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Catalytic, aerobic depolymerization of epoxy thermoset composites†

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We present catalytic, aerobic conditions for depolymerizing amine-linked epoxy thermoset matrix polymers commonly used in high-performance carbon fiber-reinforced polymer (CFRP) materials. Unlike other recycling methods, this process preserves the fibers aligned and woven in the same pattern as the parent material and returns valuable materials from the thermoset matrix.

Carbon fiber-reinforced polymers (CFRPs) are composite materials composed of long, continuous strands of highly engineered carbon fibers (CFs) embedded within a thermoset polymer matrix. These materials have superior strength-to-weight ratios and longer service lives than conventional structural metals.¹ FRPs are thus widely used in aircraft, wind turbine blades, and recreational equipment, with global consumption exceeding 128.5 kilotons in 2018.² The irreversible curing process of the amine-linked epoxy thermoset matrices prevents component separation or recycling *via* heating or remolding, as is possible with some thermoplastics. Currently, there is no effective recycling method for end-of-life CFRP waste, nor is there a means of recycling the *ca.* 30% of material discarded as scrap during manufacturing of many CFRP composite products.³ Landfilling is widespread practice.

A small fraction of CFRP waste is recycled, generally by pyrolysis or solvolysis, although reports of chemical depolymerization are beginning to appear.⁴ Pyrolysis downcycles composites by heating to temperatures up to 700 °C, thus destroying the matrix and leaving low value, disordered, short

fiber mats. Solvolysis methods aim to dissolve the thermoset matrix, which becomes plausible only at or near supercritical conditions. In some limited cases, this leaves CFs for collection and repurposing, although typically with damage to the physical properties of the fibers. Chemical depolymerization methods attempt to disassemble the matrix into constituent monomers for re-use, freeing the CFs for subsequent reprocessing with little downcycling, if any. Of these methods, both pyrolysis and solvolysis are energetically demanding, eliminate the value of the matrix, and downcycle the CFs, thus limiting the value of the recyclates and capping (or eliminating) the value available to support the cost of remanufacturing the material. Chemical depolymerization can preserve ordered, long CF materials if mild conditions can be realized for the breadth of chemical motifs that pervade the CFRP matrix systems in commercial use.

Alternative strategies to improve CFRP recyclability utilize resins containing reversible, dynamic covalent bond exchange processes such as vitrimers or covalent adaptable networks. This allows them to act as conventional thermosets under normal operating conditions, but may be reprocessed like a thermoplastic when exposed to a stress, like heat, for extended periods of time.⁵ Though clever and beneficial, these composites cannot be used for high-performance applications, so there is still a large need to recycle matrices found in current composites.

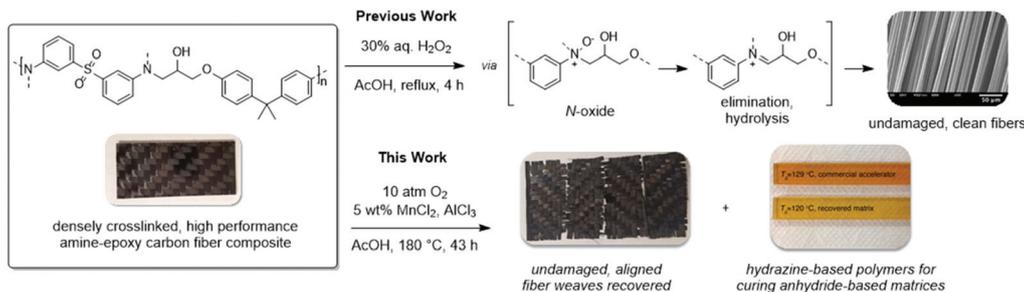
Strategies for chemical depolymerization of CFRPs commonly rely on strongly acidic, basic, or oxidative conditions to cleave the matrix.^{1,4} With few molecular-level studies known for these reactions, our group determined a mechanism for peroxide-mediated decomposition of epoxy-based CFRPs (Scheme 1, top).⁶ We found that peroxide utilizes the very C–N bond that is the basis of the thermoset polymerization reaction as the target for attack, initially by a fast oxidation of the nitrogen, then through a slower, catalytic solvolysis of the polymer. CFs recovered from the reaction appeared undamaged by the oxidative and acidic conditions of the process, although the polymer matrix was destroyed in the reaction. The latter is a

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Scheme 1 Reaction conditions and results of (top) our previously reported recycling process and (bottom) our new aerobic depolymerization process.

common feature of all methods that we have encountered for recovery of CFs from amine-linked epoxy composites.

