcing of epoxy polymers could thus have the double positive effect of Bisphenol A replacement and renewable resources use. Therefore, the access to biobased, aromatic

* Corresponding author. Tel.: +33 4 67144327.
E-mail address: sylvain.caillol@enscm.fr (S. Caillol).

http://dx.doi.org/10.1016/j.eurpolymj.2014.10.011
0014-3057/

and non-harmful epoxy monomers is a hot topic and a challenge that needs to be addressed. For these reasons, the biosourcing of epoxy polymers received a great deal of attention [6].

Vegetables oils are currently the most employed renewable resources in the chemical industry. Epoxidation of these oils is usually performed by oxidizing the natural-ly-occuring unsaturations alongside the hydrocarbon chain with peroxides. Vegetable epoxidized oils were used in numerous works [3] as epoxy prepolymers. They lead to a cross-linked network either *via* a catalyzed ionic pathway (epoxy ring opening) or by reaction with hardeners such as amines, acids, or anhydrides. Epoxidized vegetable oils are without doubt the most advanced solution when it comes to biobased epoxy polymers. However, the materials formed have intrinsically low T_g as they are based on long and flexible hydrocarbon chains. This property is not suitable for high thermo-mechanical stress applications. Indeed, as mentioned previously, more stable aromatic compounds such as DGEBA are preferred.

Cycloaliphatic structures, being less flexible than their non-cyclic counterparts, could be used to circumvent this problem. Rosin is the solid nonvolatile fraction of the oleoresin obtained from coniferous trees. Rosin is a complex mixture, mostly of abietic- and pimaric-type resin acids (or rosin acids) with characteristic cycloaliphatic structures. Some works report the preparation of epoxy polymers from abietic acid [8,9] as an abundant component of rosin. However, abietic acid extraction is problematic. Also, it is a monofunctional compound; it must thus be chemically modified in order to obtain a polymer.

Biobased cycloaliphatic compounds can also be derived from saccharides. Glycidyl ethers and crotyl ethers of sucrose were prepared and crosslinked with diethylene tetraamine to lead to epoxy polymers [10]. These sucrose-based epoxy monomers could not be prepared by the usual one-step reaction with epichlorohydrin. They were instead prepared in a two-step process by sucrose allylation or crotylation followed by epoxidation with a peroxide. The actual conversion of double bonds to epoxide was rather low, especially for allylated products.

Isosorbide, another cycloaliphatic, saccharide-derived compound was used for the preparation of isosorbide diepoxy [11]. This diglycidyl ether was prepared by the allylation–oxydation method described previously and also by reaction between isosorbide and epichlorohydrin. This epoxy monomer was cross-linked with isophorone diamine and displayed fairly good properties but still not on the level of DGEBA-based materials. However, isosorbide diepoxy is hygroscopic and water uptake upon storage might impact negatively the polymer properties.

Through this tendency of aliphatic biobased monomers to not reach the thermo-mechanical properties attained by their petroleum-based counterparts, it is clear that biobased aromatic building-blocks are necessary.

Furan derivatives present a five-membered aromatic heterocycle. They are obtained by dehydration of saccharides. Their availability and aromatic structure make them good candidates to be used in epoxy polymers even if only few studies report that kind of use. One of these works report the reaction of epichlorohydrin with furan-2,5-dimethanol to prepare the interesting diglycidyl ether product [12]. This epoxy monomer was photo-polymerized with a cationic initiator. Unfortunately, the materials obtained could not be compared to other works as the thermo-mechanical properties were not fully investigated.

Literature also reports interesting works based on biobased phenolic compounds. Cardanol is an abundant biobased phenol extracted from the cashew nutshell, already industrially produced and currently extensively studied [13]. Epoxy prepolymers from cardanol are available, such as novolac resins prepared by cardanol and formaldehyde reaction, followed by glycidylation [14]. However, cardanol bears a C_{15} unsaturated aliphatic chain on the *meta* position. This structure leads, as in the case of epoxidized vegetable oils, to low T_g polymers [15].

The potential of biobased 4-hydroxybenzoic acid, prepared by biological means, was investigated for the preparation of epoxy polymers in a comprehensive work [16]. Multiple polymers were prepared, all exhibiting good thermo-mechanical properties. One must note, though, that even if promising results were obtained, the bio-production of this compound is not a mature technology yet.

Tannins are polyphenols found in most plants. They are complex polymers with a variety of structures. They can be roughly classified as condensed tannins and hydrolysable tannins. Condensed tannins have a flavonoid-like repeat unit. Catechin, a molecular flavonoid compound, was used as a model for condensed tannins and was glycidylated [17,18] with epichlorohydrin and used to obtain high T_g epoxy polymers. Hydrolysable tannins are basically gallic acid (3,4,5-hydroxybenzoic acid) molecules esterified onto a sugar. Gallic acid can thus be retrieved by hydrolysis and was glycidylated to prepare a multifunctional an epoxy monomer that was polymerized to also give high T_g epoxy polymers [19,20].

Lignin is the most abundant aromatic feedstock in nature and is currently being extensively studied [21]. It is a

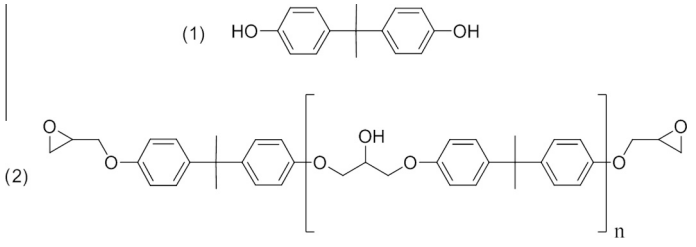


Fig. 1. Bisphenol A (**1**) and DGEBA (**2**) structures.

complex cross-linked polymer that has already been utilized to synthesize epoxy polymers [22]. Unfortunately, despite a great deal of work, efficient lignin depolymerization remains a challenge [23]. Moreover, due to lignin complexity, precise structural analysis is limited and processability depends on its solubility and molecular weight. Thus, molecular structures are preferable.

Eugenol is one the many monoaromatic structures that can be obtained from lignin. An interesting diepoxy monomer was prepared from eugenol and cross-linked with a rosin-based hardener, leading to an epoxy polymer having a high content of renewable carbon [24]. Despite the good properties obtained for the polymer, the functionalization of eugenol is a three-step process involving the use of not-so-environmentally-friendly reactants for the double bond oxidation of eugenol. Also, there is no mature technology allowing the production of eugenol from lignin yet.

The only monoaromatic compound currently industrially produced from lignin is vanillin. For instance, Borregaard Company is the second largest vanillin producer in the world and they use a vanillin-from-lignin process. Therefore, vanillin has a huge potential as a biobased building block for polymer chemistry. Despite this potential, there is only a handful of works reporting the use of vanillin in the polymer field and even less works about the synthesis of vanillin-based epoxy monomers. In one of these works, a difunctional monomer was obtained by "coupling" two vanillic acid molecules by esterification [20]. Vanillic acid or this difunctional diester were then allylated and oxidized either by a classical chemical oxidation or by a chemo-enzymatic process with *Candida Antarctica* lipase. The same strategy of esterification to prepare bis- and tris-phenols was applied to ethyl dihydroferulate obtained from vanillin [25]. In this work, *Candida Antarctica* lipase was also used, but as a transesterification catalyst. The bis- and tris-phenols synthesized were allylated and authors envisaged the preparation of epoxy monomers. This "coupling" strategy to prepare multifunctional phenols was applied directly to aldehyde moieties of vanillin [22]. In a first step, a diacetal was prepared from vanillin and pentaerythritol and in a second step, a diglycidyl ether was formed. In another work, vanillin was reacted with a diamine to obtain a dienamine that was glycidylated in a second step [26]. In a previous paper [4], our team investigated the functionalization of vanillin and its derivatives at different oxidation states, getting rid of the "coupling" step. These molecules formed a platform of potential biobased difunctional monomers for different kind of polymers, including epoxy polymers.

The present work directly continues the efforts engaged on using vanillin as a biobased building-block. More precisely, Fig. 2 shows the vanillin (**1**) derivatives methoxyhydroquinone (**2**), vanillic acid (**3**) and vanillyl alcohol (**4**) that were glycidylated to obtain the previously described [4] biobased epoxy monomers DiGlycidyl Ether of MethoxyHydroquinone (DGEMHY, **5**), DiglycidylEther of Vanillic Acid (DGEVAC, **6**), and DiGlycidyl Ether of Vanillyl Alcohol (DGEVA, **7**).

These epoxy monomers are aromatic and difunctional, which makes them worth to investigate as DGEBA substitutes. All these epoxy compounds were cross-linked with the same common industrial hardener IsoPhorone DiAmine (IPDA), for comparison purposes. Thermo-mechanical properties of the materials obtained were investigated and effects of monomer structure on these properties are discussed. Finally, a comparison of key parameters of the materials prepared with the industrial DGEBA–IPDA was performed.

2. Experimental

2.1. Materials and methods

Vanillin (99%) and vanillic acid (99%) was purchased from ABCR. Sodium percarbonate $Na_2CO_3 \cdot 1.5H_2O_2$

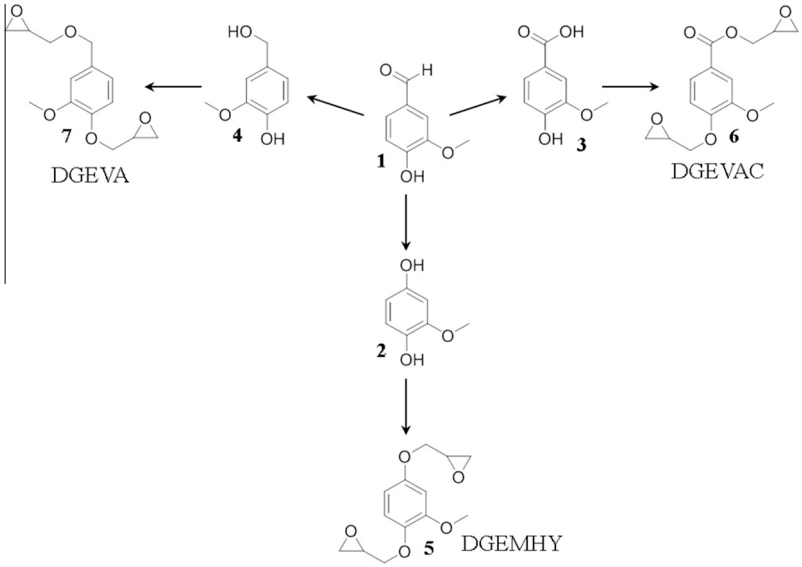


Fig. 2. Epoxy monomers prepared from vanillin derivatives.

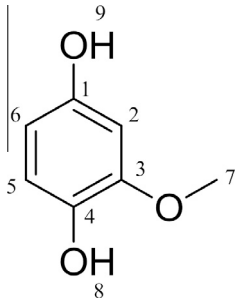


Fig. 3. Methoxyhydroquinone (**2**).

(available H_2O_2 20–30%), vanillyl alcohol (98%), triethylbenzylammonium chloride (TEBAC) (99%), anhydrous sodium sulfate Na_2SO_4 (99%), HCl (37.5 wt.%), DiGlycidyl Ether of Bisphenol A (DGEBA, 99%), and all solvents used (>99.5%) were purchased from Sigma–Aldrich. Epichlorohydrin (>99%) was purchased from Fluka. Sodium hydroxide NaOH (99%) was purchased from Fisher. All reactants were used as received.

^1H and ^{13}C (APT mode) NMR spectra were recorded on a 400 MHz Brucker Aspect Spectrometer at room temperature. Deuterated solvents used are given for each molecule. Chemical shifts are in ppm. Silica gel flash chromatography was performed on a Grace Davison Reveleris device. Melting points were measured on an Electrothermal digital melting point apparatus. MS measurements were performed on a Waters Synapt G2-S High Resolution Mass Spectrometer (HRMS) equipped with an ESI ionization source.

2.2. Synthesis of methoxyhydroquinone (2) from vanillin (**1**)

A two-necked round-bottomed flask was charged with a 0.25 mol L^{-1} solution of 1.0 eq. of vanillin in THF. 40 vol.% of deionized water was added. The mixture was degased with nitrogen. 1.1 eq. of sodium percarbonate ($Na_2CO_3{\cdot}1.5H_2O_2$) was then added by portions under nitrogen and agitation. The reaction was conducted for 3 h at room temperature. Portions of a 0.1 mol L^{-1} solution of HCl were added to the mixture under vigorous stirring until reaching pH = 3 to quench the reaction. THF was evaporated and the product in aqueous layer was extracted with ethyl acetate. The organic layers were combined, was washed with brine, dried on anhydrous Na_2SO_4 and ethyl acetate was removed on rotary evaporator.

The product (**Fig. 3**) was characterized by ^1H NMR, ^{13}C NMR and HRMS.

Methoxyhydroquinone (97%; black solid, m.p. 88 °C).

^1H NMR (400.1 MHz, acetone-d6, ppm) δ: 3.77 (s, 3H, H_7); 6.27 (dd, $^3J_{H6H5}$ = 8.4 Hz, $^4J_{H6H2}$ = 2.6 Hz, 1H, H_6); 6.46 (d, $^4J_{H2H6}$ = 2.6 Hz, 1H, H_2); 6.63 (d, $^3J_{H5H6}$ = 8.4 Hz, 1H, H_5); 6.86 (broad s, 1H, H_8); 7.73 (broad s, 1H, H_9).

^{13}C NMR (100.6 MHz, acetone-d6, ppm) δ: 56.38 (s, C_7); 101.40 (s, C_2); 107.64 (s, C_6.); 116.13 (s, C_5.); 140.71 (s, C_4); 149.07 (s, C_3); 151.82 (s, C_1).

HRMS (*m/z*, *AP+*): $C_7H_8O_3$; Calculated 140.0473; found 140.0473.

Spectra are available in Supplementary information (**S01–02**).

2.3. Synthesis of diglycidyl ether of methoxyhydroquinone (**5**)

A round-bottomed flask was charged with methoxyhydroquinone (1.0 eq.) and TEBAC (0.1 eq.). Epichlorohydrin (10.0 eq.) was added and the mixture was stirred for 1 h after reaching 75 °C. The solution was then cooled down to room temperature. An aqueous solution of TEBAC (0.1 eq.) and NaOH (4.0 eq., 5.0 mol L^{-1}) was added and the mixture was stirred 30 min at room temperature. Ethyl acetate and deionized water were then added. The mixture was stirred and the aqueous layer was washed two more times with ethyl acetate. Organic layers were combined, rinsed with brine and dried on anhydrous Na_2SO_4. Ethyl acetate and most of the epichlorohydrin excess were removed on a rotary evaporator. Further purification was achieved by silica gel flash chromatography using a hexane/ethyl acetate gradient as eluent.

The product (**Fig. 4**) was characterized by ^1H NMR, ^{13}C NMR and HRMS.

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

^1H 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.

Spectra are available in Supplementary information (**S03–04**).

2.4. Synthesis of diglycidyl ether of vanillic acid (**6**)

A round-bottomed flask was charged with vanillic acid (1.0 eq.) and TEBAC (0.1 eq.). Epichlorohydrin (10.0 eq.) was added and the mixture was stirred for 1 h after reaching 75 °C. The solution was then cooled down to room temperature. An aqueous solution of TEBAC (0.1 eq.) and NaOH (4.0 eq., 5.0 mol L^{-1}) was added and the mixture was stirred 30 min at room temperature. Ethyl acetate and deionized water were then added. The mixture was stirred and the aqueous layer was washed two more times with ethyl acetate. Organic layers were combined, rinsed with brine and dried on anhydrous Na_2SO_4. Ethyl

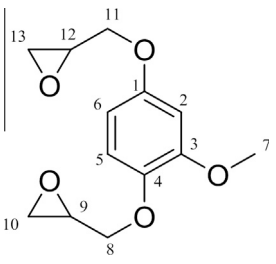


Fig. 4. Diglycidyl ether of methoxyhydroquinone (**5**).

acetate and most of the epichlorohydrin excess were removed on a rotary evaporator. Further purification was achieved by silica gel flash chromatography using a hexane/ethyl acetate gradient as eluent.

The product (Fig. 5) was characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

Diglycidyl ether of vanillic acid (85%, white solid, m.p. 77 °C).

^{1}H NMR (400.1 MHz, acetone-d6, ppm) δ: 2.73 (m, 2H, H_{10a}, H_{14a}); 2.84 (m, 2H, H_{10b}, H_{14b}); 3.31 (m, 1H, H_9); 3.36 (m, 1H, H13); 3.89 (s, 3H, H_7); 3.98 (dd, 1H, H_{8a}); 4.08 (dd, 1H, H_{12a}); 4.43 (dd, 1H, H_{8b}); 4.62 (dd, 1H, H_{12b}); 7.09 (d, $^{3}J_{H5H6}$ = 8.6 Hz, 1H, H_5); 7.56 (d, $^{4}J_{H2H6}$ = 2.0 Hz, 1H, H_2); 7.64 (dd, $^{3}J_{H6H5}$ = 8.6 Hz, $^{4}J_{H6H2}$ = 2.0 Hz, 1H, H_6).

^{13}C NMR (100.6 MHz, acetone-d6, ppm) δ: 44.50 (s, C_{14}); 44.68 (s, C_{10}); 50.00 (s, C_{13}); 50.50 (s, C_9); 56.31 (s, C_7); 66.35 (s, C_{12}); 71.12 (s, C_8); 113.38 (s, C_5); 113.47 (s, C_2); 123.72 (s, C_1); 124.28 (s, C_6); 150.28 (s, C_3); 153.64 (s, C_4); 166.32 (s, C_{11}).

HRMS (*m/z*, ES+, $[M+H^+]$): Calculated: 281.1025; Found: 281.1025.

Spectra are available in Supplementary information (S05–06).

2.5. Synthesis of diglycidyl ether of vanillyl alcohol (7)

A round-bottomed flask was charged with vanillyl alcohol (1.0 eq.) and TEBAC (0.1 eq.). Epichlorohydrin (10.0 eq.) was added and the mixture was stirred for 4 h until obtention of a limpid pink solution. This solution was cooled down to 0 °C with an ice bath. A NaOH solution (33 wt.%, 15.0 eq.) in deionized water was prepared and poured slowly into the cold mixture under vigorous stirring. The reaction was conducted overnight at room temperature (the ice bath was left to melt over time). Deionized water was added to the mixture to dilute 4 times the NaOH solution. An equal volume of ethyl acetate was added. The mixture was stirred and the aqueous layer was washed two more times with ethyl acetate. Organic layers were combined, rinsed with brine and dried on anhydrous Na_2SO_4. Ethyl acetate and most of the epichlorohydrin excess were removed on a rotary evaporator. Further purification was achieved by silica gel flash chromatography using a hexane/ethyl acetate gradient as eluent. The product (Fig. 6) was characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

Diglycidyl ether of vanillyl alcohol (89%, white solid, m.p. 53 °C).

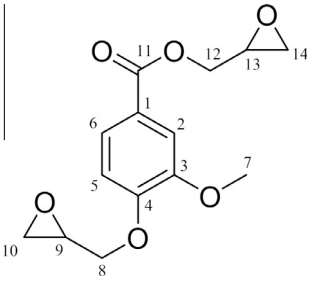


Fig. 5. Diglycidyl ether of vanillic acid (**6**).

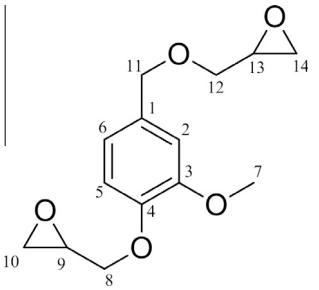


Fig. 6. Diglycidyl ether of vanillyl alcohol (**7**).

^{1}H NMR (400.1 MHz, acetone-d6, ppm) δ: 2.53 (dd, 1H, H_{14a}); 2.69 (m, 2H, H_{10a}, H_{14b}); 2.81 (m, 1H, H_{10b}); 3.10 (m, 1H, H_{13}); 3.30 (m, 2H, H_9, H_{12a}); 3.73 (dd, 1H, H_{12b}); 3.82 (s, 3H, H_7); 3.87 (dd, 1H, H_{8a}); 4.28 (dd, 1H, H_{8b}); 4.47 (d, 2H, H_{11}); 6.86 (dd, $^{3}J_{H6H5}$ = 8.0 Hz, $^{4}J_{H6H2}$ = 1.6 Hz, 1H, H_6); 6.94 (d, $^{3}J_{H5H6}$ = 8.0 Hz, 1H, H_5); 6.98 (d, $^{4}J_{H2H6}$ = 1.6 Hz, 1H, H_2).

^{13}C NMR (100.6 MHz, acetone-d6, ppm) δ: 44.16 (s, C_{14}); 44.49 (s, C_{10}); 50.76 (s, C_9); 51.28 (s, C_{13}); 56.16 (s, C_7); 71.39 (s, C_8); 71.82 (s, C_{12}); 73.42 (s, C_{11}); 112.91 (s, C_5); 114.76 (s, C_2); 120.99 (s, C_6); 132.93 (s, C_1); 148.86 (s, C_4); 150.75 (s, C_3).

HRMS (*m/z*, ASAP$^-$, $[M^-]$): Calculated: 266.1153; Found: 266.1154.

Spectra are available in Supplementary information (S07–08).

2.6. Synthesis of epoxy polymers

The diepoxy monomers synthesized are solids at room temperature. In order to avoid any inhomogeneity or air bubbles in the final material, they were first molten at a temperature of 95 °C and IPDA was then added. In the case of **5**, eight materials with varying epoxy/amine ratios ranging from 2.0/0.6 to 2.0/2.0 were prepared. **6** and **7** were formulated, also with IPDA, in a 2.0 epoxy functions for 1.0 amine function ratio.

The mixtures were thoroughly hand-stirred at 95 °C with a pre-heated stirring rod to obtain a homogeneous liquid mixture. They were then cured stepwise first for 1 h at 100 °C then for 1 h and 30 min at 125 °C and finally post-cured at 160 °C for 1 h. For comparison purposes, a material was prepared from non-oligomerized DGEBA (2.0 eq.) and also reacted with IPDA (1.0 eq). The procedure used was the same as the one described above.

2.7. DSC analyses

The thermal properties of each polymer prepared were investigated by Differential Scanning Calorimetry (DSC). All 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 pierced aluminum pans and the thermal properties were recorded at 20 °C/min. For each material sample, the thermal history was erased with a first heating ramp. The T_g value was measured on the second heating ramp at the inflexion

point of the curve. All analyses are available in Supplementary information (S09–13).

2.8. 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 3 °C/min from 50 °C to 250 °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 temperatures T_α of the α relaxation processes, corresponding to the relaxation of the networks starting to coordinate large-scale motions, 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. All analyses are available in Supplementary information (S14–17).

2.9. TGA analyses

ThermoGravimetric Analyses (TGA) were performed on a Q50 from TA Instrument. The samples were heated in an alumina crucible from room temperature to 650 °C under a nitrogen flow (60 mL/min). The experiments were carried out at a heating rate of 10 °C/min. All analyses are available in Supplementary information (S18–21).

3. Results and discussion

3.1. Syntheses of the epoxy monomers

Three vanillin derivatives in different oxidation states were used as starting points. This choice was based on the fact that lignin depolymerization often requires harsh oxidative or reductive conditions [27]. Thus, it is mandatory to consider not only vanillin itself, as it is common in the literature, but also its different oxidative states as potentially available. Methoxyhydroquinone is commercially available, it is however petro-based and relatively expensive. Here, it was synthesized from vanillin by a mild, efficient and environmentally friendly Dakin reaction. Vanillic acid can either be obtained directly from lignin depolymerization [28] or from vanillin oxidation [29]. Vanillyl alcohol can also be prepared from vanillin, by reducing it. This reaction is well-known and vanillyl alcohol was prepared from vanillin [30] and used in the polymer field.

The epoxy monomers **5**, **6**, and **7** (Fig. 2) were prepared from these vanillin derivatives. The ins-and-outs of these glycidylation reactions are described in our previous work [4]. It is worthy to note that there is only one structural difference between each of these three monomers; the impact of this difference on the thermo-mechanical properties of the final material will be investigated.

Interestingly, in their search of a biobased diepoxy monomer, Qin et al. synthesized a compound very similar to the ones described here, starting from eugenol (Fig. 7) [24].

However, the synthetic pathway from the starting compound to the diepoxy monomer involved four steps, lowering the industrial and environmental relevance compared to the two-step procedure reported here. Also, the use of *m*-ChloroPerBenzoic Acid (mCPBA) is a drawback, from an environmental point of view (multiple washing steps are necessary to remove unreacted mCPBA and *m*-chlorobenzoic acid is a by-product) and from a safety point of view (pure mCPBA is explosive). Finally, as pointed out by the authors, the current biosourcing of eugenol is mainly based on essential oil extraction from specific plants, which leads to prices prohibiting its use in polymer chemistry. Contrary to vanillin, selective lignin conversion to eugenol is not an industrial reality yet.

3.2. Syntheses of epoxy polymers

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 1.

As it can be seen, the theoretical stoichiometric epoxy/amine ratio is 2/1. However, practically, this optimal ratio can be impacted by different factors. On the one hand, the secondary amine formed might be sterically hindered and less mobile than the primary amine, especially in highly cross-linked systems, and thus less susceptible to react. In this case, an excess of amine is needed to obtain the optimal formulation. Secondly, hydroxyls formed upon epoxy ring-opening, even if less reactive than amines, might themselves react on another epoxy moiety. The optimal formulation would then require less amine than the 2/1 theoretical ratio. For these reasons, one cannot assume in the first place that a 2/1 theoretical epoxy/amine ratio is an optimal formulation and leads to polymers with optimized thermo-mechanical properties. The optimal ratio has to be experimentally determined to reach the best properties. An easy way to achieve this is to study the influence of

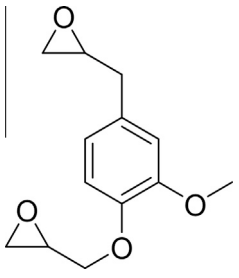
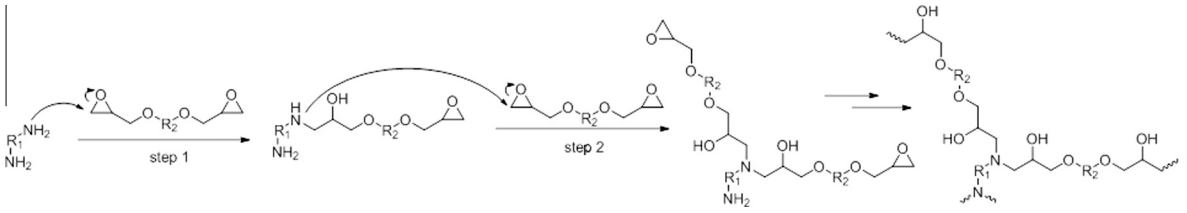


Fig. 7. Diepoxy monomer synthesized from eugenol by Qin et al. [24].



Scheme 1. Synthesis of cross-linked materials by epoxy/amine reaction.

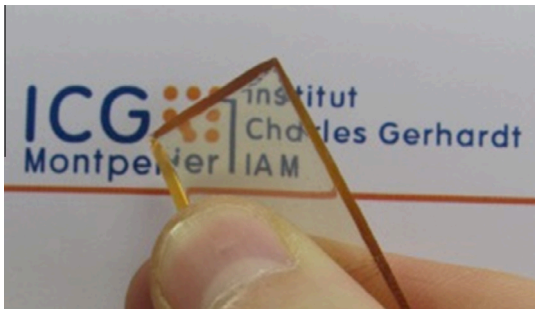


Fig. 8. Epoxy thermoset prepared from diglycidyl ether of methoxyhydroquinone and IPDA.

the epoxy/amine ratio on a given macroscopic property. For instance, Meyer et al. studied the impact of this on the T_α [31]. In this work, we selected **5**, to investigate the effect of epoxy/amine ratio variation on material properties. **5** was chosen because it is the most bulky monomer, and thus the most susceptible to differ from the theoretical ratio due to steric hindrance. Eight materials with epoxy/amine ratios ranging from 0.6/2.0 to 2.0/2.0 were prepared from **5** and IPDA and their T_g was measured by DSC. **6**- and **7**-based materials were also reacted with IPDA in a 2.0/1.0 epoxy/amine ratio in both cases.

All three diepoxy monomers were solids at room temperature and had to be reacted in a molten state. All materials were post-cured at a temperature higher than T_g to ensure complete reaction. The complete curing was confirmed by the absence of residual exothermicity on DSC thermograms of post-cured samples. This processing guaranteed the obtention of homogeneous materials as shown in Fig. 8. DGEBA-based materials were also prepared by the same method for comparison purposes.

3.3. Influence of the epoxy/amine ratio on the T_g

The influence of the epoxy/amine ratio on the T_g of the **5**-based materials was studied. Fig. 9 shows the T_g of the materials as a function of the epoxy/amine ratio used (all DSC available in Supplementary information S09).

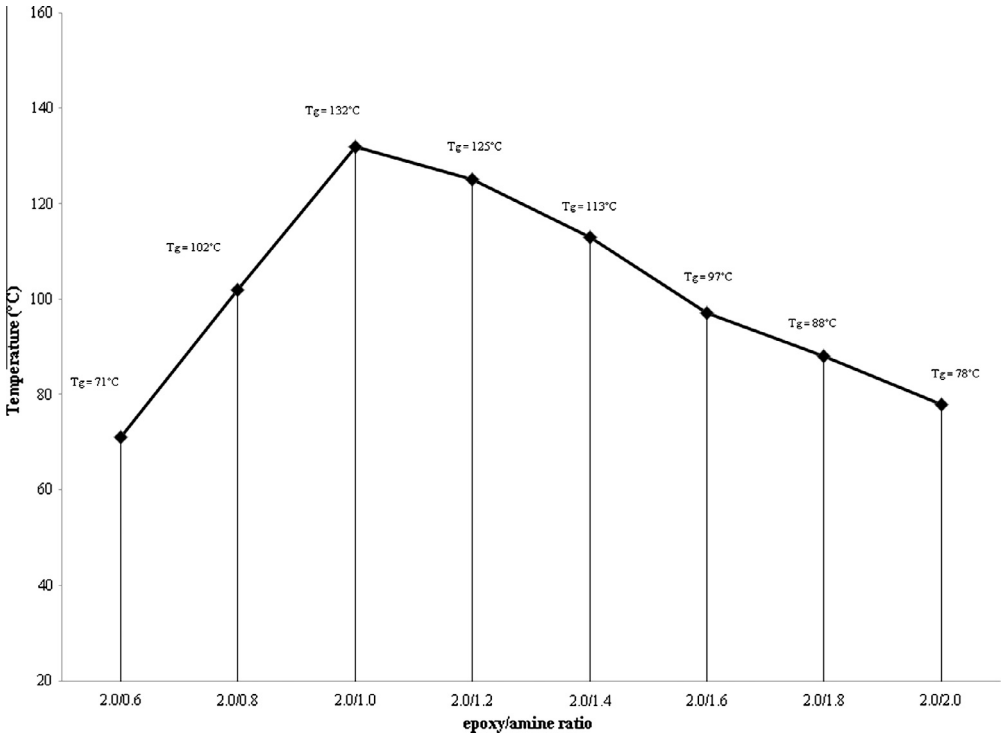


Fig. 9. T_g of the diglycidyl ether of methoxyhydroquinone-based materials as a function of the epoxy/amine ratio used.

