Towards sustainable reprocessable structural composites: benzoxazines as biobased matrices for natural fibers

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Abstract

In this work, we synthesized and investigated three fully biobased benzoxazine matrices containing exchangeable ester bonds for natural fiber composites. The thermoset properties were investigated and the transesterification behavior was assessed. The obtained polymers show high tunability. Using isosorbide as the starting building block, the thermoset exhibits a glass transition of 130 °C, a tensile modulus of 2.5 GPa, and thermal stability leading to degradation occurring after 270 °C with 31% char at 800 °C. All formulations stress relax under catalyst-free conditions within minutes with properties recovery superior to 80%. Finally, flax composites were manufactured. We highlight strong affinities between the matrices and the fibers through high mechanical performances with a modulus over 30 GPa and stress at break of 400 MPa in the longitudinal direction. 5 GPa modulus and 47 MPa stress at break were found in the transverse direction. Excellent fire retardancy properties, with self-extinguishment and UL-94 V1 classification were obtained for the isosorbide-based/flax composite. The obtained composites were able to be welded with comparable results to glued ones, paving the way to processable laminates and stable cured prepreg perfectly suited for transportation-engineered applications.

Keywords

A: Polymer-matrix composites (PMCs); A: Natural fiber composites; A: Resins ; Covalent Adaptive Network

1 Introduction

The interest in natural fibers composite (NFC) raised in the last decades to meet the sustainability goals of industries [1]. Bast fibers such as flax and hemp appear to present key properties that can compete with E-glass [2], the latter dominating the composite market [3].

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Nonetheless, matrices for such materials are still an issue and tend to hamper the greener aspect of so-called biobased composites. If thermoset matrices, such as epoxides or unsaturated polyesters, lead to satisfactory properties suitable for structural NFC [4], they are not recyclable and hardly biobased [5]. Considering such environmental issues, composites made with covalent adaptive network (CAN) matrices bring new opportunities by gathering high performances, recyclability, weldability, and reshapability [6,7]. For obvious reasons, biobased CANs are even more interesting to improve the environmental aspect [8]. Therefore, it becomes compulsory to develop sustainable alternatives to the current solutions for NFC that offer this dynamic behavior while maintaining the properties of the resulting composites.

One of the solutions could rely on (dynamic) benzoxazines (BXZ). BXZ are highly versatile monomers with high thermo-mechanical properties commonly obtained by the reaction of phenols, amine, and formaldehyde. This diversity allows the elaboration of matrices whose properties depend on the macromolecular structure of both phenol and amine. Additionally, BXZs are known for their excellent intrinsic fire retardant ability [9], a major asset for NFCs, known for their poor fire resistance [10–12]. By playing on the chemical structures of the monomer through simple molecular engineering during the monomer synthesis, dynamic moieties can be implemented to allow BXZ to become CAN [13]. The resulting matrices combine therefore the interesting performances of conventional BXZ such as high T_g and mechanical properties [14, 15] or high char yield [16] while the dynamicity allows self-healing behavior and reprocessability [17]. The thermo-mechanical properties and fire resistance of BXZ combined with the dynamicity of the network could be of high interest for matrices in NFC. Such materials could match all requirements for the sports, leisure, or transportation industries among others [18].

Surprisingly, while numerous biobased BXZ has been synthesized from agro-based phenols such as vanillin, chavicol, tyrosol, and others [19–22], only few BXZ have been studied as matrices for structural NFC with continuous fibers, and none of them bearing dynamic functions to allow reprocessing [23,24]. One of the reasons could be that BXZ usually requires high curing temperature (between 180 °C and 220 °C), limiting their implementation to natural fibers [25]. Recently, Ramdani et al. [23], reviewed natural fiber-reinforced polybenzoxazine composites. If the focus is on the excellent potential of these matrices for natural fibers and promising results, it's worth noting that all the studies reviewed so far have mainly dealt with short fibers or non-woven reinforcements. Unfortunately, these approaches tend to compromise the mechanical performance of the fibers, making them less attractive for high-performance composites.

For these reasons, we propose in this work the synthesis of dynamic biobased BXZ monomers with low viscosity and low curing temperature to act as matrices with unidirectional flax fibers. The properties were targeted to match natural fiber composite requirements. Following green chemistry principles, biobased raw materials were used to synthesize BXZ monomers under solventless conditions. Phloretic acid, paraformaldehyde, and two different biobased diols (isosorbide and PEG_{200}) were used as starting material. Sugar-derivative isosorbide and fibrous waste PEG_{200} were chosen as hydrophilic diols for good wetting to natural flax fiber. 1,12-dodecandiol, which exhibits the same molecular weight as PEG_{200} but a hydrophobic behavior, was also chosen as diol to evaluate the importance of polarity.

Isosorbide was particularly investigated following our previous work as the path seems promising for BXZ thermoset [14]. Phloretic acid, a non-toxic plant-derived natural product obtained by the modular engineering strategy in Escherichia coli [26] was chosen as the biobased phenol as it does not exhibit any substituent in ortho positions, thus promoting the ring-opening polymerization (ROP) at lower temperature [27]. Moreover, the presence of the acid function in the para-position allows the design of new features in the material. Ester moieties were integrated into the network by Fischer transesterification between the acid function of phloretic acid and hydroxyls from biobased diols to tailor the vitrimeric behavior. To complete the transesterification network, mobile hydroxyl groups were included in molecules with the use of monoethanolamine. In addition to the dynamic properties obtained by transesterification, the -OH functions decrease the polymerization temperature by a nucleophilic activation on the NR3 moieties [28].

After the synthesis of the monomers and their characterization, the investigation focused on the curing process of the monomers to showcase their potential applicability in composite industries. The properties of the polymerized networks were analyzed using mechanical, thermo-mechanical, and thermal tests. The dynamic behavior of the networks was characterized, and its reprocessing capability was demonstrated. Additionally, the impact of the backbone was explored. Unidirectional flax laminates with high impregnation quality were produced, and their mechanical properties were evaluated. The fire resistance of the laminates was also tested. Finally, leveraging the dynamic network, cured samples were welded, and the efficiency of their adhesion was assessed.

