Synthetic Design of Self-Healing Epoxy Systems

Xiwei Xu, Jin Zhu, and Songqi Ma

Abstract Epoxy resins are widely used in our life due to their excellent thermal and mechanical properties, dimensional stability, and processability, but they are inevitably impacted by chemical/physical events, which leads to micro-cracks during use. Self-healable epoxy resins can repair the micro-cracks, greatly extending the life and safety of the resin. This chapter reviews the methods of achieving self-healable epoxy resins, including embedding hollow fibers (or microcapsules) filled with healing agents, thermoplastic additives, or dynamic bonds in the epoxy networks. The self-healing mechanisms, advantages, and disadvantages of each method are summarized. Finally, the conclusion and prospect of self-healing epoxy resins are highlighted.

Keywords Epoxy resins · Extrinsic self-healing · Intrinsic self-healing · Dynamic bonds

1 Introduction

Biological tissues can self-repair when damaged. As an example, most animal skins can completely self-repair within a few hours or days when damaged to protect other subcutaneous tissues from further harm. In contrast, traditional synthetic resins are challenging to achieve self-healing when damaged and may lose or weaken their special functions such as super hydrophobicity, anti-corrosion property, antibacterial activity, and conductivity.

Resins with self-healing properties can repair damage triggered by physical or chemical events in working conditions or specific environments (such as heating) at the molecular level. It is complicated and trivial to design resin structures similar to

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living organism's self-healing and regeneration ability as a benchmark [1] because organisms possess exceptionally complex and highly synergistic cells. Cognizant of the broad application of resins, straightforward and efficient methods in imparting self-healing properties to resins received widespread attention. According to the self-healing mechanisms, we can simply divide the self-healing process into physical and chemical processes. The main physical self-healing processes include diffusion, [2] shape-memory effects, [3] the loading of superparamagnetic nanoparticles,[4] and phase-separated morphologies [5, 6]. At present, the design of self-healing systems by chemical processes including the covalent, [7–9] free-radical, [10, 11] or supramolecular [12–14] dynamic bonds have attracted significant attention from researchers.

Epoxy resin is a high-performance thermosetting resin obtained by reacting epoxide-containing monomers/oligomers with curing agents. It is often used to construct adhesives, coatings, and composites on account of its favorable mechanical performance, thermal properties, dimensional stability, and processability. However, during service, epoxy resin will inevitably be damaged by external factors, resulting in cracks at the macro or molecular scale, reducing the material's mechanical performance and even compromising its special functions, such as anti-fouling, hydrophobic, and antibacterial effects. On account of the highly and permanently cross-linked network structure of traditional epoxy resin, using physical processes (such as diffusion and shape-memory effects) alone could not achieve a satisfactory self-healing effect. Combining chemical processes with physical processes can lead to a superior self-healing effect. Through the works reported recently, the self-healing of epoxy resin can be achieved by adding hollow fiber [15–17], microcapsule[17–19], and thermoplastic additive [20] to the epoxy resin matrix, which is known as extrinsic self-healing. During the past two decades, intrinsic self-healing epoxy networks triggered by dynamic bonds have captured increasing attention. Especially since Leibler's pioneer report on vitrimers, [21] the application of dynamic chemistries in epoxy resins has been rapidly developed, and various dynamic bonds have been used to construct self-healing epoxy resins.

2 Extrinsic Self-Healing Epoxy Resins

2.1 Hollow Fiber

Most of the micro-cracks on the resins are generated when they receive an external impact. Therefore, adding appropriate hollow fibers to the epoxy resins can reduce the expansion of cracks in the resins when impacted by force. Meanwhile, adding a certain amount of self-healing agents (such as small-molecule monomer and initiator) to the hollow fibers can realize the self-repairing of cracks (Fig. 1). When cracks are generated in the epoxy resins from an external force, hollow fibers at the cracks will also be broken, and the healing agents stored in the hollow fibers will fill the
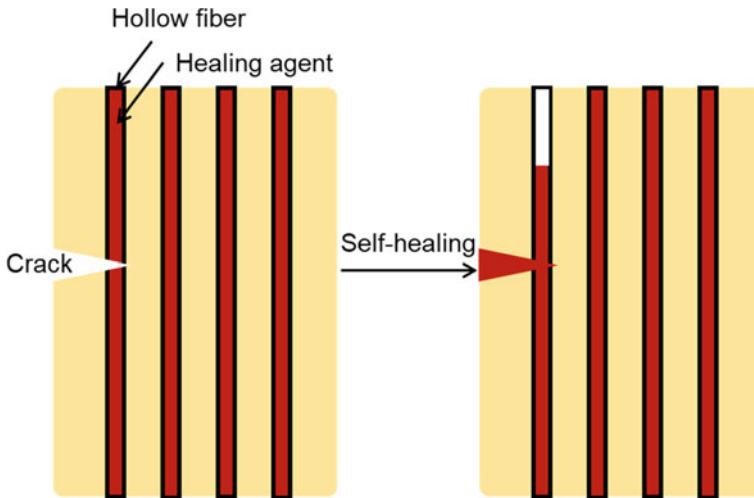
Fig. 1 Self-healable epoxy resins based on hollow fiber filled with healing agent

cracks and then quickly cure under the action of the initiator to regain the mechanical properties of the resin.

In 1996, Dry [22] developed an epoxy resin/hollow fiber composite that achieved self-healing of the internal cracks. The authors employed microscopy observation and mechanical properties analysis to characterize the self-repairing performance of the composite and found that the cracks can be controlled by hollow fiber, and the adhesive entered the crack and repaired it. In 2005, Pang and Bond [23] developed a bionic visualized seal-healing method, ultraviolet fluorescent dyes as well as the healing agent were filled into the hollow fiber, and the self-healing and impact damage was visualized through the exudation of the ultraviolet fluorescent dyes when the hollow fiber was broken. Bending tests showed that the damaged resin self-healed with high efficiency. Kling and Czigány [20] replaced the commonly used epoxy resin with unsaturated polyester resin as the healing agent to fill the hollow fiber, mainly because the curing of unsaturated polyester material was less susceptible to the mix than that of the commonly used healing agent (epoxy resin) in the reported literature. Curing of the unsaturated polyester led to a 20% increase in flexural properties.

