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ARTICLE

Magnetic Vitrimer-Based Soft Robotics

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Magnetically responsive elastomers, consisting of elastomer embedded with magnetic particles, can produce fast and reversible actuation when subjected to a magnetic field. They have been extensively explored to construct versatile remotely controllable soft robots. Nevertheless, the magnetically induced actuation strain in elastomer is typically small, which limits its broad applications. Recently, magnetic particles have been mixed with viscous fluid to enable giant magnetically induced deformation. However, their response speed is slow and the actuation is usually irreversible. In this work, we have developed magnetic vitrimer (MV), with magnetic particles mixed with polymer network containing abundant dynamic covalent bonds. At room temperature, the MV behaves like a regular magnetically responsive elastomer. When the temperature is elevated to the exchange reaction temperature of the dynamic covalent bonds, the material behaves like viscous magnetically responsive fluid, which can produce large deformation. The embedded magnetic particles and the vitrimer matrix also makes the material self-healable without requiring any direct touch. We have demonstrated that with the guidance of an externally applied magnetic field, a MV based soft robot can pass through a confined space, dramatically change its configuration, contactless self-heal, catch, secure and release a fast-moving object, and move along a planned path.

1. Introduction

Shape-morphing materials that can alter their configurations under various external stimuli, such as temperature, light, pH, humidity, electrical and magnetic fields, have been explored for diverse applications such as actuators, wearable devices, soft robotics and flexible electronics[1]. In this context, various stimuli-responsive materials have been developed, including liquid crystal elastomers[2], stimuli-responsive hydrogels[3] and shape memory polymers[4]. In particular, magnetically responsive soft materials composed of magnetic particles and polymer matrix have shown many unique and desirable features including fast response[5], reversible actuation[6], self-healing[7] and facile controllability[8], which has great potential in various applications with minimally invasive interactions[9,10].

Commonly adopted actuation mechanisms of magnetically responsive soft composite materials rely on the magnetic gradient-induced external force and magnetic field-induced torque exerting on the materials[11]. When the magnetic particles are embedded into a matrix, an external magnetic field can be used to remotely and rapidly actuate the soft composite. Recent studies have demonstrated several creative applications utilizing these composites. For example, a magnetically actuated soft continuum robot has been controlled to actively navigate and steer in confined environments[8]. Hu et al.[6] developed a small-scale magneto-elastic soft robot with silicone elastomer matrix (Ecoflex 00-10) embedded with hard magnetic neodymium-iron-boron (NdFeB) microparticles, which exhibited enhanced mobility and multimodal locomotion with controlled external magnetic field and carefully designed magnetic domain in the composite. Moreover, Kim et al.[5] fabricated magnetic responsive elastomer through 3D printing technique, enabling fast transformations between complex 3D shapes by programming ferromagnetic domains. For the examples above, elastic actuation of the polymer matrix is employed, where the material returns to its original configuration upon the removal of the magnetic field.

Limited actuation modes and deformability of elastomer-based soft actuators can be improved by substituting the elastomer matrix with viscous fluid. Viscous fluid greatly enhances the deformability of the soft actuators. Recent studies have reported the use of fluid-based magnetic responsive actuator such as ferrofluid[12] and magnetic slime[13] to build non-invasive and reconfigurable miniature robots, which shows nearly infinite deformability[14]. Thanks to the flowability of the viscous fluid, these soft actuators are capable of passing through confined spaces that are much smaller than their sizes without any damages. Moreover, fluid-based magnetic robot can generate drastic shape change under magnetic control, enabling novel functionalities including object manipulation and transportation[15–19]. For instance, Fan et al.[16] have developed collective magnetically actuated ferrofluid with multiple deformation modes such as splitting and forming various liquid-robot aggregates, which can be utilized for navigation in multi-terrain surfaces and confined spaces. Researchers have also investigated a single ferrofluid droplet

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Electronic Supplementary Information (ESI) available: Videos corresponding to Fig. 4 and 6.

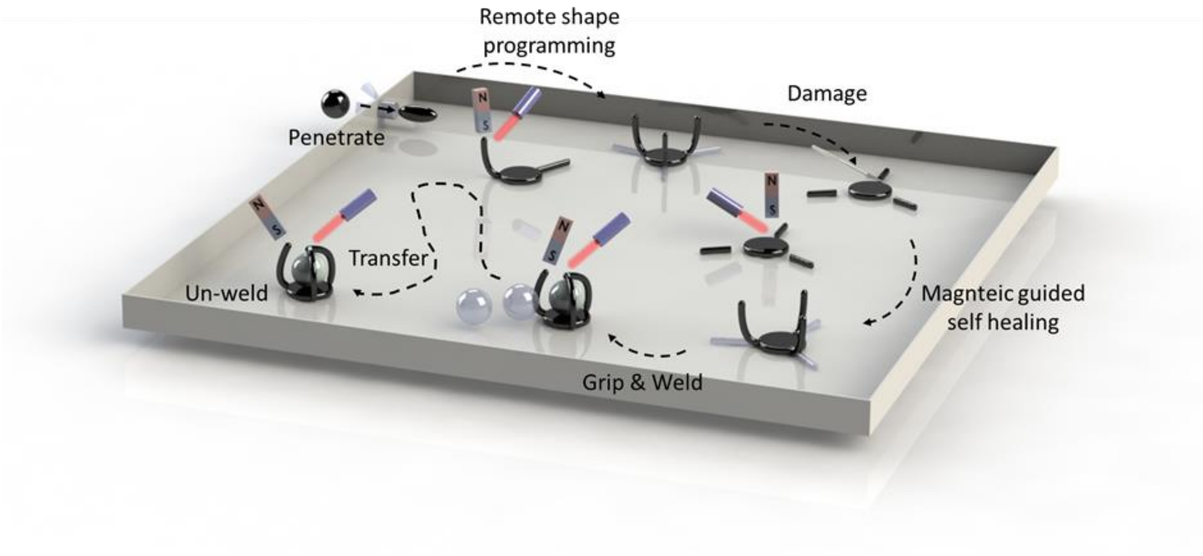

Figure 1. A magnetic vitrimer-based soft robot can squeeze itself to pass through an extremely confined space, reshape, self-heal, grip, transport and release an object.

