Mechanism of Extrinsic and Intrinsic Self-healing in Polymer Systems

Sérgio Henrique Pezzin

Abstract Self-healing materials, which can increase the lifespan of various types of products, have been researched quite intensively in recent decades. In general, self-healing polymers and composites are classified based on their mechanisms of action. While extrinsic systems depend on an external healing agent, the process takes place through reversible bonds or supramolecular interactions in intrinsic systems. In this chapter, the main mechanisms of self-healing epoxy systems, involving extrinsic and intrinsic approaches, autonomous and non-autonomous, are presented and discussed. Since the development of the first extrinsic self-healing epoxy systems, based on microcapsules and vascular networks, which are still the most studied approaches for coatings and composites, many new possibilities have been researched, especially systems involving intrinsic mechanisms. Among them, mechanisms of dynamic covalent networks based on thermally activated reversible Diels–Alder reactions and disulfide bonds, and photoreversible cross-linking have been considered. Furthermore, new trends in self-healing processes concerning vitrimers, non-covalent supramolecular systems, shape memory-assisted self-healing, and bio-based epoxy materials are introduced, looking forward to a wider range of possible applications.

Keywords Epoxy · Self-healing · Mechanism · Extrinsic · Intrinsic · Microcapsules · Vitrimers · Shape memory · Dynamic bonds · Supramolecular

1 Introduction

Self-healing materials are, simply, materials that have the built-in ability to regenerate or 'cure themselves' autonomously, that is, without human intervention. Since the early 2000s, researchers in academia and industry have begun to use several innovative scientific techniques and ideas to create a variety of materials that self-heal

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damage, thus providing a means to significantly extend their service life, increase reliability, and reduce costs.

The great initial motivation for the development of these materials was that in applications with high mechanical demand, such as in aircraft, wind blades, cars, ships, etc., they are subjected, during their useful life, to mechanical and/or thermal fatigue, exposure to ultraviolet radiation, exposure to chemicals or a combination of these factors, leading to the formation of microcracks. These microcracks are difficult to visualize and repair and can propagate along with the material, leading to premature failure [1–5]. These materials are, therefore, especially important in case of internal matrix damage in composite materials, for example, in wind blades, which are difficult to detect, and/or in which it is impossible to carry out corrective maintenance *in loco* [6].

The inspiration for the design of these materials came from nature, a field of science called 'biomimetics' and which is currently undergoing rapid development. We all know that living things, like plants and animals, can seal and heal injuries to a certain extent. In general, there is first a self-sealing phase to avoid desiccation of the cellular tissue and the attack of pathogenic microorganisms, which is followed by a self-healing phase. These processes have been the basis for, bioinspired self-healing materials [7–10], including polymer composites [11–15]. This field is also related to other biomimetic materials, such as those with self-organization, self-lubrication, and self-cleaning capacity [16].

Following these motivations and inspirations, a variety of self-healing polymer materials have been investigated, including thermosets, such as those based on epoxy [1, 17–24] and vinyl-ester [25] matrices, thermoplastics [26–28], and elastomers [29–31].

In short, it is hoped that these materials can [32]:

- regenerate autonomously and multiple times;
- regenerate defects of any size;
- perform better or equal to traditional materials;
- present lower maintenance cost and lower cost compared to other high-performance materials.

1.1 Historical Background

Although cementitious materials with self-healing properties have been used since the ancient Romans [33] and academically studied for more than one century [34], autonomous self-healing polymer materials are a product of the twenty-first century.

Before going into autonomous self-healing materials, it is worth remembering that since the middle of the last century, several researchers had already developed and tested some methods to repair/heal polymer-based materials, including composites, but which still involved some degree of human intervention. For example, pouring a curing agent into the crack [35], injection of adhesive/resin through capillary tubes [36], immersion in solvents [37, 38], or heat and pressure welding [39]. The work of researcher Carolyn Dry [36] stands out, including a 'recipe' for the development of future self-healing systems using hollow glass fibers containing the curing agent embedded in the polymer matrix, which would break by mechanical stress.

The first works involving autonomous repairing appeared in 2001. The cornerstone was laid by researchers from the University of Illinois at Urbana-Champaign (USA), who presented a self-healing polymer system consisting of an epoxy matrix containing a catalyst (Grubb's catalyst), to which microencapsulated dicyclopentadiene (DCPD), the healing agent, was added [1].

In general, 'first-generation' self-healing materials have a single chance of curing, the ability to repair only minor superficial scratches, or require heat to be repaired. Toohey et al. [40] prepared an epoxy material containing a microchannel framework containing dicyclopentadiene (DCPD) and Grubbs catalyst incorporated into the surface to address these problems. By this concept, the self-healing process can be repeated several times due to the possibility of replenishing the channels after use, but not *ad aeternum* since the polymer generated in previous cures would accumulate in the crack plane with time. It also did not fit into the more restricted concept of 'autonomous,' as it would require an external intervention to replenish the microchannel system.

From there to now, a myriad of self-healing systems based on thermoset and thermoplastic polymers has been developed [2, 11, 12, 15, 30, 41–47] for diverse types of applications in composite structural materials and coatings. The most recent approaches deal with materials that can self-heal indefinitely, for example, by shape memory effect [48–52], or by reversible cross-linking via intermolecular interactions (supramolecular chemistry) [53–56], and reversible chemical reactions [57–60].

To get an idea of the growing interest in the topic, Fig. 1 provides a profile of the number of publications in the period 2001 to 2021, and it can be noted that there is an almost exponential growth in scientific works in this area.

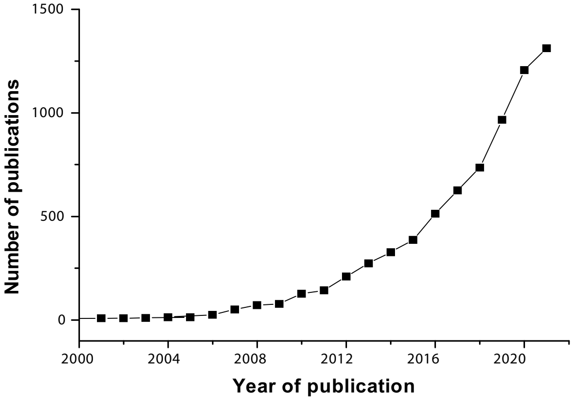


Fig. 1 Graph of the number of publications per year, from 2001 to 2021, according to a survey by "self-healing AND polymer*" with the 'web of sciences' (accessed in 15/03/2022)

1.2 Types of Self-healing Materials

Self-healing polymers generally follow a three-step process very similar to a biological response. The first response is the trigger, which occurs almost immediately after the damage occurs. The second is the transport (diffusion) of the healing agent to the affected area, which is usually also relatively quick. The third step is the physicochemical repair process, which may involve different mechanisms, such as polymerization, interchain interactions, reversible cross-linking, entanglement which will be discussed later.

Based on these different repair mechanisms, autonomous self-healing materials can be divided into three different groups: extrinsic, intrinsic, or combined [30, 47, 61–63].

Extrinsic systems are those that depend on an 'external' healing agent, normally released from microcapsules dispersed in the matrix or by vascular networks. In this process, self-healing is generally triggered by the displacement of a microcrack, and cross-linking begins at room temperature. The first generation of self-healing materials is based on these systems.

In intrinsic systems, the regeneration process takes place through the restoration of reversible bonds (covalent or ionic) or intermolecular or supramolecular interactions and/or through molecular interdiffusion processes [64, 65]. Recently, combined systems have been proposed, especially for applications in elastomers, which involve several types of intrinsic covalent (Diels–Alder, disulfide/diselenide bonds, transesterification, etc.) and non-covalent (hydrogen bonds, π-π interactions, ionic interactions, metallic coordination bonds, shape memory, etc.) processes [30, 66–68].

