



Mild chemical recycling of aerospace fiber/epoxy composite wastes and utilization of the decomposed resin

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ABSTRACT

Carbon fiber reinforced polymers (CFRPs) with high T_g (>200 °C) are indispensable for aerospace industry where high service temperature is required. Chemical recycling of the matrix polymers for these CFRP composites is more difficult than that of their low T_g analogues. In this work, an efficient approach for mild chemical recycling of CFRP with a T_g of ~210 °C was developed using a ZnCl₂/ethanol catalyst system. The high efficiency of ZnCl₂/ethanol was attributed to the strong coordination effect of ZnCl₂ with the C-N bonds and the strong swelling ability of ethanol, which worked together to break down the chemical bonds of the cross-linked polymer. Also, mild degradation temperature (<200 °C) imparted little damage to the recovered fibers. The decomposed matrix polymer (DMP) was in the oligomer form and contained multifunctional reactive groups. When DMP was used as a reactive ingredient and added up to 15 wt% to the preparation of new epoxy materials, the resulting cross-linked polymers could still retain the high strength and modulus compared to the neat polymer without addition of DMP.

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1. Introduction

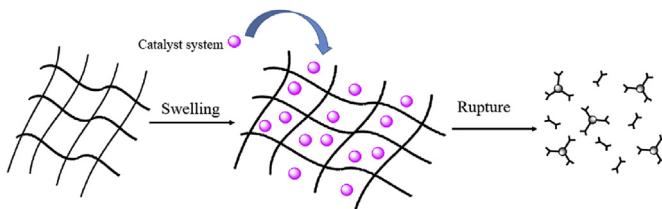
Owing to the high-modulus, high-strength and low-density, CFRP has become a preferred choice of material in the aerospace, sporting goods, automotive and wind energy industries [1–3]. However, the rapid growth of CFRP bring a great environmental and sustainable challenge. The CFRP wastes resulted from product manufacturing and post-service products cannot be recycled as easily as thermoplastics, while disposal in landfills takes no advantage of the residual value but adds burden to waste management [4]. In order to solve this problem, various recycling methods, such as mechanical recycling [5,6], pyrolysis [7], fluidized bed thermal process [8], chemical treatment in near-critical or supercritical water [9,10], have already been explored to recover

carbon fibers and cured resins. However, harsh conditions, such as high temperature (>350 °C) and high reaction pressure, are required for these recycling methods and are energy-intensive. Also, such high recycling temperature likely results in certain damages to the surface of the recovered carbon fibers. More seriously, the decomposed resin at such harsh conditions is often a complex mixture of gaseous, liquid and solid chemicals, making the viable reuse of the recycled chemicals very difficult [11].

In recent years, recycling of CFRP by chemical degradation has become a promising method to claim the residual values for both fibers and chemicals [12]. As shown in Scheme 1, chemical degradation of CFRP usually proceeds in two main stages: first, the cured resin swells in liquid solution and the catalyst permeates into the cross-linked network; second, the chemical bonds of the cured resin are cleaved, forming soluble molecules under the effect of catalysts. It is critical to develop efficient catalytic systems that are capable of permeating into the cured resins and breaking down the chemical bonds of cured resins. Early chemical degradation studies

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Scheme 1. Principle of CFRP degradation using chemical degradation method.

were focused on recycling the CFRP using strong acid [13,14] or strong alkali aqueous solutions [15,16], such as nitric acid and potassium hydroxide solutions. Use of these caustic chemicals poses potential pollution to the environment and easily causes corrosion to equipment, reducing its scalability. Recently, chemical recycling of an aliphatic amine cured bisphenol-A (BPA) epoxy in the $ZnCl_2/H_2O$ solution was performed at $220\text{ }^\circ\text{C}$ [17], which was much lower than the temperatures in most other reports. K_2CO_3 /phenol was also found to be an effective catalyst system that can well decompose BPA cured anhydride below $200\text{ }^\circ\text{C}$ [18]. However, to the best of our knowledge, all the reported mild chemical recycling technologies are used to deal with low T_g ($<150\text{ }^\circ\text{C}$) CFRPs. It is important to note that the CFRPs with high T_g ($>200\text{ }^\circ\text{C}$) are widely used in aerospace industry. Due to their stiffer backbone structures and higher crosslink densities, high T_g CFRPs are much more difficult to be recycled compared with their lower T_g analogues. There has not been a report for the degradation of high T_g ($>200\text{ }^\circ\text{C}$) epoxy systems under mild conditions (e.g. low degradation temperature ($<200\text{ }^\circ\text{C}$) and mild catalyst system).

In addition to the reaction severity of CFRP degradation, reuse of the decomposed matrix polymer (DMP) is another challenge to be resolved. The matrix resin under the harsh reaction conditions is decomposed into a complex mixture of small molecules, which show little practical values and may become secondary waste after degradation [19]. Current research on CFRP recycling is mainly focused on the recovery of carbon fibers [20–22], but utilization of the DMP is rarely explored due to the complexity of the decomposed product. Generally, CFRP comprises 30–40 wt% resin materials which are mostly epoxies, bismaleimides and unsaturated polyesters and are much more expensive than traditional thermoplastics [23]. Making utilization of DMP is beneficial to both economic value and environmental protection.

