SELECTIVE CLEAVAGE OF AMINE-LINKED EPOXY COMPOSITE MATRICES BY OXYGEN

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ABSTRACT

This presentation will describe conditions for the use of oxygen as a reagent for the selective cleavage of thermoset composites.

Carbon fiber-reinforced polymer (CFRP) composites have a prominent role in aviation, sporting goods, marine, and other manufacturing sectors and are accumulating en masse as waste, both at end-of-life and as manufacturing defects. We have recently introduced a method to use oxygen itself along with an appropriate catalyst selectively to disassemble such fully-cured composite wastes to recover both ordered carbon fiber sheets and organic materials suitable for re-manufacturing of second-life resin systems.

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1. INTRODUCTION

Fiber-reinforced polymer (FRP) composites are widely used because of their high performance and light weight relative to conventional metal alloys. Most of the polymer matrices involved are thermoset epoxies, which undergo an *irreversible* cure reaction, converting them from viscous liquids to stiff, glassy solids. The irreversibility of this curing impedes the productive reuse of scrap and recycling of end-of-life FRP composites and constitutes a growing obstacle to more wide-spread use. Amplifying the problem is the inefficiency of FRP manufacturing methods: generally, 20% to 30% of purchased material (prepreg) becomes production waste,[1] and *no standard approaches exist for reusing production waste or recycling end-of-life thermoset FRP composite products*. At present, most such composite waste is sent to landfills, often with attendant hazmat disposal fees.

The widespread use of composites creates an urgent need for new strategies for the recycling of FRP scrap and end-of-life waste. Moreover, developing catalytic chemical reactions that will gracefully deconstruct fully cured FRP matrices requires the development of chemical technology to enable catalysts and reagents to move and react within the complex solid-phase composite architecture. We have recently invented methods to enable such catalytic depolymerization of common thermoset polymers used in composites manufacturing, and our long-term goal remains to apply these catalytic

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methods to the cleavage of FRP matrix linkages in a way that enables the recovery of useful small-molecule monomers and preserves the length and order of composite fibers.

The following narrative will show how we have used three oxidative catalysis systems tuned for the cleavage of target CFRP matrix systems. We will discuss the design of the chemistry and illustrate why and how chemical structural features of a given polymer matrix inform the engineering of optimal chemical conditions for the effective cleavage of that polymer matrix.

2. EXPERIMENTATION

2.1 General 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 solvent peak. Degradation studies were performed in 8" J-young tubes (Wilmad or Norell) with Teflon valve plugs to avoid possible loss of solvent or products at elevated temperatures. GC/MS data was acquired on an Agilent 5973/HP 6900 instrument, MALDI data were obtained from a Bruker Autoflex Speed MALDI mass spectrometer and IR data were acquired on a Nicolet iS5 FTIR spectrometer. SEM photographs were recorded on a low-vacuum electron microscope (JEOL JSM-6610) with a tungsten filament. The working parameters of the recorded images, such as working distance and accelerating voltage, are recorded in the images in the main text.

2.2 In Situ Oxidation and Cleavage of Me_4DDS.

Me_4DDS[2] (5.1 mg, 17 μmol, 1 equiv, DDS = 3,3'-diamino diphenyl sulfone), acetic acid-d_4 (700 μL), and 50 μL 30% hydrogen peroxide (490 μmol, 29 equiv) were placed into a J-young NMR tube and heated in a VT NMR experiment at the temperature specified in the main text.

2.3 Composite Panel Digestion with Peroxide and $ScCl_3$ Conditions.

Resins were prepared from monomers using a 2/5 amine/epoxy molar ratio and were mixed at room temperature in clean aluminum cans until fully homogenized. By 2/5 we mean to imply that the molar ratio of epoxy groups (in epoxy monomers) to NH groups (in the amine curing agent) is 2/5. The mixture was then heated to 120 °C in a pre-heated convection oven to further improve the mixing quality, yielding a clear homogenous mixture.

An FRP panel based on a resin comprising DDS and DGEBA monomers (prepared as described above, DGEBA = diglycidyl ether of bisphenol A) was manufactured as an 8-ply composite laminate, fabricated using 2 x 2 twill weave carbon fiber fabrics (3K, 193 g/m^2, FibreGlast,) and a 1/1 amine/epoxy stoichiometric ratio matrix. Final polymer content was 45 +/- 2 wt%. The cured laminates were cut into 100 x 20 mm coupons (ca. 5 g sample) and subjected to digestion.