A new classification was proposed in 2020 [30], based on constructive criticism of the most used categories (extrinsic and intrinsic), considering the chronological order of the development of self-healing polymer materials. In this approach, the materials are classified into generations, being the 1st those based on microcapsules (extrinsic), the 2nd based on intrinsic approaches, the 3rd those presenting vascular systems (extrinsic), and the 4th those consisting of combined (essentially covalent/non-covalent intrinsic) systems.

When the material needs the application of an external stimulus such as heat and/or pressure [69, 70], light, or pH [71] for the repairing process to occur, the material is still considered self-healing but not autonomous [72–74].

2 Autonomous Self-healing Epoxy Systems: Extrinsic Approaches

In extrinsic systems, healing agents are added to the polymer matrix in microcapsules or vascular networks. In both cases, the autonomous healing process is initiated by fatigue or external damage, in the form of microcracks or fissures, which act as starting mechanisms (triggers) for self-healing. A propagating microcrack breaks the microcapsules or capillaries embedded within the polymer matrix, releasing the healing agent, which by capillary action, is deposited in the plane of the microcrack [1, 75]. Polymerization is initiated when a healing agent encounters an initiator incorporated into the matrix (a catalyst, for instance), the resin's functional groups, or another reactive compound, previously added to the matrix or also released from microcapsules/capillaries, binding the crack faces [1, 4, 19, 41].

Epoxy resins are extensively employed as matrices in self-healing polymer materials [4, 44], as, in general, there is no need for external intervention other than microcracks since polymerization/cross-linking can occur at room temperature. Extrinsic self-healing epoxy materials can achieve healing efficiencies above 100%, even when damaged severely [76].

These systems can be separated into several groups. While microcapsule-based systems only release healing agents when they are ruptured, vascular materials contain the healing agent in hollow capillary channels, which can be uni-, bi-, or three-dimensionally interconnected. When one of these capillary channels is damaged, the network can be recharged by another channel that has not been damaged (in the autonomic approach) or by an external source (non-autonomous system) [77].

2.1 Systems Based on Microcapsules

The idea of using a microencapsulated healing agent in an epoxy matrix, aiming to restore physical properties after stress is applied to the material, has attracted the interest of many researchers and various industrial segments, such as aerospace, automotive and high-tech industries [4, 73, 78–80].

Healing agents and/or hardeners/catalysts are encapsulated to be protected from environmental and matrix influences so that they can remain inactive for a long period of time. Generally, healing agents are microencapsulated by emulsification. In this process, the monomers polymerize to form an envelope that surrounds the drops of the liquid healing agent in suspension or, in the case of hollow microcapsules, that enclose air bubbles in suspension [75, 78, 81–83].

The flowchart in Fig. 2 represents the stages of development to give materials the ability to self-heal by using microencapsulated agents.

To provide this functionality, the first step is to choose a healing agent that presents a suitable chemical repairing mechanism. Next, an appropriate shell material for the preparation of microcapsules containing the healing agent and/or the hardener and the encapsulation method is determined. In the latter step, the core properties, the matrix's processing capacity, and the crack response must be considered [74]. For instance, an increase in microcapsule or catalyst content can reduce the processability due to increased resin viscosity, and, thus, care must be taken with processing conditions to minimize microcapsule breakage during mixing and mold filling stages.

In self-healing systems that employ microencapsulated healing agents, at least one component must be flowable [43, 74]. These systems can also consist of an

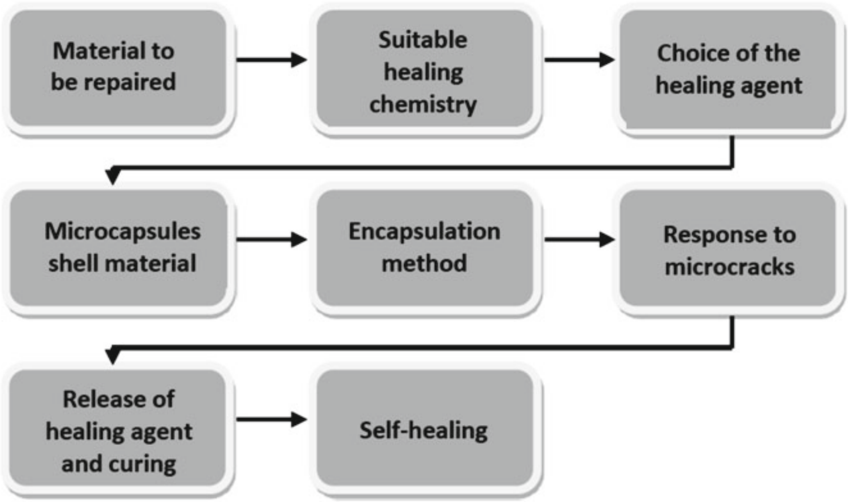
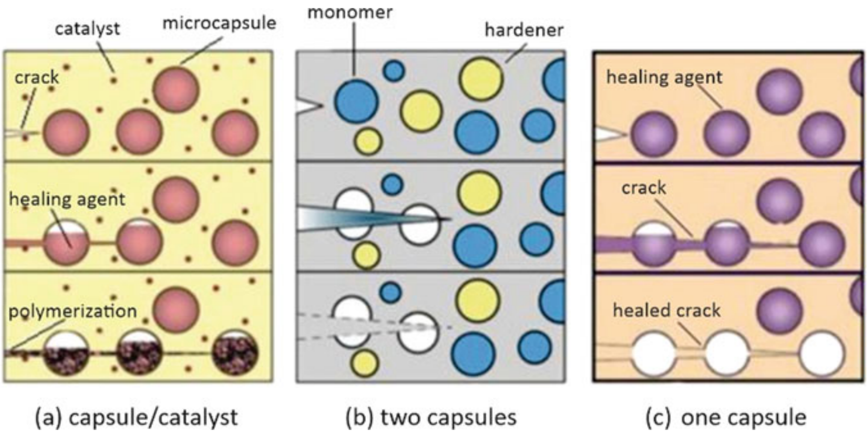


Fig. 2 Flowchart of development steps to provide self-healing capacity to polymer materials using microencapsulated curing agents

encapsulated component [1, 83, 84], two encapsulated components [17, 24, 25], or even a 'dual' system, where one component is a particle or droplets, and the other component is in the form of microcapsules [85]. Figure 3 represents the scheme of the healing mechanism of each of the systems described above.



(a) capsule/catalyst (b) two capsules (c) one capsule

Fig. 3 Microcapsule-based self-healing approaches **a** a two-component system, where one component is a particle (catalyst), and the other is a capsule (reproduced with permission [1], copyright 2001, Springer Nature); **b** a two-component encapsulated system in which the monomer and healing agent are encapsulated (based on Jin [86]); **c** encapsulated single component system

Self-healing systems of one encapsulated healing agent generally consist of a single type of microcapsule [74], in which the release of the healing agent starts a reaction with adjacent functional groups of the matrix on the fractured surface. In a two-component system, the two components are encapsulated so that one capsule can contain the resin or monomer and the other the hardener. Soon after the microcapsules rupture, due to the propagation of microcracks in the matrix, the monomer is polymerized under the action of the surrounding hardener/catalyst. In two-component systems formed by particles/droplets and capsules, at least one component must be fluid to be released with the crack propagation and react with a neighboring component, such as a catalyst. That is, these systems are formed by a reactive component that must be encapsulated and particles or droplets in a separate phase of the matrix. The closure of the crack occurs through capillarity and polymerization, which is triggered by the contact with a catalyst [74].

As already pointed out, self-healing occurs when the microcapsule breaks due to the appearance of microcracks inevitably generated in polymer materials during their time of use or external damage [1, 4, 45, 75]. For this process to take place without manual intervention and at room temperature and for the healing agent to remain intact inside the microcapsule, a catalyst/initiator can also be encapsulated or dispersed in the polymer matrix [1, 2, 4, 25]. In each case, the microcapsule disruption mechanism at the crack points offers a specific autonomous repair control [75, 84]. There are many challenges in designing microcapsule-catalyst systems. Firstly, the reactivity of the catalyst needs to be preserved even after it is dispersed in the matrix or encapsulated. In addition, the healing agent must have an adequate viscosity to completely fill the microcrack before it is polymerized [18, 87].

