

# Repairable Woven Carbon Fiber Composites with Full Recyclability Enabled by Malleable Polyimine Networks

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Carbon fiber is a lightweight graphitic material with higher tensile strength than steel and lower density than aluminum.<sup>[1]</sup> Woven and nonwoven carbon fibers can be combined with polymeric binder materials to form high-performance carbon fiber reinforced composites (CFRCs). Although the current cost of CFRCs is comparatively higher than metals, due to their excellent strength-to-weight ratios and durability, they have seen explosive growth in a large number of applications ranging from aerospace to ground transportation to sporting goods.<sup>[2]</sup> With increasing production of CFRCs, the environmental impact of these traditionally nonrecyclable materials and reduction in their material and manufacturing cost are of great concern. Typically epoxy thermosets are used as binders to produce high-performance CFRCs with superior mechanical properties (high strength/stiffness). However, the resulting CFRCs cannot generally be repaired or recycled.<sup>[3]</sup> Recycling of CFRCs (polymer binders as well as carbon fibers) has been the focus of a growing body of research over the last two decades in order to make them more cost effective and sustainable.<sup>[4–6]</sup> Many mechanical, and thermochemical approaches have been applied, mostly with the aim of recovering the valuable carbon fibers, with preservation of fiber length as a key objective. Thus far, researchers have managed to recover epoxy resins as fine powders,<sup>[4,5,7]</sup> downgraded chemical feedstocks, or downgraded thermoplastic materials.<sup>[8]</sup> However, these processes either involve the use of novel synthetic monomers<sup>[8]</sup> or energy-intensive processes (such as use of supercritical solvents), which would be difficult to scale economically.<sup>[9]</sup> The recycling difficulty comes from the irreversible nature of the epoxy thermoset resins in CFRCs.

We envision that repairability and recyclability of CFRCs could be enabled by introduction of dynamic covalent bonds in the binder material. Dynamic covalent chemistry<sup>[10,11]</sup> has been demonstrated as a promising route to recyclable covalent network materials.<sup>[12–15]</sup> Previous work has largely focused on reversible chemical links based on Diels–Alder reaction, which results in a gel-to-sol transition at high temperatures,<sup>[16]</sup> and thus is undesirable for the majority of structural applications. More recently malleable thermosets, also called covalently adaptive networks or vitrimers, have emerged as novel recyclable covalent network materials, which incorporate dynamically exchangeable covalent bonds into the polymer networks.<sup>[17–20]</sup> The rate of bond exchange exhibits an Arrhenius-like temperature dependence, enabling molding, welding, and complete recycling of the pure polymeric materials, while maintaining the crosslink density of the covalently adaptive network.<sup>[17,21,22]</sup> However, the recycling of vitrimers typically requires a mechanical process of abrasive grinding, followed by compression molding of the powdered binder above its vitrimeric transition temperature ( $T_v$ ).<sup>[23]</sup> In a fiber-reinforced composite, such a grinding action would result in complete reduction of fiber length, and thus limit the materials' potential for reuse as cheap composite fillers, rather than a replacement for virgin fibers.

Herein, we describe the preparation of fully recyclable CFRCs from woven carbon fiber sheets and malleable polyimine networks. A closed loop recycling of CFRCs is achieved through dissolution of the polyimine binder via dynamic covalent bond exchange with an excess of a monomer, resulting in the recovery of full-length fiber, as well as complete recovery and reuse of the binder material. The key to our approach is the use of covalently cross-linked yet malleable polyimines, which undergo dynamic covalent bond exchange reactions in response to chemical or physical stimuli, as binder materials. The process reported herein involves minimal energy input (magnetic stirring), and could be easily scaled up.

