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Self-Healing Polymer Composites for Structural Application

Jeetendra Kumar Banshiwal and Durgesh Nath Tripathi

Abstract

Self-healing materials are the next-generation materials for high-performance structures. To reduce the fatigue and subsequent probability of failure along with extended service life of polymer and polymer composites, the self-healing concept has great potential. Today, polymeric composites are structural matrix and prone to failure against cyclic mechanical and thermal loading. Significant degradation of polymeric structures at surficial sites can be measured by barely visible impact damage (BVID), but internal micro-cracks are not easily detectable. Various damage modes make major damage sites in composites and further lead to catastrophic failure of the structure. On-site repairing of microscopic or macroscopic damages in polymer composites is a value-added function that is offered by self-healing techniques. Different extrinsic methods including encapsulation, hollow fiber embedment, and vascular methods are preferred, and some intrinsic, dynamic bonding is created by reversible covalent networks and supramolecular interaction based on H-bonding, metal-ligand, and ionomers. This chapter is preferred on the new trends and challenges regarding the structural health monitoring of polymeric composites against external mechanical and environmental impacts and extended service life and performance by utilizing self-healing strategies.

Keywords: intrinsic and extrinsic self-healing, covalent reversible network, supramolecular interactions

1. Introduction

Polymers and fiber-reinforced polymers (FRPs) are common as structural materials due to lightweight, easy processability, and constancy against adverse environmental impacts. However, mechanical properties are associated with many variables including service time, operating temperature and pressure, molecular weight, and constitution of matrix. The long-term durability, high performance and reliability are major challenges for polymeric architecture. Limiting factors of polymer composite is relatively poor performance under impact loading due to lack of plastic deformation, which is a most prominent aspect of any vehicle component design. Low-velocity and high-velocity impacts are the critical issues for FRPs. These impacts influence on mechanical strength and stiffness along with dimensional stability. In metals, the impact energy is dissipated through elastic and plastic deformations, so structural integrity is retained intact. However, in FRPs the impact energy is dissipated in the form of damages in matrix. The impact damages in FRPs affect mainly the internal integrity as compared to superficial visible zone. On cyclic mechanical and thermal loadings, stress is applied on a matrix which released in the

form of micro-cracking. Micro-cracks degrade polymeric properties inevitably and result into the failure. Single or multiple damage modes result into damage sites and are required to repair the components to continue to the service. If microcracks are untreated, they lead to larger macroscopic cracks, and finally catastrophic loss of the structure is an adverse outcome. To resist these failures, the new-generation materials having autonomic healing capability to damage repair are needed to develop. Conventionally, different lay-up repair techniques are adopted in thermoset.

Similarly, in thermoplastics which are known for their mechanical performances, service temperature, and solvent resistance, fusion bonding techniques are used to recover mechanical integrity.

However, these repair strategies are very costly, time-consuming, followed by complicated procedure, and assisted only by expert technicians. So, we required such unique functionality which intimates the damages at nascent stage and sometimes repaired the damages. Self-healing of cracks is an eminent and efficient possible solution of these issues. In healing systems, a damage incident triggers the internal processes that generate the healing response which cured the damages. The bio-systems have damage detection and subsequent prevention techniques; those are source of innovation to design such functionality by introducing the self-healing functionality into artificial materials. These techniques are demanding for manned materials and structures and assisted by the biomimetic approaches. The major concern is focused on recovery of mechanical properties of polymer composites against quasi-static fracture. Initially, Mercier developed a self-healing rubber that can reseal on puncture damage [1]. The concept of healing is progressed with developing efficient vehicles and other systems such as space suits to protect from micrometeoroid impacts [2]. Currently, damage healing of polymer structure is being demonstrated via different approaches, which include extrinsic and intrinsic methodologies. Extrinsic methodology is being performed via encapsulation [3–8], hollow fibers [9–11], microvascular systems [12–16] and intrinsic damage healing is offered by reversible covalent bonding [17–21] and supramolecular interactions [22–30]. In extrinsic methodology, healing is restricted only once, and the delivery of healing precursor's amount is limited. To overcome the above concern, different intrinsic healing systems are developed that offer multiple healing at macroscopic damages. Multiple healing of the same crack is achieved by microvascular 3D system, thermoreversible networks, and supramolecular interaction. These strategies help to design various self-healing systems. In literature, various high-performance systems such as self-healing coating, self-healing ceramics, and self-healing metals are reported. Self-healing nanocomposites are also reported. Self-healing technology provides public safety and reduced maintenance cost of the structure. Healing approaches offer longer lasting with fault-tolerant components across various fields including coatings, electronics, robotics, transportations, energy, etc. In the following section, the author is mainly focused to elaborate current trends and the leading research field of remendable polymers for structural composites.

2. The basic principle and theory of damage healing

Mimicking biosystems, in synthetic materials, damage repair is performed by three steps including actuation of healing, later transport of healing precursors to the damage site, and finally chemical repair process occurring with contact of catalyst or curing species at an angstrom level in which matrix is restructured by bonding of cleaved bonds at the damage site. Macroscopically, healing is proceeding by two consecutive mechanics; these included physical and chemical process. In physical process, the flow of healing precursors or segmental movement of chains is

mandatory for damage repair. These events proceed continuously and are controlled by kinetics and thermodynamics. The repair event is determined by the kinetic energy of chains and entropy changes meanwhile by chain diffusions. These intrinsic properties have a great impact on entropy contribution to Gibbs free energy during repair event [31]. Another considerable factor is a free volume in a matrix which is desirable to the mobility of polymeric chains [32]. To obtain free volume, some stimuli-responsive units are also incorporated into nonreversible systems by copolymerization, and during mechanical stress, the entropy ΔS increased due to segmental mobility, and finally rebonding of cleaved sites is possible [33]. During self-healing process, voids/free volume facilitated segmental mobility of chains and matrix macromolecular chains. Void-less system are rigid and subsequently damage sensitive. Heterogeneities are critical parameters which offer the design of self-repair concept. Different types of polymers like block, branched, and/or star polymers showed self-repairs in range of nm to μm . Microphase separation and microcapsules and inorganic particles are embedded into polymers and responsible for macrodamages. In polymeric systems, heterogeneities are developed by phase separation utilized by copolymers or composite materials [27, 28, 34] and shape memory polymers [35]. In chemical process, different polymerization reactions of healing precursor or entanglement of polymer chains or reversible covalent bonding according to base matrix materials is dominant. All these stages are balanced by the damage rates to healing rate. The rate of damage is defined by various factors such as loading frequencies, strain rate, and the amplitude of stress. However, healing rate can be monitored by concentrations of precursor species and/or intrinsic temperature using varying reaction kinetics. In thermoset, encapsulation is an effective healing strategy, but in thermoplastics induced-healing is reported in which healing is possible on heating of polymers above its glass transition temperature (T_g) or using solvents by depression of the effective T_g as compared to below room temperature [36]. In autonomic healing, the healing agent is incorporated or phase separated by matrix so that the healing of crack/failure takes place without external intervention at ambient temperature. It is fully self-contained and responds to external stimuli. Healing is achieved by one-capsule system, dual-capsule system, and hollow fiber and vascular network-based system. In non-autonomic healing, human intervention is mandatory. It is inherent and intrinsically similar to biological structures. It is a partially self-contained healing system. Healing functionality is an intrinsic part of base matrix, but additional heat or radiation is required to proceed. Generally, for high healing efficiency, the healing agent forms a homogeneous mixture although it is difficult to process in terms of large-scale production in industries. The healing efficiency represents the recovery of mechanical integrity of components. To quantify healing efficiency, many definitions have been proposed. Basically, healing efficiency (η) is a ratio of change in a property of interest of materials as shown in equation no. 1.

$$\eta = \frac{f_{\text{healed}} - f_{\text{damaged}}}{f_{\text{virgin}} - f_{\text{damaged}}} \quad (1)$$

where f is the property of interest of material, and f_{healed} , f_{damaged} , and f_{virgin} are the property of interest of healed sample, the damaged sample, and the virgin sample, respectively.

