Chemical Treatment for Dissolution of Amine-Cured Epoxies at Atmospheric Pressure

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Abstract

Carbon fiber/epoxy composites have largely resisted attempts to recycle because the crosslinked polymer matrices cannot be easily separated from the fiber reinforcements. In this study, two chemical treatment methods - depolymerization and acid digestion (both at atmospheric pressure) - were employed to dissolve amine-cured epoxy formulations. Both depolymerization and acid digestion were shown to be effective dissolution processes for all amine/epoxy samples that encompassed variations in amine/epoxy stoichiometric ratio (A/E ratio), epoxy monomer functionality, and amine curing agent type. The relationship between epoxy properties and dissolution rate was determined, and the key parameters affecting thermoset matrix dissolution were identified. The dissolution rate was controlled by both the chemical reaction and diffusion rates. The components of the chemical solutions after epoxy dissolution were analyzed and identified, and protocols to quantitatively track the products after dissolution were developed. The two major cleavable sites during epoxy dissolution were the C-N and C-O bonds, and the aromatic structures of the epoxies were preserved.

Keywords: Recycling; Composites; Carbon fiber; Epoxy; Chemical treatment; Atmospheric pressure

1. Introduction

Because of increasing demand for lightweight structures in aerospace, automotive, and wind energy industries, the global demand for carbon fiber (CF) composites will grow to an estimated 146,000 ton/yr in 2020, consuming 89,000 tons of carbon fibers [1]. A major portion of the carbon fibers produced will be consumed in the production of airplanes and automobiles. The lifespan of a commercial airplane (20-30 years), and the average life expectancy of a new car (less than 10 years), pose needs and challenges for recycling. Though carbon fibers from end-of-life products retain properties similar to those of virgin fibers, little carbon fiber is recovered and re-used due to (a) a lack of viable recycling methods, and (b) insufficient market demand. As end-of-life composite waste continues to increase, the need for composite recycling methods will increase also, especially for composites with thermoset matrices that undergo an irreversible cure reaction.

Thermoset composites exhibit superior mechanical properties, good resistance to heat and corrosion, low shrinkage upon cure, and low moisture absorption. Most of these attributes derive from the thermoset nature of the matrix. After cure, thermoset matrices have cross-linked, three-dimensional structures and are generally insoluble and inert under mild-to-severe conditions [2, 3]. Thus, separating the fiber reinforcements from matrices poses challenges for composite recycling.

Because of the absence of effective methods to separate carbon fibers from thermoset matrices, end-of-life composites are commonly 1) disposed in landfills without treatment, 2) incinerated for energy, because polymer matrices can be burned at sufficiently high temperature [3], or 3) mechanically ground to produce fillers or reinforcement for lower grade composites [4,

5]. After incineration, most of the material converts to ash, fiber residue, and other solid waste, which is sent to landfills as well. Mechanical grinding has been investigated for both glass and carbon fiber-reinforced composites, although most reported research has dealt with glass fiber composites. The process of mechanical grinding is simple, but clean fibers of sufficient length generally cannot be recovered, and little value is recovered from the composites waste. Effective recycling methods are thus needed to make composite materials more sustainable.

An ideal composite recycling approach should feature ease of recovery, process robustness, recovery of fibers with near-virgin quality, low overall cost, high throughput, low gaseous emissions, and little hazardous waste. All these features may not be present in a real process because of multiple problems concerning material properties of thermoset composites, such as good thermal and chemical stability. However, some of the necessary attributes for effective recycling are being incorporated into composite recycling methods, as outlined next.

Thermal processing (pyrolysis) is now the most widely used recycling process for industrial scale recycling [4-6]. Thermal processing relies on heat to degrade polymer matrices into lower molecular weight components. Those products can be volatilized into gases, after which fibers can be separated and recovered. However, thermal processing generally requires high temperatures (450 to 700 °C) depending on the properties of the matrix, which can lead to fiber degradation and entangling. Reported data showed that during pyrolysis of CF composites at 500 ^{o}C, there was negligible degradation of fiber tensile strength [6]. However, pyrolysis above 600 ^{o}C caused severe oxidation of the carbon fiber and the tensile strength of the fibers declined by > 30% [6]. Furthermore, thermally degraded matrix (generally epoxy) often leaves residual char on fiber surfaces, even in the absence of oxygen, which reduces the interfacial bond

strength between recycled fibers and new matrix systems. Lastly, high temperature also raises the cost for recycling a material that is considered a waste product.

In chemical treatment (solvolysis), a wide range of solvents are used as a reactive medium with a catalyst or reagent to decompose the matrix into oligomers or monomers, under supercritical or atmospheric pressure. Relatively low temperature is required (compared to pyrolysis) for matrix dissolution, and clean, intact, carbon fibers can be recovered which retain 100% of the elastic modulus and 95% of the ultimate tensile strength compared to virgin carbon fibers [5]. Valuable products from the chemical feedstock can also be reused after additional treatment. Consequently, among all recycling approaches for thermoset composites, most research attention has focused on chemical treatment.

Traditionally, supercritical fluid has been used for recycling due to the unique interactions achieved between gas and liquid phases in the reaction medium, especially the high mass transfer coefficient and diffusivity. Commonly used solvents include water, ethanol, methanol, propanol, acetone, and their mixtures. Alkaline catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), are often added to accelerate the reaction rate and reduce the reaction temperatures [5, 8]. High temperature (> 250 ^{o}C) and high pressure (> 5 MPa) are required to reach supercritical conditions due to hydrogen bonds in the solution [5]. Specific reaction conditions depend on the nature of the matrix. For example, Okajima et al. attempted recycling of bisphenol A type epoxies cured with phthalic anhydride using supercritical methanol at 250-350 ^{o}C and 10 MPa [7]. They reported that the crosslinked structure of the epoxy decomposed and dissolved in supercritical methanol at > 270 ^{o}C within 1 h. When the temperature decreased to 250 ^{o}C, the epoxy dissolution time increased to 2 h. Hyde et al. used supercritical propanol as the solvent fluid to remove bisphenol A type epoxies cured

with amines from composites, using conditions above 450 ^{o}C and above 5 MPa [9]. Results showed little damage to the fibers, and the recovered fibers retained 95 % of the tensile strength of virgin fibers, despite the severe conditions. However, under supercritical conditions, reactors made of special alloys are required to withstand the high pressures and chemical corrosion. Thus, the capital costs associated with supercritical chemical treatment are generally high. Consequently, chemical treatment that can be performed under atmospheric pressure and low temperature (< 200 ^{o}C) has emerged as a research focus in thermoset composite recycling.

Chemical treatment methods for recycling thermoset composites at atmospheric pressure have been reported, often using an acidic medium, such as nitric [10] or sulfuric acid [11]. But strong acid solutions pose environmental hazards, and thus, atmospheric chemical treatment methods that require less corrosive reaction media and are easier to handle have drawn attention recently. For example, Hitachi Chemical reported a solvolytic depolymerization method conducted at atmospheric pressure for anhydride/epoxy systems, using chemical solutions comprised of alkali metal salt (catalyst) and high boiling point alcohol (solvent) [12-14]. The method was demonstrated for anhydride-cured matrices, and thus, the viability of the process for amine-cured epoxies, which are widely used in high performance composites, is unlikely. Amine/epoxy formulations lack ester groups for transesterification, a reaction essential to the Hitachi technology [14]. Thus, this approach cannot be expected to effectively dissolve amine/epoxy matrices.

