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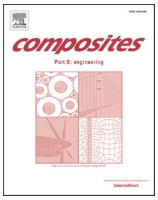

Catalyst-free malleable, degradable, bio-based epoxy thermosets and its application in recyclable carbon fiber composites

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ABSTRACT

Carbon fiber reinforced composites (CFRCs) are a kind of most potential materials due to the high strength-to-weight ratio, excellent fatigue and corrosion resistance. However, the vast majority of CFRCs prepared from carbon fiber and thermosetting matrices are difficult to be recycled and depend on limited fossil resources. Here, for the first time, we reported fully bio-based catalyst-free epoxy vitrimers for CFRCs. The epoxy vitrimers exhibited excellent malleability and could be reprocessed by compression molding. Outstanding degradability was also achieved, which enabled multiple recovery of CF from their CFRCs without damage. In addition, CFRCs regenerated from multiple recovered CF exhibited insignificant differences from the original CFRCs. This work will provide an effective method for the sound development of CFRCs from both economic and environmental aspects.

1. Introduction

Carbon fiber reinforced composites (CFRCs) are a kind of most promising materials that are widely used in automotive, aerospace, sports equipment, and other fields [1–4] due to their light weight, low density, high strength, high modulus, excellent corrosion resistance and so on [5–8]. However, the widespread applications of CFRCs have also brought about serious recycle issues for off-cuts, unused prepregs and end-of-life components [9–11]. Thermosets are usually used as matrices for preparation of CFRCs to achieve high performance. The insoluble and non-meltable feature of thermosets make it difficult to be recycled and reused like thermoplastic resins [12]. For decades, landfill and incineration are the two popular disposal methods adopted by composite industries which have led to increasing environmental awareness to identify a sustainable dispose method and provide a solution to prevent the cumulating wastes [13–17].

Among the above CFRCs, epoxy thermosets were the most widely used resin matrices because of their excellent mechanical properties, adhesion strength, thermal stability and chemical resistance [18,19]. However, the three-dimensional cross-linked networks and the high performance of epoxy thermosets made recycling of the composites inherently difficult [20,21]. Whether the high-value CF in CFRCs can be recycled depends on the nature of the resin matrix. For those recycling methods that involve in harsh conditions such as high temperature and high pressure could cause significant damage to the CF [22]. So far, efficient, and non-destructive recovery of CF from epoxy composites is still a challenge. Therefore, designing an epoxy resin degradable under mild conditions can provide a possible solution to prepare readily recyclable CFRCs which can reclaim CF without destroying chemical structure and mechanical properties [23].

One approach to prepare degradable epoxy resins is to introduce labile linkages [24], such as acetal bonds [15,25,26], Schiff base [27], carbonate bonds [28,29], sulfur-containing structures [28,30–33], ester bonds [34,35], et al. In our previous work [14,15], degradable epoxy resins containing Schiff base and cyclic acetal structure were synthesized to produce readily recyclable CFRCs from which almost non-destructive CF could be reclaimed. Zhao, Chen and coworkers [33] developed a degradable epoxy network with high content of aromatic disulfide bond, and CF was recovered from the obtained CFRCs without destroying the structure and performance. Zhang and coworkers [36]

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prepared an epoxy vitrimer internally catalyzed by hydroxyls and tertiary amines, and the recyclable CFRCs based on it was efficiently degraded in pure water at above 160 °C. Qi et al. [37] used the epoxy/carboxylic acid/$Zn(OAc)_2$ system to prepare CFRCs, the CF was reclaimed by dissolving the matrix through transesterification with ethylene glycol. However, the transesterification required high temperature (180 °C) and needed metal catalysts to accelerate the reaction which added the cost and complexity.

In addition to degradability, the development of malleable and reprocessable, especially catalyst-free epoxy thermosets matrix is also extremely important. Traditional thermosets cannot exhibit reprocessability like thermoplastic resins due to their cross-linked three-dimensional network structure. However, thermosets prepared by introducing dynamic covalent bonds into the cross-linked network, called vitrimers or covalent adaptable networks (CANs), can solve this issue [38]. Epoxy CANs based on transesterification are currently the most studied and most promising materials because the ester bond is relatively stable, and the raw materials are easily available. However, the transesterification relies too much on the addition of catalyst [39], which would bring about toxicity, incompatibility and corrosion issues [40,41]. Therefore, the development of catalyst-free epoxy CANs based on transesterification is of great significance. In recent years, the field of catalyst-free epoxy resin based on transesterification attracted attentions of some researchers, and their fruitful works have laid the foundation for this field [41–47]. However, there are few reports of catalyst-free and reprocessable epoxy vitrimers based on transesterification. Zhang et al. [41] reported the acceleration effect of hydroxyl on transesterification. While the film obtained after hot pressing still had defects. In another work, they incorporated tertiary amine and hydroxyl into an epoxy cross-linked network to accelerate transesterification. The cross-linked epoxy powder could be mixed and cured with fresh resin [48]. In our previous work, we reported a method for curing DER331 with excess cyclic anhydride monoester and successfully prepared a catalyst-free reprocessable epoxy vitrimer [49].

In addition to the recycle issue of the CFRCs, the dependence of fossil resource goes against their sustainable development. Thus, in this work, epoxy networks were synthesized completely from renewable and abundant bio-based compounds itaconic acid-based epoxy monomer, maleic anhydride, and glycerin through a simple one-pot method. The obtained epoxy cross-linked networks exhibited excellent controllable degradation and catalyst-free malleability. The thermal and mechanical properties of epoxy cross-linked networks were evaluated to determine whether it was suitable for preparing CFRCs. Moreover, CF was successfully reclaimed from the prepared CFRCs, which was further used to re-prepare CFRCs. The properties of repeatedly recovered CF and regenerated CFRCs were systemically investigated. For comparison, the epoxy network as well as the CFRCs from a commercially available petroleum-based bispenol A epoxy monomer were also investigated.