The coupon thus prepared was placed in a 1 L flask with 60.0 mL glacial acetic acid (EMD Millipore) and 10.0 mL 30% aqueous hydrogen peroxide (EMD Millipore). The resulting mixture was refluxed (110 °C bath) with additional 5.00 mL hydrogen peroxide solution portions added every hour.

Carbon fibers from the reaction mixture were separated and examined by SEM. The product mixture was screened for monomeric materials by GC/MS and MALDI mass spectroscopy, using sodium dihydroxybenzoate as the MALDI matrix.

2.4 Aerobic Homogenization of Amine-Epoxy Thermoset using $MeReO_3$ and $ScCl_3$.

Polymer blocks were prepared according to the resin formulation and curing procedure above. Blocks thus prepared were digested in acetic acid for 20 hours at 110 ºC, each with 1 wt% $ScCl_3$ and respectively containing 1 wt% $MeReO_3$ or ascorbic acid as a catalyst.

2.5 Condition Screen for Benzoxazine Polymer Cleavage.

Benzoxazine/epoxy resin (BZ 9102) was a gift from the commercial supplier, Henkel. This was used as received. Neat polymer blocks were manufactured according to the manufacturer's curing specifications. CFRP composite panels were manufactured in-house.[3]

Distilled water (5.0 mL) was added to acetic acid (5.0 mL, Millipore, used as received) in a 20 mL test tube with a Teflon stir bar (VWR), along with neat, cured, fiber-free benzoxazine matrix grounds (ca. 50 mg) that had been pulverized in a desktop coffee grinder to give a particulate size on the order of ca. 1 mm. Oxidant (0.5 molar equivalents to 1 molar equivalent of benzoxazine) and catalyst (0.5 equiv), were added to each test tube. The test tubes were then capped with a rubber septum, heated to 80 °C and stirred at 300 RPM. After 24 hours of reaction time, the resin grounds were dried in a vacuum oven for 2 hours to remove any excess solvents, then weighed.

2.6 Benzoxazine CFRP Cleavage.

A small coupon of a benzoxazine panel,[3] measuring approximately 30 mm by 15 mm, was excised from the larger composite panel by a tile saw and placed in a 500 mL round bottom flask along with of distilled water (100 mL), triflouroacetic acid (100 mL), $RuCl_3$ (11.93 mg), and $(NH_4)_2Ce(NO_3)_6$ (70.2 g). The flask was capped with a glass stopper, and the reaction was allowed to proceed for 24 hours at 60 °C (at ambient pressure) while being stirred at 360 RPM. After 24 hours, the individual fibers were removed with tweezers.

3. RESULTS

3.1 Approaches to Oxidation

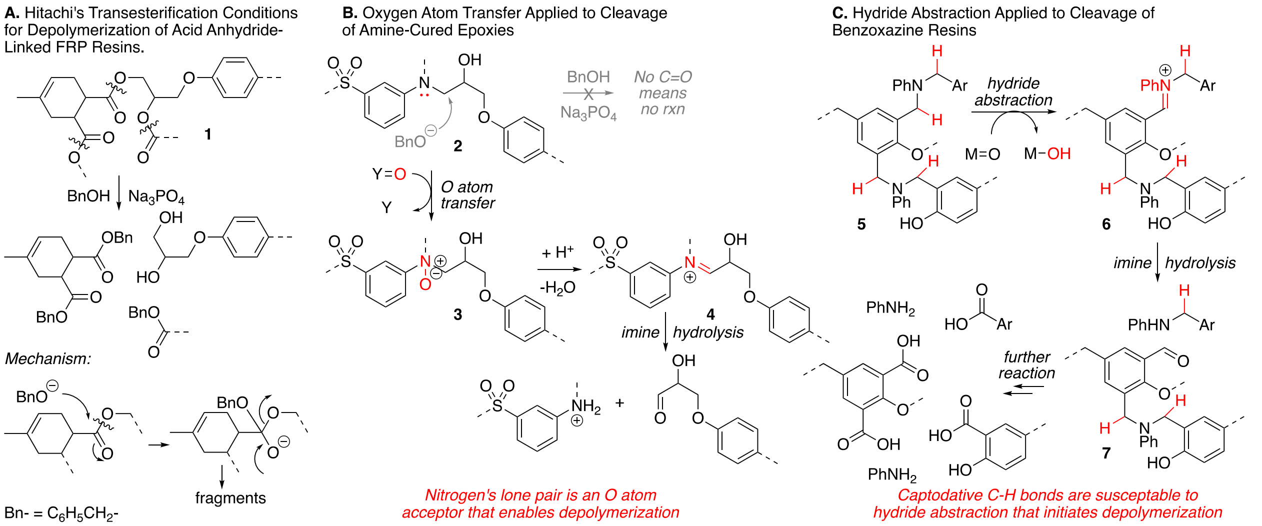
There are many chemistries that are used widely in CFRP manufacturing. Some of these have accessible recycling approaches built-in, such as the emerging class of selectively cleavable resins like Recyclamine,[4] in which a hardener, additive, or crosslinking agent[5] for an epoxy resin enables the disconnection of bonds with heat and pH to enable recycling.[6] Others have natural susceptibility to solvolysis. For example, a solvolysis process developed by Hitachi Chemical uses alkaline benzyl alcohol to cleave anhydride-cured FRP resins Scheme 1 (part A).[7] Such conditions are very well fit to anhydride-cured matrices that are linked through ester functional groups, which are easily susceptible to alkaline solvolysis. Emerging thermoplastic[8] and vitrimeric[9] resin systems also have straightforward recycling strategies built in: these materials deform upon heating and can be melt processed to an extent, thus offering a thermal strategy at end-of-life, which is typically preferable to a chemical route.

