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POUR OBTENIR LE GRADE DE

DOCTEUR DE
L'UNIVERSITÉ DE BORDEAUX

ÉCOLE DOCTORALE DES SCIENCES CHIMIQUES

SPÉCIALITÉ: Polymères

Par **Etienne SAVONNET**

**DEVELOPMENT OF BIO-BASED EPOXY THERMOSETS FOR
AEROSPACE LAUNCHERS**

Développement de réseaux époxydes biosourcés pour lanceurs aérospatiaux

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Soutenue le 16 février 2018

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Résumé

Les liaisons collées jouent un rôle prépondérant dans l'industrie aéronautique et spatiale. Le collage permet de remplacer efficacement les liaisons dites « mécaniques » de type rivetage et boulonnage, en améliorant les propriétés des surfaces assemblées. Les liaisons collées permettent notamment d'améliorer la distribution des contraintes, l'étanchéité et l'absorption des chocs au travers du joint de colle. De plus, cette technologie permet de réduire drastiquement le poids des structures et ouvre le champ des possibles à la conception de nouveau design. Afin de répondre parfaitement au cahier des charges, le joint de colle doit être constitué de matériaux pouvant répondre à de très fortes contraintes, notamment en termes de résistances thermiques et mécaniques. Pour cela, les matériaux thermodurcissables représentent la catégorie de polymères la plus adaptée pour ce type d'application. Parmi cette catégorie de matériaux, les réseaux époxydes généralement obtenus par réticulation d'un pré-polymère époxydé (aussi appelé résine) en présence d'un agent de réticulation, sont les plus largement utilisés. Aujourd'hui, plus de 75% des réseaux époxydes sont dérivés du Bisphénol-A (BPA).¹ Cependant, le BPA est soumis à des très fortes régulations en Europe car très récemment, l'agence européenne des produits chimiques (ECHA) a classé le BPA comme « substance chimique extrêmement préoccupante » en tant que perturbateur endocrinien. Par conséquent, tout industriel, importateur ou fournisseur se voit dans l'obligation de répertorier et de labéliser chacun de ses produits pouvant être constitués de BPA, comme toxique pour la reproduction catégorie CMR 1B. L'objectif des institutions est donc de réduire l'utilisation et d'encourager la substitution de ces substances chimiques. D'autre part, le BPA est une molécule produite à partir de la pétrochimie, c'est-à-dire à partir de carbone fossile comme le charbon, le pétrole et le gaz naturel. Dans un contexte de raréfaction des ressources fossiles, de la volatilité des cours du pétrole et des préoccupations environnementales liées au réchauffement climatique, l'utilisation d'une source de carbone renouvelable est primordiale. Tous ces attributs entraînent donc un risque élevé d'obsolescence du BPA.

Ainsi, le concept de bioraffinerie peut être une solution pérenne pour répondre à la fois aux problématiques environnementales et sanitaires. Par analogie avec les raffineries conventionnelles, les bioraffineries sont des installations industrielles intégrant des procédés de transformation de la biomasse en bioénergie, en production alimentaire et en molécules à valeurs ajoutées pour la chimie (Figure 1). La biomasse représente l'ensemble de la matière organique, qu'elle soit d'origine végétale ou animale. Contrairement aux ressources fossiles résultant de la transformation du carbone d'origine végétale et animale datant de plusieurs

millions d'années, l'utilisation de la biomasse ne déséquilibre pas le cycle de régénération du carbone. En effet, cette dernière constitue une source de carbone ayant un temps de régénération court évalué à quelques dizaines d'années.^{2,3}

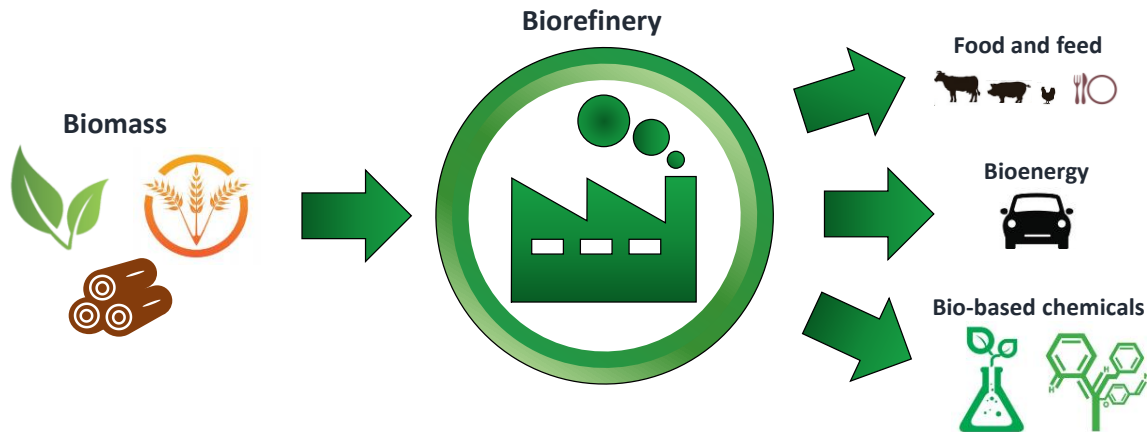


Figure 1: Représentation schématique du concept de bioraffinerie

De cette manière, la réduction de l'empreinte environnementale et la préservation de la santé des opérateurs sont des moteurs pour le développement d'alternatives biosourcées non toxiques. C'est dans ce contexte que les travaux de thèse ont été réalisés au Laboratoire de Chimie des Polymères Organiques (LCPO) et financés par ArianeGroup dans le cadre du Groupement d'Intérêt Scientifique « *Structural Assembly of Multi-Materials and Biosourced Alternatives* » (GIS SAMBA). Les objectifs de ces travaux sont donc de développer des précurseurs époxydés non toxiques, à partir de ressources renouvelables, et permettant l'accès à des réseaux possédant des propriétés thermomécaniques au moins similaires au réseau référence issu du diglycidyléther de bisphénol-A (DGEBA).

La stratégie employée pour répondre à cette problématique est de partir de ressources naturelles issues de la biomasse, tel que la lignine (Figure 2). La lignine est le second biopolymère le plus abondant sur terre et un des principaux constituants du bois, après la cellulose. Ce biopolymère est potentiellement très intéressant car sa déconstruction permet de faire de la lignine l'une des principales sources de molécules aromatiques biosourcées (source de phénols).

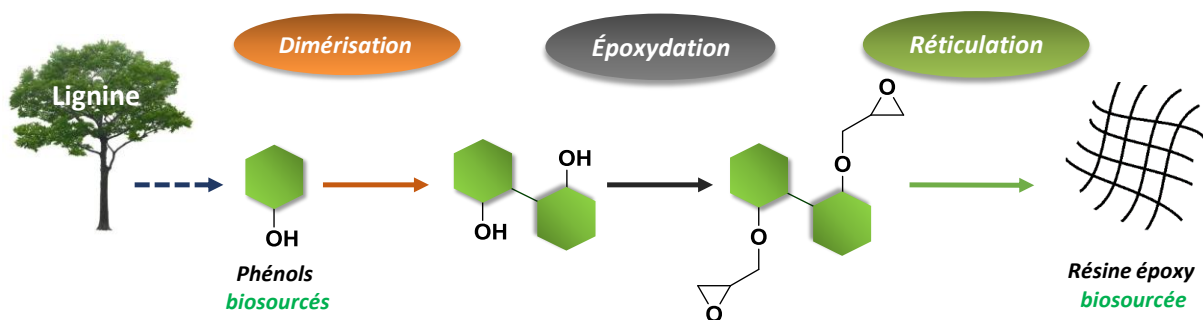


Figure 2 : Stratégie employée pour la synthèse de résines époxy biosourcées

Ces travaux de thèse sont ainsi divisés en quatre chapitres. Le **Chapitre 1** de ce manuscrit est consacré à l'état de l'art des précurseurs époxydés synthétisés à partir de ressources conventionnelles et renouvelables. Les huiles végétales, les terpènes, les tanins, les sucres, la lignine sont des sources de carbone biosourcé et peuvent être utilisées comme base pour la synthèse de précurseurs époxydés (Figure 3).

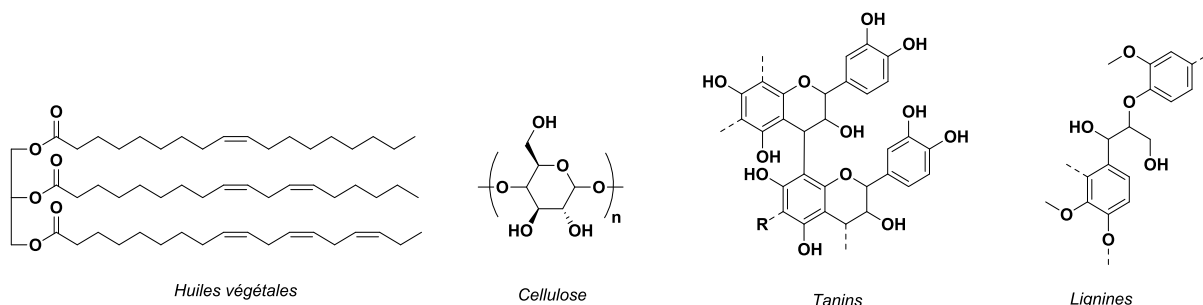


Figure 3 : Principales sources de carbone biosourcé pour la synthèse de monomères époxydés

Les huiles végétales sont considérées comme l'une des catégories les plus importantes en raison de leur abondance et de leur faible prix.^{4,5} Elles sont constituées de triglycérides possédant de longues chaînes carbonées insaturées. L'intérêt majeur de ces huiles réside dans la conversion des insaturations en groupement époxy par oxydation. Ainsi, de nombreuses études ont permis de développer, notamment à partir d'huiles de soja ou de lin époxydées, des systèmes réticulés biosourcés.^{6,7} Néanmoins, la structure aliphatique des huiles végétales ne permet pas l'obtention de matériaux possédant des propriétés thermomécaniques suffisamment élevées pour répondre à des applications hautes performances. La plupart des débouchés industriels restent ainsi limités à des applications en tant qu'additifs ou pour revêtements de surface.^{8,9}

D'autres études ont permis de souligner l'intérêt de bioressources, comme la colophane, les dérivés du glucose ou le cardanol, dans la synthèse de réseaux époxydes.¹⁰⁻¹² Ces dernières, en raison de leurs structures cycliques et/ou aromatiques, sont capables d'offrir des réseaux plus rigides, permettant d'obtenir des propriétés thermomécaniques supérieures à celles obtenues à partir des huiles végétales. Les tanins et la lignine représentent également une source de carbone biosourcé à fort potentiel.¹³⁻¹⁶ En effet, ces structures polyphénoliques peuvent être converties en composés pluri-époxydés. Les réseaux thermodurcissables biosourcés ainsi formés présentent des températures de transition vitreuse et des propriétés mécaniques similaires à ceux des réseaux équivalents issus de la référence DGEBA. Cependant, le principal frein aux développements industriels de ces nouveaux précurseurs biosourcés réside dans l'hétérogénéité et la disponibilité des structures naturelles. Ainsi, seule une substitution partielle du DGEBA est envisageable à partir de ces dérivés biosourcés. Un intérêt pour des structures chimiques biosourcées plus simples et mieux définies a alors été mis en évidence. De nombreuses études,

sur la synthèse de monomères époxydés à partir de la vanilline, ont ainsi démontré un fort potentiel pour le remplacement des composés époxydés conventionnels.¹⁷⁻¹⁹ En effet, la vanilline est la seule molécule aromatique, obtenue à partir de ressources renouvelables, produite à l'échelle industrielle.²⁰ Depuis 1962, la bioraffinerie Borregaard a développé un procédé industriel permettant, à partir de lignine, de produire chaque année environ 1500 tonnes de vanilline biosourcée. Par conséquent, la synthèse de monomères époxydés, dérivés de la vanilline, suscite un intérêt particulier et mérite une étude plus approfondie. De précédents travaux effectués au LCPO, sur le couplage oxydatif de molécules phénoliques, ont permis de synthétiser une bioplateforme de substrats potentiellement issus de la lignine. En effet, Llevot *et al.* ont développé un procédé de couplage enzymatique, utilisant la laccase *Trametes versicolor* pour produire des dimères de la vanilline, du méthyl vanillate, d'eugénol et du 2,6-diméthoxyphénol.²¹⁻²³ Le **Chapitre 2** de ce manuscrit est consacré à la synthèse de précurseurs époxydés, dérivés de ces substrats biphenoliques. Une voie de synthèse a été développée au laboratoire permettant d'époxyder ces composés phénoliques en présence d'épichlorhydrine, d'un agent de transfert de phase et d'une base. Il a ainsi été possible de synthétiser une bioplateforme de 11 précurseurs époxydés (Figure 4).

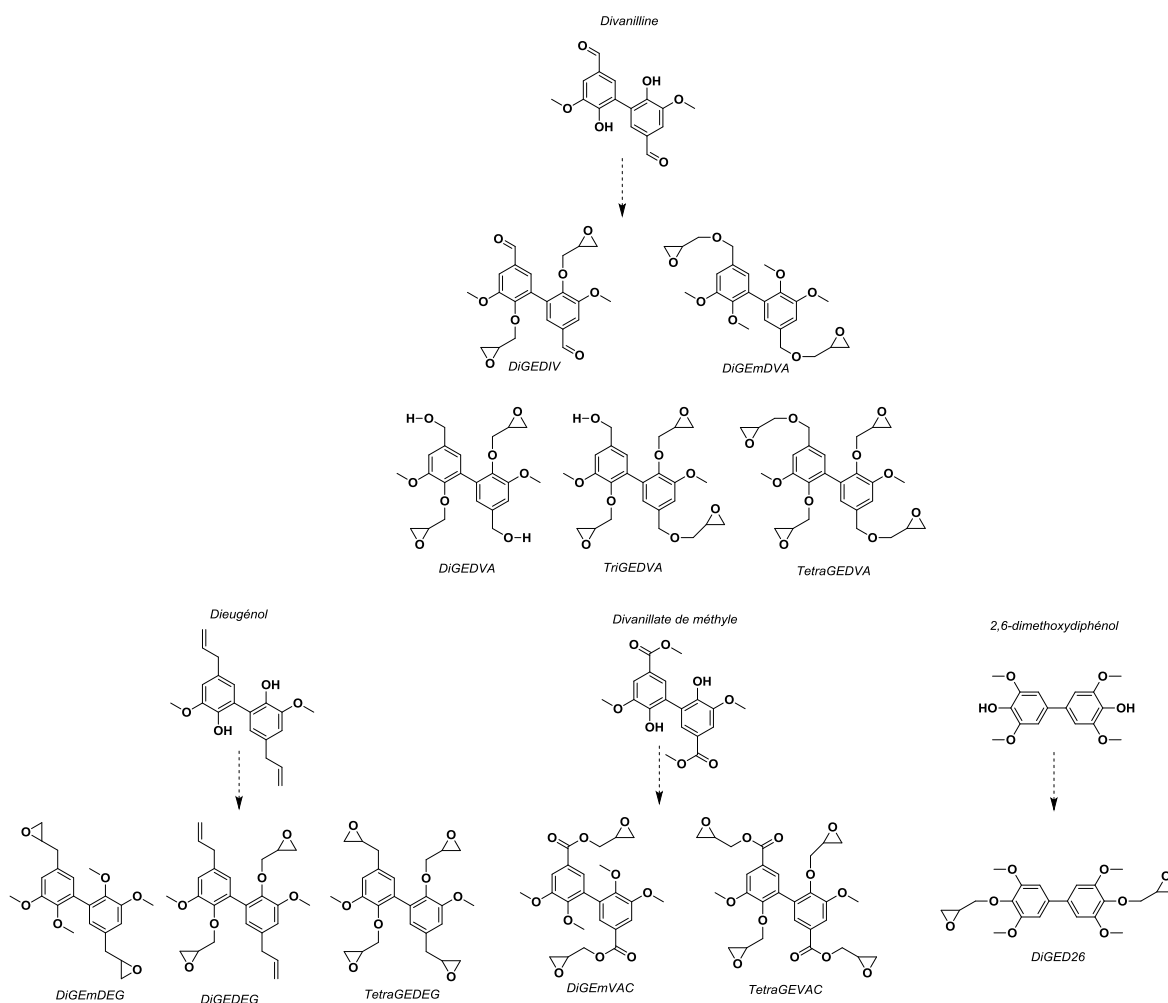


Figure 4: Bioplateforme de monomères époxydés dérivés de phénols potentiellement biosourcés

Parmi ces précurseurs, l'alcool divanillique (DVA), obtenu par réduction des fonctions aldehyde de la divanilline, a suscité un intérêt particulier. En effet, la réaction d'époxydation conduit à l'obtention de mélanges d'espèces pluri-époxydées : le diglycidyléther de l'alcool divanillique (DiGEDVA), le triglycidyléther de l'alcool divanillique (TriGEDVA) et le tétraglycidyléther de l'alcool divanillique (TétraGEDVA). Après purification par chromatographie flash, chacune des espèces de ce mélange a été isolée et caractérisée. Le DiGEDVA est un liquide extrêmement visqueux et difficilement manipulable, alors que le TetraGEDVA se trouve sous la forme d'un liquide de faible viscosité. Or, l'obtention de précurseurs époxydés de faible viscosité est un paramètre primordial pour la mise en œuvre de la résine époxy, avant l'étape de réticulation. De plus, le procédé de purification utilisé est difficilement transposable à une échelle industrielle. Ainsi, une étude approfondie des conditions de synthèse a permis d'identifier des paramètres expérimentaux permettant de mieux contrôler la formation sélective des différentes espèces pluri-époxydées. Des mélanges de compositions variées et possédant des propriétés rhéologiques contrôlables ont ainsi été obtenus. D'autres précurseurs époxydés ont également été préparés à partir de l'acide divanillique, du di-eugénol et du 2,6-diméthoxydiphénol. En règle générale, les polyglycidyléthers ont été synthétisés avec un bon rendement. Néanmoins, comme évoqué précédemment, un des paramètres clés dans la formulation de résines époxy concerne la rhéologie de ces systèmes. Or, certains des monomères époxydés synthétisés se sont révélés être des solides avec des points de fusion supérieurs à 120 °C. L'état cristallin de ces dérivés constituant un sérieux obstacle dans le développement des formulations, leur oligomérisation a été étudiée. Ainsi, des oligomères amorphes de différentes masses molaires ont été obtenus avec succès permettant d'ajuster les propriétés rhéologiques de certains de ces systèmes.

Dans la continuité du chapitre précédent, le **Chapitre 3** consiste en l'étude et la caractérisation des propriétés thermomécaniques des réseaux de polyglycidyléther dérivés de l'alcool divanillique : le DiGEDVA, le TriGEDVA, le TétraGEDVA ainsi que leurs mélanges. Ces monomères ont été sélectionnés pour leur disponibilité, leur processabilité et leur polyfonctionnalité. Les réseaux sont obtenus en mélangeant le monomère époxydé avec un agent de réticulation, possédant des fonctions antagonistes de type amine par exemple. Le durcisseur joue un rôle prédominant dans l'obtention d'un matériau possédant de bonnes propriétés thermomécaniques car il fait littéralement partie de la structure finale du réseau (Figure 5). Parmi tous les durcisseurs disponibles, nous avons décidé de travailler principalement avec les diamines. Dans une première partie, l'isophorone diamine (IPDA) a été choisie comme agent de réticulation. Ce durcisseur est une amine cyclo-aliphatique largement décrit dans la littérature scientifique.

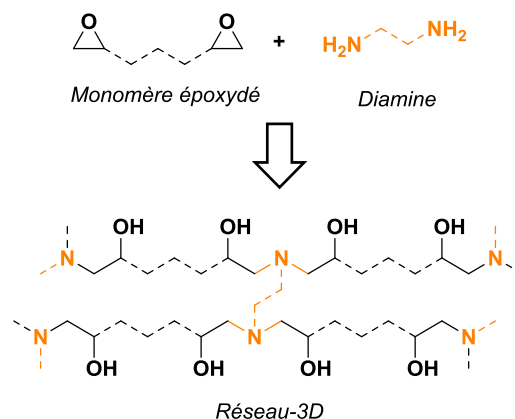


Figure 5: Représentation schématique de la formation de réseau-3D

L'analyse et la caractérisation des réseaux biosourcés obtenus avec l'IPDA ont présenté des propriétés thermomécaniques similaires voire bien supérieures à celles obtenues avec la référence de type DGEBA. La fonctionnalité accrue du TriGEDVA et du TetraGEDVA permet ainsi d'obtenir des réseaux plus denses avec des températures de transition vitreuse (T_g) plus élevées. En effet, les polyglycidyléthers de DVA ont permis de former des réseaux avec des T_g comprises entre 140 et 200 °C, alors que le réseau conventionnel réticulé dans les mêmes conditions a présenté une T_g de 155 °C.

Dans un second temps, les polyglycidyléthers de DVA ont été réticulés avec la diaminodiphénylsulfone (DDS). La DDS est une amine aromatique largement utilisée dans le domaine aéronautique, car sa structure aromatique permet d'améliorer les propriétés des réseaux formés. Différentes analyses thermiques et mécaniques (DSC, TGA, DMA et essais tractions) ont permis de caractériser et de comparer les réseaux biosourcés avec ceux obtenus à partir du système DGEBA/DDS. Les réseaux thermodurcissables biosourcés ont révélé des températures de dégradation similaires, des modules de Young compris entre 1,3 et 1,9 GPa, ainsi que des T_g allant de 204 à 312 °C, alors que le réseau de référence possède une T_g de 206 °C. De plus, des tests au feu réalisés sur les réseaux biosourcés ont démontré une aptitude à limiter la propagation de flamme. Cette propriété remarquable a pu être expliquée par la formation de coke lors de la dégradation du produit. Il s'est avéré que les réseaux biosourcés issus de la vanilline possèdent des taux de coke résiduel trois fois supérieurs (>50 %) à ceux des réseaux obtenus avec le système DGEBA/DDS.

A partir de ces résultats, plusieurs formulations basées sur le système polyglycidyléthers de DVA/DDS ont été identifiées pour des applications en tant que matériaux ablatifs composites. Ce dernier consiste en une matrice de polymères associée à des renforts, tels que des charges ou des fibres de carbone. Dans le cas des matériaux composites ablatifs, l'énergie thermique reçue conduit à la pyrolyse de la matrice et à la formation d'un résidu carboné appelé coke. La

proportion massique du polymère transformé en carbonisation est critique et doit être supérieure à 50% pour être efficace en tant que protection thermique. À cet effet, ArianeGroup a mis au point un procédé d'imprégnation des fibres de carbone sans utiliser de solvant (Figure 6). Ce procédé nécessite des conditions précises, notamment en termes de rhéologie de la résine époxy.

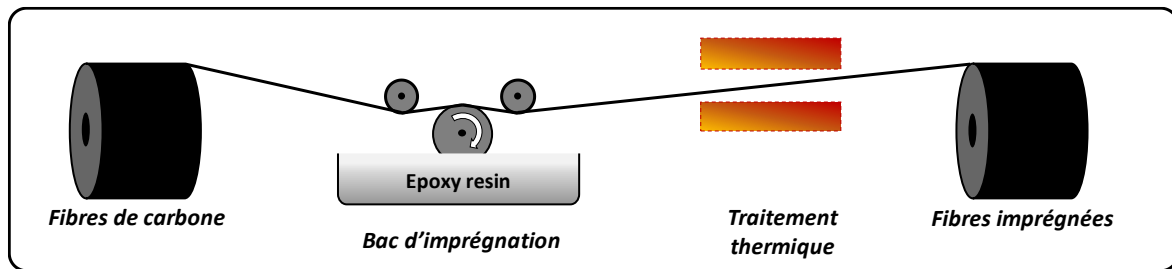


Figure 6: Représentation schématique de la ligne d'imprégnation de fibres de carbone au sein d'ArianeGroup

Plusieurs formulations ont ainsi été identifiées pour répondre aux spécifications de la ligne d'imprégnation des fibres de carbones et présentent des propriétés prometteuses pour une application en tant que matériaux composites ablatifs. Néanmoins, des investigations complémentaires sur la chaîne d'imprégnation de fibres de carbone, nécessitant au moins 1 kg de produit, sont nécessaires pour confirmer ces résultats.

Ces formulations basées sur le système polyglycidyléthers de DVA/DDS ont également été testées pour une application en tant qu'adhésifs structuraux. ArianeGroup s'intéresse à ce type de matériaux, car ils sont utilisés dans la structure de lanceurs aérospatiaux et militaires. Ils peuvent, par exemple, être utilisés pour lier ensemble un réservoir composite à une jupe de protection métallique (Figure 7). Le réservoir est destiné à recevoir et stocker le carburant tandis que la jupe assure la répartition des efforts entre les différents modules des véhicules aérospatiaux.

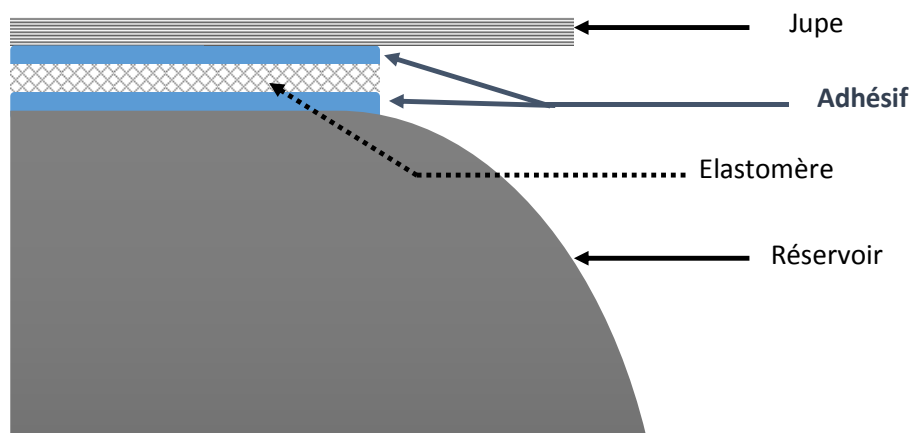


Figure 7: Collage structural du réservoir à la jupe d'un lanceur aérospatial

La formulation d'un adhésif est complexe. En plus d'un monomère réactif et d'un agent de réticulation, la formulation nécessite l'incorporation d'autres éléments, comme des charges minérales ou organiques, des plastifiants, des stabilisants. Néanmoins, des tests en cisaillement, sur des éprouvettes aluminium assemblées grâce à un joint de colle, ont permis de caractériser le comportement en tant qu'adhésif des résines biosourcées préparées. Les systèmes polyglycidyléthers de DVA/DDS ont ainsi présenté des résistances en cisaillement similaires à celles obtenus avec les réseaux DGEBA/DDS. Cependant, certaines limitations concernant notamment l'épaisseur du joint de colle sont à prendre en compte. La réalisation de nouveaux tests avec un meilleur contrôle du joint adhésif est nécessaire afin de mieux évaluer ces systèmes biosourcés pour des applications adhésives.

Enfin, le **Chapitre 4** est consacré à la synthèse de diamines aromatiques biosourcées pouvant être utilisées comme agents de réticulation dans des réactions de polyaddition avec des monomères époxydés. La première section de ce chapitre a consisté en une étude bibliographique des agents de réticulation de type amine. Une analyse bibliographique des différentes voies d'accès aux amines primaires a également été réalisée et a permis d'identifier plusieurs voies de synthèse applicables aux dérivés de la divanilline et de l'acide divanillique (Figure 8).

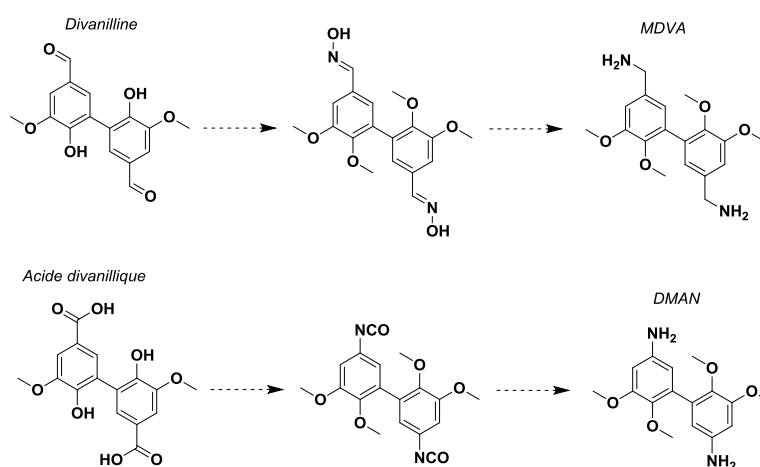


Figure 8 : Synthèse de diamines aromatiques biosourcés à partir de la divanilline et de l'acide divanillique

La première voie de synthèse envisagée a consisté en la réduction du dioxime, obtenue à partir de la divanilline. La réduction a été réalisée sous pression d'hydrogène en présence de Nickel de Raney et a permis d'obtenir la divanillylamine méthylée (MDVA). Une étude préliminaire des propriétés thermiques des réseaux obtenus par réticulation du DGEBA avec la MDVA a été réalisée. Malheureusement, la caractérisation par DSC n'a montré qu'un faible exotherme de réticulation et aucune température de transition vitreuse n'a pu être clairement observée. En parallèle, la synthèse de la 3,4-diméthoxyaniline (DMAN) a été réalisée par ré-arrangement de

Curtius de l'isocyanate dérivé de l'acide divanillique. Cependant, l'amine correspondante n'a pas pu être isolée efficacement. Néanmoins, une fraction non purifiée de DMAN a été utilisée pour réticuler la résine DGEBA. Les propriétés thermomécaniques du réseau ainsi formé présente une température de transition vitreuse de 176 °C contre 204 °C pour le système DGEBA/DDS classique. Le réseau obtenu a également révélé un taux de coke deux fois supérieur à celui du système conventionnel DGEBA/DDS. De plus, cette diamine DMAN a également été utilisée pour réticuler le TétraGEDVA. Un réseau 100 % biosourcé et présentant une température de transition vitreuse de 212 °C et un taux de coke supérieur à 48 %, a été obtenu. La synthèse de nouveaux agents de réticulation de type amine a été étudiée à partir de précurseurs phénoliques biosourcés dérivés de la vanilline. Néanmoins, l'optimisation des voies de synthèse décrites est encore nécessaire afin de mieux évaluer le potentiel de ces nouvelles diamines aromatiques biosourcées.

L'objectif de cette thèse était de développer de nouvelles résines époxy biosourcées ayant des propriétés au moins similaires à la référence DGEBA. La première partie de ce travail a ainsi permis de synthétiser une bioplateforme de monomères époxydés à partir de phénols (vanilline, méthyl vanillate, eugénol et 2,6-diméthoxyphénol) potentiellement issus de la lignine. La seconde partie de ce travail a consisté en la synthèse de réseaux époxydés à partir de ces monomères biosourcés. Les matériaux obtenus ont ainsi révélé des propriétés thermomécaniques remarquables bien supérieures à celles obtenues avec les systèmes conventionnels basés sur le DGEBA. Enfin, une étude préliminaire de la synthèse de diamines biosourcées, pouvant être utilisées comme agents de réticulation, a montré des résultats prometteurs pour l'obtention, à terme, de réseaux époxydés 100 % biosourcés.

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List of abbreviations

Techniques

DMA: Dynamic Mechanical Analysis

DSC: Differential Scanning Calorimetry

ESI: ElectroSpray ionization

FTIR: Fourier Transform Infrared spectroscopy

HPLC: High Performance Liquid Chromatography

HSQC: Heteronuclear Single Quantum Chromatography

NMR: Nuclear Magnetic Resonance spectroscopy

SEC: Size Exclusion Chromatography

SEM: Scanning electron microscopy

TGA: Thermogravimetric analysis chromatography

TLC: Thin Layer Chromatography

Chemicals

BPA: Bisphenol A

CDCl₃: Deuterated chloroform

DCM: Dichloromethane

DDS: Diaminediphenyl sulfone

DETA: Diethylenetriamine

DGEBA: Diglycidylether of bisphenol-A

DMF: Dimethylformamide

DMSO-d₆: Deuterated dimethylsulfoxide

EtOAc: Ethyl acetate

EtOH: Ethanol

HCl: Hydrochloric acid

IPDA: Isophorone diamine

K₂CO₃: Potassium carbonate

KOH: Potassium hydroxide

mCPBA: *meta*-Chloroperoxybenzoic acid

MeCN: Acetonitrile

MeOH: Methanol

NaOH: Sodium hydroxide

NaOAc: Sodium acetate

THF: Tetrahydrofuran

TEBAC: Triethylbenzylammonium chloride

TEA: Triethylamine

Characteristic parameters:

AHEW: Amine Hydrogen Equivalent Weight

ΔH : Enthalpy of reaction

D: Polydispersity

E': storage modulus

E'': loss modulus

E_a: Activation energy

EEW: Epoxide Equivalent Weight

\overline{M}_n : Number average molar mass

\overline{M}_w : Mass average molar mass

RT: Room Temperature

T: Temperature

T_{5%}: Temperature corresponding to 5 wt% loss

T_g: Glass transition temperature

T_m: Melting temperature

T _{α} : Alpha transition temperature

Others:

CMR: Carcinogenic, Mutagenic, Reprotoxic

REACH: Registration, Evaluation and Authorization and restriction of Chemical

General Introduction

Adhesive bonding of structural parts play a significant role in the aerospace industry. This technology is of critical importance in this area, because it allows improving the properties of the bonded structure, especially compared with mechanical bonding, such as riveting or bolting. Adhesive technologies improve the stress distribution, the sealing, the noise and vibration damping across the bonded joint. In addition, this technology enables the effective reduction of weight and the design of new structures.^{1,2} To fulfill the specifications of bonding structural parts, thermosetting polymers are usually necessary. According to the IUPAC definition, thermosets are polymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing under the action of external stimuli, such as heat or radiation. Among them, the epoxy networks, generally obtained by crosslinking of an epoxidized prepolymer (also called resin) in the presence of a curing agent, are the most widely used. Today, 75% of the epoxy polymers are derived from Bisphenol-A (BPA).³ However, BPA is subject to strong regulations, particularly because of its recent classification as a chemical of very high concern by European Chemical Agency (ECHA). Consequently, any industrial, importer or supplier is obliged to list and label each of its products consisting of BPA as toxic for reproduction category CMR 1B. The objective of the institutions is thus to reduce the use and encourage the development of alternatives to this chemical. In addition, BPA is a molecule produced from petrochemicals, which means from fossil carbon such as coal, oil and natural gas. In a context of dwindling fossil resources, volatile prices and environmental concerns related to the global warming, the use of renewable carbon is crucial.⁴ All these attributes entail a high risk of obsolescence of BPA.

Thus, the biorefinery concept can be a sustainable solution to meet both environmental and health issues. By analogy with petroleum refineries, biorefineries are industrial plants integrating processes for transforming biomass into bioenergy, food production and value-added molecules (Figure 9). Biomass represents all organic matter, whether of plant or animal origin. Unlike fossil resources resulting from the transformation of plant and animal carbon over millions of years, the use of biomass does not unbalance the carbon regeneration cycle. Indeed, the latter constitutes a carbon source with a short regeneration time frame of few decades.^{5,6}

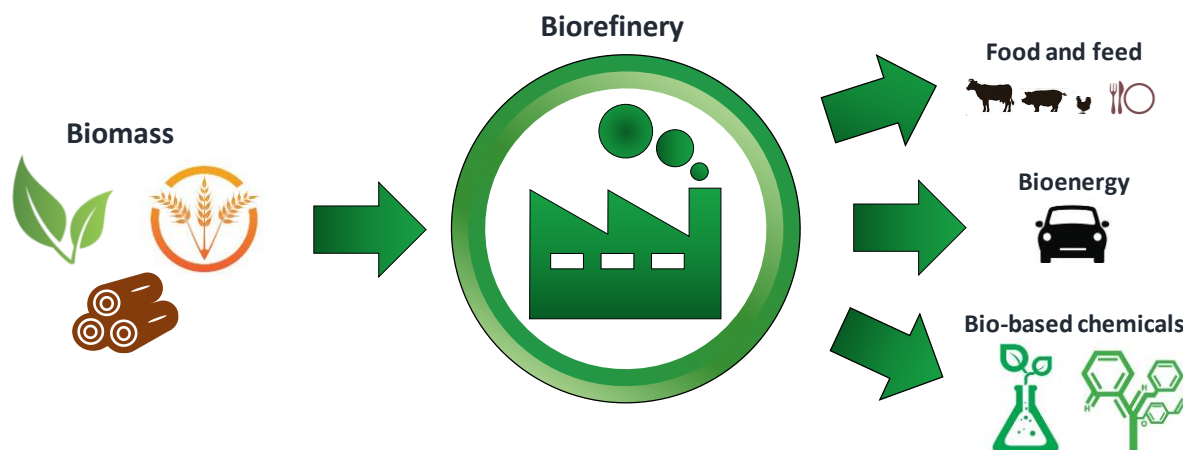


Figure 9: Schematic representation of the biorefinery concept

In this way, staying ahead of new regulations, reducing the environmental footprint and above all preserving the health of operators are driving forces to develop bio-based and non-toxic alternatives. It is in this context that this thesis was conducted in the Laboratoire de Chimie des Polymères Organiques (LCPO) and financially supported by ArianeGroup in the framework of the project « *Structural Assembly of Multi-Materials and Biosourced Alternatives* » (GIS SAMBA). The aim of this work is to develop a new epoxy thermoset being bio-based, non-toxic and exhibiting similar thermomechanical properties to DGEBA-based references.

The strategy used to overcome this issue is to start from natural resources derived from biomass, such as lignin (Figure 10). Lignin is the second most abundant biopolymer on earth and one of the main constituents of wood, after cellulose. This biopolymer is very interesting because its deconstruction makes the lignin one of the main sources of bio-based phenolic molecules.

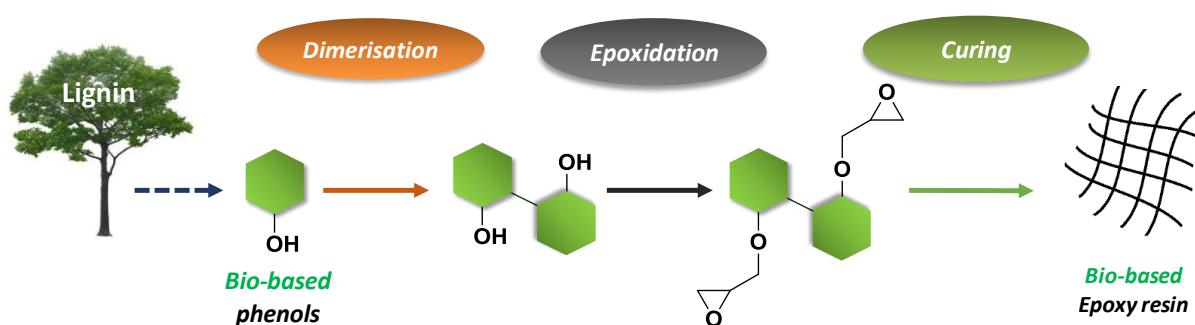


Figure 10: Overview of the strategy for the synthesis of bio-based epoxy resins

The manuscript is divided into four chapters. After an introduction dealing with structural adhesives and more precisely epoxy thermosets, the first chapter is dedicated to a literature review of bio-based epoxy monomers. This section describes the synthesis of these bio-based

epoxy monomers and the thermomechanical properties of their networks are discussed and compared with DGEBA-based references.

Previous work carried out at the LCPO, on the oxidative coupling of phenolic molecules, made available a bioplateform of phenolic substrates potentially derived from lignin. Indeed, Llevot *et al.* developed an enzymatic coupling process, using *Trametes versicolor* laccase to produce dimers of vanillin, methyl vanillate, eugenol and 2,6-dimethoxyphenol.⁷⁻⁹ The Chapter 2 of this manuscript is devoted to the synthesis and the characterization of polyglycidylethers prepared from these biphenolic molecules.

In the continuity of the previous chapter, Chapter 3 consists of the study and thermomechanical properties of polyglycidylethers networks derived from divanillyl alcohol (DVA): diglycidylether of DVA (DiGEDVA), triglycidylether of DVA (TriGEDVA), tetraglycidylether of DVA (TetraGEDVA) and their mixtures. These monomers have been selected for their availability, their processability and their polyfunctionality. The networks are obtained by mixing these epoxy monomers with amine-type curing-agent. The thermomechanical properties of DVA-based thermosets will be discussed and compared with DGEBA-based thermosets.

Finally, the Chapter 4 is dedicated to the synthesis of bio-based aromatic diamines from vanillin derivatives. After a literature survey on the bio-based amine-type curing agents and a description of the different synthetic pathways to primary amines, this section describes the synthesis of bio-based aromatic diamines and their use as curing-agent in polyaddition reaction with epoxy monomers. The preliminary characterization of the thermal properties of epoxy networks synthesized will be discussed.

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Chapter 1: State of the Art

Keywords: Structural adhesives, epoxy resins, bisphenol-A, DGEBA, epichlorohydrin, thermosets, bio-based polymers

Mots-clés: Adhésifs structuraux, réseaux polyépoxyde, bisphénol-A, DGEBA, épichlorhydrine, réseaux thermodurcissables, polymères bio-sourcés

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I. Structural Adhesives

I.1 Overview

Over the past 70 years, adhesive technologies have gained more and more importance due to the development of new performing polymeric materials. Today, the Europe adhesives market was estimated at USD (United States Dollar) 13 billion and world consumption is projected to exceed 8,2 million tons in the world by 2021.¹ Adhesives can be designed for many applications like weak temporary adhesion to very high performance for structural systems. From footwear, packaging, woodworking to construction and transportation, this versatility gives to adhesive a strong industrial application potential. This market is shared by suppliers such as 3M, Henkel, Arkema, The Dow Chemical Company and Solvay.

According to the American Section of the International Association for Testing Materials (ASTM) definition, adhesive is a substance able to hold material together by surface attachment. Structural adhesives distinguish from other adhesives by bearing very high loads and constraints.² Typically, the joints will have bond strengths of greater than 6 MPa.³ They are literally part of the structure of their assemblies and can therefore compete with old mechanical systems, such as bolt or rivet. Structural bonding are designed to meet specific requirements and offer numerous advantages like excellent mechanical performances, efficient stress distribution, good thermal properties, flexibility and vibration dampers.⁴ Adhesive assemblies are also weight-saving and very cost-effective in comparison to mechanical bonding.⁵ Among the various structural adhesives commercially available, polyurethanes, epoxy-, acrylic- and cyanoacrylate-based polymer materials represented in 2016 the most important families in terms of volume (Figure 11).

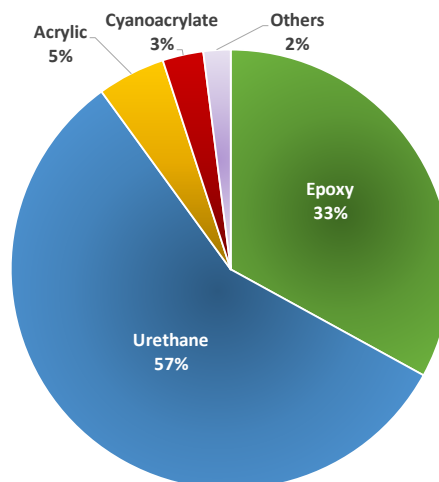
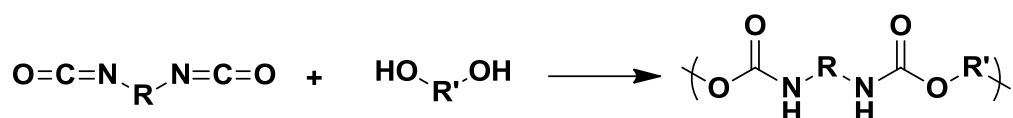


Figure 11: Global structural adhesive market in 2016^{6,7}

For structural applications, adhesives are generally 3D-materials known as thermosets. Contrarily to thermoplastics, cross-linked polymers exhibit a tridimensional structure able to support high-performance specifications. However, some thermoplastic structural adhesives such as cyanoacrylates are also strong challengers in certain market segments (see later in this chapter).²

I.2 Polyurethane structural adhesives

Polyurethanes are the major type of structural adhesive. The latter represent more than half of the global structural adhesives market in terms of volume in 2016. PUs are characterised by the presence of urethane linkages in their backbone and are generally obtained from the polyaddition of pluri-isocyanates and polyols as represented in Scheme 1.



Scheme 1: Synthesis of linear polyurethane from a di-isocyanate and a diol

PU structural adhesives can be found as one- or two-component systems. Two-component systems are generally used for high performance applications. Overall, two-component systems consist of one part containing a reactive isocyanate-terminated prepolymer and a second part generally composed of polyols. Usually, two-component PUs are cured at room temperature and then post-cured at more elevated temperature to provide the optimal bond strength.² To obtain cross-linked materials, polyfunctional monomers are required to provide the formation of a 3D-network. Polyurethanes are typically formulated as to produce segmented polymer consisting of hard and soft segments (Figure 12).

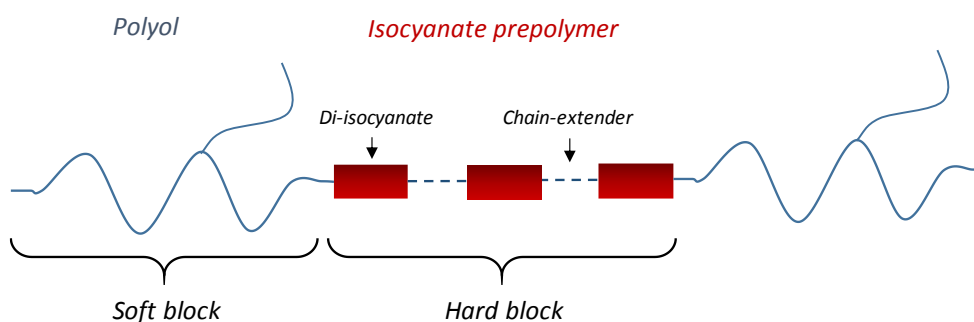


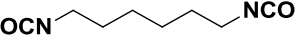
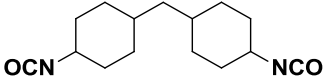
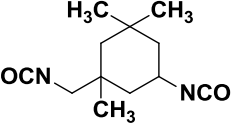
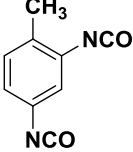
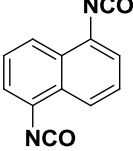
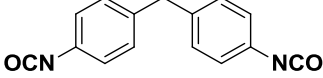
Figure 12: Schematic representation of polyurethane

Hard segment is usually composed of isocyanate-terminated prepolymer. These latter are generally obtained by reacting di-isocyanate with chain extenders, such as diol or diamine. There is few di-isocyanates industrially available, which display either aliphatic or aromatic structure (Table 1). In contrast, soft blocks consist in long-chain of polyols based on polyester

(PEP), polyether (PETP), polybutadiene, polyisobutylene or polycarbonate.⁸ As there is much larger range of polyol structures, their selection is a key factor to tune the physical properties of the final PU. For example, high molecular weight PEP with long chain lead to flexible PU. On the other hand, highly branched or low molecular weight PEP result in rigid PU with good heat and chemical resistance. However, PEP suffer from hydrolysis due to the presence of ester groups, which can lead to a decrease of the mechanical properties of PU.

Finally, their cost-efficient and ability to bond a wide variety of materials give them a competitive advantage over other product types. They provide excellent low-temperature performance, fast curing process and exhibit strong bonding on many substrates. However, polyurethane structural applications are limited due to their poor elevated-temperature performance, low solvent resistance and moisture sensitivity.^{2,3}

Table 1: Structure of various diisocyanates industrially available

Name	Structure
Hexamethylene diisocyanate (HDI)	
Hydrogenated MDI (H₁₂MDI)	
Isophorone Diisocyanate (IPDI)	
Toluene Diisocyanate (TDI)	
Naphthalene Diisocyanate (NDI)	
Methylene Diphenyl Diisocyanate (MDI)	

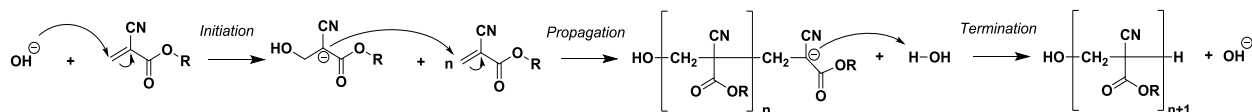
I.3 Acrylic and cyanoacrylate structural adhesives

Acrylic structural adhesives contribute substantially to structural adhesives market with about 5% in 2016 and generated profits over USD 1.5 billion in 2015.⁷ The latter are strictly two-part systems that exist in liquid to paste form adhesive. The first part consists in the reactive monomer and an accelerator. The second one contains the initiator. Formulations are often

based on methyl methacrylate monomers and are usually cured through a radical process with peroxide or hydroperoxide initiators.

Structural acrylic adhesives exhibit high shear, peel strength on variety of substrates, and are able to bond oily and unprepared surfaces. On the other hand, acrylics suffer from having a strong odour, a short pot-life and a low resistance to vibration and impact. Nevertheless, recent improvements of properties, such as less persistent odour, impact resistance or room temperature stability, make them more competitive than PU and epoxy systems in certain applications.⁹⁻¹¹

Cyanoacrylate represent another class of structural adhesives. Cyanoacrylate adhesives count for little but are maybe the most famous structural adhesives, better known as Super Glue™. Generally, methyl- or ethylcyanoacrylate esters are commonly used. Contrarily to previous structural adhesives, cyanoacrylate adhesives are thermoplastics. The latter require moisture to initiate the polymerization. More precisely, the reaction is initiated by the presence of nucleophilic impurities, such as hydroxide ions found on most substrate surfaces. This reaction takes place in three steps: initiation, propagation, and termination like all chain-growth polymerization (Scheme 2).



Scheme 2: Mechanism of polymerization of cyanoacrylate

Cyanoacrylate adhesives present several advantages. They are, for example, one-part system with no need of mixing process before to be applied. They exhibit a fast curing at room temperature and thus reach optimal bonding in seconds or minutes. Wide range of substrates, especially metals, can be bonded. However, they suffer from poor heat and moisture resistance which can be explained by their thermoplastic nature and their sensitivity to hydrolysis.¹² As major drawbacks, one can note their short shelf-life and the assembly of large areas are very complex to set up. Finally, cyanoacrylates are more intended for direct consumer applications and are very competitive on *Do-It-Yourself* (DIY) and repair market segments.

I.4 Epoxy structural adhesives

I.4.1 Introduction

At the dawn of World War II, polyepoxide materials had genesis with the reaction product of bisphenol-A and epichlorhydrin. This credit for the synthesis of the first materials designated as epoxy polymer is shared by the authors Castan and Greenlee in Europe and USA,

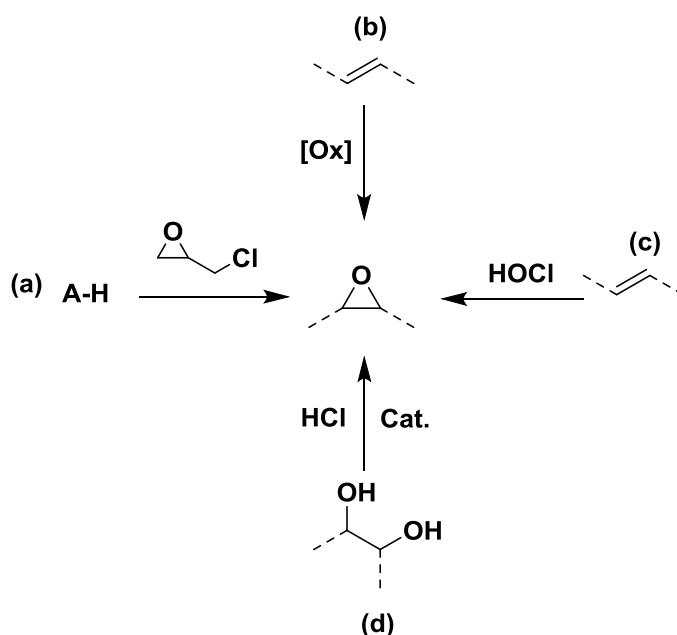
respectively. In 1947, the first epoxy monomer went in to production. Since that time, the market for epoxy compounds has constantly grown due to technology improvement and growing application demands.¹³⁻¹⁵ Today, polyepoxide materials represent in 2016 more than one third of the global structural adhesives market in terms of volume. Projections show an estimated growth of more than 6% for the next five years, which is faster than the other adhesive families.⁶

Epoxy-based structural adhesives are generally made of several compounds and the major component are an epoxy monomer and a curing-agent. They are available as both two-part and one-part systems and have the advantage to bond a variety of materials such as metal, concrete, rubber, wood and composite. They also offer the highest strength, elevated temperature, corrosion and chemical resistance and no volatiles are released upon curing.¹⁶⁻¹⁸ This versatility and outstanding properties make them valuable and leading materials for high performance applications in aircraft and aerospace industries.

Nowadays, the term epoxy resin became generic and used widely to describe both uncured and cured systems. According to the International Union of Pure and Applied Chemistry (IUPAC), the term epoxy resin is strongly discouraged. In the rest of this study, epoxy resin will be defined as the uncured monomer or oligomer containing more than one oxiran moieties.

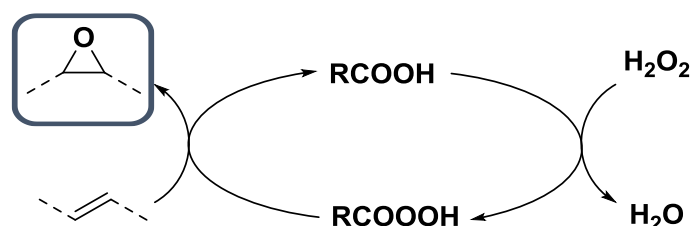
I.4.2 Synthesis of epoxy monomers

The synthesis of epoxy precursors can be achieved through various pathways. The reaction of active hydrogen-bearing compounds with epichlorhydrin (Scheme 3a) and the oxidation of unsaturated compounds (Scheme 3b) are the two main routes.



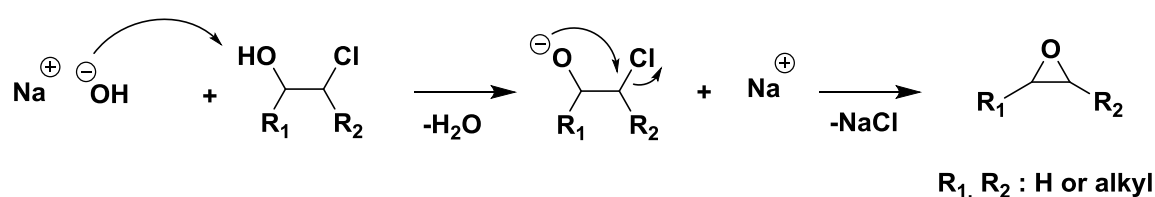
Scheme 3: General routes for the synthesis of epoxy resins

The oxidation of a double bond into the corresponding epoxy function would ideally be carried out by oxygen in the presence of a catalyst, such as metal salts, transition metal complexes or even metal organic framework (MOF).^{19,20} A typical example in industry is the synthesis of ethylene oxide from ethylene.²¹ In the case of other substrates, such as vegetable oils or butadiene derivatives, the oxygen is provided by direct addition or *in-situ* formation of peracides (Scheme 4). Generally, meta-chloroperoxybenzoic acid (mCPBA) is a very efficient oxidizing agent for this kind of reaction, but hydrogen peroxide and peracetic acid are preferred for economical and safety standpoints.²²



Scheme 4: Example of *in-situ* process for the production of epoxy from unsaturated compounds

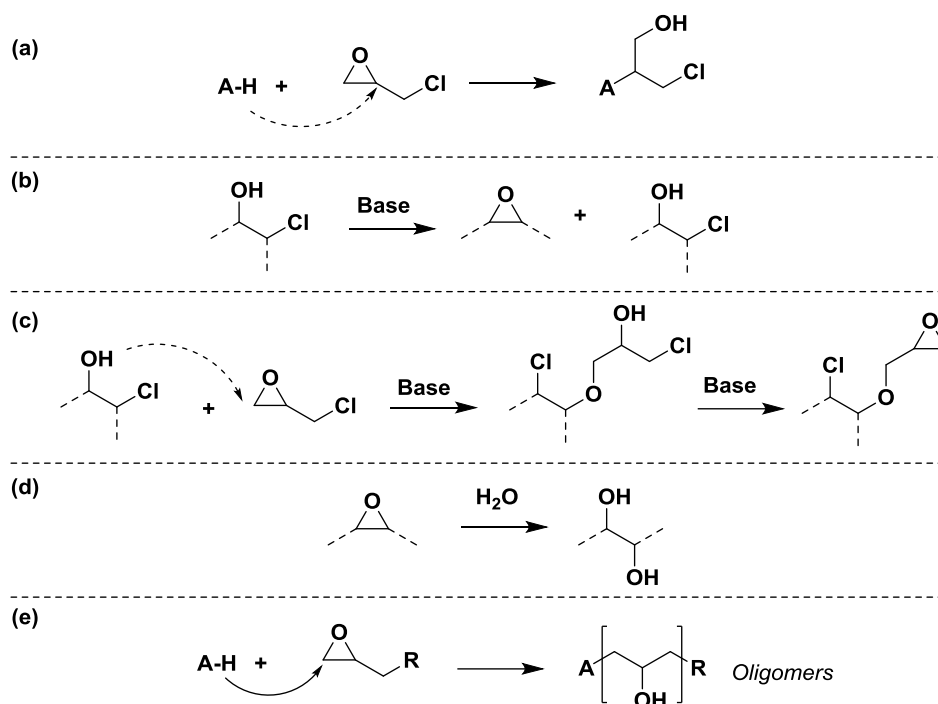
A less direct method consists in converting olefin to a chlorohydrin using hypochlorous acid (Scheme 3c).²³ In the same manner, chlorination of vicinal alcohols yield chlorohydrin intermediates, in the presence of a catalyst, typically an organic carboxylic acid (Scheme 3d).²⁴ The so-formed chlorohydrins are then dehydrohalogenated by basic treatment. This process are commonly used for the synthesis of epichlorhydrin from propylene or glycerol.¹³ However, this method is limited by the accurate control of the reaction and by the formation of by-products, such as salts and water (Scheme 5).²⁵



Scheme 5: Synthesis of epoxy compound from chlorohydrin intermediates

The synthesis of epoxy monomers from the reaction of active hydrogen-containing compounds with epichlorhydrin is by far the most common route (Scheme 3a). Starting substrates are generally phenols, alcohols, amines or carboxylic acids. The main example is the synthesis of the diglycidylether of bisphenol-A (DGEBA). In fact, 75% of epoxy resins are derived from bisphenol-A (BPA).⁴ This BPA prevalence is mainly due to a combination of high availability, low cost and relatively high performance in the resulting materials. In this way, diglycidyl ether moieties are the most commonly produced epoxy monomer types.

During the glycidylation reaction, several side-reactions can occur that decrease the properties of the resulting materials.²⁶ The main side reactions are depicted in the Scheme 6.

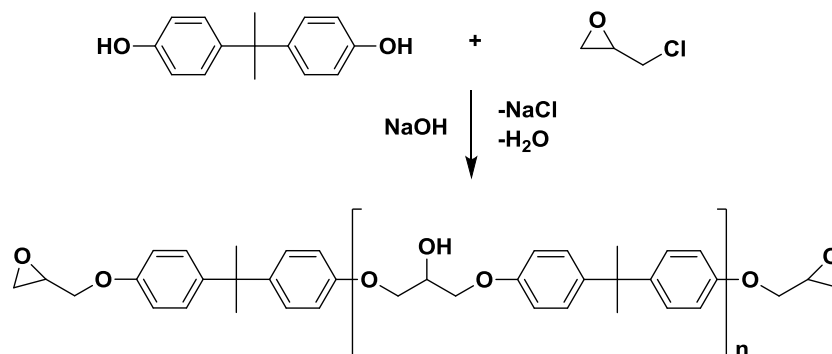


Scheme 6: Main side reactions during glycidylation (a) abnormal addition, (b) incomplete dehydrochlorination, (c) bound chloride formation, (d) hydrolysis, (e) oligomerization

The anomalous nucleophilic attack on the substituted epichlorohydrin carbon generates chlorohydrin intermediates difficult to dehydrochlorinate (Scheme 6a). The incomplete dehydrochlorination or the formation of bound chlorides by reaction of epichlorohydrin with hydroxyl groups in the polymer backbones yield hydrolysable chloride (Scheme 6b and Scheme 6c). High hydrolysable chloride content generally disabled basic catalysts or decreased electrical properties for electronic application.²⁷ A small amount of hydrolysed epoxy is also frequently reported. Vicinal diols can thus be produced during the hydrolysis of epoxy groups (Scheme 6d). Another side reaction intended or not, is the reaction of active hydrogen-containing compound with another epoxy monomer instead of epichlorohydrin yields oligomers with higher molecular weight and thus increased the viscosity (Scheme 6e).

I.4.3 Synthesis of DGEBA monomers

DGEBA is obtained by reacting BPA with epichlorohydrin in the presence of a base, such as sodium hydroxide as shown in Scheme 7. The reaction takes place in two steps: the formation of a chlorohydrin and the dehydrohalogenation of the so-formed intermediate.



Scheme 7: Synthesis of DGEBA from BPA and epichlorhydrin

The DGEBA is a mixture of oligomers in which the number of repeating units, n , lies between 0 to 35.²⁸ Variation of the molar ratio between epichlorhydrin and BPA is used to control this value. Typically, pure DGEBA ($n = 0$) is a crystalline solid with a melting point around 40 °C, whereas DGEBA with $n < 0.5$ are viscous liquids of low molecular weight. In contrast, DGEBA with $n > 0.5$ are gradually amorphous solid products of higher molecular weight.

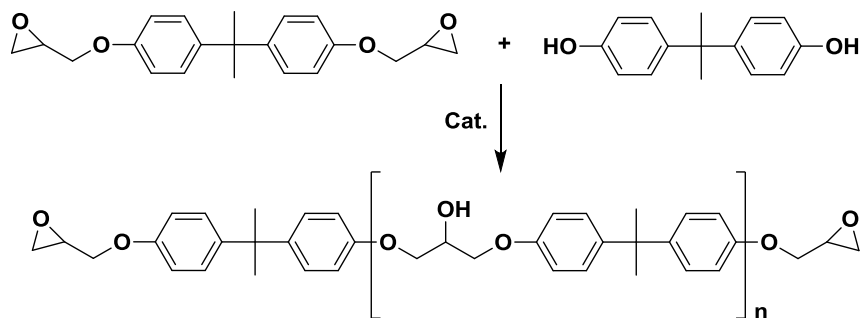
These DGEBA grades are industrially produced from different processes. Generally, the *taffy process* is used to produce low molecular weight liquid epoxy to low molecular weight solid epoxy product. This process consists in coupling BPA with epichlorhydrin in the presence of a catalyst such as sodium hydroxide in aqueous solution or a quaternary ammonium salt acting as a phase-transfer catalyst. As depicted in Table 2, the excess of epichlorhydrin is the key parameter to tune the chain length of oligomers. The resulting product is an emulsion of epoxy oligomers in water and precipitated salts, hence the term *taffy*. Organic solvent and water are then used to wash and recover the desired product. However, for higher molecular weight species this process is limited by handling of highly viscous materials.²⁹

Table 2: Effect of epichlorhydrin/BPA ratio on the M_w of epoxy oligomers^{15,30}

Epichlorhydrin:BPA ratio	n	M_w (g.mol⁻¹)	Viscosity at 25 °C (Pa.s)
10:1	< 0.1	350	4
2:1	0.1	450	16
1.4:1	0.8	790	<i>Amorphous Solid</i>
1.2:1	2	1480	<i>A.S.</i>

For that reason, the *advancement process* is preferred to synthesize higher molar mass epoxy oligomers, typically above 2000 g.mol⁻¹. This process consists in a chain-extension of low molecular weight DGEBA structures by incorporating bisphenolic moieties, such as BPA (Scheme 8). This reaction is carried out at high temperature (150 – 190 °C) in the presence of

catalyst. Usually, ammonium salt, tertiary amine or inorganic base are used to promote the reaction, but most of them are poorly selective and generate ionic impurities. Therefore, new class of catalyst derived from aryl- or alkyl phosphonium salts were preferred and proved their efficiency.^{31,32} The chain length of oligomer is then controlled by the stoichiometry ratio of the reactants. The higher the excess of BPA, the higher the molecular weight of DGEBA oligomers.^{13,14} In this way, DGEBA epoxy grades with M_w up to 20 000 $\text{g}\cdot\text{mol}^{-1}$ are easily produced.



Scheme 8: Synthesis of DGEBA oligomers using advancement process

As well as BPA, glycidylation of bisphenol-F, tetrabromobisphenol-A, methylenedianiline or *p*-aminophenol lead to a series of epoxy monomers (Figure 13). Such structures can lower the viscosity, improve thermomechanical or flame-retardancy properties of the final materials. For example, halogenated epoxy monomers, such as diglycidyl ether of tetrabromobisphenol A (DGETBBA) is extensively used in electrical and electronic applications, where flame-retardancy is mandatory. Halogenated-based flame-retardants act as flame poisons by releasing volatile halogen radicals that scavenge hydrogen radicals in the flame to form non-flammable hydrogen halide.^{33,34} Additionally, multifunctional epoxy monomers, such as tetraglycidyl ether of methylenedianiline (TGMDA), are often used to increase heat resistance, mechanical strength and glass transition temperature.³⁵

In general, structural adhesives are complex formulations requiring skilful mix of these complementary structures.

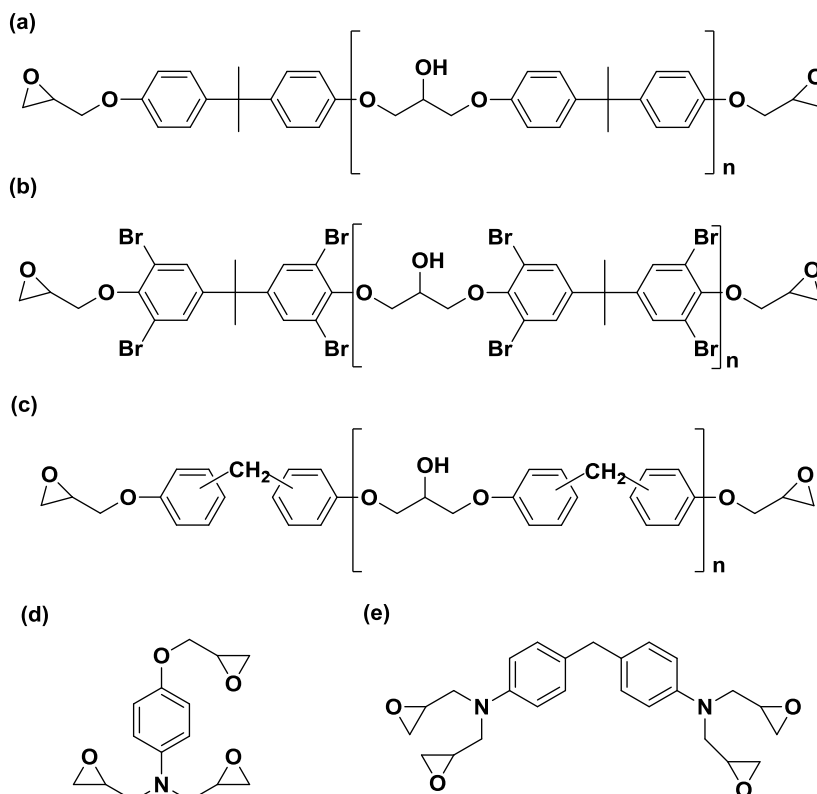
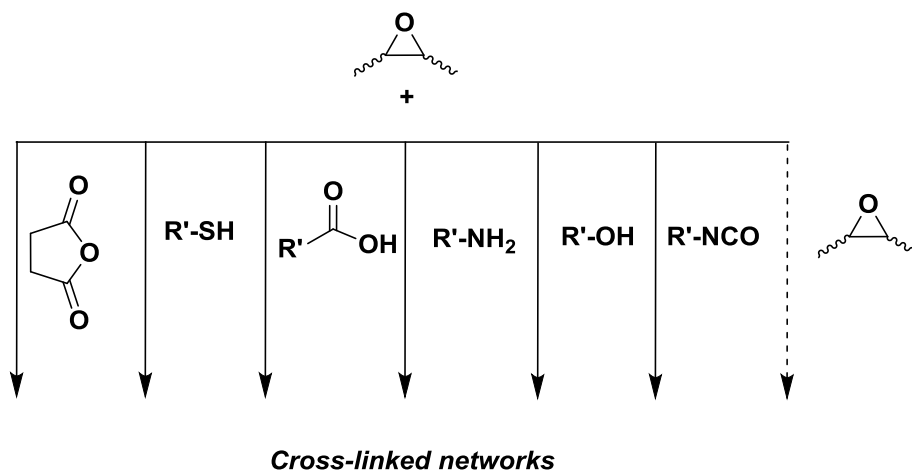


Figure 13: (a) DGEBA, (b) DGETBBA, (c) Diglycidyl ether of bisphenol F (DGEBF), (d) Triglycidyl ether of p-aminophenol, (e) TGMMA

I.4.4 Synthesis of epoxy thermosets

Epoxy thermosets are obtained by adding a curing agent (cross-linker or hardener) to epoxy monomers. Cross-linking of epoxy with hardeners yield three-dimensional insoluble and infusible networks. Thus, curing agents play a preponderant role in the final properties of the materials, as they are literally part of the structure. For that purpose, there is a wide range of hardeners available with various physical and chemical properties, processing methods and curing conditions. Conversion into three-dimensional cross-linked networks are accomplished by either direct reaction of hardener with epoxy groups, such as amine, alcohol, carboxylic acid, anhydride, thiol or by catalytic action (Scheme 9).³⁶ Reactive curing agents will act as comonomers in the polymerisation process, whereas catalytic curing agents will initiate epoxy ring-opening homopolymerization reaction. Either catalytic hardeners are Lewis acids such as boron trifluoride monoethylamine or Lewis bases such as tertiary amines. These catalytic curing agents can also be used as accelerators with other curing agents such as amines or anhydrides.³⁷



Scheme 9: Principal reactive curing agents

The most important class of reactive cross-linkers, meaning amines and anhydrides, will be discussed in the following section.

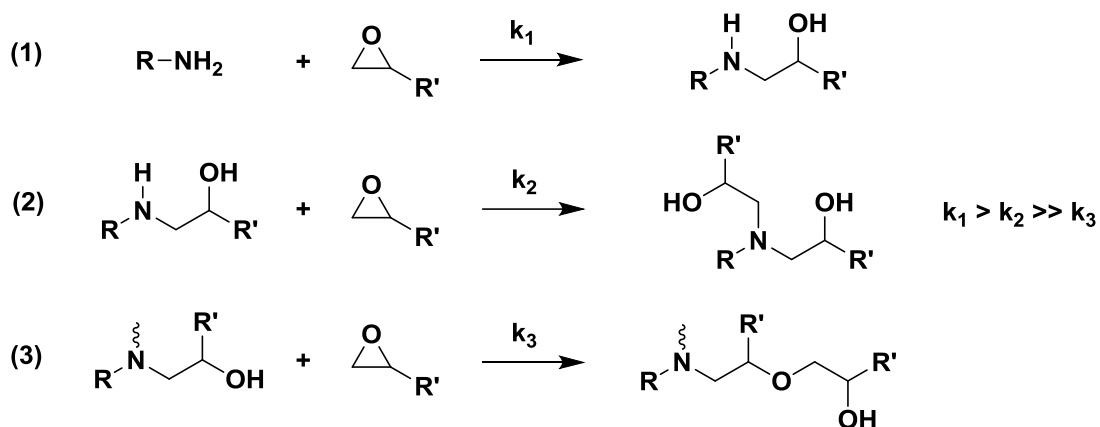
I.4.4.1 Amine cross-linkers

Amines are most widely used as curing agent for epoxy thermosets.¹³ From aliphatic, cyclo-aliphatic to aromatic amines, they provide a wide variety of structure, which can explain this predominance. Structures of typical amine hardeners are shown in Table 3. Generally, aromatic amines such as DDS or MDA are preferred to obtain high performance thermosets by enhancing the thermo-mechanical properties of the network. Consequently, they are used extensively in aerospace structures.^{38,39}

Table 3: Typical amine hardeners

Name	Structure
1,6-Hexanediamine (HDA)	
Polyetheramine (Jeffamine®)	
Diethylenetriamine (DETA)	
Triethylenetetramine (TETA)	
Isophorone diamine (IPDA)	
Methylene dianiline (MDA)	
4,4'-Diaminodiphenylsulfone (DDS)	

Polyaddition reaction occurs between N-H and epoxide functions. The mechanism involved is depicted in Scheme 10. The reaction of an epoxide group with a primary amine (1) results in the formation of a secondary alcohol and a secondary amine. The secondary amine thus formed will react with a second epoxy group to form a tertiary amine and two hydroxyl groups (2). It has been reported in the literature,^{13,40-42} that primary amines react faster than secondary amines. Etherification reaction from hydroxyl groups with epoxy function (3) has very low probability to occur without any catalyst or an excess of epoxy functions.



Scheme 10: Polyaddition reactions between an amine and an epoxy function

Aromatic amines are much less reactive towards epoxy functions in comparison to aliphatic and cycloaliphatic amines. The temperature onset (or T maximum) of the exothermic reaction discloses the reactivity of the amine: the lower this value, the higher the reactivity of the amine. This feature can also be related to the basicity of the amine. Indeed aromatic amines are less basic due to electron withdrawing effect of the aromatic ring. In reality, this latent property could be an advantage for certain applications, which require longer working life before the curing procedure. Table 4 gives values of pKa and exothermic peak of DGEBA cured with various types of amines.

Table 4: Effect of the structure on the reactivity of amine towards epoxy groups

DGEBA/Amine	DETA	IPDA	DDS
pKa ^{43,44}	10,4	10,4	2,4
Exothermic peak (°C)	95	110	225

The stoichiometry of epoxy-hardener reaction is a key parameter to obtain epoxy networks with the highest properties (Equation 1). This quotient r is defined as the ratio of molar quantity of epoxy monomer (n_{epoxy}) weighted by its functionality (f_{epoxy}) with the molar quantity of hardener ($n_{hardener}$) weighted as well by its functionality ($f_{hardener}$). Typically,

functionality of diamine is equal to 4 and functionality of di- or triepoxy monomer is to 2 and 3, respectively.

Equation 1

$$r = \frac{f_{epoxy} * n_{epoxy}}{f_{hardener} * n_{hardener}}$$

Usually, the stoichiometric ratio $r = 1$ leads to epoxy networks with the highest thermomechanical properties (Figure 14).⁴⁵ In fact, when the ratio differ from $r = 1$, the glass transition temperature (Tg) drops rapidly. For $r > 1$, epoxy functions are in excess meaning reaction (2) and etherification (3) will be promoted. Pendant chains of unreacted epoxy will help mobility of chains and thus decrease the Tg. In contrast, for $r < 1$, amine are in excess and oligomer chains will be formed, as reaction (1) is faster than (2). The cross-link density will be lower and the distance between two nodes will be higher. In this way, Tg will be lower because long macromolecular chains need less energy to move.

