

Room-temperature Self-healing and Recyclable PDMS Elastomers with Superior Mechanical Properties for Triboelectric Nanogenerators

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Electronic Supplementary Information

Abstract Polydimethylsiloxane (PDMS) is an electron-withdrawing material that is widely used in triboelectric nanogenerators (TENGs). However, PDMS has poor mechanical properties after curing and is easily damaged when subjected to long-term workloads. Thus, the long-term stable operation of TENGs under mechanical deformation cannot be guaranteed. In this work, multiple hydrogen bonds and aromatic disulfide bonds were introduced into PDMS elastomers. These elastomers exhibited high toughness (a tensile strength of 1.91 MPa and an elongation at break of 340%), good recyclability, and room-temperature self-healing properties (healing efficiency of 96.4% in 24 h). Recyclable sandwich-like triboelectric nanogenerators with excellent electrical output performance (13.5 V) and room-temperature self-healing performance (24 h, 98% recovery of self-generating performance) were prepared by utilizing the hydrogen bonding between the PDMS elastomer and MXene. The work reported herein offers theoretical guidance and a compelling strategy for developing high-performance TENG negative friction layers.

Keywords Polydimethylsiloxane; Aromatic disulfide bonds; Hydrogen bonds; Room temperature self-healing; Triboelectric nanogenerator

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INTRODUCTION

Triboelectric nanogenerators (TENGs) are environmentally friendly and low-cost energy harvesters that exhibit good energy conversion efficiencies and high output voltages. TENGs are defined by their ability to utilize ambient mechanical motions such as the movement of the human body for energy harvesting. Therefore, TENGs show good promise for application in self-powered sensors/electronics or soft electronic devices.^[1–3] However, during operation, TENGs regularly encounter external mechanical actions, including sliding, bending, pressing, and twisting. This leads to mechanical damage, which greatly shortens their service life.^[4–6] Consequently, a range of strategies has been explored for the fabrication of TENGs capable of deformation and healing. For example, electrodes with interlocking kirigami, serpentine patterns,^[7] and three-dimensional (3D) network structures have been evaluated.^[8] However, these strategies have only resulted in TENGs with 22%–310% stretchability.^[9] The preparation of TENGs that simultaneously exhibit good stretching, transparency, and self-healing properties is a notable challenge due to the material requirements and

energy conversion mechanisms of these devices.^[5]

Polydimethylsiloxane (PDMS) is a thermally stable, flexible, and intrinsically hydrophobic material with good triboelectricity properties. The desirable physicochemical properties of PDMS are caused by low interchain interactions and the nature of its siloxane bonds. Due to these properties, PDMS has been widely investigated as an electron-withdrawing material for use in TENGs.^[10,11] However, PDMS also has certain drawbacks, such as low fracture energy (less than 100 J/m²), low strength, and the formation of microcracks under external stress.^[12,13] The application of PDMS, especially as a multifunctional elastomer, has been significantly limited by these shortcomings. In addition, due to its irreversible cross-linked structure, existing commercial PDMS cannot conform to the complex and diverse shapes of biological surfaces and is not self-healing. Consequently, on-skin electronics prepared using PDMS exhibit weak performance and lack stability. Recently, synthetic polymer materials have been modified by introducing noncovalent and dynamic covalent bonds into their structure. This strategy shows great promise for the successful fabrication of polymers with self-healing properties.^[14–18] However, there is usually a trade-off between high structural robustness and efficient self-healing performance due to the conflict between free chain motion and a high degree of cross-linking. This means that the development of a new polymer material with appropriate dynamic

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bonds, mechanical robustness, and autonomous room-temperature self-healing abilities still remains a significant challenge.^[19,20]

Polymer chains that can undergo reversible chemical bond cleavage followed by chain recombination can exhibit rapid room-temperature self-healing abilities. Imine bonds can be reversibly severed and self-healed at room temperature, but materials based on these bonds exhibit unsatisfactory mechanical performance (strengths as low as 0.01 MPa).^[21] The Diels-Alder addition reaction can be used to prepare self-healing materials, but only low healing efficiency is achieved and high temperatures (>140 °C) are required.^[22] Materials with supramolecular π - π stacking have satisfactory room-temperature mechanical performance, but these materials typically have disappointing self-healing performance and excessively high glass transition temperatures (T_g s).^[23] Self-healing functionality can be achieved via the amide exchange reaction with reversible acylhydrazone bonds, but long healing times and high temperatures are required.^[24] Materials based on ion coordination bonds can be rapidly self-healed at room temperature, but these materials are susceptible at high temperatures and typically have strengths of less than 1 MPa.^[25] Compared to other dynamic bonds, disulfide bonds are capable of undergoing exchange reactions at mild temperatures, even down to room temperature. Moreover, it has been reported that aliphatic disulfide bonds exhibit lower efficiency for self-healing than aromatic disulfide bonds.^[26,27] Kim *et al.*^[28] used a simple aromatic disulfide metathesis reaction to prepare a high-strength thermoplastic polyurethane with rapid self-healing properties at room temperature. Huang *et al.*^[29] used allyl glycidyl ether (AGE) and 1,1,3,3-tetramethyldisiloxane (TMDS) to synthesize PDMS elastomers, which exhibited an excellent room-temperature self-healing efficiency of more than 95%. By introducing "sacrificial bonds" into molecular chains,^[30] the modulus and toughness of polymer materials can be greatly improved. These bonds can include metal coordination bonds, hydrogen bonds, ionic bonds, and so on. Moreover, the broken sacrificial bonds can be recovered under certain conditions. Zheng *et al.*^[31] combined sacrificial imine bonds with aromatic disulfide bonds, which acted as semi-permanent cross-linking points, to prepare PDMS elastomers that exhibited elongations at break of up to 2200%. PDMS/CNTs composites with a 1.1 MPa tensile strength have also been prepared by utilizing a CNT doping and hot pressing strategy.^[32]

PDMS is not conductive, which greatly limits the charge transport properties of TENGs. To solve this problem, conductive fillers and conductive interlayers can be incorporated into PDMS. Materials such as silver nanowires,^[33] liquid metal,^[19] carbon nanotubes and graphene have been reported. Guan *et al.*^[34,35] doped carbon nanotubes and silver nanowires into PDMS elastomers to form conductive pathways. Wang *et al.*^[36] designed PDMS elastomers using 1,2,4,5-tetrakis(trifluoromethyl)benzene as a chain extender and cross-linking agent. Then, they prepared a TENG with good ductility (50%) and high light transmittance (73%) by compounding the silver nanowires and polyethylenedioxythiophene. However, these conductive polymers often experience a "broken contact" phenomenon, resulting in charge transport instability. Therefore, to prepare TENGs with long-

term stable operation, PDMS elastomers with high strength, high toughness, and self-healing ability are urgently required. Zeraati *et al.*^[37] prepared a high conductivity (20000 S/cm) $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film by scraping and coating, which is due to the larger lateral size of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. Zhang *et al.*^[38] prepared nanocomposites with high tensile strength (237 MPa) comparable to that of superhard aluminum alloys by using MXene, which can form strong hydrogen bonds with lignin and polydopamine components. Liu *et al.*^[39] prepared a sensor with excellent conductivity by combining MXene with PDMS, and this sensor exhibited a sensitivity of up to 3.6.

