Chemical Treatment for Recycling of Amine/Epoxy Composites at Atmospheric Pressure

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Abstract: The use of fiber-reinforced composites poses significant environmental problems because most end-of-life composite waste is sent to landfills, and effective recycling technologies have drawn research attention. Our previous study demonstrated that chemical treatments at atmospheric pressure – depolymerization (benzyl alcohol/K_3PO_4 at 200°C) and acid digestion (acetic acid/H_2O_2 at 110°C) – were both effective for dissolution of amine-cured neat epoxy. In this paper, depolymerization and acid digestion were applied to amine/epoxy composites, including composites produced from lab-made and aerospace prepregs, and commercial composite waste. Findings indicated that acid digestion was more effective for highly crosslinked amine/epoxy composites than depolymerization. Furthermore, digestion occurred via reaction steps of oxygen atom transfer to the aniline groups and then bond cleavage, resulting in recovery of near-virgin quality fibers at faster dissolution rates and lower temperatures. The relationship between epoxy functionality, fiber bed architecture, fiber reinforcement, laminate thickness and matrix dissolution rate were investigated, and key parameters affecting the dissolution rate were identified. Data showed that the major rate-limiting factor for acid digestion was the diffusion rate, rather than the chemical reaction rate. Two strategies to enhance the diffusion rate – pre-treatment and mechanical shredding – were evaluated, and both were effective. Polymer matrices in pre-treated and shredded composites were homogeneously decomposed in 1 h.

Please cite the article as: Yijia Ma and S.R. Nutt, **“Chemical treatment for recycling of amine/epoxy composites at atmospheric pressure”** *Polymer Degrad & Stability* 153 307-317 (2018) DOI: **https://doi.org/10.1016/j.polymdegradstab.2018.05.011**

Key words: Recycling; Composites; Carbon fiber; Glass fiber; Epoxy; Chemical treatment; Atmospheric pressure.

1. INTRODUCTION

The global demand for carbon fiber-reinforced polymers (CFRPs) is expected to grow to 146,000 ton/yr in 2020, consuming 89,000 tons of carbon fiber [1], as the demand for lightweight materials increases. Due to the absence of effective recycling methods, most composite waste is not recycled/treated but is sent to landfills. Without a robust and effective method to recycle composites and complete the material life cycle, composite replacement of metallic parts will be limited in automotive, sporting goods, and energy industries. Consequently, effective recycling methods for CFRPs are required to reduce environmental impact and facilitate entry into sectors requiring mass production.

The objective of this work is to demonstrate and evaluate chemical treatment methods for amine/epoxy composites at atmospheric pressure that can effectively separate fibers and epoxy matrix to near-virgin quality fibers and potentially useful polymer components. The investigation focuses on amine-cured epoxies, which is the most widely used polymer matrix in high-performance composites [1,2]. A parametric study is performed that encompasses variations in chemical treatment method (depolymerization and acid digestion), matrix properties (epoxy monomer functionality and amine/epoxy molar ratio (A/E)), fiber bed architecture (2 × 2 twill weave and unidirectional (UD) fibers), and fiber type (carbon fiber (CF) and glass fiber (GF)). Key factors affecting the recycling process are identified and modified to accelerate the separation process. The long-term goal of the recycling project is to develop a catalytic method for cleavage of amine/epoxy molecules using moderate conditions (atmospheric pressure and moderate temperature) and safe chemicals. These features are critical to practical, large-scale composite recycling to recover long continuous fibers and useful chemical components, but have not been reported to date.

Recycling of epoxy composites presents a daunting challenge because the epoxies are highly cross-linked, three-dimensional structures and are insoluble and under mild conditions [3, 4]. Consequently, most efforts to recycle epoxy composites have largely focused on recovering the higher value component, the carbon fibers, discarding the polymer matrix. Currently, there are two physical recycling approaches practiced on industrial scales: mechanical grinding [5] and thermal processing [6,7]. The main advantage of physical recycling methods is that composite materials with various matrices and fiber reinforcements can be accommodated by a single process, and tuning these processes to particular matrix formulations is not necessary. However, neither method recovers any of the matrix, and both methods have inherent drawbacks, as outlined below.

Mechanical grinding produces fillers or reinforcement for lower grade composites. Though the mechanical integrity of recycled composites could be improved by careful separation and reincorporation [5], long clean fibers cannot be recovered from grinding, and market demand for ground materials is limited. Thermal processing (pyrolysis) is now the most widely used process in industrial scale recycling. Pyrolysis breaks down polymer matrices into lower molecular weight components, although the temperatures (450 - 700°C) can result in fiber degradation and char [6-8]. Analysis of the recovered material showed that pyrolysis above 600°C caused severe oxidation of the carbon fiber, and the fiber strength decreased by > 30% [6]. Furthermore, pyrolysis of the matrix left residual char on fiber surfaces, and fiber purity was less than the desired level of 99.5% [8]. Fibers recovered from thermal processing are generally chopped into short fibers for use in molding compounds and other applications, and most of the value of the continuous fibers/fabrics is lost. Due to the limited market demand for recycled short fibers, most composite materials are not being recycled today.

Recent recycling research has focused on lab-scale chemical approaches that can recover clean fibers (99.9% purity) [8] with greater than 90% strength retention [9]. For example, supercritical fluids have been evaluated for recycling due to the high mass transfer coefficient and diffusivity. High temperature (> 250°C) and high pressure (> 2.5 MPa) were used in experiments to recover fibers from composites (specific reaction conditions depend on the nature of the matrix) [8-14]. However, the aggressive conditions inevitably led to fiber degradation, and the tensile strength of recovered fibers was reduced by 1-15% [10]. Commonly used solvents have included water [10-12], methanol [13], ethanol, propanol, acetone, and their mixtures [14]. Alkaline catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), were often added to reaction systems to accelerate the reaction and reduce the reaction temperature [14]. In addition, various metal salts were employed as catalysts to cleave the C–N bonds in epoxy matrices, including $AlCl_3$, $FeCl_3$, $ZnCl_2$, $CnCl_2$, $MgCl_2$ [15-17]. Most chemical recycling methods focused on amine-cured bisphenol A type epoxies (bi-functional epoxy) [10-16], which featured relatively low crosslink density and glass transition temperature (T_g). However, Liu et al. investigated a chemical recycling method for CFRPs with high crosslink density (T_g = ~210°C) using a $ZnCl_2$/ethanol system at 180-220°C [17]. The CFRPs used were manufacturing scraps, and the main composition of the matrix was amine-cured epoxy. Results showed that a matrix degradation degree of ~90% could be achieved.

To date, chemical recycling methods have not been employed on an industrial scale recycling due to 1) the high capital costs associated with high temperature and high pressure conditions, 2) the slow recycling rates and corrosive reaction media, and/or 3) a lack of post-treatment methods for chemical solutions after recycling. There is an urgent need for effective low-pressure methods that require less corrosive reaction media and are readily scalable. The present work demonstrates chemical treatments for amine/epoxy composite recycling that can be performed under atmospheric pressure and moderate temperature (≤ 200°C).