Chemical dissolution of amine-cured epoxy formulations requires a different approach. Ma et al. conducted a parametric study of the recyclability of amine-cured epoxies using the above depolymerization conditions [15], and reported that the same depolymerization approach could also be used to fully dissolve amine-cured epoxies with high crosslink density, although

the dissolution rate was slower than for anhydride-cured epoxies. Xu et al. investigated an oxidative treatment, using a mixed solution of hydrogen peroxide and *N,N*-dimethylformamide as the reaction medium to dissolve amine/epoxy matrices with an epoxy value of 0.54–0.57 (bi-functional resin) [16]. Results showed that clean fibers were recovered, and the recovered fibers retained > 95% tensile strength. However, the dissolution of amine/epoxy matrices with higher crosslink density is more challenging, and doing so in oxidative environments has not been considered.

In the present study, we focus on chemical treatment methods at (1) atmospheric pressure and (2) low temperature (< 200 ^{o}C) for amine-cured epoxy formulations with highly crosslinked networks. These features are critical to practical, large-scale composite recycling, but have not been reported to date. Two methods - depolymerization and acid digestion - are applied to amine-cured epoxies with high crosslink densities. We show both depolymerization and acid digestion routes can achieve 100% resin dissolution in all amine/epoxy samples. Correlations between epoxy formulation and dissolution reveal that the dissolution rate is influenced not only by the chemical reaction rate, but also greatly by the diffusion rate, which has not been reported previously. Protocols are developed using NMR spectroscopy to characterize the components of the chemical solutions. We show that the two major cleavable sites during epoxy dissolution are C-N and C-O bonds. During dissolution, cured polymers are first cleaved into molecular chains with various lengths, which further react to yield oligomers or monomers. These discoveries of molecular level mechanisms of dissolution provide insights to inform further studies on amine/epoxy composite recycling optimization and development of large-scale recycling processes.

2. Experiments

Amine/epoxy resins were formulated (without toughening agents or other additives) to analyze cured epoxy dissolution by chemical treatment. The resin formations, relatively simple compared to commercial epoxy formulations, provided less complex crosslinked structures, allowing identification of the chemical reactions involved in dissolution. 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. Cured samples were subjected to (a) depolymerization and (b) acid digestion. One- and two-dimensional proton NMR spectroscopy (1H and 2H NMR) was used to identify the components of the chemical solutions after dissolution.

2.1 Resin Formulation

Resins were formulated using three types of epoxy monomers that varied in epoxy functionality. The first, bi-functional epoxy, was a diglycidyl ether of bisphenol A (DGEBA, Araldite GY 6010, Huntsman Corporation). DGEBA was a medium viscosity liquid epoxy with a chemical structure as shown in Figure 1 (a). The second was tri-functional epoxy, a triglycidyl of para-aminophenol, with medium functionality and low viscosity (Araldite MY 0510, Huntsman Corporation, Figure 1 (b)). The third was tetra-functional epoxy - tetraglycidyl-4,4'-methylenebisbenzenamine - that featured high functionality and yielded systems with good thermal stability and mechanical performance (Figure 1 (c)). Epoxy equivalent weight (EEW) was used to calculate the A/E ratio for amine curing agents and epoxy resins. The EEWs of bi-, tri- and tetra-functional epoxy monomers were 187, 101 and 113 g/eq, respectively. 1 HNMR

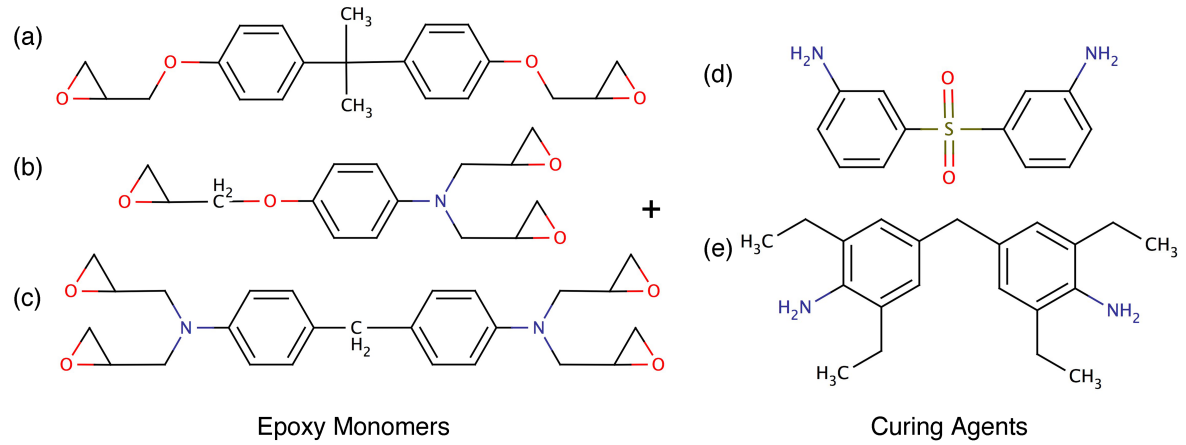


Figure 1: Epoxy monomers and amine curing agents (red and blue represent oxygen (O) and nitrogen (N), respectively)

spectra of bi-, tri- and tetra-functional epoxy monomers are shown in Supplementary Figures S4, S5, and S6, respectively.

Two types of tetra-functional, amine-based curing agent were selected to react with the epoxy monomers. Type I curing agent was diamine 3,3'-diaminodiphenyl sulfone (3,3'-DDS, Aradur®9719-1, Huntsman Corporation), a high-performance curing agent shown in Figure 1 (d). Type II was 4,4'-methylenebis (2,6-diethylaniline) (M-DEA, Sigma-Aldrich), a component often used as curing agent or chain extender (Figure 1 (e)). Amine hydrogen equivalent weight (AHEW) was used in A/E ratio calculations, and the AHEWs of 3,3'-DDS and M-DEA were 63 and 78 g/eq, respectively. A 1 HNMR spectrum of 3,3'-DDS is shown in Supplementary Figure S3.

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 A/E ratio varied from 40 % to 100 %, providing a wide range of crosslinking densities. The mixture

was then heated to 120 ^{o}C in a pre-heated convection oven to further improve the mixing quality, yielding a clear homogenous mixture.

2.2 Thermal Analysis

TGA tests were used to measure the degradation temperature of the epoxy samples. First, TGA was performed on samples to obtain a correlation of sample weight loss as a function of temperature. In each TGA test, a dynamic ramp was applied from 30 to 400 ^{o}C at a heating rate of 1.5 ^{o}C/min. From the TGA data, polymer degradation temperature was defined as the temperature at which 5% sample weight loss was achieved. The degradation temperature set an upper limit for further MDSC tests. All samples began to degrade at ~300 ^{o}C.

