Polymer Chemistry

MINIREVIEW

Intrinsic self-healing of covalent polymers through bond reconnection towards strength restoration

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Covalent polymers are widely used as structural materials because of their load-bearing capability. Integration of self-healing functionality with covalent polymers would improve stability and durability of the latter in practical engineering usage. This mini-review outlines recent developments in establishing intrinsic self-healing approaches of the materials through inter-macromolecular reactions towards strength recovery for structural application.

1 Introduction

In the past decade, development of self-healing polymers was placed on a fast track.[1–5] Various polymers have been integrated with self-healing capability, showing attractive prospects for future application as next generation materials. Unlike extrinsic self-healing that operates by the pre-embedded healing agent,[6] intrinsic self-healing is simply driven by macromolecular inter-actions and can be repeated unlimited times in principle without

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the aid of additional catalysts, monomers and special surface treatment.[7] Therefore, the strategy is quite competitive from the point of view of end-products manufacturing and usage.

Covalent polymers, constituting the majority of polymers in commercial use, mostly serve as structural materials with load-bearing capability owing to their high bonding strength. Recently, recombination of broken covalent chains across a fractured interface has been successfully demonstrated in terms of reversible macromolecular reactions in solids under the stimuli of heat and light. As a result, cracks in covalent polymers are mended in a controlled manner through chain reconnection.

Relatively speaking, however, the number of publications dealing with intrinsic self-healing of covalent polymers is less than that for extrinsic self-healing. It implies the necessity for deeper investigations of the former because of the importance of covalent polymers in modern society. Therefore, it is worth

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summarizing the achievements in this aspect so far, particularly the ability of mechanical property recovery for structural application and the corresponding chemical reactions responsible for covalent bond reconnection. It is hoped that the present mini-review will help to understand the frontier, and to form a solid basis for subsequent breakthroughs in healing chemistry, synthesis and preparation of self-healing covalent polymers as engineering structural materials. Self-healing polymer gels and supramolecular interaction aided healing are not discussed hereinafter owing to the limitation of the scope.

2 Self-healing based on thermally reversible reactions

2.1 Diels–Alder reaction

Reversible polymers share one property in common – reversibility, either in the polymerization process or in the cross-linking process.[7,8] Such a feature offers versatile possibilities of repeated healing at the molecular scale. For example, thermally reversible crosslinking behavior has been known for quite a while.[9,10] Wudl *et al.* combined this with the concept of self-healing in making healable polymers.[11,12] They synthesized highly cross-linked polymeric materials with multi-furan and multi-maleimide *via* Diels–Alder (DA) reaction. At temperatures above 120 °C, the intermonomer linkages disconnect (corresponding to the retro-DA reaction) but then reconnect upon cooling (*i.e.* DA reaction). This process is fully reversible showing recovery of fracture toughness of about 57%. The polymers are transparent and possess mechanical properties comparable to commercial epoxy and unsaturated polyesters.

Subsequently, composite panels were prepared by sandwiching the Diels–Alder monomers between fiber reinforcements.[13–18] Microcracks that were induced on the resin-rich surface of the composites disappeared after treatment at a certain temperature (*e.g.*, 180 °C (ref. 13)). Delamination was thermally remended as characterized by up to ~90% recovery of strain energy.[17] The results demonstrated the self-healing ability of the remendable polymers in both bulk form and fiber composites.

In the work by Liu and Hsieh,[19] Wudl's approach was modified. The multifunctional furan and maleimide compounds were prepared *via* simple routes, using epoxy compounds as precursors. The furan and maleimide monomers could therefore be considered as epoxy-based compounds, so as to incorporate the advantageous characteristics of epoxy resins, including solvent and chemical resistance, thermal and electrical characters, and good adherence, into their corresponding cured polymers. Furthermore, Liu and Chen prepared polyamides (PA) possessing furan pendent groups (PA-F) by reacting furfuryl amine with maleimide containing polyamides (PA-MI) *via* a Michael addition reaction.[20] Thermally reversible cross-linked polyamides were obtained from PA-MI and PA-F polyamides by means of DA and retro-DA reactions. The thermally reversible cross-linked polyamides also exhibited a self-repairing property as well as the ability of mechanical property recovery, but the healing efficiency was not quantified.

