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REVIEW

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Dynamic Oxime-Urethane Bonds, a Versatile Unit of High Performance Self-healing Polymers for Diverse Applications

Luzhi Zhang and Zhengwei You*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Shanghai Belt and Road Joint Laboratory of Advanced Fiber and Low-dimension Materials (Donghua University), College of Materials Science and Engineering, Shanghai Engineering Research Center of Nano-Biomaterials and Regenerative Medicine, Donghua University, Shanghai 201620, China

Abstract Oxime-urethane bond featuring with high reversibility even at room temperature and multiple reactivity is an emerging dynamic covalent bond, and has shown great potential for self-healing polymers, which are one of the most attractive development directions for next generation of polymeric materials. In this review, recent progresses on the oxime-urethane-based self-healing polymers, including their designs and applications in diverse fields such as biomedicine, flexible electronics, soft robots, 3D printing, protective materials, and adhesives, are summarized, and outlooks on the future development of this field are discussed.

Keywords Self-healing; Dynamic covalent bonds; Polyurethane; Covalent adaptable networks; Metal coordination

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INTRODUCTION

Living creatures can spontaneously heal wounds to reduce further damage.[1] Inspired by nature, imparting self-healing properties to materials is a promising way to solve the partial or complete failure of materials caused by the inevitable damage in service leading to extended service life, enhanced safety, and reduced maintenance cost.[2] Accordingly, self-healing materials have been extensively studied.[3−5]

In the early stage, the self-healing materials usually embed healing agents (*e.g.*, monomer, catalyst) inside. When the materials are damaged, the healing agent will be released and heal the materials.[6−8] Although these extrinsic self-healing materials have reliable healing processes, the healing times of the materials are limited due to the exhaustion of the healing agent. Intrinsic self-healing materials based on dynamic bonds can theoretically heal unlimited times, and have become the major direction of self-healing materials.[9] The dynamic bonds used to design self-healing materials include noncovalent interactions (*e.g.*, hydrogen bonds,[10−12] π-π stacking interactions,[13−15] host-guest interactions,[16,17] metal-ligand interactions,[18−21] ionic interactions,[22,23] and van der Waals forces[24,25]) and reversible covalent bonds (*e.g.*, imine exchange,[26,27] hindered urea bonds,[28,29] boroxine bonds,[30−32] disulfide bonds,[33,34] Diels-Alder reaction,[35,36] transesterification reaction,[37,38] and oxime-urethane bonds[39−41]).

Oxime is a blocking agent used in the polyurethane industry to protect isocyanates and can be removed under heating.[42,43] The oxime-urethane group (—C=N—OCONH—) consists of a carbamate group (—NHCOO—) and an imine group (—C=N—). The strong electron withdrawing of the imine bond makes the oxime-urethane bond (—O—N=) unstable and the oxime-urethane groups easily dissociate into oxime and isocyanate groups, which can react again to reform the oxime urethane group. Recently, the oxime-urethane groups have been introduced into the polymer chains to construct self-healing polymers and showed excellent properties.[39−41,44−51] This review focuses on recent progresses on the designs and applications of oxime-urethane-based self-healing polymers. Finally, the current concerns and future perspectives are also discussed.

OXIME-URETHANE-BASED SELF-HEALING POLYURETHANES

The oxime groups can be obtained from the ketone groups or cyano groups through a one-step chemical reaction. Xu and coworkers demonstrated the dynamic exchange of oxime-urethane bonds through a dissociative transcarbamoylation mechanism at high temperature (Fig. 1).[40] They synthesized a multifunctional oximes, which reacted with hexamethylene diisocyanate to prepare a class of catalyst-free poly(oxime-urethanes) (POUs). Due to the hydrogen bonding effect between solvents and oximes, the reaction rate constants in different solvents differ by up to 40 times. Notably, in dichloromethane, the oxime-urethanation showed the highest reaction conversion (99%, 3 h) and the largest second-order

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* Corresponding author, E-mail: zyou@dhu.edu.cn

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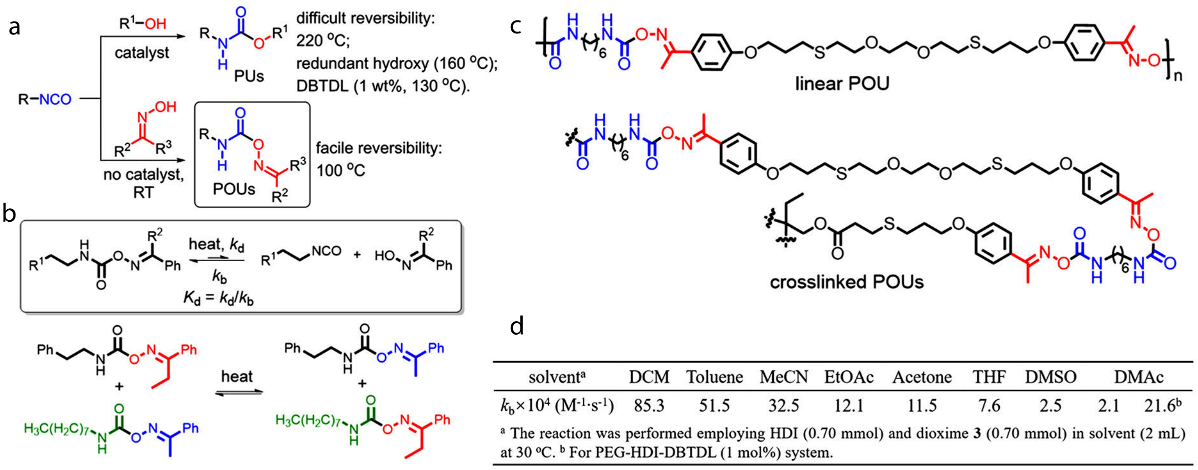

solvent^a	DCM	Toluene	MeCN	EtOAc	Acetone	THF	DMSO	DMAc	
$k_b \times 10^4$ ($M^{-1} \cdot s^{-1}$)	85.3	51.5	32.5	12.1	11.5	7.6	2.5	2.1	21.6^b

^{a} The reaction was performed employing HDI (0.70 mmol) and dioxime **3** (0.70 mmol) in solvent (2 mL) at 30 °C. ^{b} For PEG-HDI-DBTDL (1 mol%) system.