We report here the first aerobic, catalytic process to depolymerize epoxy CFRP materials that enables both recovery of ordered CF and matrix materials (Scheme 1, bottom). The new method uses catalytic aerobic oxidation to replace the peroxide of the prior system, thus both obviating the challenges of hydrogen peroxide and supercritical solvent, while simultaneously reducing the oxidative potential of the system such that matrix recycle materials can be collected. The mild nature of the reaction balances the need to intercalate reagents and catalysts into very rigid CFRP materials (glass transition temperature, $T_g > ca.$ 180 °C) while simultaneously preserving the integrity, continuity, and order of the carbon fibers. It is moreover the first method we know that enables recovery of woven fiber materials intact and preserves value from amine-linked epoxy thermoset polymers.

Our survey of literature methods for cleavage of amine-linked epoxy thermosets revealed that most involve oxygen, frequently added inadvertently, which we inferred was likely accessing a mechanism analogous what we found for hydrogen peroxide.^{7–9} With that insight, we set about to design a process based on catalytic aerobic oxidation. Discovery of our process commenced with identification of MnCl₂ and AlCl₃, respectively as catalysts for the process's oxidative and solvolytic steps. We identified these by screening catalysts against aerobic demethylation of a small molecule matrix analog, tetra-*N*-methyl-3,3'-diaminodiphenylsulfone (**1**). With some experimentation, we found that superior results were obtained with manganese and ruthenium among various chloride salts of Fe, Mn, Cu, Co, and Ru that we screened as possible oxidation catalysts. Table 1 shows representative rates of aerobic dealkylation of our model compound in the presence of air and AlCl₃ with these metal salts. Addition of salen or phenanthroline did not significantly improve performance, *vide infra*. Two Lewis acids were identified in our prior studies for solvolysis of oxidized polymer,⁶ ScCl₃ and AlCl₃, and either sufficed to degrade the model compound within 17 h in presence of MnCl₂ or RuCl₃. MnCl₂ and AlCl₃ were selected for further study due to their low cost and toxicity, and because they are naturally abundant.

NMR data collected from degradation of **1** (¹H and COSY) showed no signals related to iminic CH₂ protons when the

Table 1 Summary of catalyst screening for small molecule demethylation (conversion calculated by ¹H NMR)

10 mol% cat.
 10 mol% AlCl₃
 AcOH, open vial
 50 °C, 17 h → products

Catalyst	Conversion (%)
FeCl ₂	35%
MnCl ₂	88%
RuCl ₃	88%
CuCl	78%
CoCl ₂	87%

reaction was conducted with O₂/MnCl₂ in place of peroxide. This suggests that aerobic degradation proceeds through a somewhat different path than was observed with hydrogen peroxide. While this mechanism remains unknown, control reactions on the aerobic conditions show that both catalysts are essential. A trial conducted without manganese in presence of air shows slow color change from clear to brown, which is slowed when the headspace is flushed with an inert gas, indicating **1** is prone to aerobic oxidation, but in the absence of either catalyst, no cleavage of the molecule is observed.

To observe whether data collected from our small molecule model reactions translates to thermoset polymer degradation, we prepared fiber-free matrix blocks from 3,3'-diaminodiphenylsulfone (3,3'-DDS, **2**), a bi-directional amine curing agent composed of two anilines joined by a sulfone in the *meta*-position, and the diglycidyl ether of bisphenol A (DGEBA, **3**), a bi-directional epoxy based on bisphenol A, which are common monomers used in the manufacture of aerospace pre-impregnated (pre-preg) fiber fabrics (see ESI† for structure). The monomers were blended in a 2 : 5 ratio, which gives a lightly crosslinked solid thermoset material with a T_g of 51 °C (see ESI† for preparative details).

