# Use of a fully biobased and non-reprotoxic epoxy polymer and woven hemp fabric to prepare environmentally friendly composite materials with excellent physical properties

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## Abstract

In the future, materials will need to be biobased and produced sustainably without compromising mechanical properties. To date, in many cases, the advantages of the bio-origin of the raw material are overridden by the environmental impact of the process. In the present study, we have developed a novel composite material based on woven hemp fabric which reinforce a thermoset polymer produced from birch bark, a low-value forestry byproduct. Results show that this fully biobased composite has specific stiffness and strength equivalent to those of flax fibre-reinforced petroleum-based epoxy composites and slightly lower than glass fibre-reinforced petroleum-based epoxy composites. The sustainability of the material was also evaluated by life-cycle assessment from cradle to gate and showed significantly superior performance with respect to the potential global warming impact than commercial benchmark materials. Furthermore, toxicology studies showed no endocrine disruptive

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activities. This is an important proof of concept study demonstrating that biobased structural materials can be produced sustainably.

**Keywords:** A. Polymer-matrix composites (PMCs), B. Cure behaviour, B. Mechanical properties, Bio-based composites

**This manuscript is accompanied by a supplementary information (SI) file. SI-S# refers to the section # in the SI document.**

# 1. INTRODUCTION

Climate change is one of the major challenges faced by humanity in this century. Another challenge is that a growing population is increasing the demand for food and resources. To mitigate climate change in the face of this increased demand requires development of novel value chains that do not compete with food production, emit greenhouse gases or use finite resources. Furthermore, the production processes must be sustainable to avoid shifting the burden from raw material to production. In this context, it is necessary to develop new families of sustainable, lightweight and high-performance materials that are not derived from petroleum [1, 2]. Plant biomass is a promising raw material candidate for such developments. Indeed, the $CO_2$ sequestered by plants during growth makes this resource an excellent carbon sink and potentially allows production of carbon-neutral products. However, caution should be taken in the choice of biomass to avoid negative consequences related to effects on irrigation, eutrophication, and land-use. Major challenges remain for processing biomass into products with advanced functionalities while maintaining carbon neutrality and limiting the environmental footprint [1]. In many cases, the advantages of the bio-origin of the raw material are overridden by the environmental impact of the process [3]. It highlighs the importance of completing a comprehensive life cycle assessment (LCA) before a material and product can be labelled "environmentally friendly" [4].

Plant fibre composites (PFCs) constitute promising candidates for sustainable future materials [1, 5]. For the past 15 years, there have been tremendous interest and many technological developments involving these materials [6-10]. Among fibre crops, hemp is a notable and sustainable source of natural fibres that can be used for composite applications. Hemp is an environmentally friendly and fast-growing annual crop that fixes carbon dioxide (with absorption of approximately 1.4 to 1.6 t of $CO_2$ per tonne of hemp [11]), can be grown without the use of herbicides, pesticides or fungicides and requires no irrigation [12] or fertilizer in production [13]. This fibre plant also regenerates and improves the quality of soils by carbon sequestration. Fertilizer input is generally low [13],

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and the interventions and human power required for farming are limited. The resulting energy cost for raw hemp fibre production is estimated at approximately 5 GJ/t, approximately 7 times less than that required for the widely used glass fibres [14]. Hemp fibre constitutes an interesting alternative to synthetic fibres.

The most common matrices currently used in PFCs are polymeric, as they are lightweight and can be processed at low temperatures. Most of these matrices are produced from non-renewable resource. This strongly impairs the environmentally friendly character of the resulting composite materials. Among the traditional composite matrices, epoxy resins play key roles, and the diglycidyl ether of bisphenol A (DGEBA) is the major precursor used. The use of DGEBA has major drawbacks since bisphenol A (BPA) is an oil-derived and reprotoxic substance [15]. The reprotoxicity refers to the potential risk from a substance or a preparation which if it is inhaled or ingested or penetrates the skin may produce or increase the incidence of non-heritable adverse effects in the progeny and/or an impairment of male or female reproductive functions or capacity. BPA is a known endocrine disruptor, a substance that can interfere with our hormonal system and lead to such adverse effects. Substantial effort has been devoted during the last few years to finding a biobased alternative to DGEBA [16-22]. A variety of epoxy thermosets have been synthesized from various bioresources, either naturally occurring or biotransformed [23], such as cardanol, eugenol, vanillin, tannin acid, gallic acid, and so forth. Despite this substantial effort, no fully bio-based systems, including epoxy precursors, curing agents and additives, were commercialised so far.

More broadly, in the last decade, there has been a renaissance in biomass valorization [24, 25] for the production of low-carbon footprint chemicals production. Many studies have been directed towards efficient fractionation of lignocellulosic feedstocks, with novel directions such as 'lignin-first' methodologies [26-28]. In contrast, bark, which is a low-value feedstock currently burnt to produce energy, has received very little attention. Only a handful of reports on catalytic depolymerization and fractionation have been published [29-31]. Samec's group recently showed that ethyl guaiacol could be generated from the bark of *Quercus suber* by employing reductive catalytic fractionation [29]. However, this method required the use of a nonsustainable palladium catalyst in a fractionation process in which catalyst recovery is challenging. More recently, the same group reported organocatalytic depolymerization of bark from *Betula pendula* (birch) that was converted to biofuels with a positive LCA [30]. So, the objective of the present work is to develop a structural and fully biobased composite prepared from a sustainable and economically viable value chain based on plant biomass (Figure 1). This process combines a woven fabric produced from long hackled European hemp fibres and a biobased epoxy system constituted of a nontoxic epoxy monomer, diepoxy bis-ethylguaiacol (BG-diepoxy), derived from an abundant, renewable and undervalued

