Implementing recyclable bio- and CO_2-sourced synergetic dynamic matrices via precise control of curing and properties for natural fiber composites within industrially relevant resin transfer molding

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Abstract

The use of thermosets in natural fiber composites (NFC) presents major challenges related to their sustainability. Most alternatives struggle to meet industrial requirements relevant to conventional composite processing techniques. This study explores a synergetic copolymerization strategy that combines epoxy and CO_2-derived polyhydroxyurethanes (PHU) to allow fine-tuned polymerization kinetics, including the suitability for the RTM process. We demonstrate a synergetic catalytic effect that accelerates curing compared to each neat component. The formulation maintains a low viscosity (<5 Pa.s) at room temperature while curing within 30 minutes at 80 °C, unattainable conditions with pure PHUs. Formulations suitable for resin transfer molding (RTM) were developed and demonstrated an improvement in mechanical performances compared to the homopolymer parents. RTM-made composite achieved a fiber volume fraction of 58-60% and a porosity below 1%, making them ideal for high-quality NFCs. The influence of hybridization content was investigated, and the influence of impregnation quality was highlighted while the PHU well-supported the adhesion quality. Moreover, the catalyst-free dynamic matrix allows the reshaping after curing, and flax fibers can be easily separated without toxic reagents from the polymeric matrix under mild conditions (60 °C for 2 hours) and reused, retaining properties similar to those of virgin yarns. This strategy could broaden the application of PHU chemistry in sustainable NFC manufacturing while preserving both natural and fossil feedstocks."

Keywords: Covalent Adaptable Network; Non-Isocyanate Polyurethane; Sustainable material; Composite manufacturing; Polymerization; Oxidative recycling

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1 Introduction

Fiber-reinforced polymer composites (FRPC) provide exceptional strength-to-weight ratios compared to traditional metallic structural materials [1]. The recent advances in such materials have leveraged significant improvements in terms of structure performance, durability, and efficiency [2]. For instance, thanks to the weight savings offered by FRPC, taller wind turbines with improved electricity yields are obtained. Weight saving in the transportation industry, affords substantial fuel savings [3]. Due to their exceptional cost-to-properties ratio, the market is mainly dominated by glass fiber-based composites [4]. Nevertheless, the depletion of mineral and fossil resources [5], together with the high energy consumption required for manufacturing such fibers, pushes towards greener alternatives. Over the last decades, natural fibers (NF), particularly flax and hemp, have been viewed as valid substitutes for glass fibers [6] since they offer better environmental footprint, including biodegradability [7], similar specific properties [8], and potentially improved societal outcomes [2].

Although greener alternatives to conventionally used fibers already exist, the matrices used for FRPC remain a crucial issue from an environmental point of view. They are often the limiting factor [9]. Indeed, the polymeric matrix governs the manufacturing process required to obtain FRPC and the End-of-Life (EoL) scenarios [10]. The last decades have seen a surge in more sustainable matrices for composites, including thermosets and thermoplastics [11]. Partially biobased epoxides are now available on the market and are commonly employed with flax, such as the GreenPoxy by Sicomin [12] owing to glycerol-derived epichlorohydrin. Recently, Placet et al. reported fully biobased bis-guaiacol epoxy that demonstrated promising properties with hemp fibers [13]. While thermosets, mainly based on epoxy (EP) resins, offer the best performances for natural fibers composites (NFC), they require a long processing time [14]. Besides, the recycling of such NFC is extremely limited due to the inherent chemical and physical stabilities of the aforementioned thermosets [10]. These stabilities are desired for long service lifetimes but severely impact sustainability and circularity [15]. Recently, a fully biobased recyclable epoxy has been achieved by Barta et al. [16] and applied to flax fibers. However, the methanolysis of the network in the presence of natural fibers might be challenging and was not reported. In parallel, Rorrer et al. [17] successfully implemented a biobased epoxy-anhydride in a glass fiber wind turbine blade with exceptional results. The network was suitable for methanolysis. However, the harsh conditions (225 °C, 6 hours) would be detrimental for NFCs. So far, the recovery of natural fibers from a thermoset composite has not been successfully achieved. The EoL of NFC generally involves incineration with energy recovery and sometimes grinding and reuse as low-quality fillers, downgrading these FRPC structures. Ultimately, these natural fibers' economic and environmental values are lost [18]. Such loss of fibers that could still be used in many applications has a considerable negative impact on the environment, leading to more unnecessary material production [10].

The solutions developed must consider chemical processes and end-user requirements, including manufacturing, scalability, cost, sustainability, circularity, and final properties, to obtain industrially relevant matrix alternatives for NFCs. In that sense, Covalent Adaptive Networks (CAN) meet the prospect of reaching thermoset-like processes and properties, while incorporating dynamic moieties that can be triggered on-demand to reshape, weld, and, in some cases, cleaved the cured materials to separate the fibers from the surrounding matrix. Although research has been going on for more than 20 years, since the first works reported in the literature [19–21], industrially relevant solutions remain scarce [22]. The compounds' low availability and high cost have made scaling up unfeasible, together with a lack of compatibility with composite manufacturing processes [23].

Out-of-autoclave systems present considerable growth among the possible processes for manufacturing FRPCs due to the lower tooling and energy consumption cost, higher production rates, and improved versatility [24]. Resin Transfer Molding (RTM) is one of the essential out-of-autoclave processes as it allows fast curing rates, high fiber volume fraction, and high impregnation quality for parts up to a few meters in size with good surface finish [24]. However, to meet RTM requirements, the curing behavior of the matrix must be precisely controlled so that low viscosity for fast reinforcement impregnation (ideally below 1 Pa.s) and fast curing (within 1 h at low to moderate temperature) are needed. To the author's best knowledge, dynamic chemistries for resin transfer molding of natural fiber composites have never been explored, and even less targeting large-scale, low-cost production with potential for fiber-matrix separation. Only very recently, Schenk et al. [23, 25] explored aerograde disulfide-based EP dynamic networks for RTM of carbon fiber composites. Although efficient, the high temperatures required in their systems would lead to the deterioration of NF, and no fiber recovery was studied. Such a research gap may result from the challenge of developing innovative and more environmentally friendly materials on a large scale and at a cost suitable for composite manufacturing processes. The difficulty of matching chemical, material, and processing aspects in a parallel manner impedes the successful design of more sustainable materials, requiring a multidisciplinary approach.

Among the various emerging dynamic networks developed, polyhydroxyurethanes (PHU), a polyurethane chemistry that avoids the use of hazardous isocyanates as precursors, appear to be promising [26]. PHUs are mainly obtained from the CO_2 insertion into (bio)epoxies, leading to cyclic carbonates (CC). CCs are further polymerized with (bio)polyamines via aminolysis reactions in solution, emulsion, or bulk [27]. Besides their renewable feedstock sourcing, they possess inherent dynamicity that opens the door to new manufacturing processes and favorable EoL scenarios. In a recent work [28], our research team demonstrated that PHU could be a relevant platform for natural fiber composites (NFC) thanks to their strong hydrogen bonding, driving outstanding interfacial strength with flax. Compared to their EP counterparts, PHUs showcased substantially better thermo-mechanical properties, and NFC single-plies were effectively welded by taking advantage of the dynamic character of PHUs. However, the viscosity and the curing time displayed by the PHU were not adequate for large-scale composite manufacturing processes such as infusion or resin transfer molding [29]. Moreover, the dynamicity of PHUs remained poorly effective in the case of composites, and the use of catalysts to boost the PHU dynamicity showed limited positive effects [30], in particular, if the cost and toxicity related to their use are considered.

More recently, we unveiled the synergetic effect between conventional non-dynamic EP-amine thermosets and dynamic hydroxyurethanes thermosets, ushering a significant increase in the dynamicity of the network [31]. Although this approach is simple, fully scalable, sustainable, and cost-effective, how this hybridization approach impacts the curing process, matrix properties, and the resulting NF composite material remains unknown. In particular, a thorough understanding of curing kinetic and rheological behavior is essential for exploiting it efficiently further.