Our previous study shows that a mechanically resilient polyimine thermoset can be conveniently prepared from combination of diamine, dialdehyde, and triamine cross linkers through imine condensation in the absence of any catalyst.<sup>[24,25]</sup> We have also demonstrated that the reversibility of imine bond formation and temperature-dependent rate of the imine exchange render heat or water-driven malleability of such crosslinked polyimines. In this study, three polyimines with different properties were prepared through simple mixing of commercially available terephthaldehyde (1) and tris(2-aminoethyl)amine (2) (TREN), with various diamines. We chose to use diamines (3, 4, or 5) with different size and functionalities to tune the mechanical properties of the polyimine networks. The preparation of

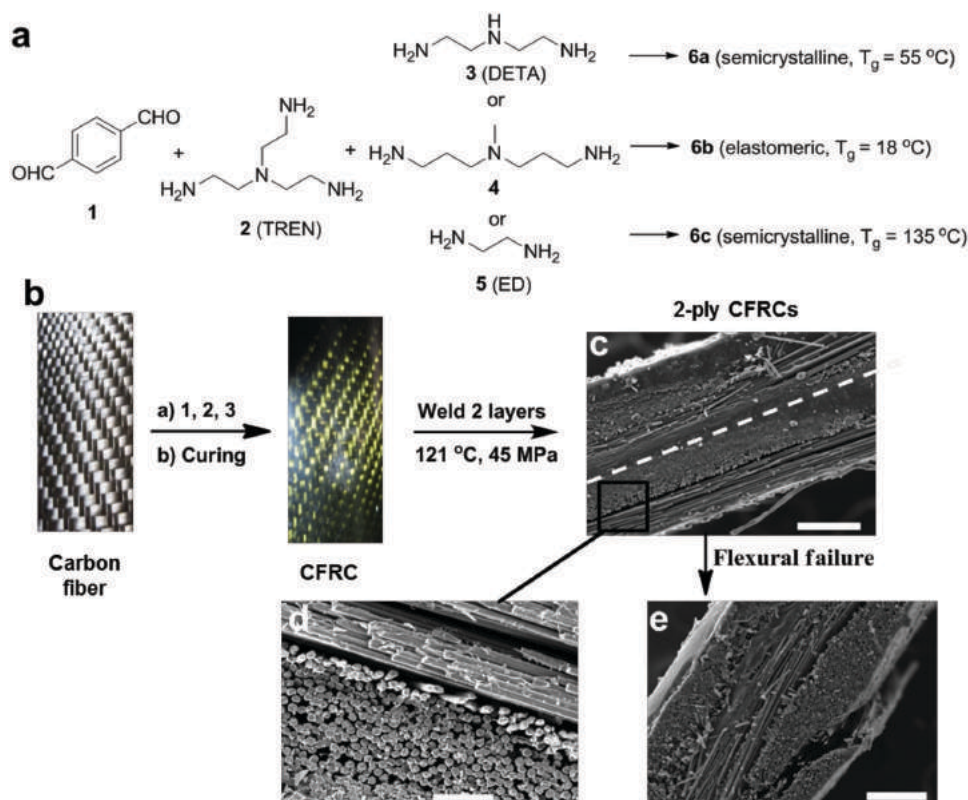
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**Figure 1.** Preparation of CFRCs, and SEM cross-cut images of multilayer devices. a) Synthesis of polyimine malleable thermosets. Different diamine monomers result in polymers with varying thermomechanical properties. b) Process of forming prototypical 1-ply and 2-ply CFRC (35 wt% **6a**) used in this study. c) SEM images of 2-ply CFRC device with a total of four tows of carbon fibers visible (two running in plane, and two tangential to the plane of the page). The white dotted line shows the interface of two layers. Running between the two woven layers is the gray amorphous polyimine binder (**6a**), showing each 1-ply CFRC sheet is perfectly welded into a coherent 2-ply CFRC device, scale bar = 200  $\mu\text{m}$ . d) close-up to show the fiber direction, scale bar = 50  $\mu\text{m}$ . e) 2-Ply CFRC device after flexural failure, scale bar = 200  $\mu\text{m}$ .

polyimines is simple. Compounds **1**, **2**, and **3** (or **4** or **5**) were mixed in ethanol, and all the volatiles were evaporated at room temperature. After curing under heat (removal of water), semicrystalline (**6a** and **6c**) or elastomeric (**6b**) polyimines were obtained (Figure 1a). In the IR spectra of polyimines **6a–c** (Figure S1, Supporting Information), we observed prominent C=N stretch at  $1637\text{ cm}^{-1}$  with the absence of C=O stretch band at  $1687\text{ cm}^{-1}$ , confirming the formation of imine bonds.

