

A Triple Crosslinking Design toward Epoxy Vitrimers and Carbon Fiber Composites of High Performance and Multi-shape Memory

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Electronic Supplementary Information

Abstract It remains a challenge to use a simple approach to fabricate a multi-shape memory material with high mechanical performances. Here, we report a triple crosslinking design to construct a multi-shape memory epoxy vitrimer (MSMEV), which exhibits high mechanical properties, multi-shape memory property and malleability. The triple crosslinking network is formed by reacting diglycidyl ether of bisphenol F (DGEBF) with 4-aminophenyl disulfide, γ -aminopropyltriethoxysilane (APTS) and poly(propylene glycol) bis(2-aminopropyl ether) (D2000). The triple crosslinking manifests triple functions: the disulfide bonds and the silyl ether linkages enable malleability of the epoxy network; the silyl ether linkages impart the network with high heterogeneity and broaden the glass transition region, leading to multi-shape memory property; a small amount of D2000 increases the modulus difference between the glassy and rubbery states, thereby improving the shape fixity ratio. Meanwhile, the high crosslinking density and rigid structure provide the MSMEV with high tensile strength and Young's modulus. Moreover, integrating carbon fibers and MSMEV results in shape memory composites. The superior mechanical properties of the composites and the recyclability of carbon fiber derived from the dissolvability of MSMEV make the composites hold great promise as structural materials in varied applications.

Keywords Multi-shape memory; Epoxy vitrimer; High mechanical performance; Triple crosslinking; Composites

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INTRODUCTION

Shape memory polymers (SMPs) are a promising class of intelligent materials that can recover the original shape in a predefined way from the temporary shape upon external stimulation such as heat, pH, light, electricity, magnetic field or moisture.^[1–10] By chemically or physically designing the network structure, SMPs can be highly tunable in shape memory effects, stimulus methods, and multifunctionality. Therefore, they hold great potential for applications in various areas including wearable textiles, aerospace exploration, electronics, 4D printing, and especially biomedicine.^[11] Recently, many studies on SMPs mainly focus on the multi-shape memory effects (MSME),^[12–14] which greatly extends the capacity of SMPs. Compared with conventional dual-shape memory polymers, multi-shape memory polymers (MSMPs) are capable of memorizing more than one temporary shape in a shape memory cycle, which is much more competitive in applications where complicated and elaborate shape designs are desired, such as

structural materials like aerospace vehicles and devices.

Fabricating polymers with multiphase^[14–17] and designing polymers with broad thermal transitions^[12,18] are two common methods to achieve MSMPs. Multiphase polymers with distinct phase transitions exhibit as-designed shape changing according to the switching stimulus of each phase. However, their fabrication inevitably requires mixtures of polymers, often of completely different natures that need separate chemistries, which greatly increases the intricacy of the synthetic procedure.^[19] Polymers with broad thermal transitions can be treated as SMPs with an infinite number of sharp transitions, which can be further regarded as an elemental memory unit with a corresponding transition temperature. Thus, temporary shapes can be programmed at multiple temperatures across their broad transitions. Without sophisticated structural design for independent transitions, the polymers with broad transitions can exhibit dual-, triple- or multi-shape memory effects (SMEs) as desired at alternate temperature in the transition window, which show higher versatility and efficiency than multiphase polymers do. In 2010, Xie reported a MSMP (thermoplastic perfluorosulphonic acid ionomer) with a glass transition as broad as 75 °C for the first time.^[12] Afterward, numerous approaches have been

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developed such as introducing interactions like hydrogen bonds or ionic bonds,^[20,21] constructing semi-interpenetrating polymer networks,^[18,22] and designing filler-induced heterogeneous network.^[23,24] However, all these SMP systems are either thermoplastic or of low crosslinking density, which are vulnerable to long-range molecular chain slippage and insufficient in mechanical performance, failing to serve as structural materials.

For thermoset polymers with high crosslinking density, epoxy resins are widely used as structural materials. If epoxy resins have combination of both SME and robust network, it can greatly improve their application value. However, it is of great challenge to achieve triple- or multi-SME for epoxy resins due to the lack of designability of the highly crosslinked network, because of which studies on triple- or multi-shape memory epoxies are very rare. Fabricating bilayers,^[25] utilizing Diels-Alder reactions^[26] and introducing the second reversible phase^[27] have been utilized to achieve triple-SME in epoxies. However, these methods are either inconvenient in the curing process or complicated in the synthetic procedure.