controlled by spatiotemporally changing the external magnetic field to deliver and manipulate delicate objects[20]. However, magnetically actuated tiny droplets often experience additional resistance from its surface tension. One recent work[13] has proposed magnetic slime as magnetic actuated soft robot with great adaptability and deformability compared with conventional magnetic droplet robot, being able to work across multiple interfaces and underwater. However, those soft actuators usually do not show reversible and elastic response, which are often needed for many tasks such as cyclic gripping and releasing items, reversible expansion/collapsing and impulsive motion based on spring-latch mechanism.

The elastomer-based and fluid-based magnetic soft actuators both have been studied extensively, but each type has certain limitations: the actuation strain of elastomer-based magnetic actuator is typically small, while the actuation of most fluid-based magnetic actuator is irreversible. To combine the characteristics of both elastomer-based actuator and fluid-based actuator, researchers have employed the polymer matrix with dynamic covalent bonds, which can rearrange their network under certain stimuli such as heat and ultraviolet (UV) irradiation[9,21,22]. Kuang et al.[23] have recently developed polymers with dynamic covalent bonds embedded with hard-magnetic particles for modular assembling and reconfigurable architectures with reprogrammable actuation modes. However, versatile and drastic permanent shape morphing have yet been demonstrated.

In this work, we have developed magnetically responsive soft composite with polymer matrix containing disulfide bonds embedded with magnetic particles. The exchange reaction of disulfide bonds occurs under heat or infrared (IR) irradiation. Consequently, disulfide bonds dynamically rearrange and the mobility of the polymer chains significantly increase[24,25]. The deformation mechanism of the magnetic vitrimer (MV) lies in its temperature-sensitive rheological behavior, which allows reversible actuation at room temperature and also drastic shape change with mild temperature increase. Besides, we used laser to remotely control local temperature field of the MV to enable local and more precise shape morphing. Furthermore, unlike most self-healing materials that need to be manually brought together[7] and subjected to a mechanical pressure[25] during the healing process, a broken MV can self-heal without being touched under the guidance of external magnetic field. As shown in **Figure 1**, we demonstrated a MV-based soft robot that can: 1) pass through a gap that is smaller than its original size, 2) dramatically transform its shape to a soft robotic gripper, 3) contactless self-heal from a permanent damage, 4) catch and secure a fast-moving object, 5) transport and release the object.

2. Results and Discussion

2.1 Fabrication and characterization of the MV

The schematics of the material preparation are shown in **Figure 2A and 2B**: we prepared the MV using epoxy monomers (EPS25, epoxy equivalent = 462 g · equiv^{-1}) with stoichiometric mixtures of two sulfhydryls: 2,2′ - (ethylenedioxy)diethanethiol (EDDET) and pentaerythritol tetrakis (3-mercaptopropionate) (PETMP). The polymer network is formed through thiol-epoxy reaction, where the EDDET with two thiol groups forms the polymer chains together with EPS25 and the PETMP with four thiol groups crosslinks the polymer chains into a network. We chose (dimethylamino)pyridine (DMAP) as the catalyst. In addition, we tuned molar ratio (γ) of thiol groups from EDDET and PETMP to tailor the crosslinking density of the MV and thus its thermomechanical properties, while maintaining the thiol group concentration the same. As shown in **Figure 2C**, as the temperature rises, the disulfide bonds can readily be cleaved and re-formed from a reduction reaction and an oxidation

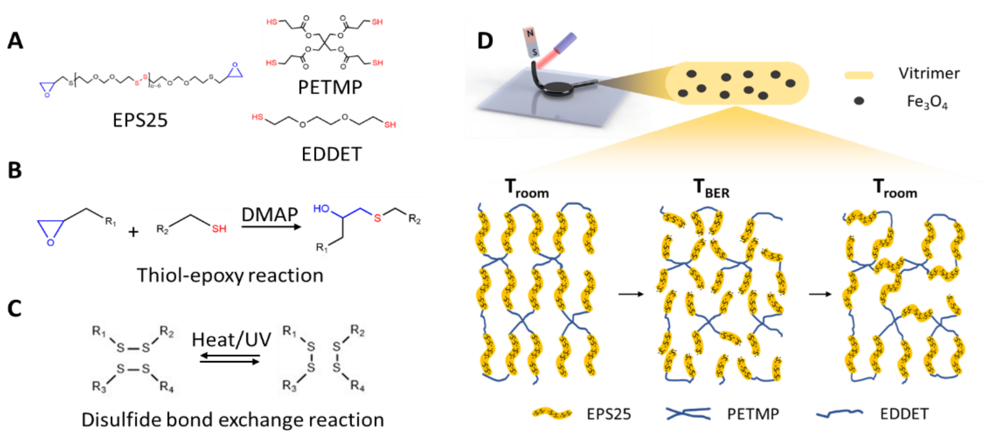

Figure 2. Preparation and molecular structure of the magnetic vitrimer used in the current study. (A) Molecular structure of the monomer EPS25, crosslinker PETMP and chain extender EDDET. (B) Crosslinking mechanism of thiol-epoxy reaction with DMAP (4-Dimethylaaminopyridine) as the catalyst. (C) Mechanism of disulfide bond exchange reaction. (D) Reconfiguration mechanism of magnetic vitrimer.

reaction, respectively[24,26], endowing the fluid-like behavior to the vitrimer.