MDSC tests were performed on each sample to measure the glass transition temperature (T_g) of the 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.

2.3 Amine-cured Epoxy Dissolution

Epoxy dissolution samples were prepared by curing specific amounts of resin in an oven via the same temperature ramp at 1.5 °C/min to 250 °C, followed by a dwell for 0.5 hour. MDSC measurements were performed again on oven-cured samples to confirm that no residual exothermic reaction peaks existed and that the T_g's of the oven cured samples were comparable to that of the MDSC-cured samples. Cured samples were then dissolved by depolymerization and

acid digestion. Epoxy dissolution time was defined as the time required to achieve complete dissolution in solvent (determined by visual observation), which marked the end of each experiment. The standard deviation of dissolution time for samples with the same formulation was below 5 %, so one sample was tested for each condition. For consistency, sample concentration used in all experiments was 10 mg/mL.

2.3.1 Approach I: 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 a weighed sample (1 g) was fluxed at 200 ^{o}C in an oil bath. Magnetic stir bars were placed in both the oil bath and the flask to homogenize the heat and concentration distribution. Nitrogen flow was employed to create an inert environment for the reaction to keep the catalyst in a reactive form. After reaction, the homogenized chemical solution was stored in a glass bottle for further analysis.

2.3.2 Approach II: Acid Digestion

Acid digestion (more accurately described as oxidative digestion) was performed using a solution of 100 mL glacial acetic acid (solvent, Sigma-Aldrich) and 10 mL hydrogen peroxide solution (oxidant, 30 % (w/w) in H_2O, Sigma-Aldrich). The same setup as depolymerization was used in acid digestion. The resultant mixture and a weighed sample (1 g) were refluxed at 110 ^{o}C, and additional hydrogen peroxide solution (30%, 5 mL) was added to the flask every hour. No nitrogen flow was used for acid digestion.

2.3.3 Pre-treatment

Pre-treatment was employed as a strategy to permeabilize (swell) the cured sample before dissolution, so that the rate-limiting effect of solvent diffusion could be reduced or eliminated. During pre-treatment, cured samples were placed in benzyl alcohol at 200 ^{o}C for 3 hours, which was more than sufficient for the sample size (1 g). After pre-treatment, the epoxy samples were softened and expanded compared to their original size. The soaking pre-treatment allowed the solvent to penetrate the crosslinked network, enabling reactant molecules to subsequently reach the cleavable bonds more easily, thus increasing dissolution rates.

2.4 Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy (Varian Mercury 400) is useful for characterizing small molecules and polymers. 1H NMR is the most sensitive NMR technique, well-suited to polymer analysis, because the large macro-molecules in polymers are generally tangled and have repeat units. 2H NMR can provide information complementary to 1H NMR in a manner that is more easily interpreted, and is often used to confirm data from 1H NMR. Chemical solutions from depolymerization and acid digestion were analyzed in 1H and 2H NMR. The liquid mixture was first purified by removing solid impurities after letting the mixture standing overnight. Next, the chemical solution (benzyl alcohol) was evaporated, and the dried sample was dissolved in deuterated dimethyl sulfoxide until a clear solution was achieved for 1H and 2H NMR analysis.

2.5 Test Matrix

Table 1 summarizes the five sets of dissolution experiments performed in this study. In Set I, the viability of depolymerization and acid digestion for epoxy dissolution was investigated using 3,3'-DDS-cured bi-functional samples. The selected A/E ratios promoted different reaction

kinetics and crosslinking densities in cured epoxies, thus affecting those properties related to crosslinked network morphology. To investigate the effect of A/E ratio on the recyclability of amine-cured epoxy, samples at A/E = 40 %, 60 %, 80 % and 100 % were tested. In Set II, the effect of diffusion was analyzed by applying pre-treatment to 3,3'-DDS-cured bi-functional epoxies at A/E = 60 %, 80 % and 100 % before acid digestion. The T_g values for those samples were similar to or greater than the reaction temperature of acid digestion, and the effect of diffusion was expected to be non-negligible. In Set III, highly crosslinked samples (produced from 3,3'-DDS-cured tri- and tetra-functional epoxies) were subjected to depolymerization and acid digestion to evaluate the effect of crosslink density. Sets IV and V were used to determine the cleavable sites during epoxy dissolution. By replacing 3,3'-DDS with M-DEA without sulfone functional groups, Sets IV and V revealed the effects of sulfone functional groups on dissolution by depolymerization and acid digestion.

Set	Amine	Epoxy	A/E Ratio	Chemical Treatment
I	3,3'-DDS	Bi-functional	40 %, 60 %, 80 %, 100 %	Approach I and Approach II
II	3,3'-DDS	Bi-functional	60 %, 80 %, 100 %	Pre-treatment + Approach II
III	3,3'-DDS	Tri-functional	40 %	Approach I and Approach II
		Tetra-functional	40 %	Approach I and Approach II
IV	M-DEA	Bi-functional	40 %, 60 %, 80 %, 100 %	Approach I and Approach II
V	M-DEA	Tri-functional	40 %	Approach I and Approach II
		Tetra-functional	40 %	Approach I and Approach II

Table 1: Test matrix for amine-cured epoxy dissolution

3. Results and Discussion

3.1 Bi-functional Epoxy Dissolution

Figure 2 (a) shows that as the A/E ratio increases from 40 % to 100 %, the dissolution time increases for both depolymerization and acid digestion processes. For a given A/E ratio (40 %, 60 % and 80 %), dissolution times for acid digestion are less than those for depolymerization, indicating a faster chemical reaction rate for acid digestion. However, for bi-functional samples with A/E = 100 %, the dissolution times for depolymerization and acid digestion are comparable.

To explain this finding, the T_g's of the cured epoxies are analyzed (Figure 2 (b)). As the A/E ratio (in bi-functional samples) increases from 40 % to 100 %, the T_g's of epoxies cured using the same cure cycle increases from 60 to 160 ^{o}C in a quasi-linear manner. The T_g is the temperature where the free volume available for chain movement has reached a minimum value, and the internal mobility of the polymer chains starts to change markedly. Thus, the material physically changes between the glassy state and the rubbery state. The increase in T_g represents the decrease in free volume and the decrease in freedom of polymer chains to achieve different physical conformations. For cured epoxy at A/E = 100 %, the T_g (160 ^{o}C) is greater than the reaction temperature for acid digestion (110 ^{o}C), so the mobility of the polymer chains is reduced compared to samples with lower A/E ratios. The low mobility of the polymer chains, as well as the decreased free volume, limits the diffusion of the solvent and reactant molecules into the crosslinked network, and thus longer dissolution time is required. For depolymerization, the reaction temperature (200 ^{o}C) is greater than the T_g's of the samples, and the dissolution rate is mainly limited by the chemical reaction rate of depolymerization.

