Basics of Self-healing Epoxy Systems—General Concepts, Behavior, and Mechanism

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Abstract Epoxies are the most versatile thermoset resins and are considered to be the hallmark of thermoset industries. The demand for epoxy resins is predicted to grow at a compound annual growth rate of 6.32% by 2030. The self-healing nature of synthetic material is an emerging field of research as it can prolong the service life of the material and thus can possess a broader range of applications. The development of self-healing epoxy resins has been inspired by the natural repairing system wherein the damage initiates autonomic healing of the wound. This chapter covers the fundamentals of the self-healing system as well as the mechanism and main approaches of self-healing, which are further divided depending on the healing chemistries involved and the type of vessels used to store the healing agent. The benefits and drawbacks of various self-healing techniques have been discussed. This chapter also reviews the existing self-healing epoxy systems published in the last decade. Lastly, the research opportunities in the near future and the challenges are discussed.

Keywords Self-healing · Epoxy resins · Intrinsic · Extrinsic · Microcapsules · Thermo-reversible crosslinks

1 Introduction

Epoxy resins are the prepolymers containing three-membered epoxy rings with an oxygen atom bonded to two interconnected carbon atoms and thus possess considerable ring strain, making them highly reactive. These epoxy rings are usually terminal, though they may lie within the chain of the molecule. The thermoset epoxy resins are a fusion of both epoxy resin and curative agent. Because of the existence of electron-rich oxygen and electron-deficient carbon atoms in the oxirane rings, the epoxide resins can undergo both electrophilic as well as nucleophilic addition reactions. Thus, epoxy resins can cross-link with one another or with a variety of hardeners/curatives

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N. Hameed et al. (eds.), *Multifunctional Epoxy Resins*, Engineering Materials,
https://doi.org/10.1007/978-981-19-6038-3_2

such as alcohols, thiols, phenols, amines, anhydrides, amides, and acids, resulting in three-dimensional cross-linked thermosetting polymers. The cross-linking density of the epoxy thermosets is responsible for the mechanical, thermal, and many other properties of the material. The process of fusion of the oxirane group and hardener is termed as curing of epoxy, and the cured epoxy thermoset resin contains no or relatively very few epoxide groups.

Epoxy resin thermosets possess excellent properties such as adhesive strength, thermal stability, chemical resistance, electrical insulation, mechanical strength, processability, flame retardance, and water tightness. These properties enable a wide range of thermosetting resin applications in aerospace and recreation industries, coatings and adhesives, printed circuit boards, potting materials for electronics, high tension electrical insulators, fiber-reinforced plastic materials, and lightweight automobile parts. Epoxy thermosets can also improve the decorative/aesthetic performance of the material. An increase in the functionality of these resins increases their reactivity and thus promotes their binding with various substrates/fibers. The epoxy resin thermosets are employed as a matrix material for fiber-based composites in renewable energy and aerospace industries. Thus, epoxy resins are important, commercially available, multipurpose thermosetting materials with high strength and firmness.

However, epoxy resin thermosets have an imperfection, as they are brittle, and minor cracks are more likely to form during their service life. These microcracks are difficult to detect because they are deep within the structure, and if not repaired, they can progress to macrocracks, causing the entire system to fail. Traditional damage repair techniques (welding and patching) are restricted to visible cracks only, are not instantaneous or autonomous, and demand a thorough inspection of the material. Epoxy systems are difficult to recycle at the end of their lives due to their highly cross-linked network architectures and thus may cause health and environmental difficulties. The epoxy resin's service life can be extended either by preventing the microcracks formation in the epoxy matrix or by repairing microcracks as soon as they form. Hence to reduce the cost of damage repair and to prolong the service life of the material, there is a need to upgrade the material to be self-healing. Over the past few decades, successful attempts have been made to synthesize epoxy-based self-healing materials, and this has attracted the interest of many researchers and scientists.

Self-healing may be defined as the material's ability to recover from damages/cracks on its own. The inspiration for self-healing in materials is derived from nature's wound and cut repairing ability in living organisms. Every living species can release the healing agents to the site of injuries and thus repair the damage by sealing and then healing the wounds. Even the plants can restore the mechanical properties along with the wound closure. The self-healing materials are supposed to imitate the capability of biotic materials to repair the wound and restore mechanical integrity.

This chapter represents an overview of the general concept of self-healing approaches, discusses various healing mechanisms along with the benefits and drawbacks of the various methods, and studies the behavior of epoxy systems with self-healing ability.

2 Approaches of Self-healing

There are numerous self-healing approaches, which are primarily classified into two categories: extrinsic self-healing and intrinsic self-healing. In these two approaches, the self-healing chemistries that the polymeric material undergoes during the crack repairing process are different. However, the mobile phase is required in both self-healing approaches so that it can flow to the site of damage and fill the crack during the healing process. In the extrinsic self-healing approach, the crack in the network structure is repaired by the release of the healing agents from the containers, which are already embedded in the polymer matrix and allow them to flow to the site of damage. The cross-linking of the healing agent results in the repair of the crack. Because the damage itself triggers the release of the healing agent from the containers, this extrinsic self-healing approach is also known as autonomous self-healing as no external intervention, such as heat, light, or moisture, is required to initiate the repair mechanism.

On the other hand, in the case of the intrinsic self-healing approach, the self-healing process is driven by the chemical bonding of the matrix. Thus, the material is designed with the inherent potential to restructure after impairment in the presence of external triggers such as heat, light, or chemicals. No stored healing agent or catalyst is required in its self-repairing chemistry. The intrinsic self-healing mechanism is considered non-autonomous, as external stimuli are required to initiate the healing process. The following sections summarize the development of self-healing polymeric materials for these two categories.

2.1 Extrinsic Self-healing Mechanism

In extrinsic self-healing, the resin matrix is not healable on its own. The repairing agent-filled micro-containers are dispersed within the matrix system in advance. When exposed to fracture, the micro-containers rupture, thereby releasing the healing agent, which travels through capillary action to the site of damage, where it is cured by the polymerization reaction, restoring the material's damage and surface integrity [1]. The healing agent must be stable for a long duration inside the micro-containers and should be able to reach the crack site via capillary action, i.e., lower viscosity. It should react quickly to seal the crack in a reasonable amount of time and have no harmful effects on the polymer matrix. The added catalyst and the curing agents present in the polymer matrix must be chemically stable within the matrix but rapidly

react when they come in contact with the healing agent. The catalyst must be stable over a wide range of applications and temperatures and well dispersed within the matrix.

This self-healing mechanism is not repeatable, and the scratch at a specific location can be healed only once [2]. The healing performance and self-healing ability of the material depend on structural and dynamic factors such as size, shape, and distribution pattern of micro-containers, flow, and incorporation of healing agents into micro-containers. In this self-healing approach, the research is mainly focused on the fracture process, repairing agent, kneading process, and matrix formulation techniques. Based on the type of micro-containers embedded within the matrix, the extrinsic self-healing technique is further divided into categories such as microencapsulation, microvascular networks, hollow fibers, or nanoparticles, which are described in detail in the upcoming sections.