Fig. 1 (a) Preparation and dynamic nature of traditional polyurethanes (PUs) (DBTDL: dibutyltin dilaurate) and POUs. (b) Oxime-enabled transcarbamoylation reaction *via* a dissociative approach. (c) The chemical structure of POUs. (d) Second-order rate constants in different solvents at 30 °C. (Reprinted with permission from Ref. [40]; Copyright (2017) American Chemical Society.)

bonding rate constant (8.5×10^{-3} $M^{-1} \cdot s^{-1}$) at 30 °C. The resultant oxime-urethane bonds were demonstrated to be reversible *via* thermally dissociative mechanism, which enabled the healing and recycling of POUs at 120 °C.

For the construction of self-healing materials, compared with aforementioned laboratory-synthesized oximes, the use of commercially available oximes can greatly simplify the synthesis and is more practical. Xia and coworkers reported a series of healable and recyclable poly(oxime-urethane) elastomers (POUs) based on commercially available dimethylglyoxime (Fig. 2).[44] The healing ratio of tensile fracture strain of POU-0.2 was almost 100% after heating for 120 min at 100 °C or 30 min at 110 °C.

Although the above-mentioned oxime-urethane-based self-healing polymer could self-heal at elevated temperature, considering that the use and damage of materials are mostly under environmental conditions, room temperature self-healing polymers are desired. Compared with chemical cross-linked networks, physical cross-linked polymer chains are easier to move at room temperature and facilitate the self-healing of polymer. Accordingly, our group designed and prepared a physical cross-linked poly(oxime-urethane) (DOU-PU) with the room temperature self-healing property (Fig. 3).[41] However, the tensile strength of DOU-PU (tensile strength ~1.6 MPa) is relatively low for actual use. Considering the ability of dimethylglyoxime unit to coordinate with metal ions, we introduced metal coordination bonds in the oxime-urethane-based polymer for the first time. The inherent hydrogen bonds in the poly(oxime-urethane) and the newly formed Cu(II)-dimethylglyoxime-urethane-complex together built "dual-hard phases", which could dissipate energy during loading, to significantly improve the mechanical properties. As a result, the tensile strength and the toughness of Cu-DOU-PU increased by 8.0 and 11.8 times of DOU-PU, respectively.

More interestingly, in addition to improving the mechanical properties, the introduction of metal ions also facilitated the self-healing of materials due to their unexpected catalytic effect on reversible oxime-urethane dissociation, which was verified by both experiment of small model reaction and density functional theory calculations.[39] Accordingly, we introduced copper ions into cross-linked poly(oxime-urethane) to ob-

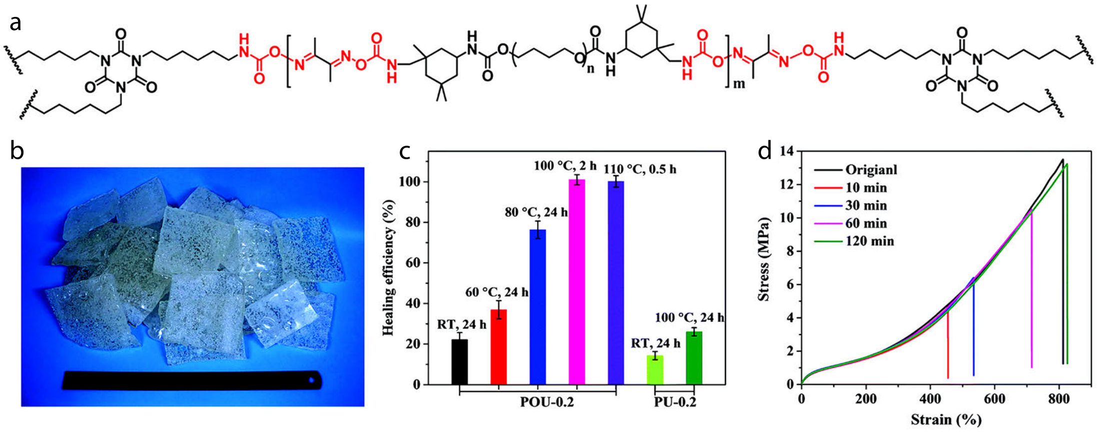

Fig. 2 (a) The chemical structure of POU. (b) Photo of 1 kg of POU. (c) Healing efficiencies of POU under different conditions. (d) The tensile strain-stress curves of original and healed POU. (Reprinted with permission from Ref. [44]; Copyright (2018) The Royal Society of Chemistry.)

tain Cu-DOU-CPU networks with triple dynamic bonds (hydrogen bonds, oxime-urethane bonds, and metal coordination bonds), which exhibited the highest mechanical strength and toughness (tensile strength up to 14.8 MPa, toughness up to 87.0 MJ·m^{-3}) among all the reported room temperature self-healing elastomers (Fig. 3). At the same time, Cu-DOU-CPU maintained a high room-temperature self-healing efficiency (92%). The design of Cu-DOU-CPU provides a novel and powerful strategy for simultaneously enhancing the typically contradictory self-healing efficiency and mechanical strength.

Besides, the oxime-urethane groups possessed the ability of diverse chemical transformation. As an example, we investigated the photolysis of poly(oxime-urethane) to generate amino groups under ultraviolet irradiation (Fig. 3). This property may have potential for applications such as construction of superhydrophobic/superhydrophobic surfaces and grafting of biologically active substances of self-healing materials.

The design principle to simultaneously enhance the tensile strength and promote self-healing properties by introducing metal coordination, has been further demonstrated by other researchers. Lu and coworkers designed a mechanically robust and autonomous self-healing network (Cu-DMG-SS) based on multiple reversible interactions including oxime-urethane bonds, disulfide bonds, hydrogen bonds and metal coordination bonds, with tensile strength of 19.5 MPa and self-healing efficiency of 83% at room temperature (Fig. 4).[50] Notably, in addition to promoting the reversible dissociation of the oxime urethane-bond, copper ions could also accelerate disulfide exchange in Cu-DMG-SS.