An optimal T_g of 132 °C is attained for an epoxy/amine ratio of 2/1. Materials with an excess of either amine or epoxy present unreacted end-groups or even free monomers. These unreacted entities are trapped inside the polymer network, creating steric hindrance as they can move and rotate freely, thus diminishing the cross-linking density and the T_g. These entities act as plasticizers. The optimal formulation is the one presenting as less unreacted functions as possible. The further away from this optimal formulation the polymer is, the more unreacted functions there is, and the lower the T_g is. The optimal ratio found corresponds to the theoretical stoichiometric ratio, confirming the polymerization reaction proposed in Scheme 1.

3.4. Relationship between monomer structure, cross-link density and polymer T_g and T_α

DSC and DMA analyses (Supplementary information S10–12 and S14–16 respectively) were performed on materials based on **5**, **6** and **7** formulated with an optimal 2.0/1.0 epoxy/amine ratio. Fig. 10 shows the T_g and T_α obtained for each of these polymers.

Numerous efforts have been made to predict the T_g of polymers since the pioneer work of Van Krevelen [32] on a group contribution method. Here we consider cross-linked epoxy polymers and as such, the papers from Stutz et al. [33] and Bellenger et al. [34] were considered especially relevant. Conclusions from these works stated that the glass transition temperature is governed essentially by three different effects:

(1) The influence of monomer(s) structure. The contribution of a given group to T_g will depend for instance on its ease of rotation, free volume, cohesive energy with the rest of the network... The influence of aromatic rings is especially important [34]: the more there is, the higher the T_g is as they are very rigid, non-rotating groups.
(2) The influence of the number of end-groups, related to the degree of curing. End-groups can rotate more freely, lowering the T_g as discussed in the previous paragraph.
(3) The influence of the cross-link density, which is the number of cross-links per unit volume. The higher it is, the more the chain mobility is restricted and the higher the T_g and T_α are.

In this study, the influence of the number of end-groups was assumed to be negligible compared to the two other effects as the 2/1 epoxy/amine ratio used for each materials was proven to give an optimal T_g. An optimal T_g indicates a degree of curing as high as possible, *i.e.* a number of end-groups as low as possible. End-groups act as plasticizers if they are not integrated in the network, lowering the T_g. The ratio used maximized the T_g, which enabled us to neglect the end-group effect.

We studied the uniaxial stretching of homogeneous and isotropic materials, on the rubbery plateau at $T_\alpha + 50$, and at very small deformations that can be considered elastic as at $T = T_\alpha + 50$, $E' \gg E''$. Under these hypotheses, the cross-link density can be obtained from Eq. (1), obtained from the theory of rubber elasticity [35]:

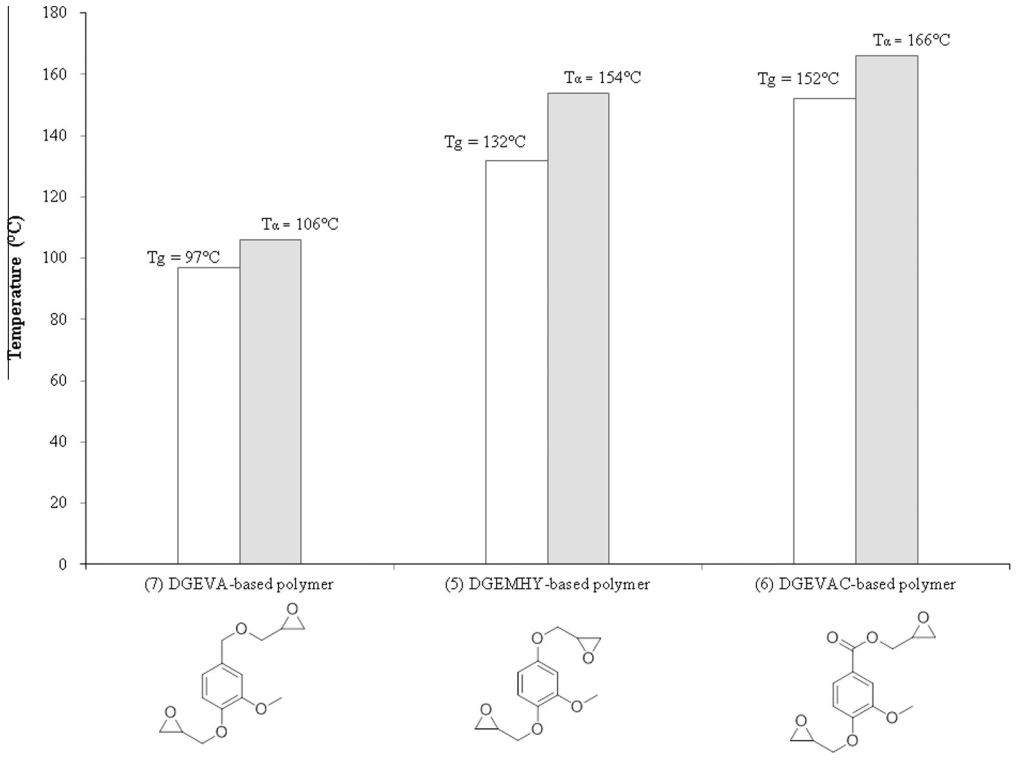


Fig. 10. T_g and T_α of the polymers synthesized from diglycidyl ethers of methoxyhydroquinone, vanillic acid, and vanillyl alcohol.

Table 1
Comparison of some key thermo-mechanical properties between vanillin-based and DGEBA-based epoxy polymers.

Material	T_g[a]	T_α[b]	E' (30 °C)[c]	d[d]	T_{deg}[e]	Char 600 °C[f]
DGEBA/IPDA	166 °C	182 °C	1.9×10^9 Pa	1.4 mmol m^{-3}	360 °C	10%
7/IPDA	97 °C	106 °C	1.5×10^9 Pa	0.7 mmol m^{-3}	361 °C	19%
5/IPDA	132 °C	154 °C	1.2×10^9 Pa	1.3 mmol m^{-3}	338 °C	20%
6/IPDA	152 °C	166 °C	2.1×10^9 Pa	1.4 mmol m^{-3}	315 °C 370 °C	14%

[a] Glass transition temperature measured by DSC.
[b] Alpha transition temperature measured by DMA.
[c] Storage modulus at 30 °C measured by DMA.
[d] Cross-link density calculated from $E'(T_\alpha + 50)$, measured by DMA.
[e] Temperature of maximum degradation rate given by TGA curve derivative under N_2.
[f] Residual mass at 600 °C given by TGA curve under N_2.

$$E'(T_\alpha + 50) = 3\left(\frac{\rho}{\overline{Mc}}\right)R(T_\alpha + 50) \quad (1)$$

with E' the storage modulus (Pa); T_α the temperature of α relaxation process, maximum of $\tan\delta$ (K); ρ the volumetric mass of the polymer (g m^{-3}); $\overline{Mc}$ the average molecular weight between cross-links; R the ideal gas constant (J K^{-1} mol^{-1}).

As pointed by Levita et al. [36], for dense epoxy networks:

$$\frac{\rho}{\overline{Mc}} = \frac{3}{2}d \quad (2)$$

with d the cross-link density, number of moles of cross-links per volume unit (mol m^{-3}).

This leads to **Eq. (3)**, linking the cross-link density d to the storage modulus above T_α:

$$E'(T_\alpha + 50) = 3\left(\frac{3}{2}d\right)R(T_\alpha + 50) \quad (3)$$

Here, we discuss the effect of monomer structural differences and cross-link density d (**Table 1**) on the T_g and T_α of the polymers prepared. As it can be seen, the **7**-based polymer has the lowest T_g (97 °C). **7** is a benzyl glycidyl ether (**Fig. 10**), meaning that the additional methylene gives the molecule more possible rotations, making it less rigid than the other two monomers. This structural difference can be linked to the lower T_g observed in the case of **7**-based materials. This result is consistent with the recent work of Hu et al. [37], in which they found a T_g 113 °C lower for materials prepared from dibenzyl glycidyl ether monomer than for materials from diphenyl glycidyl ether monomer. Additionally, the cross-link density for this polymer is two times lower than for the others, meaning chain mobility is less restricted and the T_g and T_α higher.

5, however, has a diphenolic structure, meaning it has one carbon less than **7**, and thus less possible rotations. This makes **5** more compact and more rigid than **7**. These are two different contributions to the higher T_g observed on the final material. On the one hand, the fact that the monomer is more rigid means the network as a whole will need more energy to coordinate large-scale motions, increasing the T_g. On the other hand, the fact that the monomer is shorter, more compact explains the higher cross-link density of the network and thus the higher T_g and T_α.

The highest T_g and T_α were obtained with the **6** monomer. **6** is an aromatic glycidyl ester (**Fig. 10**). It has an ester group conjugated with the aromatic ring, locking the molecule in one energetically favored conformational state. **6** has thus the biggest rigid part among the monomers studied, which explains the T_g and T_α increase from a monomer structure perspective. **6**-based polymers have a crosslink density higher than **7** with same number of carbons. This result was also attributed to the monomer structure, more flat and thus allowing a denser stacking and to the presence of hydrogen bonding to the ester group, increasing the overall energy of the network.

3.5. TGA analyses

Thermal degradations of all materials were characterized by TGA under nitrogen (Supplementary information **S18–20**). The weight loss and weight loss derivative of these materials were recorded as functions of temperature. In these conditions, the samples present a degradation starting around 300 °C. The weight loss at this temperature is around 2%. At higher temperatures, a sharp weight loss. The weight loss derivative monitors the rate of degradation as a function of temperature. These curves present peaks at which the degradation rate is maximum. In the case of **7**- and **5**-based polymers, these curves present one peak which is characteristic of a one-step weight loss. In the case of **6**, it takes place in a two-step fashion. The fact that **6** present this two-step degradation profile is attributed to the presence of the ester linkage. This ester is believed to degrade at a lower temperature than the rest of the network, explaining the first peak of degradation. The residues at 600 °C were also investigated were comprised between 14% and 20%. This parameter can be of importance, especially in fire retardation applications. TGA curves are available in Supplementary information.

3.6. Comparison to a DEGBA-based reference

Epoxy thermosets were prepared starting from derivatives of vanillin, which is a non-harmful, biobased and available compound. This is an improvement compared to current epoxy polymers based on bisphenol A, a reprotoxic compound. The choice of vanillin was also guided by its aromatic structure, necessary to reach thermo-mechanical properties comparable to current industrial epoxy

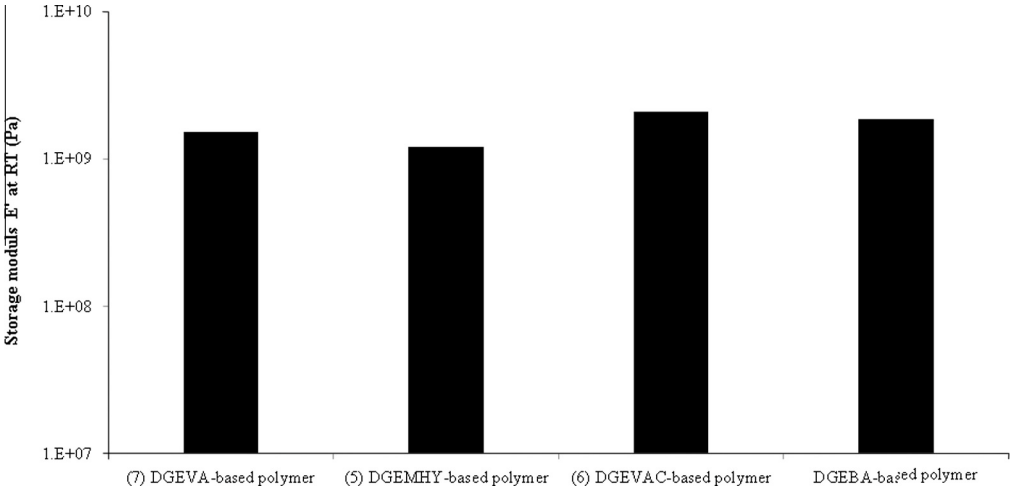


Fig. 11. Storage moduli E' at room temperature for all polymers prepared.

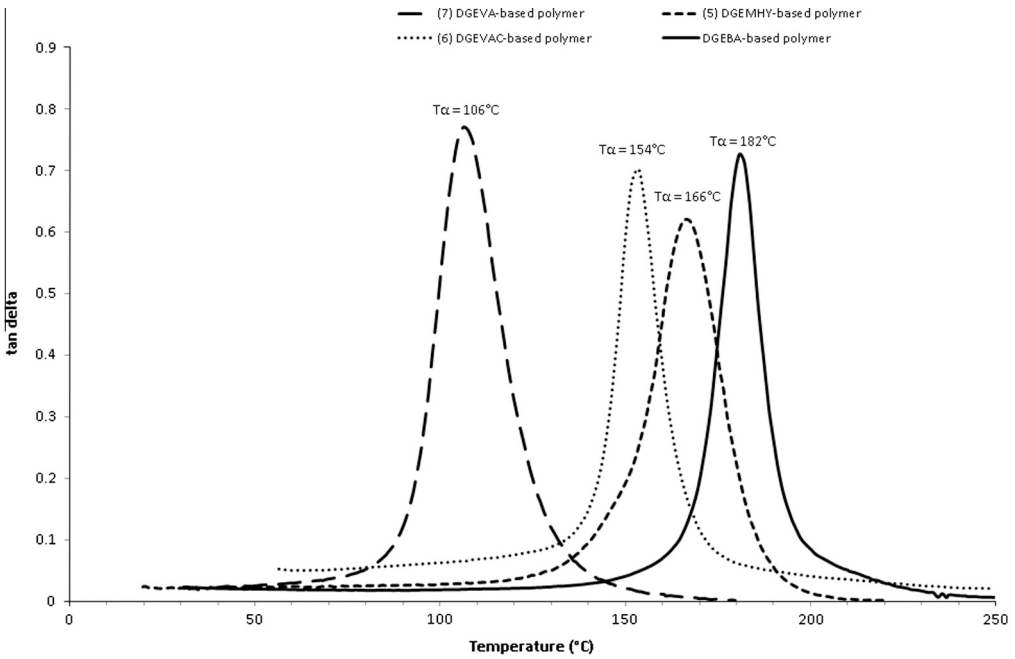


Fig. 12. Tanδ curves of synthesized polymers.

thermosets. Indeed, in order to have an industrial relevance, new biobased materials have to display good performances compared to existing systems. The properties of the materials prepared were thus compared to the industrial DGEBA/IPDA system as a reference (analyses available in Supplementary information S13, S17, and S21). Results of this comparison are summarized in Table 1.

To ensure a valid comparison, a specific attention was given to the DGEBA used. Indeed, most of the DGEBA used industrially are actually prepolymers, meaning that they are oligomers with varying length. Thus, depending on the length chosen, one can obtain with a given hardener a wide range of T_g: the longer the prepolymer is, the lower the T_g of the final material will be. This is of great industrial interest as the properties of the network can be tuned this way. However, in our case, the materials were synthesized from purely monomeric diepoxies and can only be compared to a material obtained from non-oligomerized DGEBA, which was thus used. This explains the differences in T_g and T_α given in Table 1 for the DGEBA–IPDA system compared to the literature. Indeed the T_g reported for this system is 158 °C [15] and the T_α is 160 °C [19]. In both cases, the authors used a short DGEBA oligomer, giving materials with transition temperatures lower than the ones reported here for a non-oligomerized DGEBA.

As it can be seen, the biobased materials prepared have properties close to the current industrial petrobased reference. For instance, the storage moduli at room temperature have similar values and are all >1 GPa, as shown in Fig. 11. This temperature is an interesting parameter to monitor as

it gives an idea of the mechanical properties of the polymers below T_α.

Also, the height and mid-height width of the tanδ curves are close for each material prepared as it can be seen in Fig. 12. The tan δ is the ratio between the energy irreversibly dissipated by the material (E'') and the energy stored (E'). This ratio is – as T_α – dependent on parameters like monomer structure and cross-link density. Here, the magnitude of the tanδ peak is close for all materials prepared. The small decrease of the peak height with increasing T_α can be attributed to the increasing monomer stiffness (the material will dissipate less energy by molecular motion if it is less flexible). The mid-height widths of the peaks are also very close for all materials, confirming the obtention of homogeneous materials. All three vanillin-based materials give results comparable to the DGEBA-based material.

The properties can be tuned by choosing the adapted vanillin derivative. The polymer prepared from vanillic acid displays properties very similar to the DGEBA-based reference. Transition temperatures, in particular, are the closest to the reference among the derivatives studied. The cross-link density is equivalent, and residual mass are even higher than the reference. Its maximum degradation temperature is however lower. The polymer prepared from vanillyl alcohol shows more modest thermo-mechanical properties, which are still very good for an epoxy polymer in general and for a biobased one in particular. These results indicate that Bisphenol A-based epoxy polymers could thus be replaced in many applications by renewable vanillin-based epoxy polymers.

4. Conclusion

Biobased epoxy thermosets derived from vanillin with properties close to the current Bisphenol A-based industrial reference were prepared. This work directly continues the efforts engaged by our team to use vanillin as a biobased building block for polymer chemistry [4]. Vanillin is a well-known industrially available, non-toxic, wood-derived compound. Its aromatic structure makes it particularly suitable for high performance thermosetting polymers. As the ubiquitous Bisphenol A-based epoxy ther-mosets might be restricted in future years due to Bisphenol A health hazards, vanillin-based epoxy polymers appear as an attractive biobased substitute. Three vanillin derivatives (methoxyhydroquinone, vanillic acid, and vanillyl alcohol) were glycidylated to give biobased aromatic diepoxy monomers. These monomers were polymerized with IPDA, a common industrial amine hardener. The influence of the epoxy/amine ratio on thermal properties was studied and the theoretical 2/1 ratio was found to be the optimal formulation as the resulting polymer presented the highest T_g. The relationship between monomer structure and polymer properties was also investigated and the polymer based on vanillic acid was found to have the highest transition temperatures. Finally, key parameters of these biobased polymers such as transition or degradation temperature were compared to the industrial DGEBA–IPDA system as a reference. For instance, vanillic acid-derived polymer possessed the same T_α than this reference. Overall, this comparison led to the conclusion that these renewable vanillin-based epoxy polymers could replace current Bisphenol A-based epoxy polymers in many applications.

The diepoxy monomers were all solids at room temperature, as pure DGEBA. This limits their industrial relevance because of high processing temperatures required to work in the molten state. The solution currently in use for DGEBA is the use of prepolymers – oligomers – having low T_g. This approach is directly applicable to our vanillin-derived compounds and will be investigated in future works.

Acknowledgments

The authors would like to thank the French Ministry of Research for funding this work. The authors are also grateful to Agathe Bouvet-Marchand, Mony Girault, and Thibault Derouineau for preliminary experiments.

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.2014.10.011.

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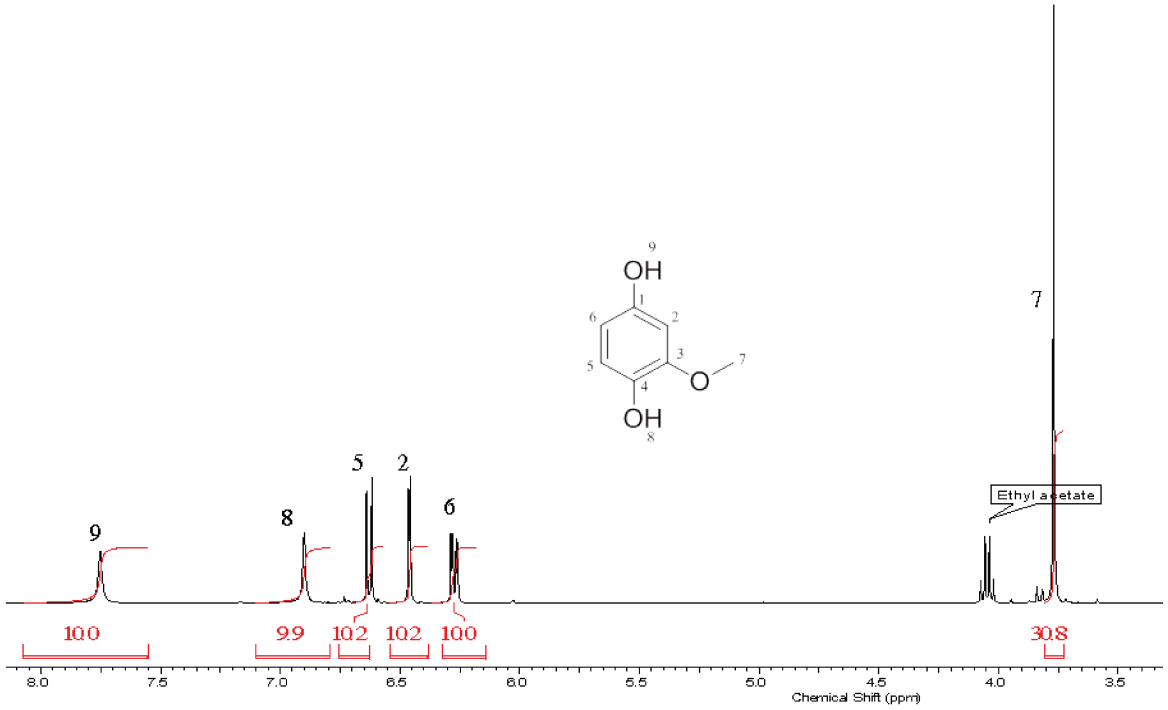
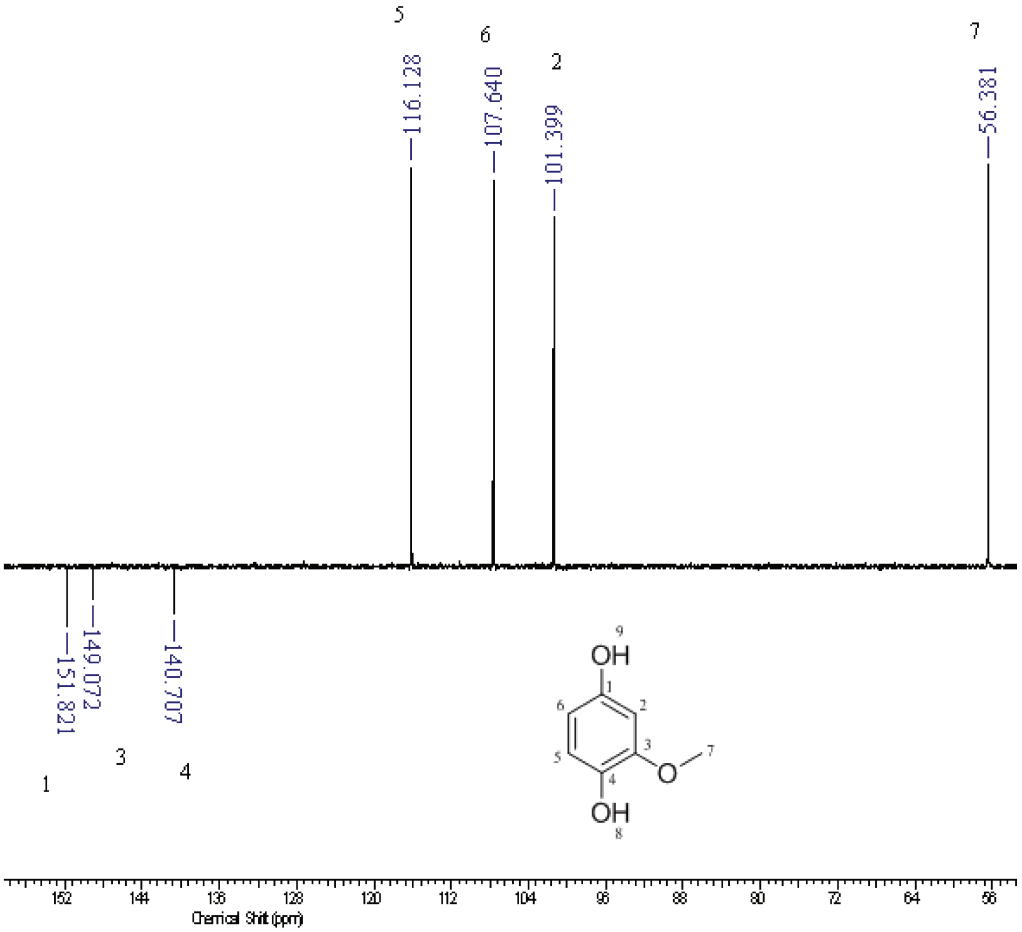
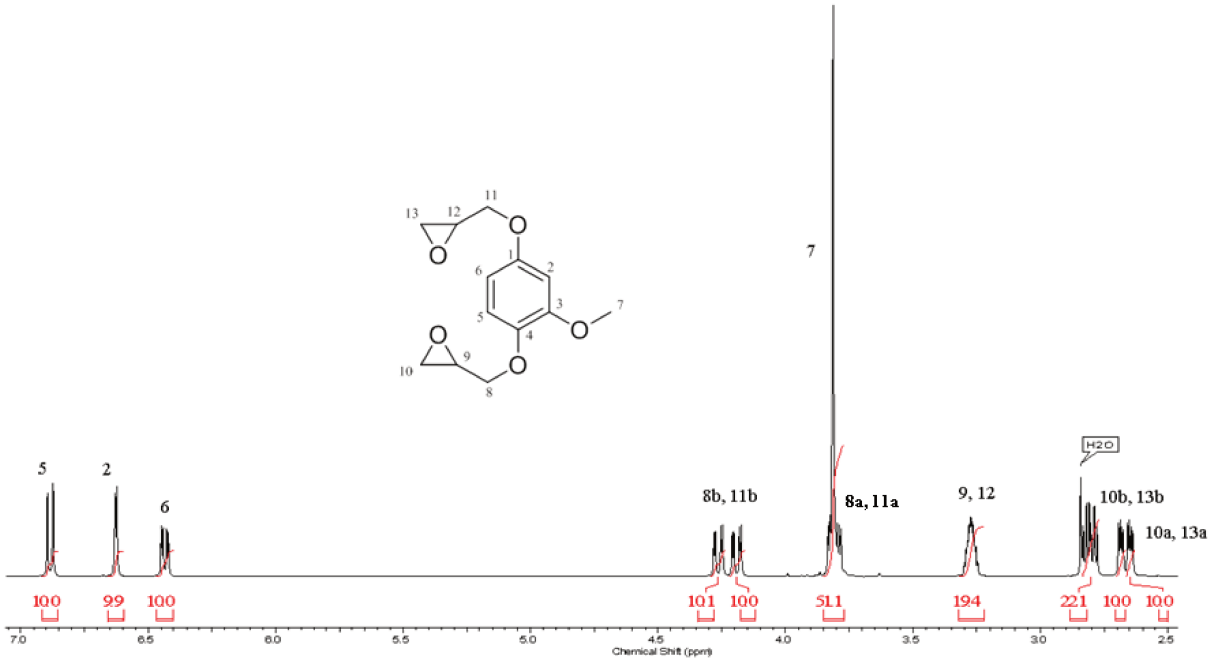
S01 - ^{1}H NMR spectrum of methoxyhydroquinone (**2**) (acetone d_6).



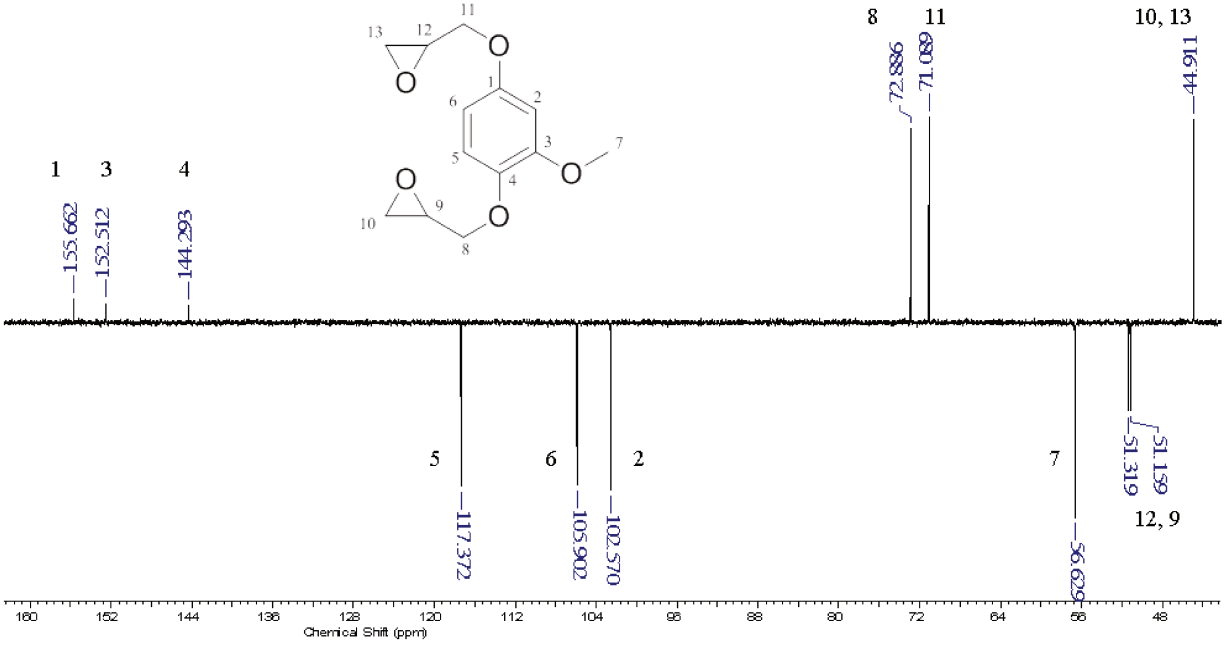
S02 - ^{13}C NMR spectrum of methoxyhydroquinone (**2**) (acetone d_6).