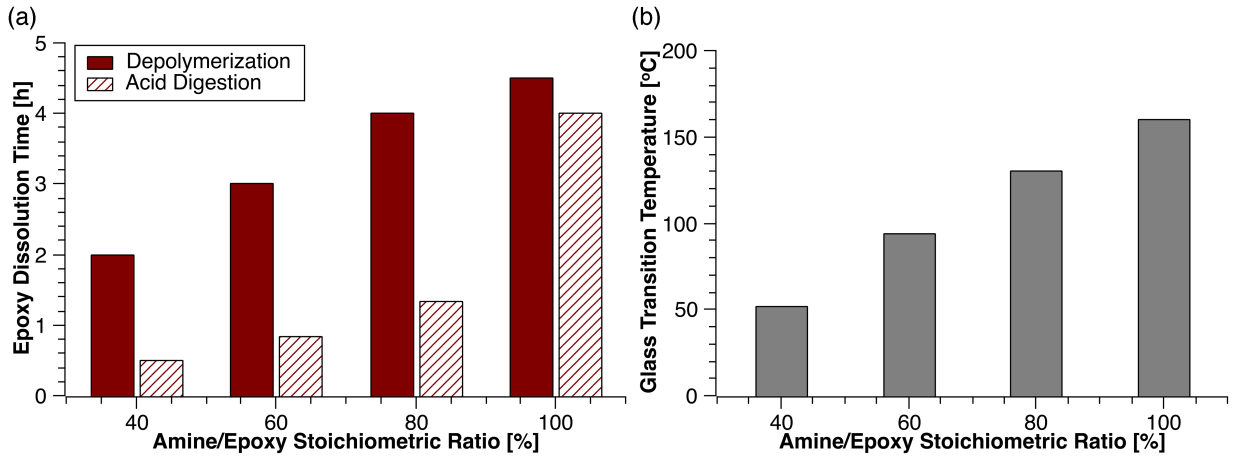


Figure 2: Effect of A/E ratio on a) dissolution time and b) T_g's for 3,3'-DDS-cured epoxies

We conclude from the above observations that both depolymerization and acid digestion are effective for amine-cured epoxy dissolution. The dissolution rate is influenced by the chemical reaction rate, and also by the diffusion rate. When the reaction temperature is less than the T_g of the epoxy, the dissolution rate is mainly determined by the diffusion rate. However, in other cases, the chemical reaction rate is the deciding factor, and the chemical reaction itself is faster for acid digestion than for depolymerization.

3.2 Effect of Diffusion

To evaluate the effect of diffusion on dissolution rate, 3,3'-DDS-cured bi-functional samples with A/E = 60 %, 80 %, 100 % are pre-treated in benzyl alcohol. Figure 3 shows that pre-treatment reduces the dissolution times for all the above formulations, even for the sample with A/E = 60 % that exhibits a T_g (95 ^{o}C) lower than the reaction temperature (110 ^{o}C). This finding indicates that the limit from diffusion exists in all cured epoxies, though the extent may vary. The sample with A/E = 100 % shows the greatest reduction due to the highest crosslink density compared to the other two amine/epoxy formulations. This observation supports the

assertion that the particularly long time required for dissolution of the sample with A/E = 100 % (Figure 2 (a)) is due to slow diffusion.

Pre-treatment experiments demonstrate that the diffusion rate plays a key role in determining epoxy dissolution rate if the reaction temperature is less than or comparable to the T_g's of the cured samples. Choice of appropriate pre-treatment solvents to better permeabilize the cured epoxies with heavily crosslinked network can effectively reduce/overcome the limit from diffusion.

3.3 Tri- and Tetra-functional Epoxy Dissolution

Tri- and tetra-functional epoxy monomers show end groups similar to bi-functional monomers (Figure 1), but differ in molecular structure. Higher functionality resins also promote more heavily crosslinked networks, which further limits diffusion of the solvent molecule. In this section, polymerization and acid digestion of 3,3'-DDS cured tri- and tetra-functional samples with A/E = 40 % are analyzed. The results are compared to the data for bi-functional samples (A/E = 40 %) to gain a more complete understanding of amine/epoxy dissolution.

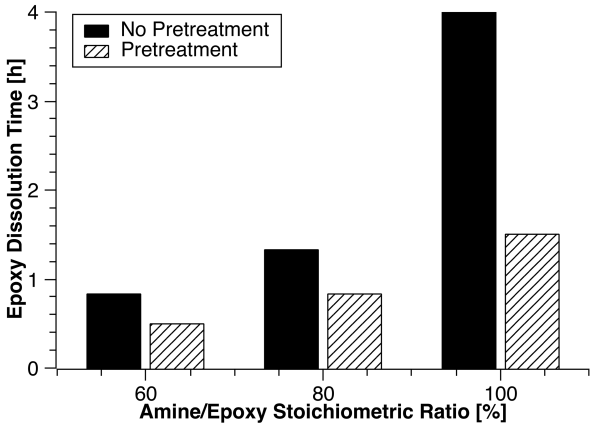


Figure 3: Effect of pre-treatment on epoxy dissolution time

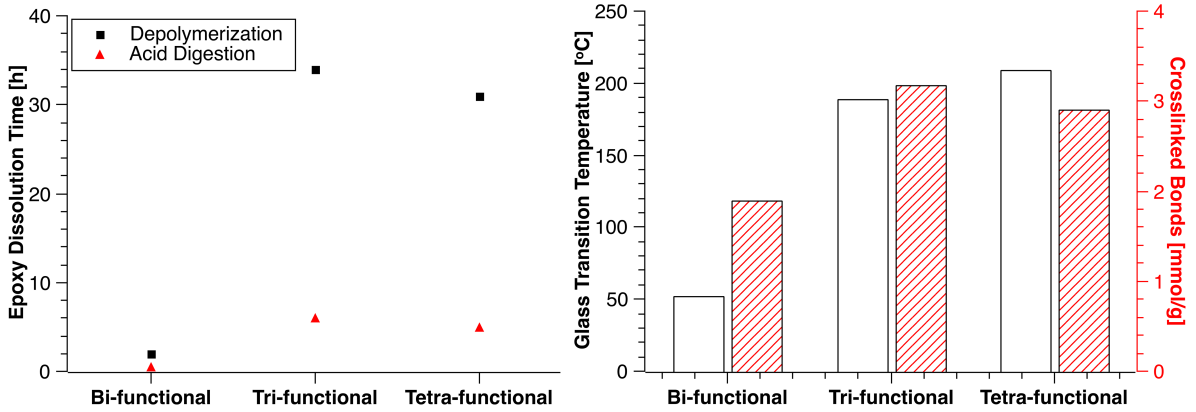


Figure 4: Effect of epoxy functionality on a) dissolution time and b) T_g's and number of crosslinked bonds for 3,3'-DDS-cured epoxies

Figure 4 (a) shows the dissolution times of 3,3'-DDS cured bi-, tri-, and tetra-functional epoxies with A/E = 40 %, indicating that all samples can be dissolved via depolymerization and acid digestion. Acid digestion again requires shorter dissolution time than depolymerization, which is attributed to the faster reaction rate and is consistent with previous discussion. The MALTI-TOF/MS data in Supplementary Figure S7 show that the maximum molecular weight of the dissolution products for tri-functional epoxy is 834 at 34 h into depolymerization, and 620 at 6 h into acid digestion, confirming that the chemical reaction rate for acid digestion rate is faster than depolymerization. For both recycling methods, the dissolution times for bi-functional epoxies are less than 4 hours. But for tri- and tetra-functional epoxies, the dissolution times are more than ten times longer than for bi-functional samples. This observation can also be attributed to the slower diffusion rate in tri- and tetra-functional epoxies.