Damage volume is a deciding factor of maximum healing efficiency of various repair systems. Each technique demonstrated diverse healing efficiency for different damage volume. Intrinsic systems are preferred to heal small damage volume and heal at molecular level due to the close proximity of damaged site which is mandatory for re-bonding of the cleaved site. Microvascular network heals large

damage volume and potentially attempts highest healing efficiency. Encapsulation strategy covered the regime between intrinsic and vascular systems. Most of the repair systems established high damage volume to low healing rate. To achieve high healing efficiency, the damage rate should be equal to damage healing. Only some systems based on capsule and intrinsic system are matched to healing rate to damage rate. The exact nature of the self-healing method to be deployed depends upon (i) the nature and location of the damage, (ii) the choice of repair resin, (iii) the influence of the operational environment, and (iv) proximity of damage site and healing precursor container. The stability and durability of the final material can be increased by repairing the damage in an autonomic way. Currently, a more dynamic strategy based on damage acceptance and management has been explored and growing exponentially shown in **Figure 1**.

Multiple healing is possible through the intrinsic approaches which have intrinsic functionality. This approach can be practical to thermoplastic, thermoset polymers and elastomers. Intrinsic self-healing is achieved by the recovery of the former interactions, with or without an external trigger. A certain magnitude of stress (i.e., chemical, mechanical, or thermal) enhanced the mobility of polymer network. On impact, the sudden drop of viscosity in matrix occurs due to transfer of impact energy in the form of heat to localized zone, which allows the local deformation and mobility of polymer chains or network. Upon cooling, network restores the initial values of viscosity, and materials achieved virgin mechanical and thermal stability. Moreover, to increase mechanical properties of intrinsic system, more than one chemical healing principle may be required to combine. The damage interfaces disappear when chain entanglements and chemical or physical cross-links formed a network as strong as the bulk material. This process can be obtained by physical and chemical interactions and a combination thereof. The most accepted theory leading to interfacial physical healing is proposed by Wool and O'Connor [37] which is based on molecular interdiffusion leading to chain entanglements. This process can occur at higher temperatures as compared to the bulk polymer glass transition temperature or through local external trigger such as a solvent and temperature beyond the melting point in thermoplastics (welding) [38]. In the case of reversible chemistries, the enhanced mobility leads to a viscous flow of the material in the vicinity of the damage site. It is remarkable that chain interdiffusion has been observed also at temperatures theoretically below the bulk T_g which highlights the potential difference in T_g between the bulk and the surface in freshly damaged materials influencing the healing process. From a mechanical and theoretical point of view, up to 100% healing of an

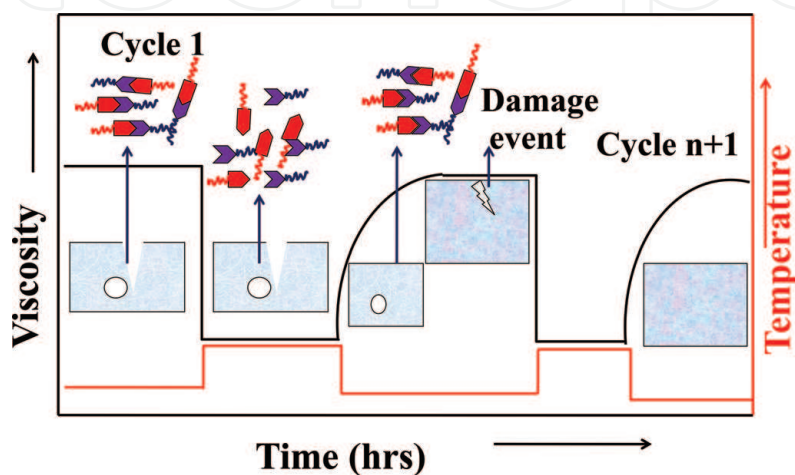


Figure 1.
The concept of damage healing using intrinsic methodology.

interface can only be obtained if the new interface has exactly the same properties as the bulk material.

3. Passive self-healing based on extrinsic techniques

In passive mode, healing is generated by incorporation of foreign functionalities. The extrinsic healing process is based on the use of a healing agent contained in the matrix as a separate phase. The healing agent is usually in the liquid state, placed into reservoirs which may be microcapsules or hollow fibers or microvascular network. In most approaches, the healing agent is used with a catalyst, which can also be encapsulated or dissolved in the matrix. Different extrinsic healing approaches are explored. In some cases, the catalyst is not required to initiate the healing process; the healing agent can also react to itself. The extrinsic healing concept is based on the response after or at the onset of damage. Current research is concerned with the improvement of healing agents in terms of compatibility and catalyst-free system with some new encapsulation techniques.

3.1 Microcapsule embedment

Encapsulation strategy is mainly studied for polymers and coating. The basic principle of strategy is healing by incorporated healing functionality or reactive constituents into capsules followed by chemical reactions. These reactions take place by various mechanisms including ring opening metathesis polymerization (ROMP) [3], cycloreversion [39], cycloaddition [40], cross-linking reactions [41], or a mechanochemical catalytic activation [42]. Damage acts as a stimulus to initiate the healing process. Damages rupture the microcapsule, and subsequent release of the core material (healing agent) is possible. The healing precursor reached at the damage site by capillary action and spreads itself over the two fracture surfaces due to the surface tension. Further, precursors interact with embedded adjacent catalysts (**Figure 3**) leading to a network formation by following the above chemistries, which terminate the further growth of crack or damage and restore mechanical integrity. White et al. [3] designed a “dicyclopentadiene (DCPD) Grubbs’ system” based on capsule healing which achieved 75% recovery of virgin fracture toughness of TDCB specimens. Capsule- and hollow fiber-based healing systems are shown in **Figure 2**.