Researchers further studied the influence of the structure of the oxime on the self-healing and mechanical properties of the material. Wei and coworkers reported an engineered self-

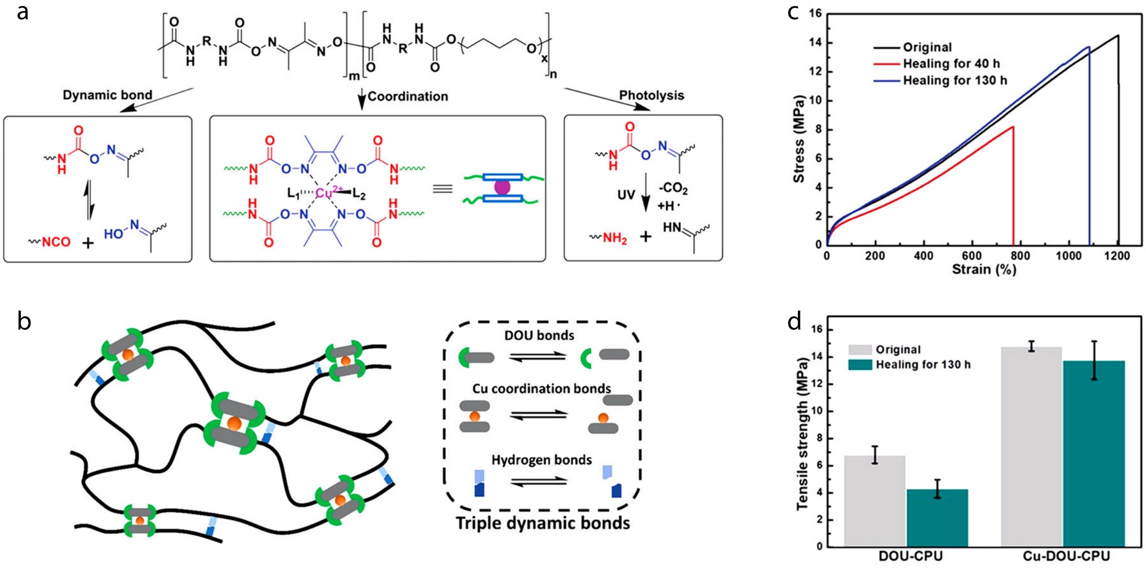

Fig. 3 (a) The chemical structure of DOU-PU and the multiple reactivities of oxime-urethane groups. (b) Schematic structure of Cu-DOU-PU. (c) The tensile strain-stress curves of original and healed Cu-DOU-PU. (d) Tensile strength of original and healed DOU-CPU and Cu-DOU-CPU. (Reprinted with permission from Refs. [39,41]; Copyright (2019) Wiley-VCH.)

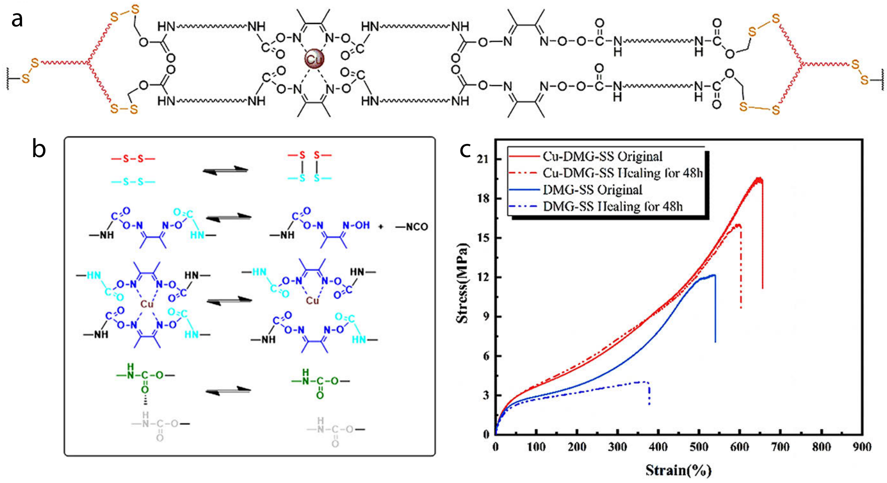

Fig. 4 (a) The chemical structure of Cu-DMG-SS. (b) Schematic of self-healing mechanism of Cu-DMG-SS. (c) The tensile strain-stress curves of original and healed DMG-SS and Cu-DMG-SS. (Reprinted with permission from Ref. [50]; Copyright (2021) Elsevier.)

healable elastomer (PDO-IP2.5) with superior mechanical properties (tensile strength up to 29.5 MPa, and toughness up to 124.9 $MJ·m^{-3}$) using 2,4-pentanedione dioxime instead of dimethylglyoxime (Fig. 5).[46] Meanwhile, the healing efficiency of tensile strength, elongation at break and toughness of PDO-IP2.5 were all over 95% after healing for 12 h at 70 °C. Compared with dimethylglyoxime, structural symmetry of 2,4-pentanedione dioxime is relatively poor. Therefore, the hard domains of PDO-IP2.5 formed by 2,4-pentanedione dioxime and isophorone isocyanate with the high steric resistance unit were loosely-packed. During the stretching process, the energy dissipation of hard segments and stress-induced crystallization of soft segment enhanced their ability to resist tension.

OXIME-URETHANE-BASED OTHER TYPES OF REPROCESSABLE POLYMERS

In addition to polyurethane, scientists have also used oxime-urethane groups to build other types of reprocessable polymers, which have potential to self-heal at high temperature. Zhang and coworkers developed a reprocessable and recyclable acrylonitrile-butadiene rubber (T-NBR) by introducing oxime-urethane bonds into the raw acrylonitrile-butadiene rubber and post-crosslinking (Fig. 6).[52] The tensile strength of resultant material was up to 4.85 MPa and exceed that of vulcanized NBR (3.18 MPa). The tensile strength of T-NBR showed a recovery ratio above 90% after the second reprocessing. This work provided a potential solution for recycle of widely used rubbers.

More recently, Zhang and coworkers prepared hydrogen bonds and oxime-urethane bonds based multi-functional polyamide vitrimers (Dx-Poly) (Fig. 7).[53] It is the first example of utilizing Ugi four-component reaction (Ugi-4CR) to fabricate polyamide vitrimers. The recovery of mechanical properties of Dx-Poly vitrimers was nearly 90% after being reprocessed at 100 °C for 30 min.

Polymers derived from vinyl monomers constitute more than half of the plastic produced every year. For the first time, we proposed a solvent-free thermal polymerization strategy for covalent adaptable networks (CANs) from vinyl monomers (Fig. 8).[54] The key was the dimethylglyoxime-urethane (DOU) cross-linker, which was miscible with vinyl monomers (*e.g.* methyl methacrylate and methyl acrylate) to polymerize DOU-CANs with superior processability, transparency and structural stability. The use of commodity raw materials and

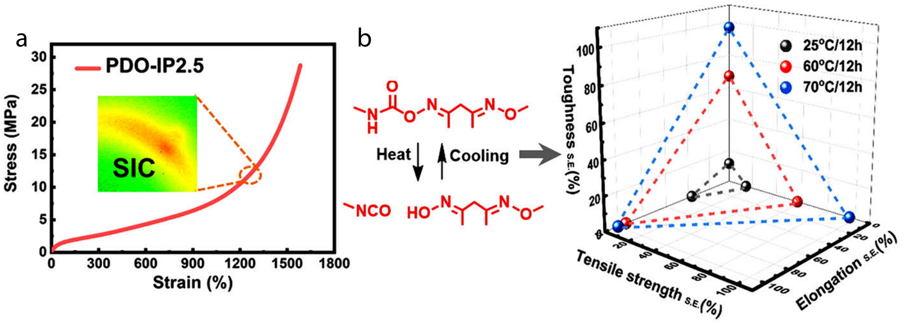

Fig. 5 (a) The tensile strain-stress curves of PDO-IP2.5 and the 2D WAXS patterns of PDO-IP2.5 with strain 1400%. (b) Schematic of self-healing mechanism and the healed mechanical properties of PDO-IP2.5. (Reprinted with permission from Ref. [46]; Copyright (2021) Elsevier.)

