Composites Part B 199 (2020) 108278

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Rapidly reprocessable, degradable epoxy vitrimer and recyclable carbon fiber reinforced thermoset composites relied on high contents of exchangeable aromatic disulfide crosslinks

Hongwei Si [a,b], Lin Zhou [b], Yeping Wu [a], Lixian Song [b], Ming Kang [b], Xiuli Zhao [a,**], Mao Chen [a,*]

[a] Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang, 621900, China
[b] State Key Laboratory of Environmental-friendly Energy Materials, Southwest University of Science and Technology, Mianyang, 621010, China

ARTICLE INFO

Keywords:
Thermosetting resin
Recycling
Polymer-matrix composites (PMCs)
Epoxy vitrimers

ABSTRACT

With large quantities of waste carbon fiber reinforced polymer (CFRP) composites generated, the development of recycling routes for CFRP composites have been driven by both environmental and economic factors. Vitrimer materials provide exciting opportunities to recycle thermosets and CFRP composites, since they can be thermally reprocessed without losing their permanently cross-linked networks. However, the poor mechanical properties, additional catalyst and time-consuming recycling process still limit their applications. Herein, the authors proposed an epoxy vitrimer with high contents of exchangeable aromatic disulfide crosslinks to overcome these limitations. This epoxy vitrimer exhibited outstanding properties with the glass transition temperature (T_g) of 147 °C and the tensile strength of 63.1 MPa. Upon heating, it released the stress from deformation more rapidly without any catalyst, resulting from the high contents of disulfide crosslinks in the network. Meanwhile, the networks exhibited excellent reprocessability and were more readily degraded by thiols. Moreover, this epoxy was applied as matrix to prepare recyclable CFRP composites. By dissolving the epoxy matrix efficiently, the carbon fibers embedded were recycled rapidly and they still exhibited outstanding mechanical properties when being reused to form CFRP composites. Results from this study may promote the wide development of cost-efficient recyclable composites in automotive, wind power and aeronautical industries.

1. Introduction

From aerospace to automobiles and from ground transportation to sporting goods, carbon fiber reinforced polymer (CFRP) composites have been widely used in various applications, because of the advantages of outstanding mechanical properties and light weight [1,2]. Among the different CFRP composites, thermosetting CFRP composites based on epoxy are often preferred or even irreplaceable when high performance is needed in quite a few fields like aircraft components, wind blade, *etc*. resulting from their structural stability, high strength, low shrinkage and solvent resistance [3–10]. Meanwhile, due to the permanently cross-linked networks and thermosetting nature, epoxies and their composites cannot be reprocessed, degraded or recycled after full curing. With the increasing consumption of thermosetting CFRPs in the worldwide, large quantities of waste CFRP composites generated from the off-cuts during manufacturing and retired components, which have already raised the urgent requirement to recycle the CFRP waste for both environmental and economic awareness [11–14].

Recent progress of dynamic chemistry makes it possible to recycle thermosetting polymers and composites [15–24]. These unconventional polymer networks rely on dynamic bonds that can react reversibly, namely covalent adaptable networks (CANs) [17,19,20,22]. The CANs could release stress from deformation, allowing the cross-linked polymers to be reprocessed, reshaped and recycled. According to the mechanism, CANs can be classified into two groups. The first group, namely“dissociative” CANs, relies on dynamic bonds that break and reform in cross-linked networks, such as Diels−Alder reactions [25,26]. When triggering the dissociation of dynamic bonds, these networks exhibit obvious decrease of viscosity, lack of solvent resistance and loss of dimensional stability. Besides the“dissociative” CANs, vitrimer materials, making use of an “associative” mechanism and pioneered by Leibler’ group [16,27], are an especially interesting approach that have

---

* Corresponding author.
** Corresponding author.
E-mail addresses: zhaoxiuli@caep.cn (X. Zhao), nkchenmao@caep.cn (M. Chen).

https://doi.org/10.1016/j.compositesb.2020.108278
Received 5 January 2020; Received in revised form 27 June 2020; Accepted 4 July 2020

potential to obtain recyclable thermoset and CFRP composites. Through exchange reactions between crosslinks, vitrimer materials can rearrange their molecular architecture thermally, while maintaining permanent organic networks, fixed cross-link density and excellent solvent resistance [21,28]. Until now, a few dynamic chemistries, such as carboxylate transesterification [13,16,28–31], transamination [32–34], transalkylation [35], transcarbamoylation [36], siloxane equilibration [37,38], disulfide metathesis [28,39–46], olefin metathesis [47,48], imine amine exchange [49–51], and dioxaborolane metathesis [52–55], have been applied to design various types of vitrimer materials. Epoxy vitrimers, relied on transesterification [11], aromatic disulfide metathesis [41] or imine amine exchange [56], have been reported to recycle CFRP composites recently. Among these, the epoxy vitrimers with aromatic disulfide crosslinks have advantages of catalyst-free and the rather rigid polymer structure over the polyester-based epoxy vitrimer. Moreover, they exhibited long-term stability in comparison with the water or moisture sensitive imine based epoxy vitrimers. However, due to the outstanding mechanical properties and high crosslink density of the aromatic disulfide epoxy vitrimers, it is time-consuming to reprocess or degrade the epoxy vitrimer. Thus, it is urgent to improve the recycling efficiency of these high performance epoxy vitrimer materials and carry forward their academic research to industrial applications.

In this paper, an epoxy vitrimer with high contents of exchangeable aromatic disulfide crosslinks was proposed to speed up the exchange reactions of disulfide bonds in networks and to improve the recycling efficiency of the epoxy vitrimers and CFRP composites. This epoxy vitrimer was synthesized from the epoxy monomer and the amine curing agent that both contained aromatic disulfide bonds, namely dual disulfide vitrimer. These networks exhibited outstanding thermal/mechanical properties and excellent solvent resistance, with the glass transition temperature (T_g) of 147 °C, the storage modulus E' of 1.72 GPa (at 30 °C) and the tensile strength of 63.1 MPa. Relied on the high contents aromatic disulfide cross-links in networks, the dual disulfide vitrimer rapidly released the stress from deformation and became reprocessable or malleable readily through the inner disulfide metathesis without any catalyst. Moreover, the dual disulfide vitrimer could be easily degraded by dithiothreitol (DTT) dilute solution through the exchange reactions with outer thiols, while its degradation process was more efficient when compared with the single disulfide vitrimer. Then, the CFRP composites based on the dual disulfide epoxy vitrimer were prepared, which exhibited outstanding mechanical properties, with the E' of 10.5 GPa and the tensile strength of 334.5 MPa. After removing the epoxy matrix efficiently, the carbon fibers were recycled integrally and reused to form CFRP composites. The reformed CFRP composites remained outstanding mechanical properties, with the E' of 8.2 GPa and the tensile strength of 320.9 MPa.