Chemical treatment methods for thermoset composites at atmospheric pressure have been reported, often using nitric acid [18]. However, strong acid solutions pose environmental hazards, leading researchers to seek methods that require less corrosive reaction media and are safer to handle. For example, Hitachi Chemical reported a solvolytic depolymerization method conducted at atmospheric pressure for anhydride/epoxy systems. The protocol involved using chemical solutions comprised of alkali metal salt (catalyst) and high boiling point alcohol (solvent) [19,20]. However, amine/epoxy formulations lack ester groups for transesterification, a reaction essential to the Hitachi technology. Thus, the solvolytic depolymerization approach cannot be used to dissolve amine/epoxy matrices.

Chemical dissolution of amine-cured epoxy formulations requires a different approach. Oxidative treatment methods using a mixed solution of hydrogen peroxide and organic solvents, such as *N,N*-dimethylformamide [21] and dilute nitric acid [22], were reported to dissolve amine/epoxy matrices. Results showed that clean fibers were separated from the matrix (amine-cured bi-functional epoxy), and the recovered fibers retained > 95% tensile strength [21]. However, dissolution of amine/epoxy matrices with higher crosslink density is more challenging, and doing so in oxidative environments has not been considered. Previous work [23-26] demonstrated that both depolymerization (benzyl alcohol/K_3PO_4 at 200°C) and acid digestion (acetic acid/H_2O_2 at 110°C) were effective for amine-cured neat epoxy with high crosslink density. The epoxy dissolution rate was controlled by both the chemical reaction rate and the diffusion rate. The reaction mechanism for oxidative degradation of amine-cured epoxies was investigated, revealing that reaction occurred by oxygen atom transfer to the linking aniline groups, and the polymers were then cleaved by an elimination and hydrolysis sequence [26].

In this study, we report methods for depolymerization and acid digestion on amine/epoxy composites and compare with similar methods applied to neat epoxy. Composites were fabricated using select epoxy formulations and fiber reinforcements, and subsequently subjected to chemical treatments to identify correlations between epoxy matrix functionality, laminate thickness, fiber bed architecture, fiber type and dissolution rates. Results show that both depolymerization and acid digestion achieve complete matrix dissolution and fibers are recovered. Acid digestion is shown to be a more effective approach for amine/epoxy composite recycling because it offers faster chemical reaction rates at lower reaction temperature, and recovers residue-free fibers. Furthermore, two strategies to improve the matrix dissolution rate – pre-treatment and mechanical shredding – were employed using both laboratory and commercial amine/epoxy composites. Both strategies effectively accelerate the diffusion rate and recover clean fibers.

2. EXPERIMENTS

Amine/epoxy resins were formulated (without toughening agents or other additives) and characterized using thermal analysis. A total of ten fiber-reinforced composite laminates were fabricated using prepregs that consist of the resin formulations with variations in crosslink density. Samples of composites produced from lab-made prepregs, composites produced from commercial aerospace prepregs (Cycom 5320-1/8HS) and commercial composite waste (provided by ELG Carbon Fibre Ltd.), were subjected to chemical treatment to evaluate speed and effectiveness of dissolution for recycling. Recovered fibers were examined by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) to determine surface quality. Residue on the fibers was analyzed using energy dispersive X-ray spectroscopy (EDS) to determine chemical composition.

2.1. Resin Formulation

Epoxy resins were formulated using three types of epoxy monomers that varied in epoxy functionality: (1) bi-functional epoxy (diglycidyl ether of bisphenol A (DGEBA), Araldite GY 6010, Huntsman, Figure 1 (a)), (2) tri-functional epoxy (triglycidyl of para-aminophenol, Araldite MY 0510, Huntsman, Figure 1 (b)), and (3) tetra-functional epoxy (tetraglycidyl-4,4'-methylenebisbenzenamine, Araldite MY 721, Huntsman, Figure 1 1 (c)). A tetra-functional, high-performance amine-based curing agent, diamine 3,3'-diaminodiphenyl sulfone (3,3'-DDS, Aradur®9719-1, Huntsman, Figure 1 (d), was selected to react with the epoxy monomers). The structure of crosslinked bi-functional epoxy from the primary and secondary amine reactions with the epoxy groups is shown in Figure 1 (e). During resin formulation, specific amounts of epoxy monomer and curing agent were mixed at room temperature in clean aluminum cans until fully homogenized. The mixing ratio of amine/epoxy (A/E) were varied from 40% to 100% (molar), providing a wide range of crosslink densities. The mixture was then heated to 120°C in a pre-heated convection oven to further improve the mixing quality, yielding a clear homogenous mixture.

2.2. Thermal Analysis

Thermal analyses, including thermogravimetric analysis (TGA, TA Instruments Q5000 IR) and modulated differential scanning calorimetry (MDSC, TA Instruments Q2000), were used to measure the thermal properties of the epoxies. TGA data showed that all resin formulations began to degrade at ~300°C. The degradation temperature set an upper limit for further MDSC tests. MDSC tests were performed on each sample to measure the glass transition temperature (T_g) of the

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cured sample. For each MDSC measurement, a ramp was applied from -60 to 300°C at a constant rate of 1.5°C/min with ±0.5°C/minute modulation. After cure, samples were heated from -60 to 300°C at a rate of 10°C/min with ±0.5°C/minute temperature modulation. The T_g of the cured epoxy was obtained from the inflection point of the last reversible heat flow signal during the ramp cycle.

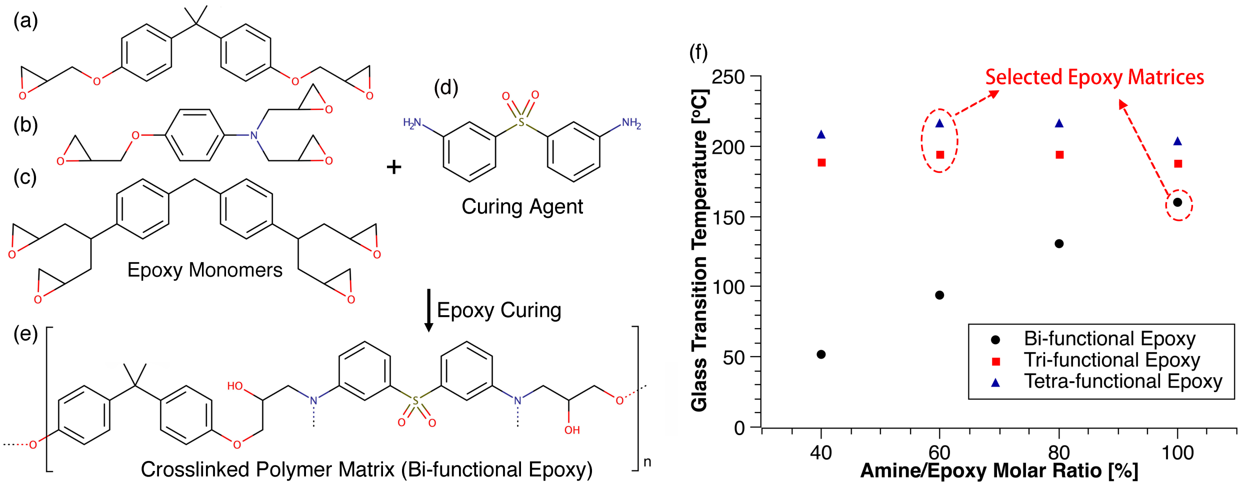

Figure 1. Resin formulations for composite matrices: (a) bi-functional epoxy, (b) tri-functional epoxy, (c) tetra-functional epoxy, (d) amine curing agent, (e) crosslinked bi-functional epoxy matrix, (f) selected epoxy matrices for composite fabrication.