The bulk of the resin systems used in aerospace and other high-performance applications involve thermoset materials with no obvious chemical vulnerability. It must be so: aerospace and high-performance resins must not include any features that would enable them to cleave or deform under high temperature or corrosive chemical conditions, or they would be poorly fit to high temperature or corrosive applications. Such materials involve amine-epoxy or other irreversible chemistries that are engineered to forge robust covalent bonds among resin monomers upon curing.

The composite recycling community has invested considerable effort to find empirical approaches to cleave robust thermoset CFRP matrices,[10] but to our observation this work has been substantially guided by material properties, thermal and pressure strategies, and solubility. As a molecular catalysis lab, we have viewed this problem from a different foundation: *find the molecular events that result in cleavage of CFRP matrices with known, but impractical, conditions, then engineer second-generation methods to realize those molecular cleavage events efficiently*.

We have approached two structurally different resin materials that are generally not susceptible to thermal or corrosive conditions: amine-cured epoxies and bis([benzo]oxazine)methane-based resins (benzoxazines). These reactions are conceptually sketched in Scheme 1 (parts B and C) along with the contrasting solvolysis mechanism exploited by the Hitachi process (part A). We will explain below why oxygen atom transfer (OAT) is well fit for oxidation and cleavage of amine linkages and hydride abstraction is effective is labializing aminomethyl-arene linkages that feature particularly weak C—H groups.

Scheme 1. Molecular Mechanisms for Cleavage of FRP Resins based on (A) Acid Anhydride, (B) Amine, and (C) Benzoxazine Curing Chemistries.

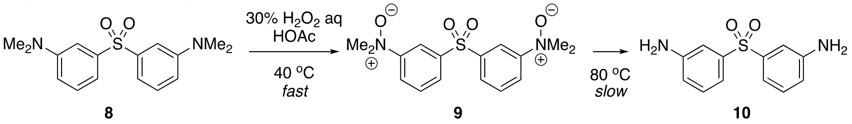


3.2 Peroxide Conditions

Our initial approach to depolymerizing CFRP epoxy matrices utilized oxidative degradation with H_2O_2, a variant of known procedures.[11] Although a reasonable starting point, the disadvantages of this method include safety, cost, and sustainability of peroxide, over-oxidation of the polymer matrix, thus destroying the value of the polymer. Nonetheless, this was a useful start for the development of our catalytic methods. We propose that this mechanism proceeds by oxygen atom transfer (OAT), followed by imine formation and imine hydrolysis (Scheme 1B). It stands to reason, therefore, that catalysts capable of accelerating either the O-atom transfer or elimination step (or both) could accelerate the degradation of these composite matrices. Ultimately, validating (or refuting) this mechanism and understanding the kinetics of the OAT reaction could help in identifying conditions that enable the use of an oxygen atom source that is more sustainable than peroxide.

