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Recycling of Composites and Prepregs by Oxidative Catalysis

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In this project we demonstrate conditions to disassemble certain carbon fiber-reinforced polymer (CFRP) composites using oxidative catalysis. Particularly, the process described herein selectively exploits oxidative vulnerabilities in amine-linked epoxy-based CFRP matrices to enable the selective depolymerization of these thermoset polymer materials to return useful fine chemicals. Concurrently, because the polymer matrix is removed, imbedded carbon fibers are released, substantially undamaged. Such recovered carbon fibers (rCF) are potentially suitable for remanufacturing into new products of value in the DoD supply chain or the public market. The recovered fine chemicals resulting from disassembly of the polymer matrix are similarly suitable for remanufacturing.

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List of Acronyms

FRP	Fiber-reinforced polymer
CFRP	Carbon fiber-reinforced polymer
rCF	Recycled carbon fiber
H_2O_2	Hydrogen peroxide
NMP	1-methyl-2-pyrrolidone

Keywords

Composites, Recycling, Catalysis, Thermoset, CFRP

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Recycling of Composites and Prepregs by Oxidative Catalysis

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Abstract

In this project we demonstrate conditions to disassemble certain carbon fiber-reinforced polymer (CFRP) composites using oxidative catalysis. Particularly, the process described herein selectively exploits oxidative vulnerabilities in amine-linked epoxy-based CFRP matrices to enable the selective depolymerization of these thermoset polymer materials to return useful fine chemicals. Concurrently, because the polymer matrix is removed, imbedded carbon fibers are released, substantially undamaged. Such recovered carbon fibers (rCF) are potentially suitable for remanufacturing into new products of value in the DoD supply chain or the public market. The recovered fine chemicals resulting from disassembly of the polymer matrix are similarly suitable for remanufacturing.

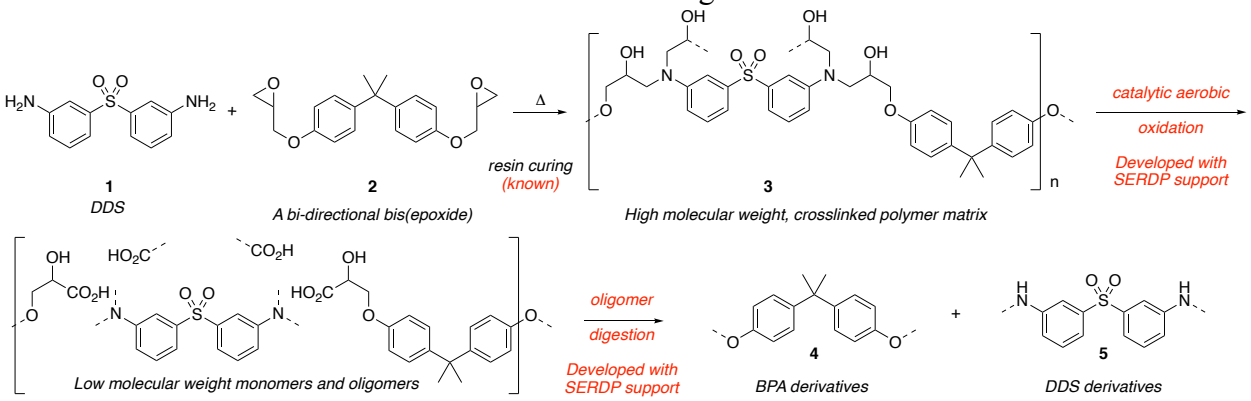
Project Objectives

As stated in the original project proposal, polymer composites are widely used across the defense services 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 FRP composite products*. At present, most composite waste is sent to landfills, often with attendant haz-mat disposal fees.

The widespread use of composites in defense applications has led to an urgent need for new strategies for the recycling of scrap and end-of-life composites. Moreover, developing catalytic reactions that will gracefully deconstruct cured FRP matrices will require the development of 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 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. Realizing this goal requires solving the problem of selective polymer cleavage using only sustainable reagents, and understanding the transport of catalysts, reagents, and products through the assembled composite material environment.