2. Experiment section

2.1. Materials

Bis(4-hydroxyphenyl) disulfide (≥98%) and 4-aminophenyl disulfide (AFD, ≥98%) were purchased from TCI. DGEBA (DER 332) was purchased from Sigma Aldrich. Dithiothreitol (DTT, ≥99%), epibromohydrin (≥98%), dimethylformamide (DMF, ≥99.8%), methanol (≥99.5%), 1,2,4-trichlorobenzene (≥99%), potassium carbonate (K_2CO_3, ≥99%), anhydrous magnesium sulfate ($MgSO_4$, ≥99.5%) and hexane (≥98%) were purchased from Aladdin Chemistry Ltd. Other chemicals were purchased from local suppliers.

2.2. Synthesis of bis(4-glycidyloxyphenyl)disulfide (BGPDS)

Typically, bis(4-hydroxyphenyl) disulfide (9.67 g, 38.6 mmol), K_2CO_3 (53.4 g, 0.386 mol), DMF (193 ml) were mixed in a 500 ml three-necked flask equipped with a reflux condenser under nitrogen atmosphere (Fig. S1). The mixture was stirred to homogeneous under 60 °C and then epibromohydrin (52.9 g, 0.386 mol) was slowly added. After reacting for >12 h, K_2CO_3 was removed by filtration. Subsequently, ~50 ml water was added to the solution and the organic layer was extracted three times with chloroform/hexane (2:3) solution. Then, a large amount of water was added to remove the remaining DMF and the bottom layer was separated and dried with anhydrous $MgSO_4$. After being concentrated and recrystallization from the methanol, white powder BGPDS was obtained.

2.3. Preparation of epoxy vitrimers

2.3.1. Dual disulfide vitrimer

Typically, stoichiometric amount of BGPDS (10.03 g, 27.70 mmol) and AFD (3.44 g, 13.85 mmol) were added into a PTFE beaker. The mixture was heated to 90 °C until phase miscibility occurred. Then, the mixture was degassed in vacuum oven and then quickly poured into a 100mm×100mm × 1.5 mm brass mold sandwiched with antiadhesive silicone paper. After being pre-cured at 110 °C for 30min and post-cured at 160 °C for 3 h under nitrogen atmosphere, the dual disulfide vitrimer that both contained aromatic disulfide bonds in epoxy monomer and curing agent was obtained.

2.3.2. Single disulfide vitrimer

To prepare the single disulfide vitrimer that only contained aromatic disulfide bonds in curing agent, stoichiometric amount of DGEBA (11.07 g, 32.52 mmol), instead of the monomer BGPDS, was used to react with AFD (4.04 g, 16.26 mmol) in the same way.

2.4. Preparation of fiber reinforced epoxy composites

In the PTFE mold, a carbon fiber fabric was immersed in the epoxy mixture of BGPDS and AFD. Then, additional epoxy mixture was used to fill the mold completely. After being placed in the 90 °C vacuum oven for 30min, the composites were pre-cured at 110 °C for 30min and post-cured at 160 °C for 3 h under nitrogen atmosphere.

2.5. Characterization

NMR was performed on Bruker AV 600 MHz Nuclear Magnetic Resonance spectrometer using the solvent of $CDCl_3$.

FTIR was performed on Nicolet 6700 Fourier transform infrared spectrometer in potassium bromide pellets.

Mass spectra was performed on a Varian 7.0T FTMS using CH_2Cl_2 as solvent.

DSC was performed on a TA Q2000 apparatus over a temperature ranging from −20 to 200 °C under nitrogen. T_g was determined at the inflection point of the curves measured at a scan rate of 10 °C/min.

TGA was performed on a TA Q500 apparatus over a temperature ranging from room temperature to 600 °C under nitrogen.

DMA was conducted on a TA RSA-G2 apparatus in the geometry of dual cantilever beam. Heating ramps of 3 °C/min were applied from 25 to 200 °C. The samples ($45 \times 12 \times 2$ mm^3) were tested at 1 Hz with a strain of 0.05%.

Solvent resistance: a sample ($10 \times 10 \times 1.5$ mm^3) was immersing in trichlorobenzene at 200 °C for 2 h to investigate its solvent resistance at high temperature. Besides, samples ($10 \times 10 \times 1.5$ mm^3) were immersing in solvents of THF, DMSO, ethanol, diethyl ether and DMF for 3 days to investigate its solvent resistance in several other solvents.

Stress-relaxation was conducted on a TA RSA-G2 rheometer using a 25 mm parallel-plate geometry on all samples with diameter of 5 mm and thickness of 1.5 mm. After a 10min temperature equilibration (from 160 to 220 °C), a 1% strain step was applied and the stress was monitored over time. To ensure a good contact of the material with the geometries, a constant normal force of 10 N was applied. According to a previous strain sweep experiment, 1% deformations were within the linear range.

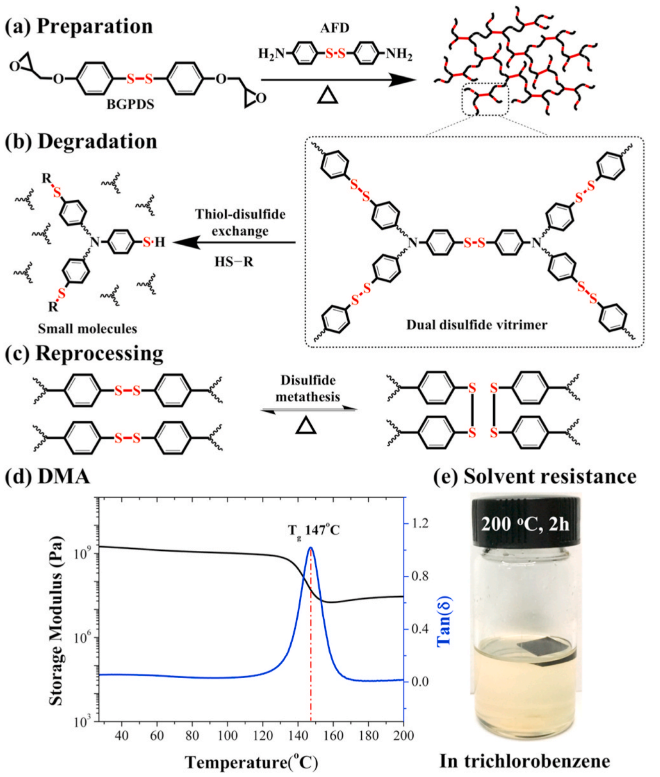

Fig. 1. Dual disulfide vitrimer: (a) preparation process and the covalently cross-linked network; (b) degradation through exchange reactions with outer thiols; (c) reprocessing through inner disulfide metathesis; (d) dynamic mechanical analysis (DMA) thermograms; (e) solvent resistance in trichlorobenzene at 200 °C.

Dilatometry was performed on rectangular samples (8mm×5mm × 1.5 mm) by using a TA RSA-G2 apparatus in the film tension geometry. The length was measured while applying heating rates of 3 °C/min from 50 to 250 °C. A weak elongational stress of 20 KPa was applied throughout the measurement to avoid buckling.

