Synergetic Hybridization Strategy to Enhance the Dynamicity of Poorly Dynamic CO_2-derived Vitrimers achieved by a Simple Copolymerization Approach

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Copolymerization allows tuning polymer's properties and a synergetic effect may be achieved for the resulting hybrid, i.e., outperforming the properties of its parents as often observed in natural materials. This synergetic concept is herein applied to enhance both dynamicity and properties of vitrimeric materials using poorly dynamic hydroxyurethane and non-dynamic epoxy thermosets. The latter generates activated hydroxyl, promoting exchange reactions 15 times faster than pure polyhydroxyurethanes. This strategy allows obtaining catalyst-free high-performance vitrimers from conventional epoxy-amine formulations and an easily scalable (bio-)CO_2-based yet poorly efficient dynamic network. The resulting hybrid network exhibits modulus retention superior to 95% with fast relaxation (<10 min). The hydroxyurethane moieties actively participate in the network to enhance the properties of the hybrid. The material can be manufactured as any conventional epoxy formulation. This new strategy to design dynamic networks opens the door to large-scale circular high-performance structural carbon fiber composites (CFRP). The CFRP can be easily reshaped and welded from flat plates to complex geometries. The network is degradable under mild conditions, facilitating the recovery and re-use of high-added-value fibers. This accessible and cost-effective approach provides a versatile range of tunable dynamic epoxides, applicable across various industries with minimal adjustments to existing marketed products.

1. Introduction

Covalent Adaptive Networks (CAN), have emerged as a promising alternative to traditional thermosets.[1] Like their traditional counterparts, CANs are crosslinked polymer networks. The difference arises from the incorporation of dynamic linkages. These dynamic linkages can be "on-demand" triggered by external factors such as temperature, pressure, pH, or light to participate in exchange reactions and ease the rearrangement of the networks, leading to the release of internal stress.[2] As a result, crosslinked polymeric materials, normally discarded after their service life, can be now reused in new second-life applications.[3] Moreover, this inherent dynamicity opens up many possibilities such as self-healing, welding, or thermoforming of the materials ushering in a wave of innovative manufacturing processes.[4]

In the last decade, various dynamic chemistries have been brought to light, namely fetched to epoxy thermosets, one of the most widespread thermosets,

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by incorporating dynamic moieties, such as disulfide metathesis,[5] transesterification,[6] siloxane,[7] boronic ester-based crosslinker,[8] transimination,[9] as well as by developing new polymer chemistries such as vinylogous urethane,[10] oxime,[11] boronic ester-based commodity polymers,[12] dynamic crosslinking of thermoplastic elastomers,[13–15] dioxazaborocane,[16] N-S acetal,[17] and many others.[18]

Despite the large range of dynamic systems, any single CAN cannot meet the overall satisfying requirements in terms of competitive properties and elevated dynamicity, being often opposite, different dynamic bonds have been implemented within these networks to get this tunability.[19] Recently, Serra et al.[20] proposed an epoxy vitrimer with dual relaxation based on imine and disulfide linkages to easily access the biobased epoxy network with intermediate properties. However, the dual vitrimer copolymerization strategy leads to the implementation of additional complex synthetic pathways that represent a major hurdle at an industrial scale.

In most cases, the resulting copolymer possesses properties in between both respective materials.[21,22] In only a few rare cases, a synergetic effect is achieved and leads to outstanding performances exceeding any expectation.[12,23] This synergetic effect is widely spread in natural materials and organisms through millennia of evolution to obtain sophisticated materials with outstanding performances and efficiency such as spider silk[24] or mussel collagen[25] but hardly predictable in man-made materials. Synergetic engineered materials are sometimes obtained from a biomimetic approach to reproduce natural behavior like hygromorph metamaterials.[26] More recently, Chen et al.[27] exploited such a synergetic copolymerization approach to unify polymerizability, recyclability, and performance properties of linear polymers. By this means, they obtained outperforming polymers with facile polymerization at room temperature with controlled structures, high performances, and fully controlled depolymerization.

To the author's best knowledge, such a synergetic approach through simple copolymerization has not been exploited in the realm of CANs. Inspired by these natural examples, we hypothesized that highly efficient dynamic networks could be obtained through simple copolymerization of easily accessible building blocks. Such a strategy would open the door to more unrestricted CANs for industrial applications, especially composite materials, and allow closed-loop structural materials. More precisely, thanks to this novel approach, we design a highly efficient dynamic network made of two distinct polymers, in which each corresponding chemistry would smoothly operate as the counterweight to the other. In such an approach, a polymer can bring dynamic linkages that normally require activation (i.e., catalyst), in a synergy manner with the other polymer that provides this catalytic effect.

Among the emerging CANs, polyhydroxyurethanes (PHU) have gained interest over the last decade as they offer an alternative to (hazardous) isocyanate-based polyurethanes.[28] The starting monomers can easily be obtained from bio- and CO_2 feedstocks by the simple quantitative carbonatation of (bio)epoxides in solvent-free and purification-free conditions.[29] PHU also includes the network dynamicity that permits potential welding and reshaping.[30] Yet, due to the stability of urethane linkages, this behavior is poorly efficient as it requires high temperature (> 160 °C) and time (> 15 h). Catalysts showed limited efficiency in improving the dynamicity.[31] We have recently observed that this dynamic network could be highly influenced by the presence of an internal catalyst that enhances relaxation times substantially.[32] In our plan to exploit this behavior efficiently, we hypothesized that copolymerizing PHUs with a polymer that could generate this internal catalyst in situ would facilitate the exchange reaction.

One of the polymers that could generate this internal catalyst upon polymerization is the widespread conventional non-dynamic epoxy-amine thermosets (EP). Indeed their curing generates hydroxyl with secondary and tertiary amines neighboring groups that could potentially accelerate the transcarbamoylation exchange reaction, thus improving the efficiency of the dynamic network.[32] Furthermore, the low viscosity of the epoxy and wide library of available building blocks allow the implementation of large-scale composite manufacturing without requiring any change from the already existing manufacturing protocols. Additionally, both being polymerized by amines, the formulation would be one-pot and one-step, without any new scarcely accessible reagents nor catalyst, valorize CO_2, and be industrially relevant.

Besides achieving this synergetic effect, the developed systems should bring some significant benefits to conventional thermoset manufacturing processes. Indeed, one of the main interests relies on the fiber-reinforced polymer (FRP) industry where CANs have shown promising outcomes by allowing welding, thermo-forming, and recycling of FRP that was before inaccessible.[18] Therefore, the ability of CAN-based FRP to be reshaped and welded could lead to a larger implementation of these high-performance materials in the demanding market such as transport.[33] Another important advantage of these CANs is the improved recyclability.[34] The possibility of recovering the high-added-value energy-intensive carbon fiber would benefit substantial economic and environmental gains.[35] Therefore, it has become necessary to develop alternatives that can offer similar performances to thermosets and additional options for manufacturing and recycling.[18] In that sense, developing economically relevant solutions that are easily accessible from renewable feedstocks, without using any hazardous reagents or complex synthesis, scalable, and with satisfying material properties must become a major effort.