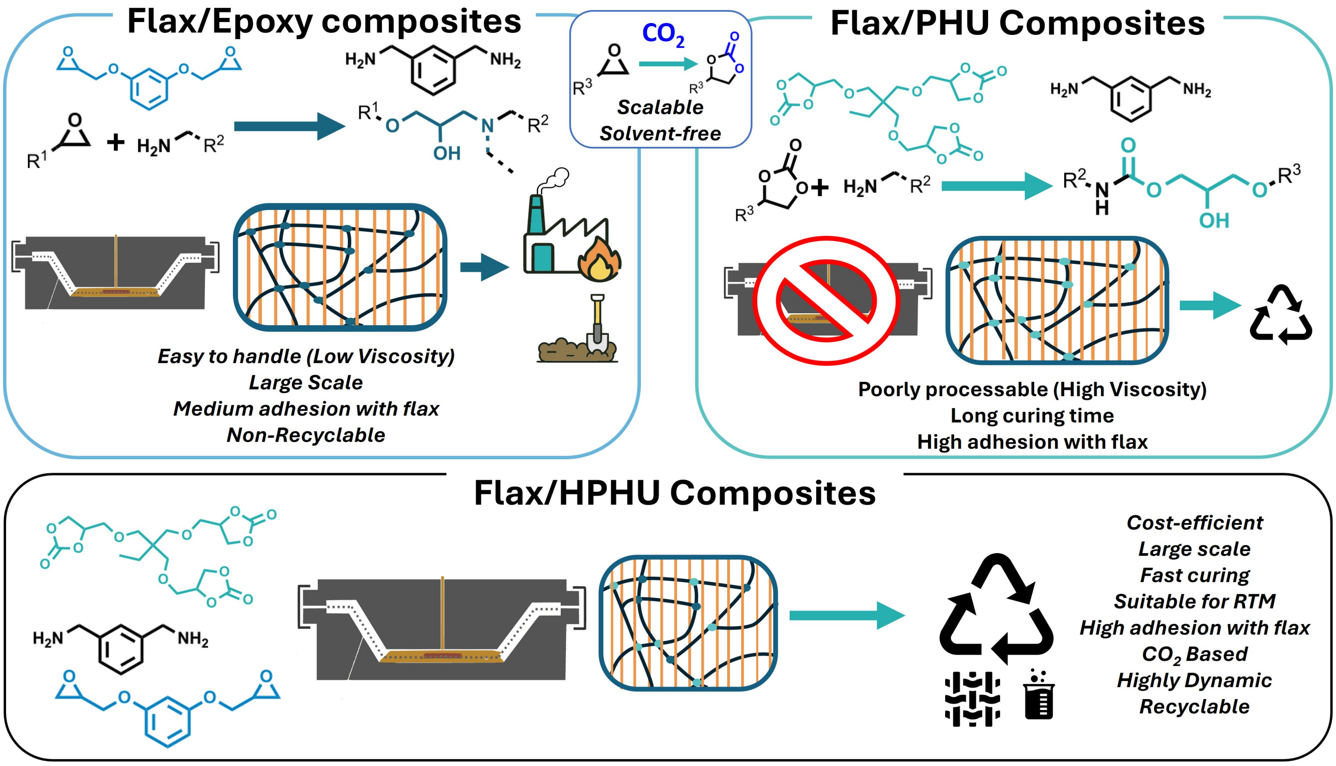

Figure 1: General scheme of the hybridization approach to introduce PHU in the composite industry.

In this work, we propose to develop and investigate this novel hybridization strategy to achieve efficient and sustainable NFC, displaying recyclability potential and meeting RTM requirements. First, model reactions were performed to investigate the mutual catalytic effect between EP and PHU by improving the aminolysis reaction rate. Then, hybrid formulations with viscosities suitable for RTM were developed, as shown in Fig. 1. In this respect, we selected building blocks for their biobased potential, wide commercial availability at a reasonable cost, and anticipated mechanical properties. The curing was then studied through rheological and calorimetric methods, particularly the EP/CC content ratio effect. Flax composites with different EP/CC ratios were then manufactured by RTM. The impregnation quality was evaluated, and their properties were assessed. The capacity of these dynamic flax-based composites to be efficiently reshaped was demonstrated. Finally, the flax fibers were recovered using a mild process to cleave the matrix and reused as reinforcing fibers into a new composite.

2 Materials and methods

2.1 Materials

Trimethylolpropane triglycidyl ether (TMPTGE, IPOX RD20, Epoxy Equivalent Weight EEW = 140 g/eq) was kindly supplied by IPOX® Chemicals. DENACOL NAGASE Chemtex kindly provided diglycidyl ether of resorcinol (RDGE, DENACOL EX201, Epoxy Equivalent Weight EEW = 117 g/eq). m-Xylylene Diamine (MXDA), glacial acetic acid, hydrogen peroxide solution (30wt% in water), ethanol (HPLC grade), butyl glycidyl ether (BGE), phenyl glycidyl ether (PGE), benzylamine, and propyl isocyanate were purchased from Sigma-Aldrich. All chemicals were used as received. Quasi-unidirectional flax woven reinforcement (FlaxDry UD180, 180 g/m^2) was bought from EcoTechnilin. Chemical synthesis of model compounds and trimethylolpropane tricarbonate are reported in supporting information (SI), section I.

2.2 Kinetic study

The model compounds were chosen to mimic the structure of common epoxy and cyclic carbonate building blocks while avoiding the crosslinking of the network. To better represent the influence of substituent, phenyl glycidyl ether (PGE) was chosen as a mono epoxy representative of phenolic epoxies such as widespread bisphenol A diglycidyl ether or resorcinol diglycidyl ether, while butyl carbonate (BGC) is a mono-carbonate representative of commonly used cyclic carbonate such as trimethylolpropane tri carbonate. The aminolysis of both BGC and PGE was monitored by ^{1}H-NMR in $CHCl_3$. For the cyclic carbonate aminolysis study, 0.5 g of BGC (2.8 mmol) was weighed in a 5 mL vial. Then, 0.307 g (2.8 mmol, 1 eq) of benzylamine (BzA) were added. In the case of the epoxy "catalyzed" formulation, 0.5 eq of mEP (0.34g) was added. The formulation was vortexed for 30 s to ensure a homogeneous mixture. Then, the vial was left under magnetic stirring at 25 °C, and an aliquot was regularly taken to be analyzed. The aminolysis rate was studied through the disappearance of the cyclic carbonate characteristic peak (4.8 ppm) and CH2-NH2 peak (3.9 ppm) related to the formed hydroxyurethane.

Similarly, in the epoxy aminolysis study, 0.5 g of PGE (3.3 mmol) was weighed in a 5 mL vial. Then, 0.357 g (3.3 mmol, 1 eq) of benzylamine (BzA) were added. In the case of the urethane "catalyzed" formulation, 0.5 eq of mU (0.21g) was added. In the case of the hydroxyurethane "catalyzed" formulation, 0.5 eq of mHU (0.265g) was added. The formulation was vortexed for 30 s to ensure a homogeneous mixture. Then, the vial was let under magnetic stirring, and an aliquot was regularly taken and analyzed. The aminolysis rate was studied through the disappearance of the epoxy characteristic peak (3.4 ppm) and CH2-NH2 peak (3.9 ppm) related to the formed amino-alcohol.

2.3 Sample preparation

2.3.1 Polymerization of the hybrid epoxy/polyhydroxyurethane networks

The epoxy monomer (resorcinol diglycidyl ether) and the cyclic carbonates (trimethylolpropane tricarbonate) were mixed in different weight ratios (0%, 25%, 50%, 75%, and 100%) and degassed before use. The amine hardener (mXDA) was added in an equimolar ratio between reacting functions using eq.1. The mixture was manually mixed for 3 minutes. The curing was performed in PTFE molds for 30 min at 80 °C followed by a post-curing step of 1 h at 160 °C to ensure complete curing.

$$m_{NH_2} = m_{monomer} \times (\%CC \times \frac{AHEW}{CEW} + \%EP \times \frac{AHEW}{EEW}) \tag{1}$$

2.3.2 Resin Transfer Molding (RTM) of flax composites

Flax composite laminates were manufactured by RTM using a single-component CIJECT 3.0 system supplied by DIATEX. An aluminum mold of 120 x 120 x 3 mm^3 was used. A Zyvax® (Chemtrend) releasing agent was employed to coat the mold and ease the unmolding. The flax quasi-unidirectional reinforcement was precisely cut to the mold size (120 x 120 mm^2) and placed into the RTM mold. A stacking sequence of $[0/(0/90)_2/\bar{0}]_S$ (11 plies) was utilized to mimic a real case scenario with a complex lay-up and different fiber orientations. The mold was then sealed by applying 30 kN pressure in a Fontjine hydraulic press. The mold was preheated for 30 min at 60 °C. In the meantime, 150 g of co-monomers (with various ratios, see section 2.3.1) and hardener were prepared by manual mixing in a disposable steel pot. The pot containing the mixture was placed into the RTM tank and injected into the mold using a nitrogen flow through PTFE tubes. Once the co-reagents mixture was going out of the tube placed at the exit of the mold, meaning its complete filling, the PTFE tubes were clamped with a steel clamp. The mold was maintained under pressure for 30 min at 80 °C. After, the plates were cooled to room temperature and later unmolded. A post-curing step of 1 h at 160 °C was performed to ensure complete curing.

2.3.3 Recovery of the natural fibers from the composite

The degradation solution was prepared by mixing acetic acid and hydrogen peroxide (30 %wt in water) in a volume ratio of 80:20. The composite material (12.4 g) was roughly cut into large pieces and put in a 500 mL round bottom flask with 250 mL of the oxidative solution. The mixture was heated to 60 °C until complete matrix degradation within 2 h under constant magnetic stirring. The fibers were then recovered by filtration and washed several times with demineralized water until a neutral pH was obtained. The fibers were dried overnight in a ventilated oven at 60 °C. The reclaimed fibers were reused as a reinforcement using the hybrid matrix (50%EP-50% PHU) by impregnation under thermo-compression. As such, 4 g of fibers were compressed to pre-shape the reinforcement. Then, 6 g of the hybrid resin mixture was poured into the mold. The composite was then pressed to 4 bar at 80 °C for 1 h and further post-cured one hour in an oven at 160 °C.

2.4 Characterization

Detailed information on the experimental characterization can be found in the second section of the supporting information.

