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DESIGN AND DEVELOPMENT OF 100% BIO-BASED HIGH-GRADE HEMP/EPOXY COMPOSITES

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ABSTRACT

In order to develop 100% bio-based high-grade epoxy composites, in this study, bio-based epoxy thermosets and hemp slivers are processed and characterized by different technologies. Epoxy resins are synthesized from the diglycidylether of Eugenol, extracted from cloves. They are cured with bio-based acid anhydrides. The physicochemical properties of the resulting epoxy resins are characterized using thermogravimetric analyses (TGA), differential scanning calorimetry (DSC), and nanoindentation. The mechanical properties of hemp fibres extracted from the slivers are also determined using tensile tests. After their processing and characterization, these bio-based constituents are then used to manufacture unidirectional composites by thermocompression. Composite specimens are tested under 3-points bending. Preliminary results show a stiffness of about 9 GPa and a strength of approximately 170 MPa for a fibres volume fraction of 22%. These mechanical properties are promising since they make this material competitive to substitute petroleum-based composites in secondary structural applications.

1 INTRODUCTION

Today, the development of bio-based products, substituting petroleum-based materials has become a major focus of academic or industrial scientists. To face the depletion of fossil resources and to preserve the environment, this change is essential. This growing awareness is especially strong in composites sectors, in particular in the field of transport, sport and leisure activities. Traditional composites made of synthetic fibres impregnated with a petrochemical matrix are left out in favour of materials extracted from biomass. A totally bio-based composite can be defined as a material made of a natural reinforcement and a polymer matrix fully synthesized from biomass.

This study focuses on developing composites with unidirectional hemp fibres and bio-based epoxy matrix for secondary structural applications. To meet the requirements of such applications, the constituents have to reach a certain level of performance. For these reasons, in this work, we proposed

to work with unidirectional non-twisted hemp yarns and epoxy polymers relating to their good mechanical properties.

One of the main issue is to substitute petrochemical resins. In fact, the most commonly used epoxy resin is a diglycidylether of bisphenol A (DGEBA). The replacement of DGEBA is of great concern to the polymers field because it is a petroleum-based epoxy resin and bisphenol A-based material have been suspected to be toxic for health [1-2]. Over the past decades more and more researchers have been engaged in developing bio-based resins to replace DGEBA [3-4]. This study focuses on processing composites with bio-based epoxy matrix and unidirectional hemp reinforcement.

The precursor used to the polymerization reaction is the Eugenol. It is extracted from cloves and then converted into its diglycidylether derivative (DGE-Eu). The synthesis and characterization of this bio-based epoxy resin was described by Qin & al. [5]. Recently we resolved the crystal structure of DGE-Eu by single-crystal X-ray diffraction [6]. In this work, the prepolymer was cured with several acids anhydrides to obtain polyepoxides with good properties in order to process hemp fibres composites. The reinforcement was processed using different technologies to produce individualized and aligned hemp fibres in the form of combed sliver laps. This reinforcement structure ensure a maximisation of the mechanical properties at the scale of the composite material. In our ongoing studies, we herein report the polymerization and the characterization of DGE-Eu-based polyepoxides cured with different acids anhydrides and the processing of hemp/epoxy bio-based composites. We also evaluate the performance of the bio-based epoxy matrix, the sliver laps of hemp fibres and the final composite for structural applications. The structural performance of DGE-Eu are compared with those obtained with the DGEBA petro-sourced resin.

2 MATERIALS AND METHODS

2.1 Materials

The polymer matrix used in this project is a polyepoxide, which was obtained from the reaction of the prepolymer DGE-Eu with acids anhydrides hardeners. A commercial anhydride was purchased from Sigma-Aldrich, 1,2-cyclohexanedicarboxylic anhydride (HHPA, 95% purity) and the second, maleopimaric anhydride (MPA) was prepared according to published procedures [5]. As the prepolymer, MPA comes from biomass. The catalyst, 1-Ethyl-4-methylimidazole (EMID; 95%), was purchased from Sigma-Aldrich.

Long hemp fibres in the form of combed sliver laps were provided by an Italian company. Their linear mass was about 15000 tex.