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wood feedstock, bark, and a hardener that can be produced from biobased furan. The thermomechanical properties of the composites produced using an optimized curing protocol are determined and compared to traditional glass fibre reinforced DGEBA-based epoxy composites. The sustainability is evaluated by life-cycle assessment (LCA) and the toxicology by endocrine activity studies.
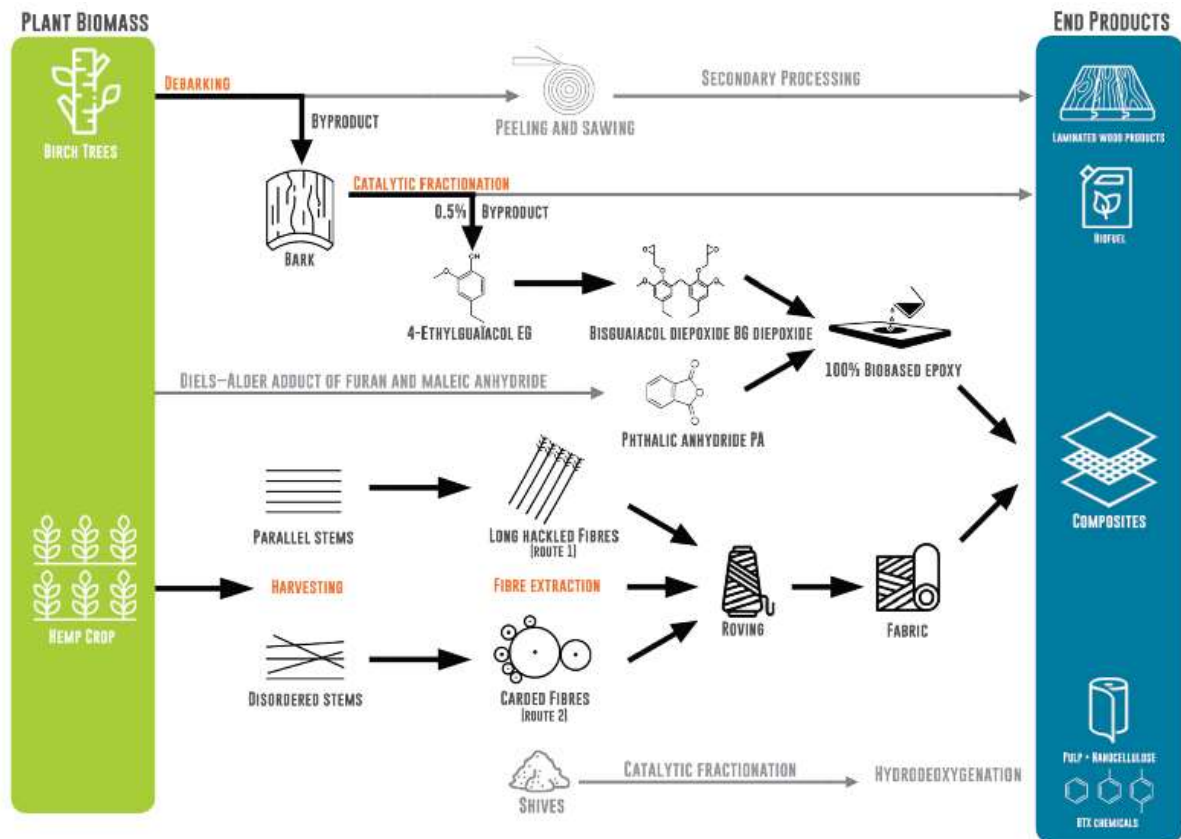


**Figure 1:** Development of structural and fully biobased composites from a sustainable and economically viable value chain based on plant biomass. The black colour represents the part of the value chain addresses in this work.

## 2. MATERIALS AND METHODS

### 2.1. Materials

All chemicals were purchased from Fischer chemicals, CCS Healthcare AB Sweden, Sigma-Aldrich, Honeywell, and VWR chemicals, and used as received (see SI).

The Biomass birch bark (Betula Pendula) was provided by Däcksta Såg, Gimo, Sweden (SI-S2).

The hemp reinforcement, a woven fabric with a balanced diagram, a satin 6 weft effect and an areal weight of approximately 350 g.m$^{-2}$, made of 100% French long scutched and hackled hemp fibres, was provided by Linificio e Canapificio Nazionale (SI-S6).

### 2.2. Production of diepoxy bisguaiacol (BG-diepoxy)

4-Ethylguaiacol was produced according to a previously published protocol [30] with the exception that the compound was isolated by distillation after solvent removal (SI-S2). 4-Ethylguaiacol was dimerized using formaldehyde and epoxidized by reaction with epichlorohydrin in the presence of $K_2CO_3$ to generate the desired diepoxy bis-ethylguaiacol (BG-diepoxy) (SI-S3).

### 2.3. BG diepoxy and DGEBA curing

Polyepoxy polymers were obtained via thermal curing according to the protocol described in Table 1 and in SI-S4. Two monomers, BG-diepoxy and DGEBA, and two anhydride hardeners, namely, methyl nadic anhydride (MNA) and phthalic anhydride (PA), were used with a molar ratio 1/1.6. They were ground in a mortar at room temperature and heated at a temperature superior to the mixture melting point, respectively 45°C - DGEBA/MNA, 65°C - BG/MNA, 110°C - DGEBA/PA and 130°C - BG/PA (SI-S4). When a homogeneous mixture was obtained, DMID catalyst was added with a molar ratio of 0.05 with respect to diepoxy monomer.

**Table 1:** Optimized curing conditions of the thermoset epoxy polymers and Tg determined by DSC and DMA (tanδ's peak)

| Epoxy systems (formulation, molar ratio and temperature of liquid state) | Optimized curing conditions | Tg (°C) (DSC) | Tg (°C) (DMA) |
|---|---|---|---|
| **DGEBA/MNA/1,2-DMID 1-1.6-0.05 Fluid liquid at 46 °C** | 30 min at 130 °C<br>15 min at 150 °C<br>Post curing 10 min at 170 °C | 154 | 165 |
| **DGEBA/PA/1,2-DMID 1-1.6-0.05 Fluid liquid at 110 °C** | 1 h at 110 °C<br>15 min at 150 °C<br>Post curing 10 min at 170 °C | 157 | 165 |
| **BG-diepoxy/MNA/1,2-DMID 1-1.6-0.05 Fluid liquid at 66 °C** | 30 min at 130 °C<br>15 min at 150 °C | 105 | 115 |
| **BG-diepoxy/PA/ 1,2-DMID 1-1.6-0.05 Fluid liquid at 130 °C** | 30 min at 120 °C<br>15 min at 150 °C | 99 | 110 |

### 2.4. DSC analysis

A TA Instruments (New Castle, DL, USA) Discovery DSC was used. Crosslinking was studied by heating the sample from 25 to 180°C at a heating rate of 5°C min-1, while the Tg was determined during the second heating of the thermoset from 20 to 180°C at a heating rate of 10°C min-1.

### 2.5. DMA studies

Dynamic mechanical analyses (DMA) were performed on rectangular samples (50×10×2 mm³) of polymers on a METRAVIB 300 apparatus with a frequency range of 0.5-5 Hz between 30°C and 210°C at 5°C intervals under isothermal conditions. A sinusoidal tensile displacement was applied on the sample with a peak-to-peak amplitude of 8 μm (SI-S7.4). For each batch, three specimens were systematically tested. A very good reproducibility of the measurements was observed. For reason of readability, in the present paper, results are presented in the manuscript for one specimen only.

### 2.6. Composite manufacturing

Composite materials were manufactured by using the different epoxy systems described above. The materials were manufactured using a hand lay-up for impregnation and thermocompression for consolidation. A woven hemp fabric recently developed for composite purposes [32, 33] was used (more details in SI-S6).

Composite plates were manufactured with a targeted mass fraction of 50%. The curing and postcuring protocols were similar to those used for the neat epoxy systems. Due to the resin loss during the thermocompression process, the measured fibre volume fractions were comprised between 38.1 and 49.3% depending on the manufactured plates. More details are given in SI-S7.

