

REVIEW

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A review on room-temperature self-healing polyurethane: synthesis, self-healing mechanism and application

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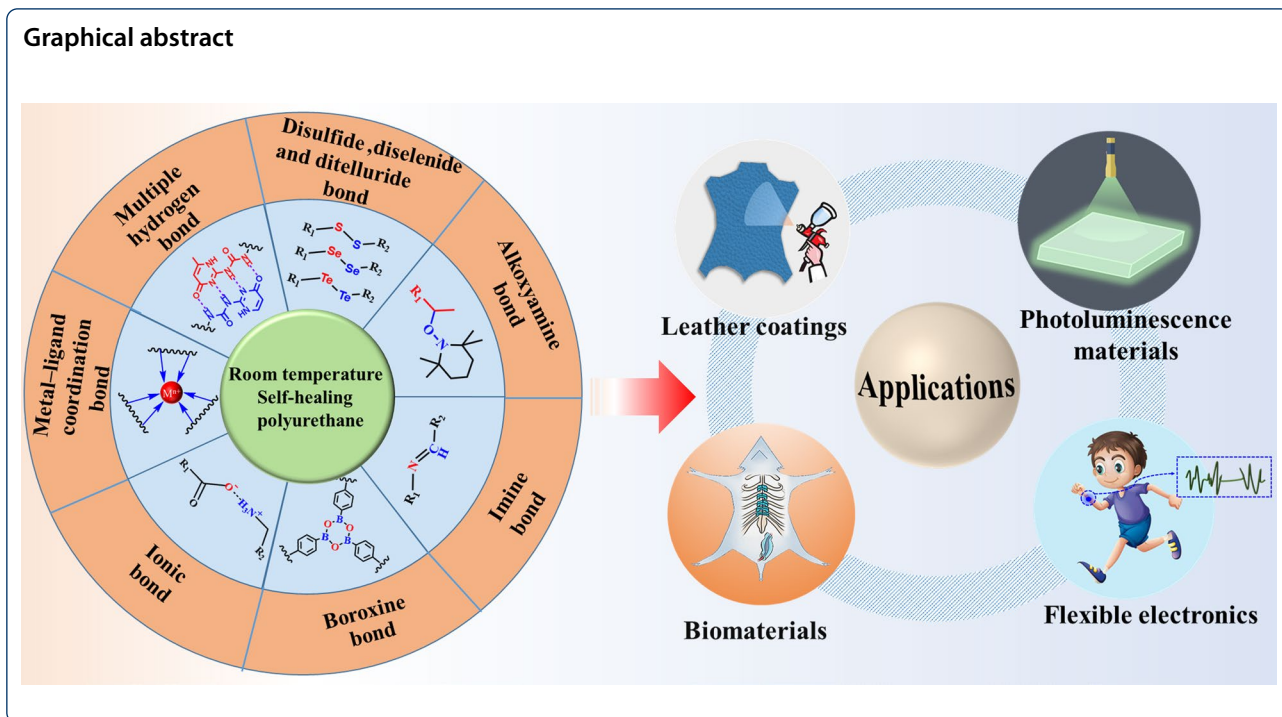
Abstract

Polyurethanes have been widely used in many fields due to their remarkable features such as excellent mechanical strength, good abrasion resistance, toughness, low temperature flexibility, etc. In recent years, room-temperature self-healing polyurethanes have been attracting broad and growing interest because under mild conditions, room-temperature self-healing polyurethanes can repair damages, thereby extending their lifetimes and reducing maintenance costs. In this paper, the recent advances of room-temperature self-healing polyurethanes based on dynamic covalent bonds, noncovalent bonds and combined dual or triple dynamic bonds are reviewed, focusing on their synthesis methods and self-healing mechanisms, and their mechanical properties, healing efficiency and healing time are also described in detail. In addition, the latest applications of room-temperature self-healing polyurethanes in the fields of leather coatings, photoluminescence materials, flexible electronics and biomaterials are summarized. Finally, the current challenges and future development directions of the room-temperature self-healing polyurethanes are highlighted. Overall, this review is expected to provide a valuable reference for the prosperous development of room-temperature self-healing polyurethanes.

Keywords: Polyurethane, Room temperature, Self-healing mechanism, Synthesis method, Application

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1 Introduction

Polyurethanes (PUs) are polymers containing urethane repeating units, which are mainly formed by addition polymerization of polyisocyanates and macropolyols in the presence of chain extenders [1]. The simplest linear polyurethane synthesis route is shown in Fig. 1a. Macropolyols (such as polyether diols, polyester diols, etc.) are often referred to as soft segments, while

isocyanates (aromatic or aliphatic) and chain extenders (small diols or diamines) are often referred to as hard segment [2]. As shown in Fig. 1b, the hard phase formed by the self-assembly of isocyanates and chain extenders through hydrogen bonds of urethane groups is dispersed in the soft phase composed of flexible polymer chains, resulting in microphase separation. The hard phase acts as a physical cross-linking point to give PUs

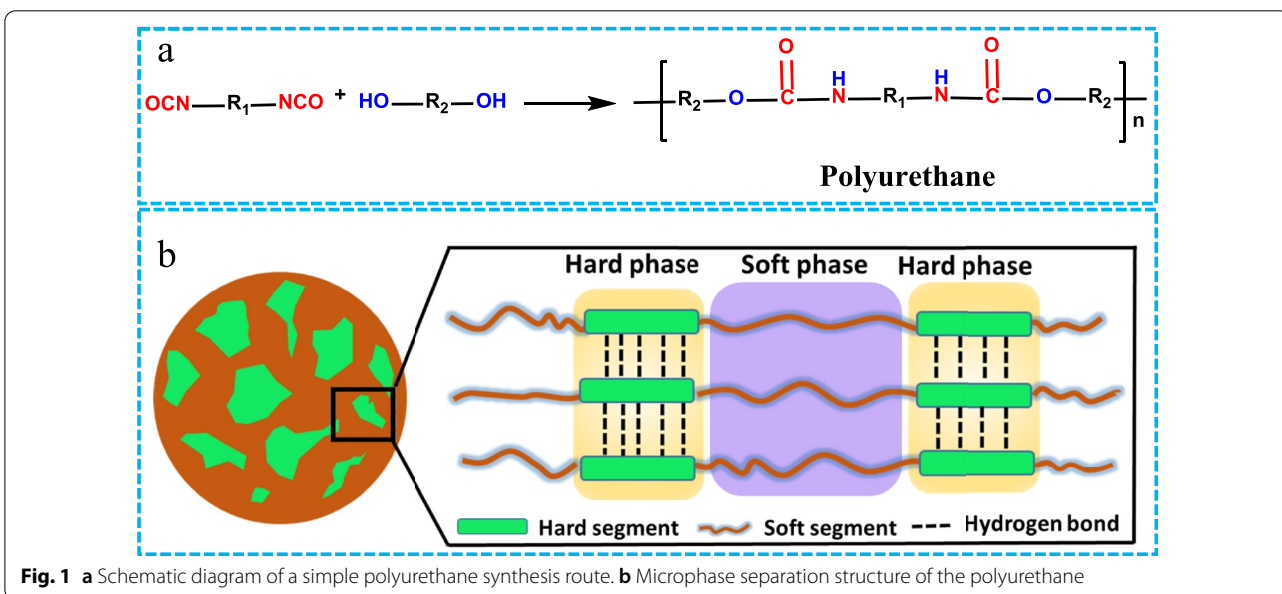


Fig. 1 a Schematic diagram of a simple polyurethane synthesis route. b Microphase separation structure of the polyurethane

good mechanical strength. At the same time, the flexible polymer chains impart flexibility and elasticity to the PUs [3]. Therefore, choosing different raw materials and relative ratios of hard and soft segments can easily tune the phase-separated structure, thereby changing the properties of polyurethanes. Thanks to easy tailoring properties of PUs, they have been widely used in many fields such as coatings [4, 5], adhesives [6], textiles [7], printing inks [8], biomaterials [9, 10], flexible electronics [11, 12], etc. However, polyurethane materials inevitably produce mechanical damages in the process of use, hence endowing them with self-healing function is of great significance to prolong the service life of materials and reduce the maintenance costs. In recent decades, self-healing polyurethanes (PUs) have been developed vigorously.

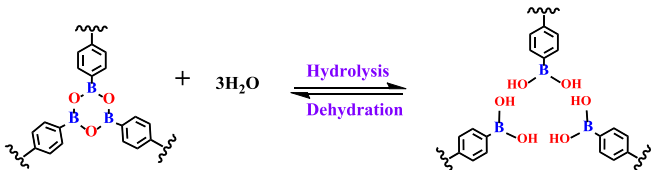
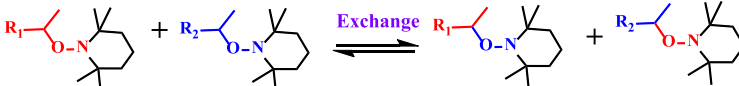
Similar to human skin, self-healing polyurethanes can repair damages or recover original functions in conditions with or without external stimuli [13]. Generally, the self-healing mechanisms of polyurethanes include two types: extrinsic self-healing and intrinsic self-healing [14, 15]. Different from the former, intrinsic self-healing mainly relies on the fracture and recombination of dynamic chemical bonds to achieve damage repair. Therefore, intrinsic self-healing possesses the advantages of no healing agents, simple preparation process and multiple healing cycles, which has attracted special attentions of numerous researchers [16, 17]. In addition, with the indepth development of intrinsic self-healing polyurethanes (PUs), the PUs with fast healing rate at room temperature and high mechanical strength can better meet the needs of practical applications, which has become an important development trend of current research [18–20]. So far, room-temperature self-healing

polyurethanes mainly rely on reversible covalent bonds (such as disulfide bonds [21–23], diselenide bonds [24–26], ditelluride bonds [27, 28], alkoxyamine bonds [29, 30], imine bonds [31–33], boroxine bonds [34–36], etc.) and noncovalent bonds (such as hydrogen bonds [37–39], metal–ligand coordination bonds [40–42], ionic bonds [43, 44], etc.) to achieve multiple healing cycles. To the best of our knowledge, the review article only focusing on room temperature self-healing has not been found so far in the literature. Materials are usually applied at room temperature, therefore, it is of great significance to pay more attention to room temperature self-healing polyurethanes from the perspective of practical application. Hence, our paper reviews the repair mechanisms and synthesis methods of room temperature self-healing polyurethanes and described their mechanical properties, healing efficiency and healing time in detail. Meanwhile, we summarize recent applications of room temperature self-healing polyurethanes in leather coatings, photoluminescence materials, flexible electronics and biomaterials. Finally, the challenges and future development directions of room temperature self-healing polyurethanes are prospected.

2 Dynamic covalent bonds

Dynamic covalent bonds have relatively high bond energy, which implies the introducing of reversible covalent bonds into the molecular chains of polyurethanes not only gives them self-healable function, but also ensures their mechanical strength. Consequently, polyurethanes based on dynamic reversible covalent bonds have been gained extensive attention. At present, the types and self-healing mechanisms of main dynamic

Table 1 Types and self-healing mechanisms of main dynamic covalent bonds for room temperature self-healing polyurethanes

Types	Self-healing mechanisms
Disulfide bond Diselenide bond Detelluride bond	$R_1-X-X-R_2 + R_3-X-X-R_4 \xrightleftharpoons[\text{X=S,Se,Te}]{\text{Exchange}} R_1-X-X-R_4 + R_2-X-X-R_3$
Imine bond	$R_1-N=C(H)-R_2 + R_3-N=C(H)-R_4 \xrightleftharpoons{\text{Exchange}} R_1-N=C(H)-R_4 + R_3-N=C(H)-R_2$
Boroxine bond	
Alkoxyamine bond	

covalent bonds used to construct room temperature self-healing polyurethanes are listed in Table 1.