To prepare a magnetically responsive vitrimer, we embedded magnetic microparticles (Fe_3O_4) into the polymer matrix, where the schematic of the MV and its reconfiguration mechanism are illustrated in **Figure 2D**. The monomers consist of abundant disulfide bonds and the bond exchange reaction (BER) becomes more active at an elevated temperature (T_{BER}), leading to increased flowability of the composite. As a result, a magnetic gradient can induce dramatic and irreversible shape change of magnetic vitrimer in a controlled manner. When the environmental temperature is dropped to the room temperature, the disulfide bond exchange reaction becomes much less active and the MV behaves like a normal elastomer. The temperature dependent behavior of the MV allows its shape reprogramability and also reversible actuation.

To evaluate the potential of using MV for soft robotics, we systematically studied the effects of the two major parameters on the thermomechanical properties of the material: the stoichiometric ratio γ of chain extender to crosslinker and the weight percentage of the magnetic particles in the composite. We varied the γ value from 0 to 1 to investigate the effect of crosslinking density on the properties of MV composite at ambient temperature (30 °C) with a fixed magnetic particle loading (10 wt%). Among all the samples, we fixed the ratio between thiol groups (from EDDET and PETMP) and epoxy groups (from EPS25) to keep the concentration of the dynamic covalent bond as a constant. As illustrated in **Figure 3A** (G_R in the relaxation shear modulus), the normalized stress relaxation for the samples with different γ values shows similar relaxation time, suggesting that the kinetics of disulfide bond exchange reaction is not affected by the crosslinking density. However, the magnitude of relaxation modulus is negatively correlated to γ. The stress vs. strain curves in **Figure 3B** show that both stiffness and strength of the MV increase as the γ value decreases. The γ value is the molar ratio of thiol group from EDDET and PETMP, where PETMP has four thiol groups and forms crosslinking junction. Therefore, the material modulus and strength increase by increasing the crosslinking density.

In addition to the γ value, the magnetic particle loading also affects the mechanical behavior of MV. In the **Figure 3C and 3D**, as the loading of magnetic particles increases from 0 wt% to 20 wt% for a given γ value (0.5), the relaxation time of the material increases by one order of magnitude and the material strength doubles. Both the mechanical property and magnetic response of the MV vary with the concentration of magnetic particles. Although higher magnetic particle concentration can enhance magnetic response, introducing too many magnetic particles to the vitrimer matrix can affect the viscoelastic properties of MV. **Figure S1** shows the viscosity of MV increases with increasing the concentration of magnetic particle. Therefore, at ambient temperature, higher magnetic particle loading increases the stiffness of the MV, requiring larger force to actuate the body, which limits the magnetic actuation capabilities of the material. Moreover, at high temperature, the viscosity will also increase with higher magnetic particle loading, which limits the flowability of the MV.

In the context of soft robotic grippers, their primary functionality is the ability to grasp or catch an object and hold against the external disturbance, and high compliance of the material can reduce control complexity. In most applications, the time scale of grasping or catching an object is typically less than a few seconds[27–29], requiring that the relaxation time of the composite at room temperature is longer than tens of seconds. On the other hand, low viscosity of MV at high temperature is desired during the shape morphing. Therefore, we chose the molar ratio (γ = 0.5) and magnetic particle loading (=10 wt%) to prepare the MV for the rest of this study, with relaxation time of around 100 seconds and secant modulus of 0.11 MPa at ambient temperature (**Figure S2**). As shown in **Figure 3E**, using the selected MV, we conducted the stress relaxation tests at