### 2.7. Bending tests

Three-point bending tests were conducted on polymer and composite samples following the ASTM D790 and D7264 standards. Rectangular samples with dimensions of 2, 12 and 100 mm in thickness, width and length, respectively, were used. More details are given in SI-S7.5. Five samples were tested for each batch.

To ensure a fair comparison between the different composite materials (which have different fibre volume fractions), the effective stiffness and strength of the fibres were determined using the following equations.

$$E_f = \frac{E_c - E_m \cdot (1 - V_f)}{V_f} \tag{1}$$

$$\sigma_f = \frac{\sigma_c - \sigma_m \cdot (1 - V_f)}{V_f} \tag{2}$$

Theoretical values of composite stiffness and strength were then computed for a fibre mass fraction of 40% using the rule of mixture, the effective properties of the fibres and the measured properties of the neat matrices.

### 2.8. Microdroplet tests

Microdroplet pull-out tests were conducted on selected very thin hemp fibres, with a diameter below 40 microns. A small droplet of resin was applied, after which the resin curing protocol was conducted. The debonding tests were performed with a micromechanical testing device (Deben), and the apparent interfacial shear strength was calculated by normalizing the failure force to the fibre-droplet contact area (SI-S7.6). The droplet size was chosen such that the embedded area was always between 20,000 and 30,000 square microns. Microdroplet debonding and pull-out tests were conducted on selected very thin hemp fibres of uniform cross-section, either on elementary fibres or on very thin bundles containing maximum three elementary fibres. For each resin system, five to ten droplet tests were conducted.

### 2.9. LCAs

An attributional LCA was performed according to ISO14040. The inventory data were retrieved from the laboratory results and GaBi, Ecoinvent 3.3, and ThinkStep databases. Additional assumptions are explained in the SI-S9. For the life cycle impact assessment, the ReCiPe 2016 Midpoint was used. The obtained results were normalized according to ReCiPe 2016 midpoint hierarchic normalization factors, which took into account the amount of equivalent impacts generated per person in 2010 for the global population.

### 2.10. Toxicology

Agonist and antagonist activities of BPA and DGEBA were measured in bioluminescent reporter cell lines as previously described [34, 35]. Briefly, HELN ER$\alpha$ and U2OS AR reporter cell lines were seeded at a density of 25,000 cells per well in 96-well white opaque tissue culture plates (Greiner CellStar). Twenty-four hours later, chemicals to be tested were added alone (agonist test) or in the presence of E2 or R1881 (antagonist test) into the wells. The cells were incubated at 37°C for 16 h. At the end of the incubation period, the culture medium was replaced with medium containing 0.3 mM luciferin. Luciferase activity was measured for 2 s in intact living cells using a plate reader (PerkinElmer Luminometer). More details are given in SI-S10.

## 3. RESULTS AND DISCUSSION

### 3.1. <u>Green chemistry route to bio-based epoxy resin precursor</u>

Ethyl guaiacol (EG) was isolated by vacuum distillation of depolymerized birch bark [30]. Even though the EG was obtained in a low yield (1.6 wt%), the remaining fraction could be converted to a biofuel to close the mass balance and divide the environmental burden. Thus, the low yield of EG can be considered sustainable and this was also confirmed by LCA, *vide infra*. A major challenge for green and sustainable chemistry [36, 37] is the use of organic solvents, where typically solvent-to-substrate ratios of 10–100 are used; this results in unsustainable mass balances, that can be evaluated by the environmental factor [38]. To address this challenge in the synthesis of bio-based precursor from EG, a two-step reaction sequence was developed in which all solvents were recycled by distillation with negligible losses (Figure 2).
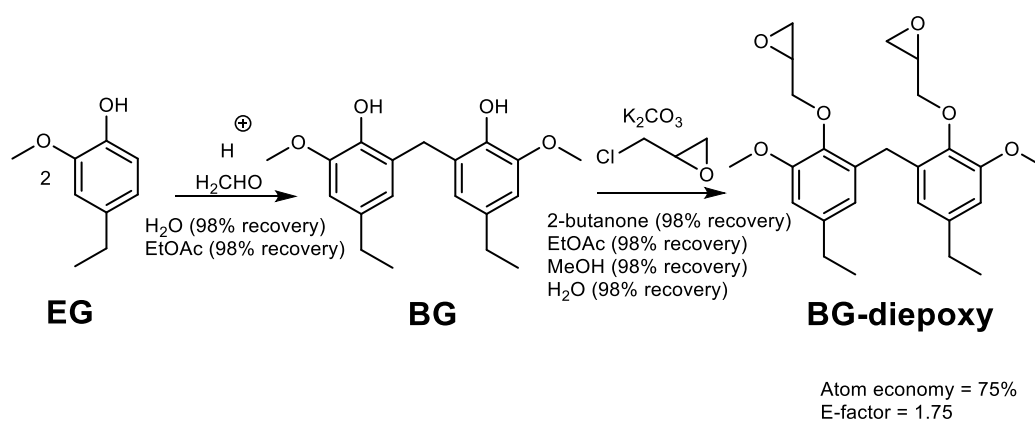


*Figure 2:* Green Chemistry pathway to dimerize monophenolic compound EG into BG and then into BG-diepoxy.

In the first step, EG was condensed with formaldehyde under slightly acidic aqueous conditions, and the bis-ethylguaiacol (BG) was efficiently extracted by ethyl acetate in quantitative yield and used without further purification in the next step. The aqueous phase was directly reused for consecutive condensation reactions, and benign ethyl acetate was recovered by distillation in 98% efficiency. The second step consisted of base-mediated substitution of epichlorohydrin to generate the desired diepoxy bis-ethylguaiacol (BG-diepoxy) using benign butanone as solvent (Figure 2). Purification was accomplished by simple precipitation using cold MeOH to yield the product in 75% yield with a solvent recovery of 98% (SI-S3-2). This gives an overall atom economy of 75% and an overall process E factor based on full mass balance including work-up and purification of 1.75. Thus, we developed a green synthetic pathway to obtain the desired BG-diepoxy from birch bark with a favourable mass

balance due to holistic valorization of the birch bark, conscious choice of solvent and efficient recycling of the same in the chemical synthesis of BG-diepoxy.