2.5 Statistical analyses

Analysis of Variance (ANOVA) was performed on the measured mechanical properties to evaluate potential statistical differences between formulations. A one-way ANOVA with a 95% confidence interval was chosen to discriminate the mechanical property discrepancies. For each property, the p-value was computed. The difference is considered statistically meaningful when the p-value is lower than 0.05. When the p-value was below 0.05, a pairwise Tukey's test was conducted to discriminate the differences between each formulation. For each test case, letters a, b, and c assemble the groups of statistical similarities.

3 Results and discussions

3.1 Mutual catalytic effect on the aminolysis of cyclic carbonates and epoxy compounds

The competition between epoxy and cyclic carbonates toward aminolysis must be first addressed. In this respect, the aminolysis of a cyclic carbonate mimicking the actual polymer building block (herein butyl carbonate - BGC) by a primary amine (benzylamine - BzA) was first studied at 25 °C. In the reference scenario, only the BGC and BzA were used. In the second scenario, 0.5 eq of an opened epoxy model (mEP, see Fig. 2) was added to see a potential catalytic effect from the formed epoxy compound within the formulation. The evolution of the BGC conversion is depicted in Fig. 2a. The aminolysis of the cyclic carbonate occurred spontaneously at room temperature with the quick conversion of 60% of the cyclic carbonate compound within 1 h. This is ascribed to the reported catalytic effect of amines that act as both reactant and catalyst [32]. However, the conversion rate significantly decreases after 2 h of reaction. 85% of conversion is reached after 5 h, and an asymptotic behavior is observed with a low extent of conversion, requiring 24 h to reach more than 99% conversion. This trend has been reported in the literature [33] and has been attributed to the effects of steric hindrance and hydrogen bonding, limiting the overall conversion of the cyclic carbonates. Additionally, the depletion of free amines reduces the initial catalytic effect, resulting in a slower reaction completion. Interestingly, a catalytic effect is observed when mEP is added. After 1 h, 75% of CC conversion was reached, and 91% after 5 h, showing a positive effect of the presence of amino-alcohols in the reaction media (Fig. 2a). Even if somewhat unexpected, this positive effect can be understood as these bases and alcohols/protic species are known to catalyze the aminolysis kinetics of cyclic carbonates [30, 34]. The amino-alcohols obtained through aminolysis of oxirane have a pKa around 10-11, providing this base-catalyst effect in addition to hydrogen bonding [35, 36]. It was also reported that basic compounds (such as triethylamine and guanidine derivatives...) stabilize the intermediary ammonium alkoxide [37] and, similarly, mEP compounds may serve as a proton-transfer (Fig. 2d). Likewise, in the case of CC aminolysis, the pendant hydroxyl group acts as a hydrogen donor and stabilizes the intermediate alkoxide together with the N-H of the urethane. Ultimately, the alkoxide deprotonates the ammonium to form the final adduct.

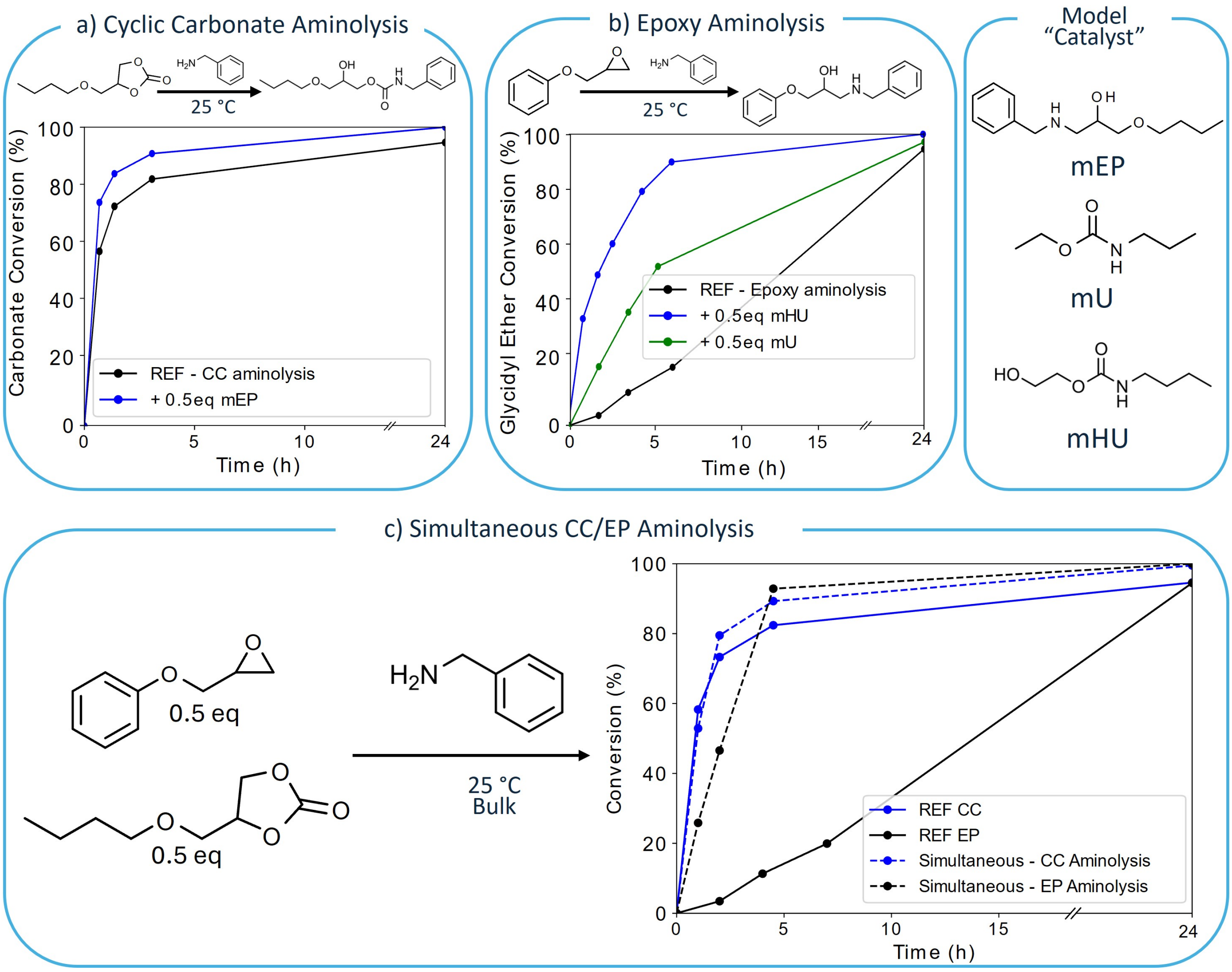

Figure 2: Model reaction kinetic study of the catalytic effect of presential epoxy and urethane compound. a) Aminolysis of cyclic carbonate, b) aminolysis of epoxy, and c) simultaneous aminolysis of epoxy and cyclic carbonate.

A similar reaction was conducted between a model epoxy (Phenyl Glycidyl Ether – PGE) and the same BzA curing amine at 25 °C. The reference uncatalyzed reaction showed a typical behavior for epoxy-amine compounds with a prolonged reaction in the early stage, reaching only 20% after 7 h but quickly evolving up to 95%. Epoxides exhibit exponential curing behavior due to the autocatalytic effect of amino-alcohols during the aminolysis. Early stages are slow, with limited spontaneous reactions happening. Still, the formation of hydroxyl compounds favors the reactions [38], thus generating a cascade effect that accelerates the curing rate [39].

Unlike epoxy aminolysis, the aminolysis of CCs is catalyzed by the presence of free primary amines, facilitating early hydroxyurethane formation. Based on this observation, we hypothesized that the formed hydroxyl compound could fasten the epoxy aminolysis. To demonstrate this, a model hydroxyurethane (mHU) was introduced into the reaction media. As initially hypothesized, a significant positive effect was detected with more than 90% conversion in 7 h, representing a reaction four times faster. In the presence of mHU, the catalytic hydroxyurethane is already present, activating the epoxy and thereby rapidly, accelerating the reaction. To discriminate the importance of the urethane moiety in the system and its role compared to the hydroxyl moiety derived from hydroxyurethane, a similar urethane compound (mU) was also tested, i.e., not bearing any alcohol moiety. Interestingly, an intermediate behavior was found at around 60% conversion within 7 h, representing a reaction 3 times faster than the reference but slower than when using mHU. However, the catalytic effect was still noticeable. The catalytic effect of mU confirms that it is not solely the hydroxyl moiety that contributes significantly to the catalytic action of mHU but urethanes also play a role in accelerating the epoxy aminolysis, more likely through hydrogen bonding.