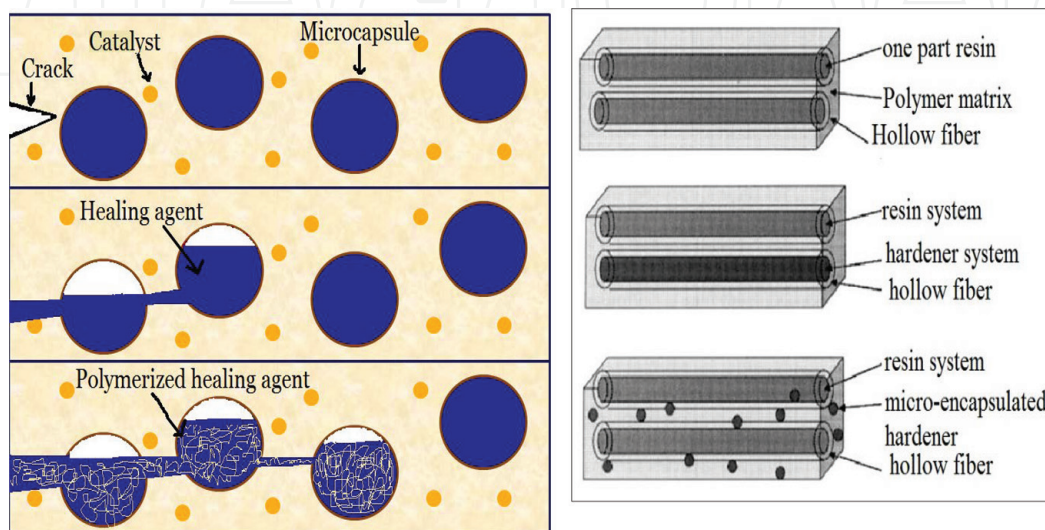


Figure 2. Demonstration of healing phenomenon. (a) Capsule-based healing [3] and (b) hollow fiber embedment [11].

Mainly, the adhesive and cohesive mechanisms are responsible for the failure of interfaces. Better healing efficiency can be achieved by improving the adhesive tendency of the poly-(DCPD) with fracture surface of the matrix without compromise with the cohesive strength of the poly-(DCPD) (shown in **Figure 4**). The average diameter of the microcapsule is ranging from ~ 300 to ~ 700 μm and shell walls with thicknesses from 5 to 20 μm . Generally, the core materials of microcapsules are made of poly(urea-formaldehyde) (PUF) [43]. The controlled release of the precursor is the typical job of encapsulation strategy. Some of the eco-friendly catalyst-free healing methods are also introduced because the catalyst-based approach is cost-ineffective and related to some compromise of mechanical properties of matrix. Various critical factors define the performance of encapsulation strategy [44, 45]. There are various different ways to proceed capsule healing; that is, (i) the encapsulated liquid agent can be combined with a dispersed catalyst, (ii) both the healing agent and the catalyst can be embedded in different capsules, (iii) the healing agent can also directly react with a functionality of the matrix under an external stimulus, and (iv) the healing agent and the catalyst can be placed in the matrix as a separate phase. Different capsule-based healing systems are summarized in **Table 1**.

The encapsulation strategy is mainly focused on meltable dispersion and in situ and interfacial encapsulation techniques for capsules. Meltable dispersion is the method of dispersing the healing agent in a melted polymer to form the capsules after solidification of the polymer [47]. In situ and interfacial techniques have been used for PUF or TETA microcapsules. In this technique, the shell is developed by polymerization at the interface of healing agent droplets and the oil-in-water emulsion.

The triggering mechanism of encapsulation strategy is validated by optical microscopy of a fracture plane showing ruptured capsules, by infrared spectroscopy (IR), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) of the fracture plane. Different microencapsulation methods are optimized such as physical methods, chemical methods, and physicochemical methods. Robust, in terms of mechanically and thermally stable, microcapsules having healing precursor have been synthesized for self-healing polyurethane matrix [48]. Triethylenetetramine (TETA) microcapsules for wear-resistant polymer composites [49] and poly(methyl methacrylate) microcapsules with high storage and thermal stability [50] have been manufactured and implemented. The switching behavior of microcapsule geometry between dry and wet condition is a critical healing phenomenon. Polydimethylsiloxane-based self-healing elastomers

S.N.	Healable systems	Healing mechanism	Ref. (s)	Healing efficiency (%)
1	DCPD/PUF-microcapsules/Grubbs catalyst	ROMP	[3, 43]	99
2	Epoxides/amine	Curing mechanism	[4]	91
3	Epoxy/DCPD-WCl ₆ catalyst	ROMP	[5]	20
4	Epoxy/mercaptan	Curing mechanism	[6]	>100
5	Polysiloxane (polydimethylsiloxane)/Pt catalyst	Polycondensation reaction	[7]	>100
6	Thiol/maleimide	Michal addition reaction	[46]	>100
7	Woven glass fabric/epoxy laminates	Epoxy/ CuBr ₂ (2-methylimidazole) ₄	[8]	68–79

Table 1.
Various self-healing systems based upon encapsulation strategy.

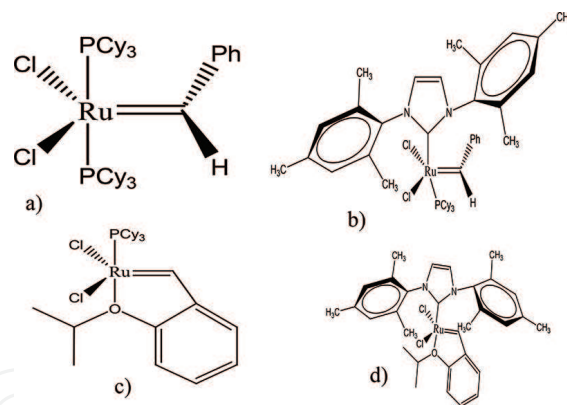


Figure 3. (a) Grubbs first generation, (b) Grubbs second generation, (c) Hoveyda-Grubbs first generation, and (d) Hoveyda-Grubbs second generation.

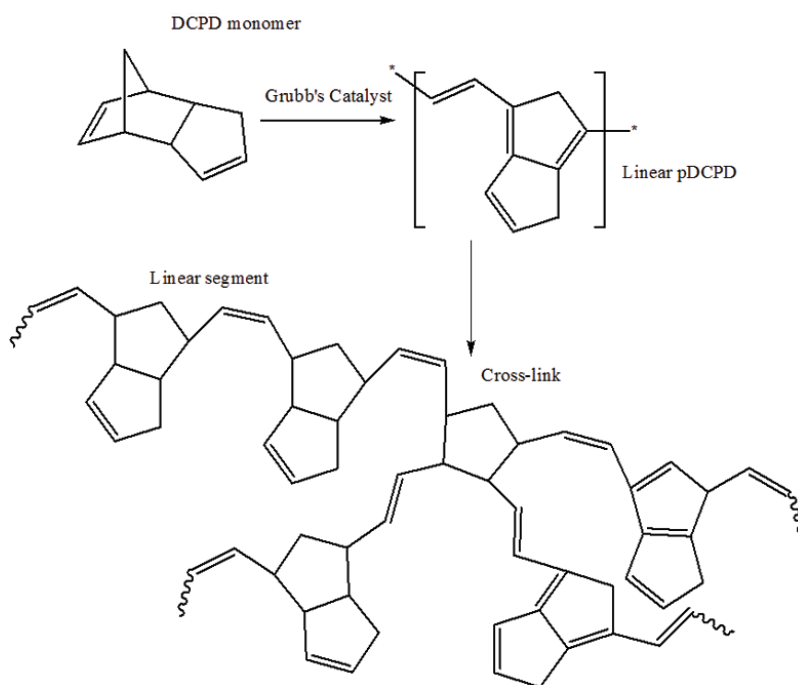


Figure 4. The ROMP of encapsulated DCPD by Grubbs catalyst [3].

also are reported [7]. Dual component self-healing epoxy system containing epoxy (DGEBA) and different variants of hardener microcapsules are investigated [51]. Various catalysts for ROMP of DCPD are shown in **Figure 3**.

