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COMMUNICATION

Fiber and Monomer Recovery from an Amine-Cured Epoxy Composite Using Molten NaOH-KOH

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We report a rapid route to reclaim carbon fiber (CF) fabric and monomeric chemicals from amine-epoxy CF-reinforced polymer (CFRP) composites. We use a reaction that occurs in molten NaOH-KOH eutectic to selectively cleave aryl ether and amine linkages, which involves two temperature-dependant mechanisms. Bisphenol-A is isolated in up to quantitative yields, and recovered CF fabric is remanufactured into 2nd-generation CFRPs.

Carbon fiber-reinforced polymer (CFRP) composites comprise carbon fibers (CFs) embedded in a polymer matrix. They exhibit exceptional strength-to-weight and stiffness-to-weight ratios, and fatigue resistance, making them excellent for aerospace applications. The carbon fiber market is expected to grow at a rate of > 8% annually, and the demand is expected to outstrip the global supply by 2030.[1] In recent years, composite recycling has garnered increasing attention because of the value that can be reclaimed from the composite matrices and fibers. However, thermoset CFRPs used in aerospace manufacturing are cured irreversibly, rendering the matrix insoluble/inert and presents a challenge for recycling. Recent advances in solvolysis have opened promising routes to recover both fibers and monomers from CFRP waste:[2, 3] in fact, we previously introduced oxidative processes to recover clean fibers from benzoxazine[4] and amine-epoxy CFRPs.[5-10] These methods respectively enable the recovery of bisphenol F tetracarboxylate via hydride abstraction[4] and bisphenol A (BPA) via oxygen atom transfer.[6] The academic community's interest in CFRP recycling is also growing, as we've witnessed an increase in composite recycling publications in just the last year. Some of these approaches accomplish full dissolution of the matrix, but most struggle with the collection of organic monomers.[11] While many technologies exist to recover oligomeric/polymeric material from composite matrices, our interviews with resin manufacturers indicate that the market will only appreciate known, existing monomers as matrix recyclates. This is necessary (1) to fully characterize the materials, (2) to assure manufacturers of product consistency, and (3) to drop into existing supply chains.

A major advancement in amine-cured epoxy CFRP recycling was the introduction of hydroxide-based methods.[12-16] We find hydroxide-based strategies to be particularly interesting, because of their ability to remove the matrix from the fibers and the potential to recover monomeric chemicals in high yields. Herein, we introduce a new hydroxide-based, solvent-free method that is the first to recover both CF fabrics and organic monomers: BPA and for the first time the linking diamine. Compared to the current state of the art, as summarized in Table S1, this method eliminates the flammability and explosivity risks associated with organic solvents under pressure (e.g., toluene, THF, and dioxane)[12, 13, 16] at high temperatures. Furthermore, higher temperature techniques (< 340 °C)[14, 15] have resulted in the degradation of organic products, and conversely, lower temperature techniques (160-190 °C) take up to 24 hours to complete while being unable to recover amine recyclates from thermoset composite substrates.[12, 13, 16] Our method is advantageous because it can recover clean fibers and monomers efficiently (220°C, 0.5 hours), thus reducing energy costs,[12, 13] and does not require the use of metal catalysts, therefore avoiding the threat of resource depletion.[16] Additionally, the ability to recover both BPA and diamines provides a valuable economic incentive.

Our process enables near-quantitative recovery of BPA from an aerospace epoxy composite (T_g > 175 °C) with concurrent collection of the linking diamine in high yields (59%). In the case of a diamine with a sulfone bond such as 3,3'-diaminodiphenylsulfone (3,3'-DDS), the collected amines