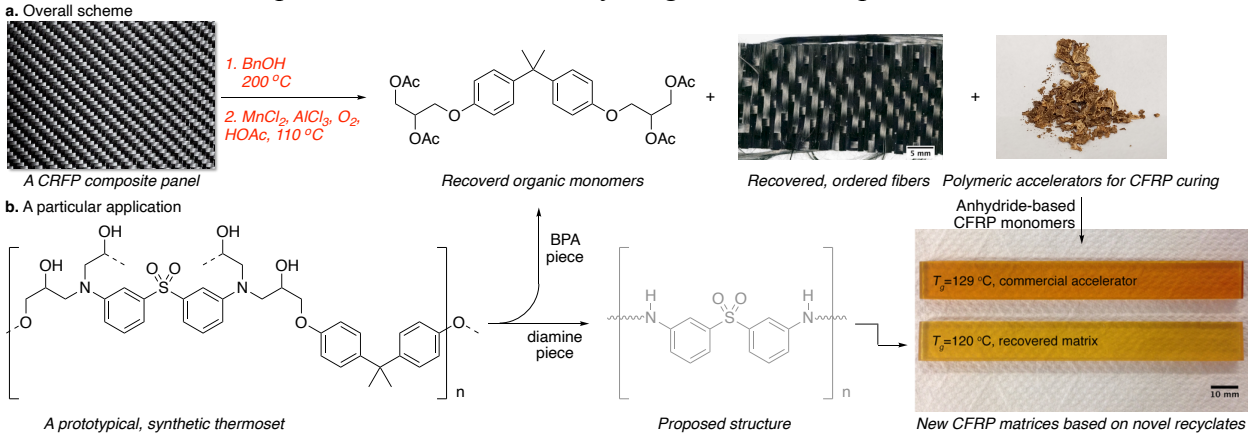
Technical Objective 1 – demonstrate use of *catalytic oxidation* selectively to disassemble thermoset epoxy matrices using sustainable reagents under mild conditions. At the outset of the project, we had identified conditions to deconstruct thermoset epoxy as shown in Scheme 1 based on hydrogen peroxide (H_2O_2).[2] With the aid of SERDP sponsorship, we have now shown that we can transition this reaction to O_2 as the oxidant, either by utilizing a molecular catalysis or a photocatalyst, which generates $^1O_2$.

Scheme 1. Chemical Structural Basis for Process Design.



Technical Objective 2 - Demonstrate effective re-isolation of engineered materials from oxidative degradation of CFRP matrices. We had previously demonstrated separation of carbon fibers from CFRP's with both epoxy and benzoxazine-based matrices.[3] We had shown that we could recover small molecules from polymer deconstruction, but that our best conditions for CFRP digestion either (1) did not drive the depolymerization reaction to full completion, and/or (2) degraded the isolable monomers that we wanted to recover. With the aid of SERDP sponsorship, *we have shown that we can collect both carbon fibers (in ordered sheets) and organic materials from the depolymerization of amine-linked epoxy-based CFRP composites*. The summary of our optimized scheme, using chemical catalysis for oxidation in this case, is shown in

Scheme 2. SERDP-Sponsored Solution to Recycling a Cured Composite Panel.

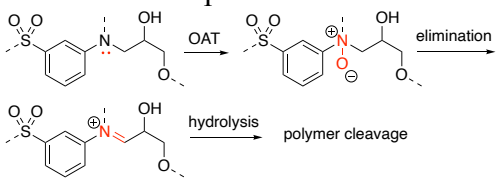


Technical Accomplishments

Key Starting Points

Our initial approach to depolymerizing CFRP epoxy matrices utilized oxidative degradation with H_2O_2, a variant of known procedures. Although a reasonable starting point, the disadvantages of this method include safety, cost, and sustainability of peroxide, over-oxidation of the polymer matrix, thus

Scheme 3. Molecular Mechanism for Cleavage of FRP Resins based on Amine-Cured Epoxies.



destroying the value in the polymer. Nonetheless, this was a useful start for the development of our catalytic methods. We pursued a mechanistic approach, which enabled an evidence-driven, hypothesis-based route to FRP resin deconstruction methodology. Our H_2O_2 conditions enabled key insights into the capability of the digestion. First, Scheme 3 shows the mechanistic model that we have developed for oxidative digestion of epoxy based CFRPs.[2] With this, we've proceeded to show catalytic aerobic conditions for the deconstruction of both epoxy-based composites.

We can recover pristine carbon fibers from digested FRP panels based on epoxy monomers. Figure 1 shows SEM images of virgin carbon fibers (left) and those that are re-isolated from a resin panel that was depolymerized by (center) solvolysis and (right) oxidative degradation. These data reveal that the strongly oxidative conditions of peroxide in acetic acid do not damage the fibers under conditions reasonable for depolymerization of a bi-directional resin.