Encapsulation techniques offered single healing due to unavailability of healing precursor into capsules which is earlier invested in damage repair. However, these are limited by processing difficulties and inhomogeneous distributions of two components. Deteriorates of some mechanical integrity is common due to the addition of external chemical constituent's limiting the strategy. To deliver a larger amount of healing agent, hollow glass fibers were used. This fiber reinforcement is based on the bleeding ability of bio-system. For polymer composite systems, the hollow fiber embedment approach has been more appropriate (**Figure 4**).

3.2 Hollow fiber embedment

Hollow fibers are used to deliver a larger amount of liquid healing agent. These are embedded within either glass fiber-reinforced plastic (GFRP) or carbon fiber-reinforced plastic (CFRP) composites. Healing-agent-filled hollow fibers

are introduced into the matrix by the vacuum-assisted resin transfer molding (VARTM) process. Vascular self-healing materials have appropriate healing agent in a network in the form of capillaries or hollow channels, which may be interconnected one dimensionally (1D), two dimensionally (2D), or three dimensionally (3D), upon damage. One-dimensional system is designed by glass pipettes that are embedded in epoxy resins [52]. Resin-filled hollow glass fibers impart healing capability on low-velocity impact damage in CFRP [9]. Large-diameter capillaries are not feasible to demonstrate damage healing. Smaller hollow glass fibers filled with resin have been also used, but they were unable to deliver the resin into the crack due to the high-viscous epoxy resins. Later, borosilicate hollow glass fibers (with diameters from 30 to 100 μm with 55% of hollowness) were produced to store the healing precursor resin. This approach offered certain advantages, such as the higher volume of healing agent to deliver, performed by different activation methods; visual inspection of the damaged site is possible, and embedment of hollow fibers to conventional reinforcing fibers is easier. The fracture of hollow fibers is mandatory to release healing precursors which limited the approach. The low viscosity of healing agent is favorable to facilitate fiber infiltration, which is necessary. The reinforcement of hollow glass fibers into CFRP also affects the coefficient of thermal expansion so that multistep fabrication stages of the hollow fiber are another challenge. A novel hybrid multi-scale carbon fiber/epoxy composite reinforced with self-healing core-shell nanofibers at interfaces has been demonstrated [10]. The ultrathin self-healing fibers were fabricated by means of co-electrospinning, in which liquid DCPD as the healing agent was enwrapped into polyacrylonitrile (PAN) to form core-shell DCPD/PAN nanofibers. To enhance the healing efficiency, vascular method is adopted in which a 3D microvascular network is developed into the matrix to store the healing agents for transport in longer distance.

3.3 The microvascular embedment

A microvascular technique is inspired from the respiratory system of livings. The incorporation of micro-channels with a diameter ranging from 1 μm to 1 mm within a polymer composite offers multiple healing. Self-healing materials that use hollow fibers or a mesoporous network are called vascular materials. Microvascular fabrication is possible by various techniques including laser micromachining, soft lithography, electrostatic discharge, fugitive inks, and hollow glass fibers. Healing precursors have been introduced into these channels either by pumping or through capillary forces. However, hollow glass fibers are restricted to the 1D network, but in order to obtain 2D and 3D interconnected networks, steel wires of ca. 0.5 mm could be used [53]. For the interface between plies in laminated composites, two-dimensional networks are suitable. Microvascular channels into polymer composites offer the benefits of added functionality and increased autonomy (i.e., the ability to distribute active healing material for crack healing which is difficult by conventional methods into monolithic materials). The introduction of sacrificial fibers into woven preforms enables the continuous fabrication of 3D microvascular composites that are both strong and multifunctional [12, 13]. To employ damage healing in microvascular systems, functional fluids that act as a healing agent are released upon fracture of vascular network. Further, the healing agent polymerized with adjacent catalyst formed a network and restricts the growth of damage. Active cooling microvascular systems continuously circulate a fluid into, through, and out of the matrix in order to absorb and remove excess heat. Replacement of some reinforcement fibers of FRPs by individual hollow fibers is a well-known method to achieve microvascular composites [54]. Schematic diagram of self-healing materials

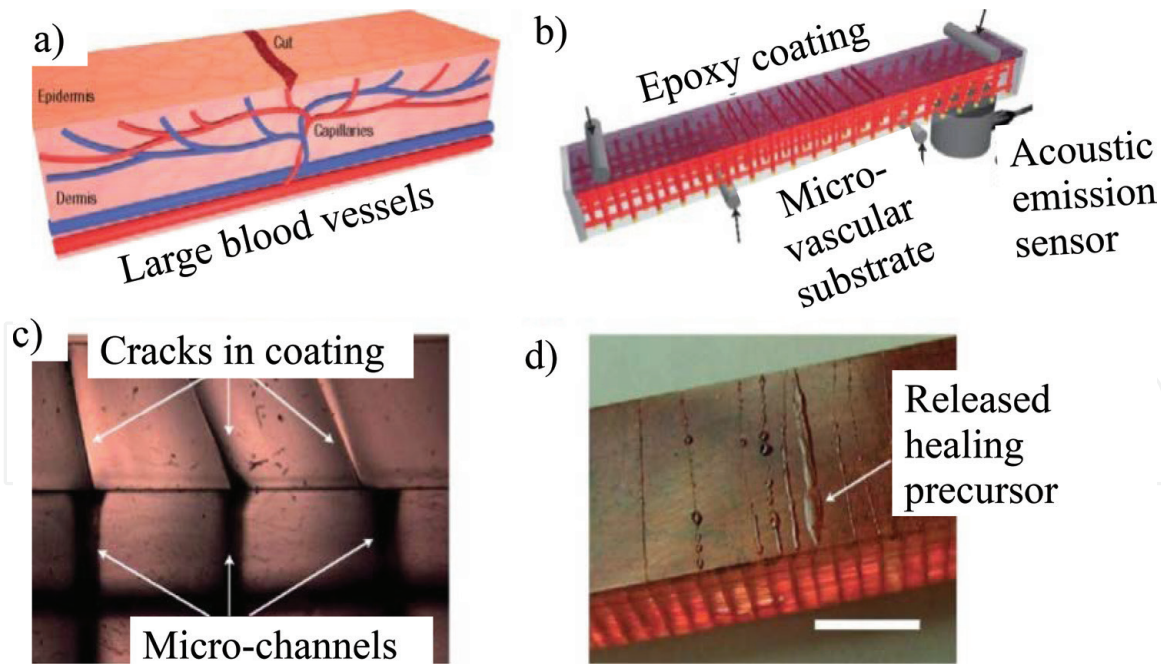


Figure 5. Schematic diagram of self-healing materials with 3D microvascular networks. (a) Capillary network in skin having a cut in the epidermis layer. (b) Vascular network into epoxy coating having catalyst in a four-point bending configuration monitored with an acoustic emission sensor. (c) Crack propagation toward micro-channel. (d) Optical image of released healing agent in the coating [15].

with 3D microvascular networks is shown in **Figure 5**. The effect of optimum size and orientation of hollow fibers in microvascular architecture in the epoxy matrix has been studied [14].