To delve into this synergetic hybridization strategy (**Figure 1**), in this work, several hybrid EP-PHU are synthesized with different epoxy/urethane ratios to demonstrate the auto-catalytic effect of the epoxy-derived amino-alcohol for the transcarbamoylation of hydroxyurethanes. First, we perform some model reactions and atomistic simulations to understand the difference between conventional transcarbamoylation and the synergetic hybridization autocatalytic approach. Later on, we investigate the (re)shapability, weldability, and recyclability of this hybrid copolymer which exhibits a fast catalyst-free adaptive behavior in comparison to the conventional epoxy and PHU network. Furthermore, we compare the properties of the hybrid systems with the analogous pristine epoxy and we show that the attained properties are similar or even superior to the traditional epoxy resin. We also demonstrate that this network can be cleaved under mild conditions allowing the recovery of the high-added value carbon fibers. The recovered fibers were characterized and re-used for

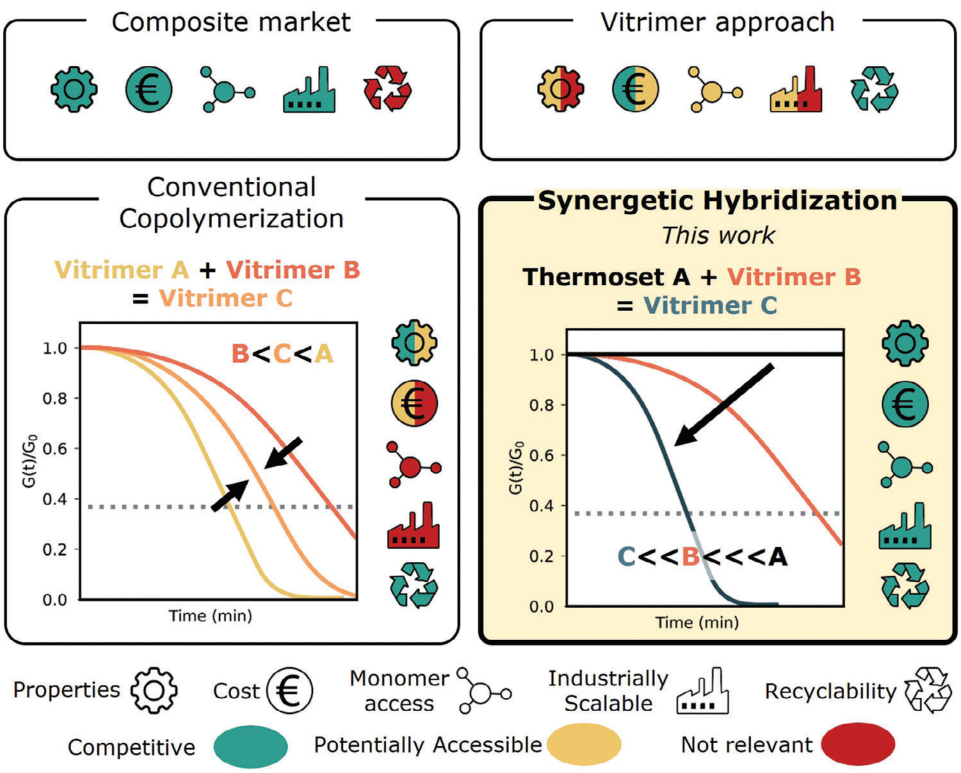

Figure 1. General scheme of the synergetic hybridization approach compared to previous work and market limitations.

manufacturing a new composite material fully closing the loop of such an innovative approach.

2. Results and Discussion

2.1. Synergetic Effect of Hydroxyurethane-Epoxy for Self-Catalyzed Transcarbamoylation

To highlight that the amino-alcohols formed by the epoxy network could efficiently take part in a fast transcarbamoylation exchange reaction, models were investigated. First, to have a better understanding about the system and its feasibility, a simple atomistic simulation was conducted. Two secondary alcohols of very similar structures, but one incorporating a neighboring amine were used, respectively called reaction A and reaction B as presented in **Figure** 2. The amino-alcohol mimics the product obtained from epoxy aminolysis. Atomic charges of the hydroxyl incorporating the amine, determined by fitting of the electrostatic potential (ESP) of the DFT-optimized isolated fragments, are found to be more negative (–0.66 e) compared to those of the secondary alcohol (–0.63 e), thus revealing higher nucleophilicity by the hydrogen bonding and the electron-withdrawing effect of the neighboring amine.[36] Furthermore, the difference in free enthalpy of the amino-alcohol-based transcarbamoylation was lower ($\Delta G_0 = = -6.70$ kJ mol^{-1}) than the conventional transcarbamoylation ($\Delta G_0 = = -3.16$ kJ mol^{-1}), see technical details in Section SI.4 (Supporting Information). This first result indicates that if the transcarbamoylation is feasible, a catalyst is required to fasten the exchange rate. In the case of the epoxy-based network, the formed amino-alcohol could be expected to play as the catalyst and the reactant and promote the network's dynamicity.

Based on these promising preliminary results, model exchange reactions were conducted as illustrated in Figure 2. No ethylene glycol (EG) generation, that would reveal the exchange reaction, was observed in the case of uncatalyzed alcohol-carbamate transcarbamoylation (reaction A, Figure S3, Supporting Information), in agreement with previous work in literature.[31] This first confirmed the impossible use of transcarbamoylation in mild conditions (temperature lower than 150 °C) without any catalyst. When the amino-alcohol compound was used (reaction B, Figures S4– S9, Supporting Information), however, EG release was quickly observed at temperatures as low as 100 °C demonstrating the positive effect of this autocatalytic system and the improvement of the exchange rate. An activation energy of 123.6 kJ mol^{-1} was calculated, correlating a previous work on catalyzed transcarbamoylation.[37] Mass spectra analysis (Figure S10, Supporting Information) confirmed that the amino-alcohol was reacting with the carbamate moieties forming the new product (m/z = 203.17) but also, to a more limited extent, was able to catalyze the primary alcohol of the hydroxyurethane and thus, forming a difunctional urethane (m/z = 283.16). Base catalysts (like triethylamine, or guanidine derivatives) are commonly used for transcarbamoylation by deprotonation of the reacting alcohol thus increasing the nucleophilicity.[37] The amino-alcohol used has a pKa around 10.5–11, similar to triethylamine, explaining the observed product. This is particularly important, as an external catalytic effect of the tertiary amine would

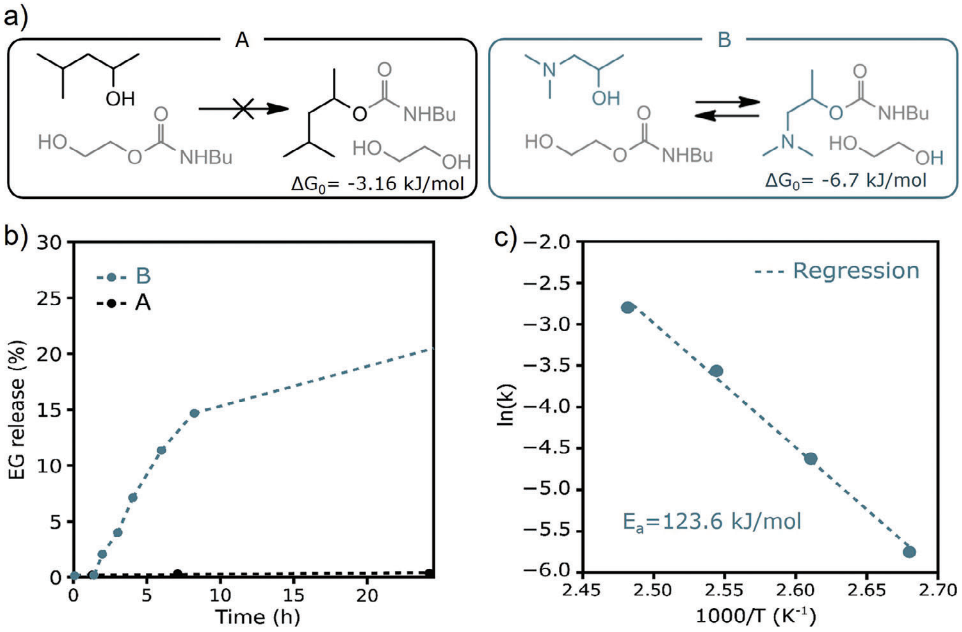

Figure 2. Design of catalyst-free efficient transcarbamoylation reaction. a) Model reaction A: Conventional uncatalyzed transcarbamoylation. Model reaction B: Internally-catalyzed amino-alcohol transcarbamoylation. b) Kinetic of the release of ethylene glycol (EG) during the exchange reaction, and c) Arrhenius plot of the internally catalyzed exchange.

probably be hindered in the copolymer network due to steric hindrance and hydrogen bonding, while the internal activation of the neighboring hydroxyl group will be encountered in the bulk material. The model reaction demonstrated the internal catalysis of epoxy-derived alcohol to act efficiently in the transcarbamoylation reaction allowing us to go on to the material scale.