2.1.1 Healant Loaded Capsules/Containers

In this mechanism of self-healing, capsules of micro-size are used as containers for the healing agent. Some researchers have also developed dual capsule-based self-healing systems in which both the healing agent as well as the curative agent or hardener are encapsulated and dispersed within the polymeric system. Many researchers have worked on developing epoxy-based self-healing coatings and studying their healing capabilities as well as other mechanical properties; a few of the research articles are listed below.

Self-healing System Having Capsule and Catalyst

Epoxy resins with capsule-based self-healing ability were first reported by White et al. [3] in 2001, which involved the use of a monomer, dicyclopentadiene (DCPD), stored in urea-formaldehyde microcapsules. A progressive crack ruptures the microcapsules, and the healing agent is released into the cracked location by capillary action, where it comes in contact with dispersed Grubb's catalyst and initiates the polymerization reaction resulting in crack repairing and restoring the material's surface integrity as shown in Fig. 1. Here, the repairing process occurs through a living ring-opening metathesis polymerization (ROMP) reaction. In terms of toughness, the healing efficiency of the material was found to be 75%. This is an autonomically self-healable material because no external stimulus is needed to initiate the repairing process as it is triggered by the propagating crack itself. DCPD is widely used as a healing agent in self-healing materials [4–6], and Grubb's catalyst is used as a catalyst in the ROMP of DCPD. White et al. made use of first-generation Grubb's catalyst, but due to low chemical and thermal stability, its applications are limited in microcapsule-based self-healing polymeric materials. To overcome this difficulty, Moore et al. [7] made use of second-generation Grubb's catalyst, Hoveyda Grubb's second-generation catalyst, and with first-generation Grubb's catalyst to compare

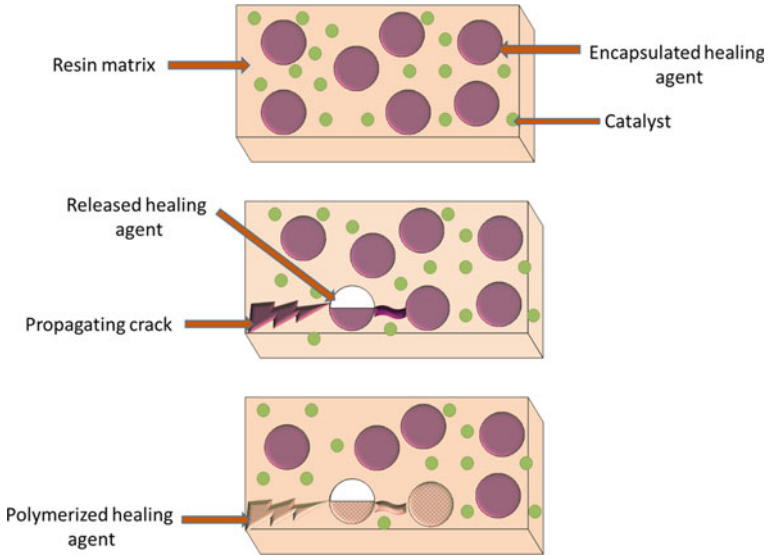

Fig. 1 Autonomic healing process for self-healing material with an embedded encapsulated healing agent and the catalyst dispersed within the composite matrix

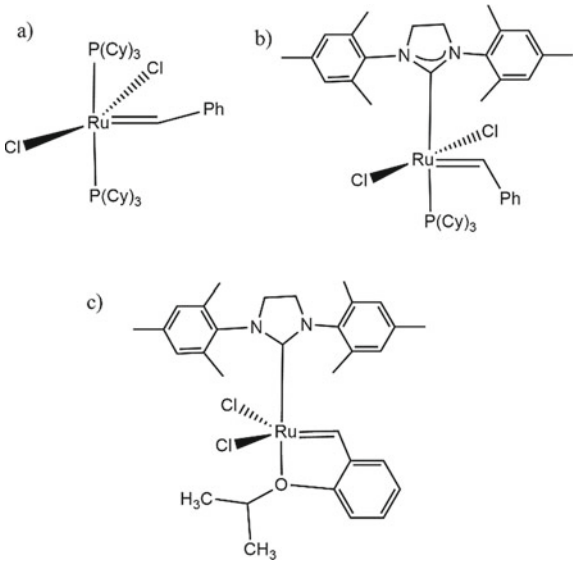

Fig. 2 Molecular structures of **a** Grubb's first-generation catalyst, **b** Grubb's second-generation catalyst, and **c** Hoveyda Grubb's second-generation catalyst

their thermal, chemical, and catalytic properties. Figure 2 represents the structures of various Grubb's catalysts.

The second-generation Grubb's catalyst was discovered to have excellent healing efficiency and thermal stability at elevated temperatures. To withstand harsh

conditions such as mechanical shear, high temperatures, and so on, the capsule's robustness must be greatly enhanced. Caruso et al. [8] created double-walled microcapsules made of PU/UF polyurethane/poly(urea-formaldehyde) microcapsules for this purpose. These double-walled microcapsules outperformed single-walled urea-formaldehyde capsules in terms of thermal stability and mechanical properties. Jin et al. [9] used a rubber toughened structural epoxy adhesive to further their research on self-healing. The self-healing ability of embedded microcapsules filled with DCPD monomer and Grubb's catalyst was demonstrated by high-temperature curing at 110 °C for 3 h. The fracture toughness of the rubber adhesive was investigated by using a width tapered double cantilever beam (WTDCB) test specimen. For 6.6 wt% of DCPD microcapsules and 10 mg of the catalyst, the healing efficiency was found to be 58%.

The poor catalytic dispersion and activation/deactivation of the catalyst, which may reduce the healing ability of the matrix, are some concerns with this capsule catalyst-based self-healing system. Thus, to preserve the catalytic reactivity of the catalyst, a wax-coated Grubb's catalyst can be used [10]. A glass-reinforced self-healing epoxy composite system can also be prepared by using DCPD capsules and paraffin wax microspheres having 10 wt% Grubb's catalyst [11]. The self-healing ability in such case accessed using a low-velocity impact test revealed that the crack length was reduced to 51% after the repair observed through fluorescent labeling.

In a very recent study, Romero-Sabat et al. [12] reported the synthesis of an extrinsic self-healing composite material with a healing efficiency of more than 100% at low or ultra-low temperatures. It is based on the ring-opening metathesis polymerization (ROMP) of 5-ethylidenenorbornene/dicyclopentadiene (ENB/DCPD) blends that can flow even at −70 °C and can react with Grubb's third-generation catalyst. The monomers, ENB/DCPD, were encapsulated within the polyurea (PU) capsules and dispersed into three commercially available epoxy resins, and there was no need to shield the metathesis catalyst. The fracture toughness analysis with tapered double cantilever beam (TDCB) for all different epoxy systems reveals that the healing efficiency was found to be more than 100% at cryogenic temperatures (−20 °C).

