Shape-programmable and healable materials and devices using thermo- and photo-responsive vitrimer

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Keywords: shape-programming, vitrimer, self-healing, printed electronics, morphable devices

Abstract

Shape morphing materials have been extensively studied to control the formation of sophisticated three-dimensional (3D) structures and devices for a broad range of applications. Various methods, including the buckling of pre-strained bilayer composites, stimuli-responsive shape-shifting of shape memory polymers, and hydrogels, have been previously employed to transform 2D sheets to 3D structures and devices. However, the residual stress locked in these shape-shifting structures will drive them to gradually revert to their original layouts upon the removal of external stimuli or constrains. Here, we report a multistimuli-responsive vitrimer (m-vitrimer) bearing thermal- and photo-reversible disulfide bonds as shape programmable and healable materials for functional 3D devices. The mechanical properties and thermomechanical properties of vitrimer were tuned by altering the disulfide content and catalyst loading. Heat and light exposure induces effective stress relaxation and network rearrangement, enabling material shape programming and healing. We demonstrate that printed flexible smart electronics are fabricated using the m-vitrimer as a matrix and printed conductive silver nanoparticles as conductive wire. The printed electronics possess good electro-mechanical properties, strong interfacial bonding, and thermal- and photo-responsive shape programming. Moreover, the m-vitrimer can be healed upon damage by heat and light, which partially restores silver conductivity and protect the electronics from further damage. The converging of multi-stimuli-responsive polymers and printed electronics for functional 3D devices have the potential of finding broad applications in smart and morphing electronics, biomedical devices, and 4D printing.

1. Introduction

Three-dimensional (3D) architectures capable of altering the shape on-demand are highly desirable in many applications, including actuators [1, 2], deployable devices [3, 4], transformable electronics [5, 6], and biomedical devices [7–9]. The most direct way to achieve shape-shifting structures is to use stimuli-responsive shape programmable materials, which can change the configuration in response to external stimuli, such as heat or light [10–13]. Diverse shape programmable materials and composites, including shape memory polymers (SMPs) [14–16], hydrogel composites [17–19], liquid crystal elastomers (LCEs) [20–22], and magnetoactive elastomers [23–26], have been extensively investigated for shape-shifting structures and devices [27]. However, there are some drawbacks to these conventional shape-programming materials. For example, hydrogels and LCEs cannot lock the programmed shape upon the removal of external stimuli. By contrast, SMP can be programmed to a temporary shape at stress-free states and then recover to their original shape under external stimuli [28–30]. Recently, Ze et al reported the magnetic SMP with integrated shape manipulation, including rapid, untethered, remote actuation, and shape locking capability [31]. However, in SMPs, the stored strain energy would drive the programmed structures to gradually recover...
its original shapes, especially near the elastic regime. Besides, buckling and strain mismatch of pre-strained and bilayer composites have been investigated for complex shape-shifting [32, 33]. For example, Rogers and coworkers exploited the pre-strained elastomers substrate and compressive buckling of two-dimensional (2D) precursors to transform the geometry into desired 3D shapes [34, 35]. But one disadvantage for this type of mechanically guided shape-shifting structures is that they cannot completely hold programmed 2D/3D shapes when releasing from the assembly platform due to the existence of residual stress. Moreover, the residual stress locked in the above shape-shifting structures may compromise the mechanical properties and material lifetime during service. Therefore, there is a need to develop reconfigurable 3D structures and devices with enhanced stability and durability to satisfy numerous applications.

In the past decade, covalent adaptive network polymers or vitrimer, containing dynamic chemical bonds in polymer networks, have emerged as a new class of functional materials with a combination of the desirable attributes of elasticity in cross-linked thermosets and fluid-like plastic flow in thermoplastics [36–40]. The bond exchange reactions (BERs) between the dynamic bonds lead to vitrimer network rearrangement upon external stimuli, enabling some interesting properties, such as material reshaping, reprocessing, and self-healing. In 2011, Leibler and coworkers introduced the epoxy vitrimer based on catalyzed transesterification for reshaping and reprocessing at elevated temperature (>130 °C) [41]. Later than, a vast array of dynamic materials using transesterification [42–44], disulfide metathesis [45–48], imine exchange [49–51], boronic esters exchange [52–54], siloxane exchange [55–57], to name a few, have been exploited to construct vitrimer with stimuli-responsive self-healing, reprocessing and recycling of structures and devices [58–61]. Recently, Xie and coworkers incorporated dynamic bonds into SMPs for shape reprogramming [62–64]. The permanent shape of SMPs can be altered via the dynamic reaction-induced plasticity. The use of stimuli-responsive vitrimer enables robust shape-programming for functional structures [65–67]. However, most of the previous vitrimer based shape-programming structures and devices respond to a single stimulus, and complex synthesis is usually involved in accommodating orthogonal dynamic reactions in the single component, which would limit their broad application.