2. Experimental

2.1. Materials

Itaconic acid (IA, Standard for AR, >99.0%), tetrabutylammonium bromide (TBAB), maleic anhydride (MA), glycerin (Standard for GC, ≥99.5%) were purchased from Aladdin Reagent, China. Bisphenol A epoxy monomer (DGEBA, trade name D.E.R.331, epoxide equivalent 182–192 g per eq.) was supplied by DOW Chemical Company, USA. All the chemicals were utilized as received unless otherwise indicated. Itaconic acid-based epoxy resin (EIA) was prepared according to our previous work [50], the epoxy value of EIA determined by ^1H NMR internal standard method was about 0.6554 eq/100 g.

2.2. Preparation of epoxy thermosets

Maleic anhydride and glycerin were uniformly mixed with EIA (or DER331) using a homogenizer and cured without any solvent or catalyst. Bubbles were removed from the mixture in a vacuum oven. After being poured into the mold, the sample were cured at 90 °C for 2 h, 120 °C for 1 h, 150 °C for 2 h, 180 °C for 2 h. The composition of each sample is summarized in Table 1 (The E, M, G, and D in the acronyms EMG and DMG represent EIA, maleic anhydride, glycerol, and DER331, respectively. The numbers following the acronyms (0, 0.76, 1, and 1.24) indicate the molar ratio of the hydroxyl group in glycerol to maleic anhydride.).

2.3. Preparation of carbon fiber composites

Vacuum infusion process was adopted to prepare carbon fiber composites. Ten layers of carbon fiber were placed on the mold layer by layer, and were covered with mold release cloth, diversion net and vacuum bag film successively. Vacuum was applied after sealing, and the pre-mixed liquid resin was pumped into the vacuum bag through the reserved pipe and infiltrated with carbon fiber. The vacuum was kept and the temperature was gradually increased to make the resin react. After reacting at 90 °C for 2 h and 120 °C for 1 h, the covering of the pre-cured carbon fiber composites was removed. The obtain pre-cured carbon fiber composites were put into a vacuum oven to post-cure at 150 °C for 2 h and 180 °C for 2 h.

2.4. Gel content test

The gel contents were determined according to ASTM D2765-16. Samples (~0.5 g) were respectively put into the Soxhlet extractor to extract with toluene for 12 h. The extracted samples were dried in a vacuum oven at 80 °C for 12 h until a constant weight were obtained. m_0 is the initial mass, m_1 is the final mass after drying; the gel content is calculated by m_1/m_0.

2.5. Reprocessing recycle of EMG

The reprocessing recycle of EMG was carried out by hot pressing using a plate vulcanizer. The shredded samples were placed between two steel sheets covered with two polyimide films and hot pressed at 190 °C under a pressure of 10 MPa for 2 h. After cooling to room temperature, recycled films were obtained.

2.6. Degradation of EMG

Each sample (50 mg) was placed in a 25-mL vial containing 10 mL sodium hydroxide aqueous solution. The degradation behavior of the epoxy resins was studied by adjusting the addition amount of glycerin in epoxy resins, the concentration of the sodium hydroxide aqueous solution and the degradation temperature.

2.7. Degradation of CF/EMG composites and recovery of CF

Virgin and repeatedly recycled CF/EMG-1 with dimensions of 10 cm (length) × 10 cm (width) × 0.25 cm (thickness) were immersed in 1 M NaOH aqueous solutions at room temperature. The reclaimed CF with

Table 1
Compositions of the epoxy thermosets.

Samples	Epoxy group/ mol	MA/ mol	Glycerol/ mol	-OH in glycerol/mol
EMG-0.76	1	1	0.253	0.76
EMG-1	1	1	0.333	1
EMG-1.24	1	1	0.413	1.24
EMG-0	1	1	0	0
DMG-1	1	1	0.333	1

original textile structure were subsequently washed with acetone and dried in a 50 °C oven for 24 h.

2.8. *Characterizations*

The temperature-dependent FTIR measurements were carried out on a NICOLET 6700 (Thermo, America) using the KBr pellet method from 25 to 250 °C. Differential scanning calorimetry (DSC1, Mettler-Toledo, Switzerland) was utilized to determine the T_g values. The cured samples with a weight of about 5 mg were used. They were heated from −25 to 180 °C at a heating rate of 10 °C min^{-1} and held for 3 min to eliminate any thermal history. Then, they were cooled to −25 °C at a cooling rate of 50 °C min^{-1}, followed by heating again to 180 °C at a heating rate of 10 °C min^{-1}. The glass transition temperature (T_g) was obtained from the second heating curve scanned from −25 °C to 180 °C at a heating rate of 10 °C min^{-1} under a N_2 atmosphere. The thermal stability was determined using a thermogravimetric analyzer (TGA, TGA/DSC1, Mettler-Toledo, Switzerland). The samples (~6 mg) were heated from 30 to 800 °C at a heating rate of 10 °C min^{-1} under N_2 atmospheres. Stress relaxation experiments were tested by a DMA (Q850, TA Instruments, America). The samples with dimensions of 30 mm (length) × 5 mm (width) × 0.3 mm (thickness) were initially preloaded by 1 × 10^{-3} N force to maintain straightness. After reaching the testing temperature, it was allowed 10 min to reach thermal equilibrium. The specimen was stretched by 1.5% on the DMA machine and the deformation was maintained throughout the test. The decrease of the stress as the function of time was recorded. The tensile properties were tested on a Universal Mechanical Testing Machine (Instron 5569A, Instron, America). For the sake of avoiding defects during cutting, the networks were cut into easy-to-cut rectangular samples to test the tensile properties. The samples with dimensions of 50 mm (length) × 5 mm (width) × 0.3 mm (thickness) were measured at a cross-head speed of 1 mm min^{-1}. At least five repeated measurements were performed for each sample. The interlaminar shear strength (ILSS) was measured with a universal testing machine (Instron 5985) according to the standard ASTM D 2344. The recorded value of ILSS for each group of specimens was averaged from five to seven successful measurements. Scanning electron microscopy (SEM) were performed using a Verios G4 UC scanning electron microscope (Thermo scientific, America). The micromorphology of CF with a conductive gold layer was observed by low-temperature fracturing under high vacuum with a voltage of 15 kV. The monofilament tensile test was conducted on a FAVIMAT+ (Textechno, Germany) at room temperature while the gauge length was 25 mm and the crosshead speed was 5 mm min^{-1}. Thirty randomly selected CF monofilaments were used for testing to achieve accuracy. An InVia Reflex Raman spectrometer (Renishaw, England) was used to compare surface chemical structure of virgin and repeatedly recycled CF with a 532 nm wavelength laser (energy: 12 mW) and exposed for 60 s.

