Catalytic, Aerobic Depolymerization of Epoxy Thermoset Composites

Carlos A. Navarro,[a] Yijia Ma,[b] Katelyn Michael,[a] Hanna Breunig,[c] Steven R. Nutt,[b] and Travis J. Williams*[a]

[a.] Loker Hydrocarbon Research Institute, Department of Chemistry
University of Southern California 837 Bloom Walk, Los Angeles, California, 90089-1661, USA. E-mail: travisw@usc.edu
[b.] MC Gill Composites Center, Mork Family Department of Chemical Engineering and Materials Science. University of Southern California, 3651 Watt Way, Los Angeles, California, 90089
[c.] Sustainable Energy Systems Group, Energy Analysis and Environmental Impacts Division
Lawrence Berkeley National Lab, 1 Cyclotron Road, 90-2012, Berkeley CA 94720

Abstract: 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.

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# Experimental Procedures

All NMR spectra were acquired on a Varian VNMRS 500 or 600 spectrometer and processed using MestreNova. All chemical shifts are reported in units of ppm and referenced to the residual ^{1}H or ^{13}C solvent peak and line-listed according to (s) singlet, (d) doublet, (t) triplet, (dd) double doublet, etc. High pressure degradations of composite panels were performed within a Series 4750 General Purpose 125 mL reactor from the Parr Instrument Company. GC/MS data was acquired on an Agilent 5973/HP 6900 instrument. Raman data was acquired on a Horiba Raman Infrared Microscope. Moderated differential scanning calorimetry experiments for characterizing glass transition temperatures were performed on a TA Instruments Q2000. Chloroform-d was purchased from Cambridge Isotopes Laboratories and used without further purification. All solvents and catalysts were purchased from commercial sources and used without further purification: bisphenol A diglycidyl ether (Huntsman), 3,3'-diaminodiphenyl sulfone (Huntsman), nitrogen gas (Airgas), oxygen gas (Airgas), hexanes (EMD Millipore), ethyl acetate (EMD Millipore), dichloromethane (EMD Millipore), benzyl alcohol (J.T. Baker), acetic acid (Macron), paraformaldehyde (EMD Millipore),sodium cyanoborohydride (Beantown Chemical), potassium hydroxide (EMD Millipore), methanol (EMD Millipore), $FeCl_2$ (Beantown Chemical), $RuCl_3$ (Strem), $MnCl_2$ (Acros Organics), CuCl (Aldrich),$CoCl_2$ (EMD Millipore), $AlCl_3$ (Beantown Chemical), and $ScCl_3$ (Alfa Aesar). Carbon fiber/epoxy prepregs used were vacuum-bag-only prepregs consisting of an eight-harness satin carbon fiber fabric T650-35 3K and toughened epoxy resin CYCOM 5320-1 with 36% resin content by weight.

Synthesis of small molecule analog, tetra-*N*-methyl-3,3'-diaminodiphenyl sulfone (1)
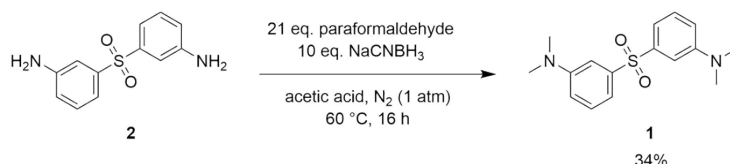
Compound **1** was prepared by charging a 50 mL round bottom flask with a magnetic stir bar, 1.00 g 3,3'-diaminodiphenyl sulfone (**2**, 4.03 mmol, 1 equiv.), 2.50 g paraformaldehyde (83.2 mmol, 21 equiv.) and 50 mL glacial acetic acid. The flask was sealed with a stopper and purged under N_2 for 20 mins. Under inert gas, 2.60 g sodium cyanoborohydride (41.3 mmol, 10.2 equiv.) was added in portions with stirring, resealed, and heated to 60 °C for 16 h. Afterwards, the reaction was neutralized using aqueous NaOH, then extracted with three portions of dichloromethane. The combined organic fractions were rinsed with brine and dried over Na_2SO_4 before concentrated on a rotary evaporator. The crude product was dry-loaded onto silica and purified through column chromatography using a hexanes – ethyl acetate gradient (100:0 – 20:80), and the isolated product was recrystallized from a 75% solution of methanol in water, 0.420 g.

