Journal of Materials Chemistry A

Recyclable CFRP with Extremely High Tg: Hydrothermal Recyclability in Pure Water and Upcycling of the Recyclates in New Composite Preparation

Journal:	*Journal of Materials Chemistry A*
Manuscript ID	TA-ART-04-2022-003161.R2
Article Type:	Paper
Date Submitted by the Author:	16-Jun-2022
Complete List of Authors:	Hao, Cheng; Washington State University, School of Mechanical and Materials Engineering & Composite Materials and Engineering Center Liu, Tuan; Shanghai Jiao Tong University, School of Biomedical Engineering; Washington State University, School of Mechanical and Materials Engineering, Composite Material and Engineering Center Liu, Wangcheng; Washington State University, School of Mechanical and Materials Engineering, Composite Material and Engineering Center Fei, Mingen; Washington State University, School of Mechanical and Materials Engineering, Composite Material and Engineering Center Shao, Lin; Washington State University, School of Mechanical and Materials Engineering, Composite Material and Engineering Center Kuang, Wenbin; Pacific Northwest National Laboratory, Energy and Environment Directorate Simmons, Kevin; Pacific Northwest National Laboratory, Energy and Environment Directorate Zhang, Jinwen; Washington State University, School of Mechanical and Materials Engineering & Composite Materials and Engineering Center

Recyclable CFRP with Extremely High T_g: Hydrothermal Recyclability in Pure Water and Upcycling of the Recyclates in New Composite Preparation

Cheng Hao,[a] Tuan Liu,[a,b,]* Wangcheng Liu,[a] Ming-en Fei,[a] Lin Shao,[a] Wenbin Kuang,[c] Kevin L. Simmons,[c] Jinwen Zhang [a,]*

[a] School of Mechanical and Materials Engineering, Composite Material and Engineering Center, Washington State University, Pullman, Washington 99164, United States

[b] School of Biomedical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

[c] Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington 99354, United States

*Corresponding authors: tuan-liu@sjtu.edu.cn and jwzhang@wsu.edu

Abstract

In recent years researchers have introduced different malleable and/or degradable thermosetting polymers to address the recyclability of traditional thermoset materials. Nonetheless, the mechanical properties and glass transition temperature (T_g) of these polymers are often compromised to achieve desired depolymerization rate. In this work, a hydrothermally recyclable epoxy/anhydride thermosetting system with superior mechanical performance and high T_g (> 200 °C) was developed for carbon fiber reinforced plastic (CFRP) applications, using triethanolamine as the co-curing agent and tetraglycidyl methylenedianiline (TGDDM) as the epoxy matrix. The hydrothermal recycling of such cured system is achieved at relatively low temperature (200 °C) without the addition of catalyst. This mild recycling process decomposes the recyclable polymer matrix into oligomer and imparts little damages to the valuable carbon fiber. Recycled carbon fiber and the decomposed polymer resin are reused to prepare new CFRP. Therefore, this study has introduced a simple and practical approach for the preparation of recyclable CFRP with high T_g and a pathway for highly efficient closed-loop recycling, which sets up a framework for the future design of sustainable polymer composites.

Keywords: Carbon fiber-reinforced polymer composites; Recyclable composites; Epoxy materials; Vitrimers; High T_g polymers.

1. Introduction

Owing to the high strength-to-weight ratio of composite materials, carbon fiber reinforced plastics (CFRP) are indispensable for aerospace, automotive, pressure vessels, and sporting goods industries. As CFRP demand continues to grow, recycling large amounts of end-of-service and left-over CFRP components emerges as a primary technical challenge. Epoxy is a common resin used for CFRP, as it provides overall good mechanical, thermal and physical properties for the composite materials. As it is for many other thermosetting polymers, however, epoxy's rigid crosslinked network structure makes the CFRP difficult to be recycled. Approximately 62,000 tons of CFRP waste from left-over and end-of-life CFRP components are landfilled or incinerated annually worldwide, which not only increases the environmental concerns but also takes no use of the residual value of the waste product.[1]

In the recent two decades, researchers have developed various CFRP recycling methods which can be classified into three categories including mechanical, thermal, and chemical recycling. In mechanical recycling, the size of CFRP waste is reduced by shredding, crushing, and milling,[1-5] and the received materials are in fine powder or fibrous form. In the thermal recycling process, CFRP materials are thermally treated at high temperatures (450 ~ 700 °C) in an inert gas atmosphere to burn off the matrix and liberate carbon fiber.[6-10] Early chemical recycling method is to decompose the matrix in strong acid (> 200 °C) or super/subcritical fluid (250 ~ 350 °C) under catalysis.[11-16] The polymer matrix is decomposed into small molecules that are difficult to reuse, and the strength of the recycled carbon fiber is reduced owing to the harsh reaction conditions. In recent years, the chemical recycling of CFRP at mild temperatures (< 220 °C) and in a neutral aqueous solution or alcoholic solvent has been reported.[17-21] The benign reaction conditions cause little damage to the carbon fibers, and the decomposed polymer matrix is in oligomer form that can be readily reused in the preparation for new polymer materials. However, these reported CFRPs that can be decomposed under mild conditions exhibited relatively low T_g (< 150 °C).[17, 20, 21] In fact, CFRP with a high T_g (> 180 °C) matrix is widely applied in aerospace and automobile industries and accounts for more than 30% of total production.[22] Due to the high crosslink density and rigid three-dimensional network, mild chemical recycling of high T_g CFRP is still challenging.[23]

The introduction of dynamic covalent bonds to the network structure is considered as a promising approach to impart malleability and enhance chemical degradability for thermosetting polymers. Disulfides, imine bonds, acetal linkages, dynamic B-O bonds, hydroxyl-ester, etc. are typical dynamic covalent bonds employed in these alternative thermosets. These bonds become interchangeable among themselves at elevated temperatures to enable malleability for the crosslinked polymers and are exchangeable with solvents containing thiols, amines, and hydroxyl groups to result in solvolytic decomposition, respectively. For example, Si et al. reported a CFRP in which the epoxy matrix contains abundant disulfide bonds.[24] The matrix of CFRP was decomposed in dithiothreitol/DMF solution at 90 °C due to the thiol-disulfide exchange reaction. The recovered carbon fiber was reused for the preparation of a new CFRP. For another example, Hashimoto prepared a recyclable CFRP using camphoric acid cured epoxidized soybean oil as the matrix resin.[25] The degradation of crosslinked matrix and the reclaim of carbon fiber were achieved by solvolysis in ethylene glycol at 190 °C for 20 hours. **Table S1** summarizes the T_g values and recycling conditions of the reported recyclable CFRP containing dynamic covalent bonds. In most cases, the polymer matrixes exhibit relatively low T_g (< 150 °C) and are degraded in environmentally unfriendly organic solvents or hydrochloric acid solution. Among various dynamic covalent exchange reactions, dynamic transesterification reaction (DTR) relied on hydroxyl-ester is probably the most applicable one for the development of recyclable polymer matrix with high T_g. The polymer matrix based on DTR is simply prepared via the curing of epoxy with carboxylic acid/anhydride which is widely adopted in industry practice. DTR usually happens at high temperatures (> 120 °C), making it possible to prepare materials with high service temperature. In our previous work, we demonstrated that tertiary amines within the structure of anhydride cured epoxy promotes the DTR and enables the chemical degradation process performed in a mild aqueous solution.[26, 27] Thus, the introduction of tertiary amines to a high T_g epoxy matrix would be a feasible way to enable high-performance CFRP with mild recyclability.