2 Material and methods

2.1 Sample preparation

2.1.1 Materials

Phloretic acid ($\geq 98\%$) was purchased from TCI. 1,12-dodecandiol (99%), isosorbide (98%), paratoluenesulfonic acid (98.5%), methyl ethyl ketone, and paraformaldehyde were obtained from VWR. PEG₂₀₀ and ethanolamine were acquired from Merck. All chemicals were used without any further purification. Unidirectional flax reinforcement (FlaxTape UD110, 110 g/m², non-woven, 40 mm x 90 m roll) was purchased from Ecotechnilin.

2.1.2 Synthesis of phloretic ester

The syntheses of PA-PEG₂₀₀, PA-DD, and PA-ISO were prepared according to the following procedure. Briefly, 120 mmol of phloretic acid was reacted with an excess of diols (72 mmol) to ensure the full conversion of phloretic acid and 1 mmol of para-toluenesulfonic acid. All the reagents were placed into a 250 ml beaker equipped with a stirring bar. The mixture was stirred at 130 °C for 24 h at 150 rpm. After cooling to room temperature, the crude product was solubilized in 200 ml of methyl ethyl ketone. Then, the solution was washed with deionized water three times to remove the catalyst and the excess of diols. The organic solvent was dried under vacuum overnight to obtain a dark red viscous product yield of 92-95%. ¹H-NMR data can be found in supporting information.

2.1.3 Synthesis of phloretic benzoxazine

The syntheses of PA-PEG₂₀₀-mea, PA-DD-mea, and PA-ISO-mea were performed using the same operating conditions for all samples. 60 mmol of Phloretic ester reacted with 120 mmol of monoethanolamine and 240 mmol of paraformaldehyde into a 250 ml beaker equipped with a stirring bar. The mixture was stirred at 150 rpm for 2 h 30 at 85 °C with an additional 30 min at 90 °C. The resulting product was a dark red viscous liquid. ¹H-NMR and FTIR data can be found in supporting information. Paraformaldehyde was preferred to formaldehyde to allow safer handling of the chemicals.

2.1.4 Curing of benzoxazine thermoset

The viscous liquid monomer was poured into silicon molds of the required shape for further testing as ascribed in Section 2.2. Then, a degassing step at 100 °C under vacuum for 15 min was applied. Afterward, samples were heated up to 160 °C for 2 h to obtain the corresponding polymerized products (Fig. 1): pPA-PEG-mea, pPA-DD-mea, pPA-ISO-mea.



Figure 1: General synthesis path from phloretic acid to benzoxazine polymer and schematic representation of the crosslinked network

2.1.5 Reprocessing of neat polymer

To assess the reprocessability of polybenzoxazine thermosets, all formulations were recycled through thermomechanical and chemical paths. For the thermomechanical reprocess, the broken tensile test samples were ground into powder in a cryomill's cryogenic vibratory mill. The powder was then poured in ASTM D638-V steel mold and pressed for 1 h at 160 °C and 6 metric tons force. Samples were then removed from the mold when still warm to ease the unmolding and tested. This reprocess was conducted twice. For chemical reprocessing, the samples were immersed in acetic acid (32%) for 24 h under agitation at 150 rpm to completely destroy the network due to the protonation of the tertiary amine [29]. The acidic medium is then removed by vacuum filtration and the residue is washed with deionized water until a neutral pH is reached. The clean polymers are dried at 100 °C overnight in an oven. Once dry, the obtained segmented polymer was thermopressed as mentioned above.

2.1.6 Composite manufacturing and sample preparation

Flax/benzoxazine composite plates (200x150 mm²) of six unidirectional plies ([0]₆ stacking sequence) were manufactured by hand lay-up and cured by thermo-compression in a teffon-coated steel mold. Uncured resins were weighted as 1.3 times the mass of fibers to impregnate each plate. The hand lay-up consists of pouring a line of uncured resin between each flax plies, see Supp. Fig. 10a, as developed by Cadu et al., to obtain high fiber volume fractions by thermocompression with relatively viscous resins [30]. Once the hand lay-up was done, the mold was placed into the press and heated up to 100 °C. At this temperature, a pressure of 5 bar was slowly applied to fully impregnate the fibers and allow the excess matrices to flow out from the opened extremities. After 15 min, the temperature was raised up to 160 °C and the plates were then cured under this pressure and temperature for 2 h. The temperature and pressure profile are illustrated in Supp. Fig. 10b. Samples were cut from the obtained plates by laser cutting and conditioned for at least three weeks at 23 °C and 50% RH prior to testing to ensure moisture equilibrium. Fiber mass was calculated from the reinforcement areal weight using equation (1). Fiber volume fraction (V_f) and void content (V_v) were calculated using equations (2) and (3) respectively.

$$m_f = A_r \times n \times S \tag{1}$$

$$\%V_f = \frac{\frac{m_f}{\rho_f}}{\frac{m_f}{\rho_f} + \frac{m_c - m_f}{\rho_m}} \tag{2}$$

$$\% V_p = 1 - \rho_c \left(\frac{w_m}{\rho_m} + \frac{w_f}{\rho_f}\right) \tag{3}$$

with n being the number of plies, A_r the areal weight of the reinforcement, S the surface of the sample, m_x the mass, ρ_x the density, and w_x the weight fraction, subscripts f, m, and c refer to fiber, matrix, and composite respectively. The density of flax was set at 1.53 g cm⁻³ as recommended in [31].

The dynamic moieties introduced in benzoxazine resins allow the composite to be welded. For this purpose, 3 samples of each formulation were welded, and the single lap-shear strength (SLSS) adhesion

was assessed. For each SLSS sample, two rectangular laminates $(100 \times 15 \text{ mm}^2)$ were put in a steel mold with an overlap of 20 mm. The mold was designed to ensure the pressure is mostly on the overlapping area as described in Supp. Fig. 15. The SLSS samples were then put into the press at 160 °C and 10 bar pressure for 1 h. For comparison purposes, a reference sample was manufactured by putting a thin layer of uncured PA-PEG-mea resin on the welding area to glue it.

2.2 Characterization

2.2.1 Chemical and morphological characterization

Fourier transform infrared (FTIR) spectra were recorded using a Fourier Transform Tensor (FTIR) 27 Spectrometer in the range 600-4000 cm⁻¹, with 2 cm⁻¹ resolution and an accumulation of 32 scans.