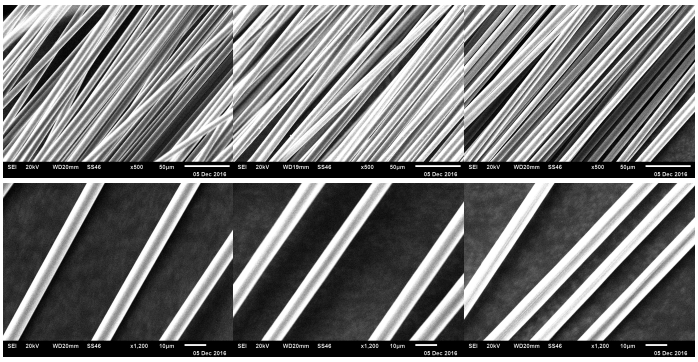


Figure 1. SEM images of carbon fibers that are (left) virgin, (center) recovered by solvolysis, and (right)

We next turned our focus to transitioning from H_2O_2 to O_2 (air), which avoids two disabling problems. 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. We then set about to develop oxygen atom transfer (OAT) conditions to affect polymer degradation *selectively*, and with *air as the oxygen source*. We showed that neat matrix blocks can be homogenized catalytically *using air as the terminal oxidant* when treated with catalysts for both OAT ($MeReO_3$)[4] and elimination ($ScCl_3$) steps in our mechanism. For example, 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 a catalyst for O-atom transfer from O_2. Further development of this observation enabled us to find conditions in which aluminum ($AlCl_3$) is the sole metal catalyst. Oxygen can be delivered as triplet O_2 at 10 atm pressure, or singlet (photoactivated) O_2 at ambient pressure. For example, treating fully cured composites with 10 atm of O_2 in place of 1 atm $O_2/MnCl_2$ removed the majority of the matrix, leaving behind fiber weaves for collection. We achieved better results by using photochemically generated singlet O_2 *at ambient pressure*. Thus, from a fully cured composite sample, singlet oxygen conditions enabled separation of the fiber plies, although each remained stiff and retained a portion of matrix. These experiments show the utility of $^1O_2$ photochemistry and may imply the importance of pressure in penetrating highly crosslinked matrices. This is a point that we propose to develop further with future sponsorship.

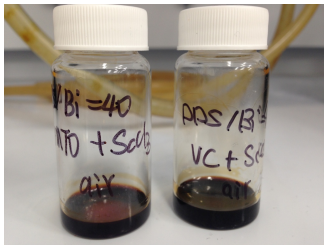


Figure 2. Amine-linked epoxy matrices are homogenized by catalytic air oxidation.

Key Success of SERDP Sponsorship: Aerobic Disassembly of a Cured CFRP

Presently we have demonstrated our ability to execute our process on a fully cured composite panel that we manufactured ourselves. 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 is readily re-used. This labialized material is then treated with our oxidative decomposition conditions. The conditions rely on O atom transfer to the matrix's linking N atom using one of (a) high pressure O_2 (ca 10 atm), (b) ambient O_2 and photolysis, or (c) OAT catalysis. Our mechanistic understanding for this process is shown in Scheme 3 above.[2] 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. The remaining liquid is pH-neutralized, which initiates precipitation of a colored polymer that accounts for about 10% of our mass. This material appears spectroscopically to be a polymer formed from hydrazine linkages formed to connect the diamine fragment when it is liberated from the matrix. We have shown that this can be re-manufactured into new composite resins for applications such as automotive parts (Scheme 2).[5] 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. We're still working out the separatory route for these materials; generally, we expect to crystallize out BPA, distill off solvent, and discard the remainder, probably ca 10% of the waste mass.