While these initial separated kinetic model reactions show promise, a final experiment was performed through the simultaneous aminolysis of epoxy and cyclic carbonate compounds. This approach acknowledges that competitive reactions may take place, limiting the catalytic behavior of each compound on the other. Thus, PGE, BGC, and BzA were mixed directly, and the hydroxyurethane and epoxy formation were monitored. The results are presented in Fig. 2c. Interestingly, we observed that the CC aminolysis is similar to the reference at the early stage, with about 60% conversion within an hour. Even if the catalytic effect is not as pronounced as in the case of the mHU-catalyzed reference that displayed a conversion of 37% in 1 h, the epoxy aminolysis in the EP/CC system was significantly faster than in the case of the reference EP (20% conversion in 1 h vs. 3%) This can be understood through the need to generate a sufficient amount of hydroxyurethane moieties to achieve a notable catalytic effect on the epoxy, therefore delaying the reaction slightly. However, after 5 h of reaction, both CC and EP reached more than 90% of conversion while the reference cases were at 80% and 15%, respectively. As a result, although some competition could have been anticipated between the aminolysis of epoxy and CC, thus hindering the full completion of one compound, a mutual catalytic effect was observed. This allowed each system to help the others in achieving higher conversion degrees more quickly. These unexpected observed features enable the future application of PHU chemistry in rapid curing processes such as RTM. We can anticipate a similar behavior at the polymer scale with the quick reaction of cyclic carbonates increasing the opening of the epoxy, thus leading to faster curing at lower temperatures.

3.2 Curing behavior of EP/CC formulations and final properties of EP-PHU copolymers

In composite manufacturing, it is essential for reactive resins to display low viscosity to efficiently impregnate the reinforcement used, ideally at room temperature. Additionally, the curing should be as fast and controlled as possible to minimize manufacturing costs, energy consumption, and thermal degradation when heating is required for curing. Although the mutual catalytic effect of EP and CC in the aminolysis reactions was effectively proven in the previous section, the situation may differ in the case of the bulk polymers. Therefore, EP/CC formulations of various compositions were prepared, in addition to the reference EP and PHU homopolymers, and their curing behavior was analyzed by DSC and rheology. The results are summarized in Fig. 3.

To achieve physical properties that align with market expectations (low viscosity, glass transition temperature of 90-100 °C, high strength...), trimethylolpropane tricarbonate (TMPTC) was selected as the cyclic carbonate monomer. The trifunctionality of the starting molecule facilitates a sufficient degree of cross-linking within the polymer network. The resorcinol diglycidyl ether (RDGE) was selected as the epoxy monomer. RDGE is a potential lignin-derivative replacement for the widespread bisphenol-A diglycidyl ether [40]. RDGE is an aromatic epoxy; therefore, it will also bring sufficient rigid substructures within the backbone. Furthermore, RDGE possesses low (melt) viscosity at room temperature to act as a reactive diluent in the formulation of the hybrid PHU. Finally, m-Xylylene Diamine (MXDA), a potential furfural bio-derived amine [41], was selected as a co-reagent between RDGE and TMPTC to further bring more aromaticity into the network, improving the mechanical and thermo-mechanical properties of the resulting material.

The viscosity of the EP/CC mixtures was measured to determine the optimal amount of epoxy diluent needed to obtain viscosity values below 10 Pa.s, which is a typical value for epoxide formulations dedicated to RTM processes. For the formulation under study, an amount superior to 25 % in mass is required (Fig. S13). Although the viscosity of neat TMPTC is high (150 Pa.s), limiting its application in many processes, adding just a small amount of epoxides can drastically lower the viscosity of the formulation by an order of magnitude. This emphasizes the effectiveness of hybrid EP-PHU by appropriately adapting and spreading the use of PHU in advanced manufacturing processes.

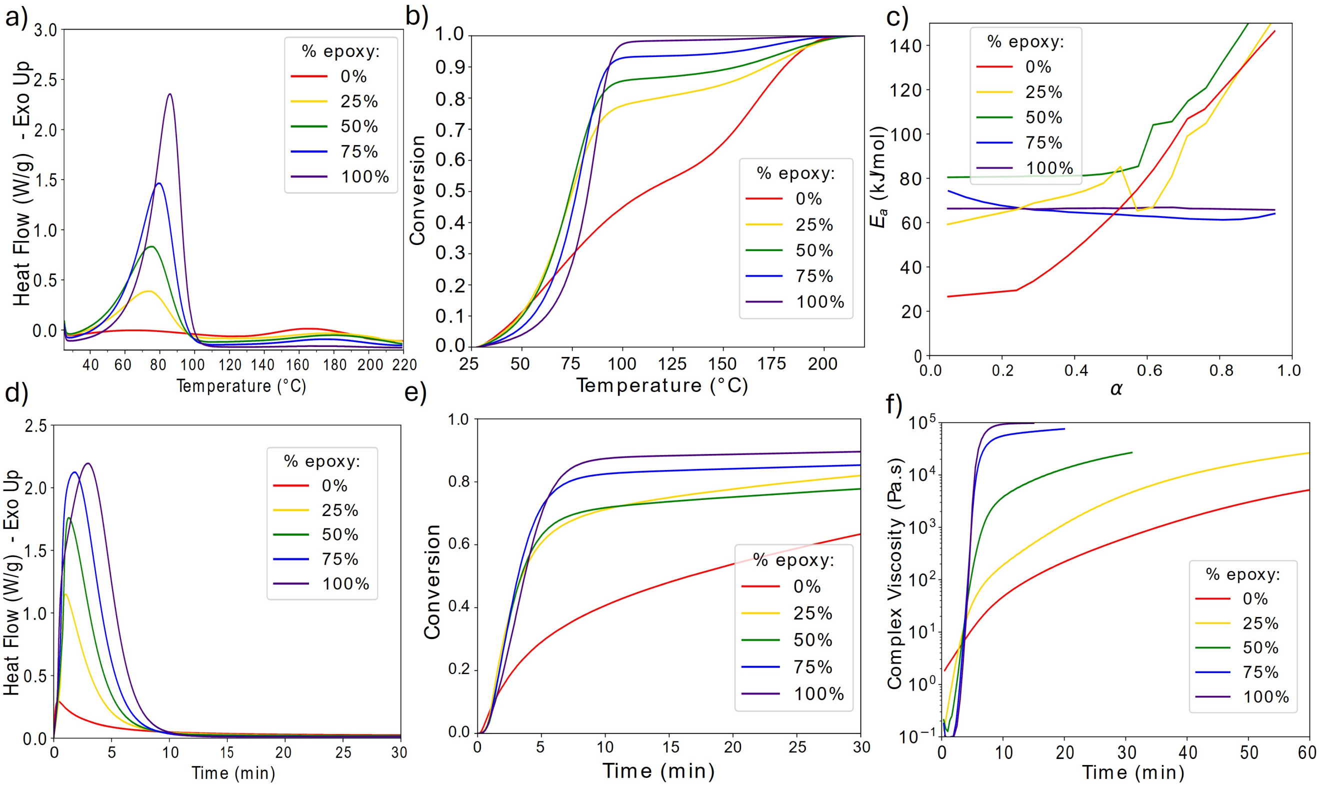

Figure 3: Curing study of the hybrid EP/CC formulations. a) Non-isothermal curing by DSC at 5 K/min, b) Conversion of non-isothermal curing c) Activation energy of the formulation as a function of conversion, d) Isothermal DSC curing at 80 °C, e) Conversion of curing at 80 °C, and f) viscosity evolution through isothermal rheology at 80 °C

Non-isothermal curing was performed on the hybrid polymer formulations to investigate the aforementioned potential catalytic effect as a function of the epoxy content. The non-isothermal curves obtained with 0, 25, 50, 75, and 100% epoxy content at 5, 10, and 20 K/min from 25 to 220 °C are presented in Fig. 3 and Fig. S14-15. Extracted data are reported in Table 1. Interestingly, the presence of hydroxyurethane led to a significant decrease in the maximum temperature peak, curing enthalpy, and offset temperature compared to neat epoxy. Additionally, the onset temperature was significantly lower and the conversion rate increased, highlighting the improvement in the curing rate compared to neat epoxy or neat PHU. PHUs are known to have a slow curing rate with a strong dependence on the temperature to reach a sufficient amount of conversion [42]. This appears evident through the conversion plot (Fig. 3b) of the non-isothermal DSC with two distinct phases of curing: one between 25 °C and 130 °C with only 50% of conversion and a second phase between 150 °C and 200 °C to finally reach full completion. This is particularly problematic for advancing PHU chemistry in composites, especially when used with biobased fibers. This highlights that prolonged curing time and high temperatures are necessary. However, when increasing the epoxy content, conversions higher than 80% are reached at temperatures lower than 80 °C. This can be understood through the catalytic effect reported earlier in this work as well as the high exothermic behavior of epoxy. The latter can generate a sufficient amount of energy to push the aminolysis forward [39].