The first studies on autonomic systems with microcapsules containing a healing agent have been reported by White and colleagues [1, 13, 18, 82]. They induced the polymerization of dicyclopentadiene (DCPD) in the presence of Grubbs catalyst (benzylidene-*bis*(tricyclohexylphosphine)dichlororuthenium) in an epoxy matrix. The healing agent, DCPD, was microencapsulated in poly(urea–formaldehyde) (PUF) by in situ polymerization in an emulsified system, forming a capsule that surrounds the liquid DCPD drops. The monomer itself is relatively unreactive, and polymerization does not occur within the microcapsule [88]. When a microcrack reaches the capsule containing DCPD and the catalyst, however, the monomer is liberated from the microcapsule and meets the bare catalyst, undergoing polymerization by ring-opening metathesis (ROMP). They found that the microcapsules effectively released the healing agent in the crack plane, inducing polymerization and damage repair. The self-healing efficiency of this system was 75% in terms of fracture toughness. These experiments paved the way for many other works using DCPD, aimed at improving the encapsulation technique and/or evaluating the effect of mechanical agitation speed, concentration, and type of surfactant [13, 25, 82, 89]. For example, Brown et al. [18, 82], varying the stirring speed from 200 to 2000 rpm, obtained capsule sizes from 10 to 1000 μm, while Blaiszik et al. [89] studied the reduction of the size of capsules to the nanoscale by modifying the agitation process with the joint use of sonication. The effects of the size and concentration of microcapsules on mechanical properties of epoxy matrices, such as fracture toughness and self-healing efficiency, have also been evaluated [3, 25, 90, 91]. These studies defined the percentages and sizes of microcapsules with the best results on the self-healing efficiencies of different epoxy matrices. An interesting variation was proposed by Skipor et al. [92], in which the catalyst is fixed to the outside wall of microcapsules filled with the healing agent. But few experimental details and results of self-healing efficiency have been given in their patent.

Other self-healing epoxy systems using diverse encapsulated healing agents, such as the epoxy resin itself [19, 93], linseed oil [94, 95], tung oil [72], poly(dimethylsiloxane)s [24, 85], polyamines [17, 24, 96], and polyurethanes [97, 98], have also been studied for both structural and coating applications. In most of these cases, the use of catalysts is not mandatory, since the healing agents can react with residual amines and/or epoxy groups within the polymer matrix [17, 75, 99]. An interesting example is the use of encapsulated amines since, due to their reactivity and solubility in water, the preparation of capsules with PUF or polyurethane shells is tricky. Jin et al. [17] developed a method to encapsulate amines by vacuum infiltration into hollow PUF microcapsules prepared by interfacial polymerization using air/water emulsions. In their work, the best results in mechanical properties were obtained using 17.5% epoxy- and amine-filled microcapsules with an average diameter of 220 μm. Weihermann et al. [24] improved this process, introducing a self-healing epoxy system based on PUF microcapsules infiltrated with an amine-functionalized poly(dimethylsiloxane) (PDMS-a). The amine-functionalized poly(dimethylsiloxane), in contact with triethylenetatramine (TETA), was able to efficiently repair the cracks by the reaction of the amine groups with epoxy rings remaining in the matrix.

Another important consideration is the change in mechanical properties and processing characteristics of epoxy matrices caused by the addition of microencapsulated healing agents/catalysts, which will depend on the volumetric fraction of the microcapsules, and the extent of the matrix/microcapsule interfacial interaction [90, 100]. However, it has been shown that epoxy resin can be significantly toughened (up to 127%) with 15 wt% of microcapsules filled with DCPD [1] or 2.5 wt% with amino-functional polydimethylsiloxane [24], and by addition of Grubbs catalyst [18]. The concentration of microcapsules for maximum toughness is greatly dependent on the mean diameter of the microcapsules, with smaller diameters providing maximum toughness at lower concentrations, as evidenced by fractographic analysis [13, 18, 75].

X-ray micro-computed tomography (μCT) is a non-destructive technique that can be very useful to evaluate self-healing materials and mechanisms, making possible bulk visualization by 3D reconstruction [101, 102]. For instance, μCT was applied to monitor the rupture of microcapsules filled with healing agents in the fracture region [75, 103], enabling the quantification of the amount of released healing agents and detecting healed and non-healed areas. Tomography using synchrotron radiation [104] showed that the rate of absorption/reaction of healing agents after fracture depends on the diameter of the microcapsule. A delay is observed for larger microcapsules due to smaller surface/volume ratios. Recently, Caballero-Peñas and coworkers [105] showed that free OH groups are responsible for self-healing of epoxy samples with different curing agents, after producing a superficial cut and heating the sample above its T_g. The authors suggested evaluating larger areas to confirm the healing mechanisms. It is also possible to follow the crack propagation as a mechanical test is performed, making is possible to obtain in situ information about how microcapsules are broken, how the healing agent fills the cracks and self-healing efficiency. μCT, in combination with electron microscopy, was also used in the study of self-healing mechanisms in epoxy systems using microencapsulated amine-functionalized polysiloxanes (PDMS-a) as healing agents [75]. When analyzing specimens after mechanical stress, it was possible to evaluate the distribution and stability of the microcapsules, as well as to recognize the trigger mechanism when a crack appears within the matrix, showing that PDMS-a was effective to heal microcracks even at room temperature. It was observed that most microcapsules with diameters >60 μm (shell thickness ca. 0.4 μm) are broken during dispersion into the epoxy matrix, in contrast to those with diameters <60 μm, which remain intact during the dispersion and curing of the resin. μCT and SEM images confirmed that the self-healing process occurs by a mechanism involving crack bowing and deflections, as shown in Fig. 4, indicating that the microcapsules are very well adhered to the polymer matrix. High fracture toughness values obtained using the same system [24] can thus be explained by this crack deflection mechanism.

The same epoxy/PDMS-a self-healing system, now in glass fiber-reinforced composites, has also been studied, under mechanical stress, using multi-contrast X-ray imaging with an inverted Hartmann mask [106]. Absorption and differential phase-contrast images revealed the distribution of glass microfibers, while scattering contrast imaging showed the changes in the inner structure of the polymer composites, indicating microfracture propagation and uniform microcapsule distribution.

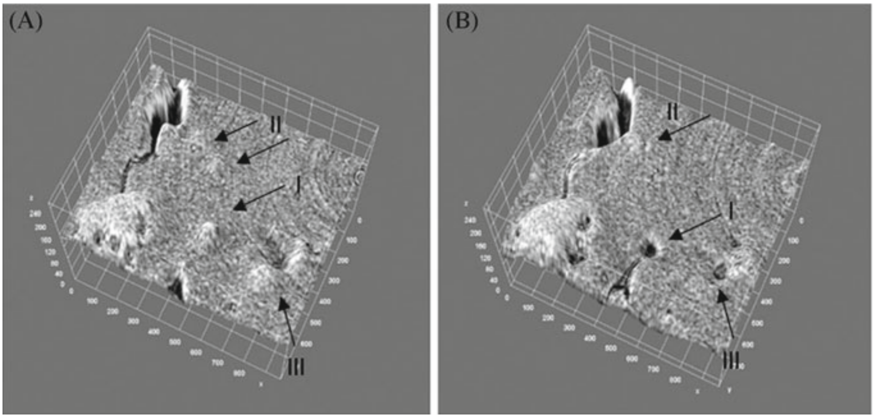


Fig. 4 **a** 3D plotting of a slice surface of an epoxy sample containing PUF microcapsules filled with PDMS-a. The light gray spots, pointed by arrows I, II, and III are microcapsules responsible for the release of the PDMS-a in the crack area; **b** 3D plotting showing cavities after the release of the healing agent (arrows II and III). Reused from [75] (Wiley-VCH GmbH, CC BY 4.0)

It was thus possible to track the self-healing triggering mechanism acting on the polymer composite under mechanical stress.