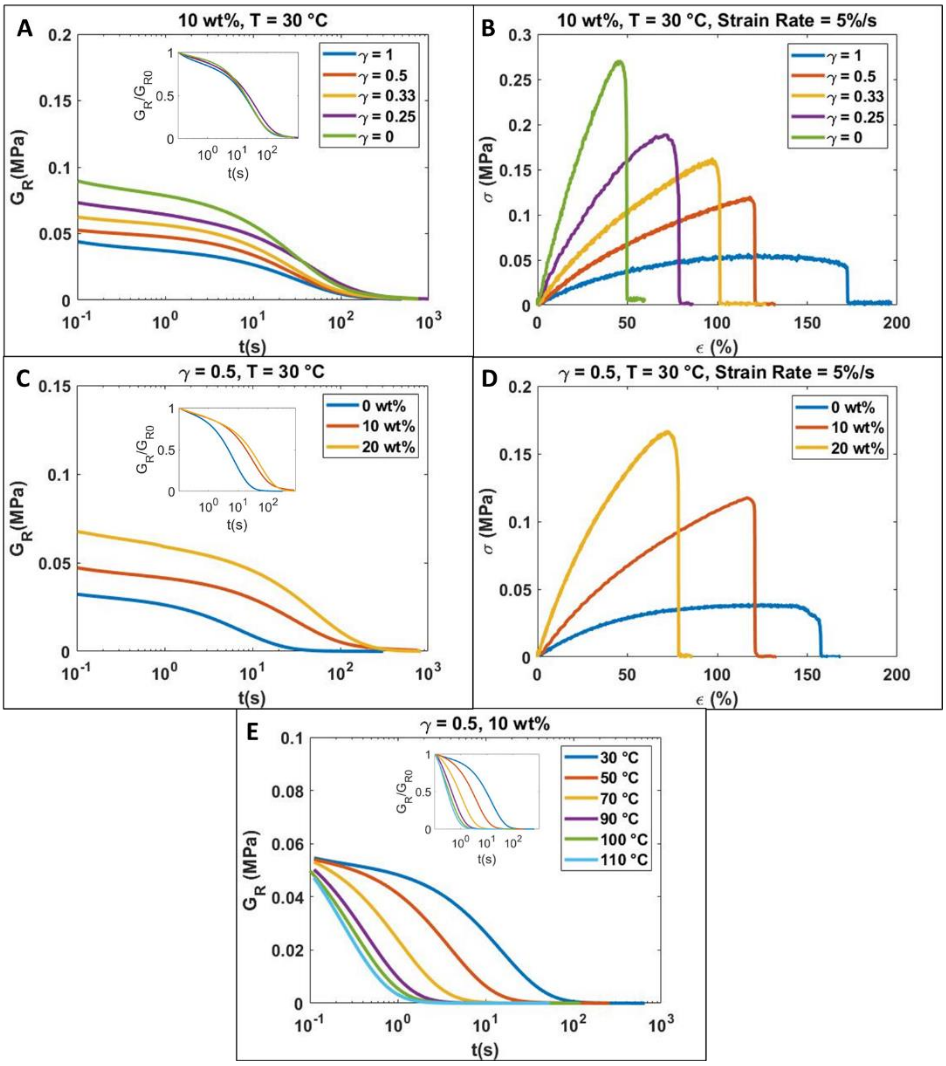

Figure 3. Thermomechanical characterizations of the MVs. (A) Stress relaxation of MVs with different chain extender-crosslinker ratio (γ) at T= 30 °C. The inset shows the normalized experimental results. (B) Uniaxial tensile testing results of MVs with different chain extender-crosslinker ratio (γ) at T= 30 °C. (C) Stress relaxation of MVs with different weight percent of magnetic particles at T= 30 °C and the inset shows the normalized results. (D) Uniaxial tensile testing results of MV with different weight percent of magnetic particle at T= 30 °C. (E) Stress relaxation of MVs at different temperatures.

different temperatures. The decrease of the relaxation time with increasing temperature is due to the accelerated disulfide bond exchange reaction at higher temperature[30].

Finally, we have also examined the possible degradation of the property of the MV during its storage. **Figure S3** shows that as the stored time increases, the storage modulus (G') increases and tan(δ) decreases. Such property degradation is mainly due to the decrease of the efficiency of the catalyst (DMAP) over time in the system[31,32].It is noted that there have been various types of vitrimers, the dynamic bond exchanging reaction of which does not need any catalyst[33]. The properties of those vitrimers are often more stable after long period of storage.

2.2 Demonstration of MV-based soft robotics

In this study, we demonstrated four distinct working modes of a MV-based soft robot: 1) passing through confined environments, 2) permanent shape morphing with remote control, 3) touchless self-healing and 4) manipulating objects as a soft gripper.

We first demonstrated the heat-enhanced flowability of the MV as shown in **Figure 4A and video 1**. A spherical MV was blocked by a narrow opening. The external magnetic field could not drive the MV to move through the opening at the room temperature because of its relatively high stiffness. When we heated the local environment to 100 °C, the disulfide bond exchange reaction became more active, leading to a significant increase of the flowability of the MV. With an applied magnetic field, the magnetic gradient-induced pulling force exerted on the MV drove it to flow through the narrow opening within around 1 min. The dimensions of the MV before and after penetrating through the small opening are shown in **Figure S4**.