In this work, we present the facile strategy that utilizes a single component thermal- and photo-responsive vitrimer to fabricate shape-programmable structures and functional devices. The scheme starts with the synthesis, characterization of mechanical and thermomechanical properties of disulfide containing epoxy vitrimer with different disulfide and catalyst loading. The effect of temperature and ultraviolet (UV) light intensity on stress relaxation were systematically investigated, and the disulfide exchange reaction mechanism under different stimuli was revealed. The 2D vitrimer structures were then integrated with printed conductive wires and electronic components, leading to printed flexible smart electronics (PFSE) with on-demand shape programming. In addition, healability of m-vitrimer was achieved under direct heat and intense pulsed light.

2. Materials and methods

2.1. Preparation of the m-vitrimer

The m-vitrimers were synthesized according to the previous literature [59]. Bisphenol A diglycidyl ether epoxy oligomer (DEGVA)(EPON 828, Hexion Inc. Pueblo, CO, USA) and a thiol based curing agent with a stoichiometric epoxide/thiol ratio were used. The thiol curing agents contain polysulfide oligomer (Thioplast G44, $M_n \sim 1100$ g mol$^{-1}$, AkzoNobel BV, Germany) and 2,2-((ethylenedioxy) diethanethiol (EDDET) with thiol molar ratio ranging from 10/0 to 2/8. The polysulfide oligomer has a sulfur content of 37–38 wt%. In addition, 0.5 or 1.0 wt% of 2, 4, 6-tris-dimethylaminomethyl phenol (Epikure 3253, Hexion Inc. Pueblo, CO, USA) was used as a catalyst. The detailed chemical composition for the samples can be seen in Table S1. The disulfide content in the m-vitrimer increases with G44 ratio. The above chemicals were manually mixed and degassed under vacuum before pouring into an aluminum mold. The resin was pre-cured at 60 °C for 2 h, then post-cured at 90 °C for 1 h in a convection oven (Model 13-247-750 G, Fisher Scientific, Pittsburgh, PA, USA). The samples were stored at room temperature for at least two days before tests. The vitrimer sample was denoted as Vx-y, where x indicates the thiol molar content from G44, and y is the catalyst weight content. The m-vitrimer containing 40% molar thiol from G44 and 0.5 wt% of catalyst was mainly used in this paper.

2.2. Printing of circuit

The printing of silver nanoparticle-based ink (ME603, DuPont Inc. USA) was conducted on a home-made direct ink writing (DIW) printing setup. The pressure in the syringe was controlled by a pressure regulator (Ultimus V, Nordson EFD, East Providence, RI, USA). Printing paths were created by computer-aided design drawings (SolidWorks, Dassault Systèmes) and converted into G-code by Repetier-Host software. A nozzle with a 0.61 mm inner diameter was used. With a pressure of 15 psi and a printing speed of 3 mm s$^{-1}$, silver
ink with consistent cross-sectional areas can be deposited on the m-vitrimer substrate. After printing, the circuit was thermally cured in a convection oven at 120 °C for 20 min.

2.3. Characterization

Scanning electron microscopic (SEM) images were acquired on a Hitachi SU8010 SEM (Hitachi Ltd, Chiyoda, Tokyo, Japan). Optical microscopic images were obtained on a 7×-90× Stereo Microscope (Amscope, Irvine, CA, USA). Fourier transform infrared (FTIR) spectra were recorded by a Nicolet iS50 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA) by averaging 32 scans at a resolution of 2 cm⁻¹. Uniaxial tension tests were performed on a universal material testing machine (Criterion Model 41, MTS, Inc. Eden Prairie, MN, USA) at room-temperature using rectangular samples with a dimension of about 30 mm × 4 mm × 1 mm. The normal tensile tests were conducted at a stretching rate of 50 mm min⁻¹. Cyclic loading/unloading and step cyclic tests were performed at a stretching rate of 30 mm min⁻¹. Temperature variant tensile tests were conducted on dynamic mechanical analysis (DMA) tester (model Q800, TA Instruments, Inc. New Castle, DE, USA) with a strain rate of 50% min⁻¹. The DMA test samples had a dimension of about 20 mm × 4 mm × 1 mm. DMA tests with temperature and time sweep were also conducted on the DMA tester using multi-strain rate mode under a constant amplitude of 30 µm, frequency of 1 Hz, and force track of 125%. The temperature sweep was performed from −50 °C to 120 °C at a heating rate of 3 °C min⁻¹. UV-DMA was conducted by mounting a UV lamp (OmniCure S2000, Lumen Dynamics, Ontario, Canada) to a DMA test. Time sweep UV-DMA was performed at room temperature with different light intensity to trace the evaluation of storage modulus upon applying and extinguishing UV irradiation. Light intensities were measured using a radiometer (IL1400A, International Light Technologies, Peabody, MA). The stress-relaxation experiments of the m-vitrimer were performed on a DMA tester. For heat-induced stress relaxation, the samples were allowed 15 min for the reaction temperature equilibrium before the test. For photo-induced stress relaxation, the UV lamp was used for UV light exposures with different light intensities. After equilibrium at predetermined condition, a constant strain of 3% was applied for the stress relaxation test. The decrease of stress was recorded, and the stress relaxation modulus was calculated and further normalized by the initial modulus.