Exploiting Friedman's iso-conversional model (see Fig. S16-20), the activation energy of the different systems was obtained as a conversion function as reported in Fig. 3c. Friedman's iso-conversional model was preferred to Ozawa's and Kissinger's models as it does not assume a constant E_a throughout the entire reaction. Instead, the activation energy depends on the extent of the reaction and thus provides a more accurate real-world representation. Moreover, Friedman's model does not assume a reaction model and thus is more suited for complex and multistep curing reactions, thus being more accurate [43, 44]. Given the observed behavior through the non-isothermal curing, particularly for the PHU, a constant E_a cannot be assumed. As expected from the previous observation, the activation energy of the neat PHU was much lower than that of the other formulations (26.5 kJ/mol vs 68.4 kJ/mol for the pure epoxy). The pure PHU shows, however, a significant and continuous increase of the activation energy after reaching 30% of conversion. This underscores a known issue with PHUs: the curing process slows down as the conversion increases, which significantly limits the complete curing and necessitates higher curing temperatures, involving higher energy consumption. This behavior is ascribed to the reduction in the amount of the catalyzing free amines and to a change in the curing mechanism, which becomes controlled by diffusion mechanism rather than kinetics [44]. This is coherent with previously reported behavior on the polymerization of thermoplastic PHUs, hindered by hydrogen bonds [45]. Additionally, the higher temperatures required to push the polymerization forward will promote uncontrolled and undesirable side reactions [26, 46]. The hybrids show an activation energy of 59.5, 82.2, and 73.5 kJ/mol from 25 to 75% of epoxy content, respectively. This result seems to contradict the expected trends as lower activation energy compared to epoxy would have been expected, given that the reaction rate is faster at the initial stage. This could be due to the limitations of Friedman's model in accurately estimating the activation energy of a complex system such as EP/CC mixtures, where different mechanisms take place and overlap with each other. However, the augmentation of the activation energy, as observed in pure PHU, resumed after 70% conversion, consistent with the decrease in the conversion rate and the further need to increase the temperature to obtain a higher curing level.

Based on the observed non-isothermal curing behavior, a temperature of 80 °C was selected as a suitable temperature for a fast and controlled curing of the hybrid formulations, limiting side reactions and reaching a high level of conversion.

The isothermal curing of the formulation was also monitored by DSC. The curves obtained regarding heat flow and curing degree as a function of time are presented in Fig. 3d-e, and key data are reported in Table 1. The maximum heat peaks appear earlier in the case of hybrid formulations compared to pure epoxy. Additionally, the offset appears much earlier, and the conversion of the resins significantly increases in the case of the hybrid EP/CC formulations compared to PHU. The PHU only reached 65 % of curing extent, consistent with previous literature work [29,35]. Conversions superior to 80% were obtained for the hybrid formulations, highlighting the positive effect of this synergy between EP and PHU chemistries. Yet, it also demonstrates that there is no need for a long curing time at 80 °C. At the same time, a post-curing step is essential to ensure the complete formation of the polymer network and, thus, structural stability. Finally, the hybrid EP/CC formulations appear to cure faster than neat PHU at potentially lower temperatures with a superior extent of curing. This makes the approach much more promising for composite manufacturing.

Table 1: DSC and rheological curing properties of the hybrid formulations

%EP			0	25	50	75	100
DSC	E_a	kJ/mol	26.5	59.5	82.2	73.5	68.4
Non-Isothermal	Tpeak	°C	66.4	74.1	75.7	79.8	85.6
5 K/min	Q_{max}	W/g	0.18	0.50	0.97	1.62	2.53
	ΔH_T	J/g	169	287	456	581	701
	Onset	°C	30.2	41.3	45.7	54.6	65.8
DSC	Peak Time	min	3.35	3.31	3.35	4.03	5.49
Isothermal	Q_max	W/g	0.29	1.15	1.76	2.12	2.19
80 °C	Offset	min	33.30	20.96	16.63	13.26	13.86
	ΔH_T	J/g	110	235	363	496	628
	Conversion (α)	%	65.0	81.8	79.6	85.4	89.5
Isothermal	η_{init}	Pa.s	44.4	6.0	4.7	4.6	6.0
Rheo	Pot Life	min	nc	2.3	7.0	11.0	12.0
25°C	Gel Time	min	>60	>60	>60	>60	36
Isothermal	η_{init}	Pa.s	2.80	0.35	0.13	0.05	0.10
Rheo	Pot Life	min	4.5	3.3	3.3	3.3	3.5
80 °C	Gel Time	min	83	41	15	5	5

Besides the DSC thermograms, the curing behavior was assessed through rheological experiments at 25°C (Fig. S21) and 80 °C (Fig. 3f and Fig. S22). The primary goal was to assess that the formulations provide sufficient time at room temperature for efficient processing and infusing through RTM while confirming the fast curing once the impregnation is performed. Values are summarised in Table 1. At 25 °C, viscosities below 6 Pa.s were obtained for epoxy content superior to 25%, which makes them particularly suited for RTM [47]. The observed rheological behavior at 25 °C directly relates to the previous model reaction and DSC. When a high content of cyclic carbonates is present, the reaction starts immediately, as observed by the continuous increase of the viscosity. The formulations containing 50 and 75% of EP are particularly noteworthy due to their low viscosities (4.6 Pa.s), extended pot life (>10 min), which allows enough time before the viscosity becomes too high to remain processable. This seems particularly adapted to allow moderate to high PHU content in the network while still remaining processable. This study at 25 °C was particularly appealing to ensure the suitability of the formulations for future impregnation processes. Notably, over an hour at 25 °C did not lead to any gelation of the hybrid formulations. Interestingly, developing pre-preg composites that are more stable at room temperature than pure epoxy pre-preg could offer significant advantages [48], especially given the dynamic behavior of such systems [31].

Finally, the curing behavior was studied at 80 °C. Similar trends to the DSC are observed, with a high curing rate for the hybrid. At 80 °C, the gel time was significantly reduced for the hybrid formulation compared to that of the pure PHU, requiring only 15 min instead of 83 min. The gel point was consistent with the DSC results where conversion higher than 60% is obtained after 10 min. This confirms that time ranging between 15 and 30 min should be enough to reach a sufficient level of curing for such hybrid systems and be further post-cured at higher temperatures, significantly reducing processing time and equipment use.

The overall results from the model compound kinetic study and the curing analysis by DSC and rheology draw a comprehensive understanding of the EP-PHU hybrid curing behavior. At the molecular level and at the early stage of polymerization, the aminolysis of cyclic carbonate happens first, generating hydroxyurethane moieties that activate the aminolysis of oxirane groups, which helps in the rapid building of a homogeneous network. This translates at the macromolecular level by gel time, happening faster than pure PHU networks with a higher conversion. While one of the challenges in composite manufacturing relies on the long curing time at elevated temperatures, with post-curing often required, the strategy enables shorter curing cycles at lower temperatures, thus increasing the efficiency of the process while diminishing operating costs.

In continuous fiber-reinforced polymers, the reinforcement primarily sustains the load [49]. Yet, the matrix is critical in transferring it to fibers. Additionally, the matrix protects the fibers and binds them together. Hence, it is essential to maintain high mechanical properties and good thermal stability in the matrix. The influence of the hybridization strategy on the pure polymer properties was therefore assessed.

Thermo-mechanical and quasi-static monotonic mechanical properties were determined. Results and complete discussion are described in section V.1. of SI. The extracted properties are summarized in Table 2. Notably, the glass transitions are significantly increased compared to the pristine PHU, reaching values similar to the epoxy, about 90 °C, being satisfactory in the case of NFCs. An increase in the glassy modulus was unveiled while the crosslinking density decreased, highlighting the positive effect of strong H-bond in the networks as observed in pure PHU [28]. In tensile, a slight increase in Young's modulus was unveiled, highlighting the positive effect of this hybrid material on tuning the processability without decreasing the final properties (stress and strain). More importantly, an increase in the modulus or glass transition often correlates to a decrease in ductility, which can be detrimental to the future structure's longevity. In the hybrid EP-PHU and as already evocated by DMA, the material incorporates "weak" H-bonds. This leads to equivalent or superior strain at break but also higher ultimate stress as the material possesses a better ability to absorb mechanical deformation with a higher stiffness [50]. This was further confirmed through Charpy impact testing, which revealed higher toughness of the hybrid materials than EP and PHU (Table 2).

Based on all the above, hybridization can be considered as a straightforward approach to exploit PHU chemistry in conventional epoxy-based materials. The overall results confirm that if pure PHUs do not fulfill the requirements of the composite industry, particularly process-wise, the hybridization strategy offers a simple yet efficient approach to overcome their limitations and can be straightforwardly implemented without compromising existing processes. It is particularly interesting that this approach not only maintains but also slightly enhances the material properties. The PHU formulations now align with the RTM process requirements, showcasing promising properties for composite applications.

Table 2: Physical properties (mean ± deviation) of hybrid EP-PHU formulations

		DMA				Tensile			Impact
% Epoxy	ρ	T_α	$E'_{25°C}$	$E'_{rubbery}$	ν'_e	E	σ	ϵ	α_{CU}
	g/cm^3	°C	MPa	MPa	mol/m^3	GPa	MPa	%	kJ/m^2
0	1.29 ± 0.01	78	3129	6.6	657	2.9 ± 0.1	100.3 ± 11.3	4.19 ± 0.81	5.7 ± 2.2 ab
25	1.27 ± 0.01	85	3441	6.1	613	3.1 ± 0.2	105.7 ± 2.4	4.23 ± 0.33	5.5 ± 1.2 ab
50	1.26 ± 0.01	94	4491	6.9	664	3.1 ± 0.1	102.9 ± 6.8	3.99 ± 0.32	5.8 ± 1.3 ab
75	1.25 ± 0.01	87	2704	6.8	663	3.0 ± 0.1	102.6 ± 3.5	4.09 ± 0.38	8.5 ± 1.5 b
100	1.25 ± 0.01	97	2560	15.9	1519	2.9 ± 0.1	88.8 ± 9.9	3.34 ± 0.47	2.8 ± 0.1 a
p-value	-	-	-	-	-	0.204	0.063	0.109	0.0003
significant	-	-	-	-	-	No	No	No	Yes

3.3 RTM manufacturing of flax-EP-PHU composites

Given the satisfying results obtained from the synergetic hybrid EP-PHU approach, with low viscosity, fast curing, and satisfying thermo-mechanical properties, RTM-made composite samples were manufactured (Fig. S27). Composites with an engineered lay-up of 11 plies were manufactured by RTM using unidirectional woven flax as the reinforcement. 25, 50, 75, and 100% of epoxy content were used as formulations. A curing protocol for RTM was developed consisting of the injection of the reaction mixture (co-monomers and hardener) for 10 min at room temperature in a 60 °C preheated mold, followed by a 30 min curing at 80 °C. An out-of-mold post-curing step was finally conducted at 160 °C for 1 h to ensure complete curing.

