Recovery and Reuse of Acid Digested Amine/Epoxy-Based Composite Matrices

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Abstract: Chemical recycling of thermoset composites has been focused largely on recovering high-value carbon fibers with property retention, while recovery and reuse of decomposed polymer matrix residues is generally overlooked, despite the fact that matrix recycling constitutes an essential component of a sustainable approach to the overall problem. Our previous study demonstrated that oxidative acid digestion can be deployed effectively to recover near-virgin quality carbon fibers from amine-cured epoxy composites. In the present study, we investigate the viability of recovery and reuse of the decomposed amine/epoxy residue after acid digestion of the matrix, effectively closing the recycling loop. We find that polymer matrix residues recovered from acid digestion solutions via neutralization and precipitation contain molecular components of the epoxies in which aromatic regions are preserved. The recovered matrix residues are blended into virgin resin formulations and two approaches are evaluate for potential reuse. Approach I utilizes the matrix residue as an accelerator for a virgin anhydride/epoxy formulation that contains no accelerator and thus cannot be self-catalyzed. We discover that adding matrix residue produces catalytic effects on the curing reaction. In general, anhydride/epoxy samples blended and cured with recovered matrix residues are homogenous and exhibit thermal and mechanical properties comparable to specimens cured with a commercial accelerator. Approach II deployed the matrix residue as a filler for virgin anhydride-

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based epoxies with a commercial accelerator to produce blended formulations. In such cases, blended formulations yielded acceptable retention of thermal and mechanical properties, provided the fraction of matrix residue added did not exceed 10 wt%.

Key words: Recycling; Reuse; Acid digestion; Composites; Epoxy; Resin formulation

1. INTRODUCTION

The increasing use of carbon fiber-reinforced polymer (CFRP) composites poses severe environmental problems. Presently, most end-of-life CFRP material is sent to landfills because there is no process technology for sustainable recycling. This issue is expected to escalate as the market for CFRPs expands [1]. Current composite recycling methods focus on recovery and reuse of the carbon fibers (only), typically by incorporating into molding compounds or stitched mats for second-use applications [2-5]. Polymer matrices in CFRPs can be of substantial value, yet they are far more difficult to recover than fibers, and few have attempted to develop reuse approaches for matrices. The absence of viable reuse routes for polymer matrices generates new sources of waste after recycling/re-use of carbon fibers, especially for recycling methods that require the use of chemical reagents.

Pyrolysis is presently the most widely used recycling method for CFRPs in industry, because the process leverages existing technology, and composite materials with various matrices are readily incorporated. Through pyrolysis, composite matrices are decomposed into lower molecular weight components at 450-700 °C. The lower molecular weight organics are burned in a combustion chamber, allowing the energy produced to be captured and reused as a supplementary energy source for pyrolysis. However, the value recovered from polymer matrices through combustion is trivial. Furthermore, data show that high temperatures can lead to fiber degradation. Pyrolysis can reduce the tensile strength of recovered fibers and leave char residue on fiber surfaces [6]. Thermal processing in air can eliminate the char residue but it also affects the mechanical properties of the fibers. Study showed that at optimum oxidization conditions, ~80% of tensile strength and modulus could be preserved [7]. Consequently, recent effort has focused on developing chemical recycling approaches that recover residue-free fibers with > 90% tensile strength retention [8-22]. Chemical recycling by selective depolymerization enables recovery of both high-quality carbon fibers and a processable mixture of solvents, catalysts, and cleaved matrix residues from which further value can be recovered. Fully utilizing such mixtures obviates adverse environmental impact, opens new fine chemical feedstocks, and increases the overall process sustainable.

Efforts to develop strategies for reuse of decomposed polymer matrix residue after chemical recycling of CFRPs have been reported in the literature. For example, Okajima et al studied mixtures of decomposed polymer matrices and virgin epoxy resins [16]. The matrices for recycling and for mixing with matrix residues were both anhydride-based epoxies, with triethylamine as the promoter. They reported that the strength of the blended polymers decreased linearly as the ratio of matrix residue increased. The addition of the decomposed matrix product had to be reduced to < 20% to retain 80% flexural strength. Liu et al also reported mechanical properties of recycled anhydride/epoxy resin prepared by degradation products obtained from anhydride-cured epoxies at different KOH concentration under subcritical methanol conditions [17]. They repoerted that compared to virgin resins, all the samples from recycled epoxy resins presented a higher flexural modulus. The flexural strength of recycled resins was comparable to that of the virgin resin at a certain KOH concentration (0.09 mol L^{-1}). Secondly, Liu et al investigated mixing decomposed polymers from amine- and anhydride-cured epoxy composites in anhydride/epoxy systems (with an accelerator) [18-19]. They reported that the glass transition temperature (T_g) and flexural strength of the mixed epoxy first increased as the amount of the decomposed matrix loading increased, then decreased. The flexural strength of mixed resins with < 15 wt% decomposed amine/epoxy matrix loadings and with < 40 wt% decomposed anhydride/epoxy matrix loadings were greater than or similar to virgin polymer samples. Similar trends were reported by Dang et al when mixing the neutralized matrix extracts from amine-cured epoxy composites in anhydride-cured epoxies [20]. The flexural strength of the blended resins was evaluated for different decomposed matrix contents, typically at 5-30 wt%.

When decomposed matrix residues are used as fillers in virgin resin formulations, the resulting polymers have shown acceptable properties, provided the mixing ratios are suitably low. However, the matrix residues recovered from CFRPs are not reused as an essential component of anything. Thus, to increase sustainability, reuse approaches for matrix residues must be developed. Moreover, the reaction mechanism for oxidative acid digestion differs from the methods reported in previous studies, leading to recovery of matrix residues with distinct molecular structures and functional groups. Consequently, the matrix residue reuse protocols for acid digestion warrant further evaluation and adjustment.

In previous studies, we demonstrated recovery of near-virgin-quality carbon fiber fabrics/arrays from amine-cured epoxy composites using oxidative acid peroxide digestion at atmospheric pressure [23-25]. The reaction mechanism for acid digestion was identified, and target catalysts were evaluated to accelerate the reaction rate [26]. In the present study, we focus on recovering the decomposed matrix residues after oxidative acid digestion at atmospheric pressure and demonstrating the feasibility of reusing the matrix residue as value-added components in virgin resin formulations, effectively closing the recycling loop with minimal downcycling. Such reuse strategies may also be applied to amine/epoxy matrix residues recovered from other recycling methods.

The decomposed polymer matrix residues preserved bisphenol A structures from the acid digestion solution and the residues were recovered via neutralization and precipitation. Two potential reuse approaches were investigated, including (a) reuse as an accelerator and (b) as a filler for virgin resin formulations. We demonstrated that the matrix residue can effectively catalyze the curing reaction of an anhydride/epoxy formulation without an accelerator. The flexural properties of anhydride-based epoxies samples cured with the matrix residue were comparable to samples cured with the commercial accelerator. We also showed that the matrix residue can be implemented as fillers for anhydride-cured epoxies with a commercial accelerator, yielding blended polymers with retention of thermal and mechanical properties.