2.4. Electrical properties characterization

The DMA tester was combined with a multimeter (Keithley2100, Keithley Instruments, Cleveland, OH, USA) to measure the electro-mechanical properties of the printed conductive wires. A rectangular m-vitrimer strip (dimension: ~30 × 3 × 1 mm) with a printed silver line on the surface was used for the tension test. To record the change of resistance, two copper electrodes connected the printed silver wire was connected to a multimeter, which was controlled by a LabVIEW data acquisition program. To calculate the resistivity of the printed silver wires after thermal curing, the image of the cross-sectional area of these wires was taken by a microscope and were analyzed by ImageJ software.

2.5. Shape programming and healing experiment

Shape programming demonstration was achieved by manually deforming the structures first or wrapped onto a surface. Heat-induced shape programming was carried out by heating using a heat gun for 2–3 min or treated in an oven at 80 °C for 10–20 min. Photo-induced shape programming was conducted by treated under UV light (light intensity: 60 mW cm⁻²) for 2–3 min. In the self-healing experiment, the m-vitrimer or printed circuit was scratched or cut completely by a sharp blade first. For completely cut samples, the crack surface was put together carefully with gentle force. In the case of thermal healing, the sample was put in an oven at 90 °C for 20 min. The healing event was also performed using a photonic sintering system (Xenon RC-847, Polytec Ltd, Wilmington, MA, USA) with high energy intense pulsed light (IPL).

3. Result and discussion

3.1. Fabrication and properties of multi-stimuli-responsive vitrimer

Among the various dynamic bonds, disulfide is very promising due to the advantages of easy fabrication from commercially available raw chemicals in a scalable manner, good chemical compatibility in diverse materials, and multiple stimuli-responsiveness, such as heat, light, and pH [68]. Here, heat- and light-responsive disulfide based vitrimer will be developed and harnessed to achieve on-demand shape programming. As shown in figure 1(a), after manually bending the vitrimer sample followed by exposure to heat or light, the straight strip can be reshaped to the stress-free bending shape. To realize this, a series of epoxy m-vitrimers containing dynamic disulfide bonds were first fabricated using commercially available chemicals, including a polysulfide oligomer (G44), DEGBA epoxy oligomer and EDDET chain extender (figure 1(b)). Tertiary amine of 2, 4, 6-tris-dimethylaminomethyl phenol acted as a catalyst for both curing...
Figure 1. Synthesis and characterization of disulfide-based epoxy m-vitrimer. (a) Schematic of the shape programming process of the m-vitrimer via disulfide BER upon heat or light irradiation. (b) Chemical structures of the monomers used to prepare the epoxy m-vitrimer: DGEBA epoxy oligomer, polysulfide cross-linker, di-thiol spacer, and amine catalyst. (c) The tensile stress-strain curves of a series of m-vitrimers containing different polysulfide and catalyst. (d) The tensile stress-strain curves of m-vitrimer (V40-0.5) for 30 repeated cycles. (e) The temperature dependence of storage modulus and tan delta of m-vitrimers V40-0.5 and V40-1.0 tested by DMA.

reaction and disulfide BER. The curing reaction between thiol and epoxide in the epoxy oligomer proceeded to form a cross-linked polymer network. FTIR spectra suggested curing reaction occurred as indicated by the complete disappearance of S-H stretching vibration (2560 cm$^{-1}$), a sharp decrease of epoxide ring stretching vibration (916 cm$^{-1}$), and a rise in intensity of hydroxyl stretching vibration (3460 cm$^{-1}$) (figure S1 (available online at stacks.iop.org/MFM/3/045001/mmedia)).