In this work, we introduced an effective chemical recycling method for a waste CFRP of high T_g (Figs. S2 and S3) and high thermal stability (Fig. S4) under mild condition ($<200\text{ }^\circ\text{C}$). The decomposed resin and recovered carbon fiber (CF) were characterized. The decomposed resin was found to be in an oligomer form; when added as a reactive ingredient for preparation of new epoxy, increased in flexural strength, T_g and fracture strain are demonstrated.

2. Experimental section

2.1. Materials

The CFRP waste was obtained from the manufacturing scraps and provided by the Boeing Company, and the main composition of the matrix is amine-cured epoxy. DER331 epoxy resin (DOW Chemical Company, EEW = 188.0 g equiv.⁻¹) was supplied by EHORN Company. Nadic methyl anhydride (99.4%) was purchased from Electron Microscopy Sciences. Zinc chloride ($ZnCl_2$), ferric chloride ($FeCl_3$), magnesium chloride ($MgCl_2$), aluminium chloride ($AlCl_3$), phosphotungstic acid (HPW), 2-ethyl-4-methylimidazole (2E4MZ, 99+, Acros Organics), and all solvents were purchased

from Fisher Scientific. All chemicals were used as received unless otherwise stated.

2.2. Characterizations

Nuclear magnetic resonance (NMR) spectra were recorded on a fully automated Varian 400-MR spectrometer (400 MHz). The sample was dissolved in $CDCl_3$ and each sample was scanned 16 times. Chemical shifts of 1H NMR peaks were reported in ppm, and the data was collected from 14 to -2 ppm . Fourier transform infrared spectroscopy (FTIR) spectra were collected on a NICOLET iS50 FTIR spectrophotometer. The specimen for FTIR experiment was prepared by grinding the sample (1 mg) and potassium bromide (KBr, 100 mg) powder in a mortar and then compressing the mixture into a disk using a mold. The sample was scanned from 4000 to 400 cm^{-1} with a resolution of 4.0 cm^{-1} for 64 times.

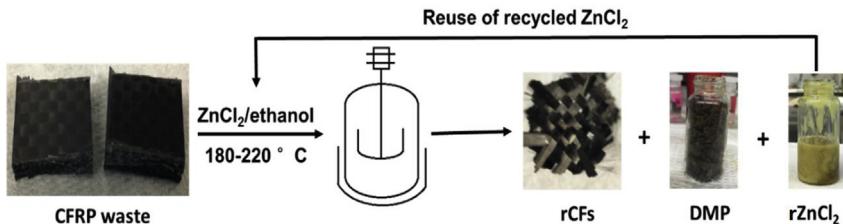
T_g values were measured using a differential scanning calorimeter (DSC 1, Mettler-Toledo, Switzerland). The sample (~5 mg) was scanned from 25 to $260\text{ }^\circ\text{C}$ at a heating rate of 10 K min^{-1} under nitrogen atmosphere. Thermal stability was measured using a TGA/DSC 1 thermo-gravimetric analyzer (TGA) and the sample (~10 mg) was scanned from 50 to $800\text{ }^\circ\text{C}$ at a heating rate of 10 K min^{-1} under nitrogen or oxygen atmosphere. Dynamic mechanical properties of the epoxy and CFRP composite were measured using a dynamic mechanical analyzer (DMA) (Q800, Thermal Instrument) in the single cantilever mode. The dimensions of the specimen were $35.0\text{ mm} \times 12.8\text{ mm} \times 3.0\text{ mm}$. The frequency was set at 1 Hz and the oscillating amplitude at $15\text{ }\mu\text{m}$. The sample was scanned from 50 to $300\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$.

Flexural strengths of cured epoxy samples were determined using an Instron 4466 test machine equipped with a 10 KN load cell, and the test procedures was carried out according to the ASTM D790-10 standard. The dimensions of the specimen were $3.2\text{ mm} \times 12.7\text{ mm} \times 125\text{ mm}$. For each sample, at least five specimens were measured. After test, fracture surfaces were coated with gold with a layer thickness of about 3 nm . The gold plated samples were then examined by scanning electron microscopy (FE SEM, Quanta 200F). For observing the surface of conductive carbon fiber, no gold plating was used.

2.3. Decomposition of CFRP

Prior to chemical decomposition, the large CFRP waste board (Fig. S1) were cut into blocks with an average size of ca. $1\text{ cm} \times 1\text{ cm} \times 1\text{ cm}$ using a power saw.

The degradation reaction was carried out in a 100-mL pressure reactor (Series 4842, Parr Instrument Company). The general procedure (Scheme 2) of the chemical recycling process is described as follows. $ZnCl_2$ /ethanol solution and CFRP wastes were directly added into a 100-mL pressure reactor. The amount of $ZnCl_2$ /ethanol solution was five times (or higher) that of CFRP wastes by weight to ensure the complete immersion of waste sample in solution. The reaction temperature was raised to a predetermined temperature, and the reaction was continued for several hours (mostly 5 h) at the temperature. The reactor was cooled down naturally to the room temperature. The reaction mixture was filtered and the insoluble was rinsed with acetone for several times. The insoluble part was the carbon fiber and/or some undecomposed resin. The filtration solution was concentrated using a rotary evaporator, and the decomposed matrix polymer (DMP) was precipitated by water. DMP was collected by filtration, washed with saturated Na_2CO_3 aqueous until no $ZnCl_2$ was detected. Subsequently, the DMP was washed with water and dried in vacuum oven at $70\text{ }^\circ\text{C}$ for 12 h, yielding a brown solid powder. The water solution of the filtration contains mainly ($ZnCl_2$) and was directly concentrated using rotary



Scheme 2. Recycling route of CFRP waste by $\text{ZnCl}_2/\text{ethanol}$ treatment.

evaporator to give a yellow solid named as recycled catalyst or rZnCl_2 .

