

Accepted Manuscript

Title: Self-healing Protective Coatings: A Review on the Principles, Chemistry, Recent Advances and Applications Outlook



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Manuscript number: **PCCC-2504-1391**

To appear in: Progresss in Color, Colorants and Coatings

Received: 20 April 2025

Final Revised: 8 June 2025

Accepted: 9 June 2025

Please cite this article as:

H. Yari, P. Kardar, R. Amini, Self-healing Protective Coatings: A Review on the Principles, Chemistry, Recent Advances and Applications Outlook, Prog. Color, Colorants, Coat., 18 (2025) XX-XXX.

DOI: 10.30509/pccc.2025.167533.1391

This is a PDF file of the unedited manuscript that has been accepted for publication. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form

**Self-healing Protective Coatings: A Review on the Principles, Chemistry, Recent
Advances and Applications Outlook**

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Abstract

The long-term functions (providing appearance and barrier protection for the underlying substrate) of polymeric protective coatings can be jeopardized by environmental damages (including corrosion and mechanical damage). Thus, self-healing coatings have emerged and developed to restore such functions in case of coating damage. Thus, a coating which can automatically repair itself ("self-healing coating") can be favorable with self-recovery of properties (i.g. mechanical, electrochemical, etc.) and accordingly extend the durability of the coating. This review discusses both extrinsic (including capsules, hollow-fibers, corrosion inhibitor loaded reservoirs) and intrinsic (reversible physical bonds such as Diels-Alder bonds, ionomers, and supramolecular polymers) approaches. Additionally, the most recent advances in the field of self-healing coatings and their associated challenges were also investigated, and the future trends were also covered. Such novel smart coatings were discussed from various perspectives, including advantages and disadvantages compared to traditional coatings, triggering mechanisms, environmental aspects, and their potential practical applications in different sectors like electronics, aircraft, automobiles, construction, and more.

Keywords: self-healing coatings; extrinsic and intrinsic approaches; reservoirs; anticorrosion coating; reversible interactions.

1. Introduction

Self-healing is introduced as the capability of a material to recover a damage without the intervention of any external factor. Several usual names, for example self-healing, intrinsic/extrinsic repair, are existed to describe this characteristic in materials [1]. The idea of self-healing in materials was inspired by the autonomous repair processes that occur in living organisms upon injury. Such idea gradually evolved over the years[2]. Over the last three decades, a great number of papers and books about self-healing materials have been published, indicating the rapid progress of the field. In 2007, Sottos and colleagues claimed that “a large part of the scientific activity worldwide is focused on this topic” and that “the future of self-healing is very bright and there is great hope for the advancement of this technology”. In addition to the new research in self-healing technology, there are also irregular reports of the commercialization of self-healing systems. Carolyn Dry and her team are considered the pioneer group in the growth of self-healing compounds [3]. In 1996, she and her colleagues developed a hollow fiber system containing a reactive fluid that, when a crack is created, is released into the damaged area and repairs the crack. Since then, various approaches have been suggested and investigated in the field of thermoset polymer repair, and among most of these self-healing systems, those based on thermal, optical, and pH stimuli, as well as mechanical rupture, have been studied the most [1].

From a mechanistic viewpoint, self-healing coatings can be classified into extrinsic and

intrinsic categories. In the former class, the self-healing systems include at least a healant compound and a carrier holding the healant. The healing agents (healers) are commonly loaded on/within the carrier/reservoir that is physically introduced into the main coating matrix (such as epoxy, PU, acrylic, etc.). Upon mechanical damage or corrosion initiation, these reservoirs rupture or chemically rearrange, discharging the embedded healing agents. The released component is solidified, filling the crack or forming a protective layer at the damaged site [1].

In the intrinsic self-healing systems, there is no externally introduced healer or carrier/reservoir components. The overall healing mechanism is founded on the formation/reformation of some dynamic physical (non-covalent) or chemical (covalent) bonds, which are intentionally installed (or tuned) on the backbone of the main coating matrix. In intrinsic systems, the healing process is inherently beholden to the reversibility of numerous linkages available on the polymer network. Compared to traditional protective coatings, which serve as passive barriers, self-healing coatings actively restore their protective function after damage, providing extended durability, reduced maintenance costs, and improved reliability. However, challenges such as higher production complexity, cost, and limited efficiency in repeated healing cycles remain.

This review provides a comprehensive overview of self-healing coating technologies, discussing their mechanisms, advantages, limitations, and practical applications. The key components and healing strategies of both extrinsic and intrinsic systems are summarized to clarify their roles and importance in developing advanced protective coatings.

2. Designing self-healing coatings

There are two main self-healing mechanisms. The first category includes materials with

“intrinsic” self-healing properties. In this category of materials, the polymers themselves can repair damage and only require an external driving force, like heat, light, etc [4]. The second category has an “extrinsic” self-healing property in which a healing agent is added to the polymer matrix [5]. Typically, the healing agent is placed inside capsules or vessels. When the polymer is damaged, this substance is released and repairs the damaged part.

The main approaches to planning self-healing coatings are as follows:

- Extrinsic healing: Release of healing agents
- Intrinsic healing: Reversible bondings

2.1. Extrinsic healing: Release of healing agents

Monomers, Inhibitors, and hardeners are typically embedded in microcapsules, hollow fibers, carriers, or channels during the manufacturing process of coating systems. When a crack occurs, these capsules are broken or triggered and the reactive healing agents by capillary force flow into the crack, where they solidify and heal the crack in the presence of atmospheric humidity/oxygen or pre-dispersed catalysts [5]. Crack growth is the main driving force of this process.

2.1.1. Microencapsulation systems

Microcapsules are the final products of encapsulating micron-sized solids, liquid droplets, or gases in a neutral shell that isolates and protects these compounds from their surroundings. Neutrality is associated to the activity of the shell with respect to the core

component. A microcapsule has two parts called the “core” and the “shell”. Capsules are spherical or irregular with different size from nanometers to micrometers. Microcapsules containing healers have been utilized together with catalysts to design self-healing polymer systems. Initial studies demonstrated the application of the healers of the microcapsules in a polyester substrate to achieve a self-healing effect. Start of capsule-based self-healing materials was made in 2001 by Professor Scott White and his colleagues[6]. Self-healing was achieved by embedding encapsulated repair agents within a polymer network containing catalysts. The shell material has a significant impact on the self-healing properties of these coatings. For example, in a research project, Karder synthesized modified capsules with various polyols and investigated the effect of polyol on capsule size and efficiency [7, 8]. The same researcher incorporated the obtained capsules in a transparent automotive clearcoat, and self-healing behaviour was observed [9]

Generally, two main categories of self-healing systems can be defined: autonomous and non-autonomous. The former refers to the healing processes that are performed without any intervention. For example, it means that the healing process is completely accomplished just by rupture of the microcapsule and consequently the polymerization of the released polymerizable agent. Mechanical rupture of microcapsules, usually caused by external forces such as scratching, is a perfect example of an autonomous self-healing mechanism. Upon mechanical exertion, the microcracks are initiated, propagated, and eventually lead to the rupture. In a very recently-published research paper, the mechanical cracking of microcapsules was mathematically simulated and concluded that the bigger and the higher the microcapsule content in the coating film give rise the higher

the self-healing efficiency [10]. Another autonomous approach is when corrosion inhibitors are released from a carrier into the defective coating (exposed substrate) and retard/omit further corrosion reactions. In such inhibitor-based scenarios, the release of the inhibitor can be triggered by various procedures such as dissolution of the carrier (like Polymer-based nanocapsules, silica nanocontainers), ion exchange method (i.e., in LDH-based reservoirs), pH-responsive release (for example, in the metal ion-capped halloysite nanotubes) [11]. The pH changes caused by anodic and cathodic corrosion reactions are the most frequent stimulant utilized in designing extrinsic self-healing materials. pH variations can protonate/deprotonate, change the material decomposition or polymer conformation (in polyelectrolytes LBL-based containers) of the container shell, allowing/stopping the release of entrapped inhibitors [11].

