Eng. Sci., 2023, **22**, 815

Engineered Science
DOI: https://dx.doi.org/10.30919/es8d815

# Dynamic Crosslinked Silicones and Their Composites: A Review

Juan Ye,[1] Hao Jin,[1] Zhaoji Zu,[1] Bing Yu,[1] Hongping Xiang[1,*] and Mingqiu Zhang[2,*]

## Abstract

The introduction of diverse dynamic bonds into the polysiloxane crosslinked networks can form dynamic crosslinked silicones and their composites, which not only maintain the good physicochemical performance of polysiloxane but also exhibit novel healing ability and reprocessability. They have shown broad application prospects in smart coatings, sensors, and flexible devices. However, the trade-off between excellent dynamic behavior and high mechanical property is challenging their practical applications. To improve this situation, recent advances that highlight the molecular structure design, property modulation, and potential application of dynamic crosslinked silicones and their composites with self-healing and reprocessing abilities are reviewed herein. Firstly, self-healing silicones are discussed according to their dynamic crosslinked network that is transforming from a single dynamic bond to multiple dynamic bonds to optimize mechanical property and self-healing efficiency. Next, the recycling or reprocessing of dynamic crosslinked silicones is also reviewed in accordance with their reprocessing methods to meet special requirements from different fields. Then, dynamic crosslinked silicone composites are discussed in terms of kinds of nanofillers to further enhance properties and broaden functionalities. What is more, the promising prospects and facing challenges dynamic crosslinked silicones and their composites are also proposed to achieve an early realization of commercial applications.

*Keywords:* Silicones and their composites; Dynamic bonds; Dynamic crosslinked network; Self-healing ability; Reprocessability.
Received: 27 November 2022; Revised: 14 January 2022; Accepted: 05 February 2022.
Article type: Review article.

## 1. Introduction

Silicone materials referred primarily to polysiloxane materials compose of inorganic –Si–O– as backbones, with at least one organic methyl, phenyl, or other functional groups as –Si– side groups, including silicone oil, silicone rubber, and silicone resin. Ascribed to their unique organic-inorganic hybrid structures, they reveal distinctive chemical and physical properties such as excellent high/low-temperature resistance, aging resistance, electrical insulation, hydrophobicity, and biocompatibility.[1-6] Utilized as rubbers, sealants, coatings, and adhesives, silicone materials have been widely applied in electronics, aerospace, healthcare, construction, transportation, 3D printing, and other fields.[7-13] Owing to the very weak interaction among polysiloxanes, silicone rubber, and silicone resin often need to be vulcanized via polycondensation at room temperature or hydrosilation under elevating circumstances, accompanied by the formation of covalent –Si–O–Si– or –Si–C– bonds.[14-16] However, the formed permanently crosslinked structures meanwhile cause difficulty to repair the internal micro-damages and recycle the waste silicones, which lead to greatly shortened service life, serious environmental pollution, and vast resource waste.

In recent years, dynamic crosslinked polymers spotlight an attractive research field, because their inherent dynamic crosslinked networks endow them with self-healing ability, recyclability, and reprocessability, enabled by reversible dissociation and recombination or metathesis of dynamic bonds under external stimuli.[17,18] Taking advantage of dynamic crosslinked networks, lots of traditional polymers, especially thermoset polymers have already become self-healable, recyclable, and reprocessable.[19-22] Recently, dynamic crosslinked silicone materials have also received increasing attention, owing to the excellent physicochemical

---

[1] *Guangdong Provincial Key Laboratory of Functional Soft Condensed Matter, School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, Guangdong, PR China.*
[2] *Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, GD HPPC Lab, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, PR China.*
**Email:* xianghongping@gdut.edu.cn (H. Xiang); ceszmq@mail.sysu.edu.cn (M. Zhang)

property of silicones and novel self-heal ability, recyclability, and reprocessability. From Table 1, many dynamic crosslinked silicone materials have been developed by virtue of diverse dynamic bonds such as hydrogen bond~~s.~~,[23,24] coordination bond,[25,26] ionic bond,[27] Diels-Alder bond,[28] disulfide bond[29,30] and imine bond.[31,32] Dynamic crosslinked silicones reveal emerging applications in flexible electronic devices, optical devices, smart coatings, sensors, and actuators.[23-34]

Notably, it is still worth noting that the trade-off between excellent dynamic behavior and good mechanical property remains a great challenge to dynamic crosslinked silicones.[33,34] Therefore, this review aims to highlight recent progress on dynamic crosslinked silicones and their composites, according to the crosslinked network design, performance modulation, and multifunctional applications (Fig. 1). Initially, self-healing silicone materials are presented.

**Table 1.** Self-healing and reprocessing condition and efficiency of diverse dynamic crosslinked silicone materials.

| Dynamic bond types | | Mechanical property | Self-healing condition and efficiency | Reprocessing condition and efficiency |
|---|---|---|---|---|
| Dynamic non-covalent bond | Hydrogen bond | 0.013 ~ 10.5 MPa [35-42] | RT ~ 100 °C, 5 min ~ 48 h； 86 ~ 100 % [35-42] | 70 °C, 12 h; 100 % [37] |
| | Metal-ligand Coordination | 0.46 ~ 3.25 MPa [43-48] | -20 ~ 100 °C, 1 ~ 72 h; 68 ~ 100 % [43-48] | 80 °C, 10M Pa, 1 h; 100 % [47] |
| | Ionic bond | 0.22 ~ 5.68 MPa [49-51] | 60 ~ 80 °C, 4 ~ 48 h; 83 ~ 90 % [49-51] | (1) 100 °C, 22 MPa, 12 h; 90 % [49](2) 100 °C, 5 min; 100 % [51] |
| | Metal-ligand coordination and hydrogen bond | 0.32 ~ 1 MPa [52,53] | RT ~ 90 °C, 1 ~ 4 h; 89 ~ 99 % [52,53] | -- |
| | Metal-ligand coordination and ionic bond | 0.15 ~ 0.73 MPa [54] | 60 °C, 8 h; 80 ~ 100 % [54] | -- |
| Dynamic covalent bond | Diels-Alder bond | 0.61 ~ 1.09 MPa [55-57] | 80 ~ 130 °C, 45 min ~ 24 h; 90 ~ 95 % [55-57] | 140 °C, 20 MPa, 1.5 h; 90 % [55] |
| | Imine bond | 0.18 ~ 2.8 MPa [58-61] | RT ~ 100 °C, 1 ~ 24 h; 93 ~ 100 % [58-61] | RT or 60 ~ 100 °C, 15 MPa; 83 ~ 85 % [58-61] |
| | Disulfide bond | 0.23 ~ 3.0 MPa [62-65] | (1) RT ~ 120°C, 30 min ~ 3 h; [63,64]<br>(2) Exposed to UV light [62,65] | (1) 150 °C, 2 h; 70 ~ 80 %; [65]<br>(2) UV radiation for 30 min [62,65] |
| | Urea and hindered urea bonds | 0.4 ~ 7.9 MPa [66, 67] | 80 ~ 120 °C, 7 ~ 24 h; 82 ~ 96 % [66, 67] | 120 °C, 10 MPa, 30 min, or 80 °C, 3 h; 90 % [66] |
| | Transesterification | 0.4 ~ 3.0MPa [68-71] | RT or 70 ~ 80°C, 30 min ~ 3 h; 70 ~ 97 % [68-71] | 80 °C, 3 h; 90 % [70] |
| | Siloxane equilibration | 0.38 ~ 1.08 MPa [72,73] | 90 ~ 105 °C, 24 h; ＞90 % [72,73] | 105 °C, 24 h; ＞90 % [73] |
| The synergy of dynamic non-covalent and covalent bonds | Imine and coordination bonds | 0.53 ~ 5.5 MPa [74, 75] | RT ~ 100 °C, 20 min ~ 6 h; ＞90 % [74,75] | 100 °C, 10 MPa, 30 min; 100 % [74] |
| | Imine and hydrogen bonds | 1 MPa [76, 77] | RT, 40 min ~ 1 h; 98.4 ~ 100 % [76,77] | -- |
| | Disulfide and hydrogen bonds | 0.06 ~ 8.6 MPa [78-80] | RT ~ 100 °C, 30 min ~ 3 h;＞93 % [78-80] | -- |
| | Disulfide and coordination bonds | 2.4 MPa | RT, 24 h; 91 % [81] | -- |
| | Boronic ester and hydrogen bonds | 7.33 MPa | 40 °C, 6 h; 97 % [82] | -- |
| | Vinylogous urethanes and coordination bonds | 7.12 MPa | 150 °C, 30 min; 84 % [83] | 150 °C, 10 MPa, 30 min; 85 % |
| | Acylhydrazone and hydrogen bonds | 1.8 MPa | RT, 48 h; 85 % [84] | 120 °C, 10 MPa, 15 min; 75 % |
| | Imine, aminal, and ionic hydrogen bonds | 12 MPa | 100 °C, 2 h; 100 % [85] | 80 °C, 10 MPa, 2 h; 95 % |
| | Imine, disulfide, and ionic hydrogen bonds | 0.42 MPa | RT, 5 h; 98 % [86] | -- |

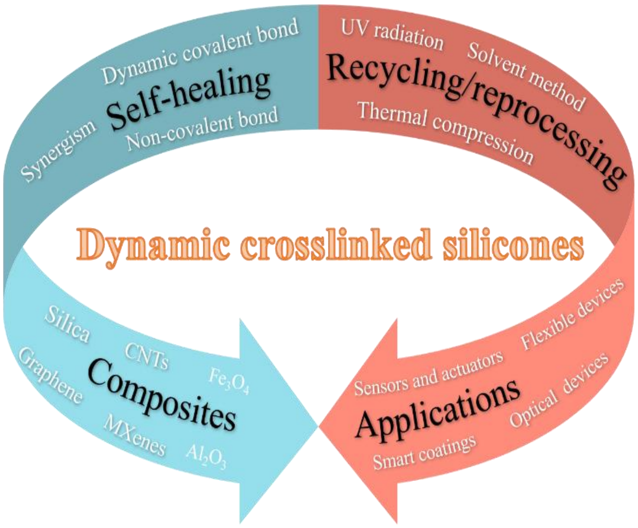

**Fig. 1** A summary illustration of this review.

according to their dynamic bonds and crosslinked networks to optimally balance mechanical performance and self-healing ability. Then, the recycling and reprocessing of silicone materials are further discussed following their processing methods. Next, dynamic crosslinked silicone composites with different nanofillers are also elaborated to enhance their mechanical properties and broaden functionalities. Lastly, the potential outlooks and facing challenges dynamic crosslinked silicone materials are also prospects

## 2. Self-healing of silicone materials

Polymers have been extensively used in modern life, but they are quite vulnerable to micro-damages caused by external stress, leading to a significant decrease in property and lifespan. To conquer these drawbacks, biomimetic self-healable polymers are designed to autonomously repair the damages and recover the virgin property.[34,87] The boom of self-healable polymers would prolong their lifespan and improve working safety, thus which is of great importance to reduce environmental pollution and resource waste. To date, self-healing polymers are realized by either extrinsic self-healing or intrinsic self-healing mechanisms.[88] Extrinsic self-healing depends on the instant chemical reactions of healing agents preloaded in microcapsules, microspheres, or microtubules dispersed into the polymer matrix.[89,90] The design and preparation of extrinsic self-healing polymers are relatively simple and easy to operate, but it is obstructed by the limited dosage of the healing agent, weak interface interaction between carrier and matrix, and unrepeatable healing ability at the same sites.[91,92] On the other side, intrinsic self-healing is achieved by diverse dynamic bonds which can reversibly rearrange the crosslinked networks and recombine the interfaces with/without the assistance of external stimuli.[22,93] Intrinsic self-healing is drawing more and more attention, because of its high healing efficiency and repeatable healing ability in the same position.[94-96]

Likewise, intrinsic self-healing silicone materials are becoming a focus research area owing to their unique properties and functions, showing great potential applications in smart coatings, optical devices, and flexible electronics.[97-99] They are successfully fabricated by integrating various dynamic non-covalent bonds (hydrogen bond, ionic bond, metal-ligand coordination interaction, *etc*.) or/and covalent bonds (disulfide bond, imine bond, Diels-Alder bond, siloxane equilibration, *etc*.) into polysiloxane crosslinked networks.[100-102]

### 2.1 Self-healing of silicone materials based on dynamic non-covalent bonds

Dynamic non-covalent bonds primarily consist of hydrogen bonds, ionic bonds, metal coordination bonds, host–guest interaction, and so on, which involve a wide range of binding energies.[103,104] Depending on their reversible dynamic nature, i.e., facile dissociation and recombination behavior with/without special stimuli like temperature, pH value, light, solvent, or catalyst, dynamic non-covalent bonds are preferably utilized in self-healing silicone materials.[19-22]

#### Hydrogen bonds

Hydrogen bonds as one of the most extensively studied non-covalent bonds due to outstanding reversibility, directivity, and sensitivity, have been popularly used in self-healing materials.[105] It is well-known that a single hydrogen bond is weak in interaction with low binding energy, which always leads to low strength and creepocity. Contrarily, multiple hydrogen bonds having higher association energy can greatly improve the mechanical properties and healing efficiency of dynamic crosslinked polymers.[106,107] Thereinto, ureidopyrimidinone (UPy), carbamate, and urea groups are representative of multiple hydrogen bonds. Self-healable silicone materials based on hydrogen bonds are primarily fabricated by the copolymerization of hydroxyl or amino groups functionalized polysiloxanes with bi- or tri-functional isocyanates, accompanied by the formation of urethane or urea linkages.[108,109] Hydrogen bonds formed between these linkages entitle silicone materials with fast self-heal ability at moderate temperatures.

For example, a multifunctional isocyanate-modified PDMS (I-PDMS) coating is developed by the copolymerization of bis(3-aminopropyl) terminated PDMS ($H_2N$-PDMS-$NH_2$) with hexamethylene diisocyanate (HDI), where physically crosslinking is formed by hydrogen bonds between the urea motifs.[35] Owing to the dynamic nature of intermolecular hydrogen bonds, the scratches within the coating are almost completely healed at 65 °C for 4 h. Furthermore, the formed low hierarchical roughness and low surface energy of PDMS segments can also mitigate corrosion and biofouling on metal substrates. Similarly, a silicone-based poly(urea-thiourea) (PDMS-P(Ua-TUa)) coating is prepared using $H_2N$-PDMS-$NH_2$, isophorone diisocyanate (IPDI) and $CS_2$ by a two-step sequential reaction (Fig. 2a).[39] After that, PDMS-P(Ua-TUa) is further mixed with tannic acid (TA), multiple hydrogen bonds formed between thiourea groups, urea groups, and TA molecules ensure a tough elastomer with an ultimate strength of 2.47 MPa and stretchability of ~1000 %. The scratches within the film completely disappear after 12 min, the repair efficiency of strength is over 98 % at ambient condition for 3 h, and the efficiency is still 95 % even in artificial seawater (Fig. 2b). Besides improving mechanical strength and self-healing ability, TA molecules also bring good antibacterial and anti-diatom activities. These works provide promising pathways toward the development of high-performance silicone-based multifunctional coatings.

Although self-healing polymers can autonomously repair damages and recover functions, they can neither warn before the damage nor visualize the suffering stress and strain. To overcome this challenge, a mechanochromic PDMS elastomer with self-heal ability is fabricated by the copolymerization of hydroxyl-terminated PDMS with spiropyran diol, diphenylmethane diisocyanate (MDI), IPDI and 1’4-butanediol (BDO) (Fig. 3).[40] Upon stretching, heating, or UV radiation, the elastomer displays a fast color variation from yellow to purple, but the color can rapidly return to yellow under white light illumination, due to the reversible sensitivity of spiropyran. With the synergetic utilization of strong hydrogen bonds from MDI and weak hydrogen bonds from IPDI, the elastomer possesses outstanding self-heal ability and mechanical performance. The tensile strength (10.5 MPa) and elongation at break (785 %) recover over 92 % at 60 °C for 24 h. This novel robust PDMS elastomer exhibits potential applications in visualized stress/strain sensing and wearable devices.

The copolymerization of functionalized PDMS with isocyanates achieves self-heal ability, but the residual isocyanates often cause the risk of irritation, anaphylaxis, and other potential harm to the human body.[110] To avoid these latent risks, the polymerization between α,ω-aminopropyl PDMS, and ethylene carbonate *via* non isocyanate reaction

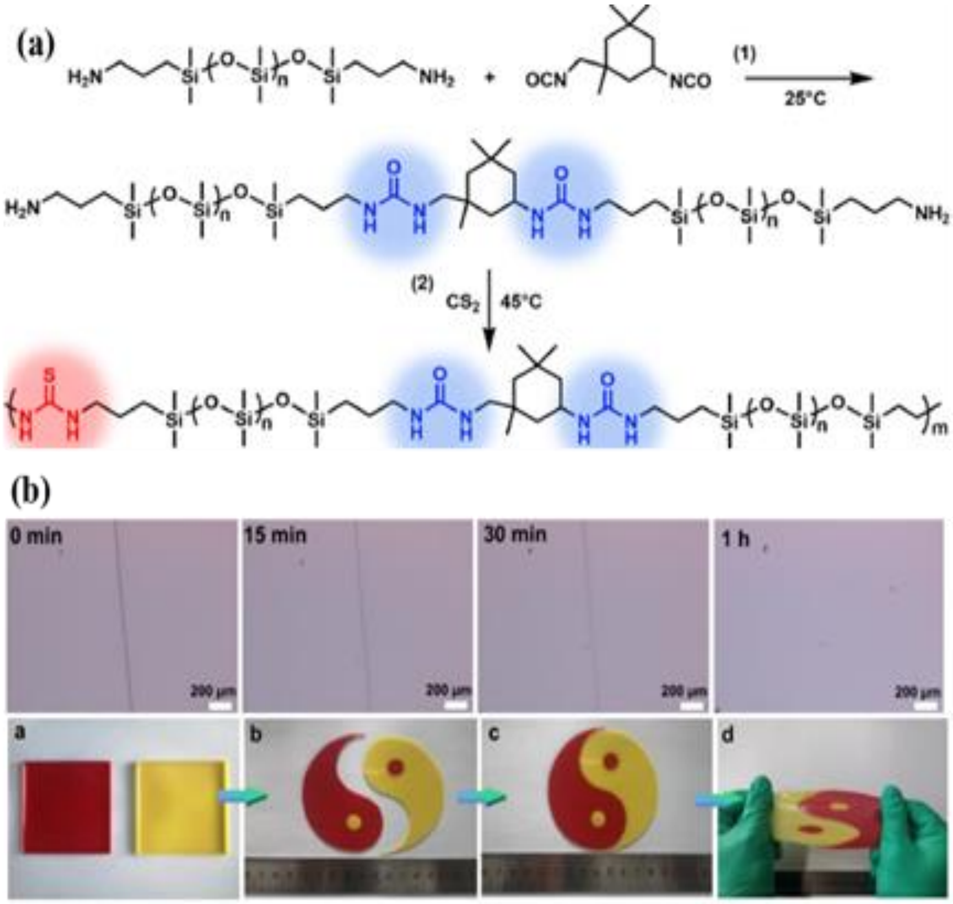

**Fig. 2** (a) Synthesis process of PDMS-P(Ua-TUa) polymers. (b) Self-healing properties of PDMS-P(Ua-TUa)-TA films. Reproduced with permission from [39], Copyright 2022 Elsevier.

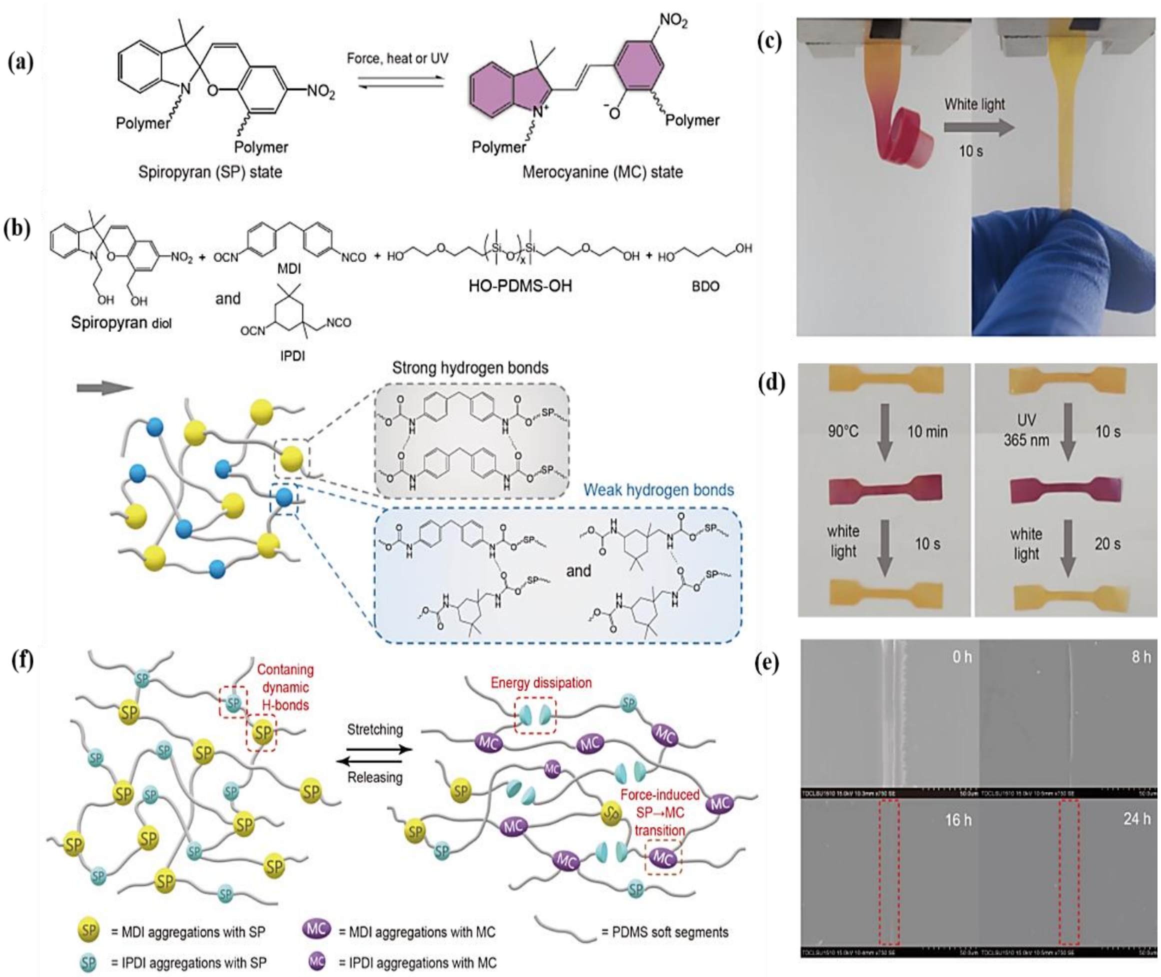

**Fig. 3** (a) Underlying mechanism of force-, thermal- and photo-induced isomerization of spiropyran. (b) Synthetic process of mechanochromic self-healing PDMS elastomer. (c) Photographs of fractured (left) and white light illuminated (right) PDMS elastomer. (d) Photographs of thermal-induced (left) and photo-induced (right) color variation of PDMS elastomer. (e) SEM images of damaged PDMS elastomer film self-healed at 60 °C. (f) Microstructure transformation of released (left) and stretched (right) mechanochromic PDMS elastomer. Reproduced with permission from [40], Copyright 2020 Springer Nature.

can also form urethane bonds.[111] The hydrogen bonds within crosslinked silicone rubber with ~0.5 MPa tensile strength lead to a repeatable self-healing efficiency of over 80 % at 80 °C for 24 h. Moreover, grafting of N-acetyl-L-cysteine (NACL) on the side chains of polyvinyl polysiloxane also enables the formation of hydrogen bonds between carboxyl and acetyl groups, where the damaged silicone material can almost fully recover its virgin tensile strength (~4 MPa) at room temperature for 24 h.[112] Meanwhile, this material reveals excellent antibacterial activity against *Staphylococcus aureus*, due to the presence of NACL.

The ureidopyrimidinone (UPy) groups able to form dimers by their complementary quadruple hydrogen bonds are often used to fabricate high-strength self-healing polymers.[113-115] To realize tunable mechanical properties, a concept of hydrogen-bond assisted multiphase assembly of siloxane oligomers is provided, where the oligomers are synthesized from UPy, $H_2N$-PDMS-$NH_2$ and a tri-functional homopolymer of HDI (Fig. 4).[37] During the assembly process, UPy dimers can further assemble into larger stacks with high crystallinity, causing a microphase-separated, semi-crystalline polymer network. The high crosslinking density and semi-crystalline properties are responsible for high mechanical strength, exhibiting tensile stress of ~4 MPa, Young´s modulus of ~48 MPa, and storage modulus of ~151 MPa at room temperature. But more importantly, unique water-enhanced healing is also observed, which is quite different from traditional self-healing material susceptible to water. This is because the low water permeability of hydrophobic PDMS phases allows water molecules to travel through the crosslinked network to exchange with UPy but meanwhile restricts the water retention, ensuring reversible dissociation and formation of hydrogen bonding. This healable material shows potential applications like actuators and smart coatings.