Inspired by previous research and the criteria for developing high-performance TENGs, the self-healing PDMS elastomers with reversible disulfide bonds and hydrogen bonds were synthesized in this work. The hard segment of these elastomers was isophorone diisocyanate (IPDI), which had a noncrystalline, asymmetric, and alicyclic structure. The soft segment of the elastomers was hydroxypropyl-terminated PDMS, which had excellent chain mobility. This enhanced the thermal resistance of the elastomers by generating separate microphases. The elastomers also contained aromatic disulfide groups, which were used as chain extenders due to their room-temperature dynamic reversibility. Flexible MXene film was incorporated in the PDMS elastomers to provide good electrical conductivity. Finally, the composite material was folded and connected with copper wires to prepare a sandwich-structured TENG device with room-temperature self-healing properties. The electrical output, room-temperature self-healing performance, and recyclability of the prepared device were studied, and a self-powered device with potential application in sustainable energy systems was demonstrated. It was demonstrated that the TENG device was still able to function after cutting due to the PDMS elastomers, which exhibited excellent self-healing abilities.

EXPERIMENTAL

Materials

Bis(4-hydroxyphenyl)disulfide (HPS), 4,4'-dihydroxybiphenyl (PPDP), isophorone diisocyanate (IPDI), and dibutyltin dilaurate (DBTDL) were purchased from Shanghai McLean Biochemical Technology Co., Ltd. Bis(3-hydroxypropyl) polydimethylsiloxane (DHPDMS) is an industrial product, and was purchased from Shandong Dayi Co., Ltd., China. Anhydrous tetrahydrofuran, anhydrous DMF, and anhydrous ethanol were purchased from Tianjin Reagents Co., Ltd., (AR grade). All solvents were fully dried and dehydrated before using (adding fresh 4 Å molecular sieve and placing for at least 72 h). Raw materials and reagents were kept in the dryer under an inert gas atmosphere.

Preparation of PDMS

PDMS was synthesized by a one-pot method. First, the stoichiometric amount of DHPDMS was placed in a vacuum oven at 110 °C for 1 h to remove the containing water. Then the DHPDMS, HPS, IPDI, and DBTDL were dissolved in anhydrous THF, and added into a four-necked round-bottomed flask equipped with a condensing device, a mechanical stirrer, a thermometer under nitrogen protection. The reaction temperature was elevated to 65 °C, and a light yellow transparent solution was obtained after 5 h. PDMS-a, PDMS-b, PDMS-c were synthesized according to the different molar fraction of HPS and IPDI. PDMS-d was syn-

thesized using PDMS-b as a reference, and the main difference between PDMS-b and PDMS-d was that PDMS-d was synthesized using 4,4'-dihydroxybiphenyl (PPDP) without disulfide bonds. The composition of PDMS is shown in Table S1 (in the electronic supplementary information, ESI).

Preparation of PDMS Elastomers

First, the weight ratio of PDMS was adjusted to 30 wt% by adding anhydrous THF; then, the solution was poured into a square tetrafluoroethylene mold (5 cm × 5 cm), and placed in a vacuum oven with the temperature of 60 °C for 6 h. After removing most of the solvents, the temperature was raised to 120 °C and maintained for 6 h. Finally, after cooling to the room temperature, the product was taken out of the oven and the yellow transparent elastomer was obtained.

Preparation of TENG Composites

First, the aqueous dispersion of MXene with a mass fraction of 10 mg/mL injected into the PDMS-b elastomer (size: 20 mm × 10 mm × 2 mm) using a syringe, and the control area was about 19 mm × 9 mm. Subsequently, the PDMS elastomer was placed in a blast oven to obtain the smooth MXene film, and the aluminum foil was attached to the edge of the MXene film and connected with copper wires. Finally, the PDMS-b elastomer was folded from one side to the other, and placed in a blast oven (60 °C, 6 h) to prepare a sandwich-shaped TENG (Fig. S1 in ESI).

Characterizations

The Fourier transform infrared spectra (FTIR), Raman spectra, rheology experiments, thermogravimetric analysis (TGA), differ-

ential scanning calorimetry (DSC), tensile mechanical tests, constant-strain cyclic tensile test, self-healing experiments, reprocessing and recyclability experiments, electrical performance tests were conducted, and the experimental details were summarized in ESI.

RESULTS AND DISCUSSION

Structural Characterization of PDMS Elastomers

Herein, a dual dynamic covalent cross-linking system was constructed by integrating aromatic dynamic disulfide bonds and sacrificial hydrogen bonds into PDMS elastomers, which endowed them with good mechanical properties, decross-linking properties, reprocessability, and a self-healing ability at room temperature. The hydrogen bonds served as reversible sacrificial bonds to dissipate energy, which endowed the PDMS elastomers with excellent stretchability and room-temperature self-healing performance. Meanwhile, the elastomers also had good reprocessing and decross-linking properties due to their aromatic disulfide bonds. The synthesis route for preparing the PDMS elastomers is shown in Fig. 1.

The isocyanate groups (N=C=O) of IPDI reacted with the hydroxyl groups of HPS and DHPDMS to form carbamate bonds, which acted as the hard segment of the PDMS elastomers. It is worth noting that the urethane bonds between the molecular chains of the PDMS elastomers were able to form hydrogen bonds, which acted as cross-linking points for the PDMS elastomers. ATR-FTIR was conducted to evaluate the synthesis of the PDMS elastomers. Based on the changing intensity of the N=C=O stretching vibration band at 2258