After curing, the m-vitrimers show different mechanical properties as evaluated by the tension tests. Figure 1(c) shows the thiol ratio in G44 and EDDET has a great effect on mechanical properties. The tensile strength and strain at break can be tuned by altering the content of polysulfide G44 (figure S2). For example, the strain at break decreases from 377% to 85% for V20-1 and V100-1, respectively. The catalyst also has an influence on the mechanical properties. The m-vitrimer with 40% of thiol from G44 show fracture strain of 250% and 300%, Young’s modulus of 3 MPa and 5 MPa for 0.5 wt% and 1.0 wt% catalyst, respectively (figure 1(c)). The m-vitrimer mainly displayed elastic response at room temperature. Figure 1(d) shows the cyclic tensile properties of the m-vitrimer of V40-0.5 for 30 repeated cycles within a maximum applied strain of 100%. In the first cycle, there is about 17% of irreversible strain. After the first cycle, the stress-strain curves show a slow increase in plastic strain. This residual strain can be attributed to both viscoelasticity and the dynamic exchange reaction of the m-vitrimer. The irreversible strain increases with the maximum applied strain, as shown in the step-cycle loading-unloading test (figure S3). Quantitative results show the plastic strain increases linearly with the applied strain (figure S4). Because the external stress can be partially released via network rearrangement even at room temperature. Given the same deformation rate, larger applied strain means longer stress relaxation time, leading to larger plastic deformation, which will be discussed later. In addition, the residual strain increases with temperature. Because disulfide BER can be accelerated at higher temperatures, resulting in enhanced plastic deformation. This effect is more obvious for the m-vitrimer with higher disulfide content. Taking the sample of V100-1 (disulfide content of 24.5 wt%) as an example, the stress-strain behavior shifts from (visco)elastic response at 30 °C to plastic response above 50 °C as indicated by an obvious yielding (figure S5). Therefore, the m-vitrimer with lower content of polysulfide and less catalyst would show better cyclic mechanical properties.

The thermomechanical properties of the m-vitrimers can also be tuned by altering the catalyst content. As shown in figure 1(e), for the m-vitrimers containing 40% of thiol from G44, when the catalyst loading is reduced from 1.0 wt% to 0.5 wt%, $T_g$ decreases from 9.8 °C to 1.8 °C, and the rubbery modulus decreases from 2.8 MPa to 2.2 MPa, respectively. This can be attributed to different network structures during curing. Above $T_g$, the m-vitrimers behave like a chemically cross-linked elastomer. Interestingly, the m-vitrimers show an elastic-to-viscoelastic-liquid transition above a critical temperature, called topology freezing transition temperature ($T_{f}$) [37, 69], owning to a short lifetime of disulfide bond at elevated temperatures. Activated by the base catalyst, disulfide BER in the m-vitrimer can be accelerated at high temperatures.
Table 1. Comparison of mechanical and thermomechanical properties of epoxy m-vitrimer with different compositions.

| Sample   | $T_g$(°C) | $T_r$(°C)b | $E_r$ (MPa)$^c$ | $E$ (MPa)$^d$ | Break strain (%) | Break strength (MPa) |
|----------|-----------|------------|----------------|--------------|-----------------|---------------------|
| V20-1    | 19.0      | 110.6      | 3.4            | 5.46 ± 0.10  | 377.4 ± 12.2    | 2.22 ± 0.09         |
| V40-1    | 9.8       | 100.0      | 2.8            | 5.16 ± 0.50  | 299.7 ± 15.1    | 1.93 ± 0.02         |
| V40-0.5  | 1.8       | 112.9      | 2.2            | 3.01 ± 0.10  | 254.7 ± 34.9    | 1.42 ± 0.06         |
| V60-1    | 8.8       | 100.2      | 3.6            | 3.59 ± 0.32  | 183.2 ± 3.0     | 1.36 ± 0.03         |
| V80-1    | −0.7      | 92.0       | 3.4            | 3.54 ± 0.13  | 102.7 ± 12.4    | 1.34 ± 0.06         |
| V100-1   | −9.0      | 90.0       | 3.2            | 5.10 ± 0.5   | 85.5 ± 12.1     | 1.07 ± 0.07         |

$^a$Sample denoted Vx-y: x molar content of thiol from polysulfide and y weight content of the catalyst.
$^b$Topology freezing transition temperature was determined by DMA with a shape decrease in storage modulus at elevated temperature.
$^c$Rubbery modulus at 60 °C.
$^d$Young's modulus at room temperature calculated by the secant modulus at 1% strain.

Lower $T_g$ suggests faster network rearrangement upon heating. The $T_r$ of the m-vitrimer decreases from 112 °C to 100 °C with the catalyst loading of 0.5 wt% to 1.0 wt%, respectively. Because a high catalyst loading can accelerate the disulfide BER. Besides, the thermomechanical properties of m-vitrimer can be tuned by changing polysulfide content. For example, $T_g$ increases from −9 °C for V100-1 to 19 °C for V20-1 (Figure S6). The rubbery modulus varies in the range of 2.8–3.6 MPa. Meanwhile, $T_r$ of m-vitrimers decreases from 110 °C (V100-1) to 90 °C (V20-1) by increasing the G44 content. The mechanical and thermomechanical properties of epoxy vitimer are summarized in table 1. Based on the above results, the m-vitrimer V40-0.5 was focused for further study because it has the lowest Young's modulus, excellent cyclic mechanical properties, good dimension stability (high $T_r$), and moderate polysulfide content (good stimuli-responsive performance).