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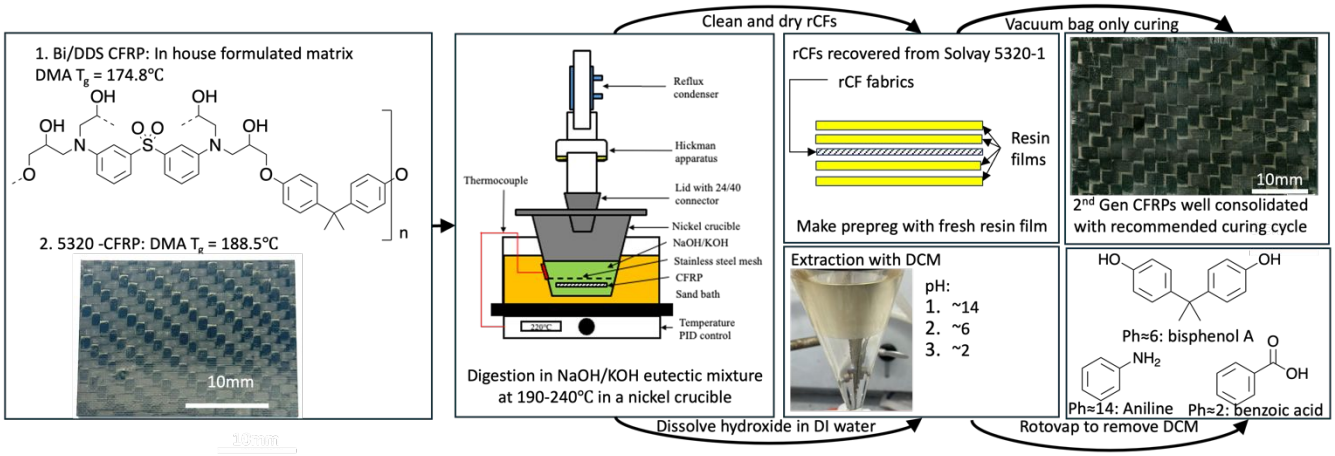


Scheme 1 NaOH-KOH eutectic recycling process for recovering and reusing CFs and monomeric chemicals from amine-epoxy CFRPs

consist of aniline and 3-aminophenol. Finally, we demonstrate that the recovered fibers can be used to produce second-generation CFRPs. Key findings from this study reveal an unreported 1,2-hydride shift during matrix degradation, conservation/recovery of the diamine monomer, and characterization of the surface chemistry of recovered fibers and understanding how that impacts the loss in short beam shear strength (SBS) of second-generation composites.

We tested our method on two separate CFRPs: first, Bi/DDS panels (T_g = 175 ℃) produced using a resin formulated in-house, comprising the diglycidyl ether of bisphenol A (DGEBA) and 3,3'-DDS (Scheme 1). Second, 5320-1 CFRP laminates (T_g = 189 ℃) were produced from commercial resin films (Solvay 5320-1) to demonstrate our method on aerospace material. Once fully cured, Bi/DDS and 5320-1 CFRPs were cut to coupons for digestion.

We use a 1:1 (mol) NaOH-KOH eutectic that serves as a solvent and reagent to accomplish CFRP matrix cleavage. The eutectic leverages a relatively low melting point (170 ℃), low volatility, and high reactivity.[17] In preparation, CFRPs produced from Bi/DDS are treated with an organic solvent to swell the matrix. Benzyl alcohol was selected as the pre-treatment solvent due to its effectiveness in swelling and environmental friendliness (Section 3a, SI). After pretreatment at 185 ℃ for 5 hours, Bi/DDS CFRPs are then digested using NaOH-KOH eutectic in a 100 mL nickel crucible equipped with a Hickman distillation head (Scheme 1). Reactions were performed at 190-240 ℃ for 15 minutes to 7 hours in a PID-controlled sand bath (section 3b(SI) and Table S5). Then, CFs were washed, dried, and weighed to calculate the matrix conversion (Table S6). We found pretreatment has a profound effect on the matrix dissolution rate as the matrix decomposition ratio of the pretreated CFRPs is greater than that of untreated ones (Table S6, entries 1-8, and Figure S5). We then compared matrix dissolution rates after three hours and found the effect is more apparent at lower temperatures: 89% vs. 6% at 190 ℃ and 99% vs. 47% at 240 ℃. We rationalize the efficacy of benzyl alcohol pretreatment as causing matrix swelling and extensive delamination of the composites (Figure S3), thus facilitating hydroxide diffusion between plies and accelerating matrix digestion. We then determined the treatment duration of the pretreated Bi/DDS CFRPs at different temperatures to be 7 hours at 190 ℃ to 15 minutes at 240 ℃ (Figure S6), and therefore selected 220 ℃ for 30 min as our optimized conditions for its reasonable duration, preservation of CF properties, and milder temperature.