The degradation degree (D_d) of resin is calculated by equation (1),

$$D_d\% = 1 - \frac{W_2 - W_1 \times 65\%}{W_1 \times 35\%} \times 100\% \quad (1)$$

where W_1 and W_2 are the weight of CFRP before and after degradation, respectively, and “ $W_1 \times 65\%$ ” and “ $W_1 \times 35\%$ ” indicate the weight of fiber and resin before degradation, respectively. The contents of resin and fiber were determined from the TGA experiment of CFRP in the oxygen atmosphere (Fig. S4) and nitric acid degradation (Table 1). The carbon fiber content was found to be ~65 wt% by both methods, indicating that the CFRP waste contained ~35 wt% of matrix resin.

2.4. Preparation of cured DER/anhydride/DMP samples

Under magnetic stirring, DMP (5, 10, 15, 20 wt% on the weight of epoxy, respectively) and DER 331 epoxy were mixed at 100 °C. After a homogeneous mixture was obtained, nadic methyl anhydride (NMA), the curing agent, was added under continuous stirring at 80 °C. For comparison, neat system (DER 331/NMA) without loading DMP was also prepared. The stoichiometry between epoxy and anhydride was fixed at a molar ratio of 1:0.8. Finally, the accelerator, 2E4MZ (1 wt% on NMA) was added. After a homogeneous mixture was formed, it was degassed and cured in metal mold. All samples were cured using a same three-step curing program: 110 °C for 2 h, 150 °C for 2 h, 180 °C for 2 h. After curing, the samples were allowed to cool on its own to room temperature.

3. Results and discussions

3.1. Chemical degradation of aerospace CFRP waste

Effects of the catalyst type and solvent type on degradation were investigated, and the results are shown in Table 1. KOH, nitric acid, and ZnCl_2 appeared to be the three most effective catalyst systems that were capable of completely degrading the CFRP matrix. KOH and nitric acid are well known corrosive chemicals and require corrosion resistant processing equipment. In contrast, the mild Lewis acid ZnCl_2 exhibited a comparable degradation efficiency as that of KOH and nitric acid. Moreover, compared with other Lewis acids, ZnCl_2 exhibited a superior catalyzing effect, while MgCl_2 , AlCl_3 and FeCl_2 only presented low degradation efficiencies. By taking into consideration both catalytic efficiency and environmental factors, ZnCl_2 is more desirable than other catalyst systems.

In addition to the catalyst selected, the solvent selected also plays an important role in the degradation of CFRP matrix. With the consideration of environmental factors, only water and ethanol as solvents were investigated. Compared with $\text{ZnCl}_2/\text{H}_2\text{O}$, $\text{ZnCl}_2/\text{ethanol}$ showed higher degradation efficiency, and only the high concentrated $\text{ZnCl}_2/\text{H}_2\text{O}$ system could achieve an almost complete degradation of the matrix. In some other reported works [24], ethanol was found to have much higher swelling ability compared with H_2O . The good swelling ability facilitates the transferring of catalyst into the matrix and eventually cleavage the cross-linked networks. In the rest sections, all reported results were based on the $\text{ZnCl}_2/\text{ethanol}$ catalyst system due to its superior performances.

The effects of reaction temperature (Fig. 1a), catalyst concentration (Fig. 1b) and reaction time (Fig. 1b) on degradation degree for $\text{ZnCl}_2/\text{ethanol}$ system were systematically investigated. The degradation degree increases with increases in reaction temperature and catalyst concentration. In Fig. 1a, the degradation degree

Table 1
Degradation of CFRP using different catalyst systems.

Entry	Catalyst (wt%)	Solvent	Temperature (°C)	Degradation degree (%)	Time (h)
1	—	H_2O	220	Swell	5
2	—	Ethanol	220	Swell	5
3	KOH (10%)	Ethanol	200	89.3	4
4	KOH (30%)	H_2O	250	32.6	3
5	Nitric acid (65%)	H_2O	80	100	10
5	Nitric acid (65%)	H_2O	80	95.6	2
6	Nitric acid (32%)	H_2O	80	94.9	2
7	Nitric acid (16%)	H_2O	80	42.4	2
8	HPW (20%)	H_2O	220	Swell	5
9	ZnCl_2 (20%)	Ethanol	220	89.8	5
10	ZnCl_2 (60%)	H_2O	250	91.8	5
11	ZnCl_2 (30%)	H_2O	250	33.7	5
12	MgCl_2 (30%)	Ethanol	220	52.1	5
13	AlCl_3 (20%)	Ethanol	220	36.2	5
14	FeCl_2 (20%)	Ethanol	220	33.0	5