Figure 4 (b) shows the T_g values for bi-, tri- and tetra-functional epoxies prepared using the same cure cycle, which are 50, 190 and 210 ^{o}C, respectively. For the bi-functional sample, the T_g is lower than the temperature for both depolymerization (200 ^{o}C) and acid digestion (110

°C), so the dissolution rate is determined primarily by the chemical reaction rate. However, for tri- and tetra-functional samples, the corresponding T_g values are greater than the reaction temperature for acid digestion, and are comparable to the reaction temperature for depolymerization. In addition, tri- and tetra-functional epoxies contain more heavily crosslinked networks than bi-functional epoxies. Thus, diffusion is rate-limiting for tri- and tetra-functional epoxy dissolution in both chemical treatment methods, and the resultant dissolution rate is slower than for bi-functional epoxies.

While cured tri-functional epoxies exhibit T_g values lower than tetra-functional epoxies (Figure 4 (b)), signifying a less heavily crosslinked network, they require longer dissolution times than tetra-functional epoxies for both depolymerization and acid digestion (Figure 4 (a)). The finding can be explained as follows. There are three main types of reactions occurring during the curing process of amine/epoxy resins (Figure 5) [20-23]. Reactions I and II are the primary (°1) and secondary (°2) amine reactions with the epoxy groups, respectively. Reaction III is an etherification reaction of the pendant hydroxyl groups formed during Reaction I with the epoxy groups. The etherification reaction is reported to be negligible at low temperature, becoming important only above 150 °C [20]. Reaction rate constants for Reaction II (°2 epoxy-amine) and Reaction III (epoxy-hydroxyl) are reportedly equal and are about one tenth the rate constant of Reaction I (°1 epoxy-amine) [21]. We can assume that the number of C-O bonds formed during cure is proportional to the number of C-N bonds, and the number of total crosslinked bonds can be expressed as equation (1) to explain the difference in dissolution times for tri- and tetra-functional epoxies.

$$\text{Number of crosslinked bonds} = (\text{A/E ratio})/(\text{EEW} + \text{A/E ratio} \times \text{AHEW}) \quad (1)$$

where:

Number of crosslinked bonds: number of C-N bonds in crosslinking (mol/g)

A/E Ratio: Amine/Epoxy stoichiometric ratio (%)

EEW: Epoxy equivalent weight (g/mol)

AHEW: Amine hydrogen equivalent weight (g/mol)

The tri-functional epoxy monomer has a lower EEW (101 g/mol) than the tetra-functional epoxy monomer (113 g/mol), and thus more crosslinked bonds exist in cured tri-functional samples with the same weight (1 g). Due to the slow diffusion rate, samples with more crosslinked bonds take longer to cleave and fully dissolve, so longer dissolution times are required for tri-functional epoxies than for tetra-functional epoxies.

3.4 Cleavable Sites

While the reaction mechanism for dissolution of anhydride-cured epoxies is triggered by transesterification [14], the mechanism for amine-cured epoxies is fundamentally different and not well understood. Chemical attack of the polymer matrix should occur at polarized carbon-

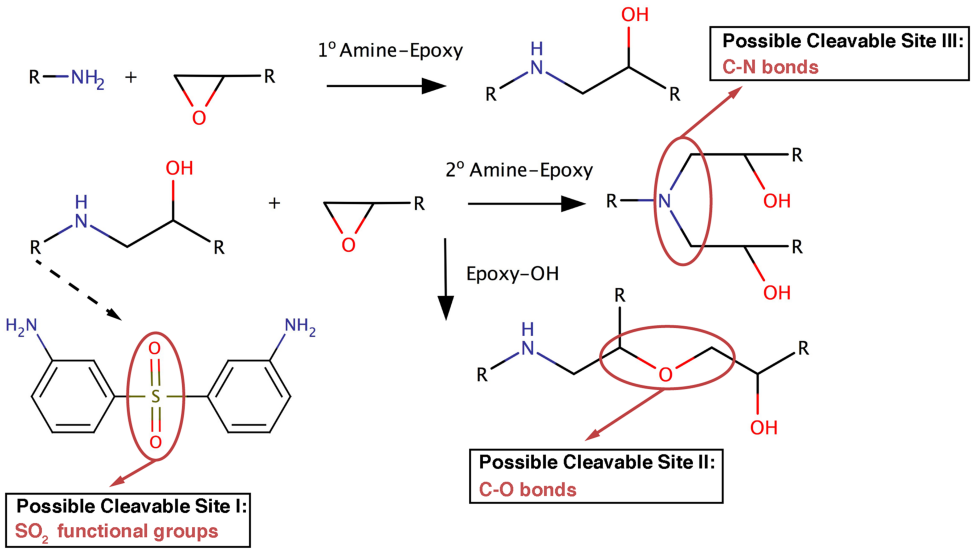


Figure 5: Possible cleavable sites in amine-cured epoxies

heteroatom linkages [17]. We envisage three groups of possible cleavable sites in amine/epoxy samples (Figure 5): (1) carbon-amine nitrogen bonds (C-N bonds) from Reactions I and II [10, 17-18], (2) ether bonds from Reaction III (C-O bonds) [17-19], and (3) sulfone functional groups (SO_2 groups) within the curing agents 3,3'-DDS [17]. To identify the cleavable sites for depolymerization and acid digestion, we analyze the three possible cleavable sites separately.

3.4.1 Sulfone functional groups

Cleavable Site I (SO_2 groups) was investigated first. To evaluate the effect of SO_2 groups, M-DEA (Figure 1 (e)), which contains no sulfone functional groups, was used as the amine curing agent (instead of 3,3'-DDS). Formulated resins were characterized, cured and subjected to both depolymerization and acid digestion. Comparison of the T_g values of M-DEA and DDS cured epoxies is provided in Supplementary Figure S1. Figure 6 (a) shows the dissolution times for bi-functional epoxies with A/E = 40 %, 60 %, 80 % and 100 %. The data indicate that all M-DEA cured bi-functional epoxies are completely dissolved by both methods.