2. EXPERIMENTS

2.1. Digestion of amine-epoxy matrices

Amine/epoxy resin formulations. A bi-functional epoxy monomer (diglycidyl ether of bisphenol A (DGEBA), Figure 1 (a), Huntsman) and an amine curing agent (diamine 3,3’-diaminodiphenyl sulfone (3,3’-DDS), Figure 1 (b), Huntsman) were selected for amine-epoxy formulations. The mixing molar ratios for amine hydrogen/epoxy groups (Amine/Epoxy ratio) were 40% (1:7.5 by weight) for neat epoxies and 100% (1:3 by weight) for composite laminates. Note that industry uses various mixing ratios, thus testing matrices with various crosslink density is necessary. Neat epoxies were cured in a convection oven using a cure cycle consisting of a 1.5 °C/min ramp to 250 °C, followed by a dwell for 0.5 hour. Composite laminates were cured using a cure cycle consisting of a 1.5 °C/min ramp rate, a 120 °C dwell of three hours, another 1.5°C/min ramp rate, and a post-cure at 180°C for three hours. Figure 1 (c) shows the crosslinked structure of amine-cured epoxy matrices. After cure, the two types of samples, neat epoxies (ca. 40 × 20 × 1 mm, pieces cut from Figure 1 (e)) and composite laminates (100 × 20 × 1 mm, Figure 1 (d)) were subjected to oxidative acid digestion.

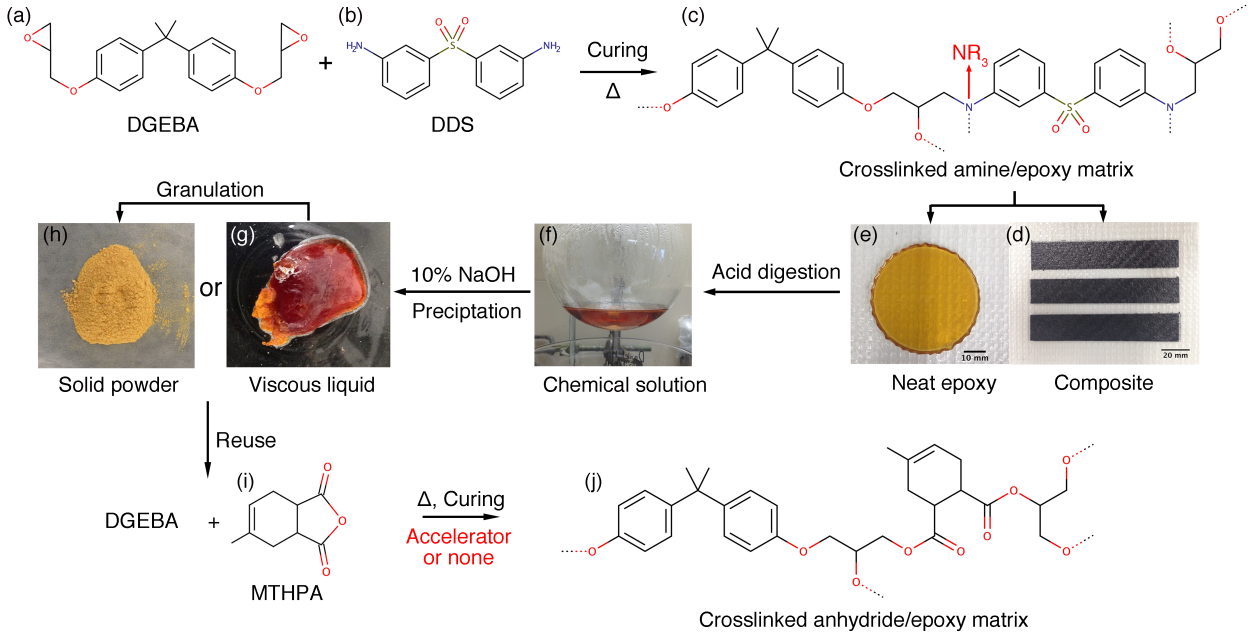

Figure 1. Recycling and reuse of amine-cured epoxy matrices.

Oxidative acid digestion. Oxidative acid digestion was performed at 110 °C using a solution of 100 mL glacial acetic acid (EMD Millipore) and 5 mL H_2O_2 solution (30 % (w/w) in H_2O, EMD Millipore). 6 g of composites or neat resin was treated for each reaction batch. Additional H_2O_2 solution (5 mL) was added to the flask every hour. The reaction times for neat epoxies were 1h (full dissolution) and 4h (over-reacted). The reaction time to reach full dissolution for composite laminates was 4 h. After reaction, the chemical feedstock (Figure 1 (f)) was neutralized using a 10%

sodium hydroxide aqueous solution. Viscous liquid or solid powder residues (Figure 1 (g)) were subsequently obtained through precipitation. The recovered viscous residues contained traces of acetic acid, which were removed by granulation and washing in water, yielding solid powder residues as well (Figure 1 (h)). After precipitation, matrix residues were further washed in water and dried at room temperature overnight for reuse. The matrix recovery rate was ca. 25% by weight. Note that matrix residues could also be recovered from solution by evaporating all the acetic acid solvent. However, the matrix residue recovered via evaporation contained much more acetic acid solvent than matrix recovered via neutralization and precipitation and was difficult to reuse in virgin resin formulations.

2.2. Reuse of decomposed matrix residues

To reuse recovered matrix residues, specific amounts of the materials were added to virgin anhydride-based epoxy formulations (Figure 1 (i)) and manually mixed at 100 °C until homogenized. Recovered matrix residues were more compatible with anhydride/epoxy systems than amine/epoxy systems because of the existence of acetic acid solvent.

Two reuse approaches were explored in this section. In Approach I, we reused recovered matrices as an accelerator for anhydride/epoxy formulations. Bi-functional epoxy (DGEBA)/Anhydride systems without an accelerator generally have low reactivity (Supplementary Figure S1 (a)), and thus the curing must be carried out in the presence of Lewis bases (such as tertiary amines) to catalyze the reaction [27-28]. In contrast, tri- (triglycidyl of para-aminophenol (TGAP)) and tetra- (tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM)) functional epoxy/anhydride systems contain tertiary amines in the epoxy monomers, and thus are self-catalyzed during cure (Supplementary Figure S1 (b) and (c)). Material recovered from amine-cured epoxies contain tertiary amines, and potentially these can be used as accelerators for the aforementioned anhydride-cured bi-functional epoxies. Therefore, anhydride/DGEBA resins without a commercial accelerator were formulated to evaluate the feasibility of using recovered amine/epoxy matrices as an accelerator. The molar ratio for anhydride/epoxy groups was 100% (9: 10 by weight). In Approach II, we reused recovered amine/epoxy matrices as a filler for anhydride/DGEBA formulations with a commercial accelerator (1-methylimidazole, Huntsman). The molar ratio for anhydride/epoxy groups was also 100%. The mixing ratios of recovered matrices ranged from 2.5-10 wt% in Approach I, and 5-10 wt% in Approach II.