Kavitha and Singha applied click chemistry to make a polymethacrylate (PMA) bearing reactive furfuryl functionality,

which was then reacted with bismaleimide (BMI) to form crosslinked poly(furfuryl methacrylate)-bismaleimide (PFM-BMI).[21] DA bonds acted as the crosslinking sites, so that the polymer can be de-crosslinked through the retro-DA reaction. Accordingly, a complete notch (knife-cut) recovery to regain the original structure was detected on the PFM-BMI film after treatment at 120 °C for 4 h.

By using the Paal–Knorr reaction of polyketones (PK) and furfurylamine, Zhang *et al.* converted polyketones to furan derivatives in bulk under mild conditions without the need for a catalyst or a solvent, whereas the degree of furan functionality can be tuned well by changing the initial reaction conditions.[22] As a result, a thermosetting material was obtained by mixing the furan-containing polymer with BMI. The furan-functionalized polyketones (PK-furan) could be repeatedly cross-linked and de-cross-linked with BMI under the stimulus of heating of injection molding. Three-point bending tests showed that the highly cross-linked polymers can be thermally remended or re-processed to complete recovery in fracture loading, whereas the remending process can be repeated multiple times without any loss in mechanical properties.

Zhang *et al.* proved that the strategy of using the DA reaction to crosslink linear semi-crystalline macromonomers can produce a multifunctional polymer coupled with triple-shape memory effect, recycling and self-healing abilities.[23] They found that the crosslinking of linear bisfuranic terminated poly(tetramethylene oxide) and poly(*p*-dioxanone) *via* tris(2-maleimide ethyl)amine was fully reversible under moderate conditions. Healing of the tensile fractured specimen (*i.e.* treatment at 150 °C for a full retro-DA reaction and 75 °C for 15 h for DA reaction) recovered ~75% of the original strength.

Besides, thermal reversibility can also be imparted to rubbers. Chen and Jiao used diglycidyl dicyclopentadienedicarboxylic acid ester (DGDCA) as a crosslinking monomer in alkyl aluminum system catalyzed copolymerization with epoxide monomers like epichlorohydrin (ECH).[24] The resultant polyether thermoplastic elastomer can be molded into sheets at 215 °C. When the opposite parts of a broken specimen were joined together, the crack became invisible under certain conditions. It means that decrosslinking of the crosslinked copolymer occurred at elevated temperatures, leading to melting and plastic flow of the cracked surface. When the material was cooled down, the Diels–Alder cycloaddition between the side group cyclopentadiene rings reconstructed the elastic crosslinking networks.

Yoshie and Watanabe developed network polymers with recyclability using telechelic prepolymers with reversible reactivity.[25] On the basis of the research, they produced an elastomer from bisfuranic terminated poly(ethylene adipate) (PEA) and tris-maleimide through the DA reaction at 60 °C.[26] The resultant polymer, PEAF2M3, possessed a glass transition temperature of −34 °C, and can be decrosslinked by a retro-DA reaction at 145 °C for 20 min. When a film sample was cut into two pieces and the cut surfaces were kept in contact with each other at 60 °C, rejoining of the cut pieces was observed. This mending was believed to be induced by the following three mechanisms. (i) The reversible cross-linking reaction bridged

the cut surfaces. At the cut front, the weak DA adducts were selectively dissociated sacrifically to release the stress so as to protect the chemical structure of the prepolymer and the linker against the scission or degradation. (ii) Exchange of the maleimide (furan) group in a DA adduct with that in another DA adduct. (iii) Entanglement of dangling chains. In a recent paper, Yoshie *et al.* synthesized a similar polymer cross-linked by the DA adducts of anthracene and maleimide.[27] They found that the forward (addition) reaction was favored at room temperature, and the reverse (dissociation) reaction was induced by mechanical stress. The mechanochemical reversibility led to 17% recovery of tensile modulus after 53 days of rehabilitation at room temperature.

The group of Lehn screened condensation reactions between various dienes and dienophiles for reversibility.[28] They found that functionalized fulvenes, bearing in particular biological groups, and cyanolefins can react rapidly and reversibly, in the temperature range of −10 to 50 °C. The results paved the way for the generation of room-temperature dynamers, *e.g.* bis(fulvene) and bis(dicyanofumarate).[29] Soft films (with a T_g lower than room temperature) of these two dynamers were cut into two pieces, and then the pieces were laid on top of each other and pressed gently to ensure a microscopic contact. Ten seconds after this the two pieces could no longer be separated by pulling them apart, but reacted to the constraint by elongating themselves. No heating was needed during the healing. It is worth noting that this room temperature self-healing took place between the surfaces of the films, not only on the freshly cut surfaces. The surface of the film represented an area at thermodynamic equilibrium, as a result of low equilibrium constants for the interaction between the fulvenes and the cyanoolefins used. The constants were high enough to permit the formation of a material made of small molecules and low enough to allow the scrambling of the chains to take place even in the condensed phase. Consequently, the dynamer constantly created new chain ends and formed new connections, thus building a material that can self-repair across all its volume, despite the fact that mechanical data were not available.