2.2 Microcapsule

Up to now, the microcapsule is one of the largest reported self-healing approaches for epoxy resin [24]. Similar to the hollow fiber method, the healing agent (often small-molecule monomers) is encapsulated in microcapsules. The catalyst for curing is evenly distributed in the resin matrix. On account of its outstanding self-healing
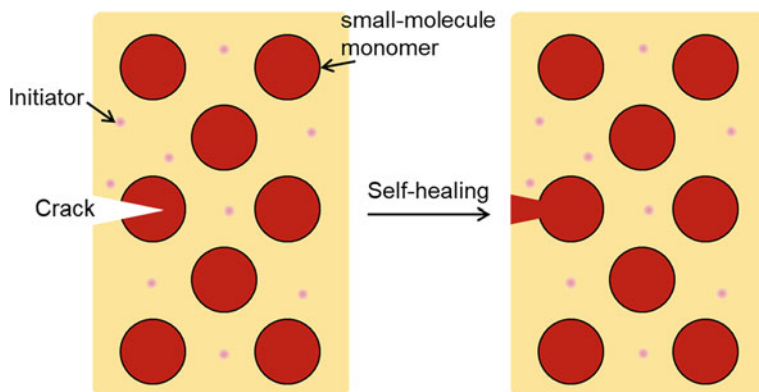
Fig. 2 Self-healable epoxy resins based on microcapsules filled with a healing agent

efficiency and no requirement of manual intervention, it is widely used in metal anti-corrosion coatings [25].

White et al. [26] innovatively developed a structural polymer material that can self-heal in a straight line without manual intervention by the microcapsule self-repairing method (Fig. 2). When a crack formed upon the damage, it would rupture the microcapsule. The self-healing agents released and interacted with the dispersed initiator (or catalyst) in the matrix, which realized polymerization and achieved a self-healing effect. According to the fracture toughness test, the willful recovery rate of the material on the fracture surface reaches 75%, which has a relatively high application value. In addition, the authors also expected their mechanism to be applied to other hard materials, including glass, ceramics, etc.

Anti-corrosion of metallic materials is of great significance both economically and ecologically [27, 28]. Anti-corrosion coatings can effectively block water and ions from corroding the metal substrates. Nevertheless, once the coating is damaged, water and ions can freely reach the metal substrate, causing rapid corrosion and eventually cracking of the coating. Adding corrosion inhibitors can improve the corrosion resistance of the coatings. However, such materials are now widely restricted by EU law because of ecological and toxicological concerns [29, 30]. Thus, it is significant to develop self-healable anti-corrosion coatings. Suryanarayana et al. [31] investigated the self-healing efficiency of epoxy coatings containing linseed oil-filled microcapsules and applied it to the anti-corrosion of metal materials. The authors prepared microcapsules in situ by urea–formaldehyde resin. The linseed oil in the microcapsules is released under the mechanical action to repair the cracks. Meanwhile, owing to the repair of the epoxy coating cracks, the metal protected by the anti-corrosion coating was re-protected.

2.3 Thermoplastic Additives

Adding thermoplastic resin or additives to the thermosetting resins is also a way to realize self-repairing for thermosetting resin/composite (Fig. 3). The above two methods (hollow fiber and microcapsule) cannot perform repeated self-repair after the resin achieves self-repair and are subject to certain restrictions in the application. In addition, the preparation process in the above two methods required the encapsulation of the healing agent, which is relatively complex and can often only be used in the preparation of composite materials. While thermoplastic particles only need to be added during the molding process of the thermosetting resin matrix, which is simpler and more efficient.

Zako and Takano [32] loaded thermoplastic particles at a volume ratio of 40% to the glass fiber/epoxy composite (GFRP) laminate. The three-point bending and tensile tests found that the addition of thermoplastic particles did not decrease mechanical properties, and since thermoplastic resins can melt at elevated temperatures, cracks in the matrix of the composite material can be self-healed. The service life of the composite material can be increased.

Meure et al. [33] developed a thermoplastic healing agent (polyethylene-co-methacrylic acid (EMAA) particles) for epoxy networks and proposed a related mechanism. Incorporating the thermoplastic additive improved the epoxy resin's breaking strength and achieved critical stress strength recovery up to 85%. They also revealed the self-healing mechanism: recovery of damaged resin's strength through the formation of a sticky EMAA layer between the EMAA particle and epoxy matrix, while swelling of the healing agent occurs during heating and forces it into the broken area of the epoxy matrix, facilitating its repair.
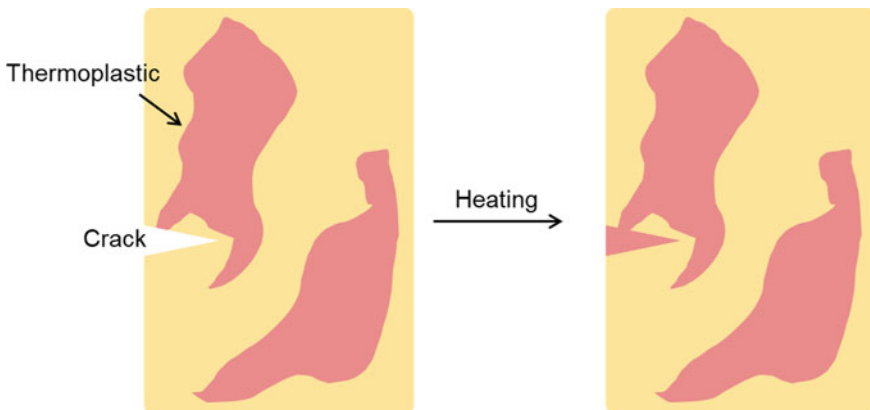