The epoxy-based CAN was built by the facile incorporation of cyclic carbonates in the starting epoxy monomer (**Figure** 3a). A diamine was used as the same crosslinking agent by reacting with both epoxy and cyclic carbonates. The cyclic carbonate aminolysis leads to a hydroxyurethane moiety (Figure S11a, Supporting Information), while the aminolysis of epoxy leads to secondary and tertiary amines with pendant free-hydroxyl (Figure S11b, Supporting Information). The hydroxyurethanes moieties act as the dynamic linkage while the epoxy-derived hydroxyl acts as the internally catalyzed alcohols to perform transcarbamoylation as represented in Figure 3a. In this work, the trimethylolpropane tricarbonate (TMPTC) was chosen as a trifunctional cyclic carbonate for its low viscosity, crosslinking ability, and potential biobased origin[38] as well as being the most widely used precursors of PHU in literature, which facilitates comparison. Resorcinol diglycidyl ether (RDGE) was chosen as a potential bio-derived epoxy monomer[39] that has proven to be a suitable replacement for the hazardous Bisphenol-A.[40] m-Xylylene diamine (mXDA), a potential furfural-derived aromatic diamine was chosen as the hardener[41] to bring stiffness and stability to the network, compatible with high-performance materials.

Several formulations of TMPTC-RDGE with different mass content of cyclic carbonates were investigated in stress relaxation (Figure 3b). Interestingly, only 10% of cyclic carbonates can already lead to some (slow) stress relaxation while the range 25–75% seems to be the most promising with relaxation times within 20 min, demonstrating the expected synergistic behavior in this range. Although previous work has highlighted that pure PHU could stress relax in catalyst-free conditions,[38] it required several hours at a temperature superior to 180 °C, leading to partial thermal degradation.[42] Herein, we report the fastest relaxation for a PHU-based dynamic network, thanks to this copolymerization strategy. The 50% content of cyclic carbonates leads to the fastest relaxation time at 180 °C in only 7 min. This can be understood as the network needs a good balance between activated hydroxyl and dynamic hydroxyurethane to perform adequately. The higher content of epoxy favors the network dynamicity as it provides a sufficient number of activated hydroxyl groups. No thermal degradation during the relaxation process was observed by isothermal dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) over 1 h at 180 °C (Figure S17), with less than 0.6 wt% loss.

The networks obtained prove to be competitive with many other systems previously reported in the literature. For instance, epoxy-disulfide-based vitrimers, one of the most efficient dynamic chemistry developed so far, were obtained by different teams[43,44] with glass transition around 120 °C. They reported relaxation times of about 10-15 min at 180 °C, analogous to the one obtained in this work. Compared to a closer chemistry, i.e. transesterification-based system, relaxation times of around 15 min at 180 °C in the presence of zinc catalyst[45,46] are commonly obtained. More recently, exploiting an internal catalysis strategy, equivalent times were reported.[6] A benchmark comparison graph and table can be found in Supporting Information (Figure S25 and Table S7, Supporting Information).

Several other monomer combinations were tested to demonstrate the versatility and efficiency of the approach thanks to the facile access to a wide library of epoxy systems suitable for many applications, including potential biobased monomers. Detailed results are presented in Section SII.2.3 (Table S2 and Figure S14

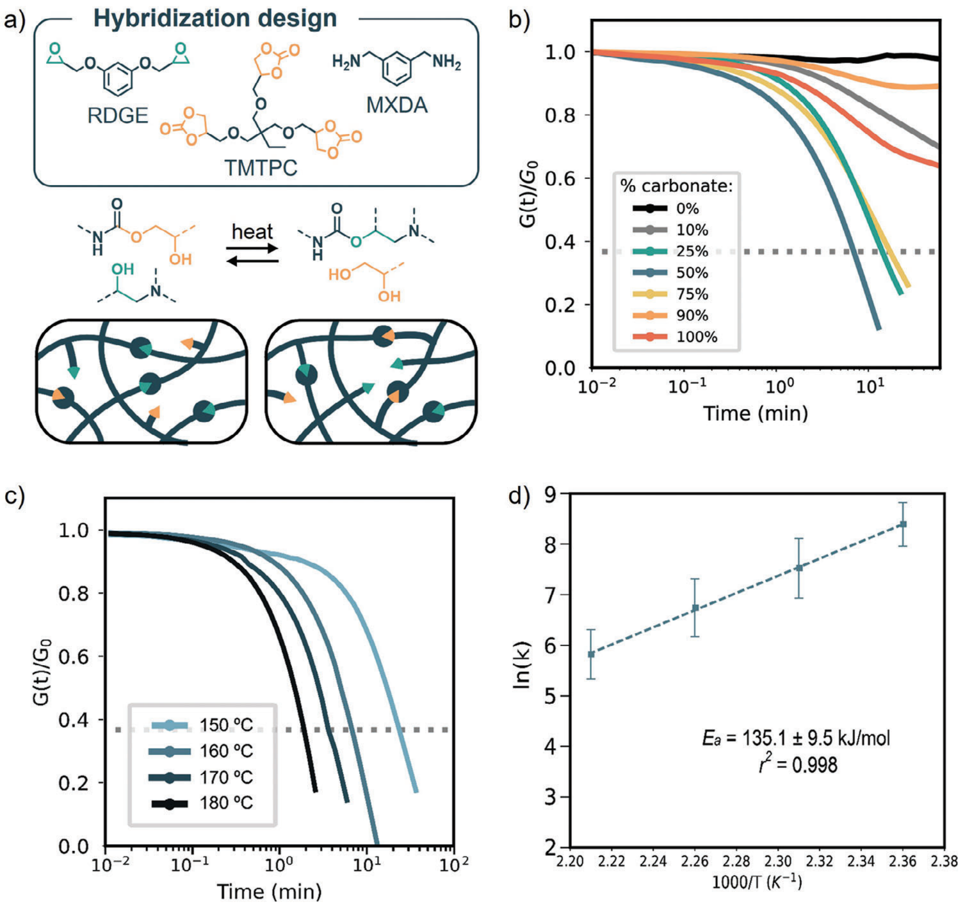

Figure 3. Design of epoxy-hydroxyurethane hybrid covalent adaptable networks. a) (Macro)molecular structure of the constituent to build the synergetic hybrid polymer with transcarbamoylation reaction, b) Stress relaxation at 180 °C of the network with a different mass content of cyclic carbonates, c) Stress relaxation of the 50/50 formulation at different temperatures and d) Arrhenius temperature–time plot from c).

and S15, Supporting Information). It is worth noting that the approach is extremely versatile and offers a wide range of properties that can be adapted to the targeted application from low glass transition (about 25 °C) to high glass transitions (about 120 °C). All formulations exhibited fast stress relaxation in catalyst-free conditions even in the case of the high glass transition and highly crosslinked network arising from the aerospace-grade epoxy 4,4'-methylenebis(diglycidylaniline). The glass transition and crosslinking density with different carbonate content but the same constituents (i.e., RDGE-TMPTC, Table S3, Supporting Information) were similar while changing the constituents led to very different crosslinking densities. In all cases, fast stress relaxations were obtained thus showing that the chain mobility has only a limited role in the overall behavior. Additionally, the rate and efficiency of the exchange reaction can be tuned through the content of cyclic carbonates. For the sake of comparison, the rest of the study focused on the 50/50 formulation out of RDGE and TMPTC.

The vitrimeric behavior was assessed for the aforementioned formulation (i.e., 50%RDGE-50%TMPTC) at several temperatures in three replicates (Figure 3c; Figure S16, Supporting Information). Although the dynamic behavior of the urethane linkage is due to both associative (transcarbamoylation) mechanism and dissociative (reverse cyclic carbonates aminolysis),[37] the main mechanism in the present work was assumed to be associative and a single decay Maxwell model stands for a sufficient approximation.[47] A good fit ($r^2 > 0.998$) was obtained with a single decay Maxwell model in the time-temperature Arrhenius plot (Figure 3d) confirming the formation of a fast relaxing catalyst-free dynamic network. Relaxation can be obtained within minutes at a temperature as low as 150 °C. The Arrhenius plot highlights a strong time-temperature dependence and thus the easy control of the relaxation through the simple temperature triggering without any catalyst side effects. The activation energy (135.1 kJ mol^{-1}) is consistent with the value obtained in the model reaction study and with literature on transcarbamoylation.[37]

The formulated networks exhibit fast and efficient stress relaxation confirming our first hypothesis, and demonstrating the interest in the copolymerization approach for epoxy to reach high dynamicity of the network through the synergy between the activated alcohols and the (hydroxy)urethane moieties. The network dynamicity being demonstrated, the material was then investigated in depth to ensure no significant modification of the properties was caused by the hybridization.