The above-mentioned self-healing polymers based on reversible DA reactions were studied as bulk materials. However, the work by Peterson *et al.* demonstrated another form of application of the polymers.[30] They synthesized a thermally reversible cross-linking gel by the addition of a stoichiometric amount of 1,1′-(methylenedi-4,1-phenylene) bismaleimide to the furfurylamine (FA)–DGEBA oligomer. Then, the gels served as a healing agent for traditional epoxy–amine thermosets. Direct application of the reversibly cross-linking network to a crack surface in an epoxy–amine thermoset resulted in the recovery of 37% of the initial epoxy–amine network's strength. Composites in which the reversibly cross-linking gel was incorporated as a secondary particulate phase recovered 21% of the initial composite strength after the first healing cycle. The healing mechanism, which was governed by the Diels–Alder reaction, lay in that heating caused the secondary gel phase to liquefy and flow into the crack surface, and upon cooling cross-links re-formed. Moreover, Peterson and co-workers utilized a *N,N*′-dimethylformamide (DMF)-based BMI solution to
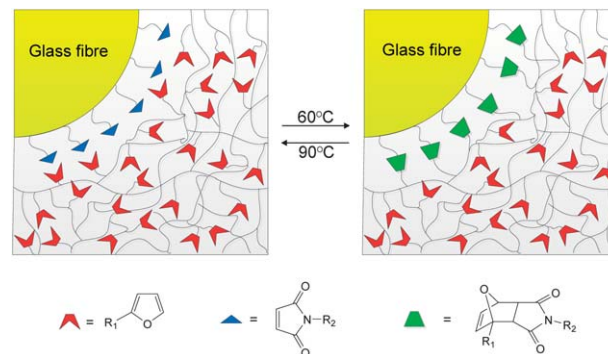
Scheme 1 Maleimide functionalization (blue triangles) of glass fiber within a furan-functionalized (red notched trapezoids) polymer network will result in a thermoreversible, and healable, fiber–network interface (adapted from ref. 32).

manually heal the furan-functionalized epoxy–amine thermosetting material that was obtained by mixing a certain amount of furfuryl glycidyl ether with the epoxy resin before curing.[31] Healing at room temperature was available as a result of physical and covalent bonding. Solvent-induced swelling and softening of the crack surfaces allowed for mechanical interlocking, while compatible functionalization of the polymer network and healing agent caused covalent bonding through the DA reaction of furans and maleimides. The authors are further considering to store BMI solutions in hollow glass fibers and polymer microcapsules for *in situ* healing. Besides, the idea has been used to build reversible interfaces in composites. That is, the reversible Diels–Alder reaction between a furan-functionalized epoxy–amine thermosetting matrix with a maleimide-functionalized glass fiber was used to impart remendability at the polymer–glass interface for potential applications in glass fiber-reinforced composites (Scheme 1).[32] At room temperature the Diels–Alder adduct is formed spontaneously and above 90 °C the adduct breaks apart to reform the original furan and maleimide moieties. Healing of the interface was investigated by single fiber microdroplet pull-out testing. Following complete failure of this interface, significant healing was observed with an overall average of 41% healing efficiency.