3. Results and discussion

3.1. *Preparation of EMG and DMG*

Maleic anhydride and glycerin were added to the synthetic itaconic acid-based epoxy (EIA) and undergo a one-pot curing reaction without additional catalysts or solvents. It was found in our previous work that the monoesterification reaction between maleic anhydride and small alcohol was relatively active that could be carried out at 90 °C [49]. In

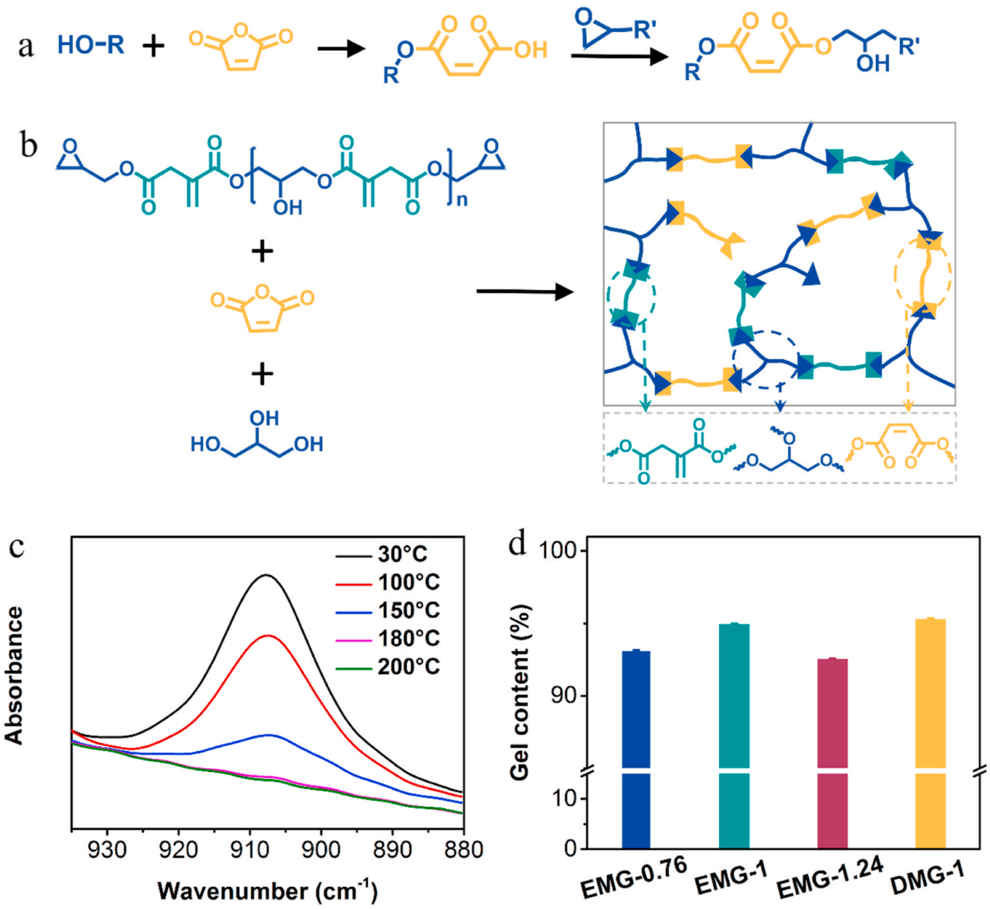

Fig. 1. (a) Reaction mechanisms during curing. (b) Schematic diagram for the preparation of the epoxy thermosets. (c) Epoxy regions (880-940 cm^{-1}) of temperature-dependent FTIR spectra at the heating rate of 2.5 °C min^{-1} for EMG-1. (d) Gel contents of the epoxy thermosets.

addition, maleic anhydride would preferentially react with the two primary hydroxyl groups of glycerol rather than the secondary hydroxyl group of EIA [41]. Therefore, during the curing process, the mono-esterification reaction between maleic anhydride and glycerin first occurred, and then the resulting anhydride monoester was cured with EIA to form cross-linked networks (Fig. 1a, Fig. 1b).

In order to obtain the optimal curing conditions to ensure complete curing reaction, temperature-dependent FTIR was employed to monitor group changes during heating. Fig. 1c and S2 show the changes of epoxy groups for the curing system of EMG-1 and DMG-1 with temperature increasing. It was found that the epoxy groups of both systems disappeared at 180 °C. Accordingly, the post-curing temperature of each sample was set to 180 °C and maintained for 2 h. Gel content is an important reference for characterizing the integrity of cross-linked network and is closely related to the performance of thermosets [51], which is presented in Fig. 1d. The high gel content of 92–96% indicates that relatively complete cross-linked networks were obtained.