Nuclear magnetic resonance (NMR) measurements were performed on a Bruker AVANCEII-500 at room temperature. The solvent was deuterated DMSO.

Gel content (GC) tests were performed in water and dioxolane by immersion at room temperature of 0.3 g of the material in 25 ml of solvent for 14 days. The sample was further dried at 100 °C in an oven for 24 h. The gel content is determined according to the equation (2.2.1).

$$GC(\%) = \frac{m_i - m_d}{m_i} \times 100 \tag{4}$$

With m_i and m_d being the initial and the dried mass, respectively. Density was evaluated by a pycnometer in ethanol.

Scanning electron microscopy (SEM) experiment was carried out by a Hitachi's STEM FEG SU8020 instrument. The resolution was 5.0 nm in general mode, and its resolution can reach 2.0 nm at 5 kv. The accelerated voltage ranged from 0.1 to 30 kV, and the magnification varied from 20 to 800k.

2.2.2 Thermal analyses

Thermogravimetric analyses (TGA) was performed using a TGA Q500 TA Instruments device. About 10 mg of each sample was scanned from 25 to 800 °C at a heating rate of 10 °C/min under N₂ gas at a flow rate of 60 mL/min.

Differential scanning calorimetry (DSC) thermograms were recorded by means of an MDSC 2920 TA Instruments apparatus operating under an inert atmosphere (N_2) with a linear heating ramp from -40 to 250 °C at 10 °C/min rate.

Fire behavior of the composites was evaluated through a UL-94 vertical burning test. Samples of dimensions of 130 mm \times 14 mm x 6 plies (as manufactured) were ignited for 10 s according to ASTM D3801-2010 in air atmosphere.

2.2.3 Mechanical and thermo-mechanical properties

Dynamic mechanical analyses (DMA) was conducted on a DMA Q800 TA Instruments analyzer. For neat matrices, DMA was performed on the rectangular sample (40x13x1 mm³) in tensile mode with an amplitude of 2 μ m at a frequency of 1 Hz, with a heating rate at 3 °C/min from 25 °C to 200 °C. The crosslinking density (ν'_e) was calculated using equation (5).

$$\nu_{E'} = \frac{E'_R}{3 \times R \times T_R} \tag{5}$$

Where E'_R is the storage modulus at rubber state (MPa), T_R the temperature at 60 °C above T_g (K), and R the gas constant. For composite samples, DMA was performed in dual-cantilever mode with a span length of 35 mm and a strain of 0.1% at a frequency of 1 Hz, with a heating rate at 3 °C/min from 25 °C to 200 °C.

Stress relaxation analyses were carried out with a DMA Q800 TA Instruments analyzer, using specimens with the same dimensions as those used for DMA tests. A constant 1% strain was applied for each test and the relaxation modulus was recorded. The stress relaxation behavior was studied at different temperatures in the range between 140 °C and 175 °C. Results were fitted using a single-phase Maxwell model using equation (6). The dynamic behavior was demonstrated through the Arrhenius relationship as shown in equation (7).

$$\frac{G(t)}{G_0} = e^{\frac{-t}{\tau^*}} \tag{6}$$

$$\tau^* = \tau_0 e^{\frac{E_a}{RT}} \tag{7}$$

Monotonic tensile tests were performed to investigate the behavior and mechanical properties of the neat matrices on a ZwickRoell Z2.5 equipment up to failure with a 2.5 kN cell force at a 1 mm/min displacement rate according to ASTM D638 standard requirements. For each formulation, five type V dog-bone shape samples were tested up to failure. Elastic Modulus was computed between 0.1% and 1.0% strain by linear regression.

Monotonic three-point bending properties and behavior of the flax/BXZ composites were studied according to ASTM D790 standards on the two main orthotropic directions of the materials (i.e. parallel and perpendicular to fiber's orientation) using a ZwickRoell Z2.5 equipment with a 2.5 kN cell force. Five 50.8x12.7x1.3 mm³ rectangular samples were tested. Tests were performed at 1 mm/min with a 0.1 MPa



Figure 2: ¹H-NMR spectra of PA-ISO-mea, PA-DD-mea and PA-PEG-mea

preload. The bending modulus (E) was computed by linear regression between 0.1 and 0.5% bending strain.

Single lap-shear strength (SLSS) adhesion was evaluated in tensile mode at a displacement rate of 1 mm/min. Three samples $(100 \times 15 \text{ mm}^2)$ with a bonded area of $20 \times 15 \text{ mm}^2$ were tested for each configuration and the average and standard deviation of the lap-shear stress were reported.

3 Results and discussions

3.1 Characterization of the benzoxazine monomers

The esterification of the phloretic acid with three different diols (PEG₂₀₀, isosorbide, and 1,12-dodecanediol) was confirmed by ¹H-NMR. The esterification of the diols by the phloretic acid is revealed with the methylene protons adjacent to the carbonyl moieties in β - and α - positions, which appeared at 2.60 and 2.73 ppm, respectively. The chemical shifts in the range of 6.67 – 6.97 ppm are associated with the aromatic ring. All the products were washed to remove the catalyst and reacted with monoethanolamine and paraformaldehyde to synthesize the monomer. The good formation of benzoxazine moieties was proved with the appearance of O-CH₂-N and Ar-CH₂-N peaks, respectively at 4.79 and 3.93 ppm, as shown in Fig. 2. Furthermore, the disappearance of the phenolic peak at 9.18 ppm confirmed the completion of the reaction. These syntheses are of particular interest as they allow facile access to a wide library of benzoxazine monomers by only playing with the structure of the diol.

3.2 Curing behavior of benzoxazine monomers

The curing behavior of PA-ISO-mea, PA-PEG-mea, and PA-DD-mea was studied via DSC, TGA, and rheological analyses. All the results are summarized in Table 1 and the thermograms are presented in

Supp. Fig. 1-3. The polymerization was also assessed using FTIR. The ring opening polymerization of the benzoxazine monomers is shown in Fig. 3a with the disappearance of the characteristic peak at 936 $\rm cm^{-1}$ (out of plane bending of H-C-H) correlated with the apparition of the new band at 875 $\rm cm^{-1}$, who is attributed to the tetrasubstituted aromatic ring. The TGA analysis demonstrated that no degradation occurred during the polymerization at 160 °C.