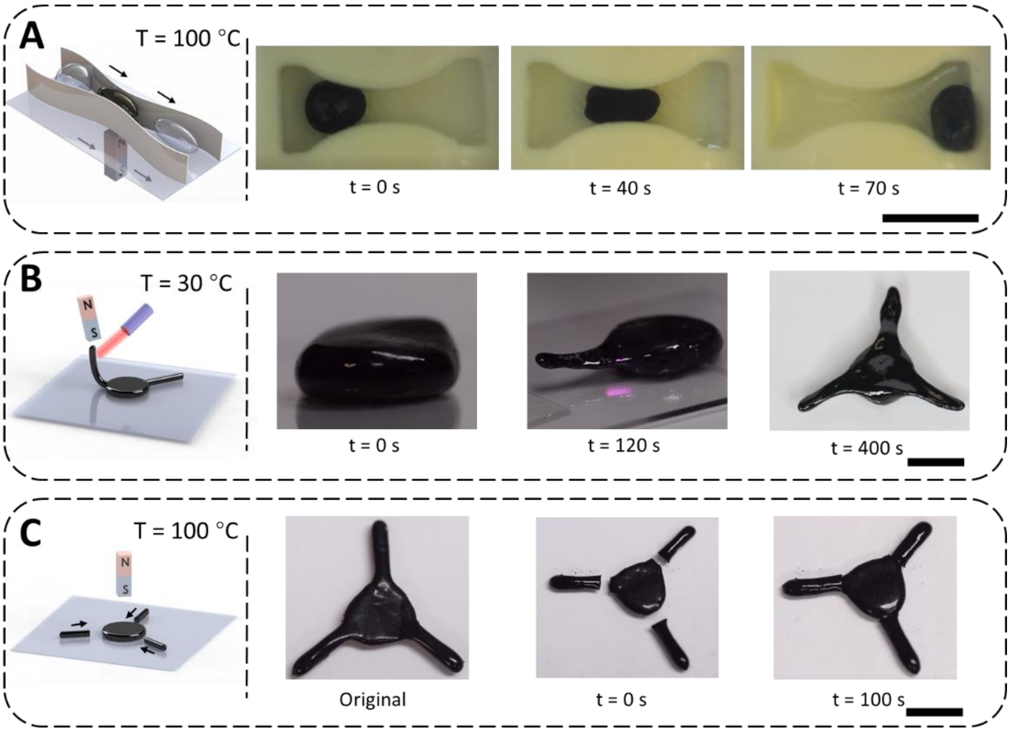

Figure 4. Heat enabled flowability, remote shape morphing and self-healing of MV. (A) At an elevated temperature (100 °C), a MV sphere can pass through a narrow opening with an applied magnetic field. Scale bar, 1 cm. (B) A MV disk can transform to a soft gripper by applying local heating with a laser beam and a magnetic field by a permanent magnet. Scale bar, 1 cm. (C) Self-healing capability of the soft gripper after severe damages. Scale bar, 1 cm.

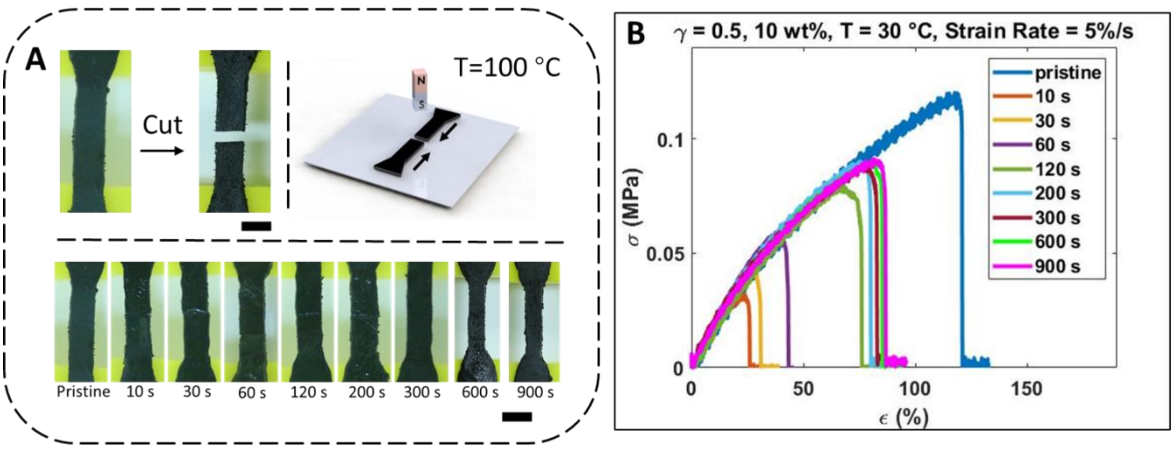

Figure 5. Magnetically assisted self-healing of MV. (A) MV strips were first cut into two parts at 30 °C. Then, assisted by the external magnetic field, the two broken parts were brought into contact and heated up at a temperature of 100 °C to trigger the dynamic bond exchange reaction. Specimens were healed for different period of times. Scale bar, 2 mm. (B) Tensile stress-strain relationship of self-healed MV strips with different healing times.

The magnetic field gradient for actuation was generated by a cubic permanent magnet (25 x 25 x 25 mm, N52 Neodymium Magnet from KJ Magnetics), which has a magnetic field density of 4000 gauss at the surface, measured by a hand-held gauss meter (TD8620, Tunkia). The MV was able to flow through the opening at a distance around 10 - 20 mm away from the surface of the magnet, where the magnetic field density ranges from 1500 to 500 gauss. After the MV robot completely went through the opening, both the thermal and magnetic fields were removed, and the material regained its elasticity.

We further extended the working mechanism of the MV to broaden its functionality by introducing localized heating, which can enhance the flowability of specific regions in the material. With the application of magnetic gradient, remote control of shape morphing could be realized in a designed fashion. As shown in **Figure 4B**, with the assistance of the local thermal field generated by an infrared laser pointer (Sky laser, PL-808-1000B) and the magnetic gradient in-line with the direction of robotic gripper 'arms', the MV could change its configuration from a disk shape to a soft robotic gripper.

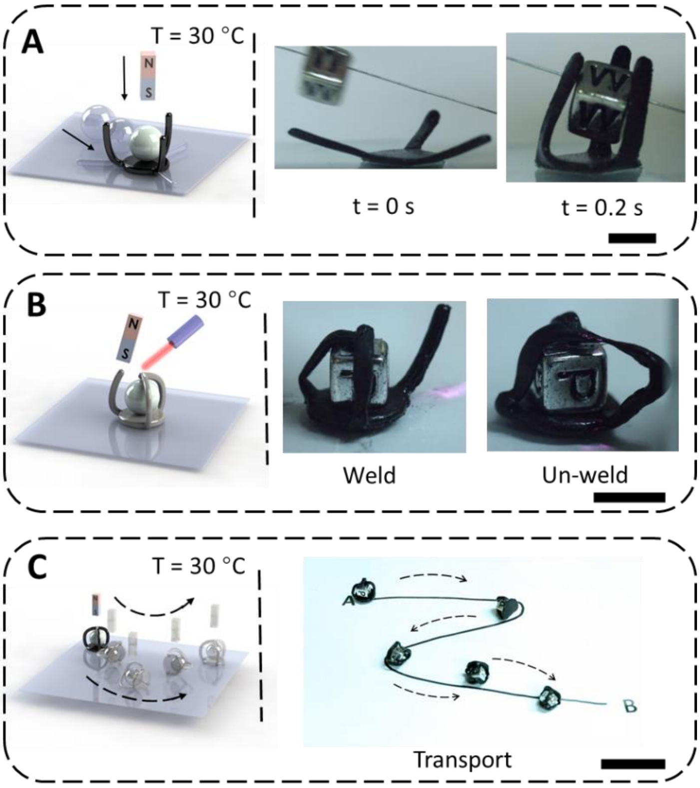

Figure 6. MV based soft gripper. (A) The soft robotic gripper can catch a moving object through fast actuation. Scale bar, 1 cm. (B) Welding/un-welding of the gripper to secure/release the object. Scale bar, 1 cm. (C) With an externally applied magnetic field, the soft robotic gripper can carry the object and move along a planned path. Scale bar, 5 cm.