In nanocontainer-based self-healing coatings, the size of the reservoir plays a crucial role in determining the final level of active protection. In a research study, it has been shown that smaller (80 nm) mesoporous SiO₂ particles filled with 2-mercaptobenzothiazole could provide higher resistance (twice) and more efficient healability compared to their larger (700 nm) counterparts [12].

The shell composition of the capsules has a wide variety of chemistry including polymeric shells (urea-formaldehyde, melamine-formaldehyde, polyurea/polyurethane, Polymethyl Methacrylate, bio-based polymers like chitosan, starch) or porous metal organic frame (MOF) materials [13, 14]

A wide range of healing agents can be utilized as the core in a capsule, depending on the matrix chemistry, the environment in which the healing process is intended to be performed, the mechanism of the healing, and the properties that are aimed to be

recovered. Such healers can be a polymer (like epoxies, polyurethanes, and Polydimethylsiloxanes), or monomeric healing agents (such as dicyclopentadiene or methacrylates), or even organic solvents that can locally swell and increase the polymeric chains mobility at the damages, rebounding the cracks [15, 16]. Corrosion inhibitors are also among the primary healing agents that are frequently used in anticorrosion smart coatings, where the corrosion process is controlled at the damaged area by on-demand active protection action of inhibitors (see section 2.1.3).

The early developing stages of self-healing materials based on incorporating various healing agents that were derived from petroleum-based compounds. Such healing materials were derived from unsustainable resources that are gradually running out. Thus, in the future outlook of self-healing materials, there is a strong driving force to shift from such non-renewable resources to renewable ones. There has been a wide range of bio-based materials that have been introduced as healing agents. For example, A bio-originated fatty acid (from Tall oil) epoxy ester healing agent was synthesized and incorporated into a urea-formaldehyde shell and finally embedded into a typical epoxy matrix[17]. The epoxy ester healing agent (**Figure 1**) has abundant C=C double bonds, enabling it to auto-oxidatively react with atmospheric oxygen upon capsule rupture and crosslink at room temperature. It was shown that this healer can fill the artificial microcracks, recovering the corrosion resistance of the epoxy coating in which the capsules had been dispersed [17].

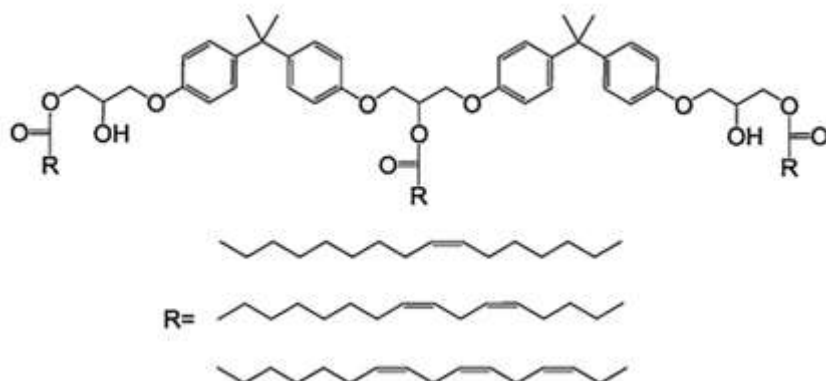


Figure 1. The chemical structure of bio-originated epoxy ester healing agent, reprinted with permission from [17], copyright 2025.

2.1.2. Hollow fiber systems

The main disadvantage of the capsule-based self-healing method is the achievement of complete healing. Because it contains a small amount of healer, when the healer is completely consumed, it is no longer able to heal later failures may occur. Further healing is only possible if there is an additional healer in the resin system when the first healing has happened.

Therefore, to obtain better healing in coating systems, another type of container was proposed by Dry and colleagues, which was capable of reserving and transporting a higher volume of healing materials [3]. Though, they reached little success utilizing this method. Later, larger diameter capillaries were implanted by Motuku and colleagues, but their efforts were also unsuccessful [18]. Bleay and colleagues utilized smaller glass fibers [19]. Materials with these glass fibers did not have the ability to carry the resin into the crack because of high-viscosity of epoxy resins and then curing was not complete. Then, Bond and his colleagues established a method to optimize the making of hollow

glass fibers and utilized these fibers as carriers for healing agents or colorants [20]. These borosilicate glass fibers had a diameter in the range of 30–100 μm with a porosity of 55%. Mahmoudi and his colleagues also used halloysite nanotubes to improve the self-healing properties of a silane coating [21, 22]. They encapsulated halloysite with praseodymium(Pr) and then dispersed it in the silane hybrid matrix. The corrosion performance of the coating was tested by salt spray and EIS tests. The characterization demonstrates the release of Pr^{3+} cation at the scratch location by creating a protective film of oxide/hydroxide of Pr [21, 22].

Crosslinked fibers are a new strategy to extend the longevity of healing cycles in the hollow fibre-based healing systems. In these systems, the interconnected fibers provide the transfer of the trapped healing agent from filled fibers (areas with high content of healing agent, intact areas) to the damaged (areas with low content of healing agent) sections, providing a more stable and more durable healing process, ready for subsequent damage occurrence [23, 24].

Recently, Fu has invented a synergetic healing approach based on PCL nanofibers loaded with halloysite nanotubes (HNT) [25]. The HNT was first synthesized and then loaded with 2-mecapobenzothiazole (MBT, as a corrosion inhibitor). The MBT-HNT nanocontainers were mixed with dissolved polycaprolactone (PCL). The final solution was electrospun onto the steel to provide a porous coating, followed by a full coverage with a typical epoxy coating. In this system, two different systems synergistically act to protect the metallic substrate upon damage: active corrosion inhibition and thermally-induced barrier repair. In case of deep scratches taking place and reaching the substrate, the pH-responsive MBT-HNT carrier instantly releases MBT, forming a protective layer

at sites where corrosion initiates. On the other hand, by a thermal treatment, PCL nanofibers liquified and flowed to fill the scratch and recover the passive barrier action. Long interconnected nanofibers filled with MBT enable the repeated healing (at least three healing-damage cycles) that can be promising for durable active protection. Due to the importance of the anticorrosion self-healing coatings, a section is specifically devoted to these inhibitor-based systems [25].