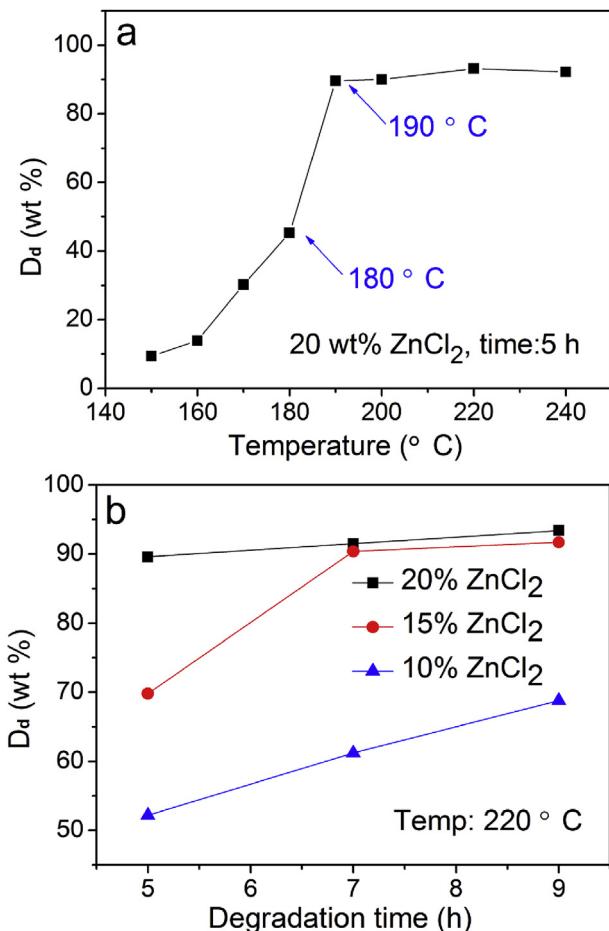


Fig. 1. Effects of temperature (a) and catalyst concentration and time (b) on degradation degree (D_d) of matrix resin in the $ZnCl_2$ /ethanol catalyst system.

exhibited a drastic increase with temperature increasing from 180 to 190 °C but remained relatively unchanged with further increase in temperature. In Fig. 1b, the degradation degree displayed a great jump with $ZnCl_2$ concentration increasing from 10 to 15 wt% in the time range of 5–9 h. At 5 h of reaction, the degradation in the 20 wt % $ZnCl_2$ solution was much faster than in the 15 wt% $ZnCl_2$ solution. When the reaction time was increased to 7 h, however, there was little difference in degradation degree between these two $ZnCl_2$ concentrations.

In comparison, reaction temperature presents the most important factor influencing degradation degree. Below 190 °C, CFRP could not be effectively decomposed even at increased catalyst concentration and prolonged reaction time. It is worth noting that the minimum degradation (190 °C) temperature correlated very well with the main glass transition of the matrix resin (190–220 °C, Figs. S2 and S3). It is well known that the onset temperature of glass transition is often defined as the minimum temperature for the movement of polymer chain segments. The DSC result in Fig. S2 reveals that the glass transition onset temperature of the matrix was ~190 °C. Below that temperature, the chain segment does not have adequate mobility, so the catalyst solution cannot effectively permeate into the crosslinked network. When the reaction temperature reaches to 190 °C, the adequate mobility of chain segments enabled effective penetration of the catalyst solution into the matrix and result in the drastic increase of degradation degree. As shown in Fig. 1b, the degradation degree could be further improved by increasing catalyst concentration or reaction time when the

degradation temperature was higher than 190 °C. Increasing the catalyst concentration can accelerate the cleavage of chemical bonds, while increasing the reaction time can allow sufficient time for achieving a higher degradation degree. However, when the catalyst concentration reached to 20 wt%, the degradation degree did not change obviously over time. By taking into consideration both economics and production efficiency, reaction at 190 °C for 5 h with a $ZnCl_2$ concentration of 20 wt% is the limiting condition that meets the requirement of a complete degradation of CFRP matrix.

The regeneration of catalyst was also investigated. After reaction, the recovered catalyst (Scheme 2) was collected. Fig. S6 shows the FTIR spectra of $ZnCl_2$ and the recovered catalyst. There was no significant difference between them, indicating that the chemical structure of the catalyst did not show obvious changes after reaction. The recovered catalyst was directly used for the next degradation reaction. Under the above mentioned limiting reaction conditions (190 °C, 5 h, and 20 wt% $ZnCl_2$ solution), use of the recycled catalyst still resulted in a degradation degree of ~90%. This result indicates that the recycled catalyst was still very effective. Regeneration and reuse of catalyst is important, because it can largely reduce the cost for industrial production and produces no secondary wastes during the entire processing process.

3.2. Analysis of the recyclates

The composition of the matrix resin for the CFRP waste was not specified by the supplier. In this study, a preliminary analysis of the matrix resin for the CFRP waste was performed. As observed, fatty N-C, aromatic N-C, and $-SO_2-$ were found in the matrix resin (Fig. 2a), suggesting that the matrix resin was likely a glycidyl epoxy cured with a $-SO_2-$ group-containing aromatic amine. It is well known that glycidyl ether and glycidyl amine are the two most