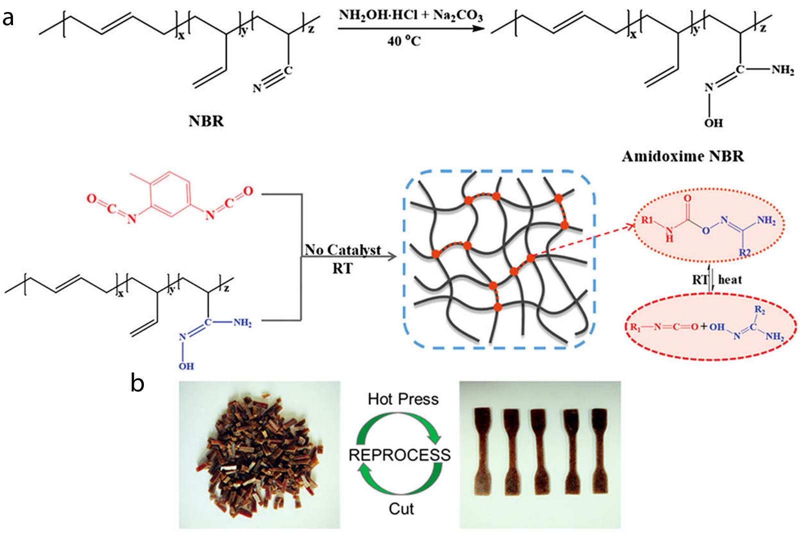

Fig. 6 (a) The synthesis of T-NBR. (b) Images of reprocessing of T-NBR. (Reprinted with permission from Ref. [52], Copyright (2019) Wiley-VCH.)

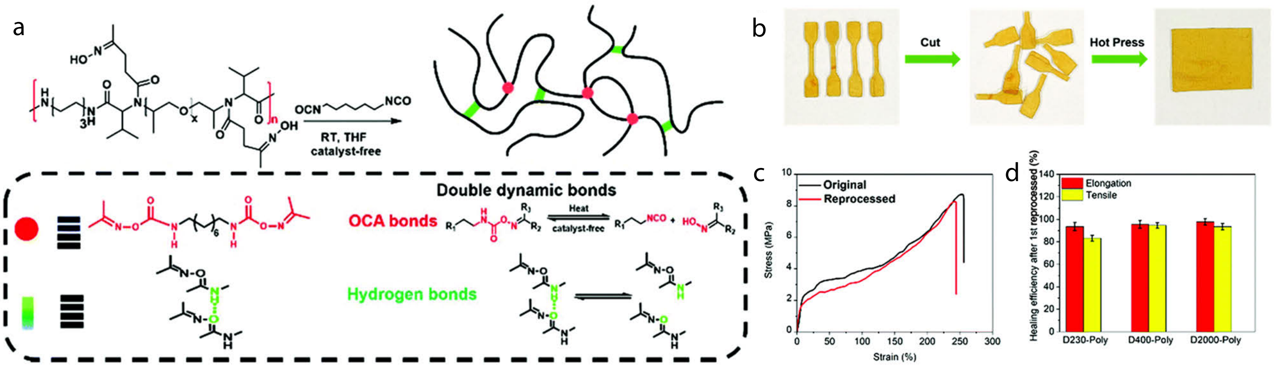

Fig. 7 (a) Schematic structure of Dx-Poly. (b) Images of reprocessing of Dx-Poly. (c) The tensile strain-stress of original and reprocessed Dx-Poly. (d) Healing efficiencies of Dx-Poly after the 1st recycling. (Reprinted with permission from Ref. [53]; Copyright (2021) The Royal Society of Chemistry.)

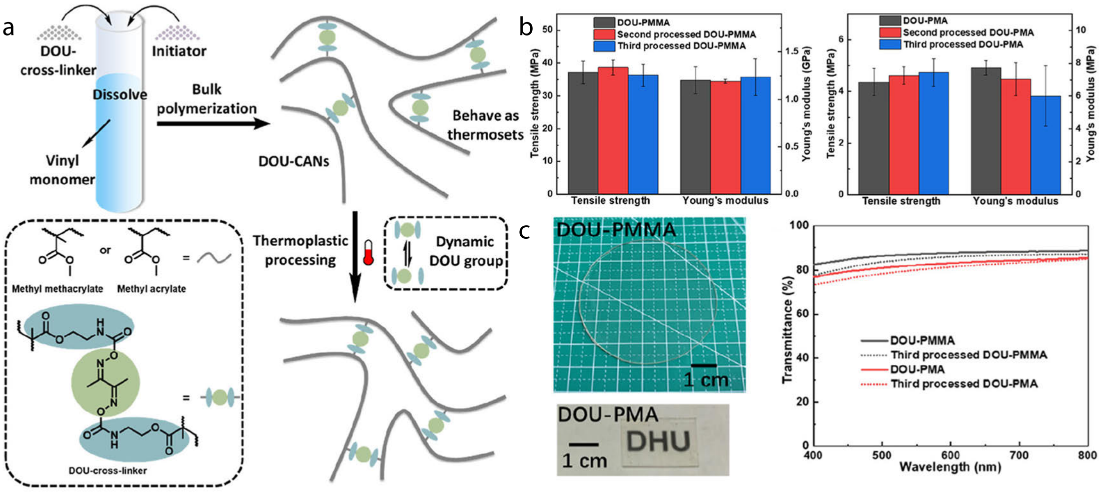

Fig. 8 (a) Schematics of synthesis and structure of DOU-CANs. (b) The tensile strength and Young's modulus of processed DOU-PMMA and DOU-PMA. (c) Photos and transmittance spectra of DOU-PMMA and DOU-PMA. (Reprinted with permission from Ref. [54]; Copyright (2021) American Chemical Society.)

simple preparation make this strategy suitable for industrial adoption.