2.3. Characterization

Characterization of recovery products was performed using multiple techniques. Modulated differential scanning calorimetry (MDSC, TA Instruments Q2000) was performed to analyze the cure reaction and the glass transition temperature (T_g) of epoxy samples after cure. Nuclear magnetic resonance spectroscopy (NMR) was used to determine the chemical structures of the recovered polymers after chemical treatment. The dried sample was dissolved in deuterated organic solvents, filtered through cotton to remove insoluble solids, and analyzed by NMR. Fourier-transform infrared spectroscopy (FTIR, Nicolet 4700) was used to monitor the crosslinking progress by observing of the peak of the oxirane ring. Flexural strength and modulus of virgin matrix and recovered matrix samples were measured by four-point bending at room temperature (Instron 5567) with a 500 N load cell following ASTM D6272-17 [29]. The epoxy sheets were cured using a cure cycle consisting of a 1.5 °C/min ramp rate, a 120 °C dwell of three hours, another 1.5 °C/min ramp rate, and a post-cure at 180 °C for three hours. Test specimen dimensions were 110 × 12.7 × 3.2 mm. Five specimens were tested for each condition.

3. RESULTS AND DISCUSSION

3.1. Recovered epoxies

Figure 2 shows that derivatized species of the glycidyl ether of bisphenol A are identified only in the one-hour digest. The ^{1}H-^{1}H homonuclear correlation spectroscopy (COSY) spectrum of the one-hour digest in acetonitrile-d_3 (Supplementary Figure S2) supports structural assignments and the conclusion that more than one para-substituted compound is present. The GC-MS data reported previously [25] also showed the existence of the bisphenol A structure in the dissolution products, confirming that the aromatic structures of the epoxies were preserved during dissolution. From the eight-hour sample, milligram quantities of 3,3'-dinitrodiphenyl sulfone were isolated, formed by the oxidation of 3,3'-diaminodiphenyl sulfone liberated during digestion. This conclusion was also supported by the ^{13}C NMR spectrum of 3,3'-dinitrodiphenyl sulfone obtained from the eight-hour digest (Supplementary Figure S3). These results indicate organic monomers liberated from the C-N bond cleavage continue to react and eventually decompose to low-value, small molecule organic compounds under the reaction conditions. Milder reagents are necessary to prevent over-oxidation of derivatized organic monomers.

We conclude from these observations that the recovered residues obtained after oxidative acid digestion contain bisphenol A from the epoxy monomer and tertiary amines from the amine-epoxy curing reaction. Thus, these components can be added to virgin epoxy formulations as accelerators and/or fillers for reuse. However, longer digesting times progressively decompose the matrix into smaller organics, reducing the value of the recovered components. Therefore, sustainable chemical recycling must not only focus on reclaiming high quality fibers, but also on recovery of useful matrix components for second-use.

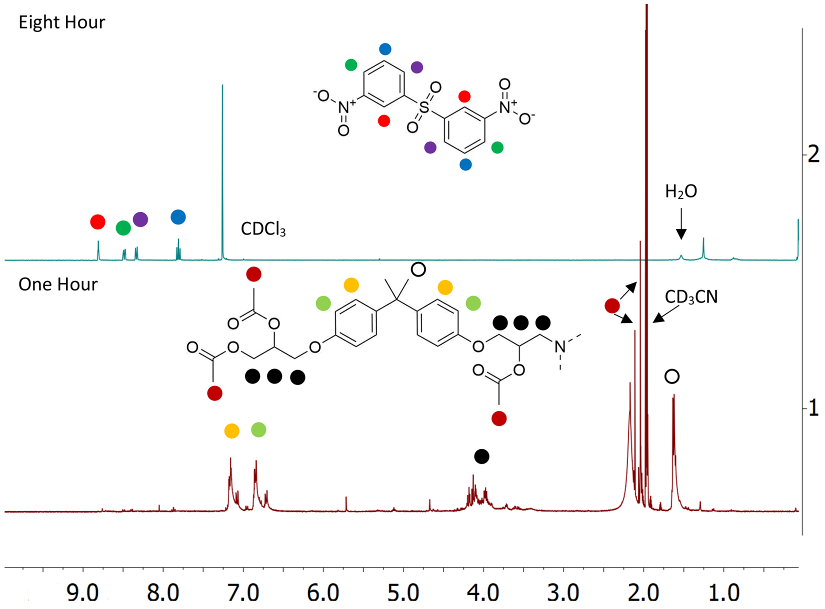

Figure 2. Stacked ^{1}H proton spectra of the one-hour (bottom) digest in d3-acetonitrile and eight-hour (top) digest in deuterated chloroform. A mixture of derivatized bisphenol A compounds containing terminal acetate esters or tertiary amine groups is predicted for the one-hour digest.

3.2. Reuse Approach I: as accelerators for anhydride/epoxy formulations

Table 1 summarizes the reactivity of the matrix residues recovered from amine-cured epoxies when used as an accelerator for anhydride-based bi-functional epoxy formulations (without a commercial accelerator). In the absence of accelerators, no exothermic chemical reaction occurred, as expected. The T_g of the epoxy with no accelerator was -40 °C after the cure cycle, confirming that the resin remained uncured. When 1 wt% commercial accelerator was added, the peak of the curing reaction occurred at 118.9 °C, and the total heat of the reaction was 311.1 J/g, yielding a cured epoxy with T_g = 126.8 °C.

When the commercial accelerator was replaced with recovered matrix residues, the curing reaction was also initiated. As the amount of the matrix residue increased, the peaks of reaction

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decreased, because a greater concentration of tertiary amines provided more reactive sites. However, the T_g and the heat of reaction of the cured epoxy first increased as the amount of the matrix residue increased, then decreased. The initial increase in T_g was attributed to the higher crosslink density resulting from an increase in tertiary amine sites. The subsequent decrease in T_g occurred when the mixing ratio reached 10 wt%, which was attributed to a greater concentration of non-reactive small molecules and short-chain polymers. Figure 3 illustrates the degree of cure as function of temperature for resin with a commercial accelerator and with various matrix residue contents. We observed that for resins with a commercial accelerator and with various matrix residue contents, the curves of degree of cure developed in similar patterns, indicating comparable cure kinetics from an accelerator and matrix residues despite their differences in peak reaction temperatures. Recovered matrices from composite laminates were also evaluated and compared with neat epoxy. Data showed that at the same mixing ratio, the cured T_g values with those two materials were comparable, indicating that the existence of fiber reinforcement did not significantly affect the properties of recovered matrices.

