DEVELOPMENT OF RAPID ELECTROLYTIC METHOD TO RECYCLE AMINE CURED EPOXY CARBON FIBER REINFORCED POLYMER COMPOSITES WITH METHYL RADICALS

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ABSTRACT

Carbon fiber reinforced polymer (CFRP) composites are uniquely essential materials in the aerospace, automobile, energy, sporting, and an increasing number of other industries. Consequently, we are amassing an accumulation of CFRP waste latent in value. Electrochemical techniques to recycle carbon fiber reinforced polymers have recently emerged as viable methods to remove the composite matrix from these materials and recover fibers. In many of these techniques, the composite is immersed in a solvent and acts as an electrochemical anode while a voltage is applied to the electrolytic cell. Still, few methods leverage the conductivity of the composite to mediate its own disassembly. We have introduced an electrolytic method that leverages this conductivity to electrolyze acetic acid to form methyl radicals that cleave the C-N bonds of the epoxy matrix and cleanly separate ordered fibers from the matrix. This talk will discuss the motivation and development for this new electrochemical method and explain the chemical mechanism through which it works.

Keywords: Recycling, Electrolysis, Epoxy
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1. INTRODUCTION

1.1 The Urgency of CFRP Recycling

Carbon-fiber reinforced polymer (CFRP) composites are characterized as exceptionally resistant to corrosion and tension while exhibiting high strength for its low weight.[1,2] These properties make them necessary materials for industries that greatly benefit from a high specific strength such as aerospace, automobile, and the renewable energy industries.[1,2] Most current aerospace CFRPs are made of a thermoset polymer that is prepared as a viscous resin that typically consists of bisepoxide monomers and a curing agent.[2] Upon heating, this resin undergoes an irreversible cure and converts that same viscous solution into a tough, rigid solid as shown in figure 1. Due to the irreversibility of the chemical cure reaction, CFRPs are notoriously difficult to recycle.[3,4] Even more alarming is the increasing mass of CFRP waste that is generated every year from large scale processes such as retiring wind turbines and from production scrap rates as high as 30% in the

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aerospace industry.[5] Over 24,000 tons of CFRP waste end up in landfills or are incinerated every year.[5] However, CFRP waste embodies latent value, because the production of carbon-fibers is an extremely energy-intensive process that involves 198-595 MJ/kg.[6] Therefore, recovering the CF fabric can significantly reduce the burden that CFRP production has on the environment.

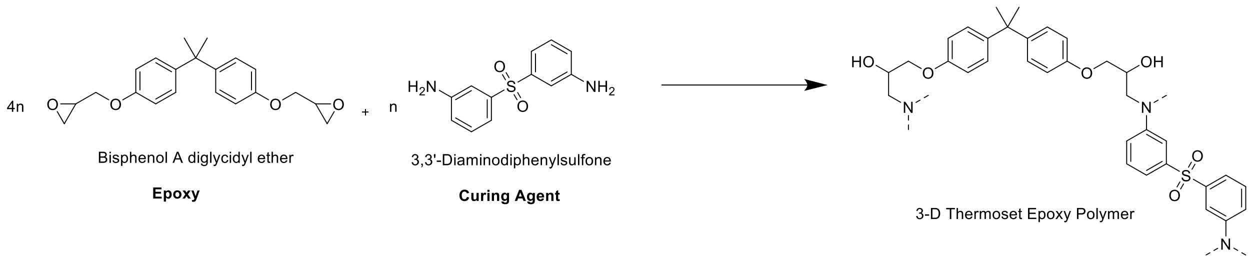

Figure 1. Typical epoxy and curing agent chemicals and mixing ratios.

1.2 Electrochemical Methods to Recycle CFRPs

There are two classes of electrochemical cells: galvanic and electrolytic.[7] The primary difference is that galvanic cells convert chemical energy into electrical energy by allowing a spontaneous oxidation reaction to occur at the anode. The electrons then flow, creating an electrical current, from the anode to the cathode where they are utilized in a reduction reaction. In an electrolytic cell, electrical energy is converted into chemical energy. The electrical potential applied to the cell will dictate which redox reaction that can take place. Application of an appropriate voltage enables nonspontaneous reactions to occur selectively.