A novel type of hollow fiber called “compartmented fibers” has been developed [55]. However, hollow fibers have a greater influence on the mechanical properties of composites than microcapsules. Indeed, using this type of fibers, a localized healing response can be activated. Vasculature-based healing allowed the efficient delivery of the healing agent and additionally healed a large area. The large-scale production of self-healing fiber-reinforced composites is not feasible due to complex vasculatures and lack of scalability. After the first healing, the network may be refilled for the next healing. Initially, a brittle polymer coating is applied to a more ductile polymer substrate which contains the interconnected network of micro-channels. In contrast, synthetic self-healing composites have high strength-to-weight ratios with less dynamic functionality.

Ultralow-temperature damage healing is achieved by incorporating a 3D microvascular network (**Figure 6**). Hollow vessels are used to deliver healing agents, and

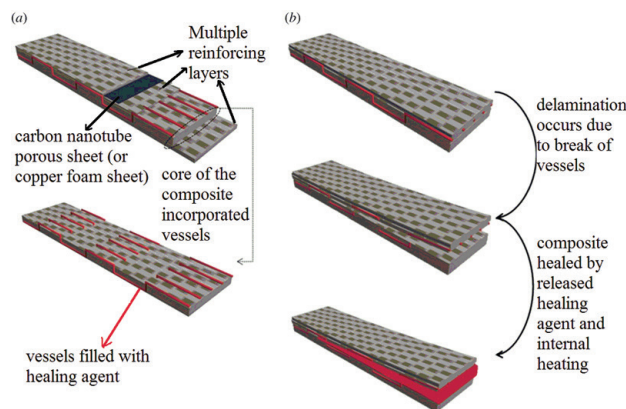


Figure 6. (a) Internal structure of the composites and (b) damage-bleeding healing process [16].

a porous conductive wire defrosts the system by internal heating, and further healing reactions are proceeded [16]. The concept may be used to develop self-healing in aerospace at high altitude having low temperature.

4. Active self-healing based on intrinsic methodology

Structurally dynamic polymers are a macromolecular system in which dynamic bonds are responsible for the restructuring of molecular architecture upon to external stimuli. Reversible bonding chemistry (i.e., covalent and non-covalent) is used to design structurally dynamic polymer systems produced to respond on macroscopic changes of material's architecture. Repeatable damage healing is demonstrated by various non-covalent interactions (reversible physical bonding), the covalent chemistries (reversible chemical bonding), and recently by their varied combination. Dynamic bonds are sensitive to specific stimulus and selectively undergo reversible bonding and de-bonding under equilibrium conditions. Intrinsic healing systems are programmed to respond to macroscopic damages. Basically, it is active methodology; healing is achieved by dynamic bonding of the polymer matrix. Intrinsic healing has specific properties of certain materials, such as molecular structures and chemical or physical bonds. The intrinsic self-healing requires human/external intervention to perform in most of the cases. The healing is possible via temporary local mobility enhancement of polymeric chains. Various modes of energy (e.g., temperature, static load, UV) are critical factors for the mobility of polymeric chains. Some chemical principles with multiple chemistries are responsible for macroscale healing. Reversible supramolecular interactions are low-energy interactions and based on hydrogen bonding, ionomer bonding, π - π interactions, or metal coordination. Two other categories of intrinsic healing systems combining physical and chemical approaches can be included: shape memory polymers and polymer blends.

4.1 Thermodynamic covalent bonding-based Diels-Alder (DA) and Retro-DA (r-DA) reactions

Cross-linked polymer networks have superior mechanical properties and thermal as well as chemical resistance as compared to their uncross-linked and linear analog. But, due to high cross-linked density, these systems are rigid and susceptible to mechanical damage. By incorporation of some dynamic covalent functionality into matrix backbone and/or in side chains, we achieved stimuli-responsive systems. Dynamic cross-linked systems have improved service life and energy efficiency and resist to foreign object impact. Basically, thermoreversible bonding is a more useful technique to load-bearing structures. It is accomplished by reversible chemical reactions upon an external stimulus. Typical dynamic bond chemistry is belonging to disulfide [56], hindered urea [57], and alkoxyamine [58] that are having flexible bonding units. A polymer (3M4F) system demonstrated self-repairing by subjecting it to heating/cooling cycles [18] shown in **Figure 7**.

In contrast, cycloaddition reaction is an efficient method to design carbon-carbon linkage without the use of catalyst. An electron-rich diene and electron-poor dienophile species play a key role to succeed DA/r-DA cycloaddition reaction. A product of DA reaction is known as DA adduct. DA adduct is the mixture of endo- and exo-diastereomers. Due to the temperature of the r-DA reaction, the exo-diastereomer is a major adduct. DA adducts have norbornane-type covalent functionality which is slightly weaker than other covalent linkages in matrix. Upon excess mechanical loading, the excess stress is transferred to weak bonding of adducts, and de-bonding