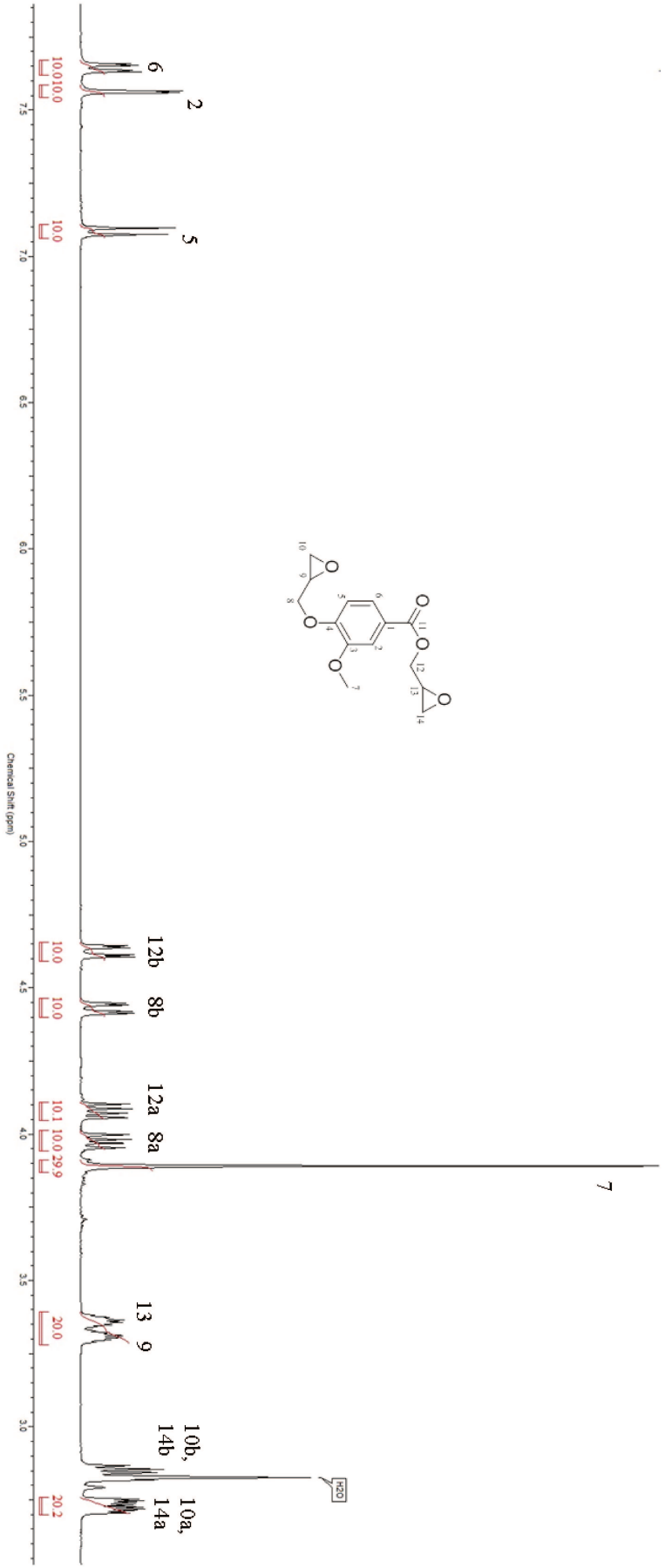
S03 - ^{1}H NMR spectrum of DGEMHY (**5**) (acetone d_6).



S04 - ^{13}C NMR spectrum of DGEMHY (**5**) (acetone d_6).



S05 - ^{1}H NMR spectrum of DGEVAC (**6**) (acetone d_6).



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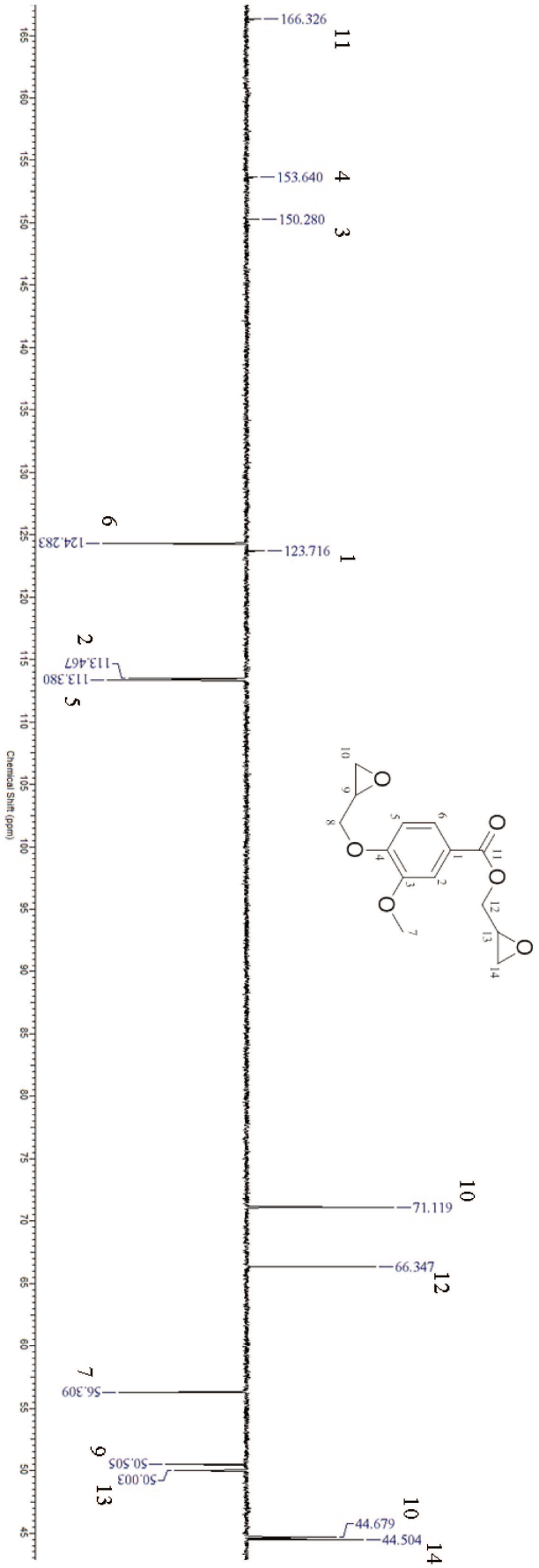
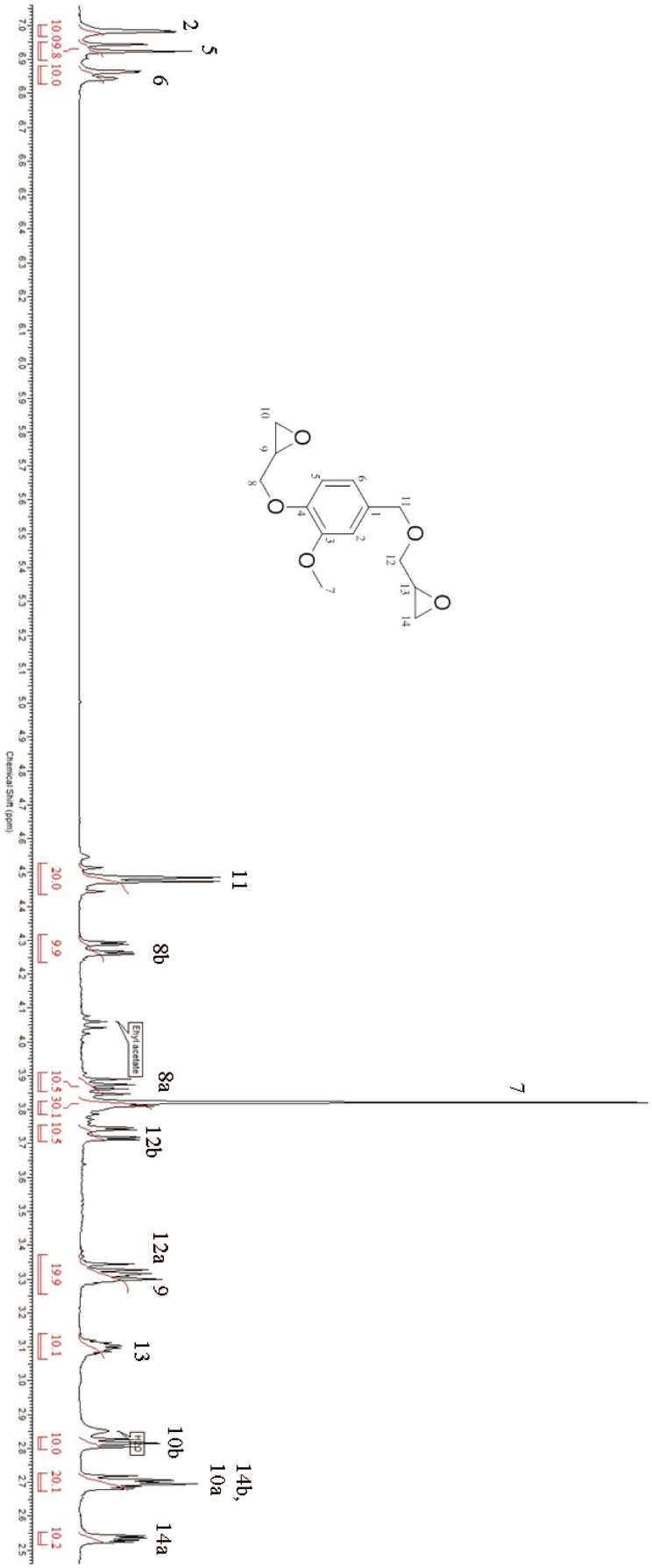
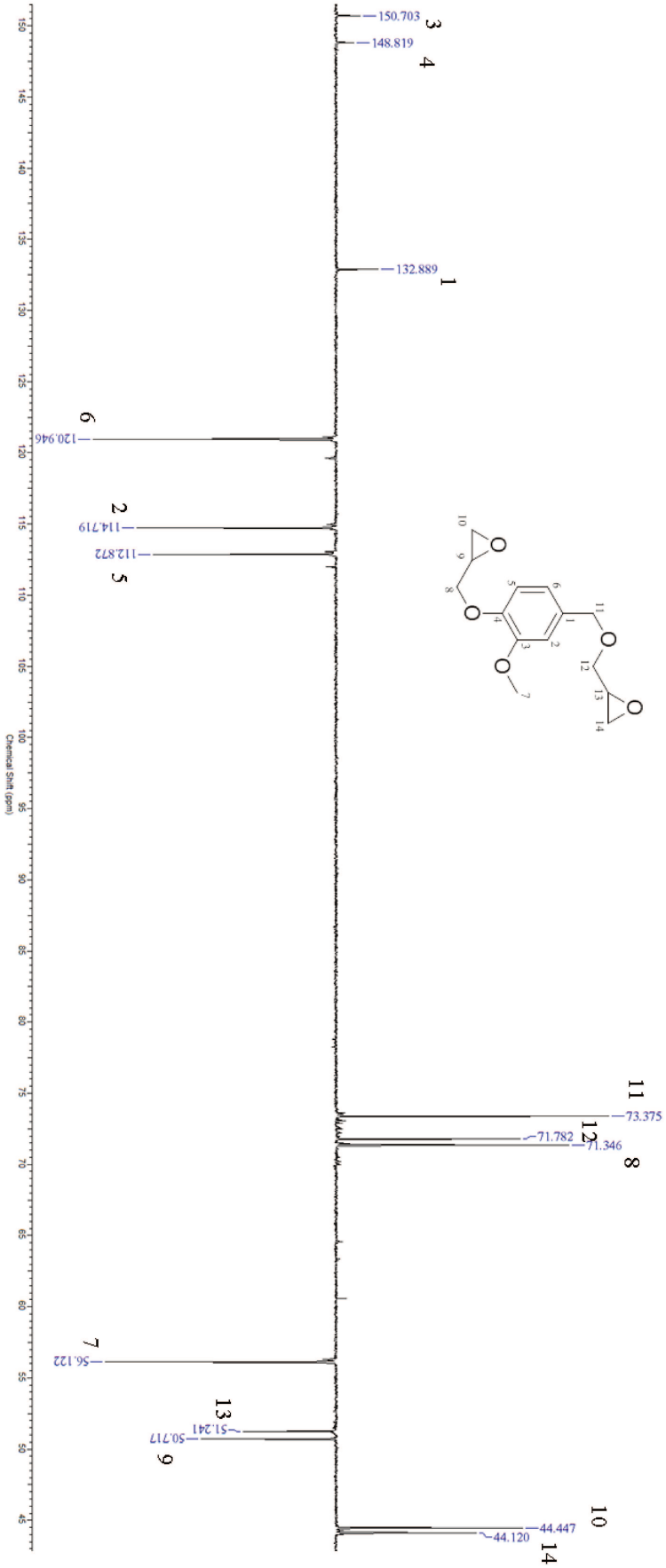


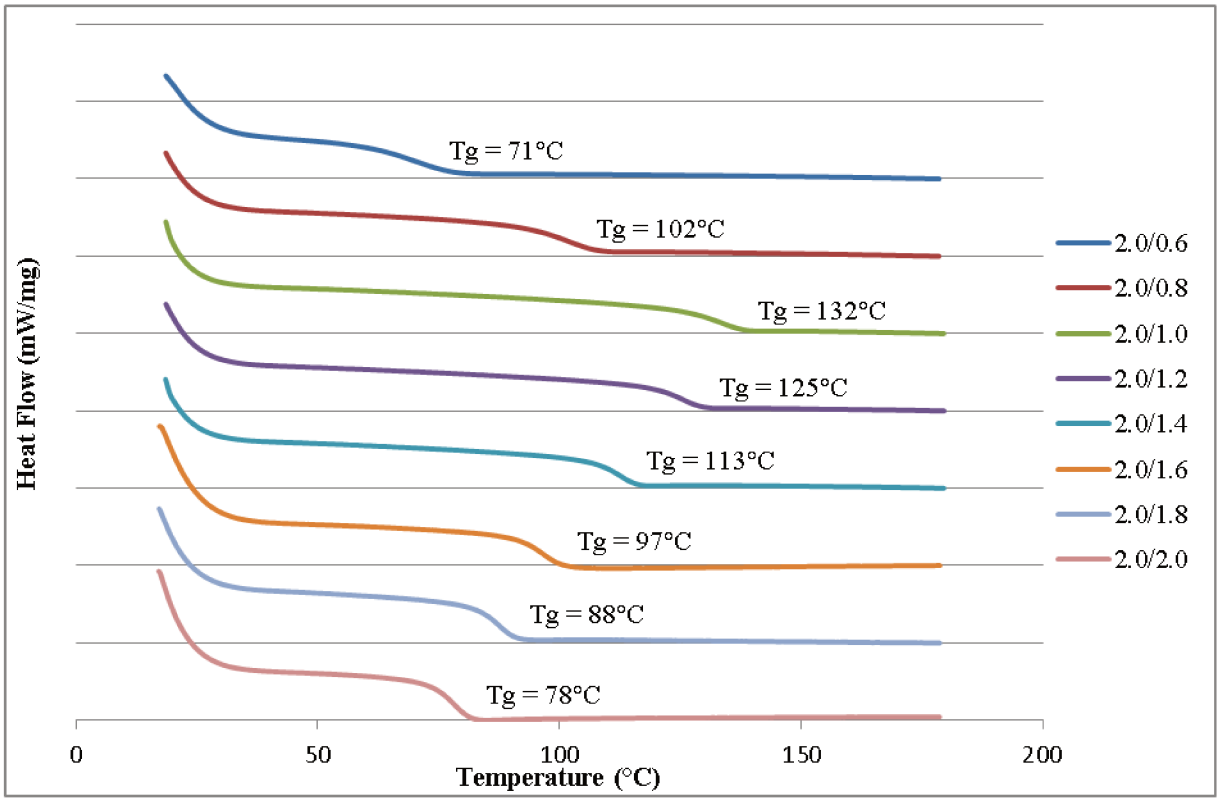
S07 - ^{1}H NMR spectrum of DGEVA (**7**) (acetone d_6).



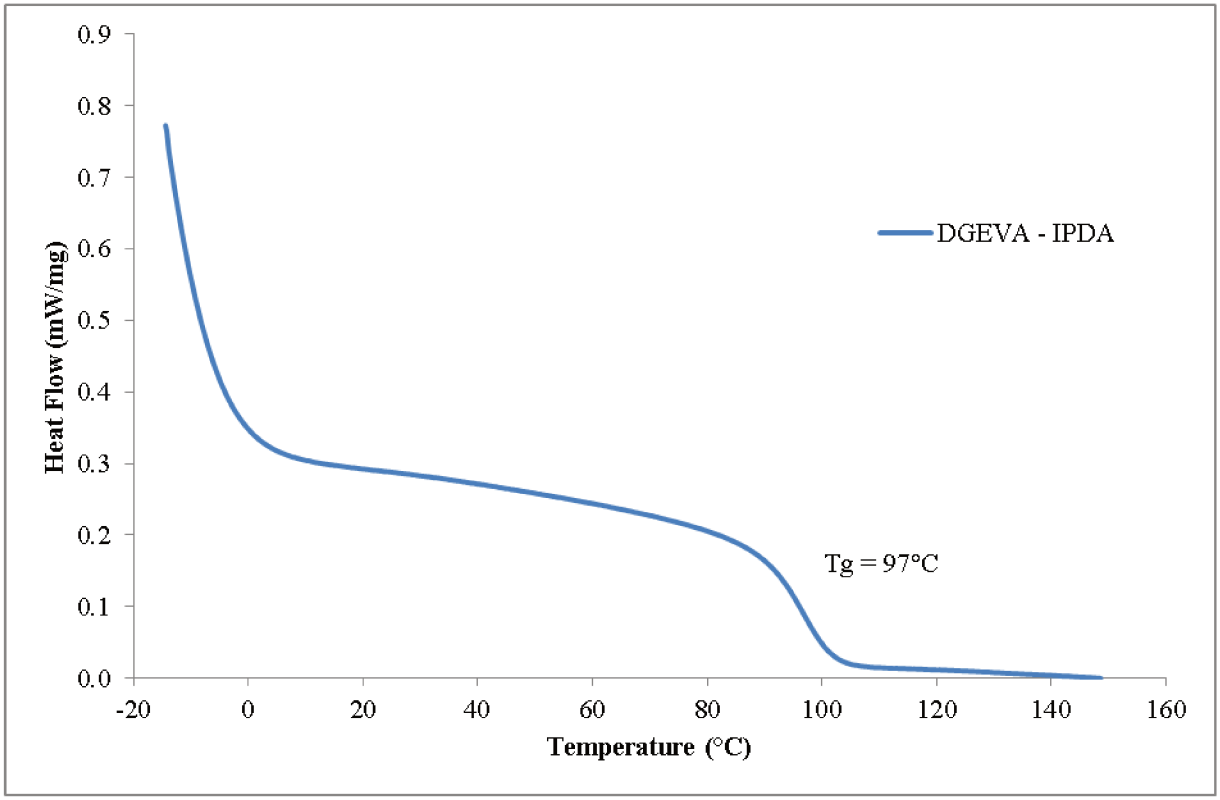
S08 - ^{13}C NMR spectrum of DGEVA (**7**) (acetone d_6).



S09 - DSC analyses for the **5** - IPDA system (ratio variation)



S10 - DSC analysis for the **7** - IPDA system (2.0/1.0 ratio)



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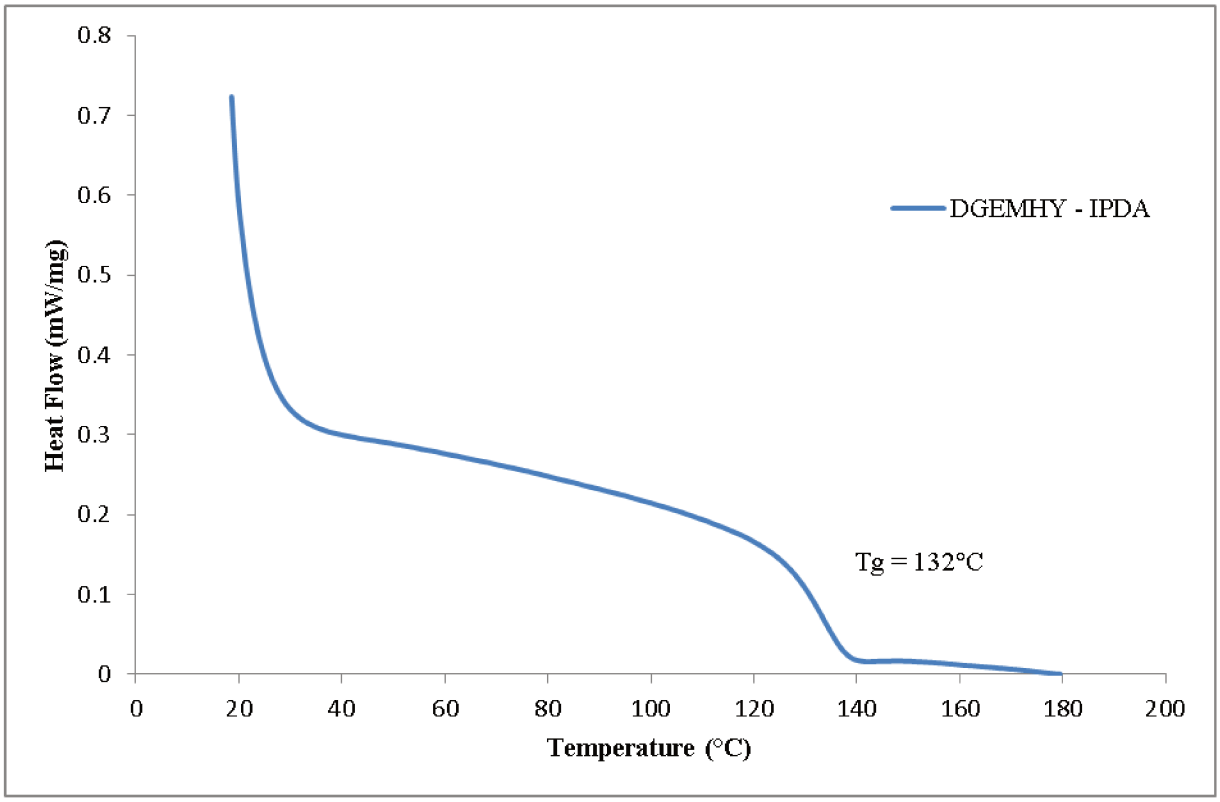

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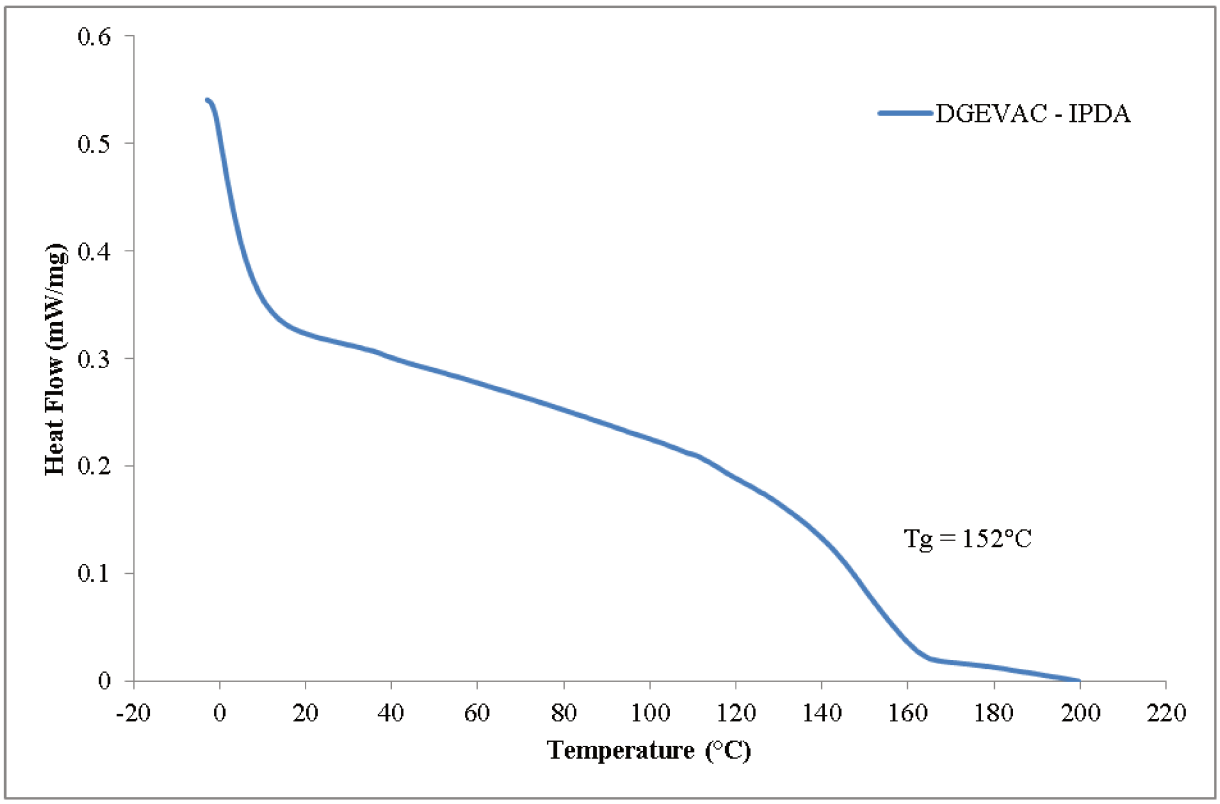

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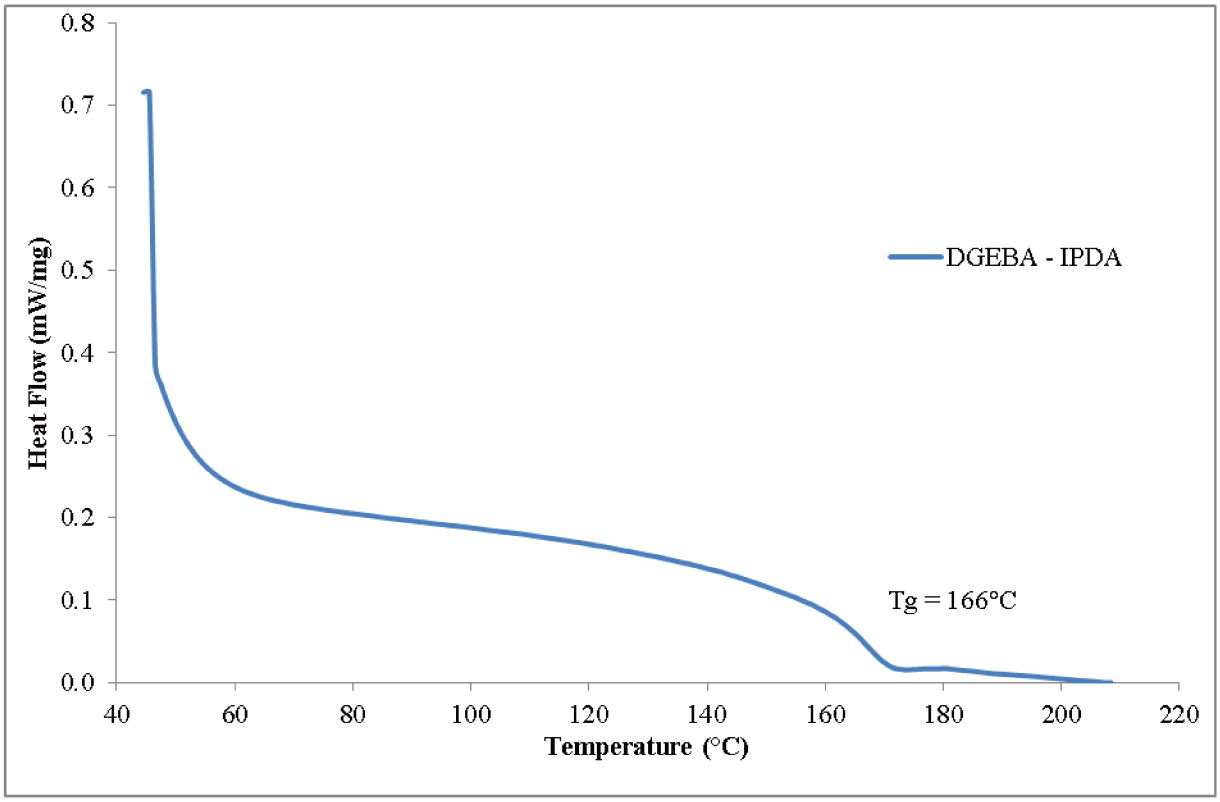
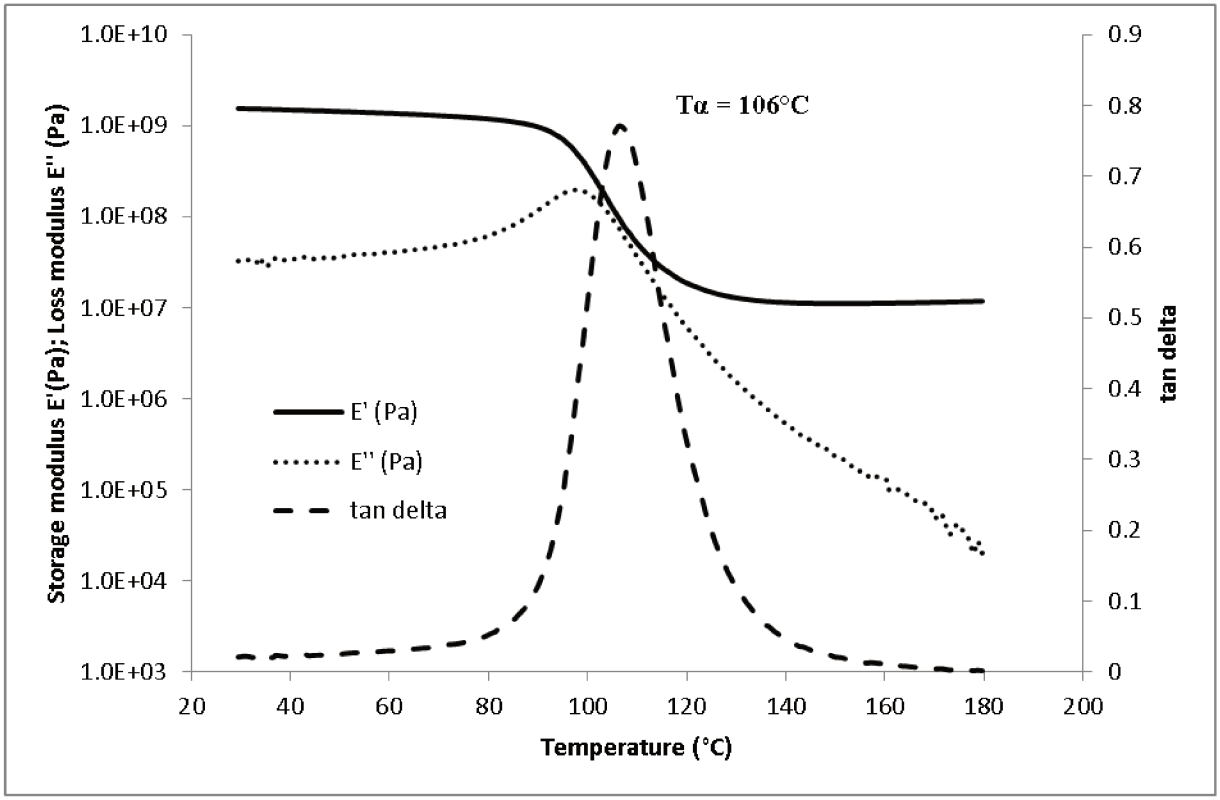


S14 - DMA analysis for the **7** - IPDA system (2.0/1.0 ratio)