1.2.1 Existing methods and limitations

CFRP electrochemical recycling methods do exist. These vary in the applied voltage, solvent, and electrolyte and ultimately result in different chemical mechanisms. Such differences in reaction chemistry result in variable quality of the respective recovered fibers and dictate the fragments of the polymer matrix that can be collected. Numerous methods employ a relatively high voltage to facilitate matrix cracking and delamination.[8,9] These techniques are successful in separating the matrix from the CF, but they reportedly used a voltage as high as 15 V and cause CF damage in the form of ruptures.[8] We disfavor such approaches, because such high potentials tend to destroy the polymer fragments of the matrix, thus obviating attempts to reclaim them, and damage the recovered fibers.

Other methods use a lower voltage and aqueous solutions to induce chemical reactions that cleave the polymer matrix.[10,11] In one system, investigators use an aqueous solution of 3% NaCl at an applied current of 4 mA, generating potentials as high as 2.6 V, but the system had a recycling rate of 33 μm/day and took up to 21 days to remove the epoxy matrix from the CFRP.[10] The investigators report that this system generates chlorine-based oxidants, which is consistent with the observation that increasing the electrolyte concentration results in chlorination and oxidation of the carbon fibers.[10]

Another method similarly uses an aqueous a 2% NaCl solution with dissolved KOH as a catalyst.[11] In this system, a current density of 3.33 A/m^2 was applied and the voltage ranged from 2.5 to 3.1 V. They report fast degradation and complete removal of the epoxy matrix, within 36 hours.[11] The report also includes the use of chlorine-based oxidants, but carbon fibers recovered therefrom suffer damage from oxidation and hydroxide intercalation, which result in swelling and increase in surface roughness.[11]

Further, we have reported methods utilizing cerium(IV) as a soluble surrogate for electrolysis. While this approach enables provocative mechanistic studies, its practicality is limited to being a step between homogeneous catalysis and electrolysis.[12]

All these techniques are intriguing, because they use the CFRP as an electrochemical anode and they all successfully separate the CF from the epoxy matrix. However, like much of the current literature, none of these reports establish the chemical mechanism that degrades the epoxy matrix. Furthermore, none endeavors to study the utility of carbon centered oxidants such as radicals to cleave the epoxy matrix. A carbon-based oxidant is strategically appealing, as it would obviate chlorination or oxidation of the recovered CF.

1.3 Proposed Method

Similar to incumbent technologies, our method utilizes minimally toxic and readily available chemicals. To avoid chlorination of CFs, we electrolyze diluted acetic acid to generate methyl radicals as the active oxidant in our system. This reaction is known as Kolbe electrolysis,[13] as shown in figure 2. Upon single electron oxidation of the carboxylate anion on the anodes surface, the intermediate radical undergoes decarboxylation to yield CO_2 and an alkyl radical. In the case of acetic acid, the alkyl radical is a methyl radical.

To deploy this reaction in CFRP recycling, we use an electrolytic cell with the CFRP as the anode and a solvent mixture of diluted aqueous acetic acid and NaCl. In this design, the anode will generate methyl radicals near its surface. These will not diffuse far from the carbon fiber electrode, because methyl radicals will oxidize the epoxy matrix rapidly, converting it to soluble polymer fragments, and will be consumed rapidly by acetic acid if they escape from the proximity of the CFRP.

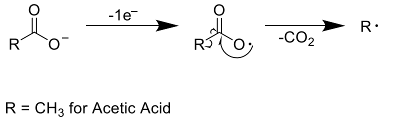

Figure 2. Kolbe electrolysis of the generation of alkyl radicals from carboxylic acids.