2.1 Disulfide, diselenide, and detelluride bonds

2.1.1 Disulfide bonds

Generally, disulfide bonds are divided into aliphatic disulfide and aromatic disulfide bonds. The abilities of two disulfide bonds to undergo metathesis reactions mainly depend on their chemical structures. Aliphatic disulfide bonds are reversibly broken and recombined under ultraviolet(UV) light stimulation, so they can be used to prepare light responsive room temperature self-healing polyurethane materials [45]. However, the UV light energy is higher than that of the conventional chemical bonds, which may lead to the decomposition of polymer chains [46]. To overcome the adverse effects of UV light, Takahara et al. [47] synthesized a thiuram disulfide (TDS) diol and introduced it into a polyurethane system. The C=S bond in thiuram disulfide group could form a p- π conjugate structure with the disulfide bond, which reduces the dissociation energy of the disulfide

bond. Therefore, the polyurethanes containing thiuram disulfide groups realized self-healing at room temperature under mild visible light. However, the synthetic process of the TDS diol was relatively complex. Notably, aromatic disulfide bonds can undergo dynamic exchange reactions at room temperature without any external stimulus. Kim et al. [48] prepared bis-isocyanate-terminated preoligomers by reacting polytetramethylene ether glycol (PTMG) with four different types of diisocyanate monomers, and then added bis(4-hydroxyphenyl) disulfide (SS) for chain extension to obtain the target polyurethanes containing aromatic disulfide bonds in the hard segment (Fig. 2a). The results showed that loosely packed IP-based hard segment domains provided the best exchange reaction efficiency for the aromatic disulfides due to the asymmetric alicyclic structure, thereby enabling polyurethanes to achieve efficient room-temperature self-healing (Fig. 2b). It can be seen from Fig. 2c, the scratches disappeared completely after healing at room temperature for 2 h. Especially, the broken circular IP-SS film sample (diameter: 46.0 mm; thickness: 2.0 mm) could hang

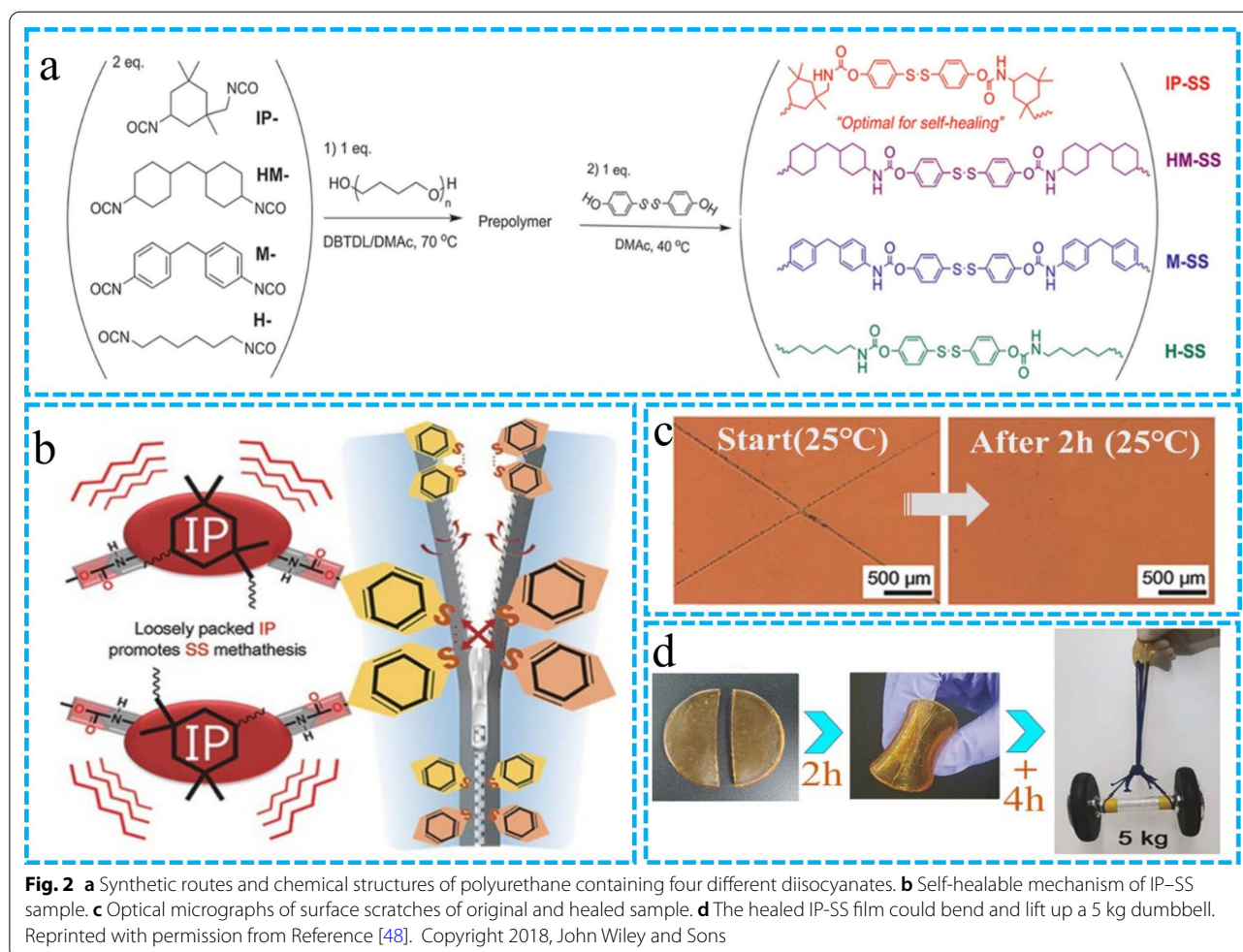
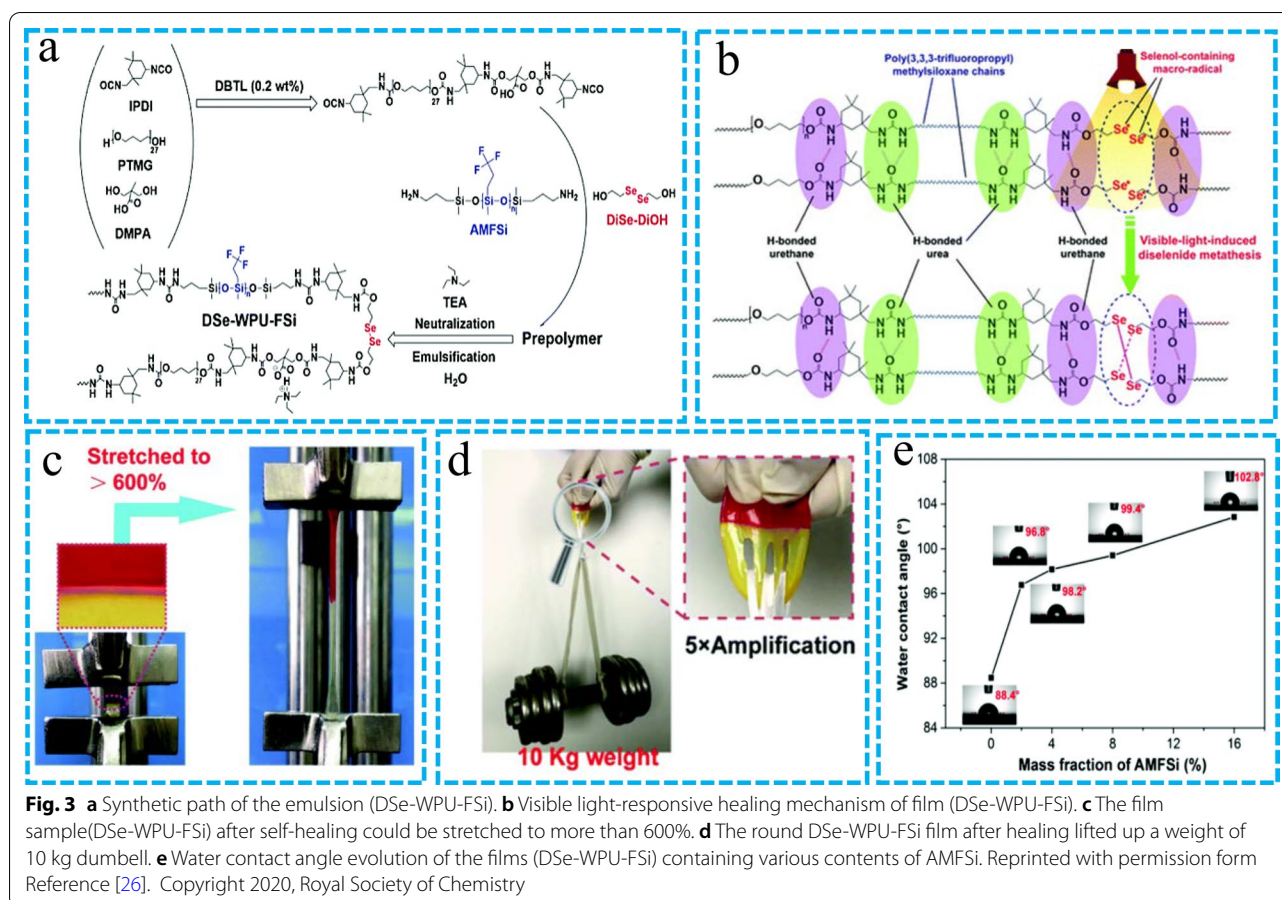


Fig. 2 a Synthetic routes and chemical structures of polyurethane containing four different diisocyanates. b Self-healing mechanism of IP-SS sample. c Optical micrographs of surface scratches of original and healed sample. d The healed IP-SS film could bend and lift up a 5 kg dumbbell. Reprinted with permission from Reference [48]. Copyright 2018, John Wiley and Sons

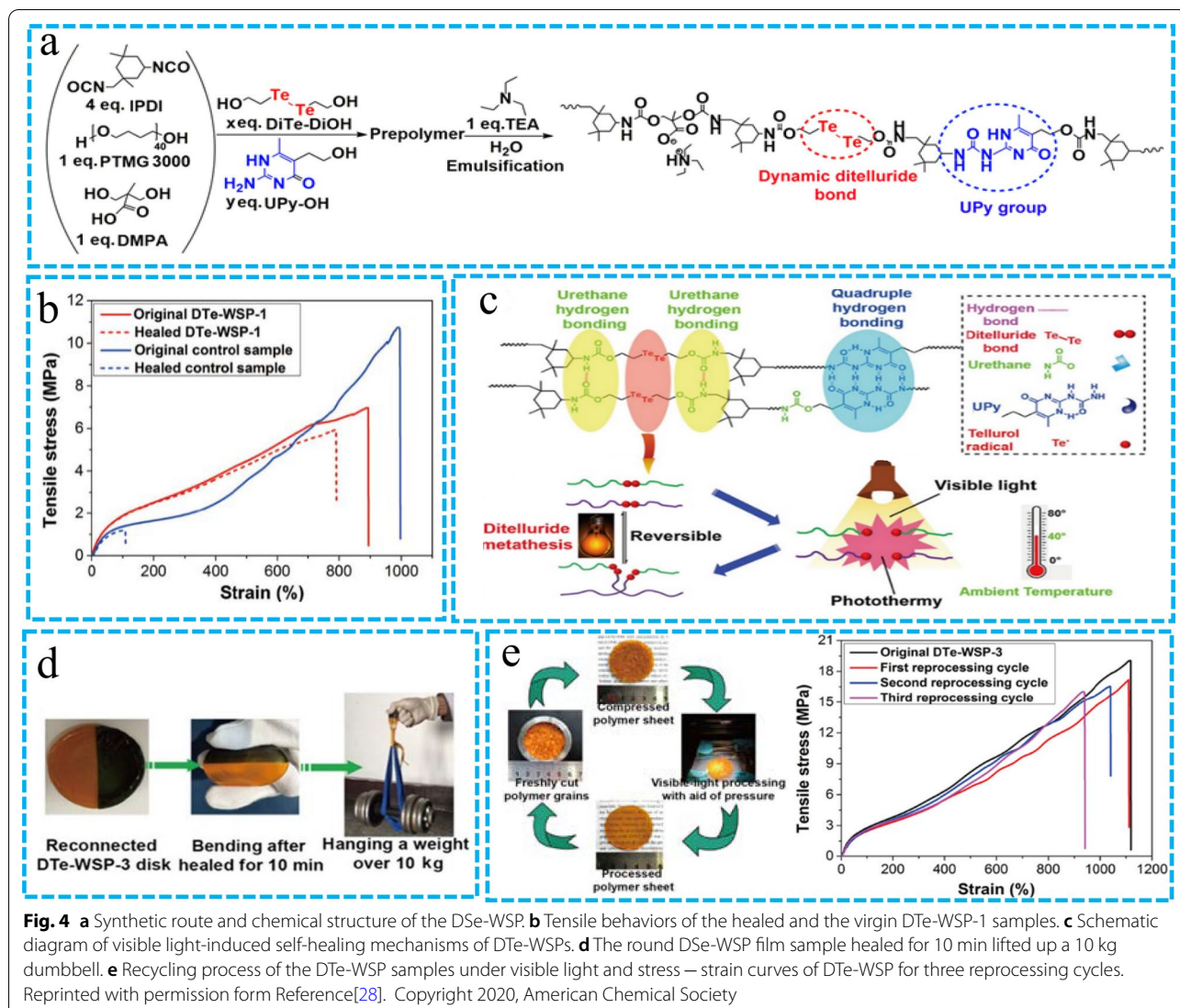


a 5 kg dumbbell after repairing at room temperature for 6 h (Fig. 2d). In addition, the resultant IP-SS displayed the outstanding mechanical properties (toughness of 26.9 MJ m^{-3} and tensile stress of 6.8 MPa), whose healing efficiency reached more than 75% within 2 h at 25°C . The introducing of diaminobenzene disulfide instead of dihydroxybenzene disulfide into polyurethane can provide better mechanical properties owing to the formation of urea bonds [49]. Furthermore, the molecular structure of diaminobenzene disulfide also affects the healing performance of the polyurethane. Huang et al. [21] introduced two kinds of diaminobenzene disulfide (2-Aminophenyl disulfide and 4-Aminophenyl disulfide) into waterborne polyurethane (WPU) and studied their effects on self-healing properties of WPU. Unlike regular linear hydrogen bonds formed by 4-aminophenyl disulfide, special Z-shaped hydrogen bonds formed by 2-aminophenyl disulfide could be exchanged effectively, contributing to adjacent disulfide metathesis. The obtained WPU possessed gratifying tensile strength (11.0 MPa) and toughness (52.1 MJ m^{-3}). In addition, the healing efficiency of tensile strength could reach more than 83% after healing at room temperature for 48 h. Aromatic disulfide bonds

have special advantages in synthesizing polyurethanes with room temperature healing function. However, aromatic disulfide monomers are so expensive that they are not suitable for industrial production. Meanwhile, the self-healing materials containing aromatic disulfide bonds have yellow appearance and low transparency [50].