In this work, we demonstrated a facile approach for the preparation of CFRP with high T_g and hydrothermal recyclability. The feedstocks used for epoxy matrix of CFRP including TGDDM epoxy resin, nadic methyl anhydride (NMA), and triethanolamine (TEOA) are all commercially available. The epoxy matrix exhibited high T_g (203 °C) and tensile strength (77.3 MPa) owing to high crosslink density and rigid backbone structure. The epoxy matrix can be efficiently degraded in pure water at a mild temperature of 200 °C due to the presence of catalytic tertiary amines originated from TGDDM and TEOA promote the hydrolysis. In addition, the free hydroxyl groups in the network structure originated from TEOA can react with the ester linkages through transesterification which destabilizes the network structure and promotes the hydrolysis. Due to the mild reaction conditions, the recycled carbon fiber (rCF) exhibits little damage. The ester bonds of polymer matrix are randomly cleaved resulting in the formation of oligomer. Both rCF and the decomposed polymer are reused to prepare new recyclable CFRP.

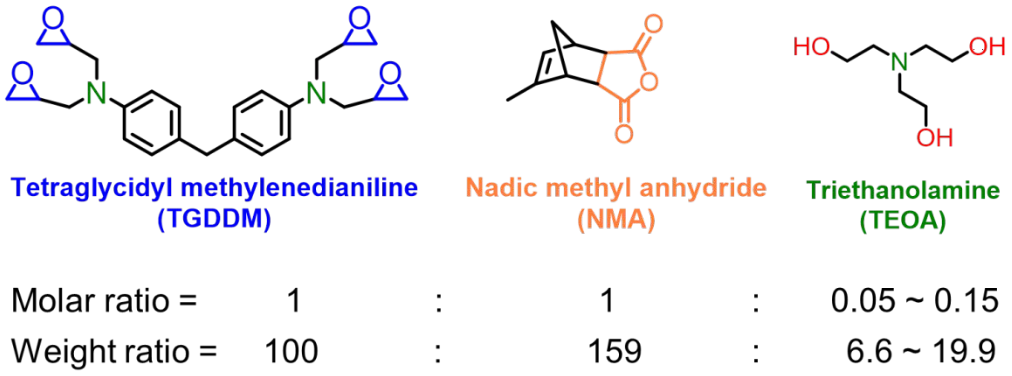
2. Experimental section

2.1 Materials

Tetraglycidyl methylenedianiline (TGDDM, Sigma-Aldrich, epoxy value = 0.89 mol 100 g^{-1}), DER 331 epoxy (DER, Olin corporation, epoxy value = 0.53 mol 100 g^{-1}), nadic methyl anhydride (NMA, Electron Microscopy Sciences), triethanolamine (TEOA, Sigma, > 99%), 2-ethyl-4-methylimidazole (2E4MI, Across Organic, > 95%), tetrabutylammonium bromide (TBAB, TCI, 98%) and epichlorohydrin (ECH, ACROS Organics, 99%) were used as received. All solvents (GR grade) were used without further purifications. Woven carbon fiber mats were purchased from Composite Envision with a tow size of 3k and weaved in 2 × 2 twills.

2.2 Preparation of recyclable epoxy matrix

TGDDM, NMA, and TEOA were mixed at room temperature (**Scheme 1**). The stoichiometric ratio between the epoxy group and anhydride group was fixed at 1:1. The molar ratio of TEOA to epoxy groups varied from 0.05 to 0.15 (**Table 1**). Based on the molar ratio of TEOA to epoxy groups, the prepared epoxies were denoted as TN-0.05TEOA, -0.1TEOA and -0.15TEOA, respectively. The mixture was degassed at 80 °C for 15 min in a vacuum oven and then transferred to a mold for curing. The curing program was 130 °C for 1 hour, 170 °C for 1 hour, and 220 °C for 2 hours. For comparison, 2E4MI was used as the catalyst instead of TEOA for the curing of DER 331 and TGDDM with NMA as references, respectively, and the resulting epoxy materials were denoted as DN-2E4MI and TN-2E4MI, respectively (**Table 1**).



Scheme 1. Chemical structures of TGDDM, NMA and TEOA. The molar ratio of functional groups and the weight ratio of the monomers are indicated.

Table 1. Formulations of TGDDM-NMA-TEOA and DER-NMA-2E4MI curing systems.

Samples	DER		TGDDM		NMA		TEOA		2E4MI
	Epoxy^a [mmol]	Mass [g]	Epoxy^a [mmol]	Mass [g]	Anhydride [mmol]	Mass [g]	[mmol]	Mass [g]	Mass [g]
TN-0.05TEOA			8.9	1	8.9	1.59	0.45	0.07	
TN-0.1TEOA			8.9	1	8.9	1.59	0.89	0.13	
TN-0.15TEOA			8.9	1	8.9	1.59	1.34	0.20	
TN-2E4MI			8.9	1	8.9	1.59			0.10
DN-2E4MI	5.3	1			5.3	0.94			0.06

^{a} Mole of epoxy group

2.3 Fabrication of CFRP

CFRP was prepared by the hand lay-up method. Woven carbon fabric mats were cut into 12 cm × 12 cm squares. The resin composed of epoxy, anhydride and TEOA was degassed at 80 °C for 15 min in a vacuum oven and then gently poured onto the fabric mats. The fabric mat was fully impregnated by the resin using a bristle roller. The impregnated fabric mats were moved to a preheated hot press and cured at 130 °C for 1 hour, 170 °C for 1 hour, and 220 °C for 2 hours with a constant pressure of 5 MPa. After the completion of curing, the cured CFRP was allowed to cool to room temperature before removal from the hot press. Two additional CFRPs fabricated with TN-2E4MI and DN-2E4MI as matrices were prepared using the same procedure as described above. Based on the matrix applied, the CFRPs prepared with virgin carbon fiber mats were named as TN-0.1TEOA-CF, TN-2E4MI-CF and DN-2E4MI-CF, while the CFRP prepared with recycled carbon fiber mat was named as TN-0.1TEOA-rCF.

2.4 Hydrothermal degradation of epoxy matrix and CFRP

The cured epoxy (~5.0 g) was ground into particles, sieved through a 10-mesh sieve, and charged into a 100 mL pressure reactor (Series 4842, Parr Instrument Company). 40 mL pure water was added to immerse the epoxy sample. The degradation reaction was performed at the predetermined temperature and heating time. After reaction, the reactor was allowed to cool down to room temperature prior to opening. The insoluble sample was rinsed with acetone for three times and dried in a vacuum oven at 80 °C for 12 hours. The aqueous solution containing the soluble degraded matrix polymer (DMP) was concentrated by a rotary evaporator and vacuum dried in oven at 80 °C for 6 hours to obtain the DMP. The degree of degradation (D_d %) was calculated according to the following equation:

$$D_d\% = \left(1 - \frac{m_1}{m_0}\right) \times 100\% \qquad (1)$$

where m_0 is the weight of the cured epoxy before degradation, and m_1 is the weight of the insoluble resin after degradation. The decomposition of CFRP was performed following the similar procedures.

2.5 Epoxidation of DMP

A round bottom flask was charged with 10 g DMP, 2.49 g TBAB, and 92.5 g ECH. The reaction solution was refluxed for 3 hours under an argon atmosphere. Afterwards, the reaction temperature was decreased to 50 °C, and 30 wt% NaOH aqueous solution (4.4 g) was added dropwise into the solution. The reaction was continued for another 6 hours. After the reaction was complete, the solution was washed with water, concentrated by a rotary evaporator, and dried in a vacuum oven to receive the brown oil-like liquid product. The dried product, denoted as rEP, possessed an epoxy value of 0.20 mol 100 g^{-1} determined by titration.