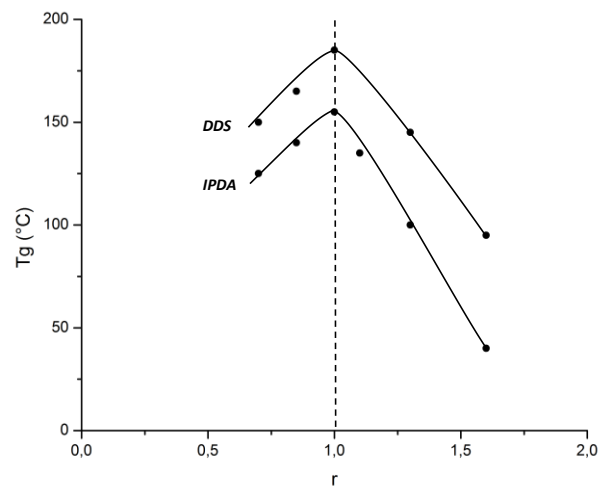


Figure 14: Glass transition temperature versus r DGEBA/DDS and DGEBA/IPDA. Adapted from Galy.⁴⁵

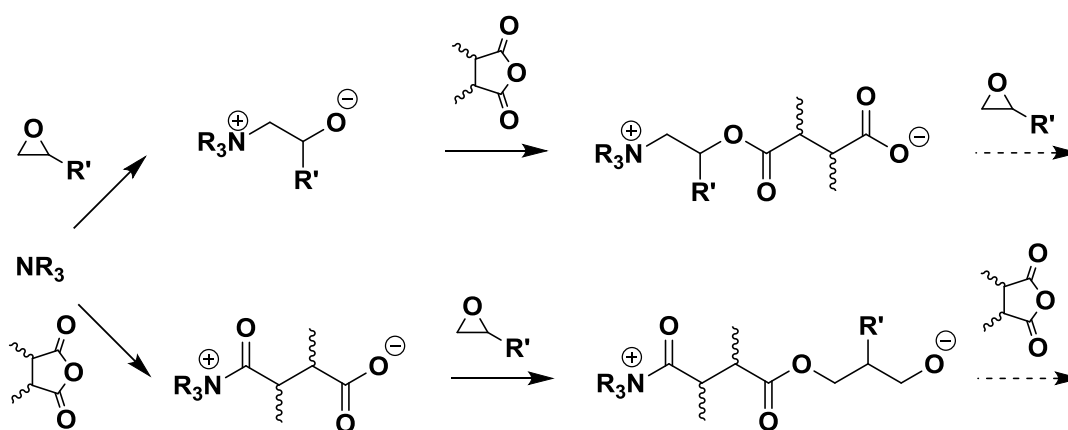
The Epoxy Equivalent Weight (EEW) is an important parameter to characterize an epoxy system in industry.⁴⁶ EEW is defined as the weight in grams of polymer containing one molar equivalent of epoxide. In theory, a molecule having two epoxy moieties has an EEW corresponding to its molecular weight divided by two. By analogy, the Amine Hydrogen Equivalent Weight (AHEW) is defined as the molecular weight of the amine divided by the number of active hydrogens (N-H). Thus, the desired stoichiometric quantity of amine, per hundred parts of resin (phr) is calculated from the following Equation 2:

Equation 2

$$phr = \frac{AHEW * 100}{EEW}$$

I.4.4.2 Anhydride cross-linkers

Anhydrides are the second largest reactants for curing epoxy monomers. They offer the advantage to be less toxic than aromatic amines and exhibit low exothermic heat of reaction. They generally require higher curing temperature than amines and the presence of a catalyst such as tertiary amines, boron trifluoride amines or ammonium salts.^{15,47,48} The mechanism involved in the curing process initiated by tertiary amines is much more complex than for amine-cured systems. Debates about the action of the catalyst either on epoxy or anhydride during the initiation step is still ongoing^{13,30,49–51}. The reaction consists in a chain-growth polymerization comprising initiation, propagation and termination or chain transfer steps. Mechanisms are shown Scheme 11. Initiation involves the reaction of the tertiary amine with anhydride or epoxy, forming a betaine or zwitterion. The resulting ion reacts with an epoxide group or an anhydride. The so-formed anion can then react with further anhydride or epoxide groups and propagation of this alternating sequence leads to the formation of a cross-linked polyester-type.



Scheme 11: Reactions involved in the epoxy-anhydride catalysed curing reaction

There is large variety of anhydrides commercially available used as epoxy hardeners. The most important structures are represented in Table 5. Among them, phthalic anhydride (PA) is the less expensive anhydride and is widely used for applications where the achievement of optimal properties is secondary. In contrast, benzophenonetetracarboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA) are multifunctional aromatic anhydrides allowing the obtention of highly cross-linked and higher thermal resistance networks. These latter have been developed especially for high temperature applications and are competitive with aromatic amines as they are less toxic.³⁶

However, contrary to amine-cured systems, anhydride cross-linkers suffer from several drawbacks. The low reactivity even at high temperature of anhydride requires the use of additional catalyst. Moreover, anhydrides are very sensitive to moisture, which limits their use

in processes that have long open time in wet environment. Once cured with epoxy, networks essentially consist in ester linkages, which are subject to hydrolysis in high humidity and temperature conditions. Consequently, anhydride-curing processes are crucial and complex. For that reasons, amine systems are generally preferred to anhydride-based ones as far as structural applications are concerned.

Table 5: Important anhydride curing agents

Name	Structure
Phtalic anhydride (PA)	
Methyltetrahydrophthalic anhydride (MTHPA)	
Methylhexahydrophthalic anhydride (MHHPA)	
Hexahydrophthalic anhydride (HHPA)	
Pyromellitic dianhydride (PMDA)	
Benzophenonetetracarboxylic dianhydride (BTDA)	

I.5 Healthcare and environmental concerns

Glycidylation reactions are essentially realised with epichlorhydrin and bisphenol-A. However, these two precursors must be handled carefully to protect the health of employees, customers and the environment.

According to the European Chemical Agency (ECHA), epichlorhydrin is classified CMR 1B, meaning that it is potentially carcinogenic for human. Today, some efforts have been done to reduce the impact of the production of epichlorhydrin on the environment.^{52,53} Solvay has successfully developed an alternative route using glycerol (Epicerol[®] process) instead of petroleum-based propylene (Figure 15).⁵⁴

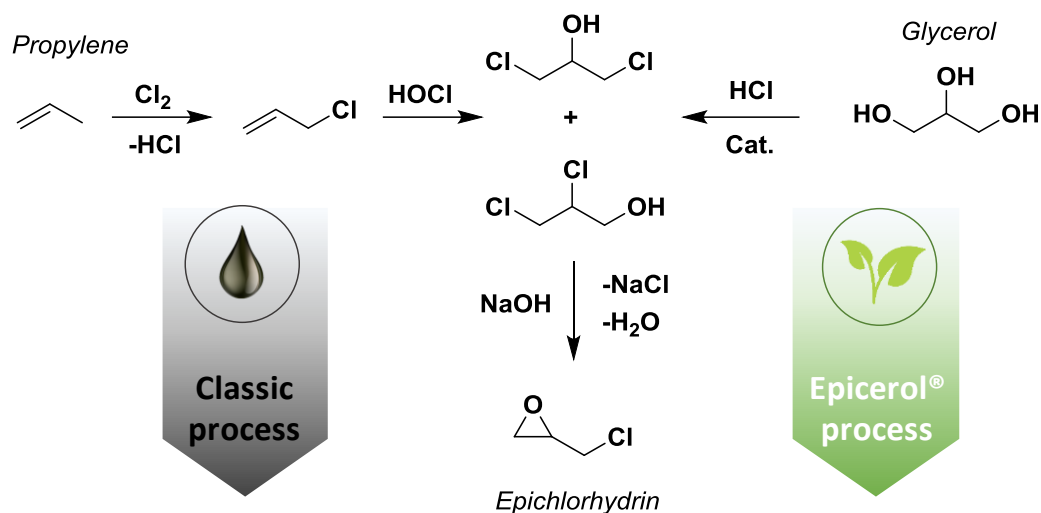
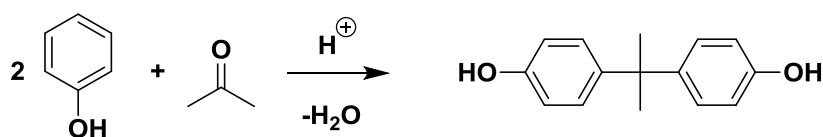


Figure 15: Synthetic processes of epichlorhydrin

Nevertheless, full alternative to epichlorhydrin in the synthesis of glycidylated epoxy resin is far to be achieved, unless radical change in the chemistry. However, Llevot *et al.* recently reported the development of catalytic system for the Tsuji-Trost allylation.⁵⁵ By using a palladium nanoparticles stabilized by poly(vinylpyrrolidone) and allyl methyl carbonate, they successfully allylated bio-based phenols in very good yields. Starting from these results, the oxidation of unsaturation could easily lead to epoxy moieties. In this ways, this new pathway could be a valuable alternative to the use of epichlorhydrin for the synthesis of epoxy monomers.

4,4'-(propane-2,2-diyl)diphenol, produced from the reaction of phenol with acetone and known as bisphenol-A, is one of the largest chemical substances produced in terms of volume and the main precursor of epoxy resins (Scheme 12). Global volume consumption of Bisphenol-A is estimated at 8 million tons in 2016 and is projected to reach 11 million tons by 2022.⁵⁶



Scheme 12: Synthesis of BPA from phenol and acetone

However, BPA is also known as endocrine disruptor. This means that BPA may interfere with the hormonal system and thereby produce harmful effects in both humans and wildlife.^{57–59} Since that, numerous debates have been raised between industry and governmental institution on whether or not BPA causes effects of concern for human. In 2008, Canada became the first country to ban the use of BPA in baby feeding bottles and toys. Subsequently a number of countries in the European Union and the United States have followed this initiative as well.^{60–}

⁶² In 2015, France has banned BPA in all food packaging, containers and utensils and, more

recently in June 2017, the European Chemicals Agency classified BPA as a substance of *very high concern* in REACH regulation, as endocrine disruptor. Consequently, all manufacturers, importers, or suppliers of BPA must classify and label mixtures containing BPA as toxic for reproduction category CMR 1B. As a result of the restriction, industrials need to replace BPA. In addition to healthcare issues, bio-based substitutes to BPA could be a solution to answer both environmental and healthcare concerns.

II. Bio-based epoxy thermosets

II.1 Introduction

The element carbon is a fundamental constituent in our society. Since the industrial revolution, fossil resources are the largest carbon source to produce energy and chemicals. Fossil resources such as coal, gas or oil are storage reservoirs, which contain carbon from plants, and animals that lived millions of years ago. Burning of fossil fuels in everyday life release very quickly the carbon into the atmosphere in the form of carbon dioxide. In this way, carbon cycle is disrupted and lead to environmental issues we are facing now.⁶³ Contrary to fossil resources, biomass induces a short carbon cycle with time frame of few decades. Resource is said renewable when its exploitation rate is similar to its regeneration rate. Therefore, short cycle using biorefinery concept and renewable resources such as biomass, could be a way to restore the equilibrium (Figure 16).

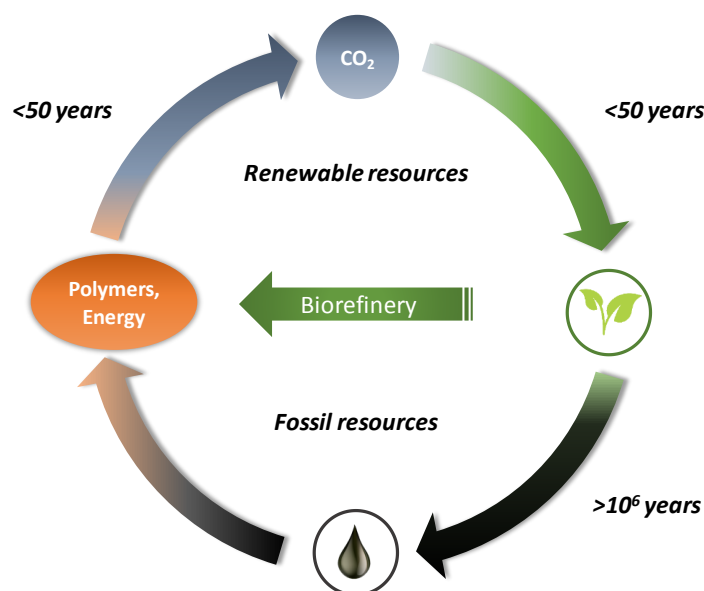


Figure 16: Graphical representation of carbon cycle

In this context of petroleum resources volatility coupled with the awareness of environmental concerns, the chemical industry urges to find solutions in order to produce

industrially viable bio-based chemicals. Recent advances in the synthesis of epoxy monomers from biomass resources such as plant oils, terpenes, glucoses, cardanol, tannins and lignins will be discussed in the next section. Literature concerning bio-based epoxy thermosets is summarized in a table at the end of this chapter.

II.2 Bio-based epoxy networks derived from vegetable oils

Natural vegetable oils are considered to be one of the most important classes of renewable sources due to their versatility, ready availability in large quantity and low price.^{64,65} They consist in a mixture of different triglycerides. As depicted in Figure 17, triglyceride is made of glycerol moiety linked to three various fatty acids.

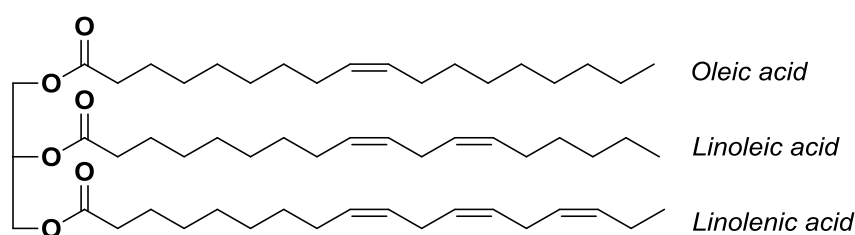


Figure 17: Example of triglyceride structures

Each oil has a unique fatty acid composition depending on its origin, growth conditions and purification process. There are five major types of fatty acids with chain lengths ranging from 16 to 18 carbons containing from 0 to 3 double bonds: palmitic, stearic, oleic, linoleic and linolenic acids. Composition of some common vegetable oils is shown in Table 6.

Table 6: Fatty acid composition of various vegetable oils⁶⁶

Oil	Fatty acid composition (%)				
	Linolenic 18:3*	Linoleic 18:2	Oleic 18:1	Stearic 18:0	Palmitic 16:0
Sunflower	1	47	42	4	6
Palm	1	10	40	4	45
Soybean	8	53	24	4	11
Linseed	57	15	19	4	5

*number of carbons : number of double bonds

Some oils, such as vernonia oil bear epoxy groups in their structure and, subsequently, can be directly used as epoxy monomers. Composition of vernonia oil can consist in almost 80% of vernolic acid (Figure 18).

Owing to its very low viscosity, vernonia oil has been mainly used as reactive diluent in epoxy coating formulations.^{67,68}

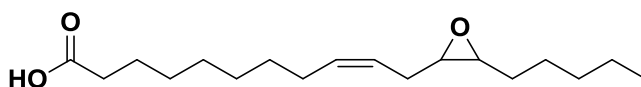


Figure 18: Structure of vernolic acid

Apart from vernonia oil, one of the major interests of vegetable oils is their ability to be epoxidized. As discussed in the previous section, double bonds can easily be converted into epoxy function through the oxidation of unsaturation. Epoxidized vegetable oil (EVO) has lower reactivity toward amine hardeners than glycidyl ether molecules, but it was reported that EVO reacts more rapidly with anhydrides or acids.⁶⁹ For this reason, most of EVO systems are cured with anhydrides. Epoxidized linseed oil (ELO) and epoxidized soybean oil (ESO) are the most widely studied EVO. Several research groups have investigated the curing of ELO and ESO into cross-linked resins with various approaches. Shibata *et al.* compared the effect of various anhydride-based curing agents, such as terpene-based acid anhydride, on the thermal and mechanical properties of ESO thermosets. Best system exhibits a T_g of 67 °C.⁷⁰

Rosch *et al.* prepared soft to rigid thermosets from ESO cured with different anhydrides in presence of catalysts. Succinic anhydride and hexahydrophthalic anhydride (HHPA) yielded highly flexible rubbery materials with glass transition temperatures below room temperature, whereas more rigid anhydrides such as maleic anhydride and PA gave polyesters with glass transition temperatures up to 73 °C.⁷¹ Other authors investigated the impact of the concentration of catalyst such as tetraethylammonium bromide (TEAB) on ESO/MHHPA thermosets. They showed that ESO thermoset with higher TEAB concentration could achieve higher storage modulus, thermal stability and glass transition temperature at about 70 °C.⁷² Based on these results, ESO is essentially used as a plasticizer or reactive diluent to modify the properties of other epoxy resins for applications as coatings and casting resins. Nevertheless, Mija *et al.* developed bio-based thermosets with remarkably good mechanical properties from ELO cured with methylhexahydrophthalic anhydride (MHHPA) or BTDA in the presence of imidazole as an initiator. The so-formed networks exhibit degradation temperature at about 340 °C and temperature of α transition at about 130 °C.⁷³ The authors demonstrated the possibility of using EVO-based materials with good impact strength and high glass transition temperature for performance applications.

In addition, it is worth noting that epoxy thermosets made from EVO are able to be decomposed by bacteria or other biological means. Numerous studies carried out to investigate the biodegradability of EVO thermosets.^{69,74–77} It was found that ester linkages present in the

triglyceride oils can be easily attacked by enzymes. The resulting products can be further decomposed into water and carbon dioxide by various micro-organisms. However, this phenomenon is controlled by the density of cross-linking and the nature of curing agents.

Vegetable oils can be successfully converted into bio-based epoxy monomers. EVO present numerous advantages such as availability, low cost or biodegradability. However, structures are made up of long aliphatic chains and generally lead to materials with low degree of cross-linking. Subsequently, EVO thermosets display lower thermomechanical properties than DGEBA-based epoxy thermosets. As a consequence, EVO are unable to compete directly with fossil derived epoxy systems and are essentially used as partial substitutes such as reactive diluents. Most industrial applications for the resulting epoxy materials remain limited to non-structural applications. More rigid structures are therefore required for high-performance applications.

II.3 Bio-based epoxy thermosets from rosin

Rosin is another highly available natural product obtained from conifer tree exudates or as a by-product of the *Kraft* process. Global production of rosin is estimated at more than 1 million ton per year. It consists of 90% of acids and 10% of neutral compounds. Acid compounds are essentially a mixture of resinic acids, containing 40 to 60 % of isomeric abietic-type acids and 10 to 30 % of pimaric-type acids.^{78,79} Typical structures are depicted in Figure 19. The presence of double bonds and COOH group make these structures very reactive. Moreover, resinic acid derivatives exhibit fused-ring system with similar rigidity to aromatic compounds. In this way, they are promising alternatives for high performance petroleum-based epoxy thermosets.⁸⁰

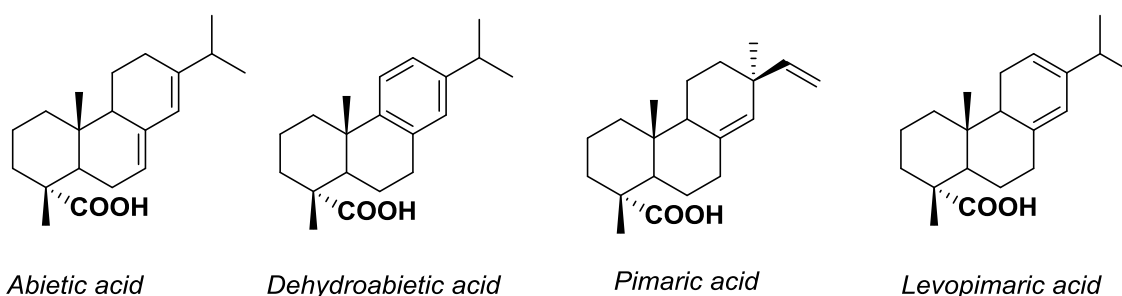
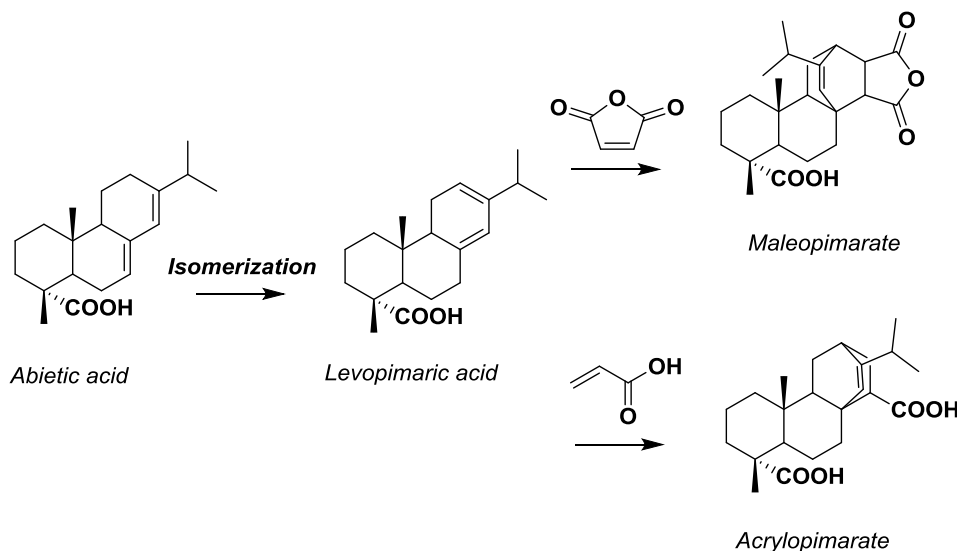


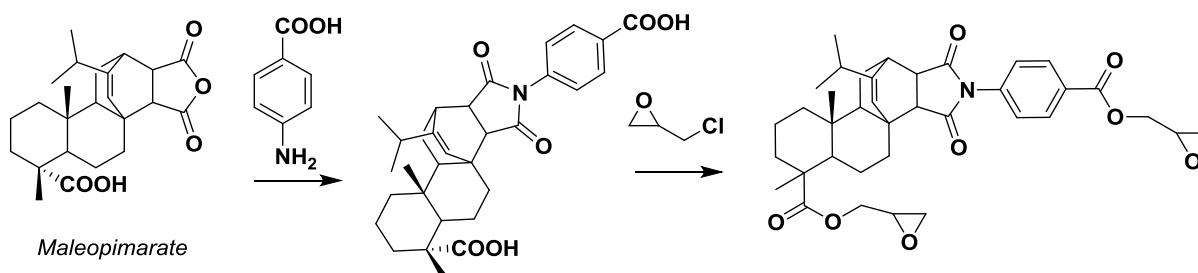
Figure 19: Typical structures of resinic acids

In order to obtain multi-functional monomers, rosin acid derivatives have been modified with various dienophiles by Diels–Alder mechanism. Synthesis of maleopimarate and acrylopimarate, obtained from abietic acid and maleic anhydride or acrylic acid, respectively, is represented in Scheme 13.



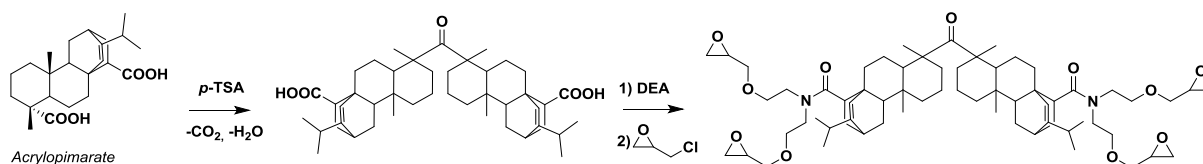
Scheme 13: Synthesis of maleopimarate and acrylopimarate from abietic acid⁸⁰

From these difunctional monomers, several authors successfully synthesized multifunctional epoxy monomers through various pathways. Liu *et al.* investigated the synthesis of bisepoxy from maleopimarate in a two-step reaction.⁸¹ The diacid was first synthesized from maleopimarate and aminobenzoic acid and then esterified with epichlorhydrin, yielding bisepoxy monomer (Scheme 14). Curing was performed with HHPA and 2-ethyl-4-methylimidazole as a catalyst. The rosin-based epoxy exhibits very similar thermomechanical properties than the DGEBA-based reference; the so-formed bio-based thermoset shows a T_{α} of 156 °C, against 144 °C for DGEBA network.



Scheme 14: Synthesis of bisepoxy monomer from maleopimarate

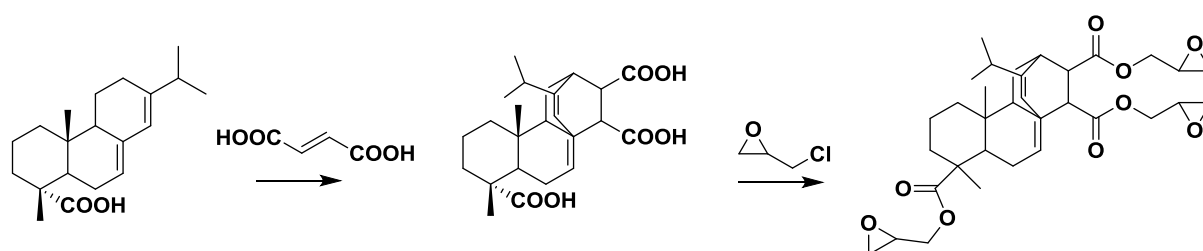
Following the same strategy, Atta *et al.* prepared tetra-functional epoxy resins from dehydrodecarboxylation of rosin acid.^{82,83} Ketones were obtained by dehydrodecarboxylation of acrylopimarate or maleopimarate catalysed by *p*-toluensulfonic acid at high temperature. In a second step, the so-formed ketones reacted with diethanolamine (DEA) yielding multifunctional hydroxyl derivatives. Epichlorhydrin was then added to produce tetraglycidylether epoxy monomers (Scheme 15). Curing was performed with poly(amide-imide) hardeners and yielded high chemical and solvent resistance epoxy networks.



Scheme 15: Synthesis of tetraglycidylether from acrylopimarate

More recently, Cramail and coworkers^{84,85} developed epoxy thermosets from Polygral, a commercial by-product of paper and forest industry which consists in a mixture of abietic acid and oligomers. Polygral was esterified in a one-pot synthesis using glycidol with carbodiimide and then cured with IPDA. The corresponding glass transition temperature exhibited a maximum value at 93 °C, which is 60 °C lower than T_g obtained with DGEBA in the same curing conditions.

Besides, Deng *et al.* developed the synthesis of trifunctional epoxy from fumaropimaric acid (FPA).⁸⁶ This latter was obtained by the Diels-Alder reaction between abietic and fumaric acids. The esterification was then performed with epichlorohydrin yielding triglycidyl ester of fumaropimaric acid. The synthetic pathway is summarised in Scheme 16. The trifunctional epoxy monomers were then cured with methyhexahydrophthalic anhydride (MHHPA). The bio-based thermoset exhibited glass transition and degradation temperatures similar than DGEBA-based thermoset. Glass transition temperature achieved a value of 166 °C against 140 °C for petroleum-based system. According to the authors, the fused-ring system and the higher degree of cross-linking greatly enhanced the thermomechanical properties. Subsequently, abietic acid derivatives show great potential in terms of properties and provide a renewable alternative to DGEBA-based epoxy resins.



Scheme 16: Synthesis of triglycidyl ester from abietic acid⁸⁶

II.4 Bio-based epoxy thermosets from glucose derivatives

II.4.1 From isosorbide

Isosorbide is one of the most promising renewable building blocks. It can be produced in a large scale from the depolymerization of cellulose or starch.⁸⁷ The schematic process is depicted on Figure 20.

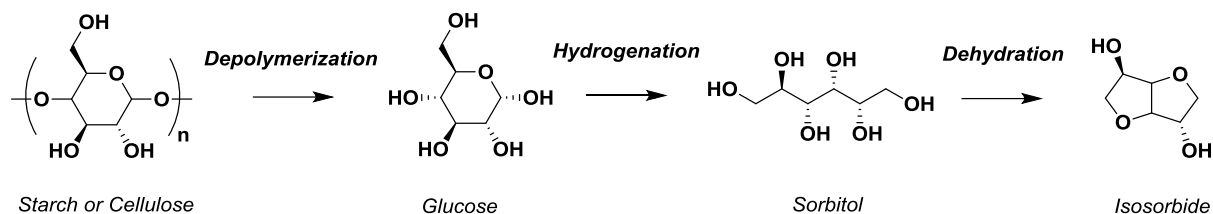
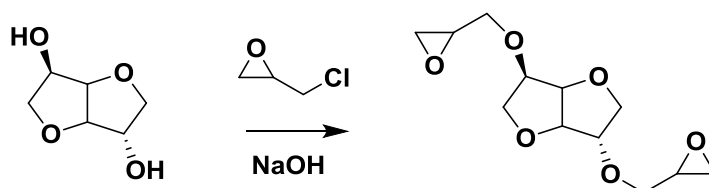


Figure 20: Upgrading process for the production of isosorbide

Since isosorbide benefits of several advantages such as low cost, non-toxicity and biodegradability, it has raised a strong interest for the development of high-performance materials.⁸⁸ In 2011, the synthesis of glycidylether of isosorbide were developed by Chrysanthos and co-workers. The epoxy precursors was cured with IPDA and compared to a conventional epoxy network based on DGEBA (Scheme 17). The bio-based reactive system exhibit a $T_g=112$ °C which is lower than the one observed for the DGEBA system (155 °C).⁸⁹ Another study carried out by Łukaszczyk demonstrated the same trend with networks cured with various hardeners such as, TETA, IPDA, or PA.⁹⁰ Following a similar strategy, Feng *et al.* also reported a decrease of T_g about 40 °C on networks synthesized from diglycidyl ether of isosorbide cured with polyetheramine.⁹¹ All authors agree that the low T_g is related to the isosorbide's hydrophilicity or refer to the fact that the aliphatic ring structure is not as rigid as the aromatic one, as in DGEBA structure.⁹²

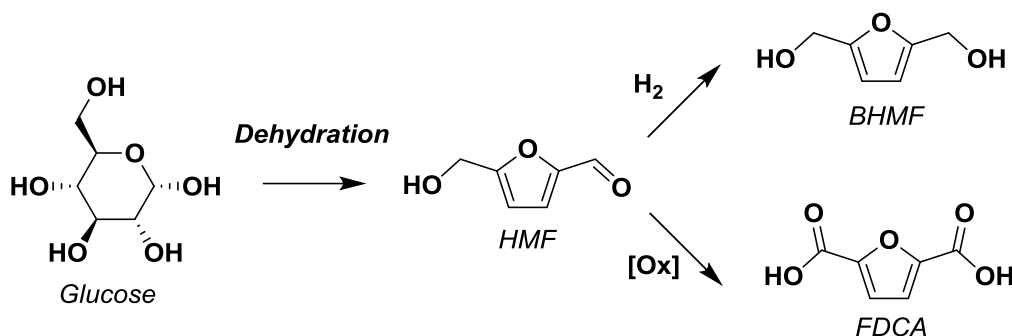


Scheme 17: Synthetic route of isosorbide diglycidyl ether via epichlorohydrin⁸⁹

However, the higher degradability character of these new materials toward water makes them valuable candidates for biomedical applications rather than high performance materials.

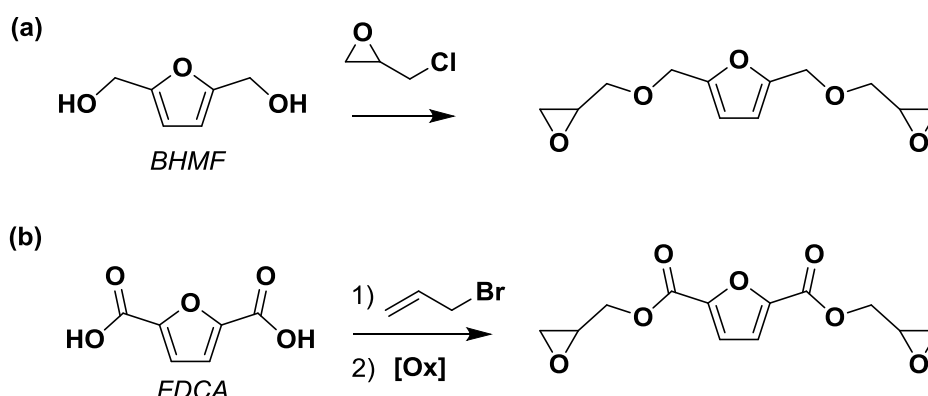
II.4.2 From furans

Furanyl building blocks have been identified as another promising chemical platforms directly derived from biomass.⁹³ Among them, hydroxymethylfurfural (HMF) derivatives such as furan-2,5-dicarboxylic acid (FDCA) and 2,5-Bis(hydroxymethyl)furan (BHMF) are rising renewable alternatives to petroleum-based epoxy thermosets due to their availability and aromatic structure. These precursors can be easily prepared in good yield from the dehydration of C6 sugars as depicted in Scheme 18.^{94,95}



Scheme 18: Synthesis of furan derivatives from glucose

In the past few years, several works reported the synthesis of furanyl-based epoxy thermosets. Palmese and co-workers successfully prepared glycidylether of BHMf by direct epoxidation with epichlorhydrin (Scheme 19a).^{96,97} After curing with 4,4'-diaminodicyclohexylmethane (PACM), the so-formed bio-based thermosets exhibited much lower T_g value than petroleum-based thermoset, 71°C and 167°C respectively. According to the authors, this difference is due to the presence of methylene groups between furan ring and glycidyl ones, which reduce the constraints in the network.



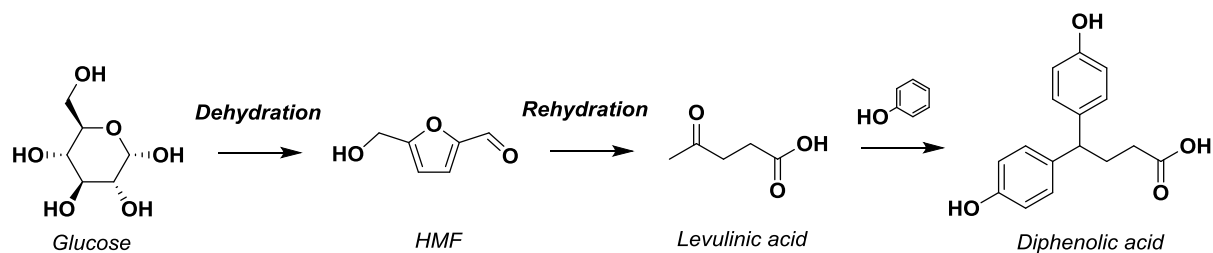
Scheme 19: Synthesis of (a) diglycidyl ether of BHMf, (b) diglycidyl ester of FDCA

In another study, Deng *et al.* reported the epoxidation of FDCA by allylation and oxidation of double bonds with *meta*-chloroperoxybenzoic acid (*m*CPBA) (Scheme 19b).⁹⁸ Epoxy monomer of FDCA was cured with MHPA and compared with DGEBA reference. Diglycidyl ester of FDCA showed a T_a value of 30°C above the one obtained with DGEBA. These results suggest that the bio-based furan ring derivatives show great potential to replace current petroleum-based epoxy thermosets.

II.4.3 From levulinic and itaconic acids

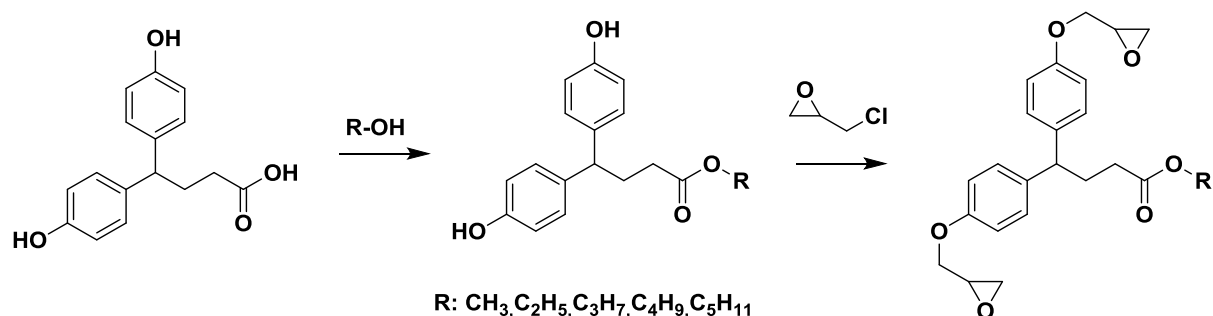
Levulinic acid (LA) is another promising starting material derived from cellulose. LA is obtained by the acid hydrolysis of C6 sugars followed by rehydration of HMF.⁹⁹ Some authors

noticed that the condensation of various phenols with LA could yield diphenolic acid (DPA) which is very close to the BPA structure (Scheme 20).^{100,101}



Scheme 20: Synthesis of diphenolic acid from levulinic acid

Based on these observations, Gross and co-workers reported the synthesis of DPA-derived epoxy monomers and investigated its curing kinetics.^{101,102} The authors first prepared a series of short chain diphenolate n-alkyl esters by esterification with a large excess of the alcohol. Glycidylation was then performed with epichlorohydrin under alkaline conditions to form diglycidyl ester of diphenolate ester (DGEDP-ester) (Scheme 21). The viscosity of epoxy monomers is a key parameter to formulate homogeneous materials. In this study, the authors demonstrated that control of the resin viscosity could be achieved by tuning the chain length of ester moieties. The so-formed bis-epoxides were then cured with IPDA and their properties compared to those from diglycidyl ether of bisphenol-A network.

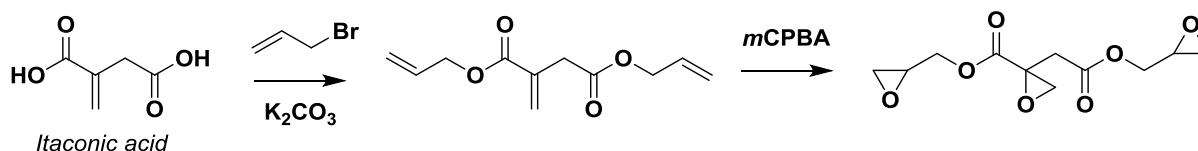


Scheme 21: Synthesis of glycidyl ether of diphenolate ester¹⁰¹

DGEDP-esters exhibit alpha transition temperature from 86 °C to 158 °C depending on the ester chain length. The cured DGEDP-methyl ester peak of the loss modulus was only 7 °C below DGEBA thermoset (164°C), whereas DGEDP-pentyl ester showed T_α of 86 °C. Other thermomechanical properties, such as Young modulus and thermal degradation were determined and found similar to the ones of DGEBA-reference. In this way, epoxy thermosets derived from DPA resins are promising alternatives for petroleum-based epoxy systems.

Itaconic acid (IA) can also be used as alternative feedstock for the synthesis of epoxy thermosets as it displays two carboxylic functions, which can easily undergo epoxidation reactions. IA is produced by fermentation of glucose in presence of *Aspergillus terreus*.^{103,104} In 2013, Songq *et al.* reported the synthesis of bio-based epoxy precursors by the esterification of IA with

epichlorhydrin.¹⁰⁵ The novel IA-based epoxy was cured with MHHPA and compared with DGEBA reference. The glass transition temperature of the bio-based system was equal to 130 °C, which is similar to the one of DGEBA thermoset cured with the same curing agent (126 °C). In another study, same authors developed a trifunctional epoxy monomers from IA in a two-step reaction (Scheme 22).¹⁰⁶ The authors first performed the allylation of acids with allyl bromide and then epoxidized the double bond with *m*CPBA.



Scheme 22: Synthesis of trifunctional epoxy monomer from itaconic acid¹⁰⁶

DSC was used to determine the glass transition temperature of the cured resins. The bio-based network exhibited a T_g of 135 °C, whereas DGEBA cured in the same conditions displayed a T_g value of 110 °C. In contrast, the thermal degradation temperatures of the itaconic-based thermosets were lower than the DGEBA/MHHPA. The authors explained this difference by the presence of easily thermally degradable polyether segments and cleavable ester bonds. As a result of these works, itaconic acid derivatives have shown great potential to partially replace the petroleum-based thermoset.

II.5 Bio-based epoxy thermosets from cardanol

The cashew nutshell is an important by-product of the cashew nuts industry. Various methods of extraction are available to extract from nutshell a dark brownish oil called cashew nutshell liquid (CNSL). This oil is considered as one of the major and economical sources of phenolic compounds and can be used as valuable raw material as petrochemical substitutes. CNSL is constituted of four different phenols: anacardic acid, cardanol, cardol and 2-methyl cardol (Figure 21).

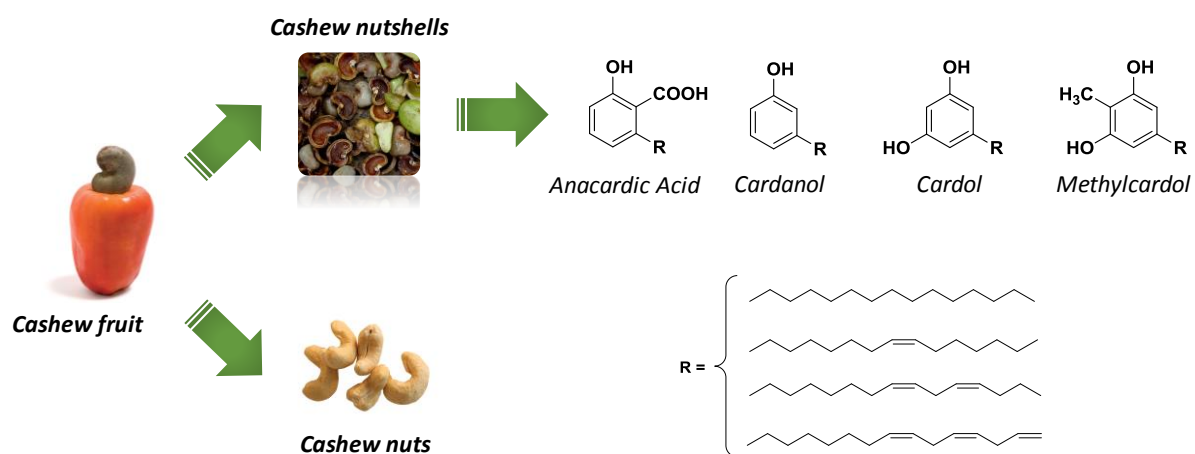


Figure 21: Upgrading process of cashew fruit

Depending on the extraction process, ratios of these phenols vary significantly. Natural CNSL is obtained by cold pressing or by solvent extraction leading to an oil containing roughly 75% of anacardic acid. On the other hand, technical extraction by roasting the nutshell followed by refining enable to recover almost 80% of cardanol.^{107,108} In fact, during the roasting process, anacardic acid is converted into cardanol by thermal decarboxylation leading to higher content cardanol CNSL. The composition of both natural and technical CNSL are summarised in Table 7.

Table 7: Composition of the phenolic components in natural and technical CNSL^{108,109}

Extraction process	Anacardic Acid (%)	Cardanol (%)	Cardol (%)	Methylcardol (%)	Polymeric Materials (%)
Natural	75	1-10	15-20	1-3	-
Technical	1-2	65-75	15-20	2-5	10

In this way, large quantities of cardanol are available. This molecule arises a wide interest as epoxy monomer. The presence of phenol and double bonds which can be epoxidized but also the aromatic ring that bring rigidity to the structure make it valuable compound for the synthesis of epoxy thermosets. Literature reports many works on the preparation of epoxy networks from cardanol. Patel *et al.* synthesized diepoxidized cardanol (DEC) by reacting the phenol with epichlorhydrin and in a second time by oxidizing the double bond with perbenzoic acid (Figure 22). They later investigated the curing behaviour of various blends of DGEBA/DEC with anhydrides and evaluated DEC as an efficient reactive diluent.¹¹⁰

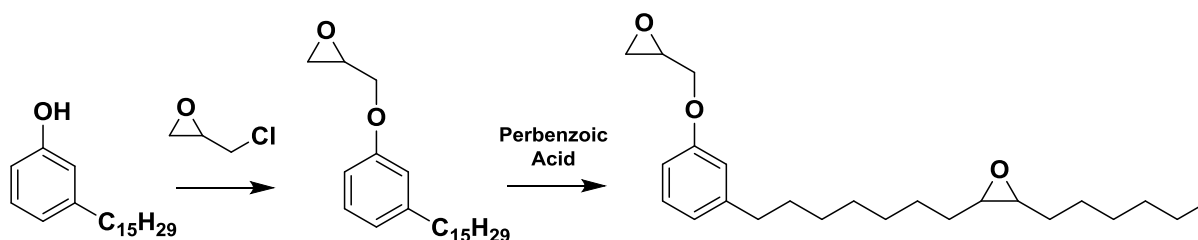


Figure 22: Synthesis of diepoxidized cardanol¹¹⁰

More recently, Jaillet *et al.* developed bio-based epoxy thermosets from commercial epoxidized cardanol called Cardolite NC-514 (Figure 23).¹⁰⁷ Bio-based epoxy prepolymer was cured with various amines and the networks compared with DGEBA thermosets. DMA analysis revealed that cardanol-based thermosets exhibited T_{α} of 59 °C, whereas DGEBA thermosets showed a T_{α} =158 °C. The authors explained this difference by the low crosslinking densities due to long aliphatic chain between the aromatic rings. These low thermal and mechanical properties do not allow the use of this compound in epoxy formulation for structural applications.

However, more studies have demonstrated the potential of cardanol-based thermosets for DGEBA alternatives in surfactant, epoxy foam and coating applications.^{111–115}

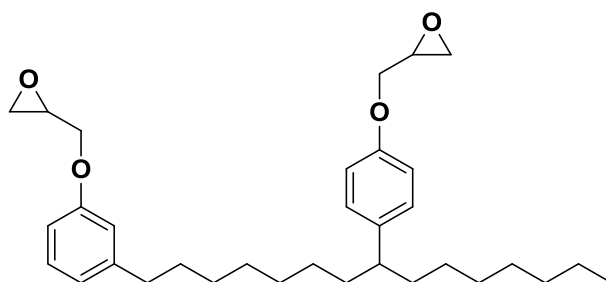


Figure 23: Structure of Cardolite NC-514

II.6 Bio-based epoxy thermosets from tannins

Tannin is a generic word to define polyphenolic compounds extracted from the barks of trees, nuts, leaves and other plants. These compounds exhibit a wide structural diversity and can be divided into three broad classes: hydrolysable, condensed and complex tannins.^{116–119} Typical structures are depicted in Figure 24. Hydrolysable tannins are molecules of low molecular weight and composed of central D-glucose esterified with gallic or ellagic acid derived, called gallotannins and ellagitannins, respectively.¹²⁰ Condensed tannins are oligomeric structures of higher molecular weights and formed by C-4 linkage of one catechin or epicatechin with C-8 or C-6 of the next monomeric catechin or epicatechin. As its name suggests, complex tannins are elaborated structures in which a catechin unit is bound to a gallotannin or an ellagitannin unit by glycosidic linkages.

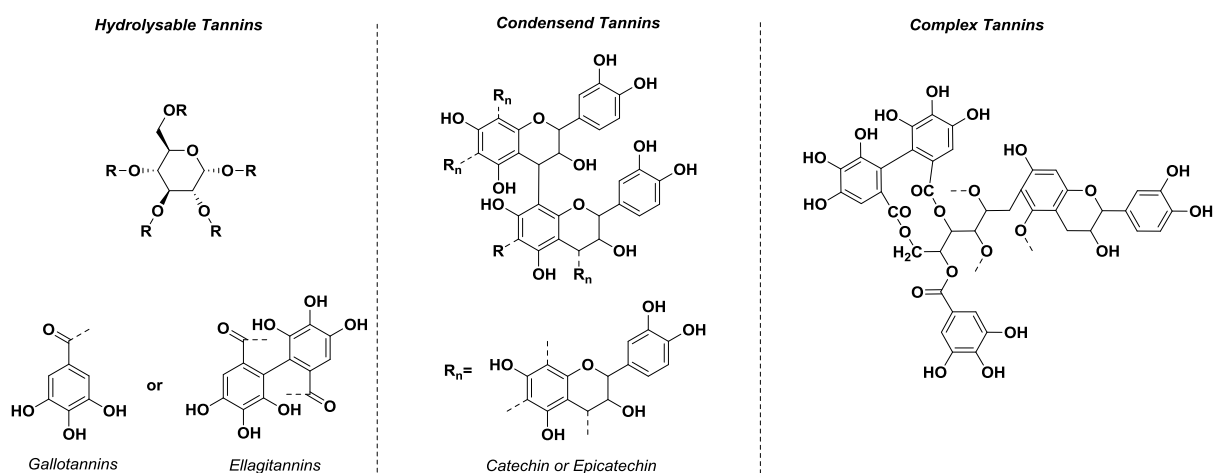
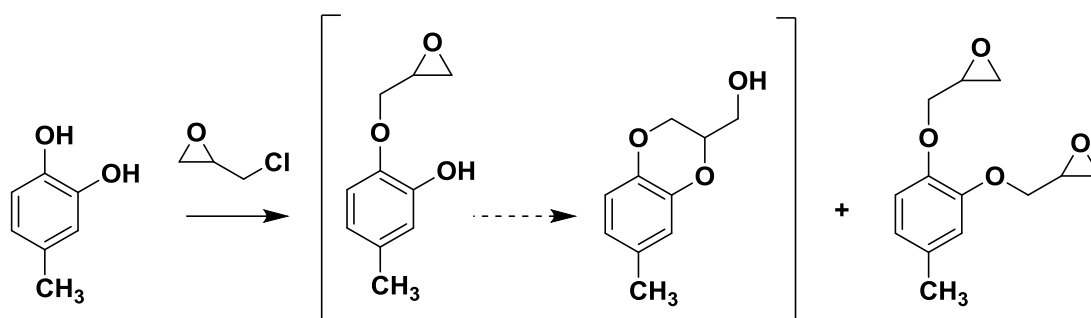


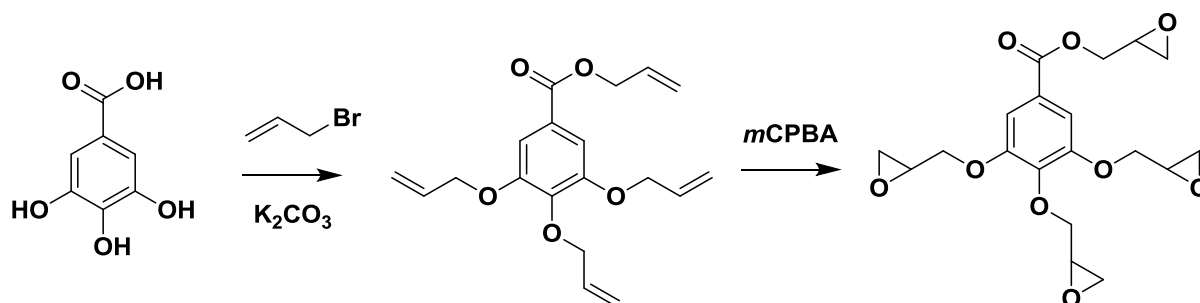
Figure 24: Classification of tannin illustrated by typical structures

In 1985, Tomita *et al.* successfully prepared the glycidylation of gallic acid using epichlorohydrin with quaternary ammonium salts as phase transfer catalyst.¹²¹ More recently, Nouailhas *et al.* investigated the glycidylation mechanisms of model phenolic compounds, such as catechin, 4-methylcatechol, gallic acid and resorcinol in order to evaluate the reactivity of tannins.^{122,123} The authors highlighted the formation of cyclic by-products during this synthesis, thus lowering the amount of epoxy groups in the expected structure (Scheme 23).



Scheme 23: Possible by-products in glycidylation reaction of tannins derivatives^{122,123}

Following another strategy, Aouf *et al.* synthesized tetraglycidylether of gallic acid in a two-step procedure: allylation of the hydroxyl groups followed by the epoxidation of resulting double bonds with *m*CPBA (Scheme 24). Using this synthetic pathway, any by-product was observed.



Scheme 24: Allylation of gallic acid followed by epoxidation¹²³

The thermo-mechanical properties of the epoxy networks obtained from the glycidyl derivative of gallic acid with IPDA show a T_g of 233 °C, value much higher than the one of DGEBA network cured in the same conditions. These outstanding properties are related to the aromatic structure and tetrafunctionality of these monomers, leading to the formation of networks with high degree of crosslinking. These studies demonstrated the feasibility of epoxy thermosets based on flavonoid building blocks.¹²³

In 2014, Benyahya *et al.* have further investigated these previous works by designing epoxy thermosets directly from green tea tannin.¹²⁴ The authors first carried out the functionalisation of the natural green tea extracted tannins with epichlorohydrin and performed the curing step

with IPDA. The so-formed bio-based thermosets exhibit T_g value and mechanical properties in the same range as DGEBA-based system.

In spite of these promising results obtained with model compounds, tannins suffer from several shortcomings. The major limitations of tannins are their diversification and availability. Depending on the plant, a wide variety of structures are present. Additionally, the polymeric nature of tannin makes the characterization and functionalization even more difficult and subsequently limits the use of direct natural tannin at an industrial scale.

II.7 Bio-based epoxy thermosets from lignins

Lignin is a major constituent of lignocellulose and represents the most abundant source of aromatic biopolymer on earth. Lignins are complex tridimensional polymers constituted of three main aromatic phenols: *p*-coumaryl, coniferyl and sinapyl alcohols also called H (hydroxyphenyl), G (guaiacyl) and S (syringyl) units, respectively (Figure 25).

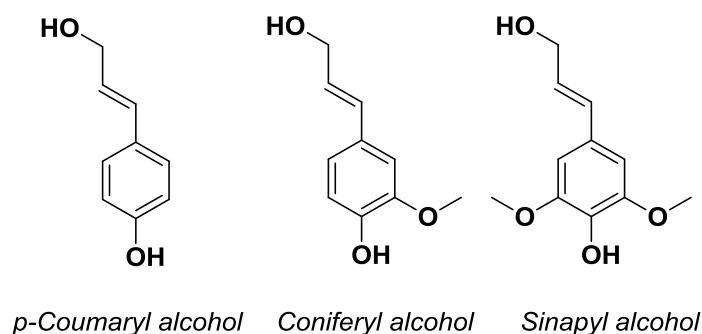


Figure 25: Basic units of lignin

The relative amount of these monolignols vary with respect to the origin of the plant; the aromaticity bringing cohesion and rigidity to the cell wall of the plant. As mentioned above, lignin is a component of the lignocellulose and an extraction process is necessary to separate lignin from the two other constituents, cellulose and hemicellulose. Extraction process has a strong impact on the structure and properties of the recovered lignins. Four industrial extraction processes are currently available to produce lignin: sulfite, kraft, organosolv and soda processes.

Sulfite process consists in the delignification of wood performed in aqueous solution in the presence of sulphur dioxide and a base. The kraft process is conducted at high pH with sodium hydroxide and sodium sulfide. Soda lignin process is based on the depolymerisation of lignins with sodium hydroxide and could be catalysed by anthraquinone. The organosolv method uses organic solvents to extract the lignin. This latter process is more environmental friendly and produces generally high purity and quality lignins. The main characteristics of the different lignins are summarised in Table 8.^{125,126}

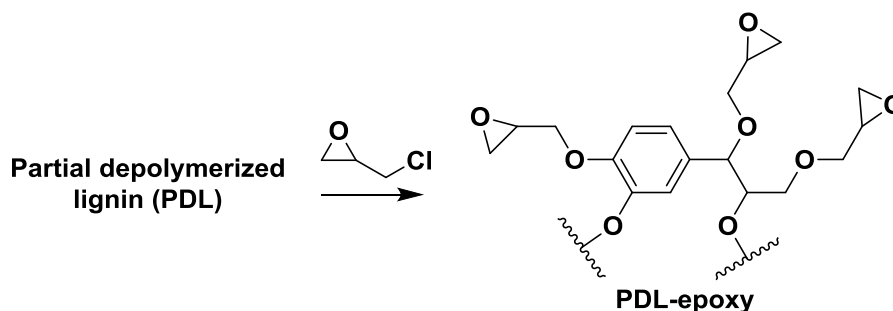
Table 8: Lignin characteristics with respect to the extraction process

Properties	Kraft lignin	Lignosulfonate	Organosolv lignin	Soda lignin
M_n (g.mol⁻¹)	1000 - 3000	5000 - 50000	<2000	800 - 3000
Dispersity	2 - 4	4 - 9	2 - 6	2 - 4
Sulfur content (%)	1-2	3 - 8	0	0
Solubility	Water (pH>10)	Water (All pH)	Water (pH>10) and organic solvent	Water (pH>10)

Today, paper industry produces almost 70 million tons per year of lignin as by-product and 95% of the lignin is burned to provide energy. Nevertheless, the high availability and aromatic feature of lignin make this biopolymer a valuable alternative to petroleum resource in the chemical and polymer industries.¹²⁷⁻¹³³

In the last decades, an increasing number of studies dealing with the synthesis of epoxy resins from lignin and derivatives has been published. As lignin is composed of many hydroxyl and phenolic functions, several authors investigated the direct epoxidation of lignin with epichlorhydrin.¹³⁴⁻¹³⁶ Asada *et al.* studied the synthesis and properties of epoxy precursors from lignin extracted with methanol from steam-exploded wood. Glycidylation with epichlorhydrin and phase transfer catalyst was performed in alkali condition. The resulting glycidylated products were cured with TD2131, a phenol novolac curing agent, and with a biomass-derived lignin hardener. In each case, the thermal decomposition temperatures of biomass-derived thermosets were found lower than those of commercial DGEBA-based thermoset (EP828). Following the same strategy, various authors successfully developed epoxy thermosets from direct epoxidation of lignin. However, only partial replacement of DGEBA in formulation led to systems with better thermomechanical properties than to those made from DGEBA alone.^{137,138} The heterogeneous structure of lignin makes functional groups less available for epoxidation and decreases the compatibility of lignin derivatives with other compounds.

Subsequently, some authors studied the epoxidation of partial depolymerized lignin (PDL) in order to increase the hydroxyl content and the miscibility of lignin with other ingredients. Zhang and coll successfully converted lignin into PDL by enzymatic hydrolysis¹³⁹ and synthesized epoxy precursors by reacting with epichlorhydrin (Scheme 25).¹⁴⁰



Scheme 25: Synthesis of polyglycidylether of partial depolymerized lignin¹⁴⁰

The thermal and mechanical properties of the PDL-epoxy cured with the Diels–Alder adduct of methyl esters of eleostearic acid and maleic anhydride (ME-MA) (Figure 26) were found higher than the ones of BPA-type epoxy cured in the same conditions. Due to its high functionality, Tg of cured PDL-epoxy (94 °C) is 60 °C higher than that of the DGEBA network (36 °C).

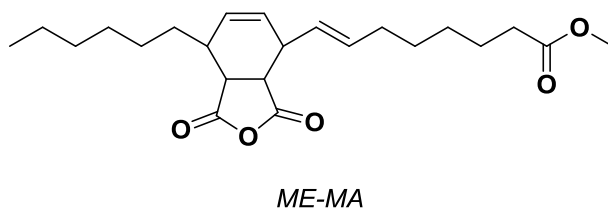


Figure 26: Chemical structure of Diels–Alder adduct of methyl esters of eleostearic acid and maleic anhydride

Despite their high functionality and aromatic structure, the structural heterogeneity and the difficulty to handle the available lignins are still limitations at the industrial scale. To overcome these constraints, deconstruction of lignin appears as a requirement in order to produce well-defined aromatics. In this way, small molecules have the best potential to serve as building blocks for high performance epoxy thermosets. Deconstruction of lignin can be achieved through two main pathways, i.e. reduction or oxidation processes. Hydrogenolysis depolymerisation of lignin involves thermal treatment in the presence of hydrogen and yields aromatic or aliphatic hydrocarbures. On the other hand, oxidation consists in the thermal treatment in the presence of oxygen and generally produce phenolic molecules (Figure 27).^{141–}

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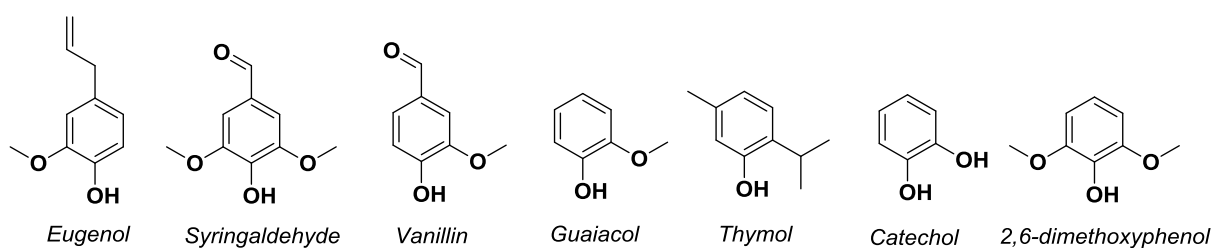
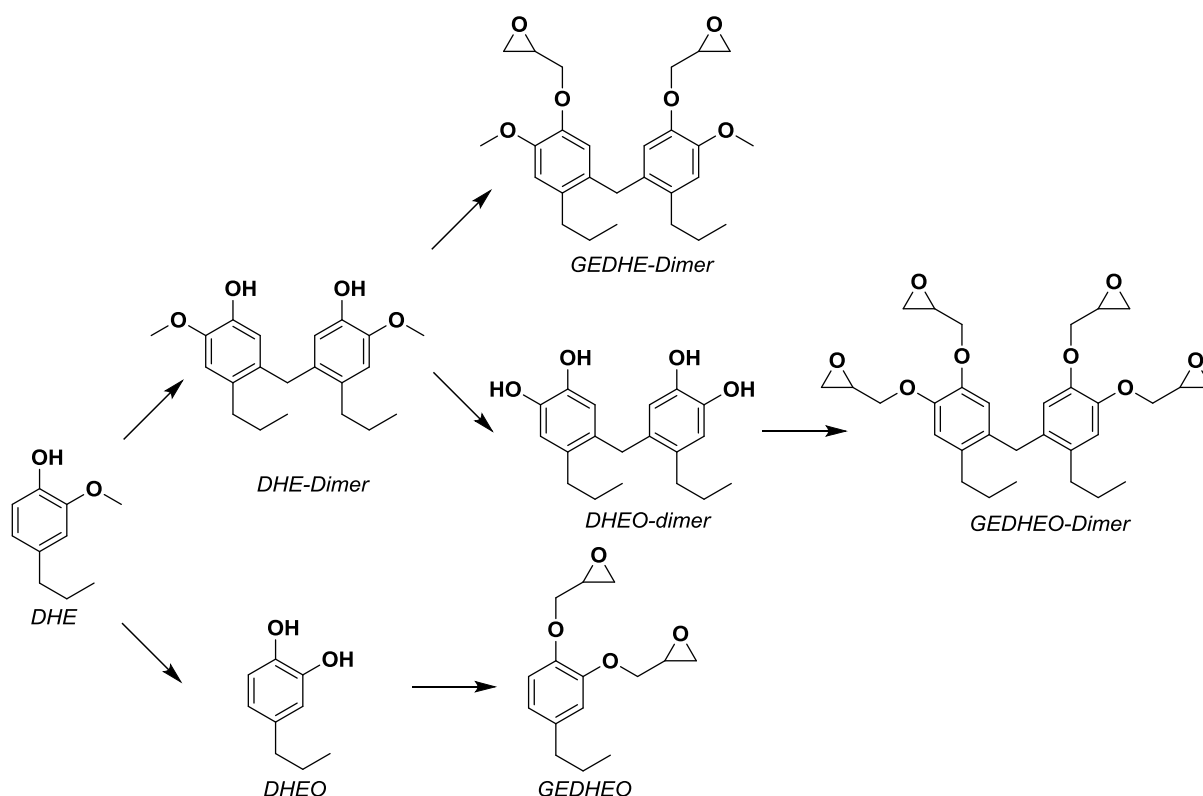


Figure 27: Principal phenolic structures derived from lignin

In 2014, Llevot *et al.* synthesized 2,6-dimethoxyphenol dimer by the laccase-catalyzed process.¹⁴⁵ From this bisphenol, diglycidylether was successfully obtained by reaction with epichlorhydrin. Epoxy precursor was cured with IPDA and thermoset exhibited a glass transition temperature of 123°C, which is slightly lower than the DGEBA reference. Nevertheless, the dimerization process involved in this work has a strong potential for the synthesis of other bio-based epoxy precursors and will be further described in the following chapter.

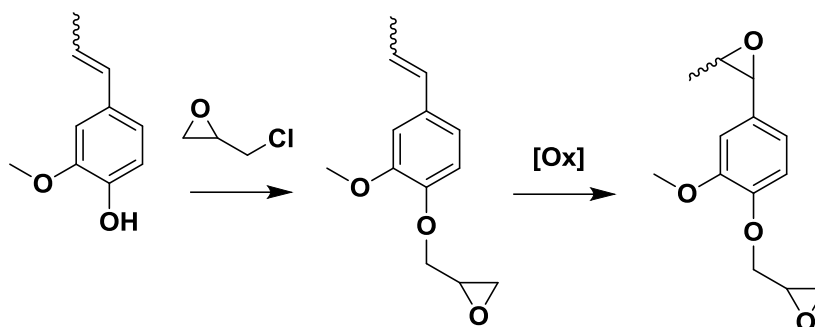
Later, Zhao *et al.* successfully developed an efficient method to convert lignin into methoxyphenol products, especially dihydroeugenol (DHE).¹⁴⁶ In another study, the authors investigated the synthesis of epoxy thermosets from DHE and derivatives cured with diethylenetriamine (DETA).¹⁴⁷ Structures of the epoxy monomers are depicted in Scheme 26. T_g of the bio-based systems follows the order: GEDHEO (40 °C) < GEDHE-Dimer (70 °C) < GEDHEO-Dimer (84 °C), which is in accordance with the cross-linking density of the formed structures. However, the presence of propylene dangling segments and of methylene bridges could increase the mobility of the chains and explain thermomechanical properties differences with traditional DGEBA-based thermosets cured in the same conditions ($T_g=138$ °C).



Scheme 26: Bio-based epoxy thermosets derived from DHE^{146,147}

More recently, Galkin *et al.* reported the fractionation of lignocellulosic biomass into iso-eugenol using an organosolv and palladium-catalyzed depolymerisation processes.¹⁴⁸

Based on this work, the same research group performed the chemical transformation of *iso*-eugenol into a prepolymer for the preparation of epoxy thermosets.¹⁴⁹ Diglycidylether derivatives (DGE-*iso*Eu) were synthesized in a two-step reaction from epichlorhydrin and oxone as oxidizing agent (Scheme 27).



Scheme 27: Synthesis of *iso*-eugenol into diglycidyl ether of *iso*-eugenol

DGE-*iso*Eu mixtures were cured with various anhydride curing agents, such as MPA, THPA or HHPA in the presence of imidazole catalyst. The best systems exhibit a T_{α} value of 120 °C which is higher than DGEBA-based thermoset cured in the same conditions (106 °C). Similar work has been carried out by Qin *et al.* on the glycidylation of eugenol. Equivalent system prepared with diglycidylether of eugenol exhibited $T_{\alpha}=114$ °C.¹⁵⁰

However, despite the promising properties exhibited by all previously described systems, they all suffer from industrial production limitations, except maybe one, i.e. vanillin as it is explained and discussed below.

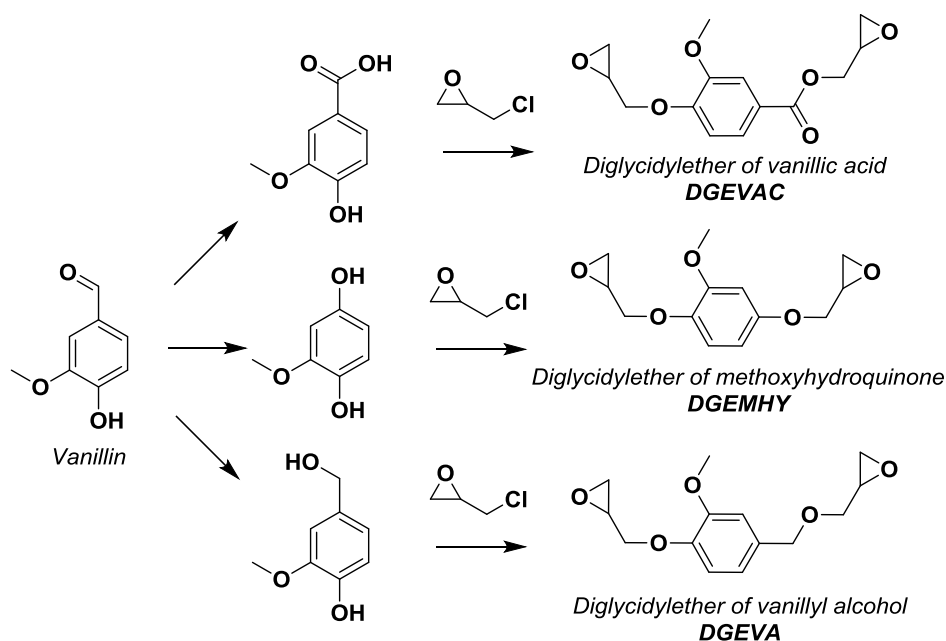
II.8 Bio-based epoxy thermosets from vanillin

Vanillin is the only aromatic compound industrially available from biomass.¹⁵¹ The annual production of vanillin reaches around 20 000 tons.¹⁵² 85% of the overall vanillin production comes from non-renewable feedstock and less than 1% stems from natural vanilla pods.¹⁵³ Nowadays, about 3000 tons of vanillin comes from lignin. Since 1962 the Borregaard's biorefinery has developed the lignin-to-vanillin process at an industrial scale.¹⁵⁴ Such process consists of treating liginosulfonate by-products of the pulp wood manufacture. Vanillin is recovered by using oxidizing agents, high pH, high temperatures and pressures in order to break up the lignin.^{155,156}

In this way, vanillin and derivatives have grown a strong interest to be used as bio-based building blocks for renewable polymers.

Several authors described the synthesis of epoxy monomers from vanillin. As an illustration, Aouf *et al.* prepared bio-based epoxy precursors from vanillic acid in a two-step reaction. The authors first synthesized allylated intermediates using allyl bromide and then oxidized these derivatives *via* chemo-enzymatic process with *Candida Antartica* lipase.¹⁵⁷ Following another strategy, Koike *et al.* reported the synthesis of epoxy monomers through the coupling of vanillin with pentaerythritol followed by glycidylation with epichlorhydrin.¹⁵⁸ Unfortunately, the thermo-mechanical properties of the so-formed networks were not evaluated.

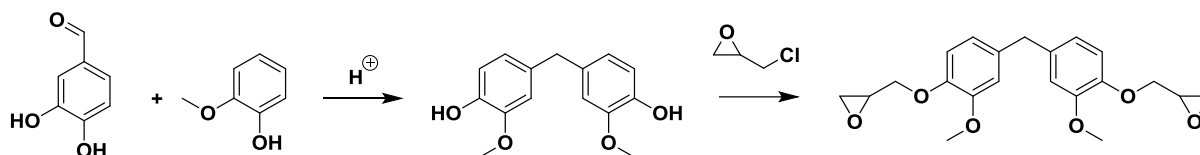
More recently, Fache *et al.* have done a complete investigation on the synthesis of bio-based epoxy thermosets from vanillin derivatives.^{159–161} The authors successfully prepared diglycidyl ethers from methoxyhydroquinone, vanillic acid and vanillyl alcohol by direct epoxidation with epichlorhydrin as depicted Scheme 28. All of these vanillin-based epoxy thermosets exhibited promising thermo-mechanical properties when cured with IPDA. The resulting networks displayed Tg values between 97°C and 152°C, whereas conventional BPA-based resins showed Tg of 166°C. According to the authors, the presence of methoxy groups on the aromatic ring could explain the decrease of the Tg when compared with DGEBA-based materials. These results are in accordance with other works which described the synthesis of vanillin-based epoxy resin from vanillyl alcohol.^{162,163}



Scheme 28: Synthesis of epoxy monomers from vanillin derivatives^{162,163}

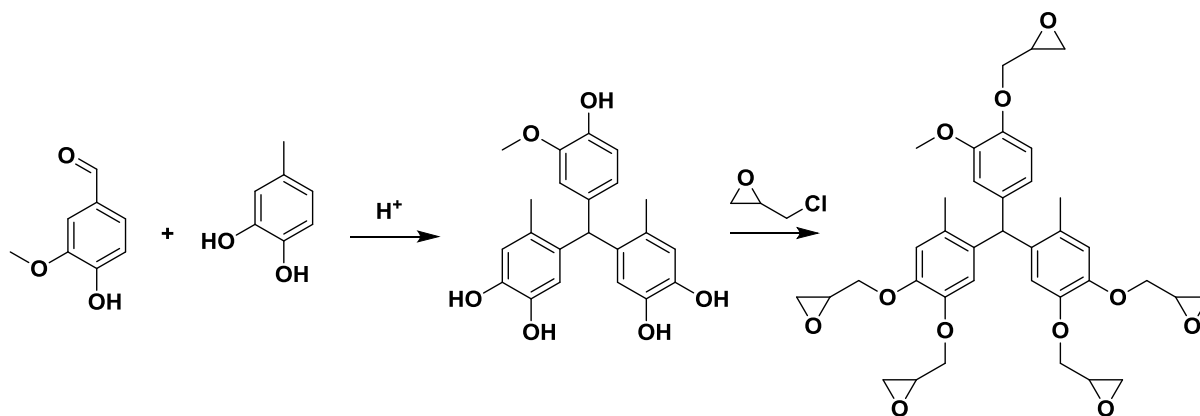
In another study, the authors evaluated the thermal properties of vanillin-based epoxides cured with IPDA.¹⁶⁴ The so-formed thermosets exhibit tuneable thermo-mechanical properties by varying the length of the oligomer and T α values all comprised between 80°C and 110°C.

Besides, Hernandez *et al.* reported the synthesis of the electrophilic aromatic condensation of vanillyl alcohol with guaiacol followed by epoxidation with epichlorhydrin to produce diglycidylether of bisguaiacol (DGEBG) (Scheme 29).¹⁶³ When cured with PACM, the DGEBG-based materials exhibit a lower Tg (104°C) than the DGEBA network (149 °C). The authors incriminated the two methoxy moieties that allow for a greater degree of rotational freedom of the polymer backbone upon heating.



Scheme 29: Synthesis of diglycidylether of bisguaiacol

In 2017, the same authors developed triphenylmethane-type phenol (TP) thermosets by condensation between aromatic aldehyde and phenol (Scheme 30).¹⁶⁵ These resulting bio-based structures were cured with DETA and exhibited excellent glassy modulus (12.3 GPa), glass transition temperature (167 °C), and thermal stability. These results were attributed to the highly functionality ($n = 5$) and highly rigidity of triphenylmethane framework. These advantageous structural properties make renewable TPs excellent precursors to epoxy thermosets for high performance applications.



Scheme 30: Example of glycidyl ether of TP from vanillin and methylcatechol

Vanillin demonstrated a great potential to provide aromatic monomers required to achieve good thermo-mechanical properties and thus answer the problematic of BPA-based thermosets. Therefore, synthesis of vanillin based epoxy monomers seems to be worth exploring.

III. Conclusion

Structural adhesives are a class of adhesives which depart from their outstanding performances in harsh conditions. They are able to compete with mechanical bonding because of numerous advantages like versatility, excellent thermomechanical properties and weight saving. Among the structural adhesives commercially available, epoxy resins represent one of the main materials. Nowadays, 75% of epoxy resins are derived from BPA. This BPA prevalence is mainly due to a combination of high availability, low cost and relatively high performance in resulting materials. In this way, diglycidyl ether is the most commonly produced epoxy resin types. However, BPA is also known as endocrine disruptor subject to strong regulation. In this context of price petroleum resources volatility coupled with the awareness of environmental concerns, the chemical industry urges to find solutions in order to produce industrially viable bio-based chemicals.