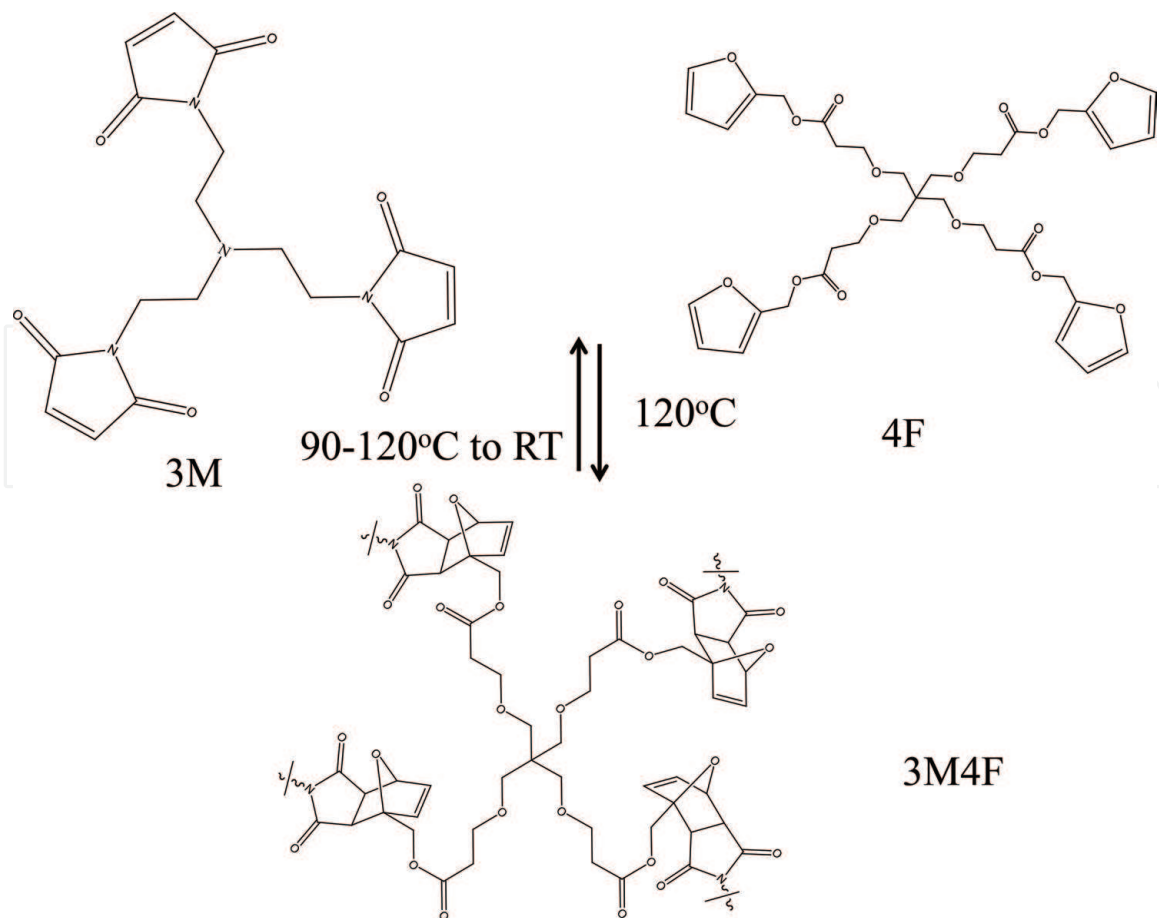


Figure 7.
 Reversible cross-linked furan-maleimide-based polymer network [18].

occurs. Upon elevated temperature, DA adducts can be dissociated into corresponding diene and dienophile moieties through r-DA reaction within the cross-linked system. Upon further cooling, re-bonding is preceded into DA adduct by reaction between corresponding diene and dienophile units. Due to thermal reversibility of DA reactions, they are frequently applied to production of remendable and recyclable materials [17–20]. The 4 + 2 cycloaddition Diels-Alder reaction is the most studied thermally controlled reaction and belongs to the group of “click reactions” that are famous for flexibility and well-organized, and selective chemical synthesis [21]. By utilizing r-DA and following DA reactions, covalent network displays a dissociation and reformation through void-filling thermoreversible process upon controlled heating. Chemically, on the basis of utilized form of diene and dienophile functionalities for DA/r-DA reaction, these systems are classified into three categories: furan-maleimide polymer systems, dicyclopentadiene-based systems, and anthracene-functionalized polymer systems. Graphene nanosheet-functionalized polyurethane-based composite has shown infrared (IR) laser-assisted self-healing, which is advantageous to flexible electronics [59]. Most of the DA cross-linked network is fabricated through step-growth poly-addition or coupling reactions of polyfurans and polymaleimides. Furan and maleimide pair is highly reactive for cycloaddition reaction and low-temperature shifting of DA/r-DA equilibrium because these moieties exist in s-cis conformation, which offered rigid system favorable for DA reaction. Furan group acts as diene, and maleimide acts as dienophile based on DA/r-DA reaction chemistry. These reactions still need an external heat source to initiate the healing process. Various healing systems based on reversible covalent bonding are presented in **Table 2**.

If the amount of damage is microscopic, capsule-based or intrinsic systems may be the best option. But, macroscopic damaged volume and vascular-based systems are

S.N.	Healable systems	Healing mechanism	Ref.	Remarks
1	Dicyclopentadiene-based polymers	DA/r-DA	[17]	Polymer side chains functionalized
2	3M4F polymer	DA/r-DA	[18]	Multivalent star-shaped systems
3	2ME4F polymer	4 + 2 DA reaction	[20]	Solvent-free synthesis
4	Anthracene-based polymers	DA/r-DA	[19]	Polymer backbone functionalized along itself
5	Thiol-modified poly [N-acetyleneimine]	Redox-reversible hydrogel system	[60]	Thiol-disulfide system (side-chain modification)
6	Polystyrene-based block copolymer	Thiol-disulfide linkage	[61]	Thiol-disulfide system (backbone modification)

Table 2.
Various self-healing systems based upon reversible covalent bonding.

efficient which allow large amounts of healing agent to be transported to the damage site. The aforementioned self-healing techniques address the repairs, mitigations, crack growth, and various damage conditions in polymer matrix. These techniques have advantages and limitations specific to applications that are summarized as follows:

- (i) These have slow healing rate.
- (ii) Additional requirement of heat/light in intrinsic systems can be good or bad depending on the application.
- (iii) The use of foreign inserts in matrix leads to detrimental effects on matrix.
- (iv) Complexity of vascular networks is a challenge.
- (v) Do not address the ballistic or hypervelocity impacts, which are great promising to space exploration upon material puncture healing.

4.2 Supramolecular noncovalent interaction-based self-healing

In materials, microscopic damages are repaired by extrinsic technology in which foreign species play a lead role in the healing process. These techniques respond to damages autonomically or stimulus-assisted phenomenon and take a shorter time to recover the strength of materials. But in the case of macroscopic damages, these extrinsic techniques are poorer in performance. Additionally, structurally covalent dynamic polymers are also requested with additional heat to clear microdamages. To overcome these issues, some significant research in the field of supramolecular systems is focused which respond to damages autonomously and recovered mechanical integrity without the addition of foreign reactive species and human intervention. In high-performance materials, macroscopic and energetic damage events are usual. These damages are healed by physical interactions. The physical interactions are noncovalent in nature and cause autonomic healing due to inherent origin. These recover about fully mechanical properties but take longer time. These noncovalent interactions recover mechanical properties almost completely but take longer time. These interactions are reversible subjected to the thermodynamic equilibrium and show additional impacts such as environmental-dependent switch properties, easy processability

S.N.	Nature of interactions	Healing system	Ref.	Remarks
1	Hydrogen bonding	DCPD/DNE/epoxy systems	[22]	Adhesion promoter used
		Polystyrene grafted with poly(acrylate amide)	[23]	Polyvalent H-bonding sites
		Ureidopyrimidinone bond—SupraPolix BV	[24]	Self-assembly mechanism
2	π - π interaction	Polydiimide/poly(siloxane) with pyrenyl end groups	[25, 26]	Flexible and self-supporting material
		Copolyimide/poly(amide) with pyrenyl end groups	[66]	Thermoreversible system
3	Ionomers	Poly(ethylene-co-methacrylic acid)/Na + ion (EMAA)	[27–30]	Self-sealing shooting range targets, tires

Table 3.
Typical supramolecular interactions and relevant self-healing polymer systems.

and self-healing behavior as compared to traditional polymers. Reversible bonding can be used to design supramolecular healable polymers and composites which respond to external stimuli such as heat [62], pressure [63], water [64], or light [65]. Various supramolecular interaction-based self-healing systems are shown in **Table 3**.