2.6 Characterizations

Fourier transform infrared (FTIR) spectra were recorded on a NICOLET iS50 FTIR spectrometer. Before the test, ~1 mg sample was ground with ~100 mg potassium bromide (KBr). The mixture was press-molded into a disc and scanned on the FTIR spectrometer from 4000 to 400 cm^{-1} for 64 times with a 4 cm^{-1} resolution. The obtained spectra were normalized based on the peak at 1509 cm^{-1} which was attributed to the benzene skeleton. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400-NMR spectrometer (400 MHz). $CDCl_3$ was used as the solvent. Differential scanning calorimetry (DSC, DSC1, Mettler-Toledo, Switzerland) was used to evaluate the curing behavior and T_g. A ~5 mg sample was sealed in a 40 μL aluminum crucible and scanned from 25 to 220 °C at a heating rate of 10 K min^{-1} under a nitrogen atmosphere. Thermal stability was examined by a thermogravimetric analyzer (TGA, TGA/DSC1, Mettler-Toledo). A ~5 mg sample was heated from 25 to 800 °C at a heating rate of 10 K min^{-1} under a nitrogen atmosphere. The viscosity of DMP was examined on a Discovery HR 2 (TA instrument) rheometer equipped with a 25 mm parallel plate geometry. Sample was scanned from 25 to 150 °C under flow mode. The heating rate was 3 K min^{-1}, and the shear rate was 1.0 s^{-1}.

Dynamic mechanical properties were tested on a dynamic mechanical analyzer (DMA, Q800, TA instrument) equipped with a single cantilever clamp. The oscillating amplitude and frequency were 15 μm and 1 Hz, respectively. Samples with dimensions of ~ 3.5 cm × 1.3 cm × 0.3 mm were scanned from 25 to 250 °C at a heating rate of 3 K min^{-1} in air. Tensile testing was performed on an Instron 4466 Universal test machine according to ASTM D638. The crosshead speed was 5 mm min^{-1}, and the gauge length of the specimen was 36.35 mm. The un-notched Izod impact test was performed on a BPI Basic Pendulum impact tester (Dynisco Polymer Test) according to ASTM D4812. For both tensile and impact tests, at least 5 repeats were performed for each formulation.

Stress relaxation tests were performed on a Discovery HR 2 (TA instrument) rheometer equipped with an 8 mm parallel plate geometry. A sample with a thickness of 0.3 mm was equilibrated at a predetermined temperature for 15 min. During the test, a 2 N normal force was applied to the sample, and a 1.5% strain was applied. The evolution of relaxation modulus with time was recorded.

3. Result and discussion

3.1 Preparation of polymer matrix with high T_g

TGDDM is a tetrafunctional epoxy resin with a rigid backbone structure. Compared with conventional DER epoxy, TGDDM tends to form a network structure with a higher crosslink density. TEOA, which possessed three hydroxyl groups and one tertiary amine, was chosen as the catalytic curing agent. In our previous study, we demonstrated that TEOA was effective in promoting the curing reaction of the epoxy-anhydride system and the thermally induced DTR in the cured epoxy.[27]

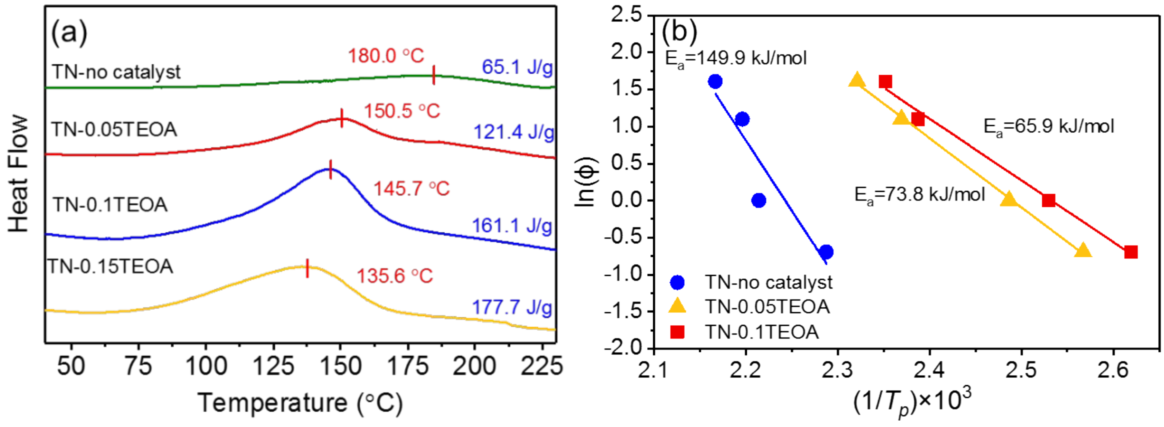


Figure 1. (a) Effects of TEOA content on the non-isothermal curing process. Enthalpies of each formulation are labeled. The DSC thermograms were obtained at the heating rate of 5K min^{-1} under nitrogen atmosphere; (b) activation energy (E_a) of different epoxy curing systems calculated based on Ozawa method.

Figure 1a shows the DSC thermograms of TN-TEOA curing systems with different TEOA contents. All formulations display a single exothermic peak. With the increasing in TEOA content, the peak temperature of exothermic curve shifted from 150.5 °C to 135.6 °C, and the enthalpy increased from 121.4 to 177.7 J g^{-1}. In contrast, only a small peak with an enthalpy of 65.1 J g^{-1} was observed for the mixture of TGDDM and NMA without TEOA. **Figure 1b** shows the activation energy (E_a) calculated based on Ozawa method.[28] As the TEOA content increased from 5 to 10 mol%, the activation energy of curing decreased from 149.9 kJ mol^{-1} to

65.9 kJ mol^{-1}, indicating that less energy is required to activate the curing reaction. These results confirm that TEOA is efficient in promoting the epoxy-anhydride curing process.

Figure S1 shows the apparent viscosities of the resin systems containing different amounts of TEOA. The viscosities at room temperature were proportional to the increasing amount of TEOA, due to the enhanced hydrogen bonding with higher TEOA loadings.[29] The viscosity profile of the resin system at around room temperature provides guidance for the processing of composite materials, and low viscosity (< 10 Pa·s) of the resin system is favorable to wet the fiber mat efficiently.[30]

3.2 Thermally induced dynamic transesterification

As illustrated in **Scheme 2**, the cured TGDDM epoxies possess abundant ester bonds, -OH groups, and catalytic tertiary amines in the network structure. The ester bonds are produced from the curing reaction of epoxy-anhydride. The -OH groups and catalytic tertiary amines are originated from TEOA, and TGDDM also possesses tertiary amines in structure. Because of these structural features, DTR between ester bonds and -OH groups could happen in the network structure under the catalysis of tertiary amines (**Scheme S1**). Stress relaxation test was applied to study the DTR (**Figure S2**). The relaxation times (τ^*) is defined as the time when the initial modulus relaxed to 1/e (37%) of its initial modulus. TN-0.1TEOA and TN-2E4MI at 200 °C showed τ^*s of 1864 and 3576 s, respectively; in contrast, DN-2E4MI can only relax 40% of its initial modulus in 6 hours. The shorter τ^* of TN-0.1TEOA compared with TN-2E4MI is due to more tertiary amines and -OH groups present in the network.[27] Because there are quite few -OH groups and tertiary amines in the network structure of DN-2E4MI, the DTR cannot efficiently perform resulting in slow relaxation rate. In addition, TGA results (**Figure**

S3) show that all samples begin to lose weight at above 250 °C, indicating that the stress relaxation behavior is the consequence of DTR instead of thermal degradation.

3.3 Mechanical performance of epoxy matrix and CFRP

Figure 2a shows the tan δ as a function of temperature for the cured epoxies. Owing to rigid backbone structure and high functionality, all the cured TGDDM epoxies show T_g (taken as the peak temperature of tan δ) values above 190 °C which is much higher than that of the reported recyclable epoxies (**Table S1**).[31-36] As the TEOA content increased from 5 to 15 mol%, T_g decreased from 224.1 to 196.0 °C (**Table S2**). The introduction of flexible TEOA moieties to the crosslinked network structure leads to the decrease of T_g. In our previous work, TEOA was used as a co-curing agent in a BPA epoxy (DER)-NMA curing system to yield a crosslinked polymer with a T_g of 134.9 °C.[27] The huge increase in T_g is this case was due to the stiffer structure of TGDDM and higher crosslink density of cured epoxies. **Figure 2b** shows the storage modulus (E') versus temperature curves. In glassy state, the E's of TN-0.05TEOA, -0.1TEOA and -0.15TEOA at 50 °C were 2.8 GPa, 2.7 GPa and 2.5 GPa, respectively. These values were much higher than that of DN-2E4MI (~ 2.0 GPa). The decrease of E' with the increase of TEOA content was due to the incorporation of flexible TEOA moieties. In the rubbery state, all the cured TGDDM epoxies exhibited a E' above 50 MPa, while the rubbery E' of DN-2E4MI was only ~26 MPa. Rubbery E' is proportional to the crosslink density of thermosetting polymers.[37] Therefore, this result confirmed a higher crosslink density of the cured TGDDM epoxies compared with that of DN-2E4MI.