3.2. *Thermal and mechanical properties of EMG and DMG*

DSC was applied to determine the glass transition temperature (T_g) of the epoxy thermosets (Fig. 2a and Fig. S3). As can be seen, the T_g values gradually decreased as the addition amount of glycerol increased, which is attributed to the increased flexibility from glycerol and the decrease of cross-link density of the networks [41]. The higher T_g of DMG-1 than that of EMG-1 is due to the higher rigidity of bisphenol A epoxy than that of EIA.

The thermal stability of the cross-linked networks was characterized by TGA (Fig. 2b). The temperature at which a 5% weight loss takes place is defined as the initial degradation temperature (T_{onset}). The T_{onset} values of EMG-0.76, EMG-1, EMG-1.24 and DMG-1 were 285 °C, 281 °C, 284 °C, 286 °C, respectively. The difference within the test error indicated that the introduction of glycerin did not affect the initial thermal stability of the epoxy resins. For each proportion of EMG, the difference in thermal weight loss at high temperature was similarly insignificant. The maximum decomposition temperature of DMG-1 was higher than that of EMG because the thermal decomposition of benzene ring proceeded at a higher temperature than that of aliphatic chains [52].

The tensile stress-strain curves of the epoxy resins are presented in Fig. 2c and the data are summarized in Table 2. The tensile strengths of EMG-1 and DMG-1 are comparable. Moreover, the elongation at break of EMG-1 was higher than that of DMG-1 due to the more flexible structure of EIA than DER. In addition, the mechanical properties of the epoxy resins can be readily adjusted by changing the addition amount of glycerin. With the increase of glycerin addition, the tensile strength and elongation at break of the epoxy resins showed a downward trend, which is consistent with the variation trend of T_g. The tensile properties of thermosets are closely related to their cross-link density and the rigidity of the chain segments [13]. Therefore, the gradual decrease in tensile strength and elongation at break are attributed to the flexible structure of glycerin and the decrease in cross-link density.

3.3. *Malleability and reprocessing recycle of EMG*

Malleability is the feature of Vitrimers or CANs that is different from

Table 2
Tensile properties of the epoxy resins.

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
EMG-0.76	80.0 ± 1.5	1841 ± 60	10.2 ± 0.2
EMG-1	70.7 ± 0.9	1654 ± 83	8.9 ± 0.1
EMG-1.24	52.0 ± 1.3	1270 ± 61	4.4 ± 0.5
DMG-1	70.8 ± 1.2	1860 ± 72	7.3 ± 0.3

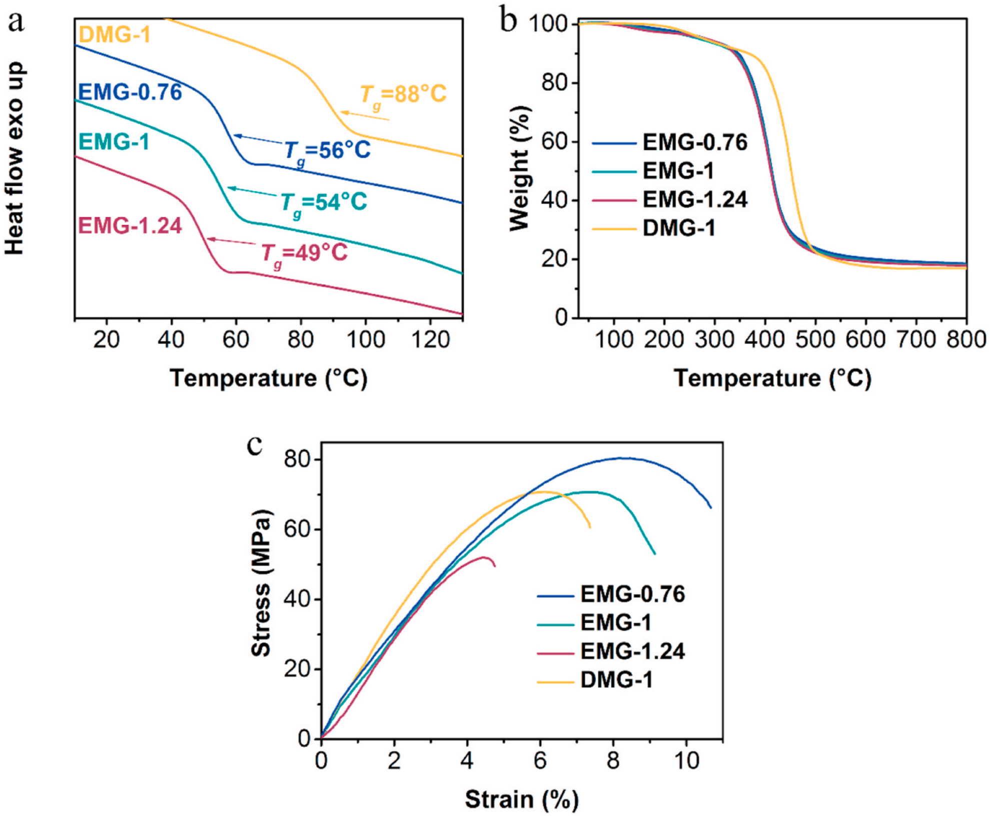

Fig. 2. (a) DSC, (b) TGA and (c) Representative tensile stress-strain curves of the epoxy thermosets.

thermosets, the theoretical basis of which can be provided by the stress relaxation test. As shown in Fig. 3a and Fig. S8, the stress relaxation rate of each sample at 180 °C followed order of EMG-1.24>EMG-1>EMG-0.76>DMG-1>EMG-0. For EMG, with increasing the addition amount of glycerol, the reprocessing rates gradually promoted, which is consistent with the result reported by Zhang's group [41]. The stress relaxation rates of EMG-1.24, EMG-1 and EMG-0.76 were faster than that of DMG-1, which is attributed to the higher content of ester bond in EMGs and their better movement ability of segment.