DSC thermogram shows the first exotherm with a maximum between 190 and 210 °C for both systems, which can be attributed to the ring opening polymerization of benzoxazine. The onset of polymerization is quite early compared to other biobased benzoxazines (210-260 °C). This is due to the involvement of the free hydroxyl group carried by the monoethanolamine, which acts as an internal catalyst [32, 33]. This was particularly desired to allow the polymerization during composite manufacturing without degrading the natural fibers. The second exotherm, located after 220 °C, corresponds to the degradation of the molecule, according to TGA analysis.

The rheological assays depict the evolution of viscosity during the polymerization (Fig. 3b). The complex viscosity decreased from room temperature to 50 °C for the PA-PEG-mea and PA-DD-mea and up to 80 °C for the PA-ISO-mea. Considering a viscosity of 1 Pa.s, common to many composite manufacturing processes [34], PA-PEG-mea and PA-DD-mea could be used for vacuum infusion as they reach the requirement at room temperature thanks to their flexible aliphatic backbone. The slightly higher viscosity of PA-PEG-mea to PA-DD-mea can be attributed to the hydrogen bonds between the ether in the PEG₂₀₀ backbone and the free hydroxyl. PA-ISO-mea, due to the stiffer isosorbide ring and its ability to form H-bonds is much more viscous at room temperature. However, these H-bonds can be broken by increasing the temperature making it flow, reaching 1 Pa.s at 67 °C. Therefore, PA-ISO-mea seems to be more adapted to Resin Transfer Molding processes or equivalent, where the uncured system can be heated prior to infusion. The ROP is clearly seen with the increase of viscosity between 165 and 200 °C, which agrees with the DSC measurements.

Interestingly, rheology and DSC highlight no substantial change in enthalpy of curing, and onset temperature, revealing that the ROP is not significantly affected by the diol used. In addition, the gel content test further confirms the formation of a crosslinked polymer network with a portion of soluble part inside the polymer matrix lower than 6% for each sample (Table 2).



Figure 3: a)FTIR spectra of pPA-ISO-mea, pPA-DD-mea and pPA-PEG-mea, b)Viscosity-temperature curves of PA-ISO-mea, PA-DD-mea and PA-PEG-mea

	Rheology			DSC			TGA	
	$\eta_{25^{\circ}C}$	$\eta_{50^{\circ}C}$	$T_{1Pas}*$	T_{onset}	T_{exo}	Enthalpy	$T_{d5\%}$	
	Pa.s	Pa.s	$^{\circ}\mathrm{C}$	$^{\circ}\mathrm{C}$	$^{\circ}\mathrm{C}$	J/g	$^{\circ}\mathrm{C}$	
PA-PEG-mea	1.2	0.1	26	125	189	53.9	212	
PA-DD-mea	0.85	0.1	25	173	210	50.0	226	
PA-ISO-mea	1160	18	67	156	192	42.5	252	
*Temperature required to reach 1 Pa.s, suitable for many composite processes								

Table 1: Polymer processing window of the benzoxazine monomers

3.3 Properties of the polybenzoxazine thermosets



Figure 4: a)Monotonic tensile behavior of the polybenzoxazine thermosets b) DMA in tension mode of the thermosets

Assessing the properties of new resins remains a key point before using them as matrices in composite applications. The crosslinked polymers were characterized through their thermal stability (TGA), thermomechanical behavior (DMA), mechanical (monotonic tensile test), and solvent resistance (GC).

The diols used in the benzoxazine system highly influence all these properties. The strong and stable cycloaliphatic ring in isosorbide limits the chain flexibility thus bringing thermal stability, and stiffness but brittleness in the network. On the opposite, flexible aliphatic chains in DD and in PEG_{200} improve ductility [25]. Moreover, while DD is highly hydrophobic due to its alkane structure, isosorbide, and PEG

are more hydrophilic thanks to their ether linkages. These considerations have a particular interest in efficiently designing specific polymers for natural fibers composites [35]. The thermal stability of BXZ thermosets was assessed by TGA and curves are depicted in Supp. Fig. 4 and results are summarized in Table 2. pPA-ISO-mea and pPA-PEG-mea showed the best thermal behavior with a $T_{d5\%}$ around 270 °C and a char yield at 800 °C near 30%. This can be attributed to the thermal stability of the cyclic isosorbide ring in the case of pPA-ISO-mea, significantly improving this behavior. In addition, the presence of ether bonds in both pPA-ISO-mea and pPA-PEG-mea also allows a better ability to char than the alkane structure of pPA-DD-mea [36]. All polymers exhibited main weight loss stages at \pm 400 °C, which can be attributed to the degradation of the main chain [37].

The alpha relaxation and crosslink density have been determined by DMA from $\tan \delta$ and storage module profiles, respectively. The results are depicted in Fig. 4 and table 2. Obviously, the incorporation of rigid segment through isosorbide increased the T_g of the system, with a tan δ maximum at 132 °C. This thermal and thermo-mechanical behavior may seem low compared to other bio-sourced benzoxazine resins [14, 16, 20], but in the context of solvent-free synthesized polymers with self-healing properties, the isosorbide sample shows better $T_{d5\%}$, higher char yield, and T_g [38]. In the same way, the presence of this short sugar-derivative in the network enhances the crosslinking density ($\nu_{E'}$) compared to the longer and more flexible PEG₂₀₀ and DD diols.

The same observations can be drawn from the monotonic tensile test. While pPA-ISO-mea formulation exhibits a brittle behavior with a high modulus of 2.5 GPa and a stress and strain at break of 54.5 MPa and 2.27% respectively, pPA-PEG-mea and pPA-DD-mea exhibit a ductile behavior with a yield point at approximately 5% strain and 15 and 25 MPa respectively. The pPA-PEG-mea reaches up to 27% strain at break while pPA-DD-mea breaks at almost 45% elongation. Thus the presence of the long and flexible aliphatic chains in the polymer networks confers high ductility and toughness to the material. On the opposite, the cyclic ring of isosorbide brings thermal stability, stiffness, and higher charring behavior but decreases the ductility. This highlights the possibility of easily tuning matrices properties by only playing on the structure of the biobased diol in the monomer synthesis [25].