2. EXPERIMENTATION

2.1 General Procedures

Synthetic details for CFRP electrolysis were originally published elsewhere; [Ref 1, Supporting Information] some additional details and adaptations are described here.[1] All synthetic procedures were conducted in a chemical fume hood with exposure to air, unless otherwise indicated. Deuterated NMR solvents were purchased from Cambridge Isotopes Laboratories. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was supplied by Supelco. Unless otherwise specified, chloroform and all reagents (including sulfuryl chloride and AIBN) are commonly available from major commercial suppliers (Sigma-Aldrich, Merck, Fischer Scientific, TCI America, Acros Organics) and used without further purification. Dichloromethane, acetonitrile and hexanes are purchased from VWR and dried in a J. C. Meyer solvent purification system with alumina/copper (II) oxide columns; dichloromethane was dried by vacuum transfer from a calcium hydride suspension. Deionized water was purified in-house using a deionizer cartridge (Philadelphia Scientific).

NMR spectra were recorded on a Varian Mercury 400, Varian VNMRS 500, or VNMRS 600, spectrometer and processed using MestReNova. All chemical shifts are reported in units of ppm and referenced to the residual 1H or 13C solvent peak and line-listed according to (s) singlet, (bs) broad singlet, (d) doublet, (t) triplet, (dd) double doublet, etc. ^{13}C spectra are delimited by carbon peaks, not carbon count. Air-sensitive NMR spectra were taken in 8" J-Young tubes (Wilmad or Norell) with Teflon valve plugs. Mass spectral data were acquired on an Agilent 6545 LC-QTOF instrument with electrospray set to positive ionization.

Pre-impregnated resin-fiber substrate materials, "prepregs" were fabricated in house or sourced from Solvay according to specified procedures. Cured CRFP panels were cut with a water jet cutter (ProtoMAX) as described. Electrolysis was mediated with a Hanmatek HM310P potentiostat.

2.2 Preparation of Amine-Cured Epoxy CFRP Panels

Epoxy equivalent weight (EEW) and amine hydrogen equivalent weight (AHEW) were used to calculate the mixing ratio of amine/epoxy. A resin of CFRP-A was formulated using the bifunctional epoxy diglycidyl ether of bisphenol A (17.95 g, EEW = 187 g/eq, Araldite GY 6010, Huntsman) and tetra-functional amine curing agent (6.05 g, 3,3′-diaminodiphenyl sulfone, AHEW = 63 g/eq, Aradur 9719-1, Huntsman). The mixing ratio of amine/epoxy was 100% (molar). After hand mixing epoxy and amine for 10 mins, the mixture was transferred into a vacuum oven (set at 120 °C) to vacuum degassing. After 10 mins, the mixture became clear and homogenous. A resin film was then prepared by spreading liquid resin onto a 203 x 203 mm release film (Airtech, Release Ease 236 TFNP), preheating at 50 °C on Wabash hot press. Prepreg was fabricated using 2 X 2 twill weave CF fabrics (FiberGlast 1069-B). One resin film was attached to each side of the CF fabric. Then, the stack was heated and pressed using a hot press at 50 °C with 20 kPa pressure for 1 min. CFRP-A panels were then laminated via a vacuum bag-only process (VBO) using 4 plies of prepreg. The curing cycle was (1) 1.5 °C /min to 120 °C, (2) hold at 120 °C for 3 hrs, (3) 1.5 °C/min to 180 °C and (4) hold at 180 °C for 3 hrs. Fully cured CFRP-A panels were then cut to 50.8 x 10.2 mm using a water-jet cutter. CFRP-B panels were fabricated using 4 plies of aerospace-grade VBO prepreg (Solvay CYCOM 5320-1, T650, PW). The cure cycle was (1) hold at 60 °C for 2 hrs, (2) 1 °C/min to 120 °C, (2) hold at 120 °C for 2 hrs, (3) 1.7 °C/min to 177 °C, and (4) hold at 177 at 120 °C for 2 hrs. Fully cured CFRP-B panels were cut into 50.8 x 10.2 mm or 76.2 x 38.1 mm samples on a water-jet cutter.