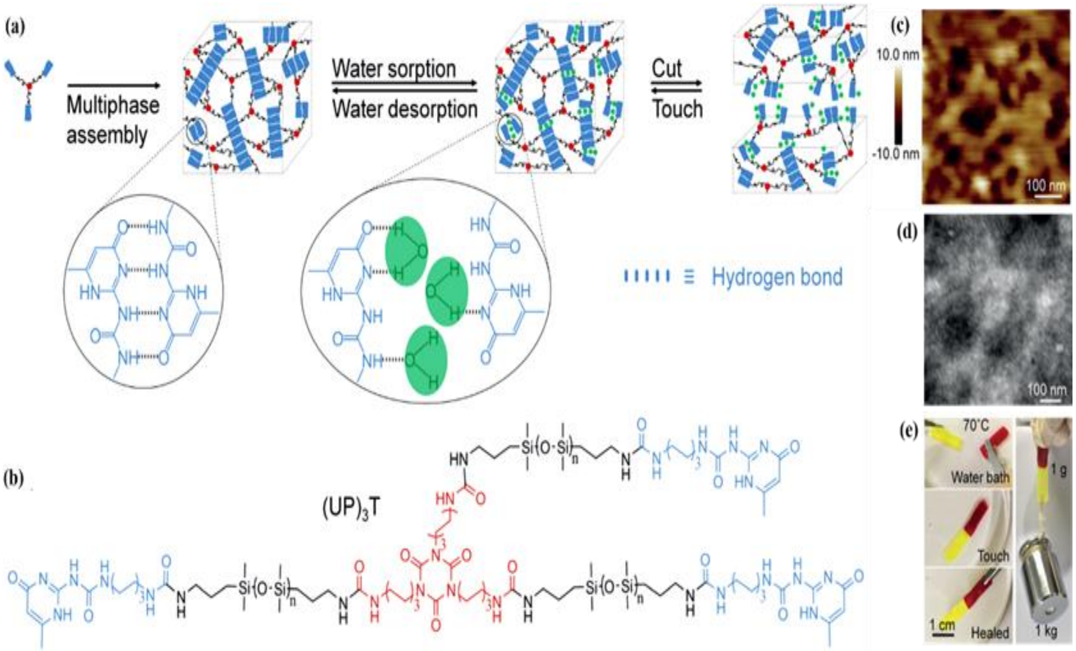

**Fig. 4** (a) Self-assembly of (UP)3T units into a 3D network via dimerization of UPy (blue) motifs and the assembly of UPy stacks. UPy dimers dissociate and exchange with water molecules (green dots) upon water sorption to release free UPy motifs at the interface. UPy dimers and stacks reform by touching two separate pieces together and finally heal by water desorption. (b) Molecular structure of siloxane oligomer (UP)3T. (c) AFM height image and (d) TEM image of the sectioned sample film, where UPy motifs are stained by osmium tetroxide and thus visualize as dark regions. (e) Two cutting pieces are touched-to-healed in a 70 °C water bath for 5 min, and the healed sample (1 g weight) can withstand a 1 kg counterweight. Reproduced with the permission from [37], Copyright 2018 Wiley.

### Metal-ligand coordination interactions

Among diverse non-covalent bonds, metal-ligand coordination interaction has a widely tunable bond strength by the combination of different metal ions and ligands.[116-118] The metal-ligand interaction is also an effective pathway to construct self-healing silicone materials due to a variety of alternative metal ions (Co$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, and Ce$^{3+}$) and ligands.[119-121] The presence of some metal ions or ligands can also give silicone materials dielectric or luminescent functions.[120,121] For example, the incorporation of a cobalt(II) triazole complex into the PDMS matrix produces a PDMS elastomer with solvatochromic behavior and self-healing ability.[121] When the elastomer film is dipped into water or methanol, its color changes from blue to light pink, because the coordination of Co(II) ion increases from four-coordinated to six-coordinated. The pink color returns to its blue color by heating for several minutes or exposure to air for a longer time. The reversible change of coordination configuration also facilitates the self-healing process, but its healing efficiency is only ~70 % after 48 h. To improve healing efficiency, cobalt(II) is replaced by Fe(III) because the lower bond strength of Fe(III)-triazole coordination is conducive to mobility.[43] The damaged elastomer regains over 90 % of mechanical strength after healing at 60 °C for 20 h, whereas the virgin strength is decreased from 1.2 to 0.4 MPa.

The facile preparation of materials like biological muscles with strong, elastic, and self-healable properties is still a great challenge. A PDMS crosslinked network with high stretchability and self-heal ability is fabricated by three different interactions between 2,6-pyridine carboxamide ligands and Fe(III) centers, including one strong pyridyl–iron bond and two weaker carboxamido–iron bonds (Fig. 5).[45] The weaker bonds can readily break and recombine, contributing to energy dissipation and self-healing, while the iron centers still maintain near the ligands by the stronger interaction, allowing for the rapid re-formation of bonds. The tensile strength (~0.25 MPa) and strain (~2000 %) fully recover after 48 h at room temperature. This highly stretchable functional silicone material has the potential application in artificial muscle.

Silicone materials should be the best candidate for fouling release coatings due to their low surface energy, but their poor fouling resistance and self-healing inability are restricting wide applications. Hence, a fouling-resistant and self-healable PDMS coating is prepared by crosslinking 2-(2-benzimidazolyl)ethanethiol (BET) ligands in PDMS chains with zinc ions *via* coordination bonds.[4] The reversible zinc-imidazole complexes not only ensure good self-healing ability

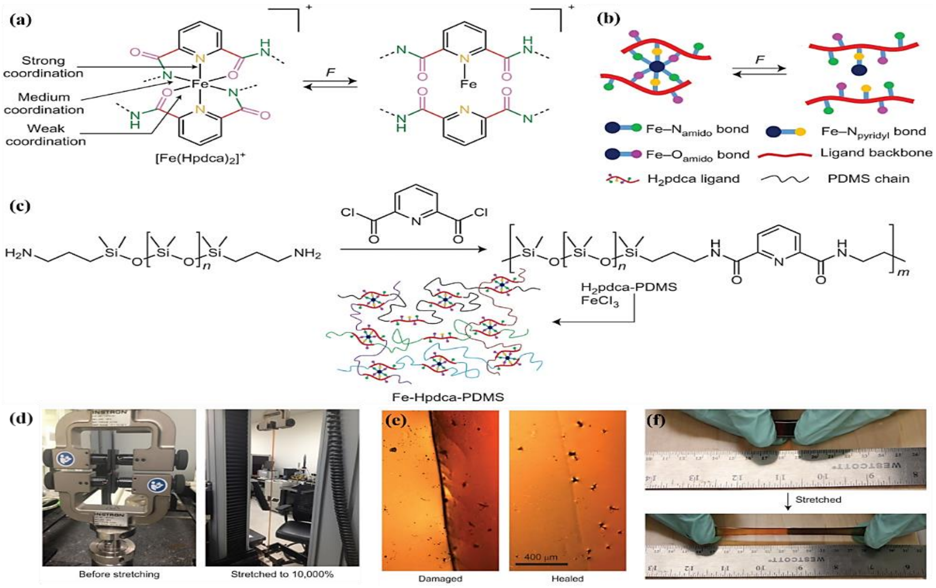

**Fig. 5** (a) Structure and (b) schematic illustration of the $[Fe(Hpdca)_2]^+$ moiety undergoing reversible dissociation and reconstruction during tensile stretching. (c) Synthesis and structure of the material, and proposed mechanism for chain folding and sliding during tensile stretching. PDMS chains with different colors represent different polymers. (d) Photographs of a film before and after stretching. (e) Microscope images of damaged and healed samples. (f) Optical images of the healed film before and after stretching. Reproduced with the permission from [45], Copyright 2016 Springer Nature.

in the air or artificial seawater at room temperature but also significantly enhance fouling resistance against marine bacteria owing to their antifouling property. This silicone material is expected to be developed as a high-performance antifouling coating.

To address the trade-off between the mechanical property (modulus and toughness) and self-heal ability, a PDMS polymer containing thermodynamically stable but kinetically labile coordination complex, i.e., Zn-Hbimcp (Hbimcp = 2,6-bis((imino)methyl)-4-chlorophenol) coordination bond is designed (Fig. 6).[46] This coordination complex reveals a relatively higher association constant, but still can undergo fast and reversible intra- and inter-molecular ligand exchange. The developed $Zn(Hbimcp)_2$-PDMS polymer achieves a high strain of 2400 % and toughness of 29.3 MJ $m^{-3}$, which can completely renew after the damage is healed at room temperature for 24 h. More importantly, this work indicates that the optimal combination of bond strength and bond dynamics plays an important role in toughness and self-heal ability.

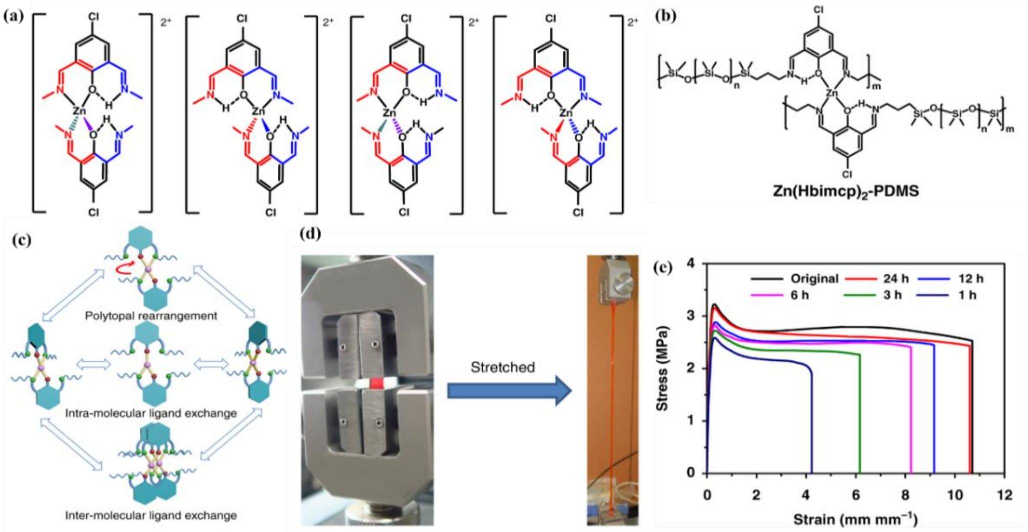

**Fig. 6** (a) Possible stereochemical structures for $[Zn(Hbimcp)_2]^{2+}$ complex. (b) Structure of polymer complex $Zn(Hbimcp)_2$-PDMS. (c) Three possible pathways for the ligand exchange process. (d) Photographs of the film before and after stretching. (e) Strain-stress curves of a film healed at room temperature at different times. Reproduced with the permission from [46], Copyright 2019 Springer Nature.

Achieving both solid-like properties and fast self-healing ability is still a great challenge, because of slow diffusion dynamics. A design concept of taking advantage of weak but abundant coordination bonds can achieve rigid and healable materials (Fig. 7).[44] The coordination bond between Zn(II) and carboxylate is relatively weak but still stronger than a hydrogen bond. Thereout, the carboxyl group-functionalized PDMS (PDMS-COOH) polymer is crosslinked by abundant Zn(II)-carboxylate interactions, becoming very strong and rigid at room temperature. Owing to the fast thermal-reversibility of coordination equilibrium, the flexural strength (~10 MPa) of this polymer fully regains at 80 °C for 4 h after damage. As well, this rigid material can also be 3D printed into various shapes (such as 3D, NJU), because it can turn into a viscous liquid when heated but quickly become a rigid solid upon cooling. Beyond the common self-heal ability, the dynamic characteristic of coordination bonds also enables simple or small 3D components to be assembled into irregular or large parts that are otherwise difficult to be fabricated. Moreover, graphene/silicone composite can be printed on various substrates and into various shapes, like an electrical circuit on paper. The obtained circuit can further be reshaped into diverse shapes such as arches and scrolls after heating and cooling. This silicone material will be used in orthopedic immobilization, conductive composites, and adhesives.

## Ionic bonds

In some cases, ionic bonds or ionic associations can serve as a more effective mechanism to achieve self-heal ability and higher strength, compared to hydrogen bonding interactions. For instance, a self-healable supramolecular silicone elastomer is prepared by neutralizing aminopropyl functionalized PDMS (PAPMS) with organic or inorganic acids to form ion-association complexes as cross-linkages.[122] The maximum tensile stress (~4 MPa) of the elastomer recovers over 80 % after healing for 10 s with the assistance of methanol or chloroform. To overcome the slow crosslinking rate of traditional curing technics of silicone materials, our group takes advantage of UV-curing technology to rapidly form self-healable silicone elastomers (Fig. 8).[49] The primary covalent network rapidly formed by thiol-ene UV-curing between thiol and vinyl functionalized polysiloxanes can maintain structural stability, while a dynamic ionic crosslinked network formed between carboxyl and amido functionalized polysiloxanes endows self-heal ability. The tensile strength recovers over 90 % after the damaged samples are kept at 100 °C for 12 h. What is more, the excellent transparency (over 90 %) of silicone elastomer in visible light is resistant to hydrothermal treatment, which ensures the potential application of optical adhesives. Moreover, this elastomer can be UV-curing 3D printed into complicated samples, and they still can be self-healed after damage.

Thermoplastic elastomers (TPEs) show promising applications in actuators, soft robots, and electronic skins, but it is still a challenge to prepare high-strength self-healable thermoplastic silicone elastomers (TPSEs).[123] Crosslinking of

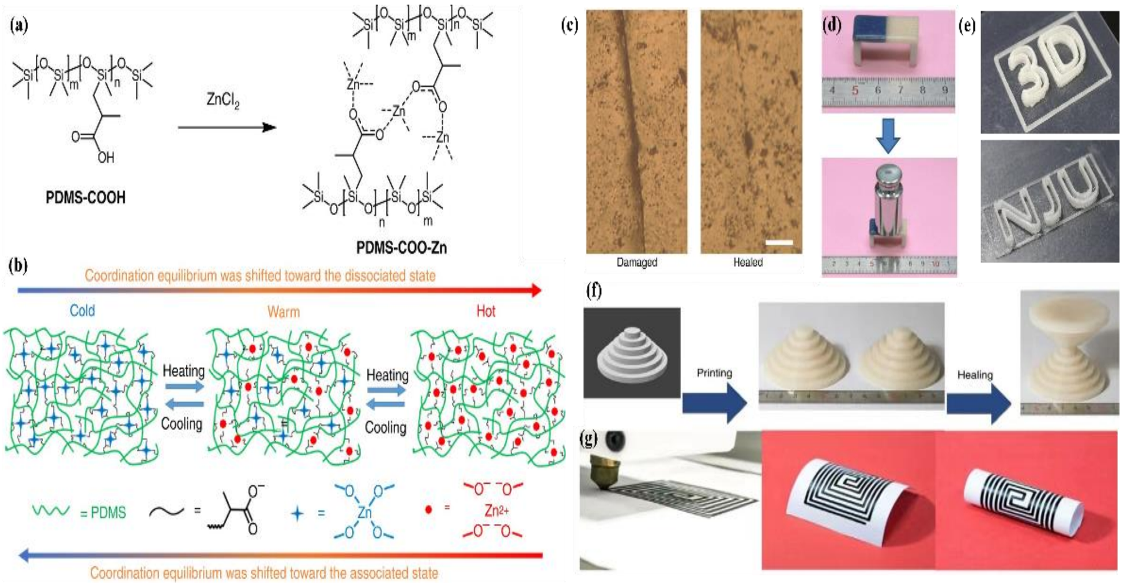

Fig. 7 (a) Synthesis and structure of PDMS-COO-Zn polymer. (b) Schematic structure of the polymer network at different temperatures. (c) Microscopic images of a film before (left) and after (right) healing at 80 °C for 4 h. (d) The weight-bearing test of PDMS-COO-Zn polymer after healing. (e) Various 3D objects were printed from the PDMS-COO-Zn polymer. (f) The irregular objects obtained by 3D printing. (g) An electrical circuit based on the PDMS-COO-Zn/ graphene composite could be printed on paper, and the as-prepared device can be reshaped. Reproduced with the permission from [44], Copyright 2018 Springer Nature.

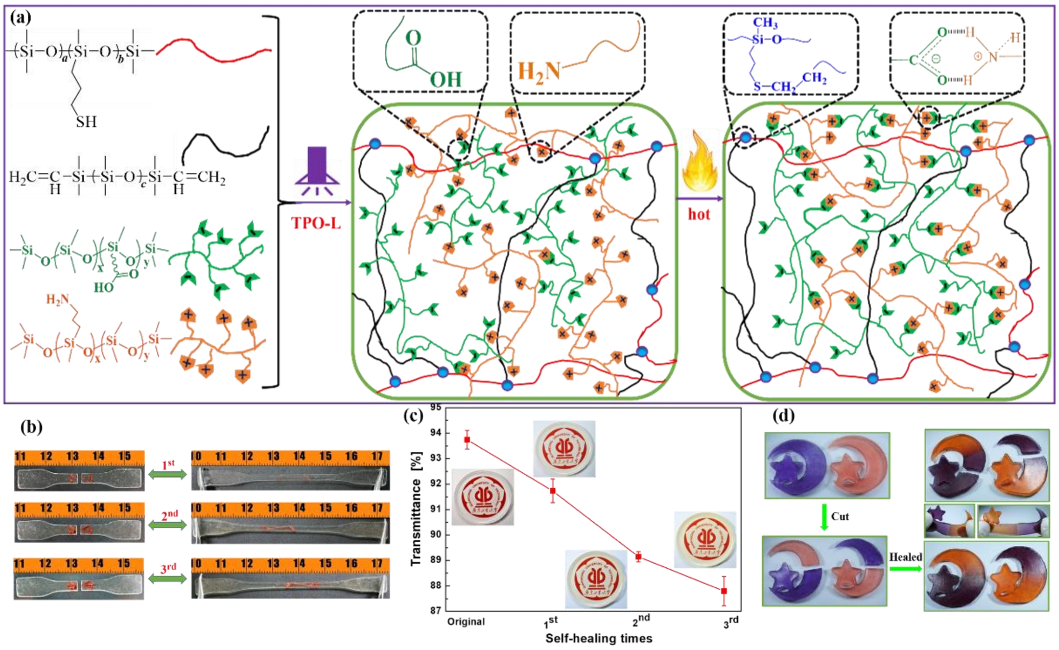

**Fig. 8** (a) Schematic illustration of dual-crosslinked networks of silicone elastomers. (b) Repeated macro-repairing of damaged samples. (c) The transmittance of silicone elastomers after different healing times. (d) Photographs for self-healing of 3D printed “Ascendant”. Reproduced with the permission from [49], Copyright 2020 Elsevier.

carboxylic acid-functionalized PDMS (PDMS-*g*-COOH) with zinc oxide (ZnO) *via* coulombic interactions can form strong, stretchable, and self-healable TPSEs.[51] The prepared PDMS-*g*-COOH/ZnO composites have an excellent tensile strength of 5 MPa, strain of 1300 %, and healing efficiency of ~84 % at 80 °C for 4 h. This facile approach provides new insights into high-performance multifunctional TPSEs. Moreover, a colorless, transparent, and healable PDMS elastomer is also successfully realized by the gradient Zn(II)–carboxylate interactions.[47] The small and weak ionic aggregates preferentially sacrifice to dissipate energy under external loading, but the large and stiff aggregates impart the elastomer with high strength and elasticity. The maximum tensile stress of ~3 MPa and strain of 1000 % fully recover after healing at 80 ~ 100 °C for 1 ~ 2 h. This PDMS elastomer can be used as an adhesive for optical devices.

Common stimuli like heat and light are inapplicable to self-healing materials in some cases, such that heat can damage heat-sensitive components while light hardly reaches the inside of materials. To address this challenge, a gas-plastic elastomer with an ionically crosslinked silicone network is fabricated, which exhibits a high mechanical strength of up to ~3.5 MPa in the air (Fig. 9).[124] The crosslinking sites of ionic aggregates can be softened by $CO_2$ gas, dramatically promoting the rearrangement of crosslinked networks. The virgin mechanical strength is quickly re-established in the exchange of $CO_2$ with air, self-healing is thus achieved at room temperature and even at −20 °C. This special gas-plastic behavior is particularly beneficial to the development of special self-healing materials because the gas not only can permeate the inside of materials but also will not break down the components.

## The synergy of different non-covalent bonds

The bond energy of single non-covalent interaction is very low, which is conducive to the diffusion and recombination of molecular chains, achieving better self-heal ability, but it often causes the instability of the material. If two or more different non-covalent interactions are effectively combined, these disadvantages will be overcome.[52-54,125,126]

Dielectric elastomer with a high dielectric constant ($\varepsilon'$) and healing ability can enhance their resistance to high driving voltages and damages during repetitive actuation cycles. For this goal, a self-healable dielectric silicone elastomer is constructed by $Fe^{3+}/COO^-$ coordination interaction between carboxylated polymethylvinylsiloxane (PMVS-COOH) and $FeCl_3$, and hydrogen bonding interaction between carboxyl groups.[52] Besides coordination crosslinking of PMVS-COOH, $FeCl_3$ also promotes dipole polarization by disrupting some hydrogen bonds and releasing carboxyl groups, causing a significant increase of $\varepsilon'$. The as-prepared elastomer shows a comparatively high $\varepsilon'$ of 12.3 at 104 Hz. The mechanical properties of damaged samples fully regain at room temperature for 1 h, owing to the high chain mobility and robust dual dynamic networks. On the other side, the combinations of metal-catechol complexes and hydrogen

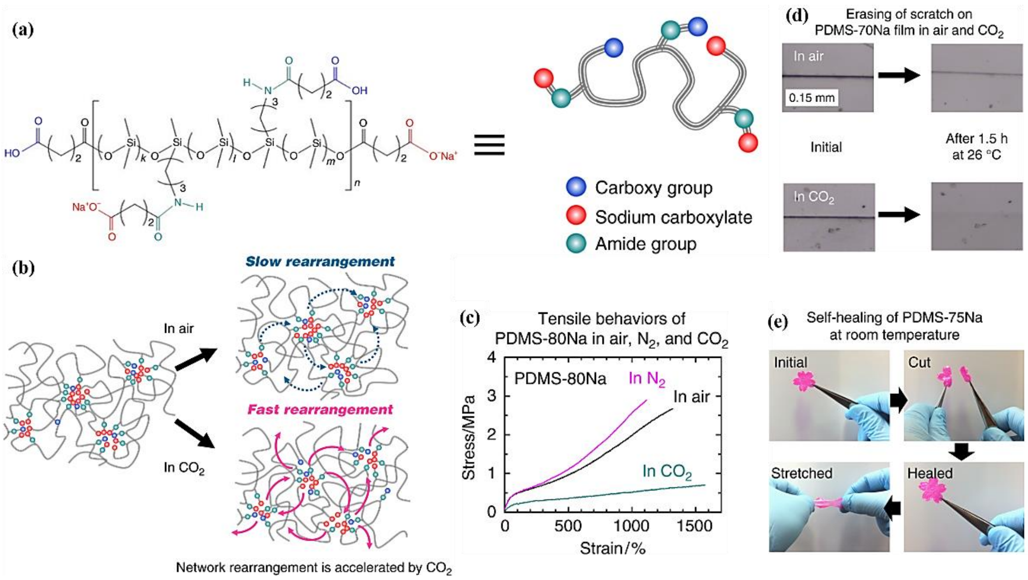

**Fig. 9** (a) Chemical structure and schematic illustration of PDMS-xNa. (b) Schematic illustration for slow and fast rearrangement of ionic crosslinks in air and $CO_2$, respectively. The plasticization of ionic aggregates by CO2 gas promotes rapid network rearrangement. (c) Stress-strain curves of PDMS-80Na tested at 27 ± 1 °C in air, $N_2$, and $CO_2$. (d) Optical microscopic images of a razor scratch on a PDMS-70Na film surface healed at 26 °C for 1.5 h in air and in $CO_2$. (e) Photographs of self-healing behavior of cherry blossom-shaped PDMS-75Na film at 26 °C. Reproduced with the permission from [124], Copyright 2019 Springer Nature.

bonds,[125] metal-imidazole complexes and hydrogen bonds,[4] catechol-Zn coordination bonds and hydrogen bonds,[126] or metal-diaminopyridine complexes and hydrogen bonds,[53] enable mechanically tunable and damage-healable silicone materials. They are promising in various areas across life and industry such as superhydrophobic coatings and flexible sensors.

Moreover, a dynamic silicone elastomer is facilely prepared by mixing PDMS-COOH, PDMS-$NH_2$, and $AlCl_3$, where the carboxyl groups react with amino groups and $Al^{3+}$ ions to form common ionic bonds and coordinated ionic bonds, respectively.[54] The carboxyl-$Al^{3+}$ interactions improve the mechanical properties, while the dense common ionic networks maintain the integrity of the dynamic crosslinking network. This dual crosslinked elastomer has better mechanical strength (~0.73 MPa) than the control sample with single ionic bonds, and the strength recovers over 80 % at 60 °C for 8 h. A dielectric silicone elastomer (SiR-SN) with large actuated strain (SA) and good self-healing ability is also constructed by hydrogen bonds and ionic bonds between carboxyl-modified polymethylvinylsiloxane (PMS-*g*-COOH) and PDMS-$NH_2$.[12] Distinctively, self-healing at 80 °C causes the recombination of hydrogen bonds and thus the recovery of network structure, while self-healing at 100 °C results in the conversion of hydrogen bonds into ionic bonds and thus the change of network structure. Therefore, the recovery of 115 % tensile strength and 100 % SA at a given electric field is achieved at 80 °C for 5 h. Besides, a polysiloxane-supported ionogel is prepared by a physically dual-crosslinked network based on ionic aggregates among [2-(methacryloyloxy)ethyl] trimethylammonium chloride (METAC) and hydrogen bonds between poly(aminopropylmethylsiloxane) (PAPMS) and tannic acid (TA).[127] This ionogel with an ionic conductivity of 1.19 mS $cm^{-1}$ can recover 83 % of properties within 12 h at room temperature or even at subzero temperature.

The self-healing of robust silicone elastomer used for wearable electronic devices activated by body temperature is quite attractive but a challenge. A strategy of the double physical crosslinking network containing at least three competitive interactions is proposed to gain this elastomer (Fig. 10).[128] The chain-extending reaction between $H_2N$-PDMS-$NH_2$ and 2,4′-tolylene diisocyanate (TDI) produces urea-contained PDMS (PDMS-U), enabling the formation of hydrogen bonding and urea/metal ion coordination interaction. Mixing of PDMS-U with carboxylic acid functionalized PDMS (PDMS-C) and different metal ions thus produces PDMS elastomer with three competitive interactions, i.e., hydrogen bonding between urea motifs, urea/metal ion and COO−/metal ion coordination interactions. The optimum tensile strength, breaking strain, and toughness of crosslinked elastomer are 4.0 MPa, 776 %, and 16.0 MJ $m^{-3}$, respectively. Its self-healing efficiency at body temperature (37°C, 8 h) reaches 98 %. Hence, this robust elastomer can be used as a flexible substrate for healable electrodes.