Reprocessing: samples in powder were placed into a steel mold sandwiched with anti-adhesive silicone paper. Then, the mold was preheated 10min and the reprocessing was conducted by hot pressing in 1 h at 180 °C.

Degradation: samples (10 × 10 × 1.5 mm^3) were immersing in dithiothreitol/DMF (0.1 mg/ml) dilute solution at various temperature (30–90 °C). The residual weight of solid samples were recorded over time.

Recycling: the fiber reinforced epoxy composites were immersed into 0.1 mg/ml DTT/DMF solution at 90 °C to dissolve the epoxy resin and to recycle the carbon fiber fabric. After being further washed and dried, the recycled carbon fibers were reused to form fiber reinforced composites.

Tensile tests: all the tests were performed on dogbone samples (8mm×2mm × 1.5 mm) by using a Universal Materials Testing Machine ETM104B at a strain rate of 2 mm/min, at room temperature.

3. Results & discussions

3.1. Synthesis & characterizations

As a demonstration, an epoxy vitrimer with high contents of exchangeable aromatic disulfide crosslinks was synthesized by classical epoxy chemistry: reaction of bis(4-glycidyloxyphenyl) disulfide (BGPDS) and 4-aminophenyl disulfide (AFD) (Fig. 1a). The dynamic monomer BGPDS was synthesized via Williamson ether synthesis [57] and characterized by the ^1H, ^{13}C NMR, FTIR and mass spectra in advance (Fig. S2, S3, S4, S5). It is notable that the peak at 912 cm^{-1} (δ_{CO}) in FTIR spectra corresponding to the epoxy peak (Fig. S4) and the molecular weight of BGPDS from mass spectra was determined to be 362 g/mol, while Na^+ (23 g/mol) should be excluded (Fig. S5). As the epoxy monomer BGPDS and the amine curing agent AFD both contain dynamic

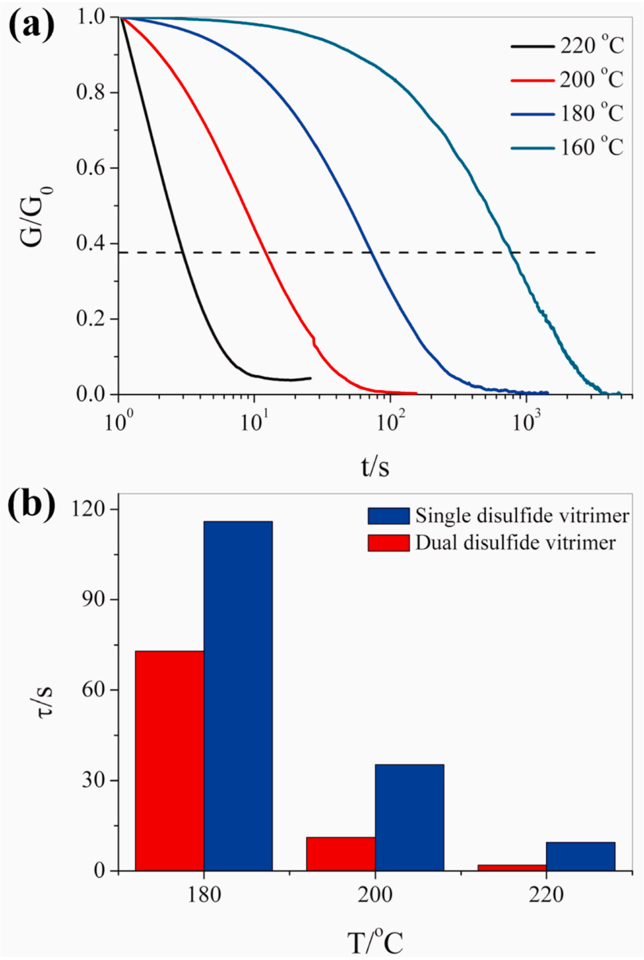

Fig. 2. (a) Stress relaxation behavior of the dual disulfide vitrimer from 160 to 220 °C; (b) Relaxation times τ of the dual disulfide vitrimer and single disulfide vitrimer at various temperatures.

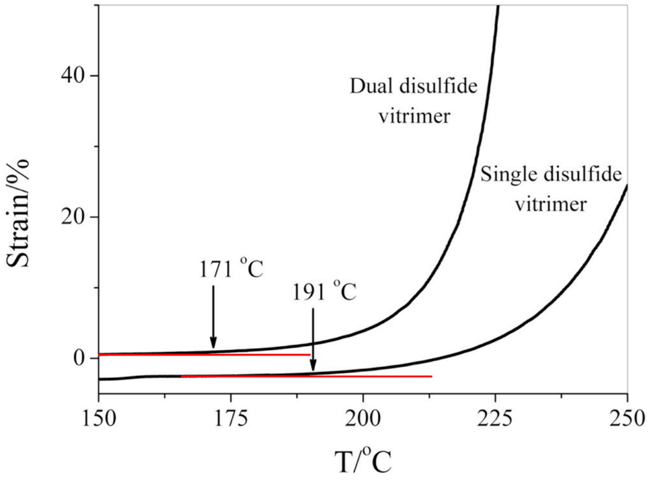

Fig. 3. Dilatometry experiments and the temperature of malleability of dual disulfide vitrimer (top) and single disulfide vitrimer (bottom).

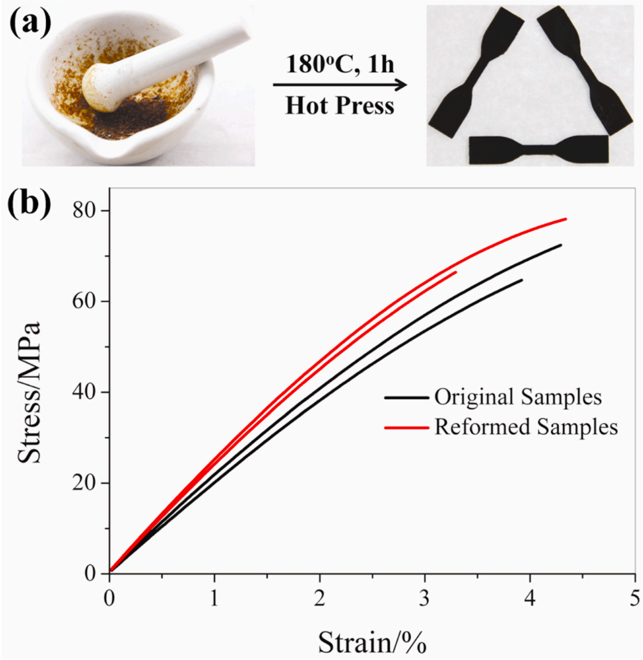

Fig. 4. (a) Reprocessing of the dual disulfide vitrimer by hot pressing; (b) Mechanical properties of the original samples and the reformed ones by tensile tests.

aromatic disulfide bonds, this epoxy vitrimer was named “dual disulfide vitrimer”, in which the content of aromatic disulfide bonds was much higher. In addition, a reference epoxy vitrimer was synthesized from AFD and the conventional epoxy monomer DGEBA, resulting in less content of dynamic disulfide bonds in the network, which was named “single disulfide vitrimer” here.