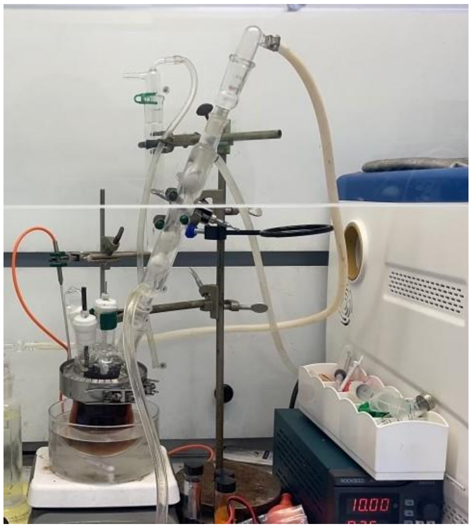

Figure 3. Electrolysis vessel during a reaction.

2.3 Reaction Development and Optimization

A CFRP sample was clamped by a PTFE (Teflon) platinum electrode holder and connected to a DC potentiostat as the anode, while a graphite rod served as the cathode as pictured in figure 3. The electrodes were immersed in the electrolyte solution containing acetic acid (AcOH), NaCl, and DI water with an attached condenser. Optimization experiments were performed under fixed amperage so that the rate of each trial was comparable.

Optimal conditions were found to be 11.6 M AcOH and 1 M NaCl. These conditions yielded the cleanest fibers within the quickest time. During these trials, the voltage fluctuated between 4-5 V as seen in figure 4.

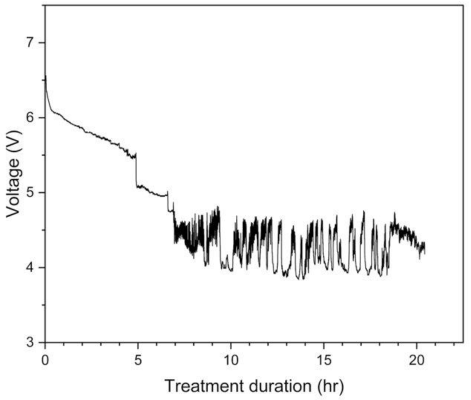

Figure 4. 11.6 M AcOH and 1 M NaCl fixed amperage trial displaying voltage change over time.

During the first five hours of the process, it appears that the insulative material of the polymer requires a higher voltage once the process initiates. Upon removing that insulative barrier the conductive carbon fiber has enough contact with the solvent that oxidation of acetate ions here should be appropriate. Therefore, we believe the operating voltage to induce reactive radicals is 4 volts. The variation in voltage is likely due to the charge capacitance in the CFRP. This stops upon sufficient matrix removal.

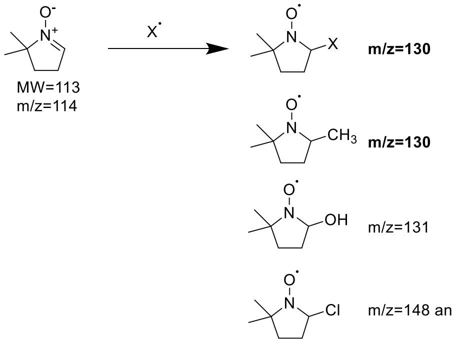

Figure 5. DMPO radical trap experiment. Here the captured radical adduct produces the same signal as the methyl radical adduct.

2.4 Methyl Radical is the Active Oxidant

To identify the active oxidant in our system we prepared an experiment employing the radical spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO). A spin trap is a molecular tool that is used to react with radicals to form a stable radical adduct that can be identified in mass spectrometry (Figure 5). In this experiment we are capturing the active radical in our system and recording the signal the radical adduct produces in mass spectrometry. This signal appears at m/z = 130. We then ran a series of control experiments in which we treat DMPO with a methyl radical, hydroxyl radical, and chlorine radical and record each of their respective mass spectra. Based on these data, only the methyl radical-DMPO adduct signal matches the one acquired from CFRP electrolysis. The experiments were prepared as follows.