Fig. 3 Self-healable epoxy resins based on thermoplastic additives

3   Intrinsic Self-Healing Epoxy Resins

The damage to traditional epoxy resin often needs to be repaired by welding, gluing, and other methods. Adding hollow fiber or microcapsule filled with healing agents and thermoplastic resin can be an extension of this traditional repair method. During the past two decades, dynamic bonds-based self-healable epoxy resins have made great progress. Here is a theory about self-healing properties that are instructive for developing self-healable epoxy resins from dynamic bonds. From the point of thermodynamics, to realize the resin's self-repairing process, it is indispensable to satisfy the change of Gibbs free energy (ΔG ($=\Delta H - T\Delta S$) < 0) of the whole process. The above-mentioned self-repairing process mainly follows two processes: (1) breakage of the molecular chains at the rupture when a physical or chemical event damaged the material, and (2) thermal motion and diffusion of the molecular chains when the interface distance was appropriate, and under the premise that the two interfaces are fused by the exchange between the dynamic bonds on the molecular chain. In this process, due to the exchange reaction, the enthalpy value before and after the reaction was almost unchanged, so the ΔH in this process was almost zero. However, the change in the degree of the disorder before and after the reaction was significant. The increase in the degree of disorder leads to the migration of molecular chains on the fracture surface to the gap and eventually fused. Since ΔH can hardly change greatly, ΔG can be assumed as ($-T\Delta S$). For the sake of increasing the driving force for self-repairing, it was a feasible idea to increase the amount of disorder. Reducing the number of atoms in repeating units between two dynamic bonds can increase the degree of disorder (ΔS) in the process of dynamic bond exchange and molecular chain migration, and there are some efficient approaches such as increasing the dynamic bond content and designing dynamic bonds on the main chain instead of side chains. In addition, as shown in Fig. 4, increasing the flexibility of the molecular chain of the polymer network is also beneficial to the increase of ΔS. The relationships between the length of the repeating unit of the molecular chain, the flexibility of the chain segment and the change of Gibbs free energy (ΔG) are shown in Fig. 4.

   The above-mentioned methods for realizing the self-healing feature of epoxy resins are all by adding external healing agents. As a result, the currently commercial epoxy resin can be directly modified, the research is relatively mature, and they are widely used. However, these methods still have some difficult problems to solve. For example, the first two methods (hollow fiber and microcapsule) can only endow the self-healing property for one time. In addition, these two methods are suitable for composite materials. They are difficult to apply in pure resin materials such as coatings, adhesives. These two methods need to add hollow fibers or microcapsules. Adding thermoplastics to thermosetting epoxy resin seems to be a better method, which can achieve self-healing multiple times, and the preparation was relatively simple, but there are still several issues. As an example, to achieve a better self-healing effect, it is essential to add a large number of thermoplastic additives [32]. In addition, the loading of a large amount of thermoplastic resin inevitably reduces
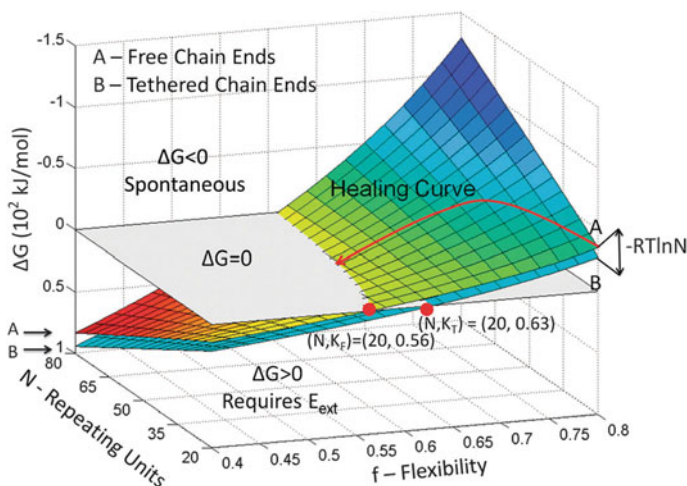
Fig. 4 Curves of ΔG versus segment number (N) in a polymeric chain and flexibility (f) for free (surface A) and tethered (surface B) chain ends *Reproduced with permission from* Yang and Urban [1]

the mechanical properties of the resin matrix. Meanwhile, this method requires the thermoplastic resins and epoxy resins with favorable compatibility, which reduces the selection range of thermoplastic resins, and after repairing, the crack is simply bonded by a thermoplastic resin with superior fluidity, which theoretically becomes a weak point. For instance, when it is used in a high-temperature environment, the thermoplastic resin tends to fail, leading to the crack breaking again.

In recent two decades, the self-healing of epoxy resins was realized by incorporating dynamic structures. The network rearrangement and the migration of molecular chains can be realized through the exchange of dynamic structures under certain conditions (such as heating, ultraviolet light), corresponding to the repairing of the resin. By introducing supramolecular chemistries such as hydrogen bonding, epoxy resin can obtain self-healing ability, while appropriate content of supramolecular bonds can enhance the mechanical performance of the epoxy resin [34, 35]. By introducing dynamic covalent bonds, self-healing can also be achieved for epoxy resins. Self-healing epoxy resins from dynamic covalent bonds have two catalogs: dissociative and associative. For the dissociative one, during the self-healing of the epoxy network or network rearrangement, dynamic covalent bonds are first dissociated, and then new dynamic covalent bonds are formed in another place. For the associative one, the cleaving and reformation of the dynamic covalent bonds occur simultaneously, and the resin's cross-link density is unchanged. Albeit there is a big difference between these two catalogs, they both can achieve effective self-healing for epoxy resins via the rational design of the molecular structure.

3.1 Supramolecular Dynamic Bonds

A hydrogen bond is a typical supramolecular dynamic bond in nature, so its strength is lower than most covalent bonds. Nevertheless, hydrogen bond-contained materials with high mechanical properties can still be designed and prepared. In recent years, urea isopyrimidone (UPy) captured great attention because it can form quadruple hydrogen bonding. Compared with ordinary hydrogen bonds, UPy-based quadruple hydrogen bonds have a stronger binding force, which is beneficial to enhancing the mechanical performance of materials. Thermosets that only use UPy-based hydrogen bonds as cross-linking points showed the same rheological characteristics as thermoplastic resins as a result of the de-bonding of hydrogen bonds at elevated temperatures [36] and possessed pretty good mechanical properties at room temperature (Fig. 5).