The polymerization of epoxy and amine was followed by FTIR, where the disappeared peak of epoxy (δ_{CO} at 912 cm^{-1}, δ_{CH} at 3058 cm^{-1}) and the new peak of hydroxyl (ν_{OH} at 3422 cm^{-1}) confirmed that the curing reaction was complete (Fig. S6). The fully cured dual disulfide vitrimer was insoluble in solvents including THF, DMSO, ethanol, diethyl ether and DMF (Fig. S7), while it exhibited excellent thermal stability with the T_{dmax} of about 300 °C (Fig. S8). The complete curing of both epoxy vitrimers were further confirmed by DSC, as no residual curing exothermic peak was observed (Fig. S9 and S10). From the DSC thermograms, comparable T_g values were determined for both epoxy vitrimers, which resulted from their similar cross-linked networks and chemical structures.

The dual disulfide vitrimer of epoxy was degradable through exchange reactions with outer thiols (Fig. 1b) and became reprocessable through inner disulfide metathesis (Fig. 1c), while their outstanding mechanical properties and excellent solvent resistance still remained. From the DMA thermograms of the dual disulfide vitrimer, it was revealed that its T_g was ~147 °C and the storage modulus E′ was ~1.72 GPa (at 30 °C) (Fig. 1d), indicating the outstanding properties of dual disulfide vitrimer. Besides, the dual disulfide vitrimer was insoluble, even being immersed in trichlorobenzene at 200 °C for 2 h (Fig. 1e), which further revealed its excellent solvent resistance and covalently cross-linked networks at elevated temperatures.

3.2. *Stress relaxation & reprocessing*

Through the reversible exchange reactions between crosslinks, vitrimer materials have the distinctive feature of releasing deformation stress at high temperature [16,28,41]. The stress release behavior was observed in dual disulfide vitrimer (Fig. 2a), which revealed the exchange reactions of aromatic disulfide bonds in networks (Fig. 1c). The dual disulfide vitrimer could relax stress completely at temperatures from 160 to 220 °C through the inner disulfide metathesis. According to our previous work [28] or other literatures [16,58], an exponential function could be used to describe the stress relaxation process of vitrimer materials, based on the Maxwell’s model of viscoelastic materials. When the modulus or stress decreased to 1/e (36.8%) of the initial value, the relaxation times (τ) of the dual disulfide vitrimer were determined, which ranged from 1.95s (220 °C) to 782s (160 °C). Taking account of the high T_g and the outstanding mechanical properties of the dual disulfide vitrimer, the stress relaxation was quite fast. Additionally, the stress relaxation of single disulfide vitrimer was also investigated (Fig. S11). By comparison, the dual disulfide vitrimer exhibited rapider stress relaxation than the single disulfide vitrimer (Fig. 2b), though they exhibited comparable T_g and E′ (Fig. S12). In other words, by increasing the contents of disulfide bonds in vitrimer network, the stress relaxation behavior was accelerated obviously. For instance, at 200 °C, the τ was ~11s in the dual disulfide vitrimer, while it was ~35s in the single disulfide vitrimer (Fig. 2b). It is known that exchange reactions between

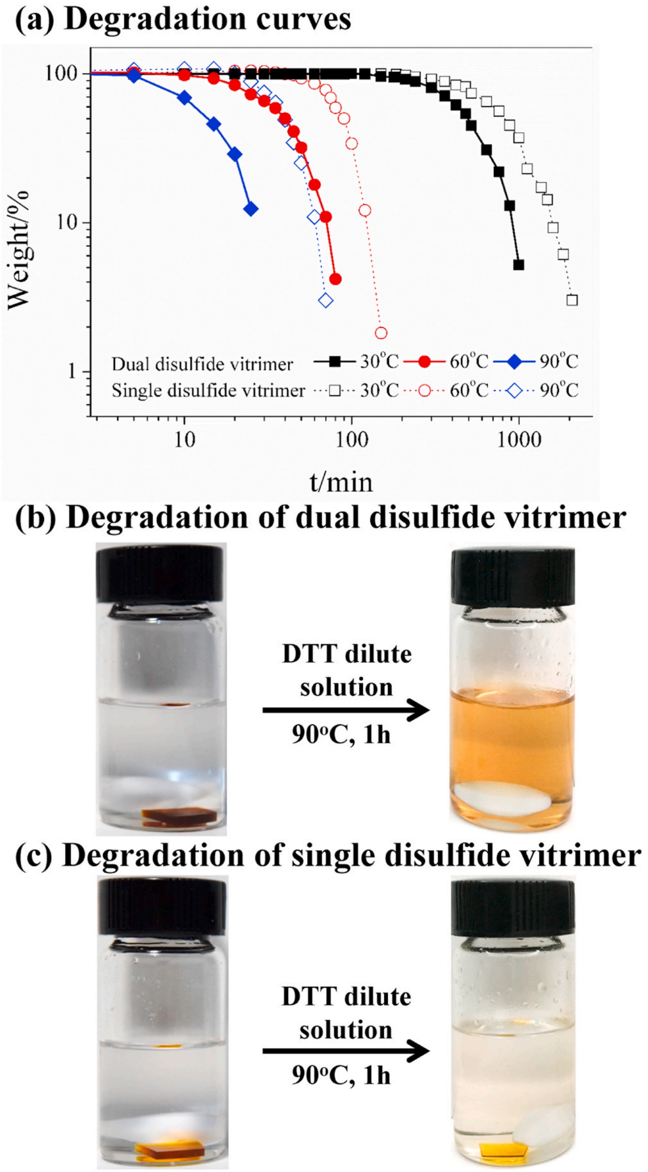

Fig. 5. (a) Degradation behavior of the dual disulfide vitrimer (solid) and the single disulfide vitrimer (dot); (b) Full degradation of the dual disulfide vitrimer at 90 °C; (c) Partially degradation of the single disulfide vitrimer at 90 °C; all the concentration of DTT dilute solution was 0.1 mg/ml.