THE APPLICATIONS OF OXIME-URETHANE-BASED SELF-HEALING POLYMERS

The unique properties of the oxime-urethane groups endow the corresponding self-healing polymers with great potential for multiple applications. The oxime-urethane-based self-healing polymers for different applications will be introduced in the following sections.

Protective Materials

Combining the multiple reactivity of the oxime-urethane groups, we fabricated a biomimetic multiple protective film based on Cu-DOU-PU with properties of self-healing, anti-counterfeiting, and puncture resistance, and an excellent adhesive ability to a widely used plastic, polyethylene (Fig. 9).[41] Accordingly, the protective film is expected to be useful for the protection of numerous valuables including electronics, diplomas, and automobiles. Wei and coworkers coated the oxime-urethane groups based PDO-2.5 polymer on the inner wall of the tire, and demonstrated the puncture-resistant and the self-healing performance of coated tire after puncture (Fig. 10).[46] These studies showed the potential of oxime-urethane based self-healing materials in the protective materials.

Flexible Electronics

Self-healing materials are highly desired for flexible electronic devices, which are typically used in dynamic environment, resulting in inevitable material damage. We prepared a stretchable and self-healable conductor using ploy(oxime-urethane) (Cu-DOU-CPU) as the sheath and liquid metal as the core. After 9 min of healing at room temperature, the severed conductor could be stretched while maintaining conductivity (Fig. 11).[39] More recently, Zhang and coworkers reported an all-solid, stretchable, and self-healable conductor based on composite of similar poly(oxime-urethane) and graphene, and showed superior mechanical properties (tensile strength: 6 MPa, maximum elongation: 1000%, toughness: 48 MJ·m^{-3}) and conductivity (Fig. 12).[48] Due to the interface compatibility and mechanical matching of the graphene and DOU-PU, the phase separation of conductive layer and DOU-PU during the stretching process was inhibited, and the conductive properties were almost consistent with the original after self-healing.

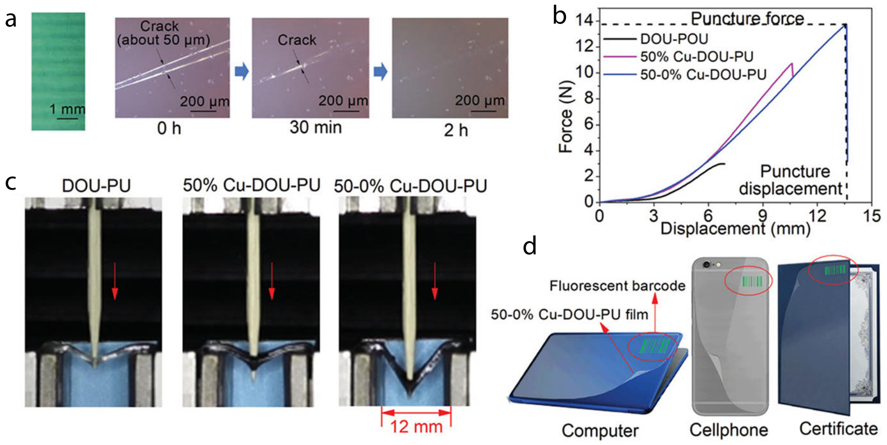

Fig. 9 (a) Images of protect film and its self-healing. (b, c) The puncture resistance of the Cu-DOU-PU films. (d) Potential applications of protective films. (Reprinted with permission from Ref. [41]; Copyright (2019) Wiley-VCH.)

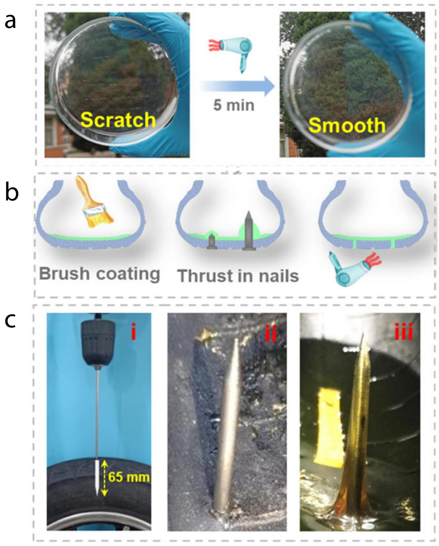

Fig. 10 (a) Images of the scratched and healed PDO-IP2.5 film. (b) Schematics of PDO-IP2.5 used as self-sealable puncture-resistant tire sealant. (c) Photos showing tire penetration. (Reprinted with permission from Ref. [46]; Copyright (2021) Elsevier.)

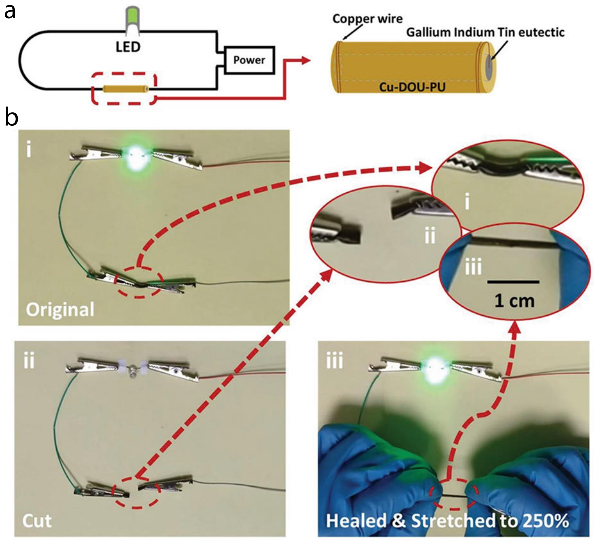

Fig. 11 (a) Schematics of the electronic circuit and the stretchable and self-healable conductor. (b) Photos of the self-healing and stretchable of the composite conductor. (Reprinted with permission from Ref. [39]; Copyright (2019) Wiley-VCH.)

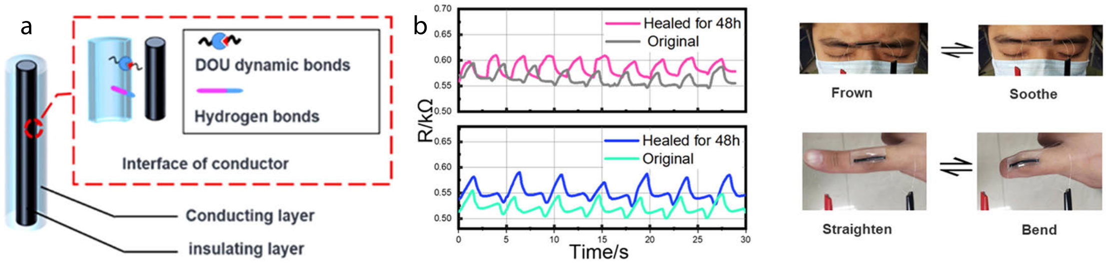

Fig. 12 (a) Schematics of the with self-healing and stretchable all-solid flexible wire. (b) Signals of original and healed conductor used as a stress sensor. (Reprinted with permission from Ref. [48]; Copyright (2021) Elsevier.)