There are not many studies on systems using polymeric nanocapsules yet [42, 89, 107, 108]. A study by Blaiszik et al. [89] showed that PUF nanocapsules (diameters 220 ± 113 nm, with a mean wall thickness of 77 nm) containing DCPD, prepared by in situ encapsulation using ultrasound, were uniform and thermally stable up to 150 °C. The encapsulation efficiency in these capsules was almost 94%, with the great advantage of allowing a much better dispersion in the epoxy matrix (up to 2% volume fraction). The authors concluded that nanocapsules exhibit damage-responsiveness, which can be useful in several applications.

2.2 *Systems Based on Vascular Networks*

By this concept, healing agents can be delivered from an external source to damage points throughout a vascular network structure, and the process could be, in principle, repeated several times due to the replenishment capacity of the channels after a regeneration. In one of the first representative works using this approach, Toohey et al. [40] prepared an epoxy material containing an array of microchannels containing dicyclopentadiene (DCPD) with Grubbs' catalyst incorporated on the surface (similar to the microcapsules approach), demonstrating the partial recovery of toughness after a fracture. The strategy can be applied to vascular systems in one (1D), two (2D), or three dimensions (3D) [40, 77, 109]. Nevertheless, several issues are still challenging [77]. The first point is the limit on the number of times the material can be healed since the polymer formed in the plane of the crack of previous cures accumulates with time, obstructing any further flow of the healing agent. The second is the upscaling of the process, as currently, only the proximity of the network channels can be healed. Furthermore, as in systems based on microcapsules, care must be taken not to damage the matrix in the formation/integration of the channels, which could lead to a worsening of the mechanical properties of the material.

2.2.1 Hollow Tube Approach

The first works on vascular systems used capillaries, i.e., hollow fibers, usually glass, embedded in a polymer matrix [10, 36, 110–113]. Part of this capillary network is filled with monomer and part with a curing agent (hardener). When material damage occurs from regular use, the tubes also crack, and monomers and hardeners are released into the matrix microcracks, promoting their repair (Fig. 5) [10]. A patent related to this concept was granted in 2006 [114].

There are important things to consider when hollow tubes are introduced into a polymer system. The first consideration is that the channels created can compromise the load-bearing capacity of the material. For instance, self-healing materials that do not need to withstand much mechanical stress allow the addition of more

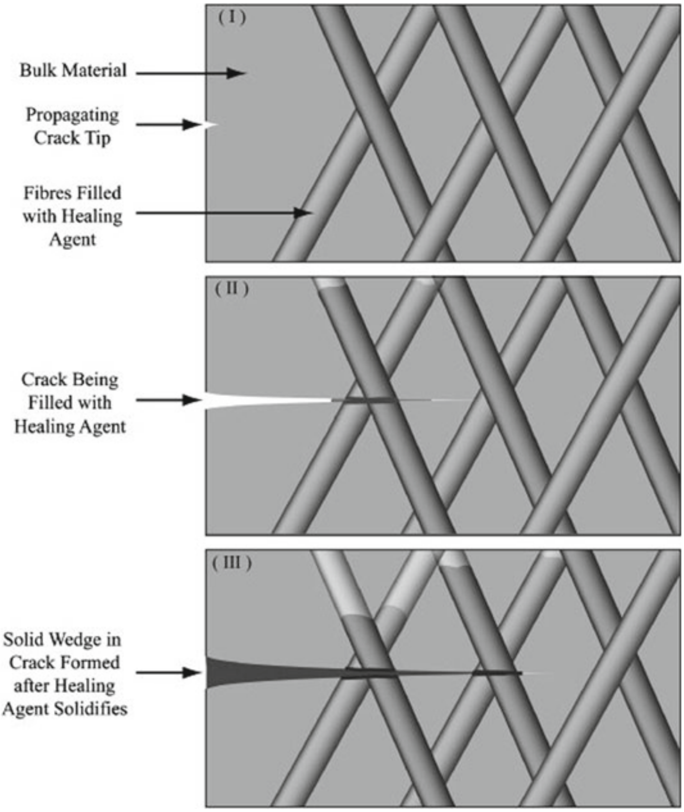


Fig. 5 Concept of self-healing mechanism in composites based on hollow fibers. Reproduced from [2] with permission from Elsevier. Copyright 2008

microchannels (hollow fibers) than structural materials designed to withstand heavy loads [109]. An interesting approach proposed for E-glass epoxy laminates is the use of sandwich structures with PVC tubes forming a vascular network housed in the core of laminate, which offers a potentially robust and replenishable system to deliver a healing agent from a remote reservoir to a region of damage [113]. Due to their high stiffness and self-healing efficiency, these sandwich structures are attractive for pressurized chambers.

It has been shown, however, that the introduction of mili- or micro-meter-sized hollow fibers into an epoxy matrix will detrimentally affect the mechanical properties due to stress concentrations. The use of carbon nanotubes (CNT) network, for instance, could avoid this problem. Sinha-Ray and coworkers [115] proposed a self-sustained Fickian diffusion method to fill CNT bores (50–100 nm) with DCPD and isophorone diisocyanate (IPDI), as healing agents, from benzene solutions. The authors also prepared core–shell polyacrylonitrile (PAN) nanofibers filled with the same healing agents (DCPD and IPDI) by electrospinning techniques and characterized their release in an epoxy matrix. The encapsulation of the healing monomers was demonstrated by fiber crush tests, confirming the filling of CNTs with IPDI and PAN with DCPD and IPDI. Microscopy techniques were used to evaluate toughening mechanisms and validate proof-of-concept epoxy composites reinforced with self-healing core–shell nanofibers at the interfaces.

Nevertheless, due to the need for more efficient methods to fill and seal narrow hollow fibers, effective placement of hollow fibers in large-scale applications, etc., this approach, although conceptually interesting, is currently less studied.

2.2.2 Discrete Channels and Interconnected Networks

Most of the more recent research on vascular systems involves the creation of micro- or submicro-channels (vascules) within the polymer matrix. Currently, the methods commonly used for vascule fabrication are micromachining, fugitive scaffold and 'lost-wax' processes, and the vaporization of sacrificial components [77]. Two types of systems are possible, those with discrete channels and those with interconnected channels [109].

Discrete channels can be constructed independently and arrayed throughout the material. There are several key points to ponder when constructing microchannels within a material, like the channel diameter and orientation, the degree of branching, and the location of branch points. Another important factor to consider is that the closer the tubes are, the lower the resistance, but the more efficient the healing [10, 109]. Interconnected three-dimensional vascular networks are in principle more efficient than discrete channels, but more difficult and expensive to be produced [109].

Machining principles to create microscale grooves have been used as the basic way to create microchannels for self-healing applications. These techniques can produce 600–700 μm channels and work very well on two-dimensional planes, but when trying to create a 3D network, they are limited [109]. However, recent developments in additive manufacturing (AM) technologies allow the fabrication of more effective, bioinspired vascular designs (VDs) [77, 116].

The direct-write assembly (DWA) or direct ink writing (DIW) is a controlled extrusion technique to design interconnected three-dimensional networks using viscoelastic inks [40, 77, 109, 117]. It works by first depositing an organic fugitive ink to a defined pattern. The structure ('scaffold') is infiltrated with epoxy, which is cured, and then the scaffolds are removed by applying heating and vacuum, creating hollow channels, generally around 200 μm. The first studies used DCPD/Grubb's catalyst or a two-part epoxy-based healing chemistry [40, 117, 118], reaching from 7 to 16 successful healing cycles at 30 °C. Hansen et al. [119] introduced the concept of interpenetrating 3D networks, achieving 30 sequential healing cycles. In another work, three-dimensional micro-scaffolds were fabricated using a computer-controlled robot, with the deposition of ink-based filaments on an epoxy substrate [120]. Liquid 5-ethylidene-2-norbornene (5E2N/CNT) containing 0.5 wt% CNT, as reinforcement, has been microinjected in the empty microfluidic networks inside an epoxy matrix with Grubb's catalyst nanoparticles. It was observed that the kinetics of the ROMP reaction of 5E2N was very effective over a relatively wide temperature range (from 15 to up to 45 °C). The results showed a significant increase in Young's modulus and hardness for CNT-loaded composites in comparison with the pure polymer.