Here, we report a triple crosslinking design to fabricate mechanically robust multi-shape memory epoxy vitrimer (MSMEV). To realize this design, 4-aminophenyl disulfide (AD), γ -aminopropyltriethoxysilane (APTS) and poly(propylene glycol) bis(2-aminopropyl ether) (D2000) are used as the crosslinking agent to cure diglycidyl ether of bisphenol F (DGEBF). Among them, AD can provide the MSMEV with high mechanical performance and dynamic properties because of its rigid structure and disulfide bonds. APTS introduces heterogeneous network and thus broadens the glass transition region of MSMEV, which leads to multi-shape memory property. Moreover, the disulfide and silyl ether linkages also enable malleability of the epoxy network. A small amount of D2000 could increase the modulus difference between the glassy and rubbery states, thereby improving the shape fixity. Ultimately, we fabricate a MSMEV with high R_f and R_r , tensile strength up to 73 MPa, and Young's modulus up to 2581 MPa. Moreover, a series of multi-shape memory composites are fabricated by integrating carbon fibers and MSMEV. The composites show superior mechanical properties and the recyclability of carbon fiber derived from the dissolvability of MSMEV, which will make the composites hold great promise to serve as structural materials in diverse applications.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol F (DGEBF, epoxy equivalent per weight-EEW=170) was purchased from Luohe Chemistry Co., Ltd. 4-Aminophenyl disulfide (AD) and mercaptoethanol were purchased from Adamas. γ -Aminopropyltriethoxysilane (APTS) and poly(propylene glycol) bis(2-aminopropyl ether) (D2000) were purchased from Aladdin®. The carbon fiber was purchased from Jiangsu Hengshen Co., Ltd. All materials were used as received without further purification.

Preparation of MSMEV

A certain amount of AD, APTS and D2000 were mixed with DGEBF. Then the mixture was mechanically stirred for 15 min

before it was degassed in a vacuum to remove air bubbles. Afterward, the degassed mixture was poured into a preheated PTFE mold. Curing was performed at 75 °C for 2 h, 125 °C for 2 h and 165 °C for 3 h.

DGEBF reacted with AD is denoted as D_0 ; DGEBF reacted with AD and D2000 is denoted as D_1 . D_0 and D_1 as the contrast samples were prepared as same as MSMEV. (The compositions of all samples are shown in Table S1 in the electronic supplementary information, ESI)

Preparation of Epoxy-carbon Fiber Composites

The epoxy-carbon fiber composites were fabricated by hand lay-up molding with the epoxy mixture and carbon fiber. The curing process was the same as that of the MSMEV.

The Recycling of Carbon Fiber

The recycling of carbon fiber was conducted by immersing the composite sheet into the *N,N'*-dimethylformamide (DMF) solution of mercaptoethanol (20 mg/mL).

Characterization

Fourier transformation infrared (FTIR) spectra were measured on Nicolet iS10 (Nicolet, America) in the range of 4000–400 cm^{-1} . ^1H -NMR spectra were collected using a Bruker AV-600 spectrometer (600 MHz) under room temperature with CD_3OD as the solvent. The molar ratio between CD_3OD and APTS was 100:1. Dynamic mechanical analysis (DMA) tests were measured on Q800 (TA instruments) in a three-point bending mode. Tests were performed in temperature scanning mode in the range of 25 °C to 250 °C at a heating rate of 3 °C/min and a frequency of 1 Hz with a strain amplitude of 30 μm . The maximum of the $\tan\delta$ was evaluated as the glass transition temperature (T_g). Moreover, stress relaxation measurements were conducted on a same instrument (1% strain). Mechanical properties were conducted on an Instron 5567 (US) tensile tester at room temperature with a strain rate of 1 mm/min.

RESULTS AND DISCUSSION

Fabrication and Network Structure Study of MSMEV

We used 4-aminophenyl disulfide (AD), γ -aminopropyltriethoxysilane (APTS) and poly(propylene glycol) bis(2-aminopropyl ether) (D2000) to cure diglycidyl ether of bisphenol F (DGEBF), resulting in a triple crosslinking network of MSMEV (Fig. 1a). The FTIR results confirm the formation of the cross-link structure of MSMEV (Fig. S1 in ESI). To illustrate the importance of the triple crosslinking network, a control sample of AD crosslinked DGEBF (D_0) was fabricated. DMA measurement shows that the $\tan\delta$ peak of D_0 is not broad (Fig. 1b), and moreover the difference between the glassy modulus (E_g) and rubbery modulus (E_r) is not large, as indicated by the small $(1-E_r/E_g)$ in Fig. 1(c). For shape memory polymer, a high value of $(1-E_r/E_g)$ is required, as it strongly correlates with shape fixity and shape recovery.^[28] To increase the modulus difference, a small amount of D2000 was used together with AD to crosslink DGEBF, generating another control sample, D_1 . Clearly, the presence of D2000 decreases the crosslinking density of D_1 , leading to the evident decreased E_r , but the E_g does not change much. Consequently, D_1 shows higher $(1-E_r/E_g)$ than D_0 , while the width of the $\tan\delta$ peak is not improved. To address this issue, APTS was introduced in addition to AD and D2000, and the