^{1}**H NMR** (500 MHz, Chloroform-d) δ 7.29 (appt, J = 8.0 Hz, 2H), 7.25 (dd, J = 2.6, 1.8 Hz, 2H), 7.20 (dt, J = 7.7, 1.2 Hz, 2H), 6.83 – 6.80 (m, 2H), 3.00 (s, 12H).
^{13}**C NMR** (500 MHz, Chloroform-d) δ 150.54, 142.45, 129.71, 116.06, 114.90, 110.24, 40.32.
FTIR ν_{max}/cm^{-1} 3430 (OH, water), 2894, 1416, 1360 (CH$_3$), 1296, 1066 (S=O).
mp 129.3 – 130.8 °C
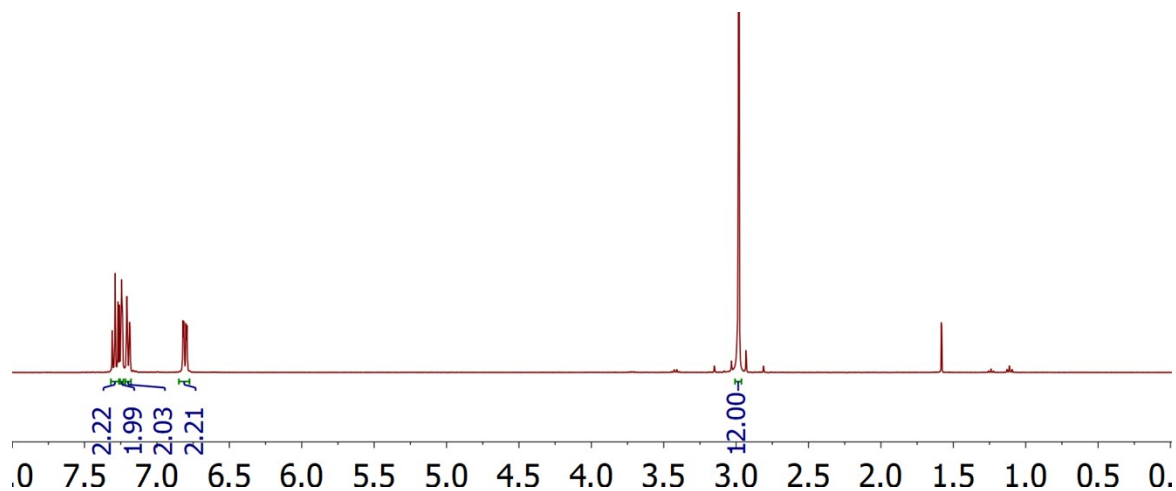**GC/MS** for $C_{16}H_{20}N_2O_2S$: calc'd 304.1, found 304.1 g/mol.

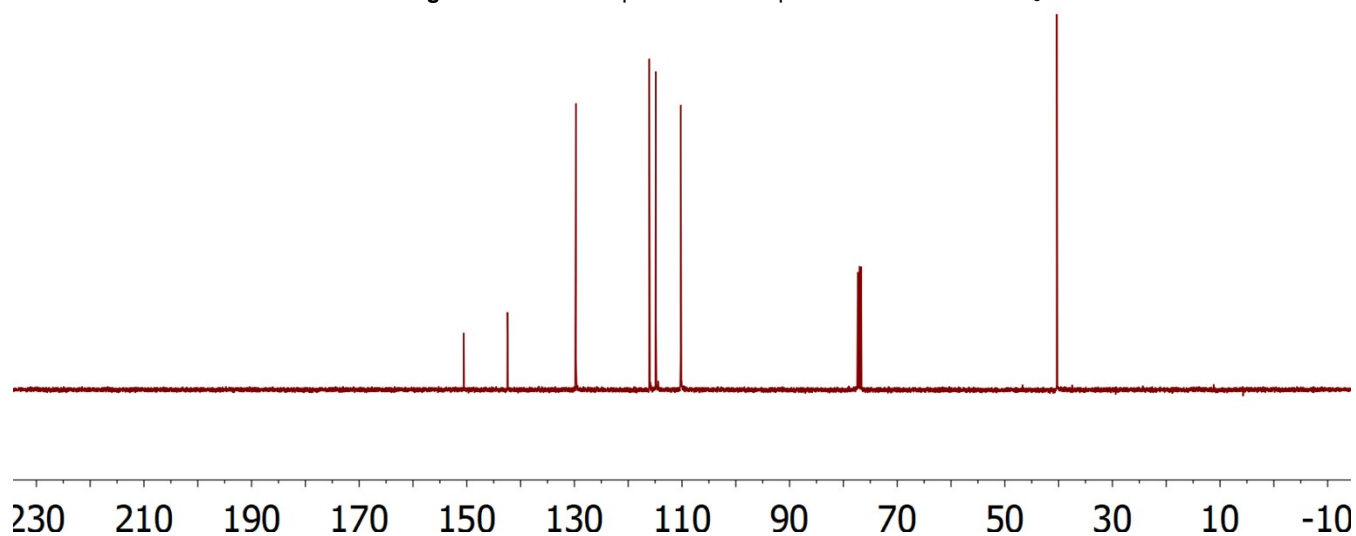**Figure S1.** ^1H NMR spectrum of compound **1** at 25 °C in CDCl$_3$.

Figure S2. ^{13}C NMR spectrum of compound **1** at 25 °C in CDCl$_3$.

Catalyst screening studies.

A series of catalysts and ligands were screened for aerobic demethylation of **1**. To an 8-dram vial, 50.0 mg **1** (0.164 mmol, 1 equiv.), 3.4 mg RuCl$_3$ (0.0164 mmol, 0.1 equiv.), 1 mL of a 0.0164 M solution of AlCl$_3$ in glacial acetic acid (0.0164 mmol, 0.1 equiv.), and an additional 2 mL glacial acetic acid (3 mL final volume). The open vial was heated in an oil bath at 50 °C for 17 h. After, a 0.3 mL aliquot was removed and placed into an NMR tube containing 0.7 mL chloroform-d and 3.0 μL of 1,2-dichloroethane (0.0379 mmol, 0.23 equiv.). From its ^1H NMR spectra, the intensity of the aromatic and methyl protons of **1** were compared to the internal standard 1,2-dichloroethane to calculate the amount of **1** remaining. This process was repeated for other metal salts: FeCl$_2$, MnCl$_2$, CuCl, and CoCl$_2$. Some trials added an extra 10 mol% of 1,10-phenanthroline or *N,N'*-ethylenebis(salicylimine).