Another method to create channels with diameters around 0,5 mm is the incorporation of PTFE-coated steel [121, 122], or solder [8] wires, silicone tubing [123], or polyamide strings [124] in carbon (or glass) fiber-reinforced epoxy laminates. After the laminate curing process, the wires/strings are pulled out of the matrix (or removed by heating and vacuum), leaving behind hollow channels (vascules). This kind of process is called 'lost-wax' [77]. In most cases, the healing agent is manually injected from an external source into the vascules, but Norris and colleagues [125] proposed an autonomous system with a low-pressure sensor connected to the vascules, which triggered a peristaltic pump that circulated the healing agent (a premixed low-viscosity epoxy resin). The fatigue behavior of such systems has been also studied [126]. However, a rapid loss in stiffness after 2500 cycles was reported, which was attributed to the low performance of the epoxy system (low-viscosity resin). A view of the integration of these vascular networks is shown in Fig. 6.

In the vaporization of sacrificial component (VaSC) approach, polylactide (PLA) filaments treated with tin oxalate, as a catalyst for thermal decomposition, are woven through layers of fiber-reinforced polymer laminates. After the laminate curing cycle, the composite is heated above 200 °C under a vacuum, leaving behind empty channels in the form of a 3D vascular network that can be filled with healing agents [77]. An advantage of this method is that the interference in the architecture of the composite is minimized, as the sacrificial PLA fibers replace part of the preform carbon (or glass) fibers. Tests using double cantilever beam (DCB) specimens of epoxy composites reinforced with E-glass woven considering two different arrangements, parallel and

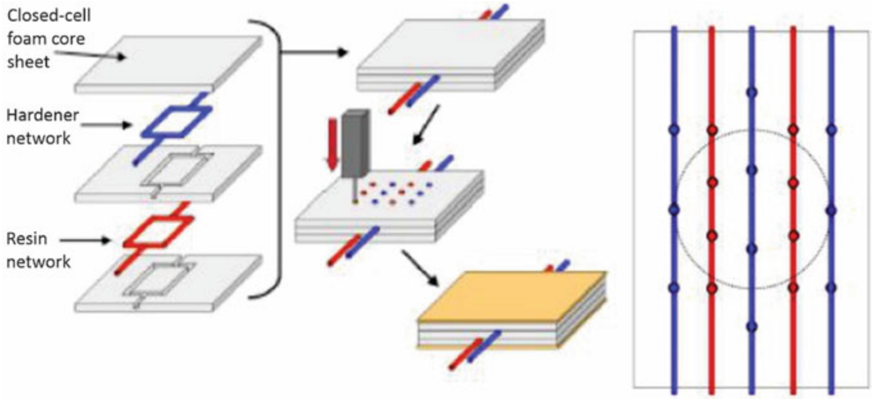


Fig. 6 Vascular network integration in composite sandwich panels (reproduced from [125] with permission from IOP Publishing, Ltd. Copyright 2012)

interpenetrating (herringbone), showed that the networks introduced via VaSC have little impact on the inherent fracture properties of the composite [127]. The dual-vascular channels filled with a two-part (resin/hardener) healing chemistry permitted the continuous delivery of the healing agents to crack planes when the samples were under load. Herringbone specimens achieved healing efficiencies above 100%, significantly higher than those reached with the parallel pattern, evidencing the importance of the vascular architecture on the healing performance. Further developments have been made by Gergely and coworkers [128], who tested VaSC with different dimensions, 0D (spheres), 1D (fibers), 2D (sheets), and 3D printed structures, and showed, by flow rate tests, that the fluid transport through these systems is viable. More recently, Cuvellier and collaborators [129] reported a study on the selection of healing agents for VaSC self-healing systems. After comparing different compositions, they found that the best healing performance is observed for TETA/trimethylolpropane triglycidyl ether (TMPTE). However, it is pointed out that an extensive swelling of the matrix with the healing agents may prevent its application in VaSC epoxy thermosets. Furthermore, the need for compatibility to promote adhesion, combined with time-consuming steps for fiber dissolution and infusion of the healing agents, make the upscaling of VaSC systems to an industrial level difficult.

3 Non-autonomous Self-healing Epoxy Systems

3.1 Thermally Induced Self-healing

It has been shown that thermosets can heal cracks or scratches via interdiffusion of dangling chains or chain slippage in the polymer network [2, 130, 131]. Due to molecular diffusion, when two parts of the same polymer are brought into contact, the interface between them gradually disappears above the glass transition temperature (T_g). This process increases the mechanical strength at the polymer–polymer interface and can heal also internal microcracks.

In one of the first reports on the healing of epoxy resin via thermally induced chain rearrangement [132], fractured resins based on bisphenol-A diglycidyl ether (DGEBA) containing methyl nadic anhydride (NMA) and benzyldimethylamine (BDMA), have been repeatedly shown to heal when heated above 150 °C. Very high healing efficiency across multiple fracture events has been verified both visually and by a double twist fracture test. The healing process only occurred when the system was heated above its T_g (120 °C) but, at higher temperatures, seemed to be independent of the healing temperature or the presence of unreacted monomer. The cure was attributed to interdiffusion/entanglement of the pendant chain ends, caused by micro-Brownian movement, with the local flow allowing a strong interfacial bond and restoration of the original surface contours. Kim and Wool [133] also presented a microscopic theory for the diffusion and randomization stages, proposing that the recovery of mechanical strength during the healing process is related to chain interdiffusion and subsequent entanglement formation.

Amorphous and semi-crystalline thermoplastics can also be used for the toughening of thermoset resins, which can generate blends with different dispersed and continuous structures, just varying the amount of thermoplastic modifier (generally with less than 15% by mass). Thermoplastic additives allow the original polymer matrix to remain unaltered, while also providing a solidifiable crack filling capable of relinking fracture surfaces [2]. Among these are co-continuous morphologies composed of thermoplastic and thermoset phases, called semi-interpenetrating polymeric networks (semi-IPNs), which are the most suitable for toughening [134]. This thermoplastic phase, in any morphology, can work for heat-induced regeneration, but semi-IPN structures are more efficient than dispersed morphology [135–137].

This approach has been tested by Zako and Takano [138], who added up to 40 vol% of small thermoplastic epoxy particles (average diameter 105 μm) in a glass fiber-reinforced composite. When the composite is heated at 120 °C for 10 min, the particles melt, flow to microcracks or internal flaws and solidify, healing the material to 100% of its original stiffness, as verified by three-point tensile and bending tests. Samples fatigued under traction until stiffness decreased by 12.5% and then heated to trigger the flow, with subsequent solidification of the incorporated thermoplastic particles, showed almost total stiffness recovery. The proposed mechanism is shown in Fig. 7.

An alternative way of using this self-healing mechanism is the use of a blend of thermoplastic and thermoset polymers, in which the matrix can contain 10–30 wt% a thermoplastic polymer [139, 140]. In this case, several factors will affect the self-healing efficiency, such as the compatibility of the two polymers. The thermoplastic healing agent should preferably be miscible with the thermoset polymer but do not chemically react with it at room temperature. Another factor is that the $T_g s$ of thermoplastic and thermoset polymers must be similar. Thermoplastic should enter the viscous regime above room temperature but not at a temperature that can cause thermal degradation of the thermoset. Another factor is the molecular mass distribution of the thermoplastic. Low molecular mass polymers diffuse faster, resulting in faster healing, while high molecular mass polymers provide better mechanical properties. Lastly is the healing temperature. Self-healing occurs by diffusion; thus, temperature influences the speed and efficiency of healing [141].