Table 1. Assessment of using matrix residues as an accelerator for anhydride/epoxy formulations

Accelerator		Peak of Reaction [°C]	Heat of reaction [J/g]	Cured T_g [°C]
Material	Ratio			
None	0	/	/	-40
Commercial accelerator	0.5 %	118.9	311.1	126.8
Matrix residue (from neat epoxies, Amine/Epoxy = 40%)	2.5 %	182.1	209.1	113.1
	5 %	170.9	222.3	114.7
	7.5 %	155.3	268.5	112.0
	10 %	159.9	218.3	103.6

Matrix residue (from composite, Amine/Epoxy = 100%)	5%	158.64	290.7	108.3

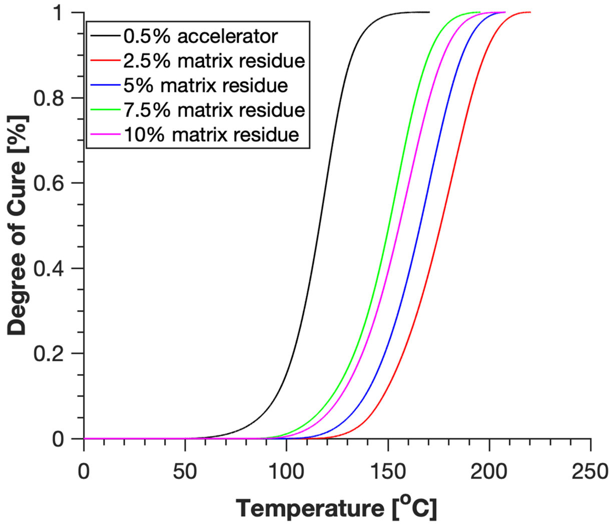

Figure 3. Degree of cure as a function of temperature for resin with a commercial accelerator and with various matrix residue contents.

Based on the peaks of reaction, heats of reaction, and cured T_g values, the optimal mixing ratio for reusing matrix residues as an accelerator in virgin anhydride-based epoxies was 5% by mass. Figure 4 shows the representative heat flows and T_g curves for anhydride/epoxy samples without an accelerator, with 0.5% commercial accelerator, and with 5% matrix residue. To verify the repeatability of these data, three anhydride/epoxy samples with 5% matrix residue loading were prepared and analyzed. The peaks of reaction, heats of reaction, and cured T_g values were 170.5 ± 0.9 °C, 255.8 ± 29.2 J/g and 117.2 ± 7.5 °C, respectively, indicating that the findings were repeatable within normal measurement bounds.

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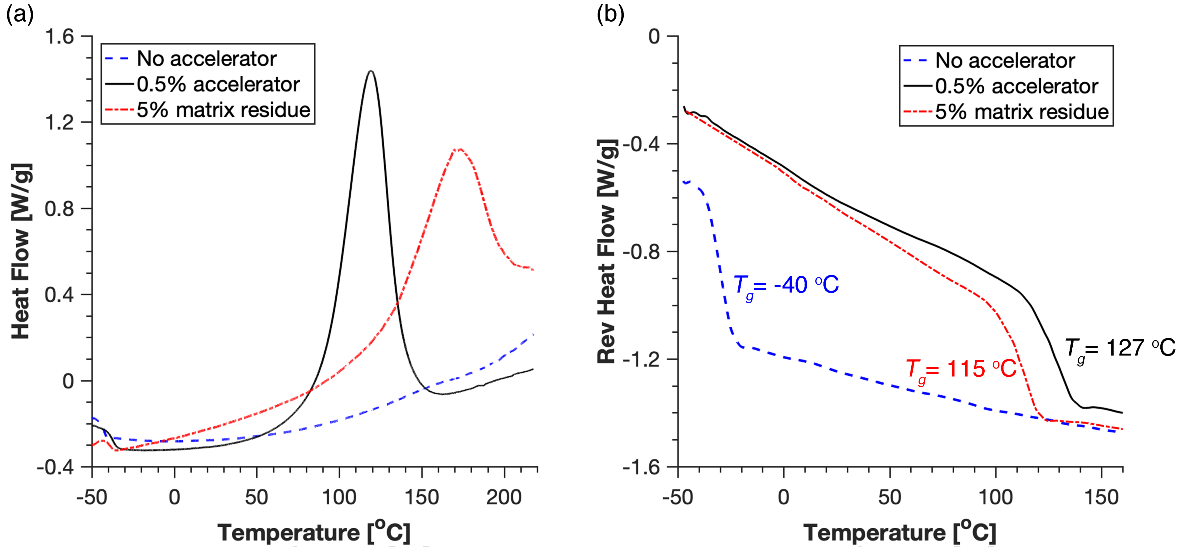

Figure 4. Reuse of recovered matrix residues as an accelerator for an anhydride-based bi-functional epoxy formulation: (a) curing reactions, (b) T_g values of cured epoxies.

Previous studies reported that $ScCl_3$ effectively accelerated the chemical reaction for acid digestion of amine-cured epoxies [26]. In this study, the effectiveness of recovered matrix residues with and without $ScCl_3$ catalyst was compared (Supplementary Figure S4). The heat flow curves during cure for anhydride-based bi-functional epoxies with matrix residues with and without $ScCl_3$ catalyst overlapped, and the cured T_g values were comparable, indicating that the existence of metal salt catalysts during acid digestion had negligible effect on the curing reaction of epoxy blends containing matrix residues.

To evaluate the flexural properties of the cured epoxies, neat epoxy specimens were prepared for four-point bending tests. Anhydride-cured bi-functional epoxy specimens cured with a commercial accelerator and with recovered bi-functional matrix residue were both homogenous and void-free (Figure 5). None of the bend test samples ruptured within the 5% strain limit required by the ASTM D6272 standard. The T_g of the specimen cured with matrix residues was ca. 10 °C below the T_g of the specimen cured with the commercial accelerator. The difference was attributed to the

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presence of small molecular segments and acetic acid residue in the recovered matrix, which was consistent with previous DSC data.

Despite the slight decrease in T_g noted above, the flexural modulus of the specimens cured with matrix residues was greater than specimens with the commercial accelerator, as shown in Figure 5. This phenomenon can be explained by a structural change in the polymer caused by reaction between hydroxyl groups in recovered matrices and epoxy monomers, introducing fragments from amine-cured epoxies into anhydride-cured epoxies. Aromatic amine-cured epoxies generally exhibit a greater storage modulus than anhydride-cured epoxies (using the same epoxy monomer) because of the higher functionality of amine, which yields a higher crosslinking density [30], as well as the rigid aromatic structures from the amine curing agents.