The activation energy (E_a) of exchange reaction was calculated according to the Arrhenius equation [42].

$\ln \tau^* = E_a / RT\text{-}\ln A$ (1)

where E_a is the activation energy for viscous flow, the relaxation time τ^* is defined as the time for the modulus to reach 1/e (0.37) of its initial modulus. R is the gas constant, T is the experimental temperature, and A is the Arrhenius prefactor. Excellent fitting for each epoxy CANs was obtained (Fig. 3b and Fig. S9). The calculated E_as of the epoxy CANs EMG-0.76, EMG-1, EMG-1.24, DMG-1 and EMG-0 are 67 kJ mol^{-1}, 64 kJ mol^{-1}, 63 kJ mol^{-1}, 77 kJ mol^{-1} and 86 kJ mol^{-1}, respectively. This result is in agreement with the result of the characteristic relaxation times.

The thermal recyclability of the epoxy resins was verified by cutting the samples into pieces and hot pressing at 190 °C under a pressure of 10 MPa for 2 h. The stress relaxation rate of thermosets can be reflected well in the reprocessing performance. As shown in Fig. 3c–d and Fig. S10–12, the cut pieces of EMG-0.76, EMG-1, and EMG-1.24 could be hot pressed into new coherent and smooth samples, while the cut pieces of DMG-1 and EMG-0 could not be hot pressed into complete films. According to literature reports, the reprocessing of epoxy vitrimers based on transesterification strongly relies on a large amount of catalyst (5–10 mol%). Zhang and coworkers [41] reported the acceleration effect of hydroxyl on transesterification for epoxy vitrimer. While their reprocessed film by hot pressing still had defects. T_g reflects the ability of chain segment movement, which can determine to a certain extent whether epoxy CANs can be reprocessed. The T_gs of EMGs with glycerin added in this work are similar to the above-mentioned epoxy vitrimer by Zhang's group [41], and both have a large number of hydroxyl groups. The difference between the two systems is that the cross-linked networks of EMG have higher content of ester bond. Thus, in this work, the epoxy network with high content of ester bond provides another method to accelerate the catalyst-free reprocessing. The large number of carboxylate and hydroxyl groups in the network brought about more

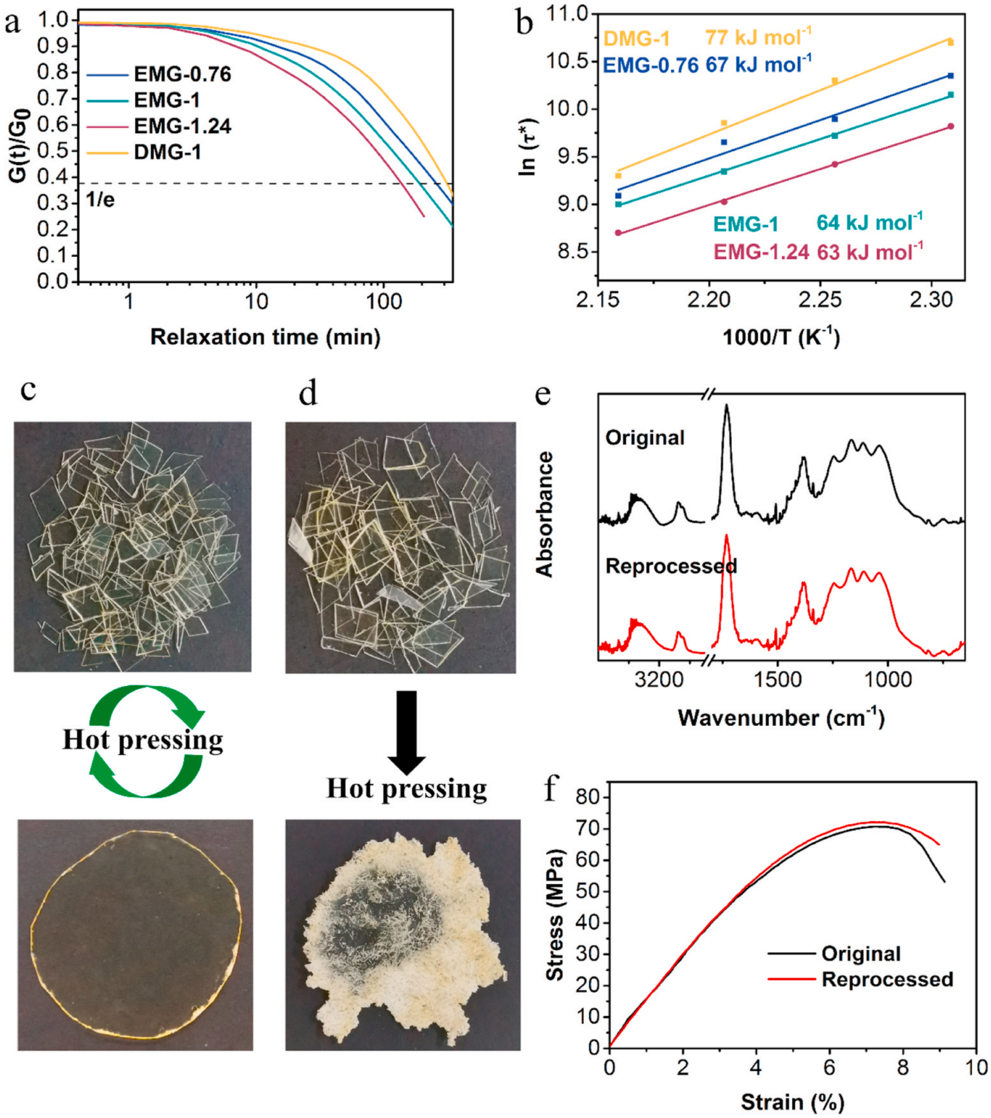

Fig. 3. (a) Stress relaxation of each sample at 180 °C. (b) Fitting of relaxation time to an Arrhenius equation. (c–d) Recycling of EMG-1 (c) and DMG-1 (d) by compression molding. (e) FTIR spectra and (f) representative tensile stress-strain curves of the original and reprocessed EMG-1.

opportunities for the occurrence of transesterification reactions. In addition, as shown in Fig. 3e–f, the structure and mechanical properties of the sample did not change significantly after reprocessing.