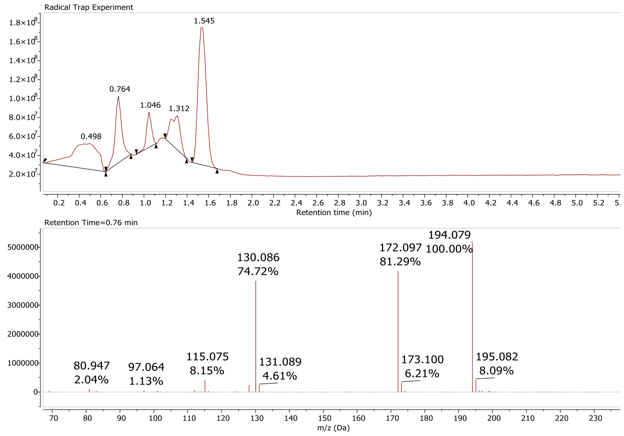

Figure 6. Acquired spectrum of captured radical from electrolysis set up.

2.4.1 Electrolysis radical capture experiment

In a 4-neck 75 mL electrolysis vessel, acetic acid (10 mL, 17.4 M) and NaCl (876.6 mg, 1 M) were dissolved in deionized water (5 mL). The electrolysis apparatus was assembled as described above, except a CF fabric was used as the anode instead of a CFRP composite and a voltage of 4 V was applied. The vessel was flushed with argon gas and allowed to react for 5 minutes. The solution was then heated to 65 °C and DMPO (15.0 mg, 31.3 µmol,8.84 mM) was added. A sample aliquot was collected after 60 minutes. Figure 6 shows the acquired mass spectrum. *The experimental radical adduct generated from the CFRP has a m/z = 130.*

2.4.2 Methyl radical positive control

In a 5 mL oven dried round bottom flask were combined acetonitrile (1.0 mL) and ditertbutylperoxide (7.0 mg, 38 µmol). The solution was heated to 130° C, then after two minutes DMPO (10 mg, 8.9 µmol) was added into the solution (8.85 mM). A sample was taken after 20 minutes and analyzed in mass spectrometry shown in figure 7. Here the methyl radical adduct signal matches the acquired signal in the electrolysis set up. The following positive control experiments were still performed to confirm the identity of the radical is the methyl radical.

2.4.3 Hydroxyl radical positive control

In a 10 mL oven dried round bottom flask were combined H_2O_2 (5.0 mL, 10 mM aq) and copper(II) chloride (400 µg, 3.0 µmol) to make [Cu] = 0.6 mM. Hepes buffer (Alfa Aesar), solid, 3.0 mg, to make 2.5 mM) was added into the solution. The resulting solution was stirred for two minutes at room temperature before DMPO (15 mg, 130 µmol, to make 27 mM) was added. An aliquot was recovered for analysis after 45 minutes. The acquired mass spectrum is shown in figure 8. It is apparent that the DMPO hydroxyl radical adduct produces a signal of m/z = 131.

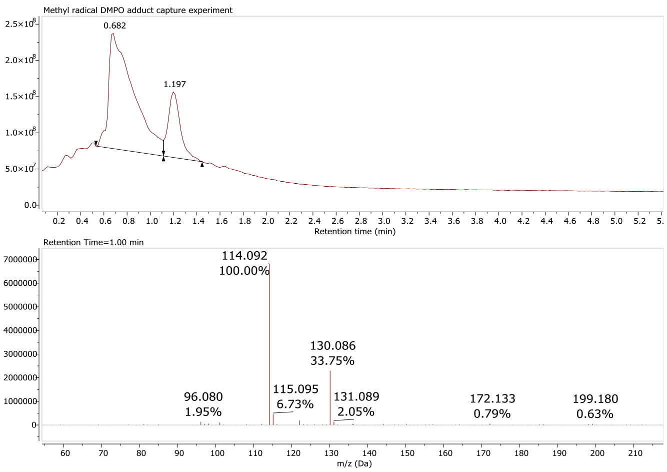

Figure 7. Acquired spectrum of methyl radical DMPO adduct.