Figure 2c and **S4** show the tensile and impact strengths of the cured epoxies, respectively. The tensile strengths of TN-0.05TEOA (65.9 MPa) and -0.1TEOA (77.2 MPa) were higher than that of DN-2E4MI (59.0 MPa) and comparable with that of TN-2E4MI (79.2 MPa). TN-0.05TEOA, TN-0.1TEOA and TN-2E4MI exhibited comparable tensile moduli at around 1.8 GPa which was higher than that of DN-2E4MI (1.32 GPa). In comparison, TN-0.1TEOA exhibited the optimum tensile property. This can be explained by the following reasons: (1) the use tetrafunctional TGDDM as matrix resin tends to yield the materials with high crosslink density and modulus; (2) the introduction of TEOA to the resin system brings abundant hydrogen bonds to the resulting network structure, thus improving the tensile strength.[38] In addition, TN-0.05TEOA and TN-0.1TEOA exhibited similar impact strengths (9.2 and 9.1 kJ m^{-2}) (**Figure S4**) which were higher than that of DN-2E4MI (7.2 kJ m^{-2}) and as good as that of TN-2E4MI (10.3 kJ m^{-2}). High impact strength of TGDDM materials is owing to the unique feature of multifunctionality that increase the content of fractional free volume and better chain flexibility with the presence of TEOA.

Figure 2d summarizes the T_g and tensile strength of the reported epoxy materials containing dynamic covalent bonds.[20, 24, 26, 39-47] It is well understood that the T_g of a thermosetting polymer is closely related to its backbone stiffness and crosslink density. In most of the reported recyclable CFRPs, the polymer matrixes are purposely designed with flexible backbone structures and low crosslink densities to achieve desired depolymerization rate under mild conditions, which consequently lead to low T_gs of the resulting materials.[48] In this study, TN-0.1TEOA exhibits the T_g of 201.3 °C and tensile strength of 77.2 MPa, and these values are higher than that of the reported epoxy materials owing to the stiff structure and high crosslink density. This exceptional performance propels us to prepare CFRP with TN-0.1TEOA as polymer matrix. Carbon fiber (CF) reinforced TN-TEOA composites with 3 plies were fabricated by the hand layup method, and the weight fraction of fiber was ~55 wt%. **Table S3** shows the mechanical properties of the prepared CFRPs. TN-0.1TEOA-CF displayed a decent tensile strength of 502 MPa which was 10% lower than that of the formulated TN-2E4MI-CF (558 MPa) and was 19% higher than that of DN-2E4MI-CF (421 MPa).

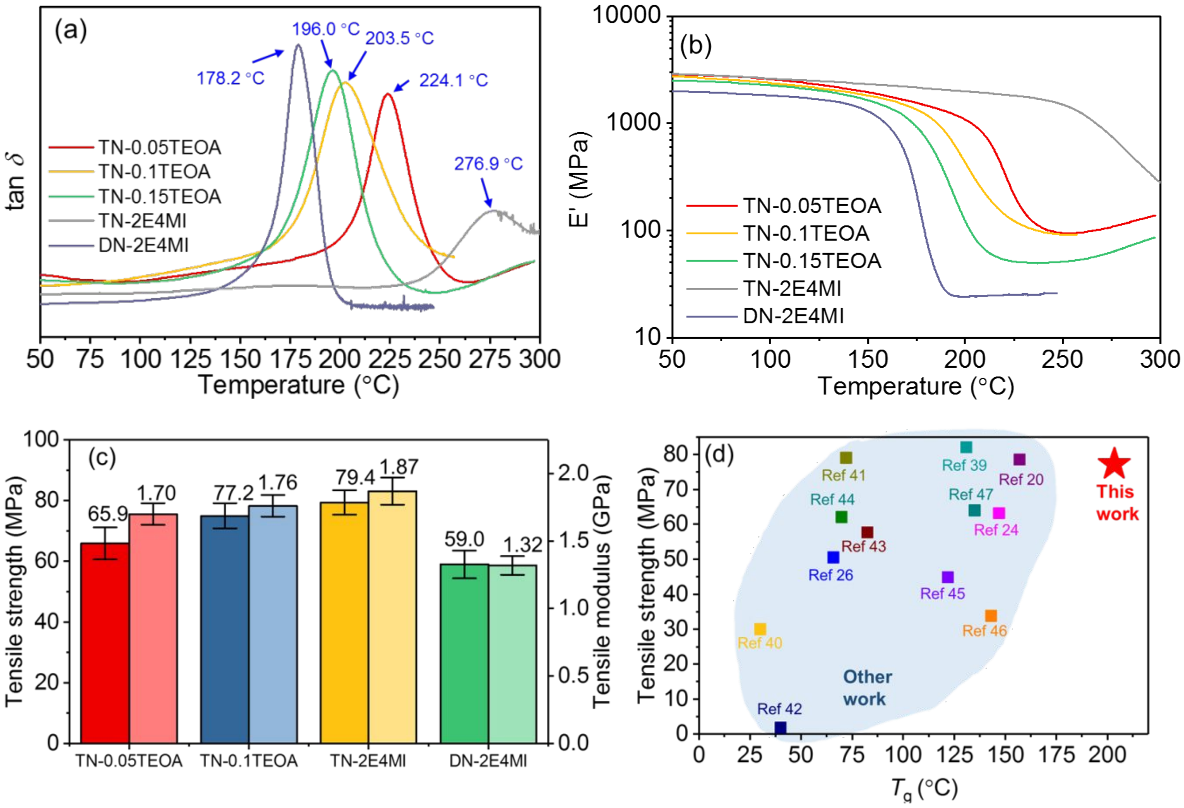
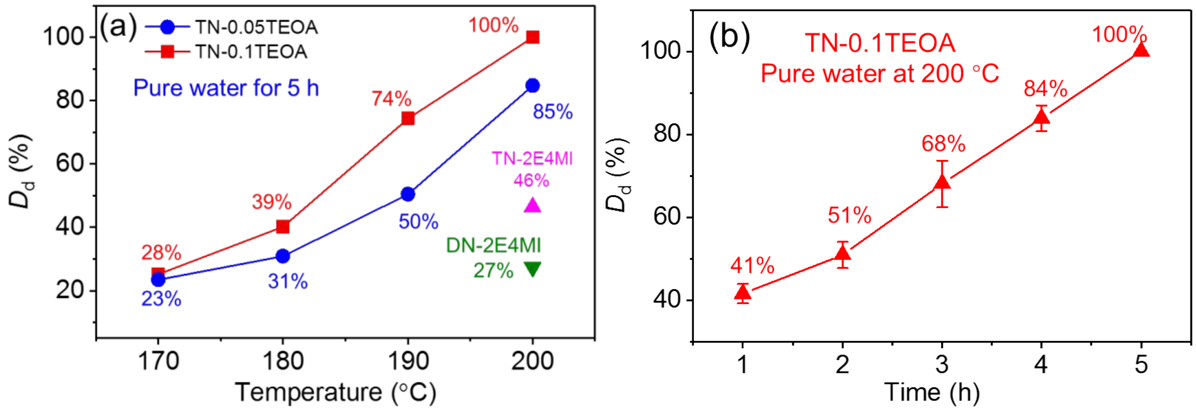


Figure 2. (a) Tan δ and (b) storage modulus (E') of the cured TN−TEOAs, TN-2E4MI and DN-2E4MI. The tests were performed at a heating rate of 3 K min^{-1}; (c) tensile properties of TN−TEOAs, TN-2E4MI and DN-2E4MI; (d) summary of T_g and tensile strength of TN-0.1TEOA and the reported recyclable epoxy materials containing dynamic covalent bonds in the network structure.

