



HAL
open science

Bio-based unidirectional composite made of flax fibre and isosorbide-based epoxy resin

Corentin Musa, Antoine Kervoelen, Pierre-Edouard Danjou, Alain Bourmaud,
François Delattre

► **To cite this version:**

Corentin Musa, Antoine Kervoelen, Pierre-Edouard Danjou, Alain Bourmaud, François Delattre. Bio-based unidirectional composite made of flax fibre and isosorbide-based epoxy resin. *Materials Letters*, 2020, 258, pp.126818. <10.1016/J.MATLET.2019.126818>. <hal-02904269>

HAL Id: hal-02904269

<https://hal.science/hal-02904269v1>

Submitted on 24 Oct 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Bio-based unidirectional composite made of flax fibre and isosorbide-based epoxy resin

Corentin Musa^a, Antoine Kervoëlen^b, Pierre-Edouard Danjou^a, Alain Bourmaud^{b,*}, François Delattre^a

^a ULCO, Université du Littoral Côte d'Opale, Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV), Dunkerque 59140, France

^b Université de Bretagne Sud, IRDL UMR CNRS 6027, Lorient, France

alain.bourmaud@univ-ubs.fr (A. Bourmaud).

Abstract

Ultrasound-assisted synthesis of diglycidyl ethers of isosorbide (DGEI) with different epoxy equivalent weight (EEW) with isophorone diamine (IPD) hardener have been performed. Interestingly, it was found that one specific epoxy formulation exhibits high reactivity with amine hardener inducing high glass transition and indentation stiffness. Associated with flax fibres, this new bio-based resin has made it possible to develop performing and promising unidirectional biocomposites with characteristics comparable to commercial petroleum-based epoxy resins.

1. Introduction

Since their advent in the thirties and until nowadays, composite materials have experienced a strong development and have conquered important industrial sectors such as automotive, aerospace, housing, etc. However, current environmental issues are pushing society to make towards sustainable development. To respond to these changes and replace finite fossil resources, the development of composites from renewable resources is of particular interest [1]. Among a large range of reinforcements and due to their availability, environmental assessment and attractive mechanical properties, flax fibres can be considered as a relevant solution to substitute E-glass fibres in Europe [2]. Epoxy resin is the most widely used polymer matrix thermoset resin. Due to its aromatic ring, giving it a high thermal stability, bisphenol A (BPA) is the most commonly used epoxy precursor and is found in 90% of crosslinked epoxy resins. Nevertheless, it is reprotoxic [3] and so requires the development of viable alternatives. Vegetable oils, proteins and polysaccharides have been studied in this way [4]. Isosorbide is considered as a viable candidate to replace BPA in thermoset materials [5]. The most convenient way to produce diglycidyl ether from an isosorbide precursor is to graft epoxy groups to isosorbide by mixing it with epichlorohydrin in basic medium. This synthesis is well known but produces a significant quantity of oligomers [6]. In a previous study, the synthesis has

been improved using high power ultrasound [7]. This work focuses on the development of new fully bio-based flax-epoxy composites. After a thermal and infrared spectroscopy characterization of the isosorbide-based epoxy resin, its mechanical properties will be investigated thanks to nanoindentation tests. The mechanical properties of unidirectional (UD) composite made of flax fibres, bio-based epoxy precursor cured with a standard diamine will be evaluated and compared to conventional solutions.

2. Materials and methods

The plant fibres used in this study are scutched textile flax (Aramis variety), cultivated in France in 2015 and obtained from Van Robaey Frères Company (Killem, France).

The ultrasound-assisted heterogeneous synthesis, chemical and structural characteristics of the bio-based epoxy prepolymers (DGEI) have been previously detailed [7]. The different resins were obtained by mixing DGEI with isophorone diamine (IPD) hardener in stoichiometric proportions (Table 1) i.e. considering that one active hydrogen of amine function reacts with one epoxy ring. A commercial Epolam 2020 (Axson) was used as a reference.

The thermal properties of epoxy resins were obtained by differential scanning calorimetry (DSC) and were carried out on a TA Instrument DSC Q1000. Samples (5–10 mg) were heated from 100 to 250 °C at 10 °C/min under nitrogen atmosphere. Infrared spectra were recorded on PerkinElmer Spectrum BXII Fourier transform infrared (FTIR) spectrometer over the wavenumber range of 4000–400 cm⁻¹.

Table 1
Thermal properties of epoxy resins.