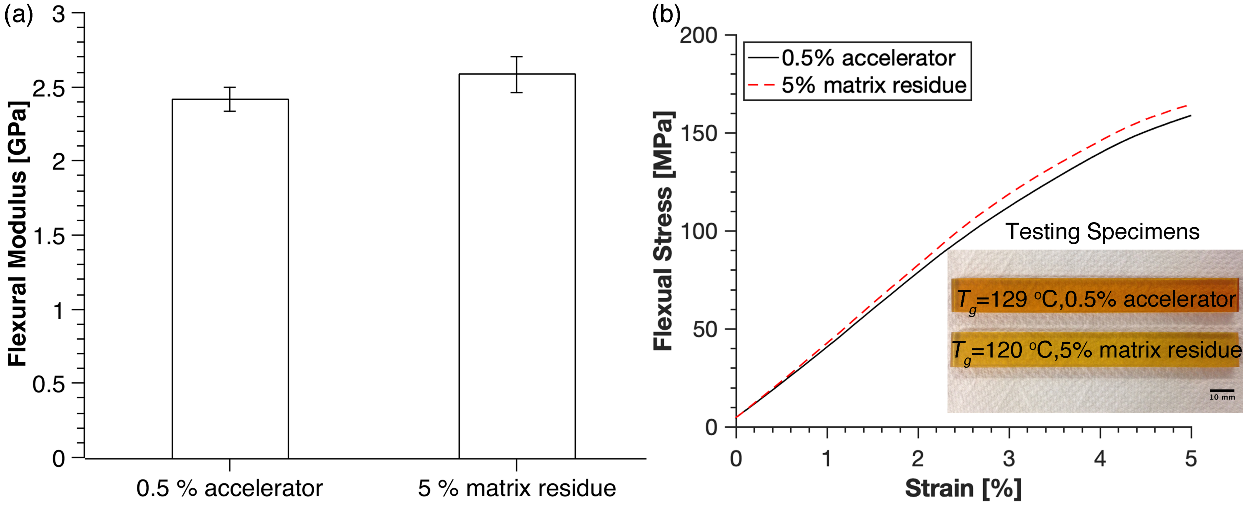

Figure 5. Flexural modulus (a) and stress-strain curves (b) for anhydride/epoxy samples cured with a commercial accelerator and recovered matrices.

The chemical reactions between bi-functional epoxy monomer (DGEBA) and the recovered matrix residue were detected via MDSC (Supplementary Figure S5). At 40 wt% (of the resin) mixing

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ratio for the recovered matrix, the reaction took place at 174.3 °C, yielding a partially cured epoxy with T_g = 26.4 °C. The peaks of reaction for DGEBA/recovered matrices and anhydride-cured DGEBA catalyzed by recovered matrices were similar, indicating that the two types of reactions occurred simultaneously during cure, and supporting our explanation. Figure 6 shows the FTIR spectra of DGEBA cured with the matrix residues. The peak at 915 cm^{-1} was assigned to C-O stretching vibration in the oxirane ring [31], which became weaker as the mixing ratio of the recovered matrix increased from 20 to 40 wt% (of the resin), confirming that the matrix residues reacted with epoxy groups. The full FTIR spectra are shown in Supplementary Figure S6.

The observations presented above demonstrate that the matrix components recovered from oxidative acid digestion can be used as accelerators for those anhydride-based epoxy formulations that are not self-catalyzed during cure. A mixing ratio of 5% by mass provides accelerators for curing anhydride-based epoxies and yields the lowest reaction temperature and highest cured T_g. Epoxy samples cured with recovered matrix residues and commercial accelerators are both homogeneous and void-free. The T_g and flexural modulus of the epoxy specimen cured with matrix residues are comparable to those of specimens cured with a commercial accelerator.

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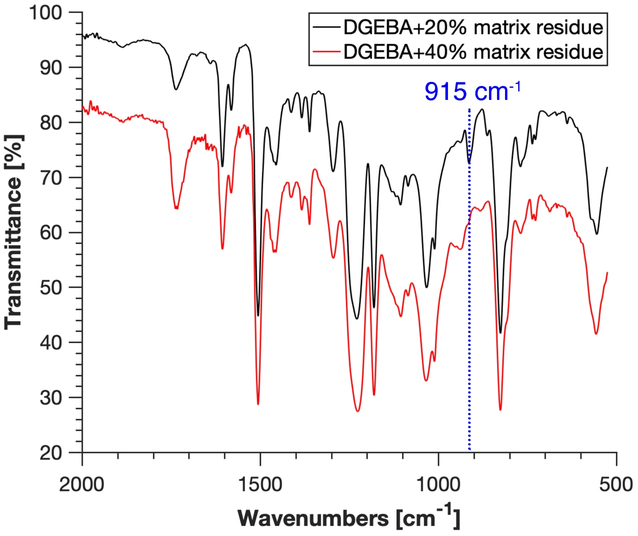

Figure 6. FTIR spectra of DGEBA/ matrix residue systems after a cure cycle.

3.3. Reuse Approach II: as fillers for epoxy resins

In this section, recovered matrix components were explored as filler additives to virgin anhydride-based epoxies with a commercial accelerator. Recovered matrix residues were blended into virgin resin formulations at mixing ratios of 5 and 10% by mass, and the thermal and mechanical properties were measured. Specimens containing both 0% and 5% residue were homogenous and void-free. However, specimens with 10% residue showed a few trapped voids because of the higher acetic acid content. The T_g values decreased as the mixing ratio of matrix residue increased. This phenomenon was ascribed to the increasing content of non-reactive small molecules and acetic acid solvent in the matrix residues. Note that the T_g values for samples with 5% recovered matrix residue as an accelerator and as a filler are comparable.

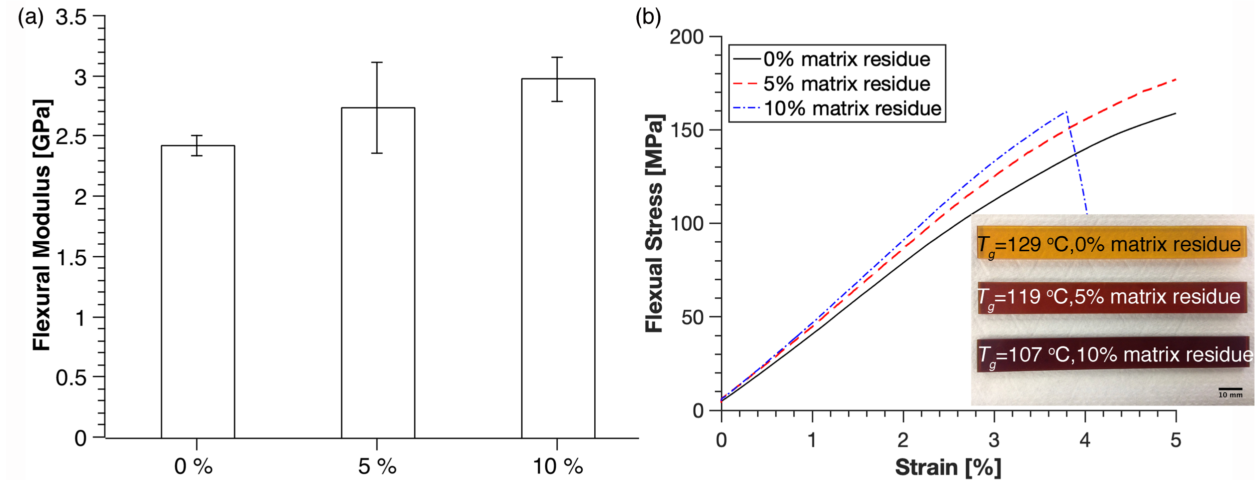

Figure 7. Flexural modulus (a) and stress-strain curves (b) for anhydride/epoxy samples with 0%, 5%, and 10% recovered matrices as fillers.