3.2. Heat- and light-induced stress relaxation and plasticity

As above-mentioned, the m-vitrimer has the capability of network rearrangement under external stimuli, which was evaluated by DMA via stress relaxation tests. Figure 2(a) shows that the normalized stress relaxation modulus gradually decreases with time at different temperatures (from 30 to 70 °C) for the m-vitrimer (V40-0.5). Because the catalyst can activate disulfide BER upon increasing temperature. According to Maxwell model, the relaxation times ($\tau$) were determined as the time required to relax to 1/e (36.7%) of the initial modulus. The relaxation time decreases with the increasing temperature. The fitted $\tau$ decreases from over 10$^4$ s at 30 °C to less than 10$^2$ s at 70 °C. The Arrhenius equation was used to fit the temperature-dependent stress relaxation time, and the activation energy was evaluated to be 81.8 ± 4.7 kJ mol$^{-1}$ (figure S7). The relaxation activation energy is affected by the reaction kinetics of disulfide BER and network structure [70]. The disulfide BER is sensitive to temperature, which is beneficial for the application. On the one hand, large $\tau$ affords excellent dimension stability at room temperature for service. On the other hand, decreasing $\tau$ at elevated temperatures allows rapid shape programming and material healing.

Heat-induced plasticity can be achieved in the m-vitrimer due to the thermal-responsive BER, which was evaluated by large strain stress relaxation tests. Figure 2(b) shows the partial stress relaxation of m-vitrimer at 60 °C. The m-vitrimer was first stretched to 100% of strain. While maintaining this strain, stress relaxation was monitored. The partial stress relaxation was obtained by controlling the relaxation for 70 s followed by the removal of the external stress to reach its equilibrium length. Subsequently, two more stress relaxation cycles (applied strain of 100% to its original length) were conducted on the same sample in a similar manner until the complete stress relaxation. It can be seen that large plastic deformation was achieved after releasing the stress at elevated temperatures. Consecutive stress relaxation cycling experiments were also conducted. As shown in figure 2(c), the m-vitrimer was stretched by 40% at 70 °C in each of three consecutive loadings. In each loading, the stress could be completely relaxed within 180 s. A prominent plasticity effect can be achieved without material integrity deterioration. Interestingly, the stress relaxation times of the three consecutive cycles are the same, and the normalized stress relaxation curves overlapped (figure S8). Therefore, the heat-induced disulfide exchange is an associative exchange reaction without changing the network cross-linking density.

Besides, BER of disulfide can proceed under light, enabling stress relaxation and network rearrangement. As shown in figure 2(d), with the UV irradiation intensity of 5 mW cm$^{-2}$, the relaxation modulus gradually decreased with $\tau$ of 1073 s at room temperature. The stress relaxation process was accelerated by increasing light intensity. The $\tau$ value decreases with increasing light intensity and then gradually levels off when light intensity is over 20 mW cm$^{-2}$ (figure S9). To further illustrate the effect of UV irradiation on the stress relaxation, intermittent UV irradiation was applied at room temperature (figure 2(e)). During a room...
temperature stress relaxation test, intermittent UV irradiation (40 mW cm\(^{-2}\)) was applied three times (at 385 s, 1060 s, and 2130 s) for about 70 s in each time. Stress relaxation is very slow without shining UV light. Upon UV irradiation, the stress drops dramatically. Quantitative analysis shows the relaxation modulus reduced over 40% of the initial value upon the first UV irradiation at 40 mW cm\(^{-2}\) for 70 s (Figure S10). Similar accelerated stress relaxation was observed using a lower light intensity (such as 10 mW/cm\(^2\)), but the relaxation modulus decayed much slower. When the light was turned off, the stress relaxation can still proceed with a slower rate. After repeating the above process three times, the initial stress could be completely released. As the sample temperature only increased around 5 °C after UV irradiation, the rapid stress relaxation was dominated by the photo-induced dynamic reaction.