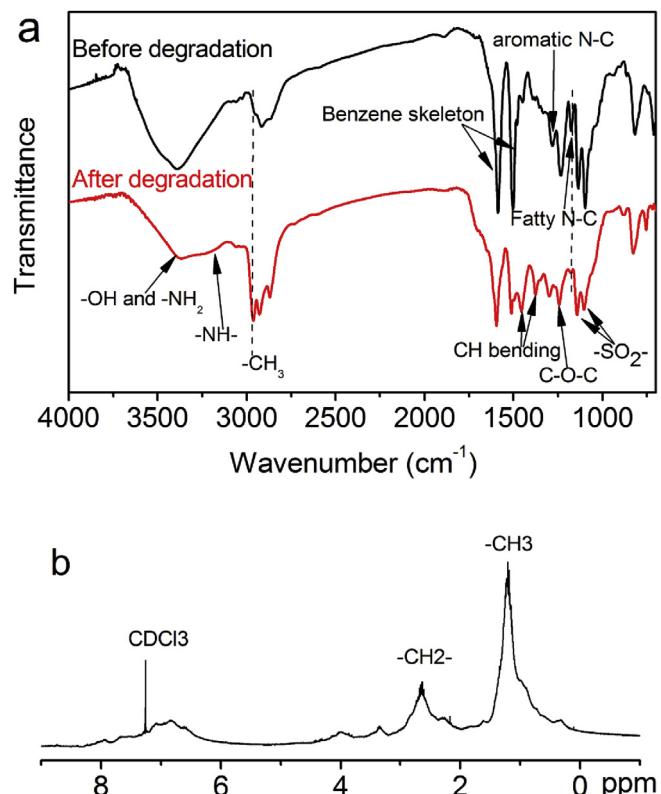


Fig. 2. (a) FTIR spectra of matrix resin before and after degradation. (b) ¹H NMR spectrum of decomposed matrix polymer (DMP).

common matrix epoxies for aerospace CFRPs. In Fig. S7, DER 331 (a DGEBA type epoxy) cured with diaminodiphenyl sulfone (DDS) exhibited an obvious aromatic ether peak at 1028 cm^{-1} in the cured resin. In contrast, the same peak was not noted in the matrix resin of the CFRP waste (Fig. 2a). The absent of aromatic ether bonds in the matrix resin indicate that the matrix resin of the waste CFRP used in this study was not a glycidyl ether based epoxy. Furthermore, the matrix resin was compared with a DDS cured *N,N'*-tetraglycidyl diaminodiphenylmethane (TGDDM). TGDDM is a typical high performance glycidyl amine epoxy. The FTIR spectra of both TGDDM curing system and the matrix resin before degradation (Figs. S7 and S8) are quite similar. Based on these evidences, it is speculated that the matrix resin was an aromatic amine/glycidyl amine epoxy curing system, and the possible structures of epoxy and curing agent are shown in Scheme 3a.

The decomposed resin from the reaction performed at $190\text{ }^\circ\text{C}$ for 5 h and with 20 wt% ZnCl_2 solution was analyzed. Fig. 2a shows the FTIR spectra. The peak intensity of aliphatic C-N at 1176 cm^{-1} exhibited a remarkable decrease after degradation, indicating the cleavage of the aliphatic C-N bond during reaction. In addition, the appearance of a broad shoulder peak at 3250 cm^{-1} implies the presence of N-H bond in the decomposed product, which also proves the cleavage of C-N bonds [24]. Meanwhile, the peaks related to ether bond (C-O-C , 1245 cm^{-1}), benzene skeleton (1595 cm^{-1} and 1512 cm^{-1}), and aromatic C-N bond (1296 cm^{-1}) remained intact after degradation. The FTIR results suggest that only the aliphatic C-N bonds in CFRP was cleaved by the ZnCl_2 /ethanol catalytic system. This selective cleavage is very important, because it can help us to better control the degradation process and obtain decomposed resin in the oligomer form, as shown in a latter section. Fig. 2b shows the ^1H NMR result of DMP. The peaks with chemical shifts from 8.5 to 6.5 ppm are attributed to the protons of the benzene rings, indicating the preservation of benzene groups during degradation reaction. Moreover, the peaks in the range of 1.6 to 0.4 ppm are attributed to $-\text{CH}_3$ after degradation. The new peaks appear at 1456 , 1377 , and 2962 cm^{-1} in FTIR (see Fig. 2a) also confirmed the generation of $-\text{CH}_3$. Apparently, these $-\text{CH}_3$ groups were derived from the cleavage of aliphatic C-N bond. During reaction, aliphatic C-N bonds are split to form $-\text{CH}_3$ and amine groups, and the possible degradation mechanism is illustrated in Scheme 3.

The molecular weight of the decomposed matrix polymer (DMP) was determined by GPC. At $190\text{ }^\circ\text{C}$, the DMP showed an average molecular weight of $\sim 650\text{ Da}$ with a polydispersity index of ~ 1.5 (Fig. 3a), indicating that the DMP was oligomer rather than