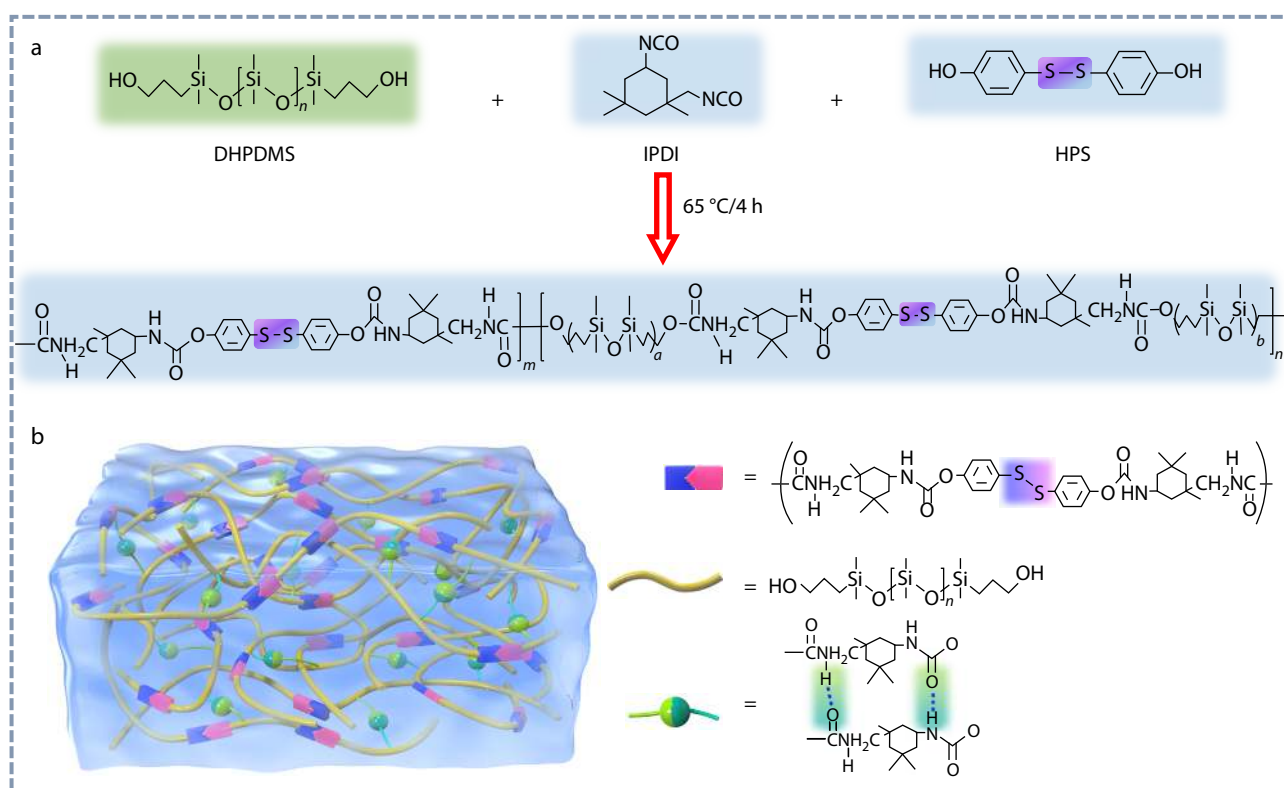


Fig. 1 Molecular structure design of PDMS elastomers: (a) Synthetic route to PDMS elastomers; (b) Schematic representation of the cross-linked network of PDMS elastomers.

cm^{-1} , the synthesis time was determined to be 4 h (Fig. 2a). The band at 3458 cm^{-1} was ascribed to $-\text{OH}$ stretching vibration. As shown in Fig. 2(b), the bands at 2258 and 3458 cm^{-1} almost disappear. Meanwhile, N-H bending vibration and C=O stretching vibration bands appear at 1546 and 1704 cm^{-1} ,^[36] respectively. This indicated that the N=C=O groups were consumed by reacting with $-\text{OH}$ groups. In addition, the stretching vibration band of Si-O-Si groups can be observed at 1020 cm^{-1} . Considering the S-S and aromatic C-S bond signals in the FTIR spectra are very weak, Raman spectroscopy was used to characterize the structure of PDMS elastomers. As shown in Fig. 2(c), an absorption band attributed to the symmetric stretching vibration of Si-O-Si is observed at 480 cm^{-1} , and a band corresponding to C=C stretching vibration was identified at 710 cm^{-1} .^[40] Compared with PDMS-a, PDMS-b, and PDMS-c elastomers, the stretching vibration absorption of C-S bonds (1100 cm^{-1}) was not detected in PDMS-d. This demonstrated that the aromatic disulfide bonds were successfully introduced into the PDMS elastomers. In summary, these results indicate the successful

synthesis of the PDMS elastomers. The visual appearance of the cured sample is shown in Fig. 2(d).

To investigate the hydrogen bonds in the PDMS elastomers, Gaussian fitting was performed on the C=O stretching vibration absorption bands at $1850\text{--}1600\text{ cm}^{-1}$. As shown in Figs. S2 and S3 (in ESI), increasing the chain extender proportion effectively improved the degree of order of the molecular chains. This resulted in a gradual increase in the relative content of ordered carbonyl groups and a gradual decrease in the content of disordered carbonyl groups. The hydrogen bonds in the PDMS-b elastomer were further evaluated using variable-temperature FTIR spectroscopy. With increasing temperature, the band at 1694 cm^{-1} (assigned to the C=O stretching vibration absorption of the urethane bonds) shifted to a higher wavenumber, whereas the band at 1540 cm^{-1} (ascribed to N-H bending vibration absorption) shifted to a lower wavenumber (Fig. 2e).^[40,41] This result indicated that the hydrogen bonds between N-H and C=O dissociated with increasing temperature, demonstrating the temperature sensitivity of the hydrogen bonds in the PDMS elas-

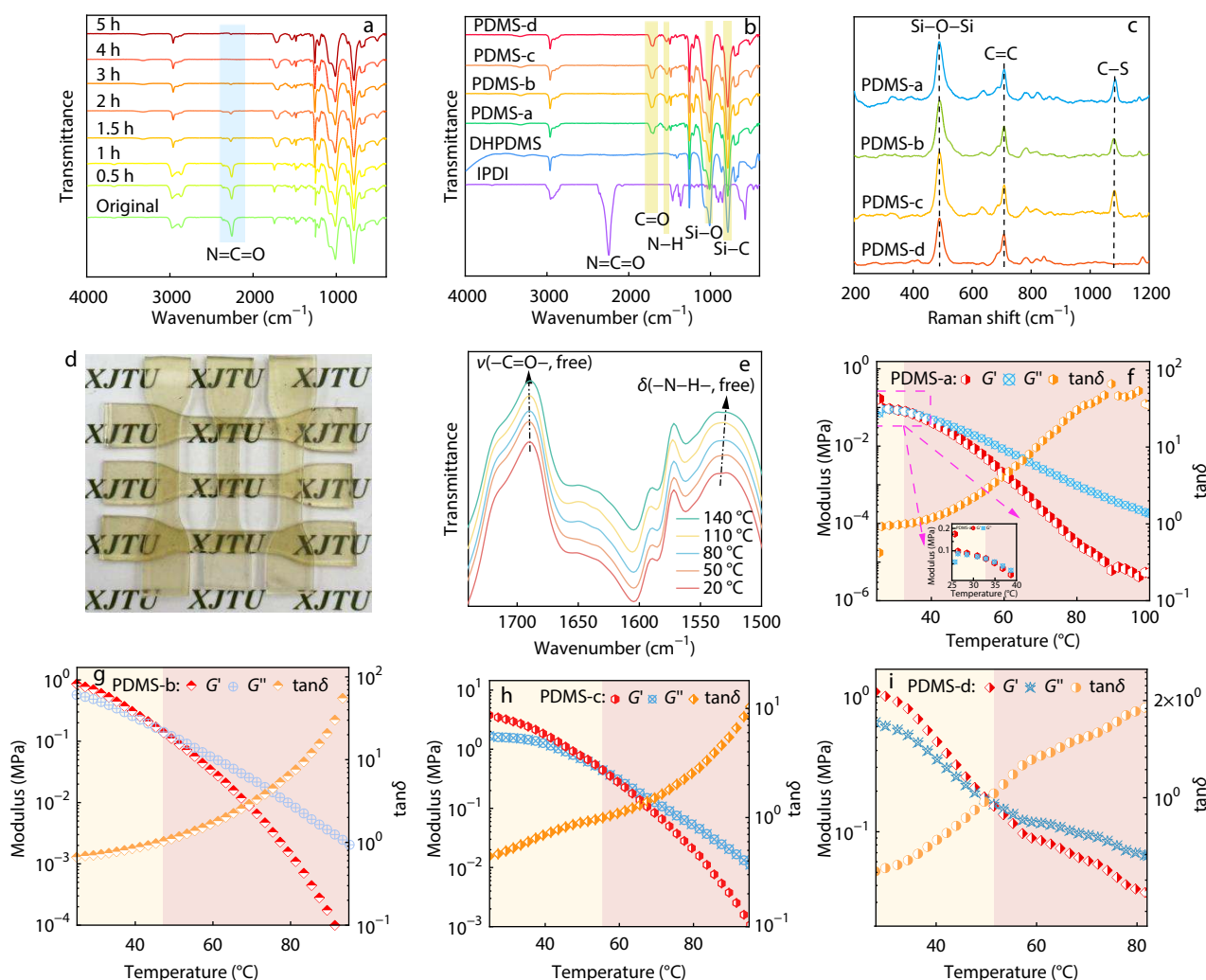


Fig. 2 (a) FTIR spectra tracking the change of N=C=O in PDMS-b elastomer; (b) FTIR spectra of PDMS elastomers; (c) Raman spectra of PDMS elastomers; (d) The appearance of the molded PDMS-b elastomer; (e) The variable temperature FTIR spectra of PDMS-b elastomer; (f–i) Rheological curves of PDMS elastomers at constant speed of temperature rising.