Since the diamines **3–5** have different lengths of backbone, they have different freedom of motion and flexibility within the network at a given temperature. When the polyimine has shorter linkers (e.g., **5**), the average flexibility and mobility of polymer chains are reduced, leading to increased crosslinking density and vice versa. As a result, drastically different glass transition temperatures ( $T_g$ ), tensile strength, and elastic modulus were observed for polyimines, **6a–c** (Table 1). The polyimine **6c** consisting of the shortest diamine **5** shows the highest  $T_g$  (145  $^{\circ}\text{C}$ ) and tensile strength ( $\approx 64\text{ MPa}$ ). On the contrary, polyimine **6b** with longest diamine **4** exhibit lowest  $T_g$  of 18  $^{\circ}\text{C}$  and tensile strength  $\approx 10\text{ MPa}$ . The  $T_g$  and tensile strength of polymer **6a** are 56  $^{\circ}\text{C}$  and 40 MPa.<sup>[24]</sup>

In order to investigate the heat-induced malleability of these polyimines, their time- and temperature-dependent relaxation modulus were tested (Figure S4, Supporting Information). Similar to previously reported **6a**,<sup>[24]</sup> the stress relaxations of

both polyimines **6b** and **6c** follow the classic time–temperature superposition (TTSP) behavior, indicating an Arrhenius-like temperature dependence of the bond exchange reactions in these polymers. It has been reported that a huge hydraulic pressure approaching GPa range would notably reduce the chain-free volume and consequently increase the shift factors of TTSP.<sup>[26–28]</sup> However, in our current study, the polyimines are subjected to uniaxial tension with small hydraulic pressure (in MPa range), therefore the impact of the stress on the free volume change of polymer chains as well as the kinetics of imine bond exchange is considered to be negligible.

**Table 1.** Mechanical properties of polyimines and composites.

	Tensile strength [MPa]	Elastic modulus [GPa]	Elongation at break [%]
Polyimine <b>6a</b>	40	1.0	5
Polyimine <b>6b</b>	10	0.13	150
Polyimine <b>6c</b>	64	0.96	22
1-ply CFRC [35 wt% <b>6a</b> ]	399 $\pm$ 85	14.2 $\pm$ 1.1	3.3 $\pm$ 0.6
2-ply CFRC [35 wt% <b>6a</b> ]	309 $\pm$ 57	12.2 $\pm$ 1.7	3.8 $\pm$ 1.2
1-ply CFRC [35 wt% <b>6c</b> ]	148 $\pm$ 7	15.5 $\pm$ 1.4	1.0 $\pm$ 0.04
2-ply CFRC [35 wt% <b>6c</b> ]	198 $\pm$ 9	12.2 $\pm$ 1.5	1.6 $\pm$ 0.1