Dual Capsule-Based Self-healing Systems

The microcapsule catalyst-based systems have some disadvantages, such as improper dissolution of the catalyst, disruption of the catalyst by the epoxy of the matrix system, the low compatibility of the DCPD and Grubb's catalyst with the matrix, and insufficient interactions of the healing agent with the catalyst. The dual capsule-based self-healing systems have been investigated to overcome these disadvantages. Here, in this category, both the healing agent and the hardener are encapsulated separately into the microcapsules, which are then dispersed evenly into the polymer matrix system. When a fracture occurs, the microcapsules rupture and the healing agent gets polymerized when it comes in contact with the hardener, thus repairing the damage. For this purpose, in 2007, Rong et al**.** synthesized an epoxy amine-based resin system in

which the DGEBA epoxy resin and imidazole hardener were both encapsulated separately and dispersed into the matrix system [13]. In this case, no catalyst is required for the polymerization reaction. The microcapsules shell wall for epoxy resin has been prepared from poly(urea-formaldehyde) PUF by the oil in water emulsion, and PUF encapsulated imidazole served as the hardener for the epoxy. The healing efficiency was accessed by the fracture toughness test and was found to be around 106%. The heat resistance self-healing epoxy composite system had also been developed by Yuan et al. using diglycidyl ether of bisphenol A (EPON 828) as a healing agent and a catalyst 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) [14]. The material used to prepare the microcapsule shell wall was poly(maleimide-formaldehyde) (PMF). The employed epoxy resin is thermally stable, and DMP-30 has low volatility, making the system self-healable and can survive in high-temperature curing conditions. The composite system showed a high level of self-repairing ability below 200 °C and healing efficiency of 72–86% even on exposure to a high temperature of 250 °C.

Li et al. [15] developed a self-healing epoxy-based system using DGEBA diglycidyl ether bisphenol A as the active ingredient. The epoxy resin and polyetheramine hardener were encapsulated in a poly(methyl methacrylate) (PMMA) shells using a water-in-oil emulsion technique. The ratio and content of microcapsules had an impact on healing efficiency. When 5 wt% of the microcapsules were dispersed within the resin system, and curing was carried out at room temperature for 24 h, the healing efficiency was found to be 43.5%. It was increased to 84.5% when the microcapsule content was raised to 15 wt%.

Our group [16] has recently developed a dual capsule-based self-healing material using a bio-based epoxy and an imidoamine curing agent. An in situ polymerization technique was used to develop melamine-formaldehyde (MF) microcapsule containers. The average size of epoxy-filled microcapsules was 83 μm, while that of hardener-filled microcapsules was 95 μm. The mild steel specimens served as coating substrates, and the self-healing coatings were prepared by using epoxy/imidoamine with 10 and 20 wt% epoxy microcapsules and both 10 wt% epoxy and 10 wt% hardener-filled microcapsules. The solvent wash analysis was used to determine the stability of microcapsules, which was found to be 98.2 and 87.5% for epoxy microcapsules-based and dual capsule-based coatings, respectively. SEM confirmed the surface morphology and the self-healing ability. The salt spray, mechanical analysis, and adhesion testing were performed on coated specimens with and without microcapsules. The self-healing coatings with both 10 wt% epoxy and 10 wt% curing agent-filled microcapsules exhibited excellent properties.

Wang [17] synthesized an epoxy composite with self-healing capabilities. Here also, the dual capsules of diglycidyl1,2-cyclohexanedicarboxylate (DGCHD) and an aliphatic amine hardener (HB-1618) were prepared. The polyetherimide was used as the shell wall material for the amine hardener microcapsules. The healing efficiency varies with the capsule concentration. With a 15% capsule concentration (6 wt% epoxy-containing and 9 wt% hardener-containing microcapsules), the efficiency was 65.6%. The hollow glass bubbles can also be used to encapsulate the epoxy and amine solutions, and a dual-part epoxy amine-based self-healing polymer

was developed by Zhang et al. [18]. The epoxy and amine solutions were encapsulated in etched, hollow glass bubbles (HGBs) and dispersed in the matrix system. The micro-compression tests were performed on a single HGB to determine its mechanical robustness and cracking ability. The HGBs were found to be much brittle as well as stronger than the PUF or PU microcapsules. The incorporated ratio of epoxy to amine HGBs was optimized to 4:1. The material showed the best healing efficiency of 62% when cured at 50 °C for 24 h, and the total HGBs content was 12.5–15.0 wt%. The healing efficiency was found to increase with increasing curing time at 50 °C, which was attributed to promote cross-linking over time as well as good diffusion of higher molecular weight chains. Corrosion-resistant, dual capsule-based self-healing epoxy coatings using epoxy resin and an amine hardener have also been reported [19], wherein the poly(styrene-*co*-acrylonitrile), SAN, was used as a shell wall material for microcapsules. Commercially available Bisphenol F epoxy resin and cycloaliphatic polyamine (EPIKURE F205-Hexion) were used as the core materials, and the material used to prepare the coating matrix was bisphenol A epoxy resin (EPON 828) and polyamidoamine curing agent (Merginamide A280). The core material was encapsulated by using the emulsion electrospray technique. Three coating samples based on microcapsule content in ratios 1, 5, and 10 wt% (in 1:1 molar ratio of epoxy and amine hardener) were dispersed within the matrix. The healing efficiency was determined with the help of electrochemical impedance spectroscopy (EIS). The coating sample with 1 wt% of microcapsule showed the best corrosion resistance with 99% self-healing efficiency.

High-temperature cured epoxy resins have a wide range of applications as structural adhesives and structural composites due to their chemical and mechanical properties. Ghazali et al. [20] studied the self-healing behavior of a dual capsule-based, high-temperature cured epoxy resin system. DGEBA resin and mercaptan hardener were loaded into the dual capsules, and 2,4,6-tris (dimethylaminomethyl)phenol (DMP-30) was used as a catalyst. The microcapsules were synthesized from poly(melamine-formaldehyde) (PMF) by in situ polymerization reaction. The mechanical behavior and self-healing abilities of the tapered double cantilever beam (TDCB) epoxy specimens were examined using mode I fracture toughness testing. When heated to 70 °C, the epoxy system recovered up to 111% of its original fracture toughness. At higher temperatures, the healant with a lower viscosity showed excellent healing ability.

The self-healing capsules are mostly made up of synthetic polymers, which can cause environmental as well as health issues. Thus, self-healing bio-capsules for encapsulating the monomers can eliminate these concerns. These bio-capsules can be prepared using alginate biopolymer. Hia et al. [21] used the electro-spraying method in order to encapsulate the epoxy (DGEBA) as well as a hardener (mercaptan/tertiary amine), respectively. The diameter of these encapsulated bio-capsules was reported to be in the range of 300–400 μm, and shell wall thickness varied from 3 to 6 μm. The core content of the epoxy and hardener microcapsules was found to be 74% and 59%, respectively. The use of scandium (III) triflate was also explored as a catalyst in the same resin system. The self-healing abilities of the two systems were accessed through the Charpy impact test. The healing efficiency of these systems was tested

by subjecting these to multiple healing cycles and was found to be in the range of 68–85% even after three/four healing cycles. The multicore internal structure of the microcapsules controls the release of the repairing agent and thus was attributed to multiple healing of the material, which is otherwise not possible in a capsule-based system.