In principle, DA reaction aided self-healing has to first undergo molecular disconnection (*i.e.* retro-DA), which results in a significant geometry change characterized by creep[33] or even an abrupt viscosity drop.[34] Continuous service of actual products would thus be affected. To prevent it from happening, Tian *et al.* proposed to construct a dual-network polymer from a bifunctional epoxy monomer (*N,N*-diglycidylfurfurylamine, DGFA), in which one furan and two epoxide groups are present for each molecule (Scheme 2(a)).[35–37] Having been reacted with bismaleimide and anhydride respectively, the epoxy is crosslinked and two types of intermonomer linkages appear in the networks (Scheme 2(b)). This molecular structure allows the cured epoxy to possess similar mechanical properties to commercial epoxies, and allows elimination of cracks through successive retro-DA and DA reaction-induced chain reconnection below the T_g of the material with healing efficiencies from 66 to 96% depending upon the chemical compositions.[37] Accordingly, distortion during crack healing is no longer perceived.
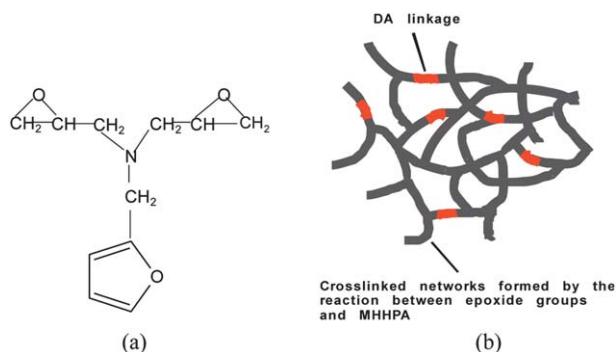
Scheme 2 (a) Structure of DGFA and (b) schematic drawing of the cured version of thermally remendable epoxy, which had respectively reacted with methyl-hexahydrophthalic anhydride (MHHPA) and N,N′(4,4′-diphenylmethane) bisma-leimide (DPMBMI), and consists of both thermally reversible and irreversible bonds.[36]

2.2 Miscellaneous reactions

Canadell *et al.* considered that the healing based on DA reversible covalent bonds usually takes place at high temperatures.[38] Therefore, they utilized another covalent bond, disulfide group, to introduce a healing functionality at lower temperatures. They incorporated disulfide links into a rubber network (*i.e.* a commercially available disulfide group-contained epoxy cured by tetrafunctional thiol), which was able to fully restore its failure strain at moderate temperatures (*e.g.* 60 °C). The key element of this self-healing concept lay in the exchange reaction of disulfide groups at certain temperatures, leading to the renewal of cross-links across damaged surfaces. It was believed that the method would be applicable to low-T_g materials, *e.g.*, polyurethanes and polyesters. In other words, the self-healing process has to take place above the T_g of the material, since the chain segments in the network need mobility to enable the interchange reaction.

Zhang and McCarthy prepared a crosslinked silicone rubber by tetramethylammonium silanolate-initiated ring-opening copolymerization of octamethylcyclotetrasiloxane and bis(hep-tamethylcyclotetrasiloxanyl)-ethane.[39] The polymer contained ethylene bridges and active silanolate end groups. The living reactive anionic species were stable to ambient atmosphere exposure and promoted thermally activated equilibration among different network isomers and cyclic oligomers. At particular composition ratios, the living silicone showed over 100% fracture toughness restoration by siloxane equilibration when the cracked compact tension specimen had been healed at 90 °C for 24 h.

In addition to the above elastomers, materials can be designed as hard at room temperature and malleable but insoluble at elevated temperatures through exchangeable links.[40,41] Leibler's group reported that with appropriate catalysts (*e.g.*, zinc acetate), the topologies of crosslinked networks from epoxy–acid and epoxy–anhydride reactions can be rearranged by transesterification exchange reactions without modification of the numbers of links and average functionality. At lower temperatures, the exchange reactions are very sluggish,

and the materials have properties of classical epoxy thermosets. At higher temperatures, however, the polymers behaved like viscoelastic liquids. Lap-shear tests indicated that these networks can be welded after treatment at 150 °C for 1 h, and 100% recovery of the mechanical property was detected after several hours.[41]

Generally, the DA reaction does not need a catalyst, so that self-healing of a polymer *via* reversible DA reaction requires substantial inputs of external energy as mentioned above. When an appropriate catalyst is present, it would be possible to develop a strategy allowing the dynamic exchange of C–C bonds under ambient conditions. Lu and Guan proved this assumption by introducing a small amount of Grubb's second-generation Ru metathesis catalyst (dissolved in dichloromethane) into a readily available polybutadiene (PBD) rubber through swelling.[42] As reflected by tensile tests, the rubber self-healed completely under appropriate conditions, because the transition-metal-catalyzed olefin metathesis reaction at fracture interfaces was efficient for shuffling C–C double bonds and resulted in establishment of new C–C double bonds between the two surfaces.