3.4. Degradation of EMGs

The EMGs can be degraded under mild alkaline conditions without organic solvents. Moreover, the addition of glycerin can accelerate the degradation of the networks. That is, the degradation rate of the networks can be readily adjusted by changing the addition amount of glycerin. Take EMG-1 as an example, the sample with size of 10 × 5 × 3.2 mm^3 was immersed in 20 mL 1 M NaOH aqueous solution. After 40 min of degradation at 50 °C, a light-yellow liquid was obtained (Fig. 4a). While DMG can be hardly degraded due to its hydrophobic benzene ring structure and lower content of ester bond than EMGs.

The concentration of NaOH aqueous solution and the degradation temperature are key factors affecting the degradation rate of epoxy resins [35], which are set as variables for studying the degradability of the cured epoxy resins, as shown in Fig. 4b–c and Fig. S13. When the concentration of NaOH aqueous solution gradually increased from 0.1 to 5 M, the degradation rate of EMG gradually increased. The degradation rate of EMG was quite slow when the concentration was further increased to 10 M. It was attributed to the fact that there was too little water in the solution to dissolve the degradation products. In addition, it can be seen from Fig. 4c that the degradation rate of EMG rose with increasing temperature. Moreover, under various degradation conditions, the degradation rate of EMG followed the order of EMG-1.24>EMG-1>EMG-0.76>EMG-0, which indicates that the addition of glycerol accelerated the degradation of the networks. The degradability of EMGs under alkaline conditions endows their recyclability, but it inevitably leads to poor alkali resistance, which needs to be considered in practical applications.

3.5. Properties and recycling of CF/EMG composite

As described above, the control sample DMG-1 is difficult to be degraded, while EMGs show excellent controllable degradation. The CF recovery of CFRCs is controlled by the degradability of the matrices [23]. Therefore, as an example, EMG-1 was used as resin matrix to prepare carbon fiber reinforced composite because of its fast degradation rate and moderate T_g. The fiber content of the CF/EMG-1 tested according to ASTM D3171-15 was 52.1 vol%. CF/EMG-1 with size of 10 cm (length) × 10 cm (width) × 0.25 cm (thickness) was immersed into 1 M NaOH aqueous solution. After degradation at room temperature for 5 h, the resin matrix was completely degraded. The recycled CF was washed with acetone to remove the remaining solution and dried in a 50 °C oven for 24 h. Finally, the recycled CF cloths were obtained, as shown in Fig. S14. Fig. 5a displays the degradation process of CF/EMG-1. The 1st recycled CF obtained above was used again to prepare CF composites and recycled in the same way for several times. TGA measurements of the CF composites and repeatedly recycled CF was used to reflect the removal degree of the epoxy resin matrix [13]. The TGA curves of virgin, 1st, 2nd and 3rd recovered CF in Fig. 5b showed excellent coincidence and stability, which proves that the resin matrix in the recycled CF was completely degraded.

In order to verify whether EMGs has the potential to be as a matrix for advanced composites, the ILSSs were measured, which would reflect the toughness of the resin matrix and the interface adhesion between the resin matrix and the reinforced fibers [53,54]. The ILSSs of 1st and 2nd recycled CF/EMG-1 were also tested and compared with that of original composite to characterize the performance of repeatedly recycled CFs. In addition, for comparison, CF/DMG-1 was also prepared. As shown in Fig. 5c, the ILSSs of CF/EMG-1, 1st, 2nd and CF/DMG-1 were 45 MPa, 44 MPa, 44 MPa and 47 MPa, respectively, which are not significantly different and are comparable to those of the CF composites reported in the literature [53]. In addition, the tensile strength, tensile modulus and elongation at break of CF/EMG-1 are 417 MPa, 31.3 GPa and 3.6%, while those of CF/DMG-1 are 423 MPa, 34.7 GPa and 2.9% (Table 3).

Recycling CF from high performance CF composites without destroying the chemical structure, mechanical property and micro morphology is currently a common challenge [14]. The premise that CF can be reused at the same level is that the resin on the surface of recycled CF is completely degraded while maintaining high performance compared to that of the original CF. Therefore, the surface morphology,