3.4 Hydrothermal recyclability of the cured epoxies

Chemical recycling of waste CFRPs in an aqueous solution has become attractive, considering that water is much greener as the reaction medium than organic solvents. Catalyst is often required to accelerate the decomposition rate of the matrix in an aqueous medium. However, recycling of the catalyst solution and removing the catalyst from the degradation product are necessary in posttreatment. It is desirable to decompose the matrix of CFRP in pure water without adding catalyst. **Figure 3a** shows the degradation degree of TN-0.05TEOA and TN-0.1TEOA at different temperatures applying pure water as reaction medium. The degradation time was fixed at 5 hours. For both samples, the D_d increased with temperature. At 170 °C, the D_d was only ~25% for both TN-0.05TEOA and TN-0.1TEOA. At 200 °C, TN-0.05TEOA exhibited the D_d of 85%, while TN-0.1TEOA was completely degraded. **Figure 3b** shows the effect of reaction time on D_d of TN-0.1TEOA at 200 °C. The D_d was ~ 41% at 1 hour and increased with time until the sample was completely decomposed at 5 hours. In contrast, the D_ds of DN-2E4MI and TN-2E4MI in pure water at 200 °C for 5 hours were 27 and 46%, respectively. Clearly, TEOA and NMA co-cured TGDDM epoxies exhibit unique and effective degradation behavior in pure water without the addition of catalyst.



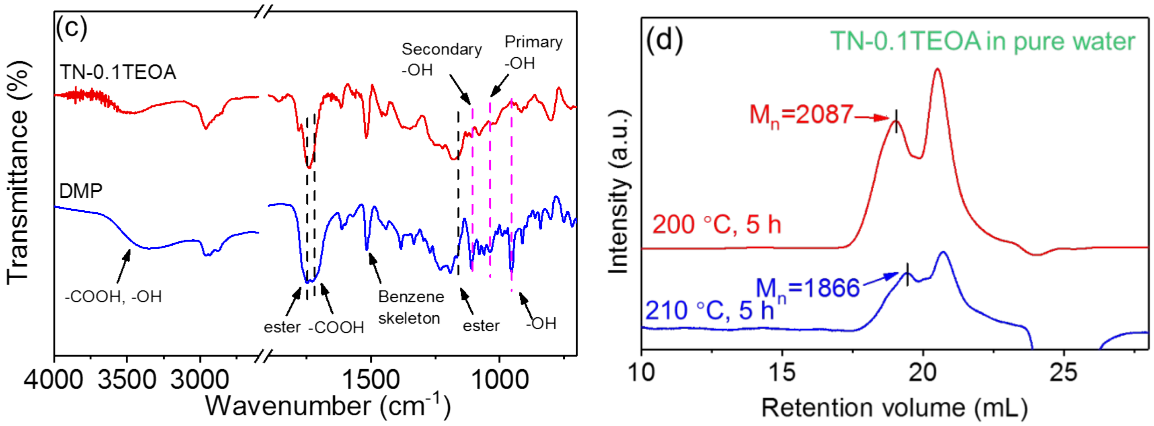


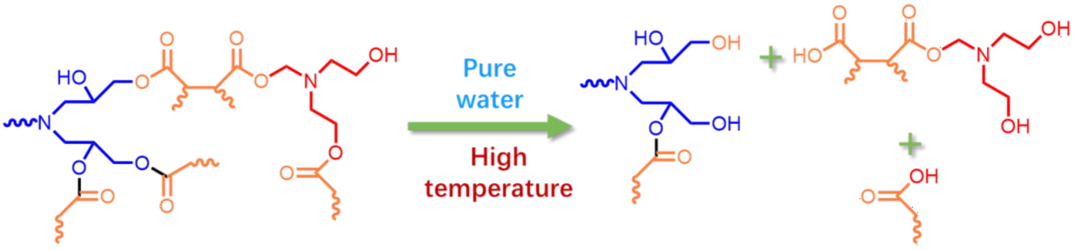
Figure 3. (a) Effects of temperature on degradation degree for TN-TEOAs, TN-2E4MI and DN-2E4MI; (b) Effects of time on the degradation degree for TN-0.1TEOA; (c) FTIR spectra of TN-0.1TEOA before and after degradation; (d) GPC curves of DMP of TN-0.1TEOA that decomposed in pure water at 200 °C and 210 °C for 5 hours.

The chemical structure of the DMP was examined by FTIR and GPC. Compared with TN-0.1TEOA, the DMP obtained from the reaction at 200 °C for 5 hours exhibited remarkable increases in peak intensity at ~ 3400, 1106 and 1035 cm^{-1} corresponding to -OH groups, and it had a new peak at 953 cm^{-1} corresponding to -COOH groups (**Figure 3c**). Meanwhile, the peak of C=O bonds at ~1750 cm^{-1} associated with ester groups in cured epoxy sample broadened and shifted to ~ 1720 cm^{-1} after degradation, which was associated with carboxyl groups. These results indicate the cleavage of ester bonds and the formation of hydroxyl and carboxyl groups during degradation (**Scheme 2**). DMP was found in oligomer form with a number-average molecular weight (M_n) of ~ 2080 Da after degradation at 200 °C for 5 hours (**Figure 3d**). When the reaction temperature was raised to 210 °C, the M_n of DMP was decreased to 1860 Da. This is because increasing temperature promotes the hydrolysis reaction resulting in DMP with lower molecular weight.

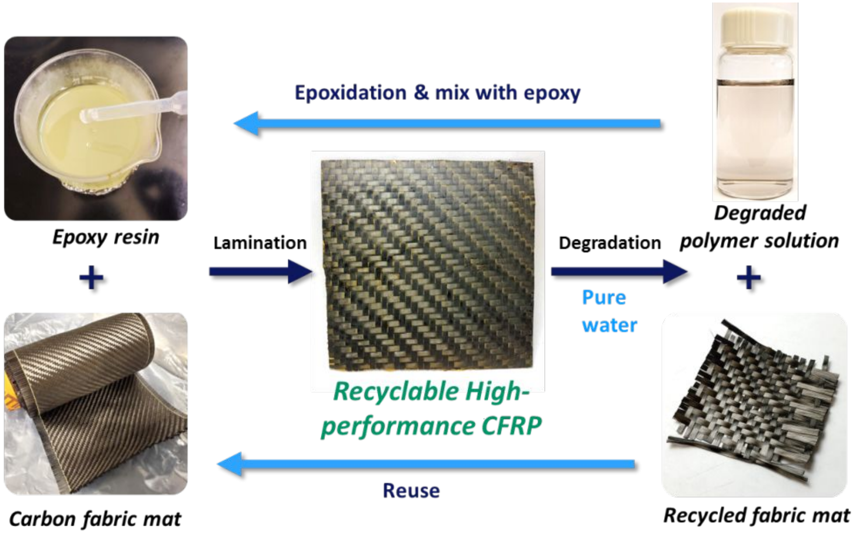
The efficient hydrolysis of ester bonds that leads to the degradation of the polymeric matrix is corresponded to the presence of catalytic tertiary amines in the epoxy matrix, which promote the hydrolysis reaction in pure water (**Scheme 2**). More tertiary amines were introduced into the crosslinked network with the addition of TEOA, so that TN-0.1TEOA possesses higher degradation efficiency than TN-0.5TEOA (**Figure 3a**). In addition, the free hydroxyl groups in the network structure originated from triethanolamine can react with the ester linkages through DTR (**Figure S2**), which destabilizes the network structure and promotes the hydrolysis reaction.