Interestingly, the pPA-ISO-mea network exhibits comparable thermo-mechanical properties as aromatic epoxy used for composite applications [39]. In particular, the results are in the range of most commonly used matrices for flax. As examples, the partially biobased GreenPoxy56[®] possess properties with glass transition around 85°C and similar mechanical properties (E= 3 GPa, σ =67 MPa, ϵ =3-5%) [40]. The non-biobased recyclable Elium[®] thermoplastic from Arkema [41] has a glass transition 100 °C, a modulus of 3.6 GPa, and stress and strain at yield of 66 MPa, and 2.8% respectively. More recently, Placet et al. proposed a fully biobased but not recyclable bisguaïacol epoxy [42] with a glass transition of 100-115 °C, a modulus of 3 GPa and stress and strain at break of 50 MPa and 2.5%. Therefore, BXZ biobased reprocessable thermosets appear to be good alternatives as matrices for natural fiber composites.

		GC		TGA		Tensile			DMA			
	$_{ m g/cm^3}^{ m ho}$	Water %	Dioxolane %	$_{^{\circ}\!\mathrm{C}}^{T_{d_{5\%}}}$	$Char_{800^{\circ}C}$	E MPa	$_{\mathrm{MPa}}^{\sigma}$	$\frac{\epsilon}{\%}$	T_{α} °C	$E'_{25^{\circ}C}$ MPa	E'_R MPa	$\nu_{E'}$ mol/L
pPA-ISO-mea	1.23	98.7	97.3	273	31	2581 ± 239	54.5 ± 13.3	2.27 ± 0.63	132	2740	15.5	1.32
pPA-PEG-mea	1.19	94.0	94.1	267	29	543 ± 35	21.1 ± 1.2	26.79 ± 3.04	64	642	7.0	0.70
pPA-DD-mea	1.16	99.4	97.0	239	25	737 ± 32	26.7 ± 1.3	44.75 ± 4.09	69	658	7.6	0.70

Table 2: Properties of the cured benzoxazine thermosets

3.4 Dynamic bond exchange and reprocessability of benzoxazine polymers



Figure 5: Transesterification mechanism occurring in the polybenzoxazine network

Stress relaxation experiments were performed to characterize the dynamic bond exchange behavior of polybenzoxazine resins. The presence of different kinds of alcohol moieties as shown in Fig. 5 in the network (alkyl and phenoxy), results in different potential transesterification mechanisms. However, alkyl alcohols are assumed to be the main responsible for the associative exchange reaction. As a consequence, a single-phase Maxwell model was used. Fig.6a-c illustrates the evolution of the normalized relaxation modulus of the BXZ networks. The Arrhenius fit shown in Fig.6d confirms the adaptive nature of the formulated networks through the time-temperature dependency with residual square superior to 0.99. The values are summarized in Table 3. The transesterification rates of the different systems, as represented by the activation energies and relaxation time, depend on the backbone of the networks. In all cases, fast relaxation times were obtained, particularly in comparison with other tertiary amines' self-catalyzed transesterification networks while maintaining better mechanical properties [28]. For example, at 160 °C, the relaxation time was 301 s for the rigid cyclic sugar derivative isosorbide, whereas the flexible aliphatic chain pPA-DD-mea and pPA-PEG-mea require only 41 s and 42 s. It highlights the predominant role of the molecular structure of the diol in the transesterification mechanism. Again, the low flexibility of the isosorbide ring limits the ability of the polymer to rearrange itself compared to the aliphatic backbone thus increasing relaxation times. The obtained activation energies are coherent with internally-catalyzed transesterification found in literature [38,43]. Interestingly, while relaxation times were longer for pPA-ISO-mea than for pPA-PEG-mea and pPA-DD-mea, the activation energy of pPA-ISO mea is lower than for the two others. This reveals that if a longer time is required to relax due to the lower mobility of the network, the isosorbide is more prone to rearrange itself when sufficient temperature is brought.



Figure 6: Dynamic network characterization by stress relaxation of a)pPA-ISO-mea, b)pPA-PEG-mea, c) pPA-DD-mea. d) Arrhenius plot and fit of the relaxation time

	E_a	r^2	$\tau_{160^\circ C}$
	$\mathrm{kJ/mol}$		s
pPA-ISO-mea	96.8	0.992	301
pPA-PEG-mea	104	0.992	41
pPA-DD-mea	121	0.999	42

Table 3: Activation energies from Arrhenius fit and relaxation time at 160 $^{\circ}$ C of the polybenzoxazine networks

The recyclability of the materials was mechanically and chemically assessed as illustrated in Fig. 7. The mechanical properties of the recycled thermosets are summarized in Table 4. Chemically, the penetration of the acid solution into the network induced local cracks inside the macromolecule and can destroy its integrity [29]. Mechanically, the ground samples can rebuild the network through the transesterification mechanism discussed. The evolution of the structure of each network is shown by FTIR in Supp. Fig.5-7.

The nature of the diol seems to have a significant impact on the chemical recyclability of the material. While the hydrophobic pPA-DD-mea sample showed no significant change in its structure, the structural evolution of the pPA-PEG-mea and pPA-ISO-mea is more evident. A significant reduction in the ester and ether peaks located at 1730 cm^{-1} and 1243 cm^{-1} respectively, was observed. In addition, the integrity of the isosorbide ring seems to be damaged, with the appearance of new bands in the fingerprint zone

(between 800 and 1150 $\rm cm^{-1}$). We hypothesize that this structural change is caused firstly by the acidic protonation of the tertiary amine into the network, but also by side reactions involving the ester units. This structural evolution would explain the changes in the mechanical and thermo-mechanical properties of the recycled material discussed further. Nevertheless, chemical recycling remains possible for all samples, allowing polymers to be segmented and reformed.



Figure 7: Reprocessing protocol of neat benzoxazine thermoset

DMA analyses confirmed the satisfying reshaping ability of the BXZ thermosets. Indeed, as shown in Supp. Fig. 8a-c, all reprocessed samples reveal an apparent and single alpha transition highlighting the homogeneity of the reshaped network. However, a drop of the tan δ values, as much as T_{α} was observed. The phenomenon is more pronounced for pPA-ISO-mea than for the two others. Such results are consistent with the previous FTIR observations that showed partial degradation of the network integrity. In all cases, the retention of the T_g remains superior to 86%.