CF fabrics can then be readily recovered and compared to virgin fabrics using SEM, XPS, and tensile tests. Based on SEM images (Figures 1, S10, and S11), the recovered CFs appeared clean and undamaged. XPS C(1s) spectroscopy shows that the C-O concentration on CF surface decreased, indicating diminution of the sizing functionalities of the fibers, as shown in Figure 2. As expected, an XPS surface elemental composition study (Table S8) showed that hydroxide treatment decreases the O/C ratio. Single-fiber tensile strength data (Figures S14, Tables S9-S14) showed that the recovered CFs retain > 92% of the strength and > 99% modulus of the virgin material.

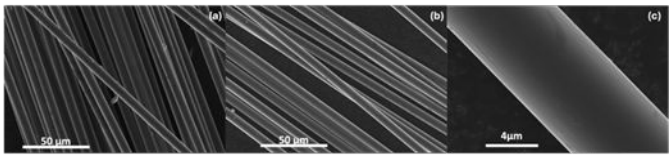


Figure 1 SEM images of fresh (a) and recycled CFs at 220℃ (b,c)

After examination of the fibers, we used the recovered fabrics as substrates to produce 2nd generation CFRPs. Figure S8 illustrates the remanufacturing process with CF fabric recovered from a 5320-1 CFRP: first, 5320-1 samples (50.8 x 38.1 mm) are digested in 140 g NaOH-KOH eutectic mixture (20 hrs, 220 ℃). Recovered CF fabrics are washed successively with acetone, deionized water, and dimethyl sulfoxide. After drying, fabrics are combined with fresh Solvay 5320-1 resin film and cured. Cross-sections of the resulting second-generation CFRPs were polished and examined with a microscope, showing complete consolidation (Figure S9) and demonstrating the viability of direct remanufacturing of CF fabric from molten NaOH-KOH conditions. Table S7 shows SBS test results of remanufactured and first-generation 5320-1 CFRPs. SBS values of remanufactured 5320-1 CFRP decreased by 23.7% compared to first-generation, indicating weaker adhesion strength between resin and recycled CFs. This is consistent with the

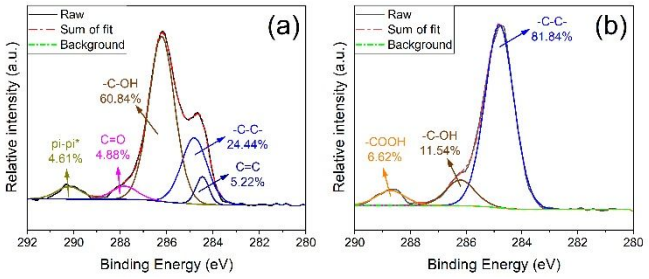


Figure 2 XPS C(1s) high resolution spectra of fresh (a) and recycled CFs at 220 ˚C (b)

diminution of sizing functionality, as observed by XPS. However sizing can be restored by nitric acid treatment.[18, 19]

We then analyzed the matrix depolymerization products, which enabled us to develop a monomer recovery procedure (Scheme 1 and Figure S15) for bisphenol A, benzoic acid, aniline, and 3-aminophenol. In the case of pretreated CFRPs, a pH-controlled extraction from the post-digestion melt provides bisphenol A (86% molar yield). The hydroxide digestion of untreated CFRPs (250-280 ℃, Table S21) gives bisphenol A (92-99%), aniline (< 30%), and 3-aminophenol (< 37%). ^{1}H NMR spectra of the crude products, as isolated by simple extraction, are shown in Figure 3. Although this separation procedure works well, note that the proposed technique consumes a considerable amount of water, acid, and/or hydroxide. To address this concern, we demonstrate ion exchange chromatography as an alternative strategy to isolate BPA (Section 8, SI). Ion exchange chromatography has proven to be advantageous in this situation, because it minimizes the amount of water and acid needed to isolate BPA, while enabling up to 91 mol% recovery of hydroxide (Table S18), determined by titration (section 8, SI).