tomers.^[42]

A rotational rheometer was used to further characterize the dissociation temperature of the hydrogen bonds. As curing progressed, the loss modulus and storage modulus gradually increased, and the system experienced a solid-fluid transition. The temperature at which the storage modulus was equivalent to the loss modulus ($G' = G''$, $\tan\delta = 1$) was regarded as the transition temperature (T_{trans}) of the cross-linked network, which was closely related to the dissociation of hydrogen bonds. It is concluded that when the temperature is lower than T_{trans} , PDMS has a solid-state structure, and the G' is higher than that of the G'' . With the increase of temperature, the G' and G'' of PDMS decreased gradually. When the temperature was higher than T_{trans} , hydrogen bonds as physical crosslinking points of PDMS elastomers, were dissociated, and the crosslinking network was destroyed. As a result, the viscosity of the elastomer decreased rapidly, and the elastomer was in a viscous flow state. At the same time, the G'' was higher than that of the G' . Guo *et al.*^[43] prepared the polydimethylsiloxane elastomer based on the hydrogen bonds and disulfide bonds, and the rheological test results also confirmed the above statement. As shown in Figs. 2(f)–2(i), the T_{trans} value of PDMS-b was 46.3 °C, which was consistent with the variable-temperature FTIR spectroscopy results. With increasing IPDI content, more urethane bonds were formed in the PDMS elastomers, leading to higher hydrogen bond content in the cross-linked network. In turn, this resulted in a higher T_{trans} . For example, the T_{trans} of PDMS-c was 55.9 °C.

Mechanical and Thermal Properties of PDMS Elastomers

Uniaxial tensile tests, cyclic tensile tests, and tensile recovery tests of the PDMS elastomers were carried out with a universal tensile test machine. Fig. 3(a) shows the stress-strain curves of the PDMS elastomers. PDMS-a, b, and c elastomers exhibited increasing tensile strength with increasing hard segment content, while their elongations at break significantly decreased. The PDMS-a and PDMS-c elastomers had tensile strength values of 0.14 and 2.54 MPa, respectively, while their elongations at break were 1250% and 153%, respectively. Young's modulus values were evaluated using the low-strain linear region of the curves. The Young's modulus values increased with increasing hard segment content. PDMS-c had a Young's modulus of 27.05 MPa (Fig. S4 in ESI), which was 25 times and 3 times higher than that of PDMS-a (1.05 MPa) and PDMS-b (9.41 MPa), respectively (Table S2 in ESI). As shown in Fig. 3(b), the work of fracture of the PDMS elastomers was calculated according to the integrated area under their stress-strain curves. With increasing IPDI and HPS content, the work of fracture of the PDMS elastomers showed an increasing then decreasing trend. The higher tensile strength and lower elongation at break with increasing hard segment content explained this trend. Compared with the PDMS-d, the PDMS-b elastomer with aromatic disulfide bonds exhibited higher elongations at break. On the one hand, the aromatic disulfide metathesis can act as the sacrificial bonds for breakage to enhance the material stretchability.^[43,44] Therefore, the stress of the elastomers was more easily released when stretched, resulting in an increase in the elongation at break. On the other hand, PDMS-b elastomer containing aromatic disulfide bonds is more softer and the glass transition temperature is

lower than that of PDMS-d elastomer.

The energy dissipation behavior of the PDMS elastomers was investigated by cyclic tensile testing to clarify the formation mechanism of hydrogen bonding. During testing, the strain increased by 50% for each cyclic test. The zone between the loading and unloading stress-strain curves obtained during the cyclic tension tests is known as the hysteresis loop (Figs. 3c and 3d), which is used to characterize the consumed mechanical energy during stretching. Due to the low elongations at break of the PDMS-c and PDMS-d elastomers (153% and 192%, respectively), only three cycles were conducted with these elastomers (Fig. S5 in ESI). With increasing hard segment content, the correspondingly higher hydrogen bond content enhanced the mechanical energy dissipation. For example, the initial (50%) cycles of PDMS-a and PDMS-b elastomers generated 0.09 and 0.33 MJ/m³ energy, respectively. When a small strain was applied, the weaker hydrogen bonds first broke and dissipated some of the energy. The number of broken hydrogen bonds increased with increasing tensile strain. Meanwhile, the aromatic disulfide bonds began to break, eventually leading to a significant increase in the dissipated mechanical energy (Fig. S6 in ESI). More mechanical energy was dissipated when a larger strain was applied, and the elastomer was unable to immediately recover its initial mechanical properties, eventually leading to the destruction of the cross-linked network. These results demonstrate that the hydrogen bonds served as physical cross-linking points, which were able to dissipate most of the energy in the form of sacrificial bonds. This also improved the mechanical properties of the PDMS elastomers.

To further evaluate the reversibility of the hydrogen bonds during the stretching of PDMS elastomers, cyclic stretching tests were performed to study the influence of cycle number on the mechanical performance of the PDMS elastomers (Figs. 3e and 3f). Hysteresis was observed in each stretching cycle, and the maximum tensile strength gradually decreased as the number of cycles increased. The dynamic covalent bonds were not fully recovered during the stretching cycles, which was because some of the dynamic covalent bonds were broken to resist the deformation caused by the external forces during stretching. As a result, the highest maximum tensile strength was achieved in the first stretching cycle, and a smaller number of sacrificial bonds was available for energy dissipation in the next cycle. Accordingly, the dissipated energy and tensile strength decreased with increasing cycle number. This stress-drop phenomenon, which is exhibited by rubber-like elastomers during cycling, is known as the "Mullins effect".^[45,46] The "Mullins effect" is a special property for the filled rubber, and the effect takes its name from the British rubber scientist Leonard Mullin who studied the phenomenon on rubbers. The characteristic of Mullins effect is that the stress-strain curve depends on the maximum load of the previous tensile process. In most cases, it can be idealized as an instantaneous irreversible softening of the stress-strain curve, as long as the increase in load exceeds all previous load maximums. The PDMS elastomers were held for 2 h at room temperature before the 7th cyclic test. As shown in Fig. S7 (in ESI), the tensile strength recovered to a certain extent compared with the previous 6 cycles. Fig. 3(g) shows the gradual