Mono Capsule-Based Self-healing System

The dual capsule system may result in poor microcapsule distribution and clustering, both of which can reduce the material's mechanical strength [22]. A new kind of self-healing system was designed wherein the solvents like methanol and ethanol are used as healing agents to repair the damage of thermoplastic polymers. This self-healing system is similar to the capsule-based healing system, where the implanted solvent capsules break during damage allowing the liquid solvent to fill the scratches and repair to occur. Caruso et al. [23] had synthesized a thermoset polymer with self-healing ability by incorporating the solvent-filled microcapsules into the epoxy composite. The solvent inside the capsules would act as a wetting agent on the surface of the polymer, resulting in swelling of the polymeric material, thus interlocking the chains across the fractured surfaces, which seal the crack and restore the mechanical properties.

The cerium nitrate is supposed to exhibit corrosion inhibition properties, and it is found that cerium ions cause the precipitation of cerium oxides or hydroxides, which obstruct the cathodic reduction reaction of metallic coatings. However, the cerium nitrate is consumed over time if it is mixed with the epoxy before being applied to the metal surfaces and thus is not in a position to recover the induced fracture during the service life of the coating. Farzi [24] made use of cerium nitrate in their self-healing epoxy-based coating system. The authors had encapsulated the cerium nitrate into the poly(urea-formaldehyde) PUF microcapsules through a two-step polymerization process, which were then embedded into the epoxy-based coating system. The self-healing performance of the system was accessed by using EIS tests in 0.6 M NaCl solutions. The EIS findings reveal that whenever the damage occurs, cerium nitrate is released from the microcapsules and results in effective healing of the cracks as the precipitates of oxide and hydroxides in the damaged region form a passive layer that inhibits the corrosion. The healing efficiency of the coatings containing 10 wt% of microcapsules was observed to be the highest, but it decreases the adhesive strength of the coatings.

The metal complexes with imidazole can be prepared easily and can be used as the latent curing agents for one-pack epoxy-based self-healing systems. The latent hardeners react with the epoxy resin on heating and do not react at room temperature. Tripathi et al. [25] synthesized a self-healing system based on microcapsules with latent curing agent functionality, wherein the latent curing agent is dispersed within the matrix phase. The epoxy resin was encapsulated in poly(urea-formaldehyde) shell-walled microcapsules. The Ni and Cu-imidazole complexes were prepared by complexation reactions of Ni and Cu chlorides with 2-methyl imidazole and were

used as latent curing agents. The epoxy composites were prepared by ultrasonication, dispersing the varying amount of epoxy-filled microcapsules (5–30 wt%) and fixed amounts of latent hardeners (1 wt%) triethylenetetramine (TETA). They were added to cure the resin at 30 °C for 24 h. The 100% healing efficiency was attained with 30 wt% of the microcapsules, but the mechanical properties of the matrix deteriorated with an increase in the capsule loading. Ma et al. [26] prepared an epoxy oxide-based (E-51) self-healing system for 4D printing. The melamine-formaldehyde (MF) microcapsules were prepared by in situ polymerization. Herein, the bisphenol A-based epoxy resin (E-51) was used as a healing agent, $Cu(MI)_4Br_2$ as a latent curing agent, and graphene oxide (GO) acted as a reinforcing phase that increased the tensile strength of the materials. The microcapsules and the latent curing agent were uniformly distributed in the matrix. The scratch healing efficiency of the material was found to be 87.22%, and the broken healing efficiency was 89.97%.

Linseed oil (LO) can act as a healing agent as it is environment friendly, shows some lubricating properties, and is economically viable. Moreover, it is air drying in nature and can polymerize with oxygen resulting in a flexible and water repellent coating layer [27]. Thus, linseed oil can provide self-healing and self-lubricating properties to the material, thus making it resistant to damage and could repair scratches after damage. Suryanarayana et al. [28] investigated the effectiveness of linseed oil as a repairing agent. The linseed oil was encapsulated within the urea-formaldehyde shell walls using the in situ polymerization technique. LO was found to be able to repair the crack and thus protect the underlying substrate from corrosion. Yang et al. [29] extended the work with linseed oil and encapsulated LO into polyurethane shell walls rather than potentially hazardous UF shells. The LO-filled polyurethane microcapsules were prepared by interfacial polymerization. Epikote 862, a commercially available epoxy resin, serves as the matrix material, and Epikure 205, a low viscosity modified cycloaliphatic amine curing agent, serves as the epoxy curing agent. The self-repairing and the self-lubricating properties of the coatings were determined by electrochemical impedance spectroscopy (EIS), salt spray analysis, and friction wear test methods. The friction wear test results revealed that the coating performance was enhanced when the microcapsule concentration reached up to 10 wt% or more. The friction coefficient was reduced to 86.8% compared to the pure epoxy coating without microcapsules.

The increased lubricating property and the wear resistance with self-healing ability can significantly extend the material's service life. To improve the mechanical damage and the wear resistance tendency of the material, the work with linseed oil has been further extended, and the self-healing ability of a polymer composite embedded with bifunctional microcapsules was also investigated [30]. The organic solvent dibutyl phthalate (DBP) and linseed oil (LO) were encapsulated into urea-formaldehyde microcapsules by in situ polymerization in an oil in water emulsion. The synthesized microcapsules possessed a dense and intact surface structure with an average size of 1.4 μm. The healing efficiency of the polymeric materials can be accessed by various characterization techniques such as AFM and 3D-scratch instrument [30]. The improved mechanical properties and repairing mechanism of the composite material were attributed to bifunctional microcapsules and lubricating

particles (LO). The material's friction coefficient was decreased by 92%, and the healing efficiency was found to be more than 96% by volume.

The mono capsule self-healing systems possess great advantages as they eliminate concerns regarding catalyst dissolution, activation/deactivation, cost, etc. However, chain mobility is essential within the cured epoxy matrix, which is difficult to achieve for a low-temperature curing system.

2.1.2 Healant Loaded Pipeline Type Containers

The disadvantage associated with the microcapsule-based self-healing mechanism is the amount of the healing agent. In achieving multiple healing with limited material, whether the healing agent has been consumed entirely or not after the first healing cycle cannot be detected. Multiple healing is possible only if a sufficient amount of healing agent remains available after a one-time scratch repair event. Thus, to attain multiple self-healing in extrinsic mechanisms, a reservoir that can store and deliver a larger amount of the healing agent should be developed. This healant loaded mechanism of self-healing uses brittle pipeline type containers filled with a polymerizable medium that should be fluid, at least at healing temperature. When the polymerizable material flows into the cracked site, it heals the crack through polymerization. Depending on the type of pipeline type containers, this type of mechanism can be further classified into two categories, viz. hollow glass tubes/glass fibers and microvascular networks, which are described in the following sections.