This chapter reviewed the literature towards the renewable resources available for the synthesis of bio-based epoxy thermosets. Vegetable oils are considered to be one of the most important classes of renewable sources due to its abundant availability and low price. However, their aliphatic structures do not allow the achievement of high performance materials. Most industrial applications for the resulting epoxy materials remain limited to non-structural applications. More rigid structures are therefore required for high-performance applications. Rosin, glucose derivatives or cardanol are other bio-based raw materials able to afford more solid networks. Nonetheless, thermo-mechanical properties were still lower than the ones of petroleum-based reference. Other bio-based raw materials such as tannins and lignins provided promising candidates for the replacement of BPA-based epoxy thermosets. However, the industrial development of these renewable resources suffer from their versatility, complexity and processability. In this way, single bio-based molecules with simple structure are required. Accordingly, vanillin is the only aromatic molecule obtained from renewable resources at an industrial scale and first academic researches demonstrated an outstanding potential of vanillin to compete with BPA.

In this context, next chapters will focus on the preparation and the characterization of new bio-based epoxy prepolymers derived from vanillin and resulting epoxy networks.

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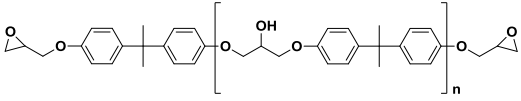
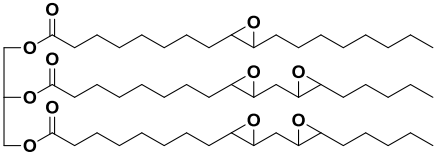
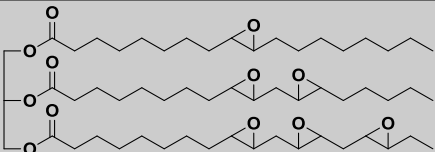
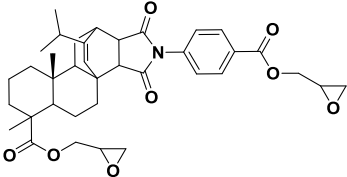
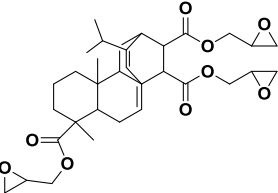
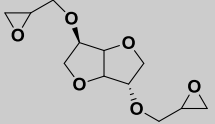
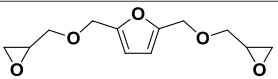
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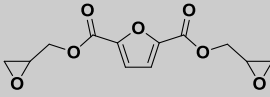
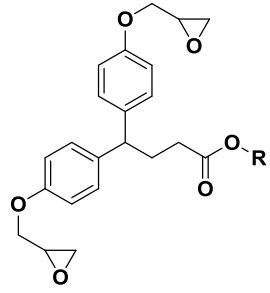
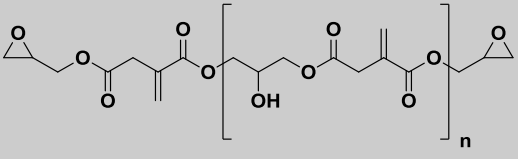
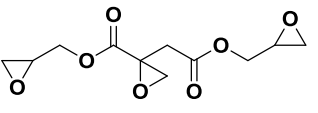
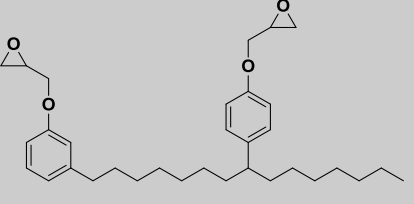
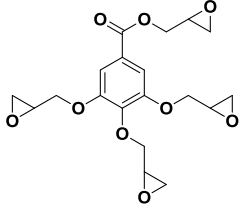
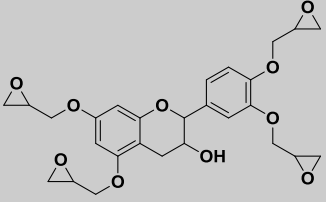
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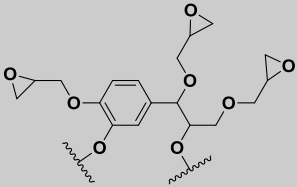
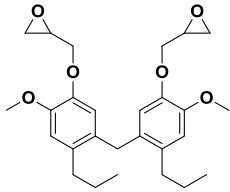
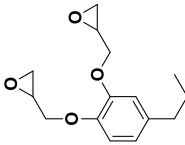
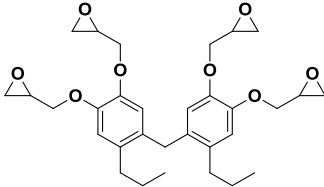
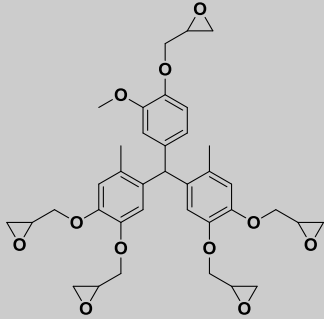
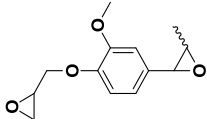
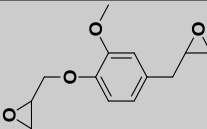
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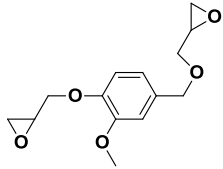
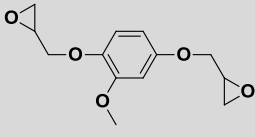
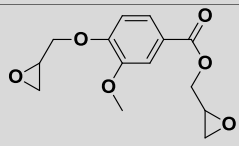
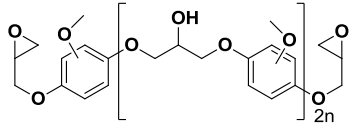
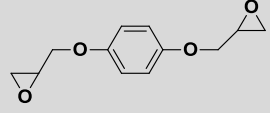
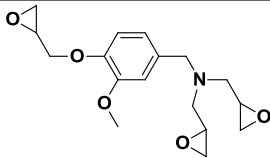
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V. Annexes

Bio-based Epoxy prepolymers	Hardeners	T _α (°C)	T _{d5%} (°C)	Ref
 <p><i>Diglycidyl ether of bisphenol A</i></p>	<i>IPDA</i>	[155-166]	360	89,101,123,161
	<i>DETA</i>	138	327	147,165
	<i>PA</i>	122	239	71166
	<i>PACM</i>	158	379	163
	<i>MHHPA</i>	[126-144]	342	86,98,167
	<i>HHPA</i>	[106-144]	330	81,149,150
 <p><i>Epoxidized soybean oil (ESO)</i></p>	<i>MHHPA</i>	70	210	72
	<i>PA</i>	73	-	71
 <p><i>Epoxidized linseedoil (ELO)</i></p>	<i>BTDA</i>	130	340	73
 <p><i>Glycidyl ester of rosin-maleic anhydride imidodicarboxylic acid</i></p>	<i>HHPA</i>	156	311	81
<i>Epoxidized Polygral</i>	<i>IPDA</i>	93 ^a	-	84,85
 <p><i>Triglycidyl ester of fumaropimaric acid</i></p>	<i>MHHPA</i>	166	328	86
 <p><i>Diglycidyl Ether of Isosorbide</i></p>	<i>IPDA</i>	112	305	89
 <p><i>Diglycidyl Ether of BHMf</i></p>	<i>PACM</i>	71	303	96,97

 <p><i>Diglycidyl ester of FDCA</i></p>	MHHPA	152	293	98
 <p><i>Diglycidyl Ether of diphenolate</i></p>	IPDA	[86-158]	363	101
 <p><i>Glycidyl Ether of itaconic acid</i></p>	MHHPA	[122-130]	326	105,168
 <p><i>Glycidyl Ether of itaconic acid</i></p>	MHHPA	109 ^a	368	106
 <p><i>Cardolite NC-514</i></p>	IPDA	59	366	107
 <p><i>TetraGlycidyl Ether of Gallic Acid</i></p>	IPDA	233	300	123
 <p><i>Tetraglycidyl ether of catechin</i></p>	IPDA	179	310	124
<p><i>Epoxidized green tea tannins</i></p>	IPDA	142	260	124

 <p>Glycidyl ether of partial depolymerized lignin</p>	<i>Maleic anhydride</i>	96	272	140
 <p>Glycidyl ether of DHE-Dimer</p>	<i>DETA</i>	40		
 <p>Glycidyl ether of DHEO</p>	<i>DETA</i>	70	138	147
 <p>Glycidyl ether of DHEO-Dimer</p>	<i>DETA</i>	84		
 <p>Polyglycidyl ether of TP</p>	<i>DETA</i>	167	270	165
 <p>Diglycidyl ether of iso-eugenol</p>	<i>HHPA</i>	120	306	149
 <p>Diglycidyl ether of eugenol</p>	<i>HHPA</i>	114	321	150

	<i>IPDA</i>	106	361	159–161
<i>Diglycidyl ether of vanillyl alcohol</i>	<i>PACM</i>	107	341	163
	<i>IPDA</i>	154	338	159–161
<i>Diglycidyl ether of methoxyhydroquinone</i>	<i>IPDA</i>	166	315	
	<i>IPDA</i>	166	315	
	<i>IPDA</i>	[80-110]	-	164
<i>Diglycidyl ether of MHY oligomers</i>	<i>PACM</i>	132	337	163
	<i>PACM</i>	111	363	
<i>Diglycidyl Ether of Bisguaiacol (DGEGB)</i>	<i>IPDA</i>	194	-	
	<i>IPDA</i>	112	-	167
<i>Triglycidylether of vanillylamine (TriGEVAM)</i>	<i>MHPPA</i>	131	-	
<i>Epoxidized Salicylic Acid (ESA)</i>	<i>DETA</i>	86	-	

^aDetermined by DSC

Chapter 2: Synthesis of bio-based epoxy precursors

Keywords: bio-based phenols, oxidative coupling, laccase, divanillin, epichlorhydrin, epoxy precursors, polyepoxydes, oligomers

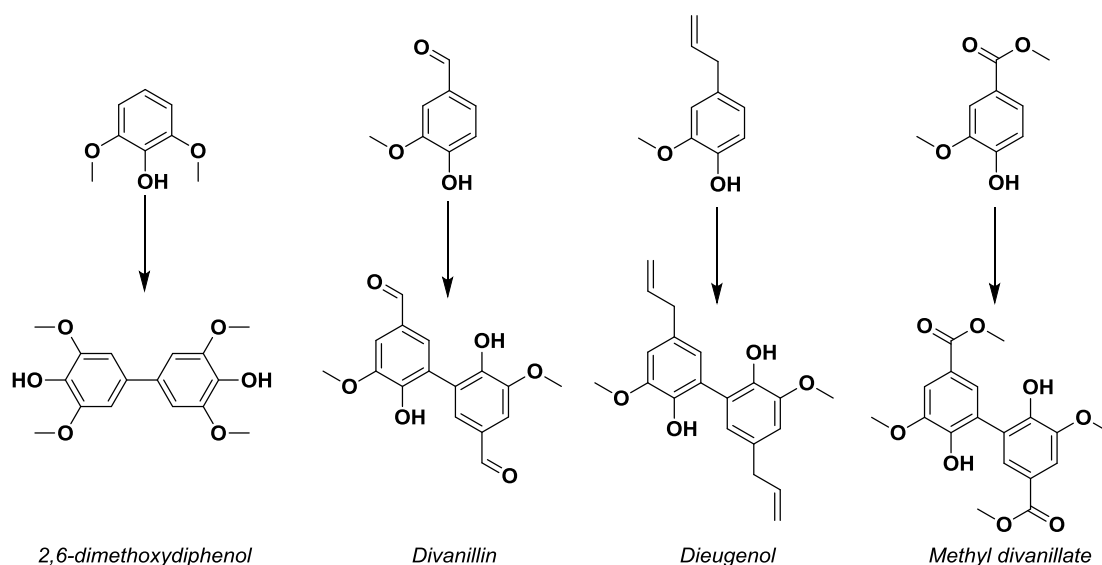
Mots-clés: phenols bio-sourcés, couplage oxydatif, laccase, divanilline, épichlorhydrin, précurseurs époxydés, polyépoxydes, oligomères

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I. Introduction

As described in the previous chapter, vanillin is a very interesting candidate for the synthesis of bio-based epoxy-precursors because it is the only non-hazardous aromatic compounds industrially available from biomass.¹ Recent works on the oxidative coupling of phenolic molecules by enzymatic catalysis have made available a bio-platform of bio-based biphenyl molecules derived from lignin.²⁻⁴ Indeed, Llevot *et al.* developed an efficient C-C enzymatic coupling process using laccase from *Trametes versicolor* to produce well-defined dimers of vanillin, methyl vanillate, eugenol and 2,6-dimethoxyphenol in high yield (Scheme 31).



Scheme 31: Platform of biphenyl compounds obtained by oxidative coupling of bio-based phenols

Based on these results, the present work is dedicated to the synthesis and the characterization of epoxy precursors from bio-based biphenyl compounds and especially from vanillin.

II. Laccase-catalysed oxidative coupling of biobased phenols

Laccases are glycoproteins available in plants, insects or fungi and are mainly used as biocatalysts for the oxidative coupling of phenolic compounds.⁵ Laccases possess four copper atoms in two active sites which can catalyse mono-electronic oxidation using oxygen as the oxidant.⁶ The overall catalytic cycle is the reduction of one molecule of oxygen to two molecules of water yielding the oxidation of phenolic substrates to produce radicals species (Figure 28).⁷

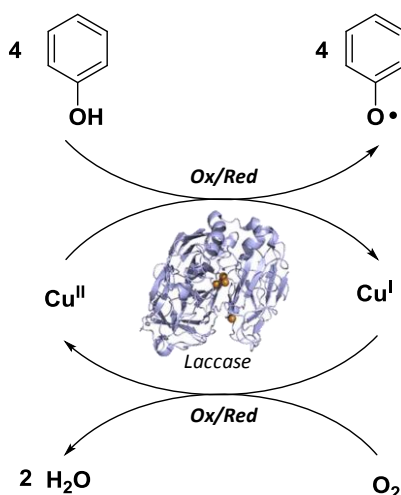
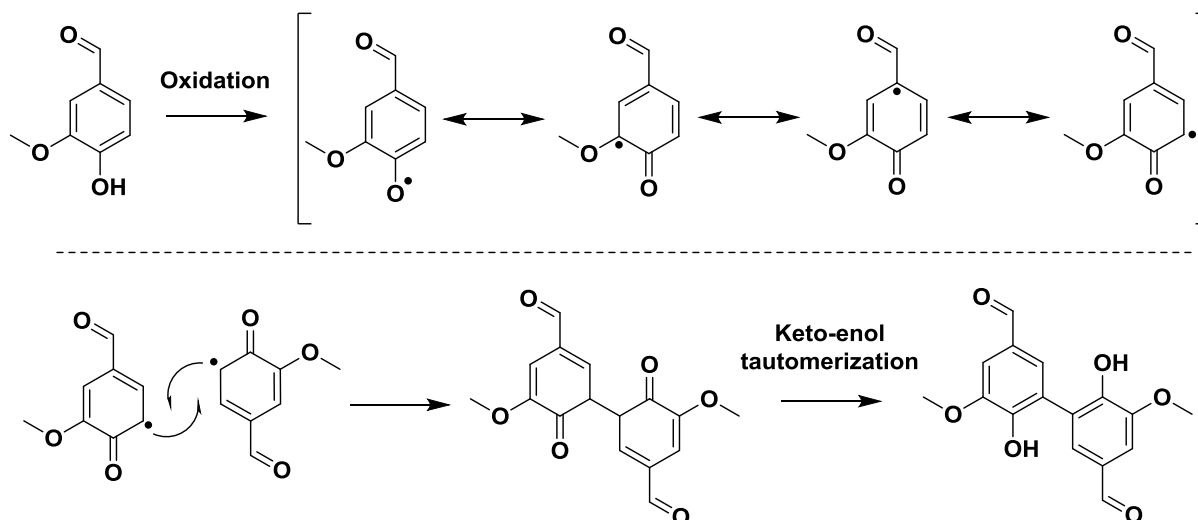


Figure 28: Catalytic cycle of laccase to produce phenolic radicals

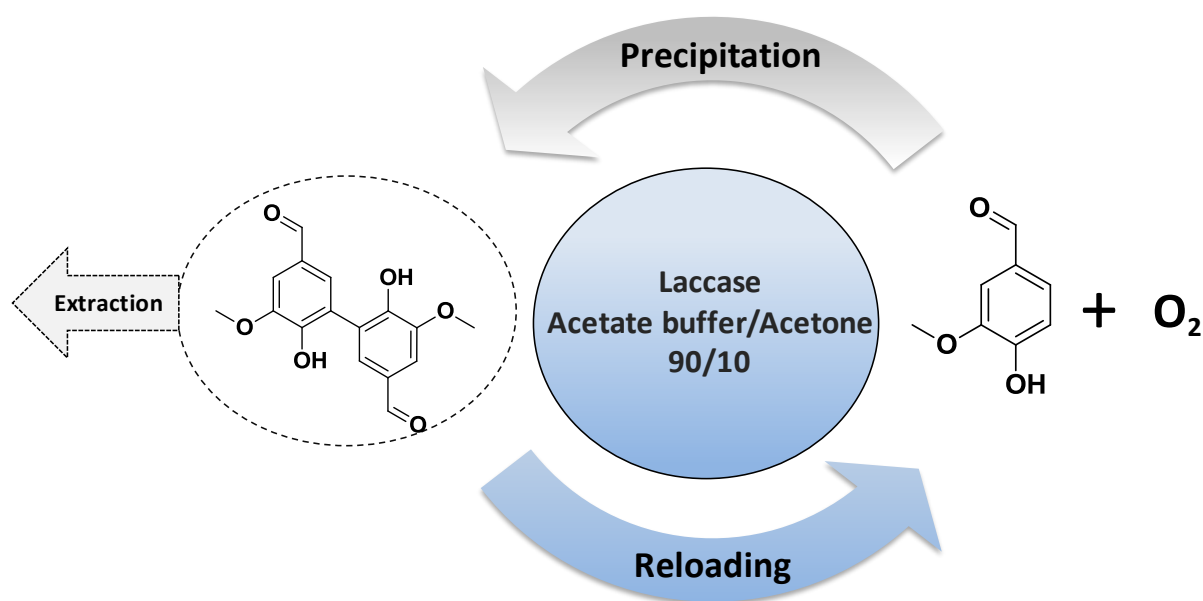
Through the oxidation of phenolic substrates, various mesomeric radical species are generated. Depending on the substitution of the aromatic ring, radicals can undergo self-coupling reactions yielding pure dimers. As an illustration, the formation of vanillin dimer is depicted Scheme 32.



Scheme 32: Laccase-catalysed vanillin dimerization mechanism

II.1 Synthesis and characterization of divanillin

As described in a previous work, Llevot *et al.* investigated the influence of various parameters, such as laccase's origin, solvent quantities, pH value, or reaction time and developed the optimum procedure for the synthesis of pure dimer.² The optimised process consists in solubilizing the monomer and the laccase in acetate buffer solution with acetone as co-solvent in saturated oxygen atmosphere at room temperature. Spontaneously, dimer precipitation starts to occur while the solvent conditions permit the phenol (vanillin) to remain soluble. After 12h, a simple filtration enables the recovery of the so-formed product. The filtrate, containing the laccase, is then refilled in oxygen and in vanillin to start again the process (Scheme 33).



Scheme 33: Self-sufficient process to synthesize dimer from vanillin

Following this procedure, divanillin was synthesized in high yield (>90%). Remaining vanillin traces were removed by reprecipitation of divanillin from alkaline water-ethanol solution with hydrochloric acid. The molecular structure of divanillin was confirmed by ¹H and ¹³C NMR spectroscopy. Only four ¹H NMR signals characterized the divanillin structure (Figure 29). The simplicity of spectrum is essentially due to the symmetry of the molecule. The singlet at 9.69 ppm represents proton of aldehydes. Aromatic protons are characterized by two doublets at 7.57 and 7.16 ppm. Labile protons of phenol are not displayed on the spectra, but protons of methoxy group are defined by the singlet at 3.76 ppm.

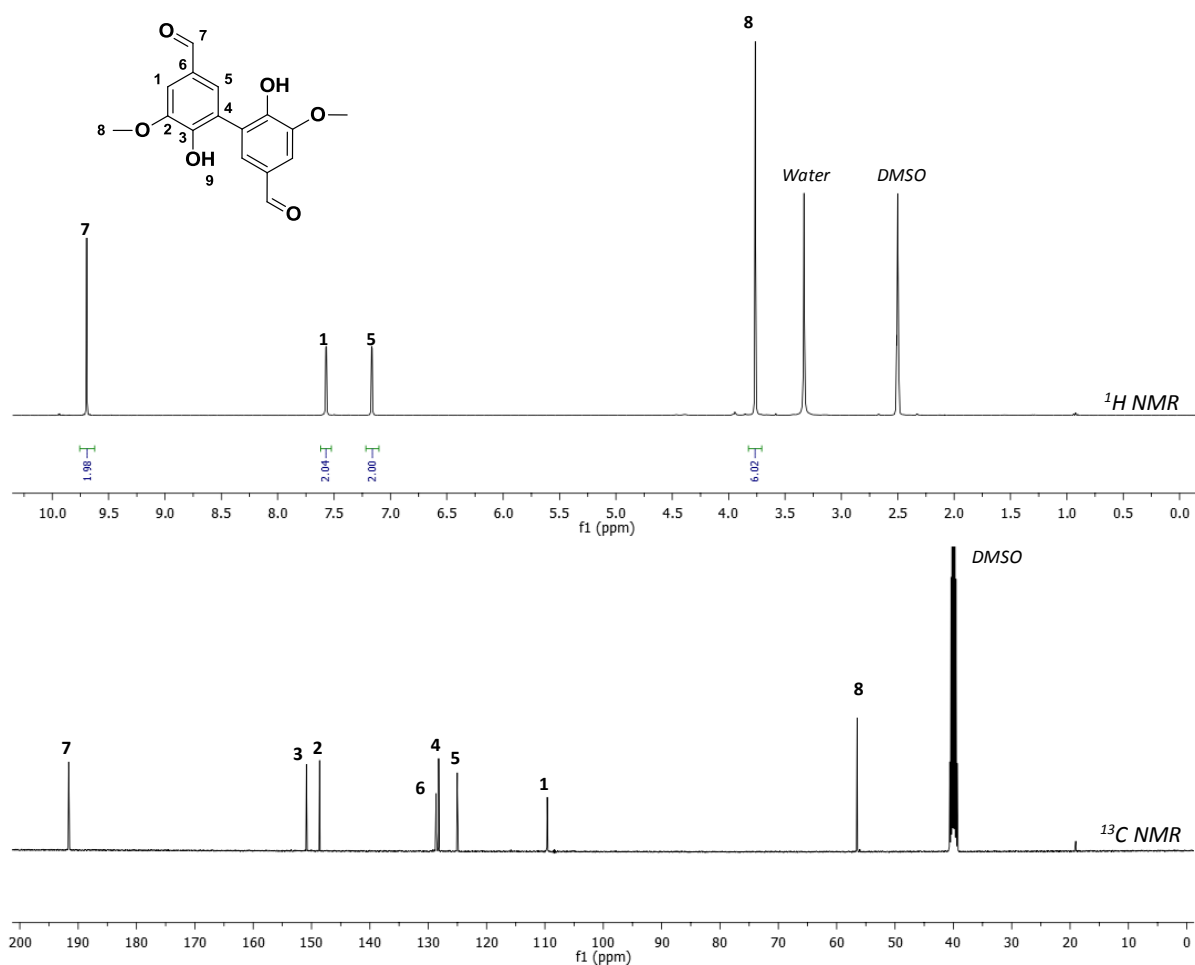
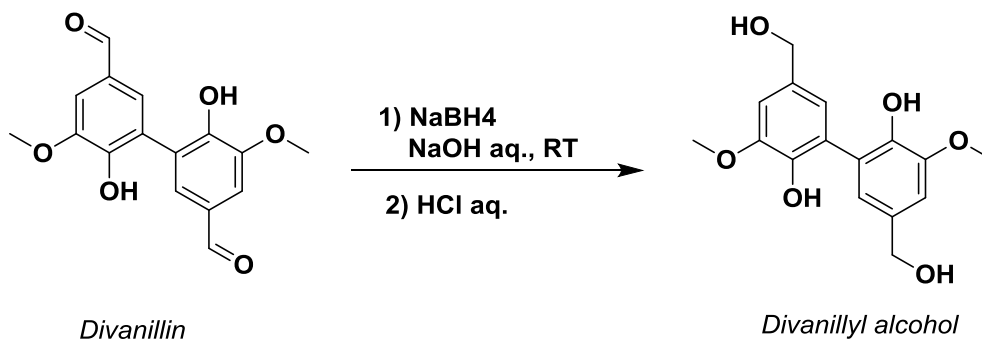


Figure 29: ^1H and ^{13}C NMR spectra of divanillin in DMSO-d_6

II.2 Synthesis and characterization of divanillyl alcohol

Aldehydes of divanillin can be reduced into benzyl alcohols using sodium borohydride as reductive agent. Divanillin aldehyde moieties undergo a nucleophilic addition of hydride yielding divanillyl alcohol (DVA) in very good yield (>90%) (Scheme 34).



Scheme 34: Reduction of divanillin with sodium borohydride

The structure of DVA was confirmed by the disappearance of the aldehyde signal at 9.69 ppm and the appearance of doublet and triplet at 4.41 ppm and 5.01 ppm, attributed to methylene

and benzyl alcohol protons, respectively. A shift of aromatic signals at 6.88 and 6.67 ppm were also observed and supported this statement (Figure 30).

The structure of the divanillin and DVA were also characterized by FTIR. Figure 31 clearly shows the absence of the C=O band at 1680 cm^{-1} attributed to the aldehyde moieties. DVA spectrum also exhibited the appearance of benzyl alcohol band at 3400 cm^{-1} .

In conclusion, divanillin and DVA displayed two and four hydroxyl moieties, respectively, which can undergo glycidylation reaction. In this way, divanillin and DVA are suitable precursors for the synthesis of epoxy prepolymers.

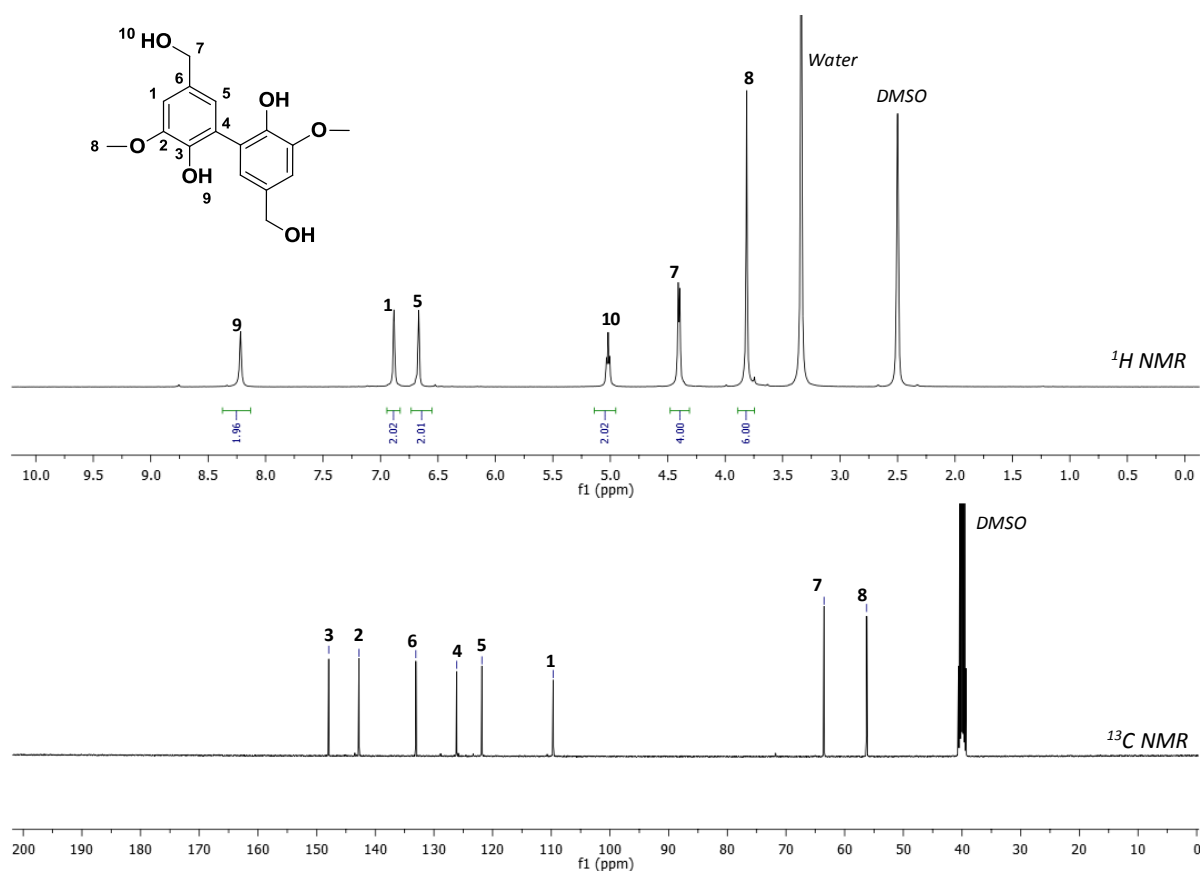


Figure 30: ^1H and ^{13}C NMR spectra of divanillyl alcohol in DMSO- d_6

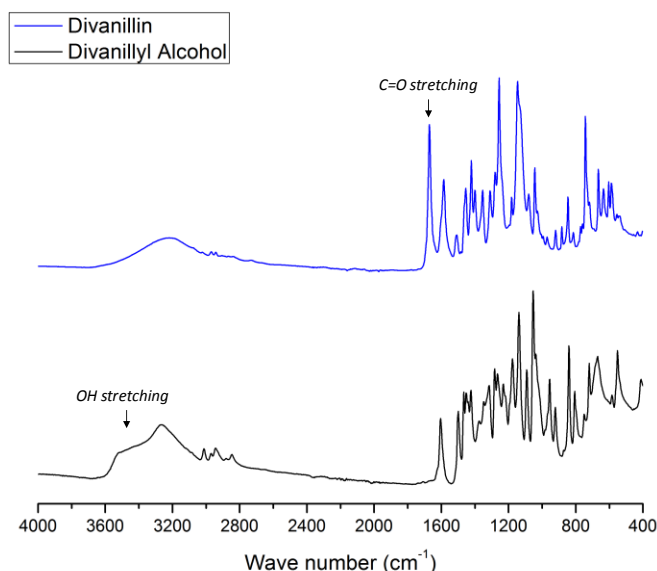


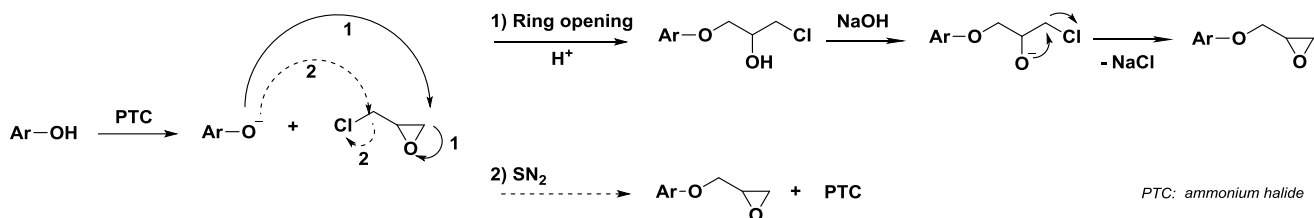
Figure 31: FTIR spectra of divanillin and divanillyl alcohol

III. Synthesis of bio-based epoxy prepolymers

III.1 Synthesis and characterization of bio-based glycidylethers derived from DVA

Several works describe the synthesis of epoxy compounds from phenolic substrates in the presence of epichlorohydrin, a phase-transfer catalyst and a base.^{9–13} Usually, a large excess of epichlorohydrin is used to prevent the formation of high molecular weight epoxy oligomers. Moreover, additional solvents are not necessary during the synthesis as epichlorohydrin acts as a reactive solvent.

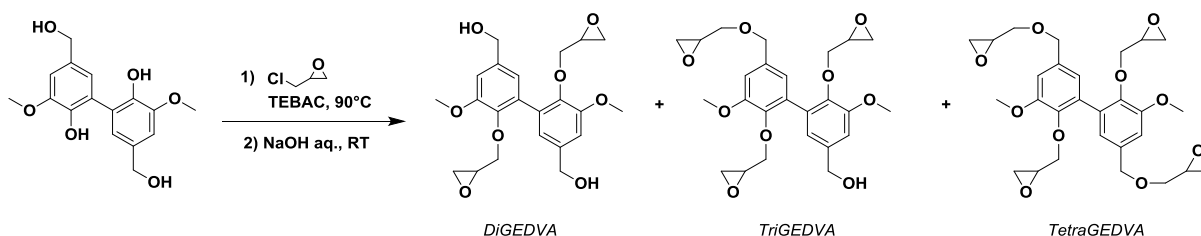
Synthetic pathway adapted for the DVA takes place in two steps. First, glycidylation reaction is carried out at 80°C with epichlorohydrin in the presence of triethylbenzylammonium chloride (TEBAC), a phase transfer catalyst (PTC). The PTC eases the nucleophilic substitution of phenol with epichlorohydrin by assisting the phenolate ion into the organic phase.¹⁴ The nucleophilic substitution can directly lead to the synthesis of epoxy moieties, but a ring-opening mechanism can also occur yielding “open-epoxy” intermediates. The second step thus consists in adding a base at room temperature in order to close the epoxy ring intermediates. Also at this step, the base is needed to deprotonate benzyl alcohols leading to their epoxidation (Scheme 35).



Scheme 35: Mechanism of glycidylation of aromatic compounds with epichlorhydrin in presence of PTC

Following this synthetic route, different epoxy prepolymers were prepared: diglycidylether of divanillyl alcohol (DiGEDVA), triglycidylether of divanillyl alcohol (TriGEDVA) and tetraglycidyl of divanillyl alcohol (TetraGEDVA) (Scheme 36).

The latter are generally obtained as a mixture at various ratios, but separation by flash chromatography, using a gradient of DCM/MeOH as eluent, enables to recover each derivatives separately.



Scheme 36: Synthesis of polyglycidylethers from epichlorhydrin and DVA

These derivatives have been characterized by ^1H NMR spectroscopy (Figure 32). The glycidylation of phenols was confirmed by the presence of signals of epoxy moieties at 2.36, 2.60, 2.95, 3.74 and 3.88 ppm. Epoxidation of benzyl alcohols of TriGEDVA and TetraGEDVA was confirmed by the characteristics signals of epoxy moieties at 2.55, 2.73, 3.14, 3.28, and 3.70 ppm and by the gradual decrease of the benzyl alcohol signal at 5.16 ppm. In addition, TriGEDVA NMR spectrum shows a duplication of aromatic and methylene signals at 6.71 and 4.47 ppm respectively, reflecting a loss in the symmetry of the molecule. ^{13}C NMR spectra of these compounds can be found in the Annexes section at the end of this chapter.

The structures of the DiGEDVA, TriGEDVA and TetraGEDVA have also been characterized by FTIR (Figure 33). Indeed, benzyl alcohol band at 3400 cm^{-1} gradually disappears with the formation of epoxide functions. In the case of TetraGEDVA, the specific band has completely vanished, while in the case of DiGEDVA the band is still visible. The CH and C=C aromatic ring stretching are also visible at 2920 cm^{-1} and 1600 cm^{-1} . Moreover, the FTIR spectrum in Figure 34 displays the noticeable band of oxirane ring at 915 cm^{-1} , which is stronger for TetraGEDVA than DiGEDVA; and additional ether band at 1100 cm^{-1} , corresponding to the glycidylation of benzyl alcohols.

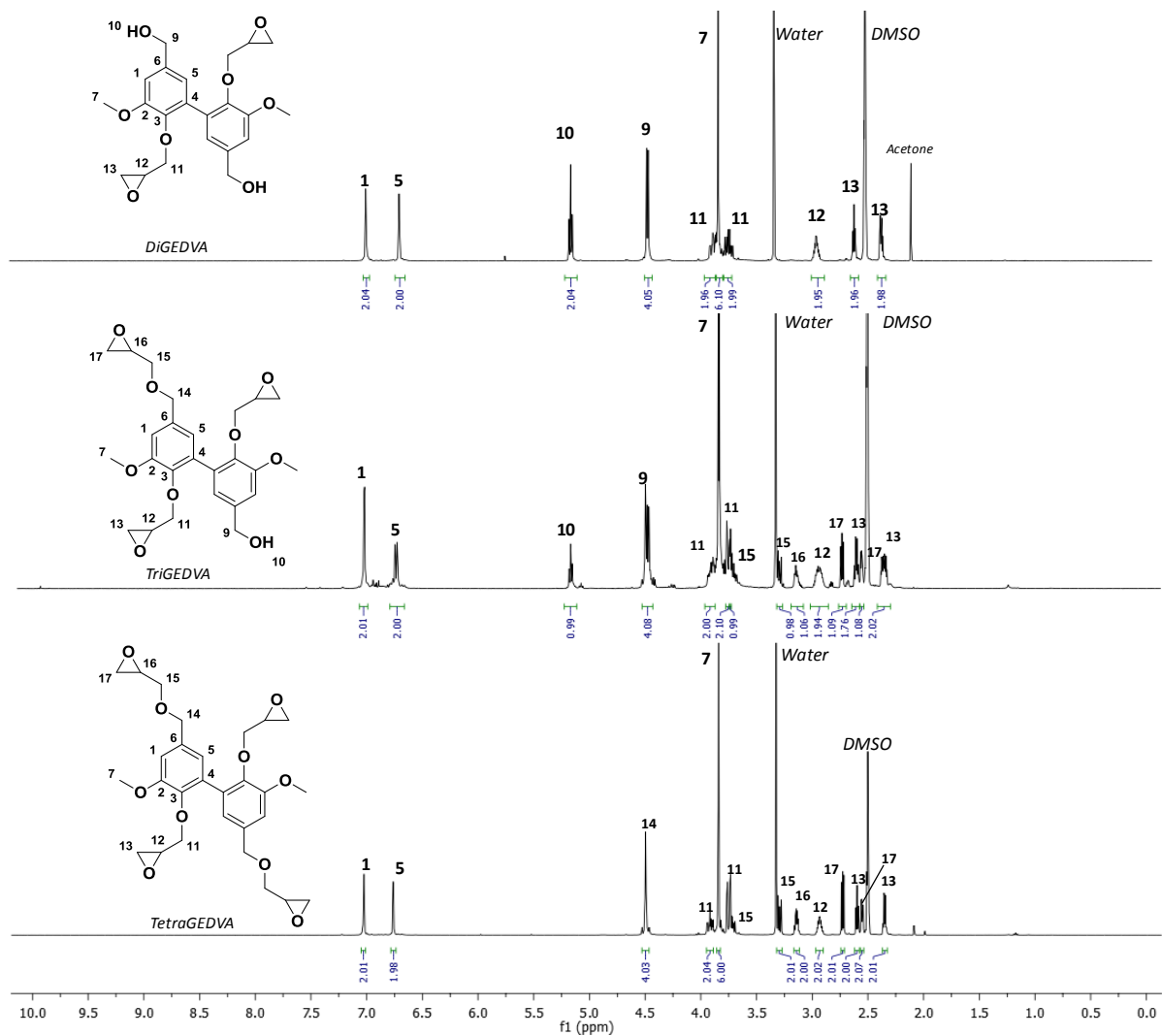


Figure 32: ^1H NMR spectra of DiGEDVA, TriGEDVA and TetraGEDVA in DMSO-d_6

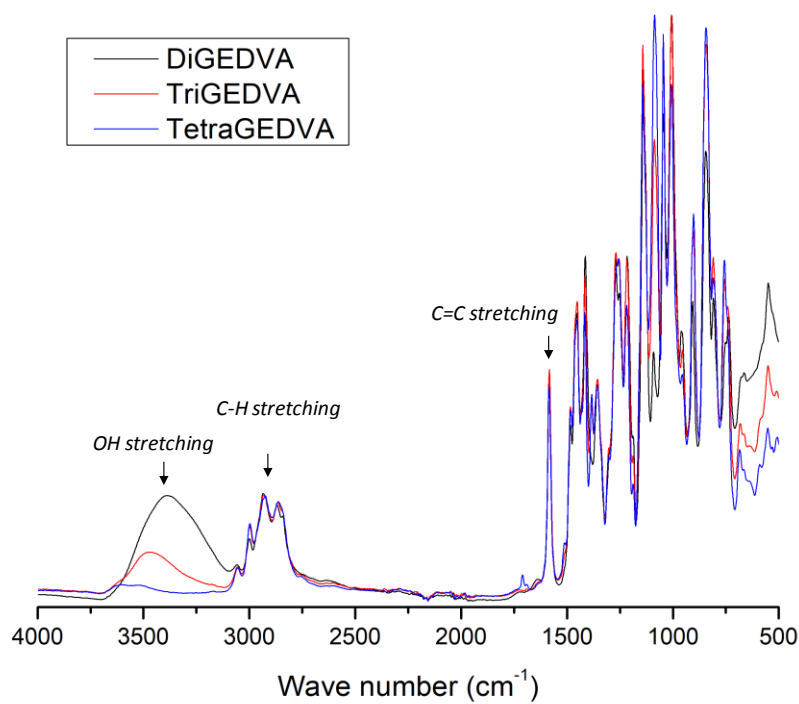


Figure 33: Characterization of DiGEDVA (black), TriGEDVA (red) and TetraGEDVA (blue) by FTIR

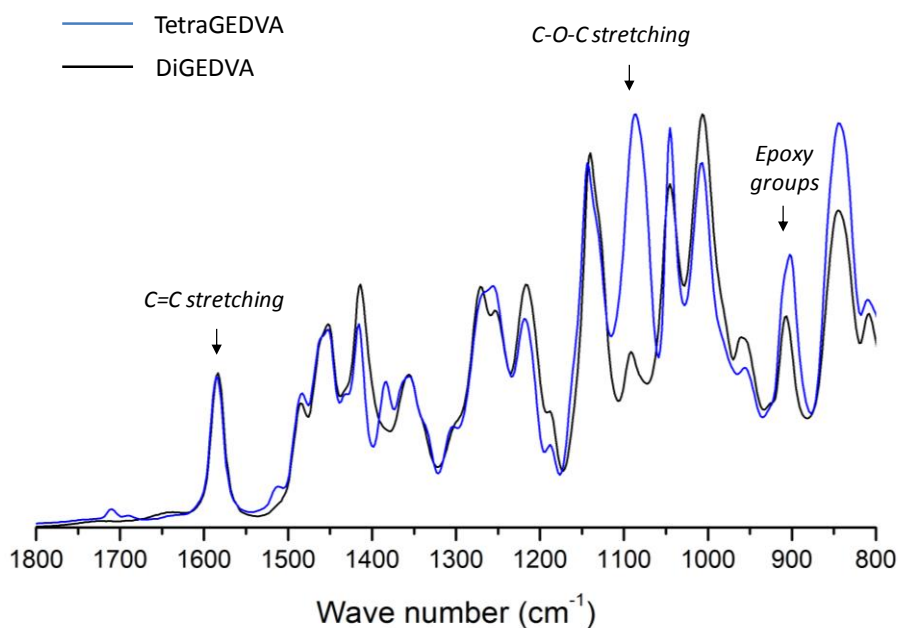


Figure 34: FTIR spectra of DiGEDVA (black) and TetraGEDVA (blue) from 800 and 1800 cm^{-1}

Nevertheless, two key parameters have been identified to govern this reaction: the sodium hydroxide content and the second step reaction duration. In this way, by tuning these two parameters, the different structures can be selectively obtained.

HPLC method was developed to quantify and characterize the different mixtures. As a first step, eluent composed of water and acetonitrile was chosen. Different compositions were tested in order to determine the best elution strength. As depicted in Figure 35, a ratio 50/50 of acetonitrile/water exhibited the best peak separation and has been selected for the rest of the study. Retention time of Di, Tri and TetraGEDVA are 3, 5 and 9 minutes, respectively, and no signal of DVA was observed during analysis. However, some fluctuations in elution times may occur due to a change in the column and evolutions of pressure inside the latter during analysis.

Subsequently, the response factors were determined using distinct solutions of DiGEDVA, TriGEDVA and TetraGEDVA at several concentrations. The latter were calculated from the slope of calibration lines and exhibited the values of 129, 122 and 128 $\text{mV.L.mg}^{-1}.\text{min}^{-1}$, respectively (Figure 36). As a result, the surface of the HPLC peak enables to determine the concentration of these various bio-based compounds in the reaction mixture.

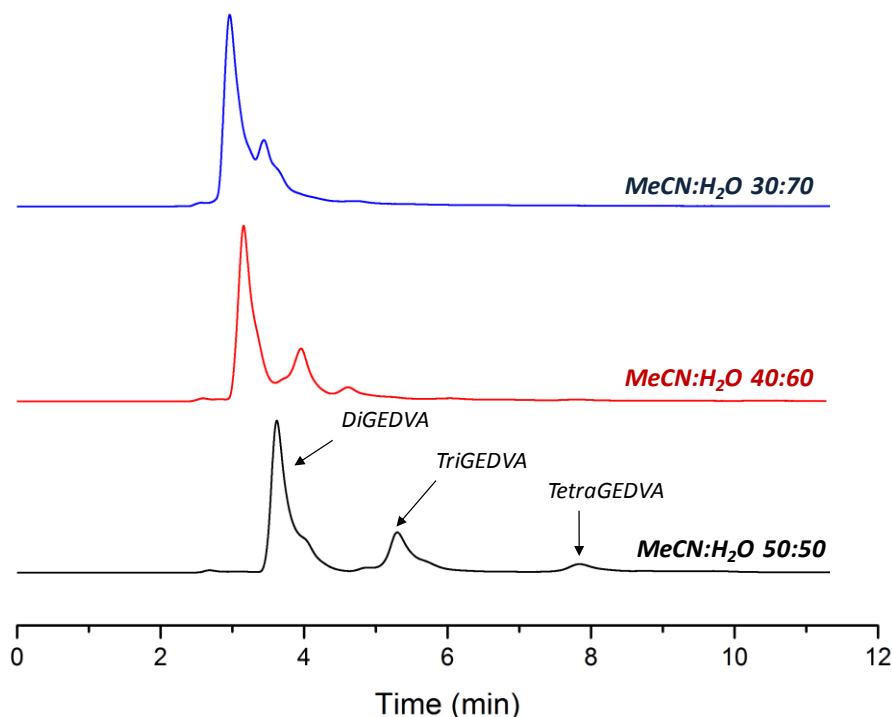


Figure 35: HPLC traces of polyglycidylethers of DVA with MeCN/Water ratio of 30/70 (blue), 40/60 (red) and 50/50 (black)

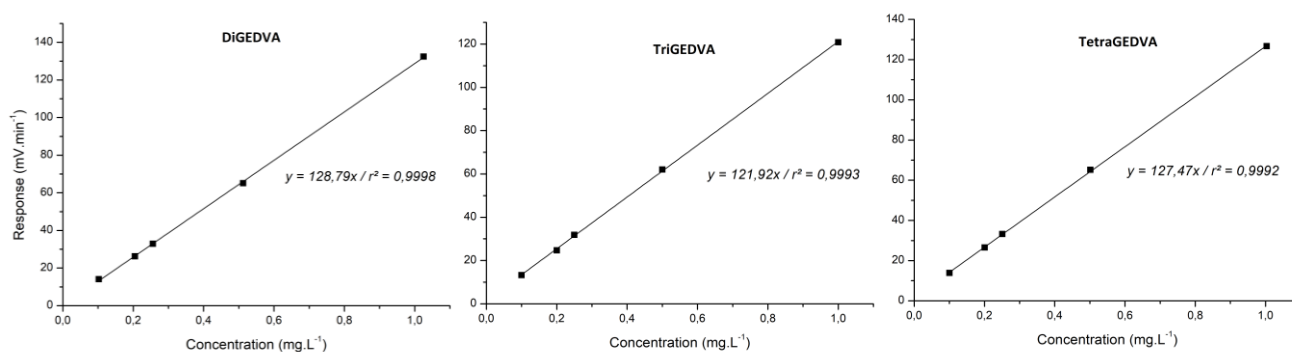


Figure 36: Determination of response factors from slope of the calibration lines of DiGEDVA, TriGEDVA and TetraGEDVA

In view of the above, kinetic studies of the reaction have been performed by HPLC. The evolution of the DVA polyglycidylethers concentration as a function of time and equivalent number of NaOH per hydroxyl group is shown on Figure 37. For a ratio NaOH/OH equal to 10, TetraGEDVA is mainly obtained with about 90 % yield. In contrast, at lower NaOH/OH ratios, DiGEDVA is mainly obtained with 80 % yield. In these different conditions, it is rather convenient to selectively obtain a majority of DiGEDVA or TetraGEDVA with very good yields.

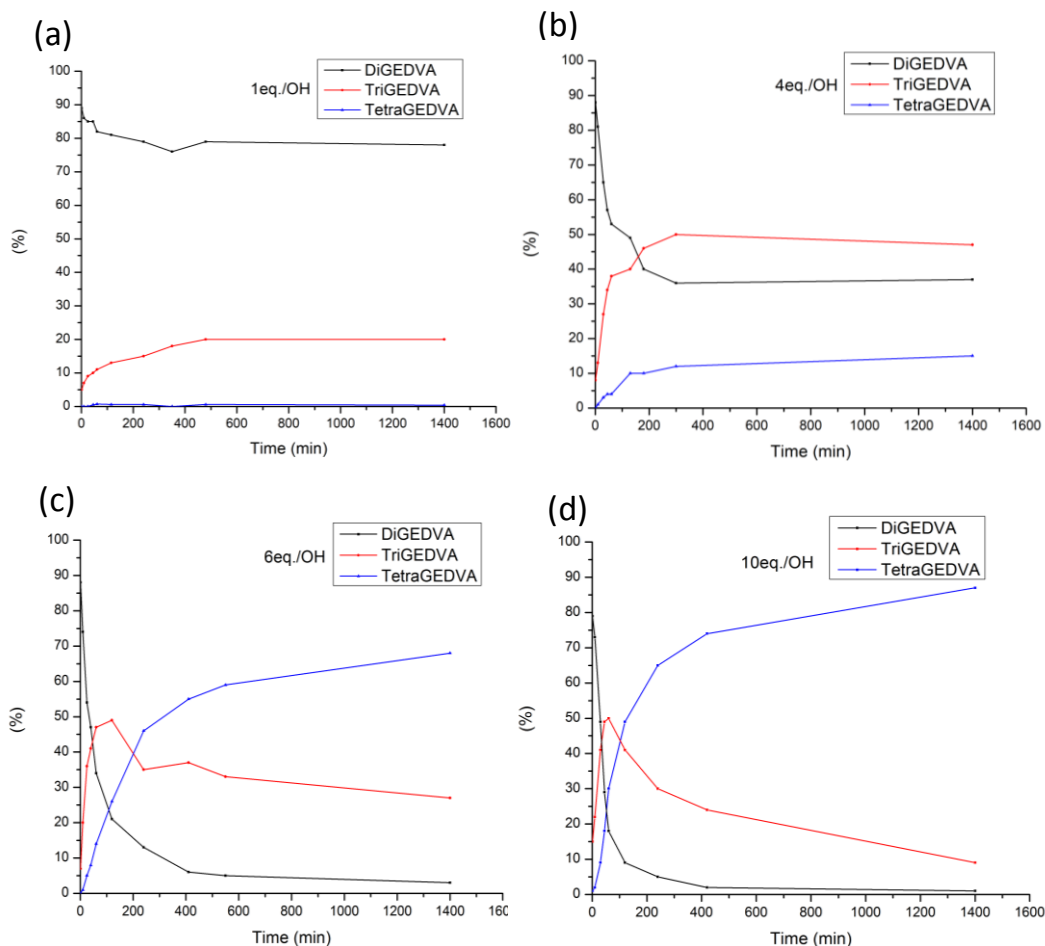


Figure 37: Concentration with time of DiGEDVA, TriGEDVA and TetraGEDVA with respect to 1 NaOH eq./OH (a), 4 NaOH eq./OH (b), 6 NaOH eq./OH (c), 10 NaOH eq./OH (d).

The processability of epoxy resins is one of the key parameter in the industrial process of these materials. In that way, the thermal and physical properties of the epoxy prepolymers were investigated (Table 9). DGEBA monomer is a solid, which can be melted into very low viscosity liquid at a temperature above 45°C. It can thus be homogeneously blended with various curing agents. On the contrary, DiGEDVA exhibits a $T_g = 16$ °C and a viscosity of 1300 Pa.s at 40 °C. By consequent, DiGEDVA is a viscous liquid at RT and its blend with a hardener is therefore quite difficult. In contrast, TetraGEDVA is much easier to handle as it exhibits a $T_g = -15$ °C and a viscosity of 2 Pa.s at 40 °C. The viscosity of the GEDVA prepolymers is thus very dependent on the number of epoxy groups carried by the molecule. This feature can be explained by the presence of two free benzylic alcohol moieties in DiGEDVA compound, which can undergo hydrogen bonding. In addition to the fact that is possible to recover Di, Tri or TetraGEDVA after separation step, the use of mixtures of these polyfunctional structures will enable to control the average properties and the processing of these resins.

The Epoxy Equivalent Weight (EEW) of bio-based epoxy prepolymers and DGEBA reference were also determined according to the standard test method.¹⁶ This method consists in the titration of epoxy with hydrogen bromide (HBr) formed *in situ*. The hydrogen bromide will react stoichiometrically with epoxy moieties to form bromohydrins. Thus, the molar quantity of HBr consumed is a measure of the epoxy content. The experimental results obtained are slightly higher than expected. This difference can be explained by the presence of by-products, such as oligomerised structures.¹⁵ In fact, this feature was confirmed by size exclusion chromatography (SEC) in THF of samples, which revealed the presence of higher molecular weight molecules. SEC traces can be found in the Annexes section at the end of this chapter. However, given to the relative errors, these results are in accordance with the chemical structure determined by NMR spectroscopy. Results are summarized in Table 9.

Table 9: Thermal and physical properties of bio-based epoxy prepolymers and DGEBA

Properties	DGEBA	Di-GEDVA	Tri-GEDVA	Tetra-GEDVA	80-20-0%*	35-50-15%	0-25-75%
T _m (°C)	45	-	-	-	-	-	-
T _g (°C)	-18	16	-6	-15	<i>nd</i>	6	-13
Viscosity at 25 °C (Pa.s)	5	>5000	975	14	>5000	1640	230
Viscosity at 40 °C (Pa.s)	1	1300	60	2	470	119	37
M _n (g.mol ⁻¹)	340	418	474	528	-	-	-
EEW th.	170	209	158	132	209	176	139
EEW exp.	171	232	164	129	250	191	150

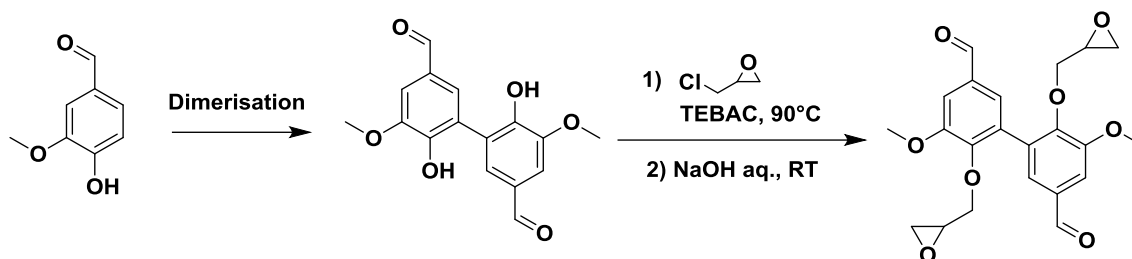
* Percentages of DiGEDVA-TriGEDVA-TetraGEDVA

III.2 Synthesis of bio-based glycidylethers derived from other bio-based phenols

As previously mentioned, other bio-based phenols are available for the synthesis of epoxy precursors. In this way, glycidylation reaction has been performed on different substrates such as 2,6-dimethoxyphenol, dieugenol, methyl divanillate or divanillin derivatives. All the derivatives synthesized were characterized by ¹H and ¹³C NMR spectroscopy.

III.2.1 Synthesis of epoxy precursors from other divanillin derivatives

In addition to polyglycidylether derived from DVA, other epoxy monomers were synthesized from vanillin. Indeed, divanillin can be directly epoxidized into diglycidylether of divanillin (DiGEDIV) (Scheme 37).



Scheme 37: Epoxidation of divanillin into diglycidylether of divanillin with epichlorhydrin

The epoxidation of divanillin was performed using epichlorhydrin following the same procedure as the one developed with DVA. The reaction time of step 1 was increased to 12 hours to obtain a complete conversion and a high yield (>90%). DiGEDIV was then characterized by ^1H NMR and ^{13}C NMR spectroscopy. The chemical structure of DiGEDIV was confirmed by the appearance of signals at 2.39, 2.61, 2.96, 3.85 and 4.18 ppm, corresponding to the protons of epoxy moieties (Figure 38).

The EEW value was also determined and displayed a value of 199 as against 207 in theory. However, DiGEDIV exhibited a viscosity at 40°C of 970 Pa.s, meaning it is a highly viscous compound at room temperature and thus difficult to handle as resin precursors.

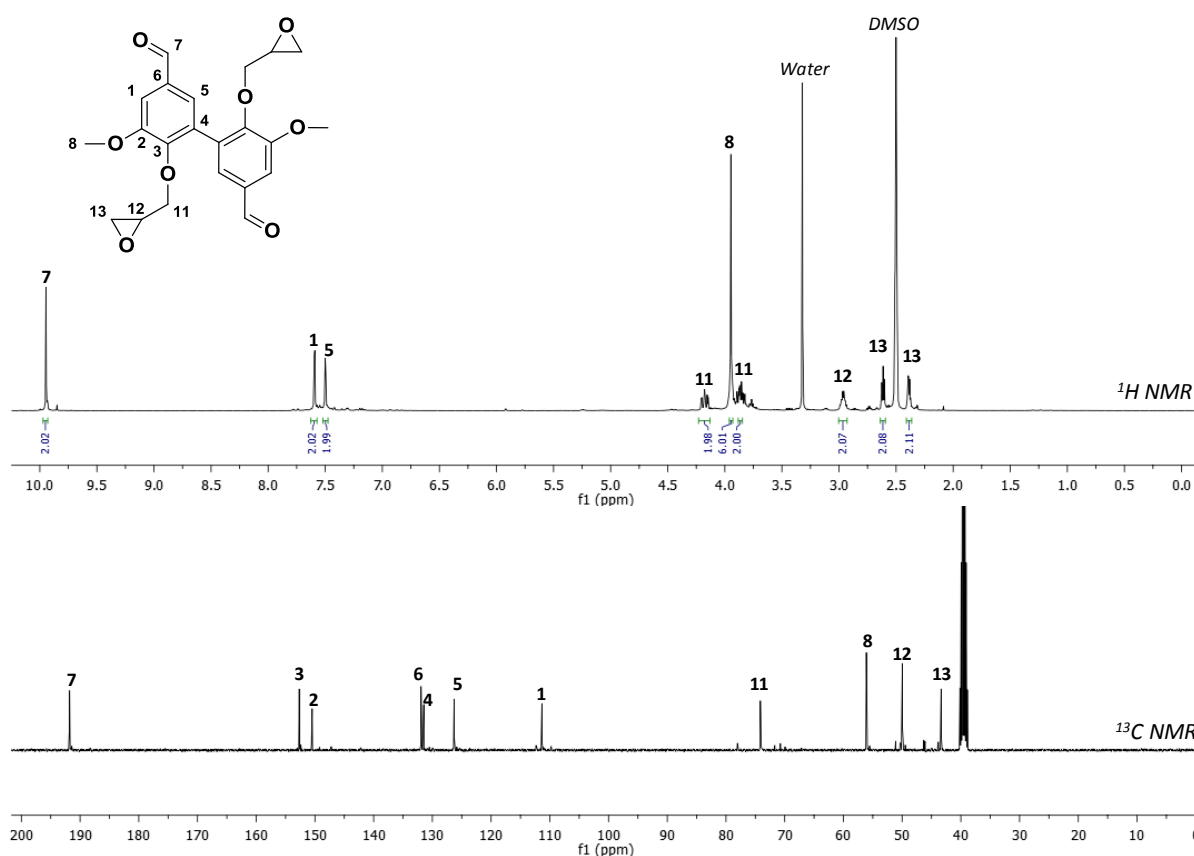
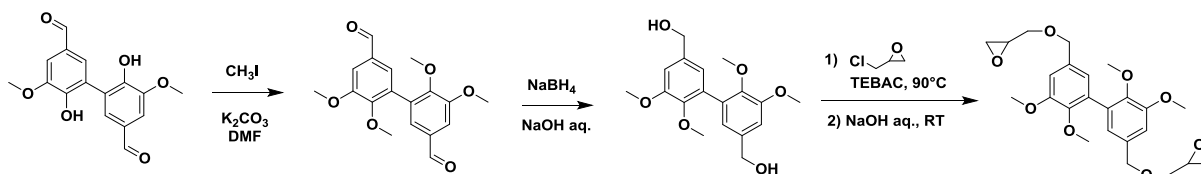


Figure 38: ^1H and ^{13}C NMR spectra of diglycidylether of divanillin in DMSO- d_6

Divanillin can also be methylated and reduced into methylated divanillyl alcohol (mDVA). This latter can undergo glycidylation reaction of its hydroxyl moieties and leading to diglycidylether of methylated divanillyl alcohol (DiGEMDVA) (Scheme 38).



Scheme 38: Synthesis of diglycidylether from methylated divanillyl alcohol

The methylation reaction was performed with iodomethane in basic conditions leading to methylated divanillin in good yield (>80%). This latter was then reduced into methylated divanillyl alcohol using sodium borohydride (>85%). ^1H and ^{13}C NMR spectra of these compounds can be found in the Annexes section at the end of this chapter.

Epoxidation of methylated divanillyl alcohol (mDVA) was performed by glycidylation reaction with epichlorohydrin and yielded a mixture of compounds. Nevertheless, DiGEMDVA was successfully isolated by flash chromatography using a gradient of DCM/MeOH as eluent (25% yield). DiGEMDVA compound was confirmed by NMR spectroscopy (Figure 39). The signals at 2.55, 2.73, 3.15, 3.31 and 3.77 ppm were attributed to the epoxy moieties. DiGEMDVA was obtained as low viscosity compound and EEW exhibited a value of 212 as against 223 in theory. However, the low reaction yield did not allow us to determine a precise viscosity value.

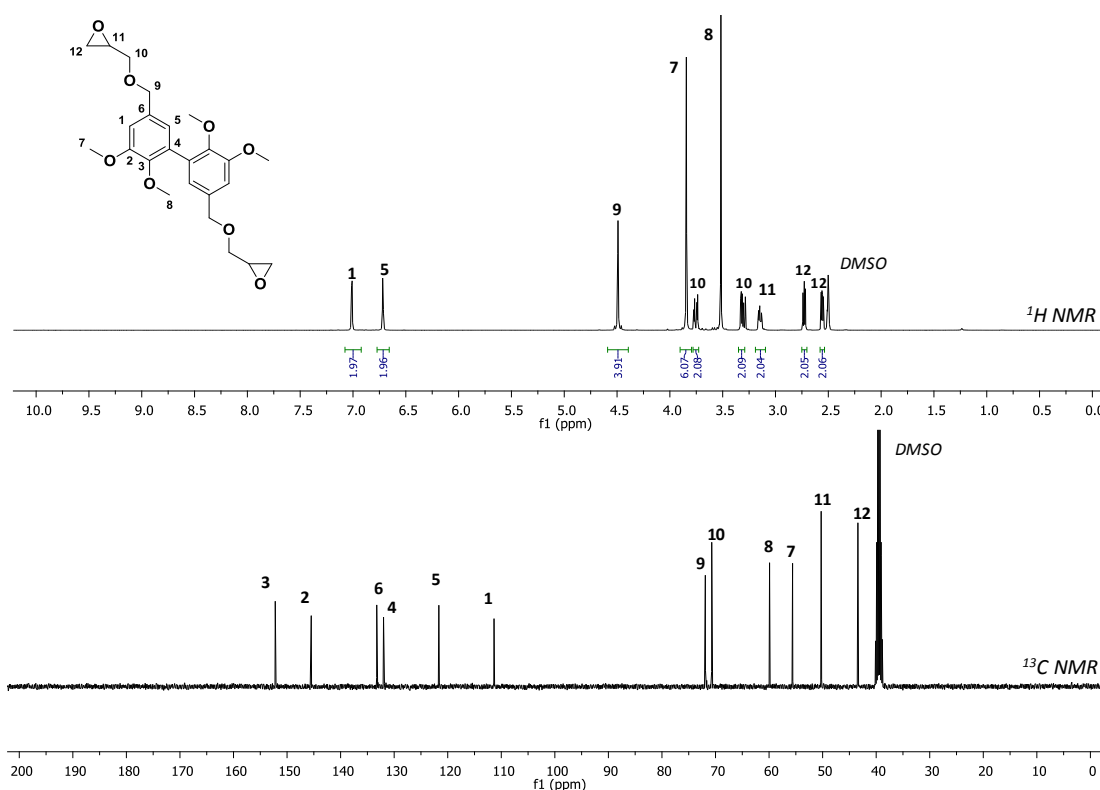
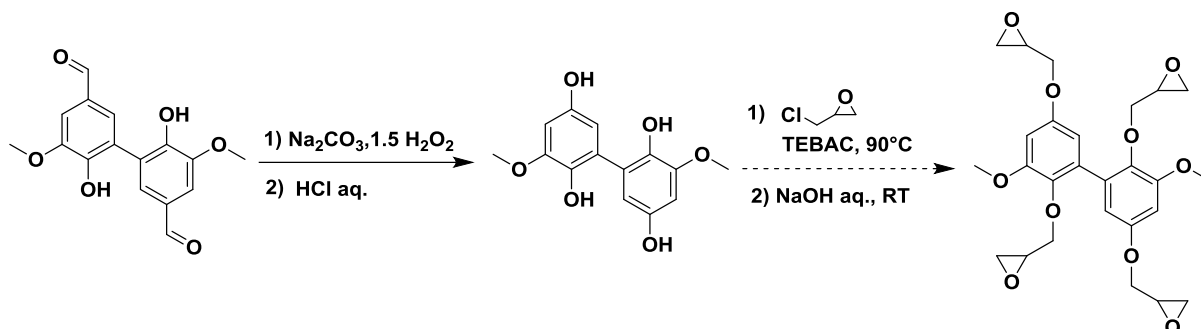


Figure 39: ^1H and ^{13}C NMR spectra of diglycidylether of methylated vanillyl alcohol in DMSO- d_6

Finally, Dakin oxidation of divanillin can lead to the dimethoxyhydroquinone intermediate and epoxidation of this latter could yield the tetraglycidylether of dimethoxyhydroquinone (Scheme 39).



Scheme 39: Synthesis of tetraglycidylether of dimethoxyhydroquinone from divanillin

Dakin oxidation was performed in the presence of sodium percarbonate in basic conditions and the mixture was then acidified in order to recover the bisphenol structure. Aqueous phase was then extracted with ethyl acetate.^{17,18} However, the desired product was recovered in low yield of 55 %. This feature could be explained by the non-total conversion of the divanillin (80 %) and the high solubility of dimethoxyhydroquinone in water phase have made the extraction process poorly efficient. Additional purification was performed through flash chromatography and the structure of dimethoxyhydroquinone was confirmed by NMR spectroscopy (Figure 40). The appearance of two new signals at 8.79 and 7.76 ppm were attributed to the hydroxyl groups.

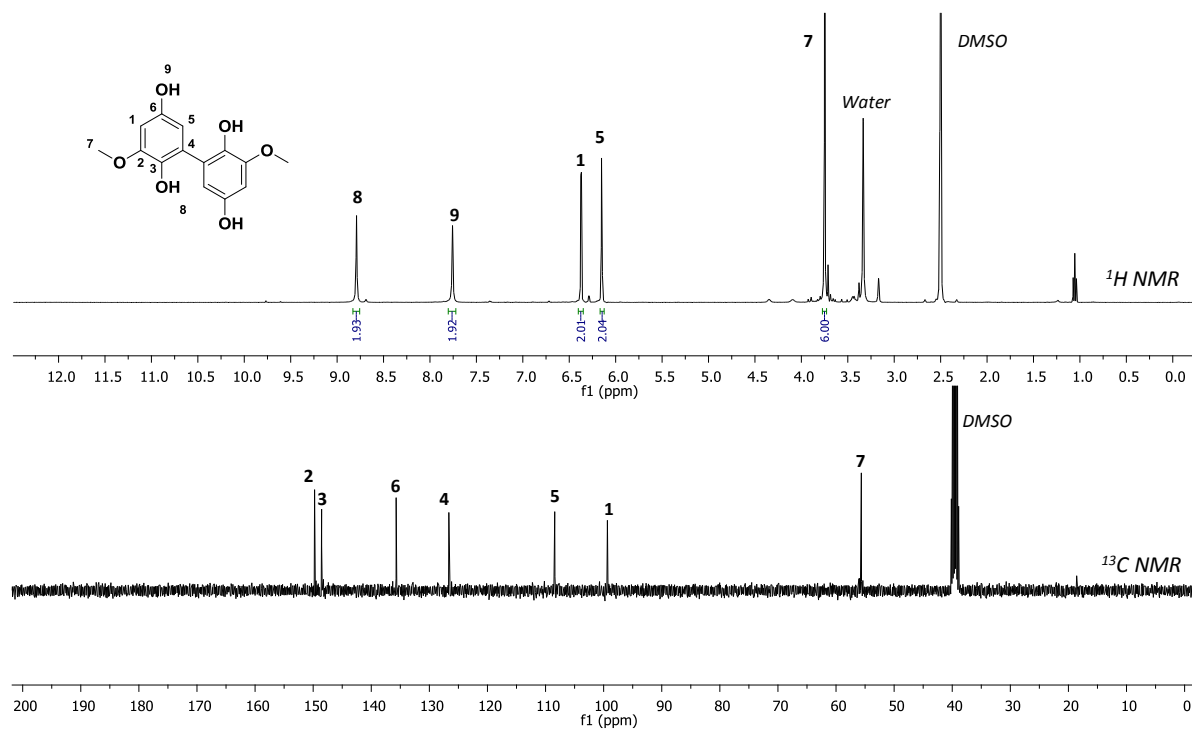


Figure 40: ^1H and ^{13}C NMR spectra of dimethoxyhydroquinone in DMSO-d_6

In addition, the synthesis of tetraglycidylether of dimethoxyhydroquinone with epichlorhydrin revealed to be difficult. Indeed, ^1H NMR spectrum exhibited the presence of several peaks, even after purification step by flash chromatography (Figure 41). These additional signals could be attributed to side products such as oligomerised or chlorinated structures.

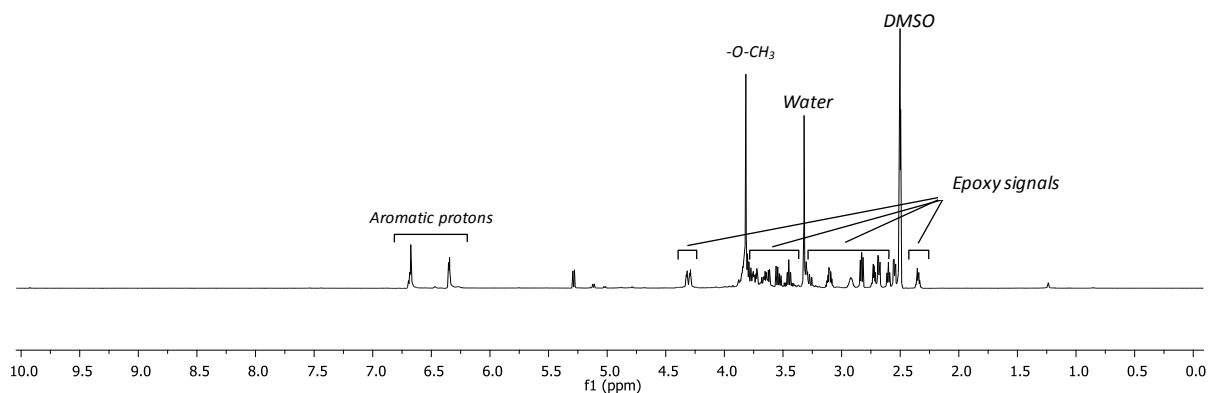
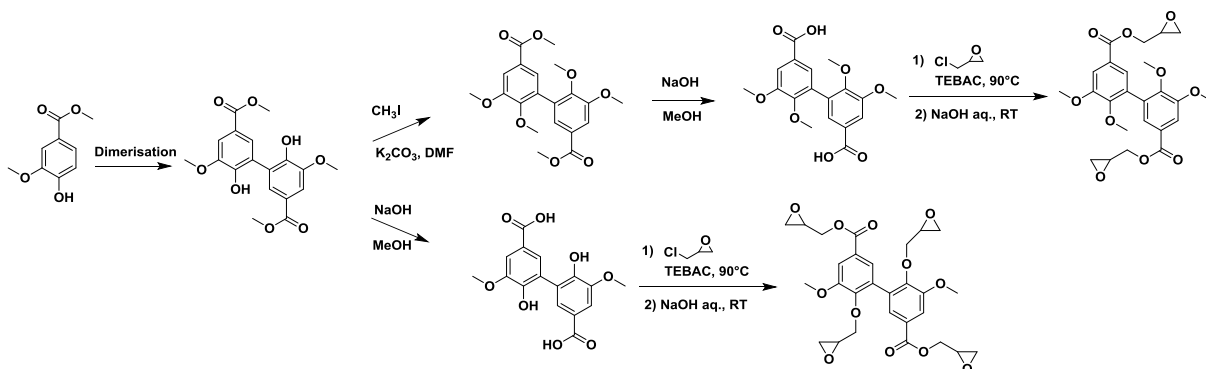


Figure 41: ^1H NMR spectra of glycidylation of dimethoxyhydroquinone in DMSO-d_6

III.2.2 Synthesis of epoxy precursors from methyl divanillate derivatives

Using the same method, the oxidative coupling of methyl vanillate catalysed by laccase leads to the formation of methyl divanillate. Methyl divanillate was then modified into several compounds by methylation of the phenol moieties, hydrolysis of esters and epoxidation. An overview of the synthesized derivatives is summarised in Scheme 40.



Scheme 40: Synthesis of polyglycidylethers from methyl vanillate

All the derivatives were obtained without any further purification step. Methyl divanillate was successfully dimerised into methyl divanillate. The characteristic signals of methyl esters, methoxy groups, aromatic protons and phenols were found at 3.80, 3.90, 7.45, 7.46 and 9.51 ppm, respectively.