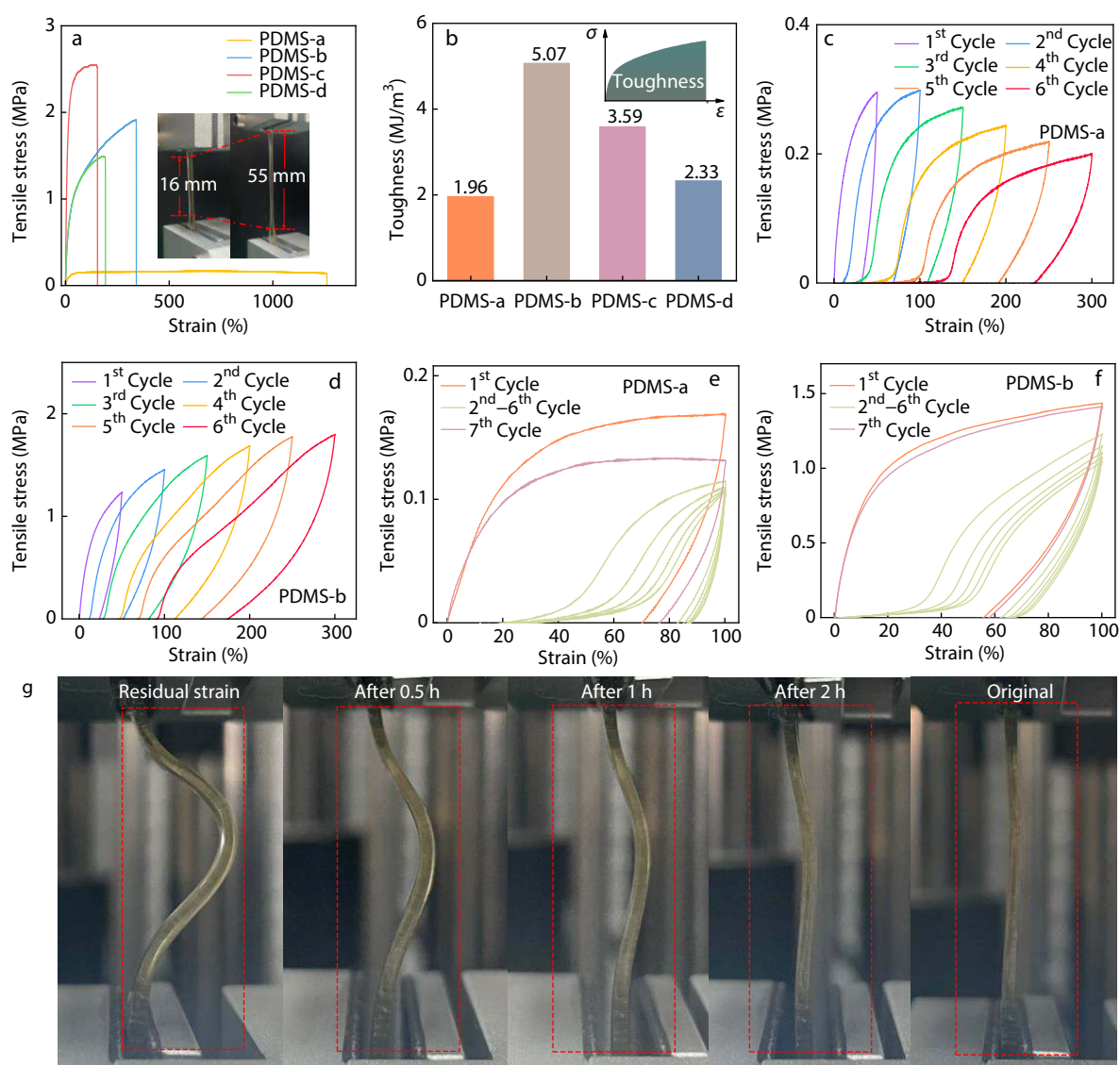


Fig. 3 (a) Stress-strain curves of the PDMS elastomers; (b) The work-to-break of PDMS elastomers; (c, d) The cycle tensile stress-strain curves of PDMS-a and PDMS-b elastomers; (e, f) Cyclic tensile curves of PDMS-a and PDMS-b elastomers at 100% strain; (g) The gradual recovery of the residual strain of the PDMS-b elastomer after held for 2 h at room temperature before the 7th cyclic test.

recovery of the residual strain of the PDMS-b elastomer after six stretching cycles. After the PDMS-b elastomer was allowed to stand for 30 min, most of the deformation was recoverable, and the full recovery of deformation required 2 h. As shown in Fig. 3(f), the loading-unloading-reloading stress-strain curves of the PDMS-b elastomer after the 7th cycle almost overlapped the original curve. Meanwhile, the tensile strength and dissipation energy of the 7th stretching cycle were comparable to those of the first cycle. These results indicated that the dissociated hydrogen bonds and disulfide bonds of the PDMS elastomers respectively underwent highly reversible association reactions and exchange reactions. Therefore, the elastomer deformation and mechanical properties of the elastomers were recoverable by allowing the samples to stand at room temperature.

Differential scanning calorimetry (DSC) was used to evaluate the glass transition temperatures (T_g) of the PDMS elas-

tomers (Fig. S8 in ESI). The intermolecular hydrogen bonds formed by N—H and C=O in the urethane bonds were conducive to the molecular chain orientation at lower temperatures, which was due to their directional nature. This resulted in the PDMS elastomers undergoing an obvious Han relaxation phenomenon.^[42] Therefore, this temperature was taken as the T_g of the PDMS elastomers. The T_g of the PDMS elastomers increased with increasing hard segment content. For example, the T_g values of PDMS-a and PDMS-c elastomers are -100 and -87 °C, respectively. These low T_g values endowed the PDMS elastomers with excellent flexibility at room temperature and better chain movement ability. This was conducive to the low-temperature self-healing of the elastomers.

The friction layers of TENGs are damaged due to local overheating during use. Therefore, the thermal properties of the PDMS elastomers were characterized by TGA (Fig. S9 in ESI). The energy of the Si—O bond (466 kJ/mol) is much higher

than that of the C—C (332 kJ/mol) and C—O (326 kJ/mol) bonds. Thus, PDMS elastomers exhibit good thermal resistance and can be used in a wide temperature range.^[47] Two obvious weight loss peaks were observed in the DTG curves of the PDMS elastomers. The low-temperature weight loss peak at about 320 °C corresponded to aromatic disulfide bond degradation, while the high-temperature peak at about 420 °C was attributed to the random depolymerization process of the polysiloxane backbone. Therefore, the thermal stability of the PDMS elastomers was significantly enhanced by the aromatic disulfide bonds. These bonds also influenced the initial degradation temperature of the elastomers. PDMS-b had a thermal decomposition temperature ($T_{5\%}$) of 260 °C, and the maximum thermal decomposition temperature ($T_{\max}$) was as high as 429.5 °C (Table S3 in ESI). Thus, it is believed that the PDMS elastomers can be used as negative friction layers to ensure the structural integrity of TENGs under long-term high-temperature operation.

Self-healing Properties of PDMS Elastomers

Polymer materials need to meet two conditions to achieve good self-healing properties. One, the polymer chain segments at the self-healing interface should have sufficient mobility, and two, dynamic covalent bonds should exist at the self-healing interface.^[48] In this work, the existence of dynamic covalent aromatic disulfide bonds, non-covalent hydrogen bonds, and good molecular chain flexibility provided the PDMS elastomers with excellent self-healing performance. Uniaxial tensile tests were conducted on the PDMS elastomers before and after self-healing to determine their healing efficiency. The ratio of the mechanical properties of each healed sample to the mechanical properties of the original sample was taken as the healing efficiency. The results revealed that the PDMS-a and PDMS-b elastomers exhibited good room-temperature self-healing performance. For example, PDMS-a exhibited healing efficiencies of 92% and 98% after healing at room temperature for 3 and 12 h, respectively (Fig. 4a). The healing efficiency of PDMS-b was 97.4% (Fig. 4b). It is worth noting that the PDMS-c and PDMS-d elastomers required higher temperatures for complete self-healing because these samples had more hydrogen bonds. For instance, PDMS-c and PDMS-d exhibited self-healing efficiencies of only 61% and 67% at room temperature for 24 h (Fig. 4c, Fig. S10 in ESI), respectively. This was because the higher IPDI and HPS content in PDMS-c and PDMS-d increased their hydrogen bonding content and cross-linking density. This greatly limited the movement of molecular chains, which affected the healing efficiency. These results also showed that the aromatic disulfide bonds were the main factor influencing the room-temperature self-healing properties of the PDMS samples in this work. It is known that the aromatic disulfide bonds can undergo room temperature exchange reactions, which has been reported in the published references. For example, Cai *et al.*^[44] prepared the room-temperature self-healing PDMS-polyurethane (PU) elastomers based on aromatic disulfide bonds, and the self-healing efficiency of PU elastomer reached 92.9% within 3 h. Kim *et al.*^[28] prepared thermoplastic polyurethane (TPU) based on aromatic disulfide bonds, after cutting the TPU film into two halves and re-splicing, the mechanical properties were restored to more than 75% of the original sample within 2 h at room temperature.