We next demonstrated the magnetically guided self-healing of the MV gripper. As shown in **Figure 4C and video 2**, the three 'arms' of the MV gripper were separated from the 'body' by a sharp blade. To initiate the self-healing process, we placed a permanent magnet on the top of the gripper and heated up the environment to 100 °C for 100 seconds. The magnetic gradient-induced pulling force allowed the broken 'arms' to move toward the main 'body' without direct applied contact. The elevated temperature accelerates the disulfide bond exchange reaction, permitting the self-healing of the MV gripper at the broken regions. Upon the removal of the magnetic and thermal field, the gripper regained its integrity and elasticity.

To further investigate the self-healing efficiency of the MV, we studied the self-healing time of MV by conducting the tensile tests. As illustrated in **Figure 5A**, the specimens were cut into two halves at ambient temperature (30 °C) by using a sharp blade. The two segments were then brought into contact with the help of an external magnetic field and put at 100 °C for various period of time. The self-healing times for the MV sample were set to 0, 10, 30, 60, 120, 200, 300, 600 and 900 seconds. We conducted tensile test at 5% s^{-1} strain rate and the results are shown in **Figure 5B**. Self-healed MVs exhibited similar strength at 120, 200,300, 600 and 900 seconds at around 0.8 MPa, which was around 80% of the pristine sample. The results also agreed with our previous measurements of the relaxation time, which was around 100 seconds, indicating that the dynamic bonds need around 100 seconds to form between separated pieces.

At last, we demonstrated the capability of the soft robotic gripper interacting with a moving object through magnetic control. As shown in **Figure 6A,** a magnetic field with a strong gradient exerted a pulling force onto the iron oxide microparticles, which could attract each 'arm' align with the magnetic field. On the other hand, the 'arm' also tended to align with the magnetic field direction, due to the body-force torque from anisotropic gripper geometry and paramagnetic torque from iron oxide anisotropic distribution. Therefore, the deformation resulted from a balance between the elastic restoring force of the gripper and magnetic force exerted onto the gripper. As shown in **video 3**, at the ambient temperature (T=30 °C), fast response of the gripper controlled by a permanent magnet allowed the soft robotic gripper to catch a fast-moving object. The gripper was also able to release the object on demand. By further harnessing the remote local shape morphing capability of MV, the soft robotic gripper could secure and release the object by 'welding' and 'un-welding' of the 'arms', as shown in **Figure 6B** and **video 4**. With careful manipulation of a magnet and a local thermal field, the tip of the 'arms' could be connected or disconnected with an object held inside. In **Figure 6C**, the welded soft robotic gripper was able to carry the object and travel along a planned route under the guidance of a magnetic field. Moreover, the soft robotic gripper could protect the object from possible mechanical damage, due to the viscoelastic nature of MV.

3. Experimental Methods

3.1 Magnetic Vitrimer Preparation

MV was prepared by cross-linking epoxy monomer with 2 different sulfhydryls. Briefly, the monomer EPS25 (ThioPlast, epoxy equivalent = 462 g · equiv^{-1}, kindly provided by Norton Functional Chemicals GmbH) and a stoichiometric mixture (γ=0.5) of two crosslinkers: 2,2'-(ethylenedioxy)diethanethiol (EDDET, >95%, Sigma Aldrich) and pentaerythritol tetrakis (3-mercaptopropionate) (PETMP, >95%, Sigma Aldrich) were manually mixed at room temperature. Then, 1 wt% of 4-DMAP (>99.0%, Sigma Aldrich) and 10 wt% of iron oxide microparticles (Fe_3O_4, >98%, d~1μm, Alpha Chemicals) were manually added and mixed into the composition to obtain a homogeneous blend, which was confirmed by the optical microscopic images in **Figure S5**. Finally, the mixture was poured into a glass petri dish and cured under 60 °C for 3 hours. As shown in **Figure S6**, the storage modulus (G') and loss modulus (G'') of MV change little after 3 hours of curing, indicating the MV is fully cured. To obtain MV sheet with desired thickness for characterization purpose, the samples and a spacer were hot-pressed by a heat press machine (Carver, Wabash) under 100 °C for 2 minutes between parchment paper. All samples were cooled to room temperature and stored at 30 °C for 24 hours before characterization.

3.2 Characterization

The uniaxial test was performed on a dynamic mechanical analysis equipment RSA-G2 (TA instruments, New Castle) using dog bone samples (effective dimension: 2 × 20 × 0.8 mm). The strain rate was 5% s^{-1}. For each sample, three specimens were tested and the average results were reported. The stress relaxation test was conducted on a rheometer DHR3 (TA instruments, New Castle) using disc samples (diameter: 20 mm, thickness: 0.8 mm). The samples were equilibrated at specified temperature for 5 minutes, and then a constant shear strain of 30% (0.015 rad) was applied to monitor the evolution of stress as a function of time. The homogeneous thermal field was created within an in-house built heating chamber including 4 polyimide heating pads (5 V, 1 W, 30 × 40 mm) with a uniform thermal field up to 130 °C. The local thermal field was generated by an infra-red laser pointer PL-808-2000 (Sky Laser, 2 W). The videos and pictures were captured using a digital camera (Cannon EOS 80D).