### 3.2. <u>Sustainable polymerization of BG-diepoxy</u>

Diepoxy resin was cured using the BG-diepoxy and two anhydride hardeners, namely, methyl nadic anhydride (MNA) and phthalic anhydride (PA) (Figure 3).
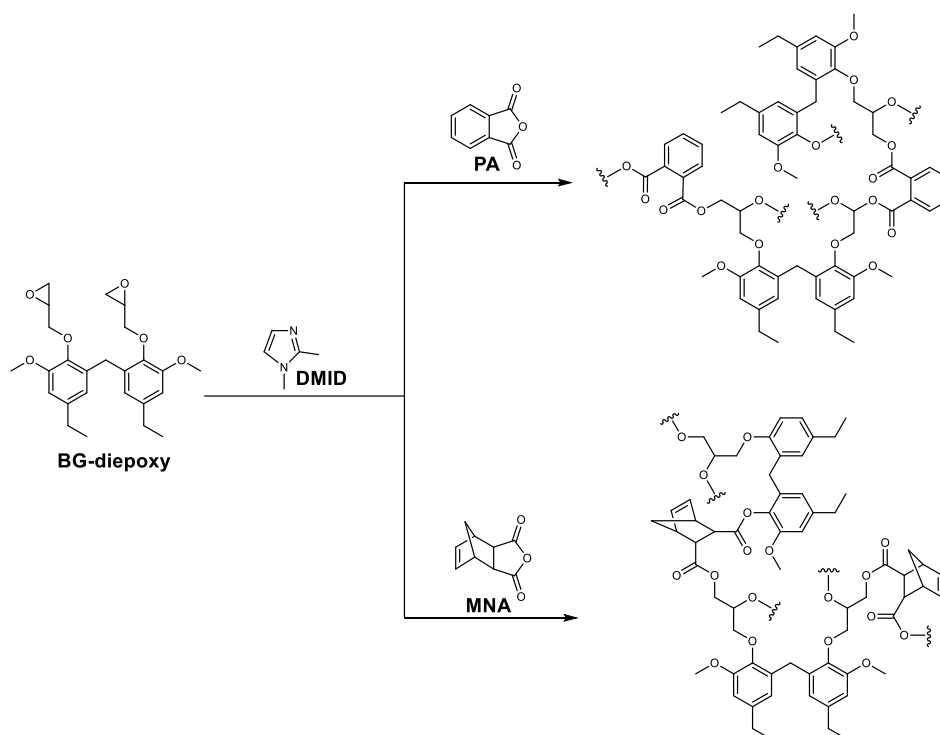


*Figure 3:* Polymerization of BG-diepoxy.

Anhydride hardeners were preferred over polyamine hardeners to avoid oxidative degradation reactions during ageing [39]. Their chemical structures containing rigid cyclic groups also ensured production of high-performance epoxy thermosets. Toxicity and bio-sourcing of these materials were also considered, and both anhydrides were determined to be compliant with the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation. While synthetic routes using MNA have been based on petroleum resources, a more sustainable route from biomass-derived starting materials was recently proposed in literature for the PA from bio-based furfural [40]. As a result, the diepoxy bisguaiacol/phthalic anhydride (BG-diepoxy/PA) system developed in this study reached a bio-based carbon content of approximately 100%.

For benchmark purposes, DGEBA resin was also cured with these two hardeners. DGEBA has a widespread use in the manufacture of polymer composites to obtain different elements of structural engineering. Formulations for the different epoxy systems studied are depicted in Table 1. The anhydride hardener/BG diepoxy molar ratio of 1.6 was chosen after optimization based on Fourier transform infrared (FTIR) analysis of the cross-linked material [41]. Indeed, under these conditions, the FTIR spectrum shows that both epoxy and anhydride functions have completely reacted (absence of anhydride and epoxy bands, see SI-S4 section, Fig.SI-5) and the glass transition temperature (Tg) of the cross-linked material determined by DSC is the highest. It should be noted that the results of this optimisation method are in good agreement with the results of epoxy dosing performed with BG diepoxy according to the standard procedure (SI-S4). Indeed, an epoxy equivalent weight (EEW) of 275 g.mol$^{-1}$ was observed instead of the theoretical value of 214 g.mol$^{-1}$. This indicated that the optimal experimentally determined molar ratio corresponded to a stoichiometric ratio of one anhydride functional group to one epoxy functional group.

The curing protocol was defined with the aim of manufacturing composites reinforced with hemp fibres. The curing reaction must occur at a temperature below 190°C to prevent fibre degradation [42]. The initial diepoxy resin/anhydride hardener/DMID catalyst mixture should also be sufficiently fluid to adequately impregnate the fibre network before initiating the cross-linking reaction. Thus, a DSC study allowed us to determine the curing temperature and to verify that, according to the proposed heating protocol, cross-linking was achieved (Figure 4A). Indeed, no exothermic reaction was detected when the cured sample was heated to determine its Tg by DSC analysis (Figure 4B). Thermogravimetric analysis (TGA) results show that the onset temperatures of degradation (T5%) for all materials were higher than 270°C (Figure 4C). These degradation temperatures are thus significantly higher than the targeted composite manufacturing temperature and the operating temperature for most of the organic matrix composite applications.
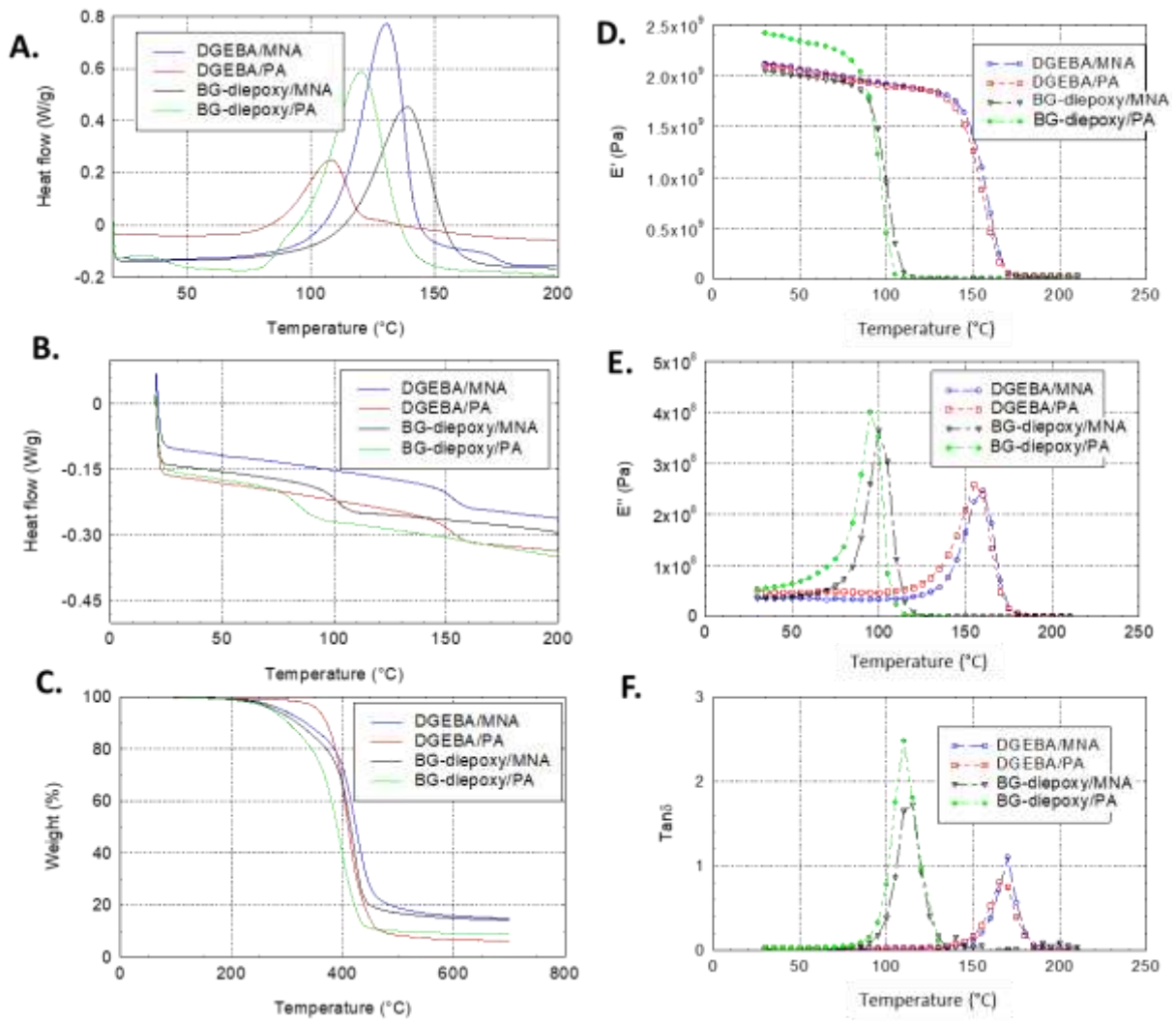
**Figure 4**: Thermomechanical properties of the thermoset epoxy polymers. DSC curing curves (heating flow vs. temperature) of the epoxy systems (A), DSC curves (heating flow vs. temperature) of the cured samples (B), thermogravimetric analysis giving the weight loss as a function of temperature (C) and DMA properties of the cured polymers: storage modulus (D), loss modulus (E) and loss factor (F) as a function of temperature.