2.1.3. Self-healing anti-corrosion coatings based on nano/micro-reservoirs

New multifunctional active coatings should quickly discharge active inhibitors on demand within a quick time after variations in the environment or the uniformity of the coating. New advances in surface chemistry and technology introduce new concepts for producing self-healing coatings by creating nano-scale carriers filled with active inhibitors in current common coatings. This design goes to new materials based on “active” host-guest constructions. Therefore, the nano reservoirs are homogeneously dispersed in the coating matrix and keep the active substances in a “captured state”. When the local environment changes or if a corrosion process is initiated at the site of coating damage, the nano-reservoirs respond to this signal and release the immobilized active material. The ideas of inhibitor nano-reservoirs are categorized into two types, which are explained below.

2.1.3.1. Coatings loaded with regular nano-reservoirs of corrosion inhibitors

In this scenario, the corrosion inhibitors are commonly kept in a micro/nano container (or on its surface) till a change in the environment or mechanical damage triggers their smart

release into the damaged site. Over more than two decades of reservoir-based self-healing anticorrosion coatings development, a wide range of reservoirs (with various chemistry, structure, and loading capacity) have been utilized. The most frequently utilized micro/nano carriers include mesoporous metal oxide, graphene oxide, layered double hydroxide, nanotubes, metal organic frameworks (MOFs), halloysite structures, hollow carbon spheres, etc [11].

A relatively easy method of inhibitor entrapment is based on the complexation of organic molecules with cyclodextrin. This method was initially proposed for the immobilized drug delivery systems. Cyclodextrin complexing agents, acting as hosts, interact with guest molecules, matching the cyclodextrin pore size. For such complex formation, some substances like heterocyclics and aromatic organics are the primary candidates. Most frequently-used inhibitors (depending on the substrate metal, such as mercaptobenzothiazole and mercaptobenzoimidazole) can be employed as guests for this complexation with cyclodextrin. For example, Khramov et al. chose these inhibitors to be added to a hybrid coating. The main aim was to protect aluminum alloys from corrosion [26]. Coating filled with the complex corrosion inhibitors exhibited much more corrosion resistance with respect to the reference coating. Formulations containing β -cyclodextrin show better corrosion protection because the equilibrium of complexation leads to slow discharge of the inhibitor. Such inhibitor/cyclodextrin compound provides a long-term inhibitor discharge without its on-demand delivery in response to any external stimulus.

Utilizing oxide nanoparticles as nano-repositories to adsorb the corrosion inhibitor on their surface can be another reserving procedure. Oxide nanoparticles not only act as a reinforcement, but also their loading results in improved barrier attributes of the coating

network. The nanoparticles in the sol-gel coating make it possible to apply a higher thickness without any risk of cracking (low cracking ability), enhancing the barrier properties. In addition, extra smart release and corrosion resistance can be obtained with a corrosion inhibitor immobilized on the oxide nanoparticles surface. The obtained sol is transformed into hybrid nanocomposite coatings with oxide nanorepositories of cerium ions by hybrid sol-gel formulation. The long-term release of the inhibitor from the surface of the oxide nanoparticles provides an improved long-term corrosion protection for the Al substrate in comparison with the sol-gel sample loaded with directly-added inhibitor. In addition, the use of oxide nanorepositories obviates the adverse impact of Ce ions on the hydrolytic stability of the hybrid coating. Inorganic corrosion inhibitor anions can also be immobilized on the nanoparticle surface, then released by an ion exchange mechanism. Corrosion inhibitors can be released via an ion-exchange mechanism, with corroding anions like chlorides and sulfates, which commonly traverse and permeate into the coating. However, a defective point for this approach is the undesired discharge of inhibitors that can be activated with harmful ions received from processes like surface cleaning.

Lashgari targeted research to promote the anticorrosion performance of epoxy coatings by two mechanisms of active inhibition and barrier. To this goal, graphene oxide (GO) nanosheets were used as a blocking agent and a substrate for the placement of the zeolite-imidazolate framework 67 (ZIF-67) [27-29]. ZIF-67 nanoparticles were synthesized as an inhibitor using cobalt ions and a dimethylimidazole linker on graphene oxide sheets (ZIF-67@GO) and then the synthesized nanoparticles were modified by 3-aminopropyltriethoxysilane (APS) for proper dispersion in the epoxy coating (ZIF-

67@GO/APS). ZIF-67@GO/APS nanoparticles were added to the epoxy coating and the anti-corrosion and self-healing properties of the coatings containing nanoparticles were evaluated using EIS, salt spray and FE-SEM/EDS tests. The results of the EIS test of the unscratched coatings showed that by modifying ZIF-67@GO with APS, after 50 days of immersion, the logarithm of the impedance at the lowest frequency increased, confirming the barrier properties enhancement. Also, the results of the FE-SEM/EDS and EIS tests of the scratched coatings showed that the influential role of ZIF-67@GO/APS in activating the self-healing properties of the epoxy coatings. With the onset of electrochemical reactions and local pH changes, cobalt cations and dimethylimidazole molecules are released from the surface of graphene oxide and form a protective film on the metal surface through interaction with -OH anions in the cathodic regions and iron cations in the anodic regions, respectively [27-29].

In a similar approach, Alipanah grew MIL-88A particles (a Metal organic frame (MOF) composed of iron(III)/fumarate) on graphene oxide (GO) [30, 31]. Active protection was also demonstrated in scratched epoxy coatings containing 0.15% of the synthesized nanocomposites using electrochemical impedance and salt spray tests. Higher adhesion values were recorded in dry and wet conditions in coatings containing hybrid particles (MIL-88A/GO). Cathodic detachment results also showed that the detachment diameter of coatings containing hybrid particles in the optimal state was reduced by 50% and 42% compared to epoxy and epoxy/graphene oxide coatings, respectively. Finally, the excellent barrier effect of modified graphene oxide sheets was confirmed using electrochemical impedance testing (Figure 2). The percentage of coating degradation was calculated using the broad frequency range analysis method. The results showed that after

105 days of immersion of the coatings in salt solution, the percentage of coating degradation for epoxy and epoxy/graphene oxide samples was 100% and 79%, respectively. While this characteristic for the epoxy coating with MIL-88A/GO hybrid particles was 4% (for the optimal particle) at the same immersion time [30, 31].