An ingenious example of heat-triggered self-healing was reported by Luo and coworkers [142], who described a polymerization-induced phase separation (PIPS) process for the preparation of a material consisting of a cross-linked epoxy matrix and a co-continuous percolating polycaprolactone phase, responsible for the healing behavior. In the concept, the damaged epoxy matrix is thermally mended by molten polycaprolactone (PCL) that wets and fills the crack surfaces. The self-healing efficiency was confirmed by tensile tests, which presented a resemblance between the virgin and the thermally mended material.

Thermoplastic polymers have also been employed as curing agents for glass fiber-reinforced epoxy composites [141, 143]. Composites containing 7–10% of poly(bisphenol-A-*co*-epichlorohydrin) (PBE) tested in several impact cure cycles

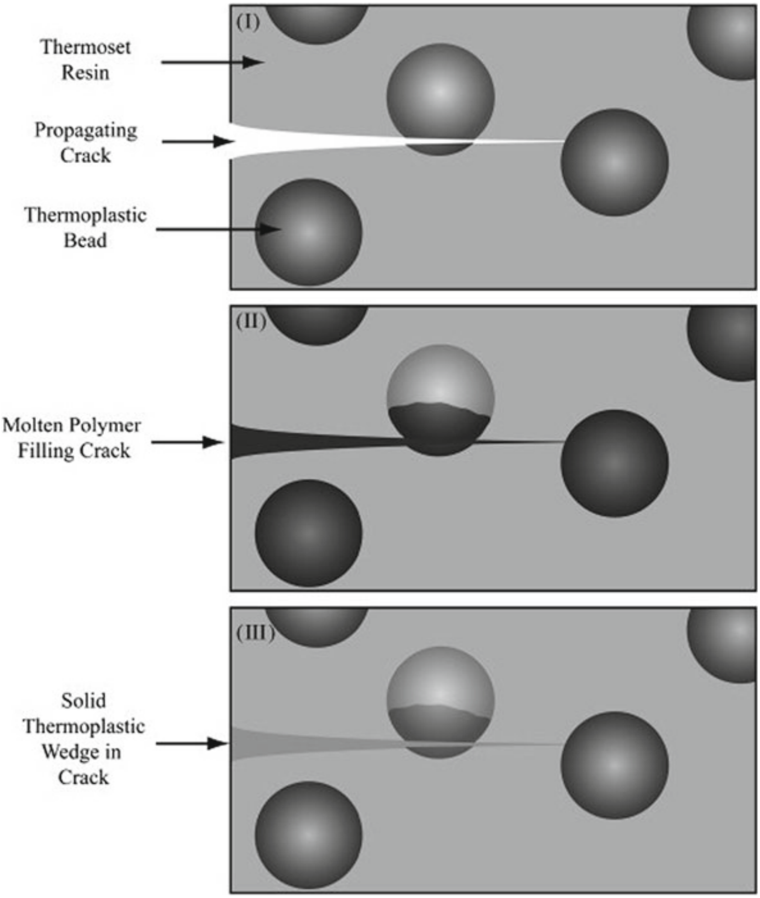


Fig. 7 Concept of healing mechanism in thermoplastic bead-based self-healing composites. Reproduced from [2] with permission from Elsevier. Copyright 2008

presented a cure efficiency of 30–50%. These values are lower than that reported in the first studies on this approach [138]. It must, however, be considered that the matrix resins and the test methods used to assess self-healing efficiency were different. Pingkarawat and coworkers [144, 145] reported the use of reactive thermoplastic additives, such as polyethylene-*co*-glycidyl methacrylate (EMAA) and polyethylene-*co*-glycidyl methacrylate (PEGMA), and two types of non-reactive additives, ethylene vinyl acetate (EVA) and acrylonitrile butadiene styrene (ABS), showing that even incompatible thermoplastic additives with high internal pressure and/or low viscosity can be also an effective crack healing agent for carbon/epoxy composites. The same group also proposed other thermally activated healing agents, such as tetra-glycidyl diamino diphenyl methane [146].

While the feasibility of this concept is proven in terms of stiffness recovery, potential problems related to the heating of thicker parts without causing excessive heat to the surface have yet to be assessed. The use of carbon nanotubes can help to solve this issue. When CNTs are incorporated into epoxy matrices, forming a percolating network, and a direct current is passed through the nanotubes, a significant change in the detection curve can indicate damage to the polymer, ‘detecting’ a crack [147]. This feature can also be used to create CNT networks that impart a self-healing function to the material. When dissolving a thermoplastic linear polymer within a thermoset epoxy matrix, forming a semi-interpenetrating network, the thermoplastic domains become movable at a certain temperature [148]. Carbon nanotubes can thus detect microcracks within the structure and be used as thermal conductors to heat the system, allowing linear polymer chains to diffuse and fill cracks in the epoxy matrix, healing the composite [143, 149].

3.2 Photoinduced Self-healing

The concept of photoinduced curing is potentially attractive because the reaction takes place at room temperature and is normally simple, fast and environmentally friendly.

The application of this approach for epoxy resins was proposed by Sriram [150] by using photoactivated catalysts for ROMP, with polymerization of norbornene (NBE) or DCPD, instead of the traditional Grubbs catalyst. The main motivation of the work was the use of a catalyst that can be easily synthesized in large quantities. Moreover, the photoactivated ring-opening metathesis polymerization reaction (PROMP) is extremely fast (<5 min), with minimal volume change. ^{1}H NMR analysis confirmed the occurrence of PROMP with DCPD and NBE at room temperature. However, no self-healing tests were reported.

Other works with photoactivated self-healing involving photoreversible crosslinks will be discussed in the next section.

4 Intrinsic Self-healing Epoxy Systems

Intrinsic approaches consider that the system can self-heal inherently. However, most intrinsic systems require an energy supply, i.e., an external trigger, such as thermal, mechanical, electrical, or photo-stimuli, to repair microcracks efficiently on the atomic/molecular level. Nonetheless, it is important to note that they differ from non-autonomic approaches due to the reversible nature of intrinsic self-healing processes. There are two main kinds of intrinsic systems, those based on reversible covalent bonds and those supported by non-covalent supramolecular approaches.

4.1 Dynamic Covalent Networks (Reversible Covalent Bond Cleavage)

4.1.1 Reversible Reticulation Systems

This concept involves a class of cross-linked polymers capable of healing internal cracks through thermo- or photoreversible covalent bonds, being suitable for the development of self-healing epoxy resins used to make fiber-reinforced composites for structural applications. The use of reversible cross-links to cure epoxy systems eliminates the need to incorporate 'reservoirs' (hollow fibers or microcapsules) containing healing agents or catalysts. However, it is usually necessary to provide heat to trigger and/or support the healing process [151–154]. As the curing agent and heat source can be integrated into these materials, they are characterized as intrinsic systems [2].

Among the thermo-reversible healing polymers, the most studied systems are those based on Diels–Alder (DA) reaction and its retro-Diels–Alder (RDA) analog (Fig. 8). DA-based systems undergo a fully reversible cycloaddition, allowing multiple cycles of crack regeneration [12, 152]. In addition, there are still other advantages over extrinsic approaches, as it eliminates the need for additional reagents, such as catalysts or monomers, or interfacial treatment at the crack surface. In general, the monomer containing the functional groups, such as furan or maleimide, forms two C–C bonds to build the polymer network through DA reaction. When heated, at temperatures normally higher than 120 °C, or under mechanical stress, the polymer chain breaks down into its monomeric units by RDA reaction. The polymer is restored (healed), again by DA reaction, after cooling, or by any other conditions that were initially used to synthesize the polymer. Two types of DA reversible polymers have been proposed: (i) systems where pendant groups, such as furan or maleimide, cross-link through successive coupling reactions; (ii) systems in which multifunctional monomers link together [66].