In contrast with the α transition results, crosslinking densities were found to be slightly increased by mechanical reprocessing and more significantly by chemical reprocessing. Being consistent with the crosslinking density, the storage modulus was also enhanced, especially after chemical recycling. As an exception, the mechanical reprocessing of pPA-ISO-mea led to a decrease of the storage modulus. Such behavior was observed by Di Mauro et al. [44] and Memon et al. [45] in vegetable oils and vanillin epoxides. They spotlighted that a slight increase in storage modulus and crosslinking density could be related to a post-curing effect induced by the applied pressure and temperature. They also observed that higher crosslinking density, such as in pPA-ISO-mea, tends to lower the exchange reaction thus the retention of the properties. Potentially, taking into consideration the decrease of the α transition and the increase of the storage modulus, being somehow opposite, and knowing that the crosslinked network possesses both alkyl and phenoxy alcohol able to participate in the transesterification, the overall network system could generate stiffer ester bond linkage than in the initial network. As discussed through FTIR, the modification of the network macromolecular structure through side reactions cannot be omitted.

Quasi-static tensile tests were further performed to assess the retention efficiency after reprocessing. The obtained stress-strain curves are presented in Supp. Fig. 8d. The retention efficiency was simply defined as the ratio between Young's modulus of the recycled specimen (E_{repro}) and Young's Modulus of the virgin sample (E_{init}). Indeed, even if the network can be restored to obtain a similar modulus, it can generate early breaking in the networks due to defects in the reprocessed samples. This early break can be attributed to both the process method but also the ability of the network to be reprocessed [46].

The monotonic tensile tests performed highlight both the retention of Young's modulus but also the modification of the ultimate mechanical properties of the network as already observed by DMA. Considering the mechanical reprocessing path, similar properties were found for each formulation and for the two reprocessing cycles. Both pPA-ISO-mea and pPA-DD-mea were found to have a modulus retention of about 80% in the two cycles. pPA-PEG was shown to retain better the modulus with recovery ranging from 0.85% to 1.1%. Such observations are likely to be attributed to the more elastomeric behavior of pPA-PEG-mea that facilitate the exchange reaction [44]. An early break was observed for the first reprocessing step of pPA-ISO-mea and pPA-PEG-mea. This decrease seems to be more process-related than due to the degradation of the network as the second reprocess leads to a better recovery of ultimate properties [6].

Chemical recycling was found to be not suitable for pPA-ISO-mea. Samples were too brittle after the pressing step and were not able to be tested in tensile. This mechanical observation further confirms FTIR results where a network degradation was uncovered. For pPA-PEG-mea and pPA-DD-mea, the chemical recycling leads to an increase in the modulus as observed in DMA, but also to higher stress at the break and a decrease in ductility. Thus, the networks were more brittle than the virgin ones. Such results could be due to the physical degradation of the network by the acidic protonation of the amine leading to a more brittle network as already highlighted by Lim et al. [29].

		Tensile			Recovery	DMA		
		E	σ	ϵ_{max}	E_{repro}/E_{init}	$E_{25°C}$	T_{α}	$\nu_{E'}$
		MPa	MPa	%		MPa	$^{\circ}\mathrm{C}$	$\mathrm{mol/L}$
pPA-ISO	As manufactured	2581 ± 239	54.5 ± 13.3	2.27 ± 0.63	-	2587	132	1.3
-mea	1st reprocess	2114 ± 45	28.5 ± 9.9	1.41 ± 0.53	0.82	1858	131	1.4
	2nd reprocess	2055 ± 44	49.1 ± 4.4	2.45 ± 0.29	0.80	2029	127	1.7
	Chemical reprocess	-	-	-	-	3101	142	1.9
pPA-PEG	As manufactured	543 ± 35	21.1 ± 1.2	27.34 ± 2.84	-	412	65	0.7
-mea	1st reprocess	596 ± 76	18.5 ± 2.6	10.03 ± 5.81	1.1	1507	63	1.0
	2nd reprocess	460 ± 19	17.3 ± 1	21.29 ± 7.84	0.85	1212	56	1.1
	Chemical reprocess	883 ± 111	26.1 ± 3.5	12.64 ± 3.99	1.63	605	60	1.0
pPA-DD	As manufactured	737 ± 32	26.7 ± 1.3	45.15 ± 3.93	-	658	69	0.7
-mea	1st reprocess	593 ± 14	21.9 ± 2.2	36.36 ± 9.1	0.81	835	58	0.7
	2nd reprocess	557 ± 48	17.8 ± 1.9	25.16 ± 9.41	0.76	1141	60	0.8
	Chemical reprocess	921 ± 41	30.1 ± 1.1	16.93 ± 5.35	1.25	1229	60	0.9

Table 4: Mechanical and thermo-mechanical properties of reprocessed benzoxazine polymers

3.5 Flax/poly(benzoxazines) composites properties and behavior

Benzoxazine monomers were used to impregnate through thermo-compression unidirectional flax fibers. The manufactured laminates' pictures are presented in Supp. Fig. 10 and the SEM cross-section are depicted in Fig. 8. All mechanical properties are summarised in Table 5.

All three resins lead to homogeneous impregnation of the flax fibers. The global aspects of the composite tend to show a satisfying process leading to good-quality laminates. SEM cross-section pictures

however highlight important initial cracks and porosities in F-pPA-PEG and F-pPA-DD laminates while F-pPA-ISO cross-sections appear to be homogeneous with only a few porosities and good dispersion of the fibers. This important difference was also observed through the calculation of V_f and V_p . All formulations lead to high fiber volume fraction with 50% for F-pPA-ISO and more than 60% for PEG and DD-based laminates, in the high range of reachable V_f for natural fibers [47]. F-pPA-ISO exhibits a low porosity level of 2.4% while the other ones range between 15% to 17% of porosities. Such a level of porosities is detrimental to the performances of the materials but is a well-known issue in NFC as already assessed in literature [48]. Indeed, it was observed that increasing fiber volume fractions in NFC tends to promote the formation of porosities [49]. Moreover, this important level of voids might be attributed to the too-low viscosity of pPA-PEG-mea and pPA-DD-mea monomers. Therefore, further optimization might be required to improve the impregnation quality [49].