As indicated by these research results, self-healing silicone materials based on non-covalent bonds can been fabricated by

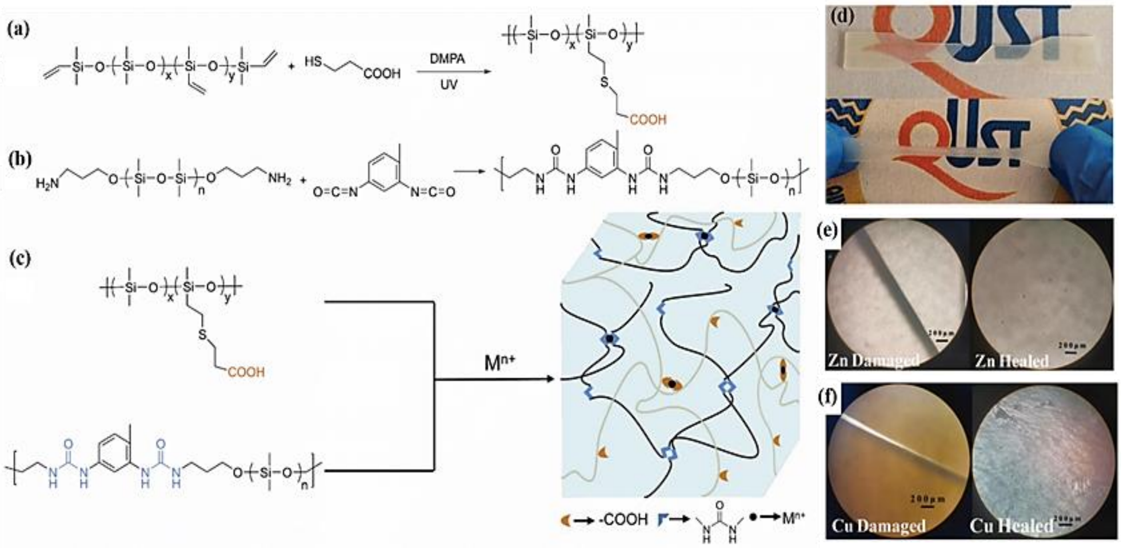

**Fig. 10** Synthetic procedure of (a) PDMS-C and (b) PDMS-U. (c) Preparation of PDMS-U/PDMS-$C_x$/$Mn^+$. (d) Photographs of PDMS-U/PDMS-$C_{0.3}$/$Zn^{2+}$ films before and after healing. (e) Microscopic images of crack surface for PDMS-U/PDMS-$C_{0.3}$/$Zn^{2+}$ elastomers before and after healing. (f) Microscopic images of crack surface for PDMS-U/PDMS-$C_{0.5}$/$Cu^{2+}$ elastomers before and after healing. Reproduced with the permission from [128], Copyright 2022 Royal Society of Chemistry.

various methods and show potential applications in many fields. The hydrogen bonds-based silicone materials reveal more easily tunable mechanical properties, and the utilization of multiple hydrogen bonds achieves higher mechanical strength and better healability.[37,40] The self-healing of ionic bonds-based silicone materials always needs heating but at lower than 100 °C, whereas their synthesis routes are quite facile by often directly mixing two components. The metal-ligand coordination bonds-based self-healing silicone materials have more choices of different metal ions and ligands to tune their mechanical strength and healing efficiency, but their preparation processes are relatively complex, due to the elaborate design and synthesis of ligands. The integration of different non-covalent bonds can synergistically regain their advantages and overcome their disadvantages, to fulfill higher healing efficiency at moderate conditions within less time.

### 2.2 Self-healing of silicone materials based on dynamic covalent bonds

Dynamic covalent bonds able to reversibly break and reform under appropriate stimuli mainly include disulfide bonds, Diels-Alder bonds, imine bonds, siloxane equilibration, *etc*.[129,130] Compared to non-covalent interactions, dynamic covalent bonds have higher bond energy and thus allow for the formation of robust materials, but remain dynamic behavior under the action of a specific stimulus.[131,132] To guarantee dynamic covalent crosslinked silicone materials with excellent healing ability, the crosslinking network parameters including the content of dynamic bonds, molecular chain mobility, and crosslinking density should be preferentially considered.[19,133,134]

#### Diels-Alder bonds

Cycloaddition is a bimolecular reaction where a diene precursor and a dienophile precursor convert into a ring molecule under heat or light stimulus, including [2+2], [4+2], [6+2], and [4+4] reactions.[135] The most widely used one in self-healing materials is the Diels-Alder reaction, which belongs to the [4+2] reaction between furan and maleimide derivatives.[136] For example, a thermally healable PDMS elastomer (PMFS) is prepared by directly crosslinking PDMS-bearing maleimide pendants (PM) with a furan-end functionalized PDMS (FS) *via* DA reaction (Fig. 11).[55] By adjusting the relative content of maleimide pendants in PM, the formed elastomers show an optimum tensile strength of 0.6 MPa. When the damaged samples are brought into contact immediately at room temperature, and successively treated at 140 °C for 3 h to dissociate DA adduct into maleimide and furan and at 80 °C for 24 h to rebond the dissociative maleimide and furan moieties into new DA adducts, its healing efficiency is higher than 90 %. Besides excellent self-heal ability, this elastomer reveals good biocompatibility, providing potential applications as artificial skin and scaffolds in the biomedical field. Additionally, the crosslinking of $H_2N$-PDMS-$NH_2$ with bis epoxide containing two DA bonds in one molecule *via* epoxy-amine reaction is another pathway to prepare self-healable PDMS elastomer, where its tensile

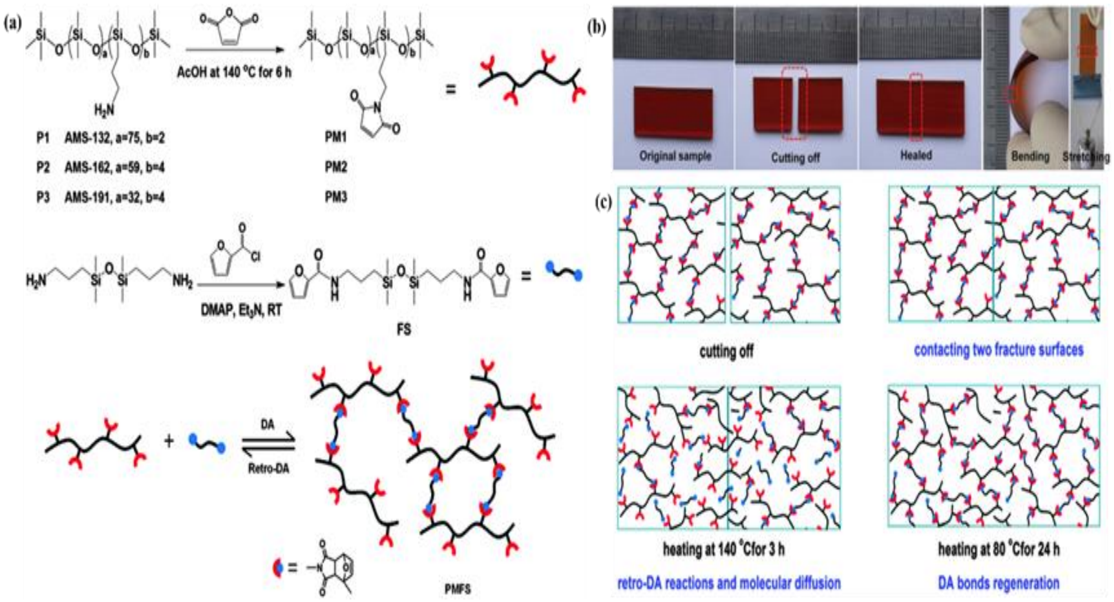

**Fig. 11** (a) Preparation process of polysiloxane elastomer PMFS containing DA bonds. (b) Photographs of the self-healing process and the healed PM3FS sample can be bent or stretched again. (c) Schematic illustration of the self-healing mechanism within PM3FS sample. Reproduced with the permission from [55], Copyright 2016 Royal Society of Chemistry.

strength of 0.8 MPa recovers ~93 % at 80 °C for 48 h.[56]

To improve the mechanical strength of thermally reversible self-healing polysiloxane elastomer based on DA bonds, hyperbranched polysiloxane (HPSis) containing furan rings is introduced, where the strength of elastomer increases from 0.2 to 0.87 Mpa.[137] Owing to multiple furan rings in HPSis, the addition of HPSis does not affect the self-heal ability, the self-healing efficiency is about 85 % at 130 °C for 10 min and 80 °C for 48 h. Moreover, the PCL segment can also enhance the mechanical properties of thermally healable poly(siloxane-urethane) elastomers with DA bonds.[138] The microphase separation structure and covalently crosslinked network endow the polymer with good tensile strength, where the strength is increased from 1 to 3 MP with 10 wt.% of PCL or ~6 MPa with 20 wt.% of PCL. However, the incorporation of PCL imposes an adverse influence on self-heal ability, because the crystalline PCL has much lower molecular mobility than PDMS, impeding the dissociation and reformation of furan and maleimide moieties at the fracture surfaces.

Although some silicone materials based on DA bonds have already realized excellent self-healing efficiency, it is notable that the self-healing process always undergoes under higher than 80 °C circumstances for a long time,[139,140] which can badly damage the e-skin components. To fulfill healing under milder conditions, the treatment with solvent vapor should be a very effective pathway for this purpose, because the gas-phase solvent molecules can penetrate the polymer and act as a plasticizer, eventually improving the polymer surface fluidity *via* dissolving retro-DA reaction products.[141] The exposure of a healable PDMS based on DA bonds to methyl ethyl ketone vapor for 1 ~ 3 min, the self-healing efficiency acquired at a much lower temperature in a shorter time is higher than that achieved by the direct heating sample at high temperatures.[141]

## Imine bonds

Compared with DA bonds, imine bonds have better dynamic characteristics enabled by reversible hydrolysis-condensation reaction, exchange reaction, or metathesis reaction, which have already been widely used in self-healing materials.[142,143] Self-healable silicone materials based on imine bonds are mainly realized by crosslinking diverse amine-functionalized PDMS with aldehyde compounds.[144,145] For example, mixing $H_2N$-PDMS-$NH_2$ and 1,3,5-triformylbenzene (TFB) produces a transparent and healable elastomer.[58] The damages can be completely repaired at room temperature for 60 min, but it's pristine tensile is only 35 kPa. The pendant amino groups in aminopropyl PDMS can also react with 1,4-phthalaldehyde (PTA) to form transparent and healable silicone elastomer.[59] The self-healing efficiency is about 95 % after 24 h at room temperature, while its original tensile strength is also only 0.18 MPa. As aldehyde-modified tetraphenylene derivatives are used as crosslinkers, the resultant PDMS elastomer exhibits fluorescence properties as well as good healing ability, but its strength is still 0.2 Mpa.[146] Moreover, a novel PDMS elastomer is prepared by crosslinking $N_2H$-PDMS-$NH_2$ with a tetra-functional biphenyl unit *via* an aldimine polycondensation reaction, which exhibits ultrafast self-healing properties.[147] The obtained material is quite tough and strong with optimal Young's modulus of 120.6 kPa and elongation of 48000 %, and the damages can be efficiently healed at room temperature within 60 s. Unlike the meticulous design and preparation of different aldehyde compounds, the extra incorporation of tri(2-aminoethyl)amine as a crosslinker into the matrix mixtures ($N_2H$-PDMS-$NH_2$ and PTA) can form vitrimer-like PDMS.[60] The tensile strength of crosslinked silicones is greatly increased to ~2.8 MPa, and the damages within the material completely disappear after 30 min at 100 °C.

As for the above-reported imine-based silicone materials, the reactivity and self-healing efficiency of imine bonds cannot be further controlled externally once they are formed. To modulate the reactivity of aldehyde functionalities, a thermally stable bifunctional diarylethene, where its ring-closed form can greatly accelerate the formation of imine bonds, is chosen as a photoswitchable crosslinker for commercially available amino-functionalized PDMS to produce a rubbery material (Fig. 12).[148] The viscoelastic and self-healing properties of the material can be reversibly tuned by illumination with UV or visible light because light can induce the reversible variation between ring-closure and ring-opening, and the former has better reactivity. The ~ 0.6 MPa of tensile stress recovers 85 % after the damaged samples are healed at room temperature for 5 h by illumination with UV light.

## Boroxine bonds

Dynamic covalent boroxine bond provides another mechanism for self-healing silicone materials because the boroxine/boronic acid equilibrium is readily controlled by temperature or the addition/removal of water or Lewis base.[149-151] As we know, the sufficient mobility of polymer chains is a key factor to facilitate self-healing, which causes a great challenge to realize self-healing in stiff polymers. Using

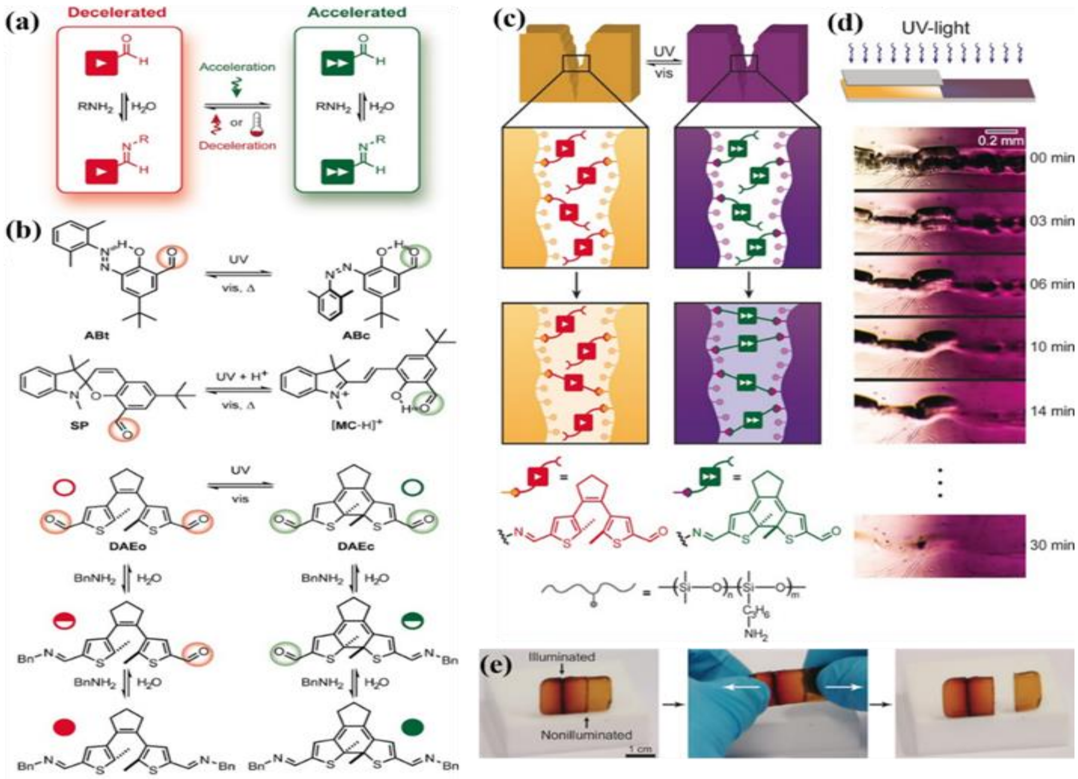

**Fig. 12** (a) The aldehyde functionality coupled to a photochromic moiety can be switched between less reactive, decelerated, and more reactive, accelerated forms (represented by red "play" and green "fast-forward" signs, respectively), upon illumination. (b) Realization of reactivity variations using different photochromic systems based on E/Z-configured azobenzene AB, spiropyran/merocyanine SP/MC, and open/closed diarylethene DAEo/DAEc. The condensation of two DAE isomers with benzylamine forms the mono- and bis-imines. (c) Schematic representation of damaged DAE@AS: Self-healing of DAEc@AS (purple, right) is accelerated compared to that of DAEo@AS (yellow, left), owing to the higher reactivity of the crosslinker in the ring-closed form. (d) The self-healing properties of DAEo@AS (yellow, left) and DAEc@AS (purple, right) in damaged polymer film varied with time. (e) Reassembly of three polymer pieces with illuminated and nonilluminated cut surfaces (left). After 30 min, both ends are pulled evenly (middle). The contact between the nonilluminated pieces ruptures before that between two illuminated surfaces (right), under ambient conditions. Reproduced with the permission from [148], Copyright 2016 Wiley.

dynamic boroxine bonds to crosslink PDMS chains into networks can produce very strong, stiff, and water-assisted self-healing silicone materials.[69] The boroxine bonds can quickly dissociate into free boronic acid upon wetting, and thus the de-crosslinking of networks promotes the molecular segments' mobility. Whereas this process is reversed by heating to remove water, and thus ~9 MPa of tensile strength is fully recovered at 70 °C for 12 h. This stiff self-healing silicone material may be used in the building industry and smart coatings. However, under some circumstances, the solvent-driven dissociation of the crosslinked network is hard to implement. Therefore, a solvent-free double-network PDMS material (DN-PDMS) is developed.[152] A covalent bottlebrush PDMS network with low crosslinking density provides ultralow stiffness, while a dynamic borate network can dissipate energy to toughen the material and heal damages to recover toughness. The high mobility of bottlebrush architecture and fast reversibility of the borate network ensures fast self-healing without any stimuli.

Beyond that, a series of impact-hardening polymers (IHPs) with stress-responsive behavior and self-heal ability at low temperatures are fabricated *via* the polycondensation of silanol-terminated PDMS with trimethoxyboroxine.[153] The stress-responsive ability of this IHP is indicated by the relative shear stiffening effect (RSTe), which is higher than in 2000. The IHP also exhibits good self-heal ability even at subzero temperatures, where self-healing efficiency reaches 80 % after 30 h at -25 °C. The excellent self-heal ability and stress-responsive property depend mainly on reversibly dynamic crosslinking of a boron compound and the reduction of entanglement density owing to the longer length of the flexible polymeric backbone.

To realize quick crosslinking of tough, transparent, and self-healable PDMS elastomer, our group utilizes the thiol-ene UV-curing between thiol-functionalized silicone resin (MDT-SH) and vinyl-terminated polysiloxane and diboronic ester to produce expectant elastomer (Fig. 13).[70] UV-curing kinetics indicate that the crosslinking is fast finished within 1 min to form an elastomer with ~3 MPa tensile strength and higher than 95 % transparency. The damaged elastomer can completely repair at 80 °C for 3 h, and the transparency is almost unaffected by the healing process. This PDMS elastomer has potential applications as flexible electronics.

## Disulfide bonds

Disulfide bonds are another type of dynamic covalent bond, which play important roles in biological activities such as the stabilization of specific protein structures.[154] The dynamic

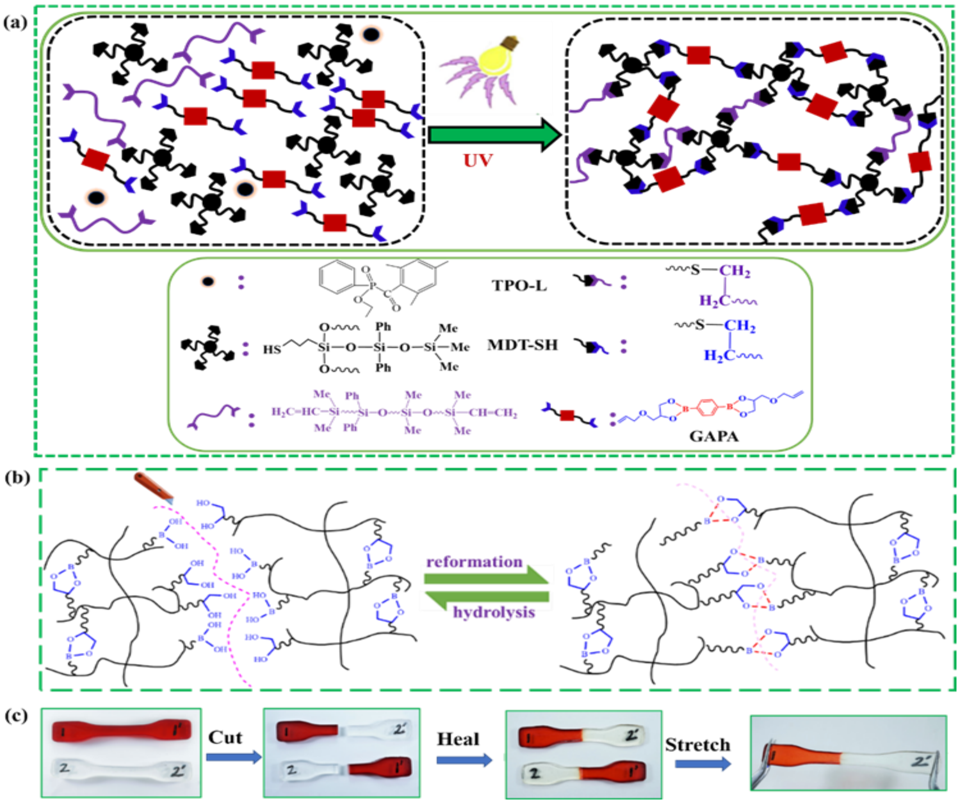

Fig. 13 (a) The UV-crosslinking process of polysiloxane elastomer. (b) Illustration of boronic ester transesterification. (c) Photographs showing the healing process of silicone elastomer. Reproduced with the permission from [70], Copyright 2021 Elsevier.

nature of the disulfide bond can be activated by UV radiation, heating, mechanical fore, or other catalysts, which have been extensively used in self-healing materials.[155-160] Making the formula of healable silicone elastomer closer to that of commercial silicone elastomer and meanwhile using the infinite, renewable, and eco-friendly sunlight energy as an external stimulus would be a feasible and sustainable strategy. Therefore, our group utilizes commercially available a ω-dihydroxyl PDMS as the matrix and disulfide bond-containing silane as the crosslinker to fabricate elastomer *via* a dealcoholized curing process which is often used in the silicone industry (Fig. 14).[62] Taking advantage of sunlight-activated disulfide metathesis, the elastomer is repeatedly self-healed without any catalyst under sunshine. This easy and eco-friendly technology for self-healing material is more likely to come true for practical application. In addition to directly incorporating disulfide bonds into silicone materials, the oxidation of thiol-terminated sulfur-containing heterochain polysiloxanes (P-SHs) with thiol-containing crosslinkers to *in-situ* form disulfide bonds is also feasible.[161] The silicone elastomer recovers over 70 % of mechanical properties after heating at 150 °C for 2 h or under UV radiation for 30 min. Inspired by this strategy, more disulfide-containing elastomers with self-heal ability will be developed.

Self-healing silicone elastomer without any extra stimuli at room temperature should be a good choice. Compared to aliphatic disulfides, aromatic disulfides actually display much higher reactivity, which can autonomously metathesize at room temperature without any external stimuli.[64,65] Therefore, a stretchable, fast self-healing PDMS elastomer is prepared by crosslinking diglycidyl ether-terminated PDMS with 4-aminophenyl disulfide (APDS).[64] The obtained elastomer has a tensile stress of 0.5 MPa, strain of over 1000 %, and healing efficiency of 95 % at room temperature. Other self-healing silicone materials based on aromatic disulfides are also prepared by crosslinking epoxy groups modified organosilicon with APDS, however, these silicones are always healed at 160 ~ 200 °C due to their rigid crosslinking networks.[162,163]

### Urea and hindered urea bonds

Although urea bonds have already been introduced into silicone materials, their dynamic behavior is too weak to fulfill self-heal ability under ambient conditions, due to the high resonance-induced stability. However, its dynamic nature can be activated and mediated by zinc salts.[67] In view of this characteristic, it is introduced into PDMS elastomer by mixing zinc salts into the mixtures of amine-functionalized PDMS and HDI or tri-HDI. The resultant elastomers reveal distinct tensile strength of ~0.4 MPa crosslinked by HDI and ~7 MPa crosslinked by tri-HDI, respectively. The samples recover over 90 % of virgin tensile strength after at 90 °C for 24 h for the

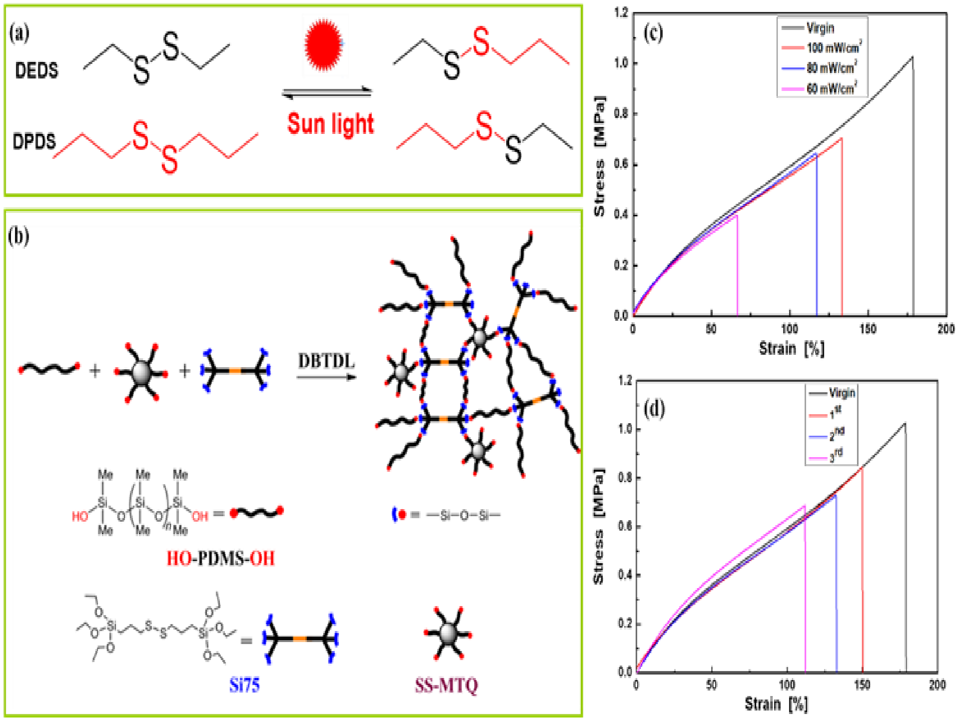

**Fig. 14** (a) Disulfide metathesis between equimolar DEDS and DPDS exposed to sunlight. (b) Synthesis of the crosslinked silicone elastomer. Tensile stress-strain curves of virgin and healed specimens under light irradiation with different conditions: (c) different light intensity, with 1.0 mm thickness for 48h; (d) repeated healing process under 100 mW/cm$^2$ with 0.75 mm for 48 h. Reproduced with permission from [62], Copyright 2017 Elsevier.

former and at 110 °C for 16 h for the latter. This dynamic polyurea is expected to have potential applications in coatings, paints, and 3D printing.[67,164]

Unlike common urea bonds, hindered urea bond, i.e., a urea bond bearing a bulk group on the nitrogen atom, shows good dynamic behavior, because the steric effect weakens the chemical bond strength of urea, thus endowing polymers with admirable healing ability under low temperature.[165] Therefore, a silicone elastomer-containing dynamic hindered urea bond is prepared from $H_2N$-PDMS-$NH_2$, HDI, and piperazine.[166] The ~3 MPa tensile strength of the formed elastomer regains 90 % under 90 °C for 12 h, and the damaged flexible sensor also restores its function at 90 °C for 24 h. Moreover, silicone materials containing dynamically hindered urea bonds can also be used as smart insulating materials for power equipment and electronic devices.[66] Both mechanical performance and dielectric properties of damaged samples recover 90 % when treated at 90 °C for 12 h, owing to the dynamic capacity of hindered urea bonds.