To evaluate the flexural properties of the cured epoxies, neat epoxy specimens were prepared for four-point bend tests. The flexural modulus of the specimens increased as the matrix residue content increased, as shown in Figure 7. The increase in modulus was attributed to the more rigid polymer chains brought by amine-epoxy structures, which was consistent the results of reusing matrix residues as an accelerator (Section **Error! Reference source not found.**). Note that the 0% and 5% specimens did not rupture within the 5% strain limit required by the ASTM D6272 standard. However, the 10% specimens ruptured within the 5% strain limit, and yielded a flexural strength of 141.5 ± 22.0 MPa. Based on the void-free condition, cured T_g value, and flexural properties, the maximum mixing ratio for reusing matrix residues as a filler in virgin anhydride-based epoxies was 10% by mass. Higher mixing ratios of matrix residue introduce additional acid content and impurities into resin systems and thus degrade resin properties [16, 18-20].

An effective process technology for recycling end-of-life CFRPs requires a high reaction rate, and three additional factors must be considered. First, a process must yield valuable recyclates after recycling. Current industrial scale pyrolysis recovers only short carbon fibers at end-of-life

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with reduced mechanical properties compared to virgin carbon fibers. Those short fibers are typically incorporated into bulk molding compounds (BMCs) or stitched mats, both of which embody much lower value than CFRPs with continuous carbon fiber reinforcement, and thus are unlikely to be eligible for subsequent recycling. Note that metals can be recycled repeatedly with negligible loss of material properties. Future recycling technologies must aim to recover near-virgin quality continuous carbon fibers (preferably without loss of organization), *as well as* high-value matrix residues.

Second, the recycling process must be economically feasible. In addition to diverting composites from landfills to comply with environmental legislation, composite recycling should include a reduction in cost/energy associated with producing virgin products to attract more recycling interest. For example, recycled aluminum and steel require 95% and 56% less energy, respectively [32]. The recovery and reuse of high-value matrix residues after chemical recycling not only closes the recycling loop, but also potentially reduce the overall cost of the process.

Finally, process scalability must be viable. Although valuable recyclates can be recovered via chemical recycling, current lab-scale processes require high pressure or hazardous reagents (corrosive or explosive). These conditions cannot be deployed readily in industry and must be modified/replaced. Mild recycling technologies also recover more value from end-of-life composites (high quality fibers and useful matrix residues), supporting and enabling the economic feasibility of recycling. The short production turnaround of chemical recycling is also a critical factor for entry into industrial scale recycling. This need is especially acute for advanced composites, which embody high intrinsic value but are difficult to recycle because of high crosslink densities.

4. CONCLUSIONS

We investigated the viability of recovering decomposed polymer matrix residues from amine-cured epoxies by acid digestion and reusing those matrix residues in virgin anhydride- based epoxy formulations. Useful matrix residues were recovered via neutralization the chemical solutions produced by oxidative acid digestion, and aromatic structures of epoxies were preserved during oxidative peroxide digestion. The recovered matrix residue had catalytic effects on the curing reaction of anhydride/epoxy formulations (without an accelerator) and could not otherwise be self-catalyzed. Furthermore, the thermal and flexural properties of anhydride-based epoxy samples cured with recovered matrix were comparable to samples cured with a commercial accelerator. We also demonstrated that the recovered matrix residue can also be reused as a filler in virgin anhydride/epoxy formulations (with a commercial accelerator), retaining thermal and mechanical properties.

The recovery of matrix residues deconstructed by oxidative acid digestion at atmospheric pressure affords opportunity to preserve useful parts of epoxy matrices *in addition* to carbon fibers, and to thus close the recycling loop. Moreover, the value recovered from matrices at least partially balances costs associated with acid digestion, rendering the process more cost effective for end-of-life recycling of composite materials, and reducing environmental impact.

However, an effective recycling process must yield valuable recyclates, be viable for scale-up, and be economically feasible. The oxidative acid digestion reaction described here does not fully satisfy these requisites. Although the acid digestion process effectively recovers near-virgin quality carbon fiber from composites, the chemical bond cleavage is not selective in the presence of H_2O_2, and thus the recovered value from the polymer matrix is limited. Moreover, H_2O_2 is a costly and explosive reagent that cannot be deployed on an industrial scale. Consequently, present efforts are devoted to seeking safer oxygen source alternatives to H_2O_2 for oxidative acid digestion that can be deployed to recover high quality fibers and more valuable polymers from amine/epoxy composites. We also aim to develop more effective catalysts to yield faster reactions, possibly sufficient to meet present and future needs. Until a more viable recycling process is developed for CFRPs, the use of composites to substitute for traditional aluminum and steel parts will be restricted, particularly in mass market applications such as automotive and infrastructure.

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Supplementary Materials

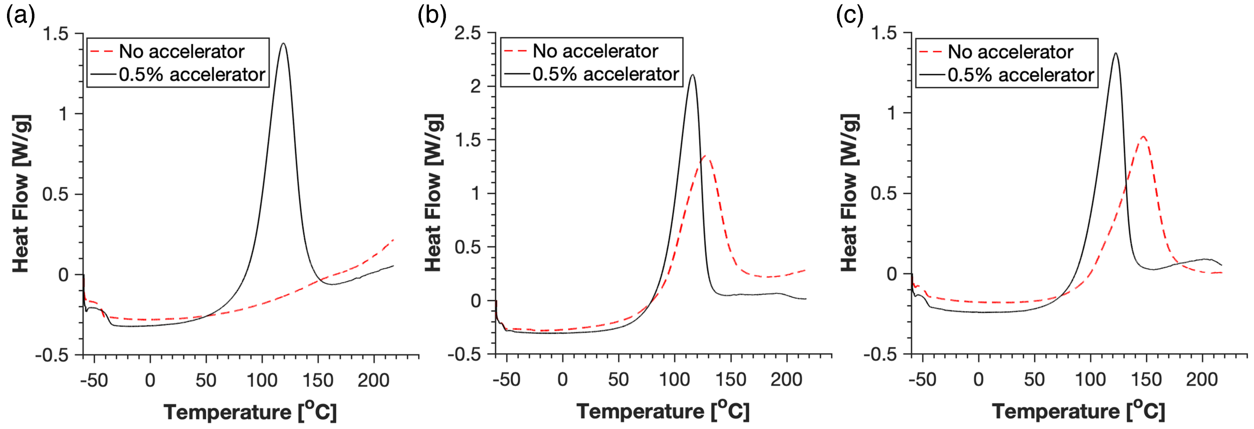

Figure S1. Effect of accelerators on curing reactions of anhydride/epoxy formulations with different epoxy monomers: (a) diglycidyl ether of bisphenol A (DGEBA), (b) triglycidyl of para-aminophenol (TGAP), (c) tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM).