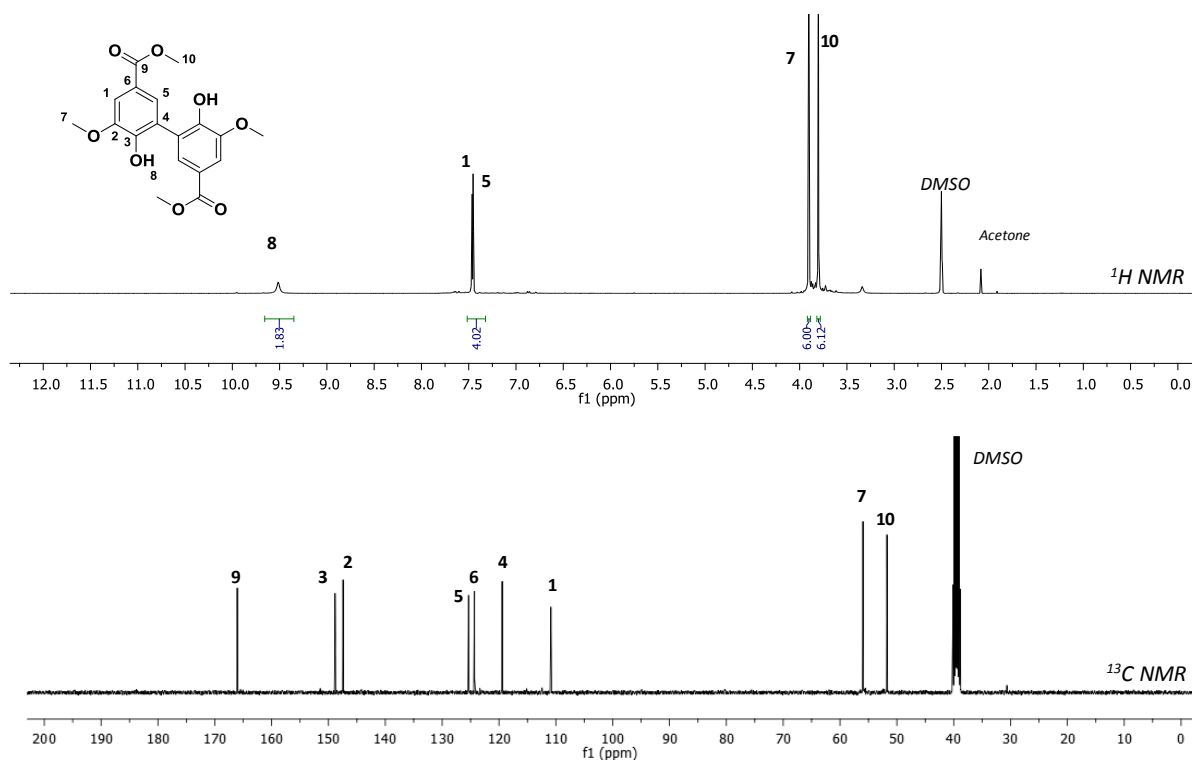


Figure 42: ^1H and ^{13}C NMR spectra of diglycidylester of methyl divanillate in DMSO-d_6

Methylation of the previous biphenyl was then performed using iodomethane under basic conditions. Methylated diester was successfully obtained in good yield (>80%) and confirmed by the appearance of additional signal at 3.62 ppm, corresponding to the methylated phenols. Thereafter, the hydrolysis of the methylated diester with sodium hydroxide yielded methylated diacid (>90%). The hydrolysis was validated by the disappearance of methyl ester signal at 3.84 ppm. ^1H and ^{13}C NMR spectra of these compounds can be found in the Annexes section at the end of this chapter.

Epoxidation of carboxylic acids was then performed using epichlorhydrin and led to the diglycidylester of methylated divanillic acid (DiGEmVAC) (>90%). Protons signals of epoxy moieties are displayed at 2.72, 2.82, 3.34, 4.08 and 4.65 ppm, which confirmed the expected structure (Figure 43). The EEW value was also determined and was found equal to 245 against 237 as theoretical value. Moreover, DiGEmVAC was found as a solid with a melting temperature of 127 °C.

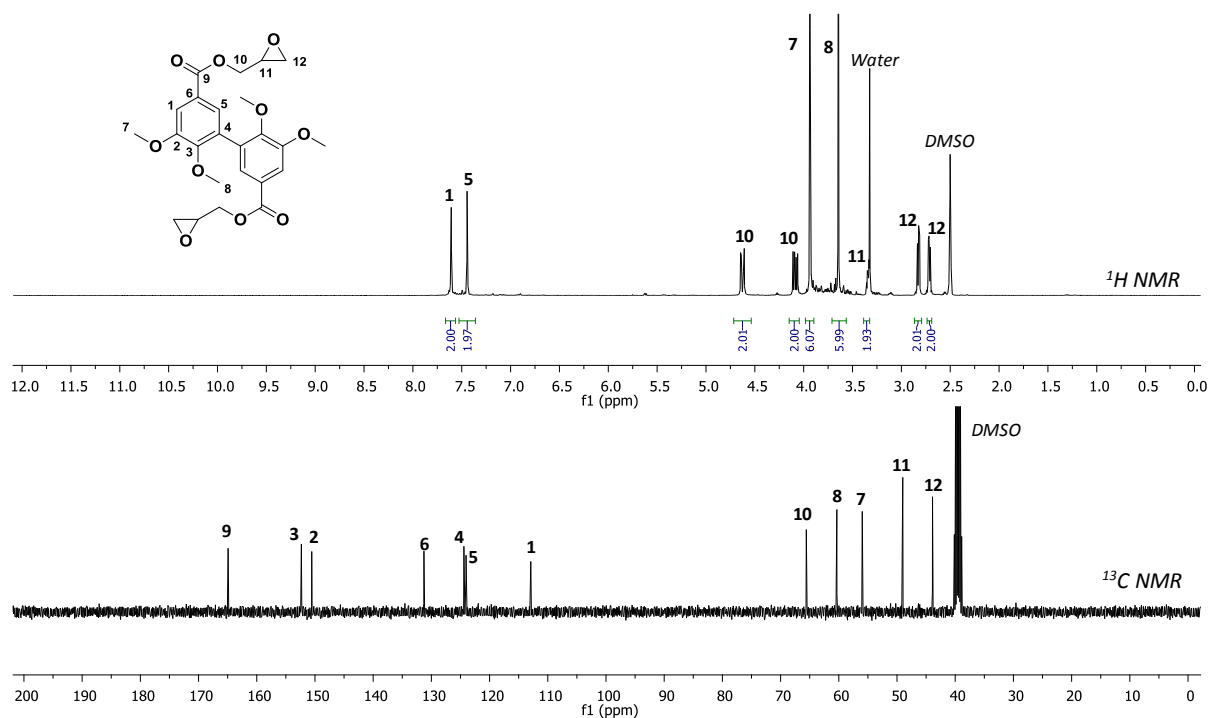


Figure 43: ^1H and ^{13}C NMR spectra of diglycidylester of methylated divanillic acid in DMSO-d_6

Following this feature, the synthesis of the tetraglycidylether of divanillic acid was performed from methyl divanillate. First, the diester was hydrolysed with sodium hydroxide and divanillic acid was obtained in a very good yield (>90%). The structure of divanillic acid was confirmed by the disappearance of the methyl ester signal at 3.84 ppm as observed by ^1H NMR (Figure 44).

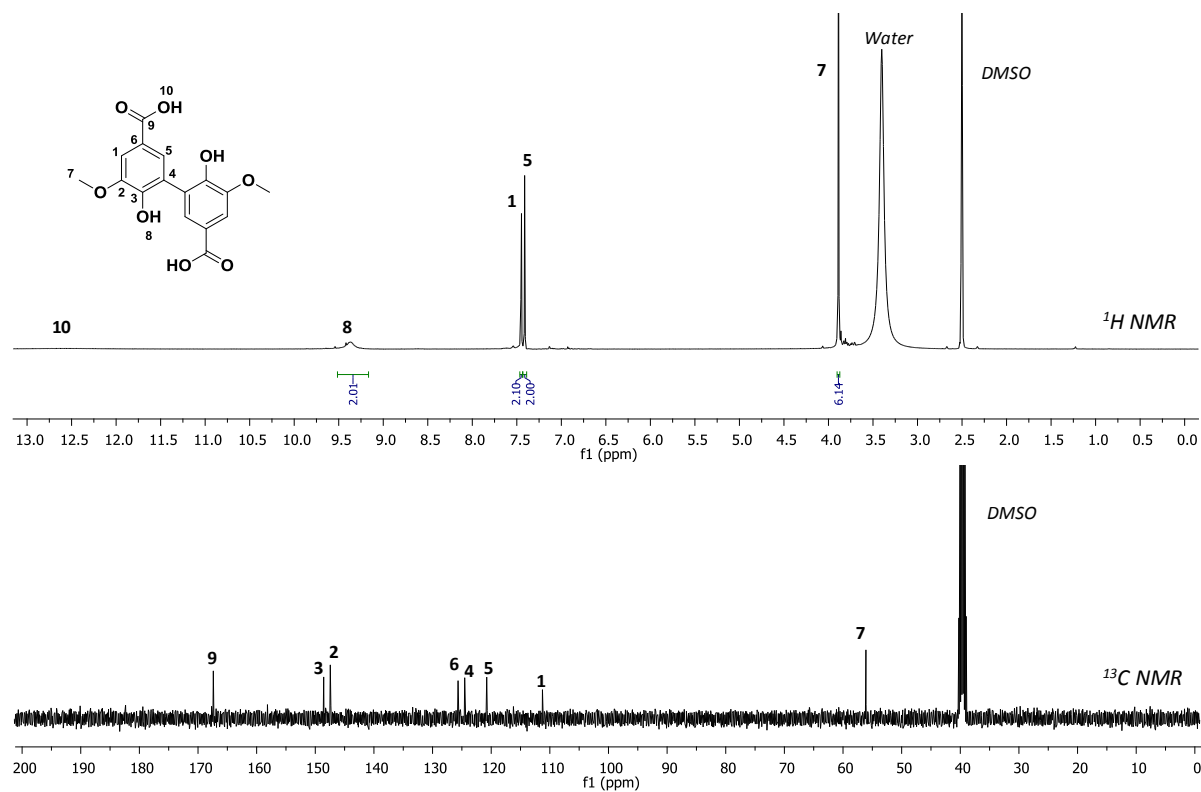


Figure 44: ^1H and ^{13}C NMR spectra of divanillic acid in DMSO-d_6

The epoxidation was then performed using epichlorohydrin in the presence of triethylbenzylammonium chloride (TEBAC) and yielded a mixture of numerous compounds. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent and enabled to recover the tetraglycidylether of divanillic acid (TetraGEVAC) (30% yield). The TetraGEVAC structure was confirmed by NMR spectroscopy (Figure 45). Glycidylation of acid functions generates new peaks at 2.73, 2.83, 3.35, 4.09 and 4.65 ppm, whereas glycidylation of phenol moieties brings new signals at 2.38, 2.62, 2.97, 3.86 and 4.15 ppm. TetraGEVAC was then found as viscous liquid, but the small amount of product did not enable further analysis to determine viscosity or EEW values.

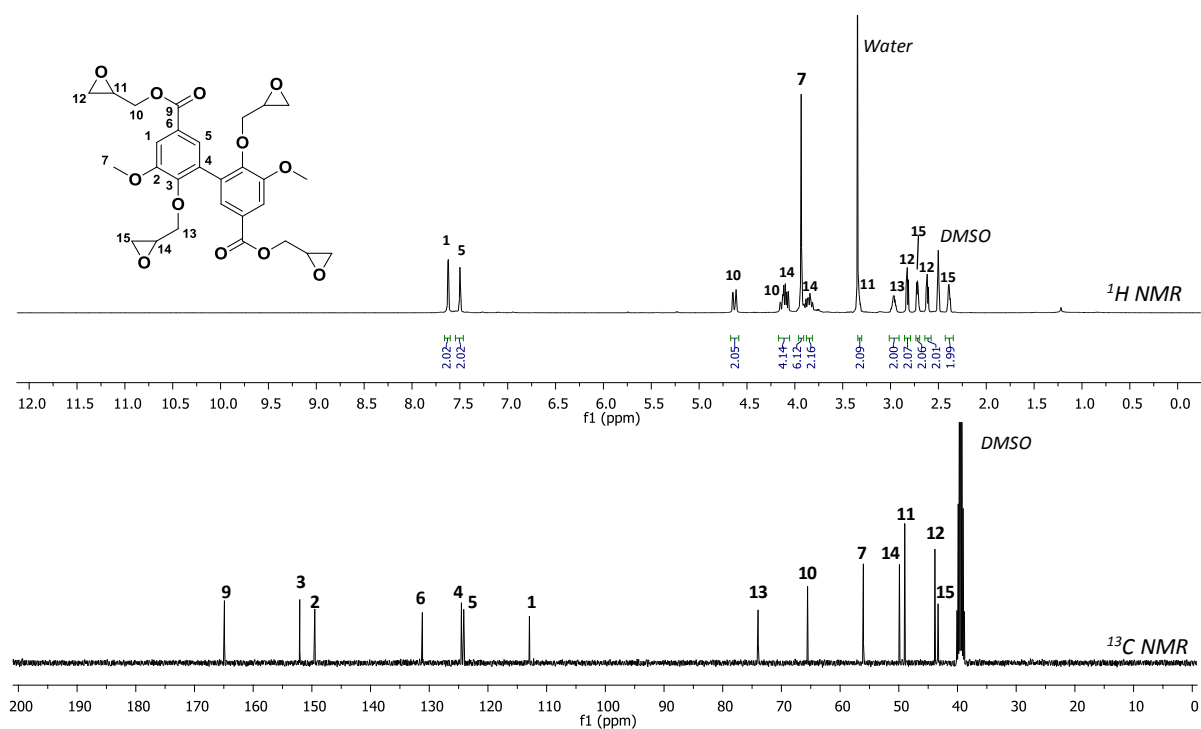
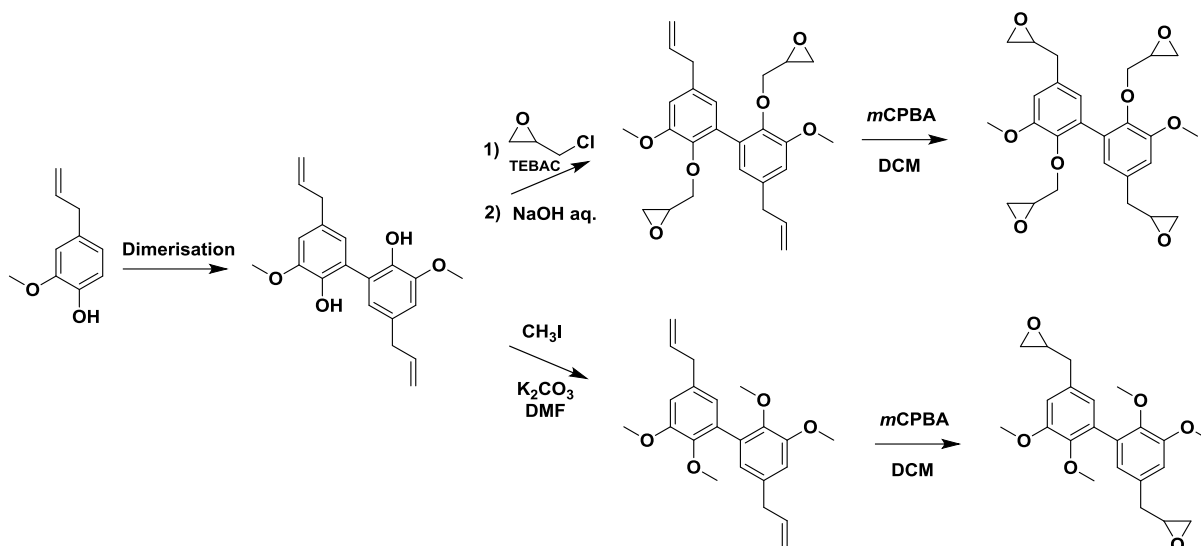


Figure 45: ¹H and ¹³C NMR spectra of tetraglycidylether of divanillic acid in DMSO-d₆

III.2.3 Synthesis of epoxy precursors from eugenol

Following the same procedure, the oxidative coupling of eugenol catalysed by laccase leads to the formation of dieugenol (DEG). Dieugenol was then derivatized into several compounds by methylation or epoxidation of phenol moiety and epoxidation of allyl group with *meta*-chloroperoxybenzoic acid (mCPBA), (Scheme 41).



Scheme 41: Synthesis of polyglycidylethers from eugenol

^1H NMR spectrum of dieugenol displayed the signals of methylene, methoxy, carbon double bonds, aromatic protons and phenols at 3.27, 3.79, 5.05, 5.93, 6.52, 6.73 and 8.16 ppm, respectively (Figure 46).

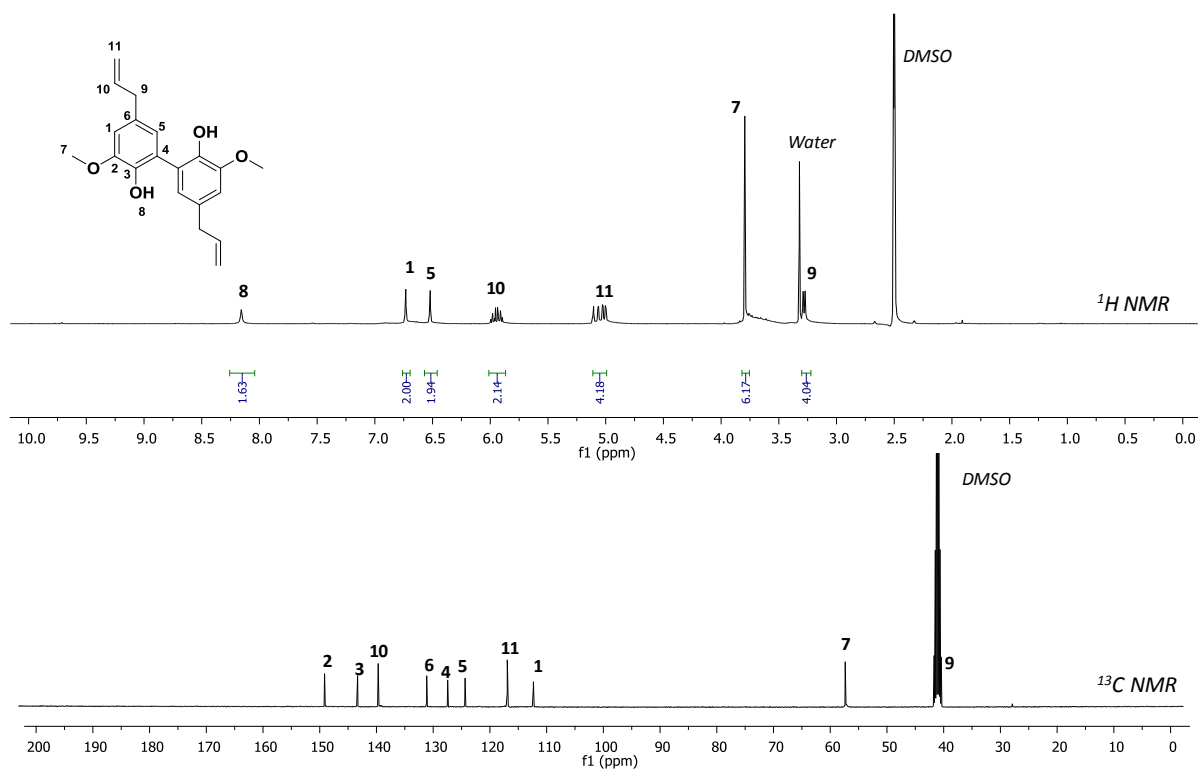


Figure 46: ^1H and ^{13}C NMR spectra of dieugenol in DMSO-d_6

Methylation of dieugenol (mDEG) was performed with iodomethane under basic conditions and led to the methylated dieugenol in yield of 50%. The structure of mDEG was confirmed by the appearance of additional signal at 3.48 ppm, corresponding to the methylated phenols. ^1H

and ^{13}C NMR spectra of these compounds can be found in the Annexes section at the end of this chapter.

The oxidation of allyl groups was performed in the presence of *m*CPBA and yielded the diglycidylether of methylated dieugenol (DimDEG) (50% yield). However, even after purification by flash chromatography using a gradient of DCM/MeOH, ^1H NMR spectrum revealed the presence of remaining signals of methylated dieugenol and only 70% of unsaturations were converted into oxirane functions (Figure 47). Nevertheless, the appearance of new signals at 2.57, 2.74 and 3.12 ppm were attributed to the epoxy moieties of DimDEG. This latter exhibited a low viscosity at room temperature, but the small amount of product synthesized did not allow us to determine a precise value of viscosity and EEW values.

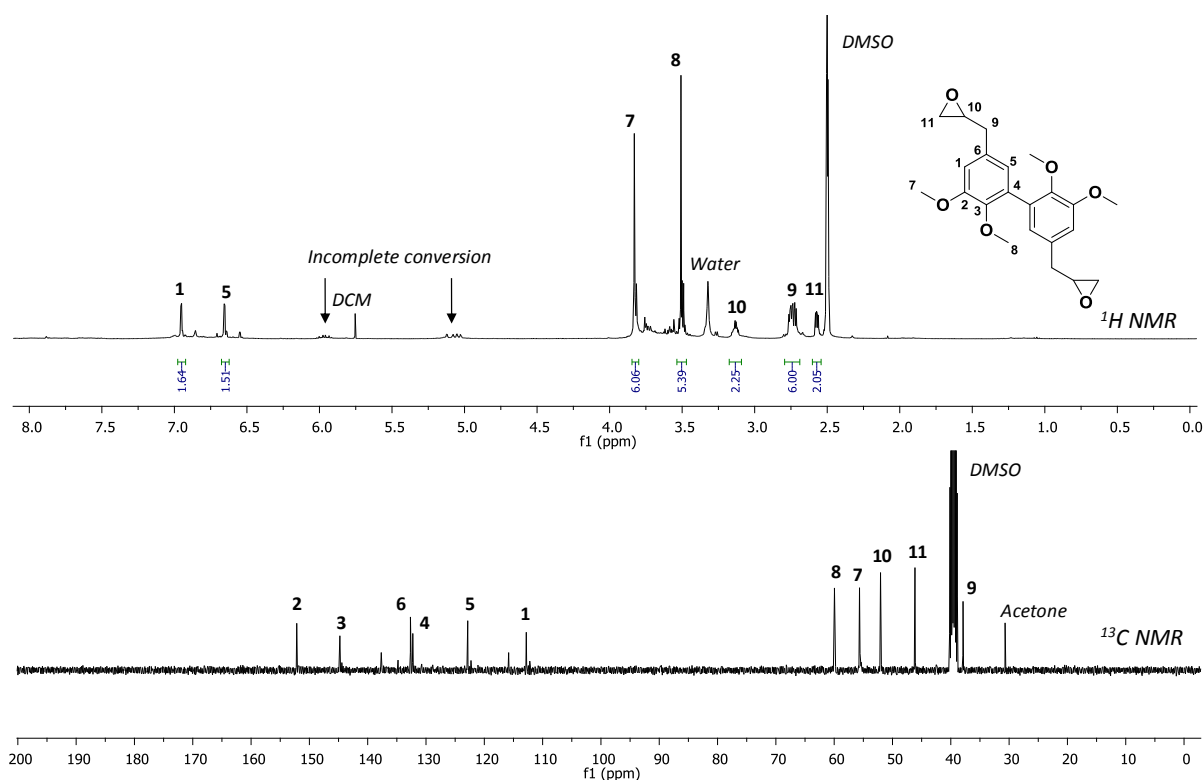


Figure 47: ^1H and ^{13}C NMR spectra of diglycidylether of methylated dieugenol in DMSO- d_6

Another polyglycidylether of dieugenol was obtained by successive epoxidation of phenols in presence of epichlorhydrin and oxidation of allyl groups with *m*CPBA. First, the epoxidation of dieugenol with epichlorhydrin led to diglycidylether of dieugenol (DiGEDEG) (75% yield) and was confirmed by NMR spectroscopy (Figure 48). The appearance of signals at 2.34, 2.58, 2.91, 3.73 and 3.88 ppm were attributed to the epoxy moieties of DiGEDEG. EEW of this latter exhibited a value of 235 against 219 as theoretical value. Tetraglycidylether of dieugenol (TetraGEDEG) was then obtained by oxidation of allyl moieties of DiGEDEG with *m*CPBA.

However, flash chromatography using DCM/MeOH gradient solvent was necessary to recover the desired product (Yield 10%). ^1H NMR spectroscopy of TetraGEDEG demonstrated the complete disappearance of signals at 3.27, 5.05 and 5.93 ppm and the appearance of new signals at 2.60, 2.77 and 3.13 ppm, attributed to the epoxy moieties. TetraGEDEG was found as low viscosity liquid, but the low amount of product did not enable further analysis to determine viscosity or EEW values.

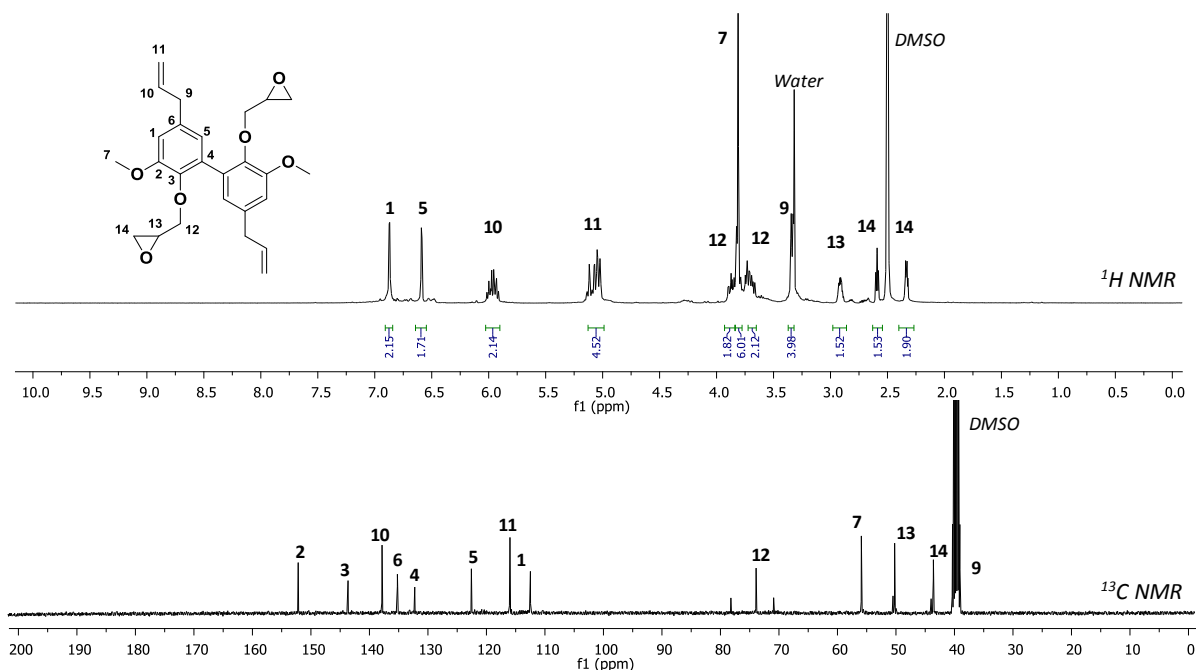


Figure 48: ^1H and ^{13}C NMR spectra of diglycidylether of dieugenol in DMSO-d_6

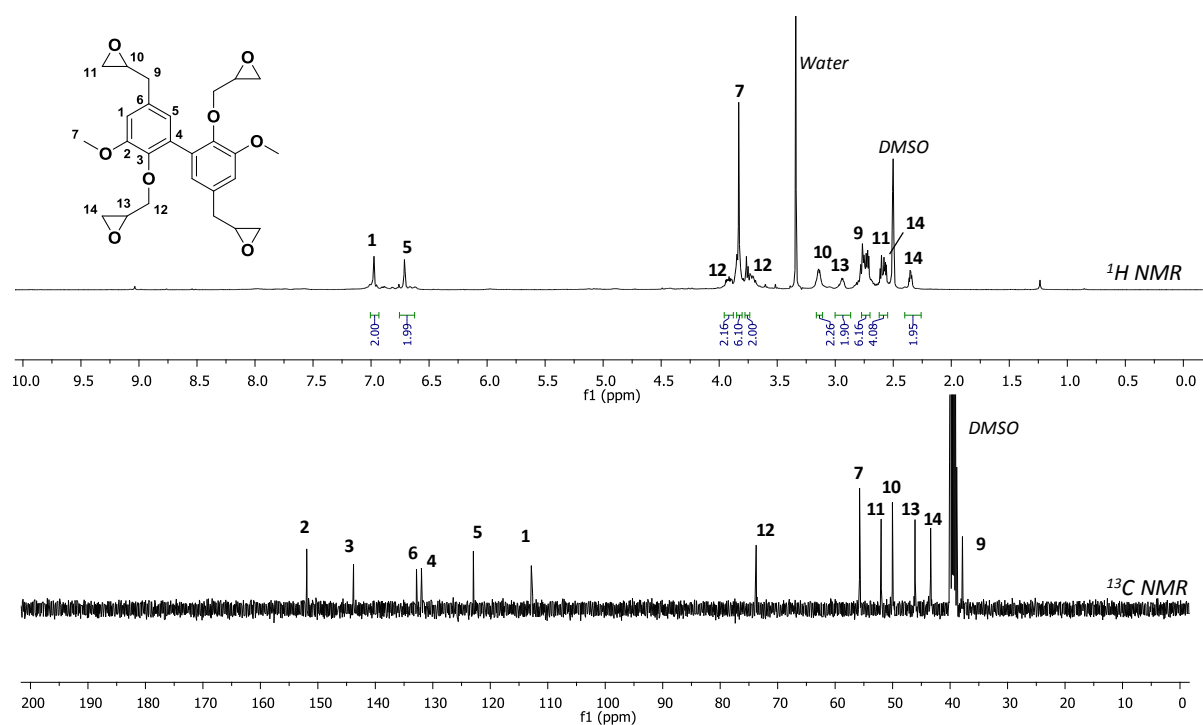
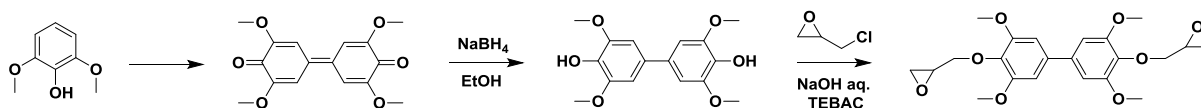


Figure 49: ^1H and ^{13}C NMR spectra of tetraglycidylether of dieugenol in DMSO-d_6

III.2.4 Synthesis of epoxy precursors from 2,6-dimethoxyphenol

In a previous work, Llevot *et al.* performed the dimerization of 2,6-dimethoxyphenol (D26) yielding the formation of 2,6-dimethoxyquinone. After reduction using sodium borohydride, 2,6-dimethoxydiphenol was obtained in a good yield (>75%). Direct epoxidation of D26 was realised and diglycidylether of D26 (DiGED26) was successfully obtained in high yield, using the same synthetic procedure as the one described for DVA derivatives (Scheme 42).



Scheme 42: Synthesis of diglycidylether from 2,6-dimethoxyphenol

2,6-dimethoxyphenol was successfully dimerized into a colourful purple solid corresponding to 2,6-dimethoxybenzoquinone. However, this compound was insoluble in DMSO-d₆ solvent, impeding ¹H NMR analysis. The reduction of quinone was successfully performed with sodium borohydride leading to D26. Protons of methoxy groups displayed a characteristic signal at 3.84 ppm and singlets at 6.82 and 8.32 ppm were attributed to aromatic protons and phenols, respectively (Figure 50).

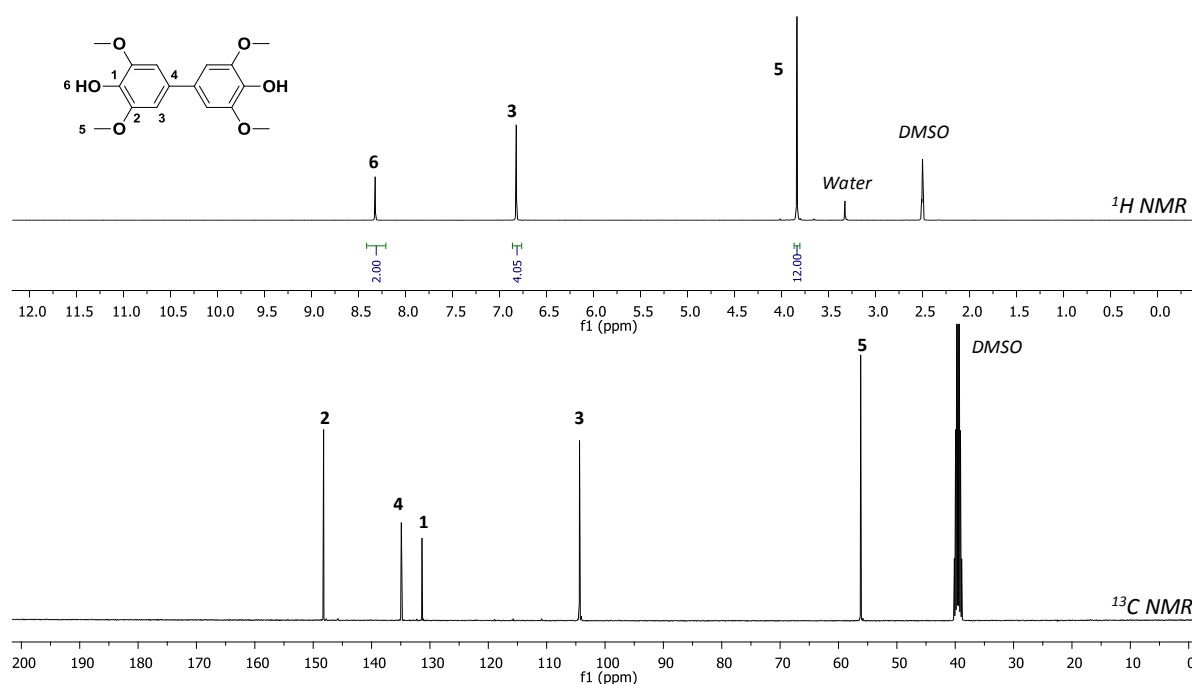


Figure 50: ¹H and ¹³C NMR spectra of 2,6-dimethoxydiphenol in DMSO-d₆

Diglycidylether of 2,6-dimethoxydiphenol (DiGED26) was then synthesized in the presence of epichlorohydrin (90% yield). The glycidylation of phenol moieties was confirmed by the presence of new signals at 2.59, 2.76, 3.27, 3.75 and 4.13 ppm, displayed on the ¹H NMR

spectrum (Figure 51). EEW displayed a value of 220 against 209 as theoretical value and supported the structure proposed. Similarly to DiGEmVAC, DiGED26 is obtained as a solid with a melting point around 120 °C.

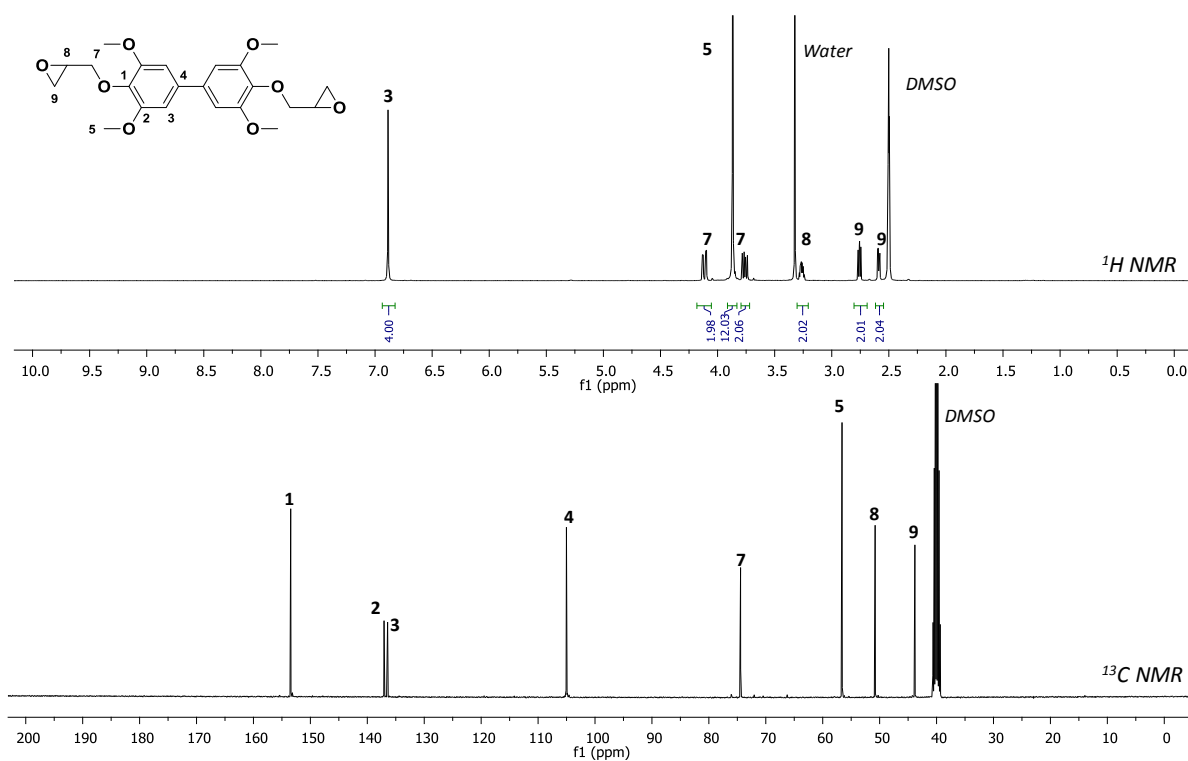


Figure 51: ^1H and ^{13}C NMR spectra of diglycidylether of 2,6-dimethoxydiphenol in DMSO- d_6

III.3 Summary of the bio-based polyglycidylethers synthesis

To sum up, a new platform of bio-based polyglycidylethers was developed from vanillin, methyl vanillate, eugenol and 2,6-dimethoxyphenol. The main characteristics of these derivatives are summarized in Table 10. As a general trend, polyglycidylethers were synthesized in a good yield, except DiGEmDVA, TetraGEVAC or TetraGEDEG. Further optimisations in terms of experimental conditions, kinetics of reaction or purification procedures would be necessary in order to recover the desired products in higher yield. Rheological behaviour of epoxy monomers is critical in the formulation of epoxy resins. Low viscosity values are often an advantage for the processing of the resin. Generally, the synthesized polyglycidylethers were obtained as solid amorphous materials. In most cases, precise viscosity values could not be determined because of the lack of compounds. However, the glass transition temperatures were measured in order to have an indication of the monomer

states at room temperature. Usually, T_g values below 0°C indicates a low viscosity monomer. In this way, TriGEDVA, TetraGEDVA, DiGEmDVA and DiGEmDEG are interesting candidates with respect to the formulation of epoxy resins. Other monomers, such as DiGEmVAC or DiGED26 were obtained as crystalline solids with high melting temperature. Unfortunately, this feature is a strong limitation as far as the formulation process is concerned. Finally, di-functional monomers were essentially synthesized. However, depending on the starting material, tri- and tetra-functional epoxy monomers were also prepared, such as TriGEDVA, TetraGEDVA, TetraGEDEG and TetraGEVAC. These latter derivatives are particularly interesting for the elaboration of highly cross-linked materials.

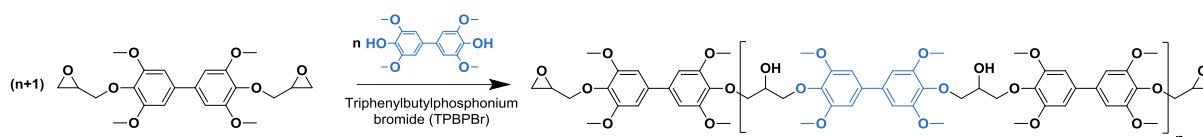
Table 10: Main characteristics and yields of bio-based polyglycidylethers

Polyglycidylether	EEW th.	EEW exp.	Molar mass (g.mol⁻¹)	T_m (°C)	T_g (°C)	Yield (%)
DiGEDIV	207	199	414	-	12	95
DiGEDVA	209	232	418	-	16	80
TriGEDVA	158	164	474	-	-6	50
TetraGEDVA	132	139	528	-	-15	80
DiGEmDVA	223	212	446	-	-20	25
DiGEDEG	219	235	438	-	<i>nd</i>	75
DiGEmDEG	193	204	386	-	-10	50
TetraGEDEG	<i>nd</i>	<i>nd</i>	470	-	<i>nd</i>	10
DiGEmVAC	237	245	474	127	-	90
TetraGEVAC	<i>nd</i>	<i>nd</i>	558	-	17	30
DiGED26	209	220	418	120	-	90

IV. Synthesis of bio-based epoxy oligomers

As already well-established with DGEBA (see Chapter 1), the oligomerisation of aromatic bisepoxides is an efficient mean to break the crystallinity of these compounds and thus tune their processability by lowering the viscosity. This reaction is controlled by the stoichiometry of reactants at high temperature in the presence of a catalyst.

This synthesis consists in a chain extension of an $(n+1)$ bisepoxide molecules by incorporating n bisphenolic moieties. Thus, the average number of monomer units per oligomer chain is $\overline{Xn} = (n + 1) + n = 2n + 1$ (Scheme 43).



Scheme 43: Oligomerisation reaction of $(n+1)$ DiGED26 with n D26

As any step-growth polymerization, the following *Carothers* equation gives the number-average value of the degree of polymerization \overline{Xn} with r the molar ratio of bisphenol/bisepoxide and assuming a complete conversion of the minor functions (Equation 3).

Equation 3

$$\overline{Xn} = \frac{(1 + r)}{(1 - r)} = 2n + 1$$

Following this feature, oligomerisation of DiGED26 were performed with different ratio r ranging from 0.1 to 0.9, in such a way that the excess of bisepoxide decreased. The conditions for the preparation of the targeted oligomers were first determined by DSC and adapted from literature (Figure 52).¹² DSC thermogram of DiGED26/D26/TPBPBr (1/0.9/0.05) showed an endothermic peak at 115°C corresponding to the melting of DiGED26 and an exothermic peak at 150°C which was attributed to the oligomerisation reaction. On the second heating cycle, the thermogram displayed only one Tg value at 93°C attributed to the oligomer synthesized ; as the reaction was completed no other peak was detected. In the following, oligomerisation reactions were performed in bulk at 140°C for 2 hours with 5wt.% of TPBPBr.

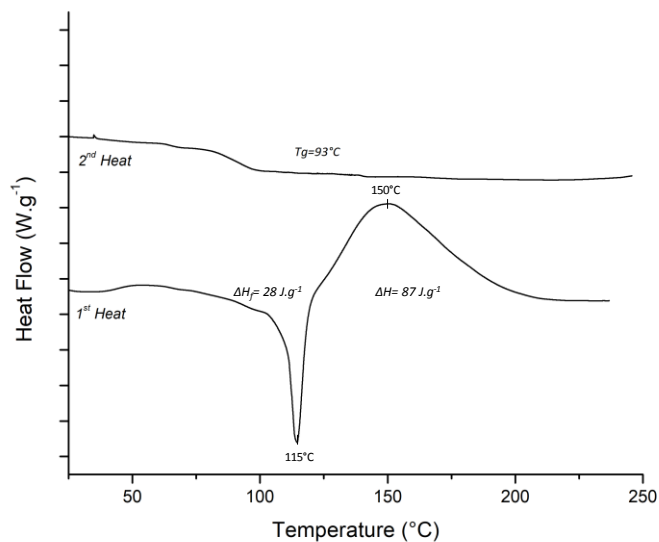


Figure 52: DSC thermograms of oligomerisation reaction with DiGED26/D26/TPBPBr (1/0.9/0.05)

The oligomerisation reactions were monitored by NMR spectroscopy at various ratios r (Figure 53). The appearance of new signals at 4.00 and 4.78 ppm were attributed to alkyl and the hydroxyl protons formed upon epoxy ring-opening, respectively.

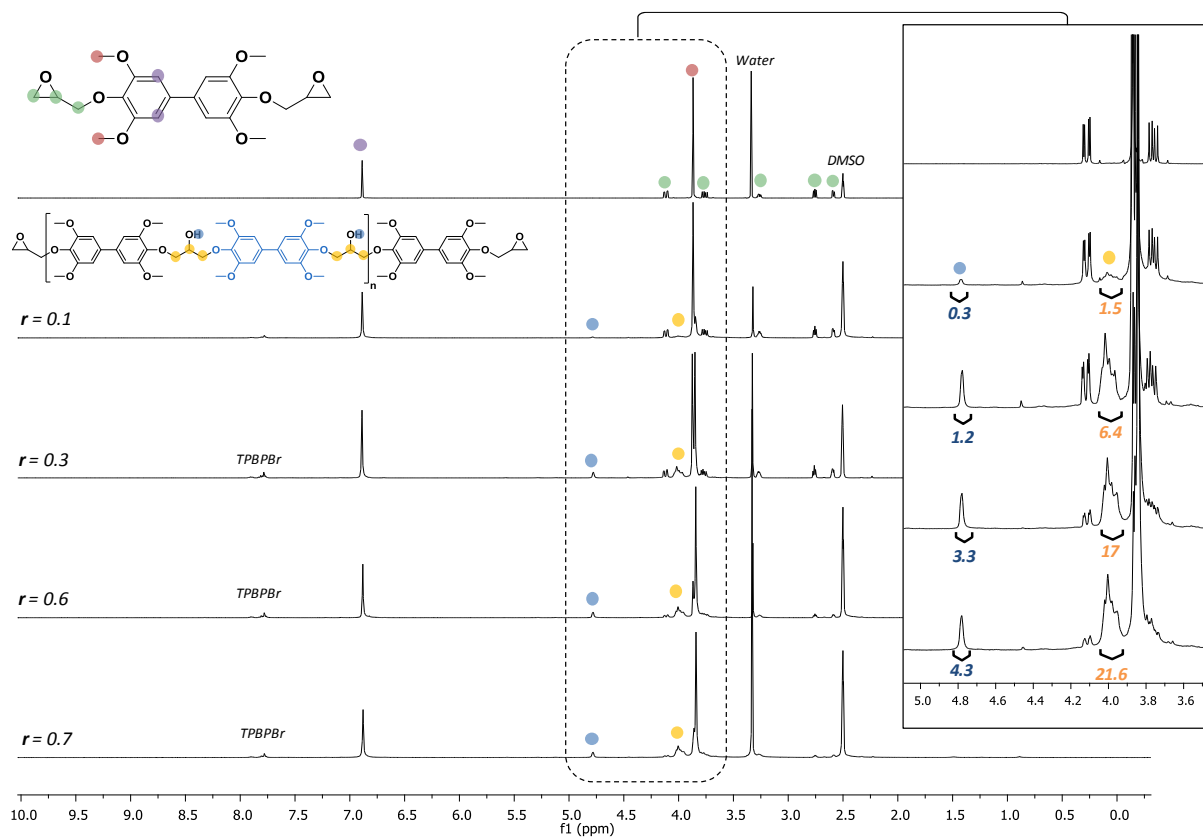


Figure 53: ^1H NMR spectra of DiGED26 and of oligomers prepared at various ratios r

Moreover, the integration of peaks enables the determination of molar mass of the oligomers. In fact, the value of the integral of hydroxyl groups at 4.78 ppm divided by two could be assimilated to the value of n , the average number of repetitive units. Therefore, the molar mass of oligomers were determined from the following Equation 4:

Equation 4

$$\overline{Mn} = 418 + 724 * n$$

This equation corresponds to the molar mass of the DiGED26 incremented with the molar mass of the repetitive unit. In addition, size exclusion chromatography (SEC) in THF was performed and enabled also to determine a value of the average molecular weight of oligomers. Theoretical values of oligomer molar mass for different ratios were calculated from Equation 3 and Equation 4. Results are summarised in Table 11.

Table 11: Average molecular weight of oligomers for various values of stoichiometry ratio r

r D26/DiGED26	\overline{Mn}_{th} (g.mol ⁻¹)	\overline{Mn}_{exp}^a (g.mol ⁻¹)	\overline{Mn}_{exp}^b (g.mol ⁻¹)	\mathbf{D}
0.9	7000	5500	5400	5,6
0.8	3900	3500	3000	2,1
0.7	1850	1950	<i>nd</i>	<i>nd</i>
0.6	1450	1600	1450	3,3
0.3	800	850	800	2,4
0.1	500	550	450	1,6

^aDetermined by ¹H NMR, ^bDetermined by SEC

In view of the above, the more the excess of DiGED26 is important the less the average molecular weight. Average molecular weight determined by ¹H NMR spectroscopy are very close to the theoretical values calculated, especially for the low molecular weight. In contrary, the variance is more important for high molecular weight. This difference could be explained by the highly viscous materials obtained for high ratio, which could lead to inhomogeneous mixture and impaired the stoichiometric ratio.

In addition, SEC provided valuable information on the distribution of molar mass of samples. Chromatograms displayed characteristic pattern of step-growth reaction with multimodal distribution of oligomers of increasing degrees of polymerization (Figure 54). Moreover, SEC traces confirmed the formation of higher molecular weight oligomers for high bisphenol/bisepoxide ratio.

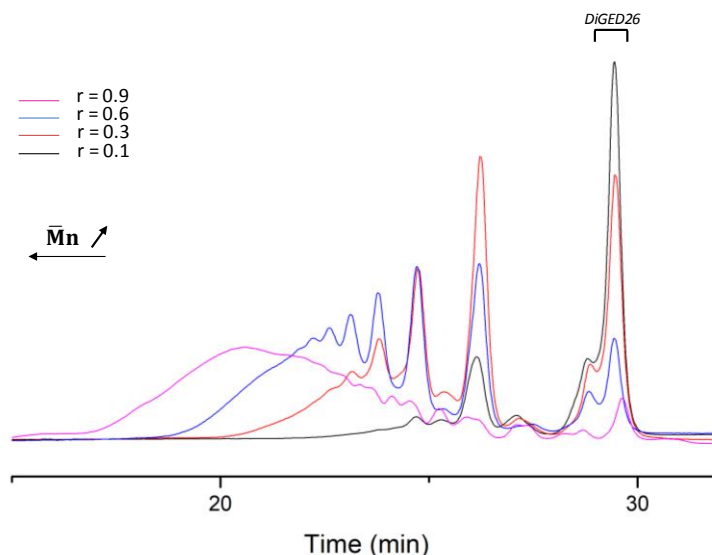


Figure 54: SEC traces of oligomers at different stoichiometric ratios

Amorphous oligomers with high T_g were obtained when ratio is close to the stoichiometric ratio $r = 1$. T_g values of the different oligomers as a function of r were determined by DSC. For ratios ranging from 0.1 to 0.9, the higher the ratio bisphenol/bisepoxide, the lower the T_g of the oligomers. As expected, the T_g decreases with the chain length down to a plateau around 20 °C. This behavior is in agreement with the Fox-Flory law indicating that T_g varies with the polymer molar mass as follows:

Equation 5

$$T_g = T_g(\infty) - \frac{K}{\bar{M}_n}$$

With $T_g(\infty)$ the value of T_g when \bar{M}_n tends to infinite value and K a constant related to the polymer. The values of K and $T_g(\infty)$ were determined from the linear regression of $T_g = f\left(\frac{1}{\bar{M}_n}\right)$ and were found equal to $-42489 \text{ }^\circ\text{C}\cdot\text{g}\cdot\text{mol}^{-1}$ and 99°C , respectively.

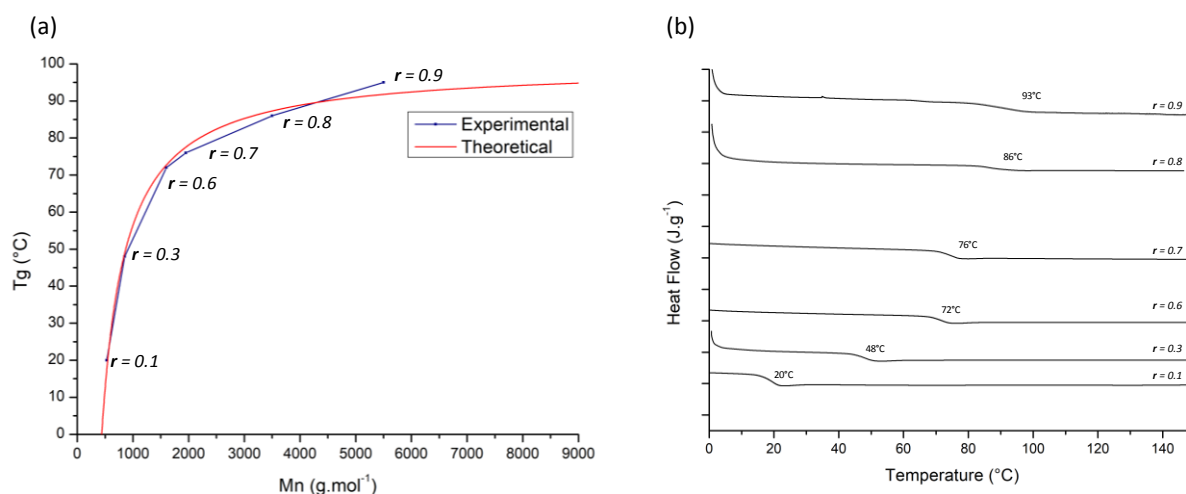
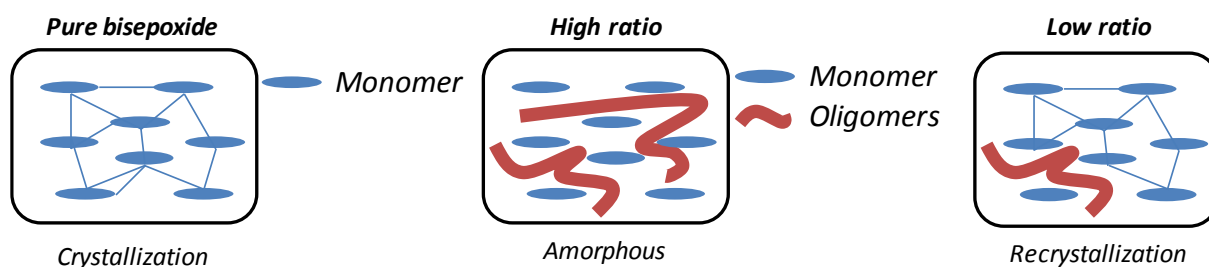


Figure 55: (a) T_g in the respect of the average molecular weight and (b) DSC thermograms of oligomers prepared at various stoichiometry ratios r

However, the recrystallization occurred almost instantly for ratio values below 0.3. This feature could be related to the high amount of monomer unreacted (see SEC traces Figure 54) and the low amount of oligomers which cannot efficiently disrupt the crystallinity of monomer (Scheme 44).



Scheme 44: Macromolecular representation of oligomers with different ratio

Finally, oligomerisation reaction is an efficient way to tune the processability of epoxy monomer. Oligomers of different chain lengths and glass transition temperatures were successfully obtained. However, recrystallization of samples occurred for low ratio bisphenol/bisepoxide. Thus, the incorporation of another kind of hydroxyl moieties, such as aliphatic diol or other bio-based bisphenols (divanillyl alcohol, dieugenol, methyl divanillate) could be a way to tune more efficiently the properties of the oligomers.

V. Conclusion

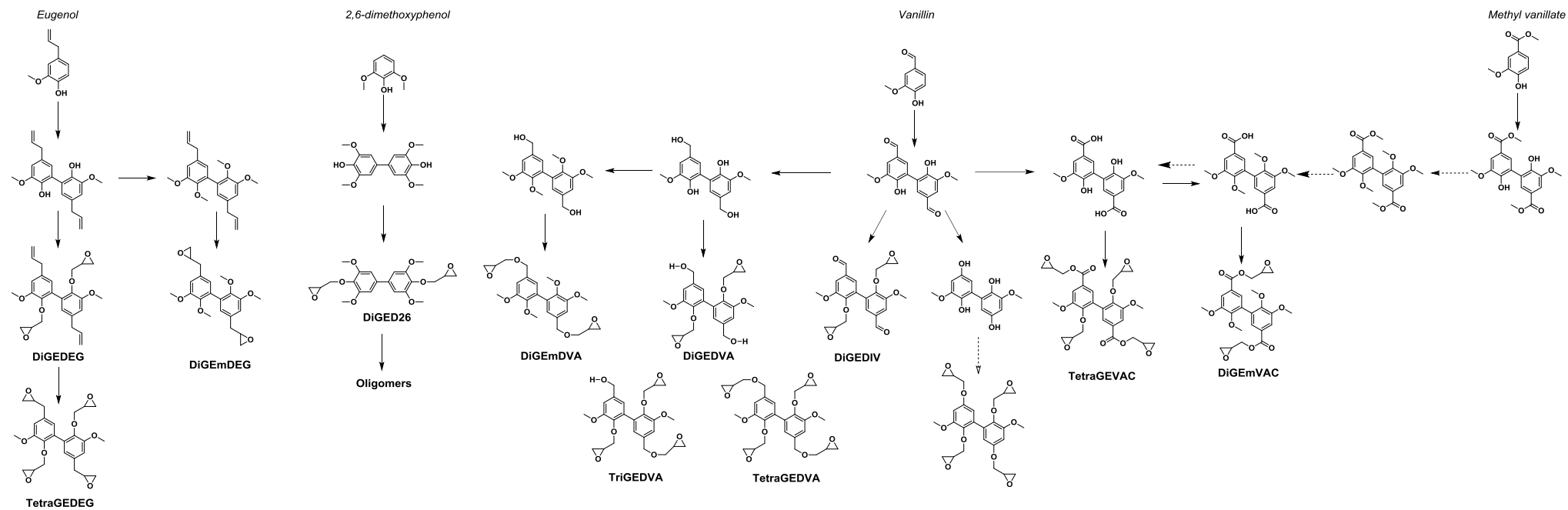
In conclusion, a platform of bio-based epoxy precursors has been synthesized from 2,6-dimethoxyphenol, eugenol, methyl vanillate and vanillin (Scheme 45).

First, the synthesis of polyglycidylethers were successfully synthesized from DVA and epichlorhydrin. In addition to the fact that is possible to recover separately DiGEDVA, TriGEDVA or TetraGEDVA, the investigation of experimental conditions of the synthesis brought to light two key parameters enabling the control of the properties and the processing of these resins.

Then, other epoxy precursors were prepared from divanilic acid, dieugenol and D26. As a general trend, polyglycidylethers were synthesized in a good yield, except DiGEmDVA, TetraGEVAC or TetraGEDEG. The amount synthesized of these latter was not high enough to fully evaluate their potential. A deepen investigation of the synthetic conditions would be required in order to fully characterise these new molecules.

In addition, epoxy monomers such as DiGEmVAC and DiGED26 were also successfully synthesized, but their high melting point is a serious obstacle in the development of epoxy formulation. Therefore, the oligomerisation of DiGED26 with D26 has been investigated. Amorphous oligomers of different molecular weights and glass transitions were successfully produced. Thus, oligomerisation reaction prove to be an efficient mean to break the crystallinity of these compounds and to tune their processability.

Following that, the next chapter will be dedicated to the synthesis of epoxy thermosets from bio-based epoxy precursors and more especially from polyglycidylethers of DVA.



Scheme 45: Bio-platform of polyglycidylethers derived from bio-based precursors

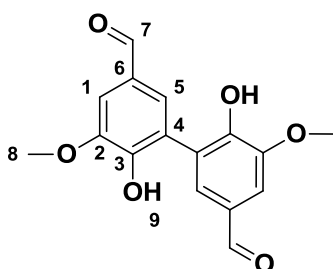
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VII. Experimental

Procedure for dimerisation of phenols

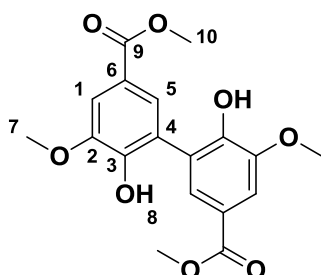
A solution of vanillin (1.5 g) in acetone (20 mL) was added to NaOAc buffer (180 mL, 0.1 M, pH 5.0). The solution was saturated in O₂ for 5 min. Laccase from *Trametes versicolor* (20 U, 12.4 mg) was added and the reaction was stirred at room temperature for 24 h. The precipitate was filtered off and the product dried overnight at 80 °C under vacuum. Yield: 90%



¹H NMR (400 MHz, DMSO, δ (ppm)): δ 9.69 (s, H₇), 7.57 (d, H₁), 7.16 (d, H₅), 3.76 (s, H₈).

¹³C NMR (400 MHz, DMSO, δ (ppm)): δ 191.62 (s, C₇), 150.88 (s, C₃), 148.61 (s, C₂), 128.64 (s, C₆), 128.21 (s, C₄), 125.02 (s, C₅), 109.6 (s, C₁), 56.25 (C₈).

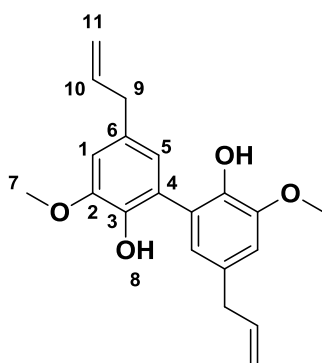
The same procedure was applied for methyl vanillate.



¹H NMR (400 MHz, DMSO, δ (ppm)): δ 9.51 (s, H₈), 7.46 (d, H₁), 7.45 (d, H₅), 3.90 (s, H₇), 3.80 (s, H₁₀).

¹³C NMR (400 MHz, DMSO, δ (ppm)): δ 166.09 (s, C₉), 148.88 (s, C₃), 147.47 (s, C₂), 125.40 (s, C₅), 124.36 (s, C₆), 119.48 (s, C₄), 110.92 (s, C₁), 56.01 (s, C₇), 51.79 (s, C₁₀).

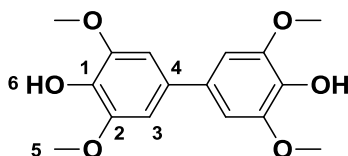
The same procedure was applied for eugenol.



^1H NMR (400 MHz, DMSO, δ (ppm)): δ 8.16 (s, H₈), 6.73 (d, H₁), 6.52 (d, H₅), 5.93 (m, H₁₀), 5.05 (m, H₁₁), 3.79 (s, H₇), 3.27 (d, H₉).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 147.61 (s, C₂), 141.79 (s, C₃), 138.15 (s, C₁₀), 129.60 (s, C₆), 125.91 (s, C₄), 122.84 (s, C₅), 115.39 (s, C₁₁), 110.79 (s, C₁), 55.82 (s, C₇), 39.23 (s, C₉).

The same procedure was applied for 2,6-dimethoxyphenol.

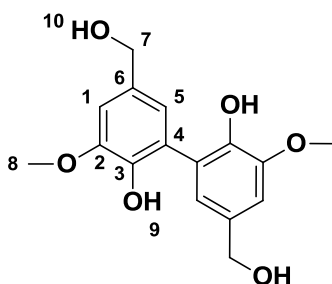


^1H NMR (400 MHz, DMSO, δ (ppm)): δ 9.93 (s, H₆), 6.82 (d, H₃), 3.84 (s, H₅).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 148.21 (s, C₂), 134.90 (s, C₄), 131.36 (s, C₁), 104.37 (s, C₃), 56.20 (s, C₅).

Reduction of divanillin

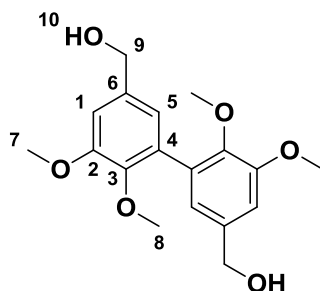
20 mmol of divanillin (\approx 6 g) were dissolved in 100 mL of NaOH (0.5M). The flask was put in an ice bath and 3.6 g of sodium borohydride (100 mmol) were added slowly. Then, the mixture was stirred at room temperature for 30 min. The solution was acidified with HCl to pH 7. The precipitate was filtered off and the product dried overnight at 80 °C under vacuum. Yield: 90%.



^1H NMR (400 MHz, DMSO, δ (ppm)): δ 8.22 (s, H₉), 6.88 (d, H₁), 6.67 (d, H₅), 5.01 (t, H₁₀), 4.41 (d, H₇), 3.82 (s, H₈).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 147.94 (s, C₃), 142.77 (s, C₂), 133.08 (s, C₆), 125.92 (s, C₄), 121.83 (s, C₅), 109.50 (s, C₁), 63.38 (s, C₇), 56.25 (s, C₈).

The same procedure was applied for methylate divanillin.

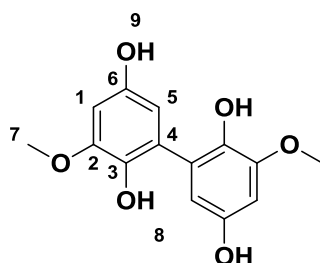


^1H NMR (400 MHz, DMSO, δ (ppm)): δ 6.99 (d, H₁), 6.67 (d, H₅), 5.15 (s, H₁₀), 4.47 (s, H₉), 3.83 (s, H₇), 3.50 (s, H₈).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 152.00 (s, C₃), 144.81 (s, C₂), 137.64 (s, C₆), 132.12 (s, C₄), 120.33 (s, C₅), 110.18 (s, C₁), 62.63 (s, C₉), 59.91 (s, C₈), 55.52 (C₇).

Oxidation of divanillin

6 mmol of divanillin (\approx 1 g) were dissolved in 10 mL of NaOH (0.5M). Sodium percarbonate (7 mmol) were added slowly. Then, the mixture was stirred at room temperature for 12 hours. The solution was acidified with HCl to pH 3 and the aqueous phase was extracted with ethyl acetate. The organic phases were collected and washed with water and dried on MgSO₄. Ethyl acetate was removed under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent. Yield: <50%.

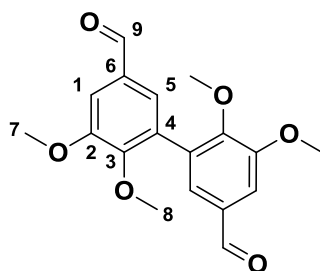


^1H NMR (400 MHz, DMSO, δ (ppm)): δ 8.79 (s, H₈), 7.76 (s, H₉), 6.38 (d, H₁), 6.15 (d, H₅), 3.75 (s, H₇).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 149.76 (s, C₃), 148.62 (s, C₂), 135.77 (s, C₆), 126.65 (s, C₄), 108.35 (s, C₅), 99.35 (s, C₃), 55.65 (s, C₇).

Procedure for methylation

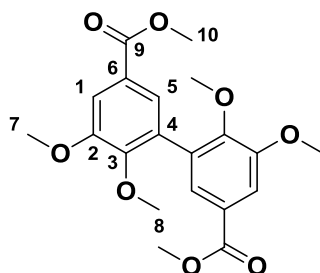
26 mmol of divanillin and 15,2 g of potassium carbonate (110 mmol) were dissolved in 120 mL of DMF. 9,6 ml of iodomethane (158 mmol) were slowly added to the mixture. After 15 h at 80 °C, mixture was filtered and the resulting solution poured into cold water. The methylated compound, which precipitated was filtered off and dried under vacuum. Yield: 80%.



^1H NMR (400 MHz, DMSO, δ (ppm)): δ 9.94 (d, H₉), 7.58 (d, H₁), 7.45 (d, H₅), 3.95 (s, H₇), 3.67 (s, H₈).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 191.76 (s, C₉), 152.88 (s, C₂), 151.52 (s, C₃), 131.81 (s, C₆), 131.56 (s, C₄), 126.09 (s, C₅), 111.36 (s, C₁), 60.43 (s, C₈), 55.99 (s, C₇).

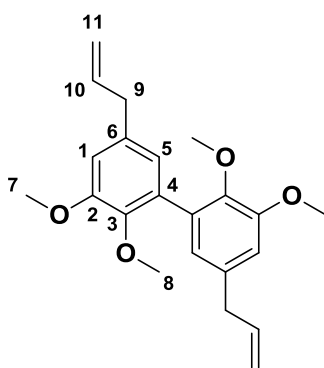
The same procedure was applied for methyl divanillate.



^1H NMR (400 MHz, DMSO, δ (ppm)): δ 7.59 (d, H₁), 7.40 (d, H₅), 3.92 (s, H₇), 3.83 (s, H₁₀), 3.62 (s, H₈).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 165.67 (s, C₉), 152.27 (s, C₃), 150.36 (s, C₂), 131.28 (s, C₆), 124.70 (s, C₄), 123.96 (s, C₅), 112.76 (s, C₁), 60.29 (s, C₈), 55.92 (s, C₇), 52.18 (C₁₀).

The same procedure was applied for dieugenol.

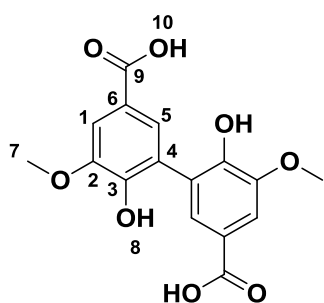


^1H NMR (400 MHz, DMSO, δ (ppm)): δ 6.85 (d, H₁), 6.54 (d, H₅), 5.96 (m, H₁₀), 5.07 (m, H₁₁), 3.81 (s, H₇), 3.48 (s, H₈), 3.34 (d, H₉).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 152.16 (s, C₂), 144.41 (s, C₃), 137.67 (s, C₁₀), 134.78 (s, C₆), 132.29 (s, C₄), 122.26 (s, C₅), 115.80 (s, C₁₁), 112.17 (s, C₁), 59.91 (s, C₇), 55.58 (s, C₈), 39.22 (s, C₉).

Procedure for ester saponification

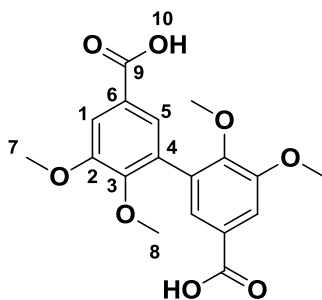
10 mmol of methyl divanillate were dissolved in 30 mL of methanol. 3g of sodium hydroxide (75 mmol) were slowly added to the mixture and warmed to reflux during 4h. After cooling down to room temperature, the solution was acidified with HCl to pH=3. The precipitate was filtered off and the product dried overnight at 80 °C under vacuum. Yield: 90%



^1H NMR (400 MHz, DMSO, δ (ppm)): δ 9.39 (s, H₈), 7.45 (d, H₁), 7.41 (d, H₅), 3.89 (s, H₇).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 167.18 (s, C₉), 148.36 (s, C₃), 147.22 (s, C₂), 125.44 (s, C₆), 124.19 (s, C₄), 120.44 (s, C₅), 111.05 (s, C₁), 55.89 (s, C₇).

The same procedure was applied for methylated methyl divanillate.



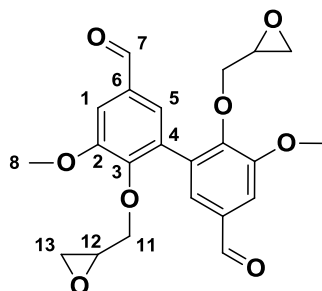
^1H NMR (400 MHz, DMSO, δ (ppm)): δ 12.94 (s, H₁₀), 7.58 (d, H₁), 7.39 (d, H₅), 3.91 (s, H₇), 3.61 (s, H₈).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 166.83 (s, C₉), 152.20 (s, C₃), 150.07 (s, C₂), 131.34 (s, C₆), 125.91 (s, C₄), 124.13 (s, C₅), 112.93 (s, C₁), 60.28 (s, C₈), 55.87 (s, C₇).

Procedure for glycidylation

Diglycidylether of divanillin

3 g of divanillin (10 mmol) were dissolved in 15 mL of epichlorohydrin. 0,3 g of tetrabutylammonium chloride (TEBAC) (0.95 mmol) were added and the solution was stirred at 80 °C for 12 h. 8 mL of a solution of NaOH (5M) (40 mmol) were added and the solution was stirred at room temperature for 1 h 30. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Yield: 90%.

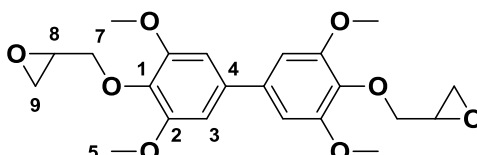


^1H NMR (400MHz, DMSO, δ (ppm)): δ 9.94 (s, H₇), 7.60 (d, H₁), 7.48 (s, H₅), 3.93 (s, H₈), 7.0 (s, H₅), 6.71 (s, H₁), 5.16 (t, H₁₀), 4.47 (d, H₇), 4.18 (m, H₁₁), 3.95 (s, H₈), 3.85 (m, H_{11b}), 2.98 (m, H₁₂), 2.61 (t, H₁₃), 2.40 (t, H_{13b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 191.79 (s, C₇), δ 152.48 (s, C₃), 150.67 (s, C₂), 131.84 (s, C₆), 131.29 (s, C₄), 126.40 (s, C₅), 111.48 (s, C₁), 74.24 (s, C₁₁), 63.14 (s, C₇), 55.89 (s, C₈), 50.12 (s, C₁₂), 43.44 (s, C₁₃).

Diglycidylether of 2,6-dimethoxydiphenol

3 g of 2,6-dimethoxydiphenol (10 mmol) were dissolved in 15 mL of epichlorohydrin. 0,3 g of tetrabutylammonium chloride (TEBAC) (0.95 mmol) were added and the solution was stirred at 80 °C for 1 h 30. 8 mL of a solution of NaOH (5M) (40 mmol) were added and the solution was stirred at room temperature for 1 h. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Yield: 90%.

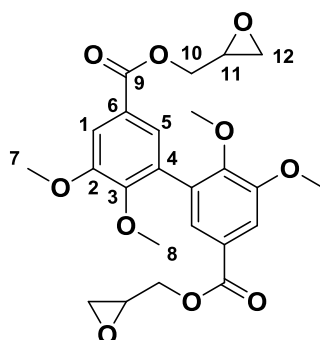


^1H NMR (400MHz, DMSO, δ (ppm)): δ 6.89 (s, H₃), 4.13 (d, H₇), 3.87 (s, H₅), 3.75 (q, H_{7b}), 3.27 (m, H₈), 2.76 (q, H₉), 2.59 (q, H_{9b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.99 (s, C₁), δ 136.59 (s, C₂), 135.97 (s, C₃), 104.56 (s, C₄), 73.97 (s, C₇), 56.14 (s, C₅), 50.33 (s, C₈), 43.35 (s, C₉).

Diglycidylether of methylated divanillic acid

0,5 g of methylated divanillic acid (1,5 mmol) was dissolved in 3 mL of epichlorohydrin. 0,1 g of tetrabutylammonium chloride (TEBAC) was added and the solution was stirred at 80 °C for 3 h. 3 mL of a solution of NaOH (5M) (15 mmol) were added and the solution was stirred at room temperature for 2 h. The product is extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Yield: 90%.

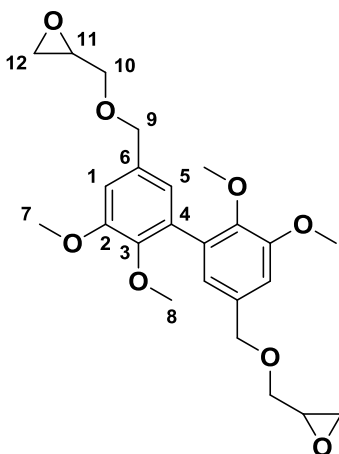


^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.61 (d, H₁), 7.45 (d, H₅), 4.65 (d, H₁₀), 4.08 (q, H_{10b}), 3.93 (s, H₇), 3.64 (m, H₈), 3.34 (m, H₁₁), 2.82 (m, H₁₂), 2.72 (m, H_{12b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 164.92 (s, C₉), 152.34 (s, C₃), 150.55 (s, C₂), 131.28 (s, C₆), 124.41 (s, C₄), 124.04 (s, C₅), 112.92 (s, C₁), 65.58 (s, C₁₀), 60.34 (s, C₈), 55.97 (s, C₇), 49.01 (s, C₁₁), 43.90 (s, C₁₂).

Diglycidylether of methylated divanillyl alcohol

0.5 g of methylated divanillyl alcohol (1,5 mmol) were dissolved in 3 mL of epichlorohydrin. 0,05 g of tetrabutylammonium chloride (TEBAC) were added and the solution was stirred at 80 °C for 1 h. 3 mL of a solution of NaOH (10M) (160 mmol) were added and the solution was stirred at room temperature for 24 h. The product is extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent. Yield: 25%.