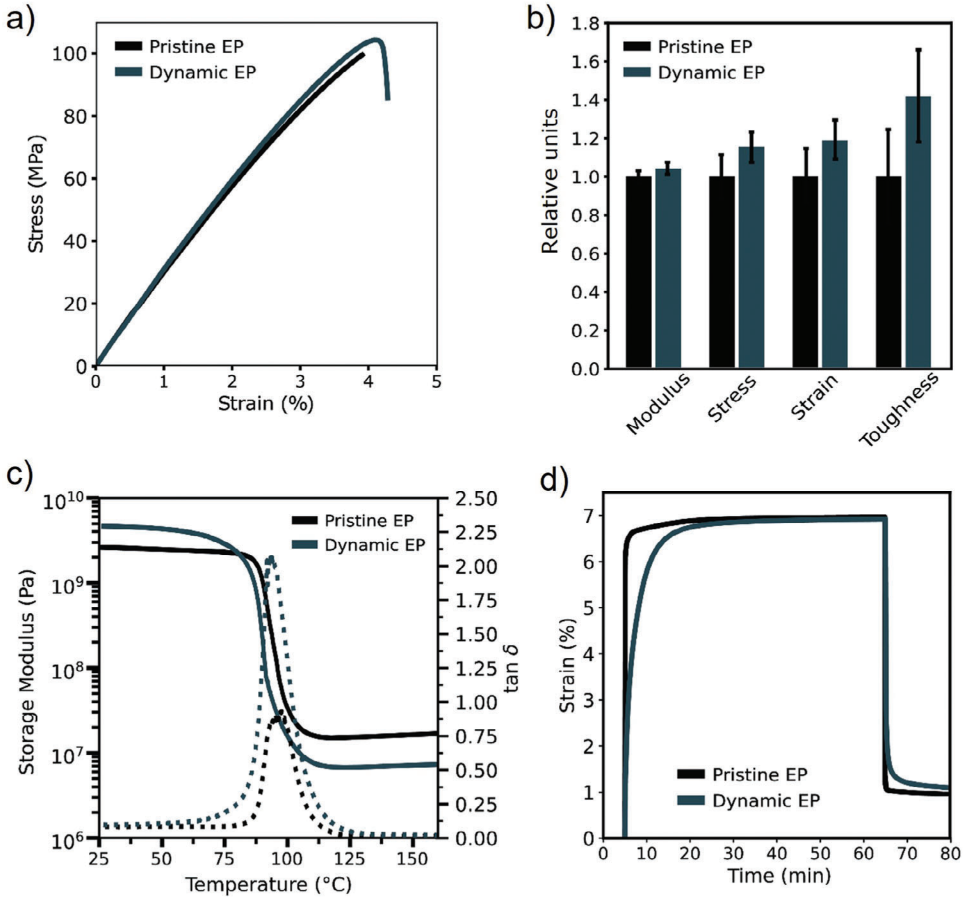

Figure 4. Mechanical and thermo-mechanical behavior of the epoxy and hybrid dynamic polymers. a) Representative tensile stress-strain curves, b) Comparative mechanical properties, normalized to the pristine epoxy, c) DMA curves, and d) Tensile creep behavior at 90 °C.

2.2. Hybrid EP-PHU Polymer: Dynamicity, Physical Properties, and Reprocessability

The pristine epoxy, consisting of RDGE-mXDA, and the dynamic epoxy, consisting of RDGE-TMPTC-mXDA, were compared. First, the mechanical properties were tested under tensile loading. The representative stress-strain curves are presented in **Figure** 4a,b and the results are summarized in Table S1 (Supporting Information). No detrimental modifications of the properties were observed. The newly formulated dynamic copolymer exhibits superior mechanical properties compared to the pristine epoxy with a high Young's modulus of 3.0 GPa (vs 2.9 GPa), admissible stress of 103 MPa (vs 89 MPa), and an admissible strain of 4.0% (vs 3.3%). The modification of the network led to an increase of the modulus by 4% and by 16% and 19% for the strain and stress respectively. These increases represent an improvement of 42% of the toughness for the new network from 1.6 to 2.3 MJ/m^{3}. This was ascribed in several works[4,48] to the stronger H-bond arising from the carbamate moieties thus maintaining a high level of stiffness, while allowing more ductility within the networks. Equally, in a recent work,[49] we highlighted the interest of pure PHU over pristine epoxy with a similar macromolecular backbone due to these stronger H-bond interactions. Lower crosslinking density PHU leads to comparable to superior thermo-mechanical properties and higher toughness than equivalent epoxy. Such can be extrapolated herein in the case of the dynamic hybrid EP where similar thermo-mechanical properties are obtained with significantly lower crosslinking density (1519 mol.m^{-3} for the pristine EP vs 664 mol.m^{-3} for the dynamic EP). For a better visualization, the internal macromolecular structure schematic representation of the dynamic EP can be found in Figure S12 (Supporting Information). This favors the potential durability of such materials by limiting the nucleation and propagation of micro-cracks,[50] in addition to the perspectives of repairability due to the dynamic nature of the newly developed copolymer network.[50]

The thermo-mechanical properties were also assessed by Dynamical Mechanical Analysis (DMA) and creep testing. The DMA (Figure 4c) displayed similar glass transitions between the pristine epoxy and the dynamic one with 97 °C and 94 °C respectively showcasing no alteration of the network and proving suitable for similar applications. Interestingly, the glassy modulus was increased for the dynamic copolymer with 4416 MPa compared to the 2314 MPa of the pristine epoxy. In addition, the crosslinking density of the dynamic copolymer was found to be substantially lower than the pristine epoxy. This is due to the implementation of the hydroxyurethane moieties through the trifunctional cyclic carbonate that lowers the crosslinking

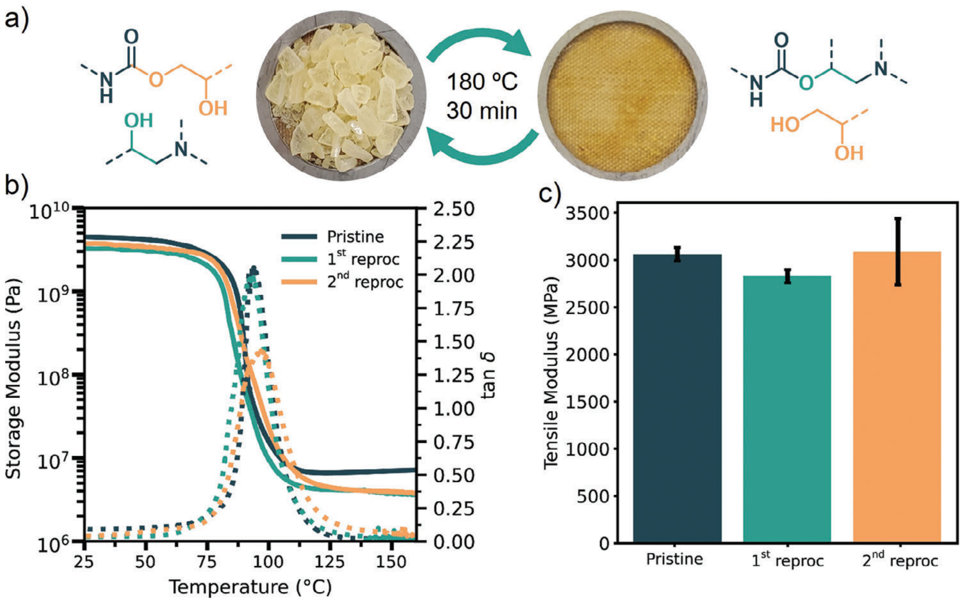

Figure 5. Thermo-mechanical recyclability of the hybrid dynamic network. a) Closed-loop thermo-mechanical recycling, b) DMA curves, and c) Tensile modulus of pristine and reprocessed hybrid dynamic networks.

density. In previous work, we reported that such lower crosslinking density in the presence of hydroxyurethane leads to stronger H-bond,[49] of high interest. The H-bond were shown to be stronger in PHUs than in epoxy networks.[38] H-bonds are secondary bonds more flexible than covalent bonding, thus, they conduct an increase of the glassy modulus while allowing more motion of the macromolecular backbone. This finally permits more ductility and toughness of the system. DMA results confirmed this trend related to our copolymerization strategy, as previously observed in tensile testing, between PHU and epoxy and the successful implementation of this toughening strategy to achieve more resilient dynamic epoxy-based materials.