Although imine linkages are often considered susceptible to cleavage by hydrolysis, the crosslinked polyimines exhibit excellent hydrolytic stability.<sup>[24]</sup> The hard glassy polyimine (**6a**) film swells and becomes flexible when it is immersed in water. Upon saturation (after  $\approx 12$  h), the swelling stays constant. Remarkably, the polymer retains its mechanical integrity even after 1 week under water at 96 °C. <sup>13</sup>C NMR spectroscopy study on the dry and water-saturated samples of polyimine **6a** failed to reveal any quantifiable hydrolysis of imine linkages in the wet samples. To simulate more practical conditions for applications, the mechanical response of polyimine sample to the atmospheric humidity was monitored in a custom built humidity chamber. We observed an incremental softening of the material with increasing atmospheric humidity (up to 90% RH, mechanical properties:  $\approx 12$  MPa, elongation at break 16%). The presence of moisture in the polyimine enables molding and reshaping of such a polymer.<sup>[24]</sup> Upon drying, the wet polyimine is restored to its original condition. The impact of moisture can theoretically be mitigated in hydrophobic polyimine formulations, and such hydrophobic polyimine networks are a focus of ongoing development efforts in our group.

Given the mechanical robustness, malleability and hydrolytic stability, the polyimines have been tested as the binder materials in CFRCs. In order to prepare carbon fiber reinforced polyimine (**6a**) composites, a single layer of twill weave carbon fiber cloth (65 wt%) was introduced to the solution of monomers (3:1.4:0.9 molar ratio of 1, 2, and 3, total 35 wt%). Evaporation of ethanol and curing to remove water under heat provided the polyimine composites (Figure 1 b). The resulting CFRC sheet (35 wt% **6a**)<sup>[29]</sup> exhibits a tensile strength of  $399 \pm 85$  MPa, a Young's modulus of  $14 \pm 1$  GPa, and an elongation at break of 3.3%  $\pm$  0.6% (Table 1, Figure S5, Supporting Information). The tensile strength and modulus are each about double what is reported for self-reinforced polypropylene composites like Milliken's Tegriss material (200 MPa and 6 GPa respectively), or Propex's Curv material (120 MPa and 4 GPa respectively), while the elongation falls between that of Tegriss (5%), and carbon fiber reinforced epoxies (typically  $<1\%$ ).<sup>[30]</sup> The mechanical properties of the polyimine composites directly correlate to the properties of polymer binder and the amount of fiber in the composite. The decrease of the fiber amount to 50 wt% in reinforced polyimine **6a** composite led to lower mechanical performance and excessive binder flow during pressing. On the other hand, the composites made from polyimine network **6c** (35 wt%) exhibit lower tensile strength ( $148 \pm 7$  MPa) and elongation at break ( $1.0\% \pm 0.046\%$ ), but slightly higher Young's modulus ( $15.5 \pm 1.4$  GPa). It should be noted that since the testing temperature of the above mechanical properties is at room temperature, the exchange of dynamic imine bonds can be considered as negligible and thus does not affect the mechanical properties. We did not test the ability of elastomeric polyimine **6b** as binders due to its inferior mechanical properties. Instead, as will be discussed in more detail later, since polyimine **6b** shows malleable flow under low pressures, it was used as adhesive layers between CFRCs to weld multiple CFRC layers and reshape them into a 3D curved shape.

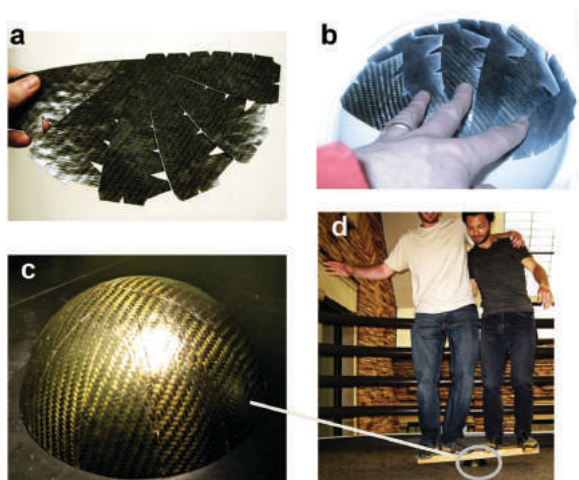
As the dynamic nature of imine bonds in the polyimine networks enables the malleability of such binder materials, we envision that multi-ply CFRCs can be obtained by simply