Conclusion

In this article, we have designed and fabricated magnetic vitrimer based soft robots. The exchange reaction activity of the dynamic bonds within the MV increases at an elevated temperature, allowing the MV soft robot to have dramatic and irreversible shape change with applied magnetic field. Such dramatic shape change enables the MV based soft robot to pass through a significantly confined space. With the laser-induced local heating and external magnetic field, the MV-based soft robot can also change its shape with control. Moreover, the combination of embedded magnetic particles and exchange reaction of the dynamic bond in the MV makes it self-healable without requiring any direct touch. At room temperature, MV behaves like a regular elastomer, and the MV based soft robotic gripper can achieve fast catching, releasing and locomotion.

Conflicts of interest

There are no conflicts to declare.

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References

1 Shintake, J.; Cacucciolo, V.; Floreano, D.; Shea, H. Soft Robotic Grippers. *Advanced Materials* **2018**, *30* (29), 1707035. https://doi.org/10.1002/adma.201707035.

2 He, Q.; Wang, Z.; Wang, Y.; Song, Z.; Cai, S. Recyclable and Self-Repairable Fluid-Driven Liquid Crystal Elastomer Actuator. *ACS Appl. Mater. Interfaces* **2020**, *12* (31), 35464–35474. https://doi.org/10.1021/acsami.0c10021.

3 Ionov, L. Hydrogel-Based Actuators: Possibilities and Limitations. *Materials Today* **2014**, *17* (10), 494–503. https://doi.org/10.1016/j.mattod.2014.07.002.

4 Meng, H.; Li, G. A Review of Stimuli-Responsive Shape Memory Polymer Composites. *Polymer* **2013**, *54* (9), 2199–2221. https://doi.org/10.1016/j.polymer.2013.02.023.

5 Kim, Y.; Yuk, H.; Zhao, R.; Chester, S. A.; Zhao, X. Printing Ferromagnetic Domains for Untethered Fast-Transforming Soft Materials. *Nature* **2018**, *558* (7709), 274–279. https://doi.org/10.1038/s41586-018-0185-0.

6 Hu, W.; Lum, G. Z.; Mastrangeli, M.; Sitti, M. Small-Scale Soft-Bodied Robot with Multimodal Locomotion. *Nature* **2018**, *554* (7690), 81–85. https://doi.org/10.1038/nature25443.

7 Ogliani, E.; Yu, L.; Javakhishvili, I.; Skov, A. L. A Thermo-Reversible Silicone Elastomer with Remotely Controlled Self-Healing. *RSC Adv.* **2018**, *8* (15), 8285–8291. https://doi.org/10.1039/C7RA13686B.

8 Kim, Y.; Parada, G. A.; Liu, S.; Zhao, X. Ferromagnetic Soft Continuum Robots. *Science Robotics* **2019**, *4* (33), eaax7329. https://doi.org/10.1126/scirobotics.aax7329.

9 Cheng, Y.; Chan, K. H.; Wang, X.-Q.; Ding, T.; Li, T.; Zhang, C.; Lu, W.; Zhou, Y.; Ho, G. W. A Fast Autonomous Healing Magnetic Elastomer for Instantly Recoverable, Modularly Programmable, and Thermorecyclable Soft Robots. *Advanced Functional Materials* **2021**, *31* (32), 2101825. https://doi.org/10.1002/adfm.202101825.

10 Ebrahimi, N.; Bi, C.; Cappelleri, D. J.; Ciuti, G.; Conn, A. T.; Faivre, D.; Habibi, N.; Hošovský, A.; Iacovacci, V.; Khalil, I. S. M.; Magdanz, V.; Misra, S.; Pawashe, C.; Rashidifar, R.; Soto-Rodriguez, P. E. D.; Fekete, Z.;