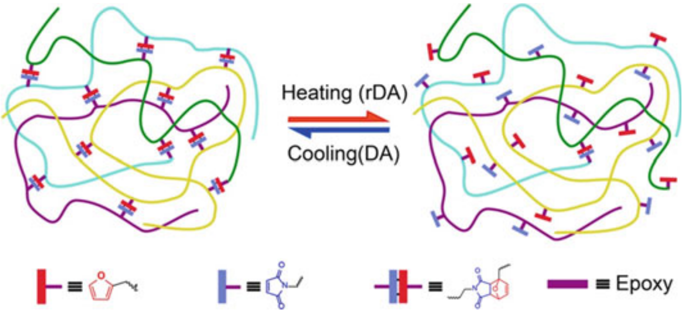


Fig. 8 Diels–Alder cross-linking agents and thermally reversible cross-linking mechanism (reproduced from [154] with permission from John Wiley and Sons. Copyright 2015)

The first works using this approach [151, 152] described the preparation of highly cross-linked and transparent materials, by DA cycloaddition of furan and maleimide (derived from DGEBA), with the thermal reversibility of the bonds due to retro-Diels–Alder reactions. The reversibility of the cross-linked structure was confirmed using solid-state ^{13}C-NMR by submitting the polymerized films to multiple heating and cooling cycles. The self-healing efficiency, quantified by fracture tests, was about 50% at 150 °C and 41% at 120 °C, but there was a drop in mechanical properties from the second to the third healing process [151]. Further improvements in the polymerization processes, for instance, the removal of reaction solvents, improved the healing efficiencies to about 80% [152]. This process has been patented [155], as well as its possible application to sports materials (thermally patchable golf balls) [156].

Looking for applications in the production of advanced composites, Liu and Hsieh [153] employed epoxy precursors to prepare multifunctional monomers containing furan and maleimide groups. These monomers present the desirable characteristics of conventional epoxy resins, such as chemical resistance, low melting point, and solubility in a range of organic solvents, allowing them to be processed similarly to commercial resins. The DA reaction regeneration mechanism has also been used to integrate conductive electromagnetic materials such as copper wires or coils into fiber-reinforced composites [157], enabling the healing of internal damage in composites through thermo-reversible covalent bonds under moderate heat application. The crack disappearance was visually observed after the samples had been heated above 80 °C for at least 6 h under a nitrogen atmosphere.

Peterson and coworkers proposed two new systems for reversible DA cross-linking in epoxy resins [158, 159]. The first one used a thermo-reversible cross-linked gel, obtained by mixing 1,10-(methylenedi-4,1-phenylene)bismaleimide to furfuryl amine and DGEBA oligomers- as a repairing agent for epoxy-amine resins. The DA healing mechanism involves liquefaction of the gel phase upon heating, which flows into the crack plane. After cooling, cross-linking is reformed, restoring the initial epoxy network structure [158]. Later, they proposed a DA system working at room temperature by the use of furan-functionalized epoxy resins with a mixture of *N,N*-dimethylformamide (DMF) to swell the epoxy network structure, and *N,N'*-(4,4'-methylenediphenyl)bismaleimide (BMI), as a DA reagent. This system enabled contact between crack surfaces, improving the strength of the repaired interface [159].

Thiol-based polymers present disulfide bonds that can be reversibly cross-linked through oxidation and reduction. Under the reducing condition, the disulfide bridges (SS) can break down and result in monomers. However, under the oxidizing condition, the thiols (SH) of each monomer form the disulfide bond, cross-linking the starting materials to reform the polymer. In one of the first works on this approach, Saegusa et al. showed a thiol-based reversible cross-linked polymer based on poly(*N*-acetylethyleneimine) [160]. Considering epoxy systems, Lei and coworkers [161] reported the curing reaction of polysulfide diglycidyl ether with diethylenetriamine using tri-*n*-buthylphosphine as a catalyst. Tensile tests showed that this epoxy cross-linked with disulfide bonds can self-heal at room temperature and without any manual intervention, but the low Tg (below room temperature) limits its applications. Other recent papers describe different possibilities using disulfide bond exchange reactions [162–164], demonstrating new features, such as reprocessability, weldability, and potential use in structural composite applications.

The formation of disulfide bonds is one of the ways to produce epoxy vitrimers [164–166]. Vitrimers are a group of polymers based on adaptive dynamic covalent networks, which fill the gap between thermoplastics and thermosets. Dissociative and associative exchanges within these networks make it possible to obtain robust 'Recyclable, Repairable, and Reshapable' (3R) materials, which maintain their original structural properties and mechanical resistance [165, 167]. The bond exchanges in these cross-linked species as a response to externally applied stimuli, such as heat or stress, define the self-healing behavior of these materials (Fig. 9). Dissociative exchange, such as pericyclic reactions, nucleophilic transalkylation, and amine transamination, is the process by which cross-links are broken prior to recombination of the cross-linking species, thus recovering the cross-link density after the exchange, while associative exchange, such as transesterification and transamination, preserve the cross-links during the exchange by substitution reactions [168]. In addition to recycling, vitrimer materials, such as self-healing bio-epoxy [169], are very promising for medical and electronic applications [170, 171].

Photoreversible cross-linked epoxy resins containing photoactive anthracene moieties have been recently reported [172, 173]. Radl and coworkers [172] dissolved the photoactive agent in a low-viscosity monofunctional epoxy resin to obtain a photocured repairable epoxy material. The results showed that, after mechanical damage, the epoxy system under UV light (>300 nm) undergoes a photoreversible polymerization along the crack surface. Nonetheless, additional heating at 60 °C is required to induce the interdiffusion of polymer chains. A further development [173] employed two anthrylamines as crosslinkers, confirming that the healing effect is due to the photochemical reaction of the cleavage of anthracene dimers, which act as cross-linking agent, causing a transition from a rigid to a softer phase, and then to a flowable material that can fill the cracks before returning to the rigid phase.

4.2 Non-covalent Supramolecular Approaches

Self-assembly of supramolecular polymers allows the formation of new structural organizations through highly selective cooperative non-covalent interactions, such as hydrogen bonding, ionic/dipole interactions, metal coordination, and π–π stacking [174–176]. It has been shown that non-covalent cross-linked structures can be self-assembled to create supramolecular polymer networks (SPNs), which can respond to stimuli such as heat, light, pH, or electricity, i.e., be manipulated to obtain a wide variety of multifunctional materials with adequate mechanical properties [177, 178]. In other words, SPNs represent a promising approach for the development of a new generation of self-healing dynamic systems, which can allow the spontaneous formation of a three-dimensional network with fast and reversible responses to various environmental conditions.

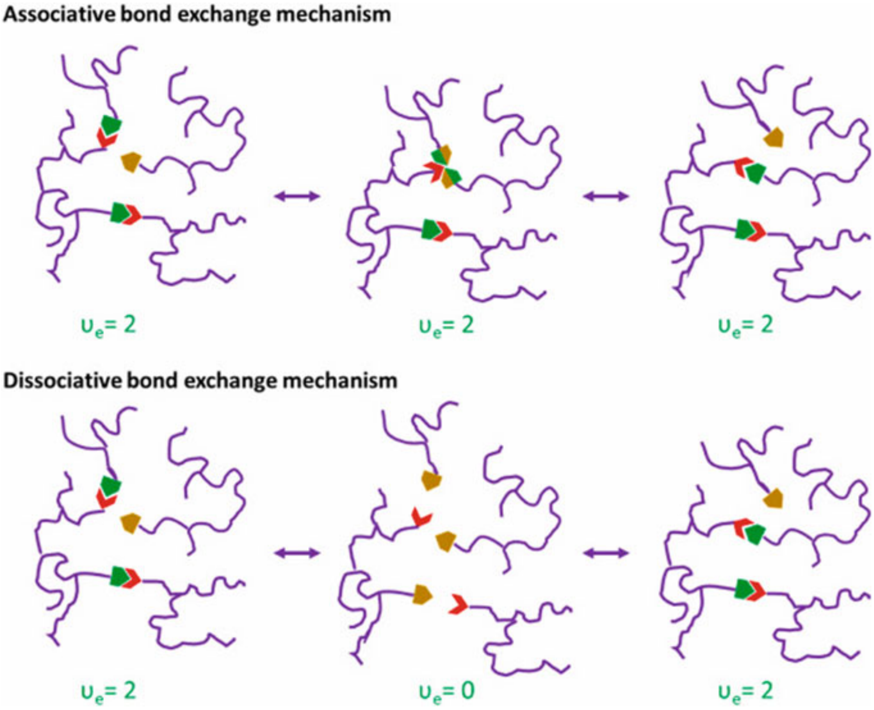


Fig. 9 Bond exchange mechanism of covalent adaptable networks, where υ_e is the cross-linking density. First is the associative bond exchange mechanism, where the overall cross-link density remains constant; i.e., cross-links are merely broken when new ones are created. Vitrimers might undergo associative or dissociative bond exchange mechanisms depending upon the covalent adaptable network present in the compound. Reproduced from [171] (Elsevier, CC-BY-NC-ND)