Figure 1 (f) shows that as the A/E ratio increased from 40% to 100%, the T_g values of bi-functional epoxies increased from 60 to 160°C due to the increase of the crosslink density. For tri- and tetra-functional, the T_g values initially increased as the A/E ratio increased because of the higher crosslink density, but then decreased due to the lower miscibility of 3,3’-DDS in tri- and tetra-functional epoxy monomers compared to bi-functional epoxy monomers. The highest T_g values of bi-, tri- and tetra-functional epoxies were 160°C (DDS/Bi = 100%), 194°C (DDS/Tri = 60%), and 217°C (DDS/Tetra = 60%), respectively. These three formulations were selected as the epoxy matrices for composite fabrication.

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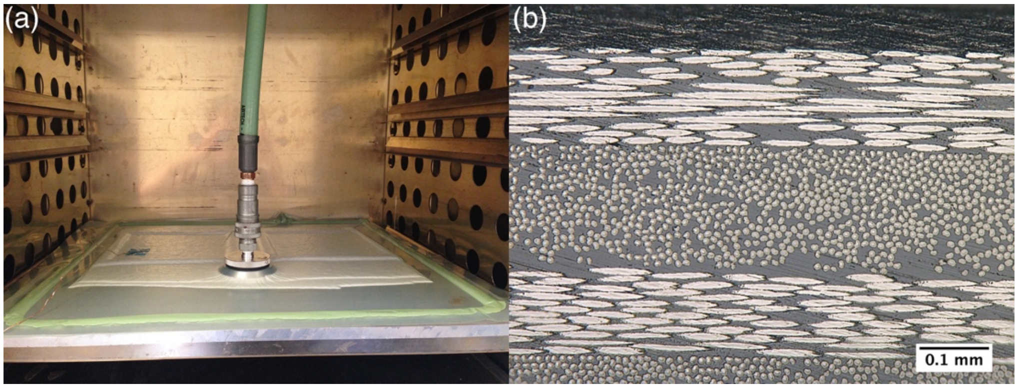

Figure 2. Composite fabrication: a) vacuum bag-only manufacturing setup, b) polished section of cured laminates.

2.3. Composite Fabrication

Composites were fabricated using the formulated epoxies and four types of fiber reinforcement: 2 × 2 twill weave CF fabric (3K, 135 g/m^2, FibreGlast), UD CF (12K, 305-325 g/m^2, FibreGlast), plain weave GF fabric (323 g/m^2, FibreGlast), stitched UD GF (955 g/m^2, FibreGlast). To fabricate composites, resin films (230 × 230 mm) were first produced by spreading resin onto release films on a heated plate (50°C). Dry fabrics (230 × 230 mm) were secured at all four edges with tape to preserve the fiber orientations. The dry fabric sheets and the resin films were stacked together with one resin film on each side of the fabric sheets. The stack was then hot pressed (Wabash) at 50°C and 100 kPa for 2 minutes. The final size of all prepregs excluding the tape edge was 200 × 200 mm, with a resin content of 45 ± 2%.

Using the prepregs above, composites laminates were fabricated via vacuum bag-only (VBO) processing. Bag edges were sealed to prevent resin bleeding, as shown in Figure 2 (a). The same cure cycles were used for all laminates, 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 180°C dwell of three hours. Final resin content in all laminates was 45 ± 2%. Cross-sectional images (Figure 2 (b)) revealed that carbon fibers

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were fully impregnated by epoxies, and the void content was < 2%. Laminates were also produced using commercial aerospace grade VBO prepreg (Cycom 5320-1 T650-35 3K 8HS 36%) using VBO processing.

2.4. Composites Recycling

Three types of composite materials were investigated: composites produced from lab-made prepregs, composites produced from commercial prepregs (Cycom 5320-1/8HS), and shredded composite waste (provided by ELG Carbon Fibre Ltd.). The cured laminates were cut into 20 × 100 mm coupons and subjected to chemical treatment. The thicknesses of the laminates fabricated from twill weave CF fabrics were 0.5 mm (2 plies), 1 mm (4 plies) and 2 mm (8 plies). The shredded composite waste was subjected to chemical treatment as received. Matrix dissolution time was used to assess the effectiveness of the chemical treatment, and was defined as the time required to fully dissolve the matrix and separate residue-free carbon fiber bundles (determined visually). Test coupons were cut from the same laminate, and the standard deviation of the dissolution time for samples with the same formulation was below 10%. After chemical treatment, the recovered fibers were rinsed in acetone (~30 ml, 5 min) and water (~30 ml, 5 min) until no residue was observed. Clean fibers were oven-dried for further analysis.

2.4.1 Depolymerization

Depolymerization, (more accurately described as alkali digestion, based on the reaction medium), was performed using a supersaturated solution of 100 mL benzyl alcohol (solvent, Sigma-Aldrich) and 7g tripotassium phosphate (catalyst, Sigma-Aldrich). Thus, a three-neck, round-bottom flask (1 L) containing the depolymerization solution and weighed composites was fluxed at 200°C in an oil bath. A magnetic stir bar was placed in the flask to homogenize the

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catalyst concentration distribution. The frequency of rotation was set at 100 rpm to minimize mechanical distortion of the fibers. Nitrogen flow was employed to create an inert environment for the reaction and to keep the catalyst in a reactive form.

2.4.2. Acid Digestion

Acid digestion (more accurately described as oxidative digestion) was performed using a solution of 100 mL glacial acetic acid (solvent, EMD Millipore) and 10 mL hydrogen peroxide solution (oxidant, 30% (w/w) in H_2O, EMD Millipore). The same setup as depolymerization was used for acid digestion, except that magnetic stir bars were not placed in the flask. The resultant mixture and a composite coupon were refluxed at 110°C, and additional hydrogen peroxide solution (5 mL) was added to the flask every hour. No nitrogen flow was used for acid digestion.

2.4.3. Pre-treatment Before Acid Digestion

An important element of this recycling method was the use of a two-step process with specific chemical substances that first physically permeabilized (swelled) the composites without disrupting the fiber weave in the polymer matrix, and second, chemically dissolved the matrix into the solvent, thus recovering near virgin-quality fibers in woven form. After pre-treatment, the rate-limiting effect of solvent diffusion was reduced or eliminated. During pre-treatment, laminates were placed in benzyl alcohol at 200°C for 4 hours. The pre-treated laminate was then subjected to acid digestion in Section **Error! Reference source not found.**.

2.5. Fiber Characterization

Scanning Electron Microscopy (SEM, JEOL JSM 7001)) was used to examine the surface quality of recovered fibers after chemical treatments. Non-conductive GFs were sputter coated with a conductive platinum layer before imaging to prevent charging of the specimen. CFs were imaged without coating. Energy-dispersive X-ray spectroscopy (EDS, JEOL JSM 7001) provided qualitative indications of the elements present in the sample, and was used to analyze the chemical composition of epoxy residues on the fibers. Observation conditions of accelerate voltages of 15-20 kV and working distances of 15-20 mm were used. Fiber surface functional groups were analyzed using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). Survey spectra in the range of 0-1200 eV were perform for each sample, followed by high resolution scans over the C1s range. Curve-fitting of the C1s spectra was performed in CasaXPS software using Gaussian-Lorentzian curves with constraints on position.