On the other hand, in a typical healing process based on DA reaction crack healing, as mentioned in Sub-section 2.1, the polymer has to be heated up to the retro-DA temperature (120 °C) for disconnecting DA bonds, which is generally higher than the glass transition temperature, and then cooled for reconnection of the DA bonds (DA reaction ≈ 80 °C). It means that the material would inevitably lose its shape as a result of (i) molecular cleavage during the first stage of healing (*i.e.*, retro-DA reaction/de-crosslinking) and (ii) drastically increased deformability due to glass transition. It is worth noting that breakage of reversible bonds and improved mobility of molecules are necessary for crack healing,[43] but distortion of end-use products is not allowed for structural applications where mechanical strength properties are critical even if self-healing is proceeding. The requirements seem to be contradictory and are hard to be satisfied simultaneously in conventional polymers. In addition to the approach of generating dual-networks of irreversible and reversible bonds and lowering the retro-DA temperature below T_g,[35–37] the healing chemistry based on dynamically reversible C–ON bonds proved to be another solution.[44] Yuan *et al.* employed alkoxyamine moieties as intermolecular links to crosslink polystyrene. Upon heating to a certain homolysis temperature, covalent bond fission and radical recombination synchronously took place among alkoxyamine moieties. Cracked parts were thus reconnected repeatedly in a single-step fashion (rather than the two-step one in the case of DA reaction) giving healing efficiencies of 65–76%, without losing the integrity and load bearing ability of the material even above T_g.

Recombination of polycarbonate (PC) chains has also been researched as one of the methods for intrinsic self-repairing materials. This method does not focus on crack healing but on molecular chain's deterioration and recombination. The PCs were treated in a steam pressure cabin at 120 °C prior to the repair.[45] As a result, the molecular weight of the PCs dropped by about 88 to 90%. After drying them in a vacuum cabin, the repairing treatment was done in an oven at 130 °C in N_2 under reduced pressure. The reduced tensile strength due to the

deterioration treatment can thus be gradually recovered, due to recombination of two broken chains under Na_2CO_3 catalyst. Similar methods were also applied for the molecular repairing of poly(phenylene ether) (PPE) and poly(ether ketone) (PEK) *via* an ester exchange reaction, and a recombination reaction of two polymer ends.[46,47]

3 Self-healing based on photoreversible reactions

In addition to thermally reversible reactions, photoreversible reactions are also important measures for realizing self-healing of polymers, despite the fact that research on photochemically self-healing polymers is at the outset. Light is clean, cheap and readily available. It would be advantageous to have polymers that unconsciously mend when exposed to environmental conditions like sunlight.[7] Similar to thermally initiated DA reactions, photoinitiated cycloaddition is also possible. Photochemical [2 + 2] and [2 + 4] cycloadditions are the most common photodimerization reactions and can be used for the photochemical healing of polymers as the reversion of the cycloaddition resulting in C=C bonds readily occurs in the solid state.[48]

In 2004, Chung *et al.* synthesized a photo-crosslinkable cinnamate monomer, 1,1,1-tris-(cinnamoyloxymethyl) ethane (TCE) bearing three optically active moieties.[49] It can crosslink to form a very hard solid *via* [2 + 2] photocycloaddition upon ultraviolet (UV) irradiation at $\lambda > 280$ nm. When the sample of TCE suffers from an impact, propagating microcracks result in cleavage of the cyclobutane ring due to its low bond strength. Re-irradiation with UV light allows recovery of the crosslinked networks (Scheme 3). Healing efficiencies in terms of flexural strength up to 14 and 26% were obtained in the case of a UV stimulus or a combination of UV light and heating (100 °C).

Taking advantage of photodimerization of cinnamoyl, Nobuhiro *et al.* also developed a photo-remendable crosslinked polymer from a cinnamoyl-telechelic poly(butylene adipate) and a tetracinnamoyl linker.[50] When the cross-linked polymer was damaged by tapping, the cinnamate dimers along the crack surfaces dissociated into cinnamate monomers. Photoirradiation of the damaged sample led to the re-dimerization of the cinnamate monomers and the mending of the network polymer along the crack surfaces. The mending process resulted in the complete recovery of the chemical structure of the polymer.

Urban and Ghosh developed a heterogeneous polyurethane network containing an oxetane-substituted derivative of chitosan (OXE-CHI) *via* the reaction with hexamethylene diisocyante (HDI) and polyethylene glycol (PEG).[51] In the case of mechanical damage of the material, the four-membered oxetane rings opened to create two reactive ends. When exposed to UV light at 302 nm wavelength, a series of covalent bond rearrangements including chitosan chain scission occurred, generating crosslinks with the reactive oxetane ends, so that the network acquired one way healability. Visual inspection of the cut on a film sample indicated that the material was capable of repairing itself in less than an hour.