Preparation and degradation of lightly crosslinked amine-epoxy polymer blocks.

Polymer cubes were prepared by mixing 3,3'-diaminodiphenylsulfone (**2**) with diglycidyl ether of bisphenol A (**3**) in a 2:5 molar ratio (T_g = 51 °C) and heated within a 120 °C oven to yield a clear, homogeneous mixture. The resin was cured via a cycle consisting of a 1.5 °C/min ramp rate to 250 °C, and a dwell for 30 min.
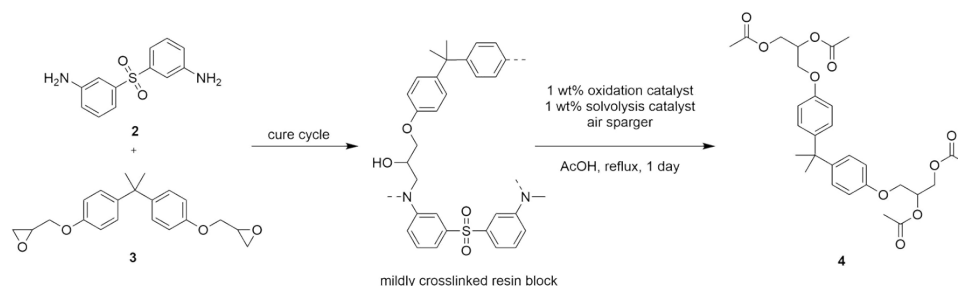
A 2.00 g resin disk of 5 cm diameter and 1 mm thickness was cut into strips and, optionally, pretreated by submerging and heating in benzyl alcohol at 110 °C for 4 h. The sample was then added to a three-neck 500 mL round bottom flask fitted with a reflux condenser, thermometer, a magnetic stir bar, and an air sparger. To the flask was added 150 mL glacial acetic acid and 0.200 g of an oxidation catalyst (MnCl$_2$ or Mn(phen)$_2$Cl$_2$) and solvolysis catalyst (AlCl$_3$ or ScCl$_3$). The reaction was heated to reflux with stirring and air bubbled into the solution for 1 day.

Reactions where the combination of catalysts homogenized the resin (MnCl$_2$ with AlCl$_3$ or ScCl$_3$), the reaction solvent was neutralized with an aqueous solution of NaOH, filtered to remove a newly formed brown precipitate, and extracted three times with ethyl acetate. The isolated precipitate was washed with water and acetone, then dried at 70 °C overnight to recover 0.021 mg polymer. Its composition revealed by elemental analysis: C, 60.99; H, 5.87; N, 1.54; S, 1.55. The combined organic fractions were rinsed with brine, dried over Na$_2$SO$_4$, and concentrated via rotary evaporator. The remaining oil was dry-loaded onto silica and purified via column chromatography using a hexanes – ethyl acetate gradient (100:0 – 20:80) to recover 0.021 mg of bisphenol A bis(diacetylglyceryl) ether (**4**).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.09 (m, 4H), 6.82 – 6.76 (m, 4H), 5.35 (dtdd, J = 6.1, 5.1, 3.9, 0.9 Hz, 2H), 4.42 (ddd, J = 12.0, 4.0, 1.0 Hz, 2H), 4.28 (ddd, J = 12.0, 6.0, 1.0 Hz, 2H), 4.09 (dd, J = 5.1, 1.0 Hz, 4H), 2.08 (dd, J = 8.7, 1.0 Hz, 12H), 1.62 (s, 6H).
¹³C NMR (101 MHz, Chloroform-*d*) δ 170.61, 170.29, 156.11, 143.77, 127.78, 113.96, 69.77, 65.96, 62.55, 41.74, 30.98, 20.96, 20.75.
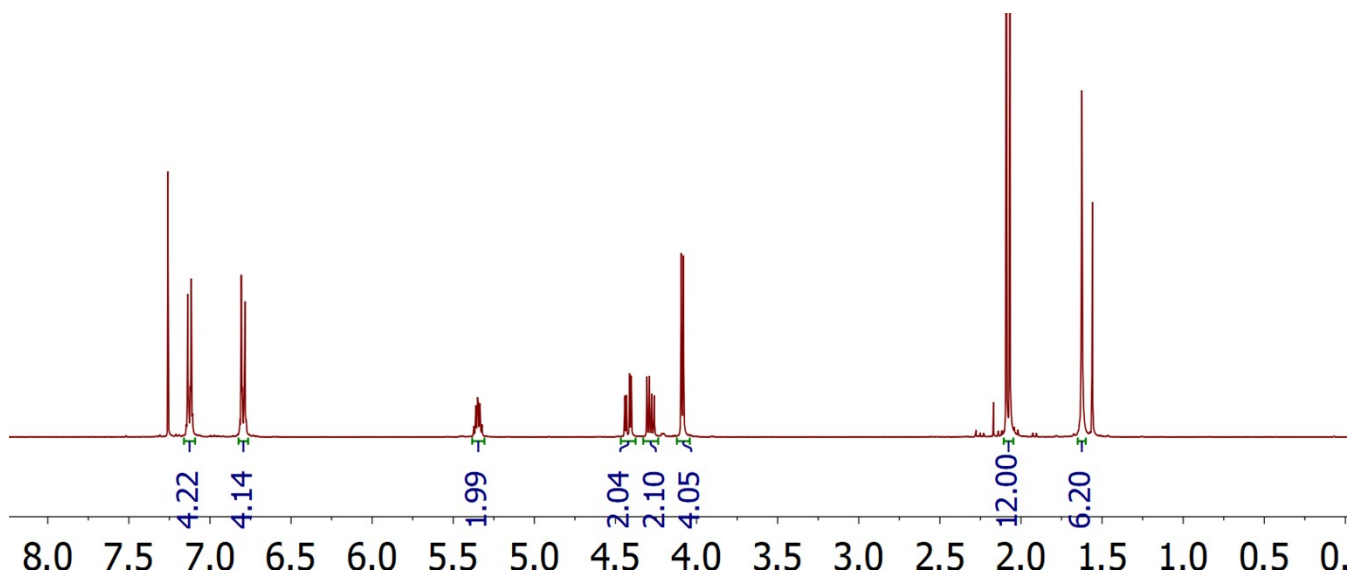