pressing multiple single layer sheets together. As a proof-of-concept, two layers of the composite sheets containing 35 wt% of **6a** were combined by simple heat pressing at 121 °C under 45 MPa pressure for 60 s. Cross-cut SEM of the 2-ply pressed samples (Figure 1c) reveals that there is no discernible interface in the binder layer sandwiched between the two woven fiber layers, indicating very efficient crosslink exchange across the interface. The mechanical properties of the 2-ply CFRC samples were investigated by three-point flexural testing (Figure S6, Supporting Information), revealing a flexural strength of up to  $255 \pm 56$  MPa, (at  $1\% \pm 0.2\%$  flexural strain) and a flexural modulus of  $32 \pm 3$  GPa. Shorter ( $\approx 30$  s), or longer pressing times (2–5 min), as well as higher temperature led to lower mechanical performance. The initial mechanical analysis of this system reveals that it is at par with commercial composite materials with applications in lightweight structural components and impact-absorbing solutions for vehicles and ballistics protection.<sup>[31]</sup> As mentioned above, we found increasing amount of binder materials in CFRC sheet (50 wt% **6a**) leads to excessive binder flow during pressing and also lower mechanical performance of 2-ply sample (Table S2, Supporting Information).

As the malleability of vitrimers is a function of reaction rate, rather than a melting transition (thermoplastics case), there can be greater flexibility in the processing temperature employed for polyimine-based CFRCs. In catalyst-containing vitrimeric networks, catalyst choice and concentration can greatly affect the  $T_v$  of the materials.<sup>[21]</sup> Alternatively, varying formulation of polyimines can achieve the same end. For example, the use of polyimine network **6c** (35 wt%) as the binder led to composites with a 50 °C higher processing temperature (heat-press welding conditions: 45 MPa, 177 °C, 60 s), compared to CFRC composed of **6a** (35 wt%). The ability to control the processing temperature for a given material represents one great advantage of using malleable polyimine as binders for advanced composite materials targeting various applications.

Commercial epoxy polymers typically require a heated curing step, which is critical to forming the permanent tough covalent network. However, such step significantly slows production cycle times. The heated welding of malleable polyimine composites described above could be disruptive to traditional notions of thermoset curing. Essentially the curing step is eliminated, as the polyimine CFRC sheets are cured prior to forming multilayer devices from the single layer sheets. Because of this, the multilayer CFRCs were formed in  $\approx 1$  min, which is the target cycle time for widespread adoption of carbon fiber reinforced composite materials in the automotive industry.

In addition to the ability to weld multiple layers of CFRCs, the fully cured malleable polyimine binder can also enable reshaping and remolding of the flat woven composite sheet into 3D curved shapes. For the purpose of demonstrating the moldable nature of the composite material, a dome shape was constructed from flat woven polyimine CFRC sheets. First, 1-ply CFRC sheet composed of 50 wt% **6a** was cut into a pattern to enable overlapping reinforcements. Multiple layers were combined and pressed in a hot (110 °C) porcelain mold. A vacuum bagging process was used. However, we found vacuum bagging, which only provides a maximum pressure of 1 atm ( $<0.1$  MPa), is unable to supply sufficient pressure for welding of the CFRCs containing 50 wt% **6a**. Therefore, a  $\approx 0.5$  mm



**Figure 2.** Molding of the CFRC sheet stock. a) Flat 1-ply CFRC (50 wt% **6a**) sheet was cut into pattern. b) The pre-cut CFRC pieces from (a) were pressed into hot (110 °C) porcelain mold via vacuum molding. The process was repeated to form a hemisphere which is three-layer thick. Polyimine **6b** was used as an adhesive interlayer between each layer of 1-ply CFRC. d) Molded sample from Figure (c) is loaded with  $\approx 150$  kg.

