



# Ferulic acid-based renewable esters and amides-containing epoxy thermosets from wheat bran and beetroot pulp: Chemo-enzymatic synthesis and thermo-mechanical properties characterization



Raphaël Ménard<sup>a,b</sup>, Sylvain Caillol<sup>b,\*\*</sup>, Florent Allais<sup>a,c,\*</sup>

<sup>a</sup> AgroParisTech, Chaire Agro-Biotechnologies Industrielles (ABI), CEBB, 3 rue des Rouges Terres, 51110 Pomacle, France

<sup>b</sup> Institut Charles Gerhardt – UMR 5253, CNRS, UM, ENSCM – 8 rue de l'Ecole Normale, 34296 Montpellier, France

<sup>c</sup> UMR 782 GMPA, INRA, AgroParisTech, CNRS, Université Paris-Saclay, Avenue Lucien Brétignières 78850 Thiverval-Grignon, France

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## ABSTRACT

In this study, ferulic acid – a natural phenolic acid present in bagasse, wheat and rice brans, and beetroot pulp – was used as renewable starting material to prepare new biobased epoxy precursors. This biobased building block was first esterified then reduced to provide ethyl dihydroferulate which was then transesterified/amidified with biobased diols, triol and diamines. *Immobilized Candida antarctica* (aka CAL-B or Novozyme 435<sup>®</sup>) was used to perform the solvent-free-transesterification/amidation under mild conditions. The phenolic architectures synthesized were then glycidylated using a TEBAC-mediated procedure to afford four biobased epoxy precursors – with various linker structures between the ferulic units – which were then cured with conventionnal and biobased diamine curing agents. The thermal and thermomechanical properties of the thermosets prepared were assessed by TGA, DSC and DMA to highlight the influence of the linker configuration (aliphatic vs cycloaliphatic), that of the epoxy functionality (di vs tri), and that of the nature of the function used for coupling ferulic units (ester vs amide) on the thermosets properties. Analyses of these thermosets revealed glass transition temperatures ranging from 32 to 85 °C and high thermal stabilities around 300 °C. The mechanical behavior of the biobased thermosets proved equivalent to that of the DGEBA-IPDA reference system at low temperatures (up to 40–100 °C depending on the epoxy precursor and diamine).

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## 1. Introduction

Among polymeric materials, epoxy resins are one of the most important players of the thermosets market. They are extensively used for their exceptional characteristics, such as excellent mechanical properties with low mass density, adhesion, thermal or chemical resistance and have many applications in adhesives industry, coatings, and electronic components. Epoxy thermosets are also used as a matrix in combination with fibers to form composites used in sports and aerospace industries (Hamerton, 1996; Petrie, 2006).

However, this kind of thermosets also suffers from some drawbacks. First, as most of polymers, the restricted availability of

petrochemical resources (Gandini, 2011; Tuck et al., 2012) does not allow us to consider current petrobased commercial systems as durable solutions. Thus, in the last fifteen years, we have observed an increasing interest for the bioresource-derived polymers including the development of some biobased industrial polymers such as RILSAN<sup>®</sup>, a biobased polyamide from ricin oil. Most of the biobased systems are derived from aliphatic resources like cellulose (Gandini, 2011), starch (Gandini, 2011) or triglycerides (Montero de Espinosa and Meier, 2011). The “greening” of the polymer market also concerns the epoxy thermosets. Indeed, the crosslinked structure of the thermosets does not allow their recycling. Currently, the thermosets are mainly valorized at the end of their life (Pickering, 2006) by mechanical process (comminution) to be re-used as filler, or by thermal process (combustion) to produce energy. This low recyclability increases the interest towards biobased thermoset systems (Raquez et al., 2010; Ma and Webster, 2015; Ma et al., 2016). Accordingly, in the last decades, many biobased epoxy thermosets have been developed from renewable raw materials. Auvergne et al. (2014) have recently presented an

\* Corresponding author at: AgroParisTech, Chaire Agro-Biotechnologies Industrielles (ABI), CEBB, 3 rue des Rouges Terres, 51110 Pomacle, France.