2.1.2 Diselenide bonds

Compared with the disulfide bonds (240 kJ/mol), the diselenide bonds possess lower energy bond (172 kJ/mol), which means that the diselenide bonds will exhibit stronger dynamic characteristics. Xu et al. [51] discovered that the diselenide bonds could be cleaved to form selenium radicals under visible light and new diselenide bonds were formed again through the exchange reaction of selenium radicals. Based on this, our group [24] synthesized a visible light-induced room temperature self-healable waterborne polyurethane (DSe-WPU) based on diselenide bonds using di(1-hydroxyethylene) diselenide (DiSe), PTMG, DMPA, IPDI and BDO. When the DSe-WPU samples were cut off and then gently placed together, the diselenide bonds in PU molecular chains on the fracture surface took place exchange reactions under



visible light, thus realizing healing at room temperature of the sample. Benefiting from the reconstruction of hydrogen bonds and diselenide metathesis, the healing efficiency of optimized DSe-WPU sample exceeded 90% during 48 h under visible light irradiation. Furthermore, our group [26] embedded flexible fluorinated siloxane units and dynamic diselenide bonds into waterborne polyurethane to prepare mechanically robust and rapid self-healable polymer networks (DSe-WPU-FSi), as shown in Fig. 3a. By optimizing the content of fluorinated siloxane units and diselenide diols, the tensile stress and toughness of the DSe-WPU-FSi reached 16.31 MPa and 68.9 MJ m^{-3} , respectively. As shown in Fig. 3b, visible-light-triggered diselenide metathesis and recombination of dual hydrogen bonds formed by urethane and urea bonds were the main factors affecting the sample repair process. Accordingly, the tensile stress healing efficiency

of the healed sample reached up to 80% after healing under visible light irradiation for 2 h. Visually, the healed film sample could be stretched more than 600% without breaking (Fig. 3c) and the healed round film sample (diameter:40 mm; thickness:1.5 mm) lifted up a weight of 10 kg dumbbell (Fig. 3d). Moreover, the highly flexible fluorinated siloxane units not only promoted healing of the sample, but also improved its water resistance properties (Fig. 3e).

2.1.3 Ditelluride bonds

The ditelluride bonds (126 kJ/mol) have lower bond energy than that of the diselenide bonds. Because the atomic radius of tellurium is larger than that of selenium, hence ditelluride bonds show more sensitive stimulus-response characteristics [52]. Therefore, the introducing of ditelluride bonds into materials can further improve

their healing rate. Recently, our group [28] synthesized waterborne polyurethanes (DTe-WSPs) combining dynamic ditelluride bonds and quadruple hydrogen bonds through polyaddition reaction of ditelluride-diol (Dite-Diol), PTMG-3000, IPDI, DMPA and 2-ureido-4-[1H]-pyri-midinone (UPy), as shown in Fig. 4a. Owing to fast exchange reaction of ditelluride bonds under visible light stimulation, the tensile stress healing efficiency of the damaged DTe-WSP-1 sample could reach 92.9% when exposed to visible light for 10 min. However, the tensile stress of the control sample without dynamic ditelluride bonds recovered only 10.8% within the same time period, as depicted in Fig. 4b. Meanwhile, quadruple hydrogen bonds formed by UPy acted as dynamic crosslinking points to improve mechanical properties of DTe-WSP. By adjusting the content of ditelluride bonds and UPy, the optimized sample simultaneously achieved supertoughness (105.2 MJ m^{-3}) and fast healing rate (85.6% healing efficiency within 10 min under visible light). The healing mechanism is shown in Fig. 4c. The rapid reconstruction of multiple hydrogen bonds on the fracture surface of material promoted the early healing and made the molecular chains containing ditelluride bonds close to accelerate the subsequent photoinduced ditelluride exchange reaction. Their synergistic effect provided an excellent healing result for the DTe-WSP. As shown in Fig. 4d, the round DSe-WSP film sample with a diameter of 40 mm and a thickness of 1.5 mm could lift

up a 10 kg dumbbell after healing at room temperature for only 10 min under visible light stimulation. Meanwhile, dynamic ditelluride bonds endowed DTe-WSPs with excellent recycling ability under visible light and the tensile strength of the DTe-WSPs sample still remains above 85% of the original value after three recycling cycles (Fig. 4e).

2.2 Imine bonds

Among the widely studied reversible covalent bonds, the imine bonds are usually formed by the dehydration condensation of aldehyde (or ketone) and amine-containing compounds (primary amines, hydrazine, and hydroxyl-mine) in the presence of an acid catalyst [53, 54]. There are three kinds of dynamic equilibria of imine bonds (Fig. 5a) including imine hydrolysis/condensation, amine-imine transimination reaction, and imine metathesis, which were widely exploited by researchers to prepare self-healing materials [55–57]. Aromatic schiff base (ASB) bond is a specific imine bond containing carbon–nitrogen double bonds and both carbon and nitrogen atoms are connected with aryl groups. The delocalization effect of π electrons on aromatic rings enables the exchange reaction of the ASB bond at room temperature (Fig. 5b) [58]. Recently, our group [59] synthesized a novel room-temperature self-healable waterborne poly-urethane (ASB-WPU) containing dynamic ASB bonds in main chain (Fig. 5c) using DiASB-DiOH,

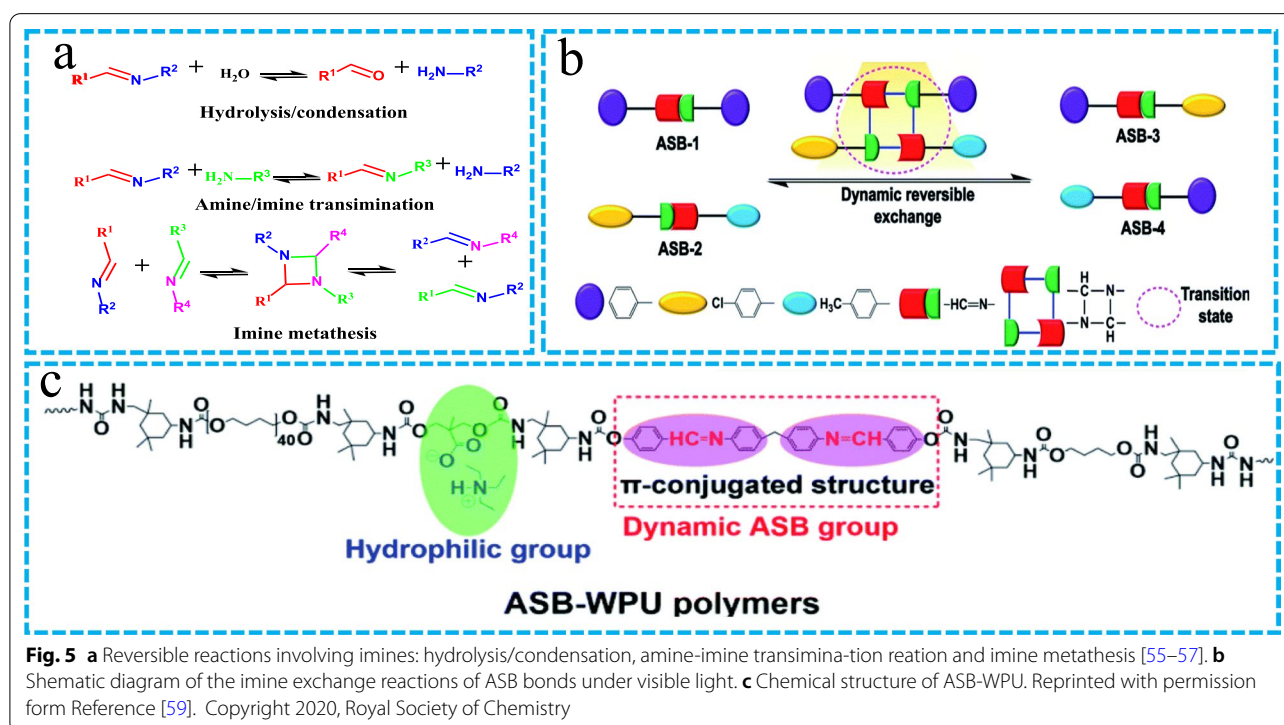


Fig. 5 a Reversible reactions involving imines: hydrolysis/condensation, amine-imine transimination reaction and imine metathesis [55–57]. b Schematic diagram of the imine exchange reactions of ASB bonds under visible light. c Chemical structure of ASB-WPU. Reprinted with permission from Reference [59]. Copyright 2020, Royal Society of Chemistry

IPDI, PTMG-3000 and DMPA. The tensile strength and toughness of ASB-WPU reached up to 14.32 MPa and 64.80 MJ m^{-3} , respectively. Taking advantage of the visible-triggered ASB bonds metathesis reactions, the tensile strength healing efficiency of the fractured sample reached 83.80% after healing for 24 h under visible light. Reversible ASB bonds have the advantages of mild synthesis conditions and no complex purification steps, but the poor stability seriously restricts their practical application.