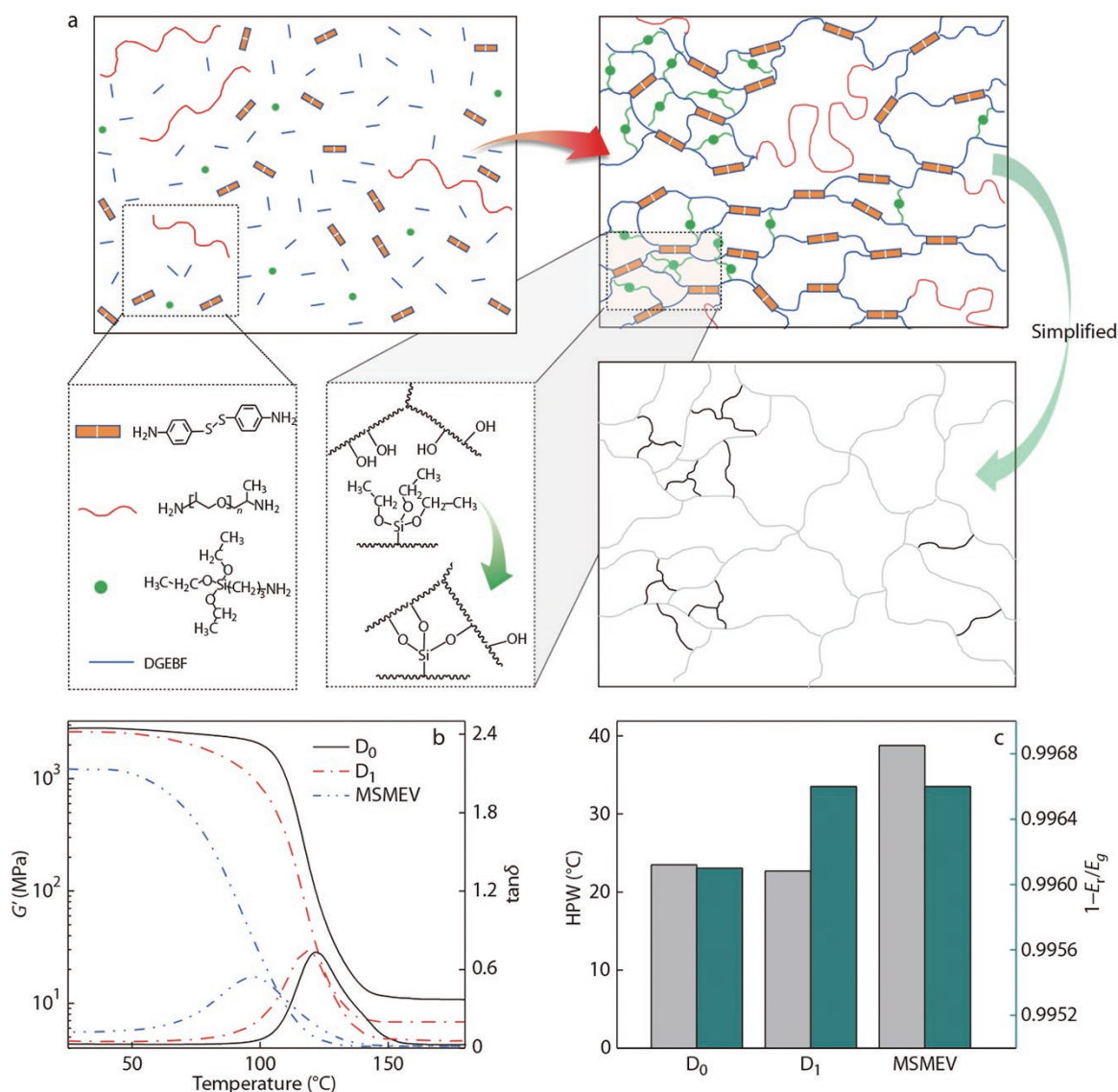


Fig. 1 Fabrication and characterization of MSMEV and the contrast samples. (a) Schematic description of the reaction process of MSMEV. (b) Storage modulus and $\tan\delta$ of MSMEV and the contrast samples. (c) HPW and $(1-E_f/E_g)$ of MSMEV and the contrast samples.

resulting polymer was designated as MSMEV.

The three adjacent alkoxyisilanes of APTS could react with the hydroxyl group produced by the ring-opening of the epoxy. To prove this reaction, we used a small-molecule model reaction between APTS and CD₃OD, and the reaction was monitored by ¹H-NMR measurements (details shown in Fig. S2 in ESI). Upon introducing APTS, we can obviously see that MSMEV shows significantly broadened $\tan\delta$ peak, which is extremely important to achieve MSMPs.^[29] Consequently, the half peak width (HPW) of MSMEV is increased by 15 °C compared with that of D₀ and D₁, as shown in Figs. 1(b) and 1(c) and Table S1 (in ESI). This phenomenon suggests that the presence of APTS increases the network heterogeneity, as APTS bears multi-functional groups which can increase the local crosslinking density.