Stimuli responsiveness [67] and a high diffusion rate of oligomeric components [68] are the main characteristic of supramolecular polymers which make them for rapid and controllable healing system. Oligomers are low-molecular-weight species that make aggregates by self-assembling and perform rheological or mechanical properties similar as polymers. The reversible non-covalent interactions can be possible by hydrogen bonding, ionic bonding, metal-ligand bonding, and π - π stacking.

4.2.1 Supramolecular chemistry based on H-bonding

H-bonding is the most popular route to achieve supramolecular polymers. Upon heat, interactions between the polymeric chains are decreased and reassembled upon cooling, and finally the non-covalent cross-linking recovered the strength and mechanical integrity. To achieve sufficient cross-linking density in polymer, a high association constant between repeating units is needed. The association constant and a reversible interaction have a reverse relation. In contrast, at the less association constant, better reversibility is achieved but having smaller assemblies and poor mechanical properties. However, individual supramolecular polymers are suffered by low mechanical strength. The mechanical strength of supramolecular system is enhanced by an increase in the number of non-covalent interaction [22] and by reinforcement with nanofiller [26]. Significantly, the interactions of matrix fiber are increased by the presence of hydrogen bond accepting functionality in matrix polymer blend. Adhesion promoter increases the amount of H-bonding of the matrix system [22]. These promoters are known as co-healing agents shown in **Figure 8**. On fracture of capsules, the DCPD monomer penetrates the networks of epoxy matrix and reacts with embedded catalyst. The formation of interpenetrated network is initiated by polymerization of DCPD which would strengthen the matrix—poly(DCPD) surface. Higher strength is obtained by entangled

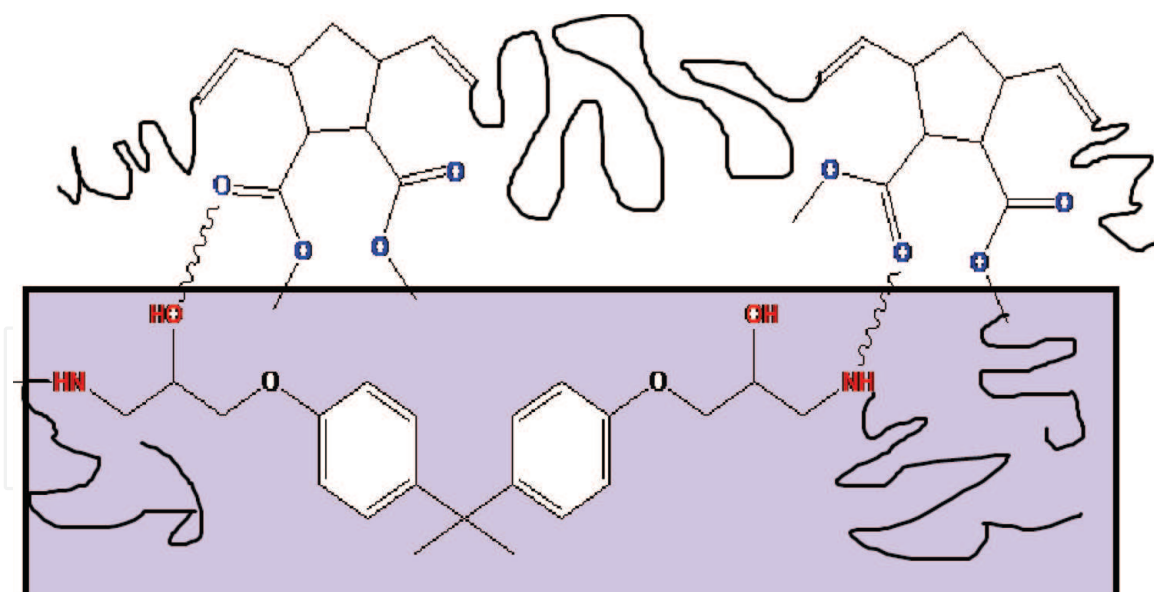


Figure 8.
Supramolecular interactions with adhesion promoter [22].

networks, and H-bonding will also improve overall bonding strength and healing efficiency. H-bonding-incorporated supramolecular system is shown in **Figure 8**.

The reinforcement of cellulose nanocrystals or cellulose nanowhiskers into polymer matrix such as poly(ethylene oxide-co-epichlorohydrin) [69] and low-density polyethylene [70] has shown improved stiffness corresponding to parental matrix materials.

4.2.2 Metal-ligand supramolecular polymers

Optical and photo physical properties of metal complexes offer to design advanced materials. Reversible behavior of metal ion and ligand bond in metal-ligand complexes attract the research community to design stimuli-responsive materials. Metallo-supramolecular polymers have low-molecular-weight species known as telechelic. These are attached with ligand end group through metal-ion linkage. These polymers can be healed upon contact of light [65, 71]. During the whole healing mechanism, supramolecular interactions and light-heat conversion happen subsequently. The temporary disentanglement of metal-ligand motifs is possible when excited electronically upon contact with UV, and further, heat energy is released. Subsequently, the average molecular weight and viscosity of system are decreased, and defect healing is resulted. Local damages can also be recovered just upon light exposure. A metallo-hydrogel based on histidine and Zn^{2+} ions is designed using coordination-driven self-assembly [72]. The hydrogel formation is instantaneous, and it exhibits stimuli-responsive behavior with respect to pH, heat, and external chemicals.

4.2.3 Supramolecular π - π interaction-assisted self-healing

A thermally triggered reversible network is achieved based on π - π stacking interactions in which end-capped π -electron-deficient groups interact with π -electron-rich aromatic backbone. The chain-folding co-polyimide (electron deficient) and pyrenyl (electron rich) end-capped polyamide chains have such π - π interactions [66]. The driving forces for producing tough, stable, healable homogeneous blend of elastomers are interpolymeric π - π stacking complexes [73]. At higher temperatures, the disengagement of the supramolecular (π - π stacking and hydrogen-bonding) interactions is possible, which leads to change in the apparent molecular