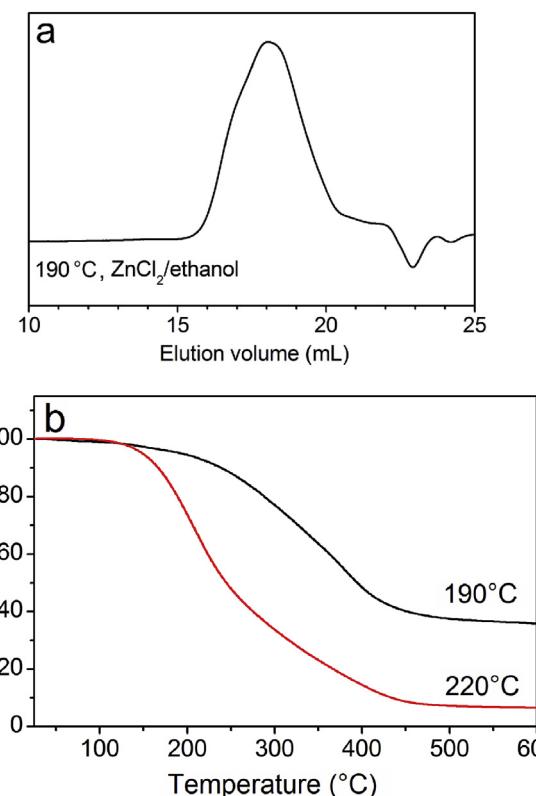
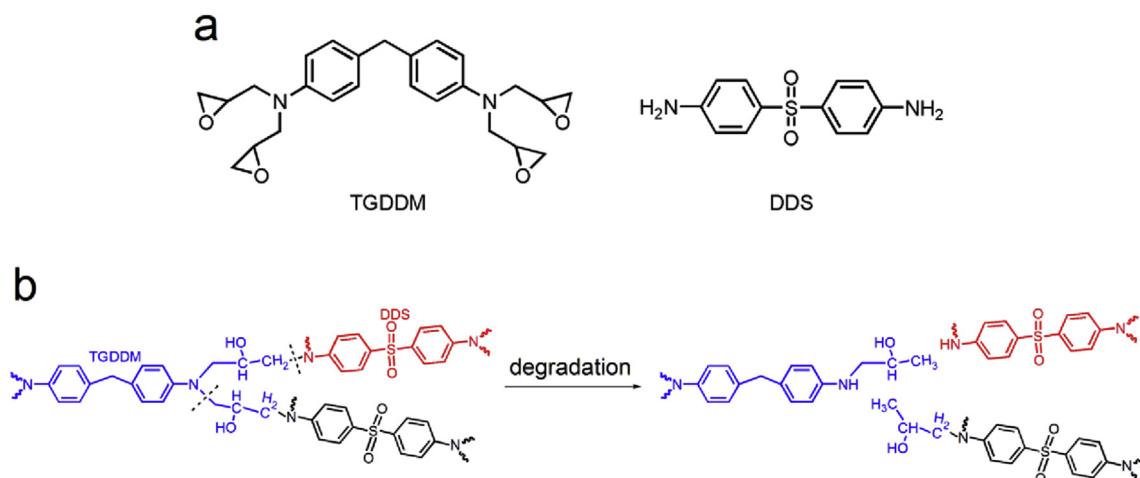


Fig. 3. (a) GPC curve of decomposed matrix polymer (DMP); (b) TGA curves of DMP obtained from different degradation temperature.

monomer. At $220\text{ }^\circ\text{C}$, the collected DMP was mostly a complex mixture of small monomers and was difficult to be determined by GPC. Higher reaction temperatures lead to more complete degradation and result in lower molecular weight product. Also, the complex mixture generated at high temperatures are difficult to be separated and may become a secondary waste. In contrast, the oligomer received from a lower degradation temperature (e.g., $190\text{ }^\circ\text{C}$) has multifunctional groups (i.e. amines and hydroxyl groups) and adequate thermal stability (see Fig. 3). These properties make the DMP suitable for being used as a reactive ingredient in new composite materials, which will be proved in section 3.3.



Scheme 3. (a) Chemical structures of the TGDDM epoxy and DDS curing agent; (b) schematic network structures of DDS cured TGDDM before and after degradation.

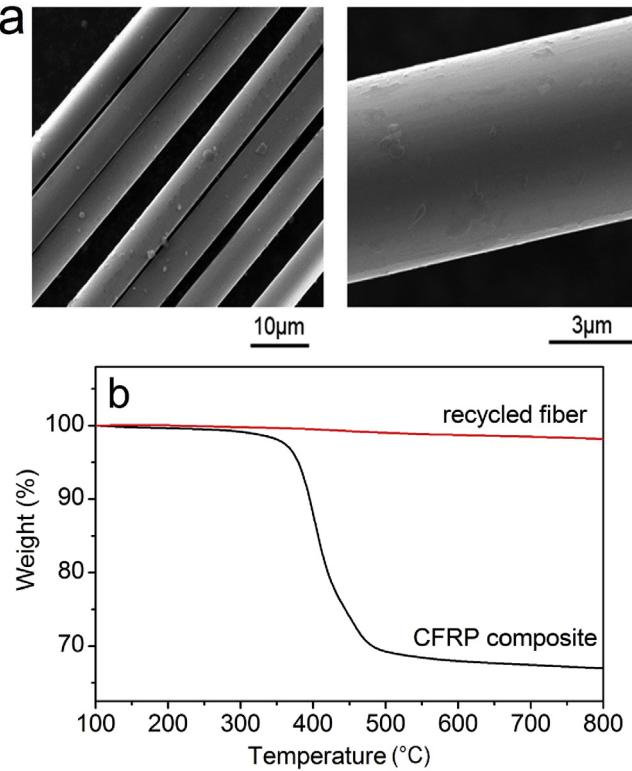


Fig. 4. (a) SEM images of recovered carbon fibers in two different scales. The recovered carbon fibers in images were recycled at 190 °C; (b) TGA curves of CFRP waste before and after degradation. TGA experiment was performed under the N₂ environment.