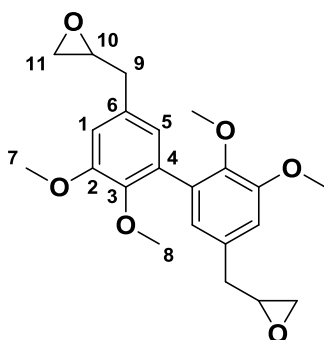
^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.01 (d, H₁), 6.72 (d, H₅), 4.49 (t, H₉), 3.84 (d, H₇), 3.77 (m, H₁₀), 3.52 (s, H₈), 3.31 (m, H_{10b}), 3.15 (m, H₁₁), 2.73 (t, H₁₂), 2.55 (m, H_{12b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.20 (s, C₃), 145.48 (s, C₂), 133.25 (s, C₆), 131.98 (s, C₄), 121.66 (s, C₅), 111.35 (s, C₁), 71.90 (s, C₉), 70.71 (s, C₁₀), 59.90 (s, C₈), 55.61 (s, C₇), 50.27 (s, C₁₁), 43.41 (s, C₁₂).

Diglycidylether of methylated dieugenol

1 g of methylated dieugenol were dissolved in 15 mL of cold DCM. 1g of mCPBA were dissolved in 7,5 mL of cold DCM and added slowly to the solution of methylated dieugenol. The mixture was then stirred at room temperature for 24 h. The organic phase was washed two times with a saturated solution of NaHCO₃ and three with water. Dichloromethane was removed

from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent. Yield: 50%.

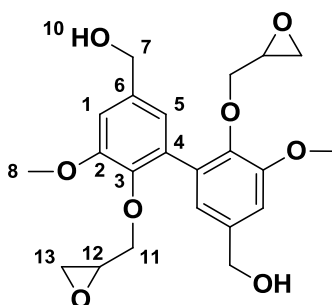


^1H NMR (400MHz, DMSO, δ (ppm)): δ 6.95 (d, H₁), 6.66 (d, H₅), 3.83 (s, H₇), 3.51 (s, H₈), 3.12 (m, H₁₀), 2.74 (m, H₉), 2.57 (m, H₁₁).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.15 (s, C₂), 144.77 (s, C₃), 132.67 (s, C₆), 132.24 (s, C₄), 122.84 (s, C₅), 112.80 (s, C₁), 59.95 (s, C₈), 55.65 (s, C₇), 52.05 (s, C₁₀), 46.15 (s, C₁₁), 37.90 (s, C₉).

Diglycidylether of divanillyl alcohol

3 g of divanillyl alcohol (10 mmol) were dissolved in 15 mL of epichlorohydrin. 0,3 g of tetrabutylammonium chloride (TEBAC) (0.95 mmol) were added and the solution was stirred at 80 °C for 1 h 30. 8 mL of a solution of NaOH (5M) (40 mmol) were added and the solution was stirred at room temperature for 1 h. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent. Yield: 80%.

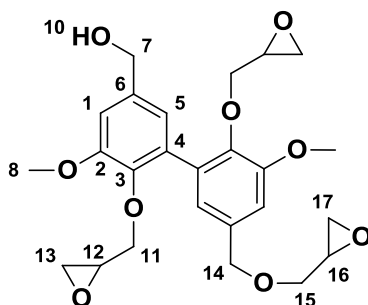


^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.0 (d, H₁), 6.71 (d, H₅), 5.16 (t, H₁₀), 4.47 (d, H₇), 3.88 (m, H₁₁), 3.83 (s, H₈), 3.74 (m, H_{11b}), 2.95 (m, H₁₂), 2.6 (t, H₁₃), 2.36 (t, H_{13b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.33 (s, C₃), 144.47 (s, C₂), 138.26 (s, C₆), 132.59 (s, C₄), 120.86 (s, C₅), 110.79 (s, C₁), 74.22 (s, C₁₁), 63.14 (s, C₇), 56.18 (s, C₈), 50.53 (s, C₁₂), 43.97 (s, C₁₃).

Triglycidylether of divanillyl alcohol

3 g of divanillyl alcohol (10 mmol) were dissolved in 15 mL of epichlorohydrin. 0,3 g of tetrabutylammonium chloride (TEBAC) (0.95 mmol) were added and the solution was stirred at 80 °C for 1 h 30. 8 mL of a solution of NaOH (5M) (40 mmol) were added and the solution was stirred at room temperature for 4 h 30. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent.



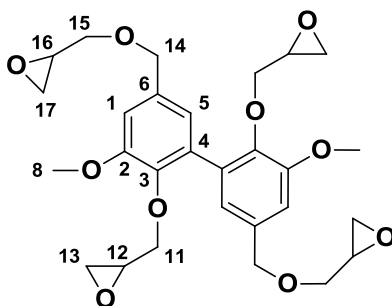
^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.01 (d, H₁), 6.75 (d, H₅), 5.18 (t, H₁₀), 4.47 (d, H₇, H₁₄), 3.92 (m, H₁₁), 3.84 (s, H₈), 3.76 (m, H_{11b}), 3.69 (m, H₁₅), 3.29 (m, H_{15b}), 3.14 (m, H₁₆), 2.97 (m, H₁₂), 2.72 (m, H₁₇), 2.6 (m, H₁₃), 2.5 (m, H_{17b}), 2.36 (m, H_{13b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.02 (s, C_{3'}), δ 151.89 (s, C₃), 144.38 (s, C_{2'}), 143.68 (s, C₂), 138.12 (s, C_{6'}), 133.39 (s, C₆), 132.06 (s, C_{4'}), 131.76 (s, C₄), 121.78 (s, C_{5'}), 120.26 (s, C₅), 111.55 (s, C_{1'}), 110.46 (s, C₁), 73.85 (s, C₁₄), 71.81 (s, C₁₅), 70.79 (s, C₁₁), 62.67 (s, C₇), 55.90 (s, C₈), 50.42 (s, C₁₂), 50.16 (s, C₁₆), 43.42 (s, C₁₃, C₁₇).

Tetraglycidylether of divanillyl alcohol

3 g of divanillyl alcohol (10 mmol) were dissolved in 15 mL of epichlorohydrin. 0,3 g of tetrabutylammonium chloride (TEBAC) (0.95 mmol) were added and the solution was stirred at 80 °C for 1 h 30. 16 mL of a solution of NaOH (10M) (160 mmol) were added and the solution was stirred at room temperature for 24 h. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed

from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent. Yield: 80%.

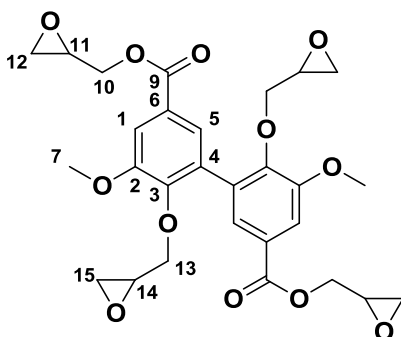


^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.02 (d, H₁), 6.76 (d, H₅), 4.50 (s, H₁₄), 3.92 (m, H₁₁), 3.86 (s, H₈), 3.76 (m, H_{11b}), 3.70 (m, H₁₅), 3.28 (m, H_{15b}), 3.14 (m, H₁₆), 2.97 (m, H₁₂), 2.73 (m, H₁₇), 2.60 (m, H₁₃), 2.55 (m, H_{17b}), 2.35 (m, H_{13b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.10 (s, C₃), 144.51 (s, C₂), 133.51 (s, C₆), 131.81 (s, C₄), 121.83 (s, C₅), 111.52 (s, C₁), 73.77 (s, C₁₄), 71.90 (s, C₁₅), 63.14 (s, C₁₁), 55.79 (s, C₈), 50.30 (s, C₁₂), 50.03 (s, C₁₆), 43.44 (s, C₁₃ C₁₇).

Tetraglycidylether of divanillic acid

1.5 mmol of divanillic acid were dissolved in 5 mL of epichlorohydrin. 0,1 g of tetrabutylammonium chloride (TEBAC) were added and the solution was stirred at 80 °C for 2h. 5 mL of a solution of NaOH (5M) were added and the solution was stirred at room temperature for 24 h. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent. Yield: 30%.

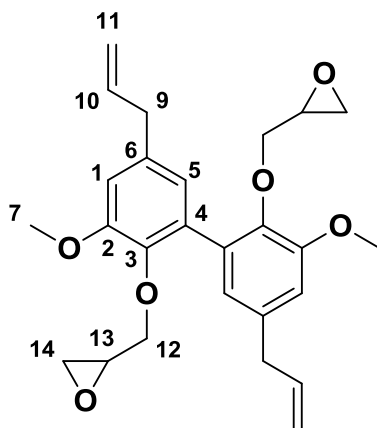


^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.63 (d, H₁), 7.50 (d, H₅), 4.65 (d, H₁₀), 4.15 (m, H_{10b}), 4.09 (s, H₁₄), 3.94 (m, H₇), 3.86 (m, H_{14b}), 3.35 (m, H₁₁), 2.97 (m, H₁₃), 2.83 (m, H₁₂), 2.73 (m, H₁₅), 2.62 (m, H_{12b}), 2.38 (m, H_{15b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 164.94 (s, C₉), 152.12 (s, C₃), 149.56 (s, C₂), 131.23 (s, C₆), 124.57 (s, C₄), 124.18 (s, C₅), 112.98 (s, C₁), 74.01 (s, C₁₃), 56.08 (s, C₁₀), 50.24 (s, C₇), 49.94 (s, C₁₄), 49.04 (s, C₁₁), 43.90 (s, C₁₂), 43.36 (s, C₁₅).

Diglycidylether of dieugenol

3 g of dieugenol were dissolved in 15 mL of epichlorohydrin. 0,3 g of tetrabutylammonium chloride (TEBAC) (0.95 mmol) were added and the solution was stirred at 80 °C for 24 h. 8 mL of a solution of NaOH (5 M) (40 mmol) were added and the solution was stirred at room temperature for 2 h. The product was extracted with dichloromethane and washed with water. Dichloromethane and epichlorohydrin were removed from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent. Yield: 75%.

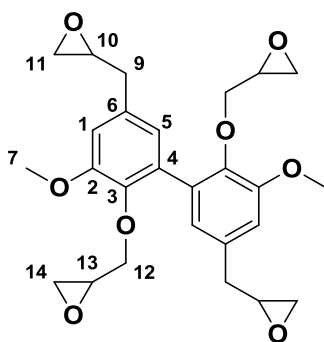


^1H NMR (400MHz, DMSO, δ (ppm)): δ 6.87 (d, H₁), 6.59 (d, H₅), 5.96 (m, H₁₀), 5.02 (m, H₁₁), 3.87 (s, H₁₂), 3.81 (s, H₇), 3.73 (s, H_{12b}), 3.35 (d, H₉), 2.93 (d, H₁₃), 2.59 (d, H₁₄), 2.34 (d, H_{14b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 151.99 (s, C₂), 143.47 (s, C₃), 137.66 (s, C₁₀), 135.03 (s, C₆), 132.09 (s, C₄), 122.39 (s, C₅), 115.79 (s, C₁₁), 112.30 (s, C₁), 73.72 (s, C₁₂), 55.73 (s, C₇), 50.04 (s, C₁₃), 43.41 (s, C₁₄), 39.22 (s, C₉).

Tetraglycidylether of dieugenol

0,5 g of DiGEDEG were dissolved in 7,5 mL of cold DCM. 1g of mCPBA were dissolved in 7,5 mL of cold DCM and added slowly to the solution of DiGEDEG. The mixture was then stirred at room temperature during 24 h. The organic phase was then washed two times with saturated solution of NaHCO₃ and three with water. Dichloromethane were removed from the organic phase under vacuum. Further purification was achieved by flash chromatography using dichloromethane/methanol gradient solvent. Yield: 10%.



^1H NMR (400MHz, DMSO, δ (ppm)): δ 6.98 (d, H₁), 6.71 (d, H₅), 3.93 (m, H₁₂), 3.83 (s, H₇), 3.73 (m, H₁₂), 3.13 (m, H₁₀), 2.94 (m, H₁₃), 2.77 (m, H₉ H₁₁), 2.60 (m, H_{11b} H₁₄), 2.36 (m, H_{14b}).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 151.94 (s, C₂), 143.79 (s, C₃), 132.84 (s, C₆), 131.98 (s, C₄), 122.94 (s, C₅), 112.86 (s, C₁), 73.74 (s, C₁₂), 55.75 (s, C₇), 51.98 (s, C₁₁), 50.03 (s, C₁₀), 46.10 (s, C₁₃), 43.39 (s, C₁₄), 37.5 (s, C₉).

Procedure for titration of epoxy content

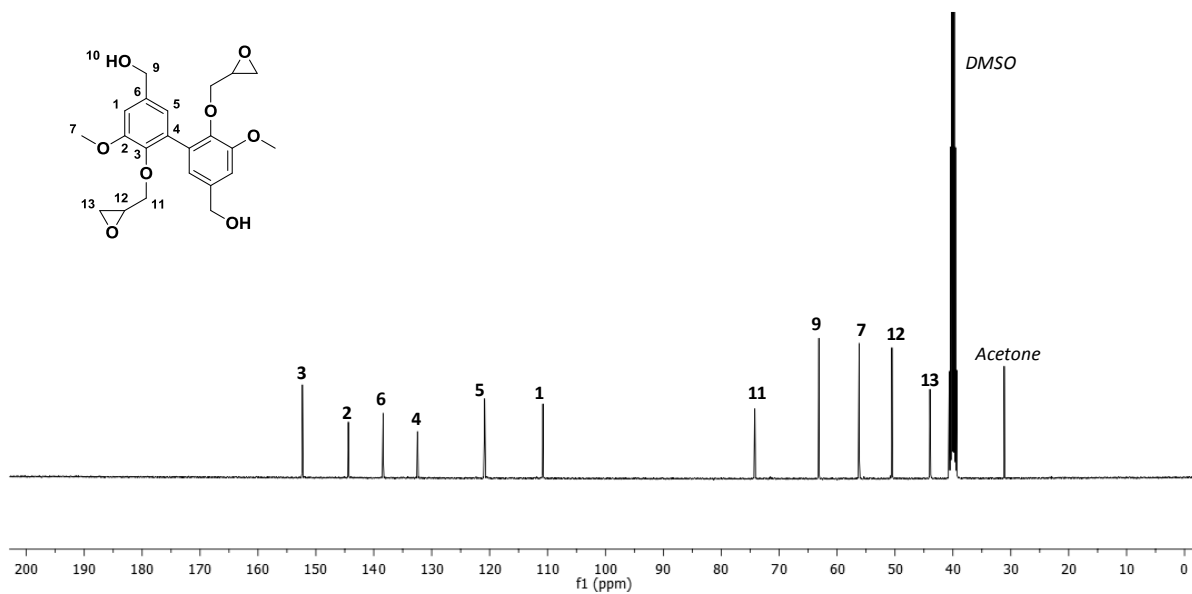
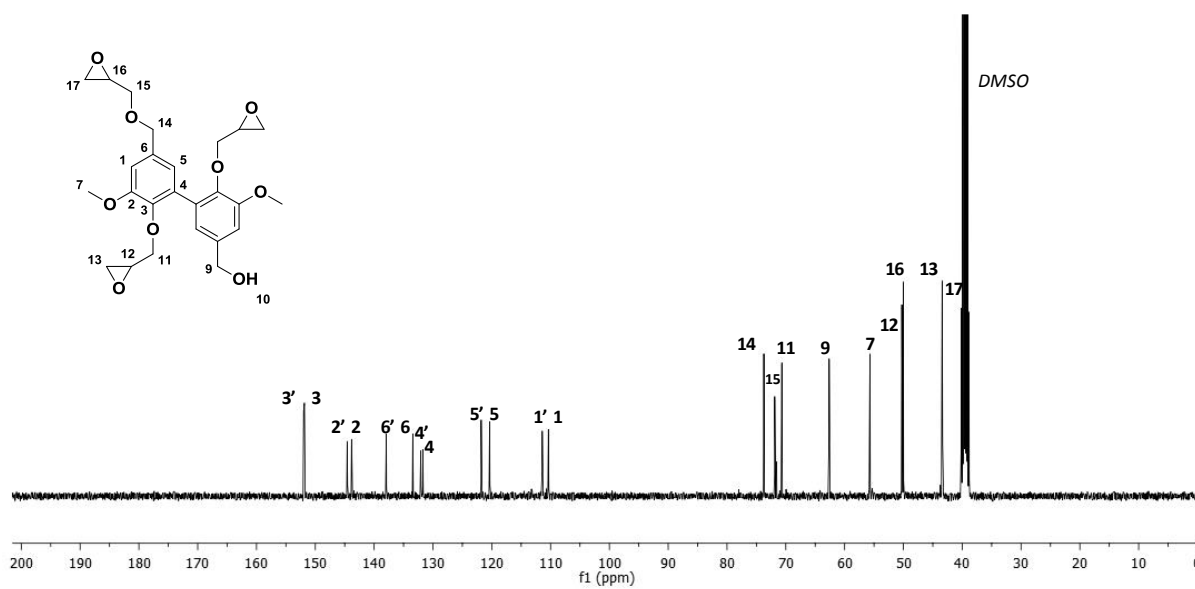
200 mg of epoxy monomer were dissolved in 10 mL of DCM. 3 drops of a 0,1% solution of crystal violet in glacial acetic acid and 2,5 mL of 25% solution of tetraethylammonium bromide in glacial acetic acid were added to the mixture. Titration was performed with 0.1N perchloric acid reagent to a sharp blue to green end point which is stable for 30 s. Volume of perchloric acid reagent used to titrate the samples was recorded.

Calculation of the epoxy equivalent weight: $EEW = \frac{1000*w}{V*N}$ with V the titrated volume in mL, N the normality of the perchloric solution and w the mass of epoxy monomer in g.

Procedure for oligomerisation

1 g of diglycidylether of D26 (2,4 mmol) was melted into a schlenk at 120 °C. Established quantities of D26 or DVA were added under magnetic stirring into the schlenk. 5 % in weight of triphenylbutylphosphonium bromide were added to the mixture and stirred during 2 h at 140 °C.

VIII. Annexes

Figure S1: ^{13}C NMR spectrum of diglycidyl ether of divanillyl alcohol in DMSO- d_6 Figure S2: ^{13}C NMR spectrum of triglycidyl ether of divanillyl alcohol in DMSO- d_6

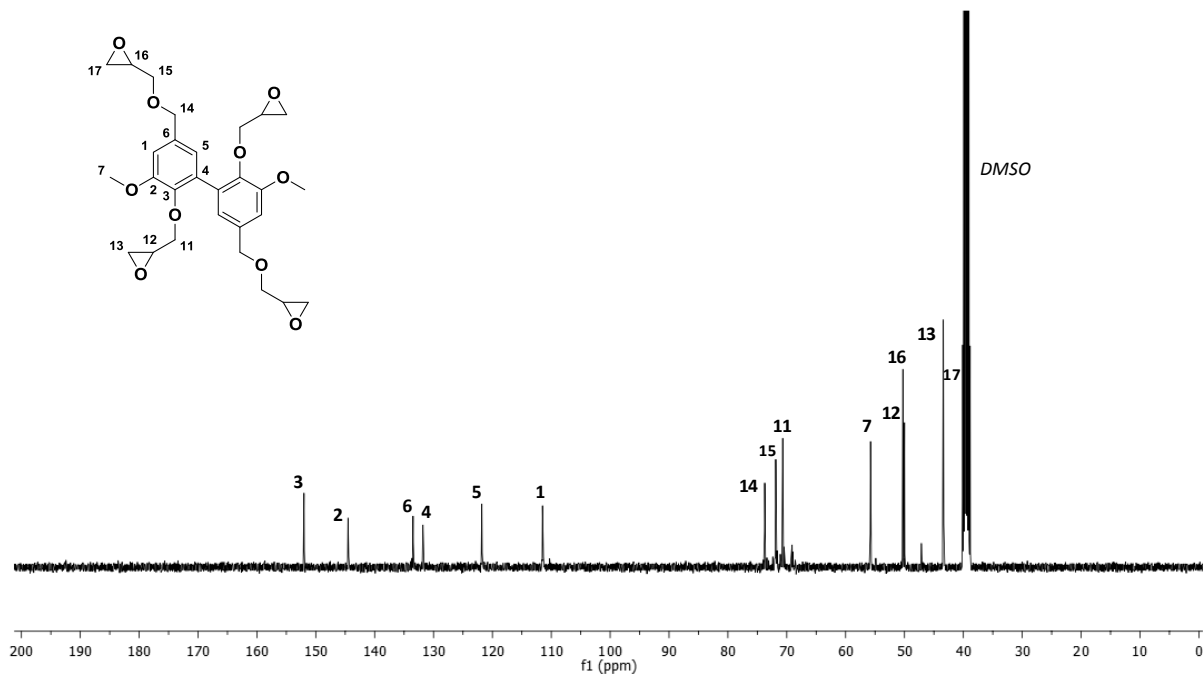


Figure S3: ^{13}C NMR spectrum of tetraglycidyl ether of divanillyl alcohol in DMSO-d_6

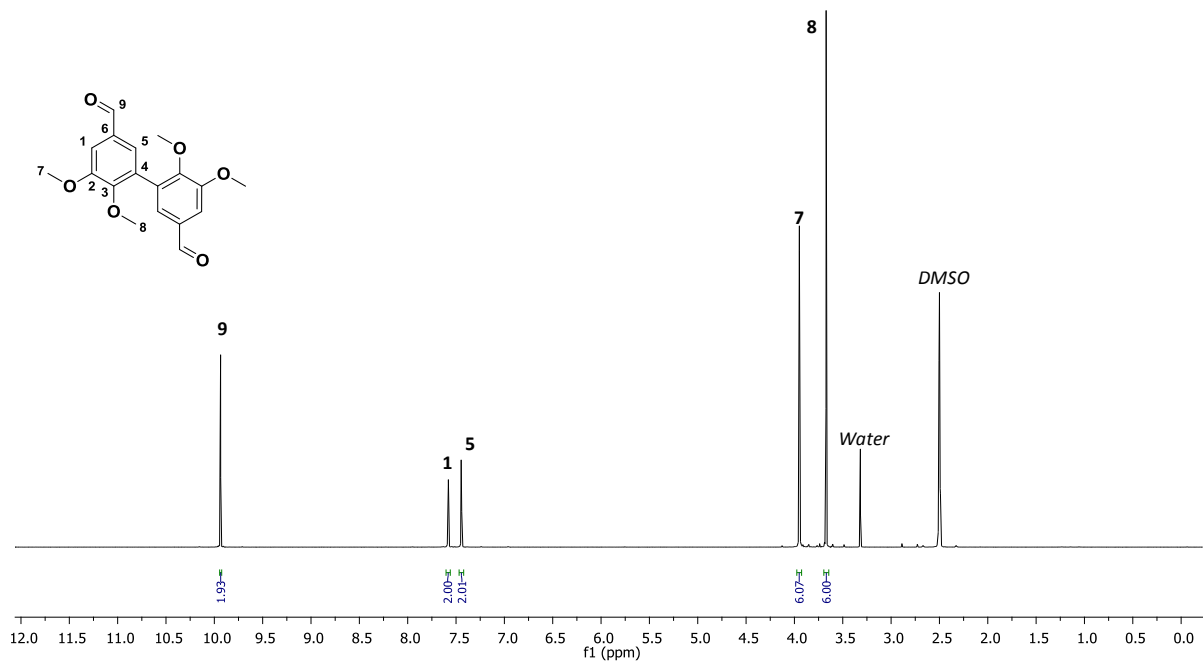


Figure S4: ^1H NMR spectrum of methylated divanillin in DMSO-d_6

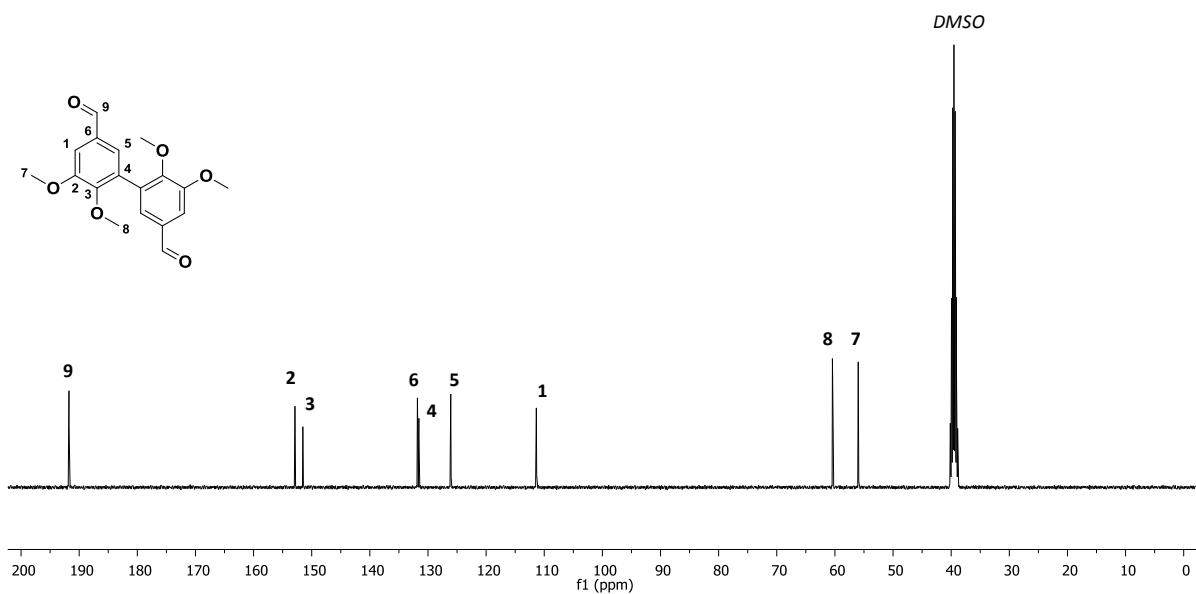


Figure S5: ¹³C NMR spectrum of methylated divanillin in DMSO-d₆

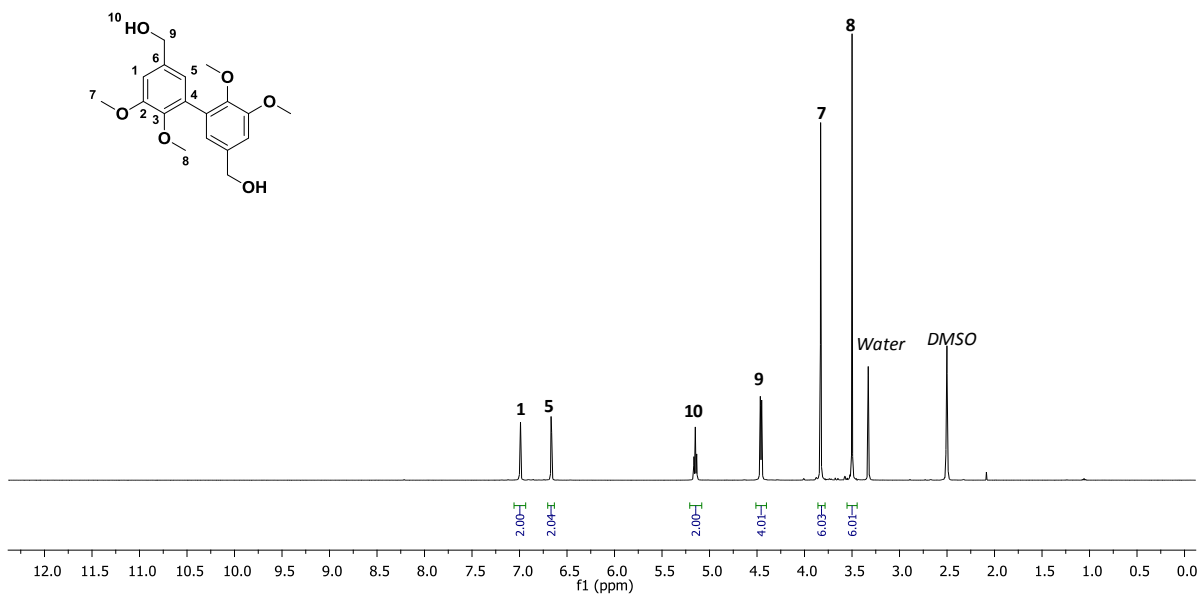


Figure S6: ¹H NMR spectrum of methylated divanillyl alcohol in DMSO-d₆

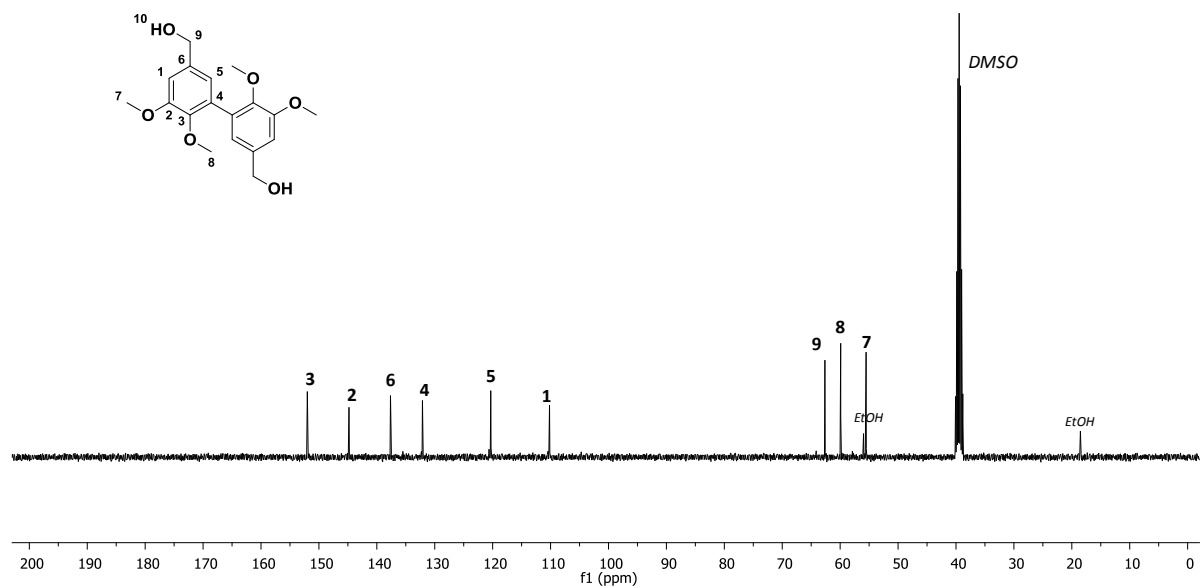


Figure S7: ^{13}C NMR spectrum of methylated divanillyl alcohol in DMSO-d_6

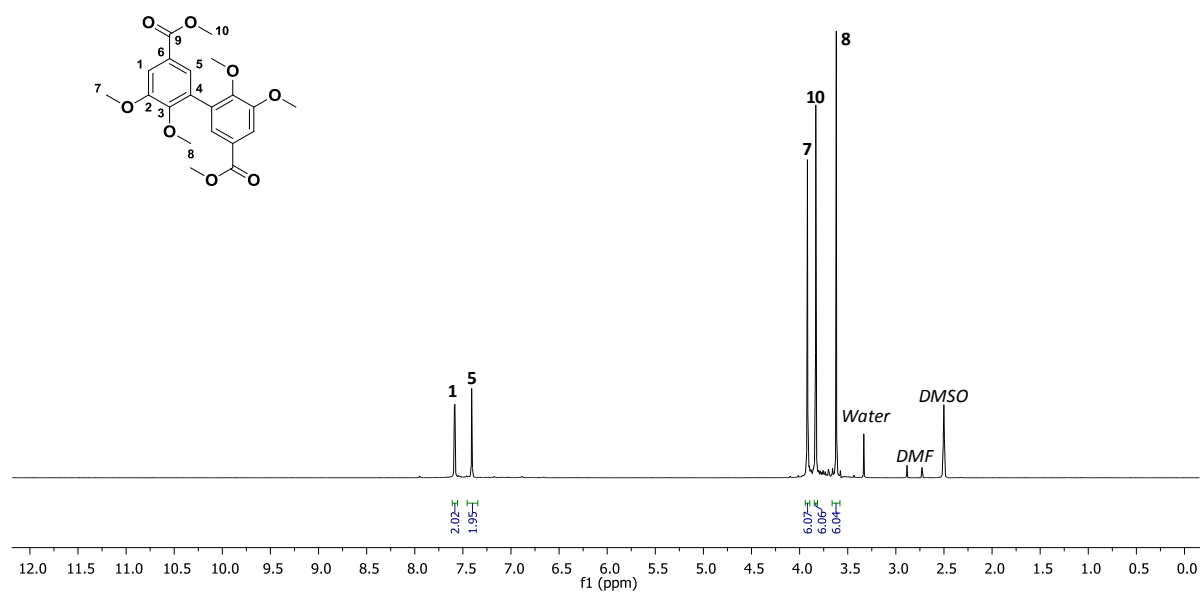


Figure S8: ^1H NMR spectrum of methylated methyl divanillate in DMSO-d_6

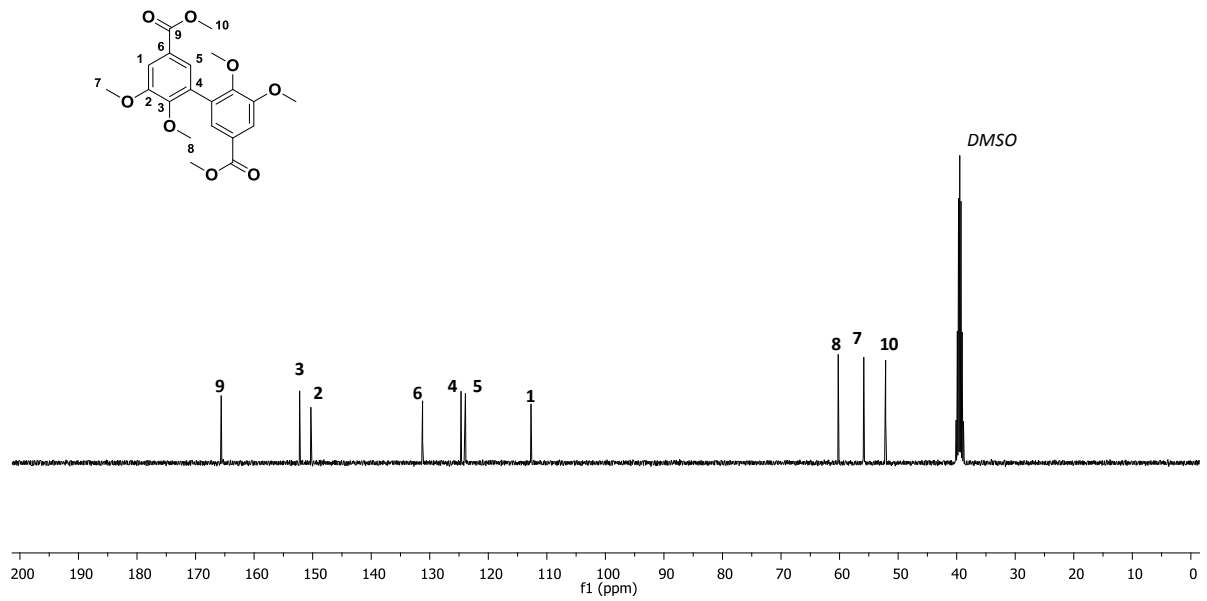


Figure S9: ¹³C NMR spectrum of methylated methyl divanillate in DMSO-d₆

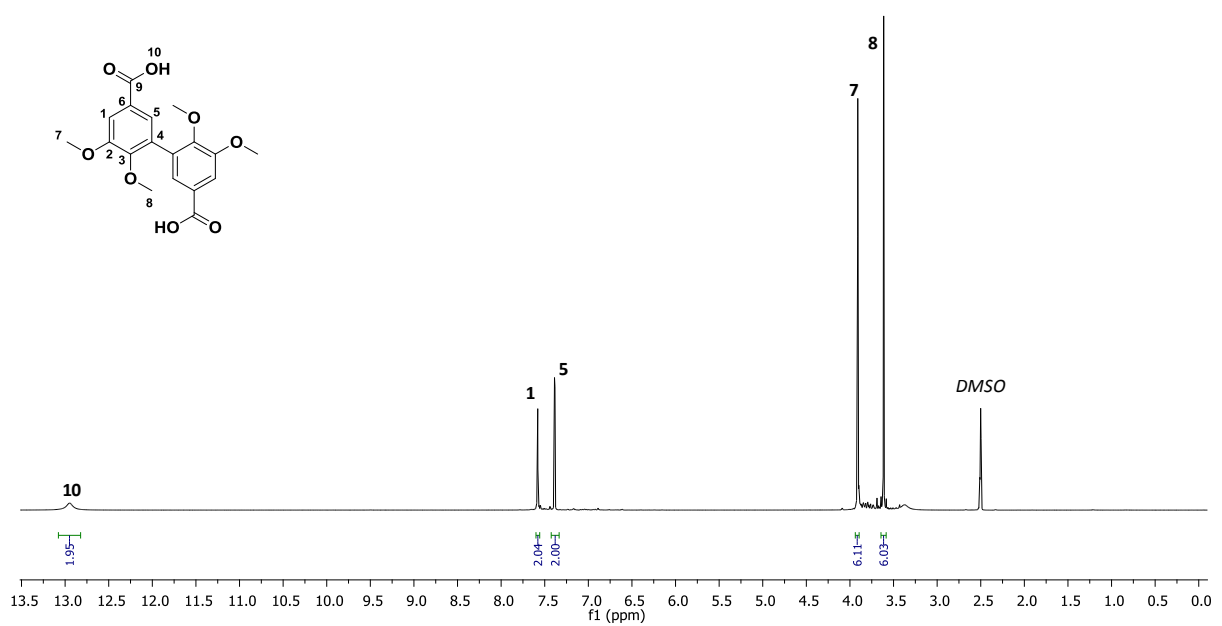


Figure S10: ¹H NMR spectrum of methylated divanillic acid in DMSO-d₆

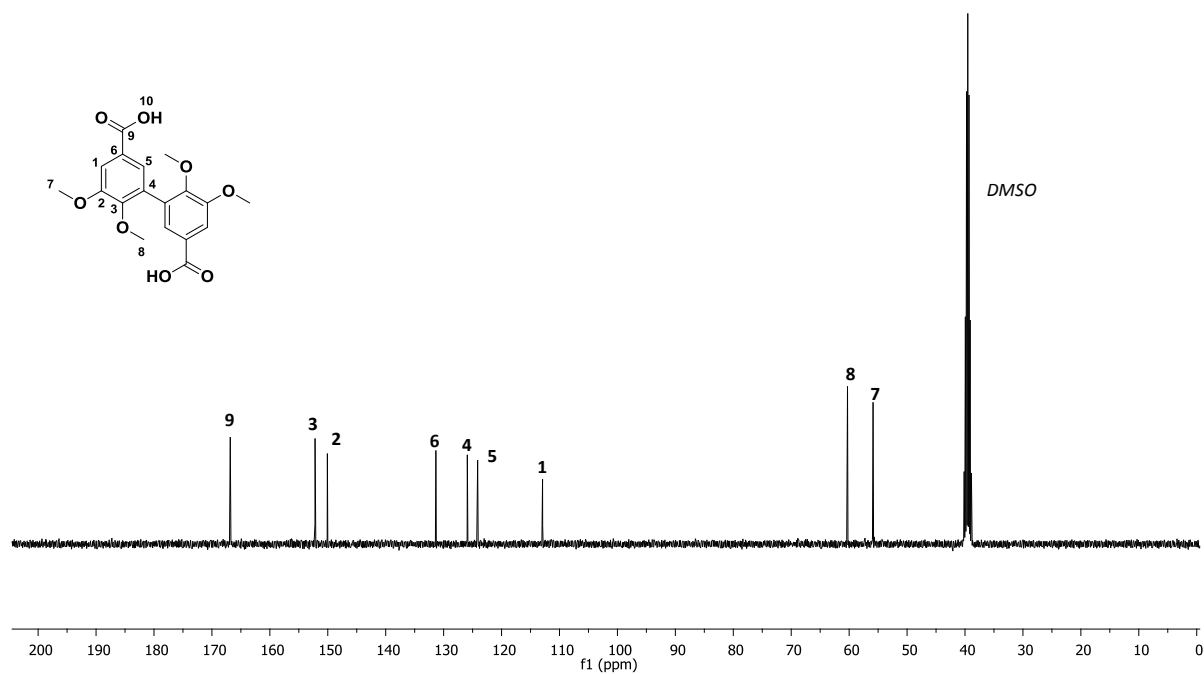


Figure S11: ^{13}C NMR spectrum of methylated divanillic acid in DMSO- d_6

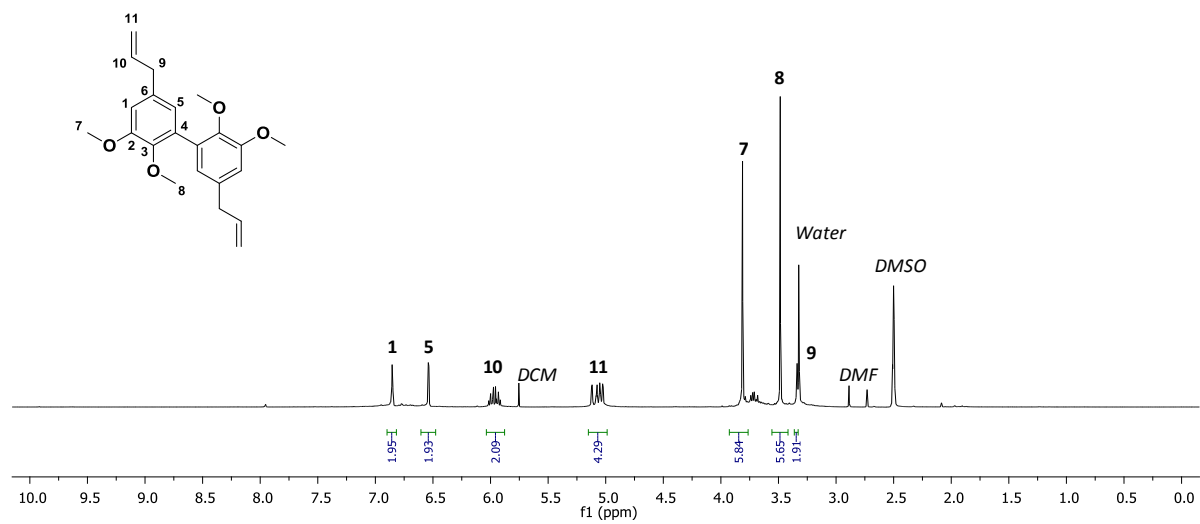


Figure S12: ^1H NMR spectrum of methylated dieugenol in DMSO- d_6

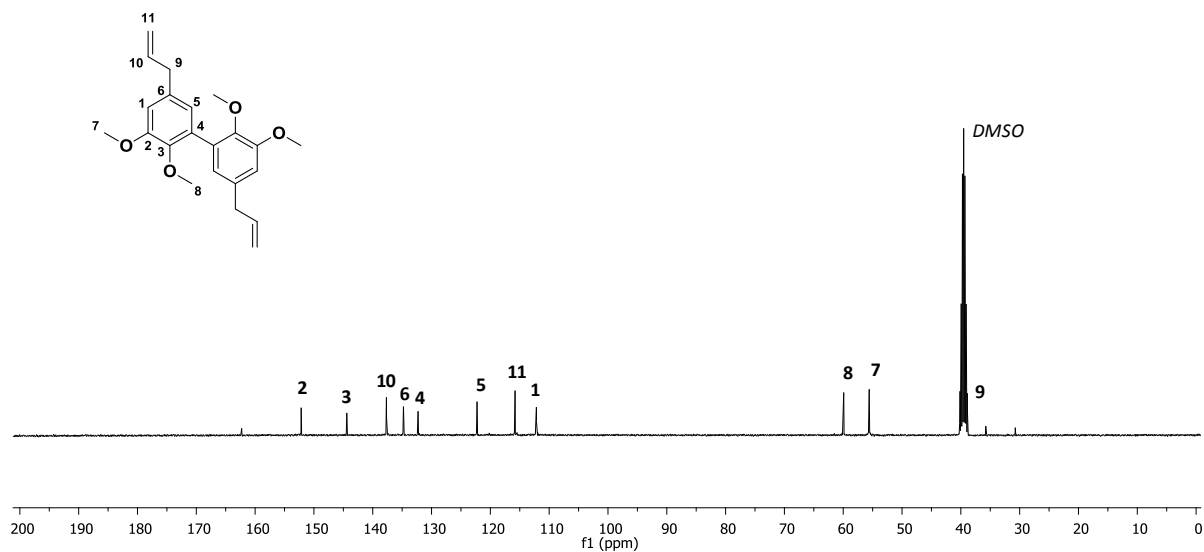


Figure S13: ^{13}C NMR spectrum of methylated dieugenol in DMSO- d_6

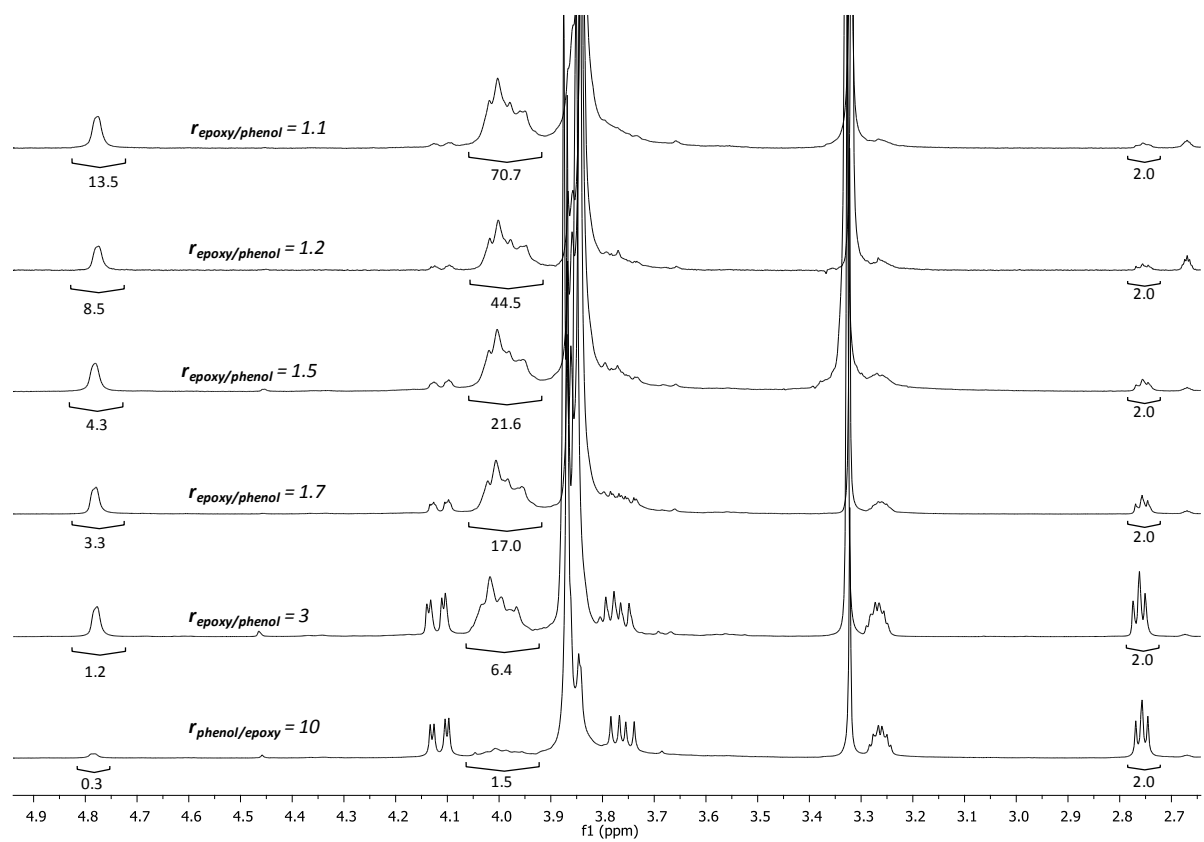


Figure S14: ^1H NMR spectra of DiGED26 oligomers prepared at various stoichiometry ratios r

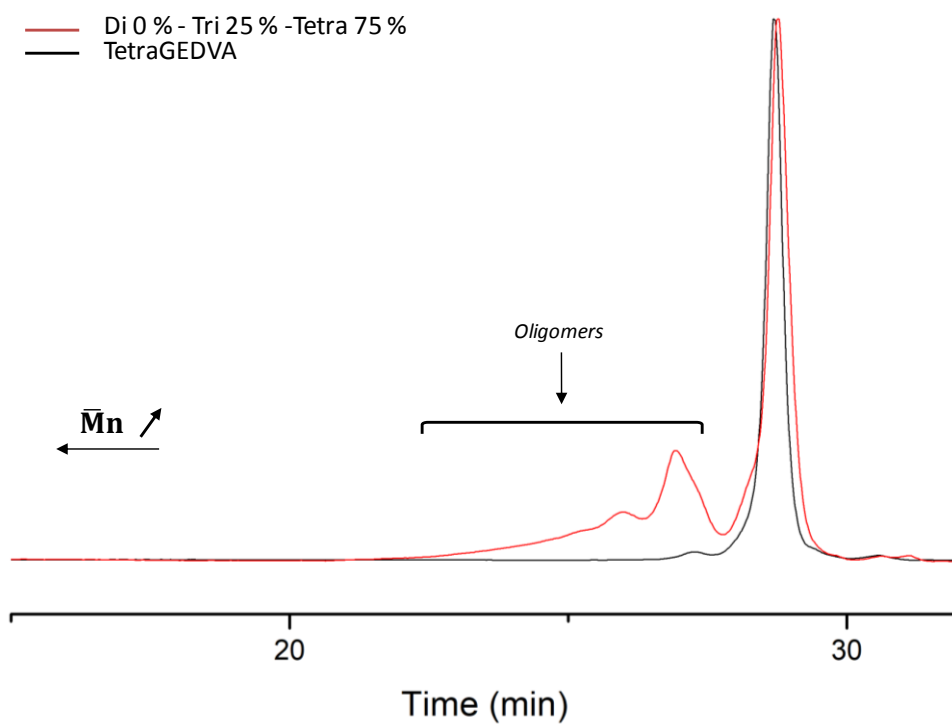


Figure S15: SEC traces in THF of TetraGEDVA purified by flash chromatography and mixture of 25%TriGEDVA-75%TetraGEDVA

Chapter 3: Synthesis of bio-based epoxy thermosets derived from divanillin

Keywords: thermoset, 3D-network, bio-based polyglycidylethers, thermomechanical properties, glass transition temperature, reactive diluent

Mots-clés: thermodurcissables, réseaux epoxydés, polyglycidylether bio-sourcés, propriétés thermomécaniques, température de transition vitreuse, diluent réactif

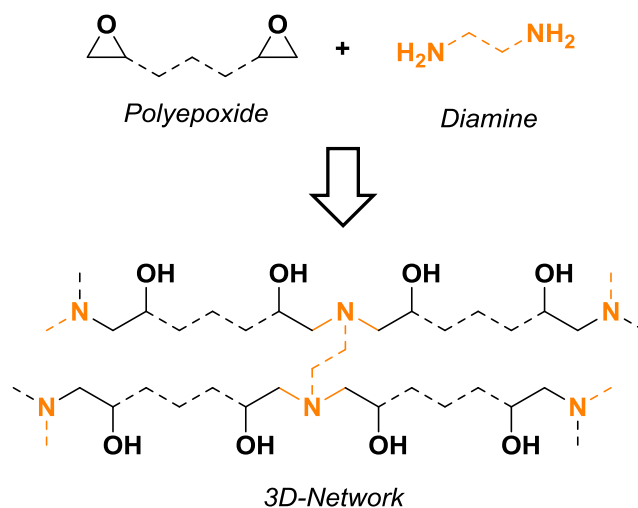
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I. Introduction

In this chapter, the synthesis of epoxy thermosets from bio-based epoxy precursors will be discussed. The thermomechanical properties of networks based on polyglycidylethers of divanillyl alcohol were investigated and compared with DGEBA reference. These structures, described in the previous chapter, have been selected for their availability, processability and polyfunctionality.

Polyepoxide networks are obtained by reacting together epoxy-based monomers with a curing agent, the whole average functionality being higher than 2. The curing agent or hardener plays a predominant role in the properties of the material, as it is literally part of the final structure (Scheme 46). Among the possible hardeners, it was decided to mainly work with diamine derivatives. Indeed, diamines are the most widely used hardeners. From coating applications with aliphatic diamine providing flexibility and rapid cure to high performance application with aromatic diamine providing chemical and thermal resistance, this versatility enables their use in various applications. In this study, isophorone diamine (IPDA) and 4,4'-diaminodiphenylsulfone (DDS), have been selected in the course of epoxy thermosets synthesis. IPDA is a liquid cyclo-aliphatic diamine widely used in the literature for its easy processability, whereas DDS is a solid aromatic diamine extensively used in aeronautic industry for enhancing the average properties. The thermomechanical properties of epoxy networks cured with these diamines will be further discuss in the following sections.

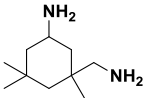


Scheme 46: Curing of polyepoxide with diamine curing agent

II. Synthesis and characterizations of epoxy networks cured with IPDA

The control of the stoichiometry ratio in between epoxy and N-H functions is a key parameter to obtain thermosets with controlled properties. As described in the previous chapter, the stoichiometric ratio $r=1$ leads to thermosets with the highest thermomechanical properties.¹ IPDA is a cyclo-aliphatic liquid diamine of low viscosity. Principal properties and structure of IPDA are depicted in Table 12.

Table 12: Structure and properties of IPDA

Isophorone diamine	
Molar mass (g.mol ⁻¹)	170
Density (g.cm ⁻³)	0,924
Viscosity at 25°C (Pa.s)	0,02
Boiling point (°C)	247
Appearance	Colorless liquid

The polyglycidylethers of divanillyl alcohol have been cured with IPDA and compared with DGEBA/IPDA system. Their thermal and thermomechanical properties were investigated by DSC, TGA and DMA in order to determine some properties, such as the curing onset, the glass transition and the degradation temperatures. Tensile tests were also performed on the different networks to determine Young's modulus and elongation at break of the networks.

II.1 Synthesis and characterization of epoxy networks by DSC

The reactions between polyglycidylethers of divanillyl alcohol (DiGEDVA, TriGEDVA, TetraGEDVA) and IPDA were performed in DSC capsules and compared with DGEBA system. As mentioned in the previous chapter, DiGEDVA, TriGEDVA and TetraGEDVA exhibited very different viscosities. As DiGEDVA is a highly viscous material, some difficulty has been encountered to obtain homogeneous mixture when blended with IPDA. In contrast, TetraGEDVA is a low viscosity liquid, which make easier the mixture with IPDA.

The glass transition temperatures of DGEBA/IPDA and TriGEDVA/IPDA thermosets at different epoxy/N-H ratios were determined. As expected, the highest Tg was obtained for the stoichiometric ratio $r = 1$ (Figure 56a).

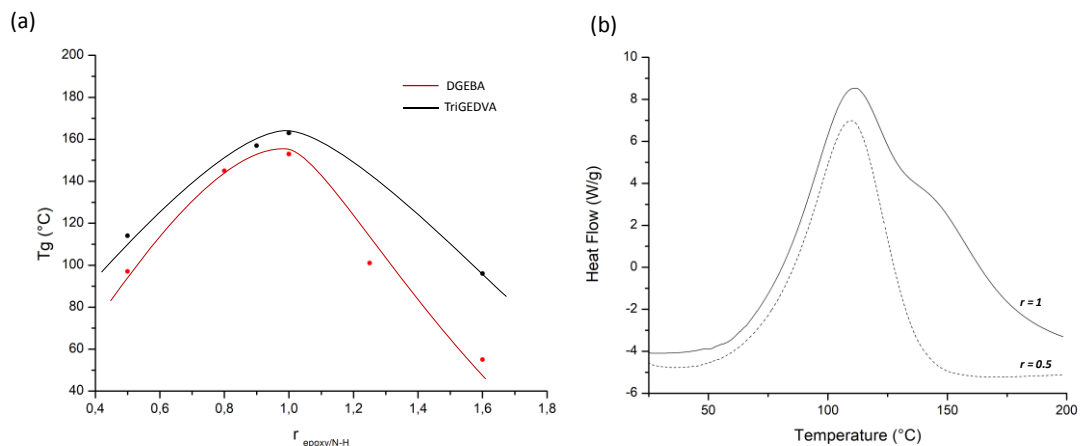


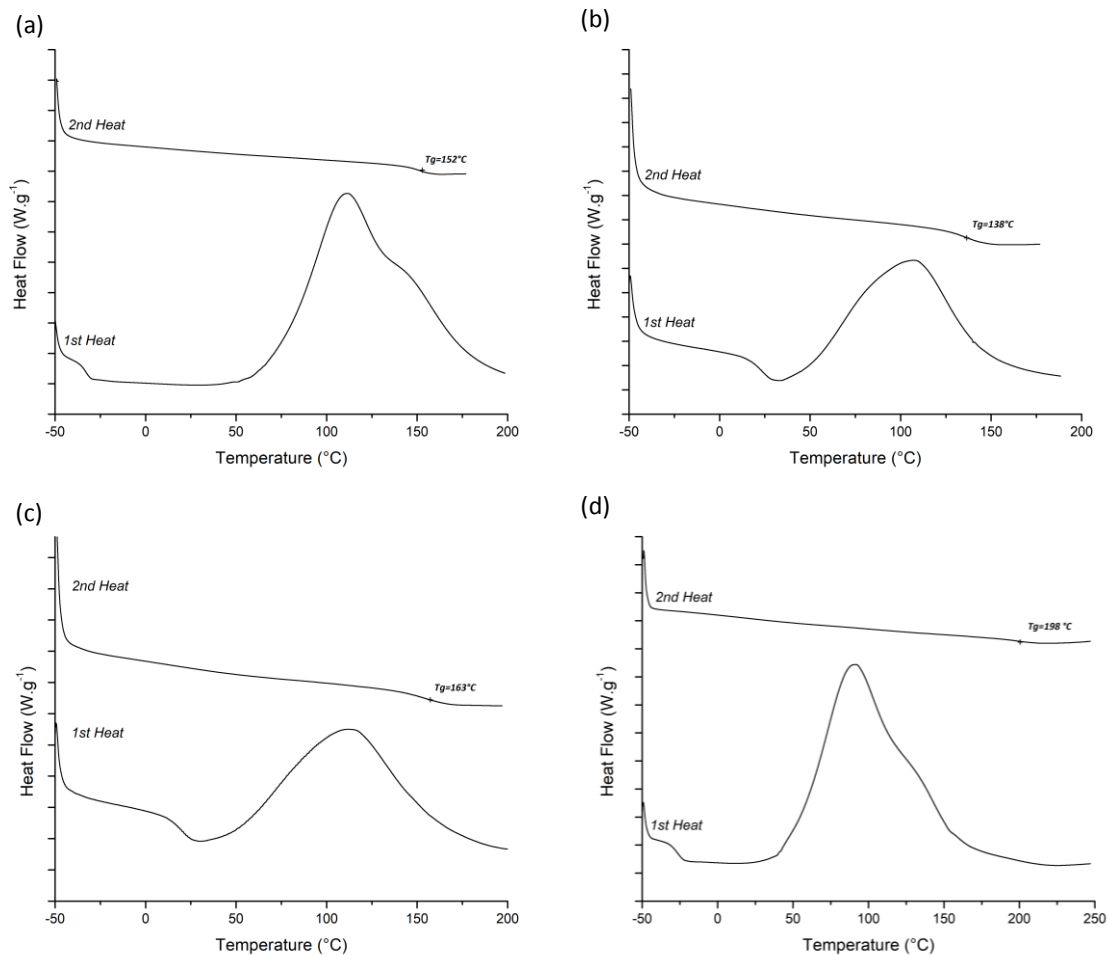
Figure 56: (a) Glass transition temperature as a function of the epoxy/N-H ratio for DGEBA and TriGEDVA cured with IPDA, (b) DSC thermograms of DGEBA/IPDA for different ratio r

In addition, it is worth noting that for $r = 1$, the DSC thermograms exhibited two exothermic peaks, whereas for $r = 0.5$ the second exothermic peak disappeared (Figure 56b). This feature could be explained by the difference of reactivity between the primary amine of IPDA and secondary amino moieties formed upon the curing. Indeed, for $r < 1$ amine function are in excess and primary amine will first react with oxirane until no more epoxy moieties will be available. Thus, only the reaction of primary amine will occur. In the other case, amine are in default and primary amine will first react followed by secondary amines until amine hydrogens are exhausted. This hypothesis is in agreement with observations described in the literature.¹ The stoichiometric ratio $r = 1$ will be used for all the following formulations in this chapter.

Other parameters of the curing reactions with respect to the epoxy precursor are summarized in Table 13 and Figure 57. All the bio-based thermosets show an onset temperature (beginning of curing reaction) lower than the DGEBA-based system, in agreement with a higher reactivity of these epoxy precursors towards amino group at RT. In terms of energy released during the curing, TetraGEDVA exhibited enthalpy of reaction similar to the DGEBA reference. In contrast, DiGEDVA exhibited a much lower total heat reaction. This feature can be explained by the fact that reaction with IPDA may have already started during the mixing process before the DSC analysis. The so-formed epoxy networks exhibited T_g ranging from 138 to 198 °C. The glass transition temperature of the networks issued from DiGEDVA could be underestimated. Indeed, the high viscosity of the DiGEDVA led to an inhomogeneous mixture when mixed with IPDA and the ratio epoxy/amine may have been distorted.

Table 13: Thermal properties of epoxy thermosets cured with IPDA

Epoxy prepolymer/IPDA	T _{Onset} (°C)	T _{Exotherm} (°C)	ΔH (J.g ⁻¹)	ΔH (kJ.mol ⁻¹)	E _a (kJ.mol ⁻¹)	T _g (°C)
DGEBA	73	111	430	91	42	152
DiGEDVA	47	107	180	45	<i>nd</i>	138
TriGEDVA	40	84	324	65	<i>nd</i>	163
TetraGEDVA	50	92	426	75	40	198

Figure 57: DSC thermograms of (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA cured with IPDA for $r = 1$

Based on Kissinger's theory,² the activation energy (E_a) of the curing reaction has been calculated from the peak temperatures at different heating rates using Equation 6:

Equation 6

$$\frac{d\left(\frac{\ln\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{E_a}{R}$$

where R is the gas constant ($8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$), β is the heating rate in K.min^{-1} and T_p is the exothermic peak temperature in K.

The activation energy can be determined by the slope of the linear relationship between $\ln(\beta/Tp^2)$ and $1/Tp$ at different heating rates of 10, 15, 20 and 25 K.min⁻¹ (Figure 58). Results are summarised in the Table 13. Unfortunately, the energy of activation of DiGEDVA and TriGEDVA were not determined because the reaction with IPDA may have already started during the mixing process and thus impaired the calculation. In contrast, DGEBA and TetraGEDVA exhibited a similar energy of activation of 42 and 40 kJ.mol⁻¹, respectively. These values are slightly lower than the ones found in the literature for DGEBA/IPDA systems. Generally, curing of epoxy resins with amines proceeds with activation energy between 50 and 58 kJ/mol.³

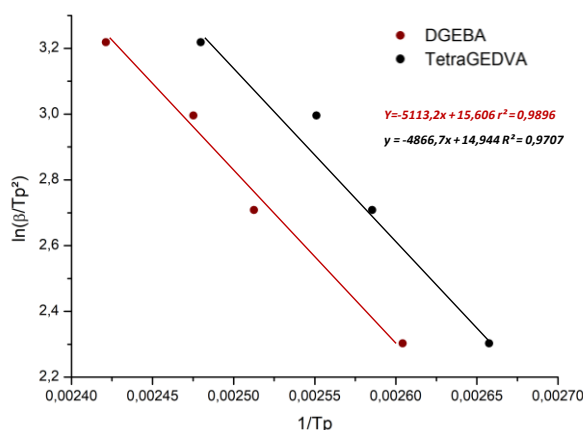


Figure 58: Linear plot based on Kissinger's equation for DGEBA and TetraGEDVA cured with IPDA

The curing kinetics of DGEBA and TetraGEDVA with IPDA was investigated by DSC. The percentage of curing was calculated from the ratio of the residual enthalpy of reaction with its initial value at t_0 . As displayed on Figure 57, systems cured with IPDA revealed two exothermic peaks, a first one at 100 °C and a second at 140 °C, corresponding to the difference of reactivity between the primary and secondary amino moieties of IPDA. Following this feature, curing was performed for 1h at 100 °C followed by a post-curing at 140 °C for again 1h. Overall, DGEBA and TetraGEDVA monomers displayed the same kinetics of curing. After one hour at 100 °C, 95% of the exothermic peak has disappeared and after one hour of post-curing at 140 °C the completion of the reaction was achieved (Figure 59).

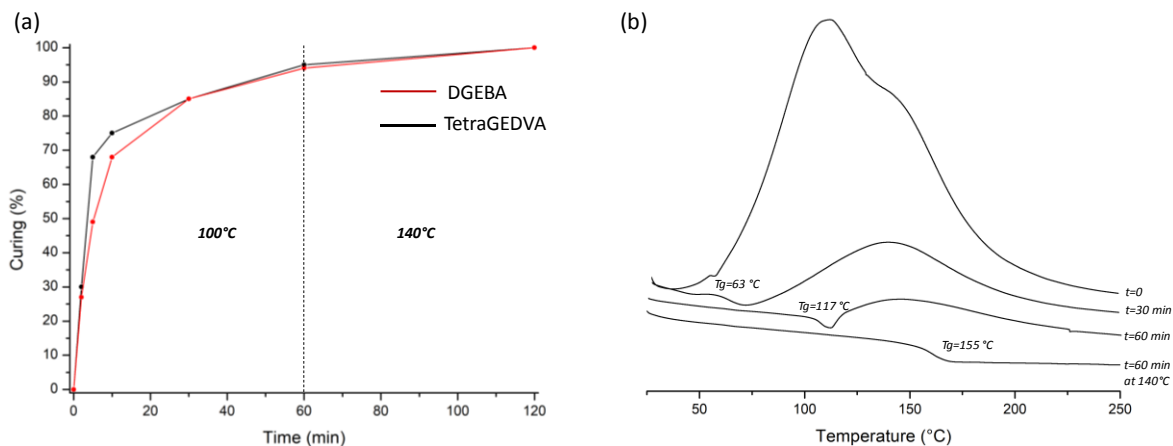


Figure 59: (a) Curing progress of DGEBA and TetraGEDVA with IPDA, (b) DSC thermograms of DGEBA/IPDA during curing for $r = 1$

Swelling tests in THF were also performed and results obtained for the various cured epoxy polymers are given in Table 15. The swelling percentage is calculated as the following equation:⁴

Equation 7

$$\text{Swelling (\%)} = \frac{(w_{sw} - w_D)}{w_D} * 100$$

The soluble part of networks is calculated as the following equation:

Equation 8

$$\text{Soluble part (\%)} = \left(1 - \frac{w_D}{w_0}\right) * 100$$

The swelling percentages of bio-based resins range from 0,3 to 0,4 % and 2 % for DGEBA-based resin. Swelling percentage is an indication of the degree of cross-linking. High cross-linked networks display low distance between nodes and then low solvent absorption. The soluble part of the various resins is null. These values indicate a fully cured network and the absence of residual products, which can potentially be released.

Table 14: Swelling properties of epoxy resins cured with IPDA

Epoxy prepolymer /IPDA	Swelling in THF (%)	Soluble fraction (%)
DGEBA	2,0	0
DiGEDVA	0,4	0,4
TriGEDVA	0,3	0,3
TetraGEDVA	0,3	0,3

II.2 Characterization of epoxy thermosets by DMA and mechanical analysis

The thermomechanical features of the epoxy networks were determined by dynamic mechanical analysis (DMA) using three-point bending geometry. Data are gathered in Table 15.

From DMA, the maximum of tan delta called alpha transition (T_α) corresponding to the transition from a glassy to a rubbery state could be determined and the density of cross-linking (ν) could be calculated from the following equation according to rubber-like elasticity theory:⁵

Equation 9

$$\nu = \frac{E'(T_{\alpha+30})}{\phi \cdot R \cdot T_{\alpha+30}}$$

with T_α the maximum of tan delta, E' the storage modulus of the network at $T_\alpha + 30$ K, ϕ the front factor approximately equal to 1 in Flory theory⁶ and $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ the gas constant.

Bio-based epoxy thermosets exhibited a T_α from 140 to 200 °C. These values are essentially influenced by the structure of the epoxy prepolymers. The cross-linking density of TetraGEDVA-based network is almost five times higher than DiGEDVA-based and two times higher than TriGEDVA-based network. These results are in accordance with the swelling test results previously described. Indeed, TriGEDVA-based and TetraGEDVA-based networks exhibited higher T_α certainly because of the additional epoxy groups increasing the network density. Epoxy networks with high cross-linking density have a reduced mobility, which lead to higher T_α . In comparison with DGEBA-based thermoset, TetraGEDVA, TriGEDVA and DiGEDVA showed higher or comparable T_g and T_α .

Table 15: Thermomechanical properties of epoxy networks formed after curing with IPDA for $r = 1$

Epoxy prepolymer/IPDA	T_α (°C)	E' (GPa)	$E'(T_{\alpha+30})$ (GPa)	ν ($10^3 \text{ mol}\cdot\text{m}^{-3}$)
DGEBA	155	1,7	0,035	9,2
DiGEDVA	140	1,9	0,035	9,5
TriGEDVA	177	2,4	0,10	25
TetraGEDVA	200	2,1	0,21	49

Figure 60 shows the profile of DMA curves obtained for epoxy networks formed after curing of the epoxy precursors, DGEBA, DiGEDVA, TriGEDVA and TetraGEDVA with IPDA.

It is worth noting that the intensity of the tan delta of DiGEDVA/IPDA system exhibits a value of almost 1 whereas TetraGEDVA/IPDA system shows a value below 0,2. This feature could be attributed to the higher cross-linked density of TetraGEDVA/IPDA networks. Indeed, tan delta is the ratio between loss and storage modulus, representing the way in which a material

absorbs and disperses energy. Following that, a low cross-linked material will have the ability to dissipate more energy by deformation and thus will exhibit a higher tan delta value than a more cross-linked and rigid network.

Moreover, DGEBA/IPDA and TetraGEDVA/IPDA systems exhibited a broad tan delta. This feature could be explained by the heterogeneity of the networks thus formed. A post curing treatment at higher temperature could be a way to promote mobility in the network and unify the curing.

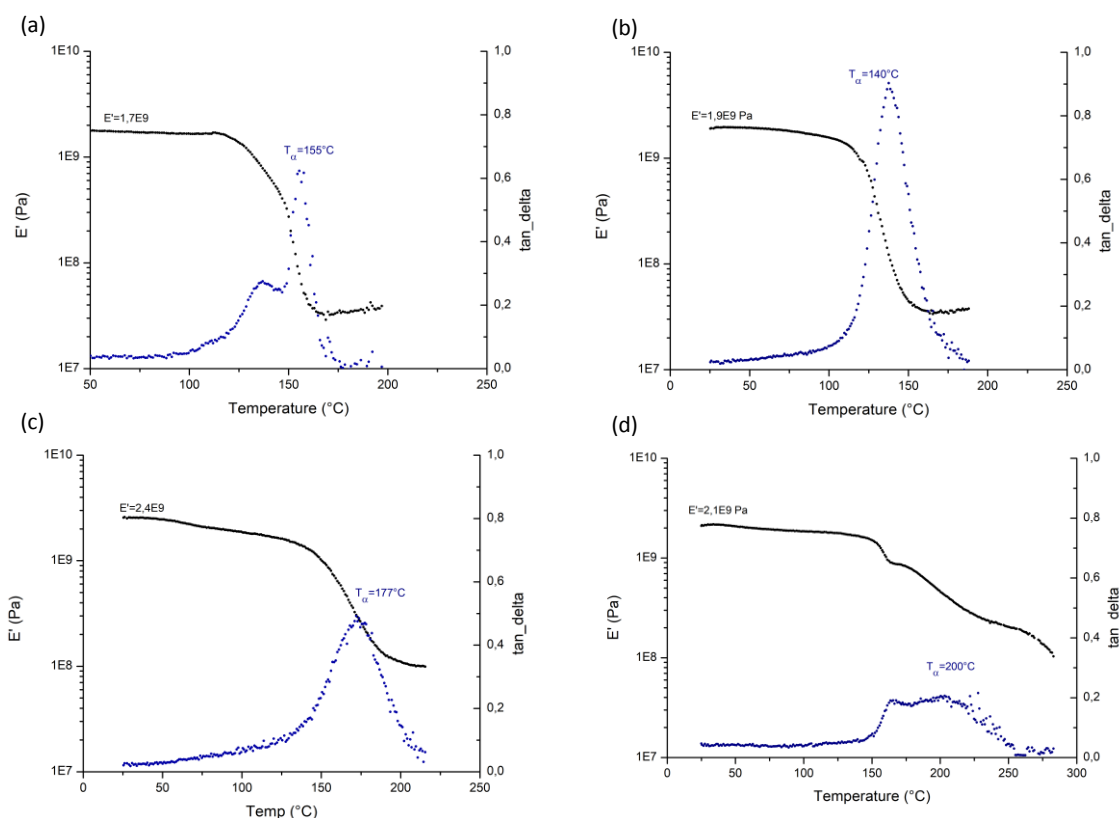
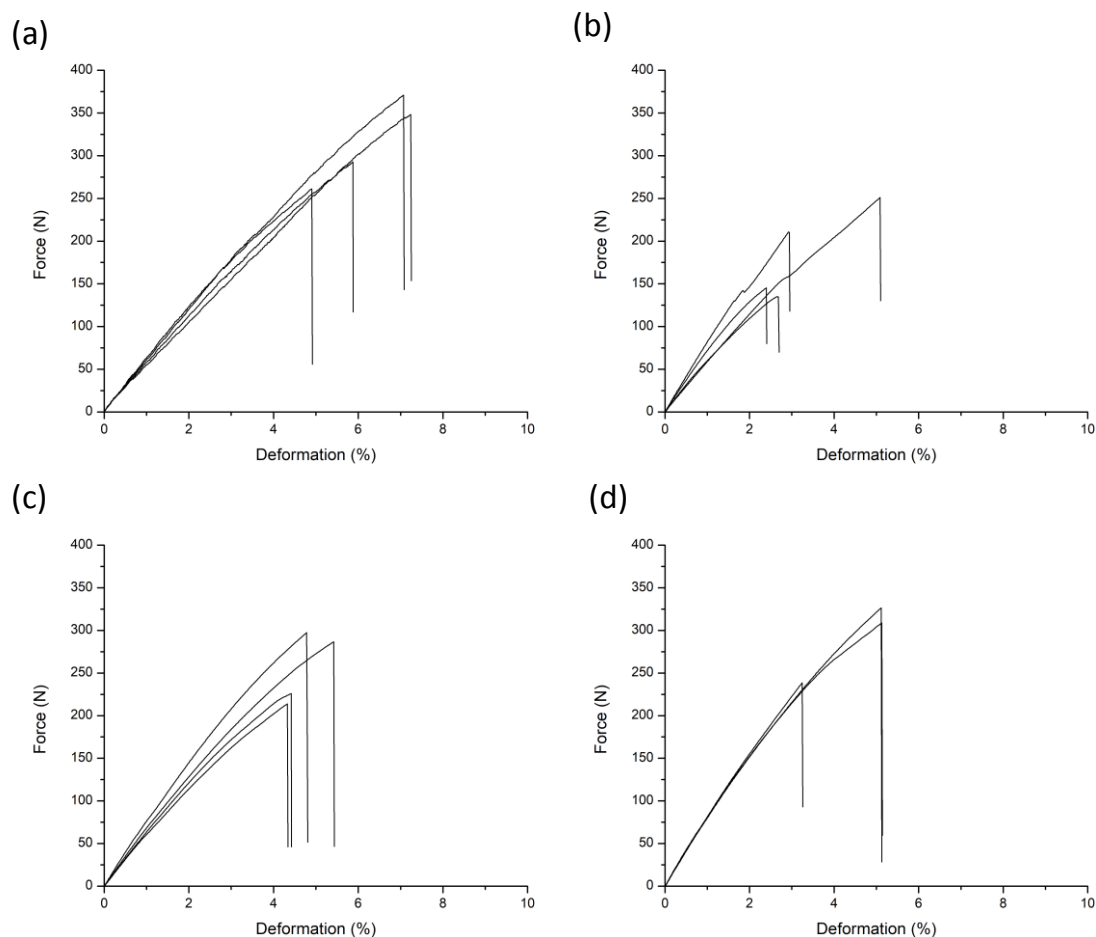


Figure 60: DMA traces of epoxy networks formed after curing with IPDA (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA

Tensile tests were also performed on DVA- and DGEBA-based thermosets. Results are summarised in Table 16 and Figure 61. DGEBA-based thermoset exhibits a Young's modulus of 1300 MPa and an elongation at break of 6%. In the other case, Young's modulus of DVA-based thermosets are ranging from 1400 to 1900 MPa and elongation at break from 4% to 5%. Once again, the increase of the Young's modulus could be related to the increasing cross-linked density of the bio-based thermosets. In addition, DGEBA-based thermoset shows a slightly higher elongation at break. This feature could be explained by the presence of the methylene bridge between the two aromatic rings of the DGEBA, giving a bit more flexibility to the networks in comparison with the direct C-C bonding of bio-based epoxy monomers.