2.6. Test Matrix

Error! Reference source not found. summarizes the four sets of recycling experiments performed. In Set I, the viability of depolymerization and acid digestion for recycling composites produced from lab-made prepregs (epoxy DDS/Bi = 100%) was evaluated. The matrix dissolution rate and the properties of the composites, including laminate thickness (2, 4, 8 plies), fiber bed architecture (2 ×2 twill weave and UD fibers) and the effect of diffusion, were analyzed and correlated. Advantages and drawbacks of both methods were determined. In Set II, the effect of epoxy functionality on matrix dissolution rate was evaluated by subjecting laminates with tri- (DDS/Tri = 60%) and tetra- (DDS/Tetra = 60%) functional matrices to acid digestion. Tri- and tetra-functional epoxy matrices featured T_g*'s* comparable to high-performance epoxy matrices, and thus provided indications of the suitability of acid digestion for recycling aerospace composites. In Set III, the effect of fiber reinforcement type was investigated, by replacing CF reinforcements with GFs. Thus, Set III revealed difference in matrix dissolution rate during acid digestion and depolymerization for CF and GF composites. Set IV was used to determine the viability of acid digestion for commercial composite recycling by using two types of composite materials: composites produced from commercial prepregs and shredded composite waste.

Table 1. Test matrix

Set	Reinforcement	Matrix	Method	Pre-treatment	No. of Plies
I	CF/Twill Weave	DDS/Bi=100%	Acid Digestion	Yes and No	2, 4, and 8
	CF/Twill Weave	DDS/Bi=100%	Depolymerization	No	2, 4, and 8
	CF/UD	DDS/Bi=100%	Acid Digestion	No	2, and 4
II	CF/Twill Weave	DDS/Tri=60%	Acid Digestion	No	4
	CF/Twill Weave	DDS/Tetra=60%	Acid Digestion	No	4
III	GF/UD	DDS/Bi=100%	Acid Digestion	Yes and No	1 and 2
	GF/UD	DDS/Bi=100%	Depolymerization	No	2
	GF/Plain Weave	DDS/Bi=100%	Acid Digestion	Yes and No	4
	GF/Plain Weave	DDS/Bi=100%	Depolymerization	No	4
IV	CF/8 Harness Satin	5320-1	Acid Digestion	Yes	8
	CF/Shredded	epoxy	Acid Digestion	No	/

3. RESULTS AND DISCUSSION

3.1. Recycling Methods: Depolymerization vs. Acid Digestion

For depolymerization, Figure 3 shows that the matrix dissolution time increased slowly in a quasi-linear manner as the number of plies in the laminate increased. The reaction temperature for depolymerization (200°C) was greater than the matrix T_g values (DDS/Bi = 100%, T_g = 160°C), so the matrix dissolution rate was limited primarily by the chemical reaction rate. In contrast, for acid digestion, the matrix dissolution time increased sharply with number of plies (Figure 3). The time required for dissolution in a 4-ply laminate was twice the time required for a 2-ply laminate, indicating that the dissolution rate for acid digestion was diffusion-limited. Note that the reaction temperature (110°C) in this case was lower than the matrix T_g's values (160°C). Epoxy residue on fibers was typically present between central plies, and not within fiber tows, indicating that diffusion was rate-limiting in the chemical treatment. Furthermore, the matrix dissolution time required for an 8-ply laminate was more than 4 times that of a 2-ply laminate (Figure 3). The extended dissolution time was due to the increased water content introduced by H_2O_2 from both the H_2O_2 aqueous solution (major) and the chemical reaction (minor). As water content increased, the reaction temperature fell below 110°C, reducing the chemical reaction rate. In thin laminates (2 and 4 plies), water content had a negligible effect, and acid digestion yielded a faster overall dissolution rate than depolymerization.

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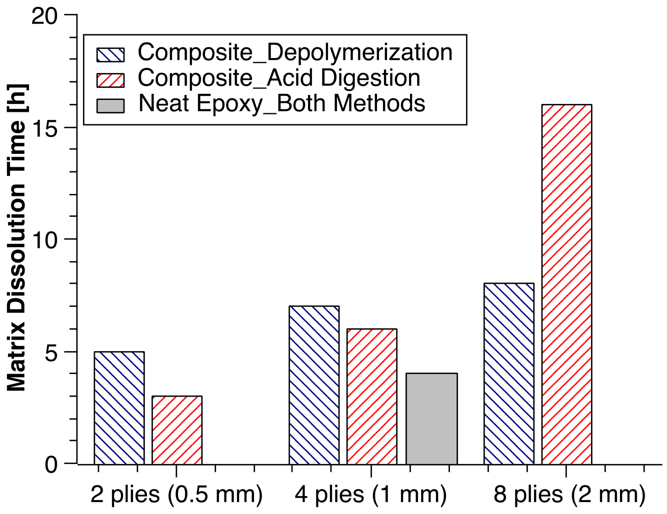

Figure 3. Effect of thickness on epoxy matrix (DDS/Bi =100%) dissolution rate

Similar trends were reported previously for neat epoxy dissolution [23]. When the reaction temperature was less than the epoxy T_g, the dissolution rate depended primarily on the diffusion rate. However, in other cases, the chemical reaction rate was the rate-limiting factor, and the chemical reaction was faster for acid digestion than for depolymerization. Figure 3 shows a comparison of the dissolution time for a composite (4 plies, ~1 g resin content) and neat epoxy (~1 g) of the same thickness. The matrix dissolution time was slightly greater than that in neat epoxy for both depolymerization and acid digestion, indicating that fiber reinforcement retarded the dissolution rate.

Figure 4 compares the surface properties of virgin fibers and recovered fibers after depolymerization and acid digestion. The SEM images reveal that the virgin fiber surfaces were smoother than those of recovered fibers because chemical treatment removed fiber sizing. (Sizing is a mixture of chemicals applied to optimize the surface chemistry.) No significant defects or residues were observed on the recovered fibers after acid digestion. Fibers recovered after depolymerization showed occasional residue, and EDS spectra (Supplementary figure S1) revealed

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that the residue was primarily undissolved catalyst (K_3PO_4). To identify the surface functional groups of recovered carbon fibers, XPS spectra of virgin fibers and recovered fibers were analyzed, as shown in Figure 4. All survey scans (Figure 4 (a)) showed three main peaks: carbon (284.6 eV), nitrogen (400.5 eV) and oxygen (532.0 eV). In the C1s high resolution spectra (Figure 4 (b), (c) and (d)), the peaks at ~ 284.8, 286.4 and 288.9 eV were assigned to C-C, C-OH and COOH groups, respectively. Percentages of those functional groups on carbon fiber surface are shown in Table 2. We observe that the percentages of the C-OH groups decrease (compared to virgin carbon fiber) for carbon fibers recovered via both depolymerization and acid digestion. This finding indicates removal of sizing from fiber surfaces, which is consistent with the SEM images shown in Figure 4. Furthermore, the percentage of the COOH group increases in fibers recovered via acid digestion (Figure 4 (d)) due to the strong oxidative environment during the reaction.