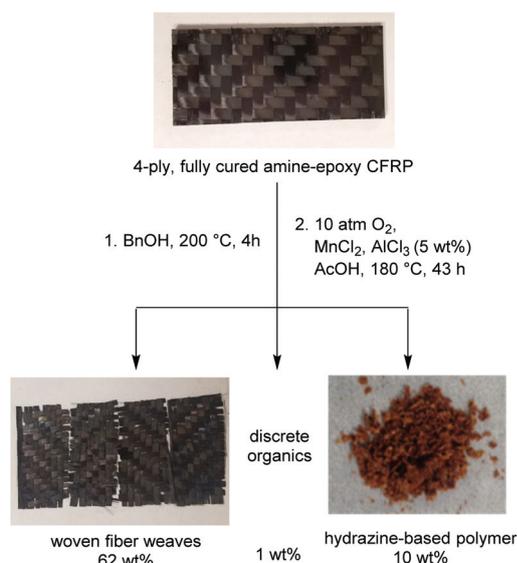
Upon attempting to disassemble these neat polymer samples, we found that a pre-treatment step with an appropriate solvent is essential to labializing the polymer. Thus, these blocks were pre-treated in benzyl alcohol at 110 °C for 4 h before catalysts were applied. This is known to weaken the

adhesion between plies of CFRP materials and introduce sites for reagents to intercalate.¹⁰ In fact, we have observed that metal salt transport through CFRPs seems to be facilitated by the channels of the fibers and inhibited by continuous polymer layers,¹¹ even in a system with no pre-treatment step. In the present case, polymer degradation reactions in acetic acid did not degrade the matrix, even at reaction temperatures above its T_g , without benzyl alcohol pre-treatment.

Once pre-treated, matrix block samples were homogenized overnight using $MnCl_2$ and either $ScCl_3$ or $AlCl_3$, with a continuous stream of air at reflux. While we examined ligated species, e.g. $Mn(phen)_2Cl_2$,¹² these did not enable reaction. Whilst this was effective with our small molecule model, we conclude that metal salts intercalate the swollen matrix sufficiently for reaction, but coordination complexes do not. Both catalysts are required: when either the oxidation or solvolysis catalyst is absent, just over half of the sample was degraded. This is difficult to quantify whereas solvent swelling cannot easily be separated from polymer homogenization. As expected, control experiments without oxygen supply failed to degrade the material.

We demonstrated our overall process by manufacturing 4-ply, fully crosslinked amine-epoxy composite panels of size 40 mm × 17 mm by curing 2 and 3 to a final T_g of 160 °C (1 : 3 weight ratio, see ESI† for preparative details). We chose to begin with panels prepared in-house, because the polymer structures of existing commercial materials are proprietary, and we wanted to be sure of the structure of our panels in the experiment.

Our fully cured composite panels, like those found in end-of-life CFRP waste, have higher T_g s than our neat polymer materials, thus making reagent and catalyst intercalation more challenging with the composite panels. To mitigate this, we



Scheme 2 Reaction conditions and products of the aerobic digestion of a fully cured amine-epoxy carbon fiber composite. Recovered mass of recyclates are relative to the weight of the initial composite sample.

begin our process (Scheme 2) by swelling the panels in benzyl alcohol for 4 h at 200 °C, thus converting the rigid matrix to a pliable consistency. After pre-treatment in benzyl alcohol, applying 10 atm of O₂ at 180 °C in acetic acid with $MnCl_2$ and $AlCl_3$ for 43 h fully removes the matrix, leaving behind clean, woven fibers. The resulting solution can be neutralized to yield a brown precipitate. See ESI† for procedural details.

The overall mass balance of recovered recyclates is very good. Typical commercial aerospace CFRP pre-preg materials have ca. 65–70 wt% carbon fibers. In our model system, we recover 62% of the mass of our composite as the woven fiber sheets, which represents quantitative recovery of the fibers. An additional 11 wt% of the overall composite is recovered as organic materials that are products of the thermoset matrix (*vide infra*), giving an overall 73% minimal mass efficiency for the process. The remaining mass comprises small molecules in the digest solution. We are currently optimizing our process to reclaim a higher portion of these organics.

Analysis of the virgin and recycled fibers *via* Raman spectroscopy revealed minor shifts of the D and G band of less than 4 wavenumbers and a small increase of the intensity ratio R (I_D/I_G), indicating little modification to the graphitic structure of the fibers (Fig. S7 and Table S1†). The recovered carbon fiber fabric weaves are also largely clean of polymer residues and represent a new class of recycled CF (Fig. 1). Unlike other reclaimed CF materials whose fiber lengths are difficult to control,¹³ our fiber length is generally preserved, preventing its conversion into lower-value random short-fiber mats as are recovered from pyrolysis processes.¹⁴ The fibers remain woven in their original architecture, which has very high value as CF weaving during manufacturing is an energy-intensive process.¹⁵ We are not aware of other methods for CFRP degradation that preserve the order of the imbedded CF fabric.