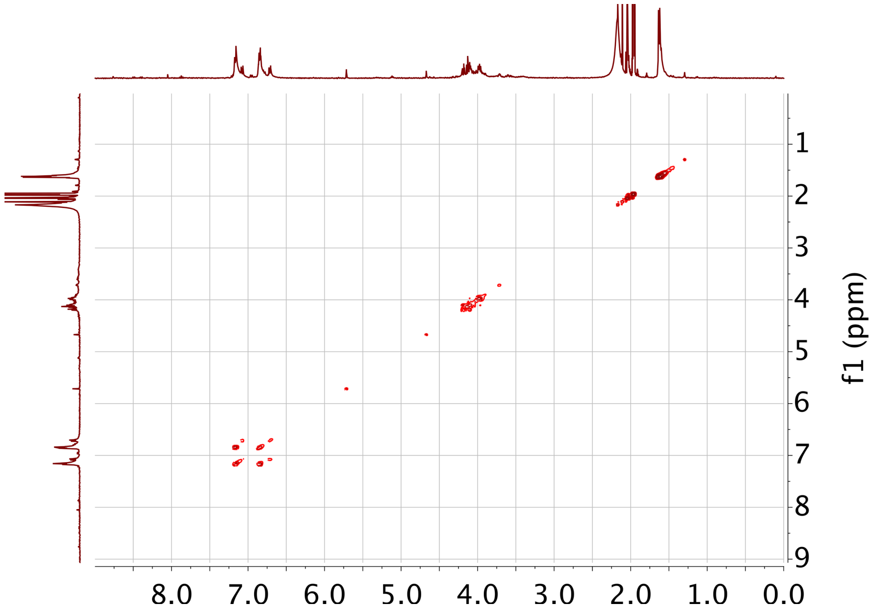

Figure S2. ^{1}H-^{1}H homonuclear correlation spectroscopy (COSY) spectrum of the one-hour digest in d_3-acetonitrile supporting structural assignments and the statement that more than one para-substituted compound is present.

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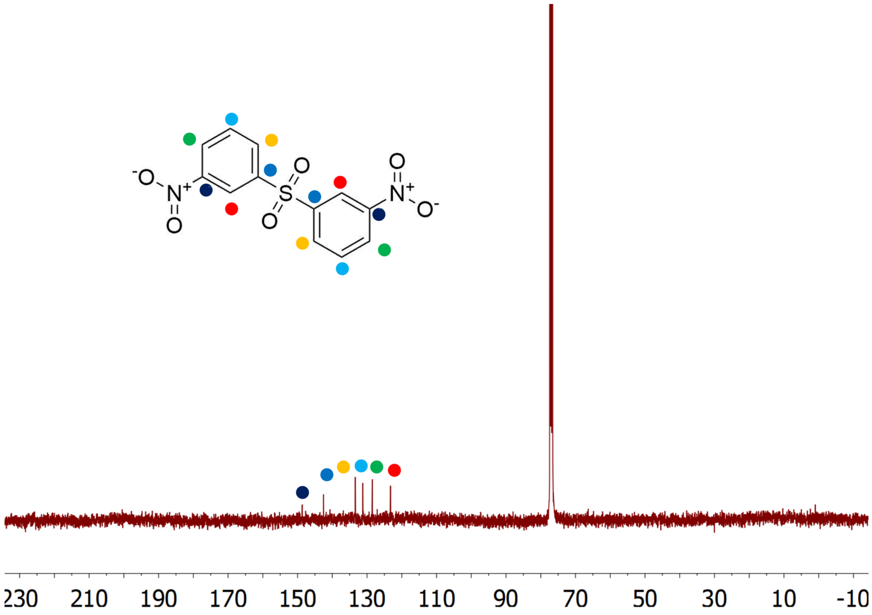

Figure S3. ^{13}C NMR spectrum of 3,3'-dinitrodiphenyl sulfone obtained from the eight-hour digest in deuterated chloroform.

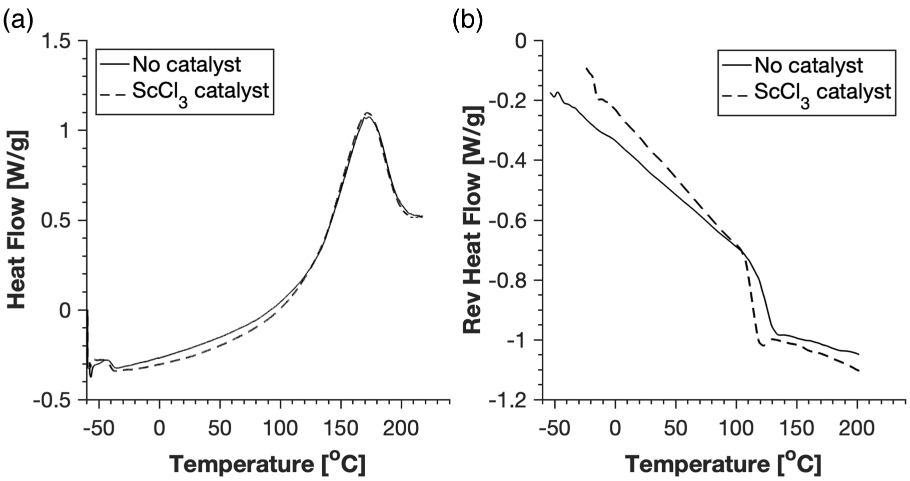

Figure S4. Comparison of (a) curing reactions and (b) T_g values for anhydride-based bi-functional epoxies with matrix residues without and with $ScCl_3$ catalyst.

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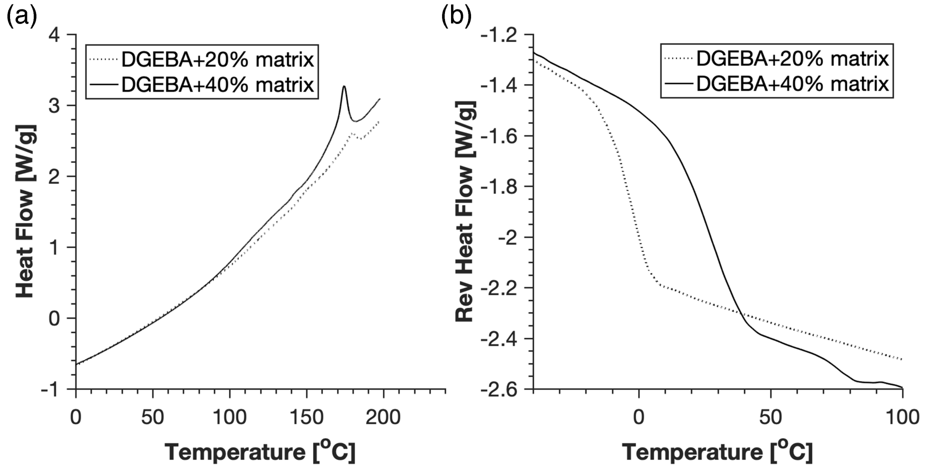

Figure S5. (a) Curing reactions and (b) T_g values of DGEBA/recovered matrix residue systems.