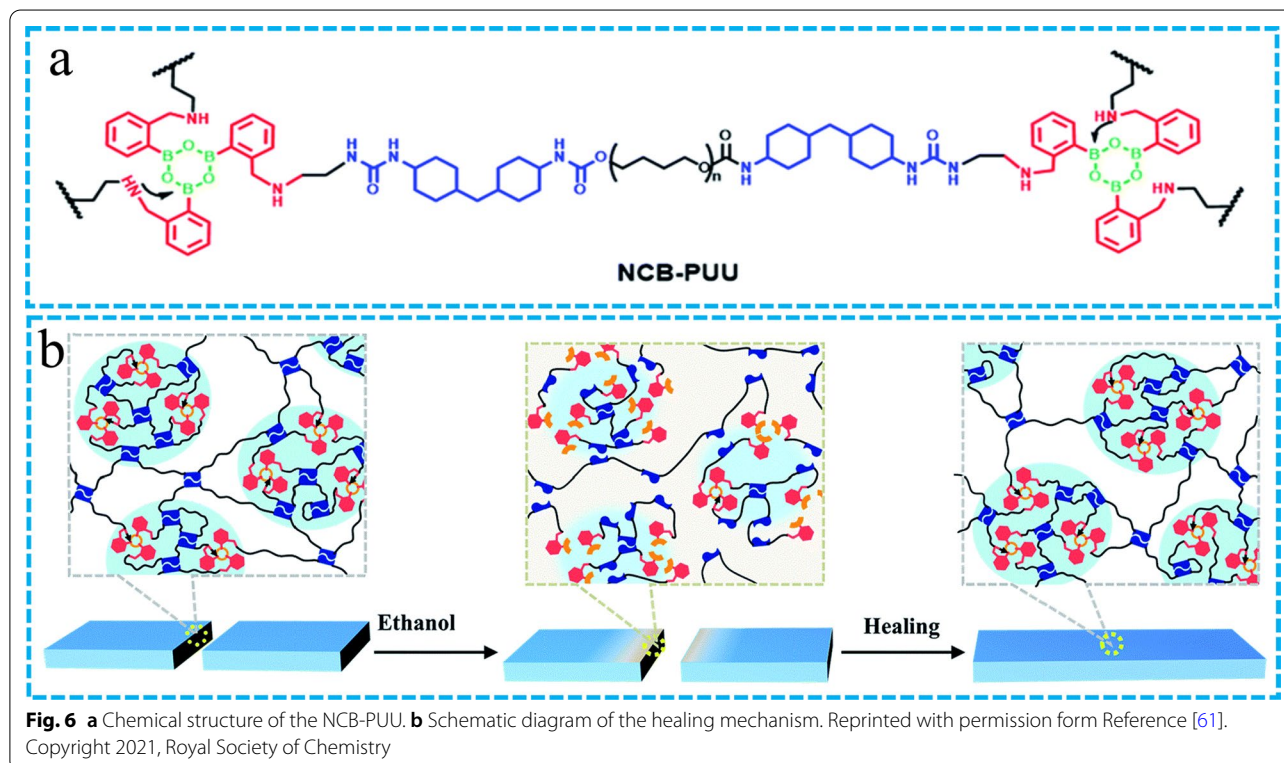
2.3 Boroxine bonds

Boroxine bonds formed by dehydration and condensation of phenylboric acids are common dynamic chemical bonds and possess special tripodal molecular architecture. Compared with borate ester bonds, boroxine bonds can increase the crosslinking density of self-healing polymers and improve their mechanical properties. However, when the boroxine bonds are hydrolyzed to form phenylboronic acids, it is usually necessary to raise the temperature to complete the condensation reaction of phenylboric acids, so the self-healing polymer materials based on boroxine bonds completed the self-healing process at relatively high temperature [60]. Sun et al. [34] reported a nitrogen-coordinated boroxine bond and the coordination interaction of N–B could accelerate the hydrolysis and condensation of dynamic boroxine

bonds at room temperature because the acidity of boric acid can be reduced by B–N coordination interaction. Recently, Sun et al. [61] incorporated nitrogen-coordinated boroxine bonds (NCBs) into polyurethane-urea materials (NCB-PUU) to construct a polymer network with room-temperature self-healing ability, as shown in Fig. 6a. The tripodal NCBs enabled polyurethane-urea to generate highly cross-linked three-dimensional network structures, thus it displayed outstanding mechanical properties with a tensile stress of $\sim 47 \text{ MPa}$ and a toughness of $\sim 190 \text{ MJ m}^{-3}$. Since NCBs and hydrogen bonds were broken in the presence of ethanol and rebuilt with the volatilization of ethanol (Fig. 6b), the fractured NCB-PUU sample could restore about 100% its tensile strength after healing at room temperature for 8h with the aid of ethanol. Although the polyurethanes containing nitrogen-coordinated boroxine bonds have superior room temperature self-healable performances, the materials have the defects of poor solvent resistance and water resistance.

2.4 Alkoxyamine bonds

Generally, alkoxyamine (C–ON) bonds in alkoxyamine derivatives can be cleaved to form carbon radicals and oxygen radicals at relatively high temperature ($60 \sim 120^\circ\text{C}$), and then carbon radicals and oxygen radicals can recombine [62]. Therefore, polymers containing alkoxyamine bonds could achieve self-healing



ability at relatively high temperature through the breaking and recombination of C–ON bonds [63]. In order to reduce cleavage temperature of C–ON bonds, Zhang et al. [29] introduced the nitrile group with strong electron absorption ability into the carbon atom of the C–ON bond to synthesize a diol monomer CTPO, and then CTPO reacted with polyethylene glycol (PEG-2000) and IPDI to synthesize a room-temperature self-healing polyurethane (ICPEG2000) (Fig. 7a). The nitrile groups could decrease the bond energy of C–ON bonds, thus leading to cleavage and reorganization of C–ON bonds at room temperature (Fig. 7b). The healing

mechanism is shown in Fig. 7c, benefiting from the reversibility of C–ON bonds and good movement ability of PEG-2000 macromolecules, the impact strength of the damaged ICPEG-2000 sample could reach 93.4% of the original value after healing at room temperature for 48 h.

3 Dynamic noncovalent bonds

Generally, the strength of dynamic noncovalent bonds is lower than that of dynamic covalent bonds, so they can dissociate and recombine rapidly, endowing polymer materials with fast room-temperature self-healing ability.

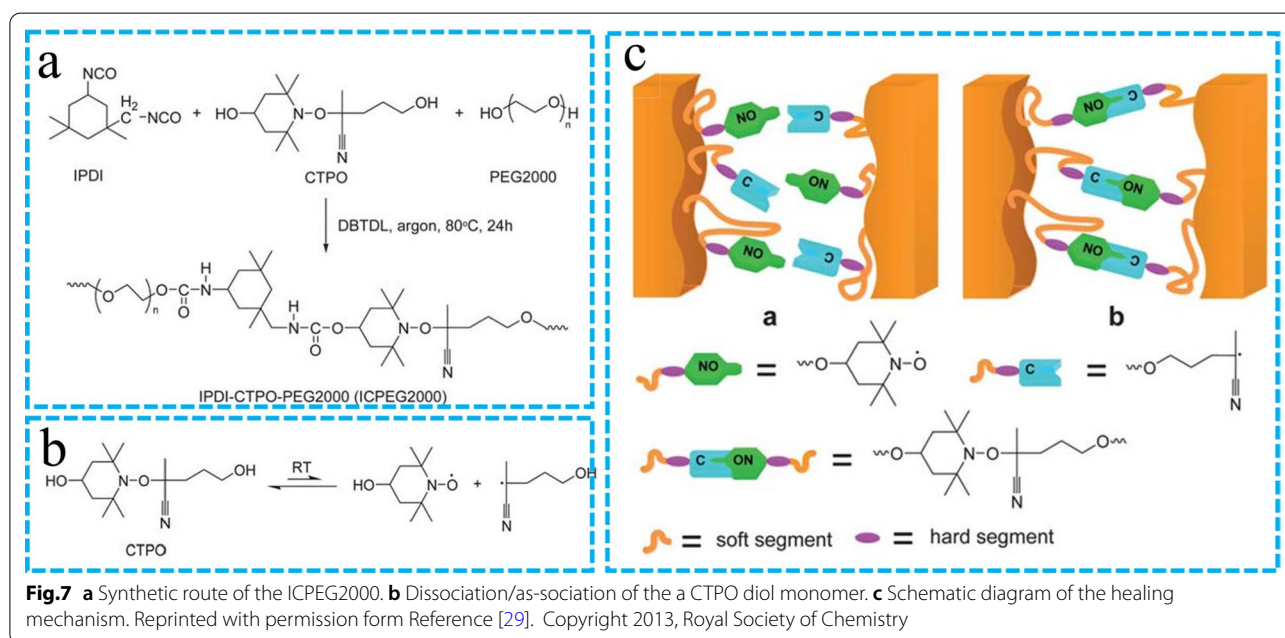


Table 2 Types and self-healing mechanisms of main dynamic noncovalent bonds for room-temperature self-healing polyurethanes

Types	Self-healing mechanisms
Multiple hydrogen bonds	
Metal–ligand coordination bond	
Ionic bond	

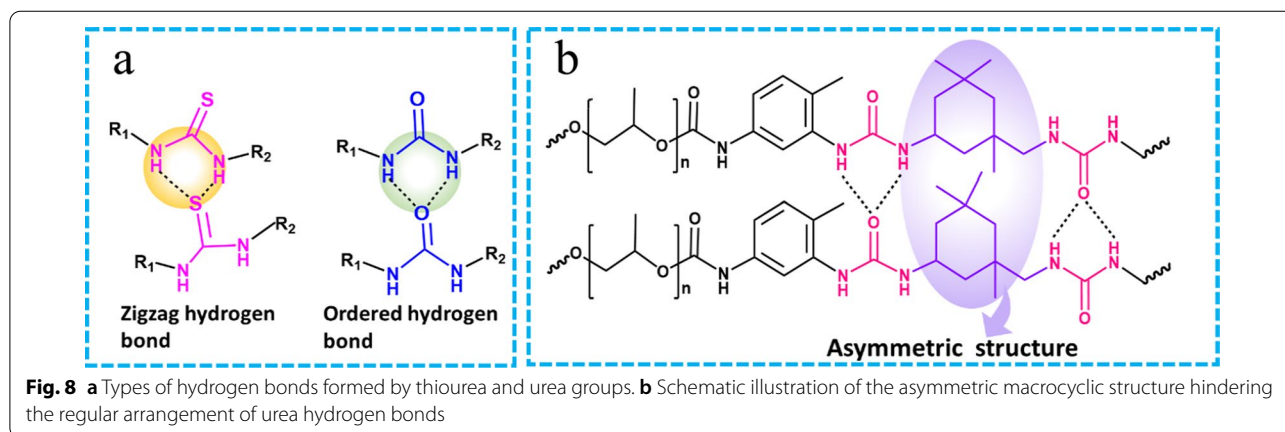
In recent years, polyurethane materials containing different dynamic noncovalent bonds have developed rapidly. At present, the types and healing mechanisms of main dynamic noncovalent bonds used to construct room temperature self-healing polyurethanes are listed in Table 2.

3.1 Multiple hydrogen bonds

The hydrogen bond is generally expressed as $X-H\cdots Y$, where $X-H$ represents the proton donor (X atom with strong electronegativity) and Y (Y atom with lone pair electron) refers to proton acceptor [64]. Hydrogen bond is a weak dynamic reversible noncovalent bond and its bond energy is only one tenth of that of $C-C$ covalent bond (400 kJ/mol). Thus, the hydrogen bonds are easily broken and reformed at room temperature, so the polymers containing hydrogen bonds possess room temperature self-healing properties [37–39]. Generally, hydrogen bonds widely exist between the molecular chains of polyurethanes, which are mainly formed by self-assembly of proton donors ($N-H$) and proton receptors ($C=O$) in carbamate groups or urea groups. However, most of the hydrogen bonds in polyurethane materials are single hydrogen bonds, and the bond energy of single hydrogen bonds is weak [65]. Consequently, polyurethane materials relying only on these single hydrogen bonds have low strength and slow room temperature healing rate, which is difficult to be applied in practice. Therefore, people turn their attention to the construction of multiple hydrogen bond systems with stronger forces and more binding sites [66]. Multiple hydrogen bonds not only provide abundant cross-linking points for polymer networks, but also rapidly recombine between the material fracture interfaces to rebuild the polymer networks. Compared with simple hydrogen bonds, multiple hydrogen bonds enable the materials to have better mechanical properties and higher healing efficiency.

However, not all multiple hydrogen-bonded polymers can achieve self-healing at room temperature because highly ordered multiple hydrogen bonds will make the polymer chains arrange orderly, leading to crystallization. Although ordered multiple hydrogen bonds can significantly improve the mechanical properties of materials, they hinder the motion of chain segments and require higher temperature to activate, which has a negative impact on the room temperature repair performances of the materials. To avoid such a scenario, Aida et al. [67] designed a mechanically robust yet readily repairable poly(ether-thioureas) material. As shown in Fig. 8a, in contrast to the ordered multiple hydrogen bonds formed by urea groups, thiourea groups in the molecular structure anomalously formed a less ordered zigzag hydrogen-bonded array, so that they did not induce crystallization. Therefore, the molecular chain structure remained amorphous, even if there were lots of thiourea hydrogen bonds inside the material. Meanwhile, the activation energy of thiourea hydrogen bond exchange reaction was also reduced through the sliding movement of triethylene glycol connecting thiourea units, which facilitates the reconnection of the fractured part during compression. As a result, the synthesized material not only possessed distinguished mechanical performances with a modulus of ≈ 1.4 GPa, a tensile stress of ≈ 40 MPa and a strain at break of $\approx 393\%$, but also could be capable of healing completely under compression at room temperature within 6 h.