After degradation reaction, the matrix resin was almost completely removed from the carbon fibers. In Fig. 4a, the SEM micrographs of the recovered CFs showed fairly smooth surfaces, suggesting a better completion of the removal of matrix resin. In addition, the smooth surface also suggests that the degradation process imparts little damage to the fiber. Therefore, the recycled fiber can be directly used as high performance reinforcement for new composite materials. In addition, some spots on the fiber were probably due to a little residual matrix resin. TGA was used to evaluate the weight ratio of the residual resin. As noted in Fig. 4b, the recycled fiber showed a weight loss <5% when the temperature was increased to 800 °C, indicating a satisfied degradation efficiency.

3.3. Reuse of decomposed matrix polymer in epoxy resin

As mentioned above, DMP have many amine and hydroxyl groups which are capable of reacting with fresh DER epoxy resins. In this study, use of DMP as a reactive ingredient for preparation of epoxy resins was attempted. Because the DMP was a solid and has a broad T_g from 60 to 100 °C (Fig. S5), its mixing with the epoxy resin (DER 331) was performed at 100 °C. During the mixing process, the amine groups and hydroxyl groups on DMP could react with epoxy groups on DER, leading to an increased viscosity. In order to lower the viscosity, NMA, a liquid anhydride, was selected as curing agent. NMA can largely decrease the viscosity of mixture, and it also has high reactivity with both hydroxyl groups and amine groups during the subsequent curing process.

The storage moduli (G') and $\tan \delta$ of the sample containing different DMP contents as functions of temperature are shown in Fig. 5a and b, respectively. Each curve shows a clear transition from glass plateaus to rubbery plateaus. T_g s as defined by the peak

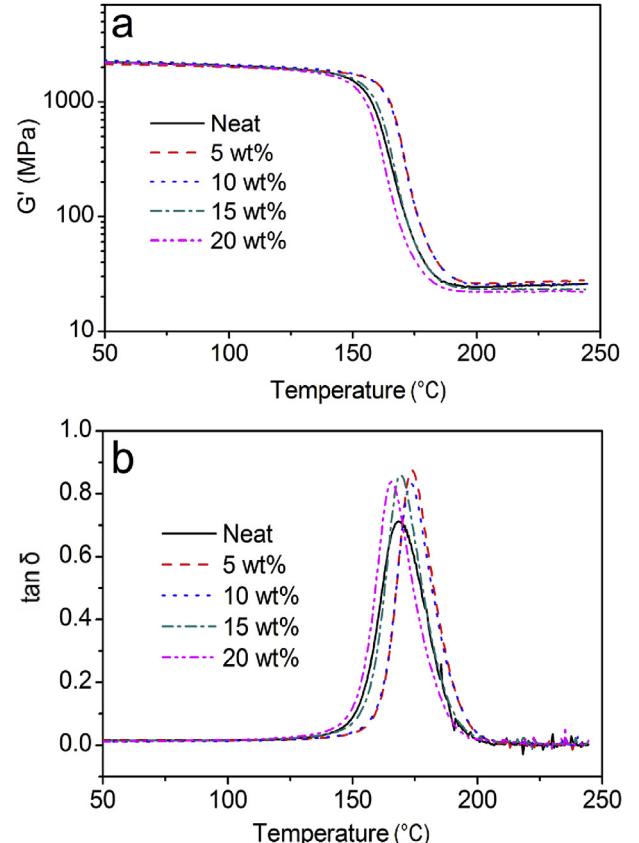


Fig. 5. Effects of decomposed matrix polymer (DMP) resin content in the composition on the dynamic properties of cured DER 331/NMA samples (a) storage modulus (G') and (b) loss tangent ($\tan \delta$).

temperatures of $\tan \delta$ are listed in Table 2. Clearly, for each composition, only one $\tan \delta$ peak was noted, suggesting an adequate miscibility between the DMP and DER resin. At 5 wt% DMP loading, the cured sample showed notable increases in T_g . However, as the loading of DMP increase from 10 to 20 wt%, T_g decreased monotonically. In Fig. 6b, the spectrum of NMA cured DER 331 still showed a weak peak at $\sim 910\text{ cm}^{-1}$ which belongs to the epoxy group; in contrast, with an addition of 5 wt% DMP to the system, the peak intensity at $\sim 910\text{ cm}^{-1}$ became much weaker. This result indicates that the reactive amines and hydroxyls on DMP consumed most of the rest unreacted epoxy groups during the curing process, resulting in a more complete network and hence higher T_g . For samples with higher DMP loadings (>10 wt%), the decrease in T_g could be related to the significant amount of aliphatic moieties (Scheme 2, Fig. 2a) in DMP.

Effect of DMP content in the resin on flexural strength and modulus were evaluated, and the results are shown in Table 2. The flexural strength showed a significant (~14%) increase at 5 wt% DMP loading. It decreased slowly with DMP content increasing to 10 and 15 wt%, but was still higher than or similar to that of the sample without DMP loading. However, the strength precipitated dramatically at 20 wt% DMP. The relative independence of flexural modulus on DMP content was consistent with the DMA result on the storage modulus in the glass region. Fig. 7 shows the representative stress-strain curves of DER epoxy samples with different DMP loadings. All samples displayed clear yield points at a similar yield strain of ~2.0%. Compared to the neat DER epoxy sample, the compositions with 5 and 10 wt% DMP exhibited kind of higher strain at break but the sample with 15 wt% DMP showed almost the

Table 2

Mechanical properties of cured DER 331/NMA containing different content of DMP.