Consecutive large strain stress relaxation was also achieved by UV irradiation. As shown in figure 2(f), the m-vitrimer was first stretched to 40% of strain at room temperature followed by shining UV light (20 mW/cm\(^2\)). After about 600 s, complete stress relaxation was observed, and another 40% of strain was applied. Finally, a plastic strain of 160% can be achieved after four cycles. It is noted that, under constant UV irradiation, the stress relaxation time decreases from 174 s to 51 s for the first and fourth testing cycles, respectively (figure S10). This can be attributed to a different reaction mechanism comparing with the heat-induced disulfide exchange reactions. To understand the unique stress relaxation behavior under UV light, the evolution of storage modulus (G') under UV irradiation was measured by UV-DMA. Figure 2(g) shows G' decreases 0.45 MPa during 10 min of light exposure (light intensity of 20 mW cm\(^{-2}\)) during the DMA test. This can be ascribed to the rise in temperature and bond cleavage. The G' decreases around 0.10 MPa when the temperature changes from 27 °C to 32 °C (figure S11). Therefore, the drop of G' is mainly attributed to the disulfide bond cleavage by UV irradiation. After turning off the UV light, the G' recovers 0.1 MPa within 10 min. To further study the reversibility of disulfide exchange, the G' was monitored by

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**Figure 2.** Stress relaxation and reaction mechanism of epoxy m-vitrimer via disulfide exchange under heat and light. (a) Experimental result and Maxwell model fitting of stress relaxation curves at various temperatures. (b) Partial stress relaxation and shape retention at 60 °C. (c) Consecutive stress relaxation cycles at 70 °C. (d) Stress relaxation under various UV light intensities at room temperature. (e) Partial stress relaxation of m-vitrimer using intermittent UV irradiation (40 mW cm\(^{-2}\)) for about 70 s each time at room temperature. (f) Consecutive stress relaxation cycles with UV irradiation of 20 mW cm\(^{-2}\) for four cycles. (g) Time-dependent storage modulus evolution during and after UV irradiation (20 mW cm\(^{-2}\)) for 10 min at room temperature. (h) Time-dependent storage modulus under intermittent UV irradiation (20 mW cm\(^{-2}\)) with alternating 5 min UV on and off for eight cycles at room temperature. The storage modulus was further monitored after turning off UV light after 10 h. (i) Mechanisms of thermo- and photo-reversible disulfide exchange reactions.
applying repeated intermittent UV irradiation. As shown in figure 2(h), the G’ shows cyclic decrease and increase during the UV light on and off cycles. The G’ decreasing (UV on) rate is fast in the first cycles (0.059 MPa min\(^{-1}\)) and then slows down with more cycles (0.038 MPa min\(^{-1}\) in the fourth cycle). In contrast, the G’ recovery (UV off) rate increases from 0.014 MPa min\(^{-1}\) in the first cycle to 0.027 MPa min\(^{-1}\) in the fourth cycle. After five cycles, the decreasing and the increasing rate of G’ becomes comparable. Using a lower light intensity (10 mW cm\(^{-2}\)) exposure, G’ decreases at a slower speed (0.028–0.014 MPa min\(^{-1}\)), and similar reversibility was observed (figure S12). Interestingly, the G’ can recover substantially at ambient conditions after an extended time (such as 10 h), indicating excellent reversibility.

On the basis of the above results, different mechanisms of heat and light-induced disulfide exchange were summarized in figure 2(i). The heat-induced disulfide exchange involves the formation of sulfur-based anions by a base catalyst [71]. The sulfur-based anion is an intermediate state with a very short lifetime. The disulfide bond cleavage and formation simultaneously occur. In contrast, the light-induced disulfide exchange follows a radical-mediated process [71, 72]. Upon light-irradiation, the disulfide bond breaks into two active sulfur-centered radicals that would attack other disulfides through exchange reactions. As the sulfur-centered radical has a longer lifetime, continuous light radiation can cleave more disulfide bonds in m-vitrimer and generates an increasing amount of free sulfur-centered radicals. Moreover, the free sulfur-centered radical is relatively stable and can be recombined for long enough time. Compared with the previous photo-induced plasticity using allyl sulfides [73], there are two advantages: first, the m-vitrimer is cost-effective without using any complicated synthesis; second, no photoinitiator is needed to activate the dynamic reaction, which enables unlimited BER.

3.3. Properties of printed circuits

The above epoxy m-vitrimer was utilized as a substrate for printed circuits. The silver ink was printed onto the epoxy m-vitrimer substrate using a home-made DIW printer (figure S14). As shown in figure 3(a), the silver ink was deposited on the m-vitrimer film by a pneumatic controlling system (video S1). After printing and thermal curing, the printed circuit composed of conductive silver wires on m-vitrimer substrate was obtained (figure 3(b)). The micromorphology and the cross-section of the silver wire were observed by SEM (figure 3(c)). The wire is flat after curing, and the silver nanoparticles are annealed to form a conductive network. The silver particle has good contact and bonding with the epoxy m-vitrimer. The tensile test further suggests the good mechanical properties and excellent interfacial bonding of the printed circuit. The printed circuit shows a breaking strain as high as 150% (figure S15). The fracture strain and modulus of the silver wire using a similar curing condition were reported to be around 160% and 100 MPa [74], respectively. Upon fracture, microcracks were formed in the silver without interface debonding (figure S16). The good interfacial bonding can be attributed to the strong interaction between sulfide and silver, such as thiol-silver interaction [75].