The viscoelastic properties of composite matrices, as well as their evolution as a function of temperature, are also of primary importance for the development of composite materials. Their suitability with the composite manufacturing process, the design criterion and the service life conditions has to be verified. The viscoelastic properties of the different epoxy systems were then characterised using dynamic mechanical analysis (DMA). The storage modulus (E'), loss modulus (E'') and the loss factor (tanδ) were measured as a function of temperature. The storage modulus of the BG-diepoxy-based epoxy systems is comparable to those obtained with the DGEBA-

based epoxy systems and ranged between 2 and 2.5 GPa, at ambient temperature (Figure 4). The glass transition temperature (Tg) was then determined from the tanδ's peak. Tg is the critical temperature at which the transition between glassy and rubbery state occurs. It is one of the most important parameters when selecting composite matrix since dramatic changes in any polymer chain mobility take place at and above Tg. The use temperature for practical applications is generally required to be below the glass transition temperature, so that the material at use is in rigid solid state. For the BG-diepoxy-based epoxy systems, Tg was lower to those obtained with the DGEBA-based epoxy systems (100-115°C vs. 155-165°C, Figures 4A, 4E and 4F) but suitable for PFCs used in structural applications.

### 3.3. <u>**Mechanical performance of bio-based composites**</u>

For structural applications, the crucial properties of composite materials are stiffness, strength, toughness, fatigue resistance, vibration damping and hygro-thermal stability and durability. In the process of research and development of new materials, the performance under monotonic loading are generally primarily evaluated. Thus, the quasi-static bending characteristics of the epoxy polymers and composites were then characterized. The reinforcement potential of hemp fabric was obvious (Figure 5A), with increases of approximately 3.75 to 4 times for the E-modulus and approximately 1.9 to 3.5 times for the strength when compared to the polymer matrix alone. For the BG-diepoxy/PA epoxy polymer, the bending modulus (3.2 GPa) was comparable to those of the other tested epoxy systems, particularly the DGEBA-based systems; the bending strength and strain at failure were lower (by approximately 35%), reflecting a more brittle nature. The average bending strength and strain values obtained, which were 46 MPa and 1.46%, respectively, were still suitable for composite applications, and it is interesting to observe that this behaviour was no longer observed for the composite materials. Indeed, the bending properties of the fully bio-based system (BG-diepoxy/PA) with a fibre mass fraction of 55% were approximately 14.7 GPa, 160 MPa and 2.7% for the Young's modulus (Figure 5B), bending strength (Figure 5C) and strain at failure (Figure 5D), respectively. The estimated values for a fibre volume fraction of 40% are similar to those for the DGEBA-based composites. The specific properties (dividing the mechanical properties by the density of the material) were also on the same order of magnitude as those for woven glass fibre-reinforced epoxy composites. The specific properties are crucial quantities when selecting materials in mechanical design [43]. The specific bending rigidity and strength of the woven hemp fibre-reinforced BG-diepoxy/PA composites were 9.5 GPa.m$^3$.kg$^{-}$1 and 105