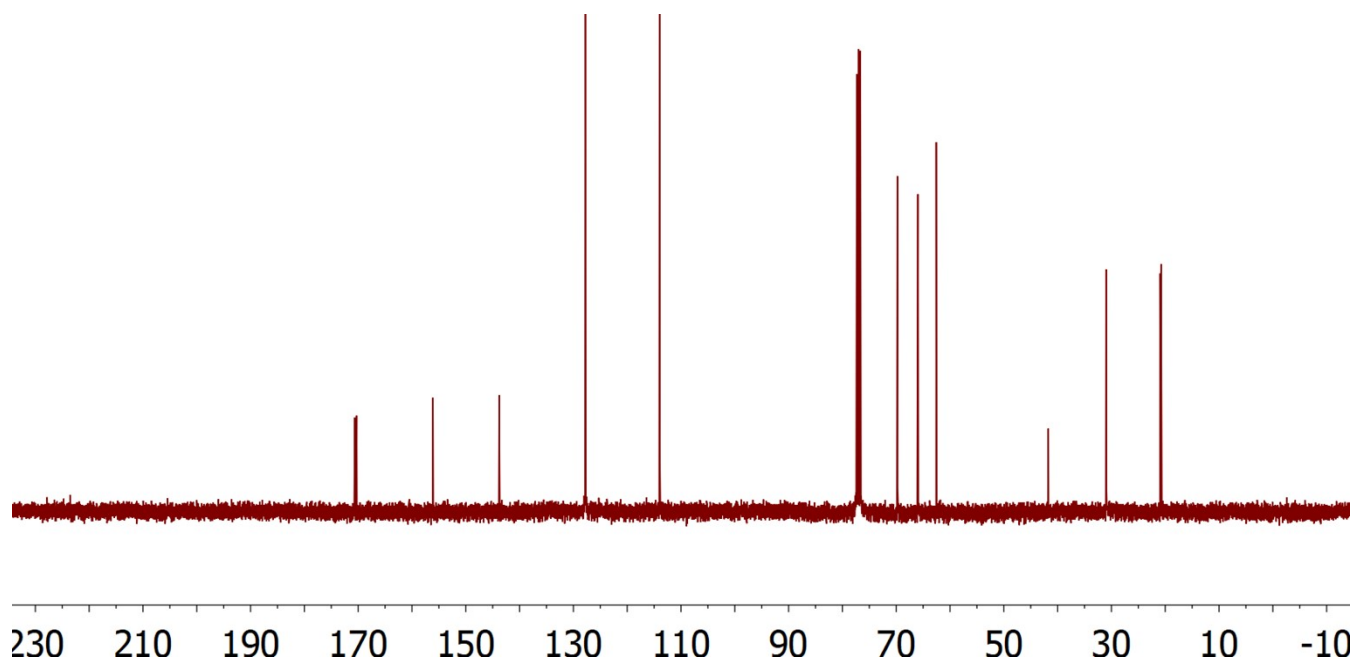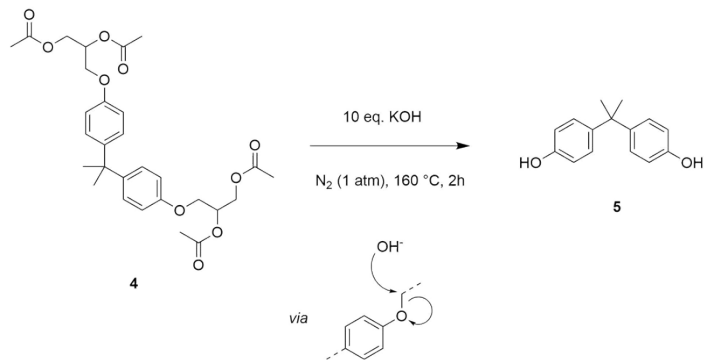**Figure S3.** ¹H NMR spectrum of compound **4** at 25 °C in CDCl₃.

Figure S4. ^{13}C NMR spectrum of compound **4** at 25 °C in CDCl$_3$.