Conventional amine cured TGDDM exhibits a high T_g (> 200 °C).[49, 50] However, amine cured epoxies are constructed by stable C-N, ether, and C-C-C bonds, making them very hard to be chemically recycled. In our previous study, a CFRP with amine-cured epoxy matrix was decomposed at 190 °C using 20 wt% $ZnCl_2$/ethanol solution.[23] In contrast, the cured epoxy in this study was decomposed at much milder conditions (in pure water at 200 °C). In addition, conventional anhydride cured BPA epoxy is not degradable in water at 200 °C without a catalyst.[51] In our previous study, TEOA was employed to a curing system based on BPA epoxy and NMA, and the resulting cured epoxy was degradable in pure water at 200 °C; however, the cured epoxy exhibited a relatively low T_g of 135 °C.[27] In another study, a dimer acid cured TGDDM was decomposed in pure water, which was explained by the catalytic effect of tertiary amines originated from TGDDM as well as the thermally induced DTR which destabilized the network structure.[52] However, that epoxy exhibited a low T_g (9.3 °C) due to the flexible backbone structure and low crosslink density.

Therefore, the degradation results for different formulations in this study emphasize the importance of TGDDM and TEOA. With the addition of TEOA in TGDDM resin system, the cured epoxy resin not only possesses high T_g and high tensile strength, but it also has the hydrothermal recyclability that synergistically catalyzed by tertiary amines originated from TGDDM and TEOA. These merits propel us to investigate the recycling of CFRP with TN-0.1TEOA as the matrix polymer.



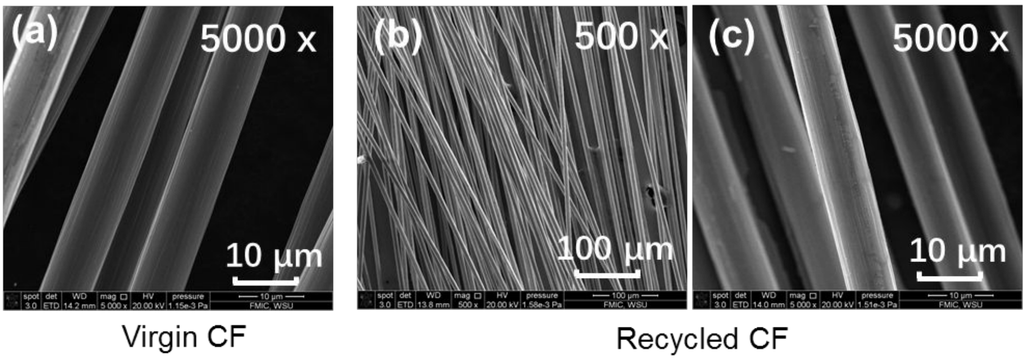
Scheme 2. Schematic illustration of hydrolysis of ester bonds in the epoxy polymer matrix in pure water.



Scheme 3. Illustration of chemical recycling of CFRP with TN-TEOA as matrix and reuse of the recycled carbon fiber and the decomposed polymer for new recyclable CFRP.

3.5 Recyclability of carbon fiber-reinforced TN-0.1TEOA composites

The improved hydrolysis of the TEOA co-cured TGDDM favors the recyclability of the resulting CFRP in mild conditions (**Scheme 3**). After the depolymerization of the crosslinked matrix in pure water at 200 °C, the insoluble carbon fiber cloths were collected easily from the aqueous reaction medium, while the decomposed polymer was soluble in solution and collected by rotary evaporation. The woven carbon fiber cloth was unaffected by the recycling process and fiber tow retains the same condition. The fiber reinforcement was subject to very little damage since the degradation was conducted at mild conditions. SEM images of both reclaimed carbon fiber and neat carbon fiber show no visible residue resin on the surface of fiber (**Figures 4a, b and c**). **Figure 4d** shows the stress-strain curves obtained from single fiber tension tests. The tensile strength of rCF was 2609 ± 351 MPa, which was 94% that of the neat carbon fiber (2790 ± 366 MPa). These results indicate that the mechanical properties of carbon fiber were barely affected during the recycling process. **Figure 4e** shows that no weight loss occurred in the TGA curve of rCF, indicating the clean surface of recycled carbon fiber. **Figure S5** also shows the derivative of TGA (DTG) curve of rCF is straight, further proving no weight loss in the heating process.



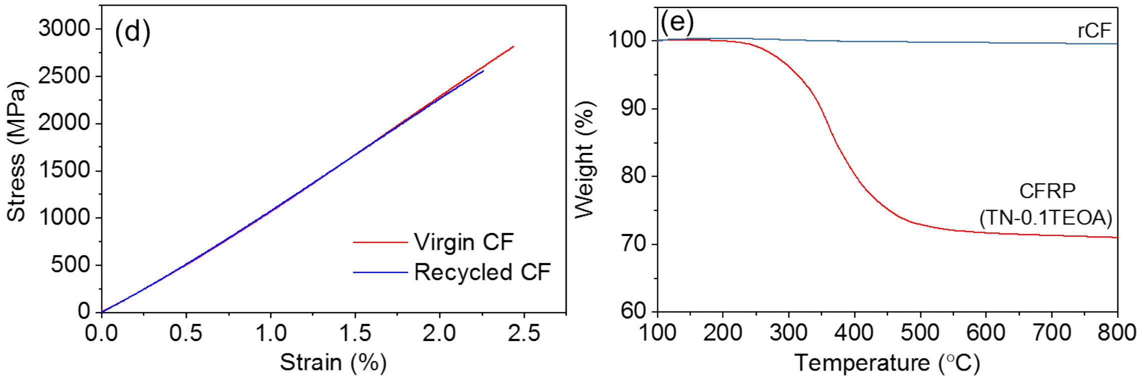


Figure 4. SEM images of (a) virgin CF and (b) (c) recycled CF; (d) single textile tension test of virgin and recycled CF; (e) TGA curves of TN-0.1TEOA composite and rCF. Recycled carbon fiber was recycled from TN-0.1TEOA-CF at 200 °C in water.

3.6 Upcycling of DMP and rCF

As aforementioned, DMP was in the oligomer form and contains a large number of hydroxyl groups, so it can participate in the epoxy/anhydride curing system to react with both components. Moreover, the upcycling of DMP was achieved by the virtue of the inherent tertiary amines; thus, the cured epoxy resin containing DMP moieties should also possess hydrothermal recyclability. However, the high viscosity of DMP results in difficulties in mixing and poor miscibility.

In this study, to reduce the viscosity and improve the miscibility and reactivity, DMP was chemically modified with ECH to introduce epoxide groups, and the resultant epoxy was named as rEP (**Scheme S3**). The chemical structure and viscosity characterization results (**Figure S6** and **S7**) demonstrate the successful conversion of hydroxyl groups to epoxide groups, which dramatically decreased the viscosity. The reduction in viscosity is due to the consumption of hydroxyl groups that reduce the number of hydrogen bonds. rEP was mixed with virgin DER epoxy resin in a large content (10, 20, 30 wt%), and the obtained cured materials were denoted as DN-10rEP, -20rEP and -30rEP. Formulations of the new epoxy resin system are presented in **Table S4**. The viscosity of resin mixture was low and suitable for processing (**Figure S8**). DSC thermograms of resin mixture exhibit identical peak temperatures (**Figure S9**), which indicates rEP and DER have a similar curing reactivity. **Figure 5a** shows tan δ of the cured epoxies. T_g decreased with an increase of rEP content in the compositions. DMP is in oligomer and possesses flexible structural units originated from NMA and TEOA, making it is more flexible than BPA epoxy and TGDDM as well. In addition, a single peak is observed in each composition, suggesting the excellent mixing of rEP and DER as well as the homogenous crosslinked structure. **Figure S10** shows the storage modulus (E') as the function of temperature, there is also a single transition from glass state to rubbery state. **Figure S11** and **Table S5** show the tensile and impact properties of the cured epoxies with rEP. With the increasing rEP content, the tensile strength decreased from 59.0 to 30.3 MPa, while the impact strength is firstly improved to 14.6 kJ m^{-2} then decreased 5.9 kJ m^{-2}.