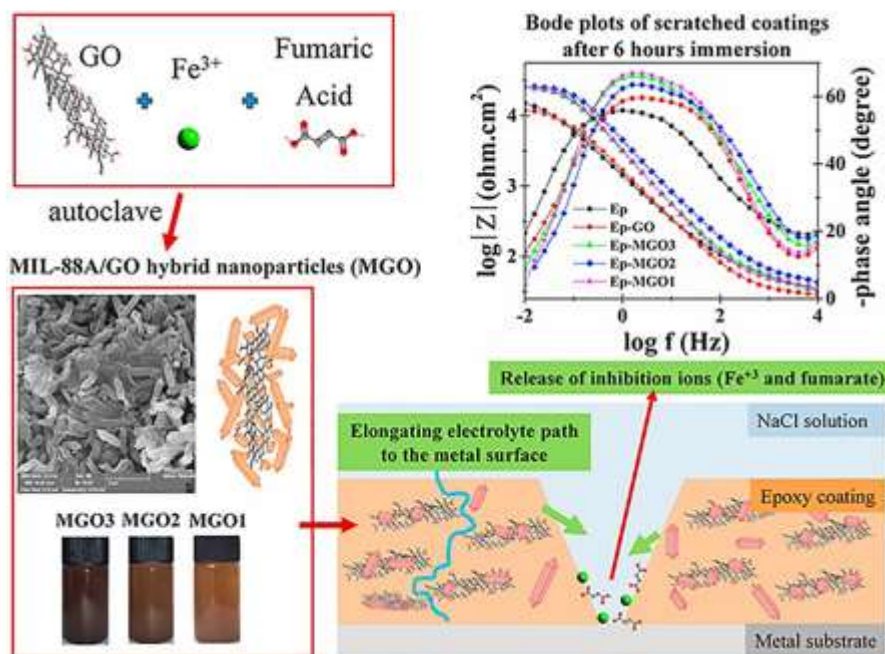


Figure 2. MIL-88A synthesis and its release upon corrosion initiation, reprinted with permission from [31], copyright 2025.

In a complicated scenario, Pezeshk-Fallah implemented a multiplayer active inhibition mechanism (consisting of a combination of inorganic and organic inhibitors) to promote the long-term corrosion resistance of epoxy coatings [32]. In this regard, zeolite-8 imidazolate framework (ZIF-8) nanoparticles were used once as corrosion inhibitor and again as nanocarrier for loading corrosion inhibitor (benzo-triazole (BTA)). Zn-based metal-organic frameworks were synthesized using four precursors (zinc nitrate hexahydrate (ZIF-8-N), zinc gluconate (ZIF-8-G), zinc acetate dihydrate (ZIF-8-A) and

zinc chloride (ZIF-8-C)) by co-precipitation/hydrothermal methods and then vacuum method was used for BTA loading (BTA@ZIF-8). ZIF-8 and BTA@ZIF-8 nanoparticles were added to the epoxy coating and the anti-corrosion and self-healing properties of the coatings containing nanoparticles were evaluated using EIS, salt spray and FE-SEM/EDS tests. Zinc acetate salt was determined as the ideal precursor among all tested ones due to its high specific surface area ($2164 \text{ m}^2.\text{g}^{-1}$) and slow release rate. The results of FE-SEM/EDS and EIS tests of scratched coatings showed that the presence of ZIF-8 and BTA@ZIF-8 in the epoxy coating causes self-healing properties in these coatings. So that with the start of electrochemical reactions and local pH change, zinc cations, BTA and dimethylimidazole molecules are released and form a protective film on the metal surface through interaction with -OH anions in the cathodic regions and iron cations in the anodic regions, respectively. According to these results, the two samples ZIF-8-A and BTA@ZIF-8-A had the best self-healing performance [32].

2.1.3.2. Coatings with inhibitors based on ion exchange systems

When corrosion inhibitors are loaded on the porous carriers composed of a hollow internal cellular structure, even greater filling capacity is achieved. The material with a hollow cellular structure can be provided with zeolite or carbon or silica clay. Zeolite-based particles are also favorable reservoirs, as their cations entrapped within the structure can easily exchange with the inhibitor cations designed in the synthesis media.

Another option, as exchangeable ions, are inhibitory inorganic cations. Since such cation-exchanged pigments are completely insoluble, a merit of this method is that osmotic blistering is prevented. In pigments capable of anion exchange that can hold anionic

inhibitors, a transformation condition is revealed. In this case, the attacking corrosive chloride ions can stimulate the release of the inhibitor. These pigments have dual functions, first, they absorb the aggressive Cl ions, and also release the inhibitor ions in the reaction. The absorption of chlorides from an attacking electrolyte near a damage reduces the attack of the corrosive substance and slows down the corrosion processes.

The layered double hydroxide (LDH)s, as an anion-exchangeable structure, can host the anion-based inhibitors. The inhibitory efficiency of a hydrotalcite pigment filled with benzotriazolate, ethyl xanthate and oxalate anions were investigated against the filiform corrosion of organically coated aluminum [33]. The inhibitors were ranked from an efficiency viewpoint so that the benzotriazole exhibited the highest efficiency and the ethyl xanthate showed the lowest. On the other hand, they present less efficiency compared to chromate-based pigment, and their practical application are unclear. However, hydrotalcite pigments exchanged with organic anion-based inhibitors require further studies for self-healing anti-corrosion systems.

2.1.3.3. Coatings with inhibitors based on layer-by-layer shells

An attractive candidate that allows controllable release and is stimulated by corrosion-related phenomena is shells assembled via layer-by-layer procedure. Nano-scale reservoirs with controllable inhibitor release or storage can be precisely fabricated by layer-by-layer assembly. In this approach, oppositely charged materials like polyelectrolytes are deposited on the surface of a template material alternatively by such step-by-step from aqueous and non-aqueous solutions. Layer-by-layer films with one or more polyelectrolyte monolayers deposited on the surface of a sacrificial pattern provide permeability restriction of the inhibitor. Storing corrosion inhibitors in such a layered

structure has two main merits: inhibitor isolation and omitting its adverse impact on the coating uniformity and controlling its release by tuning the polyelectrolyte permeability triggered by local changes in acidity/basicity and humidity level of the corrosion environment. An alteration in pH can be the best stimulus to activate inhibitor release because corrosion initiation results in local variation in pH in the vicinity of cathodic and anodic areas. Therefore, a self-healing coating containing polyelectrolyte carriers can be responsive to the onset of corrosion and initiate an on-demand self-healing action at the corrosion sites.

Yang and co-workers encapsulated the triazole inhibitor to form pp-perfluorohexane and pp-pyrrole layers using radio frequency and plasma discharge [34]. The prepared reservoirs were introduced as a pigment in a protective coating based on waterborne epoxy. This coating could slowly release the inhibitor and fulfill the requirements of a coating to guarantee the long-term active protection. Release of the inhibitor occurs only when it is mechanically broken.

Zheludkevich et al also designed a self-healing smart anti-corrosion coating utilizing layer-by-layer nanorepositories [35]. They targeted the silica nanoparticles as a template core and, via a sequential deposition approach, applied macromolecular polyelectrolyte and benzotriazole alternatively. While the charge of silica-based core was negative, the positively-charged polyethyleneimine was efficiently deposited in the first step to create an inhibitor-rich bilayer. While one bilayer cannot guarantee long-term self-healing, three or more bilayers greatly endanger the nanorepositories stability during coating application, increasing their agglomeration. Such nanorepositories cannot prevent spontaneous leakage, so after 60 days of erosion, the nanoparticle reservoirs still contain

benzotriazole at 80% of the initial inhibitor content [35].