Samples	T_g ^a (°C)	Half peak width of $\tan \delta$ (°C)	Flexural strength (MPa)	Flexural modulus (MPa)
Neat DER331	168.4	21.1	99 ± 2	2371 ± 64
5 wt% DMP	173.8	16.7	113 ± 3	2818 ± 226
10 wt% DMP	173.4	17.1	109 ± 1	2404 ± 172
15 wt% DMP	169.2	17.5	102 ± 2	2401 ± 61
20 wt% DMP	165.6	18.4	-43.7 ± 17 ^b	2357 ± 113

^a The peak temperature at $\tan \delta$.

^b The sample with 20 wt% DMP was very brittle and exhibited high standard deviation.

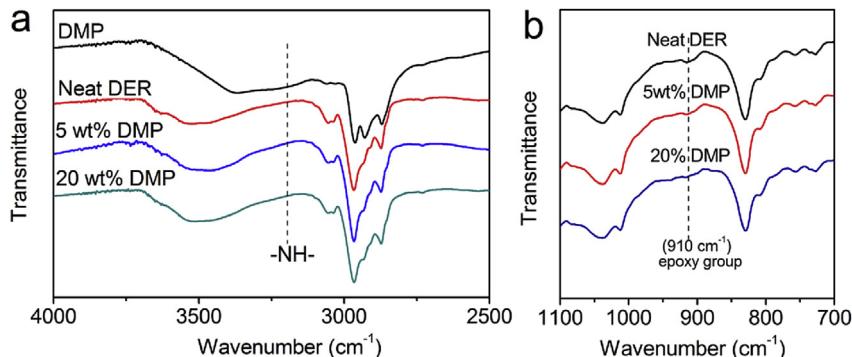


Fig. 6. Normalized FTIR spectra of decomposed matrix polymer (DMP), cured DER/NMA containing different amount of DMP, (a) from 4000 to 2500 cm^{-1} ; (b) from 1100 to 700 cm^{-1} . The peak at 1608 cm^{-1} (not shown) associated with the benzene groups is used as internal standard.

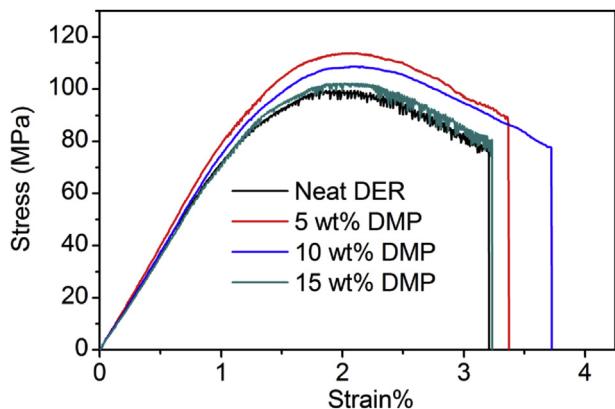


Fig. 7. Stress-strain curves of the cured DER/NMA containing different amount of DMP.

same strain at break. Overall, the strain at break was still fairly small (<4%) for all the compositions. The strain at break is always very sensitive to the defects in structures. At relatively low loadings (≤ 15 wt%), the multifunctional DMP might be mixed well with the other ingredients of the composition and contribute to the formation of a uniform cross-linked structure, resulting in the cured materials retaining the high strength and similar strain at break. At high DMP loadings (> 15 wt%), inadequate mixing might present in the composition, which led to formation of defects in the materials and hence greatly decreased the strength.

4. Conclusions

In this work, an effective mild chemical recycling method of CFRP waste has been identified and reuse of the recycled matrix compound in preparation of new epoxy materials has also been demonstrated. A CFRP waste of high T_g (> 210 °C) was effectively decomposed using a mild chemical recycling method. The

decomposition of the matrix polymer was performed at a relatively low reaction temperature (190 °C) using a benign $\text{ZnCl}_2/\text{ethanol}$ catalyst system. At this temperature this catalyst system is capable of selectively cleaving the aliphatic C-N bonds in the cross-linked network structure and turning the epoxy polymer into organic solvent soluble oligomers. After reaction, the catalyst can be conveniently recycled and still exhibits satisfactory high catalyst efficiency for degradation of new batch of CFRP waste. The recovered carbon fibers showed clean and smooth surface, suggesting little damage to the fibers after degradation reaction. The decomposed matrix polymer (DMP) contains amine groups and hydroxyl groups and can serve as a reactive ingredient in preparation of new epoxy materials without sacrificing the mechanical properties at a certain level of incorporation. The results indicate that with an up to 15 wt% addition of DMP in the composition the resulting new epoxy materials could still retain high mechanical properties. This excellent performance is probably attributed to the good mixing of DMP in the composition and effective involvement of the multi-functional DMP in the curing of the resin. This study demonstrates that the DMP is a promising additive for epoxy resins.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymdegradstab.2017.03.017>.

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