Figure 8: Transverse SEM images of the flax/benzoxazines laminates for a) F-pPA-ISO, b) F-pPA-PEG and c) F-pPA-DD matrices

The low viscosity of these resins could furthermore be of particular interest in other composite manufacturing methods such as resin transfer molding, and vacuum infusion [34]. It is worth noting that in order to keep consistency in the analyses, laminates were tested as manufactured. However, the vitrimeric behavior of the resins might be of particular interest in such cases to allow a post-processing step to consolidate the laminates and decrease the level of porosity [7].

Mechanical properties were evaluated through monotonic three-point bending up to structural failure in the two main orthotropic directions (referred to as F0 and F90) as shown in Fig. 9.

The three-point behavior of the laminates in the longitudinal direction is typical of the one observed with the same reinforcement as it is mainly driven by the properties of the fibers [50]. Interestingly, F-pPA-ISO reached 33 GPa of modulus, 418 MPa of stress, and 1.92% of strain at break which is to the authors' best knowledge the highest performance range reached for such material [50,51]. F0-pPA-PEG and F0-pPA-DD have slightly lower performances with a modulus of 29 and 25 GPa and stress at break of 281 and 257 MPa respectively. These results, even significantly lower than those obtained with the pPA-ISO-mea resins remain in the high range of materials found in previous studies. These lower properties can be first attributed to the deleterious level of porosities significantly affecting the ultimate performances [48]. However, the less hydrophilic nature of the DD diol can also explain the lower affinities between the fiber and the matrix, lowering both modulus and strength [52]. Indeed, the ether bond in the isosorbide and PEG backbones promotes H-bonding with the hydroxyl of flax cellulose leading to a stronger interface. On the contrary, the non-polar backbone of DD leads to lower affinity and consequently lower stress transfer between the fiber and the matrix.

Such observations correlate with the transversal properties of the laminates. Indeed, it is well known that when a unidirectional laminate is subjected to a load applied in the perpendicular direction to the main fiber's orientation, these fibers tend to act as a defect more than a reinforcement [53]. It is even more observable with natural fiber due to the low interfacial strength between the fiber and the matrix [35]. Thus, transverse properties can be a macroscopic view of the quality of the fiber-matrix interface strength within the laminate. It is noting that the F-pPA-ISO materials demonstrate outstanding performances in this orientation with a modulus of 5.2 GPa, stress and strain at break of 46.6 MPa and 1.1% respectively. This is again in the highest range of properties observed for such materials, commonly exhibiting a bending modulus of 2-3 GPa, and stress at break around 30 MPa [50, 51].

For F90-PA-ISO, strain and stress are slightly lower (14% decrease of stress and 55% of strain) than those of the neat matrices due to stress concentration and the rigidity of NF in the transverse direction leading to early break [54]. However, the modulus is increased up to 108% highlighting the strong adhesion between fibers and matrices. Similarly, pPA-PEG-mea and pPA-DD-mea matrices face an increase of the modulus of 214% and 71% respectively, and only a low decrease of the stress at break of 2% and 18% highlighting also the good affinity of both matrices. This effect remains more pronounced when a hydrophilic diol (PEG and ISO) is used due to additional H-bonds at the interface. Regardless, it can be noted that the hydroxyl functions of the cellulose can react in catalyst-free conditions with the ester linkage of BXZ monomer through transesterification [55] leading to high energy covalent bonding between the fiber and the matrix, explaining also the excellent properties in the transverse direction of all formulations.



Figure 9: Monotonic three-point bending behavior of the flax/benzoxazines composites for $a)[0]_6$ and b) [90]₆ laminates

	$ ho m g/cm^3$	V_f %	V_p %	E GPa	σ MPa	$\epsilon \ \%$
F0-pPA-ISO	1.35 ± 0.02	50.0 ± 2.5	2.4 ± 0.5	33.2 ± 0.8	418.0 ± 7.4	1.92 ± 0.04
F0-pPA-PEG	1.18 ± 0.01	57.8 ± 7.9	14.9 ± 1.7	28.8 ± 2.7	280.7 ± 13.8	1.75 ± 0.14
F0-pPA-DD	1.15 ± 0.01	59.9 ± 10.2	16.8 ± 2.3	25.0 ± 2.1	257.3 ± 16.1	1.98 ± 0.22
F90-pPA-ISO	1.35 ± 0.02	53.2 ± 2.0	2.7 ± 0.4	5.2 ± 0.5	46.6 ± 3.4	1.06 ± 0.23
F90-pPA-PEG	1.18 ± 0.01	63.6 ± 1.7	14.9 ± 0.3	1.7 ± 0.2	20.7 ± 3.0	1.54 ± 0.24
F90-pPA-DD	1.15 ± 0.01	62.2 ± 1.6	16.1 ± 0.3	1.3 ± 0.1	22.1 ± 1.3	2.29 ± 0.15

Table 5: Longitudinal (F0) and transverse (F90) mechanical properties of the flax/benzoxazine composites

DMA was performed in dual cantilever mode on both neat matrices and composites in the two orthotropic directions between 25 °C and 200 °C. The results are depicted in Supp. Fig. 11 and 12.

DMA is a useful tool to assess the thermo-mechanical stability of the material but also to compare the alpha transition (T_{α}) of the materials. Indeed, T_{α} expressed as the ratio between the loss and storage modulus can be seen as an overview of the network's mobility [56]. Thus increasing the fiber/matrix interface strength leads to a reduction in the damping factor but can also be seen in a shift in α temperature [57]. Interestingly, a positive shift of $\tan \delta$ was found in the case of the hydrophilic diols (PEG and ISO) while it is negative for the pPA-DD-mea formulation. This corroborates previous observations where the H-bonds promoted by the hydrophilic backbone increased the properties in bending.