Shape Memory Properties of MSMEV

To study the shape memory properties of MSMEV, stress-

controlled cyclic thermomechanical testing was performed. In the dual-shape memory test, the MSMEV exhibits ideal shape fixity ratio (R_f) (95.6%) and shape recovery ratio (R_r) (97.0%) during the first dual-shape memory cycle (Fig. S3 in ESI). After four consecutive shape memory cycles, the R_f and R_r are 94.8% and 94.1%, respectively, indicating high repeatability and durability, which are vital for many potential applications such as actuator and aerospace equipment. Moreover, the MSMEV exhibits triple-SMEs under employing separated deformation temperatures (T_{dS}) and fixity temperatures (T_{fS}) within the glass transition window (Fig. S4 in ESI). First, the sample is elongated from the permanent shape (ϵ_A) to $\epsilon_{B,load}$ (8.31%) at T_{d1} (130 °C) and cooled to T_{f1} (72 °C) to obtain the first temporary shape (ϵ_B) with R_f (A→B) of 77.8%. Next, the sample is further elongated at T_{d2} (72 °C) to $\epsilon_{C,load}$ (12.8%) and cooled to T_{f2} (25 °C) to fix the second temporary shape (ϵ_C) with R_f (B→C) of 92.8%. Then, as the temperature rises to the first recovery temperature

($T_{f1}=72\text{ }^{\circ}\text{C}$), the ϵ_C slowly recovers to ϵ_B with $R_f(C\rightarrow B)$ of 93.4%. Upon further heating to T_{f2} ($130\text{ }^{\circ}\text{C}$), the permanent shape A with $R_f(B\rightarrow A)$ of 87.1% is recovered from the first temporary shape B.

Further, a representative quadruple-SME of MSMEV is studied by a similar method (Fig. 2a). The sample is deformed from its permanent shape sequentially at T_{d1} , T_{d2} and T_{d3} . The corresponding T_{ds} are 120, 85 and $72\text{ }^{\circ}\text{C}$, respectively. Quantitatively, $R_f(A\rightarrow B)$ of the first temporary shape (ϵ_A) is 72.0%,

while $R_f(B\rightarrow C)$ and $R_f(C\rightarrow D)$ are up to 77.6% and 97.4%, respectively. During the subsequent heating process, the sample recovers from shape D to shape C, shape B and shape A step by step at $T_{f1}=72\text{ }^{\circ}\text{C}$, $T_{f2}=85\text{ }^{\circ}\text{C}$, and $T_{f3}=130\text{ }^{\circ}\text{C}$, successively. Quantitatively, the $R_f(D\rightarrow C)$ is 87.5%, while $R_f(C\rightarrow B)$ and $R_f(B\rightarrow A)$ are 82.4% and 93.4%, respectively.

The multi-shape memory property of MSMEV samples can also be illustrated visually by the shape design of different patterns. First, we fabricated a piece of MSMEV sample and