PDMS-c and PDMS-d showed increasingly improved self-healing performance with increasing temperature (Fig. S11 in ESI). Higher temperatures were more conducive to enhancing molecular chain movements, which promoted the dissociation and association of hydrogen bonds as well as the bond exchange reactions of the aromatic disulfide bonds. At elevated temperatures of 45 and 60 °C, the PDMS-c elastomer exhibited self-healing efficiencies of 60% and 97%, respectively. In addition, the mechanical properties of PDMS-b were compared with those of other reported PDMS elastomers with room-temperature self-healing properties (Fig. 4d). PDMS-b compared very favorably to these materials, especially with better tensile strength than any other similar material that has been currently reported.

Optical microscopy was used to study the fracture and recombination properties of the PDMS-b elastomer at room temperature after different healing times (Fig. 4e). This analysis allowed the self-healing performance of this elastomer to be analyzed in detail at the molecular bond scale. As the contact time reached 12 h, slight scratches were still observed on the surface of PDMS-b, but these scratches almost disappeared after 24 h of healing. This indicated room-temperature healing for 24 h was sufficient for completely removing the scratches on the PDMS-b surface. Next, the PDMS-b sample was cut into two sections, and the two damaged ends were brought into contact to heal for 24 h at room temperature (Fig. 4f). The two separate pieces of PDMS-b were completely joined together after 24 h, and the healed sample was able to support a 200 g weight. This PDMS elastomer exhibited superb self-healing performance at room temperature, which was mostly due to the synergy of the bonds in the polymer framework (the abundant dynamic aromatic disulfide bonds and hydrogen bonds) (Fig. 4g). This synergy enabled the rapid room-temperature reconstruction of the network. The low T_g of the PDMS elastomer also enhanced its self-healing properties.

Recyclability of PDMS Elastomers

Good reprocessability is very important for the recycling and reuse of polymers. Therefore, the recyclability and reprocessing properties of the PDMS-b elastomer were investigated. Due to its highly dynamic hydrogen bonds and aromatic disulfide bonds, superb recyclability was achieved under mild conditions, enabling this material to be reprocessed in a solid state. First, the PDMS-b sample was cut into smaller pieces. Next, the bulk PDMS-b sample was reformed by hot-pressing the smaller pieces at 25 °C for 2 h under a pressure of 10 MPa. The reprocessed elastomer exhibited adequate optical transparency (Fig. 5a). This process was repeated for several times, and the recycled elastomers were then evaluated in terms of their structural and mechanical properties. FTIR and tensile tests were performed after each reprocessing cycle (Figs. 5b and 5c, Table S4 in ESI). Notably, no discernible changes in the chemical structure and mechanical properties were observed over three reprocessing cycles. The excellent reprocessing properties of the PDMS elastomer can be explained by the following reasons. When the elastomer was cut into small fragments, the disulfide bonds and hydrogen bonds in the polymer network were destroyed. Due to the flexibility of the molecular chains as well as the dynamic reversibility of the hydrogen bonds and disulfide

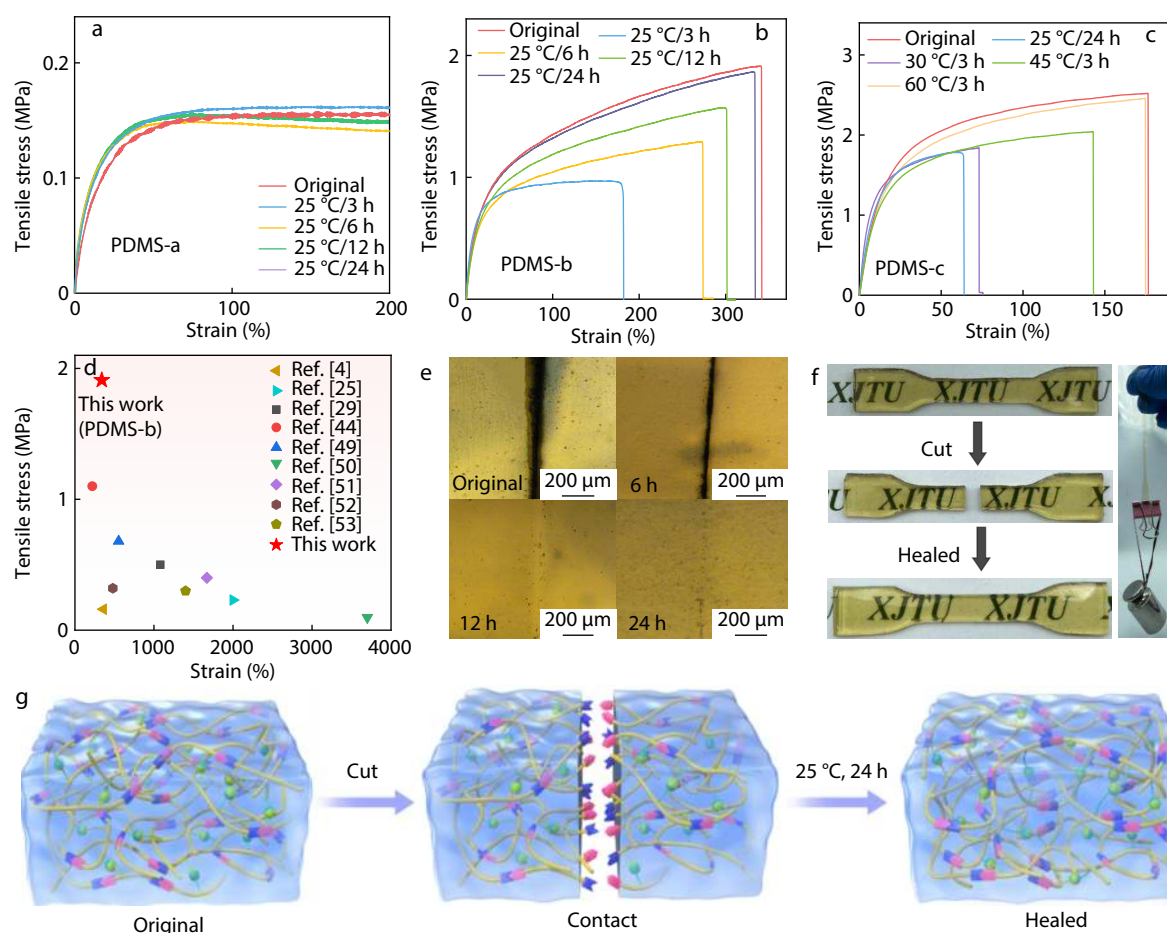


Fig. 4 (a, b) Stress-strain curves of PDMS-a and PDMS-b elastomers at room temperature for different healing times; (c) Stress-strain curves of PDMS-c elastomer at different temperatures for 3 h; (d) The comparison of the mechanical properties of PDMS-b elastomer and other PDMS elastomers with room-temperature self-healing properties; (e) Optical microscope observation of the room-temperature self-healing process of PDMS-b elastomer; (f) Photographs demonstrating the self-healing process of PDMS-b elastomer (g) Schematic diagram of the room-temperature self-healing process of PDMS-b elastomer.

bonds, the reconstruction of the network was gradually realized. Therefore, the recovered mechanical performance was comparable to that of the original sample. However, this solid-phase recycling method has significant limitations in actual applications.