Zhang et al. [37] used UPy-modified bisphenol-A epoxy resin to prepare cross-linked supramolecular polymers through epoxy curing reaction and formation of hydrogen bonds between UPys (Fig. 6). This epoxy resin can be self-healed at the cut point after heating (90°C) for 2 h, and high self-repairing efficiency was reached (99%). At the same time, the epoxy resin had excellent mechanical properties (elongation at break was 247%, and tensile strength was 3.10 MPa). This resin was also applied to self-healable conductive composites. Sun et al. [35] applied the epoxy resin containing UPy to the reusable hot melt adhesive (Fig. 7). They grafted UPy to bisphenol-A epoxy resin by chemical modification and prepared reusable adhesive through epoxy curing and hydrogen bonding between UPys. The SEA had ultra-high bonding performance with a bonding strength of 10 MPa. Meanwhile, the SEA can also be reused by heating at 80°C for 5 min through the dynamic exchange of hydrogen bonds, and it can be reused six times with 80% maintained mechanical properties.
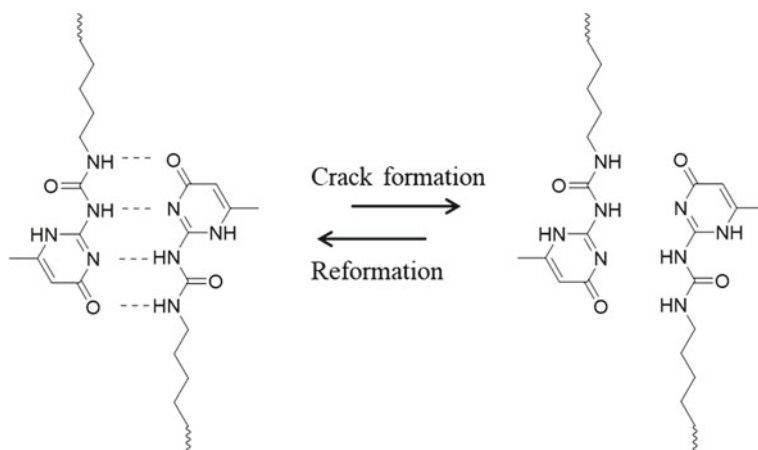

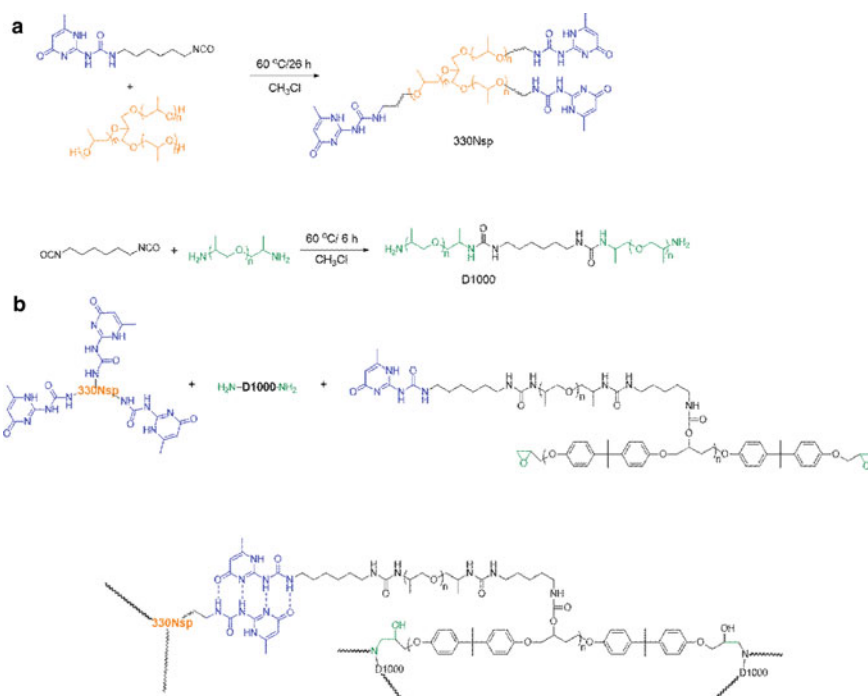**Fig. 5** Thermal dynamic exchange of urea isopyrimidone (UPy)

Fig. 6 Preparation of the UPy-based self-healing epoxy resin [37]
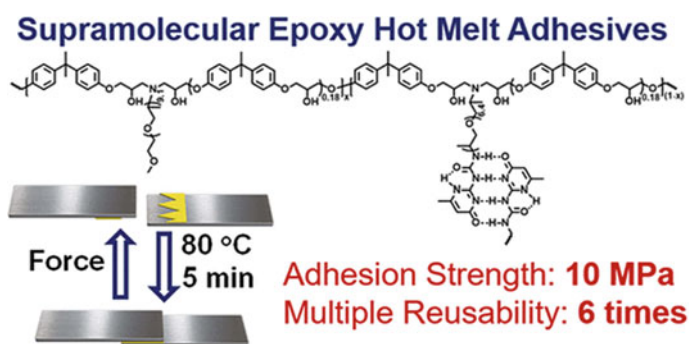

Fig. 7 Reusable hot melt adhesive based on supramolecular epoxy *Reproduced with permission from* Sun et al. [35]