Differencing from the design of Aida et al. Wang et al. [68] fabricated a novel polyurethane-urea elastomer using tolylene 2,4-diisocyanate terminated poly(propylene glycol) and isophorone diamine through a simple one-step polycondensation. Isophorone diamine reacted with isocyanate to form a polyurea structure, which can form multiple hydrogen bonds to improve the strength and toughness of the material. At the same



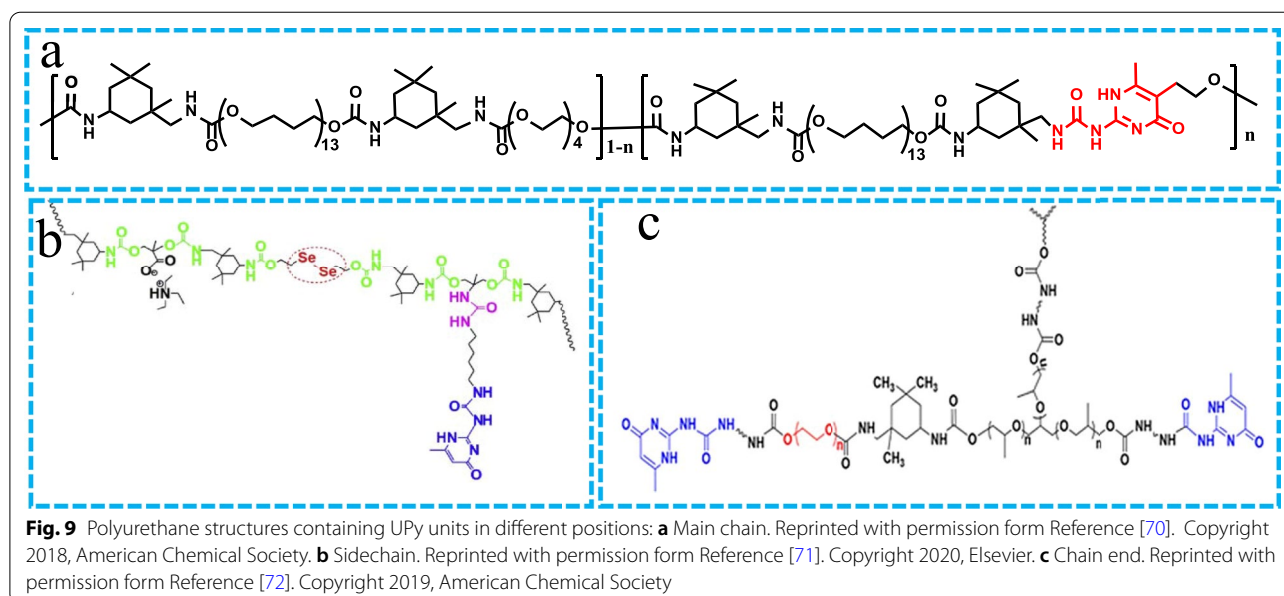
time, the steric hindrance effect of asymmetric macrocyclic structure of isophorone diamine hindered the regular arrangement of multiple hydrogen bonds (Fig. 8b), which makes the hard segments difficult to crystallize and improves the dynamics of hard segments at room temperature. Thus, the synthesized polyurethane-urea exhibited excellent mechanical properties (breaking stress of 4.83 MPa, elongation at break of 2010% and toughness of 65.49 MJ m^{-3}). In addition, the scratches on surface of the damaged sample almost disappeared after 48 h at room temperature and its toughness could be fully recovered. The above design strategies provide novel perspectives for designing fast room temperature self-healable polyurethanes with high mechanical strength by choosing motifs that can form irregular multiple hydrogen bonds or using steric hindrance effects to destroy the regular arrangements of multiple hydrogen bonds.

Besides the multiple hydrogen bonds formed by the above-mentioned urea groups, the 2-ureido-4-pyrimidone (UPy) motifs that can form quadruple hydrogen bonds have also been introduced into the mainchain, sidechain and chain end of the polymer chains for the construction of room temperature self-healing polyurethanes [69]. Bao et al. [70] introduced UPy units of the varying amounts (from 0 to 30 mol %) in the polymer mainchains to prepare polyurethanes (SPMs 0–3) via condensation polymerization of polytetramethylene glycol (PTMG), isophorone diisocyanate (IPDI) and UPy units (Fig. 9a). The quadruple hydrogen bonds formed by UPy units significantly improved the mechanical strength of the material. Compared with SPM-0 (0% UPy) that behaved as a viscoelastic fluid, SPM-3 (30% UPy) showed

the strain at break of 3100% and tensile strength of 3.74 MPa. Benefiting from reversible quadruple hydrogen bonds and soft PTMG segments, the healing efficiency of SPM-2 (20% UPy) fracture strain reached 88% of the original value ($\sim 15,000\%$) after healing for 48 h at room temperature. However, the tensile stress of SPM-2 was only 0.91 MPa.

The multiple hydrogen bonds in the main chain can effectively increase the mechanical properties of the polymers, but they have relatively strong restrictions on the movement of the main chain which may slow down self-healing rate. Recently, our group [71] introduced UPy units into the sidechains of polymers to prepare room-temperature self-healing waterborne polyurethanes (DSe-WSP) (Fig. 9b). Thanks to interactions of quadruple hydrogen bonds formed by UPy, the tensile strength, fracture strain and toughness increased from 12.54 MPa, 707.6% and 49.0 MJ m^{-3} for DSe-WSP-1 (without UPy) to 15.34 MPa, 762.3% and 69.1 MJ m^{-3} for DSe-WSP-3 (with 2.5% UPy), respectively, displaying the reinforcing and toughening effects of quadruple hydrogen bonds. Due to reversible nature of quadruple hydrogen bonds, the healing efficiency of tensile stress significantly increased from 64.1% (DSe-WPU-1) to 83.9% (DSe-WSP-3) after healing for 2 h at room temperature.

The end part of macromolecular chain is less bound than the middle part of the chain and has greater motion ability, which means that multiple hydrogen-bonding motifs that located at the chain end may be better for room temperature self-healing rate of polymer. Pan et al. [72] synthesized isocyanate terminated prepolymers using PEG-diol, PPG-triol and IPDI, and then added

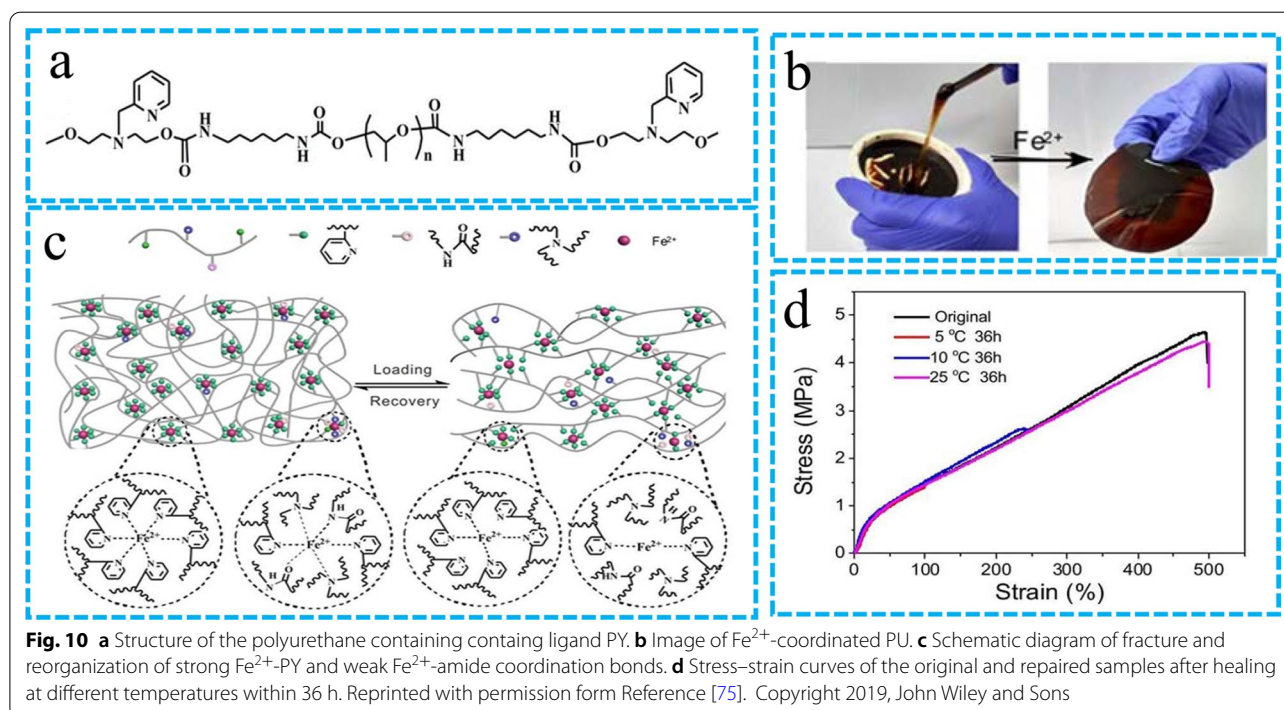


2-amino-4-hydroxy-6-methylpyrimidine (AHMP) for the end-capping reaction to obtain a series of UPy terminated self-healing polyurethane elastomers (PU-AHMP) (Fig. 9c). The quadruple hydrogen bonds formed at the chain end could significantly improve the mechanical strength of the materials. The Young's modulus of PU-AHMP increased from 1.86 ± 0.16 MPa (PU1/5-AHMP-0) to 3.02 ± 0.10 MPa (PU1/5-AHMP-0.5). In addition, the optimized sample had remarkable healing capacity based on reversible quadruple hydrogen bonds of UPy, where the end-capping effect of UPy could avoid the formation of cross-linkings in the middle of the chain structure, effectively reducing obstruction to the movement of the chain segments. Accordingly, the healing efficiency of the elongation at break reached 97% after 1440 min at room temperature. Quadruple hydrogen bond units (UPy) have been introduced into different positions of different polyurethane networks to synthesize a series of room-temperature self-healable polyurethanes. However, the influence of multiple hydrogen bonds at different positions within the same polyurethane network on room temperature self-healing performance still needs to be further studied.

3.2 Metal–ligand coordination bonds

As typical dynamic noncovalent bonds, metal–ligand coordination bonds have moderate bond energy, which is between vander waals force and covalent bond energy and there are a large number of easily available ligands

and metal ions, which makes them very attractive in the field of self-healing materials [73]. Metal–ligand coordination bonds with moderate bond energy offer two advantages: on the one hand, they are weaker than the strong dynamic covalent bonds and show more rapid dissociation and reorganization, thus giving the materials better self-healing ability; On the other hand, they have higher strength than the general dynamic noncovalent bonds which enables the materials to have better mechanical properties [40–42]. Therefore, the introduction of coordination bonds into materials is considered as an ideal method to give them desirable mechanical properties and room temperature self-healing capacity. Bao et al. [74] synthesized polyurethanes containing β -diketonate ligands in the main chain through step polymerization of curcumin, PTMG, IPDI and BDO, and then added europium (III) trifluoromethanesulfonate ($\text{Eu}(\text{CF}_3\text{SO}_3)_3$) for coordination assembly to obtain room-temperature self-healing polyurethanes containing metal–ligand bonds and hydrogen bonds. Benefiting from dual dynamic bonds and microphase separation structure, the optimized polyurethane sample possessed excellent mechanical properties with tensile stress of 1.8 MPa and fracture strain $\approx 900\%$. Due to the dynamic reversibility of hydrogen bonds and coordination bonds, the fracture strain of damaged material could be recover to 98% after healing at room temperature for 48 h. Gai et al. [75] synthesized a polyurethane containing ligand PY via polyaddition reaction using N-(2-Pyridylmethyl)



iminodiethanol (PY), hexamethylene diisocyanate (HDI) and poly (pro-pylene glycol) (PPG) (Fig. 10a), which was then coordinated with Fe^{2+} to form a metal-coordinated polymer (Fig. 10b). By adjusting the molar ratios of monomers and Fe^{2+} dosage, the optimized polyurethane showed tensile stress of 4.6 MPa, strain at break of 498% and Young's modulus of 3.2 MPa, respectively. The cleavage and recombination of the strong Fe^{2+} -PY and weak Fe^{2+} -amide coordination bonds endowed PU with excellent room temperature self-healing capacity (Fig. 10c). The self-healing efficiency (as calculated with tensile stress) of the fractured samples reached approximately 96% at room temperature and 30% at low temperature (5°C), as shown in Fig. 10d. As mentioned above, the properties of self-healing polyurethanes are affected by the type of metal ions. Recently, Xu et al. [76] introduced dopamine into the end of polyurethane chain and then added CaCl_2 to form a polymer material containing Ca^{2+} -catechol coordination bonds. Rheological experiments indicated that the Ca^{2+} -catechol coordination bonds could dissociate and associate obviously at room temperature with the aid of seawater. Based on this, the toughness of the damaged polymer could be recovered to 84% after 24 h healing at room temperature.