Hollow Glass Fibers

The incorporation of the self-healing functionality to the fiber-reinforced composites will make the materials scratch resistant, corrosion resistant, self-healable, and provide high strength. The various containers used as a reservoir for the healing agents in the composite materials are hollow nanofibers, carbon nanotubes, halloysite nanotubes (HNT), hollow glass fibers, and titanium dioxide nanotubes (TNTs). The internal diameter and the wall roughness of the containers are responsible for the flowing tendency of the healing agent within the containers. The large-sized vessels are very convenient for repairing large damage zones. The epoxy-based chemicals are used as healing agents for this type of mechanism as they can flow easily on heating and can be cured by epoxy hardeners. The smart composites of hollow glass fibers can be produced using two approaches, viz. (1) the whole fiber is filled with one-part curing resin and (2) a two-part system with hardener filling fiber and resin filling fiber. The pipeline type containers filled with both healing agent and the hardener are dispersed within the matrix system, and the self-healing process is depicted in Fig. 3.

The hollow fibers can be used as containers for the healing agent and the structural reinforcement for the matrix. The hollow fibers are also commercially available. Self-healing HGF/epoxy reinforced composites with smaller diameters (internal diameter

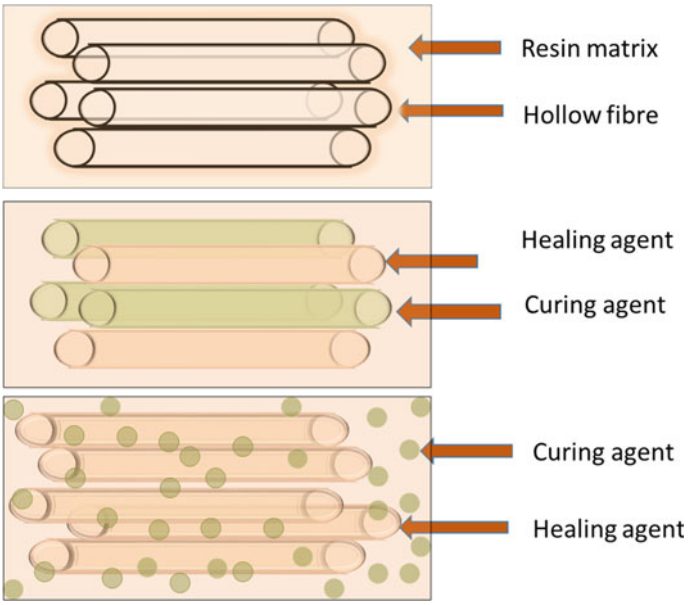

Fig. 3 Hollow fiber/pipeline type containers for the healing agent and hardener

of 5 μm and outer diameter of ca. 15 μm) have been reported [31]. The commercially available (Hollex S2 glass fiber) HGFs act as both containers and structural reinforcement material. The laminates of a thickness of 6.5 mm were prepared by the unidirectional prepreg material. The epoxy resin was incorporated in one fiber direction and the hardener in the other direction. Before encapsulation, hardener and epoxy resin are mixed with acetone so that the viscosity of the material can be reduced and it can flow easily to the site of damage where the curing takes place. Inorganic nanomaterials such as mesoporous silica SBS-15 and TiO_2 nanotubes (TNTs) have been reported in the preparation of self-healing epoxy coatings [32]. The epoxy healing agent was encapsulated within TiO_2 nanotubes, and the amine hardener was encapsulated in the mesoporous silica. The encapsulation techniques used for epoxy and the hardener are vacuum loading processes and shaking incubation for 24 h. The containers were dispersed within the epoxy matrix and then coated on a carbon steel substrate. The self-healing potential of the matrix was investigated by using electrochemical impedance spectroscopy (EIS), and the material's anticorrosive property was recovered to 57% within 5 days. Zhu et al. [33] prepared a self-pressurized healing system of glass fiber/epoxy composite by using plastic polypropylene (PP) tubes as containers for epoxy/mercaptan healing and foaming agents. On decomposition at 70 °C, the foaming agent produces gas within the sealed PP tubes, increasing the pressure inside the tubes. Whenever there is damage to the composite, the pressurized fluid inside the PP tubes bursts out and thus spreads out over a large cracked plane. The author reported an enhanced repairing efficiency compared to the case

without pressurization and gives details of the factors such as tube spacing, forming time, and forming agent on healing performance. A multifunctional nanocomposite coating was reported in 2019 [34], where the epoxy resin matrix was reinforced by the halloysite nanotubes (HNTs). The linseed oil was encapsulated into urea-formaldehyde microcapsules that served as the repairing agent, and the added sodium nitrate acted as a corrosion inhibitor. The Doctor's blade method was used to apply the nanocomposite epoxy coatings on mild steel specimens. The coating material could effectively restore its mechanical integrity, and the quick release of the healing agent and inhibitor in response to external stimuli results in good healing efficiency as well as the corrosion resistance of the steel specimen. This multifunctional epoxy nanocomposite coating system finds its application in the oil and gas industries as a corrosion protector.

The polyester resins can also be used as healing agents and, thus, filled within the hollow glass fibers (HGFs). The Polimal 1058 (a polyester resin) has been reported to work as a healing agent by Kling et al. [35]. They prepared a damage detection and self-healing epoxy composite embedded with thin hollow glass fibers of an internal diameter of 56 μm. A UV fluorescent dye was used as a visual indicator for damage detection under UV illumination. The composites were fabricated by two different methods, viz. hand layup (HLU) and vacuum-assisted resin transfer molding (VARTM). The falling weight impact testing machine damaged the prepared samples to investigate the repairing process. The damaged HLU and VARTM samples were heated at 60 and 23 °C for 12 and 120 h, respectively, for the repairing process. When compared to a reference sample without healing, the sample with the embedded healing agent showed a 20% enhancement in the bending properties after repair.

Some advantages of the hollow fiber approach of self-healing include the higher volume of repairing agent available to heal the damages, visual inspection of the damage sites, easy mixing, and tailoring of the hollow fibers with the conventional reinforcing fiber. On the other hand, some of the disadvantages include a requisite multistep fabrication and the need for low viscosity resins during fiber infiltration.

Vascular Network

The biomimetic approach of incorporating microvascular networks into composite materials develops a new type of self-healing materials. Here, in this microvascular approach of self-healing, the repairing agent is stored within the hollow channels or brittle vessels or a network of capillaries that are interconnected in 1D, 2D, or 3D. The healing agent-filled networks are distributed throughout the resin matrix as shown in Fig. 4. When the smaller vessels are damaged, they rupture and release the repairing agent, which flows to the site of damage and eventually fills the crack. The main advantage of this approach is the availability of a large quantity of repairing agents and thus the ability to repair large damaged areas. Multiple healing can be achieved by this approach because the damaged region has multiple connectivities to the healing agent. The disadvantage of this approach is that during the repairing process, the cross-linked material may jam up the micro-pipes from the damaged