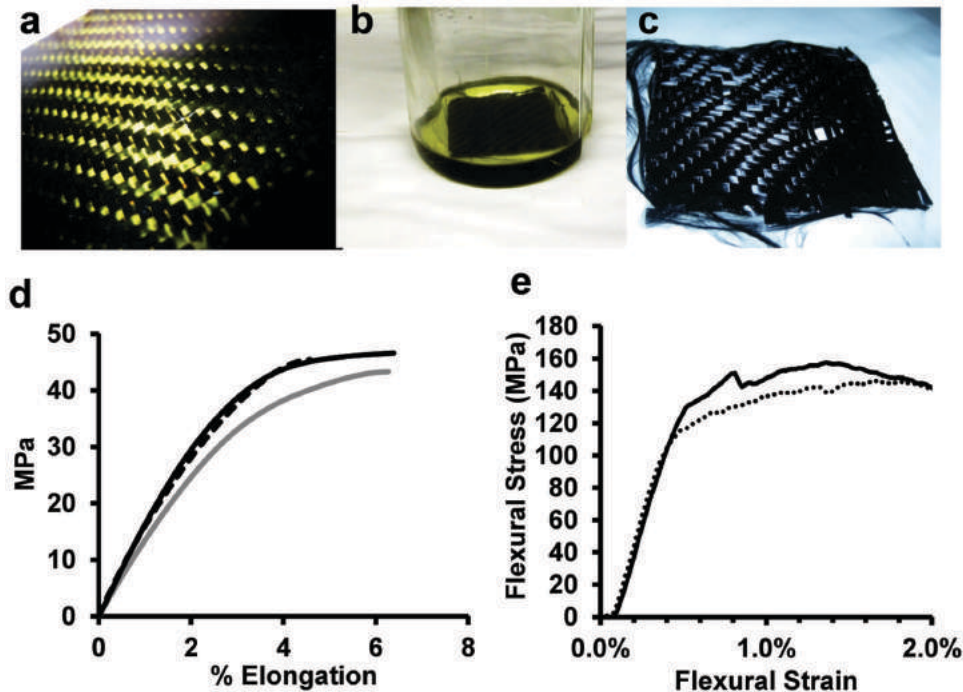
thick film of elastomeric (up to 180% elongation at break) polyimine **6b** was added as an adhesive interlayer between each of 1-ply CFRC (50 wt% **6a**) sheets, leading to successful welding of a dome shape using a hot porcelain mold and vacuum bag. **Figure 2** shows the process as well as the resulting 3-ply CFRCs (three 1-ply CFRC sheets plus 2 elastomeric interlayers) with hemispherical structure which exhibits smooth 3D curvature and is strong enough to bear the weight of two adults ( $\approx 150$  kg, **Figure 2d**). Three-point flexural testing showed that the 2-ply CFRCs formed using such an elastomeric interlayer have a flexural strength of  $95 \pm 11$  MPa, and modulus of  $7.3 \pm 0.5$  GPa (**Figure S9**, Supporting Information). It should be noted that significantly higher flexural strength and modulus could be achieved when the CFRC sheets are welded directly at higher pressures. The demonstrated moldable nature of the CFRCs containing the polyimine binder and their effective welding conditions suggest that industrial compression molding of multilayer CFRCs into complex curved shapes is possible with short cycle times, on the order of 1 min.

We then explored the recyclability of such carbon fiber reinforced polyimines. Within a polyimine network with near-perfect stoichiometric balance among aldehyde and amine units, bond exchange reactions enable stress relaxation of the material, leading to their malleable character. We found that this stoichiometric balance can be upset by introducing an excess of free primary amine groups (e.g., excess diamine monomer). Transimination reactions among the excess diamine monomers and the imine-linked network can lead to increased end groups within the matrix, thus reducing the molecular weight and solubilizing the network. We envisioned that such a depolymerization mechanism could enable efficient recycling of CFRCs. To our great delight, simple immersion of CFRC samples in neat diethylenetriamine (DETA) (**3**) led to complete dissolution of the polyimine binder (**6a**). The depolymerization of polyimine **6a** was monitored by  $^1\text{H}$  NMR spectroscopy (**Figure S10**, Supporting Information). Upon the addition