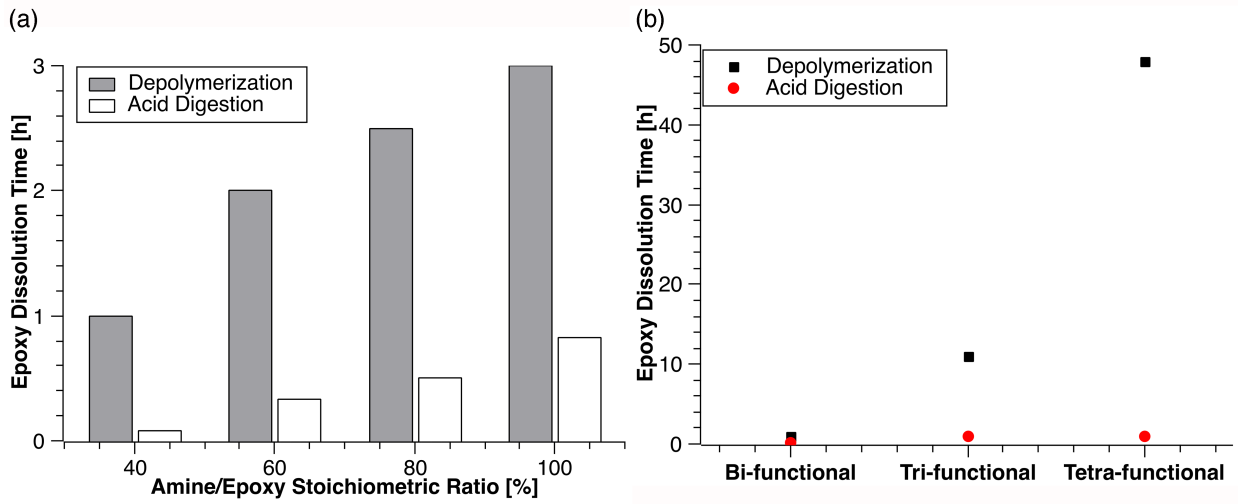


Figure 6: Dissolution times for M-DEA-cured epoxies: a) effect of A/E ratio (bi-functional epoxy), b) effect of epoxy functionality (A/E = 40%)

M-DEA-cured tri- and tetra-functional epoxies with A/E = 40 % are also subjected to depolymerization and acid digestion. Figure 6 (b) shows the dissolution times for tri- and tetra-functional samples with A/E = 40 %, which confirms that depolymerization and acid digestion processes dissolve cured epoxies with high functionality that contain no sulfone functional groups. The data demonstrate that the absence of SO_2 groups does not affect the dissolution properties, and the SO_2 groups are not the dominant cleavable sites for depolymerization or acid digestion.

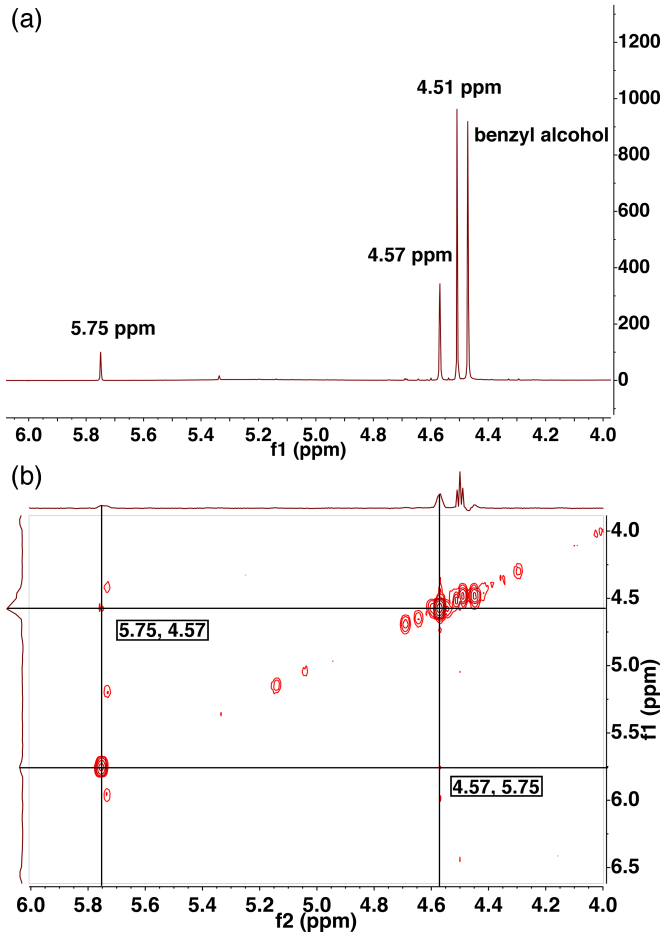


Figure 7: Qualitative a) 1H and b) 2H NMR spectrum analyses of dissolution products (26 h depolymerization) of tri-functional epoxy in DMSO at room temperature (32 scans)

3.4.2 C-N and C-O bonds

Possible cleavable Sites II (C-N bonds) and III (C-O bonds) were considered next. 1H and 2H NMR were performed to analyze the chemical components after epoxy dissolution. Signals from the 4-6 ppm region were analyzed, as multiple signals in the aromatic region produced overlapping peaks. Figure 7 (a) shows four major peaks in the 4-6 ppm region from the depolymerized solution of tri-functional epoxies. The peak at 4.47 ppm corresponds to the secondary carbon hydrogen of the benzyl alcohol solvent residue, and the peaks at 4.51, 4.57 and 5.75 ppm correspond to the epoxy components in the chemical solutions.

2H NMR (gCOSY, Figure 7 (b)) shows J coupling between peaks 4.57 and 5.75 ppm. Depolymerization is characterized by breaking the polymer chain backbone, so that after dissolution, the products are similar to the parent material, yet the crosslined structures are still distinguishable [17]. Therefore, the peaks at 4.57 and 5.75 ppm correspond to the protons of the unreacted crosslinked units. The peak at 4.51 ppm does not show any correlation to other peaks, indicating that the peak corresponds to protons in the cleaved bonds.

To confirm the assertion above, the NMR data were analyzed quantitatively. The plot in Figure 8 (a) shows that as reaction time increases, the peak intensity at 4.51 ppm increases, using the peak at 4.57 ppm as a reference. Integrating the area under the peak, which represents the number of the corresponding protons, the number of protons at 4.51 ppm increases with time. Cleaved bonds increase as reaction continues, indicating that the peak at 4.51 ppm corresponds to protons in the cleaved bonds. Figure 8 (b) shows the ratio of the protons at 5.75 and 4.57 ppm. The ratio remains constant (~ 0.25) during depolymerization for all samples, providing further evidence that the two correlated peaks (5.75 and 4.57 ppm) correspond to the crosslinked structures in the cured epoxies.

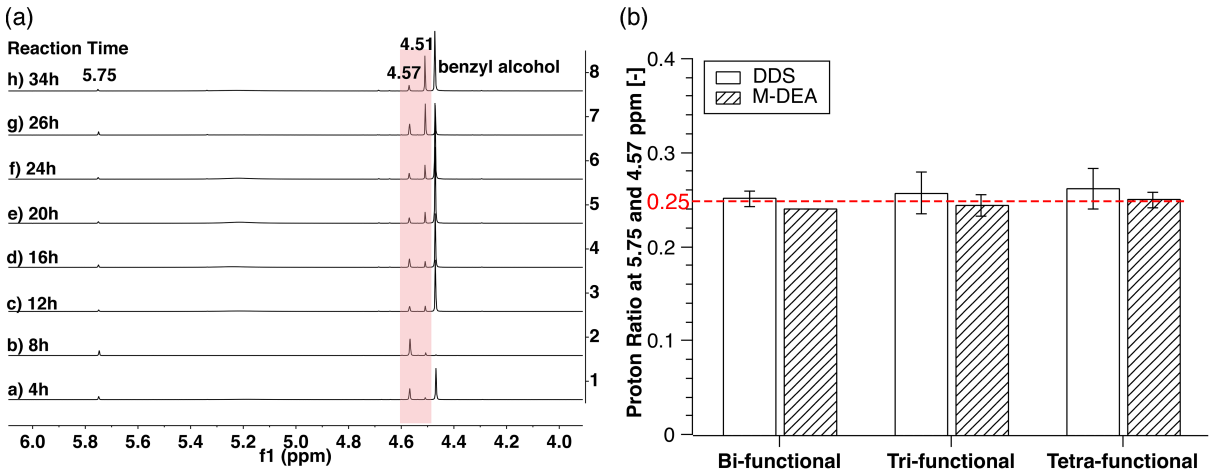


Figure 8: Quantitative 1H NMR spectrum analyses of dissolution products of tri-functional epoxy in DMSO at room temperature (32 scans) at peaks: a) 4.51 ppm, b) 5.75 and 4.57 ppm