UPy is suitable for preparing self-healing epoxy resins with high performance, but the chemical structure of UPy is still complex, and the synthesis route is cumbersome. In addition to the UPy-based hydrogen bonding, there are other common hydrogen bonds or supramolecular chemistries used in self-healing epoxy resins [38]. For instance, Kostopoulos et al. [39] introduced the hydrogen bond-based self-healing
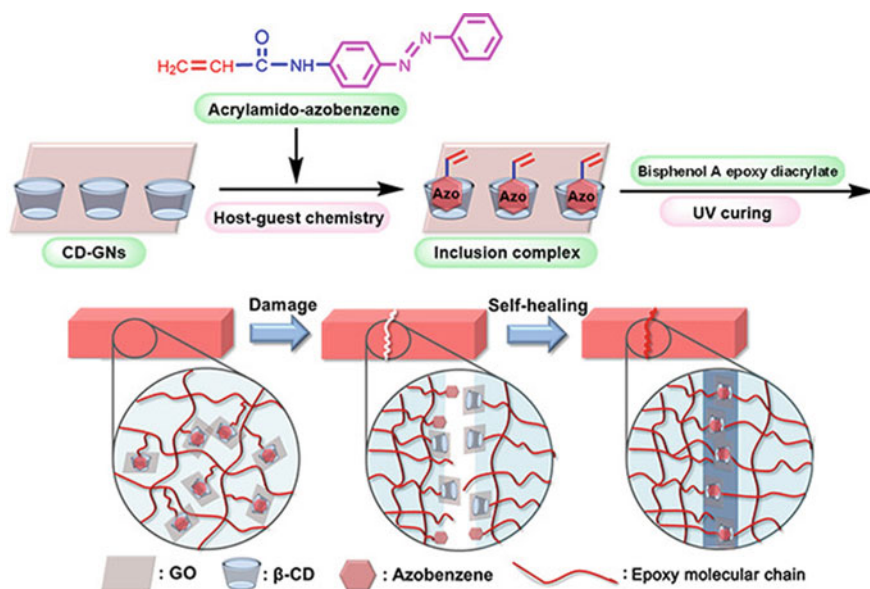
Fig. 8 The preparation process of the host–guest epoxy system and Schematic diagram of its self-healing process *Reproduced with permission from* Hu et al. [40]

epoxy resin into carbon fiber composites, and the self-healing performance was greatly improved after adding hydrogen-bonded supramolecular polymers. The host–guest system is a widely studied supramolecular chemistry. Hu et al. [40] introduced a host–guest system into an epoxy resin system, the obtained epoxy resin can achieve self-healing at 120°C with self-healing efficiency as high as 79.2%, but its synthetic method was relatively complicated (Fig. 8). For the sake of achieving epoxy resins combining excellent anti-corrosion performance and self-repairing performance, Boumezgane et al. [41] combined the advantages of supramolecular bonds (ionic dynamic bonds) and microcapsules (Fig. 9). The amino/carboxyl groups terminated PDMS was introduced into epoxy resin systems, and microcapsules were formed in situ. The surface damage of the resin released the functional PDMS oligomers to form supramolecular ionic networks, which endowed self-repairing capabilities and improved the anti-corrosion performance of the anti-corrosion coating on scratches.

3.2 Reversible Diels–Alder (DA) Addition

Diels–Alder (DA) adduct is generated by the cycloaddition of the conjugated diene system with the alkene or alkyne bond. Unlike the hydrogen bond mentioned above, the DA adduct was a kind of dynamic covalent structure, with larger bond energy than the hydrogen bond. Therefore, it is more suitable to prepare high-performance epoxy
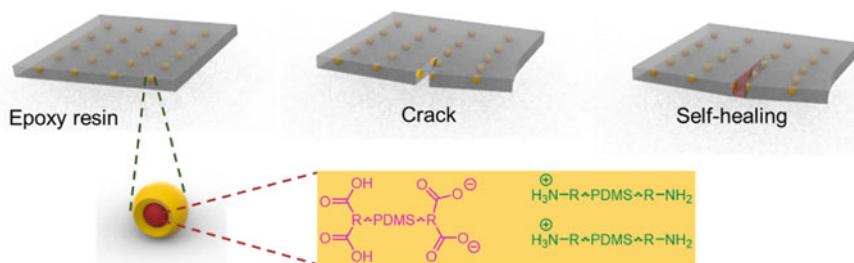
Fig. 9 Anti-corrosion epoxy resin based on ionic dynamic bond and microcapsules

resins. At high temperatures, the DA system dissociates to realize the easy migration of a part of the chain segments and further realize the self-healing of cracks. When the temperature drops, the decomposed conjugated diene system, and the alkene or alkyne bond undergo a cycloaddition reaction again to recover the resin's mechanical performance.

Chen et al. [7] first reported a cross-linked polymer that can be healed in a mild condition through disconnection and reconnection of DA adducts. The authors investigated the reversibility of Diels–Alder (DA) cross-linking by solid-state NMR, which demonstrated that DA adducts could decompose above 120°C and form at low temperatures. Further, they exposed the relationship between the rate of the formation of DA adduct and temperature. Taking advantage of this feature of DA adducts, Kuang et al. [42] prepared a DA adduct-containing diamine and further reacted with a commercial epoxy to produce an epoxy network with outstanding reprocessing and repeated self-healing. Cross-linked epoxy resins containing DA adducts can essentially behave like typical thermosets at room temperature, which cannot be dissolved in solvents. Nevertheless, it can be reprocessed quickly at high temperatures like thermoplastics. This is ascribed to the cleavage of the DA adduct at elevated temperature, which makes the resin reversibly switch between the cross-linked state and the linear structure.

Peterson et al. [43] developed a DA adduct-based reversibly cross-linked gel that can be utilized to repair epoxy resins. This gel can apply to the crack surface directly, and the resin's mechanical performance was recovered by 37%. Being heated, on account of the DA adduct's dissociation, the gel transformed into a fluid oligomer that diffused into the resin's crack, and the molecular chains of the oligomers also entangled with the chain segment on the crack surface. As the temperature dropped, the furan groups on the oligomers re-reacted with maleimide groups to rebuild a complete network structure (Fig. 10).