Creep is a known problematic side effect of CAN as the ability of the network to flow leads them to be subjected to creep behavior like thermoplastic and contrary to thermosets.[51] This behavior is strongly dependent on the chemistry involved, the design of the monomer, and the thermal sensitivity of the exchange mechanism. A highly dynamic mechanism will lead to important creep while poor dynamicity involves negligible creep.[52] Interestingly, as the transcarbamoylation is strongly dependent on the temperature and shows little dynamicity at low temperatures, it can be expected that no creep will happen in the operating window of our formulated network. Indeed, thermosets for composite applications are expected to be used at temperatures lower than the glass transition. Therefore, creep experiments (Figure 4d) were conducted at 90 °C, only a few degrees before the alpha transition. The viscous behavior of the CAN was somehow more pronounced than the pristine epoxy with an observable delayed deformation to the applied stress. Interestingly, the strain and recovery were identical to the epoxy one, highlighting no creep sensitivity of the dynamic copolymer up to its glass transition.

Overall, the copolymerization approach through the implementation of dynamic hydroxyurethane implies no alteration of the properties with even some improvement in the epoxy network and is thus attractive to implement CAN in market applications quickly. Additionally, the results in this work were compared to other dynamic chemistries as a function of dynamicity versus properties (see Table S7, Supporting Information). The approach was shown to be competitive regarding relaxation speed and properties while providing easier access to the starting building blocks.

The reprocessability of the dynamic copolymer was therefore assessed. The polymer was thermo-mechanically reprocessed twice and tested by DMA and tensile testing. Homogeneous samples were obtained as shown in **Figure 5a** underlining the ability of the material to be efficiently reprocessed. The recycled sample was dived into THF solvent for 6 weeks (Figure S18), after which no destruction or cleavage of the network was observed highlighting the formation of covalent bonding during the reprocessing. SEM micrograph of the cryogenically-fractured cross-section of the reprocessed hybrid epoxy network (Figure S19, Supporting Information) demonstrates the efficient welding of the material, even at the core of the polymeric network. The thermomechanical behavior was similar between pristine and reprocessed samples. DMA curves (Figure 5c) were comparable after two reprocessing steps with no change in the glass transition, behavior, and glassy modulus. The rubbery modulus was however found to be lower, representing a slight decrease of the crosslinking density, consistent with the mechanical grinding of the polymer that leads to some irreversible damages in the dynamic copolymer[53] (potential breaking of C–C bonds). Moreover, it is important to note the transcarbamoylation between amino-alcohol and hydroxyurethane leads first to a urethane and a pendant vicinal diol. It was shown in section 2.1 that the amine in the networks can catalyze alcohols to some extent, such as forming vicinal diol. In that sense, an equilibrium is formed and no further change in crosslinking density is observed between the first and second recycling steps. However, this slight change in the structure can also explain the partial loss of crosslinking density. As already observed by DMA, the tensile Young's modulus was almost fully

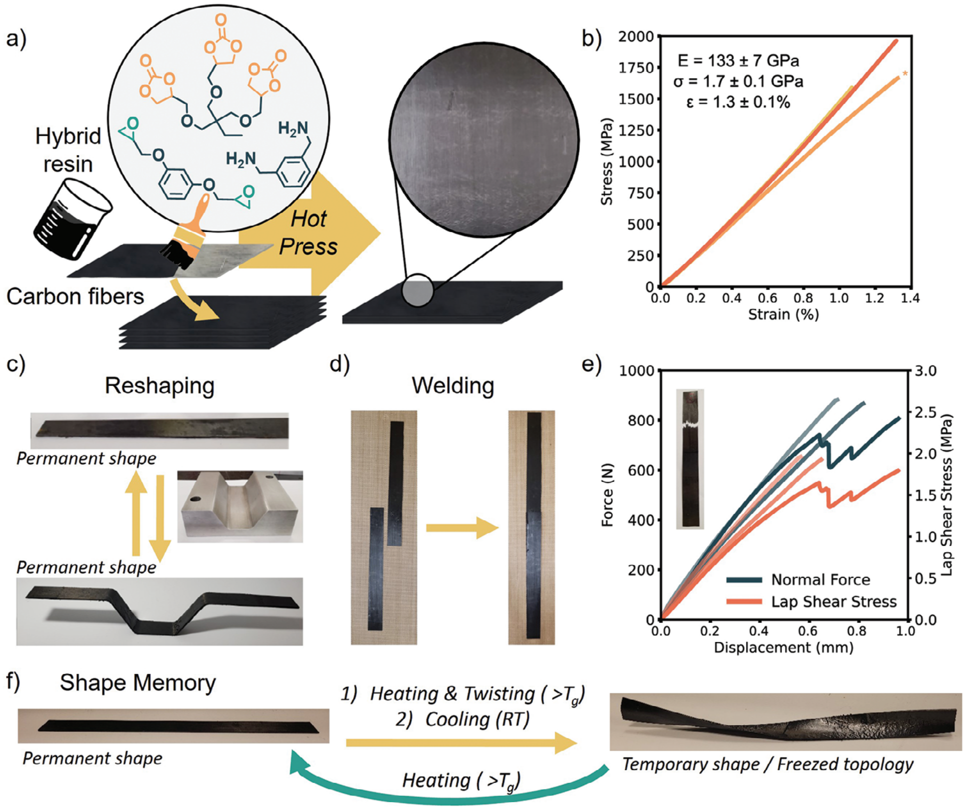

Figure 6. Carbon Fiber Reinforced Vitrimer. a) Schematic representation of the impregnation process, b) Tensile stress-strain curves of the manufactured composites (*sample did not break), c) Reshaping of the carbon composites, d) Welding of single-ply composites, e) Adhesion strength of the welded composites (Inset: representative broken sample), and f) Shape-memory ability of the carbon composite.

recovered with an efficiency of 92% on the first recycling cycle and 100% on the second one. The strain and stress at break were more significantly affected by the recycling process, with a recovery of around 40% (Figure S20, Supporting Information) due to the irreversible damages induced by the mechanical grinding and potential defects linked to the reprocessing and sample preparation methodology. In particular, the recovery of properties for hard, dynamic polymers with high modulus and admissible strength is known to be much less efficient than in the case of elastomeric CANs due to the sensitivity of the material to local defects, lower ductility thus toughness and the high force and energy involved within the materials.[54]

The dynamic copolymer exhibits promising potential for future applications with the ability to be healed, reshaped, and reprocessed. In particular, it opens many doors in the realm of composite manufacturing where welding and reshapability are particularly beneficial.

2.3. Application of Hybrid EP-PHU Polymers in High-Performance Composites: Fabrication, Properties, and Features Provided by the Dynamicity

CANs represent a breakthrough in the composite industry as they allow high-performance materials to be reshaped and welded, impossible with conventional thermosets. Thus, prepregs and semi-finished parts can be manufactured by infusing reinforcement using conventional tooling. Complex shapes and final parts could be later obtained by exploiting the fast exchange mechanism.

In that sense, carbon fiber-reinforced composites were manufactured by thermo-compression using the investigated epoxy CAN. The composite impregnation was possible with high quality as translated through the high fiber volume fraction ($V_f = 63.8 \pm 0.8\%$) and the low porosity content ($V_p = 1.0 \pm 1.0\%$).