Various supramolecular epoxy systems have been reported in the literature [179–182]. Sordo and coworkers [179] described supramolecular epoxy-based rubbers incorporating a large number of physical cross-links through cooperative hydrogen bonds and chemical cross-links, looking for materials resistant to solvents and creep. Starting from a single reactive prepolymer, functionalized with hydrogen-bonding groups, a series of networks presenting different ratios of diepoxide and tetraepoxide were prepared (Fig. 10). The introduction of tetrafunctional epoxide, using 2-methylimidazole as the catalyst, gave rise to gelled materials with high rigidity and tensile strength and improved creep resistance. All materials presented self-healing, with 50–100% complete recovery in a day depending on tetraepoxide content.

Epoxy-based coatings with tailored hydrogen bonds have been prepared and studied by Villani and coworkers [180], who introduced physical cross-links (hydrogen bonds into an epoxy-amine network) by the incorporation of amide groups. These cross-links promoted enhanced temporary local network mobility and relaxation of the mechanical stresses, without significant changes in modulus and adhesion

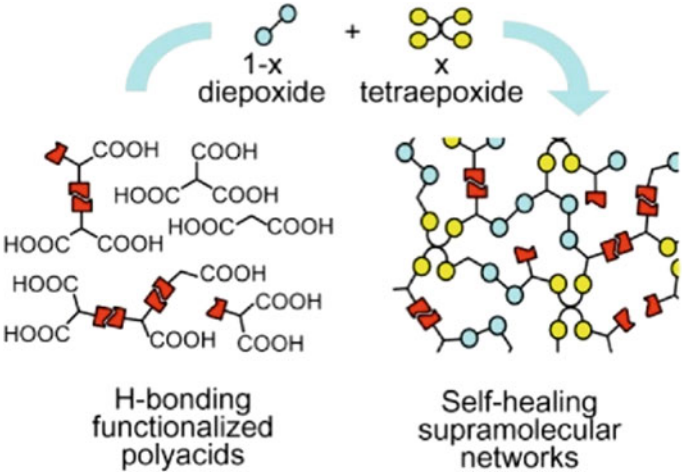


Fig. 10 Synthetic strategy used to generate insoluble hybrid networks containing a fixed amount of terminal H-bonding groups and a tunable number of cross-links. Step 1: partial amidation of poly(carboxylic acid)s with a fixed amount of an H-bonding molecule. Step 2: cross-linking with a variable amount of the difunctional DGEBA and tetrafunctional TGMDA epoxy resins. Reprinted (adapted) with permission from [Sordo, F., Mougnier, S.-J., Loureiro, N., Tournilhac, F., Michaud, V.: Design of self-healing supramolecular rubbers with a tunable number of chemical cross-links. Macromolecules 2015, 48, 4394]. Copyright 2015 American Chemical Society

behavior. The reversibility of hydrogen bonds also resulted in the efficient healing of superficial scratches with no detrimental effect on the adhesion properties.

Guadagno and coworkers [181] also developed structural self-healing resins based on dynamic hydrogen bonds supported by carbon nanotubes to enhance mechanical properties. A rubber-toughened epoxy matrix was filled with multi-wall carbon nanotubes (MWCNTs) covalently functionalized with barbiturate and thymine, which act as reversible healing agents due to simultaneous donor/acceptor character. Strong, attractive interactions between the rubber phase, finely dispersed in the matrix, and MWCNT walls have been formed due to reversible MWCNTs-bridges throughout the matrix. Healing efficiencies higher than 50% were reported for the epoxy resin loaded with 0.5 wt% MWCNTs functionalized with barbituric acid or thymine groups.

Shape memory polymers such as those described by Lendlein and Kelch [48] may also be considered for self-healing materials, the so-called shape memory-assisted self-healing (SMASH) [175]. This approach typically requires heating for healing to occur and is applicable to repairing superficial scratches, for example. Shape memory epoxy resin and its composites, including SMASH materials, have been recently reviewed by Luo and coworkers [183]. In one of the examples, self-healing coatings were prepared by inserting electrospinning thermoplastic poly(ε-caprolactone) (PCL) fibers into a shape memory epoxy matrix [184]. The self-healing of the coating after mechanical damage was triggered by heating, which promotes the shape recovery of the matrix by approximating the crack surfaces, while the melting and subsequent flow of the PCL fibers were responsible to relink the crack.

The self-healing efficiency, at room temperature, of shape memory epoxy/graphene nanocomposites has been also studied [185]. The authors reported an improvement in the scratch resistance of the nanocomposite materials, which was attributed to the in-plane fracture resistance of the graphene sheets. It was concluded that the incorporation of graphene resulted in significant improvement in different properties compared to the pure shape memory epoxy matrix.

5 Conclusions

The state of the art on the extrinsic and intrinsic self-healing mechanisms for epoxy systems has been reviewed. New technologies involving dynamic bonds, supramolecular arrangements, and shape memory-assisted self-healing open a myriad of options in the development of epoxy materials for applications in medicine, electronics, and transportation (automotive, aeronautical, and naval industries). For instance, the reversible recovery characteristics of shape memory polymers have great potential in biomedical, driving sensing, and other fields, while multifunctional and high-performance integrated self-healing composite materials are promising in the aerospace field.

Although the interest in microcapsule-based systems, especially for coatings, and in vascular systems, with 3D architectures manufactured by VaSC, continues, there is a current trend toward the development of structures by 3D printing and recyclable epoxy vitrimers. The ability to control cross-link density and defects in epoxy networks will permit the achievement of materials with a better compromise between self-healing ability, mechanical properties, such as strength, toughness, creep resistance, and fatigue, and multifunctional features, such as recyclability, thermal and electrical transport, weldability, piezoelectricity, and tribological control. Self-healing nano-systems involving reactive nanoparticles (for covalent or non-covalent supramolecular dynamic systems) or the incorporation of nanocapsules/nanovascules, are going to be much enhanced and will probably guide many efforts of researchers in this field. Modeling using computer simulation is also an open field that can significantly assist in the creation of innovative multifunctional self-healing materials [186]. Intelligent design for material structure-performance-function integration and synergistic combinations brings big opportunities for new developments.

Nevertheless, a lot of work has yet to be done to produce cost-effective self-healing materials. In special, the development of commercially viable chemical systems/healing agents and testing protocols to better assess and understand the material properties over its lifetime (e.g., fatigue and post-reprocessing cycles).

Last but not least, in the search toward a more sustainable society, there is today a great interest in replacing, entirely or at least partially, epoxy polymers from petroleum products for bio-based resins. For instance, it was shown that shape memory self-healing bio epoxy could also have degradable and recyclable properties [165, 168]. It must also be highlighted that the main purpose of self-healing materials is to effectively extend their lifetime, being an important way to reduce waste.

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