The strain-dependent resistance of the circuit was measured during a tension test. As shown in figure 3(e), the resistance of the printed wire increases slowly at low strain and changes more dramatically at a higher strain. For example, the resistance increases five times after stretching to 30% (figure S17). At a strain of 140%, the resistance increase to about 300 times its original resistance. The change of resistance after deformation could be attributed to both decrease in cross-sectional area and forming microcracks (figure S16). The cycling performance of the printed circuit was also tested. The circuit with a printed wire on the m-vitrimer substrate was cyclically loaded/unloaded using the DMA tester. During the test, the samples were elongated and relaxed at 1.5 MPa min\(^{-1}\); at the end of each cycle, the samples were left unloaded for 30 s to provide the relaxation for the silver wire to recover. Figure 3(f) shows the cyclic stress-strain curves for 100 cycles under controlled stress mode (0.22 MPa). For the first cycle, the maximum strain is about 5%. The relatively residual strain of the circuit would decrease, and the stress-strain curves would gradually overlap. After 100 cycles, the maximum residual strain increased to 14.5%. Therefore, the residual strain increased by nearly 10% in 100 cycles after the first cycle. This is attributed to the material plasticity by the disulfide exchange. Figure 3(f) shows the actual resistance of the cured silver wire on the vitrimer elastomer for the cyclic test. The resistance increases with the number of cycles during the loaded/unloaded cyclic test. In each cycle, the sample was first stretched then unloaded to recover, and the resistance would fluctuate between a minimum and maximum value. After allowing for relaxation at the released state, the resistance would substantially recover. The resistance at the strain minima increased from 0.2 Ω to 0.5 and 2.1 Ω after the 30th and 100th unloading cycle, respectively. These results suggest good cycling electro-mechanical properties of the printed circuits.

3.4. Shape programming of printed electronics

Based on the above results, highly deformable and shape programmable printed electronics can be fabricated. The stimuli-induced plasticity of the m-vitrimer enables shape programming of the printed
circuit from 2D to 3D configurations, such as from flat films to Sine, helical, and semi-sphere shape, using direct heating (figure S18). As shown in figure 4(a), a printed 2D circuit was linked into a circuit with an LED on. The 2D circuit was first wrapped onto a cylinder surface manually followed by treating with a heat gun for about 2 min (video S2). After cooling, the circuit adapted to the free-standing bending shape without losing conductivity. As the mechanical property of the circuit was maintained, the programmed circuit is still flexible and deformable.

Besides, UV irradiation could also be utilized to induce plastic deformation for shape programming (video S3). Figure 4(b) shows the 2D film can also be programmed into 3D shape using UV light. The 2D circuit was bent by a glass slide followed by exposure to UV irradiation (~60 mW cm$^{-2}$) from the top for 2 min. After the removal of the glass slide, the circuit transformed into a free-standing bending shape. Similarly, shape programming to recover the flat shape could also be achieved by both direct heating and UV light. During all of the shaping programming process, the good conductivity was maintained.

Furthermore, we demonstrate the Miura-ori design can be utilized to enhance the shape programming capacity of the printed electronic devices. Figure 4(c) shows a flat electronic device with a conductive wire, and an LED on a flat Miura-ori structure was designed and fabricated using the m-vitrimer substrate with the printed silver wire. The device was manually folded and then exposed to UV light (~60 mW cm$^{-2}$) for 2 min to program the permanent shape via photo-induced plasticity. Upon force removal, a free-standing and highly deformable 3D shaped Miura-ori device was obtained according to the design shape. Owning to the good electric-mechanical properties and excellent reversibility of dynamic disulfide, the shape programming of the printed flexible circuit can be repeated many times.

3.5. Self-healing behavior

Despite the excellent cycling performance, self-healing is desirable to further enhance the durability and lifetime of the devices. Owning to the disulfide BER, the epoxy m-vitrimer is capable of healing the crack upon heating or light irradiation, which was evaluated by tensile tests. Figure 5(a) shows the tensile stress-strain curves of the virgin m-vitrimer and healed samples under different healing conditions. The m-vitrimer elastomer was first cut and then healed by direct heating. The sample can be completely healed by direct heating in an oven at 90 °C for 20 min. To accelerate healing speed, the high energy IPL was used instead of UV light for photo induced healing. As shown in figure 5(b), a strip sample was completely cut using a sharp
Figure 4. Images of heat- and light-induced shape programming of printed electronics. (a) An initially printed flat circuit was programmed to a free-standing bending shape by wrapping on to a cylinder followed by treating with a heat gun for about 2 min. (b) A printed flat shape circuit was programmed to a bending shape by compressing with a glass slide followed by exposure to UV irradiation for about 2 min. (c) A flat Miura-ori structured printed electronics was programmed into a free-standing 3D configuration after manually deformed and shining UV light. The scale bars are 1 cm.