Table 16: Mechanical properties of epoxy networks formed after curing with IPDA for $r = 1$

Epoxy prepolymer/IPDA	Young's modulus (MPa)	Elongation at break (%)
DGEBA	1350 ± 100	$6,3 \pm 1,1$
DiGEDVA	1450 ± 200	$3,3 \pm 1$
TriGEDVA	1550 ± 150	$4,7 \pm 0,5$
TetraGEDVA	1900 ± 20	$4,5 \pm 1$

**Figure 61: Tensile test traces of (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA cured with IPDA for $r = 1$**

II.3 Thermal stability of epoxy thermosets

The thermal degradation features of these networks were investigated by thermogravimetric analysis (TGA). From the two degradation temperatures weight loss $T_{d5\%}$ and $T_{d30\%}$, it is possible to calculate the statistic heat-resistant index (T_s) as follows:⁷

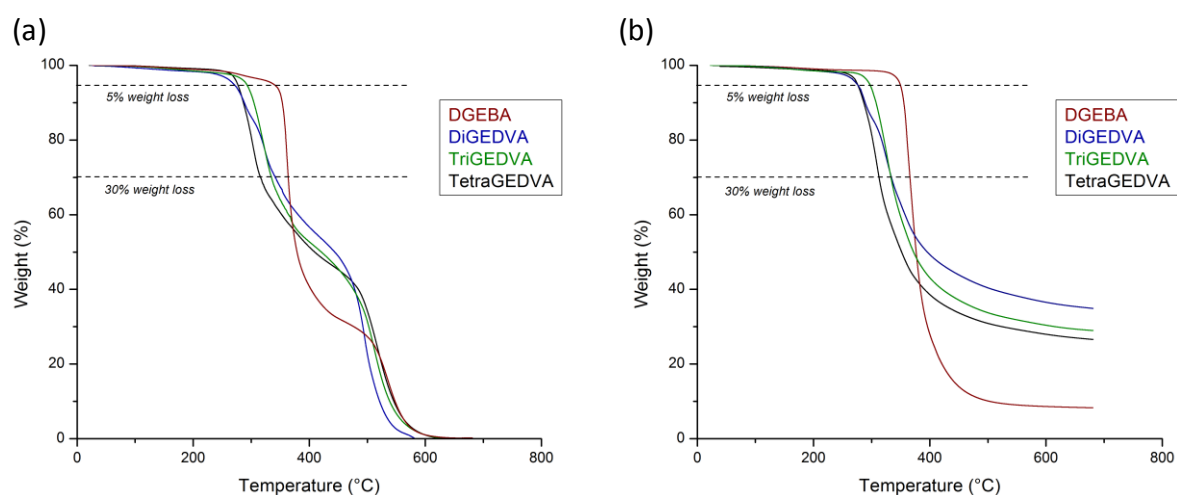
Equation 10

$$T_s = 0.49 \cdot (T_{d5\%} + 0.6 \cdot (T_{d30\%} - T_{d5\%}))$$

The statistic heat-resistant index (T_s) represents an indication of the thermal stability of an epoxy thermosets. The thermal decomposition behaviours under air of the DVA-based epoxy/IPDA and DGEBA-based epoxy/IPDA networks are given in Table 17 and Figure 62. First, the thermal degradation of bio-based networks under air starts around 275 °C with about 40% weight loss followed by a second weight loss around 60 % at 500 °C. The thermal degradation of DGEBA-based resins starts at around 330 °C with about 70 wt% loss followed by a second at 500 °C (30 wt% loss). The values of statistic heat-resistance index for the bio-based networks are 20 °C lower than the ones of DGEBA-based network. Some authors indicated that the faster heat degradation of DVA-based system may be caused by the degradation of methoxy groups on the aromatic rings.^{4,8}

Table 17: Thermal degradation of epoxy resins cured with IPDA under air and N₂

Epoxy prepolymer /IPDA	T _d 5% (°C)		T _d 30% (°C)		T _s		Char ₇₀₀ (%)	
	Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂
DGEBA	336	349	364	366	172	176	1,1	8
DiGEDVA	273	275	337	334	153	152	0,5	32
TriGEDVA	292	296	335	333	156	155	0,9	28
TetraGEDVA	275	276	316	313	147	146	1,1	24

Figure 62: TGA thermograms of epoxy prepolymers cured with IPDA under air (a) and N₂ (b)

The thermal degradation of epoxy network was also investigated under nitrogen (Table 17). The latter showed a single step of degradation process, which starts around 275 °C and 350 °C

for the DVA-based and DGEBA-based networks, respectively. The residual mass at 700 °C is ranging from 24 to 32 % for the bio-based epoxy prepolymers while DGEBA-based network has a residual mass at 700 °C of 8 %. Some authors reported that the char formation is related to the cross-linking density of networks.⁹ This feature is in accordance with results obtained with TetraGEDVA and TriGEDVA, which exhibit high density of network due to the increasing number of epoxy groups. However, DiGEDVA formulation exhibited the highest char content, whereas its network density is equivalent to DGEBA. This difference could be explained by the fact that the free benzyl alcohols on the DiGEDVA structure can react at high temperature and formed an even higher density network and thus a higher char yield. This hypothesis has been verified by DSC. Indeed, DSC thermograms of DiGEDVA monomer revealed the presence of an exothermic peak at 220°C during the first heat and a glass transition at 97 °C on the second heating ramp.

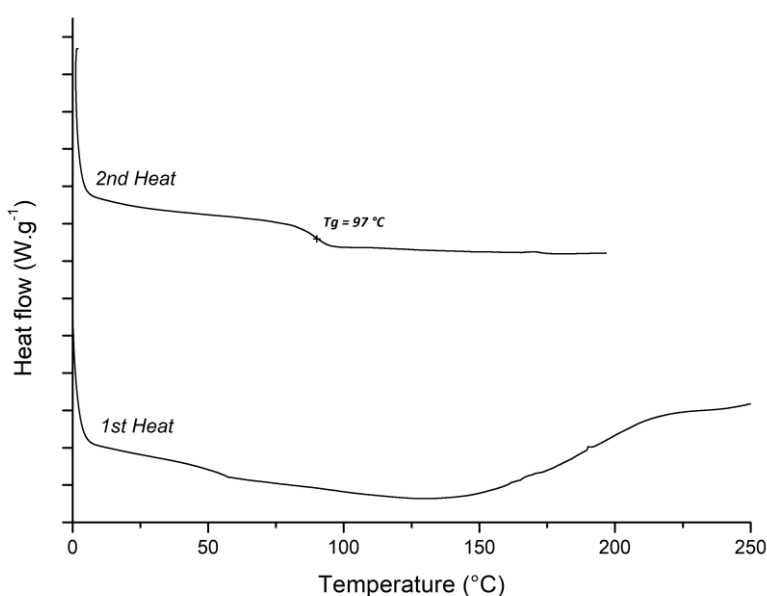


Figure 63: DSC thermograms of DiGEDVA monomer

As mentioned at the beginning of this chapter, viscosity of the bio-based epoxy monomers exhibit various values. The DiGEDVA mixture with IPDA were particularly difficult. Following this feature, several formulations consisted in different proportions of DiGEDVA, TriGEDVA and TetraGEDVA were realised and cured with IPDA. The same analysis of the thermomechanical properties of these different blends cured with IPDA were investigated using DSC, TGA, DMA and tensile tests. Main results are summarized in Table 18.

Table 18: Thermomechanical properties of epoxy networks cured with IPDA for $r = 1$

Epoxy prepolymer /IPDA	T_g^a (°C)	T_α^b (°C)	T_s^c (°C)	Young's modulus ^d (MPa)
DGEBA	152	155	176	1337 ± 102
Di 60%-Tri 20%-Tetra 20%	153	157	155	1489 ± 66
Di 20%-Tri 60%-Tetra 20%	166	171	155	1216 ± 75
Di 20%-Tri 20%-Tetra 60%	187	197	154	1545 ± 110

^adetermined by DSC, ^bdetermined by DMA, ^cdetermined by TGA under air, ^ddetermined by tensile test

As could be anticipated, formulations containing a large amount of TetraGEDVA or TriGEDVA led to the thermosets with the highest thermomechanical properties, in terms of glass transition temperature, alpha transition and Young's modulus (Figure 64). Therefore, the formulation of mixture of the different bio-based monomers can be an efficient way to tune the average properties of the epoxy thermosets

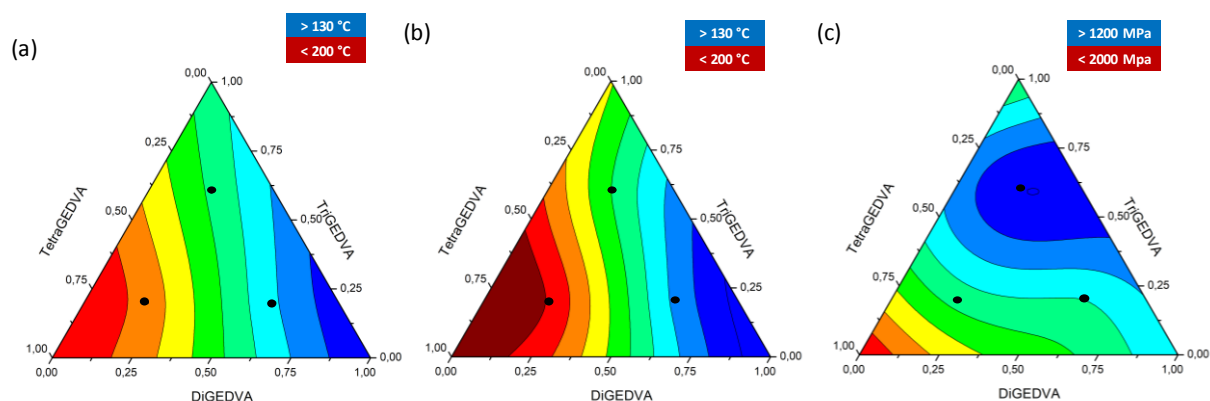


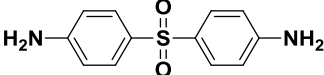
Figure 64: Ternary diagram of (a) T_g determined by DSC, (b) T_α determined by DMA and (c) Young's modulus determined by tensile test for different DVA-based monomer blends

In conclusion, these different results confirmed that bio-based structures derived from DVA are promising candidates to replace DGEBA precursor. Indeed, DVA-based networks displayed thermomechanical properties similar or even higher than the petroleum-based reference. However, principal limitation of these formulations was their very short pot-life due to the high reactivity of IPDA curing agent with bio-based epoxy precursors. Subsequently, another kind of amine hardener is required.

III. Thermomechanical properties of epoxy networks cured with DDS

4,4'-diaminodiphenylsulfone (DDS) is a well-known hardener used in aerospace industry. It is a very interesting curing agent because it brings additional aromatic structure to the network and thus enhances the mechanical properties of the final material. Moreover, due to its high melting point, DDS is a latent curing agent, which allows a longer pot-life than IPDA systems. The structure and main properties of DDS are given in Table 19.

Table 19: Structure and properties of DDS

4,4'-Diaminodiphenylsulfone	
Molar mass (g.mol ⁻¹)	248
Melting point (°C)	175
Appearance	Crystalline powder

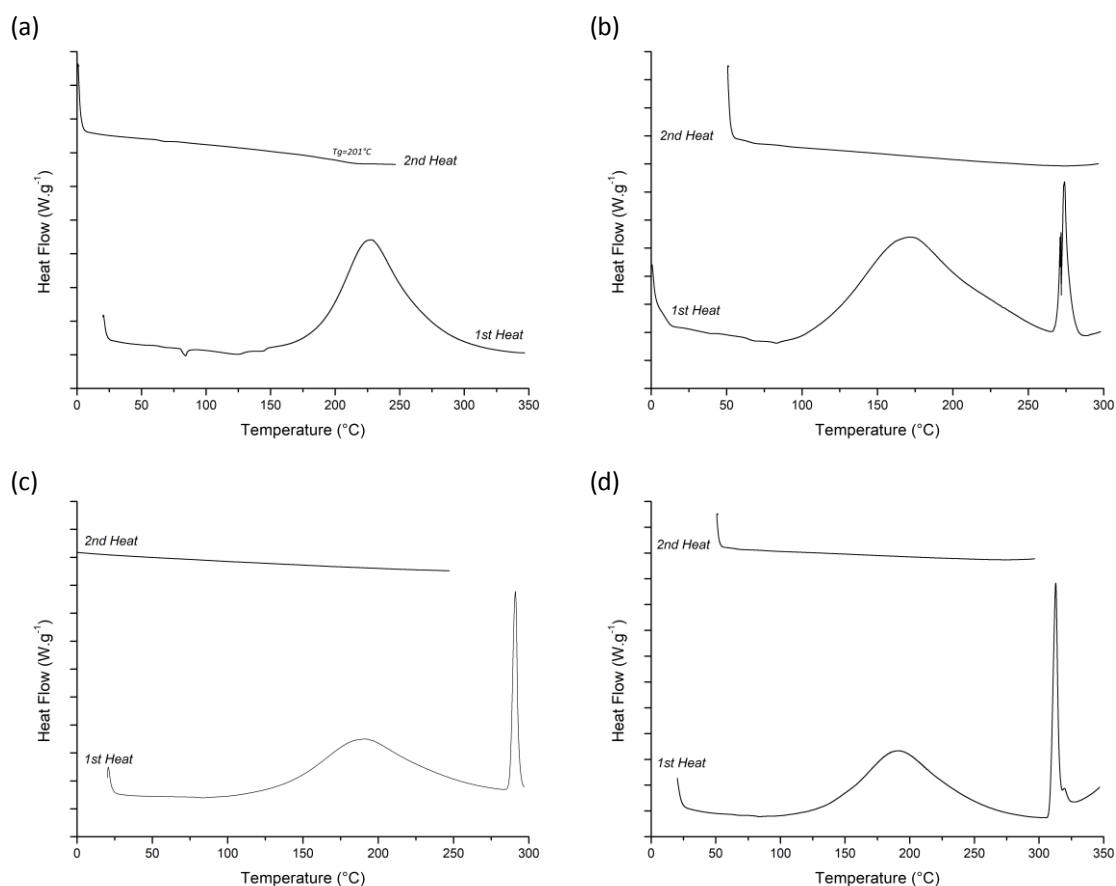
The polyglycidylethers of divanillyl alcohols have been cured with DDS and compared with DGEBA-based system. Their thermomechanical properties were investigated by DSC, TGA and DMA. Tensile tests were also performed on the different networks to collect information on the Young's modulus and elongation at break.

III.1 Characterization of epoxy thermosets by DSC

The curing reactions were performed in DSC capsules in order to determine the reactivity of the different systems (Table 20 and Figure 65). As can be seen on Figure 8, onset temperatures in the case of networks formed by curing with DDS are much higher than the ones cured with IPDA, confirming the latent property of DDS. In the same way, the curing behaviour of DVA-based thermosets with DDS show an onset temperature lower than DGEBA-based thermoset, in accord with a higher reactivity of bio-based epoxy monomers towards amino group at lower temperature. The enthalpies of reaction per mole of bio-based epoxy precursor are in the same range of DGEBA reference, which demonstrates a same reactivity of epoxy groups. However, DSC thermograms did not show clear glass transition temperature (T_g). This feature could be explained by the higher rigidity of the segments between the nodes, induced by the aromatic structure of the DDS. In addition, DSC thermograms of DVA-based thermosets exhibited a second exothermic peak. This feature will be described later in this chapter.

Table 20: Thermal properties of epoxy networks formed by curing with DDS for $r = 1$

Epoxy prepolymer/DDS	T _{Onset} (°C)	T _{Exotherm} (°C)	ΔH (J.g ⁻¹)	ΔH (kJ.mol ⁻¹)	E _a (kJ.mol ⁻¹)	T _g (°C)
DGEBA	184	226	355	83	67	201
DiGEDVA	110	170	301	82	69	*
TriGEDVA	136	192	416	92	69	*
TetraGEDVA	165	208	459	89	69	*

*T_g not observed**Figure 65: DSC thermograms of (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA cured with DDS for $r = 1$**

As described in the previous section, the activation energy (E_a) of the curing reaction has been calculated from the DVA- and DGEBA-based networks. Results are summarised in Table 20. DGEBA and polyglycidylethers of DVA exhibited a similar energy of activation, 67 and 69 kJ.mol⁻¹, respectively, and no difference was noticed between the bio-based epoxy monomers. Nevertheless, this value is in accordance with those found in the literature.¹⁰ In comparison with energy of activation determined for IPDA systems, these values are much higher. These results can be correlated with the latent property of DDS systems, which required more energy to initiate the curing reaction.

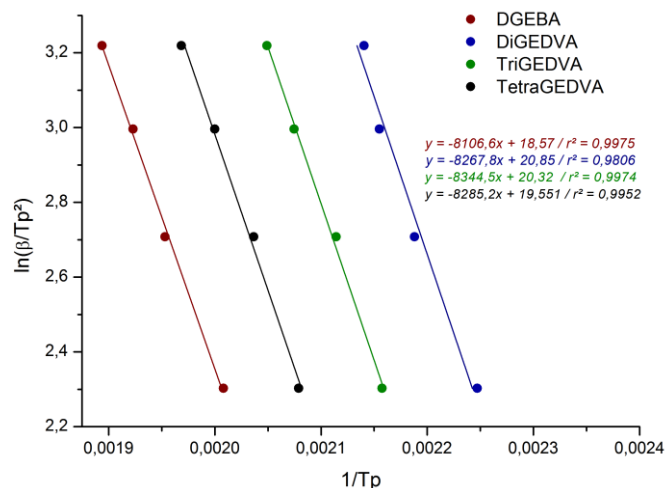


Figure 66: Linear plot based on Kissinger's equation for epoxy precursors cured with DDS

Kinetic study of the curing with DDS at 180 °C of epoxy precursors was monitored by DSC (Figure 67). This temperature has been selected as it corresponds to the onset temperature of DGEBA/DDS system in agreement of the DDS melting temperature. The curing percentage has been calculated from the ratio of the residual enthalpy of reaction with its initial value at t_0 . Figure 68 exhibits the gradual decrease of the exothermic peak of DGEBA/DDS as a function of the curing time at 180 °C. In the meantime, it is also possible to follow the glass transition temperature increase with the curing time. As expected, DVA-based epoxy precursors are cured faster than DGEBA. After 90 min all networks are fully cured, except of TetraGEDVA/DDS, which exhibited residual exotherm. This statement could be explained by the very low mobility of the network, induced by a very high cross-linking. Post-cured at a higher temperature may be necessary to promote mobility to the system and thus fully cure the system.

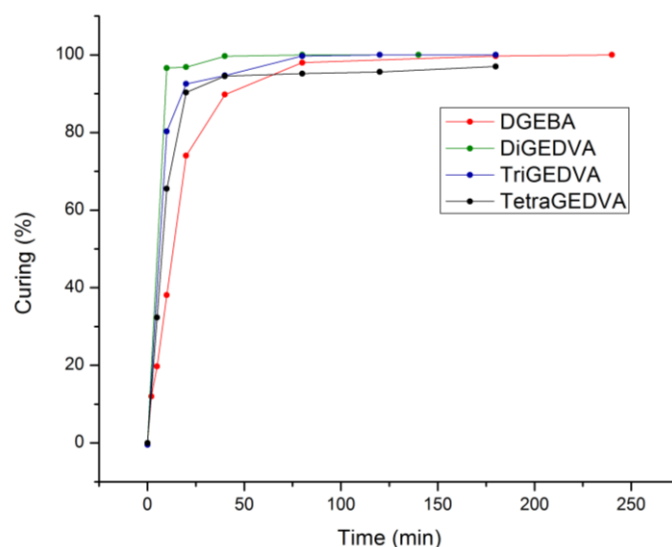


Figure 67: Curing progress of DVA-based epoxy precursors and DGEBA in the presence of DDS at 180°C

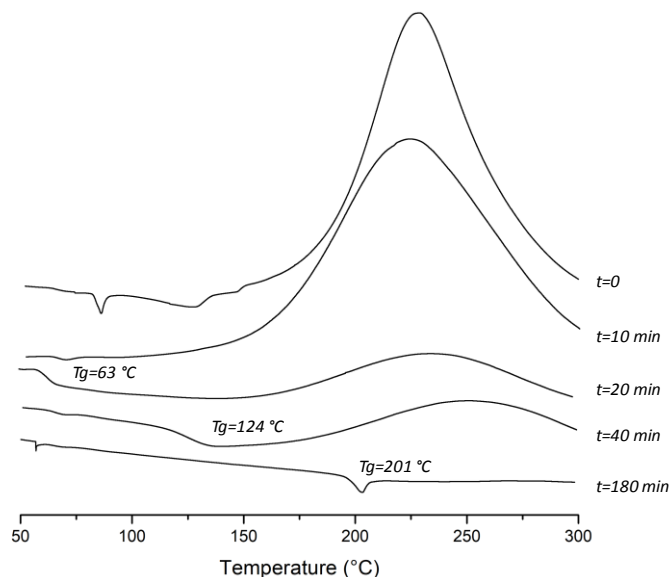


Figure 68: DSC thermograms of DGEBA/DDS during curing at 180 °C

III.2 Characterization of epoxy thermosets by FTIR spectroscopy

The synthesis of epoxy thermosets have also been characterized by FTIR spectroscopy. The following figure displays the FTIR spectra of an uncured and cured TetraGEDVA/DDS system for stoichiometric ratio (Figure 69). The uncured resin exhibits characteristic oxirane ring signals, the C=C and CH stretching of aromatic groups at 915, 1510 and 2920 cm^{-1} , respectively. Primary amine bands of DDS are visible at 1610, 3240, 337 and 3471 cm^{-1} . After 2h at 180°C, the TetraGEDVA/DDS FTIR spectrum exhibits the appearance of new signal at 3500 cm^{-1} , corresponding to hydroxyl groups formed upon the polyaddition of amines with epoxy groups. The disappearance of primary amine bands, previously cited, and the disappearance of epoxy signals at 915 cm^{-1} confirmed the formation of a cross-linked network.

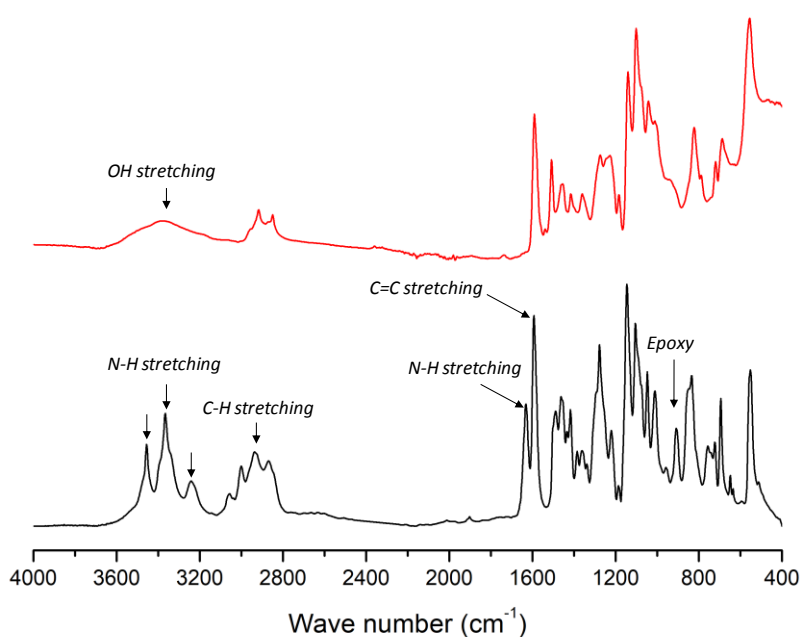


Figure 69: FTIR spectra of uncured (black) and cured (red) TetraGEDVA/DDS system

In addition, the curing reaction of TetraGEDVA/DDS system has also been followed by FTIR spectroscopy. The mixture was deposited between two NaCl crystals and placed in oven at 180 °C for different periods. Figure 70 shows the gradual disappearance of the epoxy signal at 915 cm⁻¹. This diminution of the characteristic signal of epoxy is correlated to the progressive consumption of oxirane moieties involved in the formation of the cross-linked network. The kinetics of the curing determined by FTIR seems to be slightly quicker than the kinetics determined by DSC. Indeed, after 60 minutes, the signal at 915 cm⁻¹ is almost vanished. This feature could be explained by the very thin layer of sample deposited between the NaCl crystals, which can induce a faster curing.

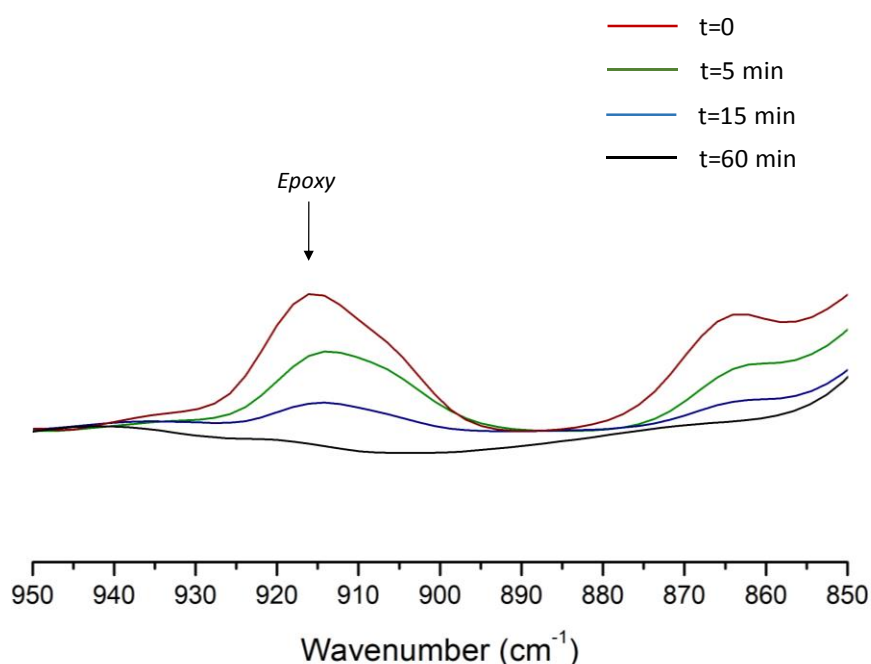


Figure 70: Zoom between 950 and 850 cm⁻¹ of FTIR spectra of TetraGEDVA/DDS systems cured at 180 °C for $r = 1$ at various time

III.3 Characterization of epoxy thermosets by DMA and mechanical analysis

Dynamical mechanical analysis (DMA) using three-point bending geometry have been performed on the different thermosets. Data are gathered in Table 21 and Figure 71. Regarding the kinetics of curing previously described, the curing procedure of the sample was 30 min at 110°C, in order to liquefy the mixture, followed by 2h at 180°C.

DGEBA and DiGEDVA exhibited clear alpha transition at 209 and 206 °C, respectively, whereas TriGEDVA system displayed a wide alpha transition, which can be explained by the presence of the heterogeneity of the so-formed networks. In addition, TetraGEDVA did not show clear T_{α} . This observation could be related to the fact that degradation of the samples

occurred before or in the same range of the alpha transition temperature. In addition, DMA curves exhibit an increase of the storage modulus instead of the rubbery plateau expected after the alpha transition. This feature will be discussed in the next section.

Table 21: Mechanical and thermomechanical features of epoxy thermosets cured with DDS

Epoxy prepolymer/DDS	T_{α} (°C)	E' (GPa)	$E'(T_{\alpha}+30)$ (GPa)	ν (10^3mol.m^{-3})
DGEBA	209	1,6	0,051	11,7
DiGEDVA	206	1,5	-	-
TriGEDVA	257	1,4	-	-
TetraGEDVA	312	1,9	-	-

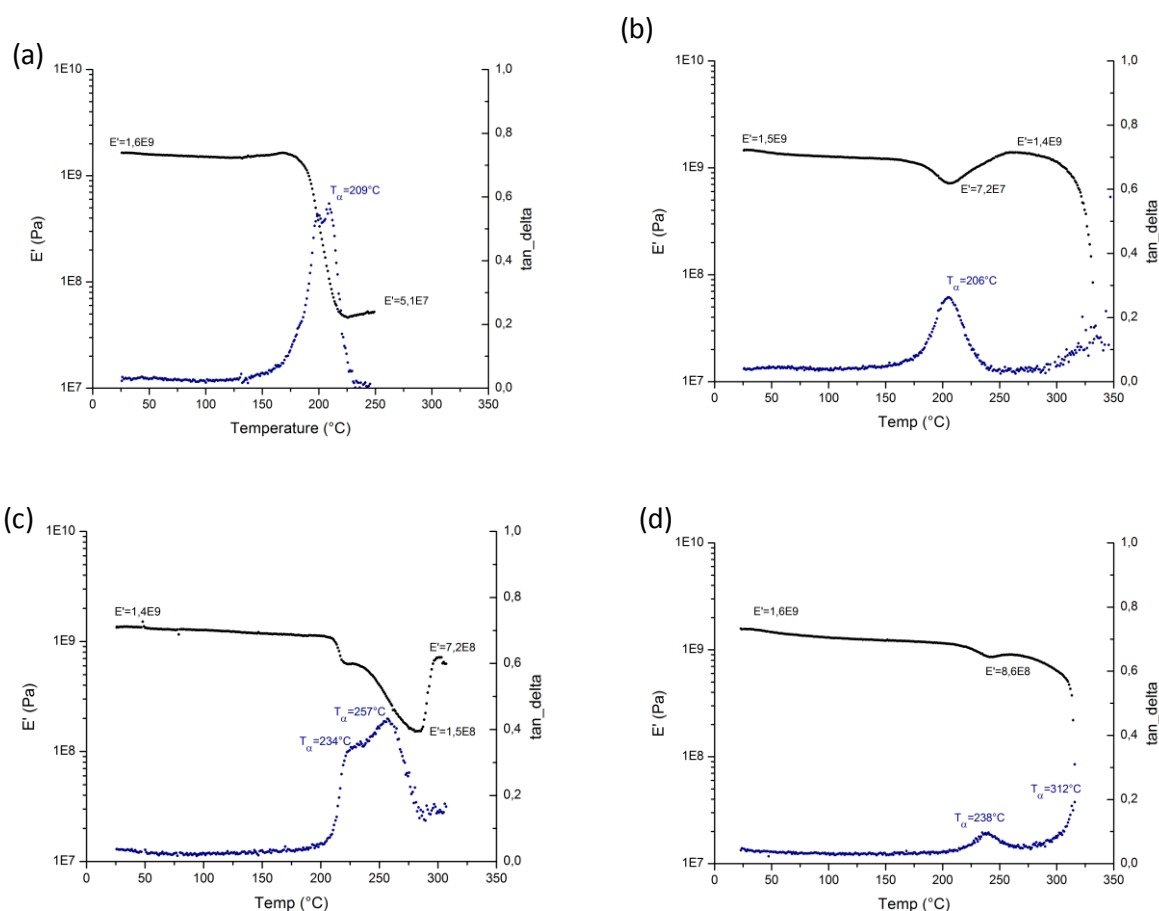


Figure 71: DMA of epoxy networks respectively obtained from (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA cured with DDS for $r = 1$

Consequently, the calculation of the network density was not possible regarding the profile of DMA curves. However, swelling tests of the so-formed networks were realised and are presented in Table 22. The swelling percentage ranged from 0,5 to 1,7 % and 2,4 % for DVA- and DGEBA-based thermosets, respectively. These results attested of the high cross-link density of all the networks. In addition, the soluble fraction in THF of the various networks

were roughly null, in accord with a fully cross-linked material and the absence of residual products.

Table 22: Swelling properties in THF of epoxy thermosets cured with DDS

Epoxy prepolymer/DDS	Swelling (%)	Soluble part (%)
DGEBA	2,4	0
DiGEDVA	1,7	1
TriGEDVA	0,5	0,5
TetraGEDVA	0,5	0

Tensile tests were also performed on DVA- and DGEBA-based thermosets. Results are summarised in Table 23 and Figure 61. DGEBA-based thermoset exhibits a Young's modulus of 1400 MPa and an elongation at break of 5%. In the same way, Young's modulus of DVA-based thermosets are ranging from 1400 to 1900 MPa and elongation at break around 4%. Once again, the increase of the Young's modulus could be related to the increasing cross-linked density of the bio-based thermosets. In addition, thermosets cured with DDS exhibit a slightly lower elongation at break than IPDA systems. This feature could be explained by the structure of DDS, which promotes more rigidity to the networks inducing more brittle materials.

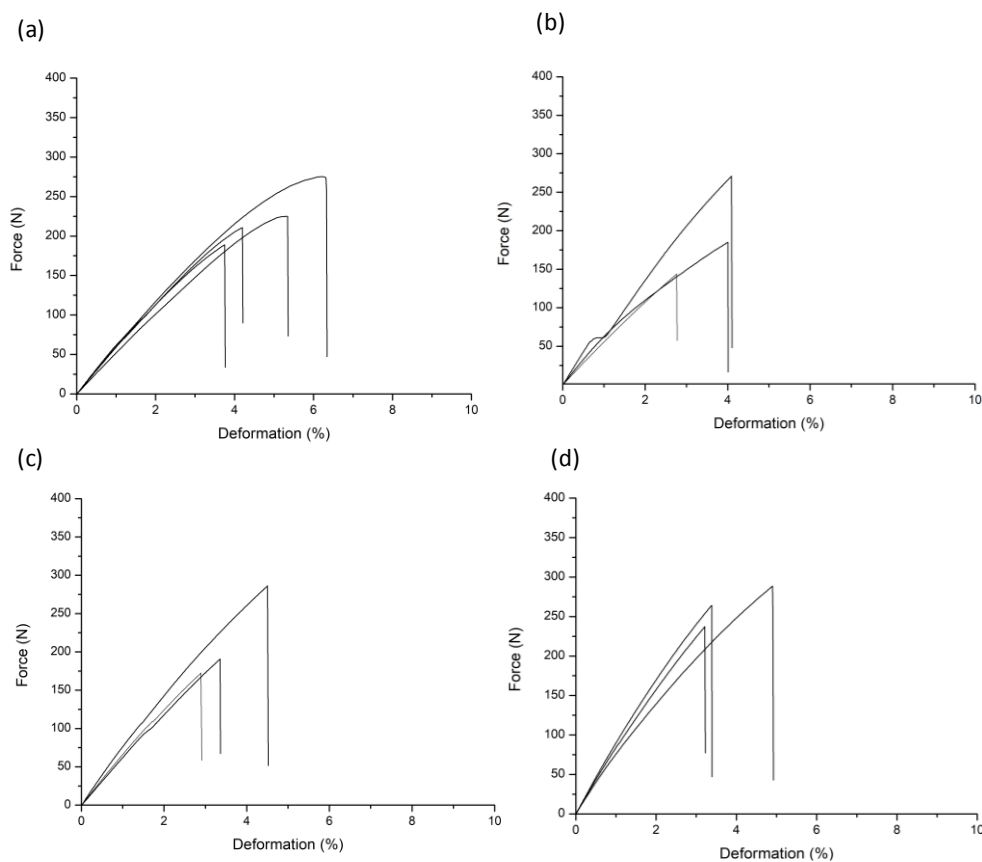


Figure 72: Tensile test traces of (a) DGEBA, (b) DiGEDVA, (c) TriGEDVA and (d) TetraGEDVA cured with DDS for $r = 1$

Table 23: Mechanical properties of epoxy networks formed after curing with DDS for $r = 1$

Epoxy prepolymer/DDS	Young's modulus (MPa)	Elongation at break (%)
DGEBA	1390 ± 110	5,2 ± 0,9
DiGEDVA	1475 ± 250	3,6 ± 0,7
TriGEDVA	1450 ± 200	3,6 ± 0,8
TetraGEDVA	1750 ± 150	4,2 ± 0,7

III.4 Thermal stability of epoxy thermosets

The thermal stability under air and nitrogen of DVA-based and DGEBA-based epoxy networks are shown in Table 24 and Figure 73.

Table 24: Thermal degradation of epoxy resins cured with DDS under Air and N₂

Epoxy prepolymer /DDS	T _{d5%} (°C)		T _{d30%} (°C)		T _s		Char ₆₀₀ (%)		Char ₉₀₀ (%)	
	Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂
DGEBA	381	380	407	403	194	193	3,7		16	
DiGEDVA	314	278	419	378	185	183	2,3		51	
TriGEDVA	319	307	409	399	183	178	5,9		49	
TetraGEDVA	326	326	406	400	180	181	11		48	

In comparison with the IPDA systems, the thermal behaviour of DDS-based networks are very similar with a shift of roughly 50 °C towards higher temperatures in agreement with a higher thermal stability. Indeed, a first thermal degradation of such epoxy networks under air starts around 320 °C with about 35 wt% loss and a second around 500 °C with a weight loss around 65 %. Thermal degradation of DGEBA-based resins starts around 380 °C with about 65 wt% loss and a second around 500 °C with a weight loss around 35 %. The values of statistic heat-resistance index for bio-based precursors are only 10 °C lower than DGEBA-based network, which induced a similar thermal stability. The thermal degradation of these networks was also studied under nitrogen. The latter showed a single step of degradation process, which starts around 300 °C for DVA-based epoxy prepolymers and at 380 °C for DGEBA-based resin. The residual mass at 900 °C is above 50% for DVA-based epoxy networks while DGEBA-based network has a residual mass at 900 °C of 16 %. Thanks to the additional aromatic structure brought by DDS, the char content increases by 20 % in comparison to IPDA systems. In addition, the C-C bond between the two aromatic rings of polyglycidylethers of DVA could also favour the increase of the char yield. High char residue value indicates good flame retardancy properties of the materials.¹¹ Consequently, flaming test have been realised on DVA-based samples to check this statement. In direct contact with flame, DGEBA-based thermoset

burned and the combustion spread rapidly to the rest of the sample. Contrarily, in the case of DVA-based thermosets, the combustion was rapidly stopped by the direct formation of a char layer on the materials (Figure 74).

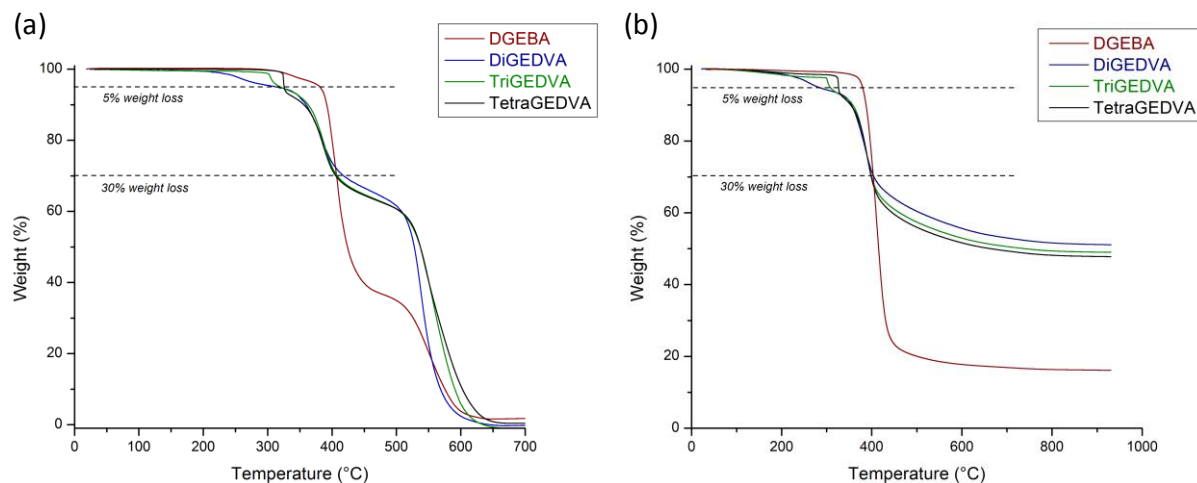


Figure 73: TGA thermograms of DGEBA and DVA-based prepolymers cured with DDS under (a) air and (b) N₂

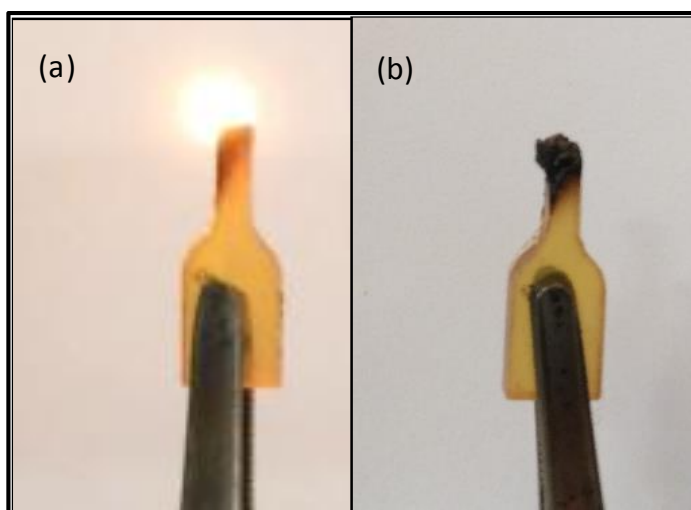


Figure 74: Flaming test of DVA-based epoxy thermoset (a) sample during combustion, (b) extinguished sample by the formation of black char layer

The char obtained was found compact and non-friable. In addition, elemental analysis of char residue has been performed and compared with TetraGEDVA/DDS system before degradation (Figure 75). This method enables the quantitative determination of carbon, hydrogen, nitrogen, oxygen and sulphur content. Results obtained from the analysis of DVA-based thermoset are very consistent with those obtained by calculation. In addition, this elemental analysis enables to confirm that the char obtained is mainly composed of carbon. Therefore, the flame-retardant

properties induced by the formation of a rich carbon layer during degradation of these materials could raise a particular interest for applications, such as matrices for thermal protection.

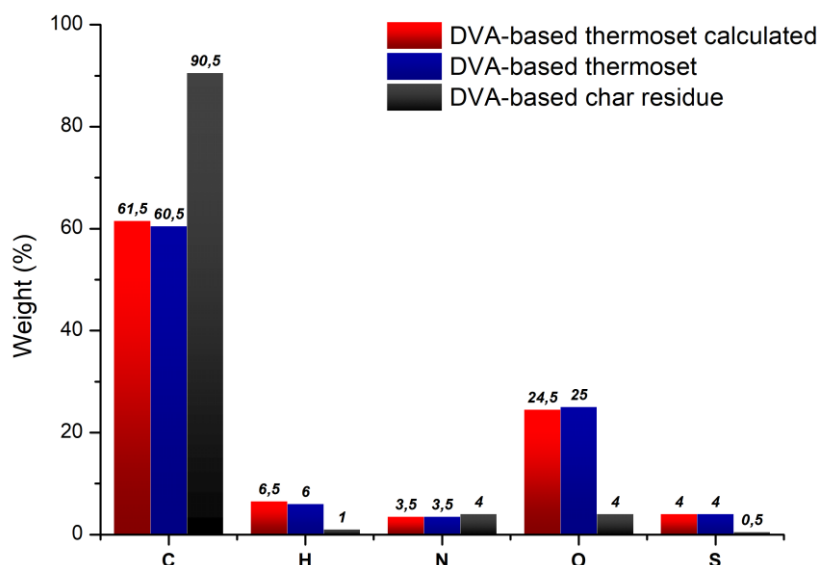


Figure 75: Elemental analysis of DVA-based thermoset before and after thermal degradation

III.5 Analysis of the second exothermic peak

As mentioned previously, DSC traces of DVA-based precursors cured with DDS displayed an unexpected and highly exothermic peak at 275, 291 and 313 °C with an increasing enthalpy of 30, 70 and 90 J.g⁻¹ for DiGEDVA, TriGEDVA and TetraGEDVA, respectively (Figure 76). This feature was not observed with DGEBA/DDS system. The first exothermic peak was attributed to the reaction of N-H functions with epoxy ones, but no clear explanation was found to explain the second peak. One hypothesis would be to attribute this exothermic peak to the homopolymerisation of unreacted epoxy moieties catalysed by the *in situ* tertiary amine formed during the curing. In fact, Levchik *et al.* observed a similar exothermic phenomenon at 307 °C when tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) was heated up without any curing agents or catalysts.¹² The authors attributed this peak to the homopolymerisation of TGDDM.

The energy of activation (E_a) corresponding to this exotherm was determined using the Kissinger's theory. The value obtained was equal to 82 kJ.mol⁻¹ and could well be attributed to a homopolymerization process, which required more energy to occur. Moreover, DiGEDVA and TriGEDVA DMA traces displayed an increase of the elastic modulus at roughly the same temperature of the occurrence of this exothermic peak observed on DSC trace. This observation could be related to the increasing of the network density induced by an additional reaction.

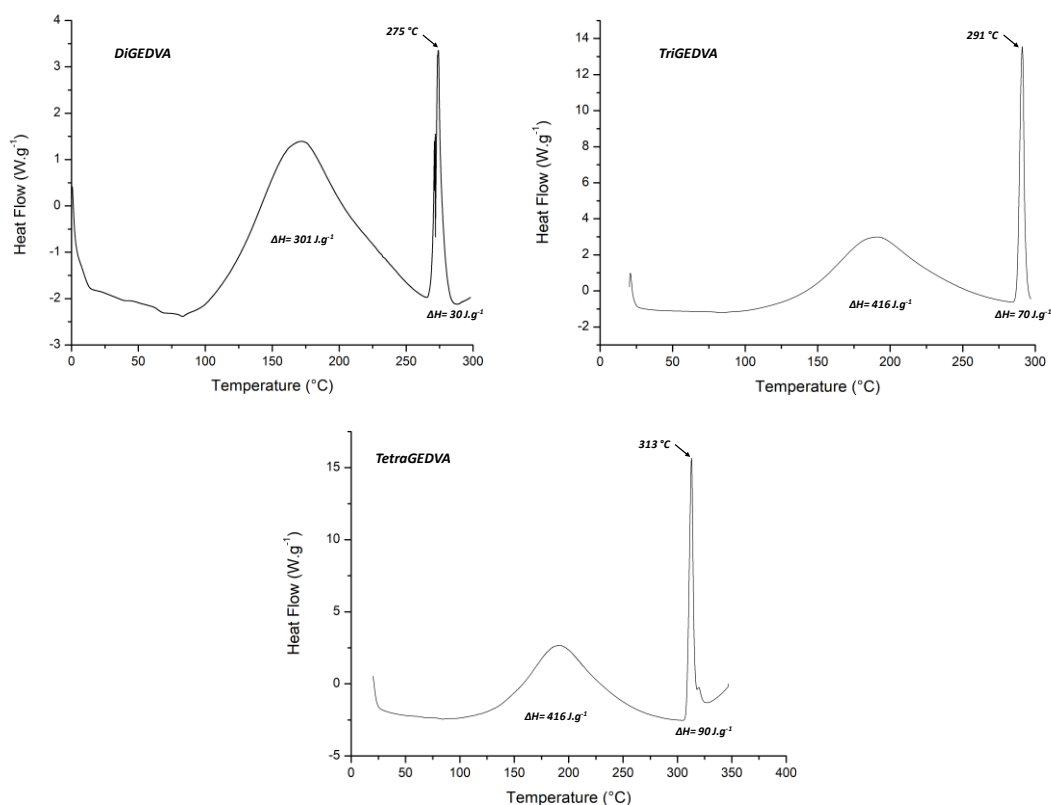


Figure 76: DSC thermograms at the first heat of DiGEDVA, TriGEDVA and TetraGEDVA cured with DDS

Another hypothesis would be to attribute this event to a degradation phenomenon. However, such degradation is usually characterized on DSC thermograms by a gradual increase of the heat flow and not by a sharp exothermic peak. Nevertheless, when the DSC and TGA thermograms are superimposed, the exothermic peak is located just before a 6 to 8 wt% weight loss degradation, which could be attributed to the degradation of methoxy group of DVA-based molecules (Figure 77).

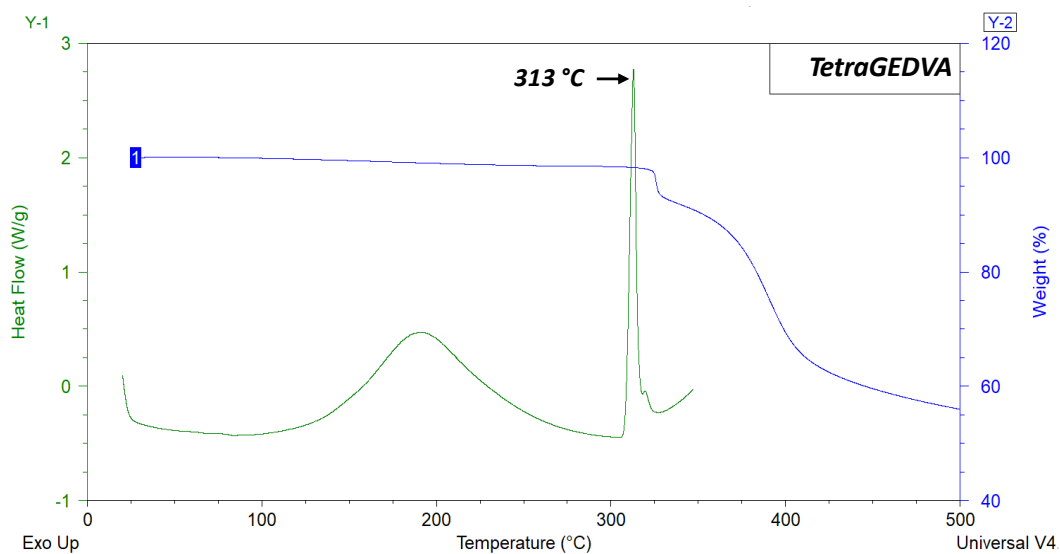


Figure 77: Superimposed TGA curves and DSC thermograms of TetraGEDVA cured with DDS

In addition, it was also around this temperature that a gradual colour change, from yellow to brown and then black, has been observed during DMA analyses (see Figure 78). Yellow sample correspond to cured thermosets; brown sample correspond to the beginning of the colour change during the DMA analyses and black specimen correspond to the char residue recover after TGA under nitrogen.

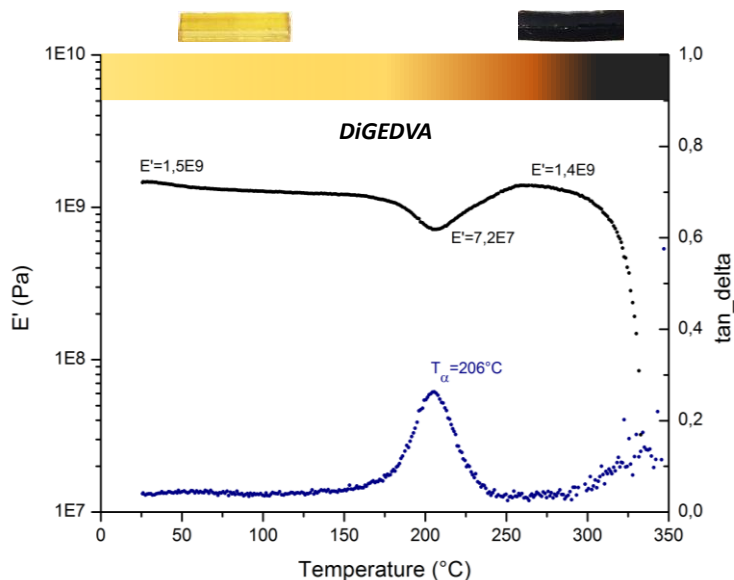


Figure 78: Colour changes during DMA analysis of DiGEDVA/DDS system

FTIR analysis were also performed on yellow, brown and black specimens. As shown on Figure 79, no significant difference was noticed between initial and brown samples. In contrast, the FTIR spectrum of char highlights the degradation process by revealing the disappearances of most of the functional groups. Nevertheless, some signals remain visible at 1510 and 2920 cm^{-1} , which can be attributed to the presence of aromatic patterns.

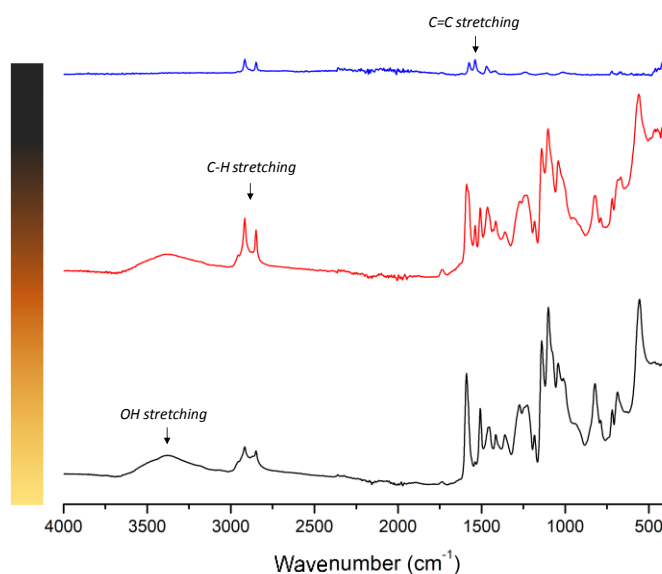


Figure 79: FTIR spectra of DiGEDVA/DDS thermoset (black), brown sample (red) and DiGEDVA/DDS char residue (blue)

However, at this stage no clear evidence enables to confirm these hypotheses. The thermal degradation analysis coupled with mass spectrometry could be a way to further investigate this phenomenon.

In conclusion, the previous described polyglycidylether of DVA exhibited remarkable properties in terms of glass transition temperatures and char yields. Following that, the next section will be dedicated to the development of these DVA-based epoxy formulations for ArianeGroup' purposes.

IV. Applications

Results discussed in the previous sections were concerning the synthesis of epoxy networks from 'pure' di-, tri- or tetra-glycidylethers of DVA. However, as already discussed, the purification of these derivatives requires a tedious procedure using flash chromatography, which is not transposable at an industrial scale. Moreover, from a green chemistry viewpoint, it makes sense to reduce the number of steps to produce the final product. As mentioned in the chapter 2, the synthesis of epoxy prepolymers derived from DVA can be controlled and leads to a mixture in different proportions of DiGEDVA, TriGEDVA and TetraGEDVA. Those proportions can be controlled and accurately determined using HPLC. The EEW value of these mixtures can be readily determined in order to add the right amount of hardener in the formulation and thus to obtain cross-linked networks with optimal thermomechanical properties.

From this feature, several crude mixtures have been prepared and the thermal properties of corresponding thermoset obtained by curing with DDS were compared. Data are gathered in Table 25.

Table 25: Thermomechanical properties of DVA blends thermosets

Blends of DVA-based Epoxy prepolymer	Viscosity at 40°C (Pa.s)	Tα^a (°C)	Char₉₀₀^b (%)
Di 80% -Tri 20% - Tetra 0% (Resin C)	471	<i>nd</i>	50
Di 35% -Tri 50% -Tetra 15% (Resin B)	119	232	50
Di 0% -Tri 25% -Tetra 75% (Resin A)	37	280	51

^acured with DDS and determined by DMA, ^bcured with DDS and determined by TGA under N₂

The mixture consisted of 25 wt% of TriGEDVA and 75 wt% of TetraGEDVA (Resin A) displays the lowest viscosity values of 37 Pa.s. In comparison, mixture of 80/20/0 Di-/Tri-/TetraGEDVA (Resin C) and 35/50/15 Di-/Tri-/TetraGEDVA (Resin B) exhibit viscosity values of 471 and 119 Pa.s, respectively. Moreover, alpha transition of thermoset obtained from Resin A cured with DDS displays a T_{α} of 280 °C, whereas thermoset obtained from Resin B shows a T_{α} of 232 °C. No significant difference was noticed concerning the thermal degradation and the char residue after degradation. Therefore, these results confirmed that blends composed of a majority of TetraGEDVA monomers are the most interesting in terms of rheology and glass transition temperatures. Thus, the Resin A/DDS epoxy thermoset will be investigated for different types of applications, such as structural composite and adhesive applications.

IV.1 Matrices for composite applications

Regarding to the high char residue displayed by polyglycidylethers of DVA/DDS systems, the characterization of these DVA-based epoxy thermosets for heat shield applications was investigated. ArianeGroup has essentially two technologies to fulfil this role: reusable thermal protection materials and ablative thermal protection materials. This latter consists in a matrix of thermoset polymers reinforced with charges or carbon fibers. In the case of ablative composite materials, the thermal energy received leads to the pyrolysis of the matrix and the formation of a carbon residue called char. The mass proportion of polymer converted into char is critical and must be greater than 50% to be efficient as thermal protection.

For that purpose, ArianeGroup developed a carbon fiber impregnation process without the use of solvent (Figure 80). This process requires sophisticated conditions, especially in terms of rheology of the epoxy system. The impregnation process consists in bringing the epoxy system to the desired viscosity by heating it at a maximum temperature of 65°C. At this temperature, the system must displayed a viscosity below 2 Pa.s during at least 2 hours in order to meet with the specific requirements. In this way, the viscosity of formulations is a key parameter in this process.

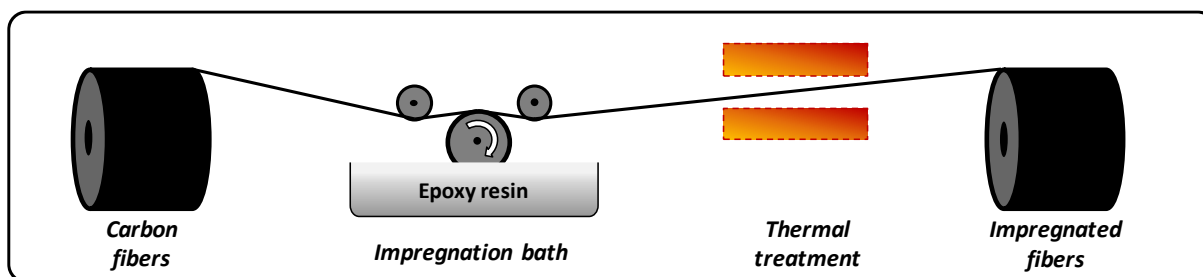


Figure 80: Simplified representation of impregnation process of carbon fibres within ArianeGroup

The uncured Resin A/DDS system was deposited between two plate-plate geometries of a rheometer and a ramp temperature was applied, in order to follow the variation of the viscosity with the respect of the temperature (Figure 81a). The same procedure was performed for a given temperature and variation of the viscosity was plotted over time (Figure 81b). Unfortunately, the Resin A/DDS system is out of the scope with respect to the requirements cited above. It exhibited a viscosity below the 2 Pa.s but for a temperature of 85°C, which is 20 °C higher than the maximum authorized. Subsequently, the curing process starts to occur at this working temperature and initial viscosity increases rapidly and exceeds 2 Pa.s after only 60 minutes (Figure 81).

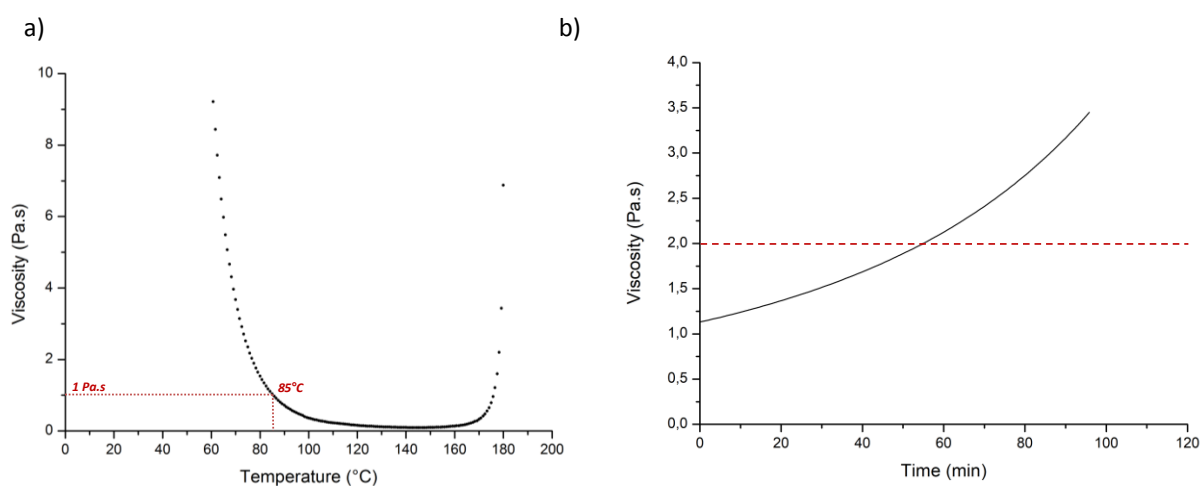
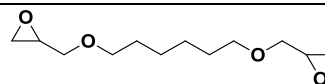


Figure 81: Variation of the viscosity of Resin A/DDS system (a) according to the temperature and (b) according to the time at 85 °C

To overcome this issue, one considered solution was to add a reactive diluent in the formulation in order to decrease the viscosity. As described in a previous chapter, there is a wide range of bio-based reactive diluent available, such as epoxidized soybean oil or cardanol-based epoxy. However, we have selected the, diglycidyl ether of hexanediol (DGEH) with a clear structure, in order to obtain well-defined networks. The structure and main properties of DGEH are depicted in Table 26.

Table 26: Structure and properties of DGEH

Diglycidylether of 1,6 hexanediol	
Molar mass (g.mol ⁻¹)	230
Density (g.cm ⁻³)	1,076
Viscosity at 25°C (Pa.s)	0,02
Boiling point (°C)	329
Appearance	Colorless liquid



The influence of DGEH on the viscosity and thermomechanical properties of the formulations was investigated. Several amounts of DGEH from 0 to 25 wt% were added to Resin A; the variation of the viscosity within the temperature was represented on Figure 82a. As expected, the higher the amount of reactive diluent, the lower the viscosity. Moreover, Figure 82b confirmed that Resin A and formulations containing 5 and 10 % of DGEH are out of the scope as such formulations display a 1Pa.s viscosity temperature above the limitation at 65°C. In contrast, the viscosity is kept below the 2 Pa.s threshold for 2h in the case of formulations containing 15 wt% and 25 wt % DGEH (Figure 83). Therefore, formulation containing at least 15% of DGEH can meet the requirements for the impregnation line.

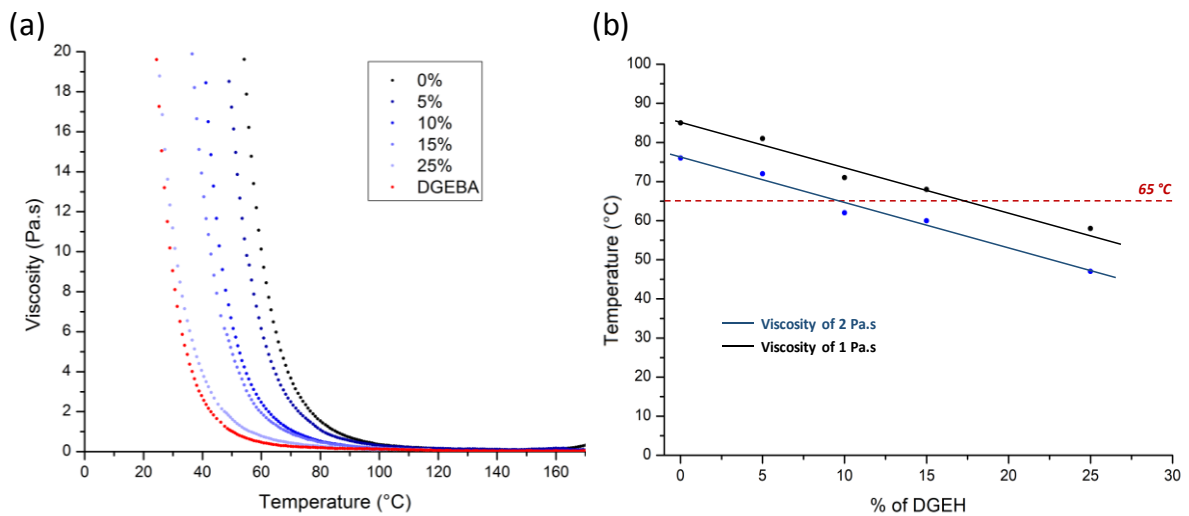


Figure 82: (a) Variation of the viscosity with temperature and (b) Variation of the temperature to reach a viscosity of 1 and 2 Pa.s for formulations containing various amount of DGEH

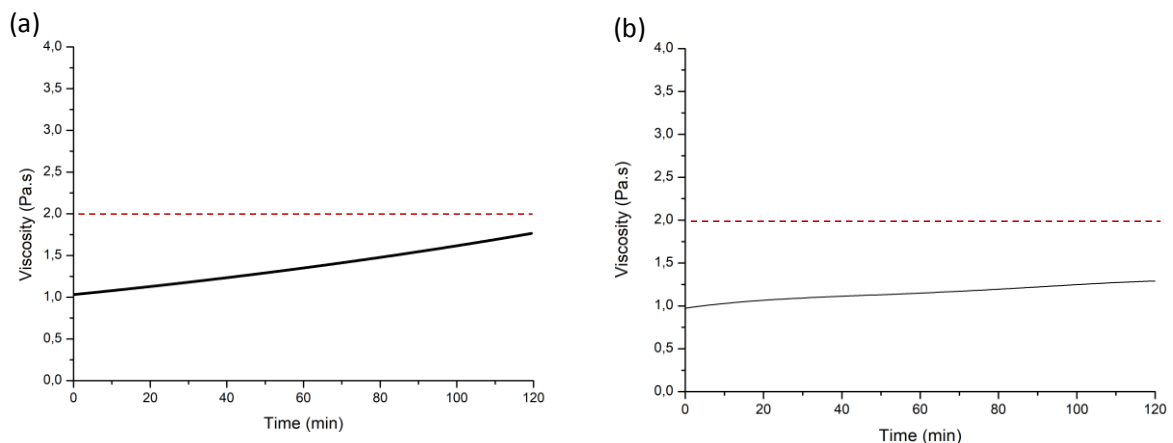


Figure 83: Variation of the viscosity of (a) Resin A + 15 % DGEH and (b) Resin A + 25 % DGEH according to the time

However, the addition of DGEH has also affected other thermomechanical properties. DSC, TGA, DMA and tensile tests have been performed on different formulations to investigate the

impact of the reactive diluent on the properties. As summarised in Table 27, the thermal properties determined by DSC did not exhibit significant difference between the formulations.

Table 27: Thermal properties of DVA-based with various amount of DGEH cured with DDS for $r = 1$

Epoxy prepolymer/DDS	T _{Onset} (°C)	T _{Exotherm} (°C)	ΔH (J.g ⁻¹)	ΔH (kJ.mol ⁻¹)	T _{Exotherm 2} (°C)	ΔH ₂ (J.g ⁻¹)
Resin A	154	203	408	86	317	85
Resin A+5% DGEH	152	204	392	82	-	-
Resin A+10% DGEH	159	205	381	79	303	98
Resin A+15% DGEH	156	206	400	82	292	92
Resin A+25% DGEH	155	206	403	81	292	87

The maximum temperature of the second exothermic peak was only decreasing with the increase of DGEH percentage in the formulation. The temperature difference between Resin A and the formulation containing 25% of DGEH was almost 30 °C. Once again, the observation of the glass transition temperature was not possible (Figure 84). As previously described, this feature could be explained by the high cross-linking density of the network formed.

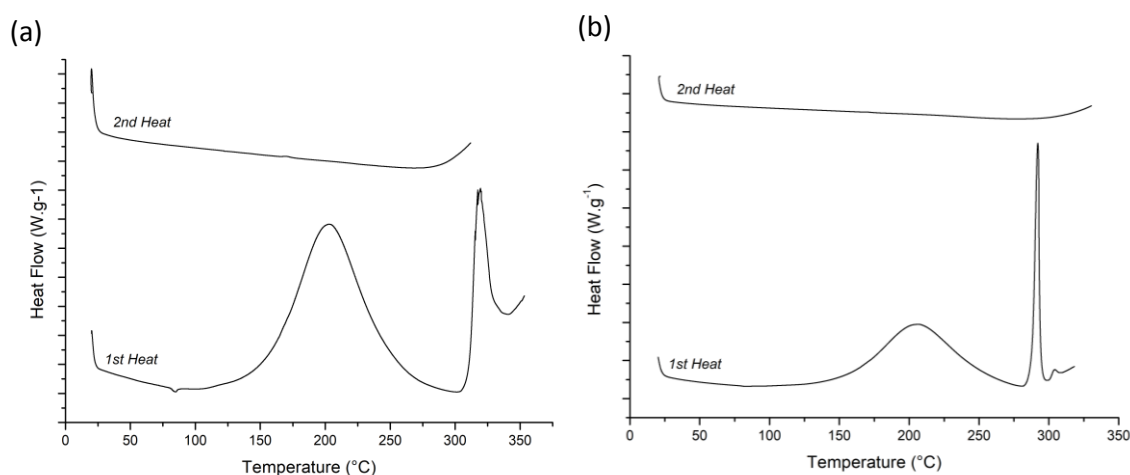


Figure 84: DSC thermograms of (a) Resin A and (b) Resin A+25% DGEH cured with DDS

Besides, dynamic mechanical analysis using three-point bending geometry were performed on the different thermosets and enabled the determination of the alpha transition temperature (T_α). Results are displayed in Table 28 and Figure 85. Curing procedure of the sample was identical as the one previously described, *i.e.* 30 min at 110°C followed by 2h at 180°C. Overall, the epoxy networks exhibited a decrease of the T_α up to 80°C for the formulation containing the highest amount of DGEH. This feature could be logically explained by the fact that DGEH “softens” the materials by incorporating linear segments in the cross-linked network and thus resulting in a decrease of the T_α . This trend is commonly reported when diluents are used.¹³

In addition, tensile tests have also been performed on these DVA-based thermosets (Table 28 and Figure 86). Young's modulus are ranging from 1150 to 1350 MPa and elongations at break from 4 to 5%, but no significant difference was noticed in these two parameters according to the amount of DGEH.

Table 28: Thermomechanical properties of DVA-based with various amount of DGEH cured with DDS for $r = 1$

Epoxy prepolymer/DDS	T_{α}^a (°C)	Young's modulus ^b (MPa)	Elongation at break ^b (%)
Resin A	280	1350 ± 170	4,6 ± 0,1
Resin A+5% DGEH	263	1170 ± 40	4,9 ± 1,0
Resin A+10%DGEH	240	1200 ± 100	4,1 ± 1,0
Resin A+15% DGEH	223	1150 ± 100	5,2 ± 1,0
Resin A+25% DGEH	201	1170 ± 80	4,5 ± 1,0

^adetermined by DMA, ^bdetermined by tensile test

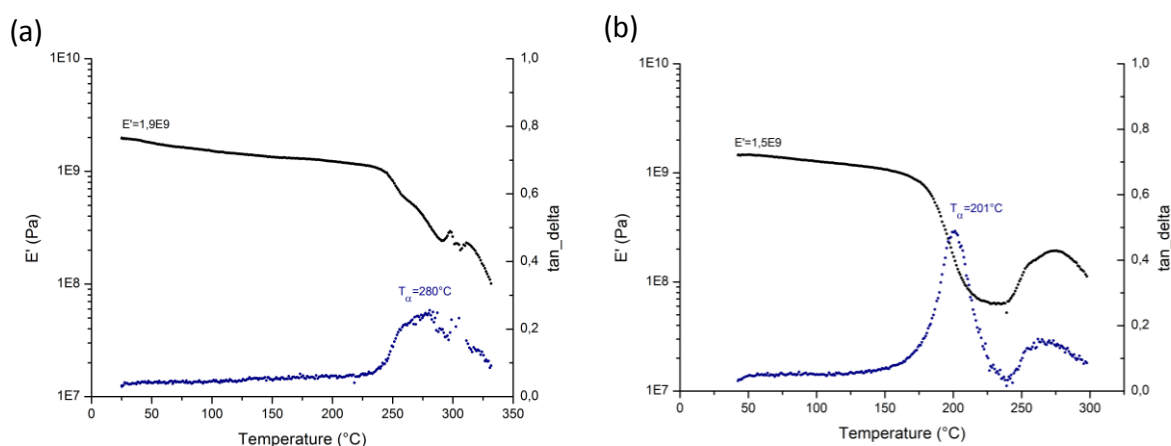


Figure 85: DMA traces of (a) Resin A and (b) Resin A + 25% DGEH cured with DDS

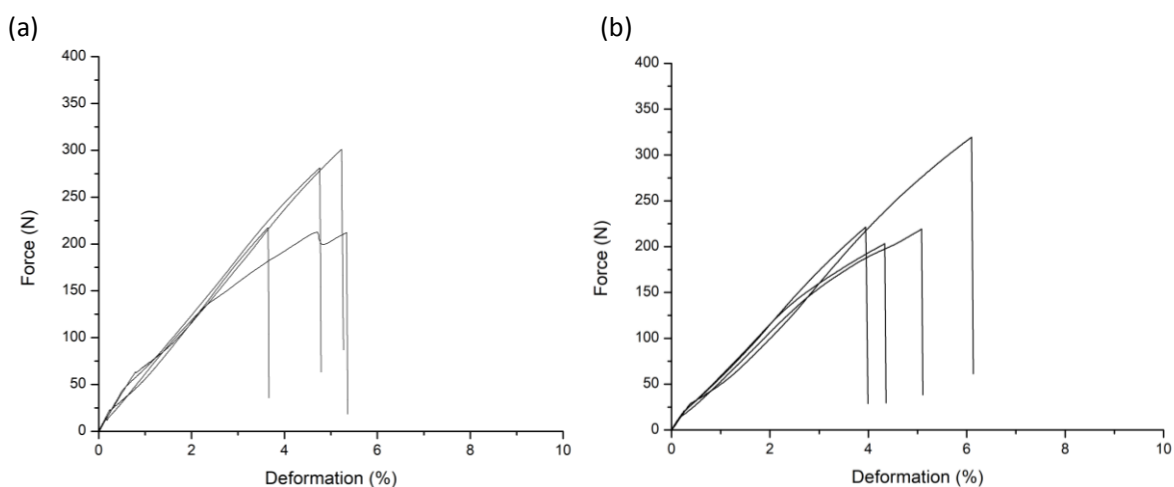


Figure 86: Tensile test traces of (a) Resin A and (b) Resin A + 25% of DGEH cured with DDS for $r = 1$

The thermal degradation feature was also investigated by thermogravimetric analysis under nitrogen (Table 29). The increase of DGEH amount leads to a slight reduction of the temperature of degradation and a reduction of the char content at 900°C. The statistic heat-resistant index (Ts) displayed a maximum difference of 10 between Resin A and Resin A + 25% DGEH, revealing a decrease of the thermal stability of high content DGEH formulation.