Since the DA addition reaction occurs on the crack surface, the healing effect between cracks is extremely sensitive to the distance between the crack surfaces. An effective way to reduce the crack distance is to expand and soften the material. Peterson et al. [44] invented a room temperature self-healing agent (a solution containing bismaleimide (BMI)) for DA adduct-containing thermosetting polymer. Solvent swelled and softened the crack surface, which led to the physical bonding of
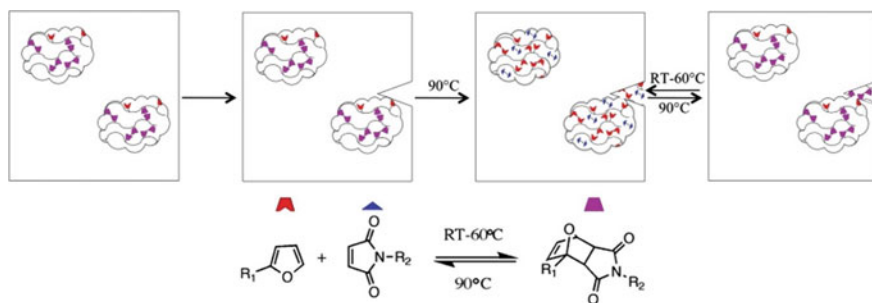
Fig. 10 DA adduct-based reversibly cross-linked gel as the secondary healing phase to repair epoxy networks *Reproduced with permission from* Peterson et al. [43]
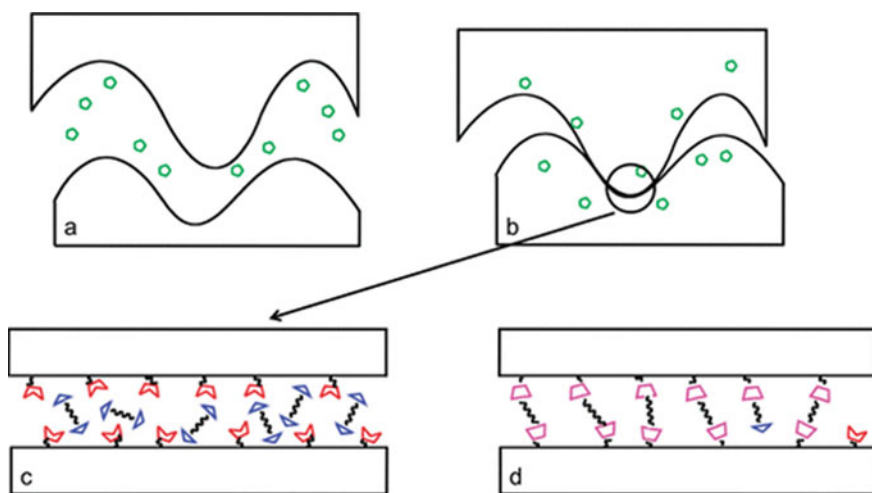

Fig. 11 Room temperature self-healing agent for DA adduct-containing thermosetting polymer. Green pentagon: solvent molecules, red notched trapezoid: furan, blue triangle: maleimide, and magenta trapezoid: DA adduct *Reproduced with permission from* Peterson et al. [44]

the cracks, and then chemical bonding from the DA addition reaction also occurred at room temperature as the crack width is less than the length of BMI (Fig. 11). The physical bonding contributed to 28.4% healing efficiency, and chemical bonding led to another 41.6% healing efficiency.

3.3 *Disulfide Bond Exchange*

In recent years, self-healable epoxy resins based on disulfide bonds have received extensive attention from researchers. Unlike DA addition, during the healing process,

the disulfide bond does not undergo significant dissociation at high temperatures. However, it undergoes a rapid exchange reaction, so the cross-link density of the material does not decrease significantly. Consequently, no annealing is necessary to realize self-healing for disulfide bond-based self-healing epoxy resins, while DA adduct-based ones often require a long time of annealing to achieve favorable recovery of mechanical properties.

Lei et al. [45] added tri-*n*-butylphosphine (TBP) into an epoxy resin containing disulfide bonds. TBP could catalyze the metathesis exchange of disulfide bonds at room temperature under alkaline conditions. Through this reaction, the cross-linked epoxy resin containing disulfide bonds can self-heal at room temperature (Fig. 12), which is demonstrated by the repeated recovery of tensile strength. In addition, this polymer can also realize the network rearrangement through the dynamic exchange of disulfide bonds, and the reprocessed resin maintains the original mechanical performance. Without a TBP catalyst or disulfide bond, the control group failed to achieve self-healing or reprocessing.

Memon and Wei [46] designed and synthesized an epoxy resin containing a disulfide bond. Through the curing reaction of this epoxy resin and methyl hexahydrophthalic anhydride, disulfide bonds were introduced into the epoxy network (Fig. 13). The obtained epoxy network possesses excellent thermal properties and mechanical performance. Via the reversible bonding of disulfide bonds, the resin can realize welding repair and remodeling processing. After reprocessing three times, the resin maintained mechanical performance well with a recovery of > 90%. This resin can also be degraded in a solution containing sulfhydryl groups to yield oligomers.
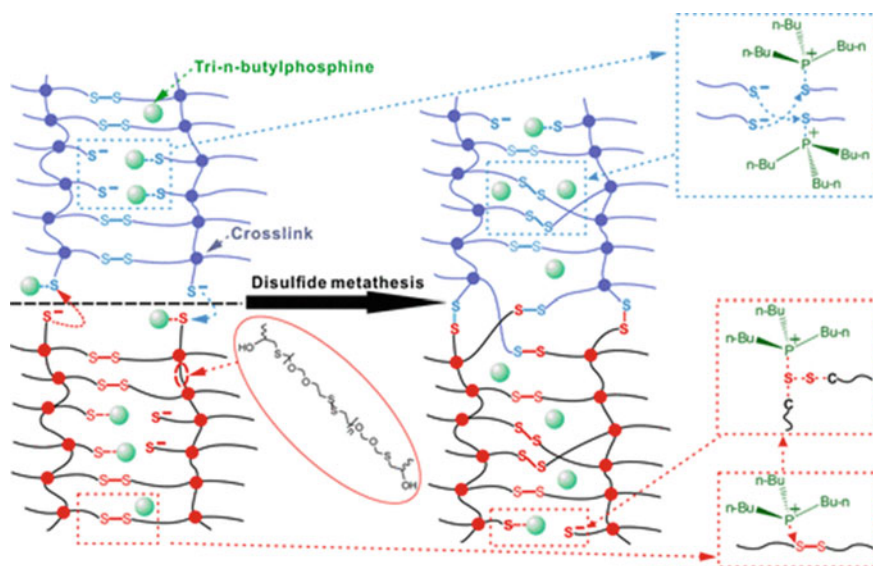