Ramezanzadeh and his colleagues also coated graphene oxide nanoparticles with polyaniline and then nettle and used them in epoxy coatings [36]. The results showed that composites made of graphene oxide-polyaniline and epoxy had significantly better active protection than pure coatings, since the barrier function and adhesion of the coating were improved thanks to the aniline polymer. Polyaniline in the structure of the designed nanoparticles added self-healing properties to scratched epoxy coatings, and a protective coating layer was formed at the site of the artificial scratch that prevented corrosion from progressing to the coating substrate and its delamination. Finally, when the particles were coated with the herbal inhibitor nettle, inhibitory properties were added to these nanocomposites in addition to self-healing properties [37].

2.2. Reversible bondings (intrinsic healing)

Crosslinks, which are mostly irreversible linkages, are formed to obtain structural characteristics to withstand mechanical, chemical, and environmental damage. Materials with a high crosslink density have disadvantages such as brittleness and tend to crack. One way to create processability in polymers is to tune reversible bonds in polymer systems. In addition to recyclability and recycling, designing reversible bonds in the polymer structure can endow network healability. To trigger reversibility and consequent self-healing, an external stimulus like thermal, optical, or chemical activation is required. While several mechanisms can be exploited for intrinsically reversible bondings, the most important ones (reversible covalent bonds, ionic polymers and supramolecular macromolecules) for achieving reversibility in crosslinked polymeric materials are

discussed in the following subsections.

2.2.1. Reversible covalent Bonds

While most covalent bonds are irreversible, some ones can be dynamic and reversible by changes in the environment they are exposed to. These bondings are Diels-Alder Bonds (temperature-sensitive), Disulfide Bonds (responsive to light, heat, or a reductant), imine bonds (pH-sensitive), Boronic Ester Bonds (pH/temperature sensitive), Hydrazone Bonds (pH responsive) and Urea-Urethane Bonds (heat sensitive). In the following section, as an example, only the Diels-Alder chemistry is explained and the rest can be found here [38-40].

The main group of thermos-responsive polymers is synthesized based on using Diels-Alder reactions. The basis of this is the reaction of a diene and a dienophile (Figure 3). Crosslinking of furanic polymers with maleimide or polymers with pendant maleimide groups at low temperatures is a frequently-used example of such self-healing polymers [41].

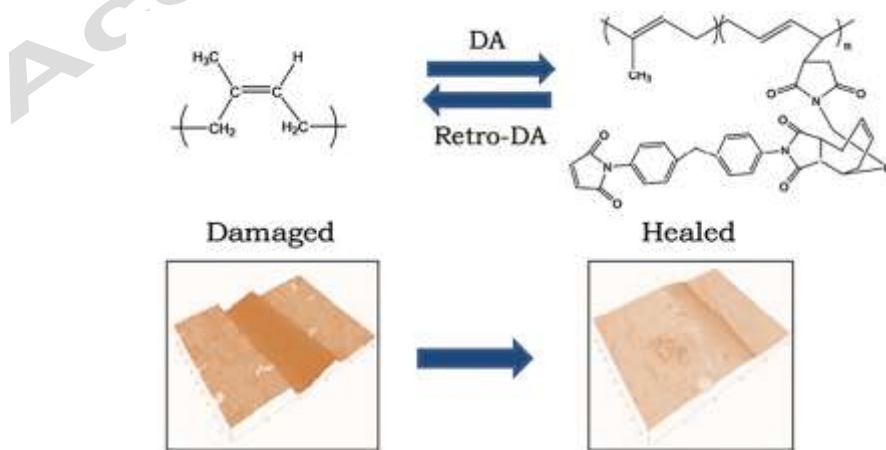


Figure 3. Scheme for crosslinking furanic polymers with maleimide, reprinted with permission from [41], copyright 2025.

The retro-Diels-Alder reaction occurs at high temperatures to break the chemical bonds of the formed networks and reverse the crosslinks. Wudl and co-workers were the first to demonstrate this strategy for the design of thermally modifiable polymers [42]. Since their discovery, various groups around the world have researched this field. Chang and co-workers first reported photoinduced crack healing [43]. They used the photocyclic addition reaction of cinnamoyl groups to achieve the self-healing property. Postiglione and his colleagues synthesized a self-healing polymer network based on three- and two-component furan resins using the retro-Diels-Alder reaction[44]. These researchers significantly improved their self-healing properties by adding a small amount of a suitable plasticizer such as benzyl alcohol. In another study, the fabrication of retro Diels-Alder polymer networks from bio-based materials (organosolv lignin) was targeted to meet the increasing demand for greener materials [45]. In this study, a lignin-based coating with thermally reversible self-healing properties and strong anti-corrosion performance was manufactured (Figure 4) [45].

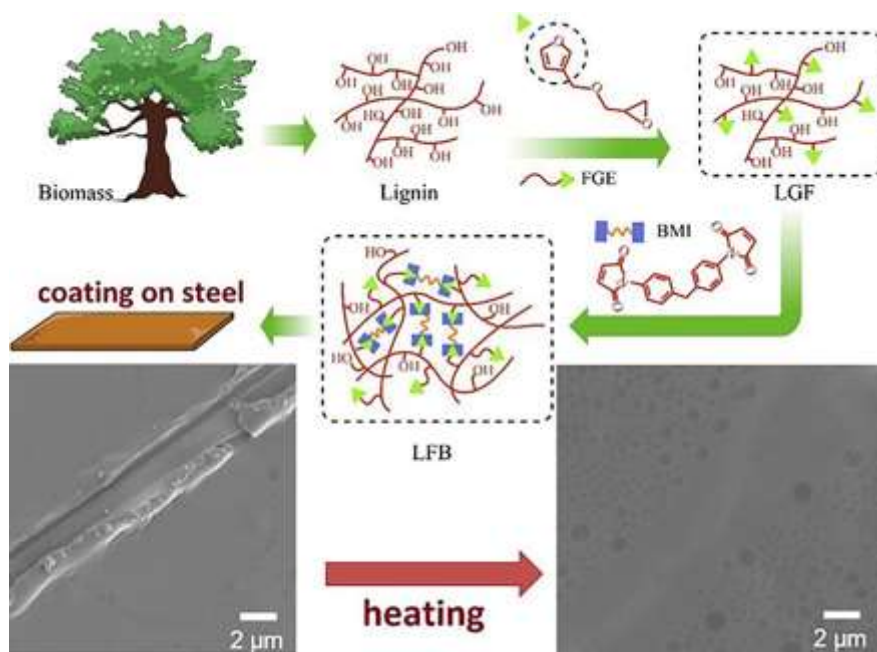


Figure 4. A schematic representation of a lignin-based coating with thermally reversible self-healing properties, reprinted with permission from [45], copyright 2025.

2.2.2. Non-covalent reversible bonds

Despite most chemical covalent bonds being irreversible, physical bondings (such as Electrostatic or Ionic Interactions, hydrogen bonding, Pi-Pi Stacking, hydrophobic interactions, etc.) are completely reversible with a moderate alteration in the surrounding environment, like temperature, pH, saline concentration, etc. These bondings are individually weak, but can be tailored or designed in macromolecular structures to fabricate a very strong network, endowing mechanical characteristics as powerful as typical covalently-linked polymers [46, 47]. Such physical bondings and chemistry can be considered to implement a dynamic backbone that can be assembled/disassembled in response to its environment. Some of these chemistries are discussed in the following sections.