Table 29: Thermal degradation under N₂ of DVA-based with various amount of DGEH cured with DDS for $r = 1$

Epoxy prepolymer/DDS	T _{d5%} (°C)	T _{d30%} (°C)	T _s	Char ₉₀₀ (%)
Resin A	336	404	185	51
Resin A+5% DGEH	319	396	179	50
Resin A+10% DGEH	305	390	174	49
Resin A+15% DGEH	311	392	176	47
Resin A+25% DGEH	306	389	174	45

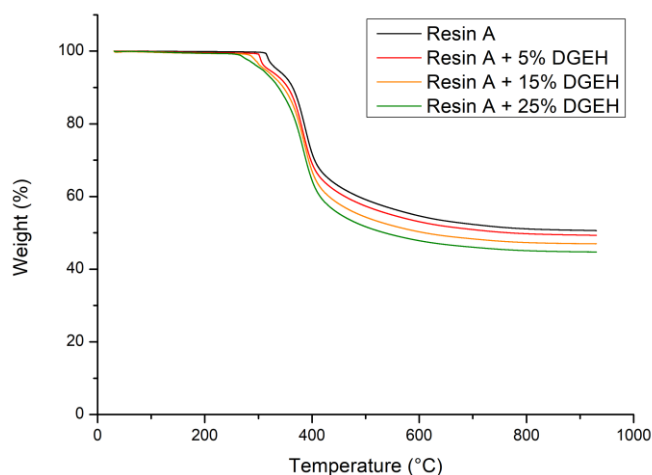
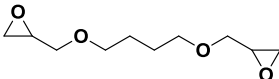


Figure 87: TGA thermograms under N₂ of DVA-based with various amount of DGEH cured with DDS for $r = 1$

Contrary to what can be expected, only 5% drop of char yield was noticed between the Resin A and the formulation with the highest amount of DGEH. From this feature, other reactive diluents, such as diglycidylether of 1,4-butanediol (DGEBD) and DGEBA were added at a ratio of 25 wt% in formulation. The structure and main properties of DGEBD and DGEBA are depicted in Table 30.

Table 30: Structure and properties of DGEBD and DGEBA

Diglycidylether of 1,4 butanediol		DGEBA
Molar mass (g.mol ⁻¹)	202	370
Density (g.cm ⁻³)	1.1	1.16
Viscosity at 25°C (Pa.s)	0,015	1
Boiling point (°C)	266	42*
Appearance	Colorless liquid	Colorless liquid

* *Melting point*

In this way, the influence of the chemical structure of reactive diluent on the char content could be compared (Table 31). The addition of 25 wt.% of DGEBD and DGEBA permitted to increase the glass transition temperature of 10 and 30 °C, respectively. This feature could be explained by the lesser mobility of the chains induced by the incorporation of shorter alkyl segments or aromatic rings in the network. However, no real influence was observed on the char yield, which means that the char content is not strongly dependent on the network density of the bio-based thermosets.

Table 31: Glass transition temperature and char residue of formulations cured with DDS

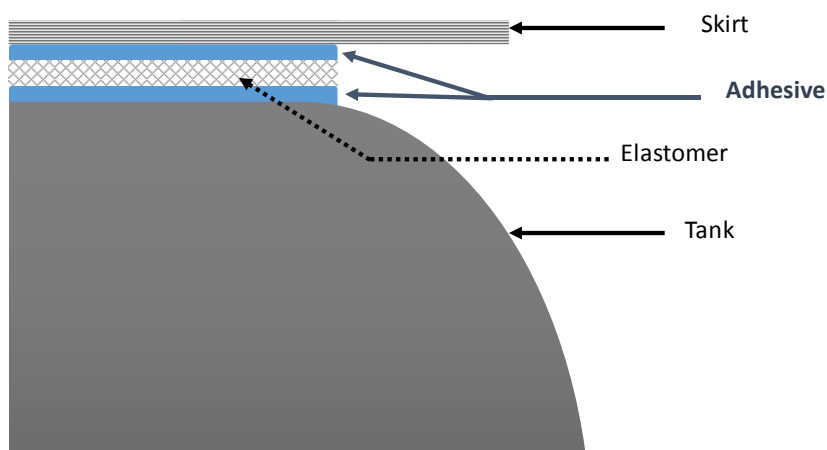
Properties	Resin A	Resin A +25% DGEH	Resin A +25% DGEBD	Resin A +25% DGEBA
T_g (°C)^a	280	201	210	229
Char₉₀₀ (%)^b	50	45	45	44

^adetermined by DMA, ^bdetermined by TGA under N₂

In conclusion, the addition of a reactive diluent in the Resin A was necessary to adjust the viscosity of formulations in order to meet the requirements of the impregnation line. Thus, formulations containing at least 15 wt.% of DGEH were identified as compatible with the temperature and viscosity specifications. Nevertheless, the incorporation of reactive diluent induced a decrease of the thermal properties, such as glass transition temperature and the char residue. However, the epoxy thermoset obtained with 15 wt% of DGEH still displayed a T_g above 200 °C and a char yield above 45%. Finally, these DVA-based epoxy thermosets displayed promising properties for an application as ablative composite materials. Nevertheless, further investigations, especially on the carbon fiber impregnation line, which requires at least one kilogram of resin, are necessary to confirm these results. In this way, the scale-up of the synthesis of DVA-based epoxy prepolymers is scheduled and would be realised in the first semester 2018.

IV.2 Formulations for structural adhesive applications

The structural adhesive bonding is a reference technology in the aerospace industry as it enables to improve the properties of the bonded structure, especially compared with old mechanical bonding, such as riveting or bolting. Adhesive technologies improve the stress distribution, the sealing, the noise and vibration damping across the bonded joint. In addition, this technology enables the effective reduction of the weight and the design of new structures.^{14,15} One of the major and emblematic application of this technology for ArianeGroup is the bonding of the launcher tank with the skirt (Scheme 47). The tank is intended for receiving and storing the fuel whereas the skirt ensures the strains distribution between the different modules of the aerospace vehicles. Indeed, the adhesive is used to bind together the composite tank with an elastomer part and the elastomer with the metal skirt. The difficulty of this bonding lies in the heterogeneity of the various components.



Scheme 47: Structural adhesive bonding of a launcher tank with the skirt

Moreover, the formulation of a complete adhesive is complex and involves a precise mixture of numerous compounds, such as epoxy monomers, hardeners, viscosity modifiers or charges. Currently, Redux 322 or FM300, respectively sell by 3M and Cytec, are typical structural adhesives used for this kind of applications. Regarding the information commercially available and deformation works, their composition revealed the presence of mixture of different epoxy monomers, curing agents, catalysts, but also thermoplastic polymers, flame retardant agent and aluminium charge for thermal conductivity. In addition, these formulations are generally supported on a film in the purpose of improving the application of the adhesive on the surface to assembly.

In view of the complexity of the formulation of a complete adhesive, the aim of this study is to evaluate the potential of DVA-based thermosets in adhesive application by comparing simple formulations consist of epoxy monomers and a curing agent.

The evaluation of bonded joints could be achieved by numerous test methods. Tensile, peel and shear tests are commonly used to characterize a reliable adhesive joint and are essentially comparative methods (Figure 88).¹⁶

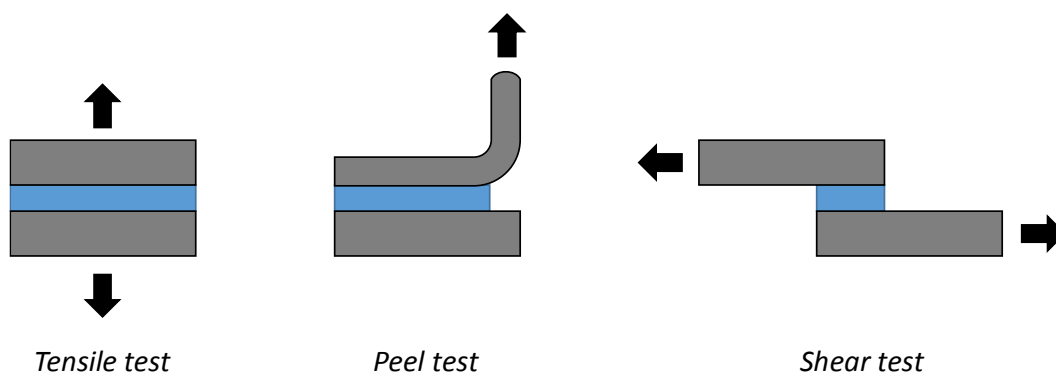


Figure 88: Mechanical test methods of adhesive joints

These latter determine stresses caused by the applied of loads and measure the strength required to break the bond. The nature of the fracture (adhesive, cohesive, or substrate fracture) provides also valuable information. Therefore, these characteristics allow assessing the quality of the adhesive bond.

Generally, shear testing are commonly used because they are easy to implement. Among them, the lap shear tests consist in two specimens overlapped by a certain length. Thus, the adhesive forms a layer between the overlap area. The most common lap shear test is the single-lap used for metallic substrates, but this test can also be performed on a variety of others substrates, such as wood, plastic or composite. From this feature, Resin A and formulations containing extent amount of DGEH were tested and compared with DGEBA-based thermoset cured with DDS. Lap shear tests have been performed on aluminum specimens in order to have direct information on the adhesive behaviour of the formulations. The ASTM D1002, which specifies lap shear for metal to metal, was used as reference (Figure 89).

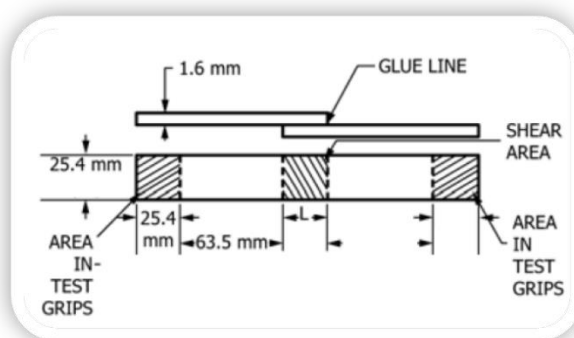


Figure 89: Lap shear test specimens according to ASTM D1002

Two aluminium specimens were bonded together with DVA-based and DGEBA-based formulations. After cured during 4 h at 180 °C, metal specimens were placed in the grips of a

tensile testing machine and pulled until failure. Results obtained are summarised in Table 32 and Figure 90.

Table 32: Lap shear test results of DGEBA and DVA-based epoxy monomers cured with DDS

Epoxy prepolymer	Shear Strength (MPa)	Elongation at break (%)	Young's Modulus (MPa)
DGEBA	$8,8 \pm 0,5$	$0,8 \pm 0,1$	2090 ± 380
Resin A	$6,9 \pm 0,4$	$0,5 \pm 0,1$	2480 ± 60
Resin A+10%DGEH	$10,0 \pm 0,3$	$0,9 \pm 0,1$	2120 ± 230
Resin A+25%DGEH	$9,7 \pm 1$	$0,9 \pm 0,1$	2290 ± 100

In comparison to the DGEBA-based system, Resin A epoxy network exhibited a lower shear strength of 6,9 MPa, a shorter elongation at break of 0,5 %, but a higher Young's modulus value of 2474 MPa. This feature could be explained by the high cross-linked density of Resin A-based thermoset, which could induce a more brittle material and explain the early failure of the joint. In contrast, when diglycidylether of hexane diol (DGEH) was added to the formulation, DVA-based epoxy thermosets exhibited a higher shear strength and elongation at break at around 10 MPa and 1 %, respectively. As explained previously, the incorporation of aliphatic alkyl segments in the network could bring some flexibility making the joint less brittle and thus more efficient.

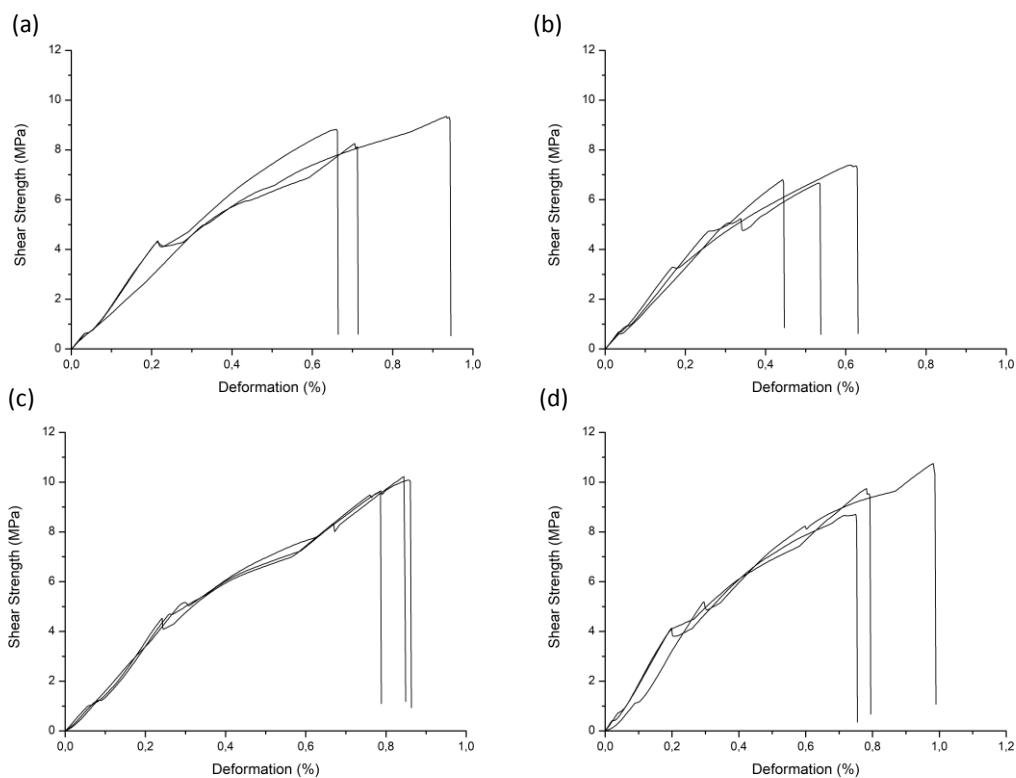


Figure 90: Lap-shear test traces of (a) DGEBA, (b) Resin A, (c) Resin A + 10% DGEH and (d) Resin A + 25% DGEH cured with IPDA for $r = 1$

However, some limitations were observed for the characterization of the adhesive strength. The procedure used enables the obtention of thin adhesive joints (0.05 mm) and for this thickness, the visual appreciation of the rupture characteristics is not relevant. In addition, the majority of the adhesive applied on the surface flowed off the overlap area and accumulated on the edge. Figure 91 showed an example of fracture faces of samples. Nevertheless, adhesive materials were found on the both faces of the aluminium samples, which suggested cohesive failures.

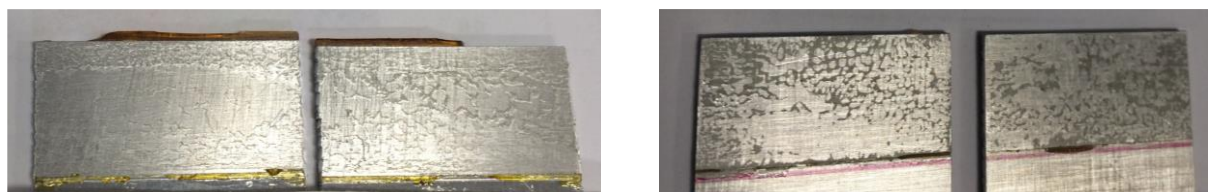


Figure 91: Fracture faces of DGEBA (left) and Resin A (right) cured with DDS

In conclusion, the preliminary adhesive behaviour of bio-based formulations exhibited similar characteristics than DGEBA reference. However, the method of characterization was limited by the thickness of the adhesive joint. The realisation of new tests with a higher and better control of the adhesive joint would be necessary to fully characterize these bio-based materials for structural adhesive applications.

V. Conclusion

In this chapter, the thermo-mechanical properties of polyglycidylethers of DVA, cured with diamine hardeners, were investigated and compared with DGEBA thermosets. The first section was dedicated to the obtention and the characterization of epoxy thermosets cured with isophorone diamine, a cycloaliphatic diamine. DSC, TGA, DMA and tensile tests revealed that DVA-based epoxy thermosets displayed at least similar thermo-mechanical properties than DGEBA thermoset. Thermosets from polyglycidylethers of DVA exhibited T_g ranging from 140 to 200 °C, whereas DGEBA thermosets displayed a T_g of 155 °C.

In the second part, same polyglycidylethers of DVA were cured with diaminodiphenylsulfone (DDS), an aromatic diamine. Thermosets from polyglycidylethers of DVA exhibited T_g ranging from 204 to 312 °C, whereas DGEBA thermosets displayed at T_g of 206 °C. Moreover, the DVA-based thermosets displayed a char residue above 50%, which induced promising flame-retardant properties.

Finally, characterizations of bio-based formulations were performed for two different ArianeGroup applications: the ablative composite materials and structural adhesives. Regarding the high char residue displayed by the DVA-based networks, several formulations were identified to fulfil the specifications of the impregnation line. In a near future, the scale-up of the synthesis of bio-based epoxy prepolymers would be necessary to confirm results on demonstrator. Adhesive tests were also performed by evaluating the lap shear strength required to separate two aluminium specimens. DVA-based thermosets displayed similar shear strength than DGEBA-based thermoset. However, limitations concerning the adhesive joint thickness of specimens were reported and accomplishment of new tests with a larger and better control of the adhesive joint would be necessary to fully characterize these bio-based materials for structural adhesive applications.

At last, the polyglycidylethers of DVA exhibited remarkable properties in terms of glass transition temperatures and thermal degradation temperatures. They also demonstrated their ability to be used as ablative resin by exhibiting very high char content. Therefore, the polyglycidylethers of DVA could be valuable and better alternatives to DGEBA than current bio-based epoxy monomers.

VI. Experimental

Calculation of the EEW of a mixture of epoxy monomers

$$EEW_{mix} = \frac{100}{\frac{m_1}{EEW_1} + \frac{m_2}{EEW_2}}$$

m: mass of epoxy monomer 1 in gram

EEW: Epoxy Equivalent Weight

Calculation of the stoichiometric ratio $r = 1$

For 100 g of epoxy monomer, x g amount of amine curing-agent is necessary to achieve the stoichiometric ratio epoxy/ N-H $r = 1$

$$phr = \frac{AHEW}{EEW} * 100$$

phr = parts per hundred

AHEW: Amine Hydrogen Equivalent Weight

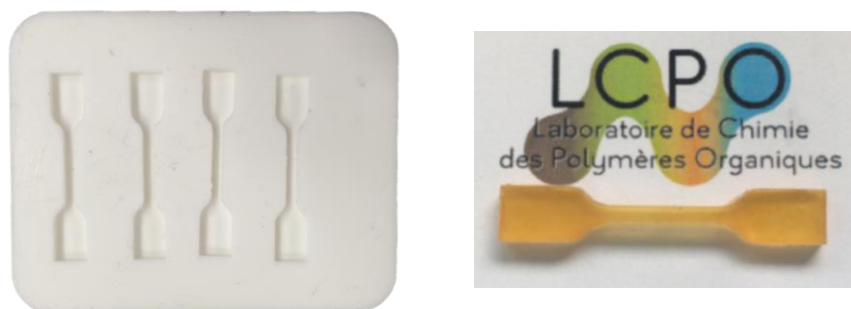
EEW: Epoxy Equivalent Weight

Swelling tests procedure

After immersion into THF for 24 h, the swollen samples were dried between paper sheets and weighted again (w_{sw}). The samples were dried at 60 °C for 24 h and weighted (w_D).

Samples preparation for tensile test analysis of epoxy thermosets cured with IPDA

Epoxy prepolymers were mixed vigorously with stoichiometric amount of curing agent. The mixture was poured into a silicon mould. Sample was degased at room temperature or with a minimum of heat under vacuum. Silicon mould was then heated in an oven during 1h at 100 °C followed by 1h 140°C.



Samples preparation for tensile test analysis of epoxy thermosets cured with DDS

Epoxy prepolymers were mixed vigorously with stoichiometric amount of curing agent. The mixture was poured into a silicon mould. Sample was degased at room temperature or with a minimum of heat under vacuum. Silicon mould was then heated in oven during 30 min at 110 °C and 2h at 180 °C.

Samples preparation for lap shear tests

Aluminium plates were degreased with methylethyl ketone (MEK) and dried 15 min at room temperature. Testing areas were sanded with Scotch Brite Minnesota type A and degreased a second time with MEK. After 15 min at room temperature, adhesive formulation is applied on both surfaces with spatula. Aluminum plates were then inserted in the tool with 0,6 bar of pressure and heated in an oven at 180 °C during 4h. After cooling, aluminum plates are processed to obtain aluminum specimens.



VII. References

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Chapter 4: Synthesis of bio-based curing- agents derived from divanillin

Keywords: curing agent, bio-based amine, polyamine, epoxy, thermoset

Mots-clés : agent de réticulation, amine bio-sourcée, polyamine, époxy, thermodurs

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I. Introduction

Epoxy thermosets are the products of the reaction between epoxy-based monomers or prepolymers with curing agents. The cross-linking agents are significant in terms of mass fraction as the latter can represent up to 50% of the formulations. Many efforts are currently done to find bio-based alternatives to traditional epoxy monomers derived from fossil resources and in particular bisphenol-A. With similar objectives, some studies report the synthesis of bio-based anhydride- or acid-type curing agents from renewable resources, such as vegetable oils,¹ rosin,²⁻⁵ terpenes,⁶ tannins^{7,8} or lignins.⁹ However, the development of bio-based amine-type curing-agents is still limited.

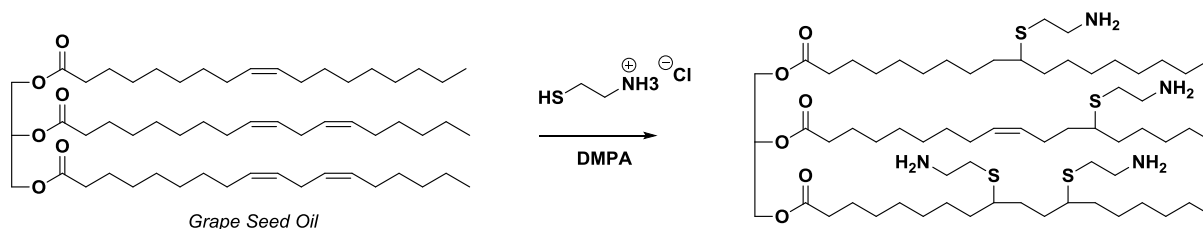
In the following of this chapter, a literature survey dealing with bio-based amine curing-agent for epoxy systems will be presented and the main synthetic routes to amine derivatives will be discussed. Finally, the synthesis of new bio-based amines derived from divanillin will be investigated and new fully vanillin-based epoxy thermosets will be presented.

II. Literature Survey on bio-based amines

II.1 Bio-based amine-type curing agent

The synthesis of amine derivatives as curing agents for epoxy thermosets could be achieved from many renewable resources, such as vegetable oils, cardanol, chitosans, terpenes or lignins.

Stemmelen *et al.* successfully developed the synthesis of amine curing agent from Grape Seed Oil (GSO).¹⁰ For that purpose, the authors investigated the thiol-ene reaction of unsaturated GSO with cysteamine hydrochloride (CAHC) by UV-initiation (Scheme 48). They successfully synthesized polyamine GSO with an average number of amine units per triglyceride close to 4.

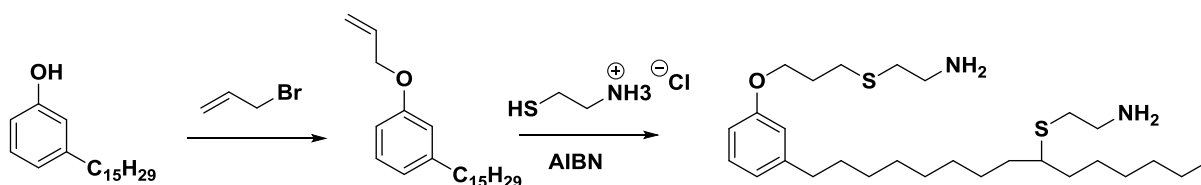


Scheme 48: Synthesis of polyamine GSO by thiol-ene reaction¹⁰

Such polyamine was then employed as hardener and cured with Epoxidized Linseed Oil (ELO). The thermomechanical properties of fully bio-based cured polymer exhibited a glass transition temperature of -38 °C. According to the authors, this very low Tg value is a direct consequence of the flexibility of long aliphatic chains constituting the vegetable oil.

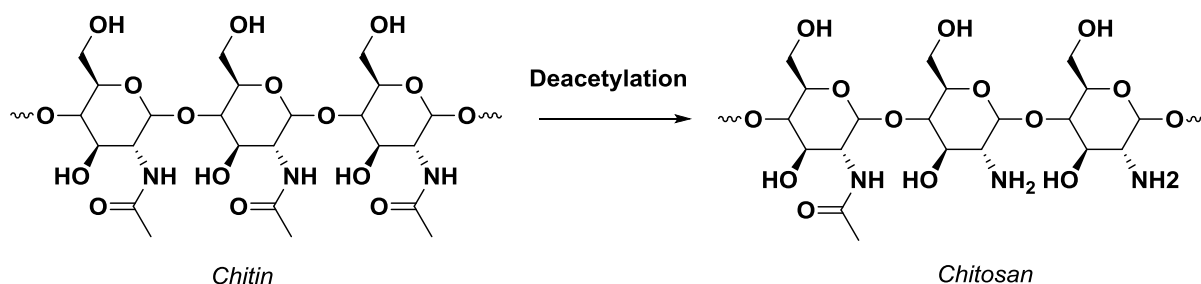
Following the same strategy, Cornille *et al.* reported the synthesis of polyamine from the thiol-ene coupling of modified bio-based pentaerythritol with cysteamine hydrochloride (CAHC).¹¹ Epoxy/amine networks were prepared from DGEBA and exhibited glass transition temperature close to 60 °C, a thermal degradation temperature of 300 °C (Td5%) and a char content at 500 °C of 18 %. These values are similar to DGEBA thermosets cured with IPDA, except for the Tg, which is 100 °C lower than the DGEBA reference (155 °C).

Other authors investigated the synthesis of amine-functionalized cardanol from cardanol and cysteamine by thiol-ene reaction (Scheme 49).¹² Fully bio-based epoxy thermosets were then obtained by curing diamine cardanol with epoxidized cardanol (NC-514). Again, the thermomechanical properties of this fully cardanol-based epoxy network remains low with Tg values close to 19 °C and storage modulus at 20°C of 1,4 MPa. In contrast, materials obtained by curing in the same conditions NC-514 with IPDA exhibit a Tg of 59 °C and a storage modulus of 1218 MPa.



Scheme 49: Synthesis of amine-functionalised cardanol¹²

Chitin is another interesting renewable resource for the synthesis of polyamine. Indeed, chitosan can be produced by the deacetylation of chitin in basic conditions (Scheme 50).¹³ The so-formed chitosans have a degree of deacetylation ranging from 50 to 90%.¹⁴



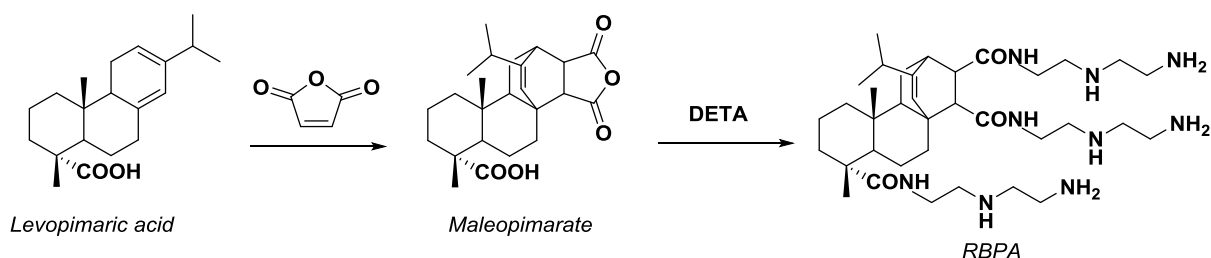
Scheme 50: Production of chitosan by deacetylation of chitin

Boutevin and coll. reported the use of chitosan as curing agent for epoxy thermosets.¹⁵ The polyaddition reaction between chitosan and DGEBA was performed in suspension in aqueous acidic solution (pH < 6). The epoxy network exhibited a glass transition temperature of 38 °C and a maximum degradation temperature of 420 °C. Overall, the design of such polyamines is more destined for coating applications than for high performance epoxy thermosets.

Nevertheless, the authors developed a more environmentally friendly process for the synthesis of bio-based, biocompatible and water-soluble amino hardener, which can be used for curing waterborne epoxy prepolymers.

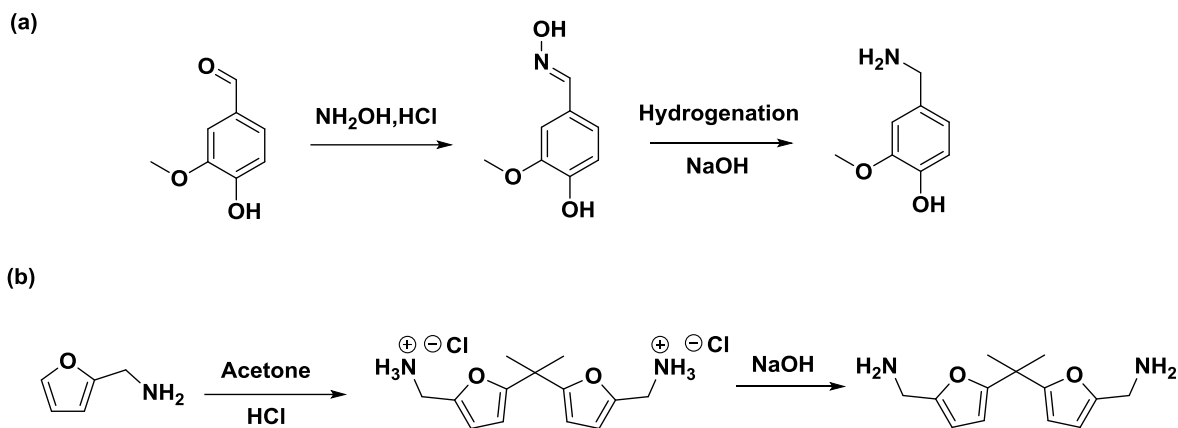
In 2011, Wang *et al.* described the synthesis of a rosin-based imidoamine-type as curing agent for epoxy systems.¹⁶ The authors successfully synthesized maleopimaric acid imidoamine (MPAIA) by the imidation of maleopimarate with ethylenediamine. DGEBA 1075 was then cured with MPAIA and methylenedianiline (DDM), a commercial aromatic amine. The bio-based epoxy thermoset displayed a Tg of 117 °C against 99 °C for the petroleum-based system. Moreover, the epoxy monomer cured with MPAIA exhibited similar thermal degradation temperature to the DGEBA 1075/DDM systems (380 °C).

Following a similar strategy, Mi *et al.* reported the synthesis of rosin-based poly(amidoamine) (RBPA) from the reaction between maleopimarate and diethylentriamine (DETA) (Scheme 51).¹⁷ The glass transition temperature of the DGEBA/RBPA epoxy thermoset exhibit a value of 147 °C.



Scheme 51: Synthesis of rosin-based poly(amidoamine)¹⁷

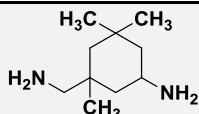
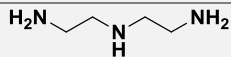
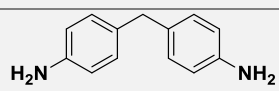
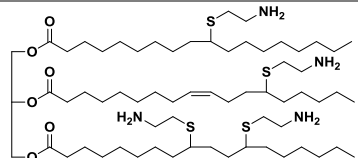
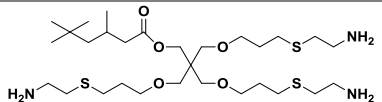
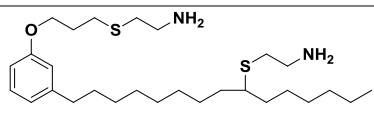
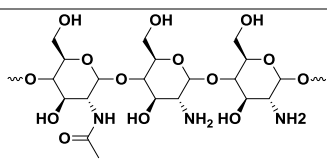
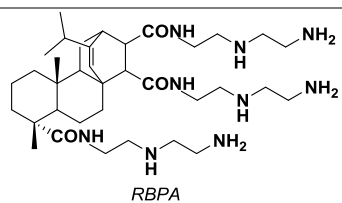
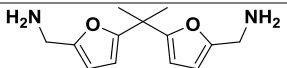
More recently, Fache *et al.* successfully derivatized vanillin into one amine compound. Vanillin was first converted into vanillyloxime and then reduced into vanillylamine (Scheme 52a).¹⁸ However, the mono-functionality of the vanillin-based amine does not permit the formation of a cross-linked network. In the same study, the authors also performed the synthesis of bis(furfuryl)amine from bio-based furfurylamine (Scheme 52b). In the same way, bis(furfuryl)amine was used as curing agent with DGEBA. The bio-based network exhibited a glass transition temperature of 111 °C, which is lower than DGEBA/IPDA network (155 °C). This decrease of Tg value could be attributed to the presence of a methylene group between the amine group and the furan ring which brings some flexibility to the epoxy network.



Scheme 52: (a) Synthesis of vanillylamin from vanillin, (b) synthesis of bis(furfuryl)amine¹⁸

In conclusion, the thermomechanical properties of epoxy thermosets issued from bio-based curing agents remain low in comparison to the ones obtained from conventional hardeners like IPDA. Nevertheless, rigid substrates, such as rosin or furfuryl derivatives, appear more suitable for the elaboration of epoxy thermosets with high T_g values and thermal degradation temperatures. A list of the different bio-based systems developed so far in the course of epoxy thermosets is given in Table 33. In this way, there is a growing interest to find bio-based reactive amines leading to epoxy thermosets with high thermomechanical properties. With this objective, the next section presents the numerous synthetic pathways to prepare primary amines from various starting materials.

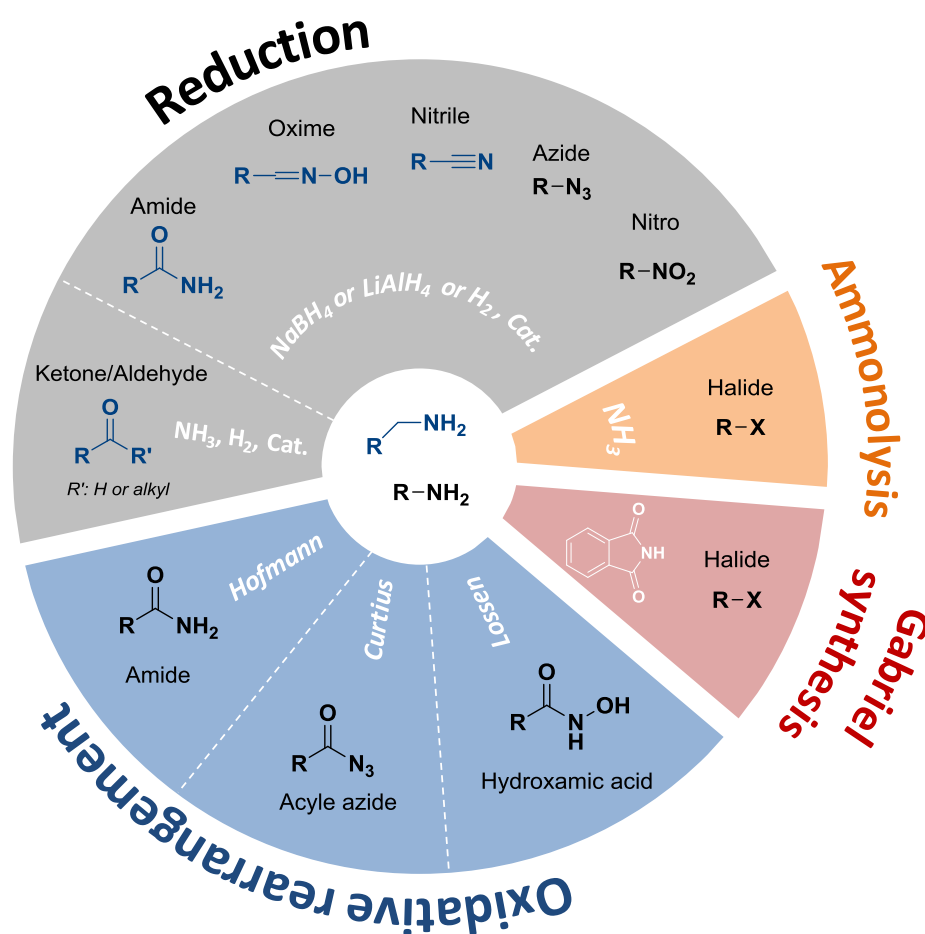
Table 33: Overview of bio-based amine-type curing-agents for epoxy thermosets

Bio-based amine curing-agents	Epoxy prepolymers	Tg (°C)	Ref
 Isophorone diamine (IPDA)	DGEBA	[155-166]	19-22
 Diethylenetriamine (DETA)	DGEBA	138	24,25
 Methylenedianiline (MDA)	DGEBA 1075	99	16
 Amine-functionalised GSO	ELO	-38	10
 Amine-functionalised pentaerythritol	DGEBA	57	11
 Amine-functionalised cardanol	NC-514	19	12
 Chitosan	DGEBA	38	15
Maleopimaric acid imidoamine (MPAIA)	DGEBA 1075	117	16
 RBPA	DGEBA	147	17
 Bis(furfuryl)amine	DGEBA	111	18

II.2 Routes to primary amines

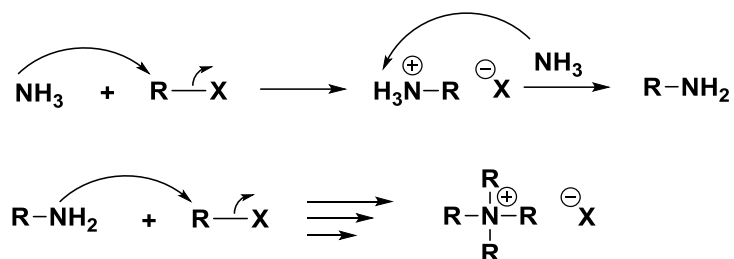
Primary amines can be prepared from various starting materials and through numerous synthetic pathways already described in organic chemistry (Scheme 53).^{26,27}

The principal pathway for preparing a primary amine is the reduction of various compound such as azide, amide,²⁸ aldehyde and ketone,²⁹ nitrile,^{30,31} nitro, oxime.^{18,32} The reduction step is generally performed with strong hydride donors such as aluminum or boran hydrides. The reduction reaction can also be carried out by catalytic hydrogenation in the presence of a metal catalyst, such as platinum, palladium or nickel. Moreover, the reduction of nitro compounds can also be performed following a milder approach using iron, zinc, tin, or tin(II) chloride in acidic conditions, without the use of high temperature or pressure conditions.



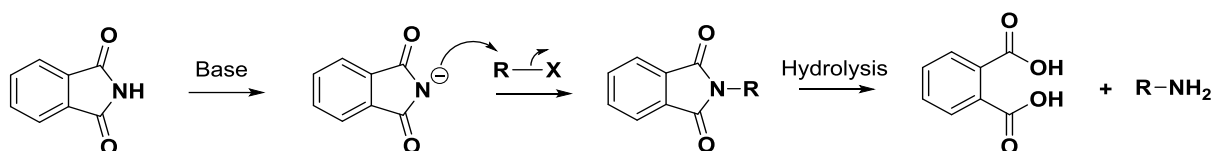
Scheme 53: Screening of starting materials for the synthesis of primary amines

Halogenated compounds can be converted into primary amines through ammonolysis reaction. Such a reaction consists in the nucleophilic substitution of halide with ammonia (Scheme 54). However, this method suffers from some limitations as the so-formed primary amine can undergo further alkylation yielding secondary, tertiary and quaternary amines.



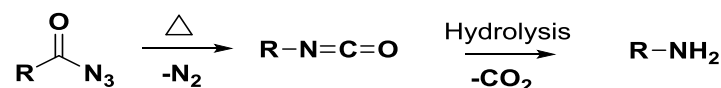
Scheme 54: General mechanism for the ammonolysis of halide compounds

Another alternative to the synthesis of primary amines is the *Gabriel synthesis*. The amine synthesis is achieved through the nucleophilic substitution of alkyl halide with phthalimide in the presence of a base, followed by acidic or basic hydrolysis (Scheme 55). Alternatively, hydrolysis with hydrazine has been developed to improve the hydrolysis step, but the separation of side-products, such as phthalhydrazide is challenging. In addition, the *Gabriel synthesis* suffers from poor atom-economy with the use of phthalimide derivatives.



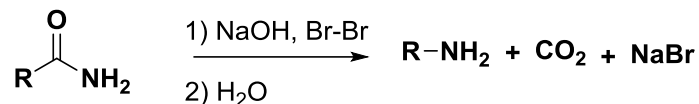
Scheme 55: Gabriel synthesis for the obtention of amine

Alternative methods for the preparation of primary amines involve oxidative rearrangements. For instance, the *Curtius rearrangement* is realised from acyl azide moiety.³³ Usually, acyl azide moiety is converted into isocyanate by heating and the latter is then reduced to amine through hydrolysis (Scheme 56). This method proved to be efficient and is widely used in the pharmaceutical industry for the production of drugs and therapeutic compounds.^{34,35} However, the principal limitation of this method is the careful handling of azide compounds, which can be explosive.



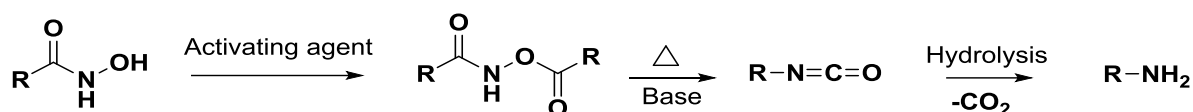
Scheme 56: Curtius rearrangement of acyl azide into amine

Similarly, amide can undergo *Hofmann rearrangement*.³⁶ Hofmann rearrangement occurs when a primary amide is treated with dibromide and a base. The overall mechanism is depicted in Scheme 57. Generally, the *Hofmann rearrangement* gives high yields of both arylamines and alkylamines.



Scheme 57: Hofmann rearrangement of amide into amine

Finally, primary amines can be prepared from hydroxamic acid through the *Lossen rearrangement*. Hydroxamic acid is converted into isocyanate via the formation of an O-acyl, -sulfonyl, or -phosphoryl intermediate using an activating agent (Scheme 58). Unfortunately, this method yield also to the formation of by-products, such as ureas or carbamates. Recently, several studies demonstrated the interesting synthesis of amines through a self-propagative Lossen rearrangement without the use of activating agent.^{37,38} Its mechanism will be further described in the next sections.



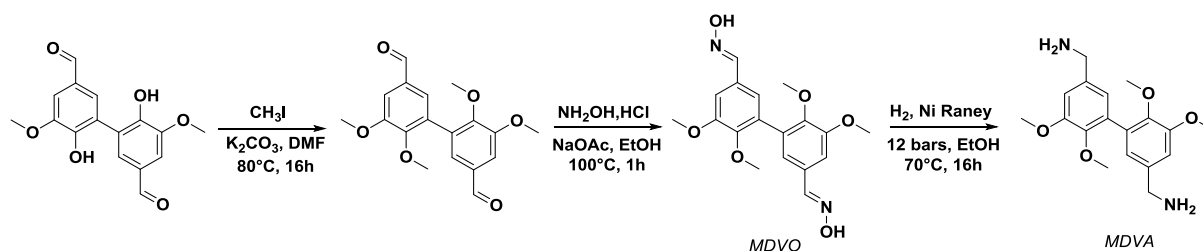
Scheme 58: Lossen rearrangement of hydroxamic acid into amine

As a conclusion, several methods for the preparation of amines have been reported. However, only few can be applied to the bio-based substrates of our interest, which present functional moieties, such as aldehydes, esters and acids. Among the bio-platform derived from vanillin available in the laboratory, divanillin or methyl divanillate could be interesting precursors for the synthesis of primary aromatic diamines. Therefore, three synthetic pathways have been identified for the synthesis of bio-based aromatic amines. In the following, the preparation of divanillin-based hardener through the reduction of oxime, the oxidative rearrangement of hydroxamic acid or acyl azide moieties will be presented.

III. Synthesis of bio-based amines from vanillin derivatives

III.1 Synthesis of amine from reduction of oxime

As described in the previous chapter, vanillin can easily be dimerized into divanillin. The so formed divanillin displays two aldehyde functions which can undergo chemical reaction to get divanillyloxime. A synthetic pathway adapted from literature has been developed and is depicted on Scheme 59.^{18,32}



Scheme 59: Synthesis of methylated divanillylamine from divanillin

First, the alkylation of phenol moiety was performed in the presence of iodomethane and a weak base leading to methylated divanillin in a very good yield (>95%). Then, the oximation step was consisting in the reaction of aldehyde functions with hydroxylamine hydrochloride in the presence of sodium acetate to yield methylated divanillyloxime (MDVO) (>95%). The structure of this intermediate was confirmed by ¹H and ¹³C NMR spectroscopy (Figure 92).

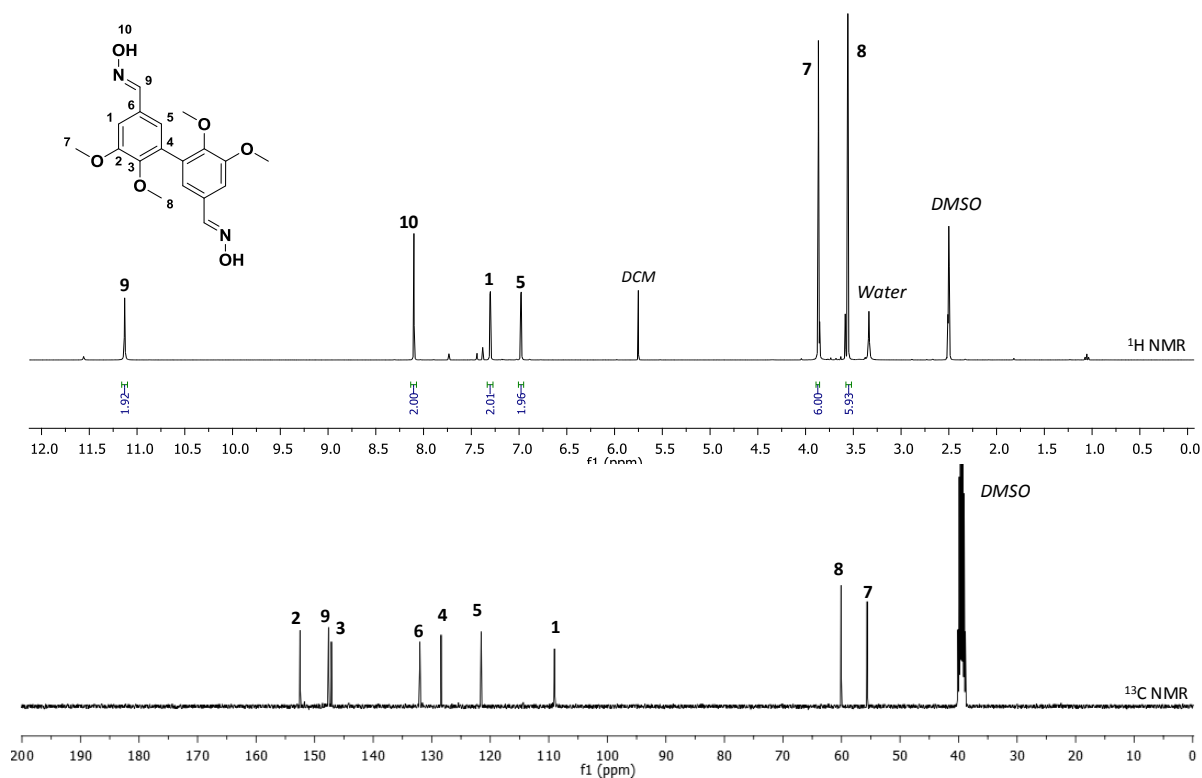


Figure 92: ¹H and ¹³C NMR spectra of methylated divanillyloxime in DMSO-d₆

The appearance of a signal at 3.67 ppm was attributed to the methylated phenols and new signals at 8.10 and 11.13 ppm were attributed to the oxime moieties of methylated divanillyloxime (MDVO).

Finally, the so formed oxime was then reduced into methylated divanillylamine (MDVA) by hydrogenation. The reaction was performed during 16 h at 70 °C under 12 bars of pressure in the presence of Nickel Raney in ethanol. Reduction of the oxime yielded a pale orange solid with a melting temperature of 69 °C (DSC). ¹H NMR spectrum of this orange solid demonstrated the disappearance of oxime signals at 8.10 and 11.13 ppm and the appearance of a new signal at 3.63 ppm, corresponding probably to alpha-protons of the amine (Figure 93). ¹³C NMR spectrum exhibited also a shift of the alpha-carbon of the oxime from 147.81 to 51.62 ppm, which confirmed the reduction of oxime moieties. The attribution of the signals was also confirmed by HSQC NMR spectroscopy. NMR Spectrum can be found at the end of this chapter in the annexes section. In addition, the MDVA was also characterized by FTIR. Figure 94a shows the infra-red spectra of MDVO and MDVA from which it is possible to observe the decrease of O-H stretching signal at 3227 cm⁻¹ and the disappearance of N-O stretching at 945 cm⁻¹, corresponding to the oxime moieties. Besides, ninhydrin test, which reveals amino groups, was realized and confirmed the presence of amine moieties on MDVA (Figure 94b).³⁹ MDVA was solubilized in ethanol with few milligrams of ninhydrin and the mixture was deposited on gel silica plate. After evaporating ethanol, a purple color change was revealed, indicating the presence of amino groups.

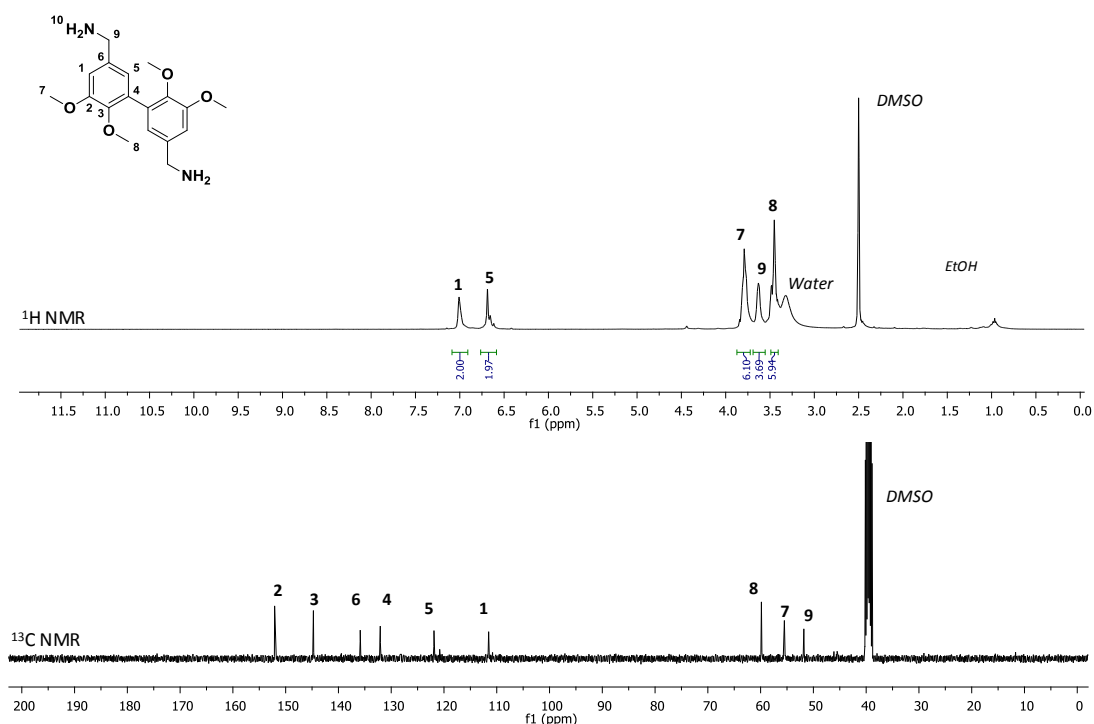


Figure 93: ¹H and ¹³C NMR spectroscopy of methylated divanillylamine in DMSO-d₆

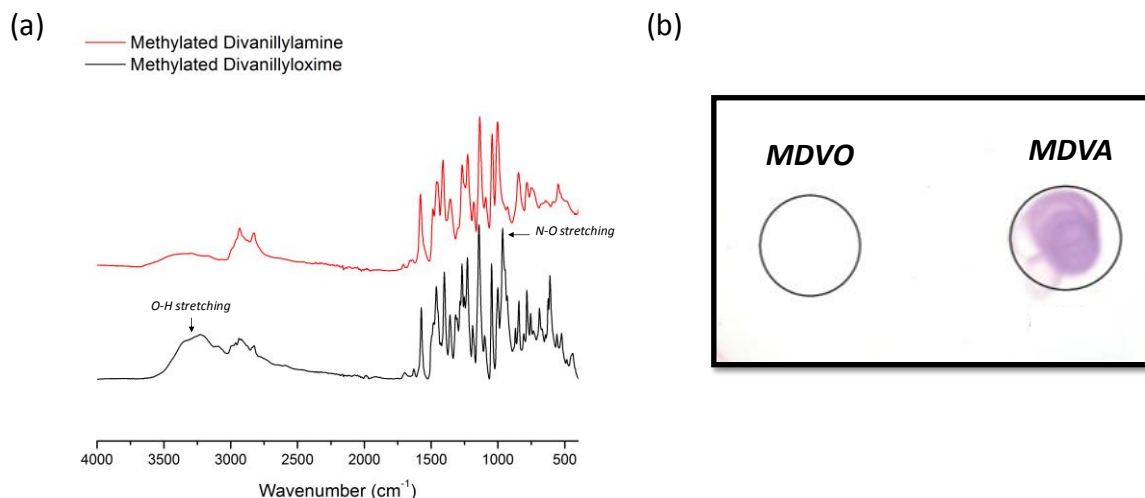
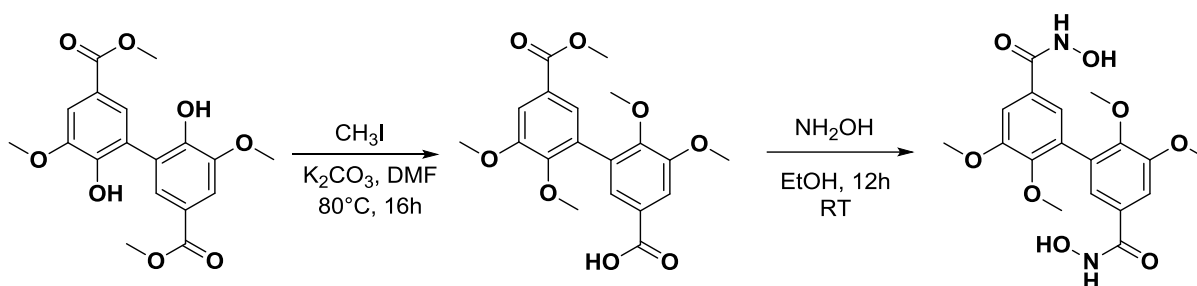


Figure 94: (a) FTIR spectra of MDVA and MDVO, (b) Ninhydrin test results of MDVO and MDVA on gel silica plate

III.2 Synthesis of amine from oxidative rearrangement

III.2.1 Lossen rearrangement

The *Lossen rearrangement* involves the synthesis of hydroxamic acid intermediate. A convenient method for the preparation of hydroxamic acids is the reaction of hydroxylamine with esters in basic conditions.^{37,40–42} As described in the previous chapter, methyl vanillate can easily be dimerised into the corresponding dimer. The synthesis of hydroxamic acid was attempted from methyl divanillate. A synthetic pathway adapted from literature has been developed and is depicted on Scheme 60.



Scheme 60: Synthesis of hydroxamic acid from methyl divanillate

Methyl divanillate was first alkylated using the same procedure described previously and was obtained in a good yield (>80%). Then, methylated diester was solubilized in methanol and a basic solution of hydroxylamine was added. More information about the experimental procedure can be found in the experimental section. As depicted on the Figure 95, the ¹H NMR spectra revealed the presence of at least two compounds. Indeed, majority of signals could be assigned to methylated divanillic acid and only small amount was attributed to the hydroxamic

acid moiety. In fact, it was estimated that 70% of the diester was converted into the diacid, whereas only 30% was converted into hydroxamic acid. One hypothesis to explain this result could be the competition between the saponification reaction of the ester and the nucleophilic reaction with hydroxylamine. However, after multiple attempts by changing experimental conditions, such as the nature of solvent, stoichiometry ratios between the reactants, reaction time and temperature, we were not able to synthesize in an efficient way the hydroxamic acid from divanillin.

Consequently, another strategy was employed for the preparation of amine. Ghosh *et al.* reported the one-pot synthesis of amines from aromatic oxime with hydroxytosyloxy iodobenzene (HTIB), in basic conditions.³⁸ HTIB is a hypervalent iodine, which is known as alternative to toxic metal oxidants in organic synthesis, such as oxidation of olefin, alpha-oxidation of carbonyl compounds or oxidative coupling.^{43,44}

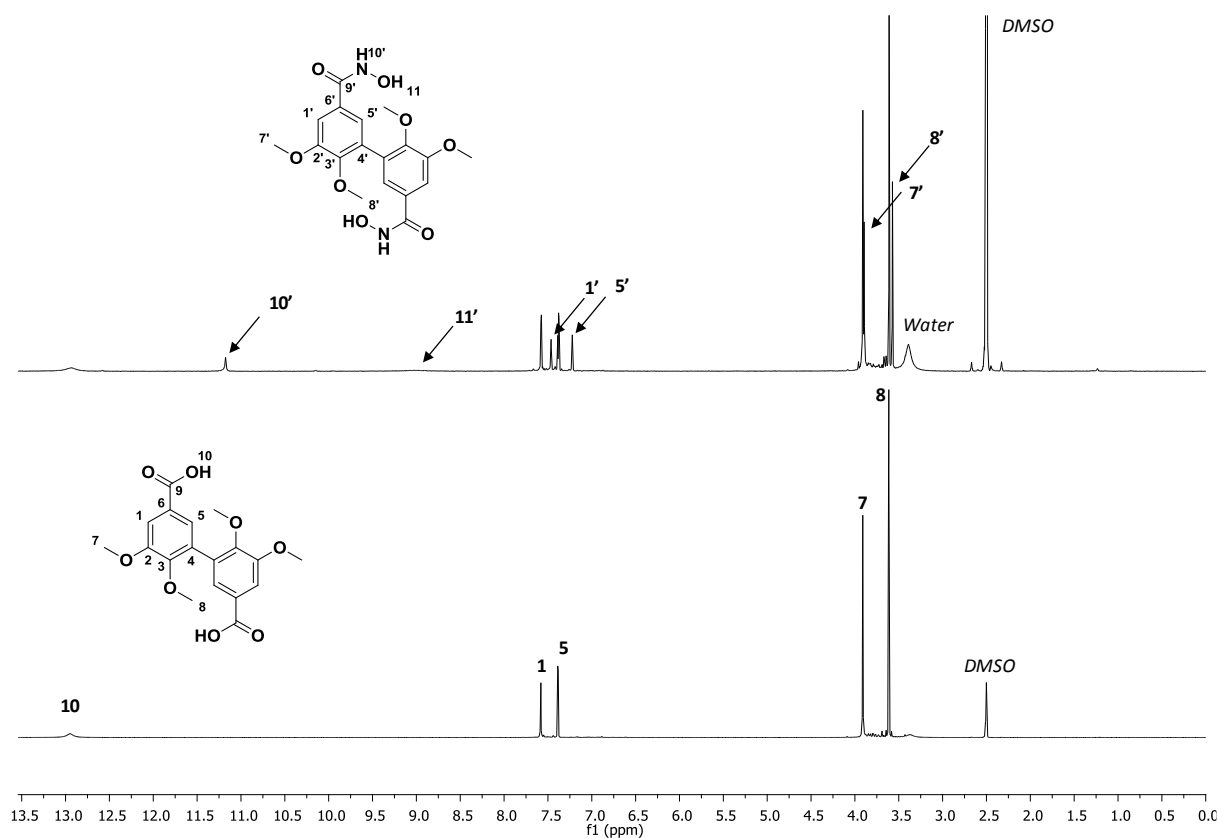
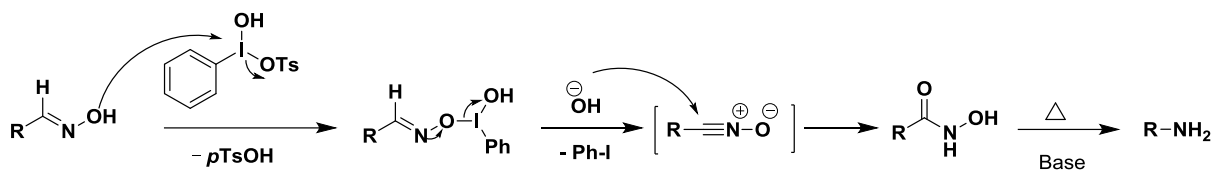


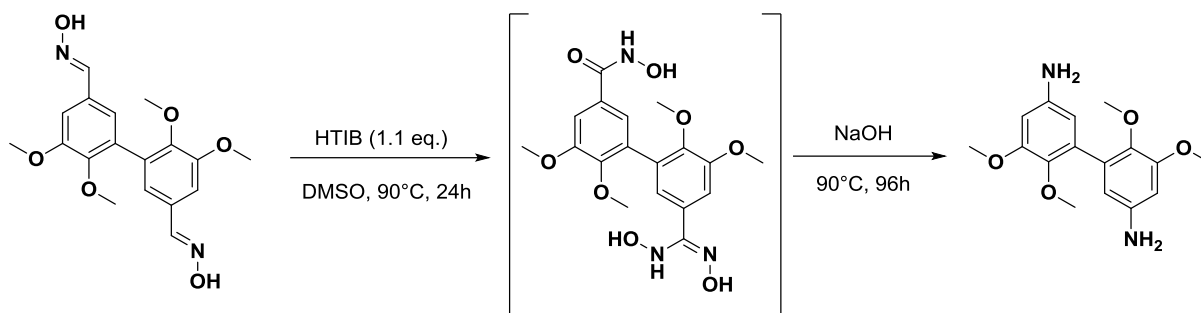
Figure 95: ¹H NMR spectra of divanillic acid (bottom) and of the reaction product of methyl divanillate with hydroxylamine (up) in DMSO-d₆

According to the authors, the oxime reacts with HTIB to form an intermediate hydroxamic acid, which then undergoes a self-propagative *Lossen rearrangement* to produce the desired amine (Scheme 61).



Scheme 61: Overall mechanism for the synthesis of amine from oxime

Therefore, methylated divanillyloxime, described in the previous section, was used as starting materials. Synthetic pathway adapted from literature has been developed and is depicted on Scheme 62. At the end of the reaction, an acid solution was added into the reaction mixture and a pale yellow solid was filtered off. The solid was solubilize in ethyl acetate and washed with demineralized water. Ethyl acetate was removed under reduced pressure and the product was characterized by ^1H NMR spectroscopy. Unfortunately, ^1H NMR spectrum of the solid was identified as the divanillic acid (Figure 96).



Scheme 62: Synthesis of 3,4-dimethoxydianiline from methylated divanillyloxime and HTIB

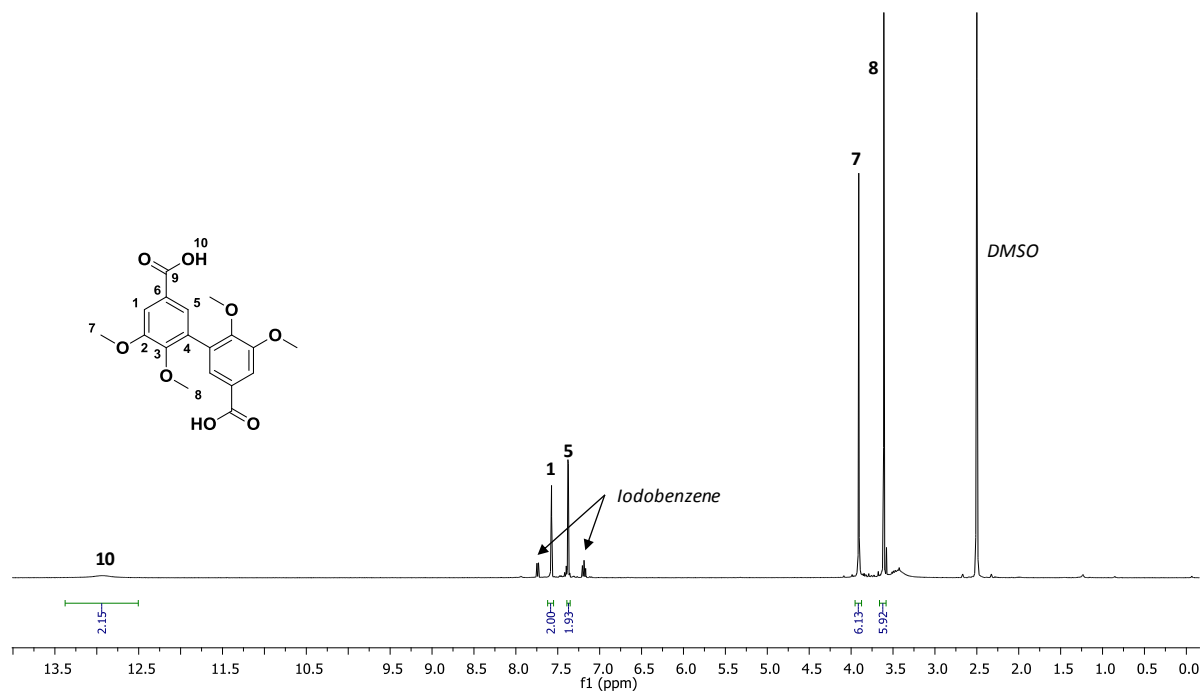
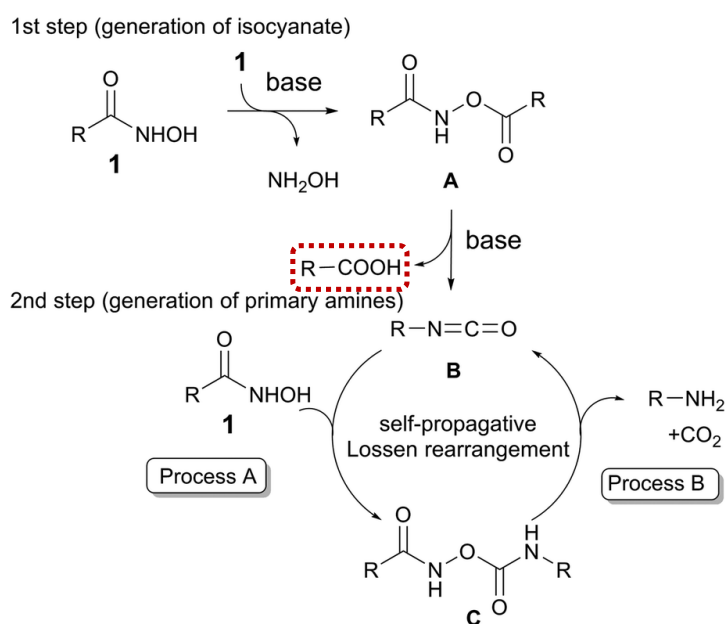


Figure 96: ^1H NMR spectrum of methylated divanillic acid obtained from divanillyloxime in DMSO-d₆

The hypothesis suggested to explain this result, could be found in the mechanism of the *self-propagative Lossen rearrangement* described by the authors (Scheme 63). First, two molecules of hydroxamic acids would react with each other in the presence of the base to give O-acyl hydroxamate. Subsequently, the rearrangement would normally give the isocyanate and release an equimolar quantity of carboxylic acid. However, the divanillic acid collected was recovered in a yield of 90%, meaning that the same amount of isocyanate should have been produced, which is impossible. Thus, the issue seems to occur before the synthesis of hydroxamate intermediate. In fact, hydroxamic acid could form the acid compound by the nucleophilic attack of hydroxide ions. In addition, this side-reaction could be induced by the difunctionality of the starting molecules which may disrupted the rearrangement and explain the formation of diacid compound instead of amine.



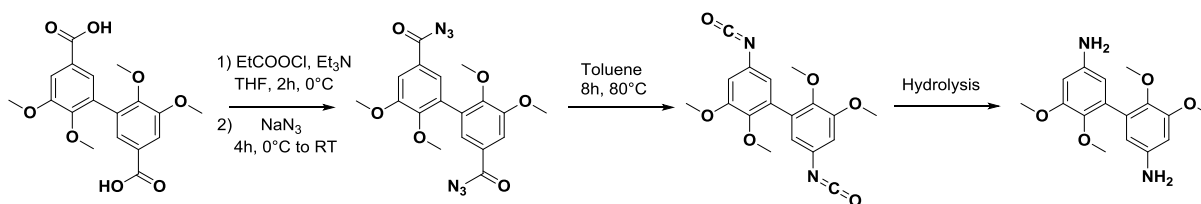
Scheme 63: Proposed mechanism of the self-propagative Lossen rearrangement³⁷

In conclusion, the synthesis of the targeted amine through a *Lossen rearrangement* could not be achieved. For that reason, another route for the preparation of aromatic primary amine was attempted.

III.2.2 Curtius rearrangement

The *Curtius rearrangement* involves the synthesis of an acyl azide intermediate. Usually carboxylic acids are precursors of acyl azides. As described in the previous chapter, methyl vanillate can easily be dimerised into the corresponding dimer and hydrolysed into the diacid. Indeed, divanillic acid would be a suitable bio-based precursor for the synthesis of amine compound through the *Curtius rearrangement*. The sequential synthetic pathway is summarised

in Scheme 64. All the intermediates were obtained without any further purification steps, except mentioned. ^1H and ^{13}C NMR spectroscopies were performed to confirm the structure of the synthesized products.



Scheme 64: Synthesis of 3,4-dimethoxydianiline from methylated divanillic acid

Methyl divanillate was first alkylated using the same procedure described previously and obtained in a good yield (>80%). Thereafter, the hydrolysis of the methylated diester with sodium hydroxide yielded the diacid (>90%). Methylated divanillic acid was then converted into acyl azide in a two-step reaction. Ethyl chloroformate was first reacted with the acid to form *in situ* an acyl chloride and sodium azide was then added to the mixture yielded the corresponding acyl azide (>60%). Finally, di-isocyanate was obtained in good yield (>80%) by simply heating the azide compound in dry toluene. The synthesis of these latter compounds was confirmed by ^1H NMR spectroscopy (Figure 97). The disappearance of the methyl ester protons at 3.38 ppm and the appearance of acid proton signals of carboxylic acid at 9.20 ppm were attributed to the formation of the methylated divanillic acid. In addition, acyl azide structure was confirmed by the disappearance of carboxylic signal at 9.20 ppm and finally the shift of the aromatic protons from 7.61 and 7.55 to 6.65 and 6.58 ppm was attributed to the so-formed di-isocyanate.

These compounds were also characterised by FTIR spectroscopy (Figure 98). Infrared spectra exhibited characteristic signal wavelengths of carboxylic acid at 1720 cm^{-1} ($-\text{C}=\text{O}$) and $2500\text{--}3300\text{ cm}^{-1}$ (O-H), acyl azide at 2140 cm^{-1} ($-\text{N}_3$) and isocyanate at 2278 cm^{-1} ($-\text{N}=\text{C}=\text{O}$).

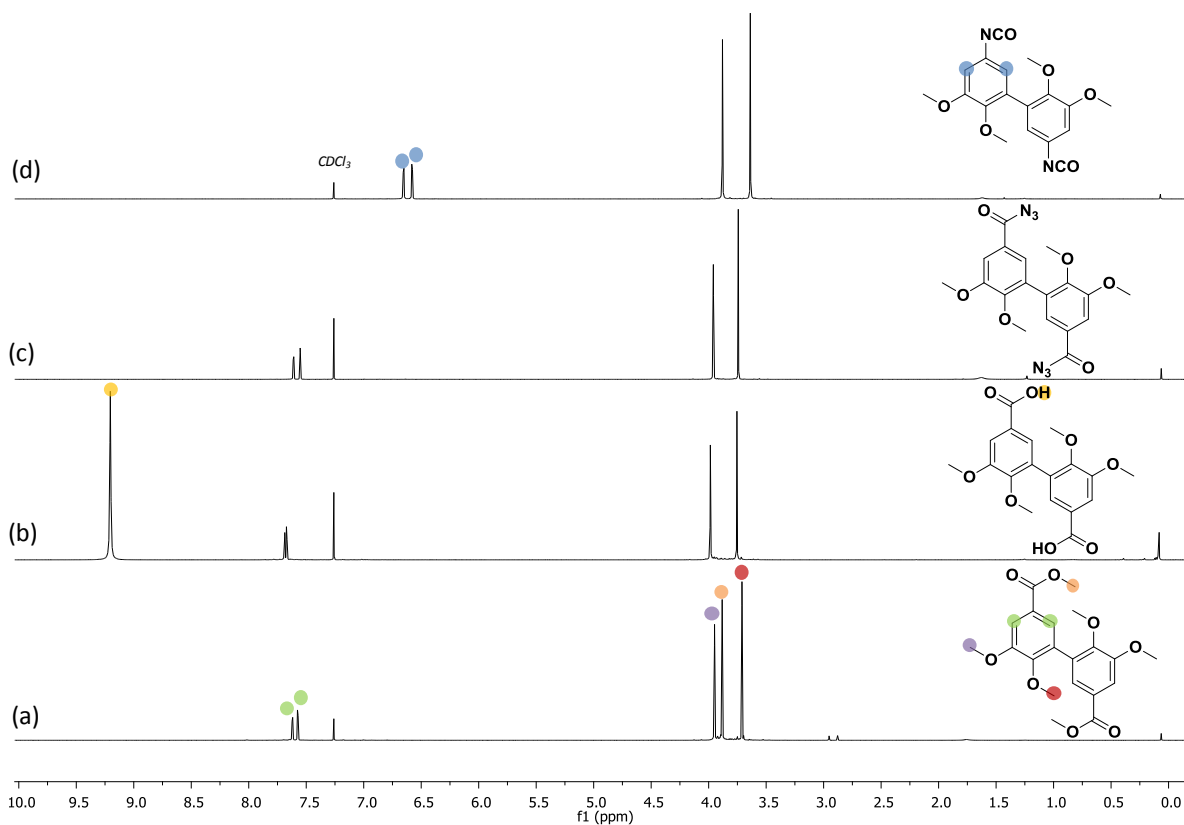


Figure 97: ^1H NMR spectra of (a) methylated diester, (b) methylated divanillic acid, (c) methylated di-acyl azide and (d) methylated di-isocyanate of vanillin in CDCl_3

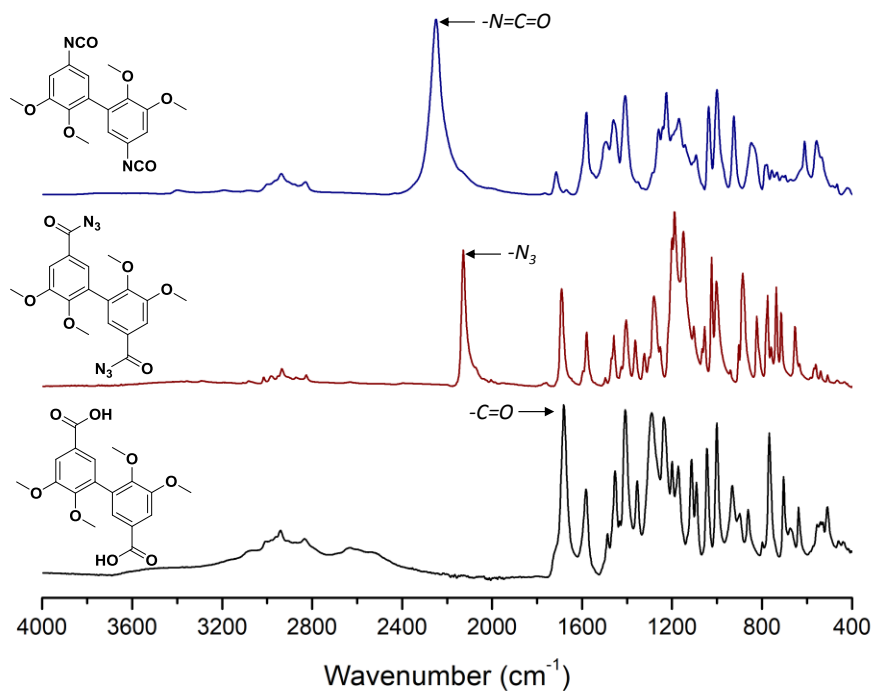


Figure 98: FTIR spectra of methylated divanillic acid, di-acyl azide and di-isocyanate

Finally, 3,4-dimethoxydianiline (DMAN) was recovered by hydrolysis in basic conditions of the corresponding di-isocyanate. After extraction with ethyl acetate and washing with water a mixture of brown and white solids was obtained. However, ^1H NMR spectroscopy of the reaction mixture revealed the presence of a by-product (Figure 99). These additional signals could be attributed to the formation of ureas, resulting of the side reaction of amine with the isocyanate or to the oxidation of the amines. Nevertheless, few milligrams of white solid were isolated and characterized by ^1H and ^{13}C NMR spectroscopy (Figure 100). ^1H NMR spectroscopy displayed protons signals of aromatic rings, amine moieties and alkylated hydroxyl groups at 6.23, 5.90, 4.79, 3.72 and 3.38 ppm, respectively. In addition, the disappearance of the C_9 carbon signals of isocyanate at 124.71 ppm, confirmed the obtention of the targeted diamine.