The incorporation of rEP in the resin system endows hydrothermal recyclability to the cured epoxies. **Figure 5b** shows the degradation degree of each sample that decomposed at 200 °C for 5 hours with pure water. FTIR and GPC (**Figure S12** and **Figure 5c**) results suggest the hydrolysis of polymer network during degradation. With the increase rEP content in the resin system, the degradation degree of the cured epoxies raised from 24.6% to over 90%. This is because higher concentration of tertiary amines incorporated by rEP yields a more complete degradation.

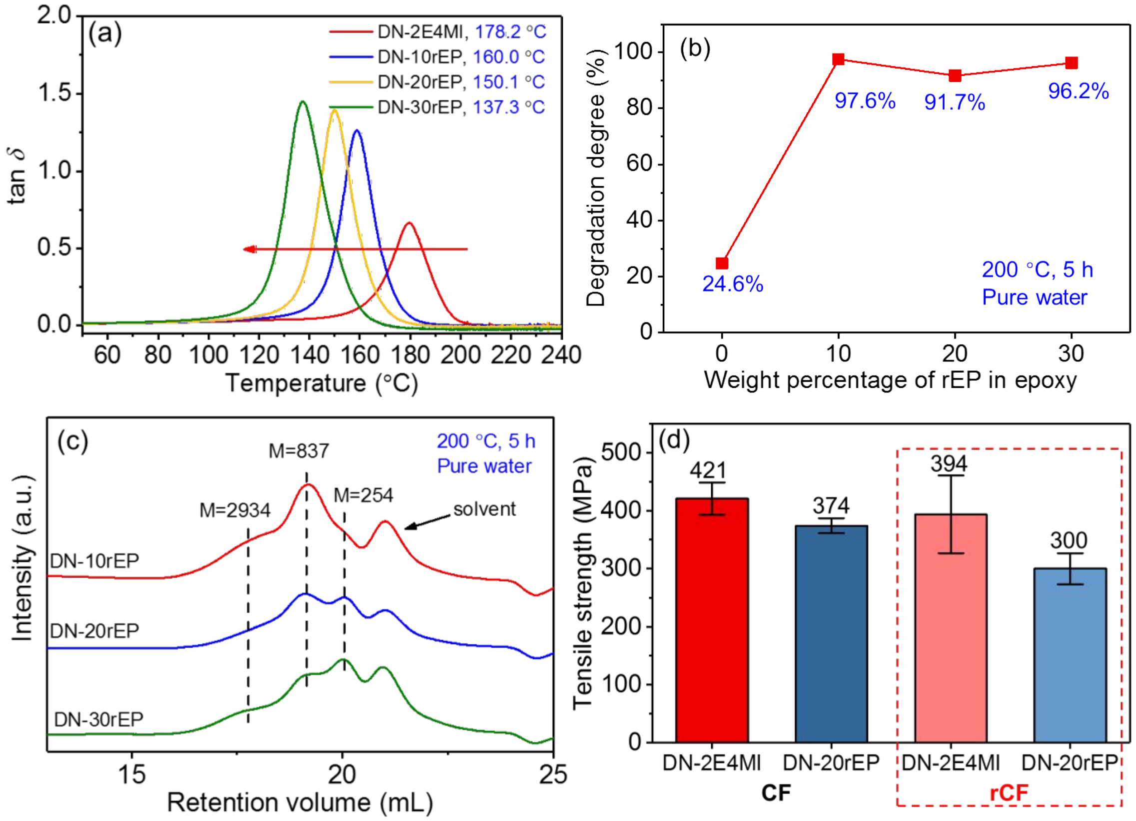


Figure 5. (a) Tan δ of the cured epoxies that uses rEP to replace part of DER epoxy resin. The tests were performed at a heating rate of 3 K min^{-1}; (b) effects of rEP content in the cured epoxy on the degradation degree; (c) GPC curves of decomposed polymer of DN-10rEP, -20rEP and -30rEP; (d) tensile strength of DN-2E4MI and DN-20rEP with 3 layers of CF and rCF.

rCF was reused to fabricate a new laminate composite with fresh epoxy resin systems. TN-0.1TEOA and DN-2E4MI were used as a matrix to prepare the CFRPs, and their tensile strengths were 437 and 394 MPa, respectively, which retained 87% and 88% of tensile strength compared with that of CFRP with virgin CF (502 and 421 MPa, **Figure 5d** and **Table S3**). Owing to the loose pattern of reclaimed fiber mat, fiber weight content of CFRP with rCF was 42% which was lower than that of CFRP with virgin CF (55%). Therefore, the decreased tensile strength was mainly due to the decreased fiber content.

Finally, we demonstrated the reuse of rCF and DMP in the preparation of DN-20rEP-rCF in which the reinforcement was rCF and the polymer matrix was DN-20rEP. DN-20rEP-rCF exhibited a tensile strength of 300 MPa which is decent for a three layers-fiber reinforcement CFRP. With the presence of rEP moiety in the matrix, the hydrothermal recyclability of DN-20rEP-rCF was achieved. After chemical recycling of DN-20rEP-rCF in pure water at 200 °C for 5 hours, the polymer matrix was completely decomposed, and the clean carbon fiber was collected (**Figure S13**), suggesting that DN-20rEP-rCF was recyclable.

4. Conclusions

In summary, a recyclable anhydride cured epoxy with high mechanical performance and high T_g (> 200 °C) was prepared through the curing of TGDDM and NMA with TEOA as catalytic co-curing agent. The high mechanical performance and high T_g (> 200 °C) were owing to the multifunctional TGDDM and stiff NMA. Inherent tertiary amines as well as the abundant hydroxyl groups originated from TEOA endowed the cured epoxy with the ability for DTR at elevated temperatures. CFRP was manufactured with this epoxy resin system and showed adequate tensile strength (501.8 MPa). The hydrothermal recycling of CFRP was achieved without the catalyst. At 200 °C, the thermally induced DTR facilitates the hydrolysis of the ester bonds in the network structure. The decomposed polymer was soluble in the reaction medium (water), while the insoluble carbon fiber was facilely collected and exhibited comparable mechanical properties as the virgin one (2609 MPa *vs*. 2790 MPa). The decomposed polymer was epoxidized to yield the recycled epoxy resin which was further mixed with fresh epoxy to generate the new epoxy resin as well as the corresponding CFRP. By virtue of the tertiary amines in rEP, the resulting epoxy matrix also possessed hydrothermal recyclability in pure water. New CFRP that is prepared with rCF showed similar tensile strength. Moreover, reuse of recyclates was achieved by the preparation of CFRP that incorporate rCF with polymer matrix that containing DMP, and it exhibited decent mechanical properties and hydrothermal recyclability. Thus, this work has developed a novel high-performance recyclable epoxy resin from the commercially available raw materials and a simple and economically viable recycling process.

Acknowledgement

The authors are grateful for the financial support from Department of Energy (DOE EERE), Office of Energy Efficiency & Renewable Energy (Award No. DE-EE0008931), and the Joint Center for Aerospace Technology Innovation (JCATI, 2019–2020). The authors also thank the financial support from the PNNL-WSU Distinguished Graduate Research Program.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Reference

1. F. Meng, E. A. Olivetti, Y. Zhao, J. C. Chang, S. J. Pickering and J. McKechnie, *ACS Sustain. Chem. Eng.*, 2018, **6**, 9854-9865.
2. S. J. Pickering, *Compos. Part A Appl. Sci. Manuf.*, 2006, **37**, 1206-1215.
3. A. Conroy, S. Halliwell and T. Reynolds, *Compos. Part A Appl. Sci. Manuf.*, 2006, **37**, 1216-1222.

4. C. E. Kouparitsas, C. N. Kartalis, P. C. Varelidis, C. J. Tsenoglou and C. D. Papaspyrides, *Polym. Compos.*, 2002, **23**, 682-689.