Jafari, A. Magnetic Actuation Methods in Bio/Soft Robotics. *Adv. Funct. Mater.* **2021**, *31* (11), 2005137. https://doi.org/10.1002/adfm.202005137.
11 Erb, R. M.; Martin, J. J.; Soheilian, R.; Pan, C.; Barber, J. R. Actuating Soft Matter with Magnetic Torque. *Advanced Functional Materials* **2016**, *26* (22), 3859–3880. https://doi.org/10.1002/adfm.201504699.
12 Zhang, X.; Sun, L.; Yu, Y.; Zhao, Y. Flexible Ferrofluids: Design and Applications. *Adv. Mater.* **2019**, *31* (51), 1903497. https://doi.org/10.1002/adma.201903497.
13 Sun, M.; Tian, C.; Mao, L.; Meng, X.; Shen, X.; Hao, B.; Wang, X.; Xie, H.; Zhang, L. Reconfigurable Magnetic Slime Robot: Deformation, Adaptability, and Multifunction. *Advanced Functional Materials n/a* (n/a), 2112508. https://doi.org/10.1002/adfm.202112508.
14 Dunne, P.; Adachi, T.; Dev, A. A.; Sorrenti, A.; Giacchetti, L.; Bonnin, A.; Bourdon, C.; Mangin, P. H.; Coey, J. M. D.; Doudin, B.; Hermans, T. M. Liquid Flow and Control without Solid Walls. *Nature* **2020**, *581* (7806), 58–62. https://doi.org/10.1038/s41586-020-2254-4.
15 Čejková, J.; Banno, T.; Hanczyc, M. M.; Štěpánek, F. Droplets As Liquid Robots. *Artificial Life* **2017**, *23* (4), 528–549. https://doi.org/10.1162/ARTL_a_00243.
16 Fan, X.; Sun, M.; Sun, L.; Xie, H. Ferrofluid Droplets as Liquid Microrobots with Multiple Deformabilities. *Advanced Functional Materials* **2020**, *30* (24), 2000138. https://doi.org/10.1002/adfm.202000138.
17 Yu, W.; Lin, H.; Wang, Y.; He, X.; Chen, N.; Sun, K.; Lo, D.; Cheng, B.; Yeung, C.; Tan, J.; Di Carlo, D.; Emaminejad, S. A Ferrobotic System for Automated Microfluidic Logistics. *Science Robotics* **2020**, *5* (39), eaba4411. https://doi.org/10.1126/scirobotics.aba4411.
18 Li, A.; Li, H.; Li, Z.; Zhao, Z.; Li, K.; Li, M.; Song, Y. Programmable Droplet Manipulation by a Magnetic-Actuated Robot. *Science Advances* **2020**, *6* (7), eaay5808. https://doi.org/10.1126/sciadv.aay5808.
19 Zhou, M.; Wu, Z.; Zhao, Y.; Yang, Q.; Ling, W.; Li, Y.; Xu, H.; Wang, C.; Huang, X. Droplets as Carriers for Flexible Electronic Devices. *Advanced Science* **2019**, *6* (24), 1901862. https://doi.org/10.1002/advs.201901862.
20 Fan, X.; Dong, X.; Karacakol, A. C.; Xie, H.; Sitti, M. Reconfigurable Multifunctional Ferrofluid Droplet Robots. *Proceedings of the National Academy of Sciences* **2020**, *117* (45), 27916–27926. https://doi.org/10.1073/pnas.2016388117.
21 Matxain, J. M.; Asua, J. M.; Ruipérez, F. Design of New Disulfide-Based Organic Compounds for the Improvement of Self-Healing Materials. *Phys. Chem. Chem. Phys.* **2016**, *18* (3), 1758–1770. https://doi.org/10.1039/C5CP06660C.
22 Kuang, X.; Wu, S.; Ze, Q.; Yue, L.; Jin, Y.; Montgomery, S. M.; Yang, F.; Qi, H. J.; Zhao, R. Magnetic Dynamic Polymers for Modular Assembling and Reconfigurable Morphing Architectures. *Advanced Materials* **2021**, *33* (30), 2102113. https://doi.org/10.1002/adma.202102113.
23 Liu, Y.-L.; Chuo, T.-W. Self-Healing Polymers Based on Thermally Reversible Diels–Alder Chemistry. *Polym. Chem.* **2013**, *4* (7), 2194–2205. https://doi.org/10.1039/C2PY20957H.
24 Canadell, J.; Goossens, H.; Klumperman, B. Self-Healing Materials Based on Disulfide Links. *Macromolecules* **2011**, *44* (8), 2536–2541. https://doi.org/10.1021/ma2001492.
25 Song, Z.; Wang, Z.; Cai, S. Mechanics of Vitrimer with Hybrid Networks. *Mechanics of Materials* **2021**, *153*, 103687. https://doi.org/10.1016/j.mechmat.2020.103687.
26 Zhang, M.; Zhao, F.; Xin, W.; Luo, Y. Room-Temperature Self-Healing and Reprocessable Waterborne Polyurethane with Dynamically Exchangeable Disulfide Bonds. *ChemistrySelect* **2020**, *5* (15), 4608–4618. https://doi.org/10.1002/slct.201904316.
27 Yuk, H.; Lin, S.; Ma, C.; Takaffoli, M.; Fang, N. X.; Zhao, X. Hydraulic Hydrogel Actuators and Robots Optically and Sonically Camouflaged in Water. *Nat Commun* **2017**, *8* (1), 14230. https://doi.org/10.1038/ncomms14230.
28 Zhang, J.; Onaizah, O.; Middleton, K.; You, L.; Diller, E. Reliable Grasping of Three-Dimensional Untethered Mobile Magnetic Microgripper for Autonomous Pick-and-Place. *IEEE Robotics and Automation Letters* **2017**, *2* (2), 835–840. https://doi.org/10.1109/LRA.2017.2657879.
29 Maffli, L.; Rosset, S.; Ghilardi, M.; Carpi, F.; Shea, H. Ultrafast All-Polymer Electrically Tunable Silicone Lenses. *Advanced Functional Materials* **2015**, *25* (11), 1656–1665. https://doi.org/10.1002/adfm.201403942.
30 Jian, X.; Hu, Y.; Zhou, W.; Xiao, L. Self-Healing Polyurethane Based on Disulfide Bond and Hydrogen Bond. *Polymers for Advanced Technologies* **2018**, *29* (1), 463–469. https://doi.org/10.1002/pat.4135.
31 Gilbert, H. F. Protein Modifications | Disulfide Bond Formation. In *Encyclopedia of Biological Chemistry III*; Elsevier, 2013; pp 150–153. https://doi.org/10.1016/B978-0-12-819460-7.00543-0.
32 Van Zee, N. J.; Nicolaÿ, R. Vitrimers: Permanently Crosslinked Polymers with Dynamic Network Topology. *Progress in Polymer Science* **2020**, *104*, 101233. https://doi.org/10.1016/j.progpolymsci.2020.101233.
33 Krishnakumar, B.; Sanka, R. V. S. P.; Binder, W. H.; Parthasarthy, V.; Rana, S.; Karak, N. Vitrimers: Associative Dynamic Covalent Adaptive Networks in Thermoset Polymers. *Chemical Engineering Journal* **2020**, *385*, 123820. https://doi.org/10.1016/j.cej.2019.123820.