Chen and coworkers reported a stretchable and self-healing perovskite solar cell by incorporating self-healing poly(oxime-urethane) (s-PU) (Fig. 13).[47] s-PU acted as a scaffold to improve the crystallinity and passivate the grain boundaries of the perovskite film, thus improving the stretchability of the perovskite solar cell. Meanwhile, the s-PU makes the self-healing match the annealing temperature. The efficiency of the device reached 19.15%, and could be healed to 88% of original after being cyclic stretched 1000 times under a strain of 20% and thermal annealing.

Adhesives

Adhesives play an important role in industry and daily life. We used the oxime-urethane groups to construct a dynamically cross-linked polyurethane hot melt adhesive (DPU-HMA), which combined the advantages of thermoplastic and reactive polyurethane hot melt adhesives, while overcame the two shortcomings (Fig. 14).[45] DPU-HMA showed fast curing speed, high initial and final bonding strength, excellent solvent resistance, and superior bonding effect on a variety of substrates (metal, plastic, wood, composite materials). More importantly, the oxime-urethane bonds enabled DPU-HMA with the detachable and self-healing ability, which were of great

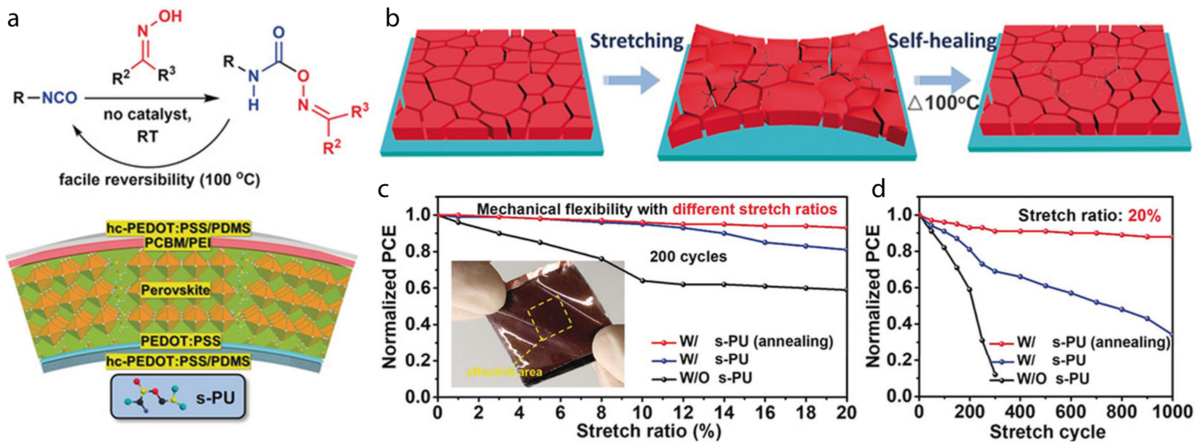

Fig. 13 Schematics of (a) the dynamic nature of the s-PU and device configuration, and (b) the self-healing process of perovskite films. (c) Normalized average power conversion efficiency of perovskite solar cells for 200 cycles. (d) Normalized average power conversion efficiency of perovskite solar cells as a function of stretching cycles with 20% stretching. (Reprinted with permission from Ref. [47]; Copyright (2020) Wiley-VCH.)

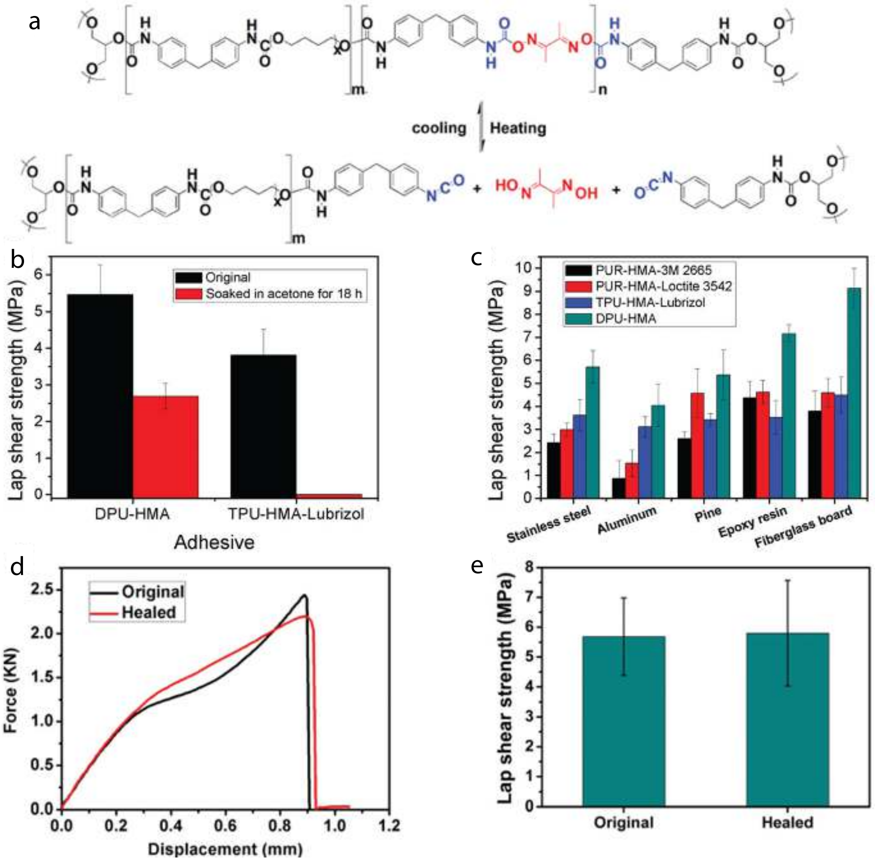

Fig. 14 (a) Schematics of synthesis and structure of DPU-HMA. (b) Lap shear strength of TPU-HMA and DPU-HMA to stainless steel. (c) Adhesion strength of DPU-HMA and other adhesives to different substrates. (d, e) The bonding effect of original and healed DPU-HMA to stainless steel. (Reprinted with permission from Ref. [45]; Copyright (2019) The Royal Society of Chemistry.)

significance for the recycle of valuable bonded devices and the extension of the service life of the materials.