To identify the specific structure of the crosslinking, details of the crosslinked network are analyzed. Recall that in bi- and tetra-functional epoxy monomers, epoxy functional groups are attached to oxygen atoms and nitrogen atoms, respectively (see Figure 1). Tri-functional epoxy monomers contain epoxy functional groups attached to both oxygen and nitrogen atoms, and thus can be considered as a mixture of bi- and tetra-functional epoxy monomers. This assertion is supported by the NMR spectra of epoxy monomers shown in Supplemenraty Figures S4, S5 and S6. At A/E = 40 %, an excess of epoxy groups exists in the resin relative to amine curing agents. Thus, both Reactions II and III occur at later stages of cure, before the epoxy groups are depleted to form C-N and C-O bonds. In Figure 9, we color mark the crosslinking of cured bi- and tetra-functional epoxies based on epoxy monomer end groups (orange and blue represent the crosslined units from epoxy-amine and epoxy-hydroxyl reactions, respectively). Note that a similar crosslinked unit structure (Figure 9 (a)) exists in all systems, regardless of epoxy functionality (bi-, tri, and tetra-functional epoxy), curing agent type (3,3'-DDS and M-DEA), or reaction type (Reactions I, II and III).

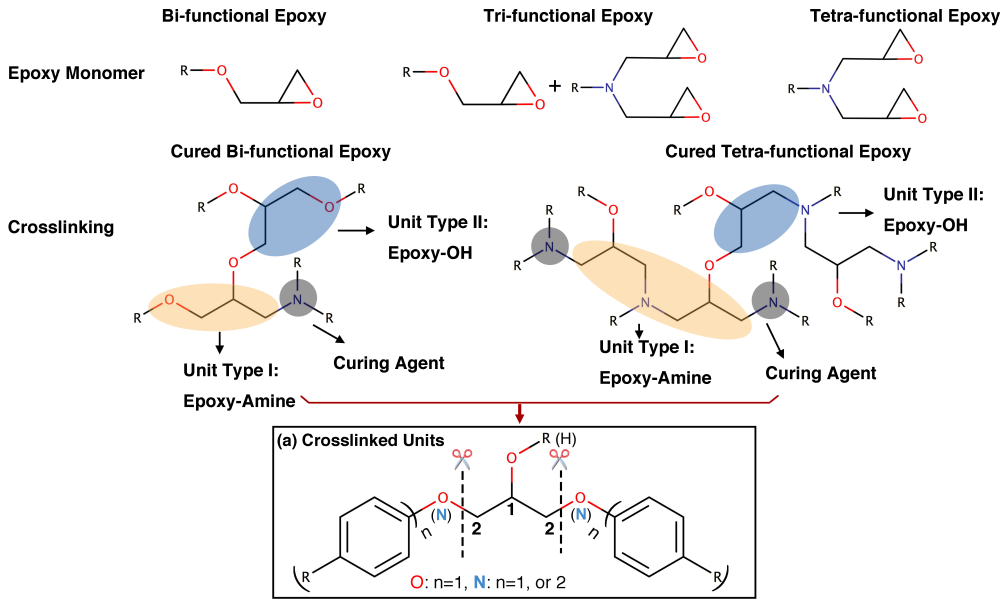


Figure 9: Molecular structure in epoxy monomers and amine-cured epoxies

This crosslinked unit contains three carbon atoms in the middle (one 3° carbon and two 2° carbons), with an oxygen atom attached to the 3° carbon atom, and one oxygen (or nitrogen) atom attached to each of the 2° carbon atoms. The oxygen atom attached to the 3° carbon atom can be bonded to hydroxyl groups, due to the slow etherification reaction at temperature < 150 °C.The ratio of the hydroxyl groups attached to the 3° carbon hydrogens and the 2° carbon hydrogens is 1:4, which is consistent with the constant proton ratio at 5.75 and 4.57 ppm. Thus,

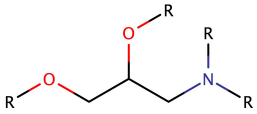
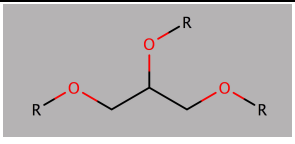
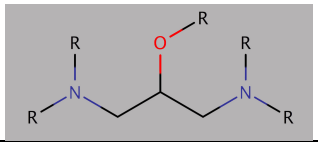
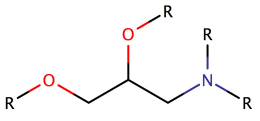
	Reactions I and II: Epoxy-Amine	Reaction III: Epoxy-OH
Cured Bi-functional Epoxy		
Cured Tetra-functional Epoxy		

Table 2: Possible cleavable crosslinked units in amine-cured epoxies with A/E = 40 %

the peaks at 5.75 and 4.57 ppm correspond to the hydroxyl groups attached to the 3^o carbon hydrogens and to the 2^o carbon hydrogens, respectively.

Table 2 summarizes the possible cleavable crosslinked units in cured bi- and tetra-functional epoxies, based on the reoccurring crosslinked units from Reactions I, II and III in (Figure 9 (a)). The functionalities (*f*'s) of these cleavable units vary from 3 – 5. In bi-functional epoxies, some crosslinked units form in Reaction III (shaded gray) that contain only C-O bonds ($f = 3$). Without breaking the C-O bonds, the shaded units for bi-functional epoxies remain intact ($f = 3$), and a less extensively crosslinked network is formed (even if the C-N bonds are cleaved), preventing complete dissolution. Previous experiments have shown that complete dissolution can be achieved for all cured bi-functional epoxies via depolymerization and acid digestion, so the C-O bonds must be cleaved during both processes.

In cured tetra-functional epoxies as shown in (Table 2), some of the crosslinked units formed in Reactions I and II (shaded gray) contain two nitrogen atoms and one oxygen atom ($f = 5$). By breaking only the C-O bonds in such crosslinked units, the shaded units in tetra-functional epoxies remain crosslinked by the C-N bonds ($f = 4$), and complete dissolution is impossible. Experiments demonstrated that cured tetra-functional epoxies were completely dissolved via both depolymerization and acid digestion. Thus, the C-N bonds must be cleaved to some extent during dissolution via depolymerization and acid digestion. The finding demonstrates that C-N bonds are also one type of cleavable site during epoxy dissolution.