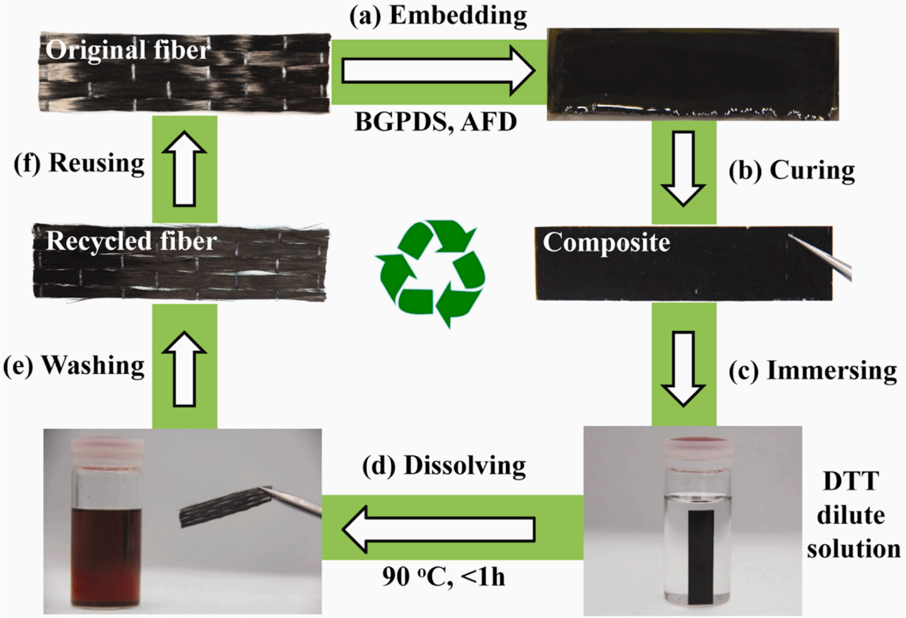

Fig. 6. The recycling process of CFRP composites based on dual disulfide vitrimer: (a) embedding the carbon fibers in epoxy matrix; (b) obtaining CFRP composites by curing; (c) immersing the CFRP composites in DTT dilute solution (0.1 mg/ml); (d) dissolving the epoxy matrix at 90 °C in 1 h; (e) washing and drying the recovered carbon fibers; (f) reusing the recycled carbon fibers to form new composites.

crosslinks lead to the recombination of polymer chains, which results in the stress relaxation of vitrimer networks. In addition, more dynamic bonds the vitrimer networks contain, easier the exchange reactions occur and more efficient the polymer chains rearrange. Thus, due to the high content of disulfide bonds in the dual disulfide vitrimer network, the exchange reactions between cross-links and the recombination of networks were faster, which led to its rapid stress relaxation.

In addition to the rapid stress relaxation, the high content of disulfide bonds in vitrimer networks also improved some other dynamic properties, such as malleability or reprocessability. It is well-known that vitrimer materials become malleable and reprocessable at the temperature of malleability, when the rate of exchange reactions between cross-links speeds up and reaches a high level. To reveal the temperature of malleability, the epoxy vitrimer were both investigated by dilatometry experiment [16,28]. It was revealed that the temperature of malleability of the dual disulfide vitrimer was determined to be 171 °C, which decreased about 20 °C when compared with the single disulfide vitrimer (Fig. 3). Because of the high content of dynamic disulfide bonds in dual disulfide vitrimer, the exchange reactions between cross-links were always rapider than that in the single disulfide vitrimer. Thus, the rate of exchange reactions between cross-links in dual disulfide vitrimer more easily reached a high level and efficiently initiated the recombination of networks, leading to the decrease of the temperature of malleability. From the acceleration of stress relaxation and the decrease of the temperature of malleability, one could expect that the dual disulfide vitrimer could be easily reprocessed upon heating.

As a common method, hot pressing was applied to study the reprocessability of epoxy vitrimers at elevated temperature. Through disulfide metathesis in the network, the dual disulfide vitrimer that was manually ground into powder, was then successfully reprocessed and remolded into the form of films or dog-bone samples at 180 °C in 1 h (Fig. 4a). To reveal the recovery efficiency, the original samples and the reprocessed ones were subjected to tensile tests. As shown in Fig. 4b and Fig. S13, the stress of the original samples at break were 63.15 ± 10.1 MPa, while 56.9 ± 17.7 MPa for the reformed samples. These results indicated that the dual disulfide vitrimer could be efficiently reprocessed by hot pressing and their outstanding mechanical properties could be fully recovered.

3.3. *Degradation & recycling*

Due to the inner exchange reactions between cross-links at elevated temperature, vitrimer materials can release stress and become reprocessable and malleable, without losing their permanently cross-linked networks, outstanding mechanical properties and excellent solvent resistance. Besides, when the dynamic cross-links react with the outer reactive molecules in solution, the vitrimer network become fully degradable and dissolvable [11,31]. Relying on the exchange reactions between thiol groups and disulfide bonds [41,59,60], thiol-based compound, such as dithiothreitol (DTT), could be used to break down the dual disulfide vitrimer effectively. As shown in Fig. 5a, the degradation kinetic process was investigated by monitoring the weight of residual solid samples, which revealed that the dual disulfide vitrimer could be dissolved in DTT dilute solution at various temperatures. The time required to dissolve the rectangular samples completely in DTT dilute solution (0.1 mg/ml) ranged from <30min (90 °C), ~90min (60 °C), to ~1120min (30 °C). The degradation process of the single disulfide vitrimer was also investigated (Fig. 5a). In comparison, the dual disulfide vitrimer was easier to be dissolved than the single disulfide vitrimer at all temperatures. In other words, with aromatic disulfide bonds both in epoxy monomers and curing agents, the efficiency of degradation of epoxy vitrimer was highly improved. For instance, the sample of the dual disulfide vitrimer was completely dissolved at 90 °C in 1 h (Fig. 5b), while the single disulfide vitrimer sample still remained at the same condition (Fig. 5c). The rapid degradation of dual disulfide vitrimer mainly resulted from two reasons, including the high content of aromatic disulfide bonds in networks and dynamic disulfide bonds in backbones. Firstly, because of the high content of aromatic disulfide bonds, the networks of dual disulfide vitrimer exhibited faster exchange reactions between the disulfide cross-links and outer free thiol groups than the single disulfide vitrimer, which resulted in the rapid degradation of cross-linked networks. Secondly, in the presence of thiols, the dual disulfide vitrimer with disulfide bonds in backbones fragmented into small molecules (Fig. 1b), while linear polymers were generated from the degradation of the single disulfide vitrimer. Since disassembling to fragments of small molecules are more effective for degradating and dissolving thermosets [57], dual disulfide vitrimer exhibited rapider