For example, Yari and his colleagues investigated in several studies the improvement of the self-healing properties of transparent automotive coatings by adding hyperbranched polymers and silsesquioxane-based nanocages that had numerous sites for inter/intramolecular hydrogen bondings within an acrylic/melamine network [48, 49].

2.2.2.1. Ionomers

A unique group of polymers called ionomers. Besides their typical hydrocarbon backbone, they have pendant acid functional groups that have been partially or completely neutralized, forming salts. While the ionic content of ionomers may vary vastly, it is commonly up to 15 mol%. The ionomers synthesis consists of two main steps: the first step is direct preparation (copolymerization of a low-functionality monomer with an unsaturated olefinic monomer), and then subsequent functionalization, resulting in a saturated polymer.

The fundamental interactions in ionic polymers typically include the attractive electrostatic forces between negatively-charged functional groups like sulfonates or carboxylates and positively-charged metallic cations. As a consequence of such attractive interaction, there is a strong tendency between ionic moieties available on the polymeric backbone, forming aggregate and cluster groups, which is opposite to the elastic forces of the chain. The mutual effects available in the aggregates/clusters are reversible, and the basic mechanism of the self-healing manner of ionomers (Figure 5) [50].

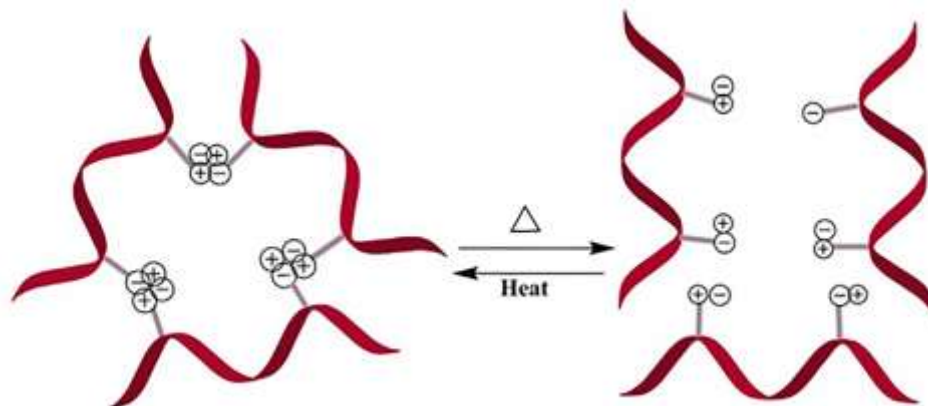


Figure 5. The schematic representation of reversible ionic interactions, reprinted with permission from [50], copyright 2025.

Varley and colleagues investigated the cluster plasticisation effect on the self-healing of a polyethylene-co-methacrylic acid-neutralized ionomer [51]. Mechanical assessment of the repair revealed that carboxylic acid modifiers diminished the elastic portion and increased the elastomeric behavior of the ionomer, thereby improving elastic repair. Meurer and colleagues introduced new bio-based ionomers with self-healing capabilities [52]. These smart materials were synthesized from itaconic acid derivatives. Studies have shown that these ionomers improve the repair efficiency by up to 99%. Luo and co-workers designed a brominated butyl rubber crosslinked with tert-butylpyridine ionomer and reinforced it with graphene nanosheets, which showed long-lasting chemical resistance and anti-corrosion properties [53]. The interactions between graphene sheets and pyridyl groups result in high interfacial interaction, increasing the graphene sheets' distribution in the polymer matrix and making it difficult for corrosive species to penetrate.

2.2.2.2. Supramolecular polymers

The polymeric behavior of traditional polymers is governed by the length and extent of entanglement of long chains or by covalent bonds within the polymer. In the last two decades, low molecular weight monomers with reversible noncovalent bonds have been developed to achieve polymer-like mechanical and rheological properties. Since noncovalent bonds can be reversibly broken and reformed, this unique category of macromolecules, called supramolecular polymers, exhibiting more and better properties compared to conventional polymers. These properties include environmental-dependent properties, better processability, and self-healing capabilities (Figure 6). Noncovalent bonds, which retain the main chain of supramolecular polymers together, can be designed in the main chain or on the side chain [54].

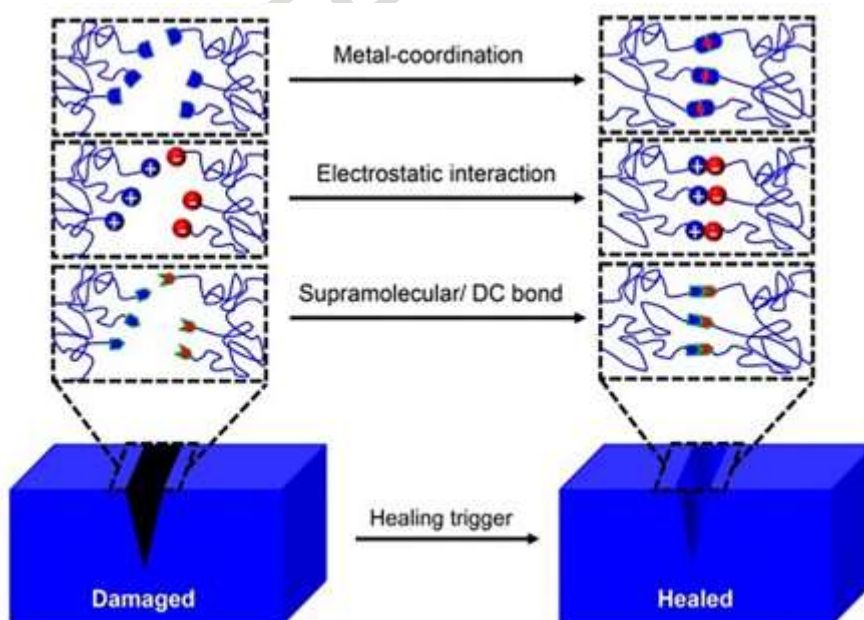


Figure 6. Schematic of the self-healing behavior of supramolecular polymers, reprinted with permission from [54] , copyright 2025.

Various types of non-covalent forces, such as hydrogen bonding, π - π , metal-ligand, hydrophobic, and electrostatic, have been employed to design supramolecules. Hydrogen bonding is the most common method to obtain supramolecular polymers. Meijer and co-workers were the first to use ureidopyrimidone monomers with non-covalent quaternary hydrogen bonding with a high degree of polymerization [55]. The properties of obtained macromolecule were similar to those of conventional polymers. The invention of such weak dynamic bondings to produce supramolecular assemblies with high aggregation constants has made this research field interesting for researchers. Ureidopyrimidone compounds are inexpensive and are also used in other polymer systems to improve processability or other functionalities. This hydrogen-bonding unit was used in the development of polysiloxane chains, polyethers, polyesters, and the like [56]. Based on the above discovery, a joint venture company from Eindhoven University of Technology has also started to explore this commercial field. In addition to hydrogen bonding, supramolecular metal-ligand bidirectional effects were also presented for the design of supramolecular polymers [57]. Metal complexes show special advantages due to their optical properties. In addition, their reversibility is tunable by using various metal ions.