3.3 Ionic bonds

Ionic bonds are formed by electrostatic interactions between cations that lose electrons and anions that gain electrons. Ionic bonds have the characteristics of non directivity and saturation and have higher interaction strength than hydrogen bonds.

The self-healable function of polyurethanes can also be realized by introducing ionic bonds. Bossion et al. [77] prepared water-dispersible non-isocyanate

polyhydroxy-urethanes from aminoalkyl-terminated poly(dimethylsiloxane), diglycerol dicarbonate and a 8-membered cyclic carbonate via phase inversion polymerization. Then multifunctional carboxylic acids were added for post-chemical modification. Taking advantage of dynamic ionic interactions of tertiary ammonium cations and carboxylate anions, the damages of the resulting film surface could be mended at room temperature for 1 h (Fig. 11). Moreover, Wen et al. [78] used N,N-bis(2-hydroxyethyl) isonicotinamide, HDI and 1,3-propanesultone as raw materials to synthesize humidity-responsive self-healable and shape-memory zwitterionic polyurethanes through polymerization and ring opening reactions. The resulting polyurethane had both N^+ cations and SO_3^- anions, which generated electrostatic interactions that endow the material with self-healing ability. Since hydration can improve the mobility of ions at the fracture surface of samples, the healing efficiency of the fracture strain reached 95% after healing at 25°C for 24 h under 90% relative humidity. Importantly, the healed polyurethane sample exhibited excellent shape memory effects with a shape fixation rate of 100% and a shape recovery rate of 88.2%. Daemi et al. [79] fabricated self-healing and biodegradable alginate-based polyurethanes based on ionic bonds by reacting NCO-terminated prepolymers containing tertiary amine cations with alginate containing carboxyl anions. The ionic interactions endowed the polyurethane with fine mechanical properties including a tensile stress of 48.1 MPa and a fracture strain of 859.5%. Meanwhile, the resulting polyurethane possessed outstanding self-healing capacity. The room temperature healing efficiency of the damaged sample was 87.3% and 70.2% in the first and third healing, respectively. The results indicated that the strong

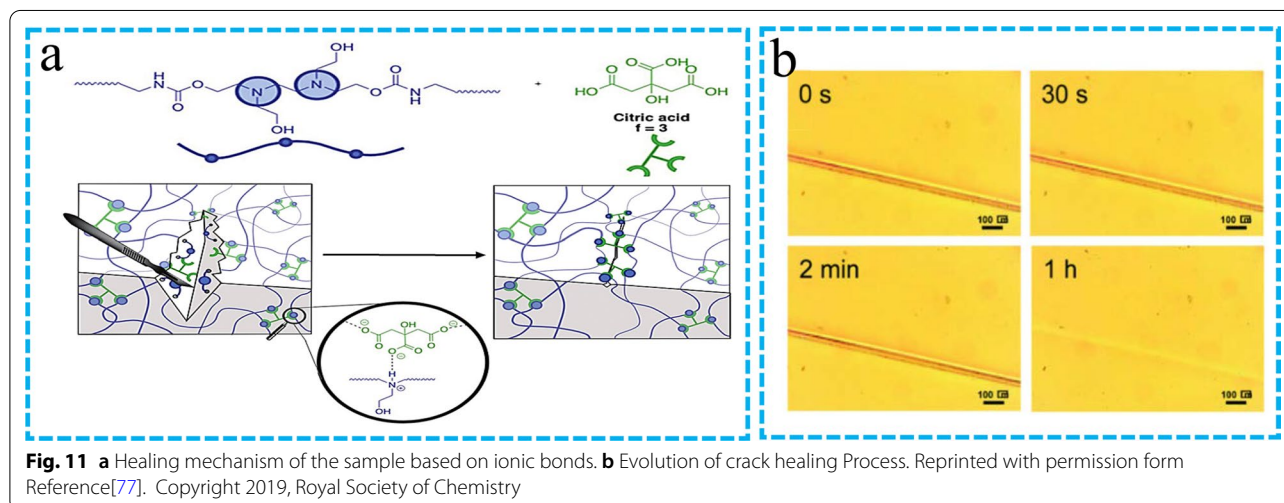


Fig. 11 a Healing mechanism of the sample based on ionic bonds. b Evolution of crack healing Process. Reprinted with permission from Reference [77]. Copyright 2019, Royal Society of Chemistry

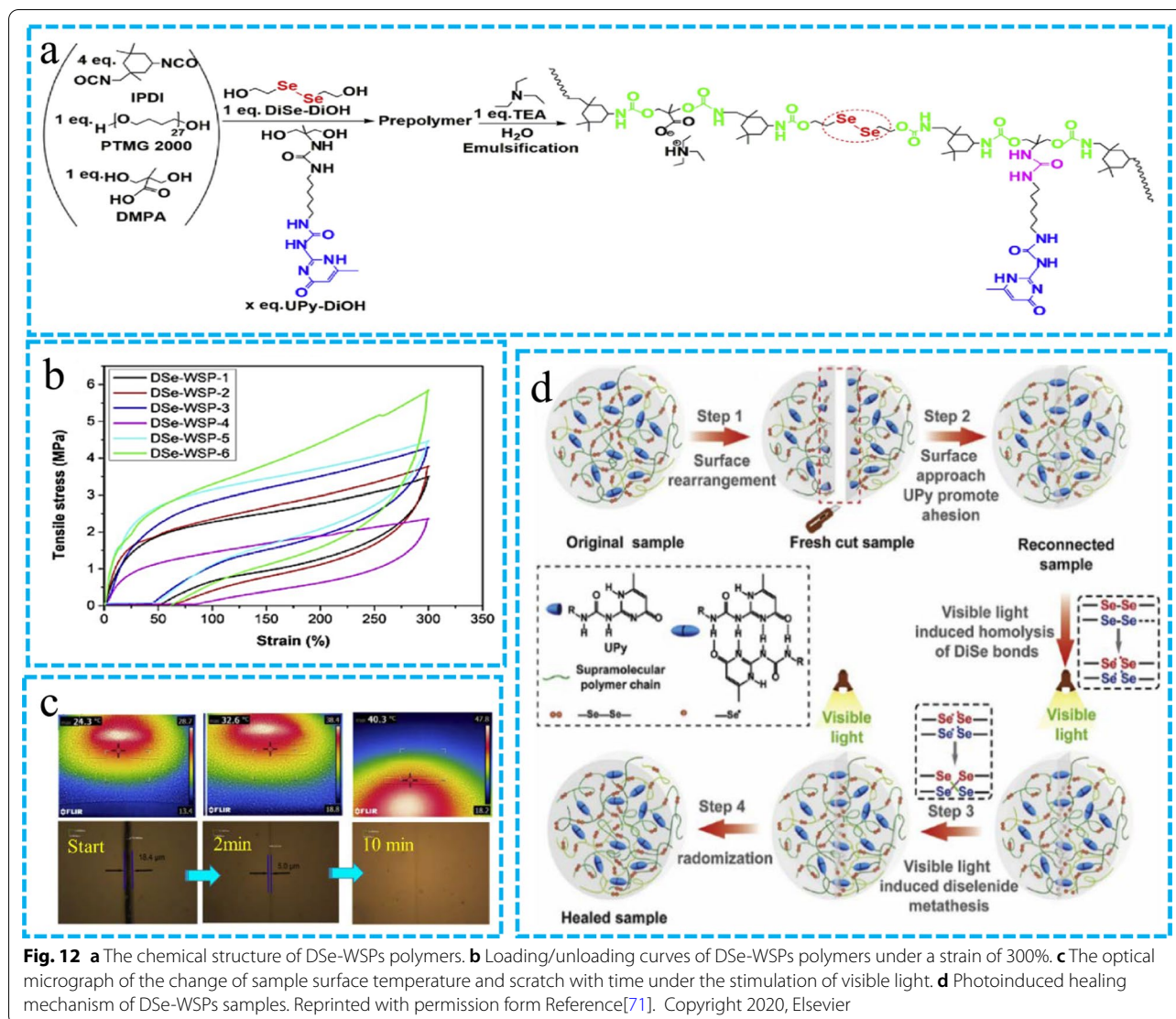


Fig. 12 a The chemical structure of DSe-WSPs polymers. b Loading/unloading curves of DSe-WSPs polymers under a strain of 300%. c The optical micrograph of the change of sample surface temperature and scratch with time under the stimulation of visible light. d Photoinduced healing mechanism of DSe-WSPs samples. Reprinted with permission from Reference[71]. Copyright 2020, Elsevier

affinity of the cationic polyurethane chain to the carboxylate anions of alginate was the main factor affecting the self-healing and mechanical properties.

4 Combined dual or triple dynamic bond systems

The materials based on weak dynamic chemical bonds have fast healing rate, but tend to have poor mechanical properties. Conversely, the materials based on strong dynamic bonds have better mechanical properties but require longer time to complete self-healing. Therefore, it is difficult for materials relying on a single dynamic chemical bond to have high self-healing rate and excellent mechanical properties at the same time. To resolve this contradiction, the combination of multiple dynamic bonds is an effective strategy [80]. Compared with a single dynamic bond, the dynamic effect of multiple dynamic bonds is stronger, which is beneficial to

the rapid healing of materials. Meanwhile, the stronger dynamic bonds can support the material structure and help to form a strong molecular network, while the weaker dynamic bonds as sacrificial bonds can preferentially break when the material is subjected to external force to dissipate energy of the system, thereby improving the toughness of the material. Recently, multiple dynamic bonds have been incorporated into polyurethane networks to optimize mechanical strength and room temperature repair efficiency.

Xu et al. [81] synthesized a novel dual dynamic cross-linked room-temperature self-healing polyurethane containing multiple hydrogen bonds and zinc-imidazole coordination bonds. The optimized PU sample displayed excellent mechanical performances (tensile strength of 10.01 MPa, stretchability of 2050% and toughness of 77.46 MJm⁻³). In this system, the weaker multiple

hydrogen bonds dissipated energy effectively to improve toughness of the polymer network, while the stronger coordination bonds could maintain the integrity of the polymer structure to improve tensile strength. Taking advantage of double dynamic interactions of zinc–imidazole coordination bonds and multiple hydrogen bonds, the healing efficiencies of tensile strength and strain at break reached 71.2–87.8%, respectively after healing at room temperature for 48 h.

Based on dynamic diselenide bonds and quadruple hydrogen bonds, our group [71] synthesized novel room temperature self-healing waterborne polyurethanes (DSe-WSPs), as shown in Fig. 12a. When the UPy groups were introduced into the WPUs, the high stretchability and robustness of materials were achieved due to formation of strong quadruple hydrogen bonds. The dissipated energy (strain of 300%) of the sample increased from 4.02 MJ m⁻³ for DSe-WSP-1(without UPy) to 4.53 MJ m⁻³ for DSe-WSP-3(with 2.5% UPy) (Fig. 12b). The results indicated that the quadruple hydrogen bonds acting as sacrifice bonds could effectively dissipate energy. The as-synthesized WPU-WSPs exhibited prominent mechanical performances (tensile strength of 15.34 MPa, fracture strain of 762.3% and toughness of 69.1 MJ m⁻³). Because of dual dynamic effects of diselenide bonds and quadruple hydrogen bonds, the DSe-WSP-3 sample exhibited fast healing behavior at room temperature. The cracks almost completely disappeared after irradiating of visible light for 10 min (Fig. 12c). The healing mechanism is shown in Fig. 12d. The fast reconstruction of quadruple hydrogen bonds promoted the close adhesion of fractured surfaces and the visible light efficiently triggered diselenide exchange reaction, so a quite fast healing process of the sample could be realized finally. Strikingly, the healed sample recovered more than 95.0% of its tensile stress under visible light (light intensity of ~200,000 Lux) for 10 min.