The monotonic tensile test assessed the static mechanical performances as shown in **Figure 6**. Extremely high mechanical performance of the carbon fiber reinforced polymer (CFRP) was obtained with 133 GPa in modulus, and 1700 MPa of stress at break. Such outstanding results were ascribed to the successful adhesion of the resin to the fibers.[55] The matrix depicts good compatibility with commercial fibers that incorporate a conventional sizing for epoxy matrix and were used without any further modification. The obtained properties were similar to typical equivalent materials in literature and industry (see benchmark in Figure S26 and Table S8, Supporting Information) showing once again that this simple copolymerization approach is a suitable path to reach industrially and economically relevant dynamic matrices for high-performance materials. In particular, PHUs have shown outstanding adhesion capabilities on many substrates,[56] including natural fibers,[49] that enhances even further the interest of the copolymerization approach to finely tune and improve the interfacial strength of composites.

The (re)shapability is illustrated in Figure 6c, where the already fully cured flat laminate was reshaped in a complex geometry within 30 min at 180 °C. The newly obtained shape was smooth and defect-free with no buckling at the edges or surface that would be indicative of a detrimental delamination. The fibers' orientation was kept. This demonstrates that the system can be extended to new shaping and manufacturing processes such as composite forging. In that sense, an easy-to-store and stable, flat pre-preg composite can be manufactured on a large scale and then shaped and welded into the final part with desired orientations within a few minutes. This would thus open the door to fast high-performance composite manufacturing processes that were up to date inaccessible due to the long time needed to cure epoxy. Additionally, it would lead to the reshaping of end-of-life structures (such as plane wings) to new second-life structures with outstanding performances and limited cost and environmental footprint. Besides, the weldability was investigated (Figure 6d,e) where two single-ply cured sheets were self-welded together by thermocompression thanks to the exchange reaction. This was only possible with the dynamic copolymer formulated where the –OH functions can thus form covalent bonding through the transcarbamoylation mechanism at the interface between the two plies. The adhesive strength was evaluated. Adhesive strength values of about 2 MPa were obtained, in the range of similar material and conventional adhesion of CFRP.[57] Interestingly, the failure did not happen in the welded area but was initiated at the welded edge due to stress concentration and propagated by splitting within the laminates. This illustrates that the welding was strong and efficient and additionally opened the door to cured pre-impregnated laminates, that could be shaped and welded in a fast process. This is of particular interest for the automotive industry, where fast processes are expected and CFRP could help reduce weight and thus energy consumption. In addition to the outstanding properties of the composite material, the dynamic matrices provide the key features to allow the efficient reshaping and welding of semi-finished parts even incorporating a high content of stiff carbon fibers with no apparent damage or structural integrity decrease. Moreover, shape memory behavior can be achieved for other specific applications such as passive actuation (Figure 6f).

2.4. End-of-Life Scenarios and Recyclability

Reshaping and welding of CFRP offers many advantages in the realm of composite structures. However, their end-of-life is a rising concern as more and more structures are reaching the end of their planned service life.

Taking advantage of the thermally activated network, the CFRP was first recycled through a simple thermo-mechanical process (Figure S21, Supporting Information). The chips were cut in parts and then pressed 30 min at 180 °C. The material obtained was tested in three-point bending tests. With a modulus of 3.7 GPa and a maximum stress of 28 MPa, the material displays mechanical properties consistent with random blocks of aligned fibers that lead to an integral material. However, the material properties are quite poor for CFRP due to stress concentration, high fiber volume fraction thus low matrix quantity to be strongly welded, and no control of the fiber orientations. It remains an open door for low-cost fast re-use of existing structures that cannot be obtained with conventional EP-based composites.

More generally, it can be expected that the structures and the composite materials at their end of first service life do not reach a sufficient safety trust level and should be downgraded. If the composite material integrity can be questioned and thus the thermomechanical recycling is not adapted, the carbon fiber could still have sufficient properties for many other applications, including semi-structural and structural ones. Moreover, the cost of carbon fibers and their detrimental environmental footprint make them the most valuable product to recover in composites with a real environmental and economic interest.[35]

In that sense, another option was investigated through chemical recycling. This pathway is more promising as it allows the recovery of the high-value carbon fibers.[58] The CFRP chips were introduced in an 80:20 mixture of (glacial) acetic acid and hydrogen peroxide (30 wt% in water). This solution generates in situ peracetic acid that can cleave the epoxy-amine linkage.[59] The solution with CFRP chips was heated to 60 °C under constant magnetic agitation. The oxidative solution destroyed the polymer integrity within 4 h, and the CFs were simply recovered by filtration, dried, and reused. Starting from 10 g of the CFRP, 6.75 g of carbon fibers were recovered, consistent with the estimated weight fraction (68–70 wt%, from both calculus and TGA analysis), and highlighting no noticeable loss of fibers in the process. The acetic acid mixture was recovered by rotary evaporation and reused for a new recycling batch (Figure S24, Supporting Information). 220 mL of the slightly diluted acetic acid solution were recovered, as already mentioned in previous studies,[59] and unveiled an 85-90% recovery of the solvent.

This way, high-value carbon fibers were retrieved under mild conditions. The recovered fibers were analyzed by SEM (**Figure** 7c), XPS (Figure 7f), TGA (Figure 7e), and FTIR (Figure S22 Supporting Information). The surface of the fibers was clean from any polymer residues as observed by SEM and FTIR, as no characteristic peak of the polymer matrix was observed. Additionally, the sizing agent was removed, which is typical for the chemical recycling of CF.[35] XPS displays the appearance of a new peak located at 288.7 eV revealing the partial oxidation of the carbon fiber surface by the oxidative treatment. The oxygen content at the CF surface increased from 19.9% to 23.8%. Such observations were already addressed by Das et al.[59] This slight oxidation at the carbon fiber surface did not lead to detrimental effects on the fibers, and, overall, the integrity of the fibers was maintained. Further, this local oxidation could be interesting in forming new bonds with amine-based matrices and acts as adhesion promoters for further use.[60] The TGA confirms the similarity between virgin and recycled CF.

To prove the possibility of valorizing such reclaimed CF in new high-added-value applications, the fibers were re-used as a non-woven mat with the dynamic copolymer matrix and tested in three-point bending (Figure 7d). The recycled material exhibits outstanding properties with a modulus close to 50 GPa, a stress at break of almost 500 MPa, and an admissible strain superior to 2.1%. The properties obtained indicate that the reclaimed fibers can be efficiently used for many applications, particularly in transportation as they exhibit properties similar to aluminum with a higher strength-to-weight ratio, promising carbon