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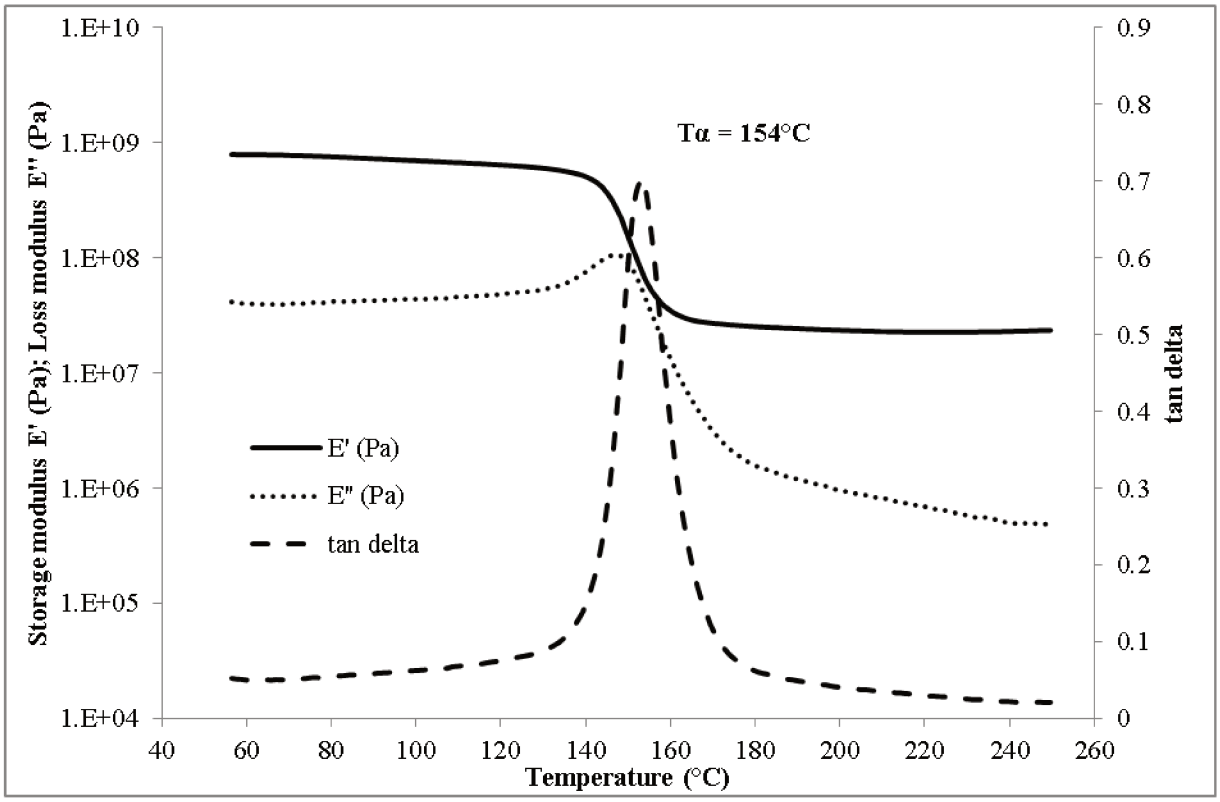

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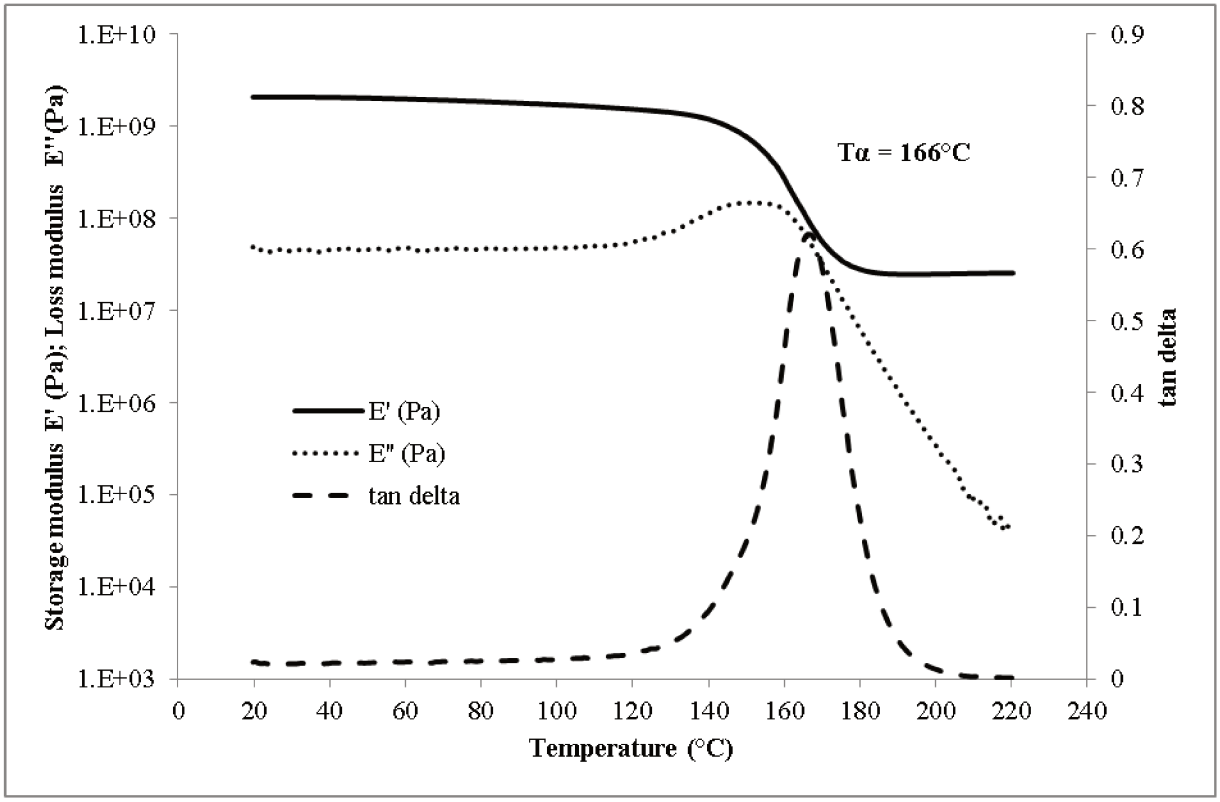
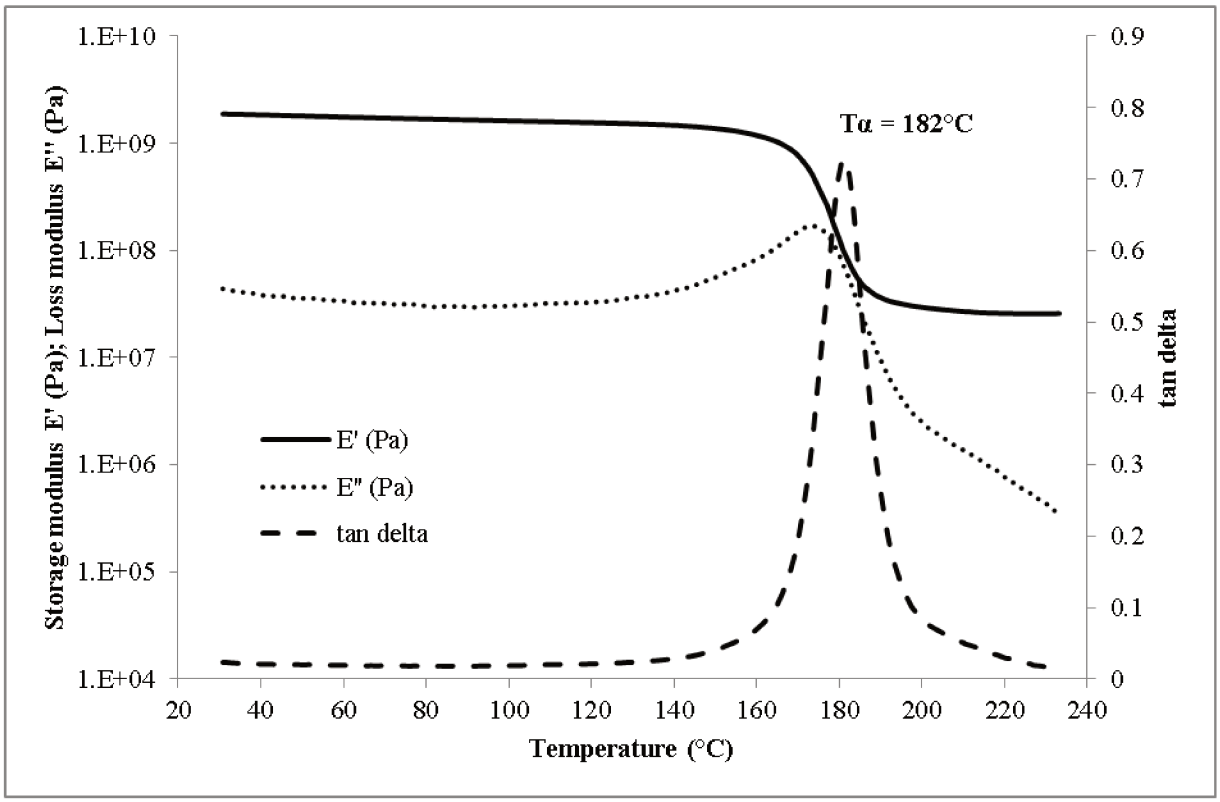
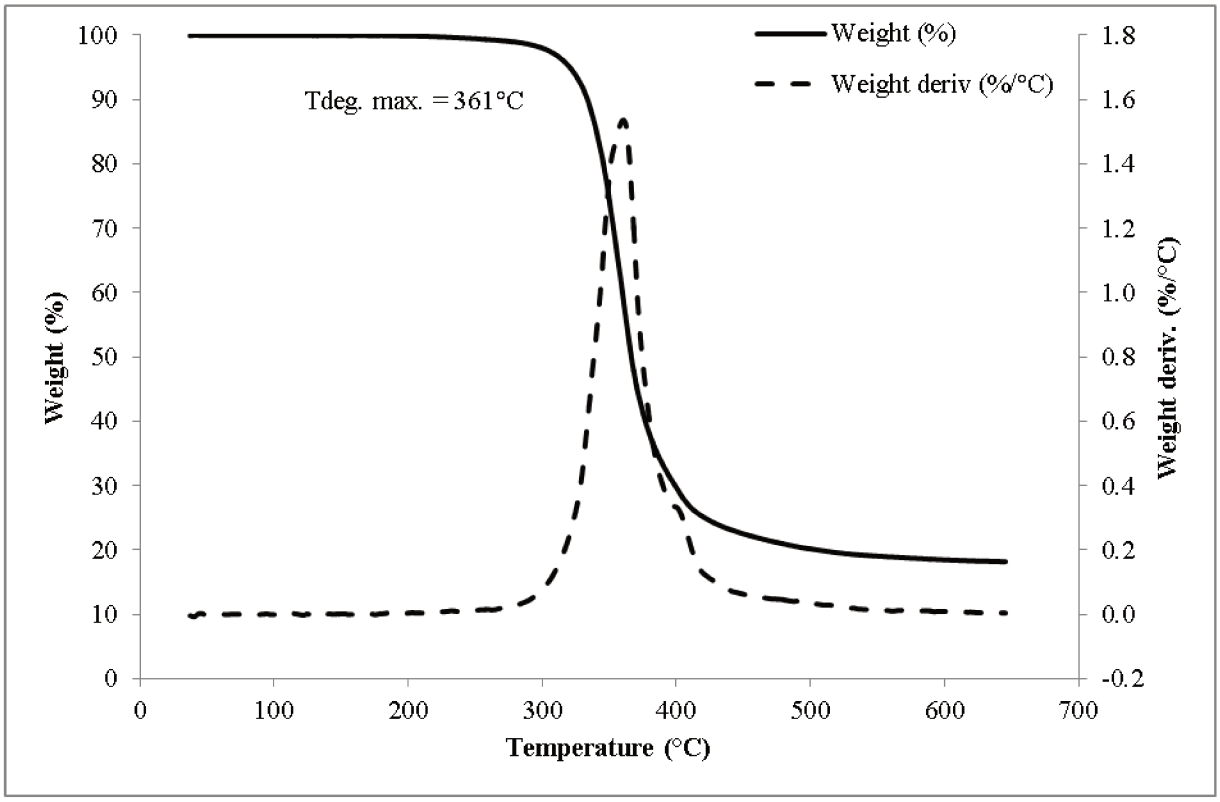


S17 - DMA analysis for the DGEBA - IPDA system (2.0/1.0 ratio)



S18 - TGA analysis for the **7** – IPDA system (2.0/1.0 ratio)



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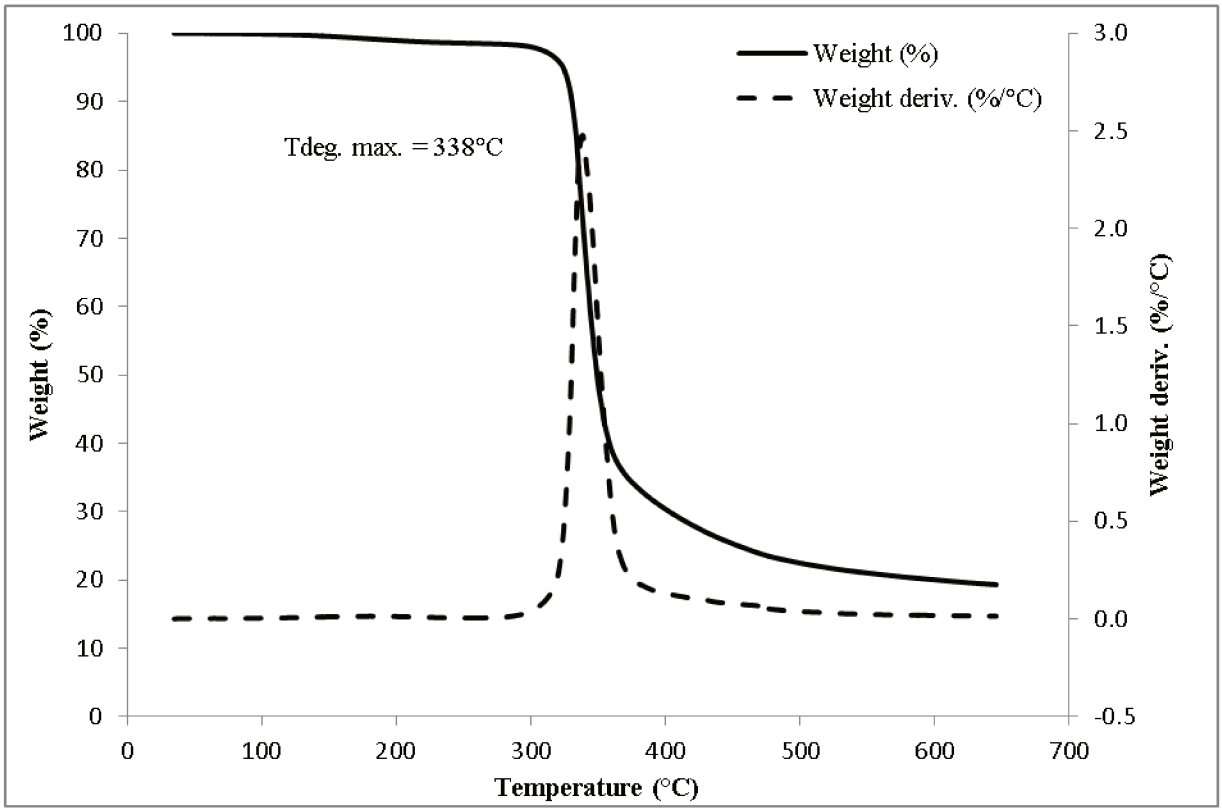
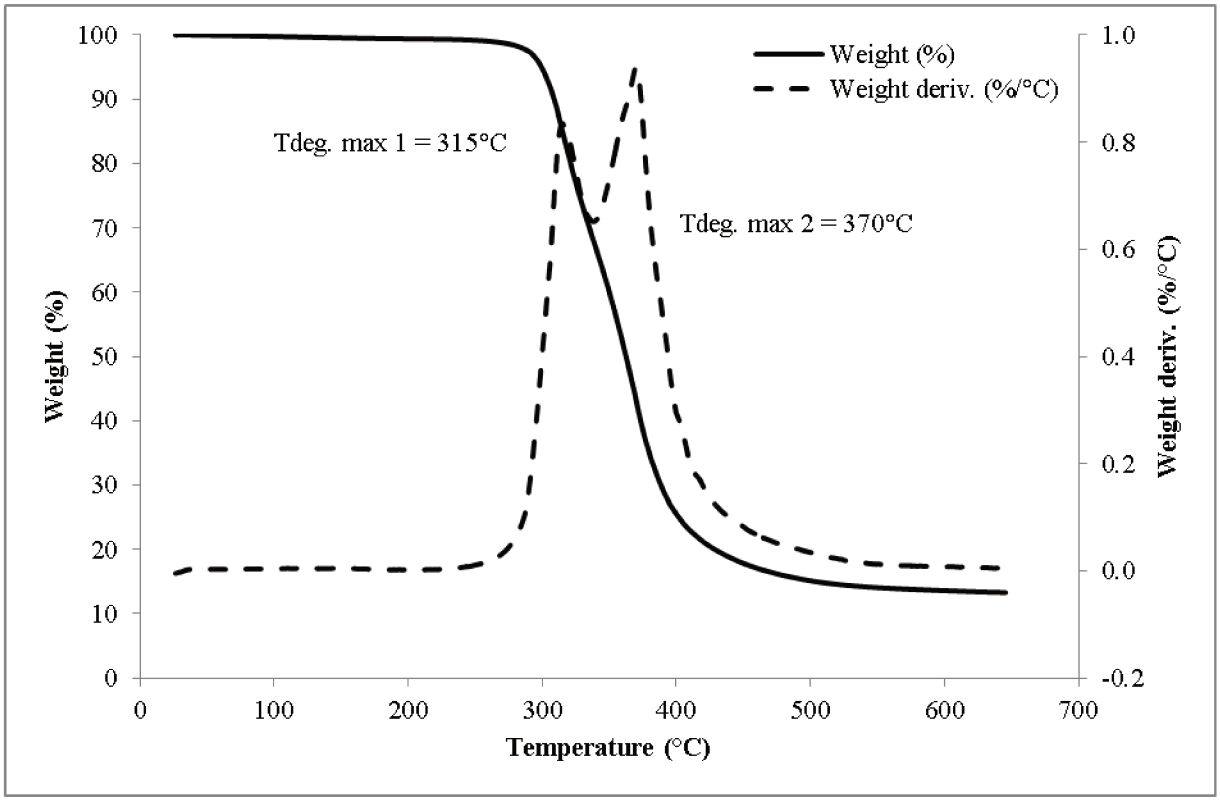
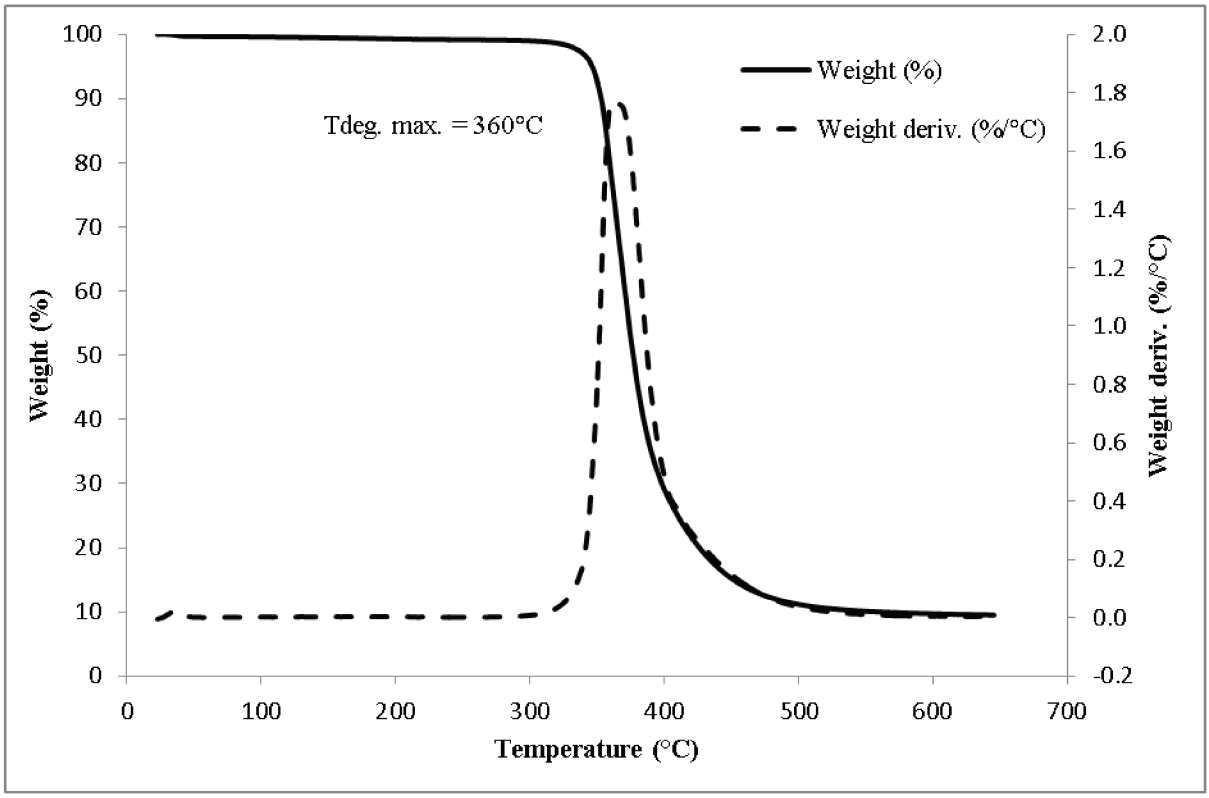


S20 - TGA analysis for the **6** – IPDA system (2.0/1.0 ratio)



S21 - TGA analysis for the DGEBA – IPDA system (2.0/1.0 ratio)



Chapter 4: Epoxy oligomers from vanillin

1. Introduction

In the previous section, vanillin-based epoxy monomers were synthesized and used to prepare epoxy thermosets. Thermal and mechanical properties of these thermosets were investigated and found to be compatible with their use in high-performance applications. The properties obtained were also dependent on the structure of the monomer used, allowing the tuning of the final properties by choosing the right monomer(s).

Versatility is actually a major requirement for epoxy thermosets. Indeed, as presented in the first chapter, epoxy thermosets formulations have to be finely tuned to reach the desired properties specific to the many applications they can fit in. Industrially, the main strategy to tune the final properties of epoxy thermosets is usually not a variation on the structure of the epoxy monomer, as DGEBA is used in 75% of the formulations, but lies in the choice of a proper length of the DGEBA pre-polymer. The main effect of a long pre-polymer will be to space the cross-link points, diminishing the cross-link density and thus decreasing the T_g and increasing the flexibility.

This section is dedicated to preparing vanillin-based epoxy pre-polymers of various lengths and to using them for the synthesis of epoxy thermosets. The first goal of this study is to evaluate the feasibility of transposing the method used industrially to prepare DGEBA pre-polymers to prepare vanillin-based epoxy oligomers. The second goal is to study the influence of the length of these oligomers on their properties and on the properties of the thermosets synthesized from them.

2. Biobased epoxy thermosets from vanillin-derived oligomers

European Polymer Journal 68 (2015) 526–535

Maxence Fache, Arnaud Viola, Rémi Auvergne, Bernard Boutevin, Sylvain Caillol *

Institut Charles Gerhardt, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France

ARTICLE INFO

Article history:
Received 29 October 2014
Received in revised form 20 February 2015
Accepted 7 March 2015
Available online 3 April 2015

Keywords:
Biobased thermosets
Vanillin
Epoxy resins
Renewable resources
Oligomers
Glass transition temperature

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

* Corresponding author. Tel.: +33 4 67144327.
E-mail address: sylvain.caillol@enscm.fr (S. Caillol).

http://dx.doi.org/10.1016/j.eurpolymj.2015.03.048
0014-3057/

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.

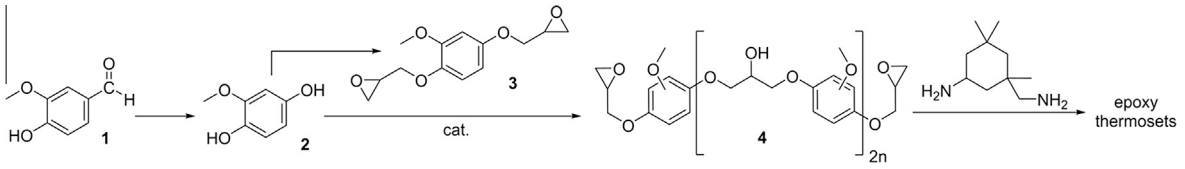
2.2. Synthesis of diglycidyl ether of methoxyhydroquinone 3

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(2*n* + 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 δ 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 δ 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.

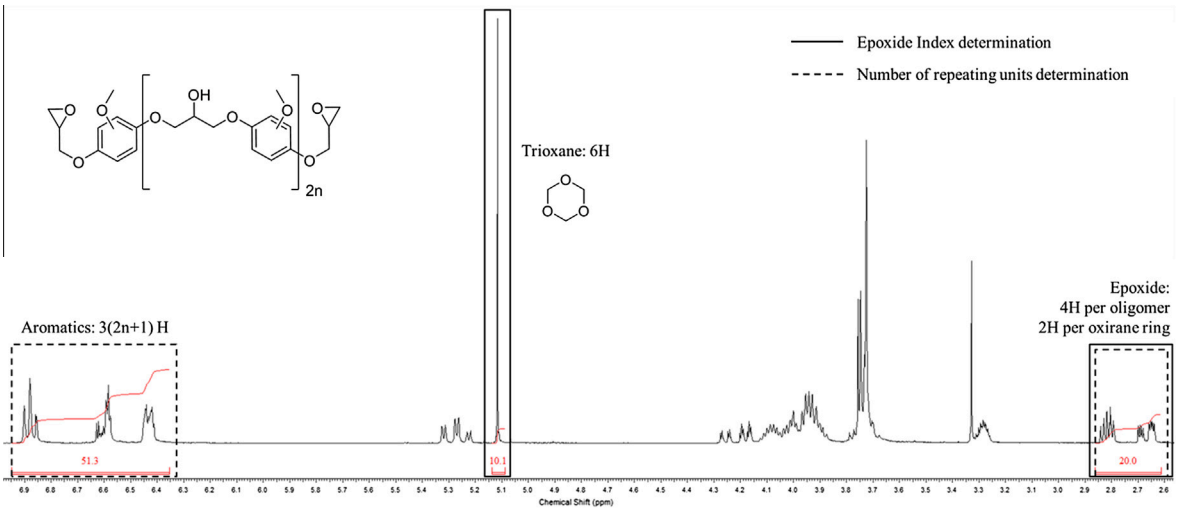


Fig. 1. ^{1}H NMR determination of epoxide index and number of repeating units of the oligomers prepared.

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, $^{3}J_{H6H5}$ = 8.8 Hz, $^{4}J_{H6H2}$ = 2.8 Hz, 1H, H_6); 6.63 (d, $^{4}J_{H2H6}$ = 2.8 Hz, 1H, H_2); 6.88 (d, $^{3}J_{H5H6}$ = 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.

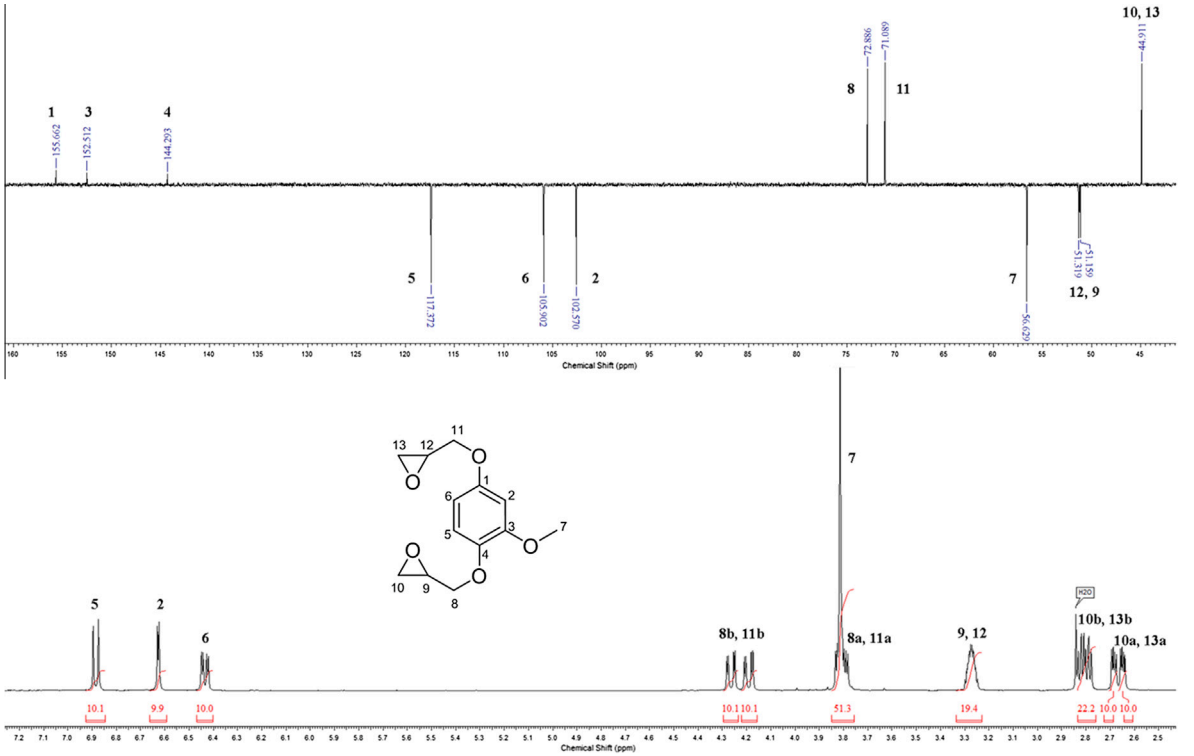


Fig. 2. ^{13}C and ^{1}H NMR characterization of diglycidyl ether of methoxyhydroquinone **3**.

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.

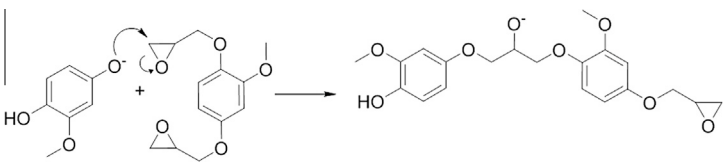
Eight samples of oligomers **4** were prepared using increasing ratios of diepoxy/diphenol (**3**/**2**) from 1.1/1 to 2/1 with the determined conditions (5 w.‰ of catalyst, 125 °C, 1 h 30 min.). Before any analysis, samples were crushed in liquid nitrogen in a mortar and placed in a vacuum desiccator. ^{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).

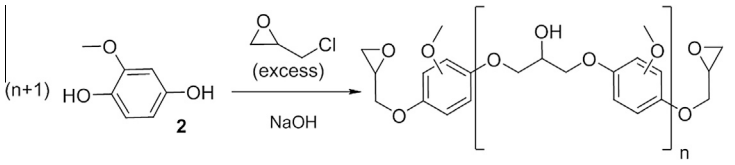
^{1}H NMR (400.1 MHz, DMSO-d6, ppm) δ: 2.67 (m, 2H, H_{10a}, H_{13a}); 2.82 (m, 2H, H_{10b}, H_{13b}); 3.28 (m, 2H, H_9, H_{12}); 3.65–3.80 (m, $2 + 3(2n + 1)$ H, H_{8a}, H_{11a}, H_7, $H_{7'}$); 3.85–4.14 (m, $5(2n)$ H, H_{14}, H_{15}, H_{16}); 4.23 (m, 2H, H_{8b}, H_{11b}); 5.2–6.35 ($3 * d$, $2n$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

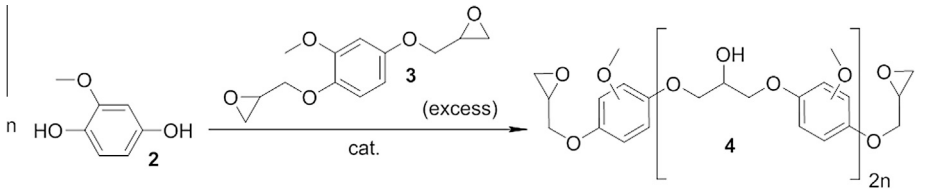
It is worthy to note that compared to the ^{1}H NMR spectrum of pure **3**, signals 14, 15, 16, and 17 have appeared. Signals 14, 15, and 16 were attributed to the glycerol ether repeating unit, which confirmed the oligomerization. Signal 17 was attributed to the proton of the hydroxyl moiety formed 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.