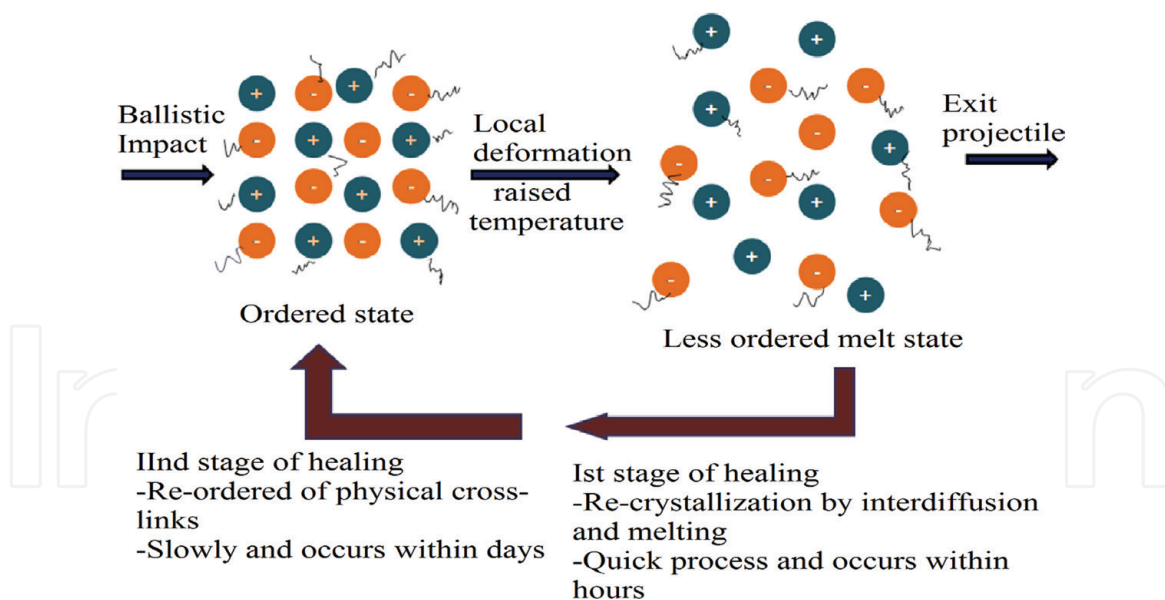


Figure 9.
Schematic diagram of ionomeric healing upon ballistic impact based on order-disorder theory of healing presented by Fall [27].

weight of the homogeneous noncovalent polymer blend and further rapid change in viscosity with temperature. A polymer blend recovered the mechanical strength by refurbishing these supramolecular interactions.

4.2.4 Supramolecular self-healing ionomers

Ionomers are polymers in which the bulk properties are governed by ionic interactions in discrete regions of the material [74]. Ionomers contain up to 15% ionic groups and respond instantaneously and autonomously in absence of external species, and additional heat or other stimuli make ionomers unique. Various bonding interactions such as ionic, dipole-dipole, or ion-dipole bonds are key factors to develop self-healing systems based on ionomers. Ballistic healing proceeds through combination of an elastic response (i.e., attain pure shape) and a viscous response (secondary polymer flow and chain entanglement) of intrinsic aggregates. Initially after impact, projectile transfers some of the impact energy to ionomer system which melts the matrix, and rest kinetic energy is stored elastically to movement, and the projectile is ejected and leaves behind the matrix with some melted portion. Finally, the hole is sealed and recovered some mechanical properties followed by crystallization and reaggregation of ionomers at the damage site. Healing process in ionomers is multistep. Initially upon high-energy impacts, the local deformation proceeded to less ordered melt state and resultant the projectile is ejected. After that, complex aggregates are formed via recrystallization of interdiffusion of intermolecular interactions. It is a quick process that happens within seconds to hours. In the second step, restructuring of physical cross-linking leads the final stage of healing; it takes longer duration as usually days to months. Some of commercial products such as React-A-Seal, Surllyn, and Nucrel have EMAA as base matrix [27]. It is a copolymer of ethylene and a vinyl monomer with an acidic group. EMAA ionomer exposed self-healing upon ballistic impact (**Figure 9**) [27, 28].

During whole mechanism “free volume” plays a great role which provides enough mobility to polymer chain rearrangement and interdiffusion. Besides, many other factors, such as impact energy, nature of ionic groups, and counterions, the neutralization degree, increased temperature during impact, the content of ionic groups and dielectric constant, and so on, also play a key role to succeed self-healing by ionomers. To enhance the healing efficiency of ionomers composites, conductive

S.N.	Healing system	Healing mechanism (photoinduced)	Ref.	Remarks
1	1,1,1-tris(cinnamoyloxy-methyl) ethane (TCE) monomer	[2 + 2] Cycloaddition	[40]	Cycloaddition of cinnamoyl groups
2	Pentaerythritol tetra (3-mercaptopropionate) and triethylene glycol divinyl ether system	Reversible cleavage of allyl sulfide linkage	[76]	Hemolytic photolysis
3	Pyridine-capped poly(methyl acrylate)s/SCS-cyclometalated dipalladium	Light-induced cis-trans isomerization	[77]	Molecular switching
4	Epoxy/SiO ₂ microcapsule	UV-triggered polymerization	[78]	Aerospace coatings
5	Chitosan polyurethane networks	Photoinduced reaction	[79]	Coating applications
6	Epoxy/nano-TiO ₂	Photoabsorbing microcapsules	[80]	Protection coatings

Table 4.
Photoinduced damage-healing system.

and magnetic fillers are added [29]. In addition to plasticizer such as zinc stearate ionic domain, the matrix properties are intact [75].

5. Photochemically induced healing chemistry

Photoinduced healing is currently demanding because of rapid, eco-friendly concept of healing of polymer matrix composites. It is induced by the application of a strong light irradiation. To damage healing, the foreign healing inserts, catalyst, or additional heat is neither required to comply with the healing process. Such system based on photochemical reactions is developed (**Table 4**).

6. Significance of healing functionality

The objective of self-healing phenomenon is focused to respond upon fracture based on quasi-static performance. In the future, self-healing materials can be used in various applications including nuclear reactors, marine structures, and various cutting tools. Self-healing aircrafts or spacecraft is currently desired in references of micrometeoroids and orbital debris protection, low-temperature repairs for aerospace structures, and re-healable fuel tanks. Cost-efficient healable wind power blades and wire insulation materials are also desirable based upon self-healing materials. Durable targets for military personnels and training are also part of self-healing ionomers which protect against ballistic penetrations.

7. Current scenario, challenges, and future perspective

Self-healing systems represent a wide interdisciplinary area and are performed by different techniques. Understanding the basic mechanism and principle of damage healing is also still a challenge for science community. Healing chemistries

have greater stabilization, higher reactivity, and fast kinetics, although many challenges still remain. Healing performance under long term in drastic environment is advantageous. Additionally, increased healing efficiency with low-cost techniques and least detrimental effect on base matrix is also challenging. To implement encapsulation technique, distribution of capsules is challenging and has adverse effects on matrix. Similarly, the fabrication of vascular network is not easy to implement. In microelectronics, optoelectronics, and robotics where damages are common as nanostructures, self-healing concept is beneficiary. Long-lasting self-healing battery, self-sealing fuel tank/tires, fad-resistant textiles, and anti-tamper electronics are future significance of self-healing technique. Sensor design with healing concept is used to structural health monitoring of components. The incorporation of self-healing concept into aerostructures is challenging and required to establish because the aerostructures always suffered mechanical and thermal loading continuously. In the future, catalyst-free and UV- or light-oriented self-healing systems are desirable.

8. Conclusive remarks

Conclusively, the self-healing techniques explore the possibility of damage detection and subsequent damage management in materials. Some technological restrictions and possible solutions are also explored. Self-healing techniques intimate damages at the early stage and recovered mechanical properties at some extent which reduces the probability of replacement and loss of structures. Currently, we are still waiting for fully self-healing systems that can show both stimuli responsiveness and healing characteristics.

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Author details

Jeetendra Kumar Banshiwal* and Durgesh Nath Tripathi
Defence Materials and Stores Research and Development Establishment, Kanpur,
India

*Address all correspondence to: jeetukumar331@gmail.com

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