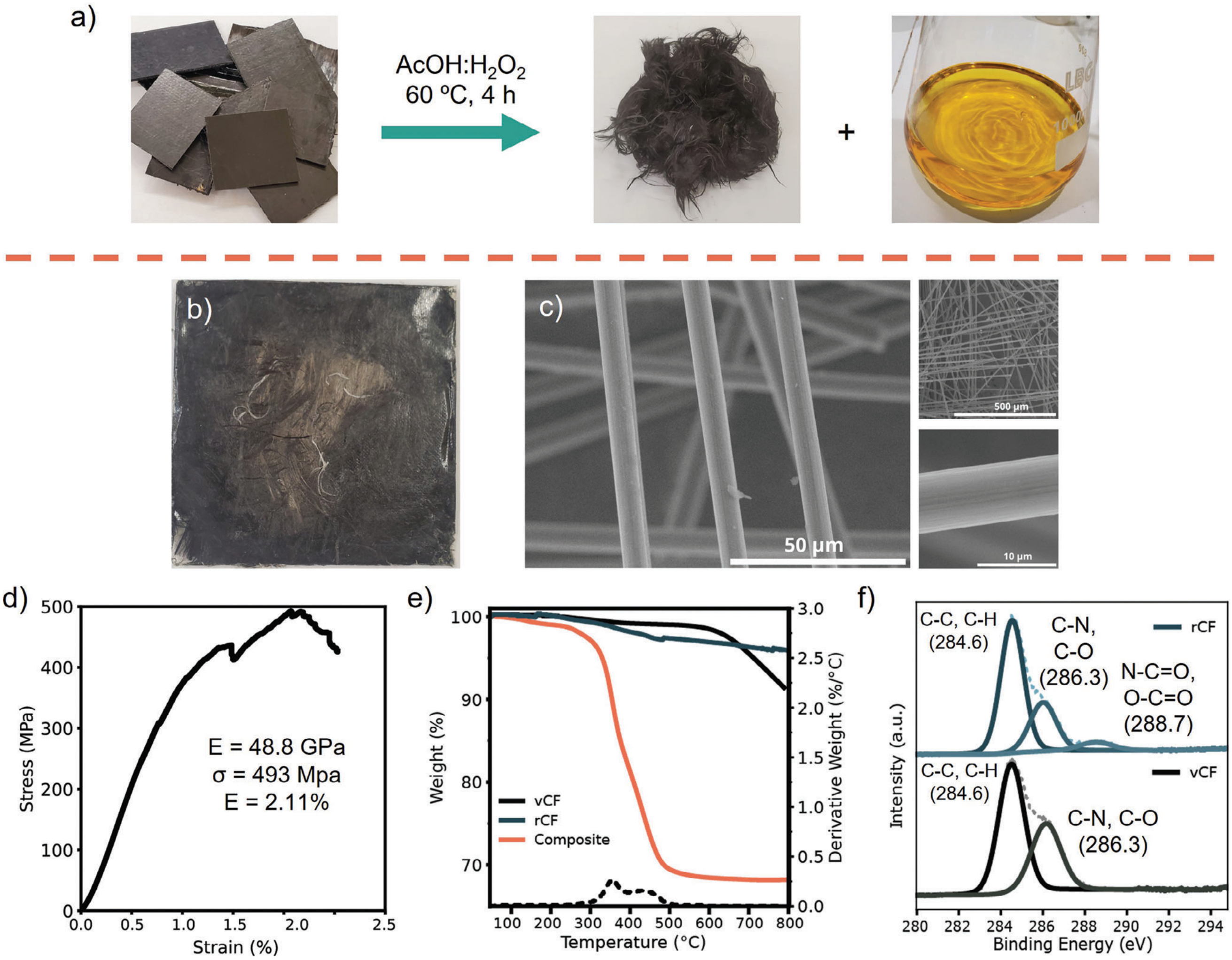

Figure 7. Recycling of CFRP. a) Chemical recycling of the composites by resin oxidation and fiber separation, b) Non-woven carbon composites fabricated from recovered fibers, c) SEM images of the recovered fibers, d) Three-point bending strain-stress curves of the chemically recycled composites, e) TGA of the composite, virgin CF and recovered CF, and f) XPS analyses of the virgin and recovered fibers.

footprint, and low cost. The mild conditions used to recover the fibers are of particular interest as they are economically relevant with low-cost, easily accessible, and recoverable reagents. Thus a new generation of recycled carbon fibers at a competitive price and interesting environmental footprint[61] could join again the market.

Regarding the chemical recyclability of the hybrid EP-PHU vitrimer, it is important to note that the matrix was cleaved in a (mild) oxidative process. Although extremely efficient, this process is not selective and leads to many potential side reactions, and therefore does not conduct a straightforward recovery of chemical building blocks. Previous works have used oxidative processes or other more selective chemical recycling paths.[59,62–64] In most cases, the identification, separation, and purification of valuable building blocks lead to low yield and a highly intensive process that can be questioned in terms of sustainability and industrial scalability. The oxidative process leads to the easy recovery of the high-value carbon fibers but also to the potential loss of the polymeric matrix.

3. Conclusion

A new strategy is proposed to obtain a highly scalable and efficient covalent adaptive network through a synergetic copolymerization approach. Non-dynamic, widely spread thermosets, e.g., epoxy-amine, and a poorly dynamic polyhydroxyurethane network can be used to form a new highly efficient network. The resulting copolymer exhibits a fast catalyst-free adaptive behavior allowing the novel network to be recycled in mild conditions. The synergetic behavior was demonstrated to arise from the amino-alcohol formed by the epoxy-amine reaction while the dynamic hydroxyurethane is obtained from the aminolysis of cyclic carbonates. The copolymer displays high tunability and promising properties, similar or superior to the pristine epoxy. The dynamic copolymer was used to manufacture carbon fiber composites that exhibit strong adhesion at the fiber/matrix interface leading to outstanding mechanical properties suitable for structural applications in conventional carbon composite uses. The cured composite could be easily reshaped from flat plates to complex geometries within half an hour and equally welded. Such scalable and efficient copolymers are extremely promising for transportation applications where large volumes are produced in intensive production lines. Finally, the copolymer can be cleaved in an oxidative process in mild conditions to recover the high-added-value carbon fibers efficiently. The carbon fibers were shown to be only slightly affected by the chemical recovery and were reused for a new composite part with remarkable properties. This innovative copolymerization approach is a promising step toward globally available epoxy-based materials with high performances and closed-loop circularity.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors have filed a provisional patent application based on this technology that names G.S., J.M.R, H.S., N.A., B.G., and C.D. as inventors.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

carbon dioxide, covalent adaptive networks, recyclable composites, recyclable thermosets, structural composites

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[1] B. Krishnakumar, R. P. Sanka, W. H. Binder, V. Parthasarthy, S. Rana, N. Karak, *Chem. Eng. J.* **2020**, *385*, 123820.
[2] J. Zheng, Z. M. Png, S. H. Ng, G. X. Tham, E. Ye, S. S. Goh, X. J. Loh, Z. Li, *Mater. Today* **2021**, *51*, 586.
[3] L. Li, X. Peng, D. Zhu, J. Zhang, P. Xiao, *Macromol. Chem. Phys.* **2023**, 2300224.
[4] R. Du, Z. Xu, C. Zhu, Y. Jiang, H. Yan, H. Wu, O. Vardoulis, Y. Cai, X. Zhu, Z. Bao, Q. Zhang, X. Jia, *Adv. Funct. Mater.* **2020**, *30*, 1907139.
[5] V. Schenk, R. D'Elia, P. Olivier, K. Labastie, M. Destarac, M. Guerre, *ACS Appl. Mater. Interfaces* **2023**, *15*, 46357.
[6] F. I. Altuna, C. E. Hoppe, R. J. Williams, *Eur. Polym. J.* **2019**, *113*, 297.
[7] T. Debsharma, V. Amfilochiou, A. A. Wróblewska, I. De Baere, W. Van Paepegem, F. E. Du Prez, *J. Am. Chem. Soc.* **2022**, *144*, 12280.
[8] W. Wu, H. Feng, L. Xie, A. Zhang, F. Liu, Z. Liu, N. Zheng, T. Xie, *Nat. Sustain.* **2024**, *7*, 1.
[9] P. Taynton, H. Ni, C. Zhu, K. Yu, S. Loob, Y. Jin, H. J. Qi, W. Zhang, *Adv. Mater.* **2016**, *28*, 2904.
[10] W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J. M. Winne, F. E. Du Prez, *Adv. Funct. Mater.* **2015**, *25*, 2451.
[11] L. Pettazzoni, M. Ximenis, F. Leonelli, G. Vozzolo, E. Bodo, F. Elizalde, H. Sardon, *Chem. Sci.* **2024**, *15*, 2359.
[12] M. A. Rahman, M. S. Karunarathna, C. C. Bowland, G. Yang, C. Gainaru, B. Li, S. Kim, V. Chawla, N. Ghezawi, H. M. Meyer, A. K. Naskar, D. Penumadu, A. P. Sokolov, T. Saito, *Cell Reports Physical Science* **2023**, *4*, 101695.
[13] Y. Liu, Z. Tang, D. Wang, S. Wu, B. Guo, *J. Mater. Chem. A* **2019**, *7*, 26867.
[14] Y. Chen, Z. Tang, X. Zhang, Y. Liu, S. Wu, B. Guo, *ACS Appl. Mater. Interfaces* **2018**, *10*, 24224.
[15] Y. Liu, Z. Tang, Y. Chen, C. Zhang, B. Guo, *ACS Appl. Mater. Interfaces* **2018**, *10*, 2992.
[16] L. Anderson, E. W. Sanders, M. G. Unthank, *Mater. Horiz.* **2023**, *10*, 889.
[17] T. Habets, G. Seychal, M. Caliari, J.-M. Raquez, H. Sardon, B. Grignard, C. Detrembleur, *J. Am. Chem. Soc.* **2023**, *145*, 25450.
[18] V. Schenk, K. Labastie, M. Destarac, P. Olivier, M. Guerre, *Mater. Adv.* **2022**, *3*, 8012.
[19] S. Engelen, N. D. Dolinski, C. Chen, E. Ghimire, C. A. Lindberg, A. E. Crolais, N. Nitta, J. M. Winne, S. J. Rowan, F. E. Du Prez, *Angew. Chem.* **2024**, *136*, 9e202318412.
[20] P. Verdugo, D. Santiago, S. De La Flor, A. Serra, *ACS Sustainable Chem. Eng.* **2024**, *12*, 5965.
[21] B. Miranda Campos, G. Fontaine, S. Bourbigot, G. Stoclet, F. Bonnet, *ACS Appl. Polym. Mater* **2022**, *4*, 6797.
[22] X.-Z. Mo, F.-X. Wei, D.-F. Tan, J.-Y. Pang, C.-B. Lan, *J. Polym. Res.* **2020**, *27*, 33.
[23] K. C. Poon, G. L. Gregory, G. S. Sulley, F. Vidal, C. K. Williams, *Adv. Mater.* **2023**, 2302825.
[24] L. Eisoldt, A. Smith, T. Scheibel, *Mater. Today* **2011**, *14*, 80.
[25] K. J. Coyne, X.-X. Qin, J. H. Waite, *Science* **1997**, *277*, 1830.
[26] A. Le Duigou, S. Requile, J. Beaugrand, F. Scarpa, M. Castro, *Smart Mater. Struct.* **2017**, *26*, 125009.
[27] C. Shi, Z.-C. Li, L. Caporaso, L. Cavallo, L. Falivene, E. Y.-X. Chen, *Chem* **2021**, *7*, 670.
[28] L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau, H. Cramail, *Chem. Rev.* **2015**, *115*, 12407.
[29] B. Grignard, S. Gennen, C. Jérôme, A. W. Kleij, C. Detrembleur, *Chem. Soc. Rev.* **2019**, *48*, 4466.
[30] S. Hu, X. Chen, J. M. Torkelson, *ACS Sustainable Chem. Eng.* **2019**, *7*, 10025.
[31] C. Bakkali-Hassani, D. Berne, P. Bron, L. Irusta, H. Sardon, V. Ladmiral, S. Caillol, *Polym. Chem.* **2023**, *14*, 3610.
[32] A. Hernández, H. A. Houck, F. Elizalde, M. Guerre, H. Sardon, F. E. Du Prez, *Eur. Polym. J.* **2022**, *168*, 111100.
[33] JEC Observer: Current trends in the global composites industry 2021-2026, *JEC Group* **2022**.
[34] E. Asmatulu, J. Twomey, M. Overcash, *J. Compos. Mater.* **2014**, *48*, 593.
[35] J. Zhang, V. S. Chevali, H. Wang, C.-H. Wang, *Composites, Part B* **2020**, *193*, 108053.