MPa.m$^3$.kg$^{-1}$, respectively, which are comparable to the specific tensile rigidity and strength of flax twill/epoxy composite (9.9 GPa.m$^3$.kg$^{-1}$; 97 MPa.m$^3$.kg$^{-1}$) and 26 to 33% lower than the specific tensile rigidity and strength glass twill/epoxy composite (12.8 GPa.m$^3$.kg$^{-1}$; 156 MPa.m$^3$.kg$^{-1}$), for a fibre volume fraction of 40% [44].
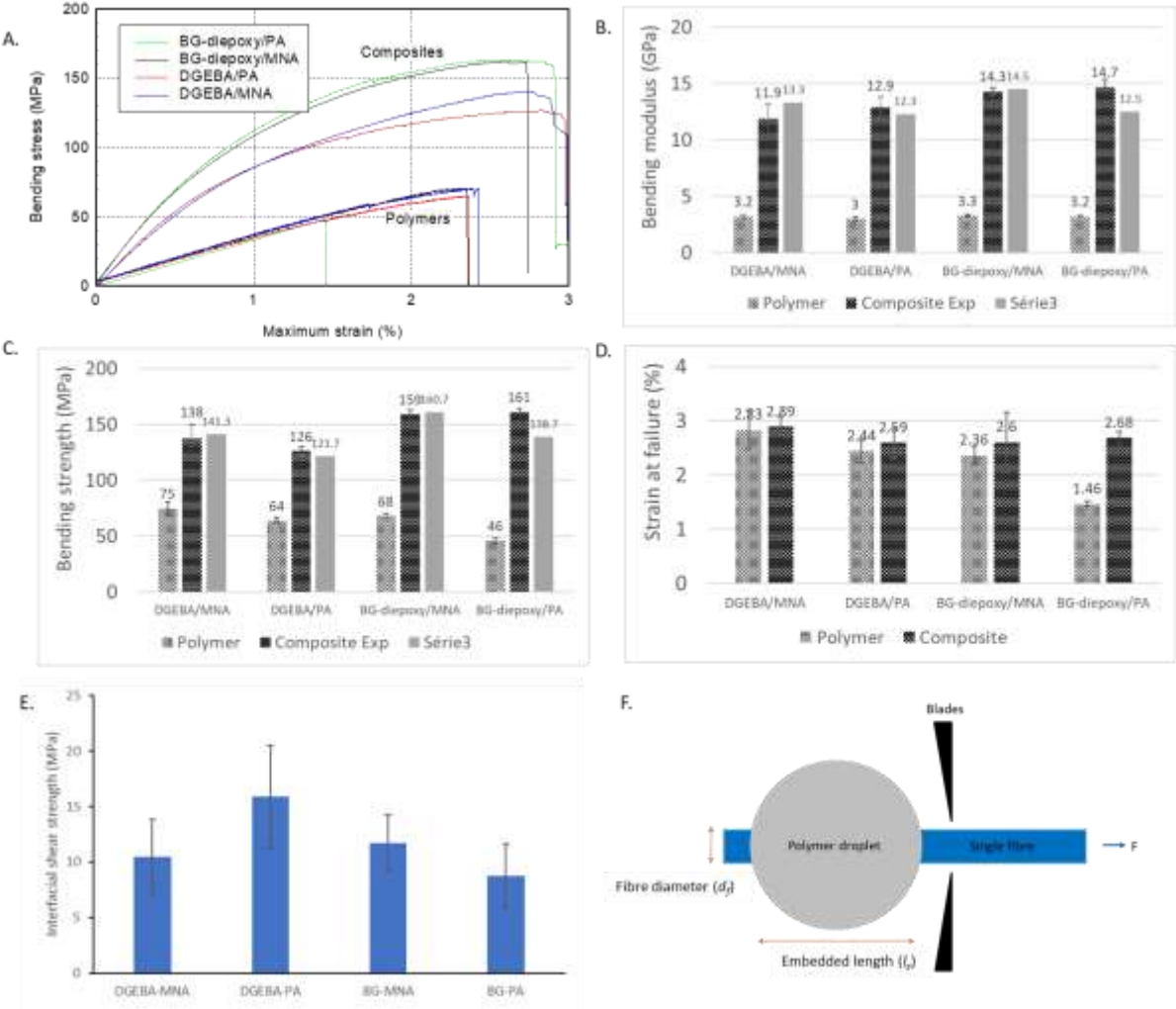


**Figure 5:** Bending properties of the epoxy polymers and composites. 3-point bending curves (A), bending modulus (B), strength (C) and strain at failure (D) of polymer and composite materials (Composite exp: experimental values, Composite Theo: theoretical values computed from experimental measurements and a rule of mixture for fibre mass fraction of 50%). Apparent microdroplet interfacial debonding shear strength (E) (values represent lower bounds because concurrent with debonding, fibre failure also occurred, and in the case of the BG systems, occasional resin failure also occurred. Thin technical hemp fibres with an average thickness of $29 \pm 5$ microns and an embedded length of $277 \pm 48$ microns). (F): Schematic representation of the microdroplet interfacial debonding test.

The observation that the Hemp/BG-diepoxy/PA composite had similar strength and strain at failure as the DGEBA-based one, while the polymer showed lower performance could be explained by an enhanced cohesion between the polymer matrix in the case of BG-diepoxy. Indeed, in composite materials, the interphase properties play a crucial role in the load transfer between the fibre and the resin and hence the global performance and durability of the composite material [45]. The degree of fibre matrix adhesion is generally measured using micromechanical experimental methods including single fibre pull out, fibre push out, fibre fragmentation and microdroplet tests [46]. In this work, the interfacial debonding shear strength was evaluated using microdroplet tests (Figure 5F). All tested systems showed good fibre-matrix adhesion (Figure 5E); no simple fibre-matrix debonding occurred, and a mixed mode of partial debonding, resin failure and, in all cases, fibre failure occurred. The BG-PA value seems lower because resin failure occurred for half of the samples, which can be attributed to the lower resin strain to failure. So, attempts to verify that cohesion between the polymer matrix is enhanced in the case of BG-diepoxy by micro-droplet testing were unfortunately not successful. So, the observation that the Hemp/BG-diepoxy/PA composite had similar strength and strain at failure as the DGEBA-based one, while the polymer showed lower performance could be explained by a modification of the reticulation and 3D network of the polymer in the presence of hemp fibres. Further studies are necessary to assess this hypothesis.

However, based on the measured properties, it can be concluded the fully-based composite proposed in this study exhibit excellent physical properties and fulfil the requirements for structural applications.