System	EEW [g.eq ⁻¹]	rIPD [%w]	DH (J/g)	T _{g0} [°C]	T _{g_{onset}} [°C]	T _{g_{peak}} [°C]
DGEDASn-IPD [6]	184	24	404	-36	-	104
Epilam2020	150	34	458	-51	80	117
DGEI180-IPD	180	19	332	-46	78	114
DGEI220-IPD	218	16	277	-30	54	95
DGEI280-IPD	280	13	170	-26	46	92

Micro-UD composites having a 62 μm section were manufactured by hot compression with a targeted fibre volume fraction of 60 ± 2%. The determination of the tensile properties was made in accordance with the NF T 25-501-2 (elementary flax fibre) and ISO-527-5 (UD composites) standards, considering the loading frame compliance. For flax fibres a 10 mm free length was chosen; the frame was clamped on a universal MTS-type tensile-testing machine equipped with a 2 N capacity load cell and loaded at a constant crosshead-displacement rate of 1 mm/min up to rupture in a laboratory with a controlled temperature (23 °C) and relative humidity (48%). Identical speed and environmental parameters were used for composite characterisation with using an extensometer to carefully control the displacement. Nanoindentation (NI) measurements were made on epoxy resin after a 1-μm polishing and a three-side pyramid (Berkovich) indenter with a continuous stiffness measurement technique was used. A 3-nm amplitude, 45 Hz oscillations and a 0.05 s⁻¹ loading rate were selected. Measurements were taken at depths to 1500 nm and indentation modulus and hardness were calculated thanks to the Oliver and Pharr method [8] by averaging 30 measurements on each sample.

3. Results and discussion

3.1. Thermal and structural characterization of bio-based epoxy resins

The thermal properties of epoxy/amine cured resins are compared to literature and standard epoxy resin (Table 1). The decreasing of EEW from 280 to 180 g.eq⁻¹ is associated with the drop of T_{g0} and the increasing of the enthalpy from 170 to 332 J.g⁻¹. Those two elements highlight the increasing of the reactivity between the prepolymers and the hardener with the increasing of the ratio of epoxy ring of prepolymer. The T_{g_{onset}} and T_{g_{peak}} increase in parallel from 46 to 78 °C and 92 to 114 °C, respectively. The increase in epoxy grafting rate produces a higher crosslinking density. Compared with the results obtained by Chrysanthos et al. (2011), the ultrasonic method allows the T_{g_{peak}} to increase from 104 to 114 °C which makes it possible to have thermal properties comparable to the standard epoxy.

The overlay of infrared spectra (Fig. 1) shows the characteristic C-O bands of the epoxy groups at 908 and 845 cm⁻¹ and OH group at 3477 cm⁻¹ on DGEI180 spectra. After curing, DGEI180-IPD spectra displays an increase of hydroxyl group (3417 cm⁻¹) a high reduction of epoxy bands and the appearance of the characteristic band of primary amine at 1642 cm⁻¹ possibly do to residual hardener. The increasing of OH groups (3017–3383 cm⁻¹) confirms the reaction between the primary amine group with oxirane leading to free hydroxyl groups. The comparison between cured epoxy resins exhibits the increasing of OH due to the increasing of oligomers in prepolymers. The slight increase of epoxy groups (834 cm⁻¹) is possibly due to the decrease of the probabilities of meeting between the N-H and oxirane groups, which in agreement with the DSC results.

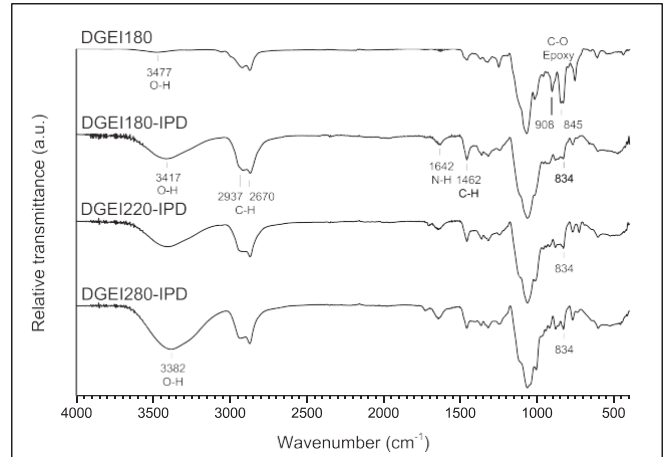


Figure 1. Overlay of infrared spectra of DGEI180 and epoxy/amine cured resins.