The thermosetting feature of traditionally covalent crosslinked polymers like silicone materials causes the inability to be 3D printed by selective laser sintering (SLS). Recently, covalent adaptable networks (CANs) provide a solution to this challenge. Thus, dynamic hindered pyrazole urea bonds containing PDMS elastomer are prepared by the copolymerization between $H_2N$-PDMS-$NH_2$, IPDI, tri-HDI, and 3-amino-5-tert-butylpyrazole (AtBuP) (Fig. 15).[164] After the elastomer is cryogenically ground into PDMS powders with appropriate particle size (~92 µm), they are can be SLS 3D printed. The damaged samples fully regain their mechanical properties (~8 MPa) after at 120 °C for 1 h and 80 °C for 6 h. More important, for traditional 3D printing polymers, the weak interlaminar bonding strength between the printed layers always leads to anisotropic mechanical strength, whereas dynamic covalent crosslinking can effectively enhance the interface interaction and reduce the anisotropy of mechanical strength. A personalized insole with complex structure and self-heal ability is 3D printed, which exhibits potential application in foot orthotics. This strategy provides a new direction for SLS 3D printing of other thermosetting polymers.

## Siloxane equilibration

All the above dynamic bonds have successfully entitled silicone materials with self-healing ability, but these bonds are exotic segments that may affect the excellent properties of silicone materials. In fact, the siloxane can be reversibly broken and recombined in the presence of an alkaline catalyst, suggesting the potentially dynamic nature. The tetramethylammonium silanol-initiated ring-opening copolymerization of octamethylcyclotetrasiloxane ($D_4$) and bis(heptamethylcyclotetrasiloxanyl)ethane (bis-$D_4$) renders crosslinked elastomer and forms active silanolate end groups (Fig. 16).[72] These "living" reactive anionic species can

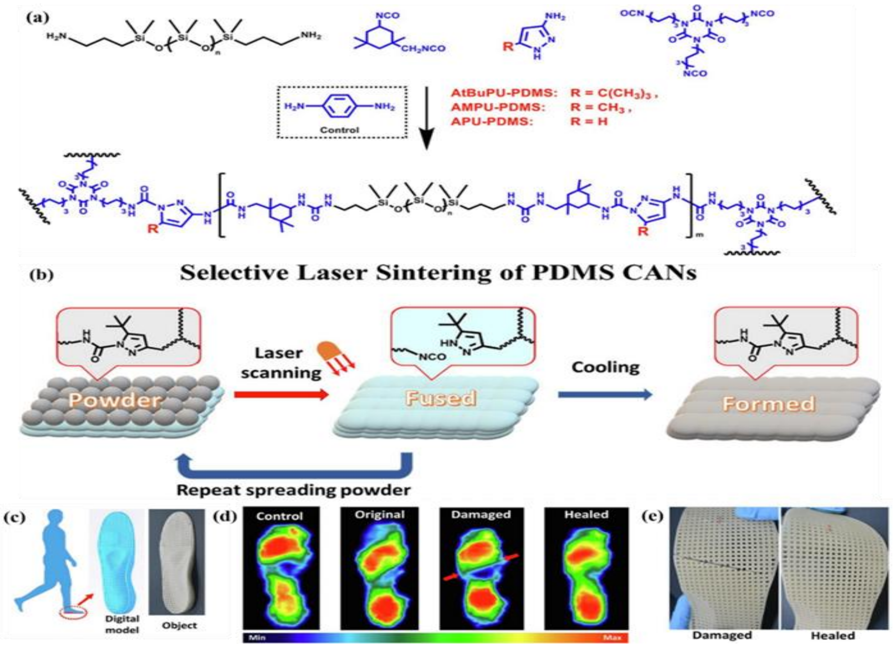

**Fig. 15** (a) Synthesis of PDMS CANs containing dynamic pyrazole urea bonds and non-dynamic control PDMS (PPDU-PDMS). (b) schematic illustration of SLS 3D printing. (c) The digital model and SLS printed object picture of AtBuPU-PDMS orthotic insole. (d) Plantar pressure distribution with the normal insole (Control) and original, damaged, healed orthopedic insoles. (The damaged area was marked by red arrows.) Colors ranging from blue to red indicate increasing pressure. (e) The practical photos of damaged and healed orthotic insole. Reproduced with the permission from [164], Copyright 2021 Elsevier.

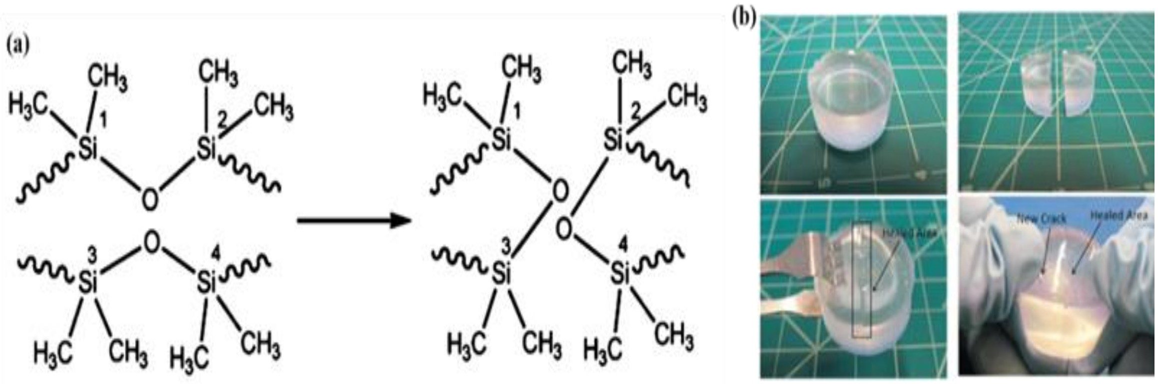

**Fig. 16** (a) Schematic illustration of siloxane equilibration. (b) Illustration of the self-healing process: the original cylindrical sample was cut in half and healed at 90 °C for 24 h the healed sample was deformed by hand, and cracking occurred at a place other than the healed area. Reproduced with s from [72], Copyright 2012 American Chemical Society.

promote thermally activated equilibration among different network isomers and cyclic oligomers. Taking advantage of siloxane equilibration, the cut elastomer is healed to restore the original strength.

Subsequently, a stronger self-healable silicone elastomer is developed, where amino groups in $H_2N$-PDMS-$NH_2$ react with multifunctional acrylates *via* amino-ene Michael addition reaction.[73]. The tetramethylammonium hydroxide is added during the preparation of elastomer to activate the dynamic nature of crosslinked networks. The tensile strength of 1.0 MPa recovers 91 % after healing at 105 °C for 24 h. In addition, self-healable silicone elastomer with tunable permittivity is also prepared by a one-step process of anionic ring-opening copolymerization of cyanopropyl-substituted cyclic siloxanes, $D_4$, and tri-$D_4$.[167] The resultant products composed of networks, linear chains, and cyclic compounds fully recover their mechanical properties and functions at 80 °C for 10 min, by virtue of active silanolate end groups leading to the rearrangement of crosslinked networks. Thus, this elastomer will be promising as artificial muscles for biomedical applications. Besides tetramethylammonium hydroxide, potassium silanolate can also activate siloxane equilibration between different linear chains. The aminopropyl side groups and potassium silanolate end groups of dual-functionalized polysiloxanes react with diglycidyl ether of ethoxylated bisphenol-A to form stiff vitrimers.[168] Owing to the dynamic behavior of siloxane equilibration catalyzed by potassium silanolate, ~50 MPa tensile stress of the vitrimers renews at 81 % after at 110 °C for 24 h.

Moreover, a superior hard, robust, transparent, and self-healable nanocomposite coating is fabricated by incorporating soft polymeric micelles into hard but quickly reversible Si−O−Si networks derived from the interaction between aminopropyl-functionalized poly(silsesquioxane) sol and triethylamine (TEA) (Fig. 17).[169] The highly cross-linked networks entitle the coating to a hardness of 0.83 GPa which is superior to those of most polymers (< 0.3 GPa), whereas the uniform dispersion of micelles into the coating reduces its Young's modulus (5.89 GPa). The scratches (~50 μm) on the coating are quickly healed within 4 min due to the dynamic reversibility of Si−O−Si networks. This strategy provides a feasible pathway to prepare multifunctional materials without trade-offs between these properties.

In general, dynamic covalent crosslinked silicone materials exhibit stronger structural stability and endurability than non-covalent crosslinked materials, but the former always needs a much higher healing temperature and longer time than the latter. The preparation of self-healing silicone materials based on imine or disulfide bonds is relatively simple owing to sufficient alternatives of precursors, meanwhile, their healing conditions are more moderate due to their better dynamic behavior. The self-healing of silicone materials based on DA bonds is often realized at higher than 80 °C for a little longer time. The fabrication of self-healing silicone materials based on siloxane equilibration is quite convenient, but it needs further research on whether the active silanolate will affect the structural stability of silicone products in service because its reactivity is even endless at room temperature.[170]

### 2.3 Self-healing of silicone materials based on dynamic non-covalent and covalent bonds

Nowadays, the synergy of the dynamic covalent bond and non-covalent bond has become a mainstream strategy to design self-healing materials, because the combinations often realize high mechanical properties and excellent self-heal ability.[34] Since a non-covalent bond has much lower bond energy than a covalent bond, the former is preferentially broken before the latter under the action of external force. Therefore, dynamic

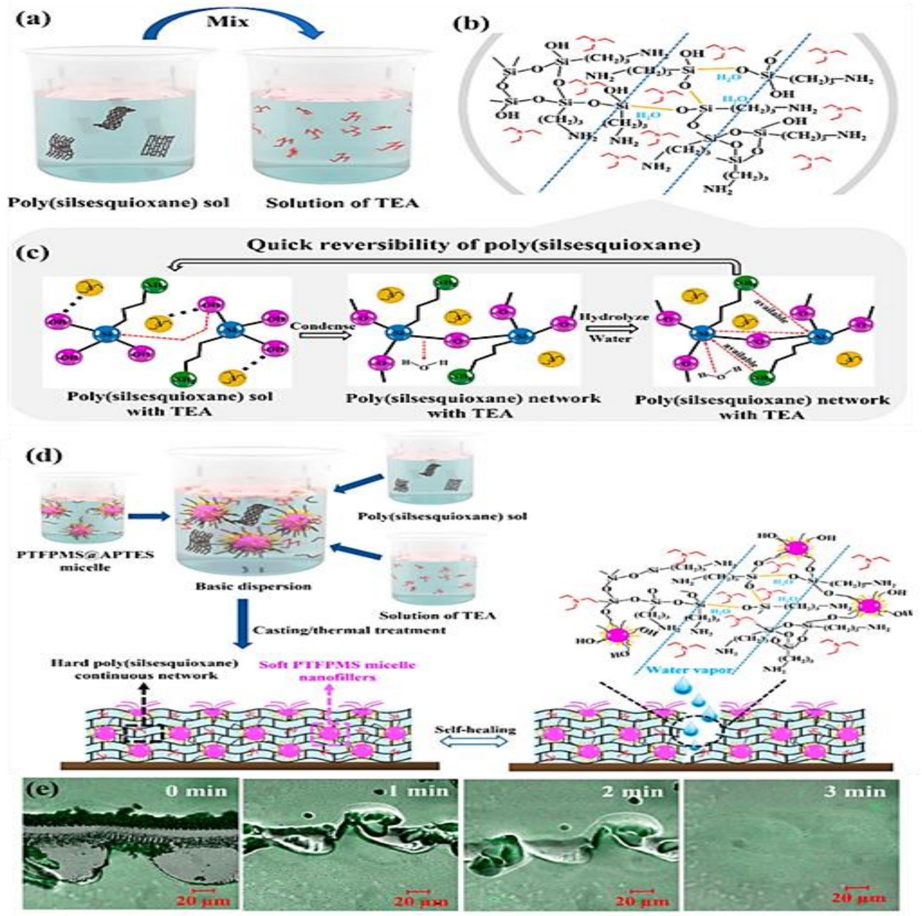

**Fig. 17** Schematic illustration of (a) the preparation and (b) molecular structure of poly(silsesquioxane) networks with TEA. (c) Schematic illustration of hydrogen bonding interactions between TEA and silanols in aqueous poly(silsesquioxane) sol (left), condensation of silanols (middle), and hydrolysis of poly(silsesquioxane) network catalyzed by free aminopropyl groups (right). (d) The preparation procedure and self-healing process of the basic nanocomposite coating. (e) The images show the self-healing process of a scratch with 50 μm width on the coating by the water vapor generated from 45 °C water. Reproduced with permission from [169], Copyright 2022 American Chemical Society.

covalent crosslinking can maintain structure stability, while non-covalent bonds can dissipate energy through reversible dissociation/recombination.[171-173] For example, the synergies of dynamic imine bonds with sacrificial hydrogen bonds,[76,77] aldehyde phenylboronic acid-Zn(II) coordination[75] or Zn(II)-amino coordination[83] endow PDMS elastomers with controllable self-heal ability and toughness. However, their tensile strength is still weak in the absence of reinforcing fillers. On the contrary, the combination of boron ester bonds and hydrogen bonds from UPy produces high-performance and self-healable silicone materials, where a maximum strength of 7.33 MPa and self-healing efficiency of 98 % are achieved.[82] This strategy is conducive to overcoming the trade-off between molecular interaction and cross-linking.

To date, it is still an interesting issue but a great challenge to develop transparent, tough, self-healable film for flexible transparent electronics. A strategy of building hierarchical crosslinked networks and dual dynamic bonds is proposed to break through this challenge.[78] The urea-containing polydimethylsiloxane (LP*x*) provides dynamic hydrogen bond cross-linkages, multi-amino terminated hyperbranched PDMS (HPSi) is used as the permanent crosslinking points and connects with LP*x* through isocyanate with exchangeable aliphatic disulfide (SS-NCO). The best comprehensive properties of tensile strength, Young's modulus, toughness, and transmittance are about 9 MPa, 200 MPa, 16 mJ $m^{-3,}$ and 88 %, respectively. The healing efficiency is still above 90 % even after three healing cycles at 100 °C for 30 min. On the other side, to guarantee dynamic interactions under harsh conditions, a self-healing, and highly stretchable silicone elastomer is prepared by synergistically incorporating strong H-bonds, weak H-bonds, and disulfide metathesis (Fig. 18).[79] The formed elastomer has a high stretchability of 14000 % within the unnotched sample and even 1300 % within the notched sample. The elastomer shows fast and excellent self-heal ability either under universal or harsh conditions, such as

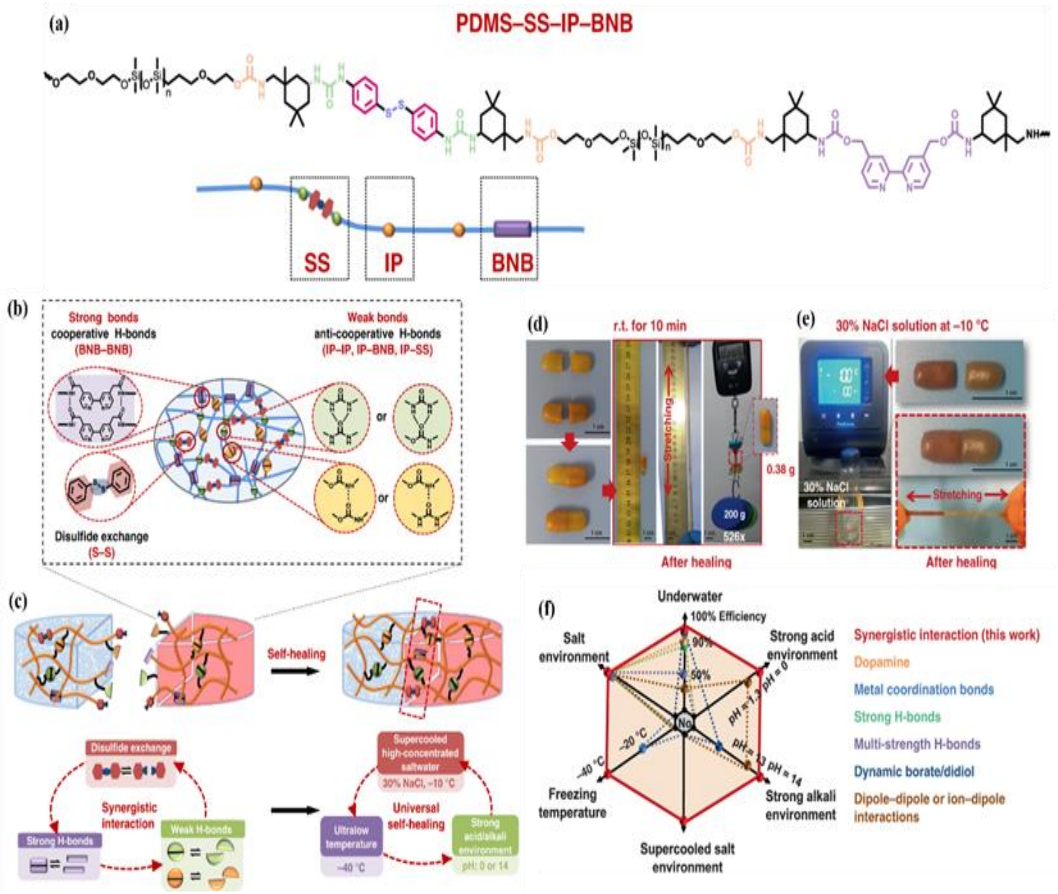

**Fig. 18** (a) Chemical structure of PDMS–SS–IP–BNB. (b) The proposed ideal structure of the supramolecular polymer network based on strong crosslinking H-bonds (BNB–BNB), weak crosslinking H-bonds (IP–IP, IP–BNB, IP–SS), and disulfide metathesis (S–S). (c) The synergistic interaction of multiple dynamic bonds contributes to the universally self-healing capability of elastomer. (d) Photographs of P3 film (left) before and (right) after self-healing and enabling high stretchability and holding a weight that is 526 times greater than that of the film. (e) Self-healing of P3 film in a 30% NaCl solution at −10 °C for 24 h. (f) A comparison between this work and previously reported self-healing materials in terms of healability in universally harsh conditions. Reproduced with the permission from [79], Copyright 2020 Springer Nature.

at room temperature (10 min for healing), ultralow temperature (−40 °C), underwater (93 % healing efficiency), supercooled high-concentrated salt water (30 % NaCl solution at −10 °C, 89 % efficiency), and strong acid (pH = 0)/alkali (pH = 14) environment (88 % or 84 % efficiency).

The combination of three or more dynamic bonds into self-healing materials will make better use of the synergistic effect, which not only easily controls mechanical strength and self-heal ability by adjusting the relative contents of various dynamic bonds, but also responds to diverse external stimuli, especially under some harsh terms.[174,175] For instance, a self-healing and high-adhesion silicone elastomer in harsh environments is also enabled by the synergistic effect of disulfide, imine, and hydrogen bonds.[86] The elastomer has excellent stretchability (368 %) and self-heal ability at room temperature (98 %, 5 h) and in water (96 % for 5 h). The elastomer also reveals high and endurable adhesion to metal and nonmetal even in harsh environments like under acidic (pH 1) and alkaline (pH 12) environments, salt water, and petroleum ether. Moreover, the synergistic interactions of the disulfide bond, hydrogen bond, and Fe-coordination bond also endow silicone elastomer with the rapid self-heal ability and high stretchability.[80] The elastomer exhibits a high stretchability of 1100 %, a tensile strength of 1.11 MPa, and a healing efficiency of 96 % at room temperature within 3 h. The combinations of the disulfide bond, zinc ion coordination bond, and weak H-bond also endow prominent stretchability of 1762 % and healing efficiency of 91 % at room temperature for 24 h.

Although the combinations of diverse dynamic bonds have greatly improved the stretchability, their tensile strengths are almost lower than 2.0 MPa. Within these developed silicone materials, dynamic non-covalent and covalent bonds often locate in segregated chain segments or independent networks, leading to the inhomogeneity of crosslinked networks and dynamic bonds. Given this, our group proposes a strategy involving the dual-crosslinking of side chains with an asymmetric chain structure to overcome the related challenges.[85] The dual-crosslinking readily undergoes between diethylenetriamine-functionalized polysiloxane (PDETAS) as the matrix and 4-formyl benzoic acid (FBA) as the crosslinker (Fig. 19). The formed crosslinked chain has an asymmetric structure, where it's one cross-linkage is strong covalent imine or aminal bond that maintains structural stability, but another one is weak non-covalent ionic hydrogen bond that confers good self-heal ability. The elastomer with a tensile strength of 12 MPa repeatedly recovers from damage when it is healed at 100 °C for 2 h. This elastomer also exhibits potential applications in flexible devices and adhesives.

At present, the synergetic integrations of diverse dynamic covalent bonds and non-covalent bonds contribute to superior healing efficiency under more moderate conditions as well as good mechanical properties and become the prevailing pathway to self-healing materials. Especially, the combinations of strong H-bonds, weak H-bonds, and disulfide metathesis achieve highly stretchable silicone elastomer, and the elastomer can realize fast healing even under many harsh conditions.[79] The integrations of imine, aminal, and ionic hydrogen bonds entitle silicone elastomer with robust mechanical strength and excellent self-healing capacity.[85]

## 3. Recycling or reprocessing of silicone materials

Nowadays, dynamic crosslinked polymeric networks have attracted more and more attention, because the reversible dissociation and recombination of networks can also entitle polymers to recyclability or reprocessability.[176,177] It means that dynamic crosslinked polymers especially thermosetting polymers like epoxy resin and vulcanized rubbers can be repeatedly recycled or reprocessed after use, which will effectively save resources and reduce environmental pollution.[178,179] Therefore, dynamic crosslinked silicone materials not only have excellent performances but also can be recycled or reprocessed after service. According to stimuli-responsive characteristics of different dynamic bonds within crosslinked silicone materials, their recycling or reprocessing technologies can be mainly divided into the hot-pressing method, solvent method, and UV radiation method.

### 3.1 Recycling or reprocessing of silicone materials by thermal compression remolding

Because thermal compression technology is a simple and feasible method, and most dynamic bonds are thermally sensitive structures, recycling or reprocessing of dynamic crosslinked silicone materials by thermal compression remolding becomes the predominant one.[176,177] As shown in

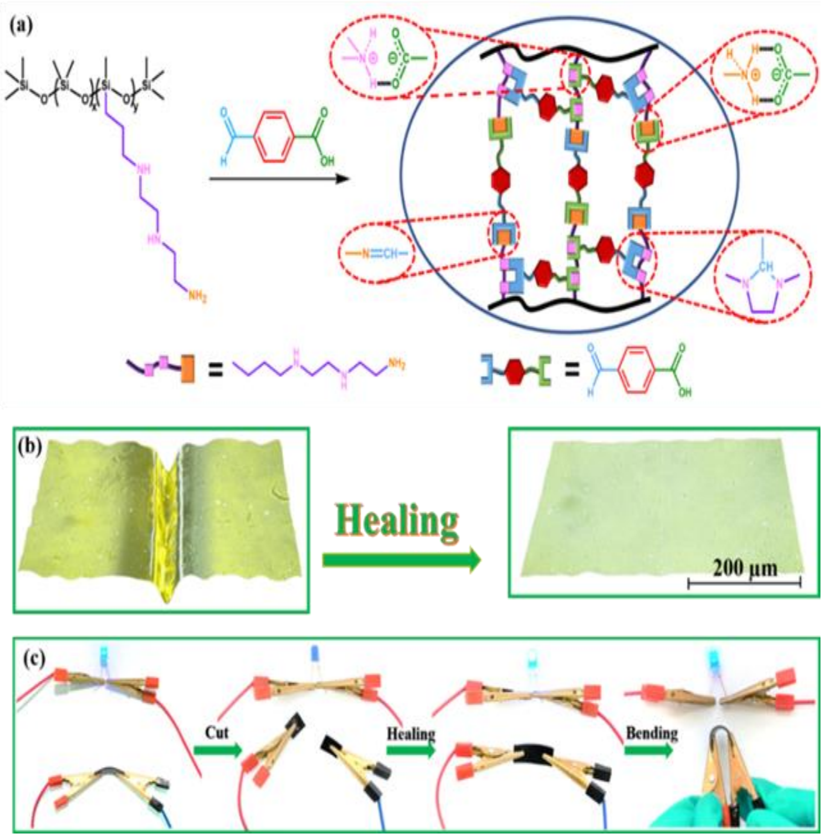

**Fig. 19** (a) A schematic illustration of the designed dual-crosslinking side chains with asymmetric chain structures in PDETAS-FBA. (b) Micrographs of a damaged sample and a sample healed at 100 °C for 2 h. (c) Photographs of the self-healing of the flexible conductive composite. Reproduced with the permission from [85], Copyright 2022 Royal Society of Chemistry.