\*\* Corresponding author.

E-mail addresses: [sylvain.caillol@enscm.fr](mailto:sylvain.caillol@enscm.fr) (S. Caillol), [florent.allais@agroparistech.fr](mailto:florent.allais@agroparistech.fr) (F. Allais).

overview of present and future trends of the biobased epoxy thermosets derived from various fractions of the biomass, such as the lipid fraction (terpene (Wu et al., 2015), oil (Supanchaiyamat et al., 2014)) and the carbohydrate one (sugar (Kovash et al., 2014), starch (Hong et al., 2014)). Diglycidyl isosorbide is already a biobased commercial product and has shown good thermomechanical properties (Chrysantos et al., 2011; Hong et al., 2014; Lukaszczyk et al., 2011). Recently, Chang et al. (2015) synthesized the first fully biobased epoxy resins from isosorbide diglycidyl ether cured by biobased hardeners. However, isosorbide requires sorbitol derived from corn syrup which competes with food production. Moreover, these aliphatic resources do not allow the access to aromatic key products that are still derived from petrochemical raw materials (Tuck et al., 2012). Auvergne et al. (2014) also described the valorization of the phenolic fraction (biophenol, tannins (Benyahya et al., 2014), vanillin (Fache et al., 2015a)) derived from lignin and other aromatic biopolymers, offering aromatic moieties and enhancing the material properties. Other teams also described different fully biobased epoxy thermosets from phenolic biobased compounds: phloroglucinol (Ménard et al., 2015), creosol (Meylemans et al., 2011), eugenol (Harvey et al., 2014), guaiacol (Hernandez et al., 2016) or vanillin/vanillyl alcohol (Fache et al., 2015a,b; Harvey et al., 2015). The literature highlights that phenolic moieties seem to be the most suitable raw material to confer competitive properties to the final thermosets.

The second main drawback of epoxy thermosets is based on the toxicity of a famous precursor: bisphenol A (BPA). Glycidylated to give DGEBA (Diglycidylether of BPA), BPA constitutes the main part of the epoxy resins industry. DGEBA based thermosets release slowly parts of free BPA, which presents health and environmental hazards (Hong et al., 2016). Indeed, BPA has recently come under attention of regulatory agencies as a potentially toxic chemical. In fact, BPA is highly bioaccumulated, linked to endocrine disruption (Odaka et al., 2008), and increases the risk of cancer (Maffini et al., 2006). Thus, increasing the sustainability of the epoxy thermosets with biobased resources and the substitution of BPA are becoming topics of increasing interest within the polymer community.

Pion et al. (2013) succeeded in developing an efficient sustainable chemo-enzymatic process to synthesize different macro (bis/tris)phenols from ferulic acid – a natural compound found in numerous non-edible bioresources such as bagasse, wheat bran and beetroot pulp – and various biobased diols under mild conditions. The valorization of ferulic acid represents a potential added value to some byproducts already used industrially for sugar production. These phenolic precursors exhibit aromatic structures needed to confer good thermoset properties, bearing two or three functionalizable hydroxyl groups (phenols). Ferulic acid derivatives have already been used successfully as polymer building blocks for the synthesis of new copolyesters (Pion et al., 2015), copoly(ester-urethane)s (Pion et al., 2015), poly(anhydride-ester)s (Ouimet et al., 2015), isocyanate-based polyurethanes (Oulame et al., 2015), and poly(ester-alkenamer)s (Barbara et al., 2016) via ADMET polymerization. However, to the best of our knowledge, only one example (Maiorana et al., 2016) of degradable epoxy thermosets derived from ferulic acid has been reported in the literature. Moreover, the estrogenic activity of that kind of ferulic derivatives have been assessed by Maiorana et al. (2016) with respect to the  $\alpha$ -human receptors (HELN hER $\alpha$ ) according to the conventional procedure (Escande et al., 2006; Molina-Molina et al., 2008) and compared to that of BPA and its analogs. The results highlight that ferulic derivatives did not exhibit the endocrino-toxicity reproached to BPA. Thus, the biobased phenolic architectures used in this study seem to be ideal candidates for BPA substitution.