5. J. Palmer, O. R. Ghita, L. Savage and K. E. Evans, *Compos. Part A Appl. Sci. Manuf.*, 2009, **40**, 490-498.

6. S. J. Pickering, R. M. Kelly, J. R. Kennerley, C. D. Rudd and N. J. Fenwick, *Compos. Sci. Technol.*, 2000, **60**, 509-523.

7. G. Marsh, *Reinf. Plast.*, 2008, **52**, 36-39.

8. L. O. Meyer, K. Schulte and E. Grove-Nielsen, *J. Compos. Mater.*, 2009, **43**, 1121-1132.

9. K. Stoeffler, S. Andjelic, N. Legros, J. Roberge and S. B. Schougaard, *Compos. Sci. Technol.*, 2013, **84**, 65-71.

10. F. A. Lopez, O. Rodriguez, F. J. Alguacil, I. Garcia-Diaz, T. A. Centeno, J. L. Garcia-Fierro and C. Gonzalez, *J. Anal. Appl. Pyrolysis*, 2013, **104**, 675-683.

11. G. Jiang, S. J. Pickering, E. H. Lester, T. A. Turner, K. H. Wong and N. A. Warrior, *Compos. Sci. Technol.*, 2009, **69**, 192-198.

12. Y. N. Kim, Y.-O. Kim, S. Y. Kim, M. Park, B. Yang, J. Kim and Y. C. Jung, *Compos. Sci. Technol.*, 2019, **173**, 66-72.

13. R. Pinero-Hernanz, C. Dodds, J. Hyde, J. Garcia-Serna, M. Poliakoff, E. Lester, M. J. Cocero, S. Kingman, S. Pickering and K. H. Wong, *Compos. Part A Appl. Sci. Manuf.*, 2008, **39**, 454-461.

14. H. Yan, C. Lu, D. Jing, C. Chang, N. Liu and X. Hou, *New Carbon Mater.*, 2016, **31**, 46-54.

15. G. Oliveux, J.-L. Bailleul, A. Gillet, O. Mantaux and G. A. Leeke, *Compos. Sci. Technol.*,

2017, **139**, 99-108.

16. H. Cheng, H. Huang, J. Zhang and D. Jing, *Fibers Polym.*, 2017, **18**, 795-805.

17. Y. Wang, X. Cui, H. Ge, Y. Yang, Y. Wang, C. Zhang, J. Li, T. Deng, Z. Qin and X. Hou, *ACS Sustain. Chem. Eng.*, 2015, **3**, 3332-3337.

18. M. Das, R. Chacko and S. Varughese, *ACS Sustain. Chem. Eng.*, 2018, **6**, 1564-1571.

19. M. Lee, D. H. Kim, J. J. Park, N. H. You and M. Goh, *Waste Manag.*, 2020, **118**, 190-196.

20. X. Kuang, Y. Zhou, Q. Shi, T. Wang and H. J. Qi, *ACS Sustain. Chem. Eng.*, 2018, **6**, 9189-9197.

21. J. Li, P. L. Xu, Y. K. Zhu, J. P. Ding, L. X. Xue and Y. Z. Wang, *Green Chem.*, 2012, **14**, 3260-3263.

22. Y. X. Yang, R. Boom, B. Irion, D. J. van Heerden, P. Kuiper and H. de Wit, *Chem. Eng. Process.*, 2012, **51**, 53-68.

23. T. Liu, M. Zhang, X. Guo, C. Liu, T. Liu, J. Xin and J. Zhang, *Polym. Degrad. Stab.*, 2017, **139**, 20-27.

24. H. Si, L. Zhou, Y. Wu, L. Song, M. Kang, X. Zhao and M. Chen, *Compos. Part B Eng.*, 2020, **199**, 108278.

25. T. Hashimoto, H. Meiji, M. Urushisaki, T. Sakaguchi, K. Kawabe, C. Tsuchida and K. Kondo, *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 3674-3681.

26. T. Liu, C. Hao, L. Shao, W. Kuang, L. Cosimbescu, K. L. Simmons and J. Zhang, *Macromol. Rapid Commun.*, 2021, **42**, e2000458.

27. C. Hao, T. Liu, S. Zhang, W. Liu, Y. Shan and J. Zhang, *Macromolecules*, 2020, **53**, 3110-3118.

28. T. Ozawa, *Polymer*, 1971, **12**, 150-158.
29. A. Guo, Y. J. Cho and Z. S. Petrovic, *J. Polym. Sci. Pol. Chem.*, 2000, **38**, 3900-3910.
30. M. R. Jamir, M. S. Majid and A. Khasri, *Sustainable composites for aerospace applications*, Elsevier, 2018, pp. 155-170.
31. J. C. Gerdeen and R. A. Rorrer, *Engineering design with polymers and composites*, CRC Press, 2011.
32. L. Lu, J. Pan and G. Li, *J. Mater. Chem. A*, 2017, **5**, 21505-21513.
33. W. Zhao, L. An and S. Wang, *Polymers*, 2021, **13**, 296.
34. C. Di Mauro, T.-N. Tran, A. Graillot and A. Mija, *ACS Sustain. Chem. Eng.*, 2020, **8**, 7690-7700.
35. J. Chen, H. Huang, J. Fan, Y. Wang, J. Yu, J. Zhu and Z. Hu, *Front. Chem.*, 2019, **7**, 632.
36. T. Liu, B. Zhao and J. Zhang, *Polymer*, 2020, **194**, 122392.
37. T. Liu, Y. Nie, R. Chen, L. Zhang, Y. Meng and X. Li, *J. Mater. Chem. A*, 2015, **3**, 1188-1198.
38. J. Yang, Z. Chen, G. Yang, S. Fu and L. Ye, *Polymer*, 2008, **49**, 3168-3175.
39. H. Memon, Y. Wei, L. Zhang, Q. Jiang and W. Liu, *Compos. Sci. Technol.*, 2020, **199**, 108314.
40. F. Ji, X. Liu, D. Sheng and Y. Yang, *Polymer*, 2020, **197**, 122514.
41. Y. Xu, S. Dai, L. Bi, J. Jiang, H. Zhang and Y. Chen, *Chem. Eng. J.*, 2022, **429**, 132518.
42. W. Zhang, J. Wu, L. Gao, B. Zhang, J. Jiang and J. Hu, *Green Chem.*, 2021, **23**, 2763-2772.
43. Y. Xu, S. Dai, H. Zhang, L. Bi, J. Jiang and Y. Chen, *ACS Sustain. Chem. Eng.*, 2021, **9**,

16281-16290.

44. Y. Liu, G. Liu, Y. Li, Y. Weng and J. Zeng, *ACS Sustain. Chem. Eng.*, 2021, **9**, 4638-4647.

45. S. Wang, B. Wang, X. Zhang, L. Wang, W. Fan, H. Li, C. Bian and X. Jing, *Appl. Surf. Sci.*, 2021, **570**, 151157.

46. Y. Wang, B. Jin, D. Ye and Z. Liu, *Eur. Polym. J.*, 2022, **162**, 110927.

47. S. Wang, X. Xing, X. Zhang, X. Wang and X. Jing, *J. Mater. Chem. A*, 2018, **6**, 10868-10878.

48. B. Wang, S. Ma, S. Yan and J. Zhu, *Green Chem.*, 2019, **21**, 5781-5796.

49. L. Guadagno, P. Lamberti, V. Tucci and L. Vertuccio, *Nanomaterials*, 2021, **11**, 833.

50. S. R. Swan, C. Creighton, B. V. Gashi, J. M. Griffin and R. J. Varley, *ACS Appl. Polym. Mater.*, 2021, **3**, 5717-5726.

51. T. Liu, X. Guo, W. Liu, C. Hao, L. Wang, W. C. Hiscox, C. Liu, C. Jin, J. Xin, J. Zhang, *Green Chem.*, 2017, **19**, 4364-4372.

52. Y. Li, T. Liu, S. Zhang, L. Shao, M. Fei, H. Yu and J. Zhang, *Green Chem.*, 2020, **22**, 870-881.