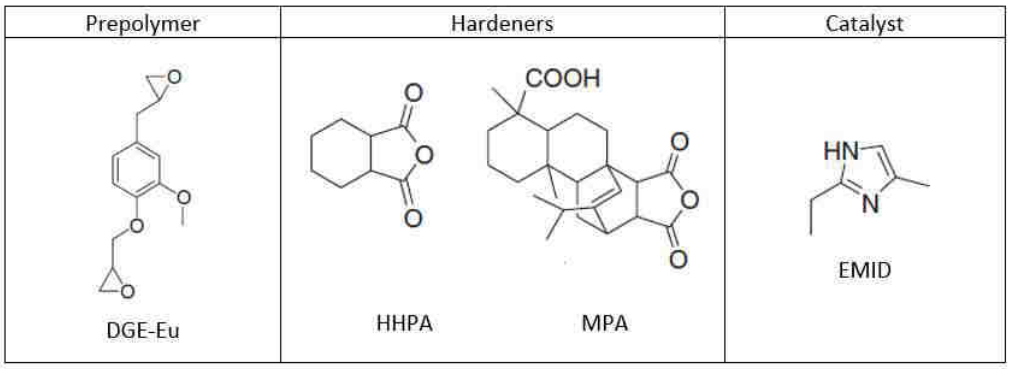

Figure 1: Constituents of bio-based epoxy thermosets

2.2 Methods

2.2.1 Processing of polyepoxides

The bio-based epoxy thermosets studied in this work are composed of DGE-Eu and anhydrides hardeners. Two different anhydrides are used. MPA is synthesized from biomass (rosin derivatives) and

HHPA is a commercial petroleum-based anhydride. The protocol for curing the epoxy monomers was the same as the one already described by Qin et al. [5]. The molar ratio corresponding for the epoxy/anhydride/catalyst combination was 1-0.8-0.012 with MPA and 1-0.8-0.08 with HHPA. These ratios are not in stoichiometry proportion because of simultaneous reactions [7].

2.2.2 Processing of hemp fibres

Combed sliver laps were drawn to obtain slivers with a linear mass of about 2200 tex, and then obtained a size of reinforcement compatible with expected applications [8].

2.2.3 Processing of bio-composites

The manufacturing of bio-composites was performed by thermocompression method. They were heated at 120°C under a pressure of 0.25 bar. These parameters have been selected based on the features of the polymerization reaction of the epoxy matrix. The dimensions of the manufactured specimens are approximately 50 × 10 × 1.5 mm. The fibres mass fraction was around 23%.

Figure 2: Manufacturing of bio-composites studied in this work

2.3 Characterization techniques

2.3.1 Differential scanning calorimetry (DSC)

DSC analyses were carried out using TA MDSC 2920 under nitrogen flow (60 mL.min^{-1}) with a sample mass of 10 ± 3 mg. To study curing reaction, samples were heated from −20 °C to 180 °C at a heating rate of 5 °C min^{-1}. To determine glass transition temperature (T_g), the cured resin was heated from −20 °C to 180 °C at a heating rate of 20 °C min^{-1}. The two combinations of polyepoxide were characterized using this technique.

2.3.2 Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed on a TA Instruments TGA Q600 thermoanalyser using aluminium pans. Samples (5-10 mg) were heated from room temperature to 800 °C at a rate of 20 °C min^{-1} under air flow (100 mL min^{-1}). Weight loss percentages were determined using the TA Universal Analysis 2000 software accompanying the instrument. The two combinations of polyepoxide were characterized using this technique.

2.3.5 Tensile tests on elementary fibres

Tensile tests were performed with a dynamic mechanical analyser (DMA Bose Electroforce 3230). Thirty to fifty single fibres, manually extracted from combed sliver laps, with a diameter of about 20 microns were tested at a constant crosshead displacement rate of 5 µm.s^{-1}. A gauge length of 10 mm was chosen. The tensile tests were carried out at a temperature of 21°C ± 2°C and a relative humidity of 50 % ± 5%. The paper frame supporting each fibre was clamped onto the testing machine and was cut before initiating each test [9]. The applied force was measured using a 20 N load sensor, with a resolution of approximately 1 mN, and the displacement was measured using a LVDT with a resolution ranging from 0.1 µm. The DMA chamber was pair up with a HumiSys humidity generator from InstruQuest INC

to control the relative humidity. Longitudinal mechanical properties (Young's modulus, ultimate strength and failure strain) of hemp fibres were determined. The fibre strain was determined using the displacement measurements and the initial length of the fibre, the tensile stress was determined using the cross-section of each fibre and the Young's modulus was computed from the initial linear section of the stress–strain curve. The cross-section area of the fibre was approximated using the average diameter and considering the fibre as perfectly cylindrical and the lumen neglected.