### 3.4. Environmental sustainability

As mentioned in the introduction, bio-based materials are far from sustainable when including the production phase [3, 47]. To ascertain that the composite material in this study was sustainable, a cradle to gate LCA was performed. The data flow and the steps considered in the LCA are performed according to the ISO 14040 standard as illustrated in SI (Figure SI-8). The GWP impact of bis-guaiacol diepoxy production was compared with other resins commonly used in composite materials, as shown in Figure 6A. BG-diepoxy resin has a 16% lower GWP impact than standard DGEBA-based epoxy resin and up to a 34% lower impact than BPA epoxy-based vinyl ester resin. The main reason for the lower GWP impact is the use of biomass instead of fossil oil as a resource, including the sequestration of $CO_2$ during the growth of the biomass, together with optimized use of reagents, which are reused and recycled where possible during the production of the resins.
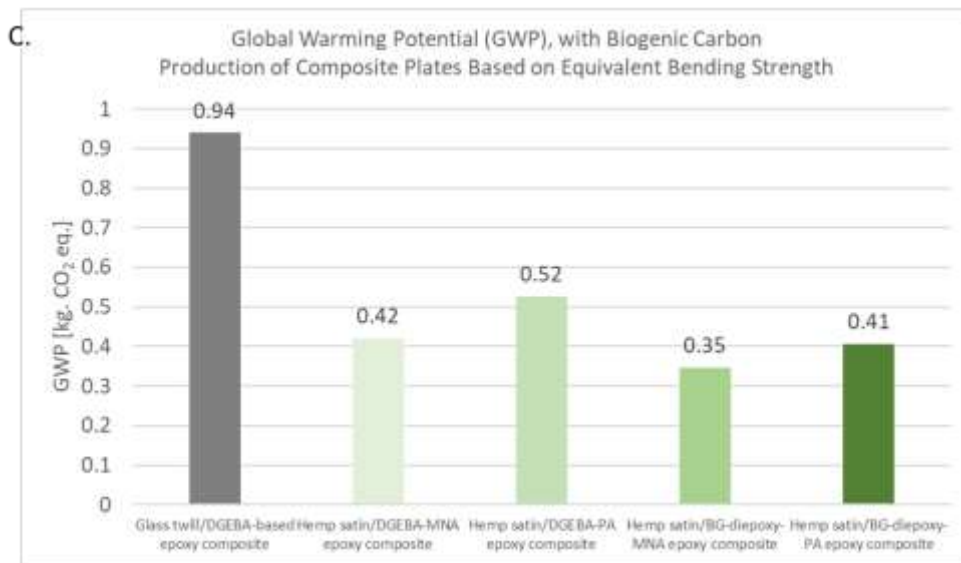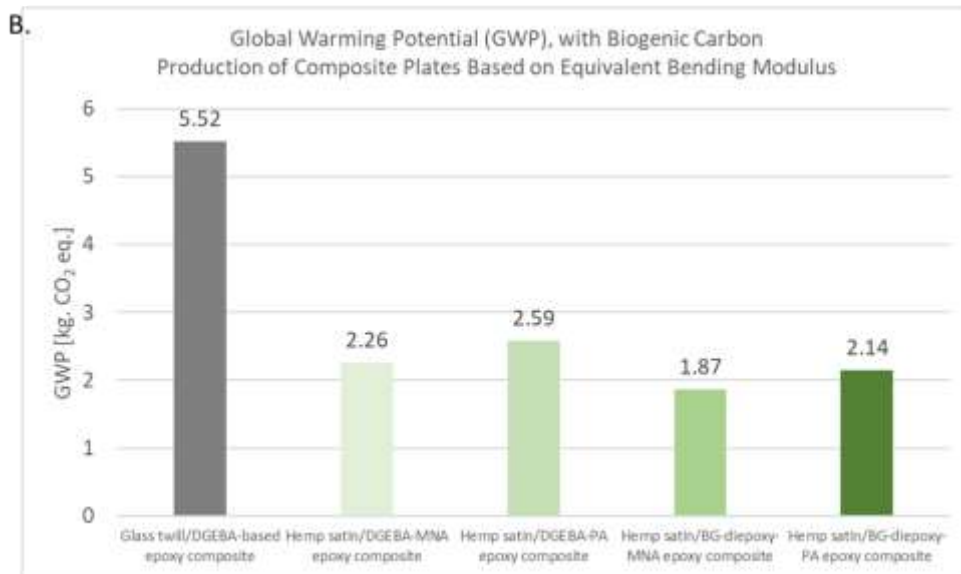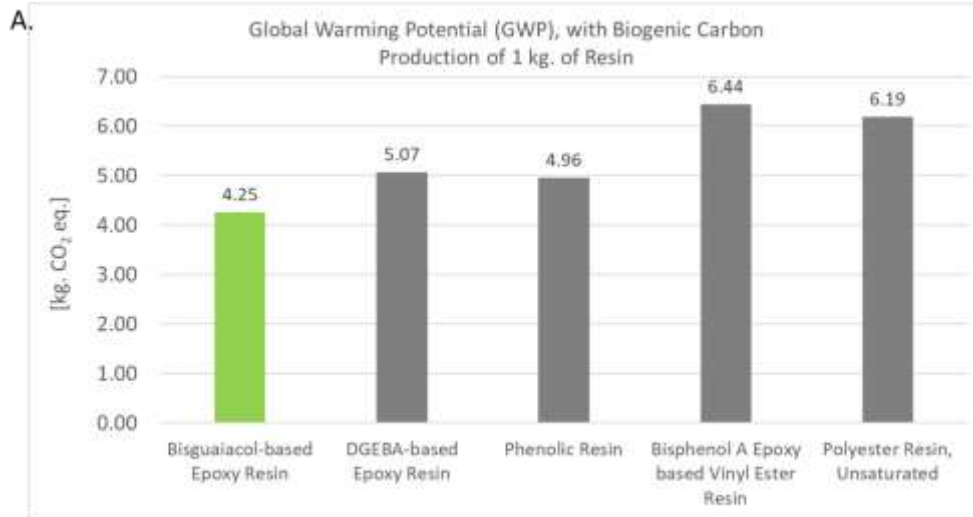
**A.**

**Global Warming Potential (GWP), with Biogenic Carbon**
**Production of 1 kg. of Resin**

| | |
|---|---|
| Bisguaiacol-based Epoxy Resin | 4.25 |
| DGEBA-based Epoxy Resin | 5.07 |
| Phenolic Resin | 4.96 |
| Bisphenol A Epoxy based Vinyl Ester Resin | 6.44 |
| Polyester Resin, Unsaturated | 6.19 |

[kg. $CO_2$ eq.]

**B.**

**Global Warming Potential (GWP), with Biogenic Carbon**
**Production of Composite Plates Based on Equivalent Bending Modulus**

GWP [kg. $CO_2$ eq.]

| | |
|---|---|
| Glass twill/DGEBA-based epoxy composite | 5.52 |
| Hemp satin/DGEBA-MNA epoxy composite | 2.26 |
| Hemp satin/DGEBA-PA epoxy composite | 2.59 |
| Hemp satin/BG-diepoxy-MNA epoxy composite | 1.87 |
| Hemp satin/BG-diepoxy-PA epoxy composite | 2.14 |

**C.**

**Global Warming Potential (GWP), with Biogenic Carbon**
**Production of Composite Plates Based on Equivalent Bending Strength**

GWP [kg. $CO_2$ eq.]

| | |
|---|---|
| Glass twill/DGEBA-based epoxy composite | 0.94 |
| Hemp satin/DGEBA-MNA epoxy composite | 0.42 |
| Hemp satin/DGEBA-PA epoxy composite | 0.52 |
| Hemp satin/BG-diepoxy-MNA epoxy composite | 0.35 |
| Hemp satin/BG-diepoxy-PA epoxy composite | 0.41 |

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*Figure 6*: GWP as determined by an LCA for (a) production of 1 kg of bis-ethylguaiacol (BG) and other resins (1) industrial epoxy resin, (2) phenolic resin, (3) BPA epoxy-based vinyl ester resin, and (4) polyester resin, unsaturated, for (b) production of one hemp fibre reinforced composite plate with (1) DGEBA/MNA with 1,2-DMID, (2) DGEBA/PA with 1,2-DMID, (3) BG-diepoxy/MNA with 1,2-DMID, (4) BG-diepoxy/PA with 1,2-DMID epoxy systems compared to a glass-fibre reinforced epoxy composite plate, all with an equivalent bending stiffness of 1 $GPa^{1/3}.dm^3$, and for (c) production of the same composite materials as (b), but now all with equivalent tensile strengths of 1 $MPa^{1/2}.dm^3$.

Moreover, the GWPs were also determined for the fully bio-based composite materials (Figure 6B and Figure 6C) described above based on a cradle-to-gate LCA including all processing steps depicted in Figure 1.

For this part of the assessment, the environmental impacts were calculated and scaled (as illustrated in the flowchart Figure SI-8) according to the performance of the materials, more specifically (1) the mass of the composites required to achieve the same bending stiffness and (2) bending strength of a thin plate, and the corresponding GWP results are reported in Figure 6B and Figure 6C, respectively. Within the bio-based epoxy systems, the BG-diepoxy/MNA system (MA-substituted system) had the lowest GWP impact in comparisons of both mechanical properties, 28 and 34% lower than the GWP impact of the DGEBA/PA system, and 66 and 63% lower than the conventional glass-fibre reinforced epoxy composite when the bending stiffness and bending strength were used as the basis for comparison respectively. Other environmental impacts resulting from the LCA showed similar trends (SI-11 and SI-12), except for eutrophication and land use.