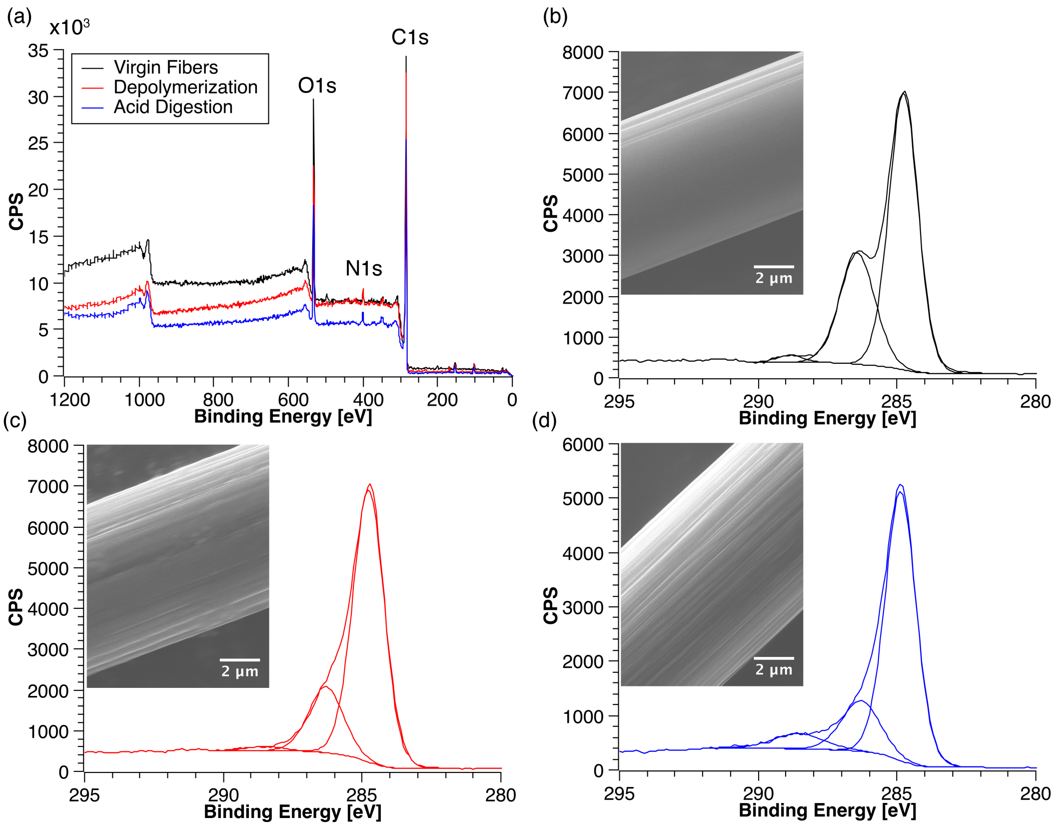

Figure 4. XPS spectra and SEM images of virgin and recovered carbon fibers: (a) XPS survey spectrum, and C1s spectra and SEM images for (b) virgin carbon fibers, (c) carbon fibers recovered from depolymerization, (d) carbon fibers recovered from acid digestion

Table 2. Percentages of functional groups on carbon fiber surface.

Samples	C-C [%]	C-OH [%]	COOH [%]
Virgin carbon fibers	66.5	32.0	1.5
Fibers recovered via depolymerization	77.8	20.8	1.4
Fibers recovered via acid digestion	75.5	17.7	6.9

The observations described above demonstrate that both depolymerization and acid digestion are potentially effective methods for recycling of amine/epoxy composites. In depolymerization, the matrix dissolution rate depends primarily on the chemical reaction rate, while for acid digestion, diffusion is rate-controlling. Acid digestion appears to be more effective than depolymerization for recycling amine/epoxy composites for five reasons: 1) faster reaction rate, because the linking aniline groups create pathways for oxygen atom transfer from H_2O_2, and the polymer can then be cleaved by elimination, 2) lower reaction temperature, 3) recovery of residue and defect-free fibers, 4) robust and convenient setup (depolymerization requires N_2 environment), and 5) clean chemical feedstock after reaction (depolymerization uses K_3PO_4 as a catalyst, which has low solubility in benzyl alcohol and leaves solid residues in the solution after reaction). Therefore, we henceforth focus on acid digestion.

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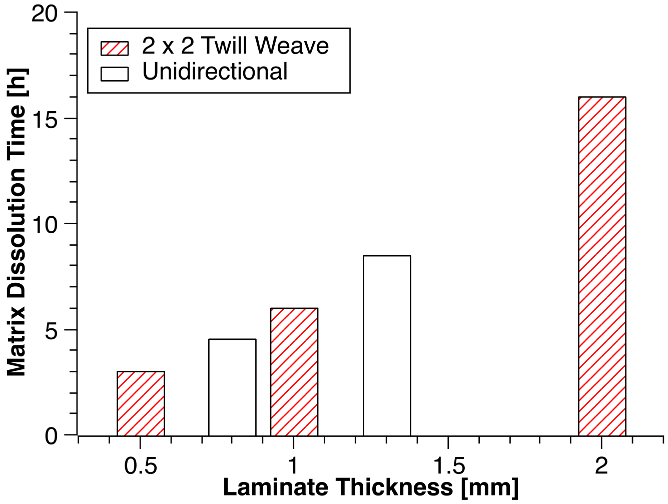

Figure 5. Effect of fiber bed architecture on epoxy matrix (DDS/Bi =100%) dissolution rate

3.2. Effect of Fiber Bed Architecture

To evaluate the effects of fiber bed architecture on matrix dissolution rate, laminates were fabricated using twill weave (135 g/m^2) and UD (305-325 g/m^2) fibers (the same epoxy matrix: DDS/Bi = 100%). (The most common fiber arrangements used in aerospace composites are UD and fabric.) Figure 5 shows that as laminate thickness increased, dissolution time increased in quasi-linear fashion for twill weave laminates. The data for UD laminates (dissolution time and laminate thickness) followed the same trend observed for twill weave laminates, indicating that fiber bed architecture had negligible effect on dissolution time or diffusion rate, and that laminate thickness was a more important parameter in determining the matrix dissolution rate.

3.3. Effect of Matrix Functionality

In this section, acid digestion of tri- and tetra-functional composites is investigated. Note that tri- and tetra-functional matrices have more heavily crosslinked networks compared to bi-functional epoxies, and this limits the diffusion of solvent molecules. The results are compared to the data for bi-functional matrix composites to gain a more complete understanding of amine/epoxy matrix dissolution. Figure 6 shows the dissolution times of bi- (T_g = 160°C), tri- (T_g = 194°C), and tetra- (T_g = 217°C) functional composites. All sample matrices dissolved in < 10 h via acid digestion, resulting in recovery of clean carbon fibers. Tri- and tetra-functional composites required comparable dissolution times, as they contained similar levels of crosslinked bonds and T_g values [23]. For bi-functional composites, the dissolution time was shorter than for tri- and tetra-functional composites. The shorter dissolution time was attributed to a more rapid diffusion rate in the bi-functional matrix, which exhibited lower T_g and crosslink density.

Composite materials in aerospace parts typically require thermally stable matrices that can tolerate high service temperatures. The T_g requirement for aerospace resin systems is generally > 160°C. For example, the selected aerospace grade VBO prepreg in this study, 5320-1/8HS, exhibits a T_g = 197 °C after post-cure. The T_g values of the tri- and tera-functional epoxy matrices used in the composites produced from lab-made prepregs were comparable to that of 5320-1/8HS. The ability to fully dissolve tri- and tetra-functional matrices demonstrates that acid digestion is a potentially viable approach for recycling of aerospace grade amine/epoxy composites. This assertion will be explored further in Section **Error! Reference source not found.**.