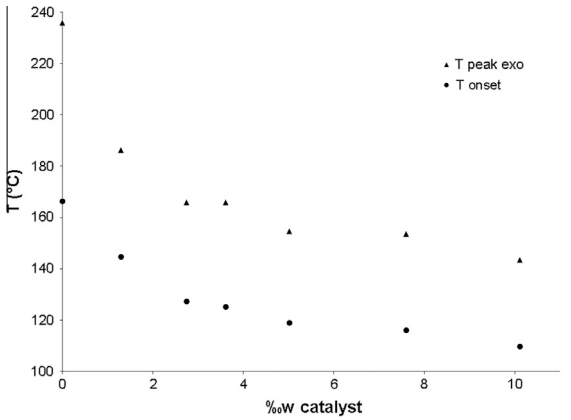


Fig. 3. Onset and exothermic peak temperatures as a function of the amount of catalyst introduced for a 1/1 mixture of **3** and **2**.

3.3. Determination of the degree of polymerization of the oligomers

The number-average value of the degree of polymerization $\overline{X}n$, 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 $\overline{X}n = 2n + 1$ (Eq. (1)). There is $2n$ repeating units plus one diepoxy monomer accounting for the chain-ends (Scheme 4).

$$\overline{X}n = \frac{1+r}{1+r-2rp} = 2n+1 \qquad (1)$$

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 $\overline{M}n$, 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). $\overline{M}n$ can thus be replaced in Eq. (2):

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

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-

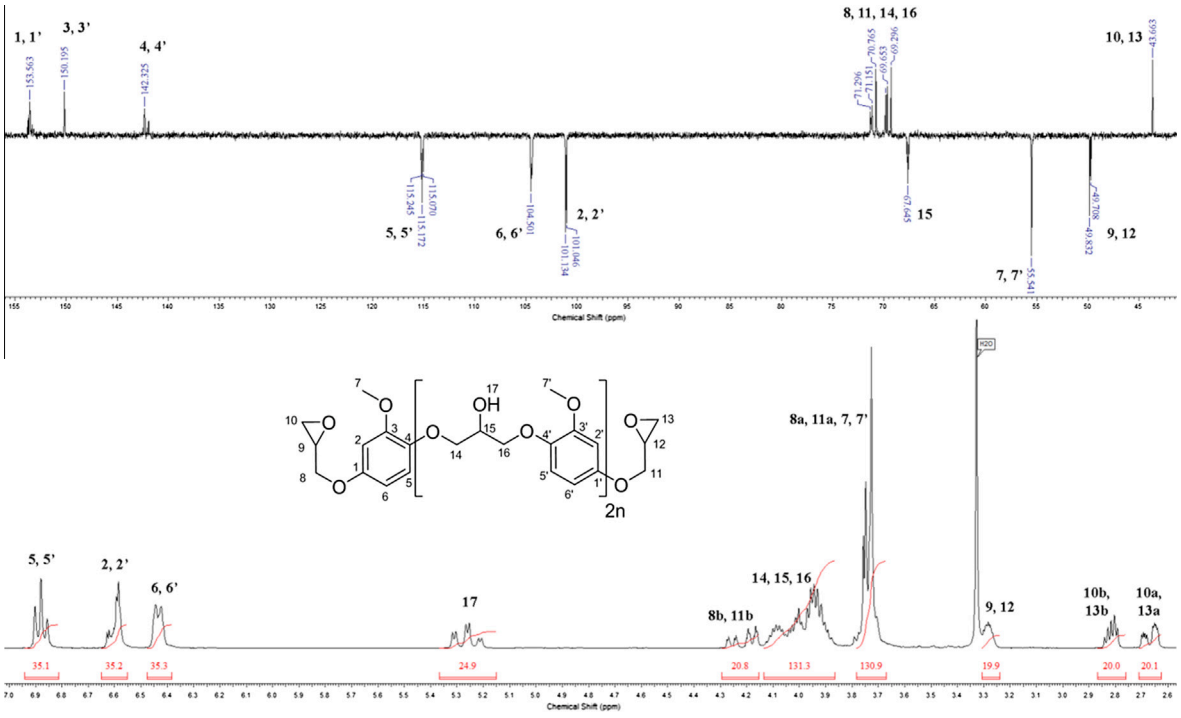


Fig. 4. Oligomers **4** of diglycidyl ether of methoxyhydroquinone.

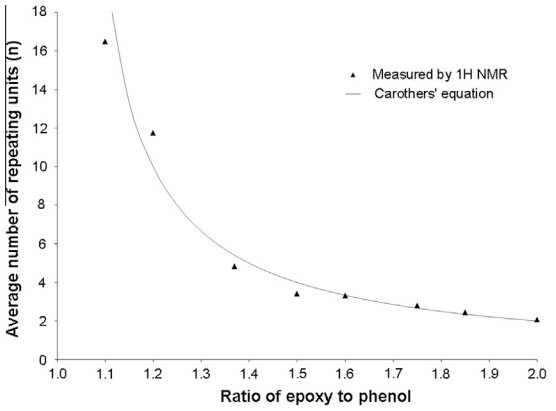


Fig. 5. Experimental and calculated degree of polymerization of oligomers as a function of the reactants ratio.

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):

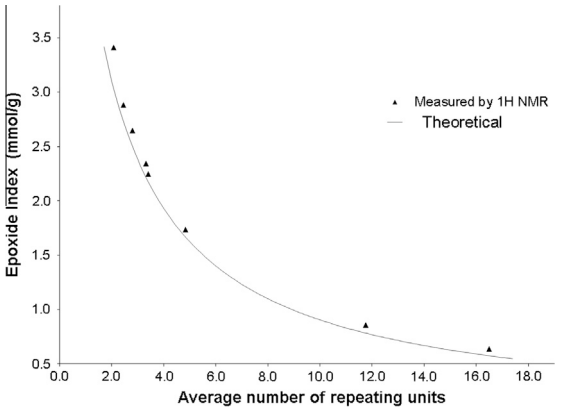
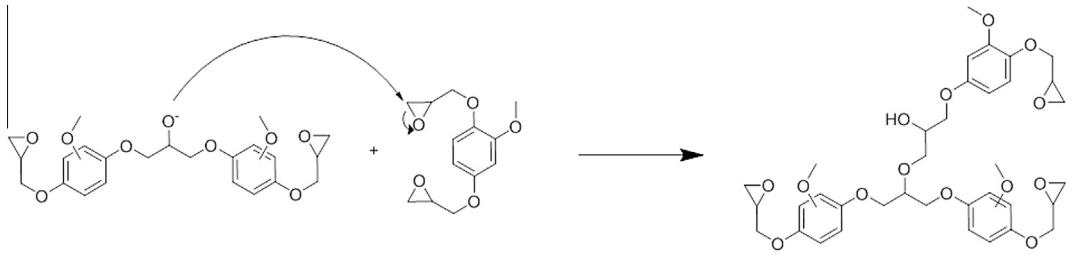


Fig. 6. Epoxide index as a function of the average number of repeating units of the oligomers.



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

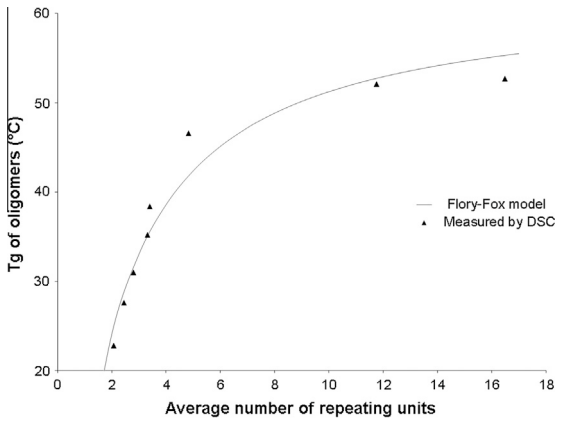


Fig. 7. T_g of the oligomers **4** as a function of the average number of repeating units.

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

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, $T_g(\infty) = 6\,2$ °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 oli-gomer with 0 repeating units, i.e. of only the chain ends (see **Scheme 4**). In our case $T_g(0) = -35$ °C.

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

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 reac-tants. The T_g of the oligomers prepared can thus be con-trolled and predicted from the diepoxy/diphenol ratio. The T_g values agreed with visual observations: long oligo-mers 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], w e 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**.

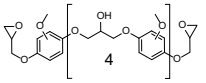
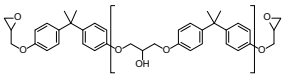
The experimental values of the T_g of the monomers were measured by DSC, on the second heating ramp of either **3** or pure DGEBA (no oligomerization). They are both negative, which is expected in the case of the T_g of molecules. They are also close to $T_g(0)$ values and follow the same trend, i.e.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

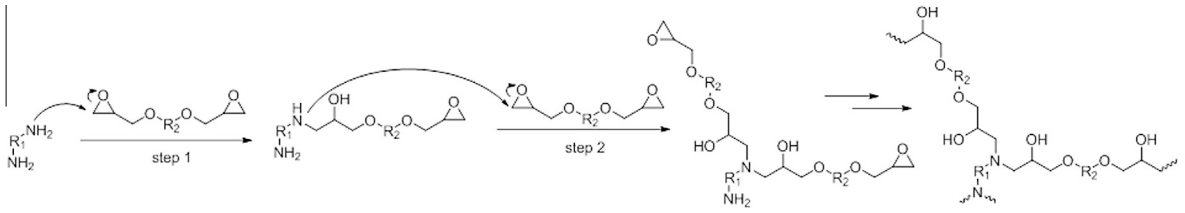
3.6. Synthesis of epoxy materials: polymerization of oligomers with IPDA

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.

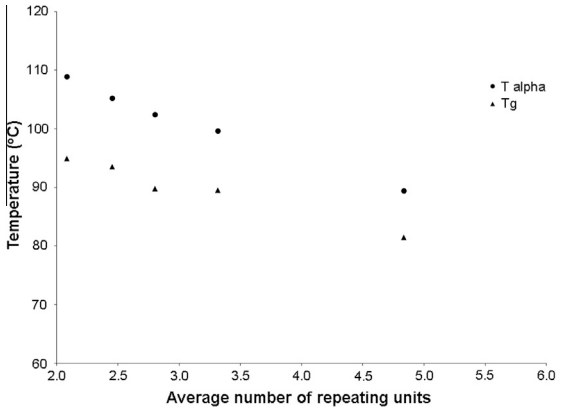


Fig. 8. T_g and T_α of the materials prepared from oligomers **4** as a function of their average number of repeating units.

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.

Acknowledgements

The authors would like to thank the French Ministry of Research for funding this work. The authors are also grateful to Christine Joly-Duhamel for fruitful discussions on dynamic mechanical analysis.

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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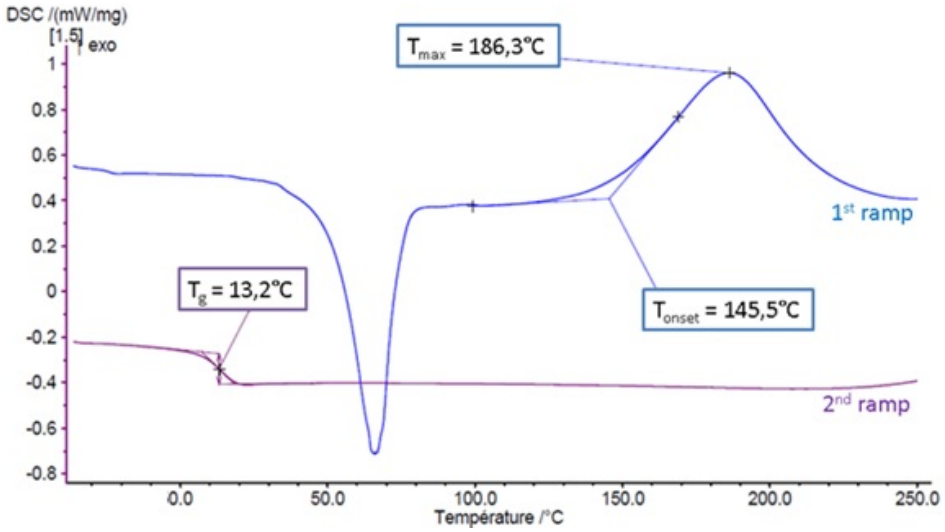
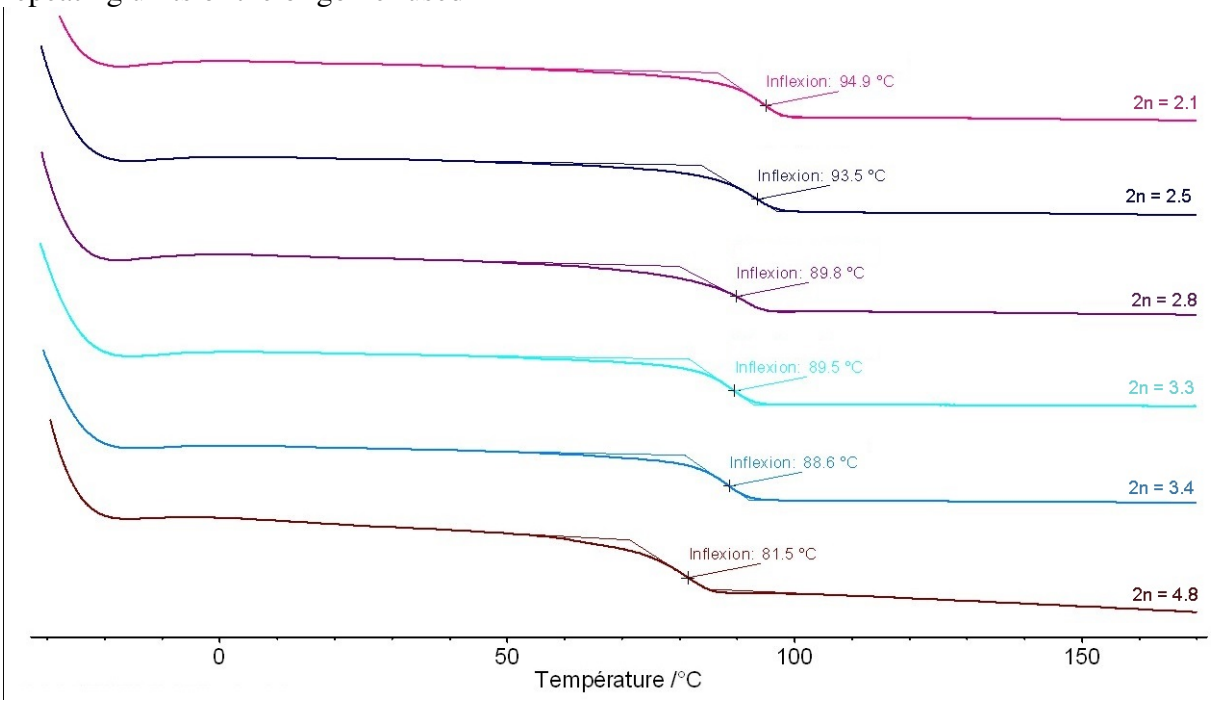
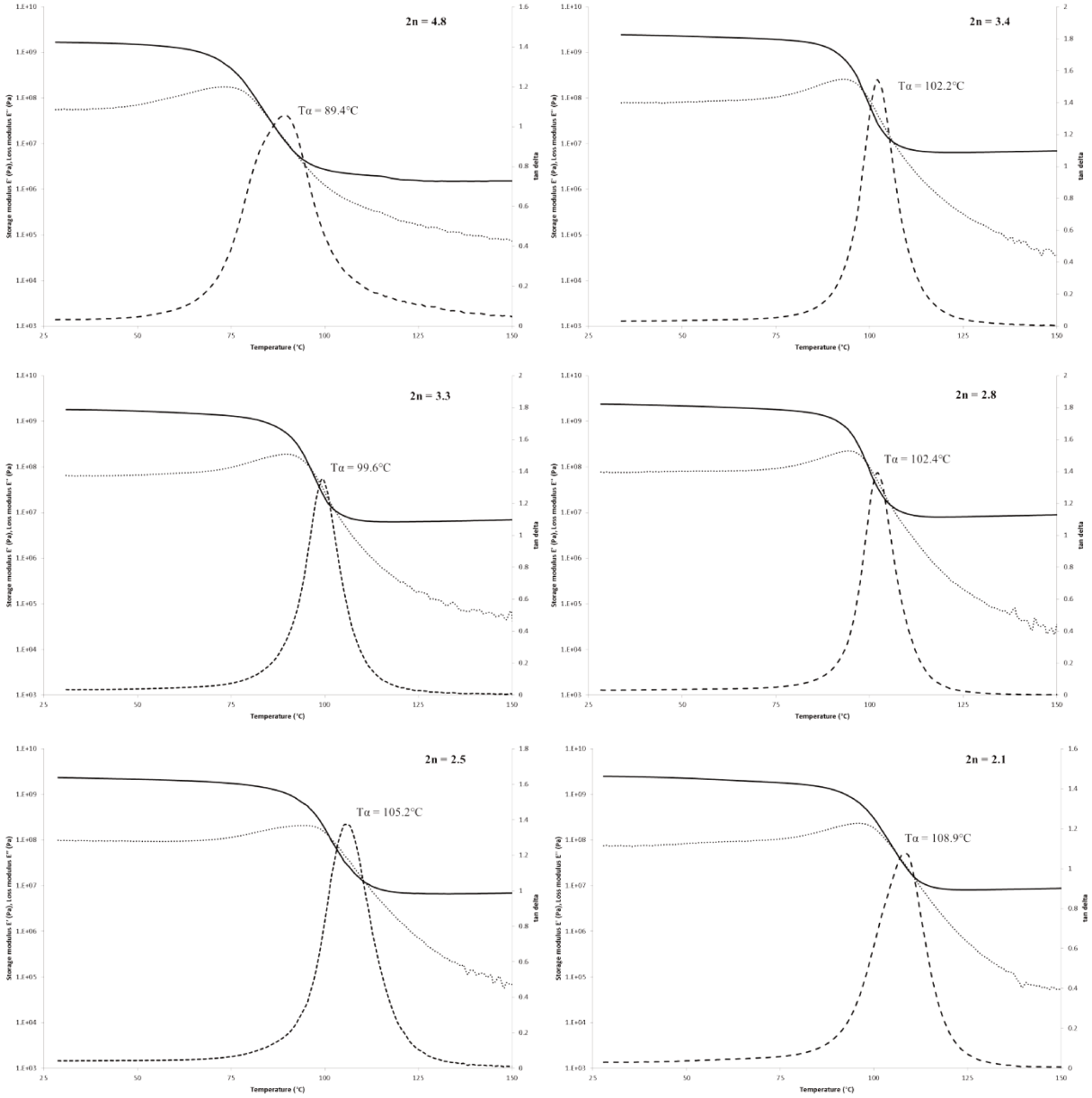
S01 – Determination of the parameters of the oligomerization reaction by DSC (10°C/min, 1‰w. cat.)



S02 – DSC analysis for epoxy materials (10°C/min) as a function of the average number of repeating units of the oligomer used



S03 – DMA analysis for epoxy materials (2°C/min, 1Hz) as a function of the average number of repeating units of the oligomer used



Chapter 5: Epoxy cross-linker and amine hardeners

1. Introduction

The previous chapter dealt with the preparation of vanillin-derived epoxy oligomers. Industrially, using oligomers of various lengths is one of the methods used to modulate the properties of epoxy thermosets. It was found that preparing vanillin-based epoxy oligomers could be achieved by the same method currently used in industry. The reaction is a polyaddition between a diphenol and a diepoxide. It was also found that the properties of the final material could be controlled to a certain extent by varying the length of the epoxy oligomer used.

Versatility being one of the strong points of epoxy thermosets, finding convenient ways to attain specified properties is one of the conditions to the development of bio-based epoxy formulations. The use of epoxy oligomers of various lengths has been explored, but there are other methods that are used in industry. Among them, choosing the right hardener structure and controlling the cross-link density by adding multi-functional epoxy monomers are convenient ones. Widening the pool of bio-based amine hardeners and epoxy cross-linkers is thus an important step in the development of bio-based epoxy thermosets.

This section deals with the synthesis of bio-based amines based on furfural and vanillin and their evaluation, along with other potentially bio-based amines, as hardeners for epoxy thermosets. The synthesis of a tri-functional, vanillin-based epoxy monomer is also reported. The effects of these compounds on epoxy thermosets was compared to commercial references and was investigated in terms of structure-property relationships.

2. Amine hardeners and epoxy cross-linker from aromatic renewable resources

Maxence Fache [a], Camille Montérémal [a], Bernard Boutevin [a], Sylvain Caillol *[a]

[a] *Institut Charles Gerhardt, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'Ecole Normale, 34296 M ontpellier, France*
** Corresponding author: Tel.: +33 4 67144327. E-mail address: sylvain.caillol@enscm.fr (S. Caillol)*

Abstract
Bio-based epoxy thermosets are currently extensively investigated. In order for bio-based epoxy formulations to be industrially relevant, the properties of the resulting thermosets have to be conveniently controllable. This can be achieved by choosing the right hardener. Thus, amine hardeners have been synthesized based on potentially bio-sourced vanillin and furfural. These compounds are also aromatic, a structural characteristic important to reach good thermo-mechanical properties. A tri-functional, vanillin-derived epoxy cross-linker has also been synthesized. Multi-functional epoxy monomers can increase the cross-link density of the network, which is another convenient way to control the final properties. Epoxy thermosets have been prepared from bio-based epoxy monomers and hardeners, as well as from compounds commonly used in industry serving as references. The properties of these polymers have been investigated and structure-property relationships discussed.

Keywords
Amine hardener; vanillin; furfural; bio-based; epoxy

1. Introduction

Epoxy thermosets are an important class of polymers in industry. They are used in many different applications such as coatings in the marine, automobile, or food-packaging industries, or as matrices in structural composites.[1] They are also used as adhesives, or in the electronic industry, for example in printed wiring boards.[1] These applications take advantage of the versatility of epoxy polymers. Indeed, they can be tailored to achieve the specific properties required by these various applications. Thus, epoxy polymers can provide thermosets with excellent mechanical strength and toughness; outstanding chemical, moisture, and corrosion resistance; good thermal, adhesive, or dielectric properties.[1]
Many epoxy thermosets are prepared from the reaction of an epoxy monomer or pre-polymer (resin) with a co-monomer (hardener). 75% of the epoxy resins produced worldwide are based on the DiGlyciDylEther of Bisphenol A (DGEBA)[1], itself based on bisphenol A. Bisphenol A is a category 1B (presumed) reprotoxic compound under EU regulation.[2] Thus, its substitution in epoxy thermosets attracted a lot of attention recently.[3-7] On top of this problematic, a more general drive for the substitution of petro-based compounds for bio-based ones is also an actively investigated area of research.
Preparing epoxy thermosets from renewable resources is a burning issue as it would tackle both problematics at the same time. Lots of research works deal with this subject.[8-11] The most studied biomass-derived raw materials are vegetable oils[12] and cycloaliphatics like isosorbide[7]. However, in certain thermo-mechanically demanding applications, aromatic raw materials are needed in order to impart the required properties to the thermoset (high Tg for instance). Therefore, bio-based aromatics are needed to prepare renewable epoxy thermosets. DGEBA itself is a bis-phenolic compound; bio-based aromatics – more specifically phenolics – are thus needed also in the context of bisphenol A substitution.
The most available sources of phenolics in Nature are lignin, tannins, and Cashew NutShell Liquid (CNSL).[13] CNSL is composed of phenolics substituted with a C_{15} alkyl chain.[14] These long aliphatic segments impart flexibility and thus do not solve the problem of thermo-mechanical properties. Lignin and tannins are poly(phenolics) with a complex and variable structure. Their functionalization and use as epoxy resins, even if investigated[15, 16], is made tricky by their variable, polymeric nature and is not a mature technology yet.

Molecular aromatics obtained on a large scale from renewable resources are scarce. Vanillin obtained by lignin depolymerization is one of the only molecular phenolic compounds available from biomass at an industrial scale.[17] Therefore, the use of this compound for renewable polymer synthesis attracted a lot of attention recently.[18] The contributions of our team on this subject dealt mainly with the use of vanillin to prepare epoxy thermosets with good properties.[3, 19-21]

Furfural is an interesting bio-based compound obtained by the acidic dehydration of pentoses, for instance xylose.[22] Thus, it is widely available and has been identified as a key renewable building-block, from which other bio-based compounds can be prepared.[22, 23] The furanic moiety displays interesting features such as the ability to act as diene in Diels-Alder reactions or the fact that it is aromatic. Furanic compounds have already been employed to prepare epoxy thermosets with good properties.[24-26] Both vanillin and furfural are bio-based aromatic aldehydes that can be further functionalized to prepare compounds relevant for epoxy thermosets.

Versatility is one of the strong points of epoxy polymers. Attaining different properties can be achieved in many different ways. One of these methods, that is convenient from an industrial standpoint, is to increase the overall functionality of a given epoxy formulation to increase the cross-link density and reach a higher T_g. Adding a tri- or tetra-epoxy compound to a base difunctional epoxy resin increases the overall functionality. Multi-functional epoxy compounds are thus of high industrial importance.

Hardeners can also play a major role when it comes to thermo-mechanical properties of epoxy thermosets. The main epoxy hardeners include mercaptans, carboxylic acids, anhydrides, amines, and phenols.[1] Amines are the most used ones[1], but they are used for different reasons that depend on their structures. Aliphatic amines are very reactive, they can even provide room-temperature curing.[27] The main advantage of cycloaliphatic amines is their versatility: they display a good balance between reactivity and final properties. Aromatic amines are the least reactive but provide good heat and chemical resistance.[27] Hardener structure and functionality strongly impacts the material final properties. Having a large choice of possible hardeners with various structures, functionalities, and reactivity is thus of the highest importance to modulate the properties of epoxy thermosets. Amine hardeners based on various bio-resources, like amino-acids (tryptophan, lysine)[28, 29], vegetable oils[12], isosorbide[30], or chitosan[31] are scarce in the literature. Only few bio-based commercial solutions exist and they are only partially bio-based, such as Mannich adducts of cardanol (phenalkamines), or poly(amido-amines) prepared by amidification of dimers of fatty acids

In order to be accepted as viable solutions, bio-based epoxy formulations need to have the same versatility as current formulations. To modulate the final properties of epoxy thermosets as much as it is done today with petro-based hardeners, the number and variety of bio-based amine hardeners available to "play with" must be increased. On top of increasing this number, it is also of the highest importance to compare their properties with existing systems.

There are thus two goals to this work:

1. Synthesize new, potentially bio-based amine hardeners based on furfural and vanillin, prepare bio-based epoxy thermosets from them, and investigate their structure-property relationships.
2. Synthesize a bio-based tri-epoxy compound and investigate its potential as an epoxy cross-linker to increase the T_g of bio-based epoxy thermosets.

2. Experimental

2.1. Materials

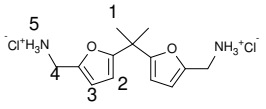
Furfurylamine **1** (≥99%), acetone (≥99.5%), HCl (≥37%w.), hydroxylamine hydrochloride (99%), anhydrous sodium acetate (99%), activated Pd/C (10%w.), sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$, available H_2O_2 20–30%), TriEthylBenzylAmmonium Chloride (TEBAC, 99%), sodium hydroxide (NaOH, ≥98%), and all solvents used were purchased from Sigma-Aldrich. Vanillin **4** (99%) was purchased from ABCR. Epichlorohydrin (≥99%) was purchased from Fluka. All reactives were used as received.

^{1}H NMR spectra were recorded at a frequency of 400.2 MHz and ^{13}C (APT mode) NMR spectra at a frequency of 100.6 MHz on a Brucker Aspect Spectrometer at room temperature. Deuterated solvents used are given for each molecule. Chemical shifts are in ppm. Silica gel flash chromatography was performed on a Grace Davison Reveleris device.

*2.2. Bis(furfurylammonium chloride) A (**2**)*

Furfurylamine **1** (2.1 eq.) was introduced in a two-necked round-bottomed flask equipped with a reflux condenser and cooled down to 0°C with an ice bath. An 18%w. aqueous solution of HCl (5 eq.) was then added dropwise to **1**. Once this addition was completed, the temperature was risen to 25°C and the mixture was stirred for 15 min. Acetone (1.0 eq.) was then added to the mixture. The temperature was risen to 40°C. Additional aliquots of acetone (0.4 eq.) were added to the mixture after 3 and 5 days. The reaction was stopped after 7 days when the conversion of **1** to **2** was complete. To isolate **2**, a sample of the crude mixture was taken, concentrated under reduced pressure and poured dropwise in a large volume of acetone while stirring. The precipitate of **2** formed that was harvested and dried.

Bis(furfurylammonium chloride) A (**2**)



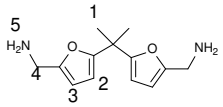
Yield : N.D.; Aspect : white to brownish solid.

^{1}H NMR (DMSO-d6): 1.59 (s, 6H, H_1); 4.00 (broad q, 4H, H_4); 6.17 (d, 4H, H_2); 6.44 (d, 4H, H_3); 8.48 (broad s, 6H, H_5).

*2.3. Bisfurfurylamine A (**3**)*

The crude mixture of **2** was cooled down to 25°C and deionized water was added. The pH was adjusted to 10 with a 15%w. aqueous solution of NaOH. The mixture was extracted thrice with dichloromethane. The organic fractions were collected, washed with brine, dried on anhydrous $MgSO_4$ and dichloromethane was removed under reduced pressure to yield **3**.

Bis(furfurylamine) A (**3**)



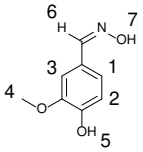
Yield : 90%; Aspect : Yellow to brown oil.

^{1}H NMR (DMSO-d6): 1.54 (s, 6H, H_1); 1.76 (broad s, 4H, H_5); 3.59 (s, 4H, H_4); 5.98 (d, 4h, H_2); 6.06 (d, 4H, H_3)

*2.4. Synthesis of vanillyloxime (**5**)*

Hydroxylamine hydrochloride (1.1 eq.) and sodium acetate (2.0 eq.) were weighed in a round-bottomed flask and dissolved in deionized water to reach a concentration in hydroxylamine hydrochloride of 50 g.L^{-1}. Vanillin **4** (1.0 eq.) was suspended in the solution. The temperature was risen to 100°C and maintained for 1 hour. The mixture became a clear, transparent solution. Upon cooling down to 25°C, a white, crystalline precipitate of **5** formed. It was filtered off and oven-dried at 40°C under reduced pressure overnight.

Vanillyloxime (**5**)



Yield : 93%; Aspect : white crystalline powder.

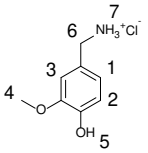
^{1}H NMR (DMSO-d6): 3.77 (s, 3H, H_4); 6.77 (d, $^3JH_2H_1$ = 8.0 Hz, 1H, H_2); 6.96 (dd, $^3JH_1H_2$ = 8.0 Hz, $^4JH_1H_3$ = 2.0 Hz, 1H, H_1); 7.16 (d, $^4JH_1H_3$ = 2.0 Hz, 1H, H_3) ; 7.99 (s, 1H, H_6) ; 9.34 (broad s, 1H, H_5) ; 10.83 (broad s, 1H, H_7).