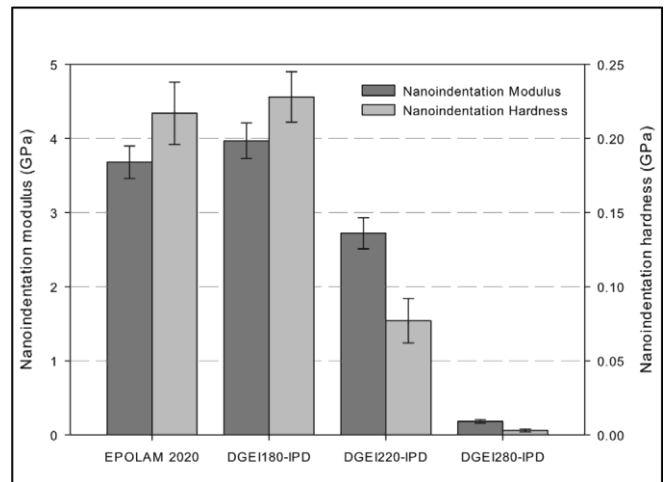


Figure 2. Comparison of nanoindentation modulus and hardness of epoxy resins cured with different epoxy content and to a standard epoxy Epilam[®].

3.2. Nanomechanical characterization of the epoxy resins

Fig. 2 shows average NI modulus and hardness obtained in both commercial Epilam2020 and isosorbide-based epoxy resins. Interestingly, one can notice that DGEI180-IPD exhibits a slightly improved mechanical performance compared to the standard Epilam 2020 epoxy resin. These two systems exhibit similar glass transition temperatures, 78 and 80 °C for DGEI180-IPD and Epilam 2020, respectively. NI mechanical properties of home-made resins regularly decrease with the increase of EEW, a drastic drop of NI modulus and hardness (94% and 98%, respectively) is noticed for DGEI280-IPD compared to DGEI180-IPD; as expected, a pronounced correlation between mechanical performances and glass transition temperature is observed, the NI modulus and hardness being negatively correlated with the EEW values. Indeed, a lower

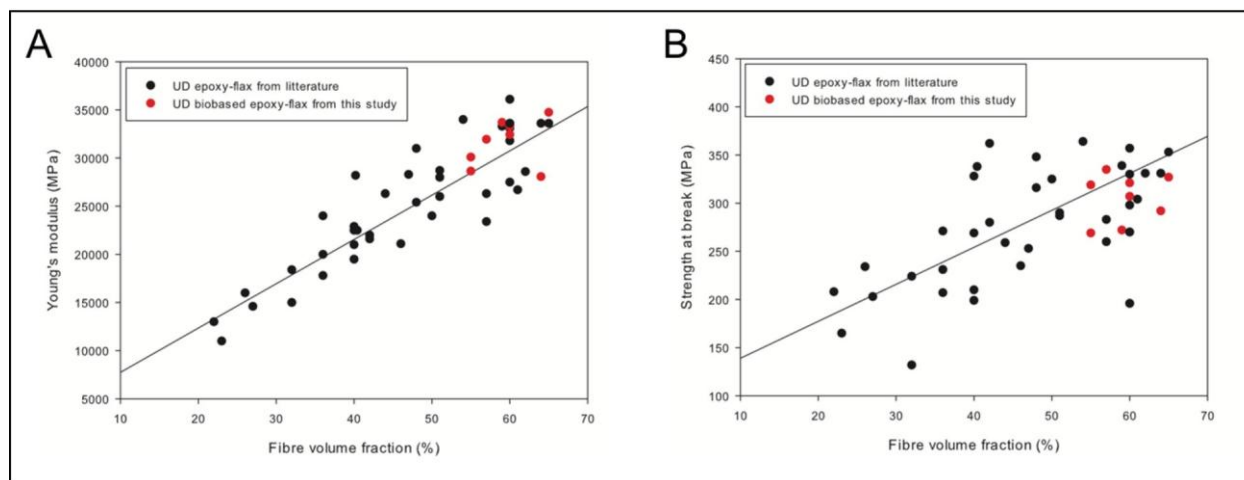


Figure 3. Comparison of biobased epoxy-flax composite with literature data (all materials are UD composites made of flax fibres and epoxy matrix) [10].

glass transition temperature induces higher polymer chain mobility and a softness behaviour, logically impacting mechanical performance. A more pronounced decrease is noticed for the hardness, compared to the modulus; indeed, hardness calculation is directly linked with the theoretical contact area between the indenter and the material. In case of defects such as voids, porosities within the sample, the hardness can be underestimated inducing low NI values.