PDMS elastomers cross-linked with hydrogen bonds can be dissolved in most organic solvents and only swelled in water (Fig. S12 in ESI). The gel fraction and swelling ratio of PDMS-a, PDMS-b and PDMS-c in water at room temperature for 24 h were tested as well (Fig. S13 and Table S5 in ESI). Consequently, the liquid-phase recycling of PDMS-b can be realized. Compared with the other synthesized PDMS elastomers, the PDMS-b elastomer exhibited higher tensile strength (1.91 MPa), superior toughness (work to fracture of 5.07 MJ/m³), and excellent room-temperature self-healing efficiency (96%). Therefore, the liquid-phase recyclability of PDMS-b was evaluated. The PDMS-b elastomer was added to THF solution, which was left to stand at room temperature for 24 h (Fig. 5d). Then, the recovered solution was re-cured to obtain a dumb-bell-shaped sample. Figs. 5(e) and 5(f) show that the structural and mechanical properties of the recycled sample were comparable to those of virgin samples even after three recycling cycles. After recycling, the PDMS-b elastomer had a ten-

sile strength of 1.87 MPa, which was 98.9% of the original value (Table S5 in ESI). Furthermore, the elongation at break of the recycled sample was 335%, which was 97.9% of the elongation at break of the original sample. Overall, these results indicate that the PDMS-b elastomer is highly suitable for both solid-phase reprocessing and liquid-phase recycling *via* exchange reactions with the aromatic disulfide bonds without any catalyst.

TENG Performance

TENGs are emerging green energy devices, and the selection of the negative friction layer in a TENG is vitally important for improving its electrical output performance and protection performance. It is well-known that the negative friction layer of TENGs is easily damaged by extrusion or the friction caused by external mechanical forces. Therefore, this layer requires good toughness. If the negative friction layer in a TENG is damaged, the electrical output of the TENG will be severely affected. Therefore, the aim of this research was to develop a PDMS elastomer with excellent comprehensive performance for use as the negative friction layer of a TENG.

In this work, a TENG was fabricated using the PDMS-b elastomer and flexible MXene film, and the working mechanism is

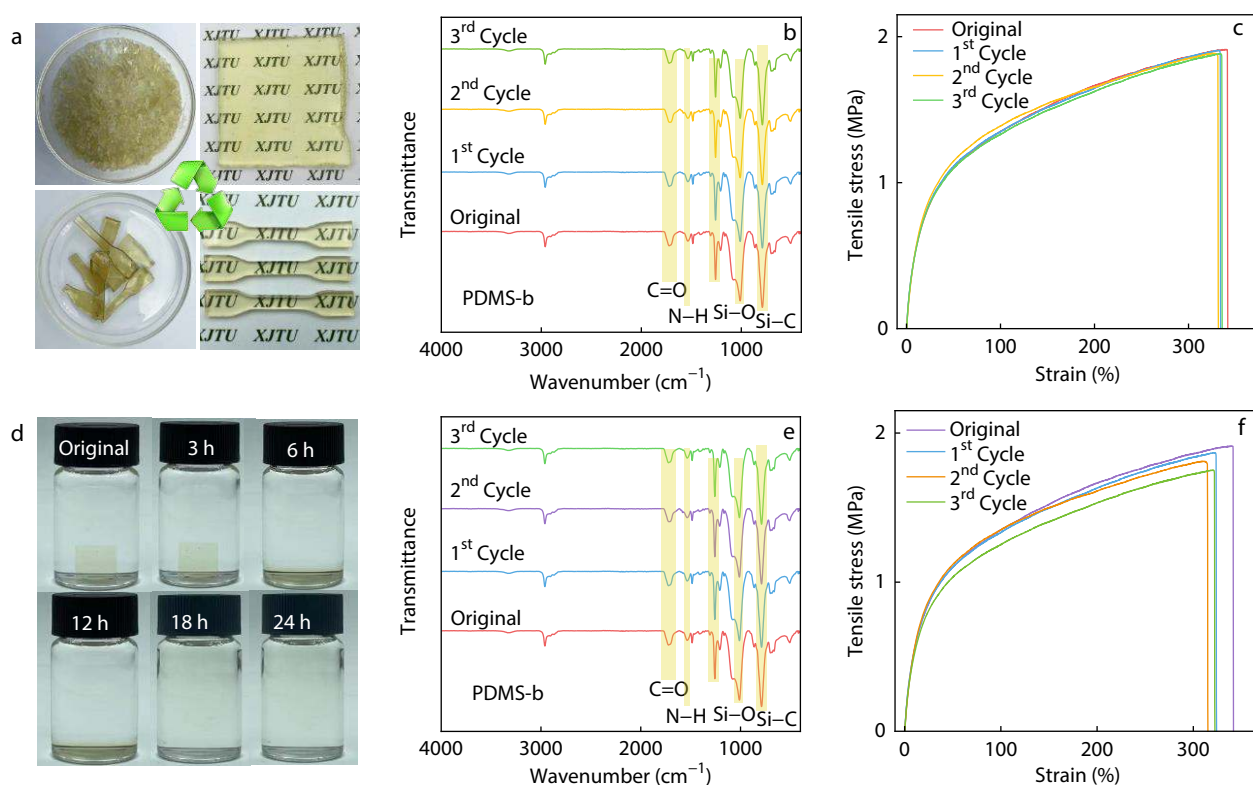


Fig. 5 (a) The solid-phase reprocessing of PDMS-b elastomer; (b) FTIR spectra of PDMS-b elastomer after reprocessed for three times through solid-phase reprocessing; (c) Stress-strain curves of PDMS-b elastomer after reprocessed for three times through solid-phase reprocessing; (d) The liquid-phase recycling of PDMS-b elastomer; (e) FTIR spectra of PDMS-b elastomer after three times of liquid phase recovery; (f) Stress-strain curves of PDMS-b elastomer after three times of liquid phase recovery.

shown in Fig. 6(a). The metal surface of a vibrator was used as the outer surface. When this surface came into contact with the TENG, charging behavior was observed due to charge transfer across the interface. This resulted in the generation of static negative charges on the PDMS-b surface and the generation of negative charges on the metal surface. Afterward, the metal and PDMS-b surfaces were separated, which generated a potential. As a result, the negatively charged PDMS elastomer surface caused the MXene electrode to become positively charged. Electrostatic equilibrium was finally attained when the acetonitrile membrane and PDMS-b layer reached the maximum separation distance. This process was reversed by moving the metal surface closer to the PDMS-b layer again, causing a current pulse in the opposite direction.^[10] As a result, an open-circuit voltage (V_{oc}) of 13.5 V was generated by the TENG through the continuous contact/separation motion (Fig. 6b). To evaluate the electric performance enhancement of PDMS with MXene conductive layer, the output voltage and short-circuit current of PDMS-TENG and MXene/PDMS-TENG. After adding the MXene electric layer, the output voltage increases by 7 times from 15 V to 100 V; the short-circuit current maximum increases from 0.3 μ A to 4.5 μ A (Fig. S14). The enhancement of TENG output performance is attributed to the fact that MXene layer makes the surface of PDMS elastomer conductive, increasing the surface charge number of PDMS elastomer.