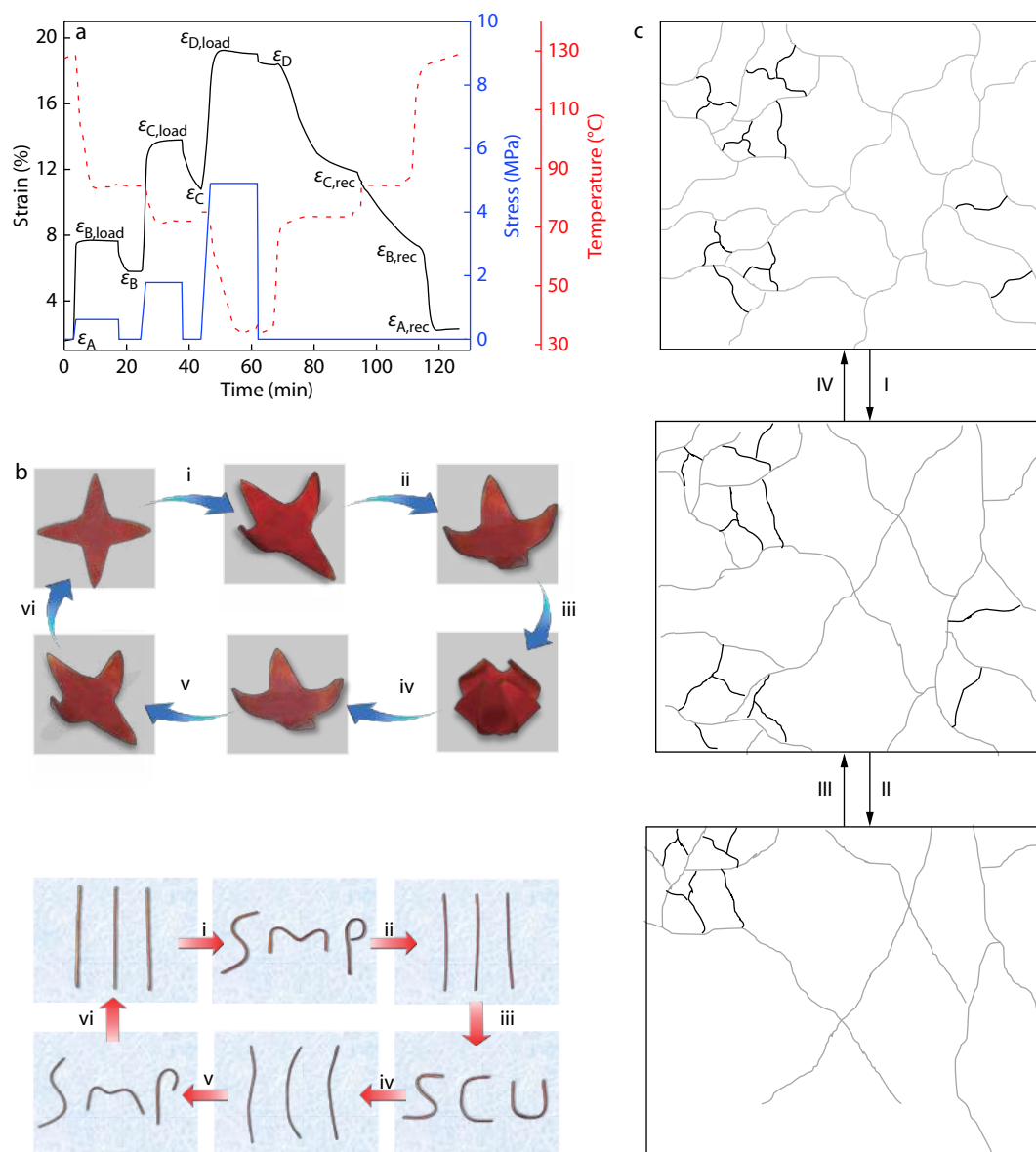


Fig. 2 Multi-shape memory study of MSMEV. (a) A typical quadruple-shape memory cycle. (b) Visual demonstration of the quadruple-shape memory performance of MSMEV: (i) deforming at $130\text{ }^{\circ}\text{C}$ and fixing at $88\text{ }^{\circ}\text{C}$; (ii) deforming at $88\text{ }^{\circ}\text{C}$ and fixing at $76\text{ }^{\circ}\text{C}$; (iii) deforming at $76\text{ }^{\circ}\text{C}$ and fixing at $25\text{ }^{\circ}\text{C}$; (iv) heating to $76\text{ }^{\circ}\text{C}$; (v) heating to $88\text{ }^{\circ}\text{C}$; and (vi) heating to $130\text{ }^{\circ}\text{C}$. (c) Schematic description of the multi-shape memory effect of MSMEV: (I) deforming the MSMEV from shape A to shape B under T_{d1} , at which all the molecular chains are unfrozen. Then cooling down to T_{f1} and the temporary shape B is fixed; (II) deforming the MSMEV under T_{f1} , at which the densely crosslinked regions are frozen while the configuration of the flexible parts is still adjustable. Then cooling down to T_{f2} and the temporary shape C is fixed; (III) heating the MSMEV from T_{f2} to T_{f1} and the sample recovers from shape C to shape B; (IV) heating the MSMEV from T_{f1} to T_{d1} and the sample recovers from shape B to shape A.

make it into a star. Taking advantage of the quadruple-SME of MSMEV, the four angles of the star can be folded up step by step by deforming and fixing the sample at different temperatures, during which three temporary shapes can be obtained (upper panel of Fig. 2b). Similarly, three MSMEV sticks can be deformed in three steps to temporary shapes of “SMP” and “SCU” via quadruple-shape programming (lower panel of Fig. 2b). In the shape recovery steps, the samples are heated to 76 and 88 °C successively, and each intermediate temporary shape can be recovered. Finally, when the samples are heated to 130 °C, the initial shapes, *i.e.* the permanent shapes, can be obtained.

The mechanism of the multi-SME of MSMEV is illustrated in Fig. 2(c). Due to the heterogeneity of the crosslinking network, a distinction exists between the densely and loosely crosslinked regions, of which the relaxation temperatures vary according to the crosslinking density. Thus, at a certain temperature within the glass transition area, a part of the crosslinking network is unfrozen because the average crosslinking density of these zones is low and the network chains can relax at this temperature, while the other parts of the network are still frozen. Thus, the broad thermal transitions can be treated as an infinite number of sharp transitions, which can be further regarded as an elemental memory unit with a corresponding transition temperature. Taking triple-SME as an example, when the deforming temperature T_{d1} is higher than T_g , the whole network is in rubber state and the deformation involves all the polymer chains in the network. Then, after cooling down to T_{f1} , the temporary shape B is fixed due to the frozen regions with higher crosslinking density even though the loosely crosslinked regions are still mobile. When another force is applied on the sample at T_{f1} , the deformation starts again due to the network reconfiguration in the rubbery zones under external forces. After the temperature decreases to T_{f2} , the whole network is in the glassy state, leading to the fixing of shape C. When the temperature raises to T_{f1} and T_{d1} successively, the relaxation of crosslinked regions with varying crosslinking densities begins to happen in sequence, leading to the successive shape recovery of shape B and shape A.