Maximal values of $\tan \delta$ are also significantly decreased when fibers are embedded, translating the high level of entanglements in the materials since the mobility of the molecular chains at the fiber/matrix interface decreases [57]. In parallel, in both fiber orientations, the gap in storage modulus between the glassy and rubbery domain was found to be less than an order of magnitude when it was superior to 2.5 orders of magnitude for neat matrices. Such observations corroborate the high affinity between the developed benzoxazines and the fibers [56] but also the interest in using a hydrophilic diol in the BXZ formulation to promote the strength of the adhesion with cellulosic fibers without any fiber treatment [58].



Figure 10: Vertical burning test of the flax benzoxazines F-pPA-ISO material.

The fire resistance of the developed materials was assessed through the simple UL-94 vertical burning test. The picture as a function of the time of the burnt materials is presented in Fig. 10 for F-pPA-ISO

and in Supp. Fig. 13 for the two others.

All laminates self-extinguished without any drop. In particular, the F-pPA-ISO material was extinguished after only 15 seconds without any significant loss of material and a surface charring. The burning behavior reaches the UL-94 V1 standard and is relatively close to V0 if we consider that the few last seconds of burning were only on the edge where the fibers are more accessible as shown in the pictures. The second ignition self-extinguished after only 3 seconds. This can be attributed to the good stability of the stable cyclic isosorbide, which is often used as a biobased platform for fire retardant compound [59].

Conversely, the aliphatic PEG and DD-based BXZ needed 25 and 35 seconds respectively to selfextinguish and the F-pPA-PEG burned again for 20 seconds on the second burning time. Consequently, the F-pPA-PEG material is classified as V1 while F-pPA-DD remains as a V2. Linear aliphatic backbones are known to have lower burning resistance due to less thermal stability and easiness of being oxidized as they are less likely to form stable aromatic compounds compared to the cyclic isosorbide [15]. However, despite being less performant than the F-pPA-ISO, they remain able to self-extinguish in low time and promote a stable char. The thermal stability and charring behavior between the different formulations were further confirmed by the TGA of the composites (Supp. Fig. 14). It was found that 26% of char at 800 °C was developed for both F-pPA-ISO and F-pPA-PEG formulations while 21% of char was formed in the F-pPA-DD system. These overall results can be compared to previous flax/benzoxazines systems with surface treatment on the fibers, that reaches 30 % char [15,23] and highlight good thermal stability and fire resistance of the F-pPA-ISO laminate.

3.6 Weldability of flax/benzoxazines composites

Covalent Adaptable Network being a major breakthrough in the composite industry to reach easier manufacturing processes and improved end-of-life [7], the crosslinked laminates were welded through thermo-compression and the single lap-shear stress was evaluated. The representative welded sample, the SEM crosscut section, and the SLSS results are shown in Fig. 11.

A good quality of welding was observed by SEM without any observable decohesion nor porosities between the two welded laminates. Interestingly, the important porosities seen after the initial manufacturing step are not observed anymore highlighting some consolidation in the materials.

The SLSS tests highlight similar adhesion between the three formulations, between 4.4 and 7.4 MPa. For the sake of comparison, we also used uncured PA-PEG-mea resin to act as an adhesive between two laminate samples and cured. These reference samples exhibit similar SLSS values as the welded samples with 5.6 MPa (20% lower than the welded F-pPA-PEG). Such values are coherent with satisfactory efficiency of the welding. The failed bonded joint area is depicted in Supp. Fig. 16. All samples underwent cohesive failure as revealed by the tearing and breaking of fibers. Such failure mode is usually preferred to adhesive failure. It translates the good crosslinking of the interphase leading to a cohesive strength higher than the interfacial strength.



Figure 11: a) Representative picture of an SLSS sample b)SEM crosscut section of welded F-pPA-PEG sample, c)Lap Shear Stress results

Finally, the developed BXZ can be shown as promising matrices for reshapable or weldable biobased composites as they allow fast rearrangement mechanisms at temperature and time lower than those leading to important fibers degradation [60]. The separation of the fiber from the matrix was possible through alkaline treatment as depicted in Supp. Fig. 17. However, it is not yet optimized and will be assessed by our team in future works.

4 Conclusion

Solventless biobased benzoxazine thermosets were successfully synthesized with dynamic functions incorporated to obtain a covalent adaptable network. The obtained monomers were able to flow with low viscosity and to cure at 160 $^{\circ}$ C within two hours.

Depending on the used diols, the properties ranged from strong and brittle to ductile thermosets, highlighting the facility to tune such materials depending on the desired application. The isosorbide-based benzoxazines show a T_g superior to 130 °C, 2 GPa modulus, 55 MPa, and 2.3% strain at the break with excellent thermal stability in both TGA and DMA making it an excellent candidate for composite applications.

The monomers were used to impregnate aligned natural flax fiber. High fiber volume fractions superior to 50% were obtained. Strong adhesion between benzoxazine matrices and flax fibers was highlighted through outstanding mechanical properties, in particular for the isosorbide-based benzoxazine, which displays an important bending modulus of 33 GPa, and stress of 418 MPa in the longitudinal direction. In the transverse direction, 5.2 GPa and 44 MPa of modulus and stress respectively, were observed. The results emphasize the importance of using a hydrophilic diol to improve the adhesion between the matrix and the natural fibers. Moreover, the isosorbide-based composites display interesting intrinsic fire retardancy properties being classified as V1.

In addition, the dynamic network behavior of those polymers was assessed. The networks were able to stress relax at 160 °C in less than 15 min. The reprocessing led to a recovery of the mechanical properties superior to 80%. Taking advantage of this feature, cured flax-BXZ laminates were successfully welded with comparable results to glued samples, paving the way to re-shapable, re-processable, and even cured biobased pre-preg for further manufacturing.

The obtained thermo-mechanical and fire properties of the final biobased material, as much as the processability, handling, and weldability of such resins make them of particular interest to make composite materials more circular. In particular, they could be of high interest to the transportation sector (automotive, indoor panels for aerospace...) where fire resistance is expected. In addition, sports and leisure (rowing, cycling, skiing...) seem also well suited for this type of material where resin transfer molding can be applied.

The dynamic network of the benzoxazine matrices previewed in this work opens many opportunities for composite materials and should be subjected to more complete investigation in the future. Taking into consideration the end-of-life of biobased composites, both mechanical and chemical recycling of the composites should be investigated and optimized in the near future by our team to reach satisfying results.

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