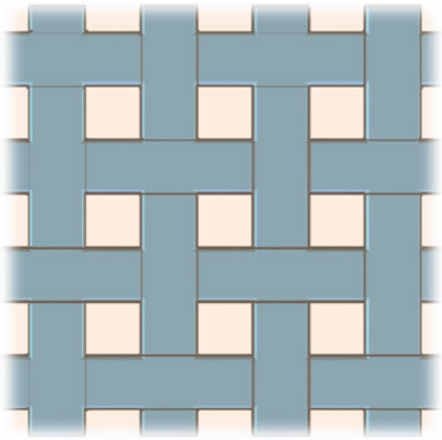

Fig. 4 Microvascular system with self-healing ability having single network specimen

region and become disconnected from the rest of the vascular system. Moreover, this network is complicated by the multistep fabrication process, and its manufacturing is more expensive than the microencapsulation technique. In 2007, Toohey et al. [36] mimicked human skin architecture and developed a first of this type, microvascular composite material by using the familiar healing combination of liquid DCPD as the repairing agent and the Grubb's catalyst, which was incorporated into a thick epoxy coating applied on the top surface of a microvascular substrate. The 200 μm wide channels were filled with DCPD healing agent. The maximum healing of 70% was attained with 10 wt% of the catalyst in the epoxy topcoat. Up to seven repeated healing cycles were demonstrated. The amount of catalyst in the top epoxy coat did not influence the healing efficiency. However, it can be a limiting factor for healing as if the catalyst is exhausted; then no healing is possible even with a continuous supply of the healing agent.

Carbon fiber-reinforced composites (CFRCs) have potential applications in aerospace and offshore wind turbines. The incorporation of self-healing ability to CFRCs may protect them from delamination. Wang et al. [37] designed self-healing CFRCs that can restore their mechanical properties by repairing the structural fibers after delamination. The short carbon fibers SCFs serve as the structural fibers here. The hollow vessels filled with the liquid healing agent were mixed with SCFs and were embedded within the material. Upon damage, the structural fiber ruptures, breaking the nearby vessels and releasing the healing agent that flows to fill the gap between the damaged surfaces. The author has compared the tensile strength of the system having pure epoxy resin as a healing agent and the epoxy resin with 13.8vol% of short carbon fibers. The tensile strength of the system with SCFs after the damage was found to be restored to 47.3% of the original tensile strength. In self-healing composites, the microvascular networks are in the in-plane direction and are normally used to transport the repairing agent into the fractured sites. The

self-healing system, where microvascular channels in the through-thickness direction are introduced into the matrix, has also been prepared [38]. The effectiveness of the through-thickness channels was evaluated by injection testing and mechanical testing. The delamination filling test, tensile test, and four-point bending test can be used to estimate the effect of microchannels on materials' strength and feasibility. The composite stiffened panels were repaired after indentation loading, and the compression testing technique was used to determine the healing ability. The compression strength of the repaired sample after indentation loading was recovered to 96% compared to the virgin specimen.

The healing efficiencies of the materials can be enhanced by using MWCNTs epoxy nanocomposite as the repairing agent for the vascular GFRPs [39]. The viscosity of the nano-modified healing agent was adjusted by using ethyl phenylacetate (EPA) solvent. The healing efficiency of the system and the effect of MWCNTs on the interlaminar fracture toughness were investigated by quasi-static mode I interlaminar fracture toughness tests. The healing efficiencies of the composite materials were found to be increased to 192% compared to the neat epoxy. The presence of the MWCNTs in the damage site may not only restrict the crack propagation after repairing but can provide reinforcement at the time of fracture toughness studies and thus is attributed to the increased healing efficiencies of the composites.

2.2 Intrinsic Self-healing Mechanism

The intrinsic self-healing materials have latent self-healing functionalities in their structures, and there is no need to store the healing agents in micro-containers. This mechanism of self-healing involves the use of some external stimuli such as photochemical, thermal, solvent, electrochemical and moisture activation to initiate the healing process, which involves the bond breaking and bond reformation of the bonds. The materials with inherent self-healing ability can repair the scratches by temporarily increasing the movement of the polymeric chain at the site of damage, allowing the material to flow to the damaged area and can repair the cracks.

Various mechanisms, such as the recombination of chain ends, reversible bond formation, molecular interdiffusion, photothermal metal-ligand complexation, host–guest interactions, and photochemical self-healing, can be used to carry out intrinsic self-healing of materials. Self-healing properties have been studied extensively in a variety of thermoplastic materials, including semicrystalline, amorphous, fiber-reinforced composites, and block copolymers. This self-healing technique requires no monomer/healing agent or catalyst, is simpler than the extrinsic technique, and is more competitive in terms of production and applications of end products.

The main advantage associated with the intrinsic self-healing mechanism is that repeated healing is possible at the same injured site of the coatings. Moreover, the self-healing functionality does not include any foreign or encapsulated healing agent. In spite of the advantages, the intrinsic system may be associated with some drawbacks, such as the flowability of the material, which improves the healing rate by eliminating

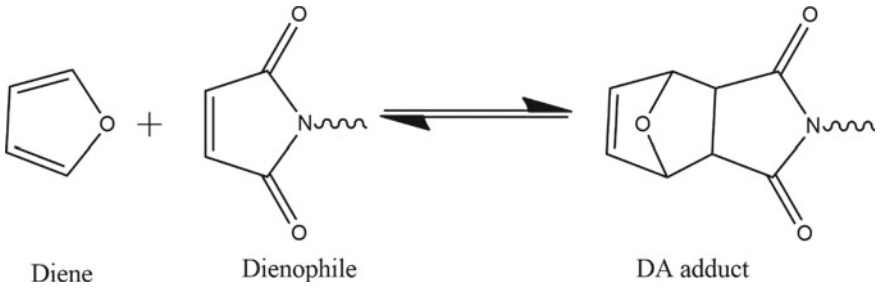

Fig. 5 Reversible Diels-Alder reaction of a diene and dienophile

the effect of damage. However, most materials with intrinsic self-healing ability are associated with higher viscosities. A high temperature is needed to overcome viscosity. Moreover, this approach is confined to small damage zones only and thus has a limited range of applications.

The different approaches to intrinsic self-healing, depending upon the type of stimuli provided to initiate the healing mechanism, are discussed in the following sections of this chapter.

2.2.1 Reversible Bond Self-healing

In most intrinsic self-healing systems, the healing is attained through reversible bonds such as Diels-Alder reactions, disulfide metathesis, hydrogen bonding, and metal-ligand bonding that have been introduced into the polymeric material.

Thermo-Reversible Cross-Links

The well-known thermally reversible cross-linking reactions are widely used in the field of polymer for the synthesis of self-mending materials. The DA cross-links are most widely used for the construction of thermo-reversible intrinsic self-healing materials due to mild reaction conditions, high yield, and excellent thermal reversibility of the DA cross-links.

The Diels-Alder reaction in Fig. 5 was discovered in 1928 and is a [4 + 2] cycloaddition reaction between the diene and dienophile through an unsymmetrical transition state.