of amine **3** to the suspension of polyimine **6a** in deuterated methanol, we observed the gradual increase of imine proton resonance intensity in the  $^1\text{H}$  NMR spectra of the mixture, indicating depolymerization of polyimine **6a** to form soluble oligomers. The loose carbon fiber material was then recovered by decanting and rinsing away the remaining binder residues with ethanol. As shown in **Figure 3c**, in addition to preserving the fiber length, it is possible to preserve the weave of woven carbon fiber. Thus dissolving in neat monomer enables 100% of the polyimine CFRC material to be recovered and recycled without consuming chemicals or energy. We also found that less DETA was required to dissolve the polyimine binder when ethanol was used as a cosolvent. The solution was stirred in a screw-cap bottle following a quick flush of nitrogen gas. The ethanol-containing recycled solution was directly combined with the solution of complementary terephthalaldehyde (**1**) and TREN (**2**) in ethanol to prepare recycled polymeric materials (**6a**) containing  $>33\%$  material from the recycled monomer solution ( $>21\%$  from the original CFRC). The recycled binder (**6a**) shows no loss of mechanical performance compared to the freshly prepared binder of the same formulation, as shown in **Figure 3d**. It should be noted that simple amines such as *n*-propyl amine can also be used to dissolve CFRCs and recover pristine carbon fibers.

In addition to the difficulty in recycling of traditional CFRCs, it is a challenge to repair them. Often, composite parts have to be completely replaced when damaged as they cannot be adequately repaired. In our three-point flexural testing, the failure mode was delamination between the binder and fiber materials (**Figure 1e**). We found that by repeating the heat pressing of the broken test samples, greater than 100% recovery of mechanical performance can be achieved (**Figure 3e**). This represents a convenient mechanism for repairing damaged composite materials. Depending on the initial welding and subsequent healing conditions, the recovery of both flexural strength and modulus ranged from 85% to 107% (**Figure S11**, Supporting Information). Broken tensile samples could not be repaired as efficiently as broken flexural samples, since binder flow cannot heal the broken fibers (**Figure S12**, Supporting Information). Such permanent damage in the composite system inevitably reduces the mechanical properties of healed samples.

In summary, we have demonstrated that the use of malleable polyimine networks as the binder component of woven carbon fiber composites enables an efficient closed-loop recycling process, in which all of the fiber and binder materials are recovered and can be directly reused. Further, the malleable nature of the binder enables moldability and weldability of woven carbon fiber composite materials. We have demonstrated that fully cured flat CFRC sheets can be molded into shapes with 3D curvature, and that multilayer devices can be built up through a simple heat-pressing process which results in perfect welding of the binder across the interface. Delamination damage can be perfectly repaired through simple heat-pressing. The use of malleable polyimines as binders in CFRCs is possibly the greenest potential approach to truly recyclable composites. Further, malleable polyimine composites enable easy repair, and can remove the time-consuming curing step from manufacture of discrete parts.



**Figure 3.** Composite recycling and repairing. a) Pristine 1-ply CFRC (50 wt% **6a**) sheet. b) 1-Ply CFRC (50 wt% **6a**) immersed in neat DETA for  $\approx 24$  h. The yellow color comes from dissolved polyimine oligomers. c) Woven carbon fiber material removed from DETA bath. d) Tensile testing of polyimine films: pristine polyimine (**6a**) film (dotted line), polyimine film prepared from recycled solution of neat DETA process (gray line), polyimine film prepared from recycled solution of DETA/ethanol process (black line). e) Repairing CFRCs: flexural stress vs. flexural strain of pristine 2-ply CFRC (35 wt% **6a**) device (dotted line), and the same broken sample after subsequent heat-press (solid line).

## Supporting Information

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

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