The obtained composites were satisfyingly impregnated, with no apparent surface defect or fiber misorientation (Fig. 4a-d). The impregnation quality was evaluated by SEM. The “between-plies” impregnation (Fig. 4e-h) and interpenetration of the matrix within the yarns (Fig. 4i-l) were investigated. The 25%EP demonstrated significantly high viscosity, which hindered complete impregnation under the current injection parameters, as indicated by the presence of a fully non-wetted area (Fig. 4a).

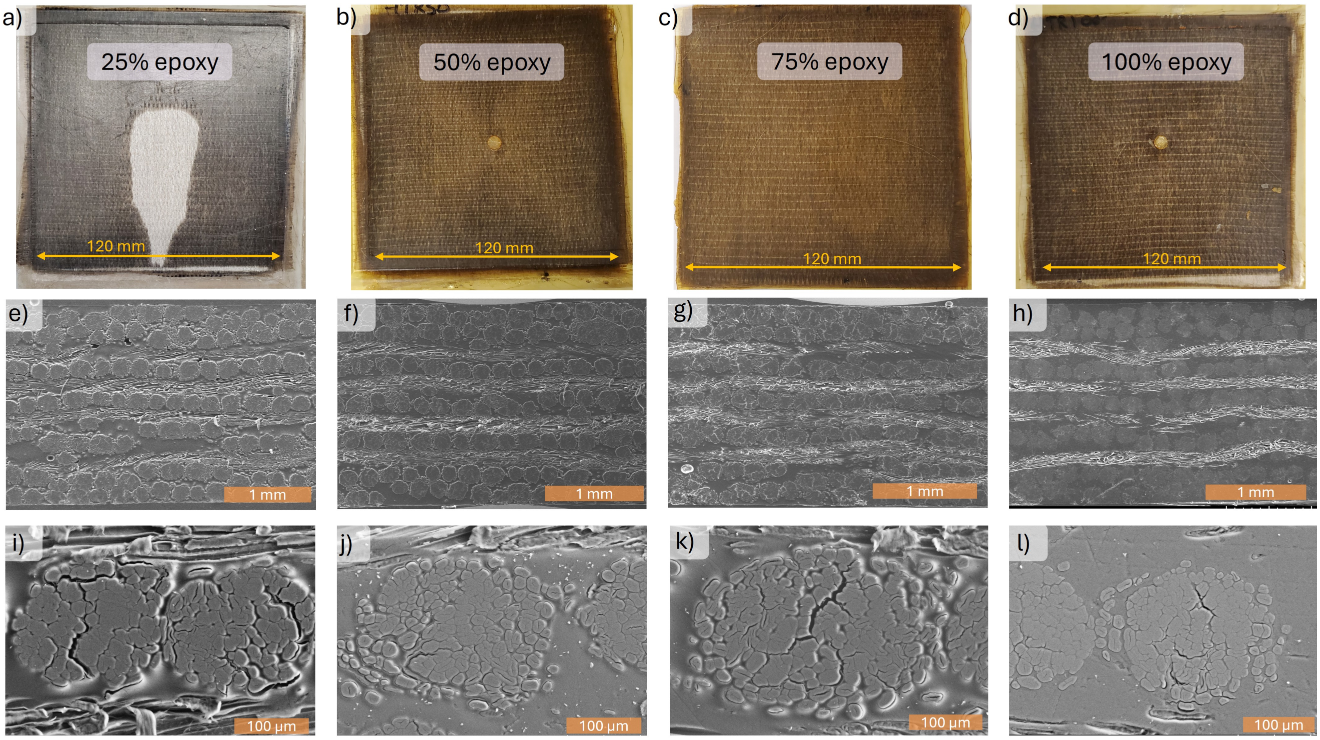

Figure 4: Resin Transfer Molding of flax reinforced hybrid EP-PHU composites. a-d) Photographs of the composite plates, e-h) SEM micrographs of crosscut sections with x30 magnifications, and i-l) SEM micrographs of crosscut sections on tows with x300 magnifications for 25,50,75 and 100% of epoxy (from left to right).

With 50% or higher contents of EP, the impregnation at the laminate scale is of high quality, homogeneuos, and defect-free. All plies are perfectly impregnated and bonded together. SEM analyses reveal high-quality impregnations for the 50%-100% EP formulations. Some issues with the fluidity and the tight twist of the fiber roving can lead to some heterogeneities in the yarn's impregnation, although they remain infrequent and do not affect high standards for flax reinforcement [51]. This could be improved in the future through simple adjustments of the formulation, components, and parameters optimization. Lower twisting of the flax yarns could also facilitate their internal wetting, further improving mechanical properties [52]. For all systems, high fiber volume fractions (V_f) ranging between 57% and 62% were obtained (Table 3), in the highest range of reported achievable V_f [53]. Notably, while high V_f has been reported to lead to high porosity content (V_p) [54], extremely low Vp were obtained, with 1% for the 25% EP system and below 0.5% for the other ones, consistent with SEM images, and showing the high suitability and consistency of hybrid EP-PHU formulations for RTM manufacturing process.

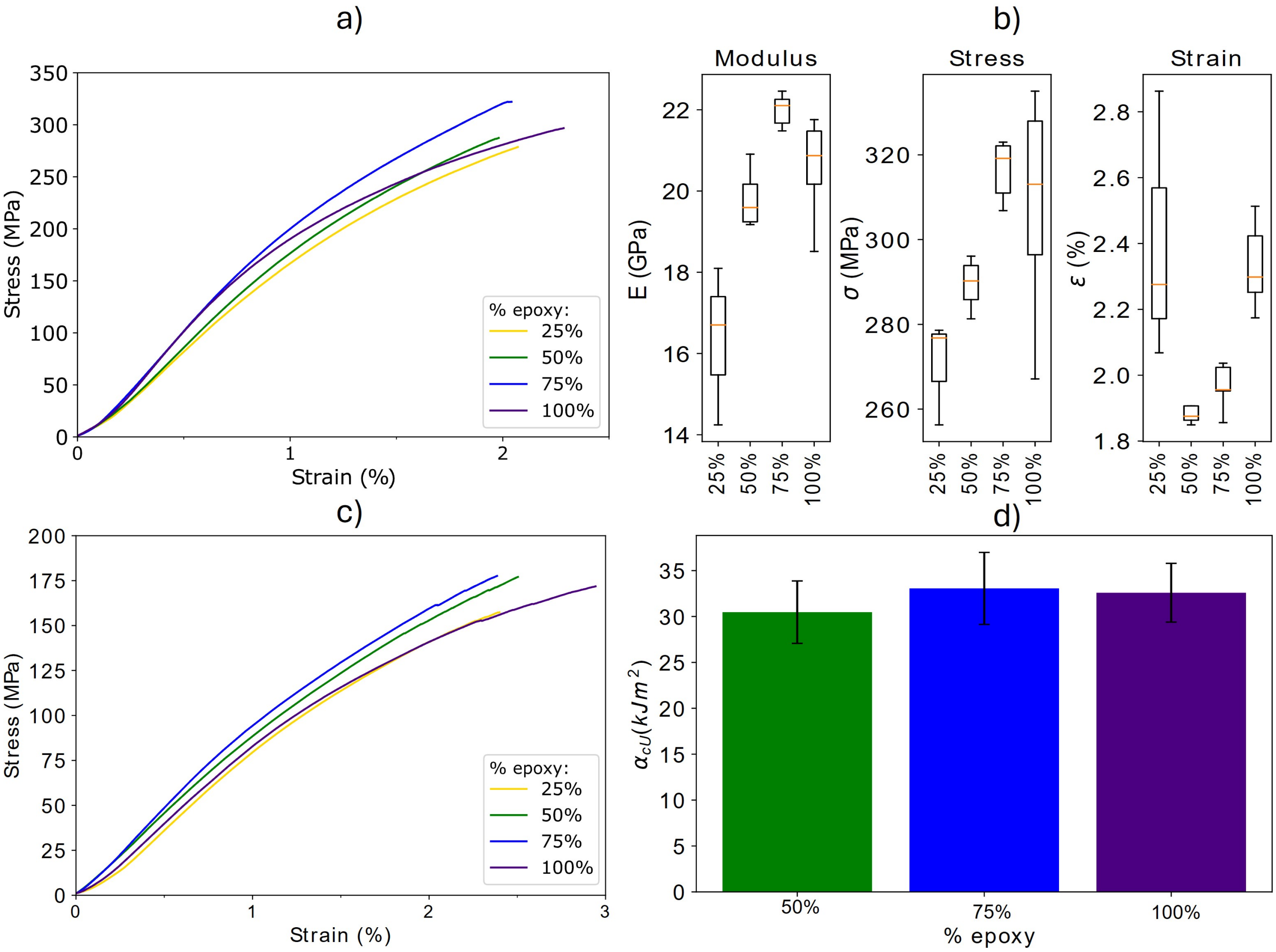

Figure 5: Mechanical properties of the RTM-manufactured flax/epoxy-PHU. a) Representative three-point bending curves in the principal direction, b) boxplot of the bending properties in the main composite direction, c) Representative three-point bending curves in the transverse direction, and d) Charpy impact results in the principal direction. (25% plate did not provide enough sample to be tested).