Fig. 20, the whole process consists of (1) cutting or pulverizing waste silicone materials into fragments or powders; (2) thermally compressing the fragments or powders to produce a bulk material under thermally-activated rearrangement and recombination of dynamic bonds within the interfaces; (3) testing the relevant properties of re-formed materials to evaluate reprocessing efficiency. Generally, recycling or reprocessing efficiency primarily depends on the thermal reversibility of dynamic bonds, crosslinking density, processing time, temperature, pressure, and particle size.[180] To date, dynamic bonds including non-covalent bonds (ionic bond, coordination bond, π-π stacking) and covalent bonds (hindered urea bond, imine bond, ester bond, vinylogous urethane bond) have been used for reprocessing or recycling silicone materials.[181-185] Silicone materials crosslinked by non-covalent bonds always have lower processing temperatures even at room temperature and shorter processing time, whereas they are inverse for dynamic covalent crosslinked silicone materials. The lower crosslinking density is conducive to molecular mobility, and smaller particle size owing to a larger specific surface area facilitates the interface interaction, together the efficiency will be improved.

For instance, a dynamically hindered urea bond containing silicone material generated from isocyanate, piperazine, and $H_2N$-PDMS-$NH_2$ can be reprocessed into smooth specimens by hot-pressing under 8 MPa pressure at 150 °C for 30 min.[164] The increasing crosslinking density enhances tensile strength but deteriorates recycling behavior, suppressing the mobility of dynamic bonds. The recycling efficiency increases with the increasing content of dynamic urea bonds, where the best efficiency is about 82 %. After two recycling cycles, the efficiency is still higher than 50 %. Our group also prepares reprocessable silicone elastomer by incorporating dynamic ionic bonds or boric acid ester bonds into thiol-ene UV-cured PDMS.[70] The resultant elastomer can be reprocessed at 80 ~ 100 °C, and the recovery of mechanical strength is still over 90 % even after three cycles, deriving from the rearrangement of crosslinked networks *via* reversible breakage and reformation of dynamic bonds. The dynamic imine bond containing vitrimer-like PDMS can also be reprocessed at 100 °C for 15 min with a pressure of 15 MPa, and the mechanical properties can be fully maintained even after three cycles.[60] The dynamic transesterification reaction can also be used to recycle silicone elastomer, where the reobtained elastomer recovers over 90 % of mechanical strength at 180 °C, 10 MPa for 40 min.[184] The coordination interaction salicylaldimine group with the $Zn^{2+}$ ion contributes to the fast reprocessing (100 °C, 5 MPa pressure, 3 min) of supramolecular silicone elastomer, where the small pieces of crosslinked elastomer can be reprocessed into new samples with no visible defects.[185] Their mechanical properties do not significantly change even after ten reprocessing cycles, indicating their robust reprocessability.

Although dynamic crosslinked silicone materials are highly attractive in various areas for good mechanical strength and aging resistance, their intrinsically high flammability limits their practical applications. Hence, it is of great significance to prepare an intrinsic flame-retardant dynamic silicone material. For this reason, phosphorus-containing compounds and dynamic phenyl borate ester bonds are integrated into silicone networks by *in-situ* polymerization.[181] The resultant materials reveal excellent flame retardance and reprocessing properties, where the limited oxygen index is 26 % with VTM-0 rating due to the N-P-Si synergistic effect, and reprocessing efficiency is over 87 % after twice cycles by firstly hot pressing at 80 °C, 10 MPa for 20 min and then placing in an oven at 60 °C for 8 h. This high-performance sustainable silicone material has great promise for fire safety behavior and reutilization in practical applications.

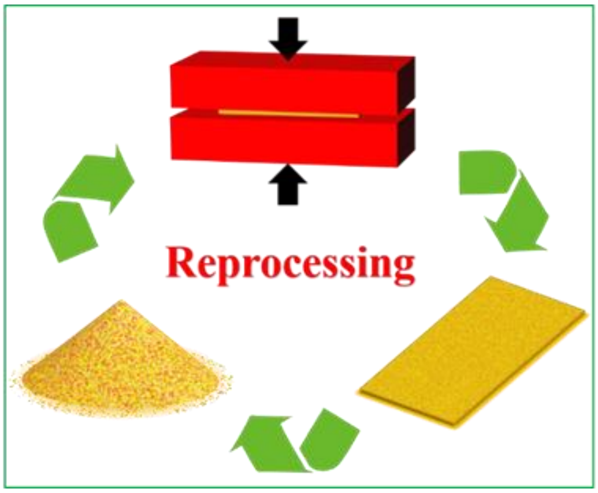

**Fig. 20** Schematic illustration of thermal compression remolding.

### 3.2 Recycling or reprocessing of silicone materials by solvent method

Regarding electronic components-encapsulated silicone materials, thermal compression technology is no longer feasible, since electronic components may be destroyed during reprocessing. At this point, the solvent method is preferable to recycle or reprocess these dynamic crosslinked silicone materials, because dynamic crosslinked networks can also be reversibly decrosslinked in appropriate solvents with/without heating or extra chemical reagents.[186,187] Thus, the electronic components or other nano-fillers can be recycled, and the broken networks can be re-crosslinked again to regain their properties after the solvent is volatilized (Fig. 21). In general, non-covalent bonds-based silicone materials can be dissolved at room temperature, while dynamic covalent crosslinked silicone materials (like imine bond,[188] DA bond [55]), especially with densely crosslinked networks, become dissolvable only with extra assistance like chemicals and heating.

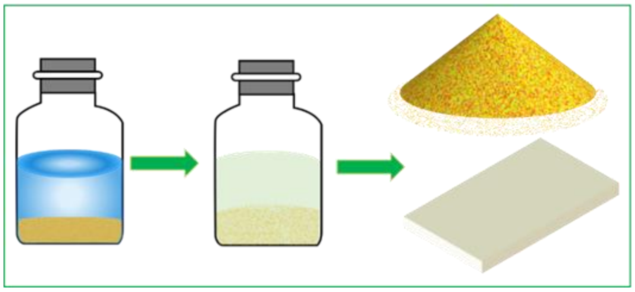

**Fig. 21** Schematic illustration of the solvent-driven reprocessing process.

For example, using non-covalent boron–nitrogen coordination bonds as a reversible crosslinking network of silicone elastomer, the elastomer can be well dissolved in *n*-butylamine.[186] After the evaporation of *n*-butylamine, a homogeneous elastomer obtains again. However, the recovery efficiency of the property is about 50 %, probably because the residual *n*-butylamine strongly destroys coordination bonds by interaction with the B atom. Taking advantage of the mild dynamic nature, imine bond crosslinked PDMS elastomer powders can rapidly dissolve into chloroform.[187] A transparent elastomer is produced again after the evaporation of the solvent, accompanied by a great recovery of mechanical properties. The dissolving process can be accelerated using acetic acid-catalyzed metathesis or butylamine-catalyzed transimination. The acid-catalyzed method recovers 90 % of Young's modulus, while it only recovers 76 % for butylamine-catalyzed recycling technology. As for DA bonds-based silicone elastomer, it is only swollen but not dissolved in toluene, chloroform, or xylene at room temperature, while a uniform solution is formed after being heated at 125 °C for 1 h, because *r*-DA reaction occurs under elevated temperature to release the furan and maleimide groups.[189] After the solution is dried at 80 °C for 48 h, a crosslinked elastomer is formed again with the recovery of 95 % mechanical strength.

Recently, flexible devices show widespread applications in human life, because of their sensitivity and lightweight, but it is still difficult to fully recycle waste flexible devices. Given this, our group utilizes an imine bond, aminal bond, and ionic hydrogen bond to fabricate a robust and re-dissolvable silicone elastomer.[85] The elastomer with lower crosslinking density can re-dissolve in THF without any extra additives at room temperature, while the densely crosslinked elastomer becomes dissolvable at 70 °C for 1 h. The regenerated elastomer exhibits similar tensile strength to its pristine. Furthermore, a flexible carbon nanotube/elastomer composite with excellent strain sensitivity can also be re-dissolved at 80 °C for 2 h and about 90 wt% of carbon nanotubes and matrix can be recycled. This robust and recyclable polysiloxane elastomer exhibits potential application in recyclable flexible devices.

### 3.3 Recycling or reprocessing of silicone materials by UV radiation

Although hot-press technology and solvent method can be used in almost all dynamic crosslinked silicone materials, hot-pressing is an energy-intensive method, and a large amount of solvent causes secondary pollution. Using renewable and eco-friendly sunlight energy or UV radiation to activate dynamic bonds should be an appropriate choice. This requires the selected dynamic bonds to have photosensitivity, where the disulfide bond is often used due to its facile reactivity.

To achieve this goal, our group utilizes commercially available disulfide bond-containing silane to crosslink a ω-dihydroxyl PDMS to produce silicone elastomer.[62] Result of sunlight-activated disulfide metathesis, the pulverized silicone elastomer powders can be recycled multiple times without any catalyst under sunshine, and ~80 % mechanical strength is regained. The smaller size of elastomer particles corresponds to higher recovery efficiency, owing to the larger specific surface and more rebinding sites. Besides, another disulfide bonds-containing silicone elastomer is prepared by the oxidation of thiol-terminated sulfur-containing heterochain polysiloxanes (P-SHs) with thiol-containing crosslinkers.[65] The resultant elastomer recovers about 70 % of mechanical strength after UV radiation (365 nm) for 30 min. Reprocessing or recycling silicone materials by sunlight or UV radiation is an environmentally friendly technology. However, it is also important to note that its reprocessing time is often longer, and reprocessing capacity is smaller compared to the hot-press method because the penetration of UV radiation within polymers especially for opaque polymers is limited.

## 4. Dynamic crosslinked silicone composites

Due to very weak interactions between polysiloxanes, silicone materials are always composited with different nanofillers to effectively enhance mechanical properties, reduce cost and give new functions.[101,190-192] However, within dynamic crosslinked silicone materials, the incorporation of large amounts of nanofillers will restrict the mobility of polymer chains, owing to strong interactions between polymer matrix and filler, which thus deteriorates self-healing and reprocessing efficiency. To break through these restrictions, the grafting of functional groups to the nanofiller surfaces allows for the formation of dynamic bonds between the nanofiller and matrix,[193] where dynamic bonds also dissociate during self-healing or reprocessing and thus contribute to chain mobility. Therefore, this surface modification strategy can maximize the balance between mechanical property and dynamic behavior.

Nanoscale silica ($SiO_2$), owing to its special optical, electricity, magnetism, and chemical characteristics, has already been widely used in plastics, rubbers, resins, pigments, ceramics, adhesives, sealants, medicine carriers, cosmetics, and antibacterial materials.[75,83,194] From Fig. 22, aminated silica (silica-$NH_2$) synthesized by grafting of 3-aminopropyl trimethoxysilane can react with (2-acetoacetoxy)ethyl methacrylate to form dynamic vinylogous urethanes and also interact with $ZnCl_2$ to form sacrificial Zn(II)-amine coordination bonds.[83] The formed dual dynamic bonds between polymer and silica not only reduce the aggregation of nanoparticles, but also facilitate stress transfer. Therefore, both the mechanical properties and dynamic behavior of PDMS composites are improved, where robust, healable, reprocessable, and shape-memory silica/PDMS composites are developed and show great application potential in smart material fields.

A well-ordered array of $SiO_2$ nanoparticles exhibits angle-independent structural colors due to their isotropic structures with short-range order, which can be used in photonic composites. To improve their compatibility, $SiO_2$ is modified with mono-triethoxysilylethyl-terminated PDMS.[194] The isotropically arranged monodispersed $SiO_2$ are then incorporated in a supramolecular elastomer based on coordination interaction between amino-terminated PDMS and cerium trichloride to produce photonic elastomer with tunable mechanical strength, angle-independent structural color, and self-heal ability. The photonic elastomer displays good mechanochromic properties while Young's modulus and elongation at break reach 0.24 MPa and 150 %, respectively. It may find applications in visualized stress or strain sensors anti-counterfeiting and wearable devices.

Self-cleaning and superhydrophobic properties are mainly associated with their wetting behavior which depends on their surface roughness and low surface energy. To achieve enhanced toughness and fast self-heal ability at room temperature, imine, and coordination bonds are employed to develop dual crosslinked silicone elastomer (imine-BZn-PDMS).[75] Mixing of imine-BZn-PDMS with $SiO_2$ nanoparticles enables the restoration of superhydrophobicity after oxidation/decomposition and improves the abrasion resistance of the superhydrophobic surface. The as-prepared HB-imine-BZn-PDMS composite exhibits superhydrophobic properties and fast self-heal ability to ruptures, pinholes, and surface oxidation, showing potential applications in skin and wearable devices.

### Carbon-based nanofillers

Graphene has excellent optical, electrical, and mechanical properties, which holds significant promise for applications in materials science, energy, and biomedicine.[195,196] To improve polymer chains' mobility and dynamic behavior, furan-functionalized graphene (G-FA) is reacted with maleic-functionalized polysiloxanes to form dynamic DA bonds (Fig. 23). It is because those DA bonds are dissociated during heating, thus promoting chain mobility and decreasing adverse

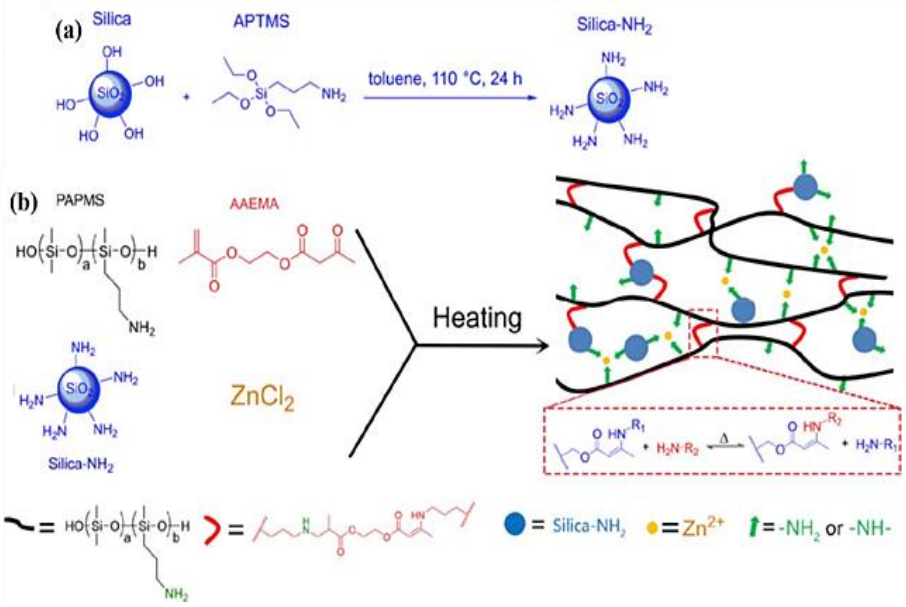

**Fig. 22** (a) Preparation route of silica-$NH_2$. (b) The preparation procedure of PDMS vitrimer composites. Reproduced with the permission from [83], Copyright 2020 Elsevier.

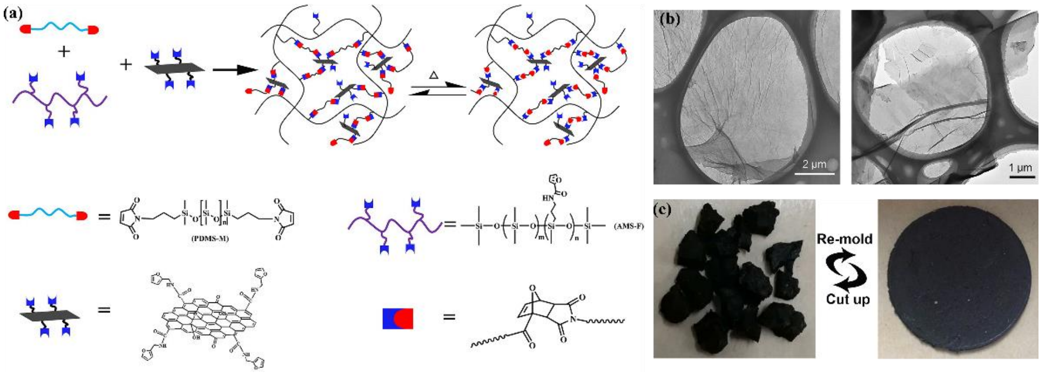

**Fig. 23** (a) Preparation process of the healable nanocomposite. (b) TEM images of GO (left) and G-FA (right). (c) The broken G-FA-reinforced nanocomposite (left) and re-molded G-FA-reinforced nanocomposite (right). Reproduced with the permission from [197], Copyright 2019 Wiley.

effects of nanofiller on healing efficiency.[197] Moreover, furan groups also improve the dispersibility of G-FA and enhance mechanical properties. The tensile strength of 0.25 MPa is improved by 140 % compared to the elastomer without G-FA. This strategy provides a practical way to fabricate nanocomposites with the excellent self-healing ability and mechanical properties.

In addition to polymer chain mobility affected by nanofillers, the interface between carbon-based nanofiller and the polymer is prone to separation under loading, which considerably decreases their properties.[198,199] Especially, the recovery of thermal conductivity is also challenging, because it is difficult to reconstruct continuous phonon transport pathways at the fracture interface between the polymer and filler. The boroxine poly(dimethylsiloxane) 2-ureido-4[1H]-pyrimidinone (BE-PDMS-UPy) polymer is composited with UPy-modified graphene aerogel (GAU).[82] The composite achieves a high mechanical strength (~40 MPa), self-healing efficiency (~80 %), and thermal conductivity (0.826 W/m·K). The H-bond crosslinking between GAU and BE-PDMS-UPy reduces interfacial thermal resistance and facilitates phonon transfer at the interface. This composite can regain high mechanical properties and efficient heat conduction by healing, particularly under extreme or inaccessible environments.

Carbon nanotubes (CNTs) show an extremely wide range of applications due to their special structure and unique physicochemical properties.[200,201] Compositing polymer matrix with modified CNTs can effectively improve the properties, but permanent covalent bonds within the interfaces make the difficult to recycle the composite. The aldehyde groups-functionalized CNTs effectively react with amino groups in PDMS to form dynamic imine bonds, which not only increases the compatibility but also makes for the complete degradation of composite and recycling of CNTs and PDMS.[202] CNTs as an efficient photothermal agents can rapidly convert NIR energy to thermal energy, potentially endowing the composite with remote-controlled ability.[61,200] Owing to strong UV absorption and shielding of CNTs, UV light gradually decreases within the composite membrane, thus forming gradient crosslinking densities. A biomimetic silicone membrane with a switchable Janus structure is prepared from anthracene-grafted 3-aminopropyl-terminated polydimethylvinylsiloxane (APT-PDMVS-g-An) and CNTs (Fig. 24), where the gradient Janus structure results from UV-induced dimerization of anthracene and UV light intensity gradient.[61] Owing to dynamic imine bonds within crosslinked networks, the PDMS-An/TFB@CNTs composite can be recycled repeatedly *via* hot-pressing or solution casting method.

Dielectric elastomer generators (DEG) able to convert mechanical energy to electrical energy are prepared by sandwiching highly deformable dielectric elastomer film between two compliant electrodes, but they are vulnerable to external stresses. Therefore, a conductive rubber electrode with high electrical conductivity (EC), healing, and recycling ability is prepared by mixing highly conductive carbon black (CB) and carbon grease (CG) into hydrogen bond crosslinked silicone rubber (SiR-SN).[203] CG and CB induce the partial phase separation of polar SiR-SN and the formation of a segregated conductive network, achieving a significantly improved EC. Compared with a common CG electrode, energy loss at 3 kV and 400 % strain of DEG from 5 phr CB/60 phr CG/SiR-SN electrode reduces by 83 %, but energy density increases by 73 %. Meanwhile, the electrodes have good healing ability to conductivity (92 % at 60 ºC for 4 h) and can be recycled 5 times without sacrificial performance.

$Ti_3C_2$ MXenes owing to good conductivity show great application potential for electronic devices.[204] Flexible conductive composites can be used as wearable strain sensors, robotics, and electronic skin, but facile preparation of

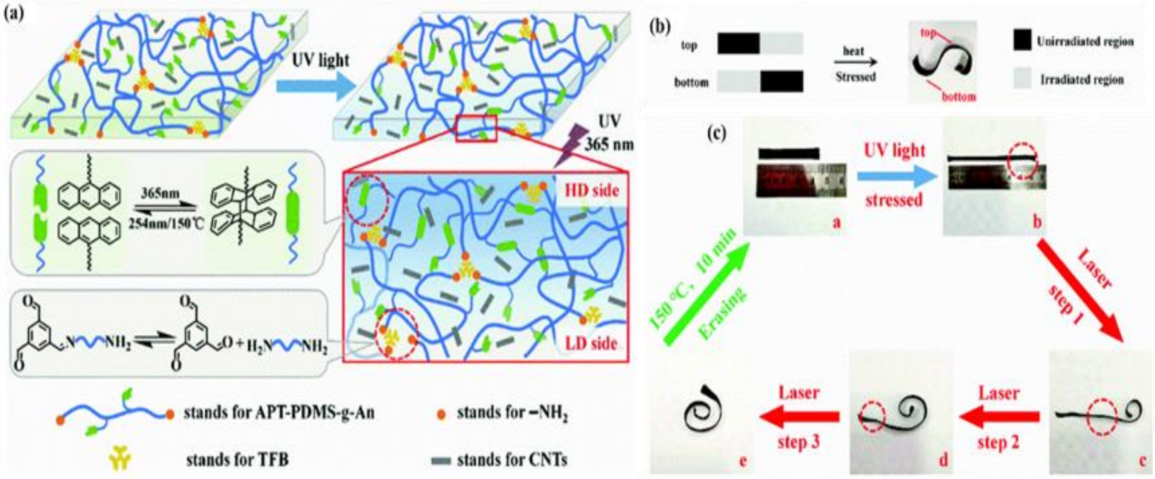

**Fig. 24** (a) Fabrication of the TFB crosslinked anthracene-grafted APT-PDMS, CNTs composite membrane PDMS-An/TFB@CNTs, and the formation of gradient Janus structure. (b) Shape reconfiguration behavior of the PDMS-An/TFB@CNTs membrane, "S" shape reconfigured via two-sided regional programming. (c) Schematic diagram of laser-triggered shape transformation process and the erasure of Janus structure. Reproduced with the permission from [61], Copyright 2022 Royal Society of Chemistry.

conductive composites with flexibility, self-healing, and sensing capability is challenging. Hence, mixing D-asparagine modifying MXenes (A-MXenes) with amino poly(dimethylsiloxane) modified by 3,4-dihydroxybenzaldehyde produces multifunctional supramolecular elastomer by hydrogen bonding (Fig. 25).[205] The uniform dispersion of A-MXenes ensures good electrical conductivity, while multiple hydrogen bonds and imine bonds endow the composite with ideal tensile properties and self-heal ability without external stimuli. The composite with 10 wt% A-MXenes shows a tensile strength and elongation of 1.81 MPa and 81 %, respectively. Both mechanical property and electrical conductivity restore 97 % at room temperature for 24 h. Moreover, the introduction of L-citrulline-modified MXenes (C-MXenes) into supramolecular silicone elastomer containing disulfide bonds and multiple hydrogen bonds also forms a flexible conductive composite for sensitive strain sensors.[206] The tensile stress and strain reach up to 4.78 MPa and 413 %, and they recover over 95 % at room temperature for 24 h. These excellent conductive silicone composites will be used in wearable sensor devices to accurately detect tiny human movements like speaking, swallowing, and pressing.

### Magnetic particles

Thermally activated self-healing silicone elastomers have been extensively studied, but direct heating is inconvenient and infeasible under some conditions. The incorporation of magnetic particles ($Fe_3O_4$) into self-healable silicone elastomer is employed to realize self-healing triggered by the indirect heating method *via* exposure to an alternating magnetic field.[38] The homogeneous presence of $Fe_3O_4$ particles does not affect significantly the viscoelastic

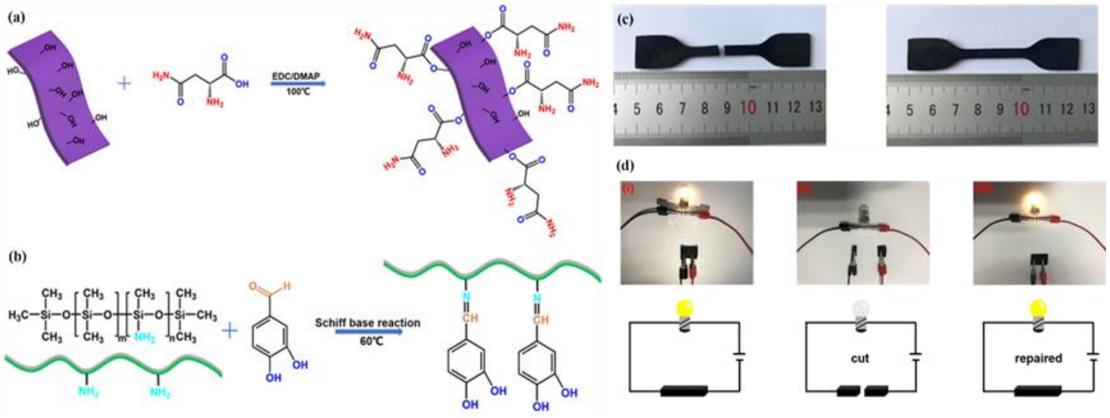

**Fig. 25** Preparation route for (a) A-MXenes and (b) D-PDMS. (c) Stereomicroscope images of 10 wt% A-MXene/D-PDMS damaged and healed samples. (d) The circuit of 10 wt% A-MXenes/D-PDMS in series with an LED lamp and the corresponding diagram: (I) virgin, (II) disconnected (open circuit), and (III) after healing. Reproduced with the permission from [205], Copyright 2020 American Chemical Society.

properties of the matrix. The damaged elastomer composite recovers 70 % of its mechanical properties after being in an alternating magnetic field at a frequency of 110.1 kHz. Besides, the incorporation of $Fe_3O_4$ particles into silicone elastomer crosslinked by hydrogen bonds can also produce self-healable magnetic actuators like magnetic robots, remote actuation, and artificial muscles.[207] Moreover, a novel magnetorheological shear-stiffening elastomer is realized by dispersing carbonyl iron particles into a shear-stiffening elastomer consisting of shear-stiffening gel (STG) and methyl vinyl silicone rubber (VMQ).[208] The storage modulus of MSTE-80 (the volume ratio of STG/VMQ of 80/20, and 8.5 vol% carbonyl iron) is increased by 425 % when applying a magnetic field of 960 mT. Due to reversible interactions of the B-O bond, the extensibility of dissected sample recovers ~40 % at 180 °C for 2 h. The reversible breakage and reconstruction of B-O bonds play an important role in shear-stiffening and self-healing performance.