3D Printing

In view of the difficulty in constructing complex structures in fused deposition modeling printing, and the size of the printed products is limited by the size of the 3D printer, we proposed a "Print-Healing" strategy to solve these problems (Fig. 15).[51] Taking poly(oxime-urethane) (Cu-DOU-CPU) as an example. Elevated temperatures accelerated the exchange reaction of dynamic bonds and promoted the topological rearrangement of the cross-linked networks. Therefore, the cross-linked

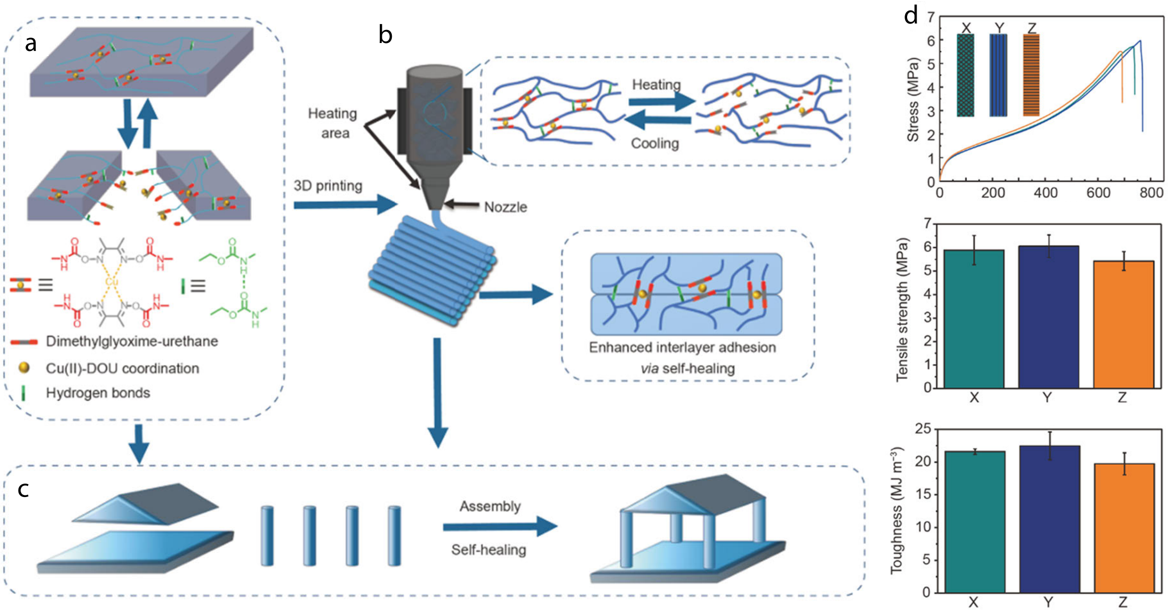

Fig. 15 (a) Schematic of Cu-DOU-CPU polymers. (b) 3D printing process of Cu-DOU-CPU. (c) Schematic of assembly of 3D-printed parts. (d) Mechanical properties of printed products in different directions. (Reprinted with permission from Ref. [51]; Copyright (2021) Springer Nature.)

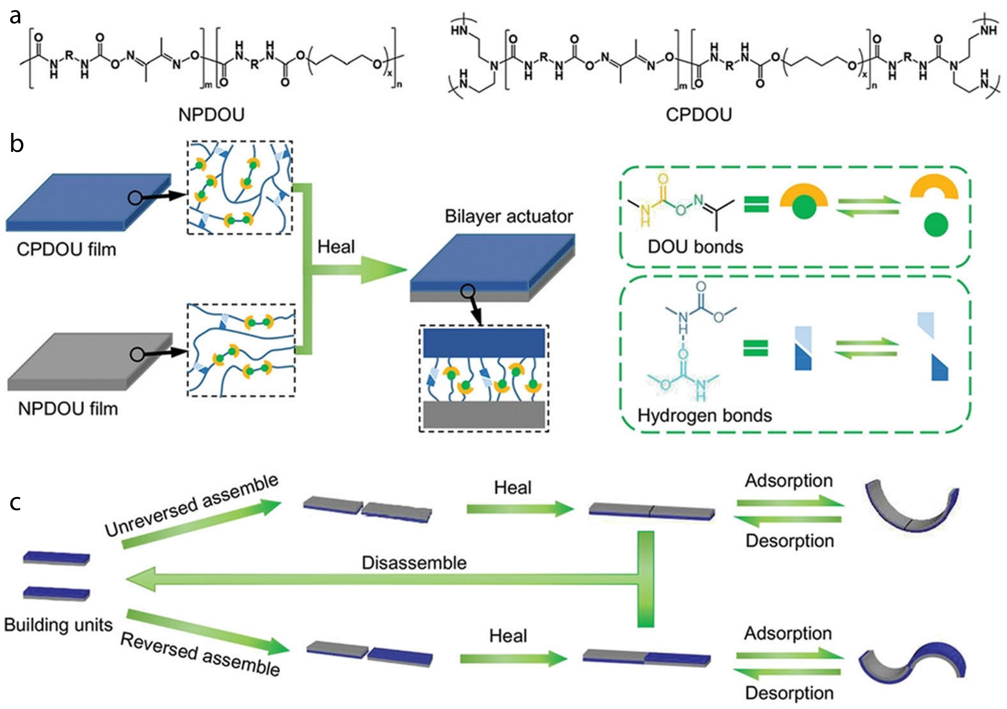

Fig. 16 (a) The chemical structure of NPDOU and CPDOU. (b) Assembly of the bilayer anisotropic actuator. (c) Schematic of the macroscopically discretionary healing-assembly strategy to achieve reconfigurable actuators. (Reprinted with permission from Ref. [49]; Copyright (2021) Wiley-VCH.)

polymer shows printability. Inspired by Lego bricks, we rationally split the complex three-dimensional structure into simple modules for printing. Then, the complete complex architectures were assembled from these modules and spliced by self-healing. Different from the relatively weak interlayer strength of products fabricated by traditional layer-by-layer accumulation printing, this strategy used dynamic bonds to form covalent bonding between layers to significantly improve the interlayer strength. Accordingly, the mechanical properties of printed products in different directions are similar.