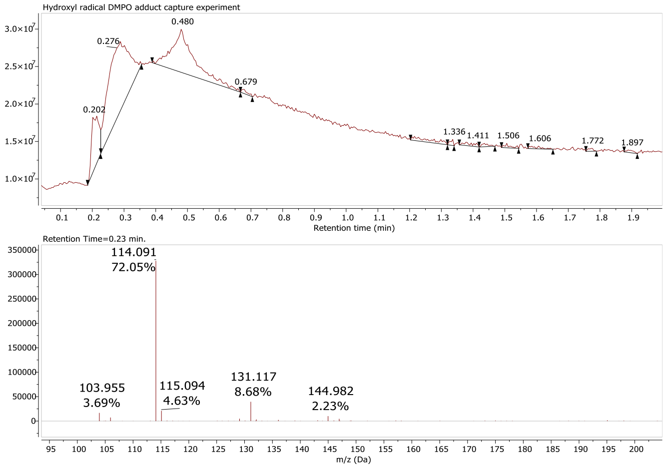

Figure 8. Acquired spectrum of hydroxyl radical DMPO adduct.

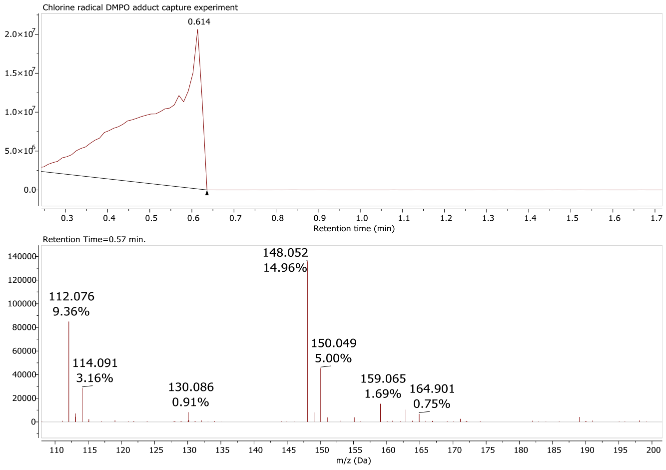

Figure 9. Acquired spectrum of chlorine radical DMPO adduct.

2.4.4 *Chlorine radical positive control*

In a 25 mL oven dried round bottom flask were combined chloroform (10 mL), sulfuryl chloride (2.0 mL, 25 mmol, 2.5 M), and azobisisobutyronitrile (AIBN, 10 mg, 61 µmol). The vessel was purged with nitrogen, a condenser was attached, and the solution was heated to 55 °C. After two minutes DMPO (15 mg, 13 µmol, 13 mM) was added. An aliquot was recovered for analysis after 20 minutes. The acquired mass spectrum is shown in figure 9. The major signals for the chlorine adduct are m/z = 148 and 150 and is observed at an appropriate isotopic abundance for chlorine.

2.5 Identifying the Sites of Bond Cleavage based on Small Molecule

A model of the epoxy polymer, Bu_4DDS (figure 10), was synthesized and exposed to our electrolysis conditions. In our glass electrolysis vessel were combined acetic acid (10.0 mL, 17.4 M) in water (5.0 mL) and NaCl (877 mg, 1M). A voltage of 4 V was applied, then Bu_4DDS was added (30 mg, 4.2 mmol, to make 64 µM). The solution was heated to 65 °C for 60 minutes before the first sample was collected. After 120 minutes, a second sample was collected. The voltage was disconnected 5 minutes thereafter.

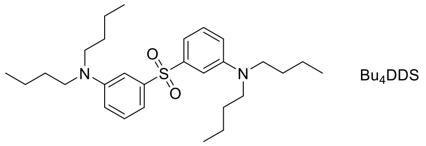

Figure 10. Small molecule matrix model.

Figure 11 displays the stacked acquired NMR spectra of pure Bu_4DDS, Bu_4DDS in the electrolysis for 1 hour, and Bu_4DDS in the electrolysis for two hours. It is shown here that the characteristic C-N signal for Bu_4DDS at δ = 3.3 ppm decreases in intensity while there is a corresponding rise of a signal at δ = 2.99 ppm. The rise of a signal at δ = 2.99 ppm is appropriate for the chemical shifts of dealkylated Bu_4DDS. This is evidence of C-N bond cleavage.