2.3.6 Flexural tests on thermosets and bio-composites

Flexural strength and stiffness were determined for the DGE-Eu-based thermosets and the DGE-Eu-based hemp fibres reinforced composites, using three-point bending test method. Tests were performed on an electodynamical testing machine (DMA Bose Electroforce 3230). The span between supports was 40.0 mm and the crosshead speed was 10 $\mu m.s^{-1}$. Flexural strength is calculated by the following equation.

$$\sigma = \frac{3FL}{2bh^2} \quad (1)$$

Where F is the maximum load (N); L is the distance between the supports or span (mm); b is the width (mm) and h is the thickness (mm) of the specimen.

Flexural modulus is determined from the initial part of the stress-deflection curve.

One specimen of DGE-Eu polyepoxide cured with HHPA and three of hemp fibres reinforced composites were tested.

3 RESULTS AND DISCUSSIONS

3.1 Characterization and performance evaluation of bio-based epoxy thermosets

The values of glass transition temperatures for each polyepoxide combination are reported in the table 1. They are indicators of the level of stiffness of the material and they depend on both the chemical structure of the polymer chain and the architecture of the polymer. We can note that the glass transition temperatures for bio-based epoxy resin (DGE-Eu) are in the same order of magnitude as values for DGEBA-based polymers (Tab. 1) [5-10]. We can see that MPA gives a better stiffness to the thermosets than HHPA.

Glass transition temperature (T_g °C)			
Epoxy resin	DGE-Eu	MPA	155
		HHPA	114
	DGEBA [5]	HHPA	106
	DGEBA [10]	MTHPA	129

Table 1: Values of glass transition temperatures for all polyepoxides combinations

Thermogravimetric analyses point out a degradation temperature corresponding to 5% weight loss of around 317°C and 321°C for DGE-Eu/MPA and DGE-Eu/HHPA polyepoxides respectively. The origin of the thermosets, bio-based or petroleum-based do not significantly influence the thermal degradation temperature. Indeed, there is no significant variation between combination with MPA or HHPA. Moreover, this result also applies to fully petroleum-based epoxy polymers [11]. The values for the degradation temperature corresponding to 5% weight loss are about 320°C.

Flexural tests were performed on DGE-Eu/HHPA polyepoxide in order to evaluate the properties of the matrix used to develop composite materials. As well as its good properties, this combination exhibits a liquid physical aspect, which facilitates the manufacturing of bio-composites. The DGE-Eu/HHPA epoxy thermosets show a flexural strength of about 90 MPa and a stiffness of approximately 3.6 GPa. They are in good accordance with typical values encountered for classical polymer materials [12].

3.3 Tensile characterization of hemp fibres

Plant fibres exhibit generally a high scattering in their mechanical properties that need to be contained by controlling the processing stages. The tensile properties of single hemp fibres with an average diameter of 20.2 ± 4.5 µm, taken from the slivers (2200 tex) are reported in the table 3. Results show that their stiffness is about 18 GPa, the mean strength is 325 MPa and the strain at failure is approximately equal to 2.05 %. Their mechanical properties are lower than those already reported in literature [13-14]. This might be explained by the process used for their transformation into slivers.

Tensile properties	*Hemp variety / Harvest year*	*Apparent modulus (GPa)*	*Stress at failure (MPa)*	*Strain at failure (%)*
Single hemp fibres from combed sliver laps	/	18.2 ± 7.2	325 ± 170	2.05 ± 0.8
Single hemp fibres from Placet & al. 2017	Fedora 17 (2013)	22.6 ± 4.5	410 ± 215	3.27 ±1.1
Single hemp fibre from Marrot & al. 2013	Fedora 17 (2007)	33.8 ± 12.2	489 ± 233	2.5 ± 1.3
Single hemp fibre from Marrot & al. 2013	Felina 32 (2009)	31.2 ± 19.7	699 ± 450	3.3 ± 1.6