In addition, a more complex room-temperature self-healing polyurethane network system based on triple dynamic bonds has also been developed. Zhang et al. [82] synthesized a dimethylglyoxime-urethane (DOU) network using PTMG-1000, IPDI, TDI, glycerol and dimethylglyoxime (DMG), and followed by addition of CuCl₂ for coordination crosslinking, resulting in a room temperature self-healing polyurethane with triple dynamic bonds (DOU bonds, hydrogen bonds, and Cu–DOU coordination bonds). The as-synthesized polyurethane showed exceedingly excellent mechanical properties with tensile stress of 14.8 MPa and toughness of 87.0 MJ m⁻³. That is because the hydrogen bonds and coordination bonds with smaller bond energy were easier to dissociate, which consumes more energy and increases toughness. Meanwhile, the relatively strong covalent bonds ensured the

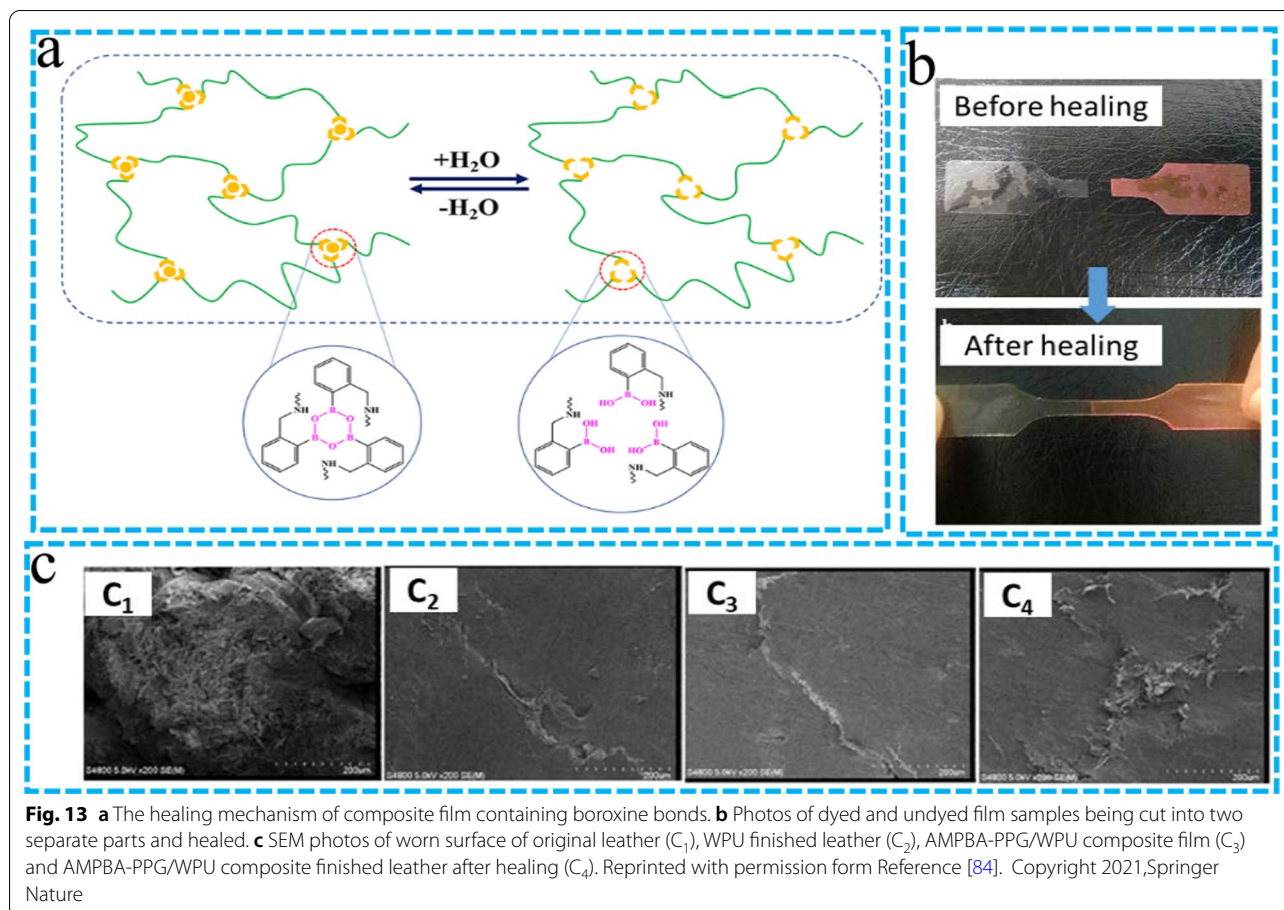
integrity and strength of the material. Particularly, the coordination bonds accelerated the exchange reaction of DOU groups. Benefiting from synergistic effect of triple dynamic bonds, the tensile stress of materials could be recovered to 13.8 MPa within 130 h at room temperature, and the healing efficiency reached 92%.

5 Current applications of room-temperature self-healing polyurethanes

5.1 Leather coatings

Polyurethanes with excellent adhesion, weather resistance and chemical corrosion resistance and decoration have been widely used in the field of leather coatings. However, it is inevitable that the leather coatings will be damaged due to external forces such as scratching and bumping, which affects their protective function and appearance. Considering the denaturation of collagen at high temperature, endowing polyurethanes with room-temperature self-healable function is of great importance to prolong the service life of leather coatings. Previously, Liang et al.[83] synthesized a self-healing waterborne polyurethane containing disulfide bonds in the main chain by using HEDS as chain extender. With the help of shape memory and disulfide bonds exchange reactions, the tensile strength healing efficiency of fractured samples could reach 80% after being treated at 60°C for 12 h. The waterborne polyurethane was coated on the leather surface to form a coating. The coating was scratched by a medical blade and treated in an oven at 60°C for 12 h. As a result, the scratches could be completely repaired, showing good self-healing ability. However, the repair temperature was relatively high.

Recently, Liu et al. [84] synthesized a boroxine-bonded cross-linked polymer network (CLP-boroxine) via dehydration and condensation of phenylboric acids terminated PPG (AMPBA-PPG). Then, a composite emulsion was prepared by mixing CLP-boroxine and WPU for leather finishing. Due to the dynamic boroxane bonds (Fig. 13a) and hydrogen bonds, the CLP-boroxine/WPU film visually displayed superior healing properties (Fig. 13b), and the tensile stress of the fractured sample could be recovered to 93.6% after healing at room temperature for 4 h under the assistance of water. Then, AMPBA-PPG/WPU composite emulsion formed a coating on leather, which improves leather performance. The CLP-boroxine effectively improved the wear-resistance of leather through the interaction between boric acid hydroxyl groups and collagen surface hydroxyl groups. The results of wear-resistance test showed that compared with pure WPU, the wear index leather coated with AMPBA-PPG/WPU composite film decreased by 11.8~15.9%. Moreover, compared with the original leather, both WPU and AMPBA-PPG/WPU coated



leather did not expose large amounts of collagen fibers after wear-resistance testing, indicating that they have excellent protective function (Fig. 13 C1-C3). Notably, the leather samples coated with AMPBA-PPG/WPU still displayed good wear-resistance after healing (Fig. 13 C4).

Room temperature self-healing polyurethanes provide great protection for leathers and extend their lifespan. However, a single self-healing function cannot meet the needs of leather coatings. It is necessary to introduce functional monomers or nanomaterials into polyurethanes to endow them with antibacterial, antifouling, flame retardant and waterproof properties, thereby improving quality and added value of leathers.

5.2 Photoluminescence materials

The introduction of photoluminescence into the room temperature self-healing polyurethanes can further broaden their application range including coating material, route signs, LED and optical anti-counterfeiting. Recently, Lei et al. [85] added polyimine(PEI) into carboxyl-type WPU to prepared cross-linked CWPU (WPU). The primary, secondary and tertiary groups in the PEI molecular structure reacted with WPU to form

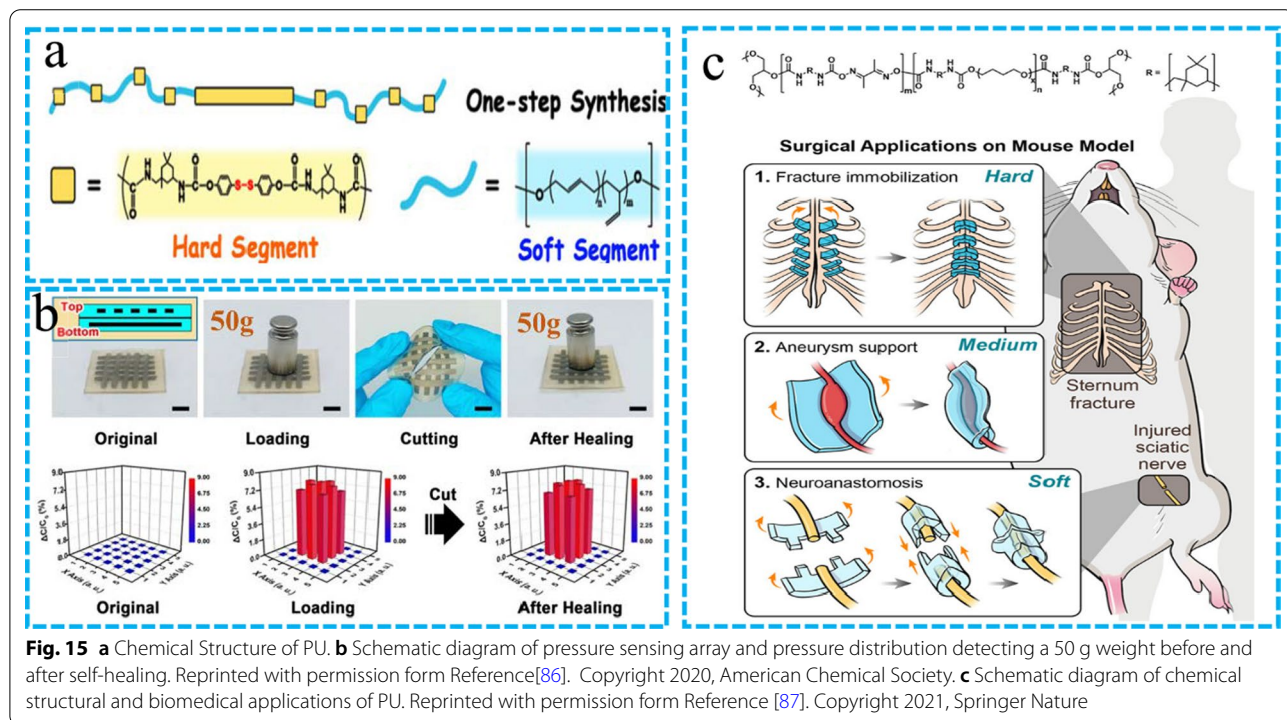
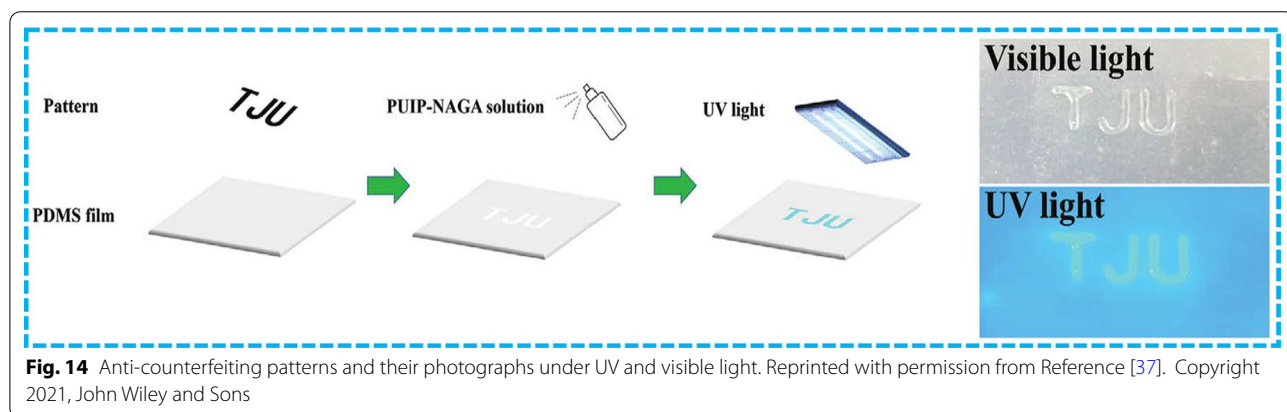
ionic bonds and hydrogen bonds, which improve healing ability and mechanical properties of WPU. The WPU showed high tensile strength of 17.12 MPa and elongation at break of 512.25%, respectively. Because of dynamic ionic bonds and hydrogen bonds, the tensile stress and fracture strain could recovered to 3.26 MPa and 450.94% after healing at 30°C for 24 h. As coating materials, the transmittances of WPU are higher than 75%, indicating their excellent optical properties. The light transmittance of the optimized WPU sample decreased from 76.76 to 17.09% after scratching, and recovered to 65.41% after healing at 30 °C for 24 h, indicating that it had good corrosion resistance. Furthermore, the carbon quantum dots (CQs) were introduced into CWPU to prepare WPU/CQs mixture, which was subsequently coated on quartz glass to form luminescent coating. Pure WPU coating did not emit light under ultraviolet light, while WPU/CQs coating emitted blue fluorescence, demonstrating that it had a new photoluminescence function.