We proceeded to show a molecular model of amine-cured epoxy matrices, in which the linking glycerol fragments within the matrix were modeled respectively as alkyl groups.[2] Kinetic data recorded by ^{1}H NMR (nuclear magnetic resonance spectroscopy) studies on Me_4DDS (**8**) revealed rapid oxygen atom transfer to form *N*-oxide intermediates (**9**) within minutes, proceeding to 50% conversion in ca. 1.5 hr at 40 °C. Prolonged heating of this intermediate oxide, Me_4DDS-*N*, *N'*-dioxide (**9**), at 80 °C for 12 hours resulted in its degradation to ca. 60% conversion. A critical and surprising conclusion came forth from this relatively simple experiment: the O-atom transfer from peroxide is much faster than elimination of the intermediate *N*-oxide.

Scheme 2. Cleavage of an Alkylated DDS under Peroxide OAT Conditions.



With some experimentation, we found that scandium(III) chloride effects rapid elimination of our intermediate dioxide **9**, and that downstream hydrolysis and polymer cleavage steps proceed rapidly relative to elimination. Still, this elimination step remains significantly slower than the preceding oxidation, so the intermediate dioxide (**9**) is readily observed.

We showed recovery pristine carbon fibers from digested FRP panels based on epoxy monomers as determined by SEM images of virgin carbon fibers (left) and those that are re-isolated from a resin panel that was depolymerized by oxidative degradation (right). These data suggest that the strongly oxidative conditions of peroxide in acetic acid do not damage the fibers.

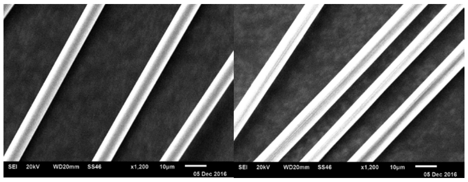


Figure 1. SEM images of carbon fibers that are (left) virgin and (right) recovered by peroxide degradation.

3.3 Oxidation Appears to be a Common, Unappreciated Feature

It is uncommon in chemical catalysis for a redox step to outrun elimination, so we found the result above illuminating. Particularly, this enabled us to understand why a number of solvolysis reactions for epoxy matrices that are based on Lewis acids (eg. zinc, magnesium) were effective when such conditions should not readily cleave carbon-nitrogen bonds: when epoxies are heated *in air or oxygen* in the presence of a Lewis acid capable of catalyzing *N*-oxide elimination, it stands to reason that the Lewis acid is not cleaving the matrix itself, but rather that there is an unseen O-atom transfer *from oxygen or air itself* that labializes the linkage. We reasoned that because OAT from air to nitrogen is spin-forbidden, and thus slow in the absence of a catalyst, the oxide intermediate would be unobserved, and practitioners might attribute the reactivity to the Lewis acid alone.

Listed in Table 1 are several examples of the degradation of amine-cured epoxy composites in the presence of a Lewis acid. In each of these cases oxygen is involved along with the Lewis acid. Entries 1 and 2 have the shortest degradation times, apparently due to the vigorous temperature and pressure. It is likely that these affect both the elimination step and oxidation steps. Although elimination is the slower step, it is important to note that oxidation must take place prior to bond cleavage and these high pressure/temperature conditions can be very strongly oxidizing. In fact, Hou points out for entries 3 and 4 that XPS data show oxidation on the recovered carbon fibers themselves.

Table 1. CFRP Cleavage Reactions Involving Lewis Acids in which Oxygen Appears to be Playing a Role.[a]

Entry	Resin	Curing Agent	Solvent	Lewis Acid	Temp	Pressure	Resin Degradation Time
1[12]	RTM6	N/A	20% acetone (aqueous)	$MgCl_2$	300˚C	16 MPa	> 95% 1 hr
2[12]	RTM6	N/A	20% acetone (aqueous)	$AlCl_3$	300˚C	16 MPa	> 95% 1 hr
3[13]	DGEBA	DMDC	HOAc	$AlCl_3$	180˚C	0.1-0.3 MPa	> 95% 6 h
4[13]	DGEBA	DMDC	HOAc	$ZnCl_2$	180˚C	0.1-0.3 MPa	Swollen 6 hr
5[14]	CFRP waste	Amine cured	EtOH	$ZnCl_2$	220˚C	N/A	90% 5 hr
6[14]	CFRP waste	Amine cured	EtOH	$FeCl_2$	220˚C	N/A	33% 5 hr
7[14]	CFRP waste	Amine cured	EtOH	$AlCl_3$	220˚C	N/A	36% 5 hr

a. DMDC = 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane. DGEBA = diglycidyl ether of bisphenol A. HOAc = acetic acid. EtOH = ethanol.