Fig. 12 Epoxy network containing disulfide bonds catalyzed by tri-n-butylphosphine *Reproduced with permission from* Lei et al. [45]
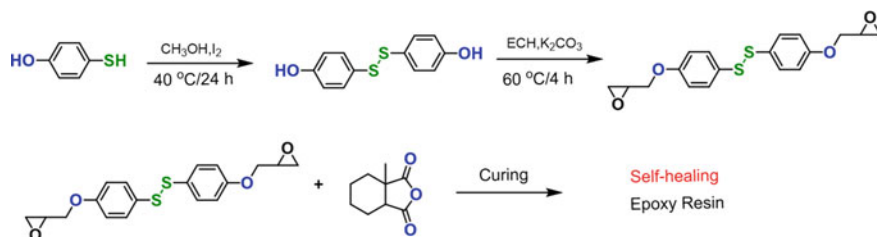
Fig. 13 Synthesis of epoxy monomer containing disulfide bond and its self-healing epoxy resin [46]

Si et al. [47] prepared an epoxy network from a diepoxy and a diamine containing aromatic disulfide bonds. High glass transition temperature (T_g, 147°C) and tensile strength (63.1 MPa) were achieved. Besides the benefit of the abundant disulfide bonds, the exchange efficiency of the network is greatly improved, enabling rapid relaxation without a catalyst. Carbon fiber composites (CFRP) based on this epoxy network could be easily degraded by small-molecule sulfhydryl compounds to obtain recycled carbon fibers, which can be reused to prepare CFRP with excellent mechanical properties.

3.4 Imine Exchange

Similar to the disulfide bond, the imine bond is also a dynamic bond with high exchange activity, which allows for rapid exchange without a catalyst via the metathesis reaction (Fig. 14) [48]. In addition, the raw materials are commonly available because they can be facilely prepared by the condensation reaction of the amino group with the aldehyde group. Lei et al. [48] first demonstrated that the self-healing of thermosets could be achieved via incorporating an imine bond.

For epoxy resins, imine bonds can be introduced into the chemical structures of epoxy monomer (Fig. 15a) or curing agents (Fig. 15b) or can be in-situ built during the formation of the cross-linked network. The introduction of imine bonds into
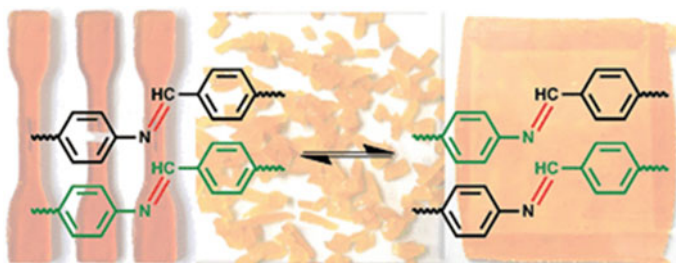

Fig. 14 Exchange mechanism of imine bond [48]

epoxy resins can provide self-healing performance without scarifying thermal and mechanical properties. In addition, imine bonds can also bring quite a few attractive features, such as antibacterial activity, [49, 50] anti-corrosion property, [51] and degradability [52, 53] etc. In 2019, Mo et al. [51] introduced the imine bond into the curing agent. The imine bond was incorporated into the epoxy network through the curing reaction of the curing agent and the epoxy monomer. The prepared epoxy resin can achieve self-healing within 1 h at 90°C, but with increasing cross-linking density of the network, the resin's healing process was hindered. Meanwhile, incorporating an imine bond also endows epoxy resin with excellent corrosion resistance. Similarly, Mai et al.[54] prepared a curing agent containing imine bonds through the reaction of vanillin with hexane-1,6-diamine and then used this curing agent to cure epoxy resins. The prepared epoxy resin can achieve self-healing within a few minutes at 90°C. The introduction of imine bonds into epoxy monomers was also a common method for preparing imine-based epoxy resins. Jiang et al. [55] prepared imine-containing epoxy monomers using 4-aminophenol and vanillin as raw materials. The cured epoxy resins can be self-healed within a few hours at 120°C and possess excellent mechanical properties, thermal stability, and solvent resistance.

To accelerate the dynamic exchange reaction and increase the self-healing efficiency, we designed an epoxy resin containing both imine bond and DA adduct [56]. The synergistic exchange effect accelerated the network rearrangement to realize the fast self-repairing and reprocessing of the epoxy resin. In addition, by adjusting the ratio of imine bond and DA adduct, the tensile strength of this material can be adjusted in the range of 10–90 MPa, which has the characteristics of a large adjustment range and good mechanical properties. Since the degree of reaction of DA adducts increases with annealing time, the authors investigated the effect of imine bonds on the formation of DA adducts and found that the formation rate of DA adducts increased when increasing imine bond content. At the same time, a series of
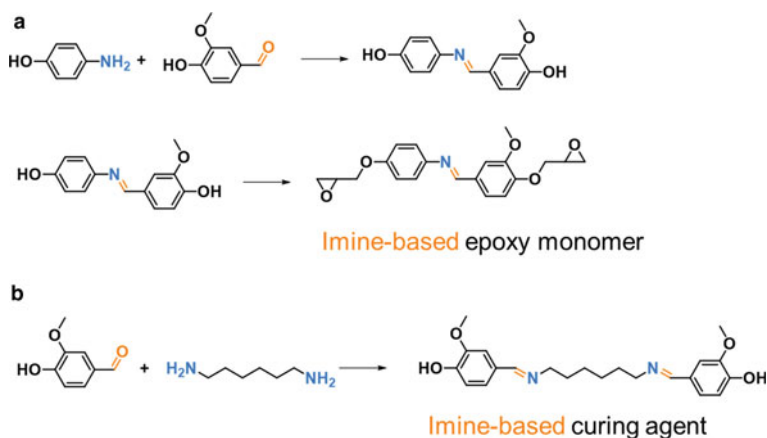

Fig. 15 Synthetic routes of imine-based epoxy monomer and curing agent

materials with various mechanical performances can be easily achieved by adjusting the annealing time.