Additionally, Yao et al. [37] synthesized a room temperature polyurethane with AIE fluorescence based on multiple hydrogen bonds using IPDI, PTMG and a T-shaped diol carrying double amide groups. The double amide

groups formed dynamic multiple hydrogen bonds, which render PU fine mechanical properties and room-temperature self-healing ability. Interestingly, the resulting PU showed strong AIE blue fluorescence under UV light irradiation, because multiple hydrogen bonding interactions led to the aggregation of tertiary amines groups, which enhances the $n-\pi^*$ transition. Furthermore, the patterns printed with the PU solution hid under visible light but emerged under UV light, demonstrating its potential as an anti-counterfeiting ink (Fig. 14).

Photoluminescence property offers potential fluorescent anti-counterfeiting function for polyurethane. Therefore, polyurethane with anti-counterfeiting and

room temperature self-healing functions can provide multiple protections for valuable products such as mobile phones, cars, computers and important certificates. However, current photoluminescent polyurethane materials mainly emit monochromatic light under the stimulation of ultraviolet light, which can be easily faked. Therefore, it is the future development direction to prepare room temperature self-healing polyurethanes with multiple luminescence properties that are difficult to be replicated and have higher anti-counterfeiting levels.



5.3 Flexible electronics

Polyurethanes are widely used as substrates of flexible electronics due to their unique flexibility. However, flexible electronic devices are damaged due to long-term bending, folding and scratching during use, which shortens the service life of the devices and reduces the reliability of devices operation. Therefore, endowing flexible electronic materials with room temperature self-healing function can not only prolong their service life, but also ensure their application reliability. Ying et al. [86] synthesized a room temperature self-healing waterproof polyurethane material and used it as a substrate for electronic skin. The polyurethane was prepared using hydroxyl-terminated polybutadiene (HTPB), Bis(4-hydroxyphenyl)-disulfide (HPS) and isophorone diisocyanate (IPDI) by one pot polycondensation reaction (Fig. 15a). Then, the galinstan was added into polyurethane matrix to prepare electronic skin. The resulting PU displayed outstanding performances (tensile stress of 11.8 MPa, elongation at break of 618% and toughness of $27.5 \pm 0.3 \text{ MJ m}^{-3}$). The hydrophobic polybutadiene segments rendered polyurethane excellent water resistance. Furthermore, due to dynamic aromatic disulfide bonds, the mechanical properties of the damaged sample healed efficiently with time and reached 93% of virgin values after healing at 25 °C for 6 h. The tensile strength of the resulting PU showed little change after 1000 cyclic stretching at 100% strain, indicating its excellent fatigue resistance. The galinstan was added into polyurethane matrix to prepare electronic skin. It is found that the prepared electronic skin had excellent hydrophobicity and self-healing properties. After immersing into water for 3 days, its shape, microstructure and electrical conductivity could remain stable. In addition, the functional of damaged electronic skin was recovered again after healing at 25°C for 6 h and it successfully distinguished the pressure distribution of a 50 g weight which was almost the same as that of the original sample, as displayed in Fig. 15b.

Si et al.[43] fabricated a flexible antenna by doping conductive silver flakes with WPU-PEI complex for communication, which had excellent electrical conductivity (4000 S cm^{-1}). A room temperature self-healing WPU-PEI complex was prepared by mixing positively charged PEI aqueous solution and negatively charged WPU emulsion. Due to ionic interactions, hydrogen bonds and polymer chain entanglement, flexible antenna possessed excellent self-healing ability. After being cut and healed at room temperature for several seconds in water, the conductivity of the antenna was recovered rapidly, because the triple non-covalent interactions quickly established the contact between the broken surfaces, though it needs

three hours to restore the mechanical properties. Plus, the conductivity of healed antenna showed excellent stable over repeated stretching (50% strain) and release cycles. Furthermore, the designed PU-PEI antennas can be used for Wi-Fi or Bluetooth.

The room-temperature self-healing polyurethanes enable the electrical and mechanical properties of flexible electronics to be restored under mild conditions. As substrates, room temperature self-healing polyurethanes have broad application prospects in the field of flexible electronics. At present, the conductivity of room temperature self-healing polyurethanes is mainly achieved in two ways: one is that the conductive materials are attached to the surface of the polymers; the other is that the conductive materials are integrated into the polymer matrix. Regarding the first way, the conductive material may fall off after many uses, which reduces the service life of the materials. With regard to the second method, the conductive material has poor compatibility with the substrate and low adhesion, which leads to the problem of delamination, thereby reducing the overall mechanical properties, electrical conductivity and self-healing properties of flexible electronics. Therefore, it is expected to develop room-temperature self-healing polyurethanes with excellent electrical conductivity by increasing the interactions between the conductive materials and the substrates surface or modifying the conductive materials to increase their compatibility with the substrates.

5.4 Biomaterials

Polyurethanes have been widely used in the field of biomaterials because of their wear resistance, low cost and chemical stability and good biocompatibility. However, biomaterials are inevitably damaged in use process, causing great harm to the life and health of patients. Endowing biomedical materials with self repairing function can not only prolong their service life, but also ensure their application security. Recently, You et al.[87] designed polyoxime urethane elastomers using DMG, PTMG, IPDI and glycerol with adjustable mechanical properties, biocompatibility, biodegradability and excellent spontaneous self-healing in physiological environment. The resulting polyurethanes could heal insitu at the lesion in vivo and assemble to form repair devices. The devices can replace sutures and wires in the traditional surgical treatments such as abdominal aortic aneurysms, nerve junctions and sternal fixation. This strategy effectively avoids the secondary damage to the lesion and surrounding tissues, greatly facilitates the surgical operation and improves the surgical effect (Fig. 15c). Eom et al.[39] synthesized self-healing carbonate polyurethanes based on dynamic aromatic disulfide bonds. It was found that the polyurethane had good healing capacity and biocompatibility.

The tensile stress, breaking strain and toughness of an optimized sample were 42.9 MPa, 480% and 75.1 MJ m⁻³, respectively, which could recover 77.2%, 82.7% and 64.6%, respectively, after healing at 35°C for 48 h. When the polyurethanes were immersed in cell culture dishes, their toxicity to cells was negligible. In addition, there is no obvious inflammation symptoms when the samples were implanted into subcutaneous regions of rats for 12 weeks. The good biocompatibility of the obtained polyurethanes demonstrated their promising application in biomedical applications.

Considering the temperature of the human body, room temperature healing performances are crucial for polyurethanes in biomaterial applications. However, achieving effective self-healing in complex physiological environments (such as the stomach with acid environment, joint cavity with high load, etc.) remains a challenge, as current room-temperature self-healing of the vast majority of polyurethanes are realized in natural environment. Moreover, the repair mechanisms and performance requirements of polyurethane materials used in different tissues need to be further explored. The self-healing polyurethanes undergo dissociation and recombination of

molecular segments during the self-healing process, and are eventually degraded in vivo. There, the toxicity to cells of the dissociated and degraded products of polyurethanes also needs to be studied intensively, which is crucial for biological safety.

6 Conclusions and outlooks

This paper reviews the recent developments of intrinsic room temperature self-healing polyurethanes based on different types healing mechanisms such as dynamic covalent bonds, non-covalent bonds, and combinatorial intrinsic mechanisms. The mechanical properties, healing efficiency, healing time of room self-healing polyurethanes are summarized in Table 3. With the adoption of new mechanisms and strategies, the mechanical properties and room-temperature self-healing ability of polyurethane materials have been significantly improved. However, there are still many challenges in practical applications. It is still a difficult problem to synthesize polyurethane materials with fast self-healing speed and high mechanical properties at room temperature. Hence, novel strategies still need to be put forward to resolve this contradiction.

Table 3 Summary of the healing mechanisms, mechanical properties, healing time and healing efficiency of room-temperature self-healing polyurethanes

Healing mechanisms	Mechanical properties			Healing time/h	Healing efficiency/%	Reference
	Tensile stress/MPa	Fracture strain/%	Toughness /MJ m ⁻³			
Disulfide bond	6.76	923	26.9	2	88.2	[48]
Disulfide bond	11.0	725	52.1	48	83.1	[21]
Disulfide bond	11.8	618	27.5	6	93	[86]
Diselenide	4.60	592	–	48	90.4	[24]
Diselenide/H-bonding	16.31	885	69.8	2	80.5	[26]
Diselenide/H-bonding	15.34	762.3	69.1	0.17	95	[71]
Ditelluride/H-bonding	19.47	114.3	105.2	0.17	85.6	[28]
Imine bond	~0.18	255	–	2	98.1	[58]
Imine bond	14.32	990	64.8	24	83.8	[59]
Boroxine bond	47	960	190	8	~100	[61]
Multiple H-bonding	4.83	2010	65.49	48	~100	[68]
Multiple H-bonding	0.91	15,000	–	48	88	[70]
Multiple H-bonding	1.93	1508	–	24	97	[72]
Coordination bond	1.8	900	–	48	98	[74]
Coordination bond	4.6	498	–	36	96	[75]
Coordination bond	1.34	430	4.4	24	84	[76]
Ionic bond	~39	~12	–	24	95	[78]
Ionic bond	48.1	859.5	–	–	87.3	[79]
Coordination/ H-bonding	10.01	2050	77.46	48	87.8	[81]
DOU bond/Coordination/ H-bonding	14.8	1200	87.0	130	92	[82]
Boroxine/ H-bonding	18.15	680	–	4	93.6	[84]
Ionic/ H-bonding	17.12	512.25	–	24	19.04	[85]

In addition, the current room-temperature self-healing polyurethanes often require complex synthesis steps and expensive functional monomers. Therefore, it is of great significance to prepare room-temperature self-healing polyurethane using simple and low-cost methods for coming industrial production. Of course, there will be good opportunities to solve the problems mentioned above with the developments of synthetic and supramolecular chemistry. Currently, a single self-healing function can not meet the development requirements of high-value materials. Therefore, introducing more functions into room-temperature self-healing polyurethane materials has broad application prospects in the future high-tech field such as artificial intelligence [12], biomedical engineering [87], high-level anti-counterfeiting [88, 89].

Abbreviations

PUs: Polyurethanes; TDS: Thiuram disulfide; PTMG: Polytetramethylene ether glycol; IP: Isophorone diisocyanate; SS: Bis(4-hydroxyphenyl) disulfide; WPU: Waterborne polyurethanes; DiSe: Di(1-hydroxyethylene) diselenide; DMPA: Dimethylolpropionic acid; IPDI: Isophorone diisocyanate; BDO: 1,4-Butanediol; FS: Fluorinated siloxane units; Dite-Diol: Ditoluride-diol; UPy: 2-Ureido-4-[1H]-pyrimidinone; ASB: Aromatic schiff base; DiASB-DiOH: *N,N'*-(4-hydroxy-benzylidene) aniline methane; DSe-WSP: Self-healing waterborne polyurethane containing diselenide bond; DTe-WSPs: Self-healing waterborne polyurethane containing ditelluride bond; AHMP: 2-Amino-4-hydroxy-6-methylpyrimidine; SPM: Supramolecular polymeric materials; PEG-diol: Polyethylene glycol; PPG-triol: Poly(propylene glycol)s; NCBs: Nitrogen-coordinated boroxines; PUUs: Poly(urea-urethane)s; C-ON: Alkoxyamine bond; CTPO: 5-Hydroxy-2-(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy)-2-methyl pentanenitrile; Eu (CF₃SO₃)₃: Europium (III) trifluoromethanesulfonate; PY: Pyridine; HDI: Hexamethylene diisocyanate; IZ/Zn: Zinc-imidazole interaction; DOU: Dimethylglyoxime; MPBA-PPG: Poly(propylene glycol) terminated with ortho-amiomethylphenyl diboric acid; CLP-boroxine: Cross-linked polymer containing boroxine; PEL: polyimine; CQs: Carbon quantum dots; HTPB: Hydroxyl-terminated polybutadiene; HPS: Bis(4-hydroxyphenyl)-disulfide; DMG: Dimethylglyoxime.

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Author contributions

YJ: Designing the outline of the draft and revising the draft from the language and logic aspects; YPL: writing this review article and summarizing the literatures; WHF and RZ: collecting references, proposing opinions. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets analyzed during the current review are available in the references, which have been specified in the article.

Declaration

Competing interests

The authors declare that they have no competing interests.

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