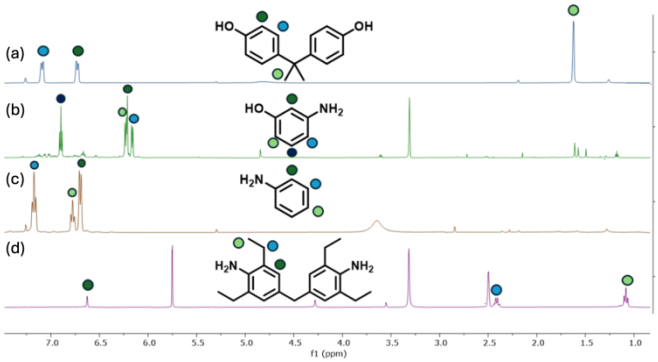
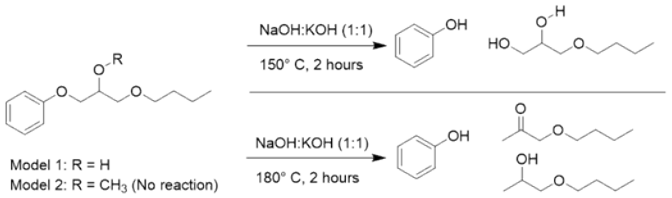
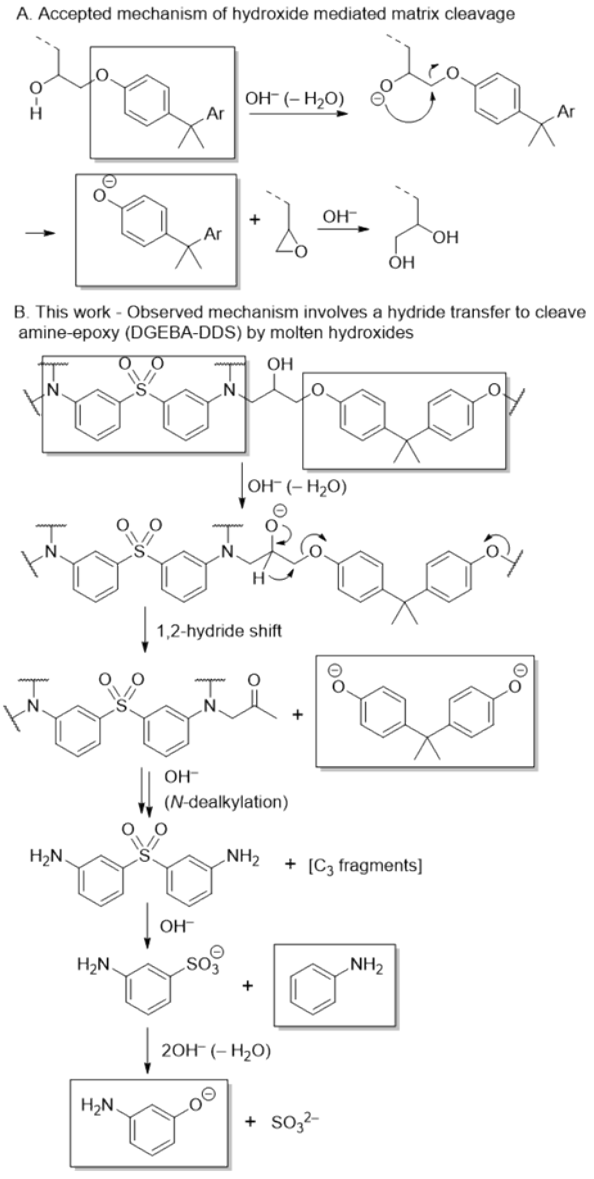