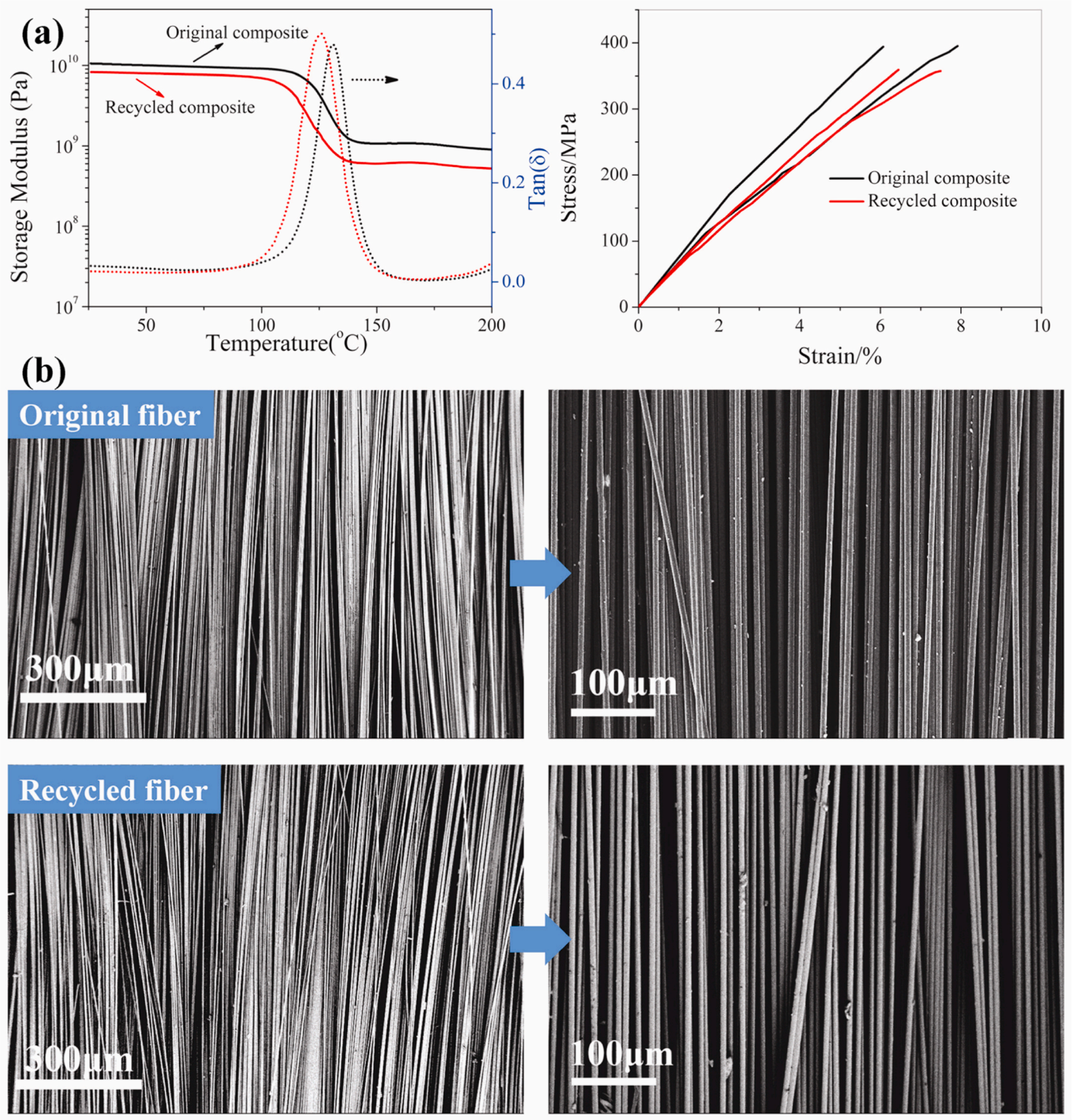

Fig. 7. (a) DMA (left) and tensile tests (right) of the original (black) and recycled (red) CFRP composites; (b) Morphology of the fresh (top) and recycled (bottom) carbon fibers by SEM. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

degradation rate than single disulfide vitrimer. Thus, the fast exchange reactions and the small molecules generated both led to the rapid degradation of dual disulfide vitrimer. The rapid degradation of dual disulfide vitrimer could be applied in the efficient recycling of thermosetting epoxy composites, such as the carbon fiber reinforced polymer (CFRP) composites.

CFRP composites based on epoxy are high performance structural materials that have been widely used in various industrial fields. Nevertheless, due to the cross-linked networks and thermosetting nature of epoxy matrix, the generated composites cannot be dissolved and the carbon fiber cannot be recycled. Owing to the efficient and selective dissolution in thiol solution, the dual disulfide epoxy vitrimer have the ability to recycle high-value carbon fibers from CFRP composites efficiently. Herein, the recyclable CFRP composites based on dual disulfide vitrimer were prepared and the recycling of the carbon fibers from composites was investigated. As shown in Fig. 6, by embedding the carbon fibers in the mixture of dynamic epoxy monomers and dynamic curing agents (Fig. 6a), the recyclable CFRP composites were obtained after full curing at elevated temperature (Fig. 6b). To integrally recover the carbon fibers from the CFRP composites, the composites were immersed in the dithiothreitol (DTT) dilute solution. The thermoset epoxy matrix was removed in less than an hour, through rapid thiol-disulfide exchange reactions. After being washed and dried (Fig. 6e), the recovered carbon fibers were reused to prepare the CFRP composites like original ones (Fig. 6f).

The original CFRP composites from the fresh carbon fibers and the reformed CFRP composites from the recovered carbon fibers both exhibited outstanding mechanical properties. As shown in Fig. 7a, the T_g of the original composite was 131 °C and the E′ was 10.5 GPa (at 30 °C). In addition, the stress at break was up to 334.5 ± 87.7 MPa (Fig. 7a). After removing the epoxy matrix of dual disulfide vitrimer, the carbon fibers were completely recycled. From the SEM images as shown in Fig. 7b and Fig. S14, it was revealed that the morphology of the recovered carbon fibers were almost the same to the fresh ones, indicating the effectively recycling of the carbon fibers. Besides, it was notable that the recycled carbon fibers were integral and did not have epoxy resins attached. From the Raman spectra, it was revealed that the recycled carbon fibers maintained the chemical details of the original carbon fibers (Fig. S15). When the recycled carbon fibers were reused to form CFRP composites, the mechanical strength of the resulted composites recovered to almost the same level as the original composites. As shown in Fig. 7a and Fig. S13, the T_g and E′ of the recycled composite was determined to be 126 °C and 8.2 GPa, while the stress strain at break was 320.9 ± 64.6 MPa. These results indicated that the reformed CFRP composites based on the recycled carbon fibers still remained their outstanding mechanical properties and could be widely used as high performance structural materials once again.

4. Conclusion

In summary, a dual disulfide vitrimer with high contents of exchangeable aromatic disulfide crosslinks was synthesized from the epoxy resin and the amine curing agent that both contained aromatic disulfide bonds. This epoxy vitrimer exhibited excellent solvent resistance and outstanding properties, with the T_g of 147 °C, the E′ of 1.72 GPa and the tensile strength of 63.1 MPa. Due to the high contents of exchangeable aromatic disulfide bonds, the dual disulfide vitrimer rapidly released the stress from deformation with τ ranged from 1.95s (220 °C) to 782s (160 °C). Meanwhile, it became reprocessable and malleable readily, with the temperature of malleability low to 171 °C. Moreover, the dual disulfide vitrimer could be easily degraded by dithiothreitol (DTT) dilute solution, while its degradation process was rapider when compared with the single disulfide vitrimer. In addition, the CFRP composites based on the dual disulfide epoxy vitrimer were prepared, which exhibited outstanding mechanical properties, with the E′ of 10.5 GPa and the tensile strength of 334.5 MPa. After removing the epoxy matrix efficiently, the carbon fibers were recycled integrally and reused to form CFRP composites. The reformed CFRP composites remained outstanding mechanical properties, with the E′ of 8.2 GPa and the tensile strength of 320.9 MPa. These results indicated the potential applications of epoxy vitrimers and their CFRP composites as cost-efficient recyclable structural composites in automotive, wind power and aeronautical industries.