## Thermal interface nanofillers

Nowadays, more and more attention is paid to environmental and energy issues. Compared to other cooling technologies, passive radiative cooling polymer coatings (PRCPCs) are regarded as a promising energy-saving strategy.[209,210] However, they are troubled by fouling and damage. In view of this, a class of multifunctional PRCPCs with passive radiative cooling, anti-fouling, and self-healing abilities are developed by mixing $Al_2O_3$ microparticles into hydrogen bonding crosslinked PDMS polymers (Fig. 26).[211] The spherical $Al_2O_3$ are selected because they show little absorption in the vis–NIR spectral range (0.4 ~ 2 μm) and thus barely generate heat under direct solar radiation, but they have strong phonon polariton resonances at middle-IR (8 ~ 20 μm), causing good emissivity. The resultant coatings exhibit good passive daytime radiative cooling with a temperature drop of ~2 °C. Meanwhile, the coatings have proper adhesion to the substrate, and excellent anti-fouling and self-healing properties, showing the application potential for thermal management.

Moreover, alumina powders are also incorporated into silicone-based thermosets crosslinked by Diels-Alder (DA) adduct as a cross-linker.[191] The resultant thermosetting polymer not only has self-healing and recycling capacity but also exhibits a low thermal resistance of 0.48 K/W. The thermal resistance of recycled samples by solution method is similar to that of virgin composite. Besides, the incorporation of $Al_2O_3$ into a dual-crosslinked silicone elastomer can form a high-thermal conductivity and fast self-healable composite.[212] The elastomer consists of thermosetting silicone rubber and heat reversibility matrix, where the former is crosslinked *via* hydrosilylation between hydrogen and vinyl functionalized PDMS, and the latter is formed by thermal-curing between amino and carboxyl functionalized PDMS. The obtained

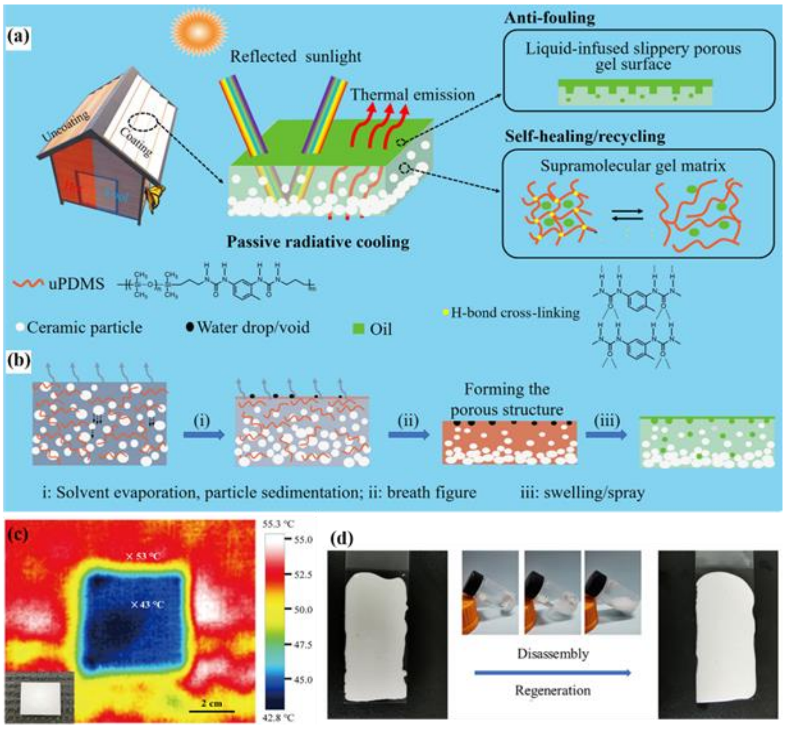

**Fig. 26** Schematic illustration of (a) functional features and (b) forming process of hybrid coatings. (c) IR images and photos of a hybrid coating at 2:00 pm under direct solar radiation. The images are obtained after the coating is exposed to solar radiation from 10:30 am. Isolar is 872 $W/m^{-2}$ at 2:00 pm. (d) Schematic illustration of the recyclability of the hybrid coatings, a hybrid coating on a glass slide (left), and its reuse (right). Reproduced with the permission from [211], Copyright 2022 American Chemical Society.

composite has an optimal thermal conductivity of 5.85 W mK$^{-1}$, and its self-healing efficiency is up to 95 % within 3 min at 90 °C, benefiting from the assistance of thermal diffusion of 3D heat conduction pathways. Hence, these works provide novel approaches to constructing multifunctional PDMS composites with longer service life and high thermal conductivity.

BN owing to its good thermal conductivity has also been often used for thermal conductive composite. Similarly, the discontinuous phonon transport pathway at the fracture interface and the interfacial thermal resistance also affect the thermal conductivity of BN-based composite.[36] To solve this challenge, hydroxylated boron nitride (mBN) is mixed with UPy-PDMS-UPy prepared by modifying $H_2N$-PDMS-$NH_2$ with UPy as end groups, to produce self-healable and thermally conductive silicone materials.[36] The hydroxyl groups on the surface of mBN can form hydrogen bonding interaction with UPy groups, improving its dispersibility and facilitating the reconstruction of thermally conductive pathways. Furthermore, a self-healing silicone/BN composite with high thermal conductivity and low electrical conductivity is realized by filling BN into DA adduct cross-linked silicones.[213] The composite with 50 wt% of BN displays high thermal conductivity, thermal diffusivity, and low dielectric dissipation factor of 0.8837 W/mK, 0.0045 cm$^2$/s, and 0.017, respectively. Meanwhile, its tensile strength is increased to 0.42 MPa by 568 %, showing a self-healing efficiency of 90 % at 135 °C for 15 min. Additionally, a conductive composite with good electrical insulation, thermal conductivity, and healability is also prepared by mixing functionalized boron nitride nanosheets (fBNNS) with silicon vitrimers containing disulfide bonds.[164] The produced composite with 66 wt% of fBNNS reveals excellent thermal conductivity of 1.41 W/mK, and healing efficiency is over 92 %. These self-healing composites reveal excellent endurable thermal management performance for high-power electronic devices.

As a whole, the introduction of diverse nanofillers into dynamic crosslinked silicone materials not only balances mechanical properties and dynamic behavior but also imparts the composite with other multi-functions. For instance, carbon-based nanofillers are mainly used for electrical conductive composites for flexible electronic devices, while thermally conductive nanofillers are primarily used for thermal interface management.

## 5. Conclusions and outlook

Recently, dynamic crosslinked silicone materials owing to their outstanding comprehensive properties, self-heal ability, and reprocessability, exhibit great application potential in smart coatings, flexible electronic devices, and other fields. So far, many kinds of dynamic crosslinked silicone materials have already been developed by integrating diverse dynamic bonds in polysiloxanes crosslinking networks. To efficiently balance mechanical property and dynamic behavior, dynamic crosslinked networks are transforming from the single dynamic non-covalent bond or covalent bond to their synergetic combinations. Hence, this review highlights an overall summary of dynamic crosslinked structural design and property manipulation of silicone materials, and their related self-heal ability, reprocessability, and other multi-functions.

Despite the tremendous advances made in crosslinking network design, property modulation, and multifunctionality, there still are some serious challenges that obstruct the large-scale production and practical applications of dynamic crosslinked silicone materials. The greatest challenge is the trade-off between constrained chain mobility and excellent dynamic behavior. The dense crosslinked network is usually conducive to high mechanical properties, whereas it will also restrict molecular chain mobility and thus reduce dynamic activities. As a result, the synergetic combinations of dynamic covalent bonds and non-covalent interactions already become an efficient pathway to achieve high mechanical properties and excellent dynamic behavior. This is because dynamic covalent bonds primarily maintain macroscopic mechanical properties, while weak non-covalent bonds as sacrificial bonds ensure dynamic behavior. On the other side, the complement of each other of different dynamic bonds also provides different healing pathways activated by temperature, sunlight, UV radiation, pH variation, or magnetic field, and enhances their resistance to harsh circumstances. Remarkably, the introduction of crystallization or orientation technology into dynamic crosslinked silicone materials is also an effective method to improve comprehensive properties, because the crystallization or orientation of polymer chain can compensate for the decrease of mechanical properties to a certain extent.[214-216]

Besides, most dynamic bonds either non-covalent bond or covalent bonds have much lower bond strength compared to inherent Si-O bond and Si-C bonds, so the existence of dynamic bonds will deteriorate excellent properties of silicone materials like high-temperature resistance, aging resistance, and weather resistance. Therefore, future intensive studies should also focus on the influence of dynamic bonds on the thermodynamics and dynamics of dynamic silicone materials.[196,217,218] Hence, developing novel dynamic structures which not only can maintain the property and stability under service but also can be effectively activated by external stimuli, should be a fundamental solution.

Furthermore, it is still worth noting that the preparation processes of most dynamic crosslinked silicone materials are quite harsh and complicated, even a mass of organic solvents is required, which also impedes large-scale production and application. The facile and simple preparation methods of dynamic crosslinked silicones based on commercially available and sustainable raw materials should be explored to meet the needs of the industry.

In addition, compositing dynamic crosslinked silicone materials with different nanofillers not only can enhance mechanical properties but also endow new functions. What needs to note is that the grating of dynamic bonds on the surface of nanofillers can improve dynamic behavior and mechanical strength, but a massive overdose of nanofillers may still deteriorate their dynamic nature. Moreover, the rapid manufacturing of dynamic crosslinked silicone materials by 3D printing technology will make them new vitality in custom-made sensors, flexible devices, *etc*.

## Acknowledgments

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 52033011, 52273104), and Guangdong Basic and Applied Basic Research Foundation (No. 2022A1515011972).

## Conflict of Interest

There is no conflict of interest.

## Supporting Information

Not applicable.

## References

[1] M. P. Wolf, G. B. Salieb-Beugelaar, P. Hunziker, PDMS with designer functionalities-properties, modifications strategies, and applications, *Progress in Polymer Science,* 2018, **83**, 97-134, doi: 10.1016/j.progpolymsci.201806001.

[2] Y. B. Guo, Y. L. Cao, Z. X. Chen, R. Li, W. Gong, W. F. Yang, Q. H. Zhang, H. Z. Wang, Fluorinated metal-organic framework as bifunctional filler toward highly improving output performance of triboelectric nanogenerators, *Nano Energy,* 2020, **70**, 104517, doi: 10.1016/j.nanoen.2020.104517.

[3] W. M. Reese, P. Burch, A. B. Korpusik, S. E. Liu, P. Loskill, P. B. Messersmith, K. E. Healy, Facile macrocyclic polyphenol barrier coatings for PDMS microfluidic devices, *Advanced Functional Materials*, 2020, **30**, 2001274, doi: 10.1002/adfm.202001274.

[4] P. Hu, Q. Xie, C. Ma, G. Zhang, Fouling resistant silicone coating with self-healing induced by metal coordination, *Chemical Engineering Journal*, 2021, **406**, 126870, doi: 10.1016/j.cej.2020.126870.

[5] A. Vitale, S. Touzeau, F. Sun, R. Bongiovanni, Compositional gradients in siloxane copolymers by photocontrolled surface segregation, *Macromolecules*, 2018, **51**, 4023-4031, doi: 10.1021/acs.macromol.8b00339.

[6] E. J. Markvicka, M. D. Bartlett, X. N. Huang, C. Majidi, An autonomously electrically self-healing liquid metal-elastomer composite for robust soft-matter robotics and electronics, *Nature Materials*, 2018, **17**, 618-625, doi: 10.1038/s41563-018-0084-7.

[7] W. Q. He, P. Liu, J. Q. Zhang, X. Yao, Emerging applications of bioinspired slippery surfaces in biomedical fields, *Chemistry – A European Journal*, 2018, **24**, 14864-14877, doi: 10.1002/chem.201801368.

[8] D. Godwinraj, S. C. George, Recent advancement in TENG polymer structures and energy efficient charge control circuits, *Advanced Industrial and Engineering Polymer Research*, 2021, **4**, 1-8, doi: 10.1016/j.aiepr.2020.12.003.

[9] S. Xia, Y. K. Chen, J. F. Tian, J. F. Shi, C. Z. Geng, H. W. Zou, M. Liang, Z. B. Li, Superior low-temperature reversible adhesion based on bio-inspired microfibrillar adhesives fabricated by phenyl containing polydimethylsiloxane elastomers, *Advanced Functional Materials,* 2021, **31**, 2101143, doi: 10.1002/adfm.202101143.

[10] G. Z. Li, G. G. Wang, Y. W. Cai, N. Sun, F. Li, H. L. Zhou, H. X. Zhao, X. N. Zhang, J. C. Han, Y. Yang, A high-performance transparent and flexible triboelectric nanogenerator based on hydrophobic composite films, *Nano Energy,* 2020, **75**, 104918, doi: 10.1016/j.nanoen.2020.104918.

[11] R. Bui, M. A. Brook, Catalyst free silicone sealants that cure underwater, *Advanced Functional Materials*, 2020, **30**, 2000737, doi: 10.1002/adfm.202000737.

[12] H. Sun, X. Liu, S. Liu, B. Yu, N. Ning, M. Tian, L. Zhang, Silicone dielectric elastomer with improved actuated strain at low electric field and high self-healing efficiency by constructing supramolecular network, *Chemical Engineering Journal*, 2020, **384**, 123242, doi: 10.1016/j.cej.2019.123242.

[13] D. Wang, X. Zhou, R. F. Song, C. Q. Fang, Z. Wang, C. X. Wang, Y. W. Huang, Freestanding silver/polypyrrole composite film for multifunctional sensor with biomimetic micropattern for physiological signals monitoring, *Chemistry – A European Journal*, 2021, **404**, 126940, doi: 10.1016/j.cej.2020.126940.

[14] X. T. Li, X. M. Zhu, J. Dong, X. Zhao, Q. H. Zhang, Preparation of low-dielectric permittivity polyimide resins with high surface activity from chemically bonded hyperbranched polysiloxane, *Chinese Journal of Polymer Science*, 2021, **39**, 1200-1210, doi: 10.1007/s10118-021-2585-0.

[15] B. Weng, D. Shang, L. J. Jin, X. Y. Sun, J. Z. Hang, Preparation and performance of silicone-based amphiphilic antifouling coating with fluorine and PEG moieties, *Acta Polymerica Sinica,* 2017, **6**, 990-998, doi: 10.11777/j.issn1000-3304.201716330.

[16] Z. Liu, P. Hong, H. P. Xiang, Z. Y. Huang, Q. H. Luo, X. J. Yang, X. X. Liu, Preparation and self-healability of silicone elastomer with dual-crosslinked network, *Acta Polymerica Sinica,* 2020, **51**, 656-669, doi: 10.11777/j.issn1000-3304.201919207.

[17] Y. You, M. Z. Rong, M. Q. Zhang, Reversibly interlocked polymer networks: design, preparation and applications, *Acta Polymerica Sinica,* 2023, **54**, 14-36, doi: 10.11777/j.issn1000-

3304.202222196.

[18] M. Q. Zhang, M. Z. Rong, Extrinsic and intrinsic approaches to self-healing polymers and polymer composites, New Jersey: John Wiley & Sons, 2022, 1-63.

[19] Z. P. Zhang, M. Z. Rong, M. Q Zhang, Polymer engineering based on reversible covalent chemistry: a promising innovative pathway towards new materials and new functionalities, *Progress in Polymer Science*, 2018, **80**, 39-93, doi: 10.1016/j.progpolymsci.201803002.

[20] Z. P. Zhang, M. Z. Rong, M. Q. Zhang, Research progress of processing of crosslinked polymers based on reversible covalent chemistry: a new challenge to the development of polymer engineering, *Acta Polymerica Sinica*, 2018, **7**, 829-853, doi: 10.11777/j.issn1000-3304.201818060.

[21] R. Ikura, J. Park, M. Osaki, H. Yamaguchi, A. Harada, Y. Takashima, Design of self-healing and self-restoring materials utilizing reversible and movable crosslinks, *NPG Asia Mater.*, 2022, **14,** 10-26, doi: 10.1038/s41427-021-00349-1.

[22] Z. M. Zhang, J. Zhao, X. Z. Yan, Synergistic covalent and supramolecular polymers, *Acta Polymerica Sinica*, 2022, **53**, 691-706, doi: 10.11777/j.issn1000-3304.2022.22049.

[23] X. W. Huang, X. F. Wang, C. Y. Shi, Y. Liu, Y. Y. Wei, Research on synthesis and self-healing properties of interpenetrating network hydrogels based on reversible covalent and reversible non-covalent bonds, *Journal of Polymer Research*, 2021, **28**, 1-13, doi: 10.1007/s10965-020-02155-9.

[24] J. S. Chen, Q. Y. Peng, T. Thundat, H. B. Zeng, Stretchable, injectable, and self-healing conductive hydrogel enabled by multiple hydrogen bonding toward wearable electronics, *Chemistry of Materials*, 2019, **31**, 4553-4563, doi: 10.1021/acs.chemmater.9b01239.

[25] W. P. Zhao, B. Dong, H. Liu, Y. M. Hu, X. Q. Zhang, Living coordination-insertion copolymerization of 1-hexene and ligated α-olefins using an α-diimine nickel catalyst and preparation of metal-ligand coordination crosslinked polymers, *Polymer Chemistry*, 2020, **11**, 2492-2501, doi: 10.1039/D0PY00224K.

[26] J. Ma, T. Zhou, T. Ma, Z. H. Yang, J. H. Yang, Q. Guo, W. Liu, Q. F. Yang, W. S. Liu, T. L. Yang, Construction of transition metal coordination polymers with free carboxyl groups and turn-on fluorescent detection for α, β-diamine, *Crystal Growth & Design*, 2020, **21**, 383-395, doi: 10.1021/acs.cgd.0c01233.

[27] H. R. Gong, Y. J. Gao, S. J. Jiang, F. Sun, Photocured materials with self-healing function through ionic interactions for flexible electronics, *ACS Applied Materials & Interfaces*, 2018, **10**, 26694-26704, doi: 10.1021/acsami.8b08884.

[28] Z. Y. Wang, H. B. Liang, H. T. Yang, L. Xiong, J. P. Zhou, S. M. Huang, C. H. Zhao, J. Zhong, X. F. Fan, UV-curable self-healing polyurethane coating based on thiol-ene and Diels-Alder double click reactions, *Progress in Organic Coatings*, 2019, **137**, 105282, doi: 10.1016/j.porgcoat.2019.105282.

[29] A. R. de Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez, I. Odriozola, Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites, *Materials Horizons*, 2016, **3**, 241-247, doi: 10.1039/D0MH90047H.

[30] Y. J. Huang, Z. Shi, H. L. Wang, J. R. Wang, Z. G. Xue, Shape-memory and self-healing polyurethane-based solid polymer electrolytes constructed from polycaprolactone segment and disulfide metathesis, *Energy Storage Materials*, 2022, **51**, 1-10, doi: 10.1016/j.ensm.202206021.

[31] H. Memon, H. Y. Liu, M. A. Rashid, L. Chen, Q. R. Jiang, L. Y. Zhang, Y. Wei, W. S. Liu, Y. P. Qiu, Vanillin-based epoxy vitrimer with high performance and closed-loop recyclability, *Macromolecules*, 2020, **53**, 621-630, doi: 10.1021/acs.macromol.9b02006.

[32] Y. H. Zhang, L. Zhang, G. T. Yang, Y. L. Yao, X. Wei, T. C. Pan, J. T. Wu, M. F. Tian, P. G. Yin, Recent advances in recyclable thermosets and thermoset composites based on covalent adaptable networks, *Journal of Materials Science & Technology*, 2021, **92**, 75-87, doi: 10.1016/j.jmst.202103043.

[33] S. Utrera-Barrios, R. Verdejo, M. A. López-Manchado, M. Hernández Santana, Evolution of self-healing elastomers, from extrinsic to combined intrinsic mechanisms: a review, *Materials Horizons*, 2020, **7**, 2882-2902, doi: 10.1039/D0MH00535E.

[34] J. Ye, Z. Q. Lin, W. J. Li, H. P. Xiang, M. Z. Rong, M. Q. Zhang, Fabrication strategies to self-healing silicone materials, *Progress in Chemistry*, 2022, 220543, doi: 10.7536/PC220543.

[35] X. Cui, Y. G. Yan, J. Huang, X. Y. Qiu, P. P. Zhang, Y. Chen, Z. F. Hu, X. B. Liang, A substrate-independent isocyanate-modified polydimethylsiloxane coating harvesting mechanical durability, self-healing ability and low surface energy with anti-corrosion/biofouling potential, *Applied Surface Science*, 2022, **579**, 152186, doi: 10.1016/j.apsusc.2021.152186.

[36] C. Chen, H. T. Yu, Y. Y. Feng, W. Feng, Polymer composite material with both thermal conduction and self-healing functions, *Acta Polymerica Sinica*, 2021, **52**, 272-280, doi: 10.11777/j.issn1000-3304.2020.20229.

[37] M. J. Liu, P. Liu, G. Lu, Z. T. Xu, X. Yao, Multiphase-assembly of siloxane oligomers with improved mechanical strength and water-enhanced healing, *Angewandte Chemie International Edition*, 2018, **57**, 11242-11246, doi: 10.1002/ange.201805206.

[38] E. Ogliani, L. Yu, I. Javakhishvili, A. L. Skov, A thermo-reversible silicone elastomer with remotely controlled self-healing, *RSC Advances*, 2018, **8**, 8285-8291, doi: 10.1039/C7RA13686B.

[39] J. W. Sun, C. Liu, J. Z. Duan, J. Liu, X. C. Dong, Y. M. Zhang, N. Wang, J. Wang, B. R. Hou, Facile fabrication of self-healing silicone-based poly(urea-thiourea)/tannic acid composite for anti-biofouling, *Journal of Materials Science & Technology*, 2022, **124**, 1-13, doi: 10.1016/j.jmst.202201026.

[40] K. F. Zhao, C. Lv, J. P. Zheng, A robust mechanochromic self-healing poly(dimethylsiloxane) elastomer, *Science China Technological Sciences*, 2020, **63**, 740-747, doi: 10.1007/s11431-019-1479-1.

[41] C. Liu, C. F. Ma, Q. Y. Xie, G. Z. Zhang, Self-repairing silicone coatings for marine anti-biofouling, *Journal of Materials Chemistry A*, 2017, **5**, 15855-15861, doi: 10.1039/C7TA05241C.

[42] J. Q. Xiong, G. Thangavel, J. X. Wang, X. R. Zhou, P. S. Lee,

Self-healable sticky porous elastomer for gas-solid interacted power generation, *Science Advances,* 2020, **6**, 4246, doi: 10.1126/sciadv.abb4246.

[43] X. Y. Jia, J. F. Mei, J. C. Lai, C. H. Li, X. Z. You, A highly stretchable polymer that can be thermally healed at mild temperature, *Macromolecular Rapid Communications,* 2016, **37**, 952, doi: 10.1002/marc.201600142.

[44] J. C. Lai, L. Li, D. P. Wang, M. H. Zhang, S. R. Mo, X. Wang, K. W. Zeng, C. H. Li, Q. Jiang, X. Z. You, J. L. Zuo, A rigid and healable polymer cross-linked by weak but abundant Zn(II)-carboxylate interactions, *Nature Communications,* 2018, **9**, 2725, doi: 10.1038/s41467-018-05285-3.

[45] C. H. Li, C. Wang, C. Keplinger, J. L. Zuo, L. H. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X. Z. You, Z. N. Bao, A highly stretchable autonomous self-healing elastomer, *Nature Communications,* 2016, **8**, 619-625, doi: 10.1038/nchem.2492.

[46] J. C. Lai, X.Y. Jia, D. P. Wang, Y. B. Deng, P. Zheng, C. H. Li, J. L. Zuo, Z. N. Bao, Thermodynamically stable whilst kinetically labile coordination bonds lead to strong and tough self-healing polymers, *Nature Communications,* 2019, **10**, 1164, doi: 10.1038/s41467-019-09130-z.

[47] L. Bai, P. Y. Qv, J. P. Zheng, Colorless, transparent, and healable silicone elastomers by introducing Zn(II)-carboxylate interactions via aza-Michael reaction, *Journal of Materials Science,* 2020, **55**, 14045-14057, doi: 10.1007/s10853-020-04997-6.

[48] Y. L. Rao, A. Chortos, R. Pfattner, F. Lissel, Y. C. Chiu, V. Feig, J. Xu, T. Kurosawa, X. Gu, C. Wang, M. Q. He, J. W. Chun, Z. N. Bao, Stretchable self-healing polymeric dielectrics cross-linked through metal-ligand coordination, *Journal of the American Chemical Society,* 2016, **138**, 6020-6027, doi: 10.1021/jacs.6b02428.

[49] Z. Liu, P. Hong, Z. Y. Huang, T. Zhang, R. J. Xu, L. J. Chen, H. P. Xiang, X. X. Liu, Self-healing, reprocessing and 3D printing of transparent and hydrolysis-resistance silicone elastomers, *Chemical Engineering Journal,* 2020, **387**, 124142, doi: 10.1016/j.cej.2020.124142.

[50] J. H. Mo, X. Y. Chen, Y. B. Fu, R. Li, Y. L. Lin, A. Q. Zhang, A solvent-free, transparent, self-healing polysiloxanes elastomer based on unsaturated carboxyl-amino ionic hydrogen bonds, *Polymer,* 2021, **228**, 123903, doi: 10.1016/j.polymer.2021.123903.

[51] J. Shi, N. Zhao, D. Yan, J. Song, W. Fu, Z. J. Li, Design of a mechanically strong and highly stretchable thermoplastic silicone elastomer based on coulombic interactions, *Journal of Materials Chemistry A,* 2020, **8**, 5943-5951, doi: 10.1039/D0TA01593H.