The cycloaddition product formed by the DA reaction exhibits both *endo* as well as *exo* isomer. When heated to a higher temperature, the DA adduct regenerates the original diene and dienophile moieties via retro-DA reaction. These broken chain lengths decrease the molecular weight and viscosity of the material at elevated temperatures, resulting in the material flow to the site of damage. When the temperature decreases to room temperature, the DA adduct's reformation occurs, and thus the cracks are sealed. These DA and retro-DA reactions can occur multiple times by decreasing or

increasing the temperature; thus, the material can undergo multiple healing cycles at the same injured site. Researchers have developed various self-healing materials with intrinsic self-healing ability using dienes such as anthracene, fulvene, pyrone, cyclopentadiene, and a maleimide unit. Nevertheless, most of the research has been focused on the Diels-Alder reaction between furan and maleimide groups. Wudl et al. [40] prepared a self-repairable epoxy polymeric material using polyfuran and polymaleimide through Diels-Alder reactions. Here, the retro-DA reaction (disconnection of the linked sites) occurs above 120 °C, and the disconnected cross-links reconnect while cooling. Wang et al. [41] synthesized a cross-linker/curing agent for the epoxy resin with diamine Diels-Alder adduct. The structure and properties of the epoxy resin with repeated self-healing ability were also analyzed. The thermo-reversible gels can also be prepared by mixing bismaleimide {1,1'-(methylenedi-4,1-phenylene)} with furfurylamine and DGEBA oligomers, as reported in [42]. This gel served as a repairing agent for epoxy amine thermosetting materials and was applied directly on the crack surface of epoxy material. The healing mechanism was controlled by the DA reaction, where heating liquifies the secondary gel that flowed to the site of damage, and cross-links were formed upon cooling and fixed the epoxy network structure.

Novolac epoxy resins, due to their excellent integrated properties, have many applications in the field of electronic packaging, and their area of applications can be broadened by introducing the self-healing functionality to the novolac epoxy resins. A new novolac epoxy resin with pendant furan groups has been reported by Li et al. [43]. The commercially available novolac epoxy resin (DEN431) had been used as the matrix material and was modified with furfuryl alcohol. The bifunctional BMI (*N*,*N*-(4,4-methylenediphenyl) dimaleimide) was used as the cross-linker for the modified novolac. The higher storage modulus and the excellent thermal stability were associated with the cross-linked epoxy resin. The thermo-reversible nature and self-repairing properties of the materials can be studied by using SEM, DSC, thermal re-solution, and gel-solution-gel transition experiments [51].

Photo-Reversible Cross-Links

Photo-reversible reactions play an important role in polymer chemistry and have excellent applications in the field of self-healing materials. This approach of self-healing is cost effective, can take place under the sunlight as no thermal treatment is needed to initiate the healing process, and can heal the repeated cracks at the same location within the polymeric material. As shown in Fig. 6, when irradiated with UV radiations of suitable wavelength, olefinic compounds such as anthracene and coumarin undergo a photo-reversible dimerization, resulting in a cyclobutene-like structure. When irradiating with UV light of a shorter wavelength, these cross-links can be reverted to the olefinic compounds. The concept of this photo-reversible cyclization/dimerization has been used by many researchers and thus prepared many polymeric materials with self-healing functionalities.

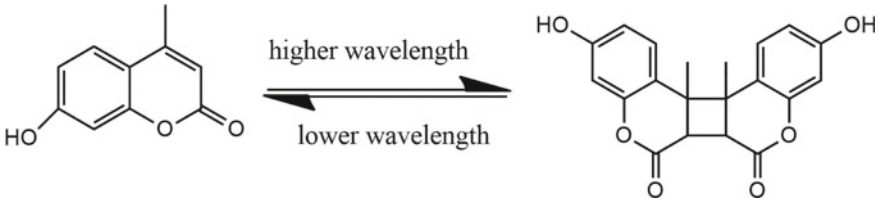

Fig. 6 Photo-reversible dimerization reaction

Simone et al. [44] synthesized a photo-curable epoxy resin with photoactive anthracene moieties by dissolving the photoactive monomer in a low viscosity epoxy derivative. The reversible bond formation and the cross-linking kinetics of the synthesized epoxy-based resin were analyzed by spectroscopic and DMA analysis. The fluorescence microscopy analysis showed that the mechanical stress causes the free anthracene moieties to diffuse on the cracked surface. The photo-reversible polymerization repairs the microscopic damages when exposed to UV light radiations ($I > 300$ nm). However, to ensure the viscoelastic flow and the polymeric chains' diffusion in the cracked zone of the material, additional heating at 60 °C was needed. The healing efficiency of the material was found to be within 84% to 100% after the first repair step. Recently, Tezel [45] synthesized a dual capsule photo-curable self-healing coating formulation based on epoxy-polyester acrylate resin. The author has encapsulated a commercial epoxy and a polyethylenimine (PEI) into microcapsules made up of poly(urea–formaldehyde) PUF and a poly(maleimide-urea–formaldehyde) PMUF shell wall materials. The sizes of the epoxy and PEI-filled microcapsules were determined with the help of a Zeta sizer and were found to be 185 and 377 nm, respectively. About 2 wt% of the microcapsules content (in 1:1 molar ratio for epoxy and PEI microcapsules) was dispersed within the coating formulation and was applied to the plexiglass substrate surface. Artificial scratches were made on the coating surfaces before exposing them to UV light for curing purposes. The scratches healed on their own after an exposure time of 48 h. This system permits the low-temperature repairing of the damages. Zhen et al. [46, 47] synthesized epoxy acrylate self-healing composite by introducing reversible dynamic host–guest chemistry into the resin structure. A β-CD/azobenzene inclusion complex (6-GMA-β-CD/AAAB) with C=C was synthesized, and the epoxy acrylate was cross-linked with this complex through free radical copolymerization by the facile UV curing process. As the complex is light responsive, upon exposure to UV radiations, the cross-linking points were unlocked, and chain mobility increased, which provided better healing abilities to the epoxy resin. Moderate heating was needed to increase the chain movement at the site of damage and initiate the host–guest interactions. The epoxy acrylate film showed excellent mechanical properties along with self-healing ability. The tensile strength of the scratched sample was recovered to 63.3% of the original value. Multiple healing is possible due to the reversible dynamic host–guest chemistry.

2.2.2 Dynamic Disulfide Bond Self-healing System

The disulfide bonds are versatile and thus gain significant attention in the self-healing chemistry due to their relatively easy implementation in the existing networks. The conventional epoxy thermosets have been synthesized with aliphatic disulfide chains obtained from thiol precursors at mild healing temperatures. Using tri-*n*-butylphosphine as a catalyst, Zang et al. [48] created an epoxy polymer of diethylenetriamine-cured polysulfide diglycidyl ether. The cross-linked epoxide polysulfides were self-repaired at room temperature without external intervention, as demonstrated by the restoration of tensile strength. The glass transition temperature of this epoxy resin was low, and thus the polymer has limited composite applications.