Table 3: Tensile properties of single hemp fibres from combed sliver laps compared to data from literature

3.4 Processing and characterization of bio-composites

DGE-EU/HHPA hemp reinforced composites were tested using flexural characterization. Stress-deflection curves are reported in Figure 3. Results show a mean strength of 171 ± 19 MPa and a mean stiffness of 8.8 ± 1.5 GPa for an average fibre volume fraction of 22.4 ± 1.6 % (Tab. 4). This volume fraction is low due to the small quantities of the synthetized polymers, which make possible only very small composite specimens to be manufactured. In such conditions, the control and tuning of constituents volume fractions are particularly difficult during the manufacturing process. In any case and as expected, we observe that incorporating hemp slivers in the bio-based matrix greatly enhances its mechanical properties. Indeed, the strength is improved by 90% and the apparent modulus by 144%. In comparison to the previous work of Islam & al. [15], we note that bending properties are in the same order of magnitude but with a lower fibre ratio. It is foreseeable that the mechanical properties of the manufactured 100% bio-based composite will be significantly improved when increasing the fibre ratio.

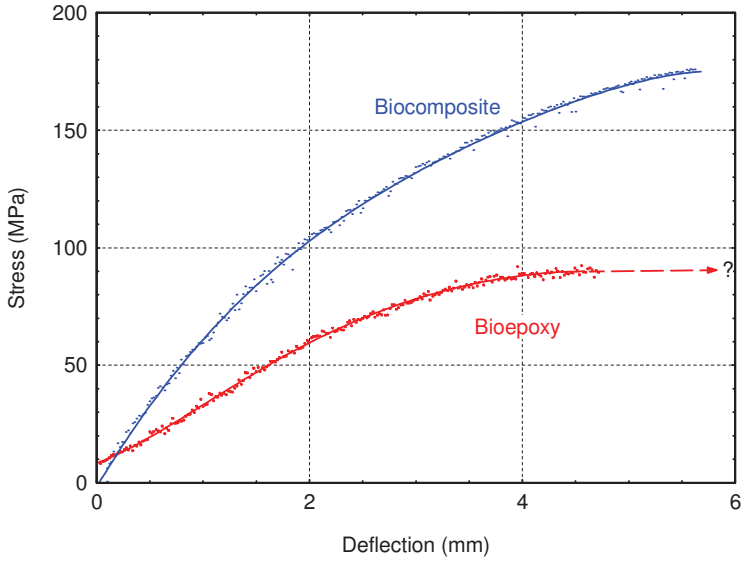

Figure 3: Stress-Deflection curve of bio-based thermoset and composite

Table 4 synthetizes the mechanical properties experimentally determined and the estimation made using the ROM (Rule Of Mixture) and the properties of the fibres and matrix. This calculation does not take into account the composite's porosity. We can observe that the experimental values are higher than the ones estimated using the ROM. This difference can certainly be attributed to the error made when determining the tensile properties of individual fibres, and in particular due to the over-estimation of the fibre cross-section area (due to lumen neglecting). This is promising results. High and interesting properties should be reached by increasing the fibres volume fraction.

	Strength (MPa)	**Stiffness (GPa)**	**Fibres content**
Experiments (mean value ± Std Deviation)	171 ± 19	8.8 ± 1.5	22.4 ± 1.6
Estimation using ROM	143	6.9	22.5

Table 4: Average tensile properties determined experimentally and using the Rule Of Mixture

4 CONCLUSIONS

The development of fully bio-based epoxy resins from Eugenol is an interesting alternative to the DGEBA-based resins. This work shows that, in addition to its bio-based origin, it exhibits physicochemical and mechanical properties that meet the needs for secondary structural applications. It makes these bio-based polymers an excellent alternative to petrochemical resin. Results also show, at the scale of composite material reinforced with unidirectional hemp fibres, mechanical properties in the same order of magnitude as some of the petroleum-based matrices reinforced with different natural fibres exposed in the literature. Therefore, these results are very promising for the development of fully bio-based epoxy matrix for composites applications. In our ongoing studies on fully bio-based composites, we work to the development of bio-composites with a prepolymer extracted from lignin and anhydrides derived from plant-based acids [16].

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