The aim of this study is to synthesize different biobased epoxy resins from various ferulic acid phenolic derivatives to evaluate the impact of the structure of the epoxys (flexibility/rigidity, function-

ality (2 or 3) and nature of the internal function (ester or amide)) on the thermal properties in order to determine structure-properties relationships. For that purpose, the hydroxyl groups of the phenolic derivatives will be functionalized by glycidylation using epichlorohydrin to provide various epoxy precursors. It is noteworthy to mention that epichlorohydrin used on this nucleophilic substitution may also be produced from biobased raw materials. Indeed, in 2007 SOLVAY® group filed patents (Krafft et al., 2005a, 2005b) on the EPICEROL™ process. Since the development of the biodiesel industry, the epichlorohydrin production from glycerol – a co-product of the biodiesel industry – has becoming economically interesting. Then, with the aim to synthesize new fully biobased epoxy thermosets, the ferulic acid-based epoxy precursors will be crosslinked by different biobased diamine hardeners such as the decane diamine produced from ricin oil or the difurfuryl amine based on furfural (Chatterjee et al., 2016), which can be produced from hemicelluloses (Shen et al., 2013; Inoue et al., 2014; Ichikawa and Namba, 2015; Bhaumik and Dhepe, 2013). Ferulic acid-based epoxy thermosets will be compared to a standard DGEBA-IPDA epoxy resin by characterizing their thermal and thermomechanical properties.

## 2. Experimental part

### 2.1. Reagents

Ferulic acid, benzyltriethyl ammonium chloride and palladium supported on carbon were supplied from Sigma-Aldrich. Glycerol, isosorbide, 1,4-butanediol were purchased from Alfa Aesar. 1,4-Butanediamine and epichlorohydrine were purchased from Acros Organics. Isophorone diamine (IPDA) was purchased from TCI. CAL-B supported on acrylic bead was purchased from Novozymes. Decane diamine (DA10) was kindly provided by Arkema. All reactants were used as received.

### 2.2. Characterizations

Silica gel flash chromatography was performed on an Interchim puriflash 4100 using a variable cyclohexane/ethyl acetate gradient of elution. Chemical structure of the prepared compounds were determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy with a Bruker Fourier Ultrashield 300 MHz spectrometer at room temperature in  $(\text{CD}_3)_2\text{CO}$  or  $(\text{CD}_3)_2\text{SO}$ . External references were trimethylsilane for  $^1\text{H}$  NMR and shifts are given in ppm. Differential Scanning Calorimetry (DSC) analyses were carried out on a TA Q20 calorimeter. Constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as the purge gas. The thermal properties were analyzed at  $10^\circ\text{C}/\text{min}$  between 20 and  $200^\circ\text{C}$  to observe the glass transition temperature determined as the inflection value in the heat capacity jump (Uncertainties:  $T_g \pm 1^\circ\text{C}$ ). Thermogravimetric analyses were performed using a TA Q500 at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere (Uncertainties:  $T_5: \pm 1^\circ\text{C}$ , w% char:  $\pm 2\%$ ). Dynamic Mechanical Analyses (DMA) were performed on a Metravib DMA 25. The DMA samples had a rectangular geometry (length: 10 mm, width: 20 mm, thickness: 2.5 mm). The span thickness of 4:1 was thus respected, in order to measure more precisely the rubbery elastic modulus, related to the crosslink rate. Indeed, McAninch et al. (2015) showed that a span thickness lower than 10:1 is adapted to the rubbery elastic modulus measurement. Uniaxial stretching of samples was performed while heating at a rate of  $3^\circ\text{C}/\text{min}$  from  $0^\circ\text{C}$  to  $200^\circ\text{C}$ , keeping frequency at 1 Hz. In order to perform measurements in the linear viscoelastic region, deformation was kept at 0.001%. The storage modulus ( $E'$ ) and  $\tan \delta$  curves as a function of temperature were recorded and analyzed using the software

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