Figure 5. Self-healing of the m-vitrimer and printed circuit. (a) Stress-strain curves of a virgin, thermally healed, and the intense pulsed light (IPL) healed m-vitrimer samples. (b) Pictures and microscopic image of cut vitrimer after healing by the IPL treatment for 30 s. (c) SEM images of scratched circuit surface before and after IPL treatment. (d) Photo and optical microscopic images showing the virgin, cut, and IPL healed printed circuit. The resistance of the silver wire at different states was marked.
blade, then the crack surface of the two pieces was carefully put together with gentle pressure. After treating
the sample with IPL for around 30 s, the broke samples can be healed with only a tiny scar on the surface, and
mechanical integrity can be restored (video S4). The quantitative mechanical property of the healed sample
is evaluated to be nearly 100% by comparing the break strain between the healed sample and virgin one. The
reason for fast heating by IPL is attributed to the high energy of photo-irradiation and photo-thermal effect
(figure S19). However, a longer IPL exposure time of 90 s results in overheating of the material, and the
material becomes softer. A shorter time for IPL exposure or thermal treatment leads to partial healing of the
material, which is not shown.

We further explored the self-healing of the printed circuit. Figure 5(c) shows the morphology of the
printed circuit with microcrack (20–30 μm in width) on both matrix and silver wire before and after treating
with IPL. The disappearance of the crack on the matrix suggests the effective crack healing of the m-vitrimer
matrix. However, the wound on the silver did not recover. This was because the temperature rise by IPL was
still too low to melt and weld the silver wire. Although the silver wire cannot be healed, it could be protected
from being further damaged after matrix healing. In the case of a complete cut, the conductivity can be
partially restored after the healing of matrix. As shown in figure 5(d), the printed circuit (4–5 cm long) with
a conductive silver wire on the m-vitrimer elastomer shows a resistance of 2.91 ± 0.07 Ω. Upon completely
cutting, the circuit broke, and the resistance increased to infinite. After putting the crack surface together
with gentle pressure, the sample was treated with IPL exposure for 30 s twice with a cooling step in between
cycles. The surface temperature is captured to be over 128 °C (figure S20). The optical microscopic images
show the matrix can be healed, and the conductive wire is physically well contacted. The healed circuit has a
measured resistance of 7.00 ± 0.23 Ω. The resistance reduces to 3.55 ± 0.01 Ω upon bending towards the
m-vitrimer matrix due to better connection by compression (figure S20). This indicates an incomplete but
still well acceptable recovery.

4. Conclusion

In summary, we present the use of multi-stimuli-responsive vitrimer (m-vitrimer) for shape-programmable
structures and smart devices with enhanced lifetime and functionality. By tuning the material composition,
m-vitrimers bearing dynamic disulfide bonds possess tunable mechanical and thermomechanical properties.
Heat and light can be used as stimuli to trigger the dynamic disulfide exchange reactions for shape
programming and material healing via different mechanisms. This single-component m-vitrimer has the
advantages of low cost, facile synthesis, and excellent reversibility. Besides, other external triggers, including
Joule heating, photo-thermal effect, inductive heating, can be easily extended to the materials by
incorporated functional particles to further enhance the multi-functionality. Moreover, the use of vitrimer
can also achieve other functional properties, including welding and recycling, enabling modular device
fabrication and enhanced sustainability. We showed the m-vitrimer can be further used as a substrate for
printed flexible smart electronics with shape-programming and healability. Printed 2D circuits could rapidly
adapt to complex 3D structures and healed upon damage under heat- or light-induced disulfide exchange
reaction. Despite the fast and good recovery of vitrimer matrix, the printed conductive wire can not be
completely restored. Future work on the printing of m-vitrimer matrix and the use of healable conductive
components, such as liquid metal and silver nanowire, will make it possible to achieve all printed, completely
healable, and programmable functional devices. The integration of printing techniques and
multi-stimuli-responsive polymers provides a new avenue to the next generation of functional 3D devices
with enhanced lifetime and functionality. This work provides a new approach to smart electronics, which can
find broad applications in morphing electronics, biomedical devices, and 4D printing.

Acknowledgments

We gratefully acknowledge the support of an AFOSR grant (AFOSR-FA9550-19-1-0151; Dr B-L’Les’ Lee,
Program Manager), a DURIP grant from AFOSR (FA9550-16-1-0160), and an Office of Naval Research grant
(N00014-20-1-2586). This work was performed in part at the Georgia Tech Institute for Electronics and
Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure, which is supported
by the National Science Foundation (ECCS-1542174).

Conflicts of interest

There are no conflicts to declare.
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