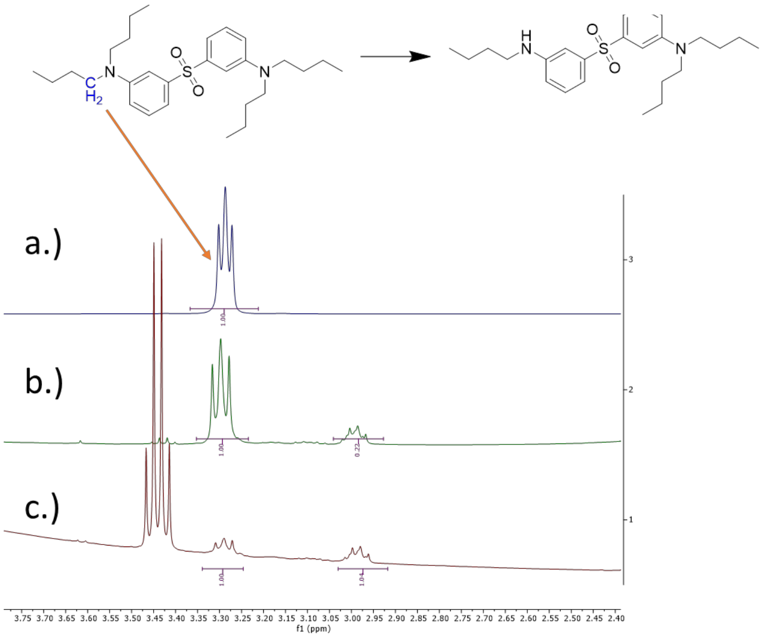

Figure 11. Degradation study of Bu_4DDS: (a): Pure Bu_4DDS (b): Bu_4DDS in electrolysis conditions for 1-hour (c): Bu_4DDS in electrolysis conditions for 2 hours.

2.6 Recycling of Carbon Fibers in Second Generation Composites

Recovered CF weaves (44.4 x 38.1 mm) and in-house formulated resin were used to remanufacture CFRPs. Loose fibers were removed or organized from the recovered weaves. Then, a layer of resin was applied to the recovered CF fabric using a brush, and a new ply of CF fabric is placed on top. The process was repeated for all 4 plies in the laminate using a vacuum bag-only process. The curing cycle was (1) 1.5 °C /min to 120 °C, (2) hold at 120 °C for 3 hours, (3) 1.5 °C/min to 180 °C and (4) hold at 180 °C for 3 hours.

2.7 Soluble Polymer Fragments

Upon its completion, the reaction leaves a dark solution containing soluble polymer fragments. Ideally, these should be converted to high value recyclates, like fine chemicals and monomers for new resin systems. These electrochemical polymer fragments can be extracted directly from the reaction solution by adding $CHCl_3$ to the completed aqueous reaction solution. A liquid-liquid extraction then enables collection of the organic layer, containing the desired polymer fragments. This material can be dried over $MgSO_4$, and the solvent is easily removed by rotary evaporation. The extracted organic residue has a ^{1}H NMR as shown in figure 12. This reveals significant disorder among the products of polymer cleavage, but the persistence of sharp peaks at 25 °C indicates that this product assortment contains small molecules. To date, we are still working to develop technology to convert these materials to useful monomers.