Mechanical and Dynamic Properties of the MSMEV Crosslinking Network

Most malleable epoxy resins have relatively inferior mechanical properties because of their low bond energy of dynamic bonds.^[30–38] However, the MSMEV exhibits high mechanical performances. The strength and Young's modulus of the virgin sample are 73.05 and 2581.1 MPa, respectively, demonstrating excellent mechanical properties derived from the rigid structure of AD and the densely crosslinked domains containing the silyl ether linkages (Fig. 3c). These mechanical properties are higher than those of most reported epoxy vitrimers^[30–38] and superior to most previously reported multi-shape memory polymers (Fig. 3d).^[39–44]

The reversible exchange of aromatic disulfides endows the crosslinking network with dynamic property. The time and temperature dependent relaxation modulus of the MSMEV is tested by DMA. At each temperature, 1% strain is applied and the relaxation modulus is monitored as a function of time. The MSMEV shows significant stress relaxation behavior

(Fig. 3a). Based on the Maxwell model, the relaxation time is defined as the time needed to achieve $G/G_0=1/e$.^[45] As the temperature increases from 140 °C to 190 °C, the relaxation time decreases stepwise. The temperature dependence of the relaxation time of MSMEV follows Arrhenius' law (Fig. 3b). According to the following equation:

$$\ln \tau = \ln \tau_0 + \frac{E_a}{RT} \quad (1)$$

an activation energy (E_a) of 95.72 kJ/mol is calculated for the MSMEV network. Furthermore, the topology freezing transition temperature (T_v), at which the transition from solid to liquid occurs because of the bond exchange reactions in the network, can be calculated according to the Maxwell relation:

$$\eta = G \cdot \tau^* \quad (2)$$

$$G = \frac{E'}{2(1 + \nu)} \quad (3)$$

where ν equal to 0.5 is the Poisson's ratio usually used for rubber, and E' is 4.01 MPa according to the DMA data.^[46–49] For MSMEV, the hypothetical T_v value obtained is 73.01 °C, which is below its T_g but much higher than the reported dynamic epoxy network based on disulfides. In the MSMEV network, the inadaptable crosslinking exists because of the reaction among epoxy, D2000 and 3-aminopropyltriethoxysilane, which results in a slower relaxation at corresponding temperature compared with the reported dynamic system.^[30–38]

The dynamic property imparts the vitrimer with malleability. To demonstrate this, we crush MSMEV samples into small pieces and hot press the pieces under 5 MPa at 200 °C for 20 min. After heat pressing, a recycled sample of full integrity can be obtained due to the exchange between the disulfide bonds (Fig. 3g). The recycled samples are subjected to tensile testing and the result is compared with that of the original sample. The average strength, Young's modulus and fracture strain of the reprocessed sample are 77.1%, 62.3% and 69.8% of those of the virgin sample, respectively, demonstrating a good recyclability (Figs. 3c, 3e and 3f). To evaluate the effect of reprocessing on the mechanical properties of MSMEV, we repeat the crushing-hot pressing cycle and the recycled samples are subjected to tensile testing again. It can be found that the mechanical properties after the second cycle of reprocessing are inferior to that of sample after the first processing cycle (Figs. 3c, 3e and 3f). Like many other vitrimers, the recovery of MSMEV is accompanied by reduction of the mechanical properties due to the simultaneous fracture of the irreversible bonds. With more reprocessing cycles, the decrease of the mechanical performance becomes more significant due to the increasing number of fractured irreversible bonds. However, compared with other recyclable epoxies which possess high recovery ratios but are not robust enough for practical applications, the MSMEV exhibits quite acceptable recovery ratios without sacrificing the mechanical performances. Such a combination of comprehensive properties makes the epoxy vitrimer hold great promise to serve as structural materials in diverse applications.

Taking advantage of the dynamic property and the shape memory property, shape fixing and recovery in the shape memory cycle and the permanent shape retention of MSMEV