Vitrimers are an emerging class of polymers having many attractive material processing properties such as healing, reshaping, and recycling. de Luzuriaga et al. [49] synthesized a dynamic epoxy vitrimer based on the reversible exchange of aromatic disulfides by using DGEBA as the epoxy monomer and AFD (4-aminophenyl disulfide) as the dynamic hardener. This system was easily applicable to fiber-reinforced polymer composites (FRPCs), as the starting materials are easily available. The synthesized FRPCs showed comparable mechanical strength in addition to new properties such as recyclability, healing ability, and re-processability when compared with reference epoxy counterparts. Zhou et al. [50] synthesized a new type of vitrimers (BDSER) having thermosetting dynamic epoxy network with double disulfide bonds. Here, the reaction between difunctional epoxy monomer having disulfide bonds and 4,4'disulfanediyldianiline (4-AFD) took place. The relaxation time of the vitrimer at 200 °C was found to be 9 s. Moreover, there was no significant loss in the chemical and thermodynamic properties of the vitrimer after three continuous cycles of breaking and compression molding.

Huang et al. [51] synthesized epoxy vitrimers by using disulfide chemistry. They made the epoxy resin system by reacting DGEBA with AFD (4-aminophenyldisulfide). The surface of the nanoparticles of silica was pre-modified either with an epoxy resin or by a thiol compound MPTMS (3-mercaptopropyltrimethoxysilane) and 3-glycidoxypropyltrimethoxysilane (GPTMS). The pre-modified nanoparticles were mixed with the resin system and were used as nanofillers. A good matrix reinforcement effect was observed with the pre-modified nanoparticles when compared with the unmodified ones. The epoxy-modified silica composites possess higher T_g values when compared to the thiol-modified silica composites. It was found that the thiol-modified nanoparticle composites possess a much faster stress relaxation rate than epoxy-modified silica composites. This may be attributed to the faster exchange rate of thiol-disulfide reactions and thus showed efficient self-healing behavior verified by the time-dependent healing experiment. The mechanical properties of the material were found to increase with an increased amount of thiol-modified silica fillers.

Li et al. [52] also investigated the self-repairing ability of the epoxy resins having exchangeable disulfide dynamic bonds. The resin material was synthesized by polymerizing two epoxies with an amine having a disulfide bond. The soft and rigid components used were poly-(ethylene glycol) diglycidyl ether (DER736), and

DGEBA. The self-healing materials with different flexibilities were obtained by tuning the content of the soft segment within the resin system. The greater the flexibility of the polymer, the lower the activation energy, glass transition temperature, and poor mechanical strength of the material, but it could possess better self-healing properties. The specimens were optimized, and the optimal specimen showed good mechanical properties as well as self-healing efficiency.

Supramolecular Self-healing

For the past few decades, supramolecular chemistry has been used for the development of self-healing polymeric materials. The rate of dynamic bond breaking and reformation via supramolecular chemistry is fast under ambient conditions. The other factors, such as chain relaxation time and bonding directionality, also have an impact on the healing efficiency of the material. The cracks in the material rupture the non-covalent bonds as they are much easier to break than covalent bonds. The damage can generate new fragments with unbonded non-covalent interactions. These fragments can further recombine by non-covalent interactions, close the cracks, and repair the damage. Depending upon the type of non-covalent bonding and supramolecular interactions involved, the healing ability of the materials may be classified into self-healing via (1) H-bonding, (2) metal-ligand interactions, (3) host-guest interactions, and (4) Π-Π stacking interactions. Nevertheless, in most of the research articles, it has been reported that one self-healing material may combine with more than one type of non-covalent interactions, deliberately or accidentally; thus, it is difficult to categorize the supramolecular healing chemistry on the basis of the interactions involved.

Significant attention has been attributed to enhancing the strength of hydrogen bonds as it is important for self-healing as well as mechanical properties of the materials. Chai et al. [53] prepared an epoxy resin with higher impact resistance by introducing the toughening agent quadruply hydrogen-bonded supramolecular polymer into the bisphenol A-based epoxy resin. The supramolecular polymer consists of poly-(propylene glycol) bis(2-aminopropyl) ether chains and 2-ureido-4[1H]-pyrimidinone (UPy) moieties. The spherical microphase-separated domains were prepared by physical blending of epoxies with the supramolecular monomers before curing. The amount of UPy supramolecular monomers strongly influences the size of the microdomain. The mechanical studies revealed that supramolecular blending could be a method for toughening epoxy resins. A significant improvement was observed in the impact strength (by 300%) of the blended epoxy compared with the neat epoxy.

Host-guest interactions result in targeted binding of dimensionally matching molecular segments. Biological systems are found to have naturally occurred host–guest interactions. These have applications in sensing, drug delivery, surface recognition, and stimuli-responsive hydrogels. The cyclodextrins (CDs), crown ethers, pillar[*n*]arenes, calixarenes (CAs), etc., are generally employed host molecules. Cyclodextrins exhibit the properties such as multi-responsiveness, water solubility,

most desired dissociation/re-association dynamics, and biocompatibility, and thus CD-modified host polymers are of significant importance.

Supramolecular elastomers were also prepared using diethylenetriamine, urea, and small carboxylic acids such as citric acid and sebacic acid [54]. The synthesized phase-separated polymers having H-bonding interactions among amide alkyl-urea and imidazolidone moieties possess self-healing ability at room temperature within 8–72 h, and the healing efficiency was found to be 31–99%. The material is non-cytotoxic and thus may have potential applications in the biomedical field.

The carboxylated cellulose nanocrystals (C-CNC) and chitosan (CT) modified epoxy natural rubber (ENR) latex are used to develop multiple hydrogen bonding bond interactions and thus can provide self-healing properties to the polymeric materials [55]. The developed material was converted into a self-healing sensor by assembling the nanostructural polymer network with carbon nanotubes. The nanostructured supramolecular self-healing sensor possesses repeatable and extremely fast self-healing ability with a high healing efficiency of 93% for the third healing cycle.

The H-bonding plays an important role in the development of supramolecular self-healing materials as the reformation of the broken bonds can take place at room temperature. However, the reformation of H-bonding has a poor tolerance for moisture, and materials healing efficiency decreases significantly in a humid environment.

3 Conclusion

With advancements in science and technology, the field of self-healing has progressively expanded over time. A large number of novel self-healing systems have been emerging with enhanced self-healing capabilities. The self-healing materials possess a broad range of applications in the food industry, agriculture, transportation, medicine, recycling, and upcycling. The developed self-healing systems showed higher healing efficiencies and thus broadening the application field of these materials. However, there are many drawbacks associated with these self-healing systems, some of which are listed below:

The main concern with the self-healing system is the harsh repairing conditions, as the material requires heating to certain temperatures, and the self-healing under normal temperature conditions is inaccessible. Moreover, the physical properties of the materials, such as flexibility, conductivity, and transparency post healing, are not very good. Thus, most of them are limited to the field of theoretical research and have no direct implementation.

The research should emphasize more on the solutions to the aforementioned shortcomings during the course of future research. Researchers should focus on developing self-healing materials by selecting low-cost starting materials, mild reaction conditions, small/simple synthetic steps, fast repairing rate, high healing efficiency, and excellent mechanical properties to be used in real-world applications.

In summary, self-healing materials have a wide array of potential applications. It may be predicted that the continuous progress in polymeric design and preparation technology of smart materials in the future will play an important role in the broader field.

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