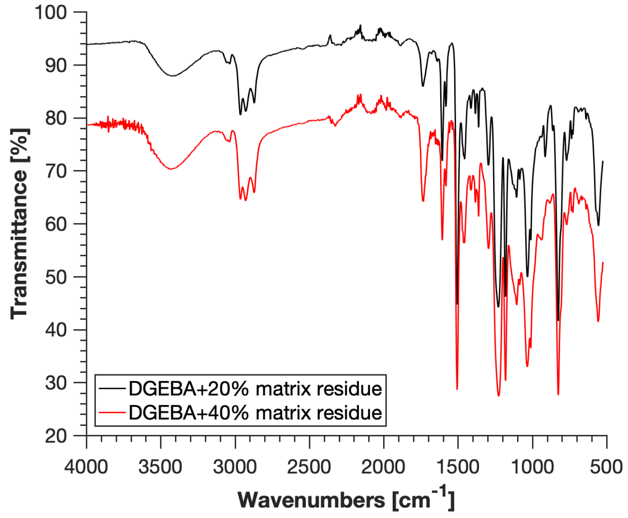

Figure S6. Full FTIR spectra of DGEBA/recovered matrix residue systems after a cure cycle.

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The recovered material is largely insoluble in organic solvents except for dipolar aprotic solvents. Attempts to study the material through NMR spectroscopy in DMSO-d6 yielded spectra with low signal-to-noise and broad peaks (Figure S7). This result is characteristic of compounds of with large molecular sizes, like polymers, resulting in short transverse (T2) relaxation and broad NMR peaks. Signals in the aromatic region (6.5 PPM – 7.5 PPM) are present, supporting the claim of aromatic groups present in the material.

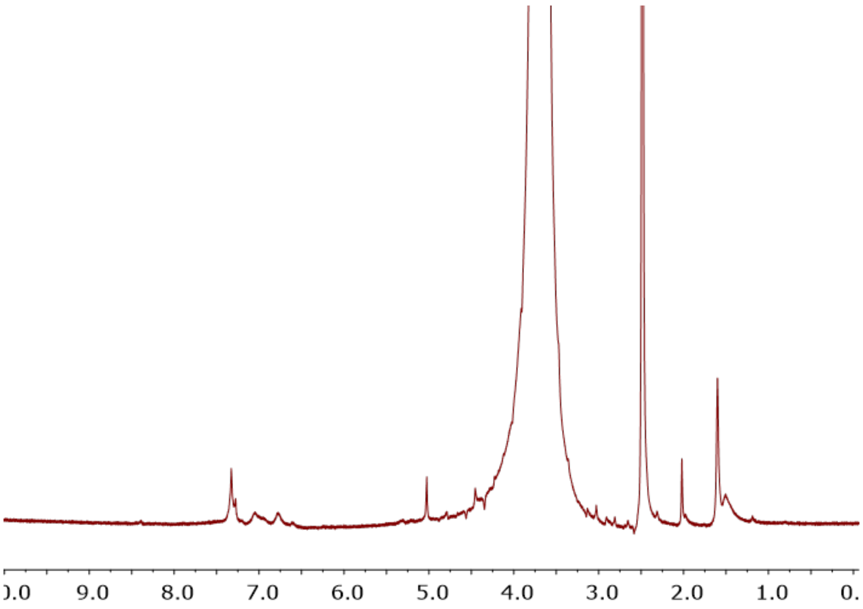

Figure S7. 1H NMR of the recovered material in DMSO-d6.

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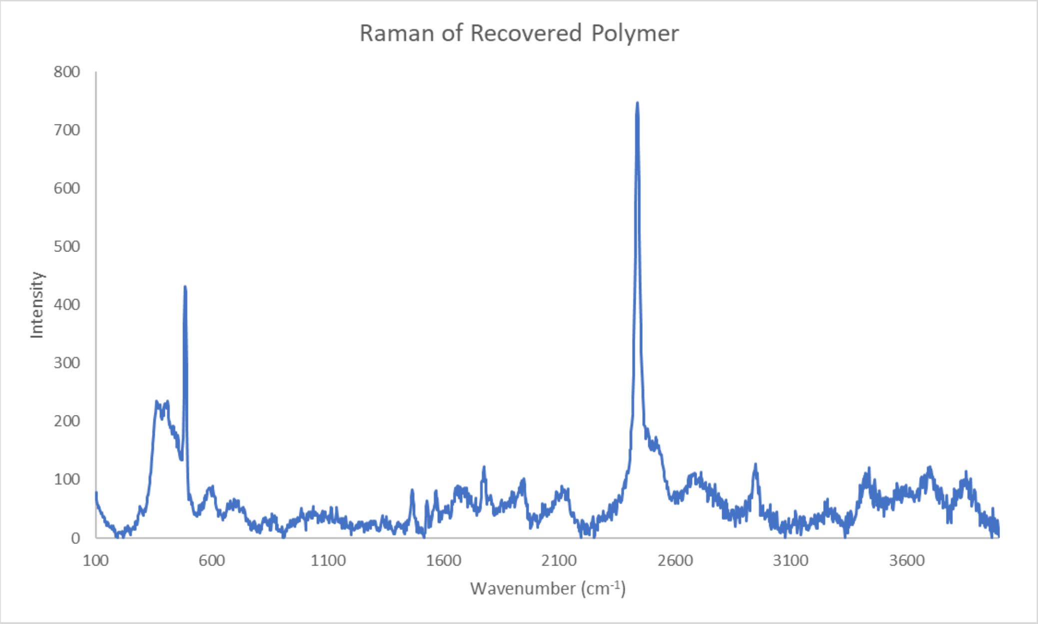

Figure S8. Raman of the recovered material.

Raman data of the polymer surface reveals a medium-strong peak at 488 cm-1 and a band centered at 415 cm-1, characteristic of the sulfone scissor vibration (Figure S8). Elemental analysis of the polymer reveals about a 2:1 nitrogen to sulfur mass ratio, which is consistent with the bis(aniline) polymerizing [Found: C, 60.99; H, 5.87; N, 1.54; S, 1.55]. There are multiple reports of transition-metal catalyzed aerobic coupling of anilines to form N-N bonds, featuring metals such as copper (J. Am. Chem. Soc. 2018, 140, 9074-9077) and iron (Angew. Chem. Int. Ed. 2017, 56, 549-553). Further, manganese oxides are known to polymerize polycyclic aromatic amines (Tetrahedron 1964, 20, 189-193), supporting the assertion that these bis(anilines) can similarly polymerize under the reaction conditions.