3. Multifunctional stimuli-responsive coatings

The previous sections thoroughly discussed two main functions (mechanical repair and corrosion inhibition) of the self-healing coating. However, other innovative functions may be endowed to the polymeric coatings rather than self-healing capabilities. Such multifunctional stimuli-responsive coatings have been reviewed in detail in [58]. The main stimulus factors include temperature, mechanical forces, humidity/water, pH,

UV/light, carbon dioxide, chemicals, magnetic fields, enzymes. various functions (such as self-healing, self-reporting, self-lubrication, antimicrobial, anti-icing, anti-fogging, self-cleaning, anti-reflection) that can be implemented in response to each stimulus [58]. surface coatings that can change their appearance, including color changes (for example, with the addition of some thermo- or electromagnetic-responsive dyes to the matrix), topology adjustment (mainly based on incorporating photosensitive Azo dyes into amorphous polymer or liquid crystal network) are categorized as materials with stimuli-responsive appearance capability. Such smart appearance-changing surface coatings can adjust their optical properties (for example in smart anti-reflective coatings), adhesion (i.e., in anti-microbial, anti-fouling, anti-icing coatings), and their wetting behavior (including superhydrophilic and superhydrophobic coatings) that can be promising for energy-saving, electronic, and medical applications[58].

4. Applications of Self-Healing Coatings

The intrinsic self-healing systems do not rely on any external materials and are triggered by a change in the environment or situation in which the coating is. Self-healing action can occur several times, although its efficiency is dependent on the level of restoration of the material to its initial state after the healing process. On the other hand, the extrinsic self-healing needs an external agent, and the healing cycles are restricted till the healing agent is consumed. The healing speed in the extrinsic approaches is usually (not always) faster than intrinsic ones, since their mechanism of action is autonomous, while the intrinsic healing is commonly (not always) non-autonomous and is activated when the stimulant(like heat, UV, etc) becomes available. Both intrinsic and extrinsic require

complicated synthesis approaches and are pricy technologies, while the latter seems to be cheaper in some specific applications. From an application viewpoint, an intrinsic scenario is preferred where longer durability is required or the clear appearance of the coating is so essential, whereas the extrinsic-based coatings are usually opaque due to the healing-agent/reservoir inclusion.

Self-healing materials are predicted to have applications in almost all industries in the future. Specific applications in various industrial sectors like automotive, aerospace, and construction have been commercialized. For example, Nissan Company has launched “Scratch Guard Coat” which is believed to be the first commercialized clear coat with self-healing and hydrophobic capabilities for car bodies [59]. It is claimed that scratches (caused by washing the car, or bird claws) can be healed and are effective for three years (**Figure 7**). The coating contains highly elastic resins that resist reaching the scratch to the underneath layers of the car. Depending on the scratch depth and the ambient temperature, complete repair happens up to ultimately 7 days. Bayer company has commercialized a coating with similar functions based on two-component polyurethane clearcoat. This coating repairs small scratches with heat (sunlight), and its technology is founded on the utilization of compact matrix with elastic bonds. For both above examples, the mentioned scratch is small, which is detectible to the unaided eye, and hence, these materials are appropriate for maintaining the coating aesthetics. The adequate energy need to overwhelmed the scratch resistance of the material is higher than thermosetting polymers (corresponding to a plastic or elastic reaction). Therefore, polymers with a high glass transition temperature and elastic reaction are suitable for healing of small scratches. In the case of small scratch failures, temperature stimulation

will improve the chains movement, and surface free energy will be so influential in self-healing efficiency [59].

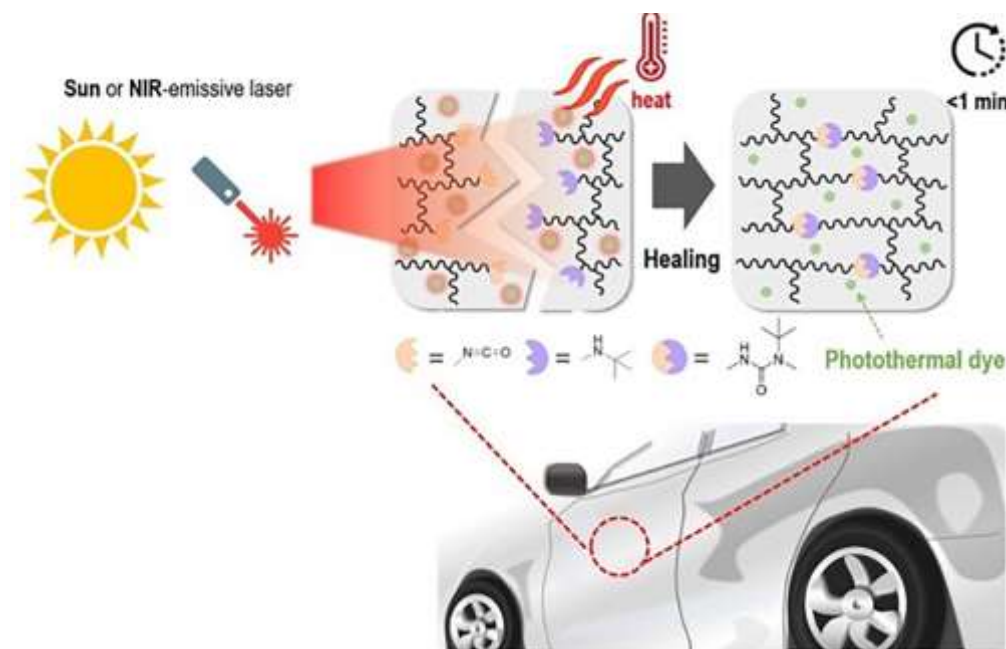


Figure 7. Schematic of the self-healing behavior of Nissan's anti-scratch coatings [59].

The next industrial sector that is considered for the application of self-healing materials is the aerospace industry (Figure 8). The use of composites in aircraft has increased rapidly in recent decades[60]. Composites reinforced with hollow fibers are an applicable solution for crack or damage recovery. Self-healing polymers have also found their way into aerospace engineering sector[61].

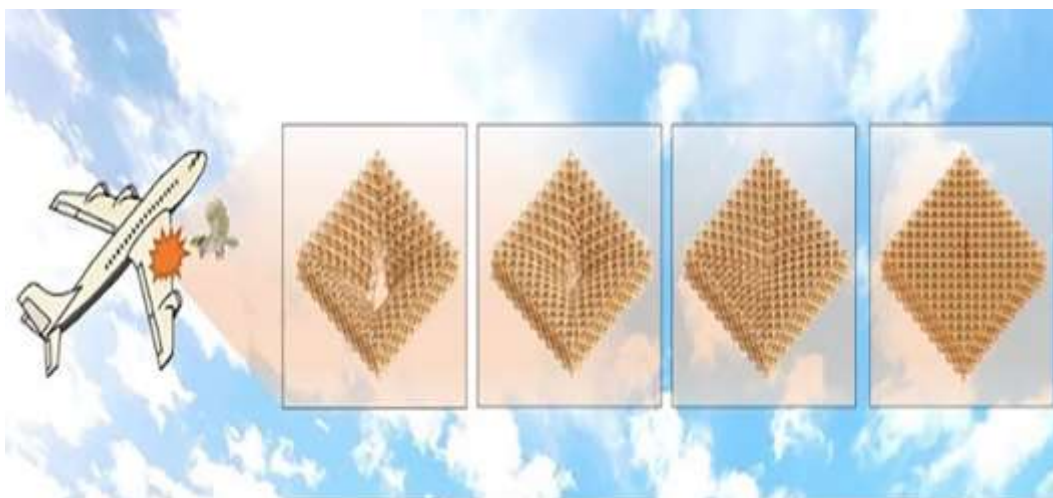


Figure 8. Schematic of the self-healing behavior of new coatings in the aerospace industry [61].