*2.5 Synthesis of vanillylammonium chloride (**6**)*

A solution of **5** (1.0 eq, 10 g.L^{-1}) in ethanol and concentrated hydrochloric acid (1.0 eq.) was prepared. 10%w. Pd/C (2 g.L^{-1}) was suspended in the solution and vacuum was applied until ethanol boiled at 25°C. The mixture was then placed under H_2 at atmospheric pressure and vigorous stirring for 4 days. The hydrogenation mixture was then filtered through Celite in a sintered glass funnel and the filtrate concentrated to dryness, giving **6**.

A sample was further purified by redissolving the white powder obtained in deionized water and adjusting the pH to 1 with an aqueous HCl solution. The solution was concentrated under reduced pressure and left to crystallize over a week. The crystals suspension was centrifuged for 5 minutes at 2000 rpm, most of the aqueous solution was pipeted off, and crystals of **6** were redissolved in ethanol. The solution was once again evaporated to dryness under reduced pressure.

Vanillylammonium chloride (**6**)



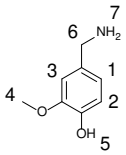
Conversion : 100% ; Yield :78%; Aspect : white powder (or small crystals if further purified).

^{1}H NMR (DMSO-d6): 3.76 (s, 3H, H_4); 3.85 (s, 2H, H_6); 6.79 (d, $^3JH_2H_1$ = 8.0 Hz, 1H, H_2); 6.84 (dd, $^3JH_1H_2$ = 8.0 Hz, $^4JH_1H_3$ = 2.0 Hz, 1H, H_1); 7.21 (d, $^4JH_1H_3$ = 2.0 Hz, 1H, H_3); 8.46 (broad s, 3H, H_7) ; 9.23 (s, 1H, H_5).

*2.6. Synthesis of vanillylamine (**7**)*

An aqueous solution of **6** was prepared by dissolving it in the minimum of deionized water. A 10%w. NaOH aqueous solution was slowly added until reaching pH = 12. The white precipitate of **7** formed was filtered. Two more precipitation by addition of sodium hydroxide solution and filtration were performed. The fractions of **7** were combined and oven-dried at 40°C under reduced pressure overnight.

Vanillylamine (**7**)



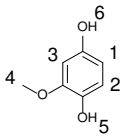
Yield : 79% ; Aspect : white powder.

^{1}H NMR (DMSO-d6): 1.80 (broad s, 2H, H_7); 3.58 (s, 2H, H_6); 3.75 (s, 3H, H_4); 6.67 (s, 2H, H_1, H_2); 6.90 (s, 1H, H_3); 8.67 (broad s, 1H, H_5).

*2.7. Synthesis of methoxyhydroquinone (**8**) and diglycidylether of methoxyhydroquinone (**9**)*

The syntheses of methoxyhydroquinone **8** and diglycidylether of methoxyhydroquinone **9** were described in our previous works.[3, 19]

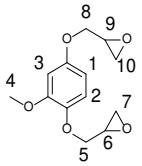
Methoxyhydroquinone (**8**)



Yield: 97% ; Aspect : brownish to black powder.

^{1}H NMR (acetone-d6): 3.77 (s, 3H, H_4); 6.27 (dd, $^3JH_1H_2$ = 8.4 Hz, $^4JH_1H_3$ = 2.8 Hz, 1H, H_1); 6.46 (d, $^4JH_1H_3$ = 2.8 Hz, 1H, H_3); 6.63 (d, $^3JH_2H_1$ = 8.4 Hz, 1H, H_2); 6.90 (broad s, 1H, H_5) ; 7.74 (broad s, 1H, H_6).

Diglycidylether of methoxyhydroquinone (**9**)

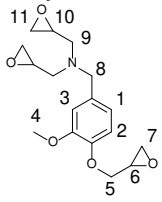


Yield : 75% ; Aspect : white powder.
^{1}H NMR (acetone-d6): 2.66 (m, 2H, H_{5a}, H_{8a}); 2.81 (m, 2H, H_{5b}, H_{8b}); 3.27 (m, 2H, H_6, H_9); 3.81 (m, 2H, H_{7a}, H_{10a}); 3.81 (s, 3H, H_4); 4.23 (m, 2H, H_{7b}, H_{10b}); 6.43 (dd, $^3JH_1H_2$ = 8.8 Hz, $^4JH_1H_3$ = 2.8 Hz, 1H, H_1); 6.63 (d, $^4JH_3H_1$ = 2.8 Hz, 1H, H_3); 6.88 (d,$^3JH_2H_1$ = 8.8 Hz, 1H, H_2).

*2.8. Synthesis of triglycidylether of vanillylamine (**10**)*

A round-bottomed flask was filled with vanillylamine **7** (1.0 eq.), TEBAC (0.15 eq.) and epichlorohydrin (30 eq.). The mixture was stirred for 4 days at 40 °C and was then cooled down to room temperature. An aqueous NaOH solution (4 eq., 5 mol.L^{-1}) was then added and the mixture was vigorously stirred 30 min at room temperature. Ethyl acetate and deionized water were added and the two phases formed were stirred for a few minutes and then separated. Extraction with ethyl acetate was repeated two more times. Organic phases containing **10** were combined, rinsed twice with brine, dried on anhydrous $MgSO_4$ and filtered. Ethyl acetate and epichlorohydrin excess were removed under reduced pressure.
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.

Triglycidylether of vanillylamine (**10**)



Yield : 83% ; Aspect : transparent, yellowish liquid.
^{1}H NMR (acetone-d6): 2.37 (dd, 1H, H_{9a}); 2.45 (m, 2H, H_{11a}); 2.57 (dd, 1H, H_{9a}); 2.67 (m, 3H, H_{11b}, H_{7a}); 2.81 (m, 2H, H_{7b}, H_{9b}), 2.94 (dd, 1H, H_{9b}); 3.05 (m, 2H, H_{10}); 3.30 (m, 1H, H_6); 3.51-3.90 (m, 2H, H_8); 3.82 (s, 3H, H_4); 3.86 (dd, 1H, H_{5a}); 4.27 (dd, 1H, H_{5b}); 6.86 (dd, $^3JH_1H_2$ = 8.4 Hz, $^4JH_1H_3$ = 1.2 Hz, 1H, H_1); 6.91 (d, $^3JH_2H_1$ = 8.4 Hz, 1H, H_2); 7.07 (d, $^4JH_1H_3$ = 1.2 Hz, 1H, H_3).

2.9. Syntheses of epoxy thermosets

The polymers **P1** to **P10** were synthesized by the reaction of the monomers shown in **Table 1**. DiGlycidylEther of BisPhenol A (DGEBA, **11**), TriGlycidylether of Para-AminoPhenol (TGPAP, **12**), and IsoPhoroneDiAmine (IPDA, **13**) were used as petro-based references as they are commonly used in industry. DecanediAmine (DA10, **14**) is a bio-based diamine obtained from castor oil and was used as obtained. Other compounds were synthesized as described previously and are also potentially bio-based as mentioned.
The amount of each reactant was calculated to reach a stoichiometric ratio, *i.e.* to have a ratio of epoxy to active H of 1 (see Results and Discussion). Prior to curing, a few milligrams of each formulation were placed in a DSC pan. They were heated at 20 °C.min^{-1} in order to determine the onset temperature of the formulations. All formulations had onset temperatures lower than 115°C, therefore they were all cured at 115°C. The only exception was **P4**. Its onset temperature was around 70°C and a curing temperature of 80°C was used.
The monomers that were liquids at 30°C (**10**, **12**, **13**, **3**) were pre-heated at 70°C. Solids (**11**, **14**, **9** with melting points respectively 45°C, 61°C, and 87°C) were molten prior to mixing with their co-monomer in order to avoid any inhomogeneity or air bubbles in the final material.
The pre-heated monomers were mixed and the mixtures were thoroughly hand-stirred with a pre-heated stirring rod to obtain a homogeneous liquid mixture. They were then poured in an aluminium mold and cured stepwise at the determined curing temperature (see Results and Discussion) first for 1 h.

Table 1 : Epoxy thermosets synthesized

	13	14	7	3
11	**P1**	**P5**	**P6**	**P7**
9	**P2**	**P8**	**P9**	**P10**
12	**P3**			
10	**P4**			

Vanillylamine **7** was handled slightly differently as its melting point (133°C) was too high to be molten before mixing. To prepare **P6** and **P9**, appropriate amounts of powdered **7** and powdered **11** (**P6**) or **9** (**P9**) were intimately mixed at 30°C. The mixture was placed in a mold, heated up to the curing temperature, and cured for 1h. A post-cure was performed at 160°C for 1h on all polymers.

2.10. DSC analyses

A Differential Scanning Calorimetry (DSC) analysis was performed on all post-cured materials in order to determine their glass transition temperature (T_g). DSC analyses were carried out using a Netzsch DSC200F3 calorimeter. Constant calibration was performed using n-Octane, indium, tin, and 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 (Tg) were determined as the inflexion point of the heat capacity jump.

2.11. TGA analyses

A Thermo-Gravimetric Analysis (TGA) was performed on all polymers in order to investigated the degradation of the materials prepared. 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) or air flow (60 mL/min). The experiments were carried out at a heating rate of 10°C/min.

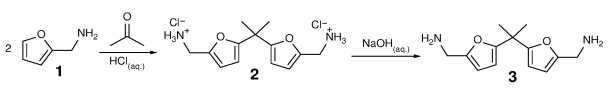
2.12. DMA analyses

Dynamic Mechanical Analyses (DMA) were carried out on polymers **P1** to **P4** 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 260°C, keeping frequency at 1 Hz. In order to perform measurements in the linear viscoelastic region, deformation was kept at 1.10^{-5} %.

3. Results and Discussion

*3.1.Synthesis of bisfurfurylamine A (**3**)*

One goal of this work is to synthesize and investigate the properties as hardeners of potentially bio-based amines. The starting compound of the synthesis of **3** is furfurylamine **1**. Furfurylamine is potentially bio-based as it can be obtained from furfural, itself obtained from the dehydration of pentoses. In this work, fufurylamine was directly purchased, however it can also be efficiently synthesized by reductive amination of furfural.[32, 33]
The overall reaction scheme for the preparation of **3** is displayed in **Scheme 1**:



Scheme 1 : Reaction scheme for the synthesis of **3**

The method employed here to prepare **3** from **1** has already been described in the literature[24, 34] and is very similar to the one used for bisphenol A synthesis. Indeed, in the case of bisphenol A, two consecutive electrophilic additions of aromatic (phenol) molecules onto acetone are performed in presence of an acid.[35] Here, the aromatic molecule used is furfurylammonium chloride. Hydrochloric acid is necessary to form electrophilic species and also to protonate **1** and form furfurylammonium chloride. Indeed, forming ammonium ions is necessary because they do not react with ketones to form ketimines, whereas amines do. Thus, the protonation of the amine acts as a protection reaction. The ^{1}H NMR spectrum of **3** is given in **Figure 1**.
BFAA is a potentially bio-based diamine that can be investigated as hardener for epoxy thermosets as it the case in this study. It could also be used for the preparation of many other polymers such as non-isocyanate polyurethanes (reaction with cyclic carbonates[36]), polyamides, polybenzoxazines etc.

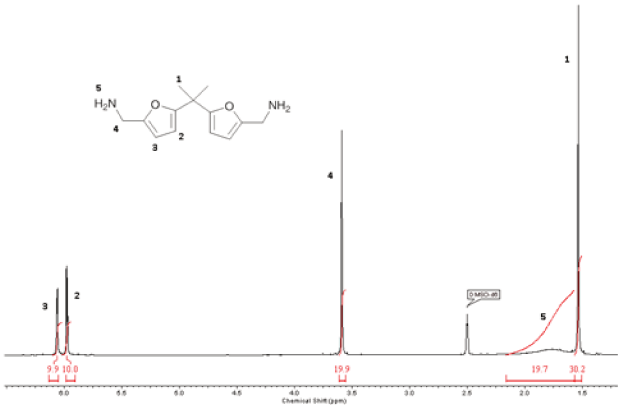
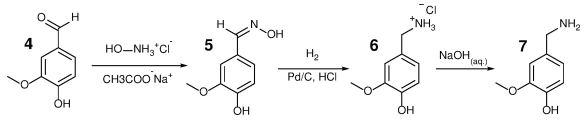


Figure 1 : ^{1}H NMR spectrum of **3**

*3.2. Synthesis of vanillylamine (**7**)*

Likewise furfural, vanillin **4** was used as a bio-based building-block. The advantages of vanillin are numerous: it is a molecular, non-hazardous compound that is already produced at an industrial from lignin (15% of the worldwide production). Thus, vanillin is an ideal candidate for the preparation of bio-based polymers. As mentioned, vanillin received a lot of attention from the polymer community.[18] Here, vanillin was employed as a starting point for the synthesis of vanillylamine **7**, a potentially bio-based hardener for epoxy thermosets.
The overall reaction scheme for the preparation of 7 is displayed in **Scheme 2**:



Scheme 2 : Reaction scheme for the synthesis of **7**

The procedure described here has been adapted from the literature.[37-39] The first step consists of the reaction of vanillin **4** with hydroxylamine hydrochloride in presence of a base (sodium acetate here) to yield vanillyloxime **5**. This step gives a high yield and the handling is simple as **5** crystallizes rapidly upon cooling down to room temperature. The second step is the reduction of **5** to vanillylammonium chloride **6**. The reactant used is H_2 -

one of the most atom-economic reducing agent – under mild conditions. Indeed, the reaction was performed at room temperature and under atmospheric pressure, which is better from a safety point of view than heated, pressurized H_2. The reaction is catalyzed by Pd/C. Amines are known to poison Pd catalysts.[40] Thus, **7** cannot be obtained directly and the presence of HCl during the reaction to form **6** is necessary. In the third step, **7** is obtained by successive precipitations of **6** in a basic aqueous solution. This method was found to be preferable to liquid-liquid extractions as the couple **6/7** has complex acido-basic reactions patterns with pKas of ammonium deprotonation and phenol deprotonation very close and difficult to determine precisely (respectively around 9 and 10[41]). The 1H NMR spectrum of 7 is given in **Figure 2**:

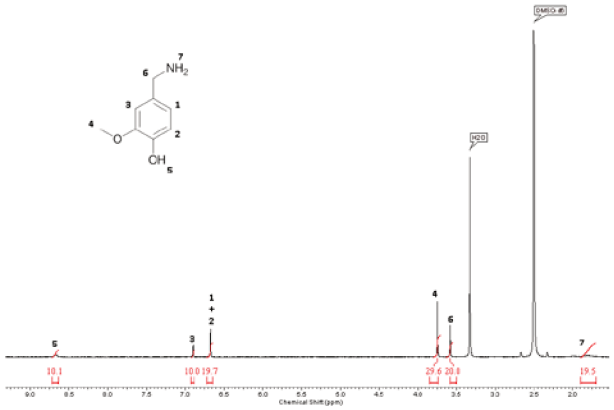
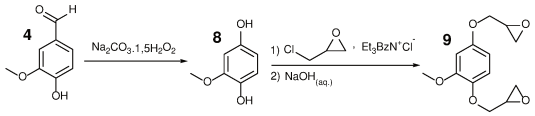


Figure 2 : ^{1}H NMR spectrum of **7**

Overall, the method based on the intermediate transformation of an aldehyde to an oxime that is then reduced under mild conditions seems to be a robust pathway to obtain amines from aldehydes. This method has even been patented in the case of the preparation of **7**.[38] Here, it was tested with furfural (results not shown), leading to furfurylammonium chloride with only a slight over-reduction of the furanic cycle. The reductive amination of vanillin and furfural is a subject of interest and very recently, Chatterjee et al. reported this reaction on both vanillin and furfural by using ammonia, H_2, and an appropriate catalytic system.[32] Their approach is very promising from a green chemistry point of view.
As already mentioned, there is a need to investigate new, bio-based amine hardeners. Having a pool of various renewable hardeners with different structures is necessary to finely tune the properties of bio-based epoxy thermosets. Thus, our team converted vanillin to vanillylamine **7** in order to investigate its potential as a bio-based hardener as well as the properties of the epoxy thermosets ensuing. Contrary to **3**, **7** is a monoamine instead of a diamine. It is still worth investigating as a cross-linker because of the presence of the phenol moiety. Indeed, phenols are also able to react with epoxy groups. [1] Thus, **7** could act as a trifunctional hardener, with reactions of the primary amine, secondary amine, and phenol groups. The reaction of all moieties to form a cross-linked thermoset with di-epoxy compounds has to be investigated (see Epoxy thermosets syntheses).

*3.3 Synthesis of diglycidylether of methoxyhydroquinone (**9**)*

Vanillin **4** was also used in previous works from our team to prepare di-epoxy monomers and oligomers.[3, 19, 20] These compounds displayed advantages brought by the use of vanillin as a building-block such as being aromatic, potentially bio-based, and available on a large scale. The overall reaction scheme for the preparation of **9** is displayed in **Scheme 3**:



Scheme 3 : Reaction scheme for the synthesis of **9**

Methoxyhydroquinone **8** was obtained by the Dakin oxidative decarboxylation of **4**. The reaction was performed at room temperature and by using sodium percarbonate as a safe and easy-to-handle oxidizing agent. Diglycidylether of methoxyhydroquinone **9** was then prepared by glycidylation of **8** with epichlorohydrin in solventless conditions. The 1H NMR spectrum of 9 is given in **Figure 3**:

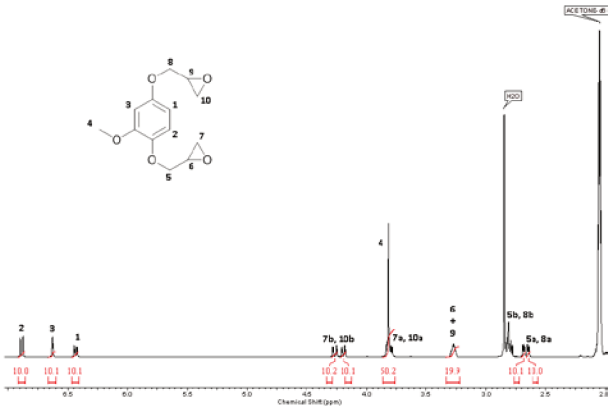


Figure 3 : ^{1}H NMR spectrum of **9**

Glycidylation is the only industrial method to prepare aromatic glycidylethers like DGEBA. Unfortunately, epichlorohydrin is a category 1B carcinogenic compound according to EU regulations. Epichlorohydrin is currently produced from renewable resources as a preparation process exists from bio-based glycerol.
The aromatic, diglycidylether structure of **9** makes it a candidate for the preparation of non-bisphenol A epoxy resins.[3] Indeed, these two criteria are major requirements when it comes to DGEBA substitution while maintaining performances. Thus, **9**, being a vanillin-based, aromatic diglycidylether monomer, could be used to tackle two current issues related to epoxy thermosets: the use of renewable resources and bisphenol A substitution.

*3.4. Synthesis of triglycidylether of vanillylamine (**10**)*

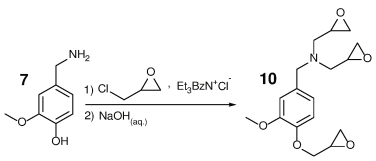
As mentioned in the introduction, to conveniently modulate the properties of epoxy thermosets, multi-functional epoxy compounds are necessary. For instance, the T_g of thermosets is affected by the following parameters[42]:

1. The epoxy monomers and hardener structures. The contribution of a given group to T_g will depend for instance on its ease of rotation, free volume, cohesive energy with the rest of the network etc.
2. The number of end-groups, related to the degree of curing. End-groups can rotate more freely, occupying more volume than fixed structures. They act as plasticizers, lowering the T_g
3. The cross-link density, which is the number of cross-links per unit volume. The higher it is, the more the chain mobility is restricted and the stiffer the network is.

Adding a tri- or tetra-epoxy compound to a base difunctional epoxy resin increases the overall functionality. The cross-link density will thus be higher at optimal curing. However, the stoichiometry and thus the overall network composition will be changed.

Compounds like TriGlycidylether of *P*-AminoPhenol (TGPAP, **12**) and TetraGlycidylether of Methylene DiAniline (TGMDA) are routinely used in industrial formulations.[1] Their aromatic structure and functionality higher than 2 bring improved thermal and chemical resistance, which is useful for instance to prepare composites for military applications.[1] They are both based on an amine that has been glycidylated twice, forming a tertiary amine. This configuration presents two advantages: the amine can bear two glycidyl moieties, which conveniently increases the functionality compared to a phenol group, and the internal tertiary amine formed acts as a built-in catalyst.[1, 43]

The numerous advantages of vanillin as a renewable aromatic have already been described and vanillylamine **7** was synthesized from it as presented above. The next step of this work was the synthesis of a tri-functional epoxy monomer from **7** by taking advantage of the amine moiety present. **7** was glycidylated by reaction with epichlorohydrin to obtain the triglycidylether derivative **10**. The reaction scheme for the preparation of **10** is displayed in **Scheme 4**:



Scheme 4 : Reaction scheme for the synthesis of **10**

It was found that an epichlorohydrin excess of 10 to 1 reactive site (phenol, primary, or secondary amine) was necessary to not form oligomers. This can be attributed to the strong reactivity of these groups towards oxirane rings. For the same reason, the temperature had to be kept relatively low (40°C) compared to the glycidylation reaction of phenols (80°C). The ^{1}H NMR spectrum of **10** is shown in **Figure 4**.

A potentially bio-based, tri-functional epoxy monomer was synthesized from vanillin. This kind of compound has not, to our knowledge, been described in the literature yet. This multi-functional epoxy monomer could provide solutions to tune the properties of bio-based epoxy thermosets and improve their versatility. It has been obtained as a liquid, which is advantageous from a formulation point of view.

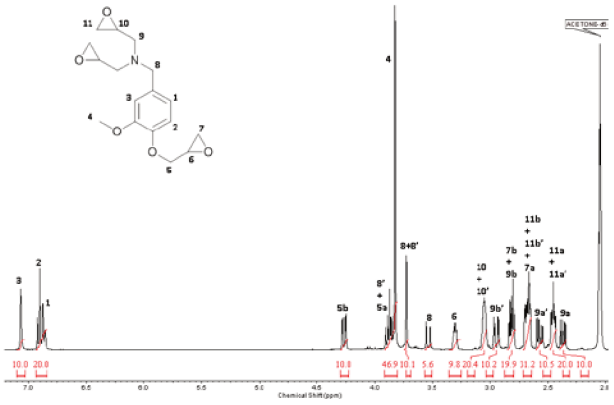


Figure 4 : ^{1}H NMR spectrum of **10**

3.5. Epoxy thermosets syntheses

The physical state of the different monomers influenced strongly the preparation method of **P1** to **P10**. Indeed, as mentioned in the experimental part, the solids had to be molten before being mixed with their epoxy or amine counterpart. More generally, in order to avoid any macro-defect such as air bubbles, epoxy resins and hardeners are liquids that are pre-heated separately. In the case of vanillylamine, this procedure could not be performed as the melting point of vanillylamine is too high. **P6** and **P10** were instead prepared from powders. The polymers prepared, even if not exempt of air bubbles, were glassy, homogeneous materials as shown in **Figure 5** This method, although not ideal to obtain thermosets without any defects in the bulk, could prove very useful to prepare coatings from powders, for instance in applications such as powder paints.

Figure 5 : Photography of **P9**

In order to obtain polymers with optimal properties, epoxy monomers and amine hardeners were mixed in stoichiometric amounts. Indeed, the theoretical ratio of two epoxy groups to one amine gives the materials with the best properties.[3] Upon reaction of a primary amine with an oxirane ring, a secondary amine is formed. This secondary amine is also able to react with another oxirane ring. Thus, amine groups can react two times; they possess two “active H”. As stated, phenols can also react with oxirane groups. Phenols are actually an

important class of compounds when it comes to epoxy thermosets: they can act as hardeners, accelerators (catalysts), or be used to increase the molecular weight of epoxy resins.[20] However, phenols are less reactive than amines and usually require higher temperatures[1]. Also, contrary to amines, they are able to react only once with oxirane rings; they have only one "active H". Thus, in the case of **7**, there are three active H. **P1** to **P10** were prepared with a ratio of epoxy groups to active H of one to one.

A stoichiometric ratio of reactants does not ensure alone optimal properties of the thermoset. The extent of the polymerization reaction is another important parameter. Indeed, one has to verify that the polymerization reaction is complete, especially in the cases of **P6** and **P9** prepared from **7**, as the phenol group is less reactive than amines. Incomplete reaction yields a lower cross-link density of the network and a high amount of chain ends that act as local plasticizers by rotating freely inside the network. Both these effects decrease the T_g of the thermoset. In order to ensure complete polymerization, **P1** to **P10** were post-cured above their T_g. The DSC analyses of the polymers after this post-cure step did not display any residual exothermicity. Thus, the polymerization reactions were considered complete.

Prior to curing, DSC analyses were performed on formulations to determine their onset temperatures. All onset temperatures were below 115°C. Thus, this temperature was chosen to cure the formulations. **P4** was the only exception as it was cured at 80°C. This temperature was chosen because it was sufficient to obtain a cured thermoset while avoiding as much as possible potential side-reactions and exothermicity arising from the aliphatic tertiary amine of **10**. The onset temperature of the **P4** formulation was the lowest of all formulations (72°C), which was attributed to the effect of the internal aliphatic tertiary amine acting as a built-in catalyst.[43] The DSC analyses of the formulations of **P4** and **P1** are displayed in **Figure 6**:

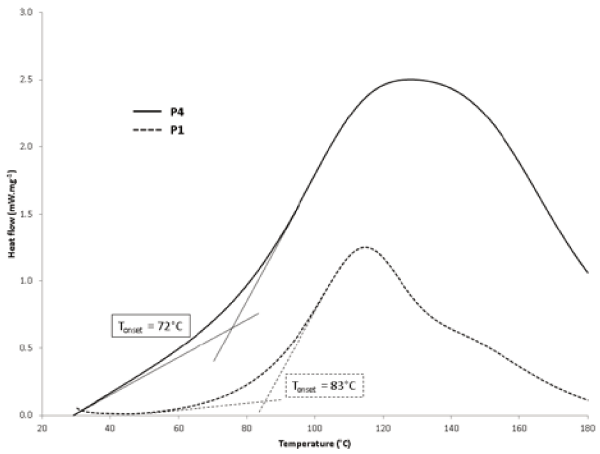


Figure 6 : DSC thermograms of **P1** and **P4** during curing

In the case of **14**, it was observed that this amine was especially susceptible to carbonation reaction upon exposure to ambient CO_2, forming white insoluble salts. This phenomenon is referred to as amine blushing and has been investigated elsewhere.[41] A quick heating well above the melting temperature was needed to avoid this reaction.

Overall, **P1** to **P10** were obtained as glassy, homogeneous materials displaying only a glass transition upon DSC analyses after post-cure. **P4** prepared from **10** is displayed as an example in **Figure 7**:

Figure 7 : Photography of **P4**

These epoxy thermosets can either be partially or fully bio-based. The monomers they are composed of are prepared from potentially renewable chemicals that were not tested previously for the synthesis of epoxy thermosets. These monomers can bring more versatility to bio-based epoxy formulations, either by being hardeners with various s structures or a new multi-functional epoxy monomer. Compounds widely used in industry were also used as references to be able to compare the properties of the polymers prepared.

3.6. Influence of the epoxy monomer on the T_g and T_α

P1 to **P4** were all prepared based on the same amine hardener, IPDA **13**. IPDA is one of the most used amine hardener in industry. It is a petro-based compound that was chosen as a reference in order to compare the properties of **P1** to **P4** and understand the effect of the epoxy monomer. Indeed, **P1** to **P4** were prepared with different epoxy monomers (respectively **9** to **12**). The T_g of **P1** to **P4** after their post-cure was determined by DSC on the second heating ramp. Results are given in **Figure 8**. No remaining exothermicity was detected by DSC. The curing was thus considered complete.

The temperatures T_α were determined at the peak maximum of the tan δ curves displayed in **Figure 9**. T_α is the temperature of the α relaxation process, which corresponds to the relaxation of the network starting to coordinate large-scale motions. This relaxation happens during the glass transition of the polymer under a given mechanical stress. T_α is commonly associated with T_g, but is measured by DMA under a mechanical stress (uniaxial stretching with f = 1Hz here). T_α results are summarized together with T_g results in **Figure 8**.

All T_α were higher than their corresponding T_g. This result was expected: the additional mechanical solicitation that is imposed to a material in a DMA analysis compared to a DSC analysis increases the temperature of the glass transition, consistently with the time-temperature superposition principle.

The thermoset **P3** based on **12** had the highest T_g and T_α (208°C and 253°C respectively). This result was explained by the high cross-link density brought by the tri-functionality of **12** as well as by its structure. It is well-known in the literature that epoxy thermosets based on aryl amines display such high performances.[43] The

amine is directly linked to the aromatic cycle, leading to a very rigid structure.

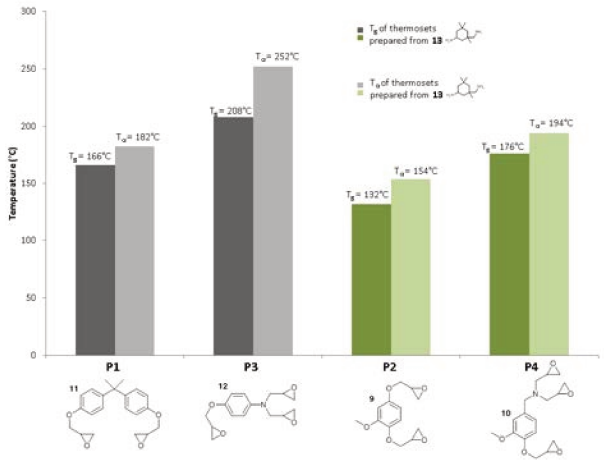


Figure 8 : T_g and T_α of **P1** to **P4**

P4 prepared from **10** had the second highest T_g and T_α (176°C and 194°C). Like in the case of **P3**, these high temperatures can be explained by the tri-functionality of **10** that increases the cross-link density. However, **10** is a benzyl amine, a structure that can adopt more spatial configurations than the locked, conjugated aryl amine structure of **12**. The additional CH_2 moiety leads to a sharp decrease of the transition temperatures. This result is consistent with the literature.[26]

P1 prepared from **11** was next with a T_g and a T_α of 166°C and 182°C respectively. **P1** transition temperatures are only slightly lower than those of **P4**, even though **P1** was prepared from a di-epoxy monomer (**11**) whereas **P4** was prepared from a tri-epoxy monomer (**10**). This fact was explained by the higher density of aromatics brought by **11**: it was introduced in a higher molar proportion than **10** in the network; and it also bears two aromatic cycles per molecule.

Finally, **P2** prepared from **9** displayed a T_g and a T_α of respectively 132°C and 154°C. **9** is also a di-epoxy but, contrary to **11**, it only bears one aromatic cycle per molecule, which can explain the lower T_g and T_α of **P2** compared to **P1**.