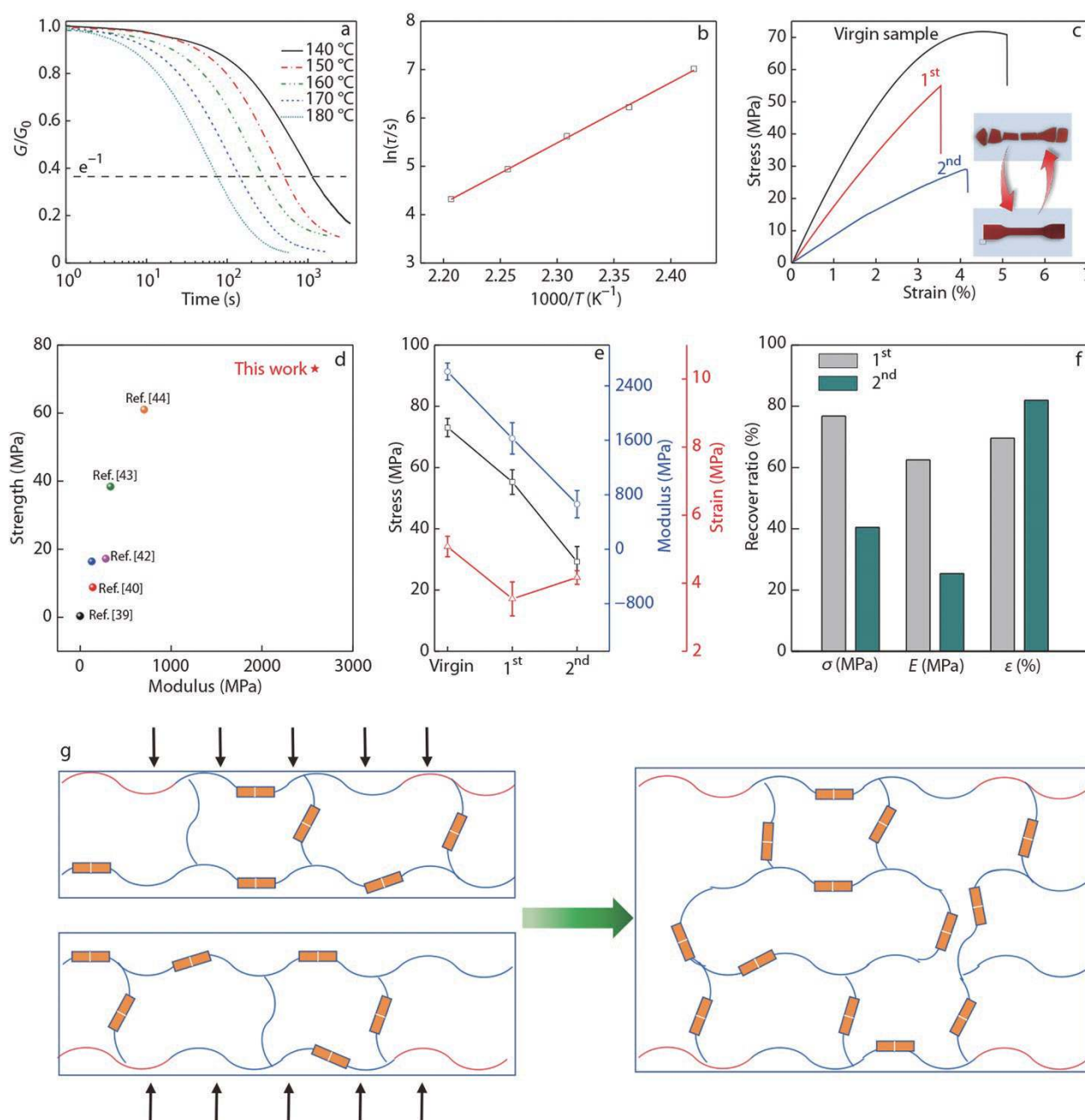


Fig. 3 Mechanical and dynamic properties of the MSMEV. (a) Normalized stress-relaxation curves of MSMEV at different temperatures. (b) Fitting of the relaxation time to the Arrhenius equation. (c) Typical stress-strain curves of the virgin and reprocessed MSMEV. (d) Comparison of strength and modulus among different multi-shape memory polymers with our work.^[39–44] (e) The mechanical properties of the virgin and reprocessed MSMEV. (f) The mechanical recovery ratios of the reprocessed MSMEV. (g) Schematic description of the reprocessing based on disulfide exchange.

can be conducted alternately throughout the cycling experiments. After one shape fixing-recovery cycle, the temperature is elevated to 180 °C and a tensile force is applied on the sample to reach a strain of 6.6%. After the tensile force is removed gradually, the tensile strain cannot recover to the initial value due to the exchanging between disulfide bonds though it slowly decreases to 5.6% due to the residual elasticity derived from the irreversible bonds in the crosslinking network. Then, another shape memory cycle can be conducted

on this permanently stretched sample under a deforming and recovering temperature of 120 °C. Accordingly, shape programming of MSMEV can be realized by deforming samples under different temperatures (Fig. S5 in ESI), which also facilitates the reprocessing of the cured materials without using molds.

Multi-shape Memory Epoxy-carbon Fiber Composites

Epoxy composites have been widely used as structural materials in various applications, such as aerospace vehicles, large