Bond dissociation energy (BDE), also commonly referred to as bond energy, is the energy required to break the bond homolytically under standard conditions, which can be used as a measure of covalent bond strength [24]. We used experimental hemolytic BDE data, collected and organized by Luo, in the ideal gas state at standard pressure and at a reference temperature of

298.15 K, to evaluate the bond strength in our epoxy crosslinking [24]. Associated BDE values are summarized in Supplementary Table S1. Although the BDE measurement conditions differ from our chemical dissolution approaches, the BDE values can be used as references to determine *relative* strength of bonds. There are three possible types of ether bond cleavage (**R**-O-R', **boldface** = dissociated atom) in the cured epoxies: 1) **R**, R'= alkyl substituents (**CH_3**–OCH_3, 351.9 J/mol), 2) **R** = alkyl substituent, R'= aryl substitute (**CH_3**–OC_6H_5, 263.2 J/mol), 3) **R** = aryl substitute, R' = alkyl substituent (**C_6H_5**–OCH_3, 418.8 J/mol). For C-N bonds, there are two possible types of bond cleavage (**R**-NH-R' or (**R**-N-R'R'', **boldface** = dissociated atom): 1) **R** = alkyl substituent, R', R''= aryl substitutes (**CH_3**–NHC_6H_5, 298.7 J/mol), 3) **R** = aryl substitute, R', R'' = alkyl substituent (**C_6H_5**–$NHCH_3$, 420.9 J/mol).

From the above data, we observe that C-O and C-N bonds with **R** = alkyl substituent and R'= aryl substitute have the lowest BDE, indicating that the bonds between O/N atoms and the secondary carbons in crosslinked units (**-C_6H_5O**-CH_2-, **-$(C_6H_5)_2N$**-CH_2-), as shown in Figure 9 (a), are more likely to be broken during dissolution. For C-S bonds in DDS, there is only one possible type of bond cleavage: (**C_6H_5**– $SO_2C_6H_5$). A similar structure (**C_6H_5**– SO_2CH_3) shows a BDE of 344.3 J/mol, which is ~50 J/mol greater than the BDEs required by C-O and C-N bonds, and thus less like to be broken during the reaction. GC-MS data in Supplementary Figure 8 confirmf the existence of the bisphenol A structure in the dissolution products, indicating that the aromatic structures of the epoxies were preserved during dissolution, and the C-O and C-N bonds were selectively cleaved.

We conclude that during dissolution, polymer chains with various lengths are first separated from the heavily crosslinked network. As the reaction continues and more polymer chains are digested, complete resin dissolution occurs gradually. The dissolved polymer chains

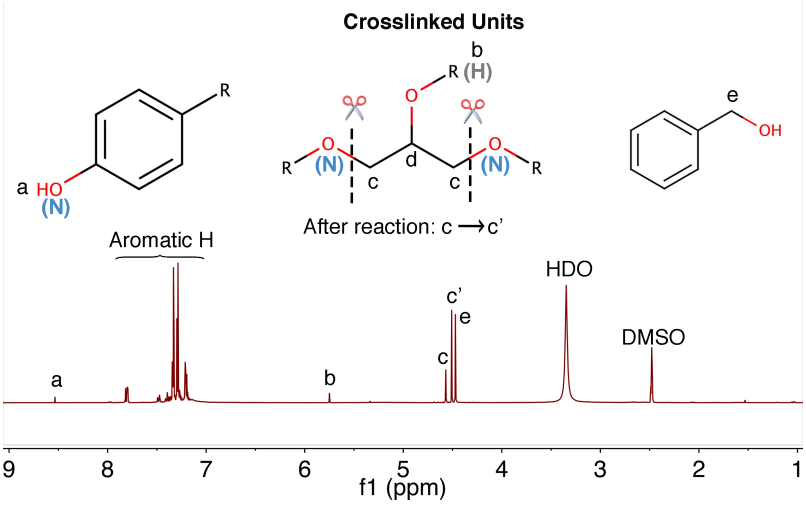


Figure 10: Assignment of 1H NMR full spectrum chemical shift of dissolution products of tri-functional epoxy in DMSO at room temperature (32 scans)

continue to react to yield progressively shorter oligomers or even monomers (Supplementary Figures S7 and S8). We find that the C-O and C-N bonds are the cleavable sites for depolymerization and acid digestion, where **-C_6H_5O-**CH_2- and **-$(C_6H_5)_2N$-**CH_2- (**boldface** = dissociated atom) are the most possible cleavable positions (Figure 9 (a)). The assignment of the full spectrum is shown in Figure 10.

4. Conclusions

We have demonstrated key aspects of amine-cured epoxy dissolution at atmospheric pressure using two chemical treatment methods: (a) depolymerization and (b) acid digestion. The insights provided are essential to developing an effective chemical treatment method for recycling amine/epoxy composites that is also practical on an industrial scale. To our knowledge, such a process has not been reported in the literature. We have also demonstrated that both depolymerization and acid digestion are effective processes for dissolving amine-cured formulations. Correlations between epoxy properties and dissolution rate were identified, and we

showed that the rates of chemical reaction and diffusion were the two factors controlling the rate of dissolution. When the reaction temperature was less than the T_g of the epoxy, the dissolution rate was determined primarily by the diffusion rate, while in other cases, the chemical reaction was the rate-controlling factor. These findings indicate that to accelerate the dissolution rate, we must understand not only chemical reactions and catalytic conditions that can cleave bonds more efficiently, but also more effective ways to permeabilize heavily crosslinked networks to accelerate diffusion.

We have also demonstrated protocols for using NMR spectroscopy to qualitatively and quantitatively track the products from chemical solutions after epoxy dissolution. The molecular-level studies clarified the process of dissolution and provide a basis for developing future strategies to employ catalysis. We showed that similar crosslinked units existed in all amine-cured epoxies with different epoxy functionality and type of curing agent. Target cleavable sites - C-O and C-N bonds - were identified for screening catalysts to achieve faster reaction rates of bond cleavage. **-C_6H_5O**-CH_2- and **-$(C_6H_5)_2N$**-CH_2- (**boldface** = dissociated atom) were the most possible cleavable positions. The aromatic structures of the epoxies were preserved during dissolution, and the C-O and C-N bonds were selectively cleaved.

The viability of depolymerization and acid digestion processes of amine-cured epoxies with high crosslink density (at atmospheric pressure) affords opportunity to recover and recycle high-value fibers from composites, as well as parts of the epoxies. Presently, prospective catalytic and permeabilization conditions are being evaluated and screened. By developing effective catalysts and permeabilization agents, we expect faster reaction rates will be possible, sufficient to meet industrial demand. Studies of depolymerization and acid digestion in amine/epoxy composites will be undertaken to understand the effects of chemical treatment on

recovered fiber quality. These efforts will furnish additional insight and more comprehensive understanding of composite recycling processes, and possibly yield an practical and scaleable solution for recycling amine/epoxy composites at atmospheric pressure.

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