[52] H. B. Sun, X. Y. Liu, S. T. Liu, B. Yu, N. Y. Ning, M. Tian, L. Q. Zhang, A supramolecular silicone dielectric elastomer with a high dielectric constant and fast and highly efficient self-healing under mild conditions, *Journal of Materials Chemistry A,* 2020, **8**, 23330-23343, doi: 10.1039/D0TA06577C.

[53] Y. F. Shao, Z. X. Li, T. W. Yu, X. X. Wang, H. N. Cui, K. Yang, Y. Y. Cui, Self-healing strain sensor based on silicone elastomer for human motion detection, *Composites Science and Technology,* 2022, **218**, 109208, doi: 10.1016/j.compscitech.2021.109208.

[54] S. Yu, H. L. Zuo, X. W. Xu, N. Y. Ning, B. Yu, L. Q. Zhang, M. Tian, Self-healable silicone elastomer based on the synergistic effect of the coordination and ionic bonds, *ACS Applied Polymer Materials,* 2021, **3**, 2667-2677, doi: 10.1021/acsapm.1c00236.

[55] J. Zhao, R. Xu, G. X. Luo, J. Wu, H. S. Xia, A self-healing, re-moldable and biocompatible crosslinked polysiloxane elastomer, *Journal of Materials Chemistry B,* 2016, **4**, 982-989, doi: 10.1039/C5TB02036K.

[56] J. Wang, C. Lv, Z. X. Li, J. P. Zheng, Facile preparation of polydimethylsiloxane elastomer with self-healing property and remoldability based on Diels-Alder Chemistry, *Macromolecular Materials and Engineering,* 2018, **303**, 1800089, doi: 10.1002/mame.201800089.

[57] L. W. Zhao, B. Jiang, Y. D. Huang, Self-healable polysiloxane/graphene nanocomposite and its application in pressure sensor, *Journal of Materials Science,* 2019, **54**, 5472-5483, doi: 10.1007/s10853-018-03233-6.

[58] B. L. Zhang, P. Zhang, H. Z. Zhang, C. Yan, Z. J. Zheng, B. Wu, Y. Yu, A transparent, highly stretchable, autonomous self-healing poly(dimethyl siloxane) elastomer, *Macromolecular Rapid Communications,* 2017, **38**, 1700110, doi: 10.1002/marc.201700110.

[59] X. Y. Lei, Y. W. Huang, S. Liang, X. L. Zhao, L. L. Liu, Preparation of highly transparent, room-temperature self-healing and recyclable silicon elastomers based on dynamic imine bond and their ion responsive properties, *Materials Letters,* 2020, **268**, 127598, doi: 10.1016/j.matlet.2020.127598.

[60] Z. B. Feng, B. Yu, J. Hu, H. L. Zuo, J. P. Li, H. B. Sun, N. Y. Ning, M. Tian, L. Q. Zhang, Multifunctional vitrimer-like polydimethylsiloxane (PDMS): recyclable, self-healable, and water-driven malleable covalent networks based on dynamic imine bond, *Industrial & Engineering Chemistry Research,* 2019, **58**, 1212-1221, doi: 10.1021/acs.iecr.8b05309.

[61] X. W. Xu, X. Y. Hao, J. Hu, W. S. Gao, N. Y. Ning, B. Yu, L. Q. Zhang, M. Tian, Recyclable silicone elastic light-triggered actuator with a reconfigurable Janus structure and self-healable performance, *Polymer Chemistry,* 2022, **13**, 829-837, doi: 10.1039/D1PY01632F.

[62] H. P. Xiang, M. Z. Rong, M. Q. Zhang, A facile method for imparting sunlight driven catalyst-free self-healability and recyclability to commercial silicone elastomer, *Polymer,* 2017, **108**, 339, doi: 10.1016/j.polymer.201612006.

[63] X. Wu, J. Li, G. Li, L. Ling, G. Zhang, R. Sun, C. P. Wong, Heat-triggered poly(siloxane-urethane)s based on disulfide bonds for self-healing application, *Journal of Applied Polymer Science,* 2018, **135**, 46532, doi: 10.1002/app.46532.

[64] L. W. Zhao, Y. Yin, B. Jiang, Z. H. Guo, C. Y. Qu, Y. D. Huang, Fast room-temperature self-healing siloxane elastomer for healable stretchable electronics, *Journal of Colloid and Interface Science,* 2020, **573**, 105-114, doi: 10.1016/j.jcis.202003125.

[65] Y. H. Huang, J. P. Yan, D. X. Wang, S. Y. Feng, C. J. Zhou, Construction of self-healing disulfide-linked silicone elastomers by thiol oxidation coupling reaction, *Polymers,* 2021, **13**, 3729,

doi: 10.3390/polym13213729.

[66] W. J. Sun, J. M. Luo, L. Zhang, Y. Chen, P. X. Li, Y. T. Zheng, Y. H. Cheng, Insulating silicones based on dynamic hindered urea bonds with high dielectric healability and recyclability, *ACS Applied Polymer Materials*, 2021, **3**, 5622-5631, doi: 10.1021/acsapm.1c00948.

[67] Z. H. Wang, S. Gangarapu, J. Escorihuela, G. X. Fei, H. Zuilhof, H. S. Xia, Dynamic covalent urea bonds and their potential for development of self-healing polymer materials, *Journal of Materials Chemistry A*, 2019, **7**, 15933-15943, doi: 10.1039/C9TA02054C.

[68] Y. J. Zuo, Z. M. Gou, C. Q. Zhang, S. Y. Feng, Polysiloxane-based autonomic self-healing elastomers obtained through dynamic boronic ester bonds prepared by thiol-ene "click" chemistry, *Macromolecular Rapid Communications*, 2016, **37**, 1052, doi: 10.1002/marc.201600155.

[69] J. C. Lai, J. F. Mei, X. Y. Jia, C. H. Li, X. Z. You, Z. Bao, A stiff and healable polymer based on dynamic-covalent boroxine bonds, *Advanced Materials*, 2016, **28**, 1602332, doi: 10.1002/adma.201602332.

[70] Z. Liu, D. S. Xiao, G. C. Liu, H. P. Xiang, M. Z. Rong, M. Q. Zhang, Self-healing and reprocessing of transparent UV-cured polysiloxane elastomer, *Progress in Organic Coatings*, 2021, **159**, 106450, doi: 10.1016/j.porgcoat.2021.106450.

[71] J. Ma, L. E. Porath, M. F. Haque, S. Sett, K. F. Rabbi, S. Nam, N. Miljkovic, C. M. Evans, Ultra-thin self-healing vitrimer coatings for durablehydrophobicity, *Nature Communications*, 2021, **12**, 5210, doi: 10.1038/s41467-021-25508-4.

[72] P. Zheng, T. J. McCarthy, A surprise from 1954: siloxane equilibration is a simple, robust, and obvious polymer self-Healing mechanism, *Journal of the American Chemical Society*, 2012, **134**, 2024-2027, doi: 10.1021/ja2113257.

[73] X. Li, R. Yu, T. Zhao, Y. Zhang, X. Yang, X. Zhao, W. Huang, A self-healing polysiloxane elastomer based on siloxane equilibration synthesized through amino-ene michael addition reaction, *European Polymer Journal*, 2018, **108**, 399-405, doi: 10.1016/j.eurpolymj.2018.09021.

[74] L. Bai, X. X.Yan, B. W. Feng, J. P. Zheng, Mechanically strong, healable, and reprocessable conductive carbon black/silicone elastomer nanocomposites based on dynamic imine bonds and sacrificial coordination bonds, *Composites Part B: Engineering*, 2021, **223**, 109123, doi: 10.1016/j.compositesb.2021.109123.

[75] Y. X. Shan, S. Liang, X. K. Mao, J. Lu, L. L. Liu, Y. W. Huang, J. X. Yang, Stretchable dual cross-linked silicon elastomer with a superhydrophobic surface and fast triple self-healing ability at room temperature, *Soft Matter.*, 2021, **17**, 4643-4652, doi: 10.1039/D0SM02175J.

[76] G. M. Chen, Z. Y. Sun, Y. M. Wang, J. Y. Zheng, S. F. Wen, J. W. Zhang, L. Wang, J. Hou, G. G. Lin, Z. F. Yue, Designed preparation of silicone protective materials with controlled self-healing and toughness properties, *Progress in Organic Coatings*, 2020, **140**, 105483, doi: 10.1016/j.porgcoat.2019.105483.

[77] P. J. Mo, Z. Y. Hu, Z. J. Mo, X. Chen, J. Yu, M. S. Selim, R. Sun, J. B. Xu, X. L. Zeng, Z. F. Hao, Fast self-healing and self-cleaning anticorrosion coating based on dynamic reversible imine and multiple hydrogen bonds, *ACS Applied Polymer Materials*, 2022, **4**, 4709-4718, doi: 10.1021/acsapm.2c00294.

[78] Y. H. Zhang, L. Yuan, G. Z. Liang, A. J. Gu, Simultaneously achieving superior foldability, mechanical strength and toughness for transparent healable polysiloxane films through building hierarchical crosslinked networks and dual dynamic bonds, *Journal of Materials Chemistry A*, 2018, **6**, 23425-23434, doi: 10.1039/C8TA07580H.

[79] H. S. Guo, Y. Han, W. Q. Zhao, J. Yang, L. Zhang, Universally autonomous self-healing elastomer with high stretchability, *Nature Communications*, 2020, **11**, 2037, doi: 10.1038/s41467-020-15949-8.

[80] X. R. Shi, K. Y. Zhang, L. W. Zhao, B. Jiang, Y. D. Huang, Robust, self-healable siloxane elastomers constructed by multiple dynamic bonds for stretchable electronics and microsystems, *Industrial & Engineering Chemistry Research*, 2021, **60**, 2154-2162, doi: 10.1021/acs.iecr.0c05238.

[81] Z. Wang, Y. T. Liu, D. J. Zhang, C. H. Gao, Y. M. Wu, Mussel-inspired self-healing PDMS/AgNPs conductive elastomer with tunable mechanical properties and efficient antibacterial performances for wearable sensor, *Composites Part B: Engineering*, 2021, **224**, 109213, doi: 10.1016/j.compositesb.2021.109213.

[82] H. T. Yu, Y. Y. Feng, L. Gao, C. Chen, Z. X. Zhang, W. Feng, Self-healing high strength and thermal conductivity of 3D graphene/PDMS composites by the optimization of multiple molecular interactions, *Macromolecules*, 2020, **53**, 7161-7170, doi: 10.1021/acs.macromol.9b02544.

[83] L. Bai, J. P. Zheng, Robust, reprocessable and shape-memory vinylogous urethane vitrimer composites enhanced by sacrificial and self-catalysis Zn(II)-ligand bonds, *Composites Science and Technology*, 2020, **190**, 108062, doi: 10.1016/j.compscitech.2020.108062.

[84] D. D. Zhang, Y. B. Ruan, B. Q. Zhang, X. Qiao, G. H. Deng, A self-healing PDMS elastomer based on acylhydrazone groups and the role of hydrogen bonds, *Polymer*, 2017, **120**, 189, doi: 10.1016/j.polymer.2017.05060.

[85] Z. Q. Lin, H. Y. Deng, Y. Hou, X. X. Liu, R. J. Xu, H. P. Xiang, Z. Q. Peng, M. Z. Rong, M. Q. Zhang, Dual-crosslinking side chains with an asymmetric chain structure: a facile pathway to a robust, self-healable, and re-dissolvable polysiloxane elastomer for recyclable flexible devices, *J. Mater. Chem. A*, 2022, **10**, 11019-11029, doi: 10.1039/D2TA01535H.

[86] S. P. Dai, M. Li, H. Yan, H. Zhu, H. W. Hu, Y. X. Zhang, G. G. Cheng, N. Y. Yuan, J. N. Ding, Self-healing silicone elastomer with stable and high adhesion in harsh environments, *Langmuir*, 2021, **37**, 13696-13702, doi: 10.1021/acs.langmuir.1c02356.

[87] M. Q. Zhang, Self-healing polymeric materials: on a winding road to success, *Chinese Journal of Polymer Science*, 2022, **40**, 1315-1316, doi: 10.1007/s10118-022-2870-6.

[88] Y. C. Yuan, T. Yin, M. Z. Rong, M. Q. Zhang, Self-healing in polymers and polymer composites. concepts, realization and outlook: a review, *Express Polymer Letters*, 2008, **2**, 238-250, doi: 10.3144/expresspolymlett.2008.29.

[89] M. Q. Zhang, M. Z. Rong, Self-healing polymer materials towards strength recovery for structural applications, *Acta Polymerica Sinica,* 2012, **11**, 1183-1199, doi: 10.3724/SP.J.1105.2012.12171.

[90] D. Y. Zhu, M. Z. Rong, M. Q. Zhang, Self-healing polymeric materials based on microencapsulated healing agents: from design to preparation, *Progress in Polymer Science,* 2015, **49**, 175-220, doi: 10.1016/j.progpolymsci.2015.07002.

[91] J. Xu, L. Zhu, Y. Nie, Y. Li, S. Wei, X. Chen, W. P. Zhao, S. Yan, Advances and challenges of self-healing elastomers: a mini review, *Materials,* 2022, **15**, 5993, doi: 10.3390/ma15175993.

[92] N. N. F. N. M. N. Kahar, A. F. Osman, E. Alosime, N. Arsat, N. A. M. Azman, A. Syamsir, Z. Itam, Z. A. A. Hamid, The versatility of polymeric materials as self-healing agents for various types of applications: a review, *Polymers,* 2021, **13**, 1194, doi: 10.3390/polym13081194.

[93] S. Kadam, S. Chavan, N. J. Kanu. An insight into advance self-healing composites, *Materials Research Express,* 2021, **8**, 052001, doi: 10.1088/2053-1591/abfba5.

[94] E. K. Kumar, S. S. Patel, V. Kumar, S. K. Panda, S. R. Mahmoud, M. Balubaid, State of art review on applications and mechanism of self-healing materials and structure, *Archives of Computational Methods in Engineering,* 2022, 1-15, doi: 10.1007/s11831-022-09827-3.

[95] Z. H. Wang, X. L. Lu, S. J. Sun, C. J. Yu, H. S. Xia, Preparation, characterization and properties of intrinsic self-healing elastomers, *Journal of Materials Chemistry B,* 2019, **7**, 4876-4926. Doi: 10.1039/C9TB00831D.

[96] S. R. Madara, N. S. Sarath Raj, C. P. Selvan, Review of research and developments in self-healing composite materials, *IOP Conference Series: Materials Science and Engineering,* 2018, **346**, 012011, doi: 10.1088/1757-899X/346/1/012011.

[97] L. Cheng, D. J. Yu, J. J. You, T. Long, S. S. Chen, C. J. Zhou, Silicone self-healing materials, *Prog. Chem.,* 2018, **30**, 1852, doi: 10.7536/PC180312.

[98] Z. H. Wang, L. Scheres, H. S. Xia, H. Zuilhof, Developments and challenges in self-healing antifouling materials, *Adv. Funct. Mater.,* 2020, **30**, 1908098, doi: 10.1002/adfm.201908098.

[99] F. Z. Kamand, B. Mehmood, R. Ghunem, M. K. Hassan, A. EI-Hag, L. AI-Sulaiti, A. Abdala, Self-healing silicones for outdoor high voltage insulation: mechanism, applications and measurements, *Energies*, 2022, **15**, 1677, doi: 10.3390/en15051677.

[100] L. Wang, L. Li, S. Feng, Research progress of silicone supramolecular materials, *Chemical Journal of Chinese Universities-Chinese*, 2021, **42**, 2111, doi: 10.7503/CJCU20210093.

[101] M. Cazacu, M. Dascalu, G. T. Stiubianu, A. Bele, C. Tugui, C. Racles, From passive to emerging smart silicones, *Reviews in Chemical Engineering*, 2022, doi: 10.1515/revce-2021-0089.

[102] B. Yi, S. Wang, C. S. Hou, X. Huang, J. X. Cui, X. Yao, Dynamic siloxane materials: from molecular engineering to emerging applications, *Chemical Engineering Journal*, 2021, **405**, 127023, doi: 0.1016/j.cej.2020.127023.

[103] A. D. O'Donnell, S. Salimi, L. R. Hart, T. S. Babra, B. W. Greenland, W. Hayes, Applications of supramolecular polymer networks, *Reviews in Chemical Engineering*, 2022, **172**, 105209, doi: 10.1016/j.reactfunctpolym.2022.105209.

[104] T. D. Clemons, S. I. Stupp, Design of materials with supramolecular polymers, *Progress in Polymer Science*, 2020, **111**, 101310, doi: 10.1016/j.progpolymsci.2020.101310.

[105] Z. L. Xie, B. L. Hu, R. W. Li, Q. C. Zhang, Hydrogen bonding in self-healing elastomers, *ACS Omega,* 2021, **6**, 9319-9333, doi: 10.1021/acsomega.1c00462.

[106] K. Buaksuntear, P. Limarun, S. Suethao, W. Smitthipong, Non-covalent interaction on the self-healing of mechanical properties in supramolecular polymers, *International Journal of Molecular Sciences,* 2022, **23**, 6902, doi: 10.3390/ijms23136902.

[107] C. J. Fan, Z. C. Huang, B. Li, X. X. Wen, E. Zheng, K. K. Yang, Y. Z. Wang, A robust self-healing polyurethane elastomer: from H-bonds and stacking interactions to well-defined microphase morphology, *International Journal of Molecular Sciences.,* 2019, **62**, 1188-1198, doi: 10.1007/s40843-019-9422-7.

[108] X. B. Lin, Q. Y. Xie, C. F. Ma, G. Z. Zhang, Self-healing, highly elastic and amphiphilic silicone-based polyurethane for antifouling coatings, *Journal of Materials Chemistry B*, 2021, **9**, 1384-1394, doi: 10.1039/D0TB02465A.

[109] W. X. Liu, D. Liu, Y. Xiao, M. Zou, L. Y. Shi, K. K. Yang, Y. Z. Wang, Healable, recyclable, and high-stretchable polydimethylsiloxane elastomer based on synergistic effects of multiple supramolecular interactions, *Macromol. Mater. Eng.*, 2022, **307**, 2200310, doi: 10.1002/mame.202200310.

[110] D. Wołosz, P. G. Parzuchowski, Biobased non-isocyanate poly(carbonate-urethane)s of exceptional strength and flexibility, *Polymer,* 2022, **254**, 125026, doi: 10.1016/j.polymer.2022.125026

[111] Y. T. Liu, K. M. Zhang, J. W. Sun, J. G. Yuan, Z. Y. Yang, C. H. Gao, Y. M. Wu, A type of hydrogen bond cross-linked silicone rubber with the thermal-induced self-healing properties based on the nonisocyanate reaction, *Industrial & Engineering Chemistry Research,* 2019, **58**, 21452-21458, doi: 10.1021/acs.iecr.9b03953.

[112] R. L. Guo, L. X. Zhou, J. W. Lin, G. X. Chen, Z. Zhou, Q. F. Li, Self-healing, high-strength and antimicrobial polysiloxane based on amino acid hydrogen bond, *Macromolecular Rapid Communications.*, 2022, 2200657, doi: 10.1002/marc.202200657.

[113] Z. J. Zhang, H. F. Mei, Q. Wang, R. Li, G. Wang, H. Wei, X. Ouyang, Self-healing polyurethane elastomer based on 2-ureido-4 [1H]-pyrimidinone, *Materials Chemistry and Physics,* 2022, **285**, 126070, doi: 10.1016/j.matchemphys.2022.126070.

[114] W. L. Gao, R. Tang, M. H. Bai, H. Z. Yu, Y. H. Ruan, J. L. Zheng, Y. J. Chen, W. G. Weng, Dynamic covalent polymer networks with mechanical and mechanoresponsive properties reinforced by strong hydrogen bonding, *Polymer Chemistry,* 2022, **13**, 2173-2177, doi: 10.1039/d2py00179a.

[115] W. Y. Fu, H. F. Mei, Z. J. Zhang, Q. Wang, R. Li, S. S. Zhang, G. J. Wang, H, Wei, C. Y. Zhang, C. G. Lin, L. Wang, Self-healing and chemical resistance polyurethane elastomers based on 2-ureido-4 [1H] pyrimidinone, *Journal of Applied Polymer*

*Science,* 2022, **39**, 52931, doi: 10.1002/app.52931.

[116] Z. X. Deng, H. Wang, P. X. Ma, B. L. Guo, Self-healing conductive hydrogels: preparation, properties and applications, *Nanoscale,* 2020, **12,** 1224-1246, doi: 10.1039/C9NR09283H.

[117] X. W. Xu, J. F. R. Guyse, V. V. Jerca, R. Hoogenboom, Metal ion selective self-assembly of a ligand functionalized polymer into [1+1] macrocyclic and supramolecular polymer structures via metal-ligand coordination, *Macromolecular Rapid Communications.,* 2020, **41**, 1900305, doi: 10.1002/marc.201900305.

[118] Y. W. Chen, S. P. Dai, H. Zhu, H. W. Hu, N. Y. Yuan, J. N. Ding, Self-healing hydrogel sensors with multiple shape memory properties for human motion monitoring, *New Journal of Chemistry*, 2021, **45**, 314-320, doi: 10.1039/D0NJ04923A.

[119] M. Tian, H. L. Zuo, J. Wang, N. Y. Ning, B. Yu, L. Q. Zhang, A silicone elastomer with optimized and tunable mechanical strength and self-healing ability based on strong and weak coordination bonds, *Polymer Chemistry*, 2020, **11**, 4047-4057, doi: 10.1039/D0PY00434K.

[120] C. H. Li, J. L. Zuo, Self-healing polymers based on coordination bonds, *Advanced Materials*, 2020, **32**, 1903762, doi: 10.1002/adma.201903762.

[121] X. Y. Jia, J. F. Mei, J. C. Lai, C. H. Li, X. Z. You, A self-healing PDMS polymer with solvatochromic properties, *Chemical Communications,* 2015, **51**, 8928-8930, doi: 10.1039/C5CC01956G.

[122] H. Lu, S. Y. Feng, Supramolecular silicone elastomers with healable and hydrophobic properties crosslinked by “salt-forming vulcanization”, *Journal of Polymer Science Part A.,* 2017, **55**, 903-911, doi: 10.1002/pola.28450.

[123] J. F. Shi, N. Zhao, W. X. Fu, Z. B. Li, A stretchable and rapidly self-healable polysiloxane elastomer based on reversible ionic hydrogen bonds, *Reactive and Functional Polymers,* 2020, **33**, 433-440, doi: 10.14133/j.cnki.1008-9357.20200228002.

[124] Y. Miwa, K. Taira, J. Kurachi, T. Udagawa, S. Kutsumizu, A gas-plastic elastomer that quickly self-heals damage with the aid of $CO_2$ gas, *Nature Communications,* 2019, **10**, 1828, doi: 10.1038/s41467-019-09826-2.

[125] B. Yi, P. Liu, C. S. Hou, C. Y. Cao, J. Q. Zhang, H. Y. Sun, X. Yao, Dual-cross-linked supramolecular polysiloxanes for mechanically tunable, damage-healable and oil-repellent polymeric coatings, *ACS Applied Materials & Interfaces,* 2019, **11**, 47382-47389, doi: 10.1021/acsami.9b17199.

[126] C. Y. Cao, B. Yi, J. Q. Zhang, C. S. Hou, Z. Y. Wang, G. Lu, X. Huang, X. Yao, Sprayable superhydrophobic coating with high processibility and rapid damage-healing nature, *Chemical Engineering Journal,* 2020, **392**, 124834, doi: 10.1016/j.cej.2020.124834.

[127] Z. X. Li, J. K. Wang, R. F. Hu, C. Lv, J. P. Zheng, A highly ionic conductive, healable, and adhesive polysiloxane-supported ionogel, *Macromolecular Rapid Communications.,* 2019, **40**, 1800776, doi: 10.1002/marc.201800776.

[128] W. J. Wang, W. P. Wang, F. Wang, X. F. Xie, G. Yi, Z. B. Li, Tough and body-temperature self-healing polysiloxane elastomers through building double physical crosslinking network via competing non-covalent interactions, *Journal of Materials Chemistry A,* 2022, **10**, 23375-23383, doi: 10.1039/D2TA06593B.

[129] S. V. Wanasinghe, O. J. Dodo, D. Konkolewicz, Dynamic bonds: adaptable timescales for responsive materials, *Angewandte Chemie International Edition,* 2022, doi: 10.1002/ange.202206938.

[130] S. Y. Zheng, G. F. Liu, Polymeric emissive materials based on dynamic covalent bonds, *Molecules,* 2022, **27**, 6635, doi: 10.3390/molecules27196635.

[131] X. X. Chen, Q. Y. Zhong, S. J. Wang, Y. S. Wu, J. D. Tan, H. X. Lei, S. Y. Huang, Y. F. Zhang, Progress in dynamic covalent polymers, *Acta Polymerica Sinica,* 2019, **50**, 469-484, doi: 10.11777/j.issn1000-3304.2019.18277.

[132] E. Morici, N. T. Dintcheva, Recycling of thermoset materials and thermoset-based composites: challenge and opportunity, *Polymers,* 2022, **14**, 4153, doi: 10.3390/polym14194153.

[133] M. Yamaguchi, D. V. Anh, A. Sunatda, Self-healing composite materials, Amsterdam: Elsevier, 2020, 87-102.

[134] M. Q. Zhang, M. Z. Rong, T. Yin, Self-healing materials: fundamentals, design strategies, and applications, *Materials Today*, 2009, **12**, 47-71, doi: 10.1016/S1369-7021(09)70143-9.

[135] Y. L. Liu, T. W. Chuo, Self-healing polymers based on thermally reversible Diels-Alder chemistry, *Polymer Chemistry,* 2013, **4**, 2194-2205, doi: 10.1039/C2PY20957H.

[136] C. R. Ratwani, A. R. Kamali, A. M. Abdelkader, Self-healing by Diels-Alder cycloaddition in advanced functional polymers: a review, *Progress in Materials Science,* 2022, **131**, 101001, doi: 10.1016/j.pmatsci.2022.101001.

[137] Q. Yan, L. W. Zhao, Q. C. Cheng, T. Zhang, B. Jiang, Y. J. Song, Y. D. Huang, Self-healing polysiloxane elastomer based on integration of covalent and reversible networks, *Industrial & Engineering Chemistry Research,* 2019, **58**, 21504-21512, doi: 10.1021/acs.iecr.9b04355.