When the friction layer of a TENG is damaged by external mechanical force during utilization, the performance of the

TENG is impacted. Therefore, the self-healing performance of the prepared TENG at room temperature was investigated. As shown in Fig. 6(c), the TENG was cut through the middle and then reconnected. After 24 h, the fracture surface of the TENG was completely healed. This was ascribed to the excellent room-temperature self-healing properties of PDMS-b. The change in the open circuit voltage was used to characterize the self-healing efficiency of the TENG (Fig. 6e). After 3 healing cycles, the TENG still achieved a similar V_{oc} as that of the pristine TENG. This also indicated that the self-generating properties of TENG were able to be healed at room temperature. The MXene layer did not have self-healing properties. However, the MXene film was still able to form an electrically conductive path during the elastomer healing process, allowing for the effective output of the voltage signal. To further evaluate the reusability of the TENG, the PDMS-b elastomer and MXene film were separated by solvent recovery method and then reassembled to form a new TENG. As shown in Fig. 6(d), anhydrous THF was used as the recovery solvent. The recovered MXene film maintained a complete structure, and the mass retention rate of MXene remained unchanged after immersion in THF for 12 h (Fig. S15 in ESI). The PDMS-b elastomer was dissolved in the THF, and the recovered solution was re-cured to form the PDMS-b elastomer, which was re-fabricated into the TENG. After three recycling cycles, the open-circuit voltage of the TENG was 12.5 V (Fig. 6f), and up to 90% of the original electrical output performance was recovered. This showed that the MXene can be reused as the

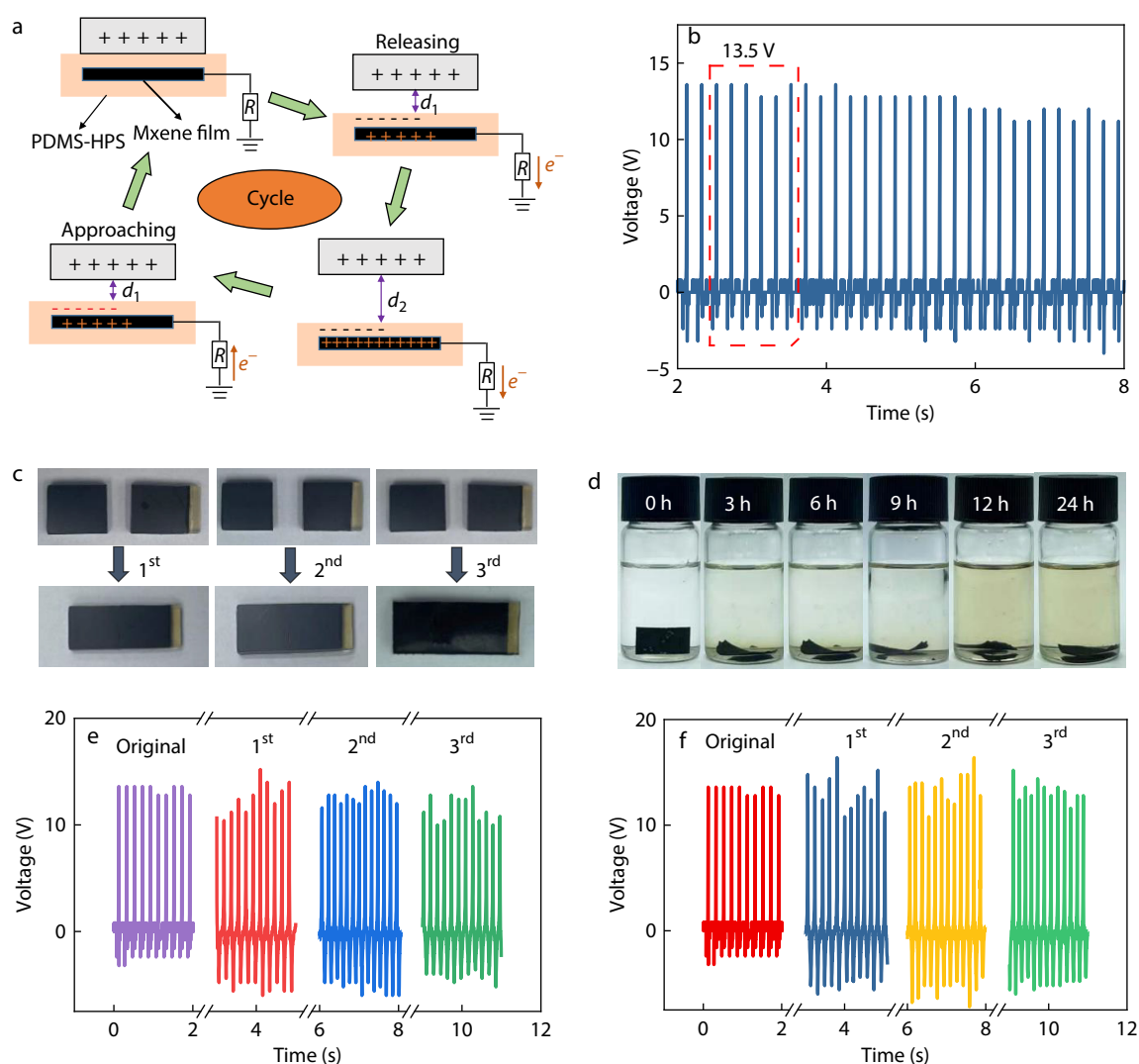


Fig. 6 (a) Assembly diagram and working principle of TENG; (b) The open circuit voltage of TENG; (c) Schematic diagram of the self-healing of TENG; (d) The solvent recovery of TENG; (e) Comparison of electrical properties of TENG before and after healing; (f) Comparison of self-generation performance of TENG before and after recovery.

conductive layer in the TENG and that the negative friction layer can be completely separated from the conductive layer. This result offers a new idea for recycling TENG devices.

CONCLUSIONS

In this work, PDMS elastomers with good mechanical properties, self-healing properties, and recyclability were prepared by introducing multiple hydrogen bonds and aromatic disulfide bonds. Hydrogen bonds were generated among the urethane bonds formed by the reaction of isocyanate groups with hydroxyl groups. The presence of these hydrogen bonds enhanced the mechanical properties of the PDMS elastomers while generating physical cross-links. For example, the tensile strength, elongation at break, and modulus of the PDMS-b elastomer were 1.91 MPa, 340%, and 9.41 MPa, respectively. Meanwhile, the aromatic disulfide bonds were able to undergo room-temperature exchange reactions. Combined with the association and dissociation properties of the hydrogen bonds, this allowed the PDMS-b elastomer to exhibit a room-temperature self-healing effi-

cy of up to 96% after 24 h. Moreover, the solid-phase reprocessing and liquid-phase recycling of the PDMS elastomer were realized *via* the exchange reactions of the aromatic disulfide bonds in the absence of a catalyst. PDMS-b samples that underwent multiple recycling cycles exhibited similar structural and mechanical properties to those of the virgin material. Finally, the PDMS-b elastomer was combined with MXene to fabricate a TENG, which exhibited an excellent electrical output (open circuit voltage of 13.5 V) as well as good room-temperature self-healing properties. In addition, a TENG recycling experiment showed that the entire MXene film could be recovered, and the electrical output performance of a recycled TENG was still nearly 92% of that of the original TENG. This study provides an effective method for fabricating self-healing negative friction layers for high-performance TENGs.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-024-3178-5>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. The author's contact information: xljing@mail.xjtu.edu.cn.

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