Conversion of 4 to bisphenol A (5)

0.100 g of **4** (0.184 mmol, 1 equiv.), 0.103 g KOH (1.84 mmol, 10 equiv.), and a stir bar was added to a 25 mL round bottom flask. The flask was sealed with a rubber septum, purged with N$_2$, and kept under an N$_2$ atmosphere. The flask was heated with stirring at 160 °C for 2 h, after which the reaction was dry-loaded onto silica and purified via column chromatography using a gradient of hexanes – ethyl acetate (100:0 – 20:80), exclusively yielding 0.041 g of **5** (98%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.03 (m, 4H), 6.81 – 6.64 (m, 4H), 4.75 (s, 2H), 1.62 (s, 8H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.27, 143.27, 127.91, 114.68, 41.67, 31.05.
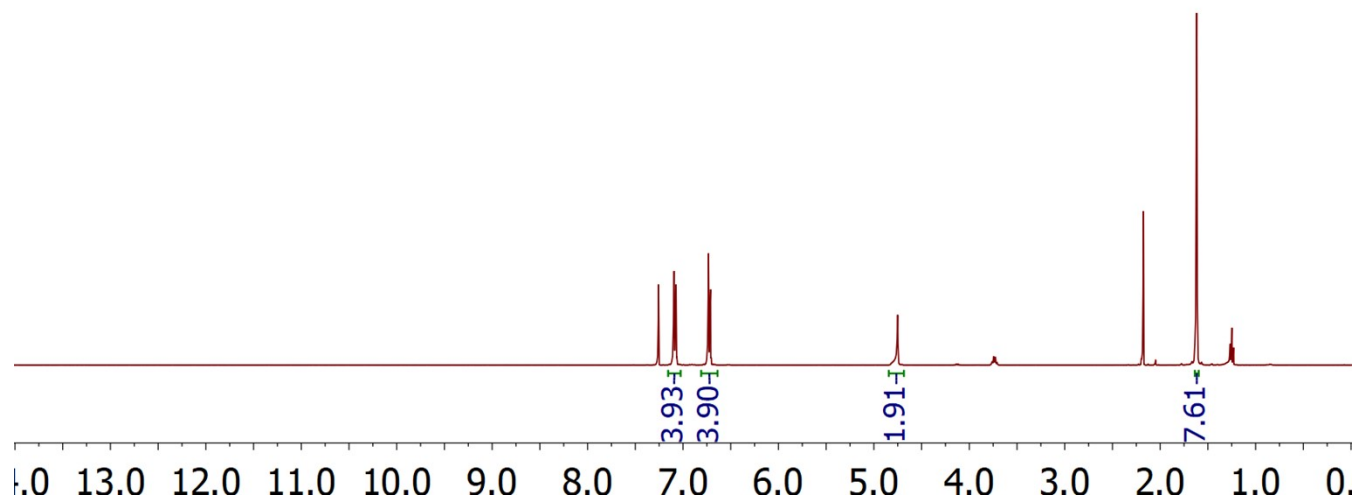
Figure S5. ¹H NMR spectrum of compound **5** at 25 °C in CDCl₃.
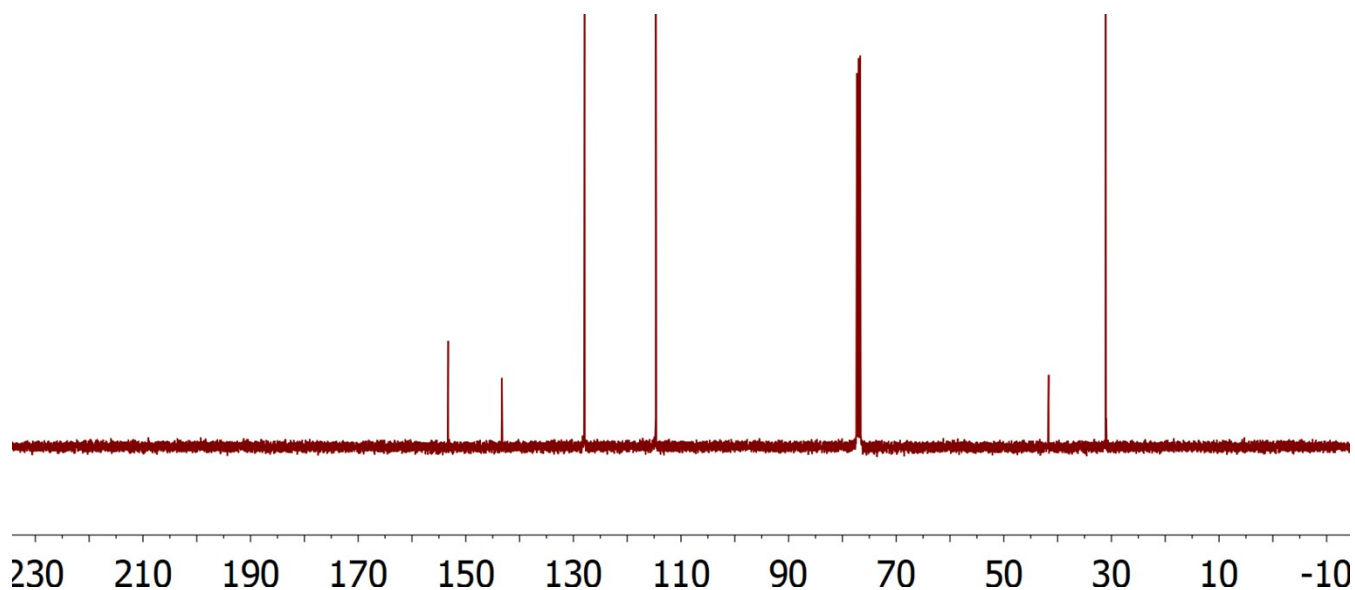
Figure S6. ¹³C NMR spectrum of compound **5** at 25 °C in CDCl₃.

Preparation and degradation of fully cross-linked amine-epoxy CFRP panels.