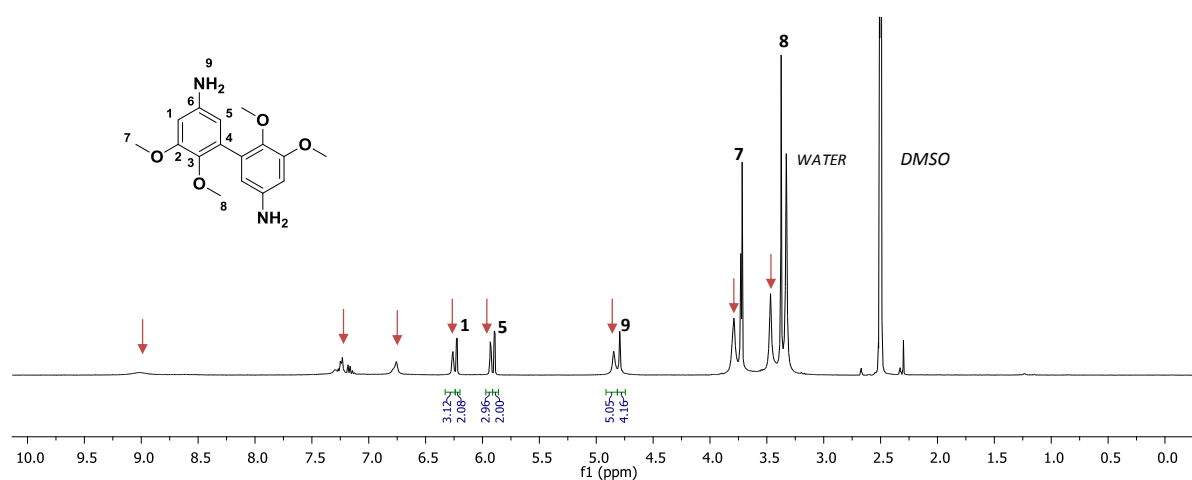


Figure 99: ^1H spectrum of 3,4-dimethoxydianiline before purification in DMSO-d_6

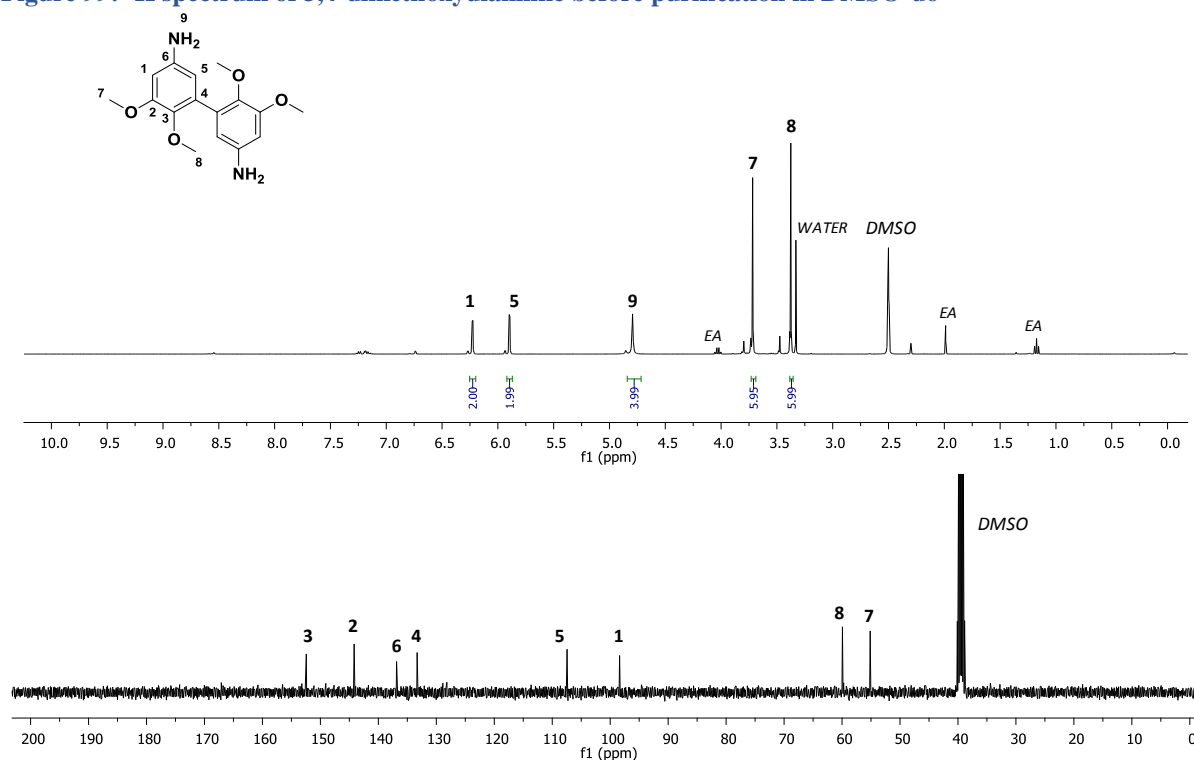


Figure 100: ^1H and ^{13}C NMR spectroscopy of 3,4-dimethoxydianiline in DMSO-d_6

DMAN was also characterised by FTIR spectroscopy (Figure 101). The following spectrum confirmed the absence of the isocyanate bands (-N=C=O) at 2278 cm^{-1} and the appearance of amino groups signals at 1610 , 3240 , 3370 and 3471 cm^{-1} .

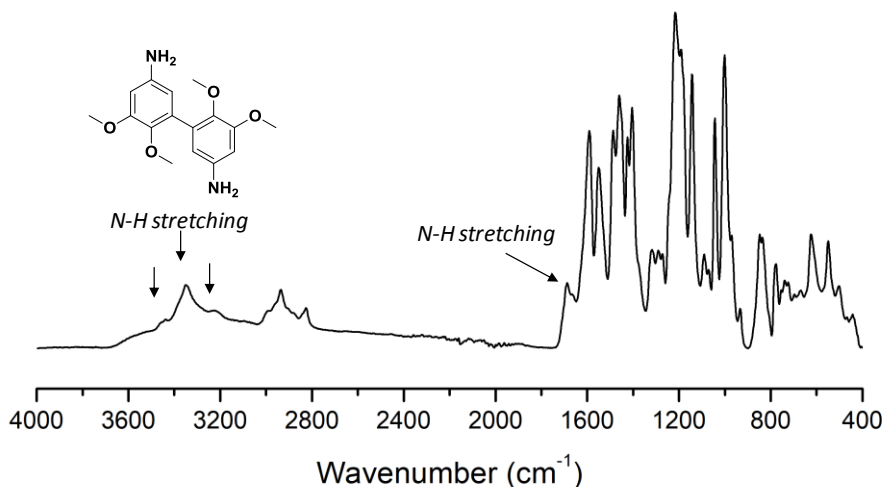


Figure 101: FTIR spectrum of 3,4-dimethoxydianiline

In conclusion, the *Curtius rearrangement* permitted to synthesize the 3,4-dimethoxydianiline from the acyl azide derived from the methyl divanillate. However, the last step of the synthesis was tedious and only a small amount of the desired product was identified as the diamine. Further investigations and optimisations in the hydrolysis step of isocyanate are required to recover the bio-based diamine in a better yield.

IV. Towards the synthesis of fully vanillin-based epoxy thermosets: Preliminary investigations

The previously synthesized di-amines, i.e. methylated divanillylamine (MDVA) and 3,4-dimethoxydianiline (DMAN) were used as curing agents for the synthesis of epoxy thermosets. As described in the previous chapter, the stoichiometric ratio leads to epoxy networks with the highest thermomechanical properties.⁴⁵ In this way, the ratio $r = 1$ has been used for the following formulations.

The DGEBA epoxy monomer was stirred vigorously with a stoichiometric amount of MDVA and the thermomechanical properties of the so-formed network were characterized by DSC and TGA. Bio-based thermoset was then compared with DGEBA/IPDA epoxy system. Results are summarised in the Table 34. Unfortunately, the characterization of bio-based epoxy networks, using DSC, showed a weak exothermic peak, corresponding to the reaction of amine with epoxy. In addition, no clear glass transition temperature was observed on this network (Figure

102a). One hypothesis to explain this result could be the poor homogeneity of the mixture between DGEBA and the solid MDVA, which impaired the stoichiometric ratio. Another explanation could be related to the side-oxidation of amine moieties of MDVA leading to the formation of amine oxide-type by-products.

Table 34: Thermomechanical properties of DGEBA cured with IPDA and MDVA

Epoxy/hardener	T _{Onset} (°C)	T _{Exotherm} (°C)	ΔH (J.g ⁻¹)	T _g (°C)	Char ₉₀₀ (%)
DGEBA/IPDA	73	111	430	152	8
DGEBA/MDVA	96	142	105	*	nd

*No T_g was clearly observed by DSC

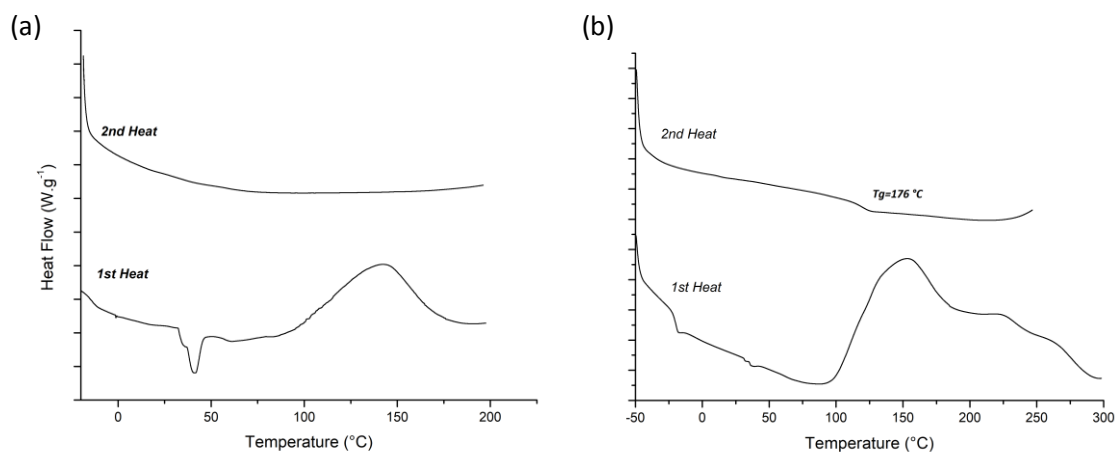


Figure 102: DSC thermograms of (a) DGEBA/MDVA and (b) DGEBA/DMAN

DGEBA epoxy monomer was also cured with bio-based DMAN. However, in view of the small amount recovered, crude DMAN was used for the curing reaction. Thermomechanical properties of network were then characterized and compared with DGEBA networks cured with DDS. Results are summarised in the Table 35 and Figure 102b. In comparison with conventional amine hardener DDS, epoxy network cured with DMAN exhibited similar properties. Indeed, glass transition temperature of thermoset cured with DMAN displayed a value 30 °C below the networks obtained with DDS. This difference can be explained by the presence of by-product compounds, which could impair the stoichiometric ratio. Interestingly, despite the presence of the by-product, the bio-based amine enabled to increase the char yield residue up to 28% (Figure 103). This statement could be explained by the C-C bonding between the two aromatic rings of DMAN, which could favour the formation of char and thus increased the residual content.

At last, a bio-based polyglycidylether TetraGEDVA, previously described in chapter 2, was cured with crude DMAN. In this way, a fully bio-based epoxy thermoset was successfully obtained. Bio-based epoxy networks exhibited promising thermomechanical properties with glass transition temperature of 212 °C and char residue of 48% (Figure 103). However, enthalpy is much lower than the enthalpy of the reaction between TetraGEDVA and DDS. Once again, the presence of undefined compounds in crude DMAN and the inhomogeneity of the mixture could explained this difference.

Table 35: Thermomechanical properties of DGEBA and TetraGEDVA cured with DDS and DMAN

Epoxy/hardener	T _{Onset} (°C)	T _{Exotherm} (°C)	ΔH (J.g ⁻¹)	ΔH (kJ.mol ⁻¹)	T _g (°C)	Char ₉₀₀ (%)
DGEBA/DDS	184	226	355	83	204	16
DGEBA/DMAN	99	153	393	95	176	28
TetraGEDVA/DDS	165	208	459	89	-	48
TetraGEDVA/DMAN	110	193	183	39	212	48

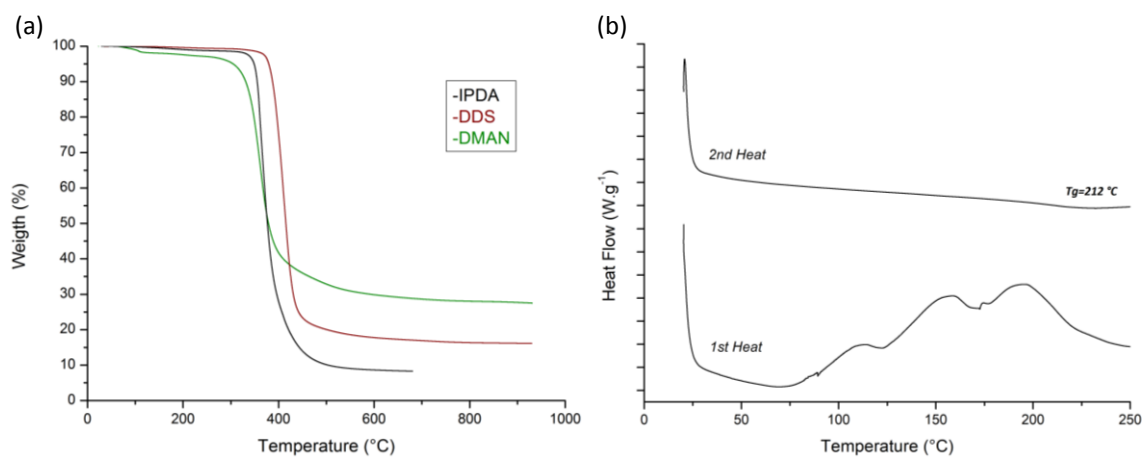


Figure 103: (a) TGA thermograms of DGEBA cured with IPDA, DDS and DMAN, (b) DSC thermograms of TetraGEDVA cured with DMAN

V. Conclusion

In conclusion, the first section of this chapter consisted in a literature survey of amine-type curing agents. This analysis revealed a lack of efficient alternative to conventional amine hardeners. Therefore, the synthesis of bio-based curing agent from divanillin derivatives was investigated. Three routes were chosen to achieve the synthesis of this diamine.

The first one consisted in the reduction of divanillyloxime obtained from divanillin. The synthesis yielded to methylated divanillylamine (MDVA) and the thermomechanical properties of epoxy precursors cured with MDVA were investigated. DGEBA epoxy prepolymers were thus cured with MDVA and the networks obtained were compared with the conventional DGEBA/IPDA system. Unfortunately, the characterization by DSC showed a weak exothermic peak, corresponding to the reaction of amine with epoxy, but no clear glass transition temperature was observed on this network.

Then, the synthesis of bio-based amine from hydroxamic acid was attempted through the *Lossen rearrangement*. Divanilic acid and divanillyloxime were used as bio-based starting materials. However, in both cases, this pathway did not permit to obtain the targeted aromatic di-amine.

Finally, the 3,4-dimethoxyaniline (DMAN) was synthesized using the oxidative rearrangement of *Curtius*. From methyl divanillate and through the synthesis of acyl azide and isocyanate intermediates, the hydrolysis of this latter yielded to 3,4-dimethoxyaniline (DMAN). However, the hydrolysis step was tedious and the corresponding amine failed to be isolated efficiently. Nevertheless, crude DMAN was used as curing agent in the polyaddition reaction with DGEBA. Interestingly, the so-formed semi bio-based thermoset exhibited a glass transition temperature of 176 °C against 204 °C for the conventional DGEBA/DDS system. Moreover, the DMAN permitted to double the char content of the network comparing to DGEBA/DDS network cured in the same conditions. Moreover, a fully bio-based epoxy thermoset was obtained by curing tetraglycidylether of divanillyl alcohol (TetraGEDVA) with DMAN. The thermomechanical properties obtained were promising as the network exhibited a glass transition temperature of 212 °C and a char residue of 48%.

Through this chapter, the synthesis of new amine-type curing agent was attempted from vanillin-based starting material. Nevertheless, further optimisations in the synthetic pathways described are necessary in order to have a better appreciation of the potential of these new bio-based aromatic diamines.

VI. References

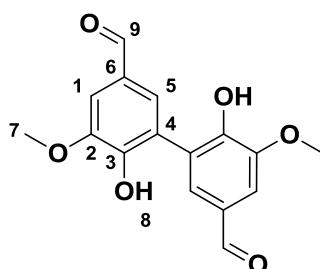
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VII. Experimental

Procedure for dimerization of phenols

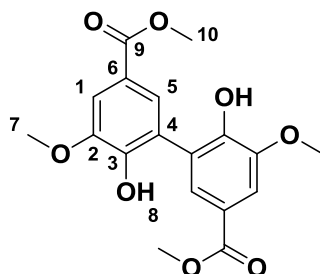
A solution of vanillin (5mmol) in acetone (20 mL) was added to NaOAc buffer (180 mL, 0.1 M, pH 5.0). The solution was saturated in O₂ for 5 min. Laccase from *Trametes versicolor* (20 U, 12.4 mg) was added and the reaction was stirred at room temperature for 24 h. The precipitate was filtered off the solution and the product dried overnight at 80 °C under vacuum. Yield: 90%



¹H NMR (400 MHz, DMSO, δ (ppm)): δ 9.69 (s, H₉), 7.57 (d, H₁), 7.16 (d, H₅), 3.76 (s, H₇).

¹³C NMR (400 MHz, DMSO, δ (ppm)): δ 191.62 (s, C₉), 150.88 (s, C₃), 148.61 (s, C₂), 128.64 (s, C₆), 128.21 (s, C₄), 125.02 (s, C₅), 109.6 (s, C₁), 56.25 (C₇).

The same procedure was applied for methyl vanillate. Yield: 90%

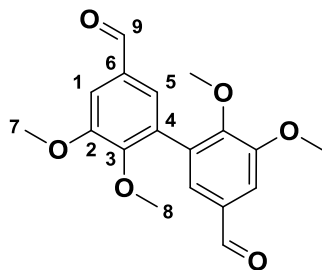


¹H NMR (400 MHz, DMSO, δ (ppm)): δ 9.51 (s, H₈), 7.46 (d, H₁), 7.45 (d, H₅), 3.90 (s, H₇), 3.80 (s, H₁₀).

¹³C NMR (400 MHz, DMSO, δ (ppm)): δ 166.09 (s, C₉), 148.88 (s, C₃), 147.47 (s, C₂), 125.40 (s, C₅), 124.36 (s, C₆), 119.48 (s, C₄), 110.92 (s, C₁), 56.01 (s, C₇), 51.79 (s, C₁₀).

Procedure for methylation

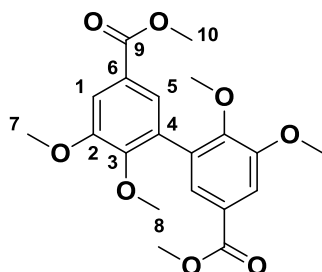
26 mmol of divanillin and 15,2 g of potassium carbonate (110 mmol) were dissolved in 120 mL of DMF. 9,6 ml of iodomethane (158 mmol) were slowly added to the mixture. After 15 h at 80 °C, mixture was filtered and the resulting solution poured into cold water. The methylated compound, which precipitated was filtered off and dried under vacuum. Yield: 80%.



^1H NMR (400 MHz, DMSO, δ (ppm)): δ 9.94 (d, H₉), 7.58 (d, H₁), 7.45 (d, H₅), 3.95 (s, H₇), 3.67 (s, H₈).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 191.76 (s, C₉), 152.88 (s, C₂), 151.52 (s, C₃), 131.81 (s, C₆), 131.56 (s, C₄), 126.09 (s, C₅), 111.36 (s, C₁), 60.43 (s, C₈), 55.99 (s, C₇).

The same procedure was applied for methylated diester. Yield: 80%

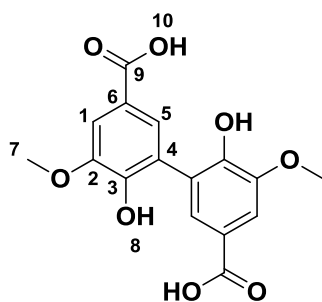


^1H NMR (400 MHz, CDCl₃, δ (ppm)): δ 7.62 (d, H₁), 7.57 (d, H₅), 3.95 (s, H₇), 3.88 (s, H₁₀), 3.71 (s, H₈).

^{13}C NMR (400 MHz, CDCl₃, δ (ppm)): δ 166.79 (s, C₉), 152.54 (s, C₃), 151.06 (s, C₂), 131.87 (s, C₆), 125.30 (s, C₄), 125.10 (s, C₅), 113.09 (s, C₁), 60.95 (s, C₈), 56.14 (s, C₇), 52.25 (C₁₀).

Procedure for ester hydrolysis

10 mmol of methylated diester were dissolved in 30 mL of methanol. 3g of sodium hydroxide (75 mmol) were slowly added to the mixture and warmed to reflux during 4h. After cooling at room temperature, the solution is acidified with HCl to pH=3. The precipitate was filtered off and the product dried overnight at 80 °C under vacuum. Yield: 90%

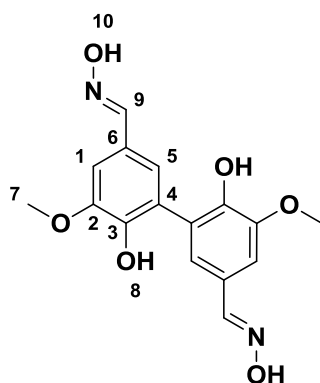


^1H NMR (400 MHz, DMSO, δ (ppm)): δ 9.39 (s, H₈), 7.45 (d, H₁), 7.41 (d, H₅), 3.89 (s, H₇).

^{13}C NMR (400 MHz, DMSO, δ (ppm)): δ 167.18 (s, C₉), 148.36 (s, C₃), 147.22 (s, C₂), 125.44 (s, C₆), 124.19 (s, C₄), 120.44 (s, C₅), 111.05 (s, C₁), 55.89 (s, C₇).

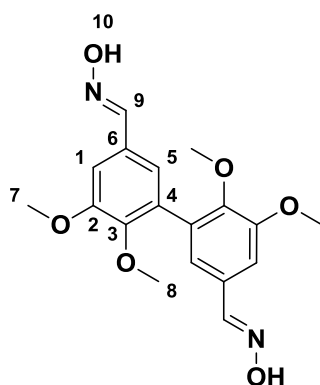
Procedure for oximation

1 g of hydroxylamine hydrochloride (7 mmol) and 2 g of sodium acetate (12 mmol) were solubilised in 20 mL of ethanol (+4 mL of water). 2 g of divanillin or methylated divanillin (6 mmol) were added to the mixture. After 2 h of magnetic stirring at 100 °C, the product is extracted with dichloromethane and washed with water and dried under vacuum. Yield: 85%



^1H NMR (400MHz, DMSO, δ (ppm)): δ 10.83 (s, H₁₀), 8.84 (s, H₈), 8.02 (s, H₉), 7.18 (s, H₄), 6.94 (s, H₅), 3.85 (s, H₇).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 148.00 (s, C₉), 147.62 (s, C₂), 145.48 (s, C₃), 125.42 (s, C₆), 123.58 (s, C₄), 123.02 (s, C₅), 107.21 (s, C₁), 56.12 (s, C₇).

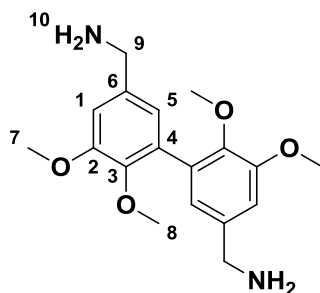


^1H NMR (400MHz, DMSO, δ (ppm)): δ 11.58 (s, H₁₀), 8.10 (s, H₉), 7.30 (d, H₁), 6.98 (d, H₅), 3.87 (s, H₇), 3.56 (s, H₈).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 152.66 (s, C₂), 147.81 (s, C₉), 147.25 (s, C₃), 131.87 (s, C₆), 128.69 (s, C₄), 121.69 (s, C₅), 108.78 (s, C₁), 59.88 (s, C₈), 55.6 (s, C₇).

Procedure for reduction of oxime

1 g of methylated divanillyloxime (2,7 mmol) and 1 mL of nickel Raney (slurry) were added in 30 mL of ethanol. The mixture was set into pressurised reactor with 10 bars of dihydrogen. After 15 h at 70 °C, the mixture was filtered and ethanol was removed under vacuum. The resulting product is extracted with dichloromethane and washed with water. Dichloromethane was removed from the organic phase under vacuum. Yield: 70%



^1H NMR (400MHz, DMSO, δ (ppm)): δ 7.04 (m, H₅), 6.69 (m, H₁), 3.79 (m, H₈), 3.63 (s, H₇), 3.48 (m, H₉).

^{13}C NMR (400MHz, DMSO, δ (ppm)): δ 151.75 (s, C₂), 144.46 (s, C₃), 136.04 (s, C₆), 132.36 (s, C₄), 121.78 (s, C₅), 111.41 (s, C₁), 60.05 (s, C₈), 55.65 (s, C₇), 51.62 (s, C₉).

Procedure for hydroxamic acid synthesis from ester

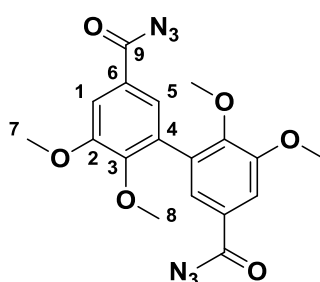
1,4 g of hydroxylamine hydrochloride were solubilised in 10 mL of MeOH and 2,3g of potassium hydroxide were dissolved in 10 mL of MeOH. Both preparations were cooled down in ice, and the alkali solution was added to the hydroxylamine solution under stirring. The precipitated salts were removed by filtration and the filtrate was added to 2g of methylated diester. Additional potassium hydroxide was added to increase the pH>10 and the mixture was stirred during 12 hours at room temperature. An aqueous solution of HCl (2M) was then added to the mixture and precipitation occurred. The solid was filtered off and washed with water.

Procedure for hydroxamic acid synthesis from oxime

1 g of methylated divanillyloxime (3 mmol) and 2,3 g of HTIB (6 mmol) were solubilised in 2 mL of DMSO and stirred at 90°C. After 24h, 0,8 g of sodium hydroxide was added to the mixture and stirred during 96h. Finally, the reaction mixture was cooled down to room temperature and 5 mL of aqueous solution of HCl (5M) was added. Precipitation occurred and the solid was filtered off and washed with water.

Procedure for acyl azide synthesis

3 mmol of methylated divanillic acid were solubilized into mixture of 15 mL of THF and 5 mL of water. The reaction mixture was cooled to 0 °C and 2,4 mL of triethylamine in 4 mL of THF was added drop-wise. 1,8 mL of ethylchloroformate was then added to the mixture and stirred during 2h at 0 °C. A solution of sodium azide (1,2g in 4 mL of water) was added drop-wise into the reaction mixture and stirred at 0 °C for 2 h and then at room temperature for 8 h. Cold water was added gradually to the reaction mixture to precipitate the solid. The precipitate was filtered off. The product was then dissolved in DCM, washed with water and dried over anhydrous magnesium sulfate. Dichloromethane was removed from the organic phase under vacuum. Yield: 60%

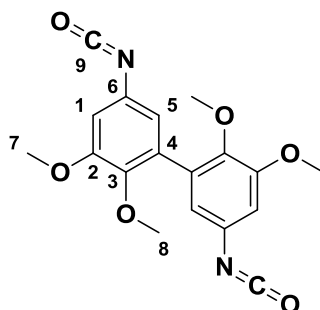


$^1\text{H NMR}$ (400 MHz, CDCl_3 , δ (ppm)): δ 7.61 (d, H_1), 7.55 (d, H_5), 3.96 (s, H_7), 3.74 (s, H_8).

$^{13}\text{C NMR}$ (400 MHz, CDCl_3 , δ (ppm)): δ 171.85 (s, C_9), 152.79 (s, C_3), 152.39 (s, C_2), 131.69 (s, C_6), 125.81 (s, C_4), 125.23 (s, C_5), 112.78 (s, C_1), 61.10 (s, C_8), 56.22 (s, C_7).

Procedure for isocyanate synthesis

Into a Schlenk tube under nitrogen atmosphere, 0.5 mmol of diazide were solubilised in 3 mL of dry toluene and stirred. The reaction mixture was heated at 80 °C for 8 h. The toluene was removed under reduced pressure at 60 °C and white oily compound was obtained. Yield: 80%

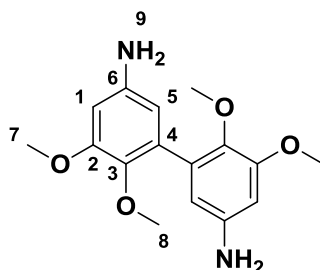


$^1\text{H NMR}$ (400 MHz, CDCl_3 , δ (ppm)): δ 6.65 (d, H_1), 6.58 (d, H_5), 3.88 (s, H_7), 3.64 (s, H_8).

$^{13}\text{C NMR}$ (400 MHz, CDCl_3 , δ (ppm)): δ 153.41 (s, C_3), 144.82 (s, C_2), 132.46 (s, C_6), 128.72 (s, C_4), 124.71 (s, C_9), 118.91 (s, C_5), 108.86 (s, C_1), 60.99 (s, C_8), 56.13 (s, C_7).

Procedure for isocyanate hydrolysis

3 mmol of a potassium hydroxide solution were added to 0.75 mmol of di-isocyanate in solution in toluene. The mixture was stirred 12h at 80 °C. Toluene was removed under reduced pressure. The product was solubilised in ethyl acetate and washed with water. Ethyl acetate was removed from the organic phase under vacuum. Yield: <10%



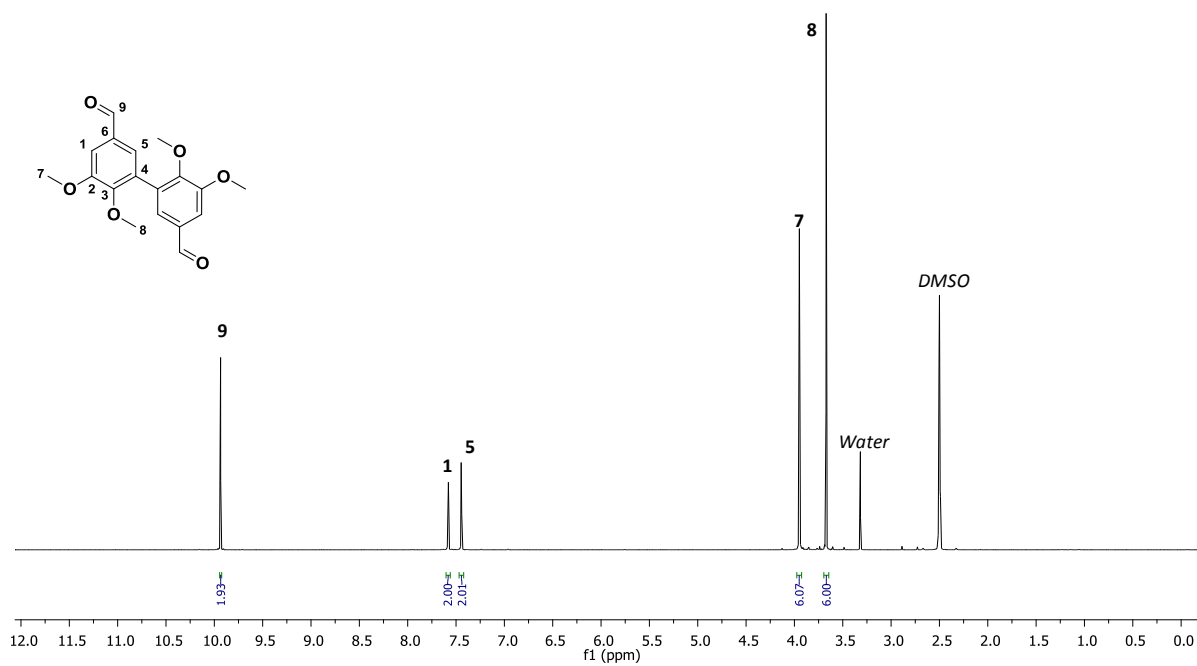
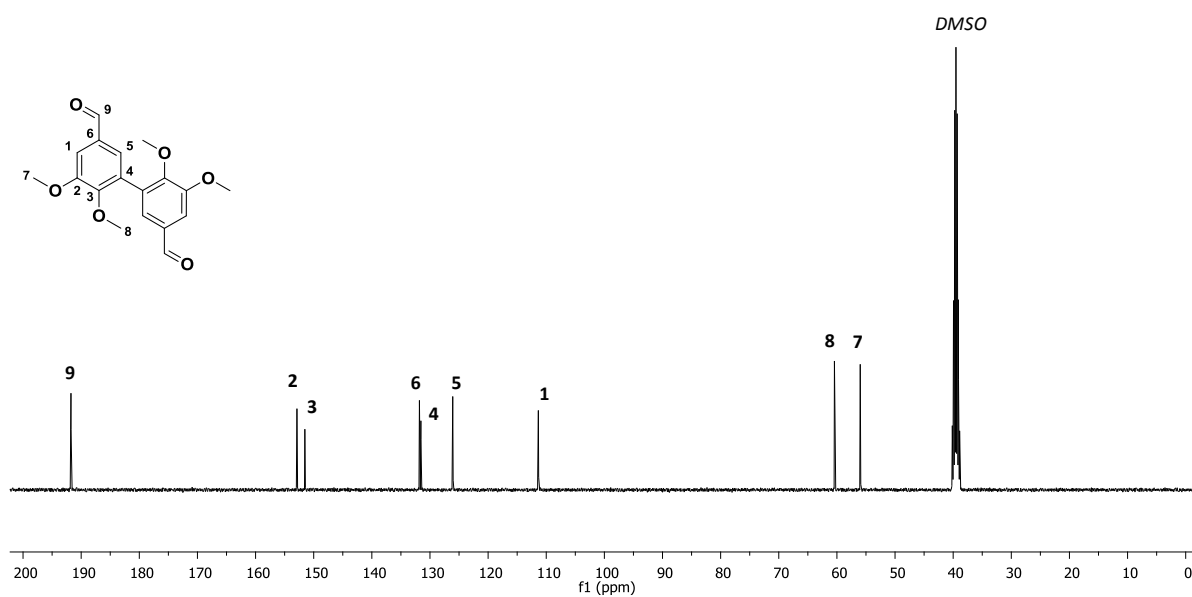
^1H NMR (400 MHz, DMSO, δ (ppm)): δ 6.23 (d, H₁), 5.90 (d, H₅), 4.79 (s, H₉), 3.72 (s, H₇), 3.38 (s, H₈).

^{13}C NMR (400 MHz, CDCl₃, δ (ppm)): δ 152.47 (s, C₃), 144.22 (s, C₂), 136.90 (s, C₆), 133.35 (s, C₄), 107.48 (s, C₅), 98.42 (s, C₁), 59.97 (s, C₈), 55.18 (s, C₇).

Procedure for epoxy resin

Epoxy monomers were mixed vigorously with stoichiometric amount ($r=1$) of IPDA, DDS, MDVA or DMAN. The mixture was then placed into an aluminium DSC pan.

VIII. Annexes

Figure S16: ¹H NMR spectrum of methylated divanillin in DMSO-d₆Figure S17: ¹³C NMR spectrum of methylated divanillin in DMSO-d₆

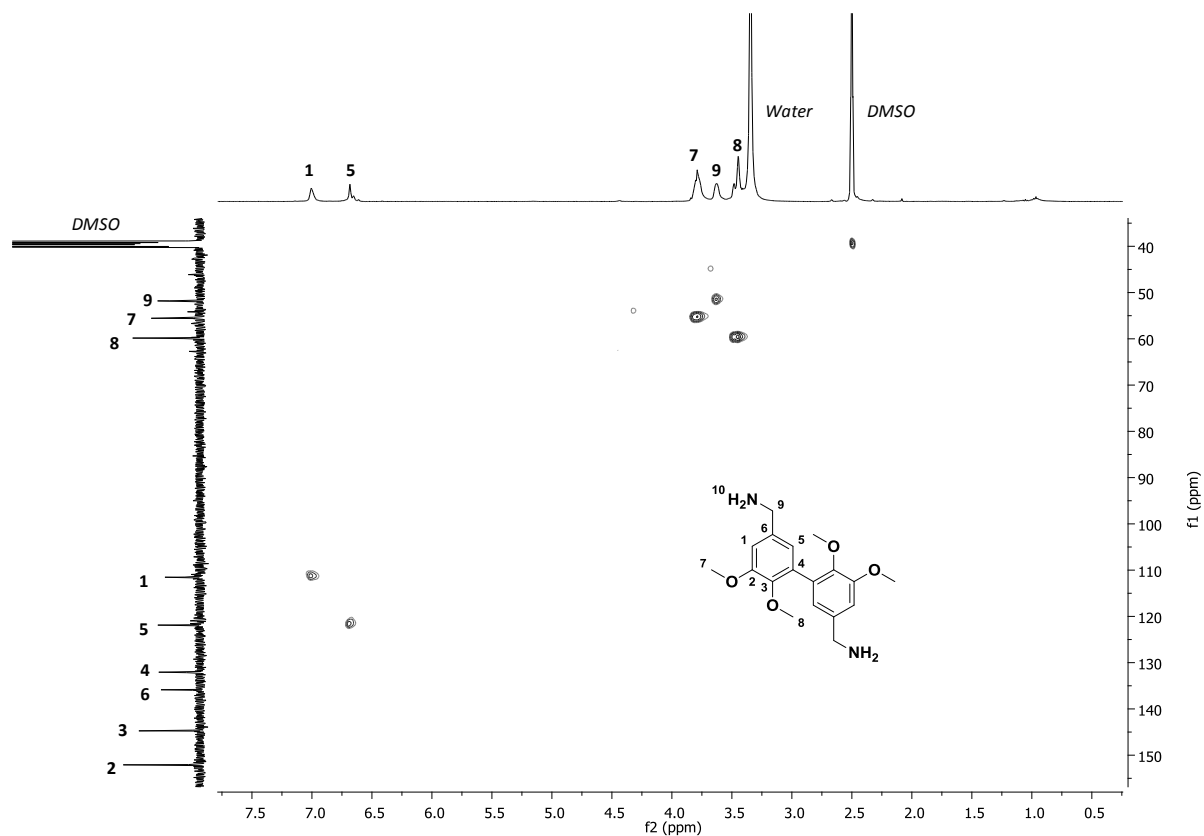


Figure S18: ¹H - ¹³C HSQC NMR spectrum of methylated divanillyl amine in DMSO-d₆

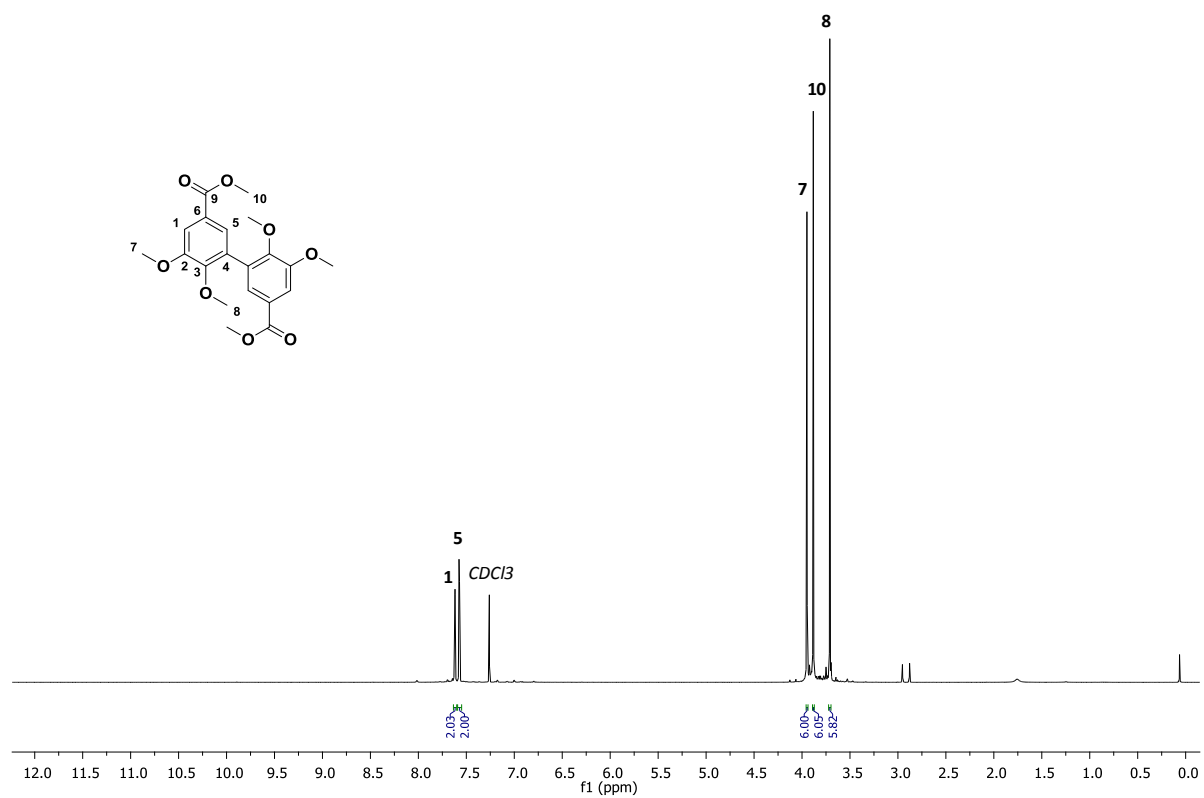


Figure S19: ¹H NMR spectrum of methylated methyl divanillate amine in CDCl₃

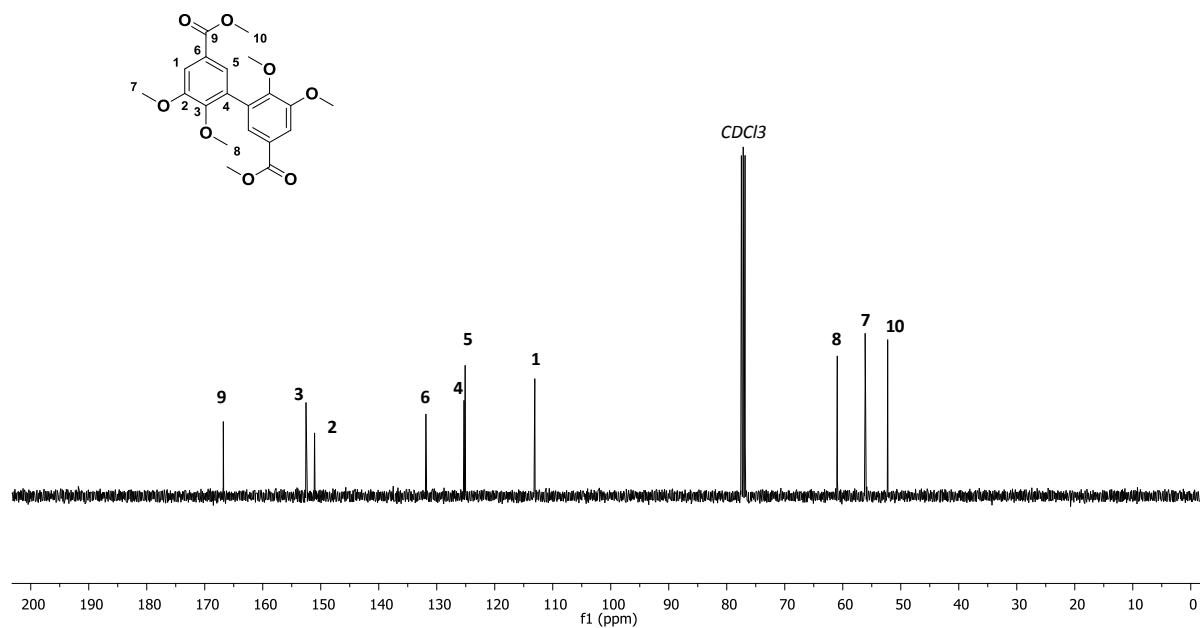


Figure S20: ^{13}C NMR spectrum of methylated methyl divanillate amine in CDCl_3

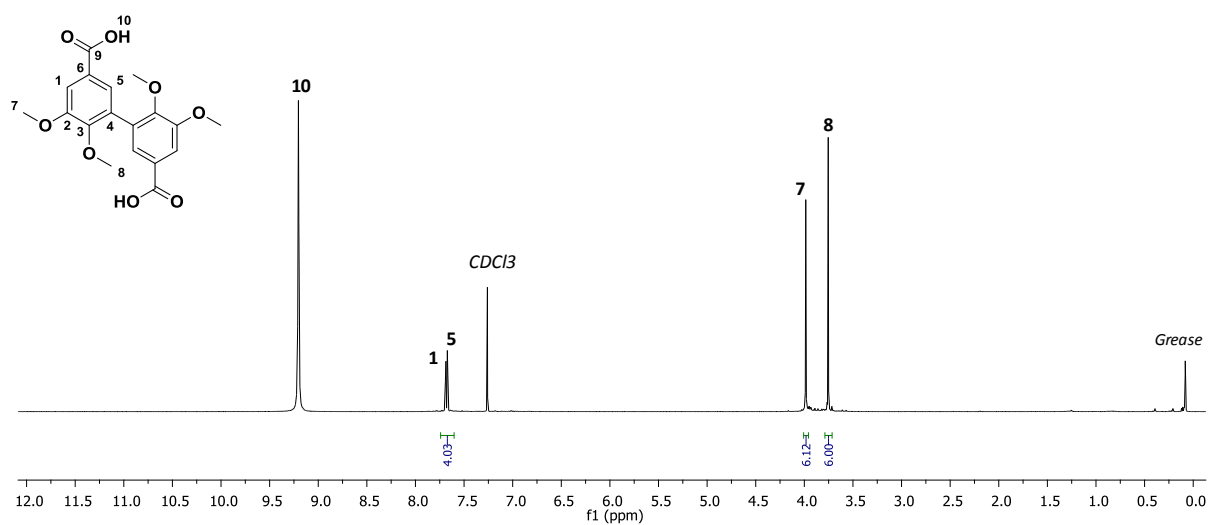


Figure S21: ^1H NMR spectrum of methylated divanillic acid in CDCl_3

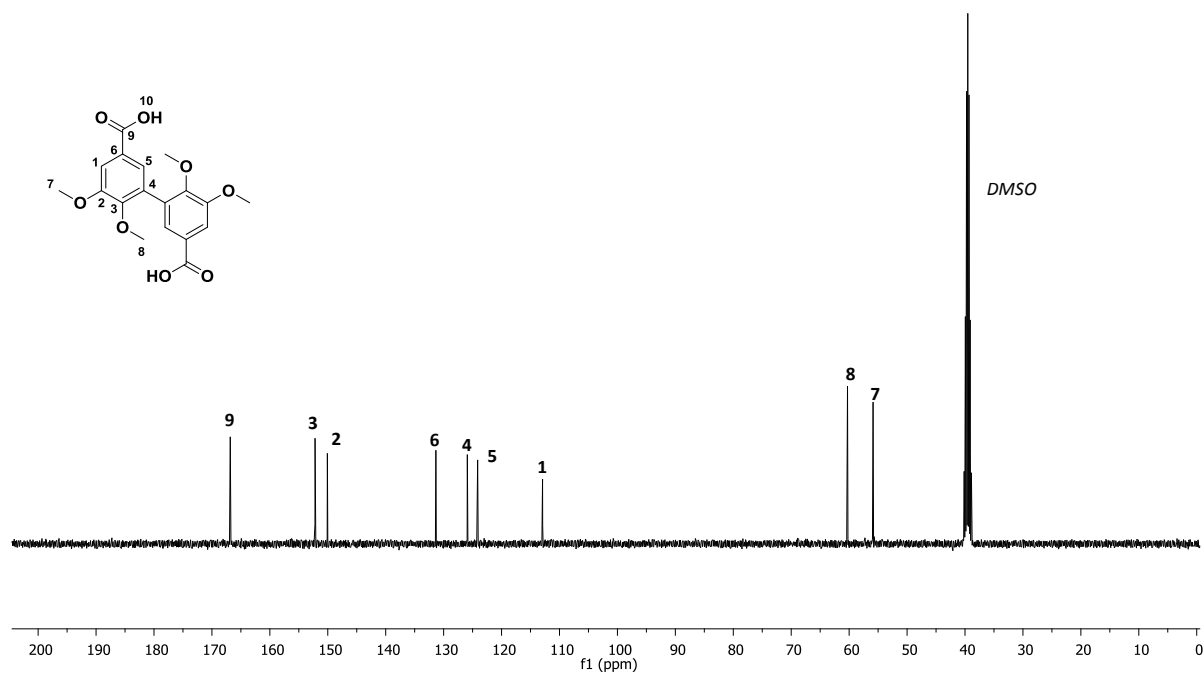


Figure S22: ^{13}C NMR spectrum of methylated divanillic acid in DMSO-d_6

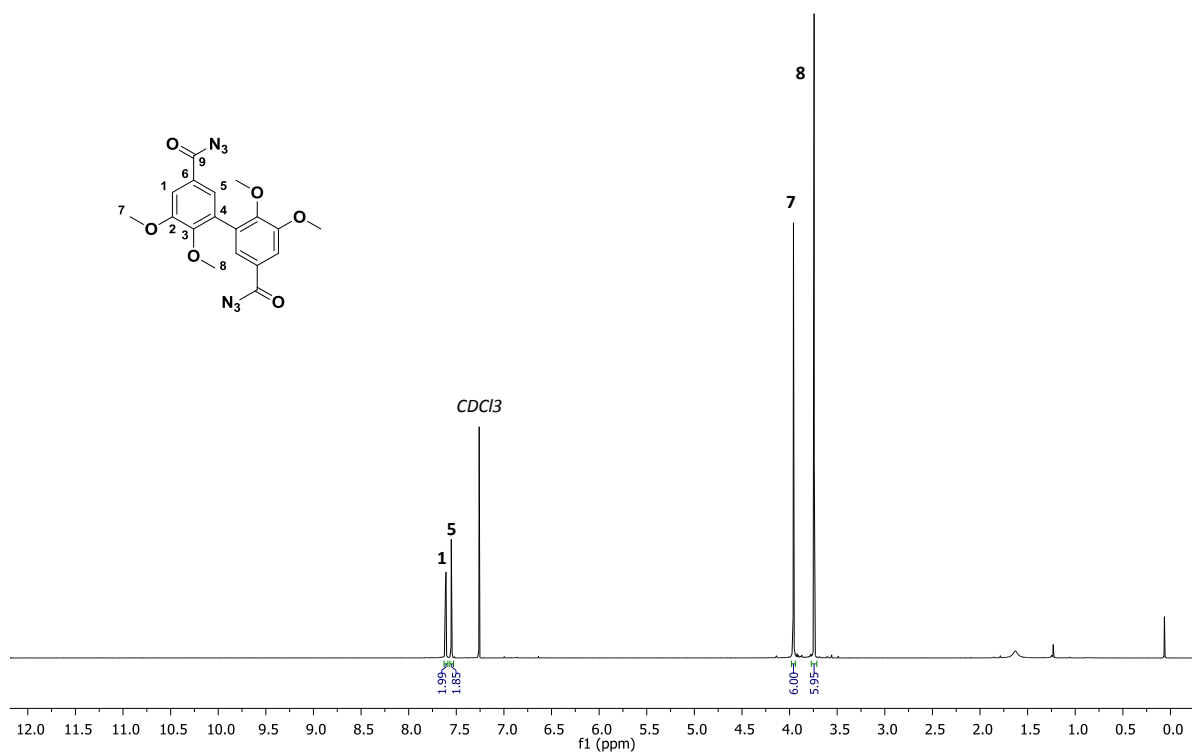


Figure S23: ^1H NMR spectrum of methylated divanillin acyl azide in CDCl_3

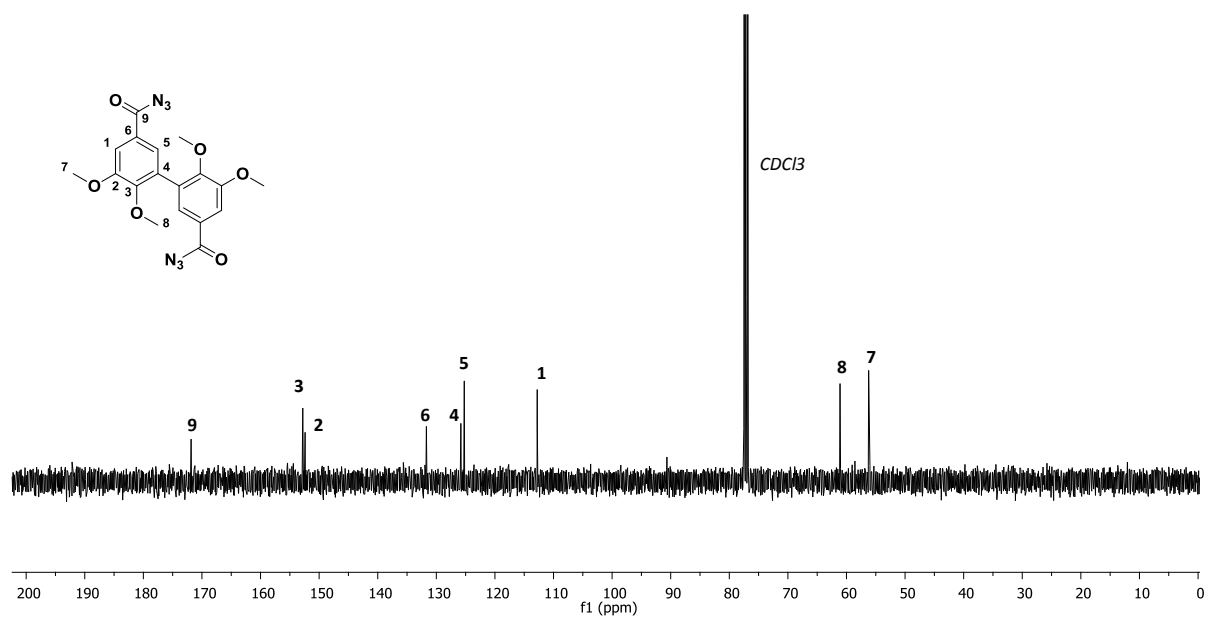


Figure S24: ^{13}C NMR spectrum of methylated divanillin acyl azide in CDCl_3

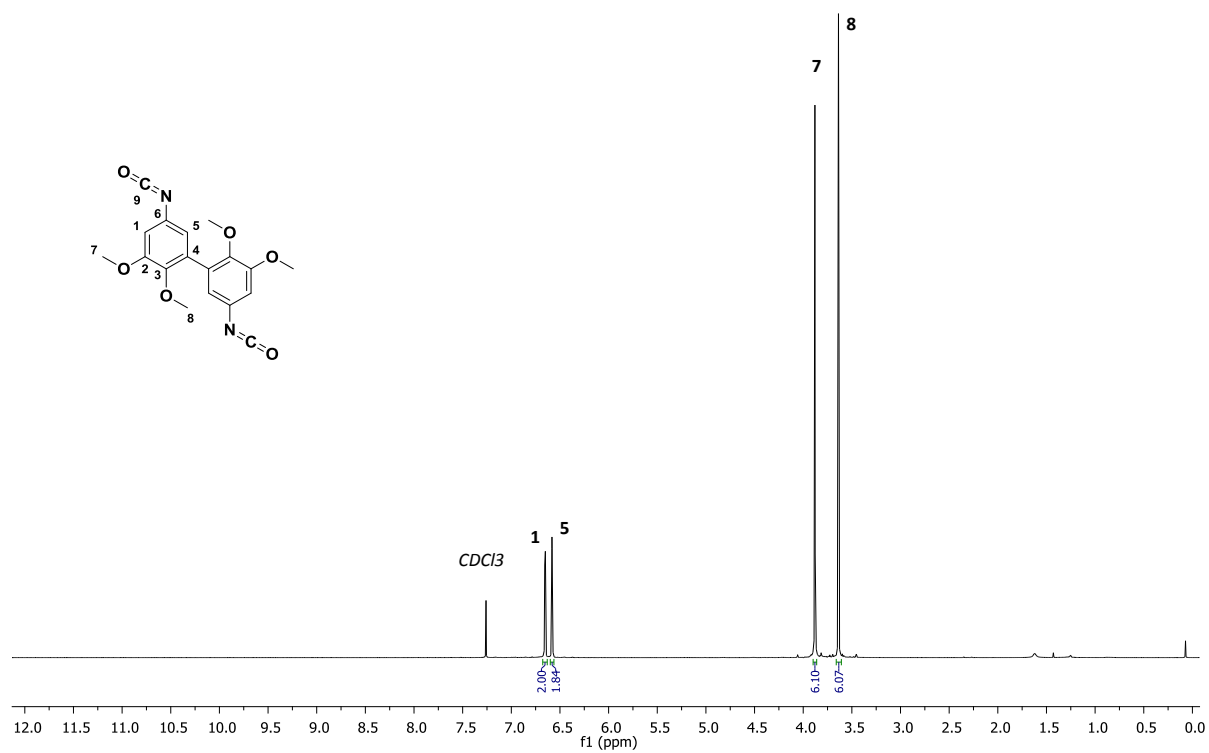


Figure S25: ^1H NMR spectrum of methylated divanillin isocyanate in CDCl_3

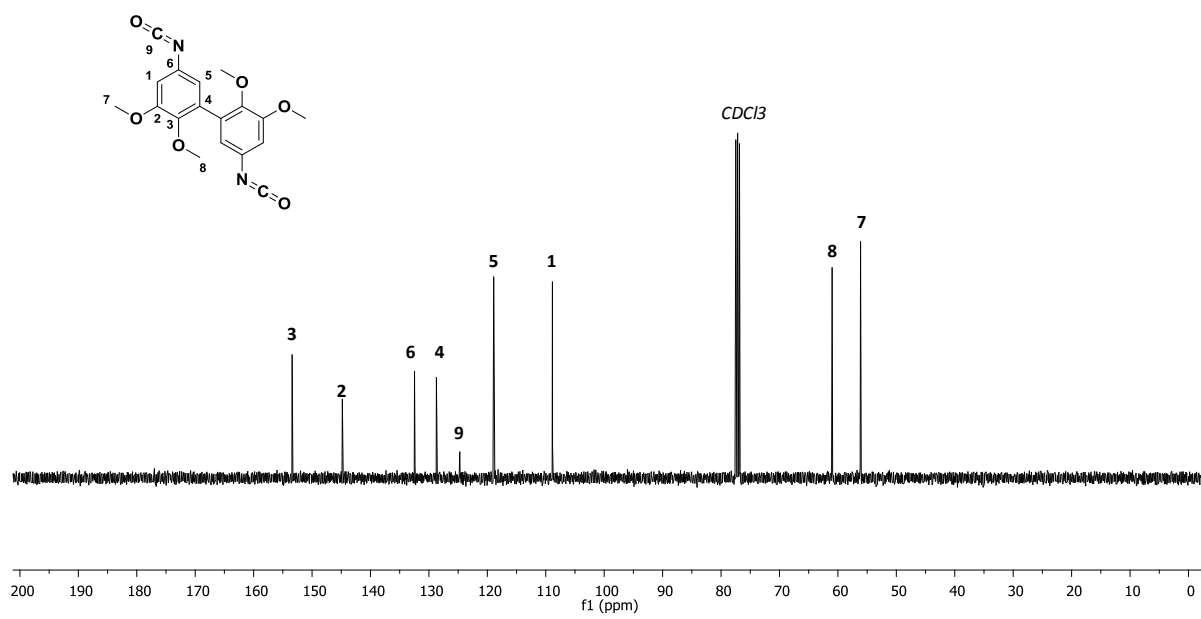


Figure S26: ^{13}C NMR spectrum of methylated divanillin isocyanate in CDCl_3

General Conclusion and Perspectives

In a context of oil prices volatility associated to the awareness of health and environmental concerns, the chemical industry urges to find solutions in order to produce industrially viable bio-based chemicals. The aim of this thesis was to develop new epoxy thermosets from renewable resources with competitive thermomechanical properties in comparison to DGEBA-based thermoset references.

The first chapter is a literature review towards the renewable resources available for the synthesis of bio-based epoxy thermosets. Vegetable oils are one of the most important classes of renewable sources due to their abundant availability and rather low price. However, their aliphatic structures do not allow the achievement of high performance materials. Thus, most industrial applications for the vegetable oil-based epoxy materials remain limited to non-structural applications. Aromatic structures, providing rigidity in the networks, are therefore required for high-performance applications. Rosin, glucose derivatives or cardanol are other bio-based raw materials able to afford this kind of networks. Nonetheless, glass transition temperatures or thermal degradation temperatures are still lower than the ones of petroleum-based reference. Other bio-based raw materials such as tannins and lignins provided promising candidates for the replacement of BPA-based epoxy thermosets. However, the industrial development of these renewable resources suffer from their versatility, complexity and processability. In this way, single bio-based molecules with well-defined structure are required. Accordingly, vanillin is the only aromatic molecule obtained from renewable resources at an industrial scale and first academic researches demonstrated the large potential of vanillin to compete with BPA.

Previous work carried out at the LCPO, on the oxidative coupling of phenolic molecules yielded bio-based biphenyl compounds potentially derived from lignin. The chapter 2 was dedicated to the synthesis and the characterization of epoxy precursors from these substrates and especially from divanillin. A synthetic route has been developed at the laboratory to epoxidize these phenolic compounds with the help of epichlorohydrin, a phase transfer agent (TEBAC) and a base (NaOH). A bio-platform composed of 11 epoxidized monomers has been successfully developed. Among them, divanillyl alcohol (DVA) aroused particular interest. In fact, the epoxidation reaction led to the production of mixtures of three derivatives: the diglycidylether of divanillyl alcohol (DiGEDVA), the triglycidylether of divanillyl alcohol (TriGEDVA) and the tetraglycidylether of divanillyl alcohol (TetraGEDVA). After purification, each of these species were isolated and characterized. DiGEDVA was found as a highly viscous

liquid ($\eta = 1300$ Pa.s) difficult to process, whereas TetraGEDVA was in the form of a low-viscosity liquid ($\eta = 4$ Pa.s). However, obtaining epoxidized monomers of low viscosity is a paramount parameter for the implementation of epoxy resin. In addition, the purification process to obtain pure monomers is difficult to transfer at an industrial scale and, from a green chemistry view-point, it is essential to reduce the number of steps to recover the final product. Following a thorough study of the synthesis conditions, experimental parameters have been optimized to better control the selective formation of the different DVA-based monomers. Different compositions of polyglycidylethers of divanillyl alcohol with controlled rheological properties have thus been prepared.

In the following, Chapter 3 investigated the thermomechanical properties of polyglycidylether networks derived from divanillyl alcohol: DiGEDVA, TriGEDVA, TetraGEDVA and their mixtures. The thermosets were cured with two kinds of diamines: isophorone diamine (IPDA) and diaminodiphenyl sulfone (DDS). Overall, the DVA-based thermosets exhibited remarkable properties in terms of glass transition temperatures (>300 °C), thermal degradation temperatures (>400 °C) and char content ($>50\%$). In addition, characterizations of the bio-based formulations were performed for two different ArianeGroup applications: as ablative composite materials and as structural adhesives. Regarding the high char residue displayed by the DVA-based networks, several formulations were identified to fulfil the specifications for the production of composite materials. However, in a near future, the scale-up of the synthesis of DVA-based monomers would be necessary to confirm results on the carbon fiber's impregnation line demonstrator. Adhesive tests were also performed by shear tests, which determine the lap shear strength required to separate two aluminum specimens. DVA-based thermosets displayed similar shear strength than DGEBA-based thermoset. However, limitations concerning the adhesive joint thickness of specimens were reported and pursue of new tests with a larger and better control of the adhesive joint would be necessary to fully characterize these bio-based materials for structural adhesive applications. In addition, this study highlighted the fact that one of the major drawbacks of using reactive compound to elaborate thermoset networks is the amount of curing agent required. Indeed, formulation generally contain up to 40 % in weight of hardener. Depending on the nature of the curing agent, the latter may have a dramatic impact on the rheology of the formulation. As for example, the viscosity of the formulations was 4 to 10 times higher with the addition of solid DDS. Following this feature, the curing of epoxy monomers without using reactive curing agent, but by using catalyst for homopolymerisation reaction of monomers could be a way to reduce the viscosity of formulations at a low level.

Finally, the last chapter was devoted to the synthesis of new bio-based aromatic amines, which can be used as curing agents in the design of epoxy thermosets. Two aromatic diamines have thus been synthesized from vanillin-derived phenolic precursors. The so-formed network exhibited a glass transition temperature of 176 °C and a char residue of 28 %, which is twice more than values obtained with the conventional DGEBA/DDS system. In addition, this diamine has also been used to cross-link TetraGEDVA epoxy monomer. A fully bio-based epoxy network has thus been synthesized and exhibited remarkable thermal properties, such as a glass transition temperature of 212 °C and a char residue greater than 48%. Nevertheless, further optimisations in the synthetic pathways would be necessary in order to have a better knowledge of the potential of these new bio-based aromatic diamines. The development of such synthetic routes to bio-based aromatic diamines also yielded di-isocyanate monomer intermediate. Such compound could be an interesting bio-based precursor for the synthesis of another kind of high performance thermoset, such as polyurethane.

To conclude, the main objective of this work, which was to develop new bio-based thermosets with similar or higher thermomechanical properties than DGEBA-based references, was achieved. The DVA-based thermosets could be valuable and realistic alternatives to DGEBA-based thermosets.

Materials and methods

Materials

Laccase from *Trametes versicolor*, benzyltriethylammonium chloride (99 %), bisphenol-A diglycidylether (D.E.R.™ 332), hydroxylamine hydrochloride (99%), tetraethylammonium bromide (98 %), 4,4'-Diaminophenyl sulfone (97 %), hydrochloric acid (37,5 %), iodomethane (99 %), potassium hydrogen phthalate (99 %), ethylchloroformate (97 %) *meta*-chlorobenzoic acid (77 %) and sodium percarbonate (available H₂O₂ 20-30%) were purchased from Sigma-Aldrich.

Epichlorohydrin (99 %), eugenol (99 %), hydroxytosyloxyiodobenzene (97%) and isophorone diamine (97 %) were purchased from TCI.

Vanillin (99 %), methyl vanillate (99 %), perchloric acid solution (0.1 N), sodium borohydride (99 %) and isophorone diamine (99 %) were purchased from Acros.

2,6-dimethoxyphenol (99 %) was purchased from Alfa Aesar.

Potassium carbonate (99 %), triethylamine (99 %), potassium hydroxide (pellet) and sodium hydroxide (pellet) were purchased from Fisher.

Diglycidylether of hexane diol (99 %) was purchased from BOC Sciences.

All products and solvents (reagent grade) were used as received, unless mentioned explicitly.

Methods

Nuclear Magnetic Resonance (NMR)

All NMR experiments were performed at 298 K on a Bruker Avance 400 spectrometer operating at 400 MHz. CDCl₃ and DMSO-d₆ were used as deuterated solvent depending on the sample and specified in the legends of spectra.

Flash chromatography

Flash chromatography was performed on a Grace Reveleris apparatus, employing silica cartridges from Grace and a dichloromethane/methanol gradient solvent equipped with ELSD and UV detectors at 254 and 280 nm.

High-performance liquid chromatography (HPLC)

High-performance liquid chromatography (HPLC) was performed using a Spectra system instrument fitted with a Phenomenex Luna 5 μ C18 100A column and compounds were detected with SpectraSYSTEM UV2000 from Thermo Separation Products. Acetonitrile: water were used as eluent.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) measurements were performed on DSC Q100 (TA Instruments). The sample was heated at a rate of 10 °C.min⁻¹. Consecutive cooling and second heating run were also performed at 10 °C.min⁻¹. The glass transition temperatures and melting points were calculated from the second heating run.

Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) measurements were performed on DMA-RSA3 system from TA instruments. The three point bending sample (width = 2 mm; thickness = 2 mm and length of fixed section = 10 mm) was heated from 25 °C to 350 °C at a heating rate of 5 °C.min⁻¹. The measurements were performed in a three-point bending mode at a frequency of 1 Hz, an initial static force of 0.5 N and a strain sweep of 0.01 %.

Thermogravimetric analyses (TGA)

Thermogravimetric analyses (TGA) were performed on TGA-Q50 system from TA instruments at a heating rate of 10 °C.min⁻¹ from room temperature to 950 °C. The analyses were investigated under air and nitrogen atmosphere with platinum pans.

Tensile test

Tensile test were performed on MTS QTest 25 system. The measurements were performed on standardized dog-bone samples (width= 2 mm; thickness = 2 mm and length of fixed section = 12 mm) using a 2500 N load cell and a crosshead speed of 1 mm.min⁻¹.

Rheological measurements

Rheological properties of prepolymers were assessed on Anton Paar MCR 301 stress controlled rheometer. Temperature was controlled on the bottom plate by Peltier effect. The geometry used for the measurement was a plate-plate (25 mm).

Rheological properties of thermosets were assessed on AR 2000 rheometer from TA Instruments. The geometry used for the measurement was a plate-plate (25 mm). The sample was heated from 25 °C to 200 °C at a heating rate of 5 °C.min⁻¹ and the measurements were performed at a shear rate of 10 s⁻¹.

Fourier Transformed Infra-Red-Attenuated Total Reflection (FTIR-ATR)

Infrared spectra were performed on a Bruker VERTEX 70 spectrometer, equipped with diamond crystal (GladiATR PIKE technologies) for attenuated total reflection mode. The spectra were acquired from 400 to 4000 cm^{-1} at room temperature using 32 scans at a resolution of 4 cm^{-1} .

Size Exclusion Chromatography (SEC)

Size exclusion chromatography analyses were performed in THF as the eluent and trichlorobenzene as a flow marker. Measurements were performed on a Waters pump equipped with Waters RI detector and Wyatt Light Scattering detector.

The separation is achieved on three Tosoh TSK gel columns (300×7.8 mm) G5000 HXL, G6000 HXL and a Multipore HXL with an exclusion limits from 500 to 40 000 000 $\text{g}\cdot\text{mol}^{-1}$, at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$. The injected volume was 100 μL . Columns' temperature was 40 $^{\circ}\text{C}$.

Développement de réseaux époxydes biosourcés pour lanceurs aérospatiaux

Résumé :

La grande majorité des résines époxy utilisées aujourd'hui sont issues ou dérivées du bisphénol-A (BPA). Cependant, le BPA est soumis à de très fortes réglementations, notamment vis-à-vis de sa récente classification comme substance chimique extrêmement préoccupante par l'agence européenne des produits chimiques (ECHA). Dans un but d'anticiper les évolutions de régulation, ArianeGroup a décidé de remplacer cette substance chimique de ces formulations. Ces travaux de thèse portent donc sur l'élaboration de nouvelles résines époxy biosourcées ayant des propriétés similaires voire supérieures aux références dérivées du bisphénol-A. Pour cela, une bioplatforme de monomères polyépoxydés issus de la vanilline, du méthyl vanillate, du 2,6-diméthoxyphénol et de l'eugénol a été développée. Ces précurseurs biosourcés ont ensuite été utilisés comme précurseurs de réseaux époxyde par réticulation avec des amines. Les réseaux réticulés biosourcés ainsi obtenus ont démontré des propriétés thermomécaniques remarquables bien supérieures à la référence de type DGEBA, notamment en termes de température de transition vitreuse ($>300\text{ °C}$) et taux de coke ($>50\%$). En parallèle de ces travaux, la synthèse de diamines biosourcées, dérivées de la divanilline, et pouvant être utilisées comme agents de réticulation de résines époxy, a été réalisée. Des réseaux époxyde entièrement biosourcés ont ainsi été synthétisés et présentent des propriétés thermomécaniques prometteuses.

Mots clés : Bisphénol-A, DGEBA, résines époxy, réseaux époxyde biosourcés, divanilline, polyaddition, transition vitreuse, taux de coke.

Development of bio-based epoxy thermosets for aerospace launchers

Abstract:

Today, most of the epoxy resins produced are derived from bisphenol-A (BPA). However, BPA is subject to strong regulations, particularly because of its recent classification as chemical of very high concern by the European Chemicals Agency (ECHA). In order to anticipate new regulations, ArianeGroup has decided to replace this substance in its applications. The aim of this thesis is to develop new bio-based epoxy thermosets with comparable thermomechanical properties as the ones issued from bisphenol-A-based materials. For this purpose, a bio-platform of epoxy monomers from vanillin, methyl vanillate, 2,6-dimethoxyphenol and eugenol was developed. These precursors were cross-linked with amines used as curing agent to obtain bio-based epoxy networks. The latter demonstrated thermomechanical properties well above the DGEBA-type reference, especially in terms of glass transition temperature ($> 300\text{ °C}$) and char content ($> 50\%$). Finally, the synthesis of bio-based diamines derived from divanillin was developed and enabled the synthesis of fully bio-based epoxy networks with promising thermomechanical properties.

Keywords: Bisphenol A, DGEBA, epoxy resins, bio-based epoxy thermosets, divanillin, polyaddition, Glass transition temperature, char content.

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