Soft Robots

Actuators have received a lot of attention in recent years and have shown great promise in many fields including soft robots. We proposed a macroscopically discretionary healing-assembly strategy for discretionarily reconfigurable actuators based on self-healing poly(oxime-urethane) (PDOU) (Fig. 16).[49] In addition to the spontaneously self-healing properties, PDOU elastomers with different cross-linking densities showed different responsivenesses to solvents. Accordingly, by assembling PDOUs with different crosslinking densities, the required corresponding actuators can be easily assembled at room temperature. Remarkably, the fabricated actuators and soft robots could be readily reprogrammed to display versatile actuation modes by easily tailoring and reassembling without external energy input. This work paves a new, simple, powerful, and universal method for constructing sophisticated soft robots.

Biomedicine

The self-healing properties of materials are also of great interest in biomedicine. We designed a self-healing poly(oxime-urethane) elastomer (SHE) with mechanically adjustable, biocompatible and biodegradable properties, and proposed to use the self-healing properties of materials to repair tissues *in vivo* for the first time (Fig. 17).[55] SHE was healed and assembled *in situ* at the lesions *in vivo* to construct repair devices, and the effectiveness for aortic aneurysm, nerve coaptation and bone immobilization in three animal models were validated. Addressing clinical issues based on the self-healing properties of materials proposed here will provide new perspective to biomedical engineering and inspire the real promising applications of self-healing materials.

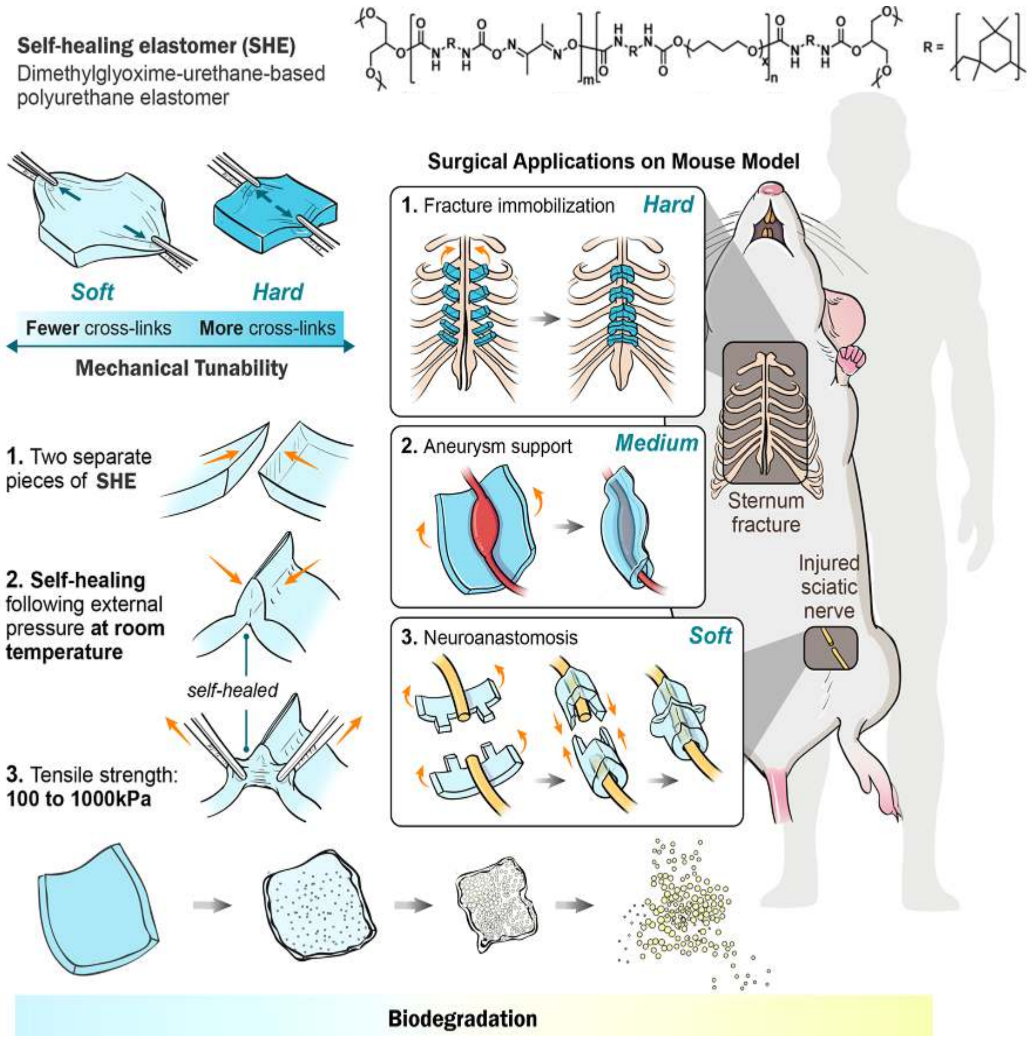

Fig. 17 Schematics of the structure and performance of poly(oxime-urethane) elastomer, and their biomedical applications *in vivo*. (Reprinted with permission from Ref. [55], Copyright (2021) Springer Nature.)

CONCLUSIONS AND OUTLOOK

In summary, the oxime-urethane bonds show the room temperature reversibility and multiple reactivity that most of the dynamic covalent bonds do not have. Furthermore, oxime urethane bond can be simply obtained by the reaction of oxime and isocyanate, both of which are widely available and have high structural diversity. A series of superior oxime-urethane-based self-healing polymers have been reported and showed great promise in multiple applications including protective materials, adhesives, stretchable devices, actuators/soft robotics, and 3D printing. Considering the dissociation properties of the oxime-urethane groups, the long-term performance of the self-healing materials based on the oxime-urethane groups remains to be in-depth studied. Except self-healing, dynamic oxime-urethane groups have also shown its power in other applications. Xu and coworkers integrated thermally reversible oxime-urethane group into the main chains of linear polyurethane to realize the melt spinning of polyurethane.[56] This work will facilitate the thermal processing of high performance polymers, whose melting temperature or viscous flow temperature is higher than their degradation temperature. More meaningfully, it has a large room to further explore the potential of oxime-urethane based polymers. For example, different metal ions (*e.g.* bioactive metals, rare earth metals) can be coordinated into corresponding polymers to enable novel biomedical or photoelectromagnetic applications.

BIOGRAPHY

Zhengwei You is a professor and the chair of the Department of Composite Materials at Donghua University. He serves as the director of Research Base of Textile Materials for Flexible Electronics and Biomedical Applications, China Textile Engineering Society. He received his PhD degree from Shanghai Institute of Organic Chemistry, CAS, and conducted research at Georgia Institute of Technology, University of Pittsburgh, and Bayer MaterialScience. His current research involves elastomers, dynamic polymers, and their 3D printing and applications in biomedicine and electronics.

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