We understand these data to indicate that many of the known examples of amine-linked epoxy CFRP depolymerization reactions probably involve a mechanism in which oxidation precedes elimination and polymer cleavage, and we suspect an *N*-oxide to be the intermediate structure.

3.4 Aerobic Conditions

We next turned our focus to transitioning from H_2O_2 to O_2 (air), which avoids two disabling problems of peroxide. 1. *Sustainability*: hydrogen peroxide is an unsustainable (expensive, explosive) reagent that will not be deployed on aircraft or automotive scale. Not only is it not sustainable, it is also a safety issue. 2. *Selectivity*: peroxide conditions degrade the matrix monomers and destroy their value. For example in the case of Scheme 2, the methyl group of **8** is ultimately converted all the way to CO_2 by hydrogen peroxide.

Our initial oxygen atom transfer (OAT) conditions affect polymer degradation *selectively*, and with *air as the oxygen source*. Thus, neat matrix blocks can be homogenized catalytically using air as the terminal oxidant when treated with catalysts for both the OAT ($MeReO_3$)[15] and elimination ($ScCl_3$) steps in our mechanism. Figure 2 shows two reactors containing matrix blocks digested in acetic acid for 20 hours at 110 °C, each with 1wt% $ScCl_3$ and respectively containing 1 wt% $MeReO_3$ or ascorbic acid as the catalyst for O-atom transfer. This experiment provided important proof of the concept that oxidative cleavage of an epoxy thermoset matrix could proceed efficiently using ambient pressure air as the O_2 source. Still, applying these conditions at scale would benefit from the displacement of higher-cost rhenium and scandium catalysis with lower cost, more abundant metals.

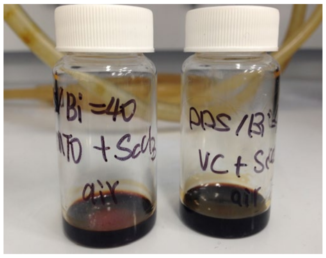


Figure 3. Amine-linked epoxy matrices are homogenized by catalytic air oxidation.

Further development of this observation enabled us to find conditions in which aluminum ($AlCl_3$) is the elimination catalyst. Oxygen is delivered at up to 10 atm pressure with $MnCl_2$ incorporated as the OAT catalyst. These conditions realize important sustainability benefits, whereas aluminum and manganese are respectively the third and fifth most abundant elements in the crust of the Earth.

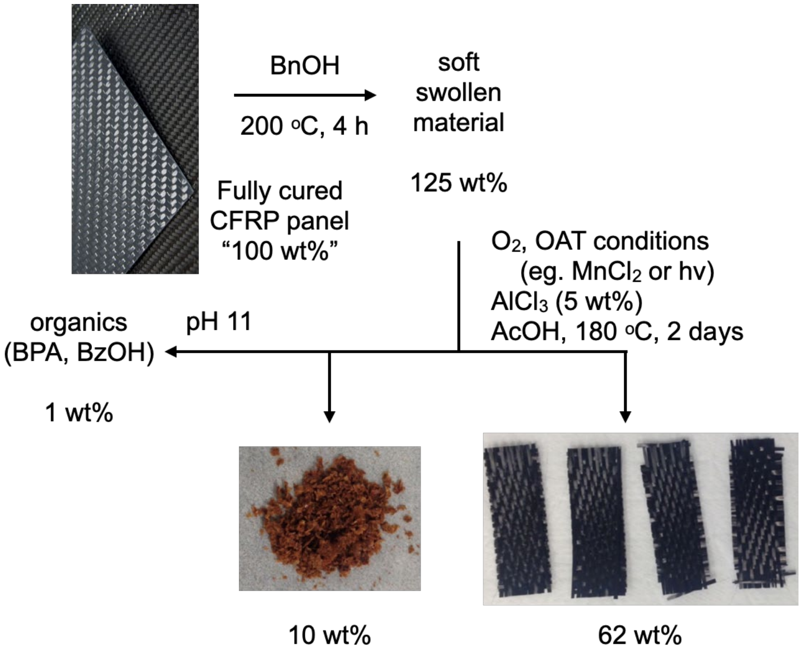


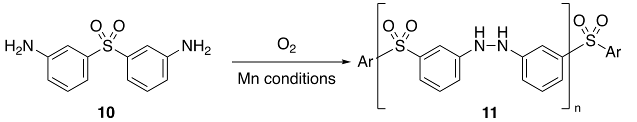
Figure 2. Schematic diagram of composite panel digestion. Mass balance indicated here were recorded in an experiment with 10 atm O_2, 5 mol% $MnCl_2$.