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.

Acknowledgements

Financial support from the National Natural Science Foundation of China (No.51603198 and No.21606213), the Foundation of China Academy of Engineering Physics (No.YZJJLX2017004) and Sichuan Science and Technology Program (No.2019YFG0455).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2020.108278.

References

[1] Peter M. Carbon fibers and their composites. USA: CRC Press; 2005.

[2] Peter WRB, Constantinos S. The structural integrity of carbon fiber composites. Switzerland: Springer; 2017.

[3] Dodiuk H, Goodman SH. Handbook of thermoset plastics. Oxford: Elsevier; 2013.

[4] Huo S, Yang S, Wang J, Cheng J, Zhang Q, Hu Y, Ding G, Zhang Q, Song P. A liquid phosphorus-containing imidazole derivative as flame-retardant curing agent for epoxy resin with enhanced thermal latency, mechanical, and flame-retardant performances. J Hazard Mater 2019;386:121984.

[5] Fang F, Huo S, Shen H, Ran S, Wang H, Song P, Fang Z. A bio-based ionic complex with different oxidation states of phosphorus for reducing flammability and smoke release of epoxy resins. Compos Commun 2020;17:104–8.

[6] Xu Z, Song P, Zhang J, Guo Q, Mai Y. Epoxy nanocomposites simultaneously strengthened and toughened by hybridization with graphene oxide and block ionomer. Compos Sci Technol 2018;168:363–70.

[7] Fang F, Ran S, Fang Z, Song P, Wang H. Improved flame resistance and thermo-mechanical properties of epoxy resin nanocomposites from functionalized graphene oxide via self-assembly in water. Compos B Eng 2019;165:406–16.

[8] Ma X, Guo W, Xu Z, Chen S, Cheng J, Zhang J, Miao M, Zhang D. Synthesis of degradable hyperbranched epoxy resins with high tensile, elongation, modulus and low-temperature resistance. Compos B Eng 2020. https://doi.org/10.1016/j.compositesb.2020.108005.

[9] Huan X, Shi K, Yan J, Lin S, Li Y, Jia X, Yang X. High performance epoxy composites prepared using recycled short carbon fiber with enhanced dispersibility and interfacial bonding through polydopamine surface-modification. Compos B Eng 2020. https://doi.org/10.1016/j.compositesb.2020.107987.

[10] Wang Y, Gao X, Wu X, Luo C. Facile synthesis of Mn_3O_4 hollow polyhedron wrapped by multiwalled carbon nanotubes as a high-efficiency microwave absorber. Ceram Int 2020;46(2):1560–8.

[11] Yu K, Shi Q, Dunn ML, Wang T, Qi HJ. Carbon fiber reinforced thermoset composite with near 100% recyclability. Adv Funct Mater 2016;26(33):6098–106.

[12] Singh N, Hui D, Singh R, Ahuja IPS, Feo L, Fraternali F. Recycling of plastic solid waste: a state of art review and future applications. Compos B Eng 2017;115: 409–22.

[13] Wang B, Ma S, Yan S, Zhu J. Readily recyclable carbon fiber reinforced composites based on degradable thermosets: a review. Green Chem 2019;21:5781–96.

[14] Ma S, Wei J, Jia Z, Yu T, Yuan W, Li Q, Wang S, You S, Liu R, Zhu J. Readily recyclable, high-performance thermosetting materials based on a lignin-derived spiro diacetal trigger. J Mater Chem A 2019;7:1233–43.

[15] Scott TF, Schneider AD, Cook WD, Bowman CN. Photoinduced plasticity in cross-linked polymers. Science 2005;308(5728):1615–7.

[16] Damien M, Mathieu C, François T, Ludwik L. Silica-like malleable materials from permanent organic networks. Science 2011;334(6058):965–8.

[17] Kloxin CJ, Scott TF, Adzima BJ, Bowman CN. Covalent adaptable networks (CANs): a unique paradigm in cross-linked polymers. Macromolecules 2010;43(6): 2643–53.

[18] Bowman CN, Kloxin CJ. Covalent adaptable networks: reversible bond structures incorporated in polymer networks. Angew Chem Int Ed 2012;51(18):4272–4.

[19] Kloxin CJ, Bowman CN. Covalent adaptable networks: smart, reconfigurable and responsive network systems. Chem Soc Rev 2013;42(17):7161–73.

[20] Zou W, Dong J, Luo Y, Zhao Q, Xie T. Dynamic covalent polymer networks: from old chemistry to modern day innovations. Adv Mater 2017;29(14):1606100.

[21] Denissen W, Winne JM, Du Prez FE. Vitrimers: permanent organic networks with glass-like fluidity. Chem Sci 2016;7:30–8.

[22] Chakma P, Konkolewicz D. Dynamic covalent bonds in polymeric materials. Angew Chem Int Ed 2019. 0 (ja).

[23] Imbernon L, Norvez S. From landfilling to vitrimer chemistry in rubber life cycle. Eur Polym J 2016;82:347–76.

[24] Krishnakumar B, Sanka RVSP, Binder WH, Parthasarthy V, Rana S, Karak N. Vitrimers: associative dynamic covalent adaptive networks in thermoset polymers. Chem Eng J 2020;385:123820.

[25] Xiangxu C, Matheus AD, Kanji O, Ajit M, Hongbin S, Steven RN, Kevin S, Wudl F. A thermally Re-mendable cross-linked polymeric material. Science 2002;295 (5560):1698–702.

[26] Yu S, Zhang R, Wu Q, Chen T, Sun P. Bio-inspired high-performance and recyclable cross-linked polymers. Adv Mater 2013;25(35):4912–7.

[27] Capelot M, Montarnal D, Tournilhac F, Leibler L. Metal-catalyzed transesterification for healing and assembling of thermosets. J Am Chem Soc 2012; 134(18):7664–7.

[28] Chen M, Zhou L, Wu Y, Zhao X, Zhang Y. Rapid stress relaxation and moderate temperature of malleability enabled by the synergy of disulfide metathesis and carboxylate transesterification in epoxy vitrimers. ACS Macro Lett 2019;8:255–60.

[29] Yang Y, Pei Z, Zhang X, Tao L, Wei Y, Ji Y. Carbon nanotube-vitrimer composite for facile and efficient photo-welding of epoxy. Chem Sci 2014;5(9):3486–92.

[30] Liu Y, Tang Z, Chen Y, Zhang C, Guo B. Engineering of β-hydroxyl esters into elastomer–nanoparticle interface toward malleable, robust, and reprocessable vitrimer composites. Acs Appl. Mater. Inter. 2018;10(3):2992–3001.