3.5   Ester Bond Exchange

In addition to the above-mentioned dynamic bonds, the ester bond is also a commonly reported dynamic bond, which can be readily introduced into the cross-linked epoxy networks through the curing reaction of epoxy monomers or oligomers with acid anhydrides or carboxylic acids. However, compared with the dynamic bonds mentioned above, the exchange efficiency of ester bonds was relatively low. Therefore, to realize the self-repairing performance of epoxy resins, it is essential to adopt catalytic methods to accelerate the exchange of ester bonds. Liu et al. [57] prepared eugenol-based epoxy monomers and then used succinic anhydride as the curing agent to prepare a dynamic network based on an ester bond (Fig. 16). The self-healing was achieved by transesterification catalyzed by zinc acetylacetonate hydrate ($Zn(acac)_2$). However, limited by the efficiency of the transesterification, the crack required to be thermally treated for 1 h (190°C) to realize partial repair. Similarly, the authors further prepared a bio-based self-healable epoxy network with a bio-based triepoxy and 4-methylcyclohexane-1,2-dicarboxylic anhydride. Self-healing was achieved within several minutes at 220°C with the catalysis of Zn^{2+} [57]. Ding et al. [58] also introduced ester bond into epoxy resins via curing of epoxy monomers with glutaric anhydride. However, owing to the low ester exchange activity, the system required to be thermally treated for two hours (200°C) to realize self-healing. Besides, the above works realized the self-repairing performance of ester bond-based epoxy resins by introducing external catalysts. Therefore, the addition of catalysts would inevitably bring about issues such as toxicity and environmental protection. Thus, several auto-catalytic systems based on tertiary amine, [59, 60] excess hydroxyl group, [61] carboxyl group [62] etc., were developed. For instance, Liu et al. [61] reported a catalyst-free self-healable epoxy resin through hyperbranched epoxy oligomers. The excess hydroxyl groups in the system catalyzed the transesterification so that the resin could achieve partial self-healing within several hours at 150°C without additional catalyst.

4   Conclusion and Prospect

There are two catalogs of self-healable epoxy resins: extrinsic and intrinsic. Extrinsic self-healable epoxy resins were based on loading hollow fibers, microcapsules, or thermoplastic additives. The mechanisms for hollow fiber and microcapsule methods are the same. Both realize self-repairing by releasing a healing agent from the broken hollow fibers or microcapsules in the cracks. For these two methods, self-healing is independent of the properties of the epoxy resins. Those with high modulus and high
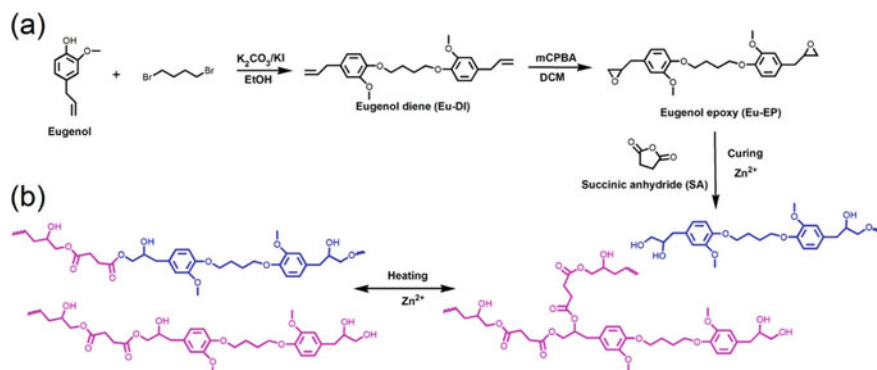
Fig. 16 a Synthesis and curing of eugenol-based epoxy monomer and **b** exchange mechanism of ester bonds in epoxy cross-linked networks [57]

T_g can also be self-healed. However, the preparation of hollow fibers and micro-capsules filled with healing agents is not easy. Loading them also affects the epoxy system's viscosity and processability, and the cracks can be self-healed only once. For the method of using thermoplastic additives, the preparation process is simple, and the cracks can be self-healed multiple times. However, it requires high loading of thermoplastic additives and favorable compatibility of thermoplastic additives and epoxy resins, and the healed cracks re-break easily at elevated temperatures.

Recent two decades witnessed the rapid development of intrinsic self-healable epoxy resins from dynamic bonds: non-covalent (supramolecular) or covalent. For the supramolecular method, hydrogen bonds, ionic dynamic bonds, or host–guest systems were applied to realize the self-repairing of epoxy resins. For the method of using dynamic covalent bonds, Diels–Alder adduct, imine bond, disulfide bond, and ester bond were commonly used to produce self-healing epoxy resins, and diselenide bond, etc. were also exploited. For the intrinsic method, the epoxy resins can be theoretically self-healed many times. Diels–Alder adduct-based self-healing epoxy resins can repair the cracks easily at elevated temperature by virtue of the cleavage of Diels–Alder adduct and the reduction of the epoxy networks' cross-link density, but to achieve enough strength of the healed cracks required further annealing. Disulfide and imine bonds as the dynamic bonds based on associative mechanisms can also provide excellent self-healing properties to the epoxy resins. While the disulfide bond is flexible, as a result, the obtained epoxy resins often exhibited relatively lower T_g and modulus compared with traditional epoxy resins. Imine bond-based self-healing epoxy resins can possess high modulus and T_g, which is attributed to the rigidity of its excellent hydrogen bonding and conjugated ability with the benzene ring. At the same time, it is easy to be thermally aged during the thermal-triggered healing process. Ester bond-based self-healing epoxy resins have attracted significant attention, especially after the first report of vitrimers. However, their self-repairing efficiency is limited on account of the slow transesterification. For the intrinsic self-healable epoxy resins, the self-repairing is often triggered by other stimuli such as

heating, UV radiation, etc. As a result, most of them are not the real self-healable ones; and it is still a challenge to achieve outstanding self-healing for those with high modulus and T_g.

In the future, self-healing efficiency should be improved. For example, the synergistic effect of two or more dynamic bonds can be utilized to accelerate the dynamic exchange and self-healing. During the service, stability and durability of the epoxy resins are also exceedingly important, so the stability or aging resistance of dynamic bond-based self-healing epoxy resins should be focused on to realize a delicate balance between self-repairing efficiency and stability. Epoxy resins are mainly from nonrenewable fossil resources, so self-healing epoxy resins from renewable bioresources should also be investigated. Materials with multiple functions are the future trend, so other functions such as flame retardancy, anti-fouling, anti-corrosion, shape-memory, recyclability, should also be introduced into self-healing epoxy resins. Although applications of self-healing epoxy resins in composite materials, anti-corrosion coatings, etc., were reported, research on specific applications' overall properties is still limited.

Conflicts of Interest There is no conflict of interest to be declared.

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