As mentioned above, materials from both DDS and bisphenol A can be recovered from the polymer digest solutions (Scheme 3). Upon neutralization of the crude digest solution, a brown precipitate is obtained. Combustion analysis data show that this comprises the DDS monomer from the original polymer matrix (Found: C, 60.99; H, 5.87; N, 1.54; S, 1.55). This is best characterized as an oxidation polymer of DDS formed *in situ* with the degradation of the original thermoset.¹⁶ Metal catalysts are known to affect this manner of aerobic coupling of anilines to form new N–N and N=N bonds,^{17–19} which appears to be the case here. The structure

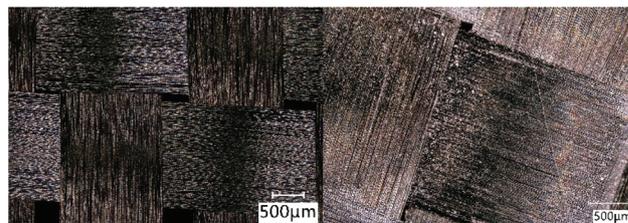
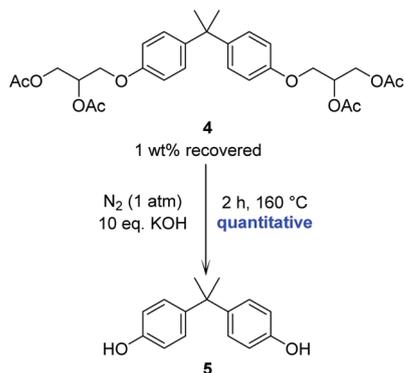


Fig. 1 Microscope imaging of (left) virgin carbon fiber weaves and (right) recycled fiber weaves recovered from the recycling reaction. Small amounts of residue are present near the weave sites.



Scheme 3 Conversion of recovered organics into commercial chemical bisphenol A through a facile one-step reaction with quantitative yields. Recovered mass of recyclates are relative to the weight of the initial composite sample.

can be confirmed by Raman and combustion analyses, particularly by a 2 : 1 ratio of nitrogen-to-sulfur in the latter. We have previously characterized this material from peroxide oxidation of analogous materials, and we have showed its unique utility as an accelerator for curing anhydride-based resins used in applications such as automotive manufacturing.¹⁶ Thus, our recovered DDS material can be upcycled into new composite materials through this path. The neutralized digestion solution from aerobic degradation contains the derivatized monomer recovered from bisphenol A, which is isolated as its bis(diacylglyceryl) ether (4). This material can be converted quantitatively to bisphenol A (5) by a neat reaction with KOH at 150 °C.

Composite product manufacturing is a characteristically inefficient process, with as much as 30% of pre-preg sheets being lost as cutting scrap.²⁰ This scrap is typically landfilled, much like end-of-life CFRPs, even though it is not fully cured. Such materials cure slowly at ambient temperature, so this waste stream represents a chemically analogous problem to that of recycling end-of-life CFRPs, but with a much lower T_g point. Thus, we applied our recycling process to partially cured pre-preg scrap. Three samples of 1-ply commercial pre-preg (Cytec 5320-1/8HS) were partially cured to varying degrees, representing different cure stages seen in pre-preg scrap waste streams. We find that a simple DMSO wash is sufficient to recover clean CF tows from ambient temperature-aged pre-pregs (Fig. 2a). The same conditions remove most of the matrix from partially cured pre-pregs of $T_g = 50$ °C (Fig. 2b). Treating these partially cleaned fibers with MnCl₂/AlCl₃ conditions in refluxing acetic acid with an air sparger (ambient pressure) gave clean fibers after one week (Fig. 2c). These data show us that our method can be applied to a commercial aerospace pre-preg, even at ambient O₂ pressure.

Lowering the high energy intensity of CFRPs is a significant challenge facing its expanded use as a structural material. To understand the viability of our proposed chemical upcycling process, we estimated life-cycle primary energy use and compared it against the primary energy use of landfilling and pyrolysis end-of-life pathways. We assumed landfilling recovers negli-