We have demonstrated process on a fully cured composite panel that we manufactured ourselves.[16] So doing, we showed that it is possible to overcome the stiffness and inertness of a fully cured amine-linked epoxy-based CFRP sample and recover products. Our initial workflow and mass balance are laid out in Figure 3. Essentially this is a 3-step process: first, composite waste is incubated in a benzyl alcohol bath, which labializes the material, apparently to enable intercalation of reagents into the material. The solvent can be readily re-used. This labialized material is then treated with our oxidative decomposition conditions.

At the conclusion of the reaction, we collect our recyclates through a purification step. Carbon fibers are recovered very easily as woven sheets. These are physically lifted from the reactor and washed with solvent. Carbon fibers account for nearly two thirds of the mass of the composite waste.

An advantage of using oxygen itself, rather than peroxide, as the oxidation source is that the organic fragments of the polymer can be recovered. Mass spectral data for the post-reaction solvent fraction of peroxide-based matrix homogenization reactions failed to reveal any intact small molecules that could be recovered. By remarkable contrast, mild aerobic conditions facilitated by manganese and aluminum co-catalysis enable recovery of pieces of both the epoxy and diamine monomers of the starting matrix. Thus, the liquid remaining after fiber recovery in Figure 3 is pH-neutralized, which initiates precipitation of a colored polymer that accounts for about 10% of our mass. This material (**11**) is itself a polymer, which is formed from oxidative coupling of the amine groups of DDS (**10**) to form hydrazine linkages when DDS is liberated from the matrix (Scheme 3). We have shown that this can be re-manufactured into new composite resins for applications such as automotive parts.[17] The remaining mass of our waste is a soluble organic fraction from which we can isolate bisphenol A, benzoic acid, and other lower-value organics.

Scheme 3. In Situ Polymerization of DDS in the presence of O_2 and Manganese.



To our knowledge, the scheme laid out in Figure 3 was *the first known route to recover intact carbon fiber sheets from fully cured composite materials*. It was also the first approach to demonstrate recovery and upcycling of organic materials from amine-linked epoxy composite matrices. These are essential to enable good mass balance in composites recycling, and the largest bulk of composite matrices in use in high-volume applications (aerospace, wind turbine blades), are based on amine-epoxy chemistry.

3.5 Benzoxazines

Bis([benzo]oxazine)methane-based FRP resins (benzoxazines) are a relatively small-market, high-performance class of composite resins that have outstanding thermal performance and excellent chemical and corrosion resistance.[18] This makes them excellent candidates for aerospace and automotive applications, particularly for high temperature tooling. Consistent with their excellent chemical resistivity, *benzoxazine-based FRPs are refractory to any of the deconstruction chemistry that has succeeded for us with epoxies*. This highlights a case of "different strokes for different folks": the chemistry of the benzoxazine matrix linkage is fundamentally an electrophilic alkylation of an aromatic ring by an iminium cation, rather than an epoxide opening. The susceptible linkage, therefore, is the aromatic aminomethyl group that results from alkylation. The chemistry of this group is fundamentally different than an alkyl aniline (in the case of epoxies) or an ester (as in the Hitachi process), so finding conditions for its efficient cleavage should logically require de novo chemical design suited specifically for the aminomethyl linkage.

Scheme 4. Benzoxazine Polymerization.

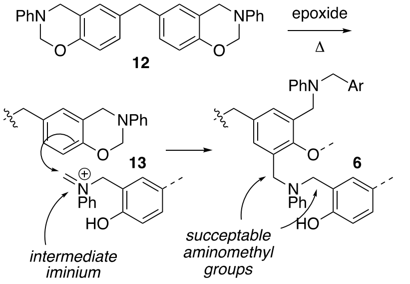


Figure 4. Homogenization of cured benzoxazine under oxidative conditions.