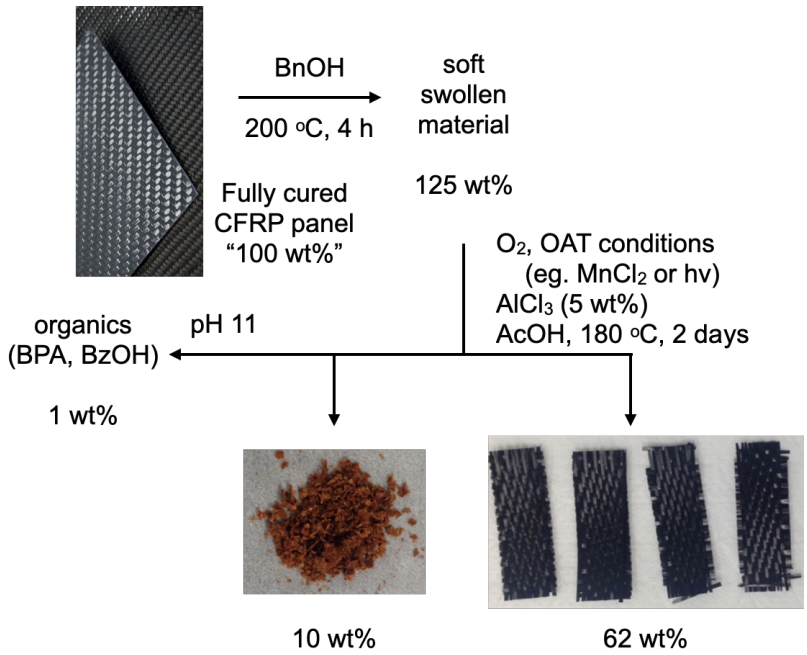


Figure 3. Schematic diagram of composite panel digestion. Mass balance indicated here were recorded in an experiment with 10 atm O_2, 5 mol% $MnCl_2$, and no photolysis.

To our knowledge, the scheme laid out in Scheme 3 is *the first known route to recover intact carbon fiber sheets from cured composite materials*. It is also the first approach that demonstrates recovery and upcycling of organic materials from amine-linked epoxy composite matrices. This is 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.

Efforts to Increase Diffusion Rate: New Pre-treatment Methods

The diffusion rate is a critical factor controlling the dissolution rate. As Scheme 2 indicates, the first step of our initial process is pre-treatment, which utilizes benzyl alcohol to permeabilize the CFRP samples to accelerate diffusion so reactant molecules can reach cleavable bonds more quickly. Figure 4 shows promising results of this strategy from our previous work[3]. However, this strategy requires processing times of 3-4 hours and relatively high temperature (200 ℃) to be effective, which potentially increases recycling cost.

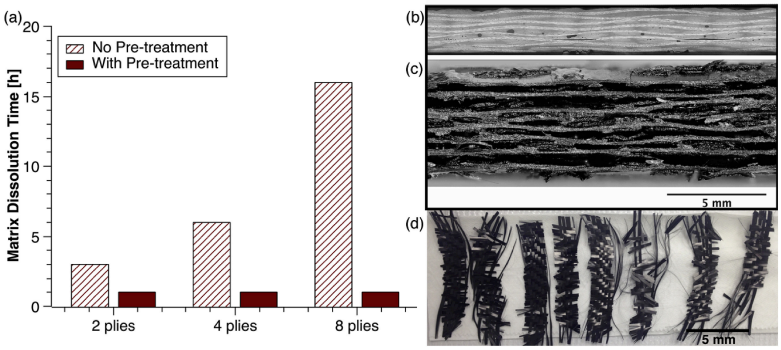
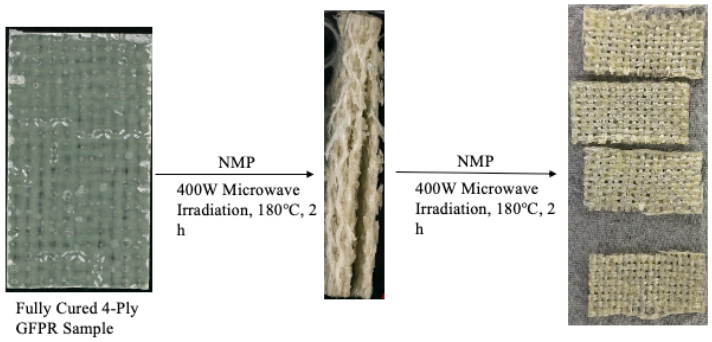


Figure 4. Effect of pre-treatment on CFRP sample dissolution rate via acid digestion (a), cross-sectional images of laminates (b) before and (c) after pre-treatment, and carbon fiber fabrics recovered from (d) an 8-ply laminate using acid digestion with pre-treatment.