All thermosets have been hardened with IPDA **13**, a very common industrial hardener. This makes **P1** an excellent industrial reference to compare to as the epoxy monomer used was the ubiquitous DGEBA **11**. **9** is a potentially bio-based, vanillin-derived di-epoxy monomer that leads to the thermoset **P2** with T_g and T_α relatively close to those of the industrial reference **P1**. **P4** has been prepared from **10**, a vanillin-derived tri-epoxy monomer, and this potentially bio-based polymer displays a T_g and a T_α higher than the industrial reference.

3.7. DMA analyses

DMA analyses of the polymers **P1** to **P4** were performed to investigate the thermo-mechanical properties of these polymers. Storage moduli E' and tan δ curves of each polymer are shown in **Figure 9**:

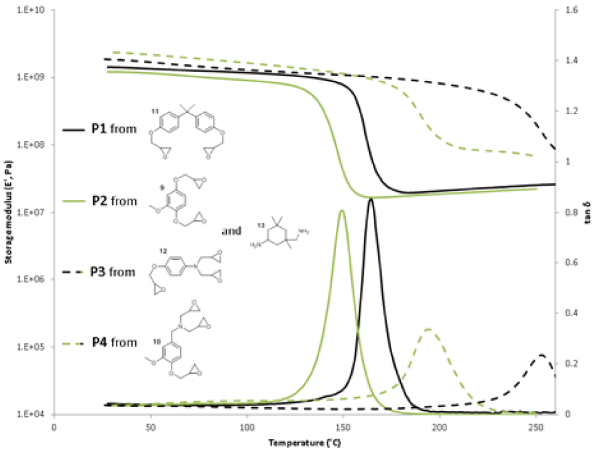


Figure 9 : Storage moduli E' and tan δ curves of **P1** to **P4**

The T_α determined at the maximum of the tan δ curves, have been commented in the previous section. Additional information can be gathered from these DMA analyses. The storage moduli E' is the elastic response of the material and is related to the mechanical energy stored per cycle upon deformation. At 30°C, the polymers were all glassy and their storage moduli were all around 1-2 GPa. **P4**, prepared from the potentially bio-based tri-epoxy monomer **10**, had the highest E'(30°C) at 2.4 GPa, higher than the industrial reference **P1**.

E' undergoes a sharp decrease upon reaching the glass transition, as large-scale molecular motions become possible. In the case of **P1** and **P2**, E' drops of two decades. However, in the case of **P3** and **P4**, the E' drop was only of one decade. This result was explained by the difference of cross-link density between these polymers. **P1** and **P2** were prepared from di-epoxy monomers whereas **P3** and **P4** were prepared from tri-epoxy monomers and are thus more cross-linked. Thermosets with a higher cross-link density lead to networks with a higher stiffness, less prone to irreversible deformations, and thus with a less pronounced E' drop during the glass transition.

Unfortunately, in the case of **P3**, the analysis could not be pursued at higher temperatures to record the values of E' on the rubbery plateau, or the end of the glass transition phenomenon. Indeed, the temperatures reached were too close to the start of the polymer degradation.

3.8. Influence of the epoxy monomer on the degradation

TGA analyses at 10°C.min^{-1} under N_2 were also performed on **P1** to **P4**. The effect of the epoxy monomer on T_{deg} was investigated. All T_{deg} were determined as the temperature at which the degradation rate is maximal. It was determined at the maximum of the derivative of the mass loss *vs.* temperature curve. TGA curves for **P1** to **P4** are shown in **Figure 10**.

P1 and **P3** had similar T_{deg} around 360°C. **P2** and **P4**, prepared from vanillin-based monomers, had also similar T_{deg} at around 340°C., only slightly lower than **P1** and **P3** prepared from the industrial references.

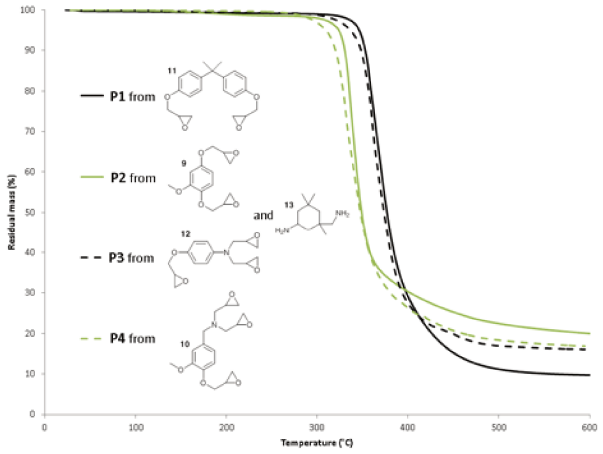


Figure 10 : TGA curves of **P1** to **P4** under N_2

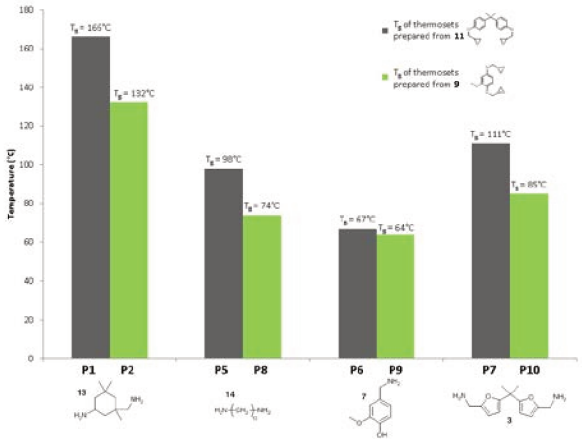


Figure 11 : Influence of the hardener on the T_g

The start of the mass loss event for bio-based thermosets **P2** and **P4** was around 280°C, whereas it was around 310°C for the industrial references **P1** and **P3**. It might be explained by the degradation of the methoxy moiety born by **9** and **10** in **P2** and **P4** respectively, but this hypothesis needs confirmation. The residual mass at 600°C, linked to the ability of the material to form char, was higher for the bio-based thermosets, especially for **P2** that had 20% of residual mass. Charring is an important feature when it comes to fire-retardation properties.

3.9. Influence of the amine hardener on the T_g

In order to investigate the properties of the amine hardeners **3**, **7**, **13**, and **14**, two series of polymers were prepared. The first series (**P1**, **P5**, **P6**, **P7**) was synthesized using DGEBA **11** as the epoxy monomer. DGEBA is the most widely used epoxy monomer in industry and was chosen to compare the properties of the thermosets prepared from various amine hardeners with the current epoxy industrial reference.
The second series of polymers (**P2**, **P8**, **P9**, **P10**) was based on **9**, a di-epoxy monomer potentially bio-based as it was prepared from vanillin and which potential in epoxy thermosets has already been demonstrated.[3]
The T_g of all post-cured polymers was determined by DSC analyses on the second heating ramp; they are displayed in **Figure 11**.
Every polymer based on **11** and a given hardener had a T_g higher than its counter-part based on **9**. These results confirm the findings on the influence of the epoxy monomer structure that have been investigated in the previous sections.
Also, importantly, the effect of the hardener employed on the T_g of the thermosets is the same, regardless of the nature of the epoxy monomer used. In other words, sorting the thermosets from the highest T_g to the lowest gives the same order in terms of hardener (**13** > **3** > **14** > **7**) for polymers of the series based on **11** and for polymers of the series based on **9**.

IPDA **13** gives thermosets **P1** and **P2** with the highest T_g (166°C and 132°C respectively). This result can be explained by multiple factors. **13** is a tetra-functional hardener, as amines can react with two epoxy groups. It is also cycloaliphatic, which means that it is more rigid than a non-cyclic compound. Finally, one amine group is directly linked to the cycle of **13**, which limits its mobility.
The hardener that gave the second highest T_g was **3**. Polymers **P7** and **P10** based on **3** displayed T_g of 98°C and 74°C respectively. **3** bears aromatic cycles that confer rigidity to the network. However, **P7** and **P10** display a T_g drastically lower than **P1** and **P2**. This result was attributed to the (bis)furfurylic structure of **3**. Like in the case of the benzyl moiety, the amine functions are separated from the cycles by a CH_2 moiety that bring mobility to the network and lowers the T_g. This result is consistent with the literature.[26]
The polymers **P5** and **P8** based on **14**, displayed T_g of respectively 98°C and 74°C. They were slightly lower than those of **P7** and **P10**. This result was attributed to the aliphatic, non-cyclic structure of **14**. It imparts mobility and flexibility to the network, and therefore lowers the T_g.
Finally, **7** gave the polymers **P6** and **P9** with the lowest T_g (67°C and 64°C respectively). Contrary to the other hardeners studied that are tetra-functional, **7** is a tri-functional compound. As such, it imparts a lower cross-link density to the network, decreasing the T_g.

3.10. Influence of the amine hardener on the degradation under N_2

TGA analyses at 10°C.min^{-1} under N_2 were performed on the polymers prepared from **11** (**P1**, **P5**, **P6**, **P7**), and on the polymers prepared from **9** (**P2**, **P8**, **P9**, **P10**), for which TGA curves are displayed respectively in **Figure 12** and **Figure 13**. The effect of the amine hardener on T_{deg} was investigated.
The polymers **P2**, **P8**, **P9**, and **P10** based on **11** did not display significant differences in their T_{deg}; they were all around 340°C. T_{deg} for **P1**, **P5**, **P6**, and **P7** are also relatively close, with a maximum difference of 24°C

between **P7** and **P5**. No relationship to the structure of the amine hardener could be made.

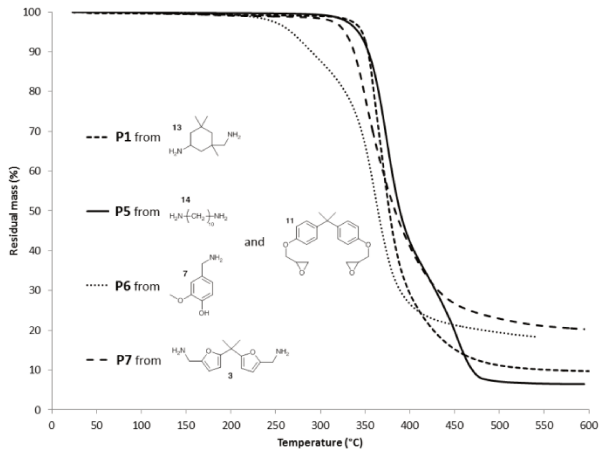


Figure 12 : TGA curves of **P1**, **P5**, **P6**, and **P7** under N_2

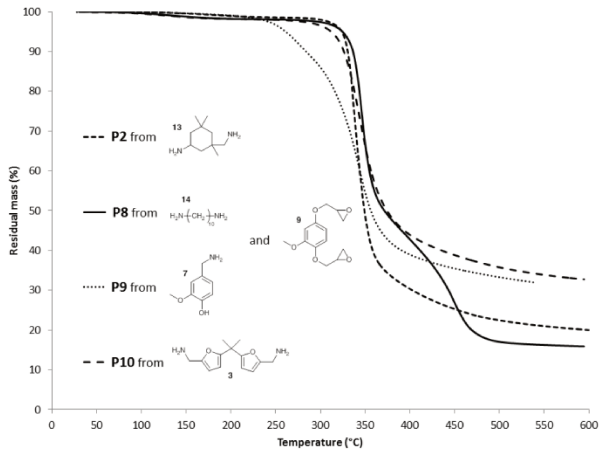


Figure 13 : TGA curves of **P1**, **P5**, **P6**, and **P7** under N_2

However, every polymer based on the di-epoxy **11** and a given hardener had higher T_{deg} than their counterparts based on **9**. This result confirms the influence of the epoxy monomer already observed and shows that the same tendency (T_{deg} higher for **11**-based polymers than for **9**-based polymers) is observable with all the hardeners tested.

Polymers **P6** and **P9** prepared from **7** start their degradation at much lower temperatures (around 230°C) than the other polymers (around 300°C). This result could be explained by the lower cross-link density of **P6** and **P9** or by degradation reactions specific to the structure of **7**.

It is also worthy to note that **P5** and **P8** prepared from **14** displayed a second degradation event at respectively 453°C and 459°C, which was attributed to a degradation mechanism specific to **14**.

Finally, the residual masses at 600°C are much higher when the amine hardener is either **7** or **3**. As mentioned, residual masses at these temperatures are due to the formation of char. Aromatic cycles are known to promote charring. This explains that polymers based on **7** and **3** show high residual char amounts. Importantly, these two monomers are bio-based and they display charring properties better than the current industrial reference.

3.11. Influence of the amine hardener on the degradation under air

P8 and **P10** are both bisphenol A-free, potentially fully bio-based epoxy thermosets. They are prepared from monomers that can be realistically processed and possess good properties such as relatively high Tg, and temperatures of maximum degradation rate under N_2 comparable to the industrial DGEBA-IPDA reference. Their degradation profiles at 10°C.min^{-1} under air have also been investigated and are shown in **Figure 14**:

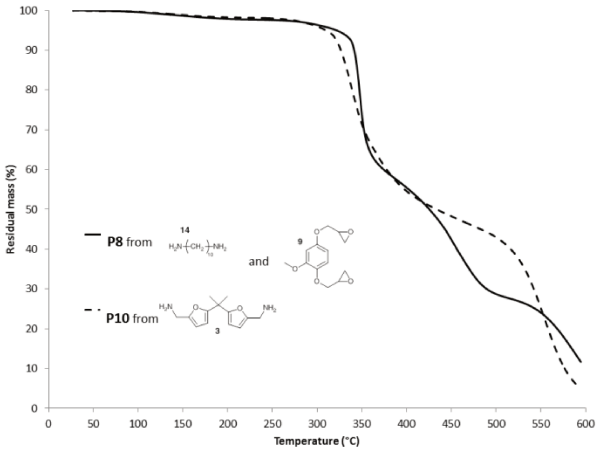


Figure 14 : TGA curves of **P8** and **P10** under air

P8 and **P10** display a first degradation step at the same temperatures than under N_2 (see **Figure 13**). However, the mass loss during this first step is around 40% while it was around 50% under N_2. **P10** displays here a second degradation step around 550°C that was not observed under N_2. This mass loss was attributed to the thermo-oxidative degradation of the material. **P8** displays the same second degradation step than under N_2, around 430°C. However, a third degradation step is observed around 570°C, also attributed to the thermo-oxidative degradation of the material. If **P10** displayed high levels of residual mass at 600°C, it is not the case under air because of this thermo-oxidative degradation step.

4. Conclusion

Aromatic structures are especially interesting to bring good thermo-mechanical properties to epoxy thermosets. Thus, vanillin and furfural, both widely available renewable aromatics, were chosen as base building-blocks for this work. The aim was to improve the versatility of bio-based epoxy formulations by different methods. The first strategy was to widen the pool of potentially bio-based amine hardeners available. The syntheses of vanillylamine and bis(furfurylamine) A were thus successfully carried out. The second strategy was to prepare a tri-functional epoxy monomer that could help increase the cross-link density and thus the T_g of epoxy networks. Triglycidylether of vanillylamine was successfully prepared, for the first time to our

knowledge. Polymers were prepared from these compounds and other various monomers, leading to bio-based epoxy thermosets. Petro-based monomers widely used in industry were also employed in this work to serve as references. In each case, homogeneous, glassy thermosets were obtained. The thermo-mechanical properties of the polymers synthesized were investigated.

The influence of the epoxy monomer was first explored. A higher functionality of the monomer lead, as expected, to more cross-linked thermosets with a higher T_g and T_α and with a smaller drop of E' during the glass transition. The structure of the monomers also impacted the thermo-mechanical properties. For instance, monomers having a benzyl structure lead to thermosets with a T_g lower than those with an aryl structure. It is worthy to note that the potentially bio-based polymer that was prepared from the triglycidylether of vanillylamine had a higher T_g than the DGEBA-IPDA industrial reference, a rare feature among bio-based epoxy thermosets. Triglycidyl ether of vanillylamne can be used as an epoxy-cross-linker to increase the cross-link density and T_g of bio-based epoxy formulations.

Tuning the final properties can also be achieved by changing the hardener. Thus, various potentially bio-based amine hardeners were also tested, with both DGEBA and a vanillin-derived di-epoxy monomer. The hardeners tested impacted the properties in the same manner with both epoxy monomers. Parameters such as the aromatic density, the functionality, and of course the hardener structure were found to strongly modify the polymer thermal properties such as the T_g or degradation profiles. Importantly, some of the polymers synthesized were bisphenol A-free, potentially fully bio-based epoxy thermosets that displayed relatively high T_g and degradation properties comparable to the DGEBA-IPDA industrial reference.

In future works, other bio-based amine hardeners should be synthesized and tested. Also, the triglycidylether of vanillylamine prepared here should be tested as an additive cross-linker in an industrial epoxy formulation.

Acknowledgments

The authors would like to thank the French Ministry of Research for funding this work.

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Chapter 6: Epoxy from lignin depolymerization mixtures

1. Introduction

The three previous chapters extensively demonstrated the real potential of using vanillin to prepare epoxy monomers. Many different applicative problems specific to epoxy thermosets have been investigated, such as the comparison to the industrial DGEBA reference, the preparation of epoxy pre-polymers, or of other various compounds of interest for industrial epoxy formulations.

However, in the process of going from biomass to industrial polymers, one could argue that up to this section, only one end of this process has been explored, namely the downstream, applicative end: the use of vanillin in epoxy polymers. This work is centered on vanillin as a renewable chemical. Therefore, exploring upstream is necessary, *i.e.* considering the reality of the lignin-to-vanillin process. More specifically, is the reality of this process compatible with preparing high-performance epoxy polymers derived from lignin-based vanillin? Indeed, as presented in the literature analysis of the first chapter, obtaining pure vanillin from the mixture issued from the alkaline oxidative depolymerization of lignin is a difficult task that implies low yields and environment-damaging steps, such as the extensive use of acids for instance. These difficulties have a consequence on the price of pure vanillin from lignin.

The following section is a published work that explores the idea of exploiting not only pure, food-grade vanillin, but mixtures obtained from the lignin-to-vanillin process that are only partially purified. This approach aims at shortening the path from biomass to polymers and at extending the pool of lignins usable from only G lignin to all lignins. The strategy employed was to prepare mixtures of G- and GS-type phenolics modelling the products obtained during the alkaline oxidative depolymerization of lignin. These mixtures were functionalized and epoxy thermosets were prepared and characterized from them.

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

M. Fache, B. Boutevin and S. Caillol*

Received 19th May 2015,
Accepted 4th August 2015

DOI: 10.1039/c5gc01070e

www.rsc.org/greenchem

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 compounds 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 the second step, they were glycidylated to obtain mixtures of epoxy monomers. Each of the components 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 monomer 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 a high value added 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 polymers[2] 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 for these high performances. In many cases, it is also because they are based on aromatic monomers, which bring stability and rigidity. Epoxy polymers are one of the most used classes 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 maintain the level of performance; (3) based on 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 aromatics.[6] Lignin is a random, three-dimensional network composed of three types of phenylpropanoid units:[7] *p*-hydroxyphenyl (H) unit, guaiacyl (G) unit, and syringyl (S) unit. These units originate from the three monolignols depicted in **Fig. 1A**.

As explained in the literature,[8] lignins from softwood (pine, spruce, 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,

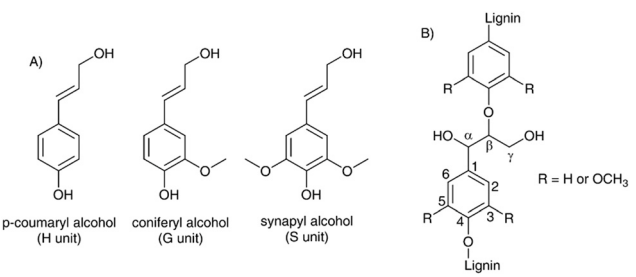


Fig. 1 Lignin monolignols (A) and a β-O-4 linkage (B).

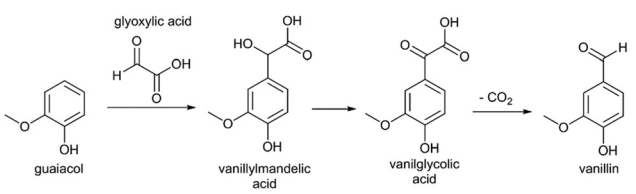
Institut Charles Gerhardt, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France. E-mail: sylvain.caillol@enscm.fr; Tel: +33 4 67144327

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 (**Fig. 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 many different types of chemical linkages,[10,11] which makes precise characterization and understanding of the reaction mechanism challenging.[7] Finally, this biopolymer is also difficult to process. To overcome these limitations, lignin 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]

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 the literature, from early patents[17–22] to more recent work.[8,14–16,23–29] The cleavage of a guaiacyl unit (G, **Fig. 1**) leads to the vanillate ion, which gives vanillin **1** after protonation. As mentioned earlier, G units are predominant in lignins from softwood (G lignins). However, in the case of lignins from hardwood (GS lignins), syringyl units (S, **Fig. 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, **Fig. 1**) can also be found in lignin, which leads to *p*-hydroxybenzaldehyde **3**. These aldehyde products are subjected 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]



Scheme 1 Outlines of the main petrochemical synthesis of vanillin.

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 treat-ment 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 $NaHSO_3$ (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**.

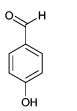
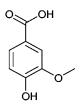
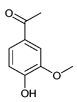
The hydrosulfite anion reacts selectively with the aldehyde moiety. The derivatives produced have a good solubility in water, as opposed to the starting aldehydes and to the other products from the crude mixture.[17] The aqueous phase must be further acidified to recover aldehydes and SO_2.[17] Apart 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 compounds,[8] drawbacks that are costly both economically and environmentally.

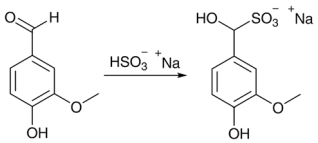
Also, this method is selective towards aldehydes, which means that *p*-hydroxybenzaldehyde and syringaldehyde[40] are extracted along with vanillin. This is especially relevant in the case of GS and HGS lignins as these compounds are major products of the depolymerization reaction. Vanillin is difficult to isolate from these compounds, as pointed out by numerous studies.[8,29–31,37] This leads to further purification steps, impacting the environmental and economic efficiency of the whole process even more.[8]

Despite these difficulties, vanillin is one of the only monoaromatic compounds readily available from biomass. Precedent studies have 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 softwood to maximize the yield in vanillin, lignin from all types of wood would be a potential feedstock. Working on mixtures instead of pure compounds to prepare

Table 1 Main products of the alkaline oxidative depolymerization of lignin in the cases of softwood and hardwood[31–36]

	Compound	Formula	Typical yields in softwood	Typical yields in hardwood
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]



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

polymers would also allow a drastic reduction in production cost – and thus a decrease in selling price.

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" in the rest of this work. In a first step, they were subjected to a green Dakin oxidation[43] 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 ^{1}H 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.

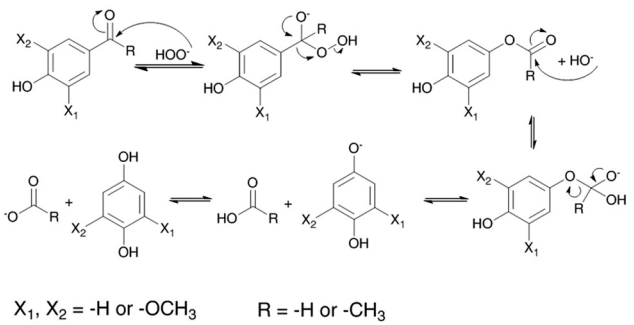
Results and discussion

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 lignin from softwood, and, on the other hand, GS lignin from hardwood. 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**.

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.



Scheme 3 Mechanism of the Dakin oxidation.

The protocol used[45] is very efficient and simple to handle. Moreover, the oxidation reagent used, sodium percarbonate, has major advantages: it is inexpensive, available on a large-scale 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 innocuousness.

Each carbonyl-containing component of the starting mixtures was first individually reacted in order to understand their reactivity and to determine the mixture 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]

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

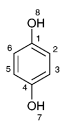
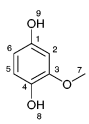
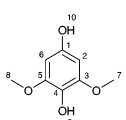
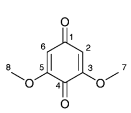
Dakin oxidation of the mixtures

The starting mixtures (Fig. 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 mixture compositions after the first step of Dakin oxidation were determined by ^{1}H NMR analysis, using the characteristic signals of each product that was found from the individual reactions. These compositions are also summarized in Fig. 2.

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 under 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**

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

Compound	Formula	Conv.	^{1}H NMR δ (400.1 MHz, 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**	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**)		91% from **6** 90% from **2**	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**)		69% from **7** 5% from **2**	3.82 (s, 6H, H_7, H_8); 5.90 (s, 2H, H_2, H_6)
		4% from **7**	$CDCl_3$: 3.83 (s, 6H, H_7, H_8); 5.86 (s, 2H, H_2, H_6)

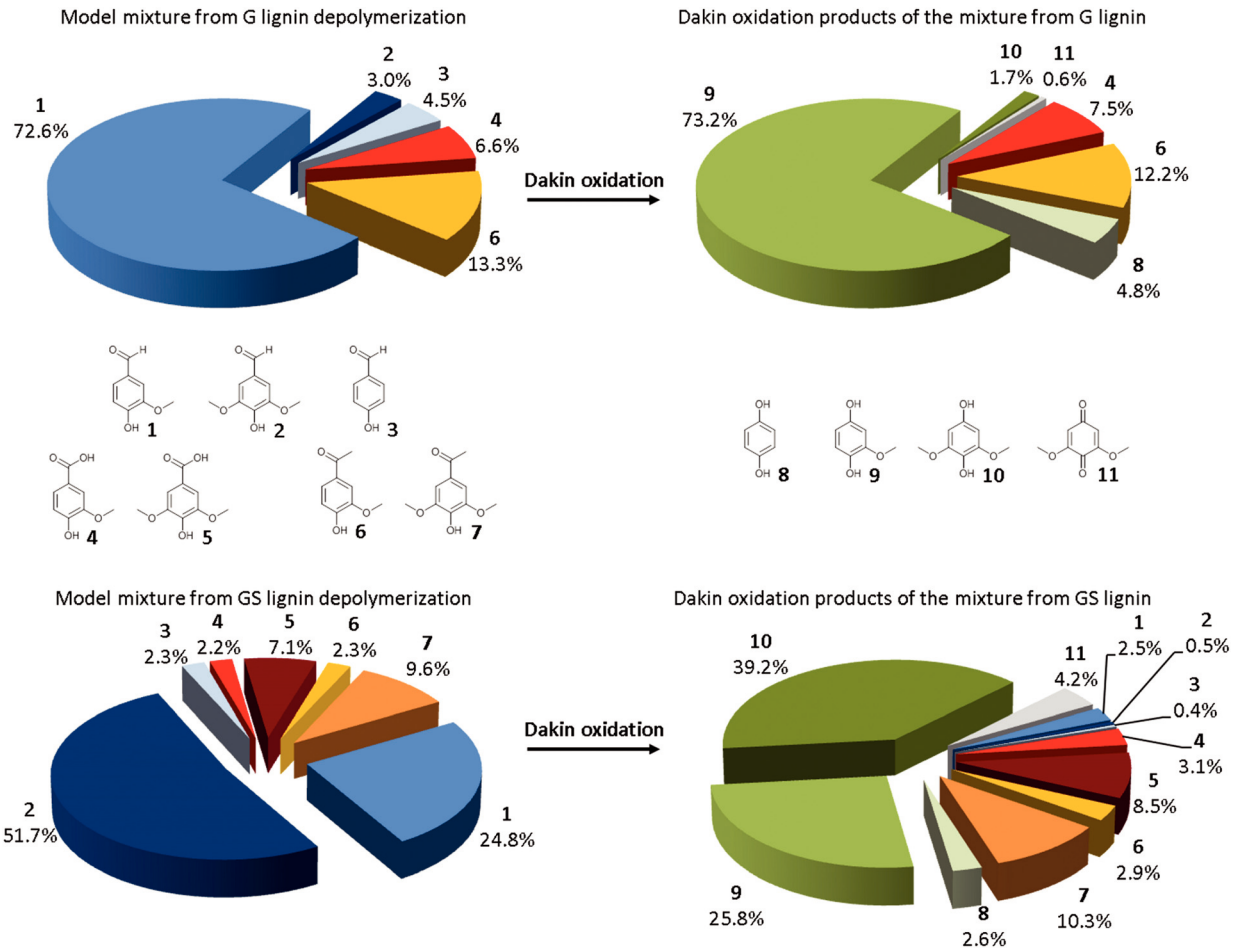


Fig. 2 Composition of the model mixtures of G- and GS-type phenolics before and after Dakin oxidation.

(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-oxidize[46] 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, decreasing 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 ($\bar{M}$(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, $\bar{f}$(G1)) of this mixture was found to be 1.87. $\bar{f}$(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 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 ($\bar{M}$(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 ($\bar{f}$(GS1)) was found to be 1.75. $\bar{f}$(GS1) is lower than $\bar{f}$(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 in the glycidylation reaction were first individually reacted and the products were characterized by ^{1}H 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.

In the first step, a phase transfer catalyst (triethylbenzylammonium chloride – TEBAC) is used to allow the phenolate ion to exist in organic solution. In the 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 the 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.

All phenolics were readily converted to epoxide products (Table 3). It is worth noting, 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**, and **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 for 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.

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 mixture compositions after this second step were determined by ^{1}H NMR analysis, using the characteristic signals of each product that were found from the individual reactions. These compositions are summarized in Fig. 3.

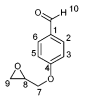
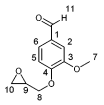
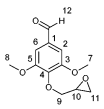
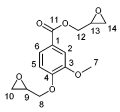
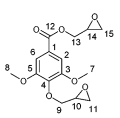
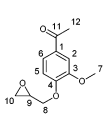
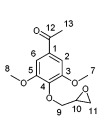
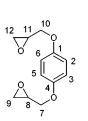
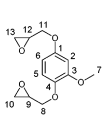
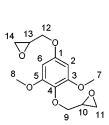
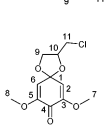
Glycidylation of the mixture of G-type phenolics

Concerning the model mixture of G-type phenolics, compounds **4**, **6**, **8**, and **9** were completely 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**, whose ^{1}H NMR signal was very low. A mean molecular mass of the glycidylated mixture of G-type phenolics ($\bar{M}$(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, $\bar{f}$(G2), was found to be 1.87. As in the case of $\bar{f}$(G1), $\bar{f}$(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 seen were observed. Indeed, compounds **1** to **9** were completely converted to their glycidylation products, *i.e.* products **12** to **20**. It is worth noting 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 described, 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 Fig. 3), which impacts the calculation of the mean molecular mass. Nevertheless, the mean molecular mass $\bar{M}$(GS2)) was estimated without taking into account **A**, and was found to be 263.2 g mol^{-1}.

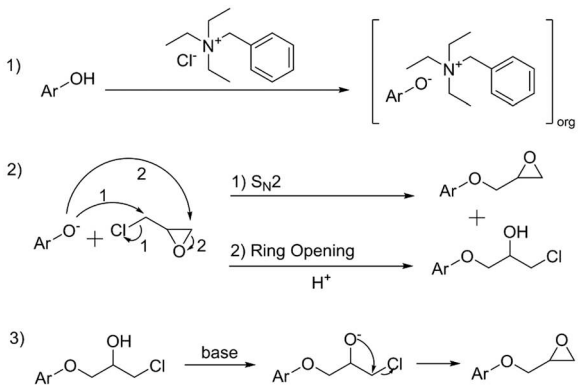
Table 3 Glycidylation products from each individual component of the oxidized mixtures

Compound	Formula	Conv.	^{1}H NMR δ (400.1 MHz, 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, 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)

In the individual reaction, no epoxy signal was detected for **A**, which means that the epoxy functionality of **A**, f(**A**) = 0. The mean epoxy functionality of the mixture of GS phenolics $\bar{f}$(GS2), was thus calculated and found to be 1.45. $\bar{f}$(GS2) is lower than 2 because of the presence of **17** (f = 1), and **22** and **A** (f = 0).