The three-point bending mechanical behavior in the two main orthotropic directions was evaluated. Representative strain-stress curves are presented in Fig. 5a-c. The lower modulus was obtained for the 25%EP composite, with 16.3 GPa due to the lower impregnation quality obtained. ANOVA was also performed (Fig. S29). 50% EP was considered statistically similar to the reference EP-based composite with 20.1 and 19.0 GPa, respectively. The formulation containing 75% EP was considered statistically improved with 22.0 GPa. The admissible strain was not affected by the different matrices. The slightly lower strain observed for 50% and 75% EP could be explained through strong interactions at the fiber-matrix interface, limiting pull-out and debonding and privileging fiber breaking. As the internal yarn impregnation is not complete, the load transfer to all fibers is limited, thus decreasing slightly the admissible stress. The ultimate stress is similar between the reference EP and the PHU-75%EP hybrid with 325 and 316 MPa, respectively. As expected, 25% of EP decreased the stress with 270 MPa due to the lower impregnation quality. As strong interactions between PHUs and cellulosic fibers were previously reported [28], the difference between the different formulations appears to be mainly process-related due to the observed lack of internal yarns impregnation, limiting efficient load transfer between the fibers. Although the interfacial adhesion between flax and the EP-PHU is expected to improve, the complexity of the reinforcement used here could lead to a counterproductive effect, potentially diminishing the anticipated benefits of the PHU chemistry. This can also corroborate the observed trends in the transverse directions (Fig.5c and Fig. S28). High modulus between 9.0 and 9.6 GPa are obtained, without any statistical significance, despite the differences in impregnation quality. Again, the stress at break was slightly diminished when a low epoxy content was used. To effectively compare the results within this study and with other works, the Classical Laminate Theory (CLT), homogenized with Chami's model, was employed to compute the global laminate stiffness matrix and determine the theoretical modulus, as reported in Table 3. The method can be found in SI (section II.10). A good agreement between theoretical and experimental results was obtained, with a ratio between 0.8 for the 25% EP hybrid and superior to 0.9 for the others, confirming the quality of the resulting composite. The results are in the highest range of the literature [55, 56]. Toughness was also assessed in the main composite direction. High toughness was obtained for all formulations, superior to 30 kJ/m^2.

In general, high mechanical properties are obtained. There are no statistical differences that could be detrimental to the reliability of hybrid EP-PHU as an alternative to existing market matrices. Additionally, further improvement can be anticipated through further parameters and formulation optimization during industrialization. The results demonstrate that following the hybridization strategy, PHU chemistry can be implemented into industrial processes with no modification of existing methods and guarantee an improvement of the curing cycle, thus production rate, and material final properties, which are a common burden of novel sustainable matrices in composites. Moreover, the building blocks are easily accessible and thus relevant to the global composite market.

Table 3: Properties (mean ± standard deviation) of RTM-made flax composites in the main lay-up and transverse directions.

					Bending			CLT		Charpy
%EP	LayUp	ρ	V_f	V_v	E	σ	ϵ	E_{CLT}	E/E_{CLT}	α_{CU}
		g/cm^3	%	%	GPa	MPa	%	GPa		kJ/m^2
25	$[0/(0/90)_2/\bar{0}]_S$	1.36 ± 0.01	57.7 ± 0.6	1 ± 0.6	16.3 ± 1.6 b	270.5 ± 10.1 b	2.40 ± 0.34	20.3	0.80	-
50	$[0/(0/90)_2/\bar{0}]_S$	1.37 ± 0.01	57.9 ± 0.4	0.2 ± 0.8	19.0 ± 0.3 a	294.8 ± 10.2 b	1.99 ± 0.12	21.1	0.90	30.5 ± 3.4
75	$[0/(0/90)_2/\bar{0}]_S$	1.37 ± 0.02	62.4 ± 0.9	0.4 ± 1.1	22.0 ± 0.4 c	316.3 ± 6.4 a	1.96 ± 0.06	22.1	0.99	33.1 ± 3.9
100	$[0/(0/90)_2/\bar{0}]_S$	1.36 ± 0.01	58.8 ± 0.4	0 ± 0.1	20.1 ± 0.4 a	325.5 ± 15.1 a	2.26 ± 0.19	21.1	0.95	32.6 ± 3.2
p value	-	-	-	-	0.0003	0.001	0.356	-	-	0.550
significant	-	-	-	-	Yes	Yes	No	-	-	No
25	$[90/(90/0)_2/\bar{9}0]_S$	1.36 ± 0.01	57.7 ± 0.6	1 ± 0.6	9.0 ± 0.2	167.1±6.9 b	2.4±0.01	9.9	0.91	-
50	$[90/(90/0)_2/\bar{9}0]_S$	1.37 ± 0.01	57.9 ± 0.4	0.2 ± 0.8	9.0 ± 0.5	166.1±10.9 b	2.35±0.18	9.0	0.84	-
75	$[90/(90/0)_2/\bar{9}0]_S$	1.37 ± 0.02	62.4 ± 0.9	0.4 ± 1.1	9.4 ± 0.6	172.3±5.6 a	2.38±0.19	9.4	0.87	-
100	$[90/(90/0)_2/\bar{9}0]_S$	1.36 ± 0.01	58.8 ± 0.4	0 ± 0.1	9.6 ± 0.1	190.1±3.5 a	2.47±0.05	9.3	0.91	-
p-value	-	-	-	-	0.240	0.007	0.736	-	-	-
significant	-	-	-	-	No	Yes	No	-	-	-

3.4 Perspectives towards the reshaping and recycling of natural fiber composites

The end-of-life of FRPCs remains a well-known and yet ongoing issue. Despite several sustainability advantages of NFC, their EoL remains problematic. The current EoL management for NFC consists of incineration, landfill, or, in the best cases, grinding them down for use as fillers in low-quality materials. Interestingly, the exploration of PHU chemistry presents opportunities in the realm. The hybrid epoxy-PHU was found to be reprocessable thanks to the dynamicity of the polyhydroxyurethane networks. Initially, PHU stood out as a poorly dynamic system, requiring harsh conditions for dynamicity [29]. This leads to the partial degradation of the natural fibers [28] and low economic or environmental interest.

Interestingly, the hybridization of PHU with EP led to a network containing both dynamic hydroxyurethane moieties and easily accessible internally catalyzed hydroxyl moieties from the epoxy network, as represented in Fig. S31. As such, a much faster and more efficient dynamicity materializes [29]. The reduction of time and temperature allows the preservation of the flax fiber integrity upon reshaping. This is not accessible through conventional epoxy. As shown in Fig. 6, an RTM-manufactured sample was heated to 180 °C and reshaped in a press using copper bars to control pressure points. From a small, flat sample, a wave-shaped composite was obtained. The fiber orientation and material integrity were kept, and no debonding or delamination was generated, contrary to the epoxy-based reference (Fig.S30).