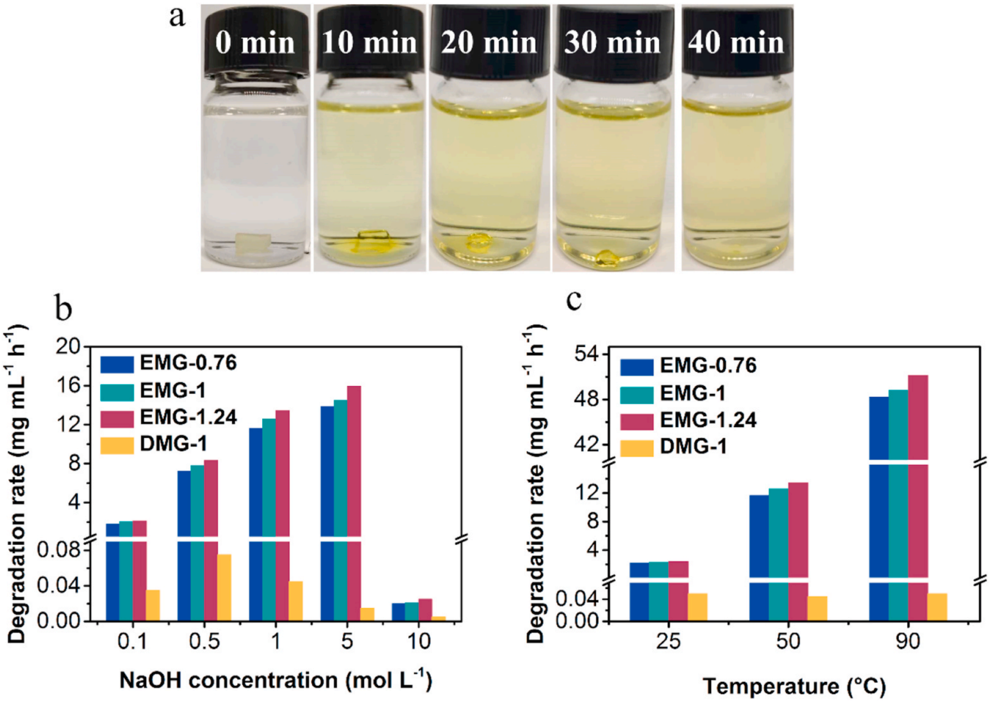

Fig. 4. (a) Degradation process of EMG-1 at different times in 1 M NaOH aqueous solution at 50 °C. (b) Degradation rates of the epoxy resins in NaOH aqueous solutions with different concentrations at 50 °C. (c) Degradation rates of the epoxy resins in 1 M NaOH aqueous solutions at different temperatures.

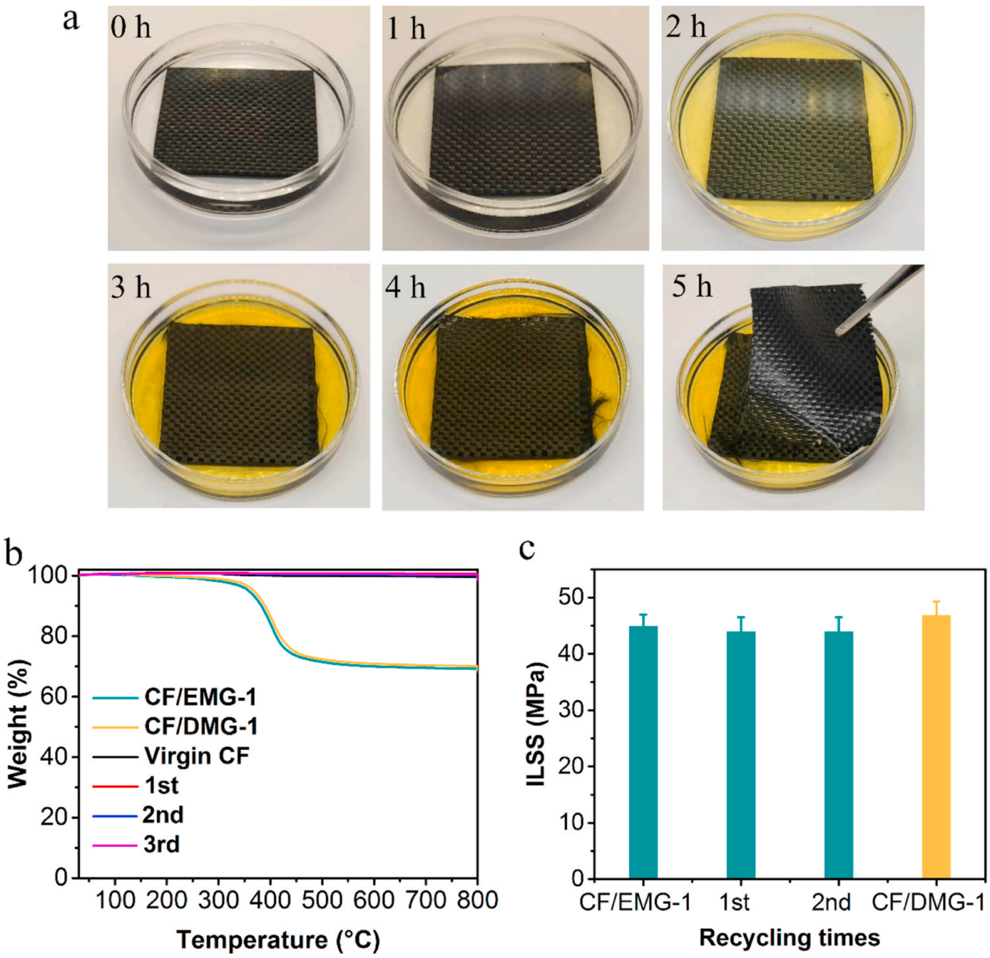

Fig. 5. (a) Degradation process of CF/EMG-1 composite with dimensions of 10 cm (length) × 10 cm (width) × 0.25 cm (thickness) in 1 M NaOH aqueous solutions at room temperature. (b) TGA curves of CF/EMG-1, CF/DMG-1, virgin and recycled CF. (c) The ILSS of CF/EMG-1, CF/DMG-1 and repeatedly recycled CF/EMG-1.

Table 3
Tensile properties of the CFRCs.