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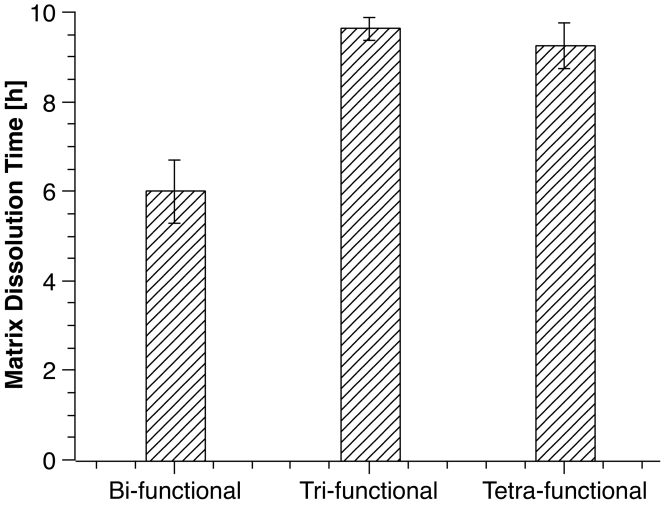

Figure 6. Effect of epoxy functionality on matrix dissolution rate

3.4. Effect of Reinforcement Types

Although CF is by far the most widely used fiber in high-performance applications, the cost of carbon fiber is generally 10-50 times that of E-glass fiber. Consequently, GF is the most commonly used reinforcement overall in industry. Results presented thus far have shown that acid digestion is effective for matrix dissolution in CF composites. In this section, we seek to understand the viability of acid digestion for glass fiber composites. Two types of E-glass fiber reinforcement were selected: UD GFs and plain weave GF fabrics. The same epoxy matrix (DDS/Bi = 100%) was used for both fiber types.

Figure 7 shows matrix dissolution time as a function of laminate thickness for CF and GF composites. For laminates with similar thickness (~1mm), the matrix dissolution time for GF composites was more than twice that of CF composites. Thicker GF laminates (~1.5 mm) were not fully dissolved even after 70 h (Figure 7), and matrix residue remained. The residue on GFs was rust red, while the residue on CFs before reaching complete dissolution was eggshell. To verify the above observation, a different type of GF reinforcement (plain weave GF fabrics) was used.

Full dissolution of the epoxy matrix in the second GF laminate (~1.4 mm) also was not achieved after 40 h. Previous recycling studies using nitric acid showed that the time required to reach the same degradation degree was longer in GF composites than in CF composites (using the same reaction temperature and acid concentration) [17,18], and these findings were consistent with our observations. Furthermore, GF composites (UD and plain weave, ~1.5 mm) were also subjected to depolymerization and results were compared with the data from acid digestion. GFs were recovered via depolymerization in ~8 h, which was comparable to CF composites, indicating that unlike acid digestion, depolymerization was effective for GF composites. To understand the relative ineffectiveness of acid digestion for GF composites, the chemical compositions of the residues were analyzed using EDS.

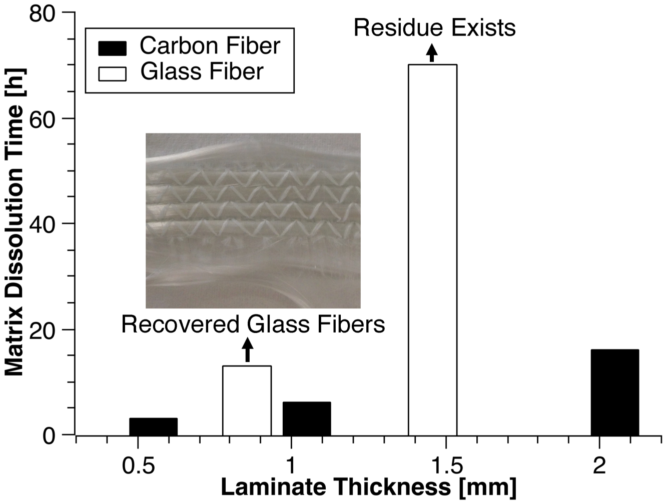

Figure 7. Effect of fiber reinforcement type on epoxy matrix (DDS/Bi =100%) dissolution rate

Figure 8 (a) shows an EDS spectrum acquired from residue from CF composites collected before reaching full dissolution via acid digestion. The three most prominent elements in the spectrum are carbon (C), oxygen (O) and sulfur (S), all of which are typical for amine-cured epoxies. In contrast, Figure 8 (b) and (c) reveal that the elements present in the residues on the GFs

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also contained silicon (Si), aluminum (Al) and calcium (Ca). These three elements, Si, Al and Ca, are related to the components in GFs (aluminum oxide (Al_2O_3), calcium oxide (CaO) and silicon dioxide (SiO_2)), indicating partial decomposition of GFs during acid digestion. Supplementary Figure S2 shows that the recovered GFs had no significant defects, and thus the extent of fiber degradation was low. Figure 8 (d) shows the presence of phosphorus (P) and potassium (K) in the residue on GFs after depolymerization, elements attributed to catalyst (K_3PO_4) contamination of the fibers. Other elements (C, O, and S) were identical to the residue on CFs, indicating that there was no degradation of the GFs in depolymerization, which matched the observation that clean GFs were recovered from depolymerization.

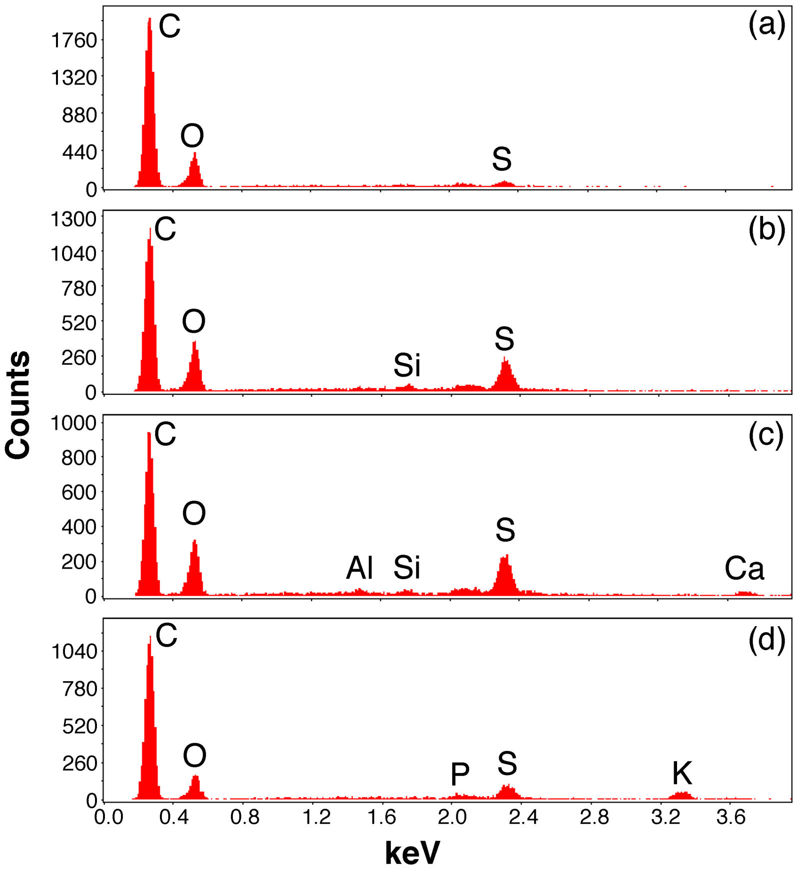

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Figure 8. EDS spectra of epoxy residues (DDS/Bi= 100%) on recovered fibers: a) CF twill weave, acid digestion, b) GF UD, acid digestion, c) GF plain weave, acid digestion, d) GF plain weave, depolymerization

We can conclude from these observations that during acid digestion, GFs are generally more susceptible to reaction than CFs. The degradation of GFs can lead to changes in chemical composition of the epoxy matrix, which prevents the matrix from reaching full dissolution. The reaction condition of depolymerization has negligible effects on both CFs and GFs, and the dissolution behavior of CF and GF composites are nearly identical.