[36] K. Yap, K. D. Krantzman, R. J. Lavrich, *J. Phys. Chem. A* **2023**, *127*, 7892.
[37] C. Bakkali-Hassani, D. Berne, V. Ladmiral, S. Caillol, *Macromolecules* **2022**, *55*, 7974.
[38] G. Seychal, C. Ocando, L. Bonnaud, J. De Winter, B. Grignard, C. Detrembleur, H. Sardon, N. Aramburu, J.-M. Raquez, *ACS Appl. Polym. Mater* **2023**, *5*, 5567.
[39] F. Ng, G. Couture, C. Philippe, B. Boutevin, S. Caillol, *Molecules* **2017**, *22*, 149.
[40] T. Debsharma, S. Engelen, I. De Baere, W. Van Paepegem, F. D. Prez, *Macromol. Rapid Commun.* **2023**, 2300020.
[41] I. Scodeller, S. Mansouri, D. Morvan, E. Muller, K. De Oliveira Vigier, R. Wischert, F. Jérôme, *Angew. Chem.* **2018**, *130*, 10670.
[42] D. J. Fortman, J. P. Brutman, C. J. Cramer, M. A. Hillmyer, W. R. Dichtel, *J. Am. Chem. Soc.* **2015**, *137*, 14019.
[43] V. Schenk, J. De Calbiac, R. D'Elia, P. Olivier, K. Labastie, M. Destarac, M. Guerre, *ACS Appl. Polym. Mater* **2024**, *6*, 6087.
[44] A. Rekondo, R. Martin, A. Ruiz De Luzuriaga, G. Cabañero, H. J. Grande, I. Odriozola, *Mater. Horiz.* **2014**, *1*, 237.
[45] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* **2011**, *334*, 965.
[46] Y. Zeng, B. Yang, Z. Luo, X. Pan, Z. Ning, *Eur. Polym. J.* **2022**, *181*, 111643.
[47] F. Meng, M. O. Saed, E. M. Terentjev, *Nat. Commun.* **2022**, *13*, 5753.
[48] R. Ghanbaralizadeh, H. Bouhendi, K. Kabiri, M. Vafayan, *J. CO2 Util.* **2016**, *16*, 225.
[49] G. Seychal, P. Nickmilder, V. Lemaur, C. Ocando, B. Grignard, P. Leclère, C. Detrembleur, R. Lazzaroni, H. Sardon, N. Aranburu, J.-M. Raquez, *Composites, Part A* **2024**, *185*, 108311.
[50] H. Perrin, R. Vaudemont, D. Del Frari, P. Verge, L. Puchot, M. Bodaghi, *Composites, Part A* **2024**, *177*, 107899.
[51] A. M. Hubbard, Y. Ren, C. R. Picu, A. Sarvestani, D. Konkolewicz, A. K. Roy, V. Varshney, D. Nepal, *ACS Appl. Polym. Mater* **2022**, *4*, 4254.
[52] F. Van Lijsebetten, K. De Bruycker, Y. Spiesschaert, J. M. Winne, F. E. Du Prez, *Angew. Chem.* **2022**, *134*, 9.
[53] K. Yu, P. Taynton, W. Zhang, M. L. Dunn, H. J. Qi, *RSC Adv.* **2014**, *4*, 10108.
[54] A. Bandegi, T. G. Gray, S. Mitchell, A. Jamei Oskouei, M. K. Sing, J. Kennedy, K. Miller McLoughlin, I. Manas-Zloczower, *Mater. Adv.* **2023**, *4*, 2648.
[55] P. Herrera-Franco, L. Drzal, *Composites* **1992**, *23*, 2.
[56] A. Gomez-Lopez, S. Panchireddy, B. Grignard, I. Calvo, C. Jerome, C. Detrembleur, H. Sardon, *ACS Sustainable Chem. Eng.* **2021**, *9*, 9541.
[57] L. An, X. Li, C. Jin, W. Zhao, Q. Shi, *Composites, Part B* **2022**, *245*, 110224.
[58] T. Liu, L. Shao, B. Zhao, Y. Chang, J. Zhang, *Macromol. Rapid Commun.* **2022**, *43*, 2200538.
[59] M. Das, R. Chacko, S. Varughese, *ACS Sustainable Chem. Eng.* **2018**, *6*, 1564.
[60] Y. Nakayama, F. Soeda, A. Ishitani, *Carbon* **1990**, *28*, 21.
[61] R. A. Witik, R. Teuscher, V. Michaud, C. Ludwig, J.-A. E. Månson, *Composites, Part A* **2013**, *49*, 89.
[62] A. Ahrens, A. Bonde, H. Sun, N. K. Wittig, H. C. D. Hammershøj, G. M. F. Batista, A. Sommerfeldt, S. Frølich, H. Birkedal, T. Skrydstrup, *Nature* **2023**, *617*, 730.
[63] Y. Ma, C. A. Navarro, T. J. Williams, S. R. Nutt, *Polym. Degrad. Stab.* **2020**, *175*, 109125.
[64] P. Xu, J. Li, J. Ding, *Compos. Sci. Technol.* **2013**, *82*, 54.