[31] Shi Q, Yu K, Kuang X, Mu X, Dunn CK, Dunn ML, Wang T, Jerry Qi H. Recyclable 3D printing of vitrimer epoxy. Mater. Horiz. 2017;4(4):598–607.

[32] Denissen W, Rivero G, Nicolaÿ R, Leibler L, Winne JM, Prez FED. Vinylogous urethane vitrimers. Adv Funct Mater 2015;25(16):2451–7.

[33] Guerre M, Taplan C, Nicolaÿ R, Winne JM, Du Prez FE. Fluorinated vitrimer elastomers with a dual temperature response. J Am Chem Soc 2018;140(41): 13272–84.

[34] Denissen W, De Baere I, Van Paepegem W, Leibler L, Winne J, Du Prez FE. Vinylogous urea vitrimers and their application in fiber reinforced composites. Macromolecules 2018;51(5):2054–64.

[35] Obadia MM, Mudraboyina BP, Serghei A, Montarnal D, Drockenmuller E. Reprocessing and recycling of highly cross-linked ion-conducting networks through transalkylation exchanges of C–N bonds. J Am Chem Soc 2015;137(18): 6078–83.

[36] Fortman DJ, Brutman JP, Cramer CJ, Hillmyer MA, Dichtel WR. Mechanically activated, catalyst-free polyhydroxyurethane vitrimers. J Am Chem Soc 2015;137 (44):14019–22.

[37] Zheng P, McCarthy TJ. A surprise from 1954 siloxane equilibration is a simple, robust, and obvious polymer self-healing mechanism. J Am Chem Soc 2012;134(4): 2024–7.

[38] Wu X, Yang X, Huang W, Yu R, Zhao X, Zhang Y. A facile access to stiff epoxy vitrimer with excellent mechanical properties via siloxane equilibration. J Mater Chem A 2018;6(22):10184–8.

[39] Lei ZQ, Xiang HP, Yuan YJ, Rong MZ, Zhang MQ. Room-temperature self-healable and remoldable cross-linked polymer based on the dynamic exchange of disulfide bonds. Chem Mater 2014;26(6):2038–46.

[40] Rekondo A, Martin R, Ruiz De Luzuriaga A, Cabanero G, Grande HJ, Odriozola I. Catalyst-free room-temperature self-healing elastomers based on aromatic disulfide metathesis. Mater. Horiz. 2014;1(2):237–40.

[41] Ruiz De Luzuriaga A, Martin R, Markaide N, Rekondo A, Cabanero G, Rodriguez J, Odriozola I. Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites. Mater. Horiz. 2016;3(3):241–7.

[42] Deng J, Kuang X, Liu R, Ding W, Wang AC, Lai Y, Dong K, Wen Z, Wang Y, Wang L, Qi HJ, Zhang T, Wang ZL. Vitrimer elastomer-based jigsaw puzzle-like healable triboelectric nanogenerator for self-powered wearable electronics. Adv Mater 2018;1705918:1–10.

[43] Zhou F, Guo Z, Wang W, Lei X, Zhang B, Zhang H, Zhang Q. Preparation of self-healing, recyclable epoxy resins and low-electrical resistance composites based on double-disulfide bond exchange. Compos Sci Technol 2018;167(1):79–85.

[44] Imbernon L, Oikonomou EK, Norvez S, Leibler L. Chemically crosslinked yet reprocessable epoxidized natural rubber via thermo-activated disulfide rearrangements. Polym Chem 2015;6(23):4271–8.

[45] Vitae IA, Vitae IOA. Aromatic disulfide crosslinks in polymer systems: self-healing, reprocessability,recyclability and more. Eur Polym J 2016;84(1):147–60.

[46] Krishnakumar B, Prasanna Sanka RVS, Binder WH, Park C, Jung J, Parthasarthy V, Rana S, Yun GJ. Catalyst free self-healable vitrimer/graphene oxide nanocomposites. Compos B Eng 2020;184:107647.

[47] Lu Y, Tournilhac F, Leibler L, Guan Z. Making insoluble polymer networks malleable via olefin metathesis. J Am Chem Soc 2012;134(20):8424–7.

[48] Lu Y, Guan Z. Olefin metathesis for effective polymer healing via dynamic exchange of strong carbon–carbon double bonds. J Am Chem Soc 2012;134(34):14226–31.

[49] Taynton P, Yu K, Shoemaker RK, Jin Y, Qi HJ, Zhang W. Heat- or water-driven malleability in a highly recyclable covalent network polymer. Adv Mater 2014;26(23):3938–42.

[50] Liu H, Zhang H, Wang H, Huang X, Huang G, Wu J. Weldable,malleable and programmable epoxy vitrimers with high mechanical properties and water insensitivity. Chem Eng J 2019;368(1):61–70.

[51] Mo R, Hu J, Huang H, Sheng X, Zhang X. Tunable, self-healing and corrosion inhibiting dynamic epoxy–polyimine network built by post-crosslinking. J Mater Chem A 2019;7(7):3031–8.

[52] Olivia R, Cromwell JC, Zhibin G. Malleable and self-healing covalent polymer networks through tunable dynamic boronic ester bonds. J Am Chem Soc 2015;137(20):6492–5.

[53] Cash JJ, Kubo T, Bapat AP, Sumerlin BS. Room-temperature self-healing polymers based on dynamic-covalent boronic esters. Macromolecules 2015;48(7):2098–106.

[54] Röttger M, Domenech T, van der Weegen R, Breuillac A, Nicolaÿ R, Leibler L, Nicolaÿ R, Leibler L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. Science 2017;356(6333):62–5.

[55] Sumerlin JJCA. Maximizing the symbiosis of static and dynamic bonds in self-healing boronic ester networks. Polym Chem 2018;9(15):2011–20.

[56] Wang S, Ma S, Li Q, Xu X, Wang B, Yuan W, Zhou S, You S, Zhu J. Facile in situ preparation of high-performance epoxy vitrimer from renewable resources and its application in nondestructive recyclable carbon fiber composite. Green Chem 2019;21(6):1484–97.

[57] Takahashi A, Ohishi T, Goseki R, Otsuka H. Degradable epoxy resins prepared from diepoxide monomer with dynamic covalent disulfide linkage. Polymer 2016;82:319–26.

[58] Shi Q, Yu K, Dunn ML, Wang T, Qi HJ. Solvent assisted pressure-free surface welding and reprocessing of malleable epoxy polymers. Macromolecules 2016;49(15):5527–37.

[59] Zhou L, Chen M, Zhao X. Rapid degradation of disulfide-based thermosets through thiol-disulfide exchange reaction. Polymer 2017;120:1–8.

[60] Johnson LM, Ledet E, Huffman ND, Swarner SL, Shepherd SD, Durham PG, Rothrock GD. Controlled degradation of disulfide-based epoxy thermosets for extreme environments. Polymer 2015;64:84–92.