3.5. Strategies to Accelerate Diffusion

The results described above demonstrate that acid digestion is a suitable candidate for recycling of amine/epoxy matrix composites - it presents a relatively fast reaction rate at a moderate reaction temperature (110°C) and yields clean fibers. However, the slow diffusion rate in heavily crosslinked matrices limits the overall matrix dissolution rate. In the following sections, two strategies to increase the diffusion rate and accelerate the process - pre-treatment and mechanical shredding - are explored.

3.5.1. Pre-treatment

The underlying purpose of pre-treatment is to accelerate dissolution by first immersing the composite in appropriate solvents before the chemical reaction. During the immersion process, the solvent penetrates the crosslinked network, enabling reactant molecules to reach cleavable bonds more easily, thus reducing/eliminating the rate-limiting effect of diffusion. Different solvents were evaluated, including benzyl alcohol, xylene, diethylene glycol dimethyl ether (DGDME), and diethylene glycol methyl ether (DGME). Trials determined that the most promising pre-treatment solvent was benzyl alcohol (solvent) at 40°C above the matrix T_g, for 1.5 hours per millimeter thickness of the laminate. The solvent pre-treatment could be applied repeatedly, as no chemical reaction occurred during this step. In the second step, pre-treated composites were subjected to chemical reaction (acid digestion) to dissolve the epoxy matrix and separate clean fibers from the matrix.

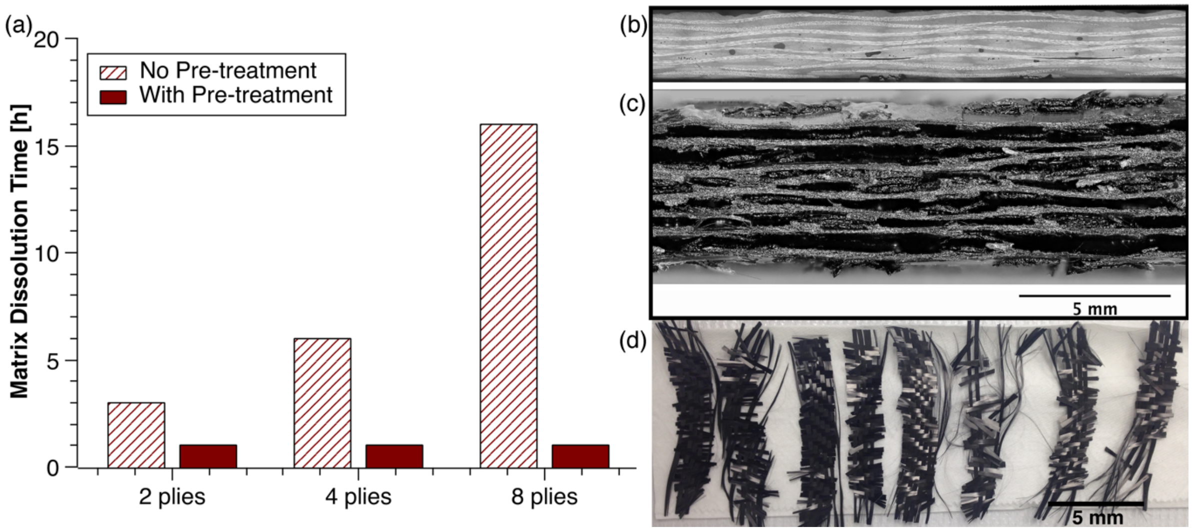

Figure 9. Effect of pre-treatment on matrix (DDS/Bi= 100%) dissolution rate via acid digestion (a), cross-sectional images of laminates (b) before and (c) after pre-treatment, and carbon fiber fabrics recovered from (d) an 8-ply laminate using acid digestion with pre-treatment.

Figure 9 (b) and (c) show that after pre-treatment at 200°C, the laminate (amine/epoxy DDS/Bi= 100%, T_g = 160°C) swelled (weight increase = 100%) and expanded in thickness (thickness increase = 120%). By applying pre-treatment prior to acid digestion, the dissolution time reduced to 1 h for all laminates, regardless of thickness (Figure 9 (a)), confirming that pre-treatment effectively removed the diffusion limit in composites. No mechanical stirring was required for the pre-treatment step or for the subsequent chemical reaction step, and the fiber arrays remained organized. Figure 9 (d) shows the fabrics recovered from an 8-ply laminates. Recall that without pre-treatment, the chemical reaction on solid composites was heterogeneous,

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initiating at the surface and progressing to the laminate center. The long dissolution time distorted and tangled the fibers, adversely affecting fiber properties. In contrast, pre-treatment before acid digestion homogeneously decomposed and dissolved the polymer matrix, preserving the fiber weave and minimizing fiber damage from abrasion. GF composites were also subjected to acid digestion after pre-treatment in benzyl alcohol. GF composite matrices reached full dissolution in 3 h, confirming the assertion that the residue on GF fibers (Figure 7 and Figure ***8***) arose from GF degradation after acid digestion (40+ h).

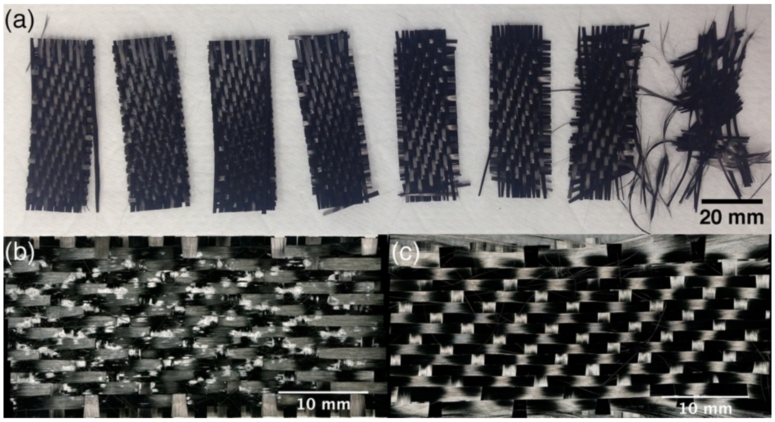

Figure 10. Carbon fiber fabrics recovered from commercial composites (5320-1/8HS): (a) separated plies, (b) recovered fabrics with toughener residue, (c) clean fabric after DMSO wash.