Figure 3 ^{1}H NMR spectra of isolated BPA (a), 3-aminophenol (b) and aniline (c) from unpretreated Bi/DDS sample digestions and MDEA (d) from Bi/MDEA digestion

To account for the formation of BPA, we explored the possibility of three chemical mechanisms: an intermediate epoxide (recently characterized independently by Skrydstrup and Beckham),[12, 13] E2 elimination, or a 1,2-hydride shift (Scheme 3). A model degradation study was conducted to probe this with our conditions. We found that reactivity between Model 1 and NaOH-KOH is consistent with two of the possible mechanisms: intermediate epoxide[12, 13] and 1,2-hydride shift. Formation of 3-butoxypropane-1,2-diol (detected by LC-MS, Figure S59) from Model 1 at 150 ℃ favors the epoxide-mediated step. However, at higher temperature (180 ℃), Model 1 generates 1-butoxypropan-2-on, suggesting the 1,2-hydride shift path. The presence of the ketone was confirmed with the annotated ^{1}H NMR, ^{13}C NMR, HMBC, and HSQC data in section



Scheme 2 Degradation of model compounds with NaOH-KOH



Scheme 3 Hydroxide-driven cleavage of CFRP matrices

11b of the SI. Additionally, no reactivity was observed with the *O*-methylated Model 2 (180 ℃). This finding highlights the necessity of the intermediate alkoxide for aryl ether cleavage

and diminishes the likelihood of an E2 path. We then rationalize the formation of amine products such as aniline and 3-aminophenol from a hydroxide-driven *N*-dealkylation of 3,3'-DDS and aryl sulfone bond cleavage. Also, the absence of 3,3'-DDS in the matrix digest is consistent with the known instability of sulfone groups to molten hydroxide.[20, 21] We then performed an experiment to confirm the instability of the sulfone by putting 3,3'-DDS under molten hydroxide conditions. Here we observed that upon heating to 190 ˚C, the sulfone was not conserved (Section 13, SI). To achieve recovery of the diamine monomer at respectable yields we recommend recycling thermoset systems without sulfone bonds. We demonstrate this in Sections 2c and 3f (SI) by manufacturing and depolymerizing a resin system cured by the diamine monomer 4,4'-methylenebis(2,6-diethylaniline) (MDEA). In this experiment, we confirmed that diamines without sulfones can be conserved (^{1}H NMR, ^{13}C NMR, MALDI, Figure S39-43) and recovered at high yields (59%, Table S22). The ^{1}H NMR spectra of the recovered diamine is shown in Figure 3. Finally, simple extraction of the pretreated reaction's acidic compounds reveals the presence of benzoic acid which can be explained by apparent hydroxide-driven benzyl alcohol dehydrogenation left over from pretreatment.[22]

In sum, this work accomplishes recovery/remanufacturing of CF fabric from aerospace composites and recovers monomers from the matrix itself. This method selectively deconstructs DGEBA-DDS/MDEA matrices to saleable monomeric units, BPA, aniline, 3-aminophenol, and MDEA. The efficient reaction degrades pretreated CFRP matrices fully within 30 minutes. Recovered CFs retain their woven architecture and tensile strength (> 92%). Despite changes to the surface chemistry of the recycled fiber fabric, we show the remanufacturing of rCF sheets isolated from hydroxide-based matrix cleavage. SBS of second-generation CFRPs were then characterized. Furthermore, we show mechanistic variation in chemical polymer cleavage depending on temperature, an insight that we are presently working to exploit.

Conflicts of interest

Williams is the founder of Closed Composites, a start-up aiming to commercialize composite materials recycling.

Data availability

The data supporting this article have been included as part of Supplementary Information.

Acknowledgement

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Data availability

The data supporting this article have been included as part of Supplementary Information.