[138] J. Zhao, R. Xu, G. X. Luo, J. Wu, H. S. Xia, Self-healing poly (siloxane-urethane) elastomers with remoldability, shape memory and biocompatibility, *Polymer Chemistry,* 2016, **7**, 7278-7286, doi: 10.1039/C6PY01499B.

[139] Y. Y. Wei, X. Y. Ma, The self-healing cross-linked polyurethane by Diels-Alder polymerization, *Adv. Polym. Technol.,* 2018, **37**, 1987-1993, doi: 10.1002/adv.21857.

[140] N. Wen, T. T. Song, Z. H. Ji, D. W. Jiang, Z. J. Wu, Y. Wang, Z. H. Guo, Recent advancements in self-healing materials: mechanicals, performances and features, *Reactive and Functional Polymers,* 2021, **168**, 105041, doi: 10.1016/j.reactfunctpolym.2021.105041.

[141] S. O. Kim, C. J. Han, Y. Kim, K. S. Kim, D. U. Kim, C. R. Lee, J. W. Kim, Fabrication of a bending-insensitive in-plane strain sensor from a reversible cross-linker-functionalized silicone polymer, *ACS Applied Materials & Interfaces,* 2020, **12**, 6516-6524, doi: 10.1021/acsami.9b21721.

[142] M. E. Belowich, J. F. Stoddart, Dynamic imine chemistry, *Chemical Society Reviews*, 2012, **41**, 2003-2024, doi: 10.1039/C2CS15305J.

[143] Z. Q. Lei, P. Xie, M. Z. Rong, M. Q. Zhang, Catalyst-free dynamic exchange of aromatic Schiff base bonds and its application to self-healing and remolding of crosslinked polymers, *Journal of Materials Chemistry A,* 2015, **3**, 19662-19668, doi: 10.1039/C5TA05788D.

[144] X. L. Chen, P. Sun, H. M. Tian, X. M. Li, C. H. Wang, J. K. Duan, Y. S. Luo, S. Li, X. M. Chen, J. Y. Shao, Self-healing and stretchable conductor based on embedded liquid metal patterns within imprintable dynamic covalent elastomer, *Journal of Materials Chemistry C,* 2022, **10**, 1039-1047, doi: 10.1039/D1TC05087G.

[145] J. Wang, J. C. Lai, X. Y. Jia, Highly stretchable and stretch-induced fluorescence chromism self-healing materials based on boroxine and dynamic imine bond, *Journal of Materials Chemistry C,* 2022, **10**, 10895-10901, doi: 10.1039/D2TC01886A.

[146] N. Wang, L. Feng, X. D. Xu, S. Y. Feng, Dynamic covalent bond cross-linked luminescent silicone elastomer with self-healing and recyclable properties, *Macromolecular Rapid Communications,* 2022, **43**, 2100885, doi: 10.1002/marc.202100885.

[147] D. P. Wang, Z. H. Zhao, C. H. Li, J. L. Zuo, An ultrafast self-healing polydimethylsiloxane elastomer with persistent sealing performance, *Materials Chemistry Frontiers,* 2019, **3**, 1411-1421, doi: 10.1039/C9QM00115H.

[148] M. Kathan, P. Kovaříček, C. Jurissek, A. Senf, A. Dallmann, A. F. Thünemann, S. Hecht, Control of imine exchange kinetics with photoswitches to modulate self-healing in polysiloxane networks by light illumination, *Angewandte Chemie International Edition,* 2016, **55**, 13882-13886, doi: 10.1002/anie.201605311.

[149] C. Liu, H. Y. Gong, W. F. Liu, B. Lu, L. Ye, Separation and recycling of functional nanoparticles using reversible boronate ester and boroxine bonds, *Industrial & Engineering Chemistry Research,* 2019, **58**, 4695-4703, doi: 10.1021/acs.iecr.9b00253.

[150] O. R. Cromwell, J. Chung, Z. Guan, Malleable and self-healing covalent polymer networks through tunable dynamic boronic ester bonds, *Journal of the American Chemical Society,* 2015, **137**, 6492-6495, doi: 10.1021/jacs.5b03551.

[151] W. A. Ogden, Z. Guan, Recyclable, strong, and highly malleable thermosets based on boroxine networks, *Journal of the American Chemical Society,* 2018, **140**, 6217-6220, doi: 10.1021/jacs.8b03257.

[152] C. Chen, H. F. Fei, J. J. Watkins, A. J. Crosby, Soft double-network polydimethylsiloxane: fast healing of fracture toughness, *Journal of Materials Chemistry A,* 2022, **10**, 11667-11675, doi: 10.1039/D2TA00887D.

[153] Y. K. Deng, X. C. Liang, X. P. Pei, K. K. Zhai, C. Wang, B. C. Zhang, Y. G. Bai, Y. M. Zhang, P. X. Wang, Y. Tan, K. Xu, Self-healing ability and application of impact hardening polymers, *Polymer Testing,* 2019, **76**, 43-53, doi: 10.1016/j.polymertesting.2019.03.007.

[154] A. Wilson, G. Gasparini, S. Matile, Functional systems with orthogonal dynamic covalent bonds, *Chemical Society Reviews,* 2014, **43**, 1948-1962, doi: 10.1039/C3CS60342C.

[155] R. W. Guo, Q. Su, J. W. Zhang, A. J. Dong, C. G. Lin, J. H. Zhang, Facile access to multisensitive and self-healing hydrogels with reversible and dynamic boronic ester and disulfide linkages, *Biomacromolecules,* 2017, **18**, 1356-1364, doi: 10.1021/acs.biomac.7b00089.

[156] Y. D. Y. Zhang, Z. Y. Ding, Y. Liu, Y. P. Zhang, S. M. Jiang, White-light-emitting hydrogels with self-healing properties and adjustable emission colors, *Journal of Colloid and Interface Science,* 2021, **582**, 825-833, doi: 10.1016/j.jcis.2020.08080.

[157] J. Ding, Z. Qiao, Y. S. Zhang, D. R. Wei, S. P. Chen, J. J. Tang, L. Chen, D. Wei, J. Sun, H. S. Fan, NIR-responsive multi-healing HMPAM/dextran/AgNWs hydrogel sensor with recoverable mechanics and conductivity for human-machine interaction, *Carbohydrate Polymers,* 2020, **247**, 116686, doi: 10.1016/j.carbpol.2020.116686.

[158] W. Y. Xu, W. Wang, S. M. Chen, R. Zhang, Y. X. Wang, Q. Zhang, L. Yuwen, W. J. Yang, L. Wang, Molybdenum disulfide ($MoS_2$) nanosheets-based hydrogels with light-triggered self-healing property for flexible sensors, *Journal of Colloid and Interface Science,* 2021, **586**, 601-612, doi: 10.1016/j.jcis.2020.10128.

[159] B. Krishnakumar, M. Singh, V. Parthasarthy, C. Park, N. G. Sahoo, G. J. Yun, S. Rana. Disulfide exchange assisted self-healing epoxy/PDMS/graphene oxide nanocomposites, *Nanoscale Advances,* 2022, **2**, 2726-2730, doi: 10.1339/d0na00282h.

[160] J. Wen, Z. Y. Jia, X. P. Zhang, M. W. Pan, J. F. Yuan, L. Zhu, Tough, thermo-responsive, biodegradable and fast self-healing polyurethane hydrogel based on microdomain-closed dynamic bonds design, *Materials Today Communications,* 2020, **25**, 101569, doi: 10.1016/j.mtcomm.2020.101569.

[161] D. Burmistrova, A. Galustyan, I. Smolyaninov, N. Berberova, Redox-mediated and microwave-assisted thiol activation: two approaches to unsymmetrical disulfides synthesis, *Journal of The Electrochemical Society,* 2022, **169**, 116501, doi: 10.1149/1945-7111/ac9d69.

[162] C. E. Yue, L. W. Zhao, L. Z. Guan, X. R. Zhang, C. Y. Qu, D. Z. Wang, L. Weng, Vitrimeric silicone composite with high thermal conductivity and high repairing efficiency as thermal interface materials, *Journal of Colloid and Interface Science,* 2022, **620**, 273-283, doi: 10.1016/j.jcis.2022.04017.

[163] W. Li, L. Xiao, Y. Wang, J. Chen, X. Nie, Self-healing silicon-containing eugenol-based epoxy resin based on disulfide bond exchange: synthesis and structure-property relationships, *Polymer,* 2021, **229**, 123967, doi: 10.1016/j.polymer.2021.123967.

[164] S. J. Sun, G. X. Fei, X. R. Wang, M. Xie, Q. F. Guo, D. H. Fu, Z. H. Wang, H. Wang, G. X. Luo, H. S. Xia, Covalent adaptable networks of polydimethylsiloxane elastomer for selective laser sintering 3D printing, *Chemical Engineering Journal,* 2021, **412**, 128675, doi: 10.1016/j.cej.2021.128675.

[165] G. Q. Zhu, J. S. Zhang, J. Huang, Y. H. Qiu, M. T. Liu, J. N. Yu, C. G. Liu, Q. Q. Shang, Y. Hu, L. H. Hu, Y. H. Zhou, Recyclable and reprintable biobased photopolymers for digital light processing 3D printing, *Chemical Engineering Journal,*

2023, **452**, 139401, doi: 10.1016/j.cej.2022.139401.

[166] W. J. Sun, L. Zhang, S. Wang, J. L. Mao, J. M. Luo, Y. Chen, Y. H. Cheng, Mechanically enhanced healable and recyclable silicone with dynamic hindered urea bond for flexible electronics, *Journal of Materials Chemistry C*, 2021, **9**, 8579-8588, doi: 10.1039/D1TC01273H.

[167] J. von Szczepanski, P. M. Danner, D. M. Opris, Self-healable, self-repairable, and recyclable electrically responsive artificial muscles, *Advanced Science*, 2022, **9**, 2202153, doi: 10.1002/advs.202202153.

[168] X. Wu, X. Yang, R. Yu, X. J. Zhao, Y. Zhang, W. Huang, A facile access to stiff epoxy vitrimers with excellent mechanical properties via siloxane equilibration, *Journal of Materials Chemistry A*, 2018, **6**, 10184-10188, doi: 10.1039/C8TA02102C.

[169] Y. Hou, G. D. Zhu, J. Cui, N. N. Wu, B. T. Zhao, J. Xu, N. Zhao, Superior hard but quickly reversible Si-O-Si network enables scalable fabrication of transparent, self-healing, robust, and programmable multifunctional nanocomposite coatings, *Journal of the American Chemical Society*, 2021, **144**, 436-445, doi: 10.1021/jacs.1c10455.

[170] W. Schmolke, N. Perner, S. Seiffert, Dynamically cross-linked polydimethylsiloxane networks with ambient-temperature self-healing, *Macromolecules*, 2015, **48**, 8781-8788, doi: 10.1021/acs.macromol.5b01666.

[171] C. Liu, Y. Z. Tan, H. P. Xu, Functional polymer materials based on dynamic covalent chemistry, *Science China Materials*, 2022, **65**, 1-18, doi: 10.1007/s40843-021-2018-y.

[172] W. J. Lee, H. G. Oh, S. H. Cha, A brief review of self-healing polyurethane based on dynamic chemistry, *Macromolecular Research*, 2021, **29**, 649-664, doi: 10.1007/s13233-021-9088-2.

[173] M. Rodin, J. Li, D. Kuckling, Dually cross-linked single networks: structures and applications, *Chemical Society Reviews*, 2021, **50**, 8147-8177, doi: 10.1039/D0CS01585G.

[174] A. M. Wemyss, C. Bowen, C. Plesse, C. Vancaeyzeele, G. T. Nguyen, F. Vidal, C. Wan, Dynamic crosslinked rubbers for a green future: a material perspective, *Materials Science and Engineering: A*, 2020, **141**, 100561, doi: 10.1016/j.mser.2020.100561.

[175] M. Podgórski, B. D. Fairbanks, B. E. Kirkpatrick, M. McBride, A. Martinez, A. Dobson, N. J. Bongiaedina, C. N. Bowman, Toward stimuli-responsive dynamic thermosets through continuous development and improvements in covalent adaptable networks (CANs), *Advanced Materials*, 2020, **32**, 1906876, doi: 10.1002/adma.201906876.

[176] W. K. Zou, J. T. Dong, Y. W. Luo, Q. Zhao, T. Xie, Dynamic covalent polymer networks: from old chemistry to modern day innovations, *Advanced Materials*, 2017, **29**, 1606100, doi: 10.1002/adma.201606100.

[177] R. L. Snyder, D. J. Fortman, G. X. de Hoe, M. A. Hillmyer, W. R. Dichtel, Reprocessable acid-degradable polycarbonate vitrimers, *Macromolecules*, 2018, **51**, 389-397, doi:10.1021/ACS.MACROMOL.7B02299.

[178] M. J. Webber, M. W. Tibbitt, Dynamic and reconfigurable materials from reversible network interactions, *Nature Reviews Materials*, 2022, **7**, 541-556, doi: 10.1038/s41578-021-00412-x.

[179] E. J. He, Y. J. Yao, Y. B. Zhang, Y. Wei, Y. Ji, Reprocessing of vitrimer, *Acta Chimica Sinica*, 2022, **80**, 1021-1041, doi: 10.6023/A22020072.

[180] A. B. Lagron, B. M. El-Zaatari, L. S. Hamachi, Characterization techniques to assess recyclability in dynamic polymer networks, *Frontiers in Materials*, 2022, **9**, 915296, doi:10.3389/fmats.2022.915296.

[181] X. Li, Q. R. Bao, K. X. Chen, R. He, Y. Liu, Q. Wang, Reprocessable flame retardant silicone polyurethane based on dynamic phenylborate ester covalent and N-P-Si synergistic effect, *ACS Sustainable Chem. Eng.*, 2022, **10**, 14174-14184, doi: 10.1021/acssuschemeng.2c03717.

[182] W. Denissen, G. Rivero, R.Nicolaÿ, L. Leibler, J. M. Winne, F. E. Du Prez, Vinylogous urethane vitrimers, *Advanced Functional Materials*, 2015, **25**, 2451-2457, doi: 10.1002/adfm.201404553.

[183] J. S. A. Ishibashi, J. A. Kalow, Vitrimeric silicone elastomers enabled by dynamic meldrum´s acid-derived cross-links, *ACS Macro Letters*, 2018, **7**, 482-486, doi: 10.1021/acsmacrolett.8b00166.

[184] H. Zhang, C. Cai, W. X. Liu, D. D. Li, J. W. Zhang, N. Zhao, J. Xu, Recyclable polydimethylsiloxane network crosslinked by dynamic transesterification reaction, *Sci. Rep.*, 2017, **7**, 1-9, doi: 10.1038/s41598-017-11485-6.

[185] P. J. Zhao, L. L. Wang, L. F. Xie, W. Y. Wang, L. L. Wang, C. Q. Zhang, L. Li, S. Y. Feng, Mechanically Strong, Autonomous Self-healing, and fully recyclable silicone coordination elastomers with unique photoluminescent properties, *Macromolecular Rapid Communications*, 2021, **42**, 2100519, doi: 10.1002/marc.202100519.

[186] J. F. Cao, D. D. Han, H. Lu, P. Zhang, S. Y. Feng, A readily self-healing and recyclable silicone elastomer via boron-nitrogen noncovalent crosslinking, *New Journal of Chemistry*, 2018, **42**, 18517-18520, doi: 10.1039/C8NJ04258F.

[187] R. Bui, M. A. Brook, Dynamic covalent schiff-base silicone polymers and elastomers, *Polymer*, 2019, **160**, 282, doi: 10.1016/j.polymer.2018.11043.

[188] R. Bui, M. A. Brook, Thermoplastic silicone elastomers from divanillin crosslinkers in a catalyst-free process, *Green Chemistry*, 2021, **23**, 5600-5608, doi: 10.1039/D1GC01696B.

[189] J. W. Kim, H. J. Jeon, S. I. Jang, H. M. Cho, Y. Kim, Recyclable thermosetting thermal pad using silicone-based polyurethane crosslinked by Diels-Alder adduct, *Applied Surface Science*, 2018, **429**, 128-133, doi: 10.1016/j.apsusc.2017.09003.

[190] R. J. Han, Y. L. Li, Q. S. Zhu, K. M. Niu, Research on the preparation and thermal stability of silicone rubber composites: a review, *Composites Part C*, 2022, **8**, 100249, doi: 10.1016/j.jcomc.2022.100249.

[191] G. Verma, N. Sheshkar, C. Pandey, A. Gupta, Recent trends of silicon elastomer-based nanocomposites and their sensing applications, *Journal of Polymer Research*, 2022, **29**, 1-26, doi: 10.1007/s10965-022-03044-z.

[192] R. Ariati, F. Sales, A. Souza, R. A. Lima, J. Ribeiro, Polydimethylsiloxane composites characterization and its

applications: a review, *Polymers,* 2021, **13**, 4258, doi: 10.3390/polym13234258.

[193] Y. Cao, M. Z. Rong, M. Q. Zhang, Covalent adaptable networks impart smart processability to multifunctional highly filled polymer composites, *Composites Part A: Applied Science and Manufacturing.,* 2021, **151**, 106647, doi: 10.1016/j.compositesa.2021.106647.

[194] H. Tan, Q. Lyu, Z. Xie, M. Li, K. Wang, K Wang, B. Xiong, L. Zhang, J. Zhu, Metallosupramolecular photonic elastomers with self-healing capability and angle-independent color, *Advanced Materials,* 2019, **31**, 1805496, doi: 10.1002/adma.201805496.

[195] A. K. Kasar, G. P. Xiong, P. L. Menezes, Graphene-reinforced metal and polymer matrix composites, *The Journal of The Minerals, Metals & Materials Society,* 2018, **70**, 829-836, doi: 10.1007/s11837-018-2823-2.

[196] D. Kuang, W. B. Hu, Research progress of graphene composites, *Journal of Inorganic Materials,* 2013, **28**, 235-246, doi: 10.3724/SP.J.1077.2013.12345.

[197] L. W. Zhao, B. Jiang, Y. D. Huang, Functionalized graphene-reinforced polysiloxane nanocomposite with improved mechanical performance and efficient healing properties, *Journal of Applied Polymer Science,* 2019, **136**, 47725, doi: 10.1002/app.47725.

[198] C. G. Pan, L. B. Liu, Q. Chen, Q. Zhang, G. L. Guo, Tough, stretchable, compressive novel polymer/graphene oxide nanocomposite hydrogels with excellent self-healing performance, *ACS Applied Materials & Interfaces,* 2017, **9**, 38052-38061, doi: 10.1021/acsami.7b12932.

[199] C. T. Cai, Y. Zhang, M. Li, Y. Chen, R. C. Zhang, X. L. Wang, Q. Wu, T. H. Chen, P. C. Sun, Multiple-responsive shape memory polyacrylonitrile/graphene nanocomposites with rapid self-healing and recycling properties, *RSC Advances,* 2018, **8**, 1225-1231, doi: 10.1039/c7ra11484b.

[200] K. Mylvaganam, L. C. Zhang, Fabrication and application of polymer composites comprising carbon nanotubes, *Recent Patents on Nanotechnology,* 2007, **1**, 59-65, doi: 10.2174/187221007779814826.

[201] F. Mohanty, S. K. Swain, Carbon nanotube embedded polymer composite: properties and applications, *Current Organic Synthesis*, 2017, **14**, 249-262, doi:10.1016/j.addma.2022.103085.

[202] C. Lv, J. K. Wang, Z. X. Li, K. F. Zhao, J. P. Zheng, Degradable, reprocessable, self-healing PDMS/CNTs nanocomposite elastomers with high stretchability and toughness based on novel dual-dynamic covalent sacrificial system, *Composites Part B: Engineering,* 2019, **177**, 107270, doi: 10.1016/j.compositesb.2019.107270.

[203] W. Zang, X. Liu, J. Li, Y. Jiang, B. Yu, H. Zou, N. Ning, M. Tian, L. Zhang, Conductive, self-healing and recyclable electrodes for dielectric elastomer generator with high energy density, *Chemical Engineering Journal,* 2022, **429**, 132258, doi: 10.1016/j.cej.2021.132258.

[204] Y. Z. Zhang, Y. Wang, Q. Jiang, J. K. El-Demellawi, H. Kim, H. N. Alshareef, MXene printing and patterned coating for device applications, *Advanced Materials*, 2020, **32**, 1908486, doi: 10.1002/adma.201908486.

[205] K. Zhang, J.Sun, J. Song, C. Gao, Z. Wang, C. Song, Y. Wu, Y. Liu, Self-healing $Ti_3C_2$ MXene/PDMS supramolecular elastomers based on small biomolecules modification for wearable sensors, *ACS Applied Materials & Interfaces,* 2020, **12**, 45306-45314, doi: 10.1021/acsami.0c13653.

[206] Z. Wang, Y. T. Liu, D. J. Zhang, K. M. Zhang, C. H. Gao. Y. M. Wu, Tough, stretchable and self-healing C-MXenes/PDMS conductive composites as sensitive strain sensors, *Composites Science and Technology,* 2021, **216**, 109042, doi: 10.1016/j.compscitech.2021.109042.

[207] H. Q. Tao, D. W. Yue, C. H. Li, A fast self-healing magnetic nanocomposite for magnetic actuators, *Macromolecular Materials and Engineering,* 2022, **307**, 2100649, doi: 0.1002/mame.202100649.

[208] Y. Wang, L. Ding, C. Zhao, S. Wang, S. Xuan, H. Jiang, X. Gong, A novel magnetorheological shear-stiffening elastomer with self-healing ability, *Composites Science and Technology.,* 2018, **168**, 303-311, doi: 10.1016/j.compscitech.2018.10.019.

[209] L. Zhou, J. Zhao, H. Huang, F. Nan, G. Zhou, Q. Ou, Flexible polymer photonic films with embedded microvoids for high-performance passive daytime radiative cooling, *ACS Photonics,* 2021, **8**, 3301-3307, doi: 10.1021/acsphotonics.1c01149.

[210] T. Wang, Y. Wu, L. Shi, X. Hu, M. Chen, L. Wu, A structural polymer for highly efficient all-day passive radiative cooling, *Nature Communication,* 2021, **12**, 365, doi: 10.1038/s41467-020-20646-7.

[211] S. H. Dong, Q. Wu, W. L. Zhang, G. F. Xia, L. Yang, J. X. Cui, Slippery passive radiative cooling supramolecular siloxane coatings, *ACS Applied Materials & Interfaces,* 2022, **14**, 4571-4578, doi: 10.1021/acsami.1c22673.

[212] Z. Y. Hu, W. J. Wu, X. Chen, Y. Z. Chen, J. L. Chen, Z. F. Hao, Flexible thermal conductive $Al_2O_3$@ siloxane composite with rapid self-healing property based on carboxyl-amine dynamic reversible bonds, *RSC Advances,* 2022, **12**, 6649-6658, doi: 10.1039/d1ra09367c.

[213] L. Zhao, X. Shi, Y. Yin, B. Jiang, Y. Huang, A self-healing silicone/BN composite with efficient healing property and improved thermal conductivities, *Composite Science Technology,* 2020, **186**, 107919, doi: 10.1016/j.compscitech.2019.107919.

[214] S. J. Yuan, Z. Q. Peng, M. Z. Rong, M. Q. Zhang, Increasing strengths of liquid crystalline polymers while minimizing anisotropy via topological rearrangement assisted bi-directional stretching of reversibly interlocked macromolecular networks, *Applied Materials Today,* 2022, **29**, 101643, doi: 10.1016/j.apmt.2022.101643.

[215] Z. P. Zhang, M Z. Rong, M, Q. Zhang, Mechanically robust, self-healable, and highly stretchable “living” crosslinked polyurethane based on a reversible C-C bond, *Advanced Functional Materials,* 2018, **28**, 1706050, doi: 10.1002/adfm.201706050.

[216] Y. M. Li, Z. P. Zhang, M. Z. Rong, M. Q. Zhang, Tailored modular assembly derived self-healing polythioureas with largely tunable properties covering plastics, elastomers and fibers,

*Nature Communications*, 2022, **13**, 2633, doi: 10.1038/s41467-022-30364-x.

[217] C. C. Hornat, M. W. Urban, Shape memory effects in self-healing polymers, *Progress in Polymer Science*, 2020, **102**, 101208, doi: 10.1016/j.progpolymsci.2020.101208.

[218] M. A. Sattar, A. Patnaik, Design principles of interfacial dynamic bonds in self-healing materials: what are the parameters? *Chemistry – An Asian Journal*, 2020, **15**, 4215-4240, doi: 10.1002/asia.202001157.

## Author Information

***Juan Ye**, graduated with her bachelor's degree from Guangdong University of Technology in 2021. She is currently pursuing a master's degree of Materials Science and Engineering in Guangdong University of Technology. Her research interest includes synthesis and application of functional polymer materials.*

***Hao Jin**, graduated with her bachelor's degree from Hunan Institute of Engineering in 2022. He is currently a postgraduate student at Guangdong University of Technology. His research interest is self-healing silicone materials.*

***Zhaoji Zu**, graduated with her bachelor's degree from Jiangsu Ocean University in 2022. He is currently a postgraduate student at Guangdong University of Technology. His research interest is 3D printing photosensitive resins.*

***Bing Yu**, graduated with her bachelor's degree from Yantai University in 2022. She is currently a postgraduate student at Guangdong University of Technology. Her research interest is biomedical polymers.*

***Hongping Xiang**, is working as Associate Professor, in School of Materials and Energy, Guangdong University of Technology since 2018. He received his Ph.D. from Sun Yat-sen University in 2015. His area of interest are functional polymers and their composite materials. In recent years, he has concentrated on self-healable polymers, solid-state recyclable rubbers, 3D printing photosensitive resins and their composites, etc.*

***Pro. Ming Qiu Zhang** has over thirty-years of systematic experience in polymers, polymer blends and polymer composites. He serves as a member of the Asian-Australasian Association for Composite Materials (AACM), Council and the standing council of Chinese Materials Research Society. In addition, Professor Zhang is on the editorial board of eight scientific journals and holds fifty-eight patents.*

**Publisher's Note**: Engineered Science Publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.