Pre-treatment was also applied to an 8-ply laminate fabricated from commercial prepreg (Cycom 5320-1/8HS). Prior experience dictated a pre-treatment temperature of 240°C (the T_g = 197°C for the cured 5320-1/8HS laminate). However, because the boiling point of benzyl alcohol is 205°C at atmospheric pressure, the pre-treatment was performed in a closed apparatus at 220°C and 5 atm. After pre-treatment, the laminate was subjected to acid digestion, and all 8 plies separated in 48 h (Figure 10 (a)). The dissolution time required will likely be much shorter if the laminate is pre-treated at a higher temperature. Images of the recovered CF fabrics (Figure 10 (b)) showed a white surface residue, which was likely attributed to polyethersulfone (PES), a commonly used toughener that is stable during acid digestion. Both 1 HNMR and FTIR spectra from the PES residue are shown in Supplementary Figures S3 (a) and (b), respectively. PES can be dissolved in amide solvents [27], such as dimethylformamide (DMF), N-Methyl-2-pyrrolidone (NMP), dimethylacetamide (DMA), as well as other organic solvents, such as dimethyl sulfoxide (DMSO). Figure 10 (c) shows the clean fabric after rinsing in DMSO. SEM images of the CFs recovered from 5320-1/8HS laminates are shown in Supplementary Figure S4.

3.5.2. Shredded Materials

Pyrolysis of composites at end-of-life is commonly preceded in practice by mechanical shredding of waste into small pieces (ELG Carbon Fibre Ltd). Shredding introduces matrix cracks and accelerates pyrolysis, but can also have benefits to chemical treatment approaches, reducing diffusion distances required for reactions. To investigate the effect of shredding on matrix dissolution rate, acid digestion was performed on shredded composite waste. The material was a blend of longer fiber tapes impregnated with matrix, clusters of loose fibers, and fine powders generated during shredding (Supplementary Figures S5 (a) and (b)). The as-received shredded material was subjected to acid digestion for 12 h. After rinsing in acetone and water, clean fibers were recovered (Supplementary Figures S5 (c) and (d). The recovered CFs (Supplementary figure S6) showed no obvious defects or residue.

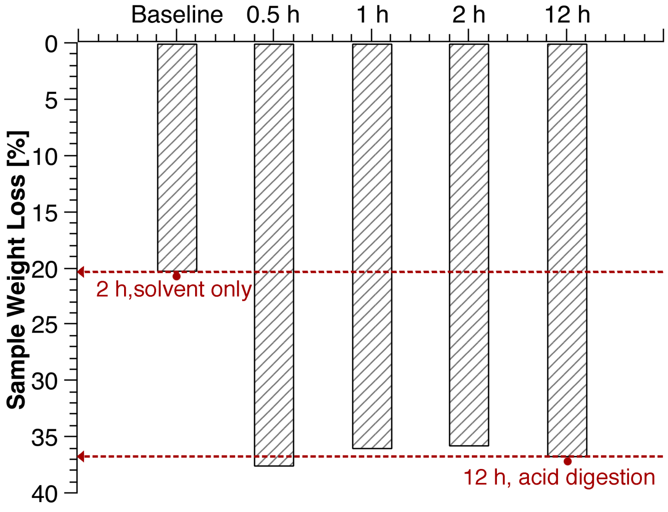

Figure 11. Matrix dissolution rate in shredded composite waste

To determine the minimum time required to reach full dissolution in shredded materials, reaction times from 0.5 - 12 h were evaluated. Figure 11 shows that using solvent (acetic acid) only, the sample weight loss after 2 h was ~20%, which was attributed to dissolution of fine powders into the solvent. After adding H_2O_2, the sample weight loss was comparable (~37%) regardless of reaction time, indicating that full matrix dissolution was achieved in as little as 0.5 h. This observation confirms that the limit of diffusion in shredded composites is negligible, and acid digestion is a viable approach for recycling of shredded composite waste. Recovered short carbon fibers are suitable for a wide range of industrial applications and processes, including injection molding and molding compounds. Short fibers can also be manufactured into non- woven mats, which offer enhanced drapeability and formability required for complex geometries.

4. CONCLUSIONS

The results presented demonstrate key aspects of matrix dissolution for both CF and GF composites (with amine-cured epoxy) using two chemical treatment methods at atmospheric pressure: (a) depolymerization (benzyl alcohol/K_3PO_4 at 200°C) and (b) acid digestion (acetic acid/H_2O_2 at 110°C). Both depolymerization and acid digestion processes dissolved amine/epoxy matrices. However, acid digestion was deemed more suitable and practical for amine/epoxy composite recycling because of 1) faster chemical reaction rate at 2) lower reaction temperature, with 3) the recovery of residue and defect-free fibers. The reaction mechanism of acid digestion (oxidative digestion) for amine-cured epoxies occurred by oxygen atom transfer to the linking aniline groups followed by bond cleavage via elimination. Furthermore, correlations between epoxy matrix functionality, fiber bed architecture, type of fiber reinforcement, and dissolution rate were identified. Acid digestion was an effective method for dissolving heavily crosslinked epoxy matrices, and fiber bed architecture had a negligible effect on dissolution rate. For GF composites, however, acid digestion caused fiber degradation.

Experiments also demonstrated that the rates of chemical reaction and diffusion were the two factors controlling matrix dissolution rate, and the diffusion limit was most significant in matrices with high crosslink density when using acid digestion. The findings indicated that the dissolution rate was accelerated by permeabilizing the heavily crosslinked networks to accelerate diffusion. Two strategies to accelerate the diffusion rate – pre-treatment and mechanical shredding – were investigated, and aerospace-grade amine/epoxy composites and commercial shredded composite waste were evaluated. Both strategies accelerated the diffusion rate, resulting in recovery of clean fibers. Furthermore, pre-treated polymer matrix was homogeneously decomposed and dissolved into solution, preserving the fibers in fabric form with negligible fiber damage.

The viability of acid digestion with pre-treatment of amine/epoxy composite at atmospheric pressure affords opportunity to recover and recycle high-value fibers from composites, while preserving useful parts of epoxy molecules. However, evaluation of this solution revealed three drawbacks. First, H_2O_2 is unstainable – it is an expensive and explosive reagent that cannot be deployed on an industrial scale. Second, the oxidative degradation reaction in H_2O_2 is not selective, and consequently, the dissolution products have little value and are thus difficult to reuse. We are currently working on acid digestion methods to recover and reuse polymers as additives for new epoxy formulations. Lastly, the pre-treatment temperature to remove diffusion limit in composite with high T_g exceeds the boiling point of the pre-treatment solvent (benzyl alcohol), which brings safety issues and adds infrastructural costs. Current efforts are devoted to seeking safer alternatives to H_2O_2 oxidation that can effectively recover fibers and valuable polymer from amine/epoxy composites, as well as permeabilization methods that requires lower temperature. The insights provided in this study has furnished additional insights and a more comprehensive understanding of amine/epoxy composite recycling processes. Development of effective catalysts and permeabilization methods may yield faster and sustainable reactions, possibly sufficient to meet present and future needs. Doing so will yield a more sustainable solution for recycling amine/epoxy composites at atmospheric pressure on an industrial scale.

Acknowledgements: This project is funded by the National Science Foundation G8 Research Project of Interdisciplinary Program on Material Efficiency, through the "Sustainable Manufacturing: Out-of-Autoclave Processing" project (CMMI-1229011). Huntsman Corporation generously donated the epoxy resins and curing agents used in this study. The authors would also like to thank Airtech International for donating the consumables used in composite manufacturing. The SEM images presented in this article were acquired at the Center for Electron Microscopy and Microanalysis at the University of Southern California. Helpful guidance for prepreg fabrication from Yixiang Zhang is appreciated. Finally, suggestions and contributions of Dr. Travis J. Williams for the thermoset composite recycling project are gratefully acknowledged.

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