Completely cured amine-epoxy panels were prepared by mixing 3,3'-diaminodiphenylsulfone and diglycidylether of bisphenol A in a 1:3 weight ratio and cured using a cure cycle consisting of a 1.5 °C/min ramp rate, a 120 °C dwell of 3 h, another 1.5 °C/min ramp rate, and a post cure at 180 °C for 3 h.
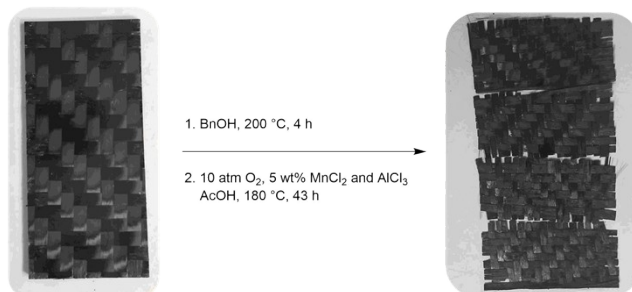
A 0.974 g 4-ply composite laminate, prepared in-house as previously described, was pre-treated by placing it in a 100 mL round bottom flask and adding benzyl alcohol until it is fully submerged (~ 40 mL). The flask was heated at 200 °C for 4 h, then the flask was removed and let cool. The softened composite was recovered from the flask, pat-dried, and rinsed with acetone. The pre-treated composite was then placed in a 125 mL Parr reactor with a stir bar, 80 mL acetic acid and 5 wt% $MnCl_2$ and $AlCl_3$. The reactor was purged with O_2 gas three times, then charged with 10 atm O_2. The vessel was left in an oil bath with magnetic stirring for 43 h. Afterwards, the reactor was removed from the oil bath and let cool to room temperature. Any remaining headspace pressure was vented, and the reactor was opened. The reaction solvent was poured into an Erlenmeyer flask, while woven fibers were removed using tweezers, washed with water and acetone, air-dried, and studied by Raman spectroscopy (0.5974 g).
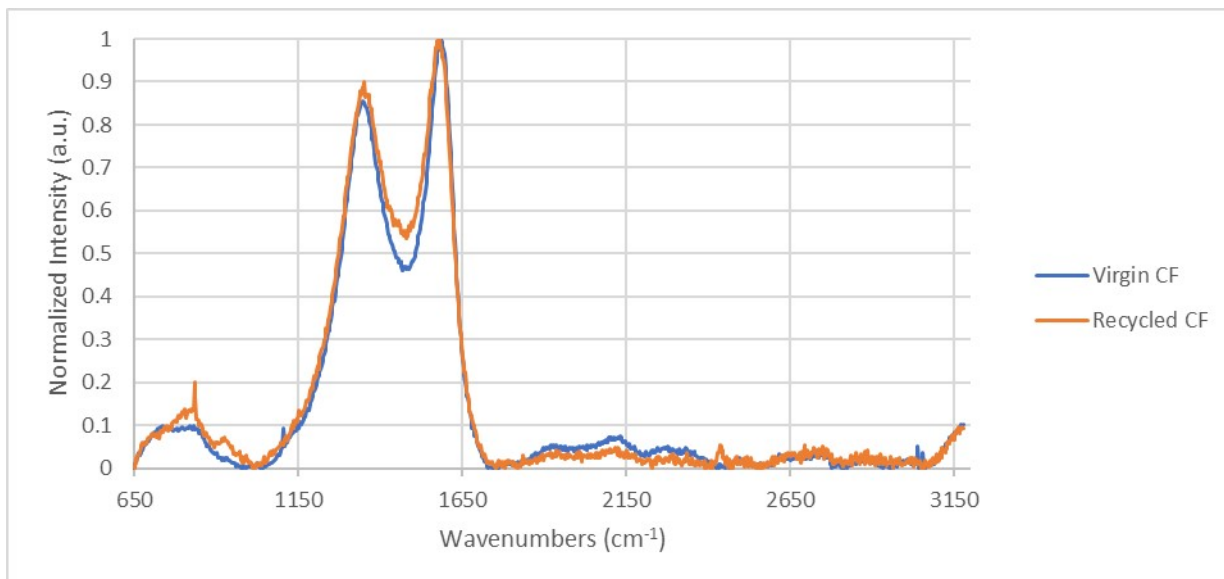

**Figure S7.** Raman spectra of virgin and recycled fibers.

Fiber Type	D band (cm^{-1})	G band (cm^{-1})	R (I$_D$/I$_G$)
Virgin	1348	1586	1.20
Recycled	1352	1584	1.22

Table S1. Raman results for the carbon fibers.

The reaction solvent was neutralized with aqueous sodium hydroxide, filtered to remove a newly formed brown precipitate, and extracted with three portions of ethyl acetate. The combined portions of ethyl acetate were washed with brine, dried over Na_2SO_4, and concentrated over rotary evaporator to yield 0.010 mg of an orange oil. The brown precipitate was rinsed with water and acetone, then dried overnight at 70 °C to recover 0.105 g of polymer.
Prepration and recycling of partially-cured pre-preg scrap.