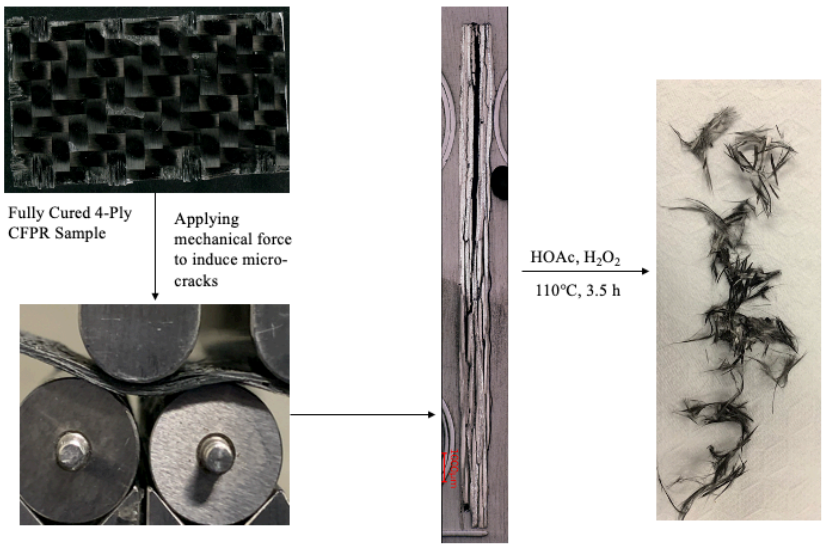
Microwave irradiation combined with polar solvents reportedly induces nano/micro-pores in epoxy networks[6], so in light of this, we subsituted 1-methyl-2-pyrrolidone (NMP) for benzyl alcohol and deployed a conventional microwave oven as a reactor so we could determine if solvents with higher polarity combined with microwave irradiation could provide a superior pre-treatment method. We swelled fully-cured, 4-ply glass fiber (GF) composite panels in the NMP solvent with microwave irradiation. Results indicated that high-polarity NMP solvent and microwave irradiation made pre-treatment more efficient (Scheme 4). All 4 layers of glass fiber sheets were separable after just 4 hours of treatment at a moderate temperature (180℃), a result of significantly increased diffusion rate. However, attempts to treat CFRP samples with microwave irradiation caused arcing, and could potentially damage carbon fibers. We are working to modify this method. Our goal is to overcome the arcing problem so that we can pre-treat CFRPs with microwave irradiation to accelerate subsequent oxidative degradation.



Scheme 4. Pre-treatment with Microwave Irradiation in NMP Solvent.

We also investigated mechanical loading to introduce micro-cracks into the composite matrix as a pre-treatment strategy. This method could reduce the total processing time and eliminate use of organic solvents. As shown in Scheme 5, fully cured, 4-ply CFRP laminates were subjected to severe flex deformation by the test fixture we made. We observed micro-cracks were introduced

in laminates. Subsequent acidic digestion results indicate that this treatment caused CFPR samples to delaminate during digestion, eliminating the limitation of diffusion rate. After mechanical pre-treatment, total processing time (3.5 hours dissolution) was less than in samples treated with organic solvents alone (4 hours pre-treatment +1 hour dissolution). However, this method also caused fiber damage, so we plan to modify this method to minimize fiber damage.



Scheme 5. Mechanical pre-treatment to accelerate matrix dissolution.

Applications to DoD Mission Effectiveness

Following on relationships forged at the 2019 SERDP symposium, we have initiated conversations with DoD stakeholders in the CFRP space. We had planned to make a visit to Dr. Ben Harvey at NAVAIR China Lake this spring to retrieve CFRP samples for which he had recycling needs. Unfortunately, that dialog has been completely sidelined by covid, and we are waiting for restrictions to open up in California so that we can pursue that need further. We have also opened a dialog with Dr. John La Scala at ARL (Aberdeen Proving Grounds), and we have arranged to receive representative samples from ARL of composite materials waste with which we can challenge our chemical recycling process. These will be sent when covid restrictions in Maryland allow.

Project Promotion

Under SERDP sponsorship, we have submitted a feature article entitled "A Structural Chemistry Look at Composites Recycling" to *Materials Horizons* (ISI 14.1 impact factor), which was solicited by invitation from the editors. This manuscript is in review. We are also preparing a review manuscript on chemical recycling of FRP thermoset composites for *Composites Part A*. We think it is important to accurately summarize the fragmented literature and present the state of the art for chemical recycling methods for the research community. SERDP sponsorship will be emphasized in this article.

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