^{1}H 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.



Scheme 4 Phenol glycidylation mechanism under solvent-free conditions.

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 paper,[44] our team reported the successful use of a ^{1}H 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-d_6. Th e^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 shown 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 $\bar{M}$ and mean functionality $\bar{f}$ as shown in eqn (1):

$$\mathrm{EEW} = \frac{1}{\mathrm{EI}} = \frac{\bar{M}}{\bar{f}} \quad (1)$$

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**.

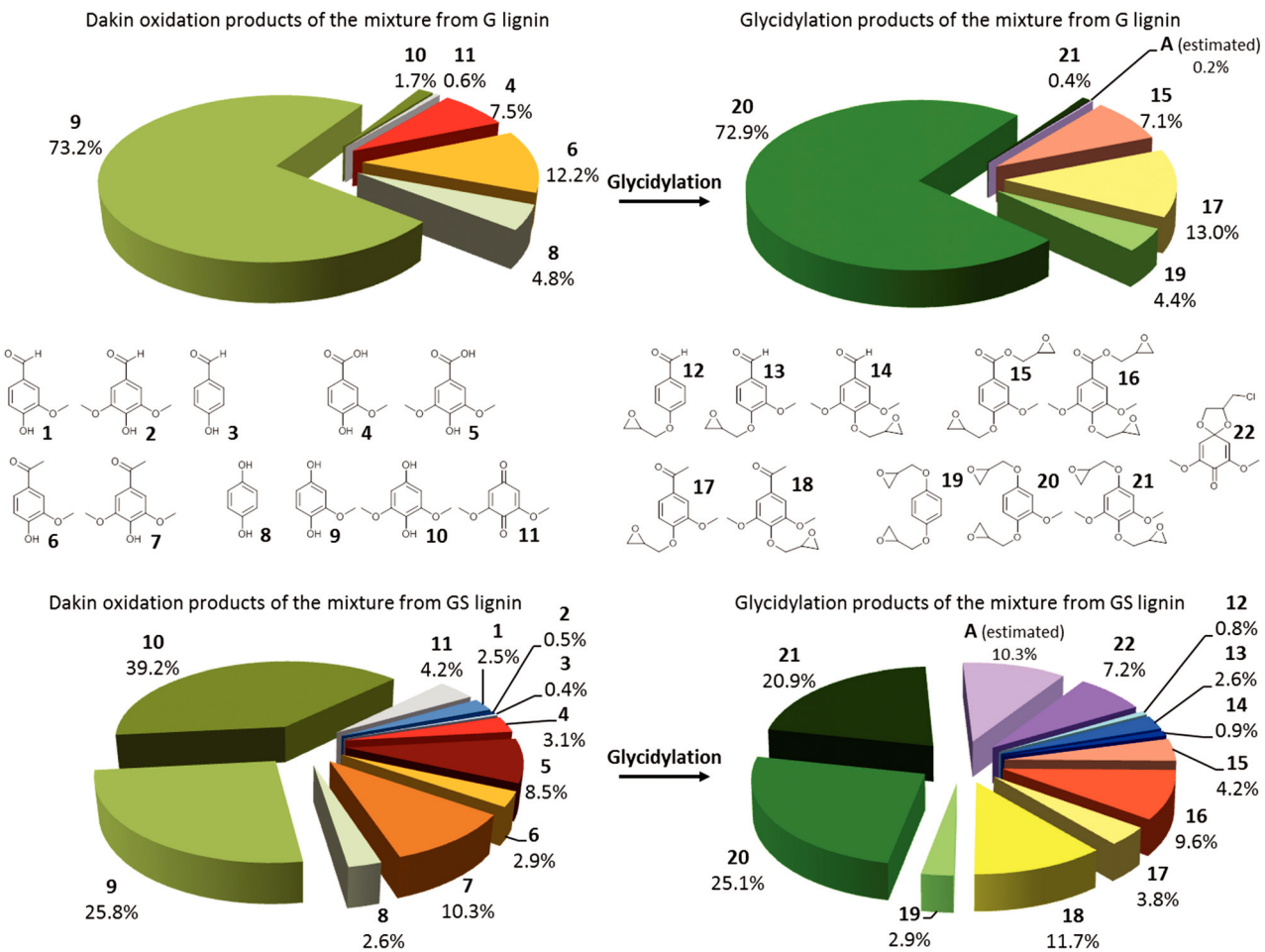


Fig. 3 Composition of the model mixtures of G- and GS-type phenolics before and after glycidylation.

Table 4 Epoxide index and epoxide equivalent weight of the glycidylated mixtures

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

EEW(GS) is higher than EEW(G) because of the lower mean functionality of the epoxy monomer mixtures. 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 **Fig. 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**.

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, and 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

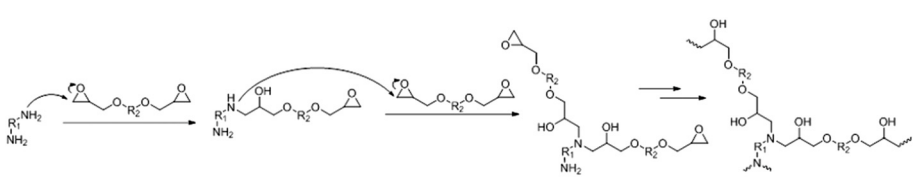
The thermal properties of the polymers prepared were investigated by DSC analyses. The thermograms obtained at 20 °C min^{-1} are displayed in **Fig. 4**.

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 113 °C and 99 °C respectively 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 (ΔC_p(G)) and of GS-type monomers (ΔC_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 thus has 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 bio-based, high-T_g epoxy polymers is a valid approach.

TGA analyses

TGA analysis was performed on both epoxy thermosets. Results are shown in **Fig. 5**.

Characteristic parameters of thermal degradation include the onset of degradation temperature (T_{onset}, °C), the



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

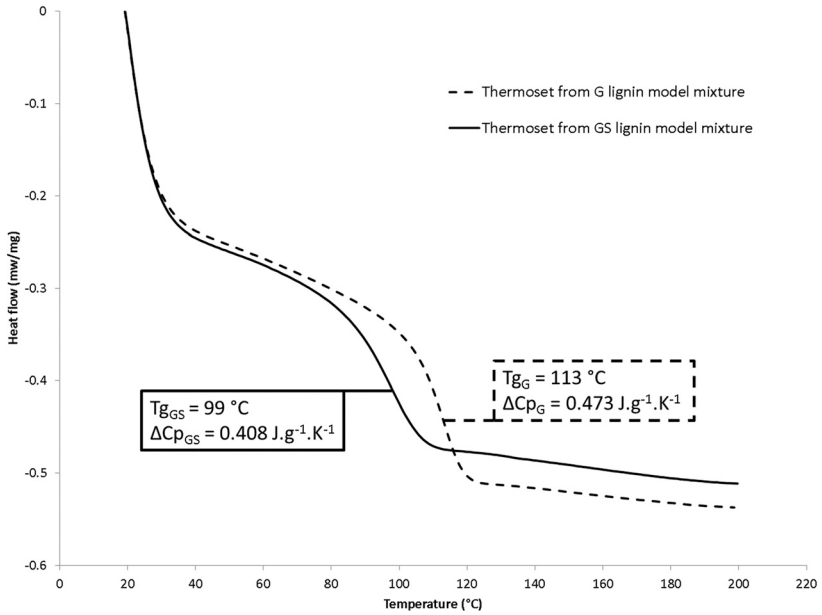


Fig. 4 DSC thermograms of the epoxy thermosets prepared from model mixtures of G- and GS-type monomers.

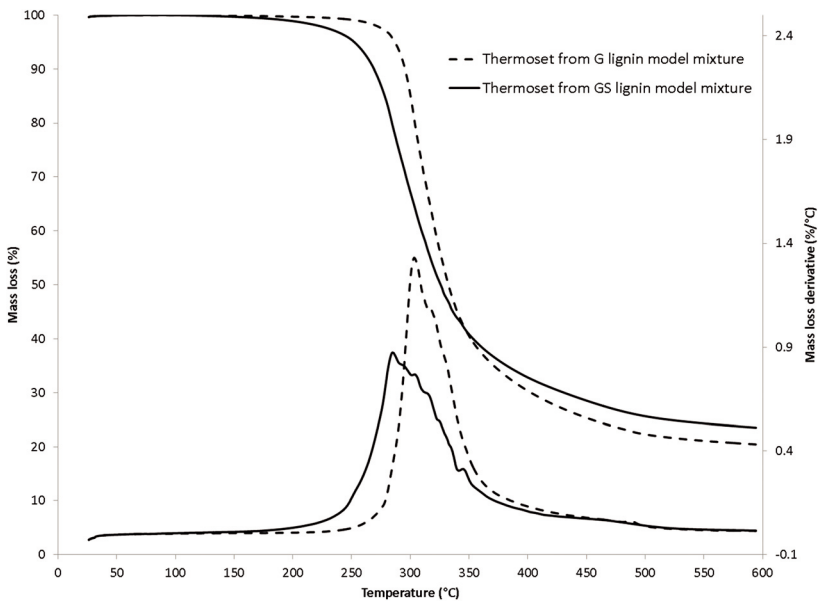


Fig. 5 TGA thermograms under N_2 and their derivatives of the epoxy thermosets prepared from model mixtures of G- and GS-type monomers.

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**.

Both polymers displayed a one-step mass loss under N_2 and an onset of degradation at 254 °C and 289 for GS-type phenolics and G-type phenolics-based polymers respectively. 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}.

Table 5 Thermal degradation characteristic parameters under N_2 of the epoxy thermosets prepared from model mixtures of G- and GS-type monomers

	T_{onset}	T_{max}	$Char_{600}$
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%

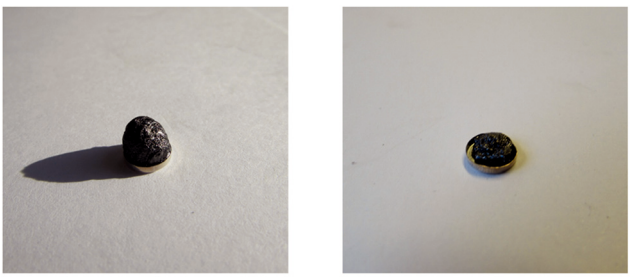


Fig. 6 Epoxy polymers from model mixtures of G- and GS-type monomers after TGA.

It is worth noting that the derivative curves of the mass loss (**Fig. 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 (**Fig. 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 **Fig. 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, combustive, and fuel transfers.[51]

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 δ of the polymers are shown in **Fig. 7**.

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_α(G) and T_α(GS) were determined as the temperatures at the peak maximum of the tan δ curves. T_α is commonly associated with the glass transition temperature T_g, which is measured by DSC under no mechanical stress. Here, T_α(G) = 117 °C and T_α(GS) = 113 °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 Glasser[52] obtained T_α 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_α thermosets than the IPDA we used.[53] T_α(G) > T_α(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. Non-functional compounds 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_α), 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 δ peak is a good indication of the homogeneity of a material: the more homogeneous the sample, the sharper the tan δ peak. Here, the polymer from the mixture of GS-type monomers displays a broader tan δ 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; that take part in the glass transition at slightly different temperatures and thus broaden the tan δ curve.

Experimental

Materials and methods

Vanillin (99%) was purchased from ABCR. Syringaldehyde (≥98%), 4-hydroxybenzaldehyde (98%), syringic acid (≥95%), acetovanillone (98%), acetosyringone (97%), sodium percarbonate $Na_2CO_3{\cdot}1.5H_2O_2$ (available H_2O_2 20–30%), epichlorohydrin (≥99%), triethylbenzylammonium chloride (TEBAC, 99%), sodium hydroxide (99%), 1,3,5-trimethoxybenzene (≥99%) and all solvents used (≥99.5%) were purchased from Sigma-

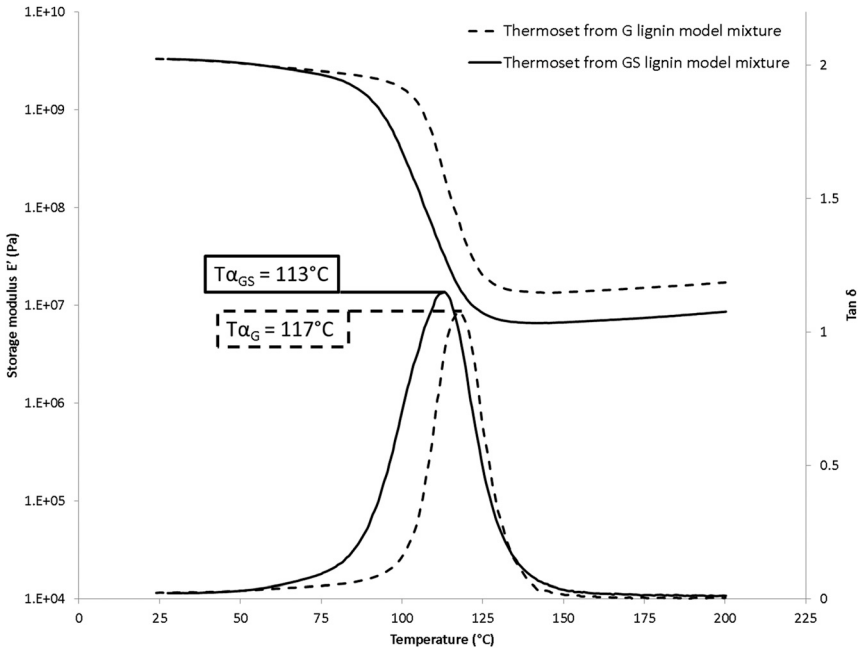


Fig. 7 DMA analyses of the epoxy thermosets prepared from model mixtures of G- and GS-type monomers.

Aldrich. Isophorone diamine (IPDA, ≥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. ^{1}H 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**, o r7 (0.25 mol L^{-1}, 1.0 eq.) in THF. In the case of model mixtures of G- and GS-type phenolics (see **Fig. 2**); the total amount of aldehyde and ketone compounds was considered as 1.0 eq. A solution of sodium percarbonate ($Na_2CO_3{\cdot}1.5H_2O_2$, 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 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 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 ^{1}H NMR (see **Fig. 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 wt%) 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 using a rotary evaporator.

Formulation and polymerization

The number of moles of epoxy groups per gram of mixture was determined using a ^{1}H NMR titration method (see Results and Discussion) successfully employed by our team in a previous paper.[44] 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 into 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 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^{-1}). The experiments were carried out at a heating rate of 10 °C min^{-1}.

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^{-1} 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 for phenolics modelling, the products obtained from G and GS lignin 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 monomer 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 value added 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 a 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 work, 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 polymers other than epoxy polymers.

Acknowledgements

The authors would like to thank the French Ministry of Research for funding this work. The authors are also grateful to Specific Polymers for providing vanillic acid.

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General Conclusion

The core of the chemical industry is the conversion of raw materials into value-added products, including fuels, platform chemicals, polymers, materials and pharmaceuticals. For now, oil is the primary feedstock. However, the oil production is predicted to level-off, even if the “when” question is still much debated. New oil-fields have to be continuously found to make up for the depletion of the ones exhausted. The exploitation of these new oil-fields presents more and more technical difficulties. Meanwhile the demand is ever rising with the global population increase. With a demand higher than the production capacity, prices will fluctuate with an overall tendency to rise. Moreover, only a few countries have access to the oil resource, others have to import the fuel and raw materials they need and are thus economically dependent. This situation leads to geopolitical tensions and increases the risk of a global economic crisis. Using renewable resources as primary feedstock could avoid the predicted shortcoming of oil and lead to price stability - due to the “renewable” part - necessary for long-term investments. A point of importance is that renewable resources are more evenly distributed on the planet than oil. Having domestic supplies could decrease the economical dependency and thus diminish tensions or the risk of a global crisis. From an environmental point of view, having local raw materials saves the fuel that would have been used for their transportation.
The question is *how* do we use renewable resources? For some time yet, the concept of bio-refinery has been described as the refining or upgrading of renewable feedstocks (biomass or food wastes) to yield fuels and commodity chemicals by means of chemical and biological processes. It is thus essentially the same principle as petroleum refining. Just as each petroleum cut has found an industrial application, each biomass fraction should be used in applications best fitting their properties, availability, purity etc. However, this might prove easier to say than to do because of the diverse, complex, and variable nature of biomass. The chemical industry is used to deal with pure, molecular compounds as raw materials. Due to the difficulties inherent to biomass, using renewable resources might imply in some cases considering complex mixtures as acceptable raw materials, or finding solutions to keep product specifications constant despite the raw material variability. In this work, this problematic became apparent in the search of bio-based compounds that could be used to prepare epoxy thermosets.

From the literature analysis performed in **Chapter 1**, the problematics identified were Bisphenol A substitution and renewable resources use (especially interesting in cross-linked materials) while keeping the level of performance. Bio-based aromatics are needed because of the rigidity and stability they can bring to the network. In Nature, the main aromatic raw materials are (poly)phenols, namely CNSL, tannins and lignin. Volumes of CNSL available are much lower than lignin or tannins and CNSL-based epoxy thermosets display glass transition temperatures too low for some applications. Tannins and lignin are difficult to handle due to their polymeric nature, complexity, and variability in structure and composition. Using a pure, di-functional, molecular compound to start with was the way that was chosen to pursue this study. This choice was made for two reasons: The first one was that it seemed the most realistic way to go given the current chemical industry mindset. The second one was that vanillin, among other manufacturing methods, is already produced industrially from wood. More specifically, it is obtained by lignin depolymerization under alkaline and oxidative conditions. Enormous amounts of lignin

are potentially available. Vanillin has thus a very unique status of being a relatively safe, molecular aromatic compound that is already produced on a large scale from biomass. This prompted many recent works to investigate vanillin as a key building-block for the synthesis of bio-based polymers. These works were summed up in a published review.

This building-block approach was put into practice to prepare a platform of vanillin-based di-functional monomers. The syntheses of these monomers are described in a published article that constitutes the **Chapter 2** of this work. The compounds prepared bear many different chemical functions that can be used to make a wide range of polymers. Bio-based aromatic monomers are very scarce in literature, making all these compounds valuable. Of particular interest are vanillin-based di-amines that could be used as bio-based hardeners or vanillin-based di-(cyclic carbonates) that could be used as monomers for the synthesis of non-isocyanate polyurethanes.

Following the problematics identified in the literature analysis, the three vanillin-based epoxy monomers prepared were investigated more closely. They are based on three vanillin derivatives in different oxidation states: vanillyl alcohol, vanillic acid, and methoxyhydroquinone, the product of the vanillin Dakin oxidation (oxidative decarboxylation). The **Chapter 3** is a published work that describes the preparation of epoxy thermosets from these monomers and their characterization. The influence of the monomers structure on the thermosets properties was investigated. For instance, it was found that the benzyl glycidyl ether structure gave an epoxy thermoset with a lower T_g compared to the phenyl glycidyl ether. Vanillin-based epoxy thermosets were also compared to a DGEBA-based thermoset cured with the same hardener, and found to have properties that could match the current industrial reference. These properties could be tuned by the right monomer choice.

Indeed, versatility is one of the main advantages of epoxy thermosets. Industrially, DGEBA pre-polymers of varying length are used to modulate the final properties of the thermoset. Long pre-polymers bring flexibility by spacing cross-links, while keeping a high density of aromatic cycles. They also lower the T_g of the thermoset. In the **Chapter 4**, this approach is transposed to vanillin-based epoxy thermosets. This published article deals with the synthesis of vanillin-based epoxy oligomers by the same process that is used industrially. It was found, as predicted by the Carothers' equation, that the reactants ratio controlled the length of the oligomers. The length in turn controlled the T_g of the oligomers, as predicted by the Flory-Fox model. Epoxy thermosets were then prepared and characterized; it was observed that the longer the oligomer, the lower the T_g.

In the **Chapter 5**, improving the versatility of bio-based epoxy formulations is still the main objective. One of the methods successfully employed in this submitted work was to use bio-based amine hardeners to prepared potentially fully bio-based thermosets and investigate their properties. One of the amine hardeners used was synthesized from vanillin and another was based on furfural. The second approach envisaged was to tune the properties of bio-based epoxy thermosets by using a vanillin-based tri-functional epoxy monomer that could act as a cross-link density modifier. All polymers prepared were compared to existing systems and structure-property relationships were established, widening the scope of solutions available to control the properties of bio-based epoxy thermosets. Importantly, potentially fully bio-based epoxy thermosets were prepared during this study.

The in-depths investigation of the previous chapters on the potential of using vanillin to prepare epoxy thermosets leads to the validation of such a concept. The **Chapter 6**, also a published work, takes a step forward by considering the sourcing of vanillin from lignin. Obtaining pure vanillin from lignin

depolymerization is a complex process, with a low-yield, and a high environmental cost. This high purity is not needed to prepare epoxy thermosets. The core idea of this work is that partially purified mixtures from the lignin-to-vanillin process could be used as raw materials, mitigating the drawbacks mentioned. Mixtures of phenolics modelling lignin depolymerization products have thus been prepared. They were submitted to a Dakin reaction to increase their phenolic content and then glycidylated to give mixtures of epoxy monomers. The reaction products were thoroughly characterized. It was found that these mixtures of epoxy monomers, once reacted with an amine hardener, gave epoxy thermosets with excellent thermo-mechanical properties, paving the way to bio-based epoxy thermosets from the lignin-to-vanillin process.

Perspectives

Looking back at the starting point of this Ph.D. work, the main general objective was to prepare thermosetting polymers from renewable resources. Epoxy thermosets were identified as priority target as the replacement of current monomers tackles both the issue of hazardous bisphenol A substitution and use of renewable compounds instead of petro-based ones. The resource chosen was bio-based aromatics, and more precisely vanillin for its numerous advantages such as industrial availability from wood. Work dealing mainly with vanillin-based epoxy thermosets was thus performed and the main general objective was met. However, answering questions led to raising others.

1. Future works

This section deals with questions that arose during this work and that should be further investigated. Additionally, from the conclusions drawn along the course of this thesis, it became clear that specific tasks of interest in the context of this work or for the field of bio-based polymers in general remained to be achieved. Future works should feature:

1. Using the compounds of the platform that were synthesized in **Chapter 2** to prepare other potentially bio-based polymers. For instance, the diamine compounds synthesized should be used as renewable amine hardeners for epoxy thermosets. However, the possibilities are not restricted to epoxy thermosets. Indeed, di(cyclic carbonates) should be used to prepare non-isocyanate polyurethanes as substituting toxic isocyanate monomers is another hot topic in the field of thermosets.
2. Performing the glycidylation of real mixtures of oxidation products from lignin depolymerization. The sequence of reactions described in **Chapter 6** should be employed on actual lignin depolymerization mixtures. The properties of the epoxy resins synthesized (for example the Epoxide Index) should be investigated. Epoxy thermosets should be prepared and their properties also investigated. Using partially refined mixtures from lignin depolymerization instead of using only one, fully isolated product such as vanillin could be profitable both economically and environmentally.
3. Developing industrial formulations adapted to specific industrial applications. Many parameters have to be taken into account when formulating. An important decision is the type of hardener to be used. A bio-based hardener like the ones developed in **Chapter 5** could be used. Amines have mainly been studied here but phenols, anhydrides, and many other can be employed, with or without catalysts. Physical properties of the formulation such as pot-life, viscosity, etc. have to be finely tuned. Parameters such as cross-link density and mechanical properties such as impact or abrasion resistance have to be investigated and optimized. Incorporation of additives (reactive diluents, toughenners, charges etc.) might be necessary.
4. Studying the polymerization reaction in more details, depending on the hardening system chosen. Indeed rheological and kinetics aspects, as well as parameters specific to the reaction such as activation energy or exothermicity, are important when it comes to industrial applications.
5. Investigating the potential of one-part epoxy formulations. Indeed, as mentioned in **Chapter 5**, the triglycidyl ether of vanillylamine synthesized was found to have self-polymerized upon storage to an insoluble material. A preliminary synthesis of the tetraglycidyl ether of bis(furfurylamine) A was also

performed and the product also self-polymerized. It was hypothesized that the tertiary amines born by these molecules acted as built-in catalysts for the anionic polymerization of epoxy groups, forming cross-linked thermosets. This hypothesis needs to be further investigated and if confirmed, the properties and polymerization kinetics of such one-part epoxy thermosets should be investigated.

6. Preparing vanillin-based thermoplastic epoxy polymers. Phenoxy resins are a class of high molecular weight thermoplastics obtained from the polyaddition reaction of diphenols with diepoxides. The same method and renewable monomers that were employed in **Chapter 4** to prepare vanillin-based oligomers should be used to synthesize vanillin-based phenoxy resins. Another way to prepare epoxy-based thermoplastic is to react a diepoxy monomer with a monofunctional amine. For instance, poly(hydroxyaminoethers) are prepared from the reaction of DGEBA with ethanolamine. Performing the same reaction with the vanillin-based diepoxy prepared in this work and a bio-based amine such as fufurylamine could provide bio-based thermoplastics with properties worth investigating.

2.Side-projects and perspectives

During this Ph.D. work, various academic collaborations on side-projects related to the use of renewable aromatics or to epoxy thermosets were also undertaken. These collaborations led to the publication of the following articles:

1. Aouf C, Nouailhas H, Fache M, Caillol S, Boutevin B, Fulcrand H. Multi-functionalization of gallic acid. Synthesis of a novel bio-based epoxy resin. European Polymer Journal. 2013; 49, 1185–1195
2. Ménard R, Negrell C, Fache M, Ferry L, Sonnier R, David G. From a bio-based phosphorus-containing epoxy monomer to fully bio-based flame-retardant thermosets. RSC Advances. 2015; 5, 70856–70867
3. Illy N, Fache M, Ménard R, Negrell C, Caillol C, David G. Phosphorylation of bio-based compounds: the state of the art. Polymer Chemistry. 2015; 6, 6257-6291

Outside of the academic scope, some of the diepoxy monomers synthesized in this work have been synthesized by the company Specific Polymers and are now commercially available on their **online catalog**. Some of the vanillin-based epoxy resins developed were tested at an R&D scale by various industrial companies and compared with their current solutions. All feedbacks on the properties of these vanillin-based epoxy resins were positive.

Projects directly derived from the findings of this Ph.D. work are underway. The first one is a collaboration project with the company Solvay, worldwide leader of vanillin production. The second one is the project of a pilot plant at a regional scale to depolymerize lignin to vanillin that would be integrated in a wood-to-lignin process already operational. This project would be partly financed by the French Environment Agency (ADEME).

Abstract

The background of this work is the synthesis of bio-based polymers, a very active area of research. Epoxy thermosets were chosen as target because of the double problematic of bisphenol A substitution and of renewable resources use. Thus, the aim of this work is to prepare bio-based epoxy thermosets and to evaluate their potential as substitutes of current formulations. In order to display good thermo-mechanical properties, these polymers have to be prepared from renewable aromatics. Indeed, aromatic cycles bring rigidity and thermal stability to the network. Vanillin is one of the only aromatic molecules available from biomass at an industrial scale. It is obtained from the alkaline oxidative depolymerization of lignin. Recently, the preparation of renewable polymers from vanillin has been intensively explored; a review on this subject was compiled. Vanillin served as a building-block to prepare a platform of derivatives bearing various functions. Di-amine, di-epoxy, or di-(cyclic carbonate) monomers – among others – were synthesized. The di-epoxy monomers prepared were cross-linked with a common amine hardener and the polymers obtained were characterized. Their thermo-mechanical properties were linked to the monomers structure. These potentially bio-based epoxy thermosets have properties comparable to the bisphenol A-based reference. In order to tune these properties, vanillin-based epoxy oligomers were synthesized by the same method as the one used industrially. The properties of these oligomers and of the thermosets prepared from them could indeed be modulated. Other means of controlling the properties were tested, like the preparation and polymerization of new bio-based amine hardeners, or of a vanillin-based, tri-functional epoxy monomer. The thermoset prepared from this last compound displayed better properties than the bisphenol A-based reference. Finally, a work more centered on the resource was performed. Mixtures of phenolic compounds modelling the products of the lignin-to-vanillin process were prepared. The use of such mixtures instead of pure vanillin could be advantageous both from an economic and an ecologic point of view. These mixtures were glycidylated, polymerized, and the materials obtained were characterized. The excellent properties displayed by these materials allow a potential integration of this strategy in a bio-refinery.

Keywords

epoxy ; bio-based ; vanillin ; polymer ; bisphenol A

Résumé

Ce travail s'inscrit dans le domaine très actif de la synthèse de polymères biosourcés. Les polymères époxy ont été choisis comme cible car ils présentent une double problématique de substitution du bisphénol A et d'utilisation de ressources renouvelables. L'objectif de ce travail est donc de préparer des polymères époxy biosourcés et d'évaluer leur potentiel en tant que substituts des solutions actuelles. Afin d'atteindre des propriétés thermo-mécaniques suffisantes, des composés naturels aromatiques doivent être utilisés. En effet, le cycle aromatique apporte rigidité et stabilité thermique au réseau. La vanilline est une des seules molécules aromatiques extraites de la biomasse qui soit disponible en quantités industrielles. Elle est obtenue par dépolymérisation en milieu basique et oxydant de lignine. Récemment, la préparation de polymères renouvelables à partir de vanilline a été intensivement explorée ; une revue sur ce sujet a été rédigée. La vanilline a servi de brique de base pour la préparation d'une plateforme de dérivés possédant des fonctionnalités variées. Des monomères diamine, diepoxy, ou dicyclocarbonate dérivés de vanilline ont – entre autres – été synthétisés. Les monomères diepoxy ont été réticulés avec un durcisseur amine commun et les polymères obtenus ont été caractérisés. Leurs propriétés thermo-mécaniques ont été reliées à la structure des monomères. Ces polymères époxy potentiellement biosourcés ont des propriétés comparables à la référence à base de bisphenol A. Afin de pouvoir moduler ces propriétés, des oligomères époxy de longueurs différentes ont été synthétisés à partir de vanilline selon la même méthode que celle utilisée industriellement. Ces oligomères et les polymères époxy qui en sont issus présentent effectivement des caractéristiques modulables. D'autres méthodes de contrôle des propriétés ont été testées, comme la préparation et la polymérisation de nouveaux durcisseurs aminés biosourcés, ou celle d'un monomère époxy trifonctionnel à partir de vanilline. Le polymère potentiellement biosourcé préparé à partir de ce dernier composé présente de meilleures propriétés que la référence à base de bisphénol A. Finalement, un travail portant plus sur la ressource a été réalisé. Des mélanges de composés phénoliques modélisant les produits obtenus lors du procédé de synthèse de vanilline à partir de lignine ont été préparés. L'utilisation de tels mélanges au lieu de la vanilline pure serait bénéfique autant économiquement qu'écologiquement. Ces mélanges ont été glycidylés, puis polymérisés, et les matériaux obtenus caractérisés. Les excellentes propriétés obtenues permettent d'envisager d'intégrer ce débouché à une bioraffinerie.

Mots-clés

Epoxy ; biosourcé ; vanilline ; polymère ; bisphénol A