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
CF/EMG-1	417 ± 26	31.3 ± 1.8	3.6 ± 0.3
CF/DMG-1	423 ± 31	34.7 ± 2.1	2.9 ± 0.1

mechanical property and chemical structure of the repeatedly recycled CF were further determined by SEM, monofilament tensile and Raman spectra, respectively. As shown in Fig. 6a, SEM images proved that the surface of the repeatedly recovered CF was clean and smooth, indicating that the resin was completely degraded. The monofilament tensile strength of 1st, 2nd and 3rd recycled CF retained 98%, 95% and 94%, as well as the retention of Young's modulus were 98%, 97% and 95%, respectively (Fig. 6b). Raman spectra also confirmed that the chemical structure of the repeatedly recycled CF was not destroyed (Fig. 6c). The structure and performance of the repeatedly recycled CF were not destroyed, thus, the performance of the repeatedly recycled CF composites could also be maintained, which had been confirmed by the above-mentioned ILSS results. The multiple recycling of CF without sacrificing performance benefits from the ready degradation under mild conditions, which will bring huge economic benefits considering the high cost of CF.

4. Conclusions

In summary, for the first time, a fully bio-based, catalyst-free malleable and readily degradable epoxy matrix for CFRC was successfully prepared. In addition, the high content of ester bond and added glycerin accelerated the matrix' relaxation and degradation. The CFRC prepared using EMG as matrix could be readily degraded under mild alkaline conditions at room temperature, and the chemical structure and mechanical properties of CF barely exhibited any perceptible change after several times of recycling circulations. Moreover, the ILSS of CFRCs prepared from repeatedly recycled CF were not significantly different from that of virgin CF/EMG-1 and were comparable to the CF composites reported in the literature. This work on catalyst-free malleable epoxy matrix and readily recycling of CF will bring economic and environmental benefits to the development of CFRCs.

Author statement

Songqi Ma: Conceptualization, Supervision, Writing - Review & Editing, Funding acquisition, Project administration. **Yanlin Liu:** Investigation, Data Curation, Validation, Writing Original Draft, Funding acquisition, Visualization. **Binbo Wang:** Investigation, Data Curation, Validation. **Tao Yu:** Data Curation. **Xiwei Xu:** Data Curation. **Qiong Li:** Data Curation. **Sheng Wang:** Data Curation. **Yingying Han:** Data Curation. **Zhen Yu:** Data Curation. **Jin Zhu:** Writing - Review & Editing.

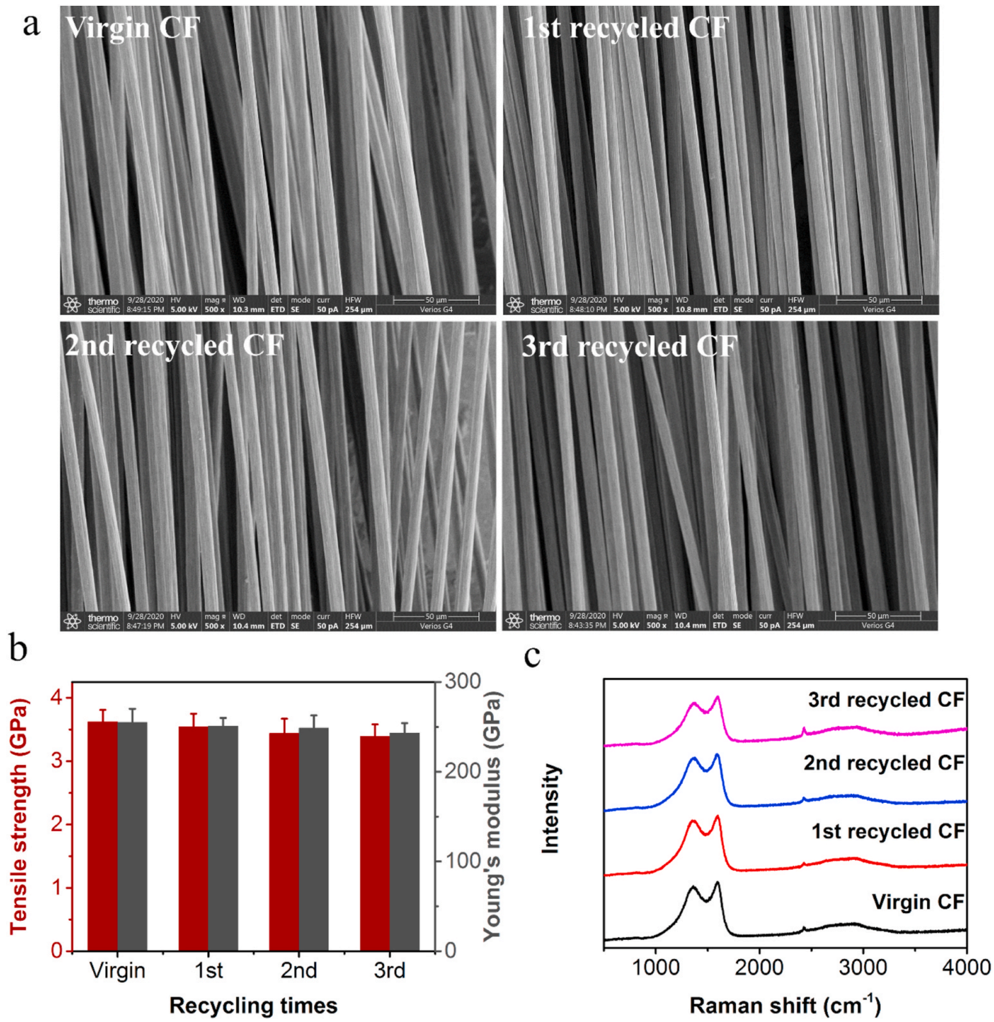

Fig. 6. (a) The SEM images of virgin and recycled CF. (b) The monofilament tensile properties of virgin and recycled CF. (c) Raman spectra of virgin and recycled CF.

Declaration of competing 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.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.compositesb.2021.108654.

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