3.3. Mechanical performances of UD composite

Fig. 3 presents the Young's modulus and tensile strength, according to the fibre volume fraction, of biocomposites performed in this study (in red) and compares them with recent literature data. In view of the thermal and mechanical results presented above, the DGEI180-IPD formulation was selected to develop these composite materials. In addition, the properties of the elementary flax fibres used were determined; with Young's modulus, stress and elongation at break values of 47.5 ± 11.7 GPa, 965 ± 373 MPa and $2.14 \pm 0.73\%$ respectively, they are well correlated to the values measured in the literature [9] on flax fibres with a similar protocol. Interestingly, whether in terms of stiffness or tensile strength, our composites offer performances comparable to literature unidirectional composites made with petroleum-based epoxy resins [10]. Regarding the stiffness, our values are even among the best composites, with values included between 270 and 340 MPa, which shows a good interfacial adhesion between the biobased resin we have developed and the flax fibres. To go further, it would be interesting to investigate the fibre-matrix interfacial shear strength and to sweep a large range of composite fibre volume fractions in a forthcoming work. Nevertheless, the results of this preliminary study validate the use of DGEI180-IPD resin for the development of structural biocomposites.

4. Conclusion

We have shown that it is possible to synthesize bio-based epoxy prepolymers with high reactivity towards amine hardener. Spectroscopic and calorimetric measurements indicate that their thermal and mechanical properties are at least as good as oil-based epoxy

precursors. The introduction of scutched flax fibres in DGEI/amine resins allowed the manufacturing of quasi fully bio-based composites. Mechanical tensile investigations on unidirectional composites have validated their use for structural applications with a Young's modulus and strength at break performance comparable with petroleum-based epoxy/flax fibres materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] N. Saba, M. Jawaid, O.Y. Alothman, M. Paridah, A. Hassan, Recent advances in epoxy resin, natural fiber-reinforced epoxy composites and their applications, *J. Reinf. Plast. Compos.* (2015), <https://doi.org/10.1177/0731684415618459>.
- [2] A. Bourmaud, J. Beaugrand, D.U. Shah, V. Placet, C. Baley, Towards the design of high-performance plant fibre composites, *Prog. Mater. Sci.* 97 (2018) 347–408, <https://doi.org/10.1016/j.pmatsci.2018.05.005>.
- [3] L.N. Vandenberg, R. Hauser, M. Marcus, N. Olea, W.V. Welshons, Human exposure to bisphenol A (BPA), *Reprod. Toxicol.* 24 (2007) 139–177, <https://doi.org/10.1016/j.reprotox.2007.07.010>.
- [4] R. Auvergne, S. Caillol, G. David, B. Boutevin, J.P. Pascault, Biobased thermosetting epoxy: Present and future, *Chem. Rev.* 114 (2014) 1082–1115, <https://doi.org/10.1021/cr3001274>.
- [5] F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup, J.P. Pascault, Polymers from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review, *Prog. Polym. Sci.* 35 (2010) 578–622, <https://doi.org/10.1016/j.progpolymsci.2009.10.001>.
- [6] M. Chrysanthos, J. Galy, J.P. Pascault, Preparation and properties of bio-based epoxy networks derived from isosorbide diglycidyl ether, *Polymer (Guildf)* 52 (2011) 3611–3620, <https://doi.org/10.1016/j.polymer.2011.06.001>.
- [7] C. Musa, P.-E. Danjou, A. Pauwels, F. Cazier-Dennin, F. Delattre, Ultrasound-assisted heterogeneous synthesis of bio-based oligo-isosorbide glycidyl ethers: towards greener epoxy precursors, *Molecules* 24 (2019) 9.
- [8] R. Scheibe, NADP⁺-malate dehydrogenase in C3-plants: Regulation and role of a light-activated enzyme, *Physiol. Plant.* 71 (1987) 393–400, <https://doi.org/10.1111/j.1399-3054.1987.tb04362.x>.
- [9] C. Baley, A. Bourmaud, Average tensile properties of French elementary flax fibers, *Mater. Lett.* 122 (2014) 159–161, <https://doi.org/10.1016/j.matlet.2014.02.030>.
- [10] A. Bourmaud, A. Le Duigou, C. Gourier, C. Baley, Influence of processing temperature on mechanical performance of unidirectional polyamide 11-flax fibre composites, *Ind. Crops Prod.* 84 (2016) 151–165, <https://doi.org/10.1016/j.indcrop.2016.02.007>.