Three types of pre-preg were prepared: room temperature aged, where the samples were left outside at room temperature for 20 days, and two degrees of partially cured pre-pregs, prepared by heating the pre-preg sample in a convection oven at 110 °C or 120 °C for 3 h. Modulated differential scanning calorimetry was used to determine the final T_g of the pre-pregs (Figure
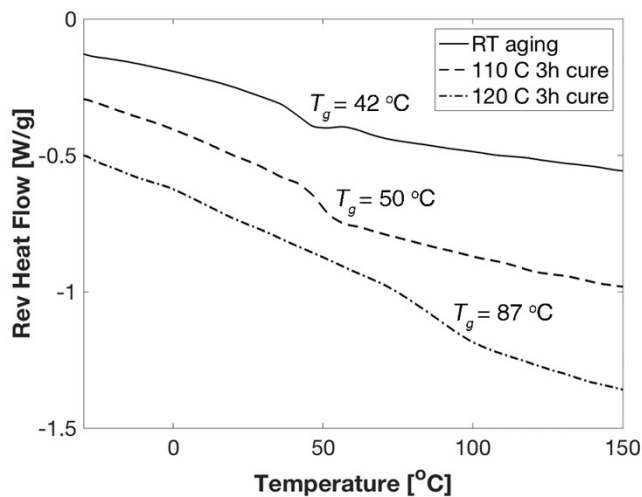
S7), revealing pre-preg aged at room temperature had a T_g of 42 °C, while those cured at 110 °C and 120 °C had T_gs of 50 °C and 87 °C, respectfully.

Figure S8. Glass transition temperature of pre-pregs aged at room temperature, cured at 110 °C for 3 h, and cured at 120 °C for 3 h.

Solvent washes were conducted by partially submerging the pre-preg into a crystallizing dish containing DMSO for a day. Undissolved epoxy matrices were recovered from solution via filtration. Clean carbon fiber fabrics were recovered from room temperature-aged samples, as well as 14 wt% of epoxy matrix. 110 °C cured pre-pregs contained fibers with matrix residues still present, as well as 22 wt% of undissolved epoxy matrix. The fabric-containing residue was treated with the aerobic recycling conditions by reacting it with 1 wt% $MnCl_2$ and $AlCl_3$ submerged in glacial acetic acid in round bottom for 7 days, after which clean fiber tows were recovered. For pre-pregs cured at 120 °C, there was almost no change after DMSO wash and only 1 wt% of undissolved epoxy was recovered. The pre-preg was similarly treated with the aerobic degradation reaction, reacting it with 1 wt% $MnCl_2$ and $AlCl_3$, submerged in glacial acetic acid within a round bottom flask for 7 days. Residue-free and soft fabrics were not recovered, though the material was noticeably softer.

Life cycle primary energy consumption study

Lowering the high energy intensity of CFRP is a significant challenge facing its expanded use as a structural material. In this analysis we estimate life-cycle primary energy consumption for our proposed recycling process and compare it with landfilling and pyrolysis end-of-life pathways. Values for pyrolysis and chemical recycling are provided for a single recycling loop, representing the theoretical limit for once-through pyrolysis. As chemical recycling preserves CF in the CF sheet and can potentially offer indefinite looping, the manufacturing of virgin CF is expected to reduce beyond what is estimated in this study. While a complete life-cycle assessment is outside the scope of this study, we note the importance of estimating raw material consumption, greenhouse gas emissions and other air pollutant emissions and their associated impacts in a future study.

Manufacturing

On-site and primary energy intensities [Btu/lb] to produce virgin carbon fibers and resin (epoxy thermoset), and for compression molding were taken from the DOE 2017 Bandwidth study on CFRP manufacturing [1]. Values were based on 2010 production data with primary energy values reflecting 32.3% energy losses from offsite electricity generation and transmission. Manufacturing processes are shown in Figure S8. Mass flows were estimated assuming the same material losses between sub-processes as reported in Das 2011, and by adjusting the CF weight content from 50% to 65% to better represent the material in this study [2].
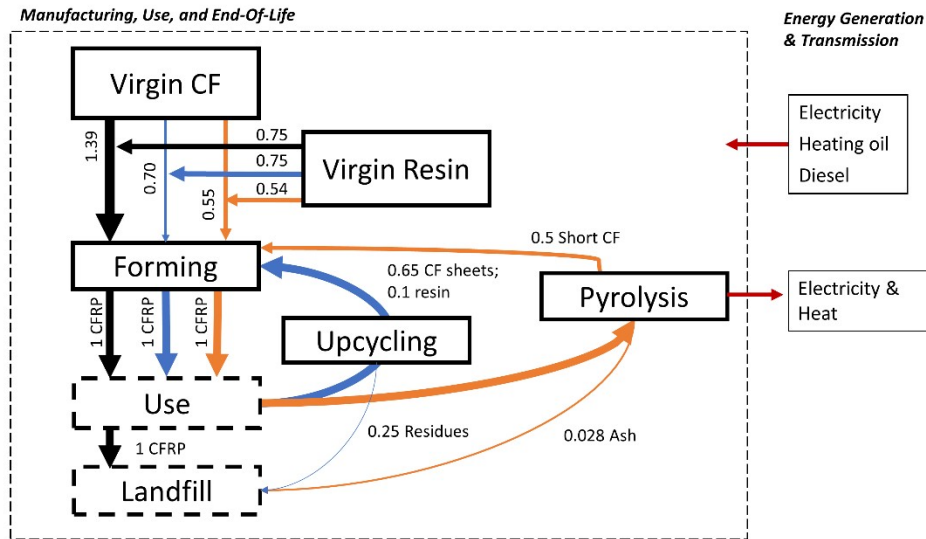
Figure S9. Processes and material flows used to model primary energy consumption. Use phase is the same for all pathways and not explicitly modeled. We assume there is no energy generated from landfill gas derived from CFRP.