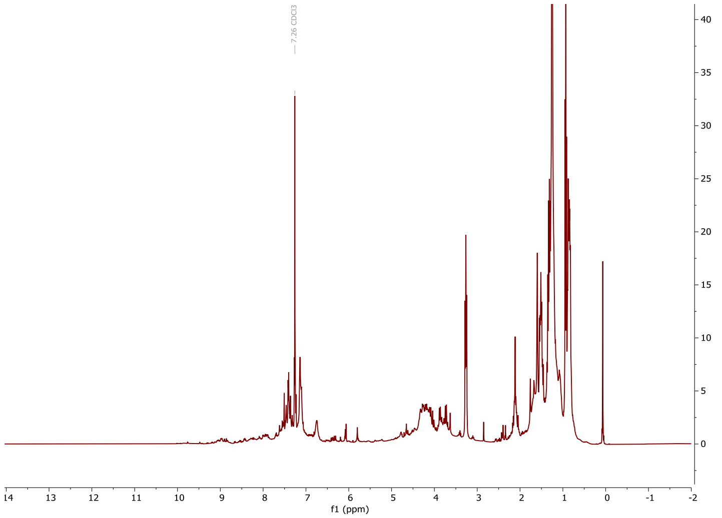

Figure 12. Chloroform extract of soluble organics from electrolysis.

3. RESULTS

3.1 Proposed Mechanism

The radical trap experiments confirm that the signal of m/z = 130 corresponds to the signal of the methyl radical DMPO adduct. Therefore, the active radical in our electrolysis set up is the methyl radical. Then from the small molecule study, we were able to confirm that this system does C-N bond cleavage. Therefore, we propose this mechanism for epoxy polymer bond cleavage shown in figure 13.

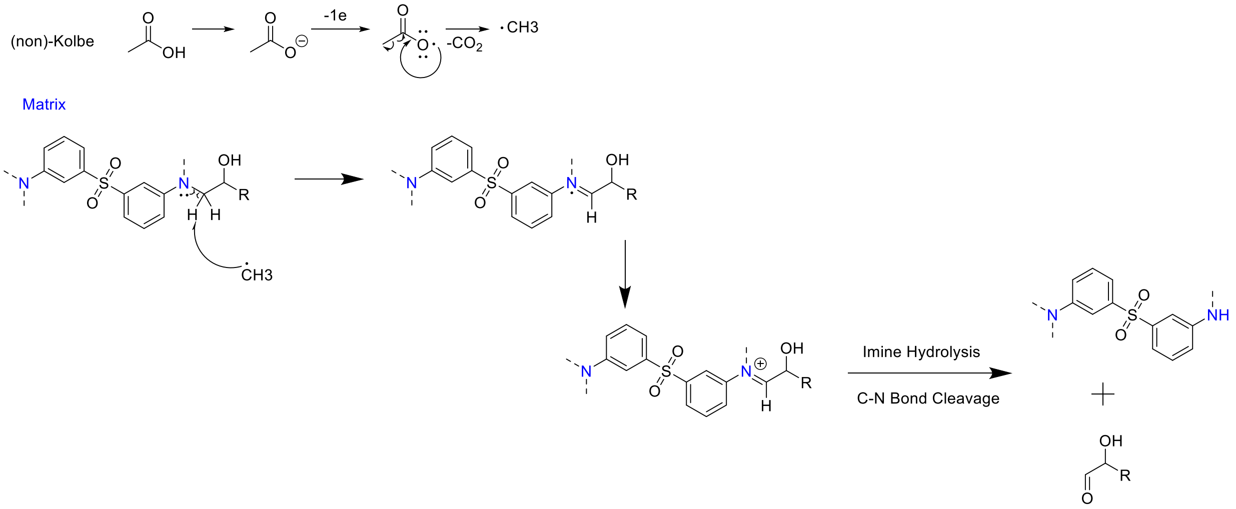

Figure 13. Proposed mechanism of epoxy polymer degradation by methyl radicals.

4. CONCLUSIONS

Our electrolysis technology is designed to take advantage of the electrolytic cell and generate a novel, rapid, and sustainable way to recycle CFRP composites. Here our optimal conditions in the electrolysis set up is to use 11.6 M AcOH, 1 M NaCl, and apply a voltage of 4 V. Based on our spin trap experiments this technique will unleash methyl radicals. From the small molecule study, it is apparent that the methyl radicals will oxidize and cleave the epoxy polymer matrix and break C-N bonds. While we have shown isolation and remanufacturing of the resulting carbon fiber fabrics, much work remains to reclaim value from the isolated polymer fragments cleaved from the CFRP matrix.

4.1 Conflict of Interest

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

4.2 Acknowledgement

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