Amamoto *et al.*[52] prepared macroscopic self-healing crosslinked polyurethanes based on radical reshuffling of thiuram disulfide (TDS) units under the stimulation of visible light at room temperature without solvent. Since the S–S bonds in the incorporated TDS units homolytically dissociate in visible light, the radical reshuffling reactions enable the reorganization of the linking units in the covalently crosslinked polymers and self-healing of significantly damaged polymers. In the meantime, to carry out the self-healing reaction in a bulk material at room temperature, the reactive TDS units, capable of re-shuffling, were incorporated in the main chain of a low T_g polyurethane. Young's moduli of the sample before and after the healing reaction were found to be almost the same. The results demonstrated that disulfide not only responds to thermal stimulus[38] but also to visible light. Such a multiple responsive nature might improve designability and controllability of new self-healing polymers.

Coumarin, a traditional perfume substance from plants, possesses attractive photo-responsiveness, and was introduced into polyurethane as a photoreversible crosslinker.[53,54] Upon mechanical damage or ultraviolet illumination at a wavelength of 254 nm, the coumarin dimers on the fractured surface that linked the polyurethane backbones with one another were cleaved, and can be reconnected *via* irradiation at 350 nm. By using this feature, cracks on the polymer were mended by ultraviolet exposure or even sunlight. Owing to the reversibility of the photocyclization of coumarin moieties, multiple cycles of crack mending were allowed, as demonstrated by both qualitative and quantitative characterization. The healing efficiencies characterized by tensile strength recovery were 70.2, 62.9 and 56.6% for the repeated healing events under UV light. This repeated photoremendability enabled the polyurethane to heal the same site in the material more than once.

In fact, photochemically remendable polymers are not limited to those quoted above. Because the main concern of this article is to focus on self-healing of covalent polymers for structural application, however, the studies of supramolecular polymers[55,56] and/or liquefaction related healing[57,58] are not included.
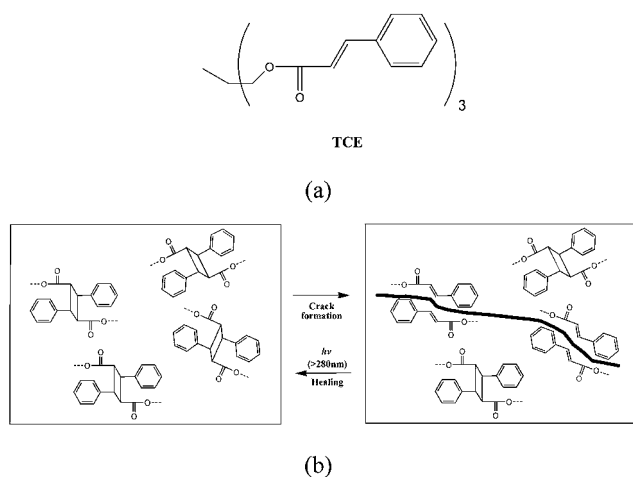
Scheme 3 (a) Chemical structure of TCE. (b) Schematic illustration of the healing concept (adapted from ref. 49).

4 Conclusions

Research on intrinsic self-healing of covalent polymers as a result of bond scission and reconnection has made substantial progress. Most concerns were focused on the DA-bond aided self-healing strategy. Modification and improvement of the methods were made from different angles. A few primary works explored other reversible chemistries, like disulfide bonds, living silicone, transesterification exchange, dynamic exchange of C–C bonds, reversible C–ON bonds, *etc.* These healing mechanisms expanded the family of intrinsic self-healing materials with reversible covalent bonds, and provided more choices for various requirements, including stronger C–C bonds and multi-functional S–S bonds. Moreover, some interesting ones like thiol–ene chemistry[59,60] and pH-sensitive reversible acylhydrazone bond formation[61] have not yet been transferred to intrinsic self-healing of damage in structural materials to restore mechanical properties.

To realize the aim of practical application, further efforts are needed to, for example, increase reproducibility of the healing performance, reduce dependency of the healing process on external stimuli, impart self-healability to common engineering materials, ensure maneuverability in practice, and maintain the original features and integrity of the materials in the course of crack healing, *etc.*

Acknowledgements

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