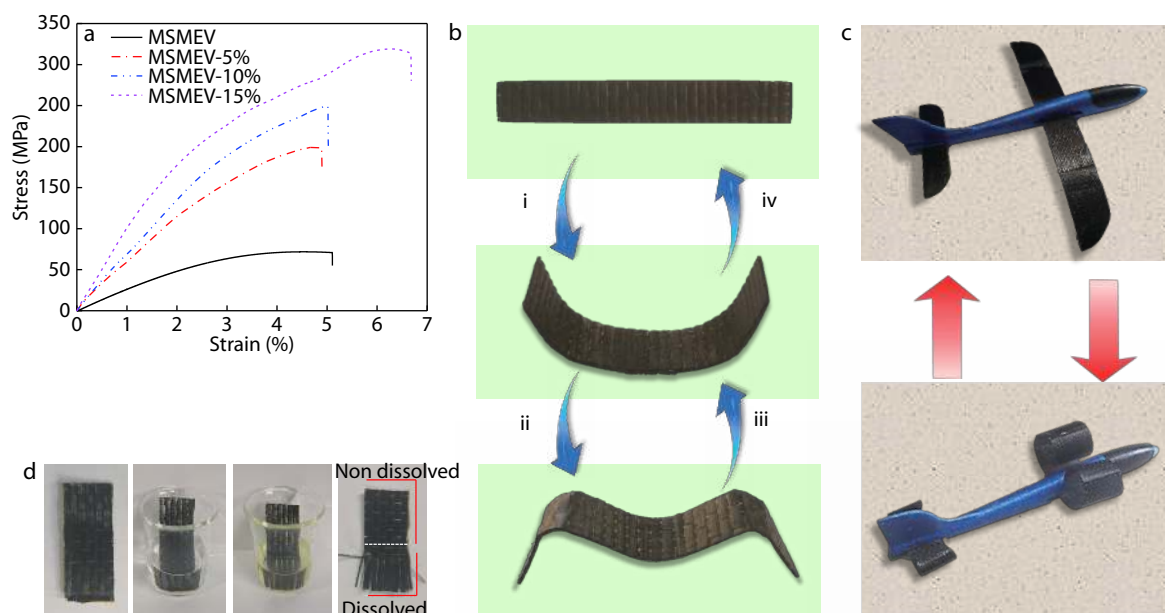


Fig. 4 Multi-shape memory study of epoxy-carbon fiber composites. (a) The stress-strain curves of the composites with different contents of carbon fiber. (b) The triple-shape memory cycle of MSMEV-5%. The conducting temperature of i and iv is 130 °C, while that of ii and iii is 70 °C. (c) The illustration of the folding-unfolding process of the pair of wings made of MSMEV-5% composite for a model aeroplane. (d) Partial dissolution of MSMEV-5% composite in a thiol containing solution.

passenger airliners, limousines, wind turbines and so on because of their ultra-high mechanical property. With multi-shape memory property and reconfigurability, the MSMEV composites can provide a new prospective in diverse applications. As shown in Fig. 4(a), the tensile strength and Young's modulus of the epoxy-carbon fiber composites are significantly increased compared with those of MSMEV: with the content of carbon fiber increasing to 15 wt%, the tensile strength and modulus of the composite increase to 320.9 MPa and 10.18 GPa, respectively, which are 339% and 294% higher than those of the MSMEV, indicating a prominent reinforcing effect of the carbon fiber. Meanwhile, the HPWs of the composites still maintain at high values. When the content of carbon fiber is below 15%, the HPW of each composite is nearly the same as that of the MSMEV, which means the composites still possess multi-shape memory property (Fig. S6 in ESI). To illustrate the triple-shape memory performance of the composites, we conduct the shape fixing and recovering test on a composite strip (Fig. 4b). The sample can be bent into "U" shape under 130 °C and fixed under 70 °C, then deformed into "M" shape under 70 °C and fixed at room temperature. Then the strip can recover to "U" shape and the original shape stepwise under 70 and 130 °C, respectively. As an exhibition of the application of the epoxy-carbon fiber composite in aerospace vehicles, we fabricate a pair of wings made of MSMEV composite for a model aeroplane. As shown in Fig. 4(c), the wings can be folded under 120 °C and fixed at room temperature. When reheated to 120 °C, the wings can well unfold. This process can save a lot of space during the storage and transportation of aerospace vehicles, while the function of the device is not affected. Moreover, due to the dynamic property of the MSMEV network, the carbon fiber can be

chemically recycled. After immersed in the DMF solution of mercaptoethanol for 24 h, the submerged part of the composite sheet exhibits a complete dissolution of the epoxy resin due to the thiol-disulfide exchange reaction (Fig. 4d). Furthermore, we weighed the recovered carbon fiber and compared with the pristine carbon fiber to examine the recovery percent. The result showed that the recovery percent can reach 100% because of the thiol-disulfide exchange reaction. The outstanding mechanical property, multi-shape memory performance and recyclability of the fillers make the composites promising when serving as structural materials.

CONCLUSIONS

In summary, we prepared a multi-shape memory epoxy vitrimer (MSMEV), which not only avoids tedious synthesis procedure, but also exhibits high mechanical property, multi-shape memory property and malleability. In the design of the crosslinking network, we cured diglycidyl ether of bisphenol F (DGEBF) with 4-aminophenyl disulfide, poly(propylene glycol) bis(2-aminopropyl ether) and γ -aminopropyltriethoxysilane. In the resulting material, the disulfide bonds and silyl ether linkages enable malleability of the epoxy network with acceptable recovery ratios, while the silyl ether linkages impart the network with higher heterogeneity and thus broadened glass transition region, endowing the epoxy resin with multi-shape memory property. Moreover, the high crosslinking density and rigid structure provide the MSMEV with high tensile strength and Young's modulus, which are higher than those of most existing epoxy vitrimers. By incorporating carbon fibers, multi-shape memory composites with superior mechanical property and recyclability of fillers can be fabricated, which hold great promise in applications as

structural materials.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2538-7>.

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