Alternative Disposal Options: Landfill

In the case where used CFRP is sent to a landfill, we assumed materials were transported 100 km prior to shredding, and then transported 300 km to a landfill. Transportation distances are assumed from Witik et al., 2013 [3]. For truck transportation of materials, we assume a class 7 truck weighing 28,000 pounds carries 75% of the remaining maximum allowed truck-weight in California (80,000 pounds), generating a payload of 39,000 pounds per truck of material. We use the EPA weight-based fuel consumption factor of 11.3 gallons/1000 ton-miles and a diesel energy density of 38.6 MJ/L. The energy intensity of the shredder was estimated from a commercial large single-shaft shredder capable of processing up to 20,000 lb/hr with an average loading rate of 30%. We believe our estimate of 0.1 MJ/kg direct energy is reasonable given Witik et al. 2013 used a value of 0.0025 MJ/kg, but energy for size reduction of PET plastics has been reported at values ranging from 1.7 to 5.2 MJ/kg primary energy. Shredders were assumed to operate on electricity and were adjusted for upstream losses. We use a scale up factor of 1.2 for diesel consumption to reflect upstream processes associated with diesel production.

Alternative Disposal Options: Pyrolysis

In the case where used CFRP is sent to a pyrolysis facility, we assumed materials were transported 1000 km prior to shredding and pyrolysis, followed by the transport of ash 300 km to a landfill, and the transport of recovered CF 1000 km for recycling. Transport and size reduction are modeled using the same assumptions as done for the landfill case. Pyrolysis is assumed to generate energy that will offset both heating oil and electricity for onsite use with no transmission losses. The energy penalty of pyrolysis of CFRP is not easily known, and as such, we assume an energy penalty equal to 10% of manufacturing virgin CF, as was assumed in Witik et al. 2013. Primary energy from the process is assumed using the same fuel to electricity ratio and upstream generation and transmission energy losses as primary manufacturing processes. The process is estimated to recover 82% of CF, in a short fiber form, and we assumed CF can only be recycled one time through this pathway due to the degradation of the fibers. While it is unclear to what extent these CF will replace virgin CF, we assumed a 50% offset resulting from this recycling pathway. The production of resin and the compression moulding sub-processes remain unchanged. We assume 8% of the resin is ash, which is sent to landfill.

Alternative Disposal Options: Chemical recycling

In the case where used CFRP is sent to a chemical recycling facility based on the process presented in this study, we assumed materials were transported 1000 km prior to hydrolysis and polymerization, followed by the transport of residuals 200 km to a landfill, and the transport of recovered CF sheets and resin 1000 km for recycling.

As industrial scale data is not available, we assume an energy intensity equal to 20% of manufacturing virgin CF and resin, as is reported for a commercial chemical recycling process. Primary energy from the process is assumed using the same fuel

to electricity ratio and upstream generation and transmission energy losses as primary manufacturing processes. Lab scale experiments presented in this study were used to determine mass flows for these life cycle stages. The process is estimated to recover 100% of CF, in a sheet form, and we assumed a 60% offset of virgin CF, and 29% offset of virgin resin. We adjusted the energy intensity of compression moulding to reflect the use of CF sheets rather than fibers by subtracting the energy intensity of sheet moulding.

Primary Energy Analysis

We find that virgin CFRP has an embodied energy of 4739 MJ/kg, with negligible energy associated with its landfilling (Figure 3, main text). A single loop pyrolysis pathway lowers the embodied energy of CFRP by 45%, with the pyrolysis process cutting the CFRP manufacturing process energy consumption by 54% due to reduced virgin material production. The pyrolysis process adds a 4% energy penalty to the new manufacturing process that uses a mix of virgin and recycled fibers. In comparison, the single loop upcycling pathway lowers the embodied energy of CFRP by 56% at 2097 MJ/kg, 20% lower than CFRP from single loop pyrolysis. The upcycling process adds a 6% energy penalty to the new manufacturing process that uses a mix of virgin CF and resin and recycled CF sheets and resin.

Key uncertainties remaining include the true energy intensity of pyrolysis and upcycling. Additionally the number of recycling cycles that both pyrolysis and upcycling can offer will play a major role on the theoretical limit of energy reduction that upcycling can offer. Assuming thousands of cycles of upcycling drives the production of virgin materials to negligible levels, would drive CFRP to an embodied energy intensity of 142 MJ/kg (95% reduction). More realistically, some virgin materials will be necessary to ensure the quality of product. Finally, the potential coupling of upcycling and pyrolysis as an end-of-life opportunity to generate energy from the upcycling residues would be important to evaluate in a future analysis.

References

1.   Office of Energy Efficiency & Renewable Energy, Bandwidth Study on Energy Use and Potential Energy Saving Opportunities in U.S. Carbon Fiber Reinforced Polymer Manufacturing Energy, U. S. D. o., Ed. Advanced Manufacturing Office: 2017.
2.   Das, S., Life cycle assessment of carbon fiber-reinforced polymer composites. *The International Journal of Life Cycle Assessment* **2011,** *16* (3), 268-282.
3.   Witik, R. A.; Teuscher, R.; Michaud, V.; Ludwig, C.; Månson, J.-A. E., Carbon fibre reinforced composite waste: An environmental assessment of recycling, energy recovery and landfilling. *Composites Part A: Applied Science and Manufacturing* **2013,** *49*, 89-99.