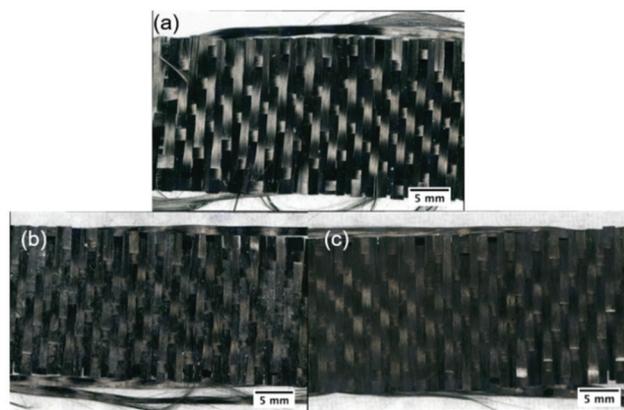


Fig. 2 Recovered fibers after 24 h DMSO wash from (a) room temperature aged pre-pregs, (b) 110 °C cured pre-pregs, with visible matrix residues, (c) 110 °C cured pre-pregs from (b) treated with aerobic conditions after 1 week, removing residual matrix.

gible energy from the CFRP, while pyrolysis incurs a 10% energy penalty of manufacturing virgin CF to recover 82% of the CF as short, disordered fibers which can be recycled only once through this pathway due to degradation.²¹ While it is unclear to what extent these recycled CF will displace virgin, we assume a 50% offset from this recycling pathway. Chemically recycling CFRPs requires an estimated 20% energy intensity of manufacturing virgin CF and resin to recover 100% of the CF as sheets, offsetting 60% of virgin CF and 29% of virgin resin. As the fibers are recovered still woven rather than disordered fibers, we adjusted the energy intensity of compression molding by subtracting the energy intensity of sheet molding.

The results of this study are summarized in Fig. 3 (see ESI† for more detail). A single loop pyrolysis pathway lowers the

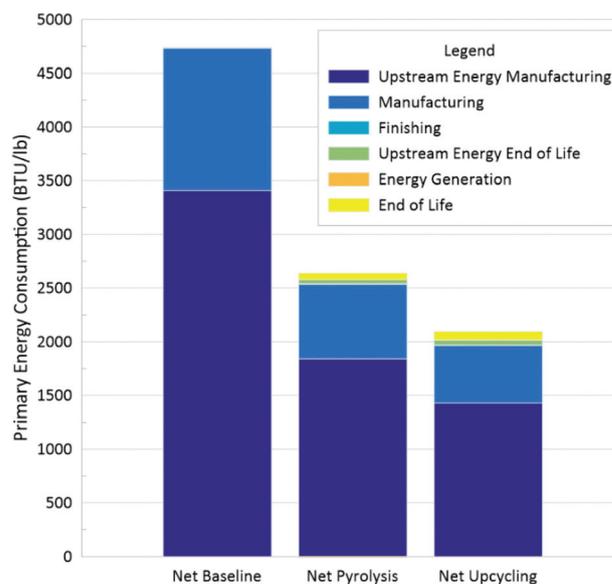


Fig. 3 Primary energy analysis comparing the baseline CFRP life cycle representing landfilling to two alternative CFRP life cycles.

total embodied energy of CFRP by 45%, while cutting the CFRP manufacturing process energy use by 54% due to reduced virgin material production. The pyrolysis process also adds a 4% energy penalty to the total manufacturing process that uses a mix of virgin and recycled fibers. In comparison, single loop chemical recycling lowers the embodied energy of CFRP by 56% at 2097 MJ kg⁻¹, 20% lower than that of pyrolysis. This chemical upcycling adds a 6% energy penalty to the total manufacturing process which uses a mix of virgin and recycled CF sheets with resin. It is worth noting these values detail a single recycling loop. This represents the theoretical limit for once-through pyrolysis, but as the detailed chemical recycling process preserves the native architecture of the CF sheet, it realistically may proceed through several recycling loops and provide greater energy reductions than what was estimated here.

In sum, we report the first catalytic, aerobic conditions for depolymerization of amine-linked epoxy thermoset matrix polymers found in high-performance CFRPs. Simple metal salts, MnCl₂ and AlCl₃, catalyze the matrix oxidation and solvolysis, respectively, ultimately cleaving the crosslinking C–N bonds, leaving undamaged CF sheets. Unlike more forcing conditions for CFRP degradation, this approach enables collection of organic materials from the polymer matrix, which are suitable for further upcycling. This technology has valuable applications in reducing the accumulating waste from pre-preg scrap and end-of-life CFRPs and providing significant energy savings by providing a valuable recycled fiber source to replace virgin CF manufacturing.

Conflicts of interest

Navarro and Williams are founders of Closed Composites LLC, a start-up aiming to commercialize the described recycling process.

Acknowledgements

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