	H_2O_2	Oxone	CAN	$NaIO_4$
$RuCl_3$	0	0	98%	0
CuOAc	0	0	5%	0
CuI	0	0	5%	0
$KRuO_4$	0	0	5%	0

Table shows percent homogenization in a solution of aqueous trifluoroacetic acid. Oxone = $KHSO_5$; CAN = $Ce(NH_4)_2(NO_3)_6$.

We invented an approach to the disassembly of benzoxazine FRPs as sketched in Scheme 1C. The chemistry works by catalytic hydride abstraction. Like O-atom transfer, this is a catalytic oxidation process, but now instead of transferring an oxygen atom from reagent to polymer, we're transferring a hydride, hydrogen with two electrons, from polymer to reagent. Like the OAT approach above, this reaction will give a hydrolyzable imine group, which will disconnect in the same was as those we propose in epoxy FRP degradation.

Development of this new chemistry required experimental demonstration of several key points. Work in the complex molecules synthesis literature shows that *N*-aryltetrahydroisoquinoline derivatives undergo facile hydride abstraction and iminium formation,[19] we reasoned that the directly analogous benzoxazine matrices should have a similar oxidative path that we could use to initiate degradation and surmount their chemical resistivity. Observing that most known catalyst systems for such reactions involve a ruthenium or copper salt in the presence of a peroxide, we devised a small screen (Figure 4) to find optimal conditions for homogenization of a cured, solid benzoxazine matrix block. While traditional OAT reagents were ineffective, we were encouraged to see that a ruthenium-based catalyst will effect full homogenization of the resin in the presence of an excess of CAN, a cerium(IV)-based, single electron oxidant. This result teaches three key lessons: 1. It is possible to overcome the chemical inertness of benzoxazine. 2. A small molecule catalyst can affect bond cleavage reactions in or on the polymer mass without pre-permeablization. 3. Single electron transfer can affect turnover of the active catalyst, thus making electrolysis a plausible, sustainable electron acceptor for oxidative degradation of the resin.[3]

Our conditions for digestion of benzoxazine composites involve 1.3 M CAN and 0.05 mol % $RuCl_3$ in 50% aqueous trifluoroacetic acid at 80 ºC. Carbon fibers survive resin removal substantially undamaged under these conditions, even in the presence of a strong oxidant, Ce^{IV}. For example, we collected carbon fibers (Figure 5), which are undamaged and retain their long-range order, although optimization remains in our washing process. We were further able to identify the small-molecule product of degradation of the benzoxazine itself. By treating the solvent milieu resulting from FRP panel depolymerization with acidic methanol, we collected bis(phenol)F-2,2',6,6'-tetracarboxylate tetramethyl ester (**14**, Figure 6) as the primary resin degradation product. NMR data (primarily ^1H and ^1H-^{13}C HMBC) are in full agreement with this structure as the degradation product, with some pieces of the resin's plasticizing epoxide also visible.

Ongoing work in this area features the transition of the chemistry away from cerium as a stoichiometric oxidant in favor of electrolysis, using the composite's imbedded carbon fibers as an electrode.

Figure 5. SEM images of fibers recovered from CAN/$RuCl_3$ digestion.

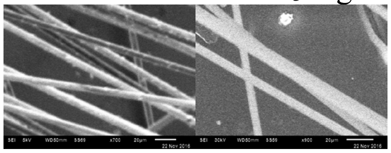
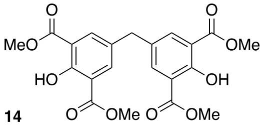


Figure 6. Depolymerized monomer **14**.



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4. CONCLUSIONS

Through these experiments we've shown how understanding chemical mechanism can lead to the discovery of new conditions for efficient and selective cleavage of CFRP thermoset matrices. Most importantly, the work exemplifies the importance of designing and matching the right conditions and molecular mechanisms to a particular thermoset polymer microstructure: when conditions are well-matched and well-tuned, selective cleavage of delicate monomers can be realized and useful organic materials can be recovered from the polymer cleavage.

Much work remains to be done in CFRP recycling, and molecular approaches such as those outlined here will play an important role. We look forward to seeing large scale chemical processes for selective production of valuable matrix recyclates and are excited to see how the market space will utilize these as new post-consumer resources.

4.1 Conflict of Interest

Williams and Navarro are part of a startup company, Closed Composites, which is working to commercialize composite recycling by oxidative catalysis.

4.2 Acknowledgement

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