### 3.5. <u>Toxicology</u>

A major concern in the development of new platform chemicals to be utilized in place of BPA is the propensity of these chemicals to interact with the human nuclear receptors and how this interaction compares to those of current bisphenol analogues. In this work, the oestrogen receptor ER$\alpha$ and androgen receptor AR activities of BG and BG-diepoxy were compared to those of BPA and DGEBA.

The agonistic potentials of the chemicals at 10 $\mu$M were monitored on ER$\alpha$ (Figure 7A) transcriptional activity by using HELN ER$\alpha$ reporter cells [34]. In these cells, BPA, which is a partial oestrogen receptor agonist [34], exhibits partial potency for luciferase activity (60% activity of the transactivation seen with oestradiol (E2) which is a partial oestrogen receptor agonist [34]). On the contrary, DGEBA, BG and BG-diepoxy were demonstrated to

be completely inactive. The antagonistic potentials of these chemicals were also assessed with HELN ERα cells in the presence of 0.1 nM E2. All of the compounds were devoid of antagonistic activity except for BPA, which being a partial agonist inhibited luciferase expression (Figure 7B).

The agonistic potentials of the chemicals at 10 μM were also monitored for AR (Figure 7C) transcriptional activity by using U2OS AR reporter cells[35]. All of the compounds were devoid of agonistic activity. The antagonistic potentials of the chemicals were also assessed with U2OS AR cells in the presence of 0.3 nM R1181. Except for BPA, all of the compounds were devoid of antagonistic activity (Figure 7D).

Together, these experiments show that BG and BG-diepoxy are devoid of (anti)estrogenic or (anti)androgenic activities.
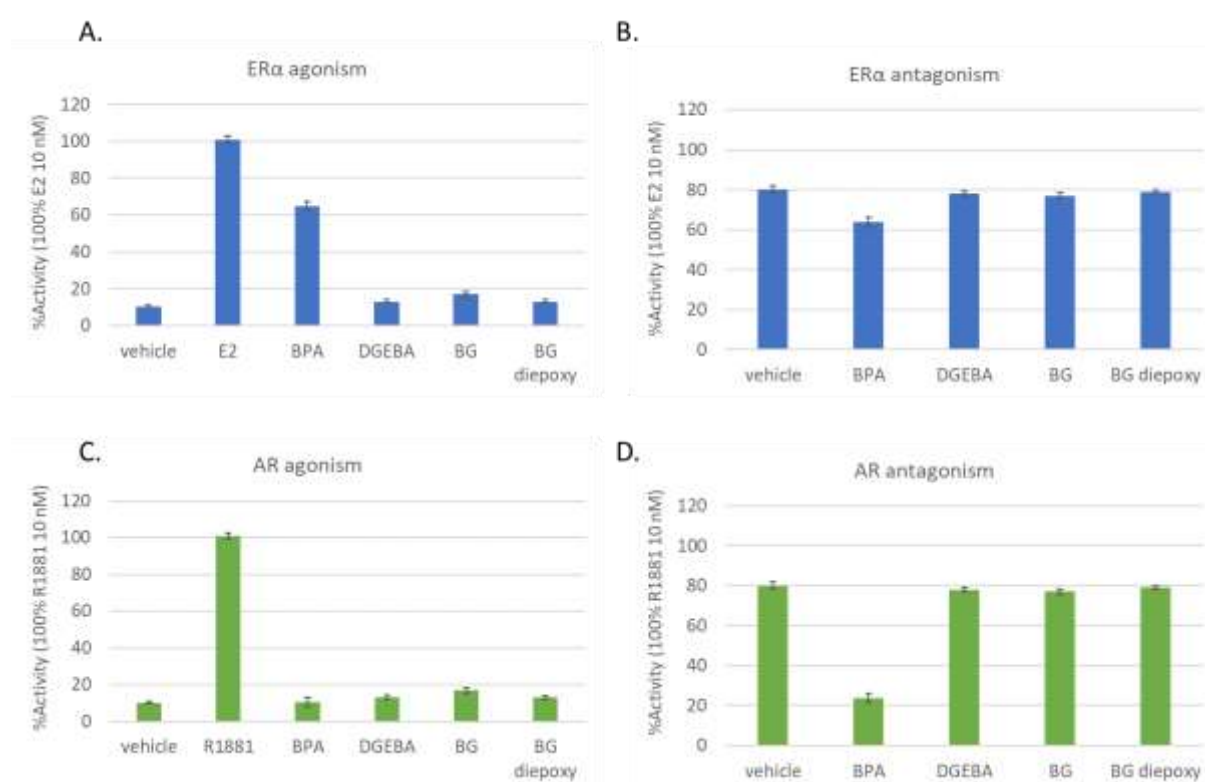


**Figure 7**: ERα and AR agonistic and antagonistic activities of BPA, DGEBA, BG and BG-diepoxy in reporter cell lines. (A) ERα agonistic activity of chemicals. The HELN ERα cells were incubated for 16 h with E2 (10 nM) or BPA, DGEBA, BG or BG-diepoxy at 10 μM. (B) ERα antagonistic activity of chemicals. The HELN ERα cells were incubated for 16 h with BPA, DGEBA, BG and BG-diepoxy at 10 μM in the presence of 0.1 nM E2. (C) AR agonistic activity of chemicals. The U2OS hAR cells were incubated for 16 h in the presence of 10 nM R1881 or BPA, DGEBA, BG and BG-diepoxy at 10 μM. (D) AR antagonistic activity of chemicals. The U2OS hAR cells

were incubated for 16 h with BPA, DGEBA, BG and BG-diepoxy at 10 μM in the presence of 0.3 nM R1881. The maximal luciferase effect was obtained with 10 nM E2 (A) and (B) and 10 nM R1181 (C) and (D). Values are expressed as the mean ± SD from triplicate experiments. Vehicle is DMSO.

## 4. CONCLUSIONS

An environmentally sustainable synthetic route to fully bio-based and nontoxic epoxy polymers is presented for the manufacture of high-performance renewable plant fibre composite materials. A nonharmful building block, EG, derived from a low-valued by-product from the sawmill and pulp and paper industries has been used. When interconnected with the hemp value chain, it maps and demonstrates a competitive and sustainable solution for replacement of glass fibre-reinforced DGEBA-based epoxy composites for engineering applications. These results show that a fully bio-based composite with comparable mechanical properties can be produced. The environmental sustainability was assessed by a cradle to gate LCA and showed benefits in GWP. The BG did not show (anti)estrogenic or (anti)androgenic activities, which is a common problem with BPA. This is an important step in the development of sustainable materials, and we hope that this inspires researchers to undertake further steps toward a bio-based economy.

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