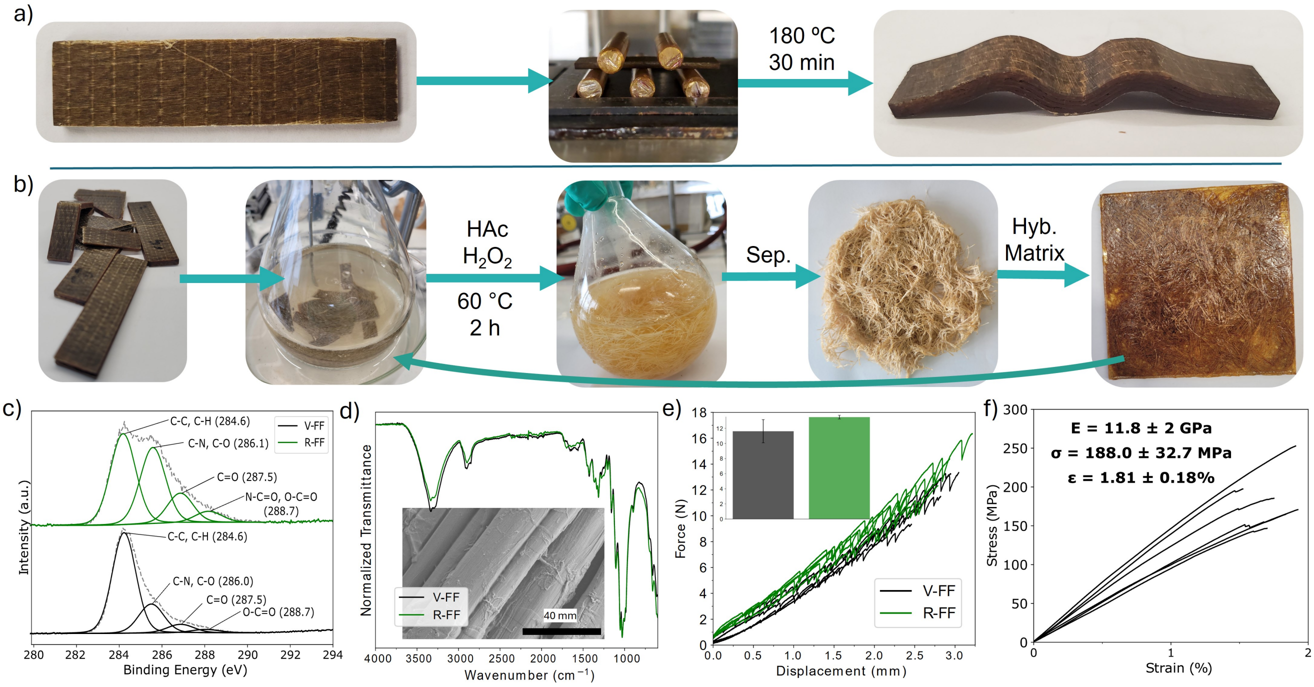

Figure 6: Exploiting the dynamic behavior of the hybrid formulations for advanced opportunities and recycling. a) Thermo-mechanical reshaping of the flax composite, b) chemical recycling and flax yarns recovery and reuse, c) XPS, d) FTIR (inset SEM of R-FF), e) tensile analyses of the virgin and recovered flax yarns, and f) bending of the manufactured composite using recovered flax yarns.

Chemical degradation of the polymer matrix under mild conditions can be an ideal solution to retrieve fibers or yarns and repurpose them in new applications. However, the severe conditions and catalysts needed to depolymerize epoxy thermosets are not adapted to natural fibers [57]. Indeed, the organic nature of such fibers makes them sensitive to strong chemical reagents and temperature. In the case of our synergetic hybrid approach, oxidative acidolysis was employed as a gentler method, avoiding the use of harsh or expensive reagents during the chemical degradation process (Fig. 6b). A solution of acetic acid and hydrogen peroxide (80:20) was prepared, and the composite samples were broken into small pieces for immersion. When heating to 60 °C, the acetic acid - hydrogen peroxide solution generates peracetic acid, a selective oxidant that effectively cleaves amine and aryl-ether linkages [58]. This process could be industrially relevant as simply feeding up the oxidative solution with hydrogen peroxide could enable to continuously degrade the matrix, while regenerating the acetic acid in the process.

Here, the network was destroyed, and the yarns could be recovered in just 2 h. Interestingly, while peracetic acid has been reported to cleave pure epoxy [59], the reaction conditions typically required longer times (4-8 h) and at higher temperatures than here. Two mechanisms contribute to depolymerizing the networks. First, the excess in acetic acid causes the network to swell [60], leading to partial physical breakdown of the network. As the crosslinking density of hybrid EP-PHU is lower than that of neat EP, which relies more on hydrogen bonds, the swelling is faster and more noticeable. Additionally, the flax fibers can significantly swell in aqueous media, initiating cracks in the matrix [61], and improving the first physical mechanism. Then, hydroxyl and acyloxy radicals can more easily cleave the C-N bonds and Ar-O-C bonds, leading to the destruction and solubilization of the thermoset.

After filtration and washing using distilled water, the flax yarns were dried. 7.3 g of fibers were recovered, representing 58.8% of the total composite mass, consistent with the flax fiber mass content (around 60-62%), indicating minor losses. As shown by the SEM images in Fig. S34 at different magnifications corresponding to reinforcement, yarns, and fiber scales, no apparent presence of polymer residues was found, and pure flax yarns were recovered. XPS was employed to characterize the fibers' surface (Fig. 6c and Fig. S35). The analysis reveals a slight modification of the surface composition with a lower carbon content (67%) compared to virgin fibers (V-FF) (81%) and a higher content of oxygen (29 vs 17%). Detailed surface survey composition can be found in Table S1 and S2. One must keep in mind that the protocol is also used in the delignification process of wood fibers [62] to obtain pure cellulose. Therefore, if some partial oxidation may occur, the main reason for this observed surface composition is the removal of lignin (carbon-rich), in favor of a more oxygen-rich cellulose. This is further confirmed by the significant augmentation of the C-O relative atomic concentration (Fig. S35, Table S1-2), which is indicative of cellulose. Even if a partial oxidation of the fiber surface is anticipated with the slight augmentation of C=0 relative, the effect is limited. Moreover, XPS represents the surface composition over a few nanometers (typically 5-10 nm). Energy-dispersive X-ray spectroscopy (EDX) was also used to analyze the surface through depth (Fig. S36, Table S3), typically, about 10 μm. In that case, almost no change in the composition was observed, highlighting that the oxidation remains significantly contained at the very surface. FTIR (Fig. 6d) and TGA analyses (Fig. S33) also confirmed no significant changes in the chemical structure of fibers, indicating the complete removal of the matrix. The recovered flax yarns were subjected to tensile testing to assess the retention of their mechanical properties and the results were compared to those of the virgin ones used in the reinforcement (Fig. 6e). Interestingly, no diminution of the tensile strength or strain was unveiled. Furthermore, R-FF showcased slightly superior mechanical properties with a 16% increase in strength (13.49 N vs 11.62 N) and 2% in displacement (Fig. S37), which corroborate with higher relative content of cellulose in the fiber. Although these differences are not statistically significant (Fig. S38), this is the first time that the chemical recovery of flax reinforcement is obtained without any major degradation, allowing their future exploration for second-life uses.

Finally, a composite was manufactured from the recovered flax fibers by thermo-compression, with a fiber volume fraction of about 45%. The fibers were not realigned and were used as non-woven, resulting in randomly oriented reinforcement. The direct comparison with the virgin materials is, therefore, not relevant. The properties of the materials were evaluated in three-point bending (Fig. 6f). Interestingly, high mechanical properties were obtained with a bending modulus of around 12 GPa, a stress at break of 188 MPa, and a strain of 1.81%, representing promising results in semi-structural applications. The materials remain competitive with other NFC despite the oxidative depolymerization process [63]. For reuse perspectives, various machines for fiber realignment [64] have been developed over the last decades, enabling the enhancement of the properties of these fibers to give a second life for these realigned recovered flax fibers again in structural applications.

4 Conclusions

Although PHUs have limited prospects in the realm of industrial structural composites despite their promising properties and beneficial feedstocks, we demonstrate that their limitations could be overcome through a simple, scalable, and straightforward hybridization strategy. Formulating EP-PHU networks leads to on-demand modular systems with tunable properties as it opens the door to the library of epoxy monomers, cyclic carbonates, and amines. Viscosity can be tuned to meet process requirements. The formulations cure faster thanks to a mutual catalyzing effect between epoxy and hydroxyurethane, initiated by the early aminolysis of cyclic carbonates. The properties of resulting networks are maintained or even improved as new H-bonds are formed in the network, resulting in an improvement of the static mechanical properties and impact toughness. Finally, the hybrid formulations were suitable for RTM-processed flax composites with complex stacking sequences. The NFC obtained exhibited high mechanical properties comparable to those of benchmark epoxy-based composites. The dynamicity of these hydroxyurethane moieties is promoted by the amino-alcohols, allowing the reshaping of the cured flax composite. Finally, we demonstrated that mild oxidative depolymerization can be applied to natural fiber composites for the extraction of natural fibers. The hybrid matrix can easily be cleaved under mild conditions to retrieve high-quality flax fibers that can be repurposed in new applications. This opens the door to more circularity in these materials.

This approach represents a reliable and consistent way to integrate CO_2-derived polyhydroxyurethane chemistry in the composite market, particularly in transportation or sports and leisure, offering new opportunities and solutions in a large and growing market where the lack of satisfying solutions hampers sustainability goals.

While emerging sustainable chemistries, in particular CANs, require a long time to be implemented in industries due to the difficulties of adapting existing processes and technologies or creating new supply chains, the results unveiled in the present work open the door to a faster implementation of PHU chemistry in industrial sustainable materials while being extremely new to composite applications. In particular, such synergetic hybrid formulations should be considered as enhanced epoxy matrices and thus would fall into already existing technology while opening new opportunities. However, it is important to note that PHU chemistry and its derivative hybrids remain extremely recent. In that sense, complementary work is still required to validate the technology through industrial proof-of-concept, applied characterization, and long-term studies. Future works should evaluate the environmental footprints of such networks, as it would also be critical for other CANs and biobased matrices, alongside techno-economic assessment. Furthermore, evaluating the performances over long service time such as weathering, stability, humidity, UV aging, fire properties, fatigue, appear crucial development for PHU-based composites but also other CAN-based materials. These challenges will be treated in the near future by our team.

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