Various applications of self-healing materials have also been found in the construction industry. For example, the use of self-repairing concretes will soon happen as a reality. Self-repairing anti-corrosion coatings for metal building composition, i.g. steel, are beneficial for achieving long service life with lower repair costs.

5. Outlook for Self-Healing Technology in Global Markets: Challenges and Future

Research Directions

Despite remarkable advancements in the self-healing coatings development, few obstacles need to be taken into consideration before their perfect commercialization and vast practical applications. Healing efficiency and repeatability an issue that restricts the long-term applicability. Most currently implemented self-healing systems exhibit restricted healing cycles. Accomplishing stable autonomous healing without a

considerable drop in healing efficiency is a vital issue. Mechanical performance trade-offs are another problem. Embedment of healing materials or installing reversible bonds in the polymer matrix can sometimes diminish the mechanical strength or durability of coatings. Mechanical properties and self-healing characteristics are routinely counteracting. Thus, optimizing self-healing capability with robust mechanical integrity is an essential challenge. Complicated manufacturing procedures and incorporating healing agents into the coating matrix have troubled their mass production. Environmental stability is still a remarkable challenge. The long-lasting self-healing coatings under aggressive situations (UV exposure, humidity, temperature fluctuations) need complementary research. Finally, conducting standardized testing procedures for assessment of healing efficiency, durability, and real-world performance is a crucial need for global industrialization. Future research should consider designing novel materials/approaches that address all the above-mentioned challenges.

From an environmentally friendly viewpoint, utilizing self-healing coatings has some merits and defects. Applying self-healing coatings can not only control the formation and release of hazardous corrosion products into the environment, but also considerably increase the periodical repair intervals and decrease the usage of unfriendly chemicals frequently used in such cleaning and repair processes.

On the contrary, the leaching out of materials used in the formulation of self-healing coating into the surrounding environment can cause some health problems for the ecosystem and raise some concern for the living creatures or even humans (for example, self-healing coatings applied as the internal layers of drinking water pipelines can directly leach out into drinking water) [62]. Additionally, the complicated processes of synthesis

and production of healing agents or final self-healing coatings involve aggressive substances that are environmentally problematic. However, there is a trend to omit or reduce the negative consequences of self-healing coatings by employing green, sustainable approaches [63, 64]. The forecast sales of self-healing composite in various applications up to 2032 are shown in Figure 9. The market share of self-healing technology in various industries is shown in Figure 10.

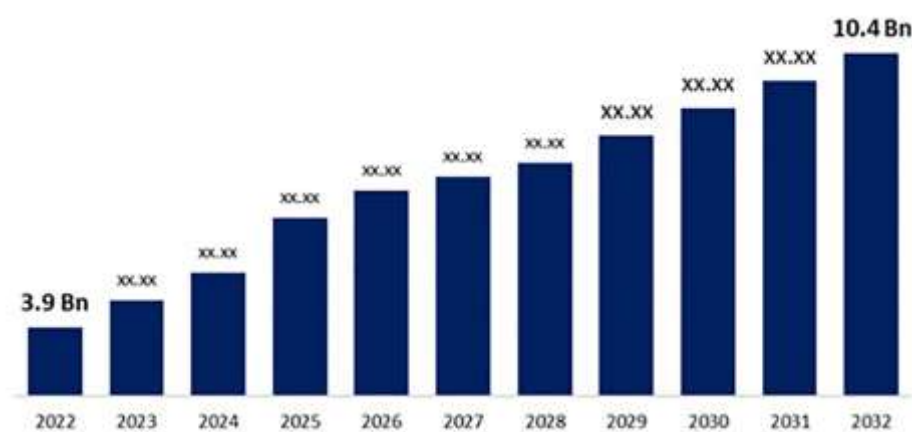


Figure 9. Development trend of the global market for self-healing technology[65].

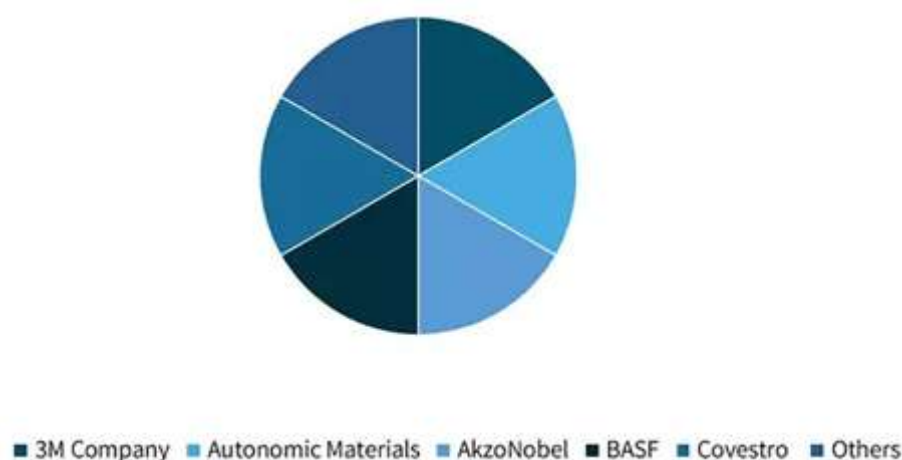


Figure 10. The market share of self-healing materials technology[66].

Figure 10 clearly demonstrates the expanding market of self-healing coatings. It has been predicted that the self-healing market will annually grow at an approximate 25% rate, reaching around 10.4 Bn US dollars by 2032. The key players of this market are AkzoNobel, Autonomic Materials Inc, Covestro, BASF and 3M Company[66].

6. References

1. Utrera-Barrios S, Verdejo R, López-Manchado MA, Hernández Santana M. Evolution of self-healing elastomers, from extrinsic to combined intrinsic mechanisms: a review. *Mater Horiz.* 2020;7(11):2882-902. <https://doi.org/10.1039/D0MH00535E>
2. van der Zwaag S, editor. *Self Healing Materials, An alternative approach to 20 centuries of materials science*. Dordrecht: Springer Netherlands; 2007; <https://doi.org/10.1007/978-1-4020-6250-6>
3. Dry C. Procedures developed for self-repair of polymer matrix composite materials. *Compos Struct.* 1996; 35(3):263-9. [https://doi.org/10.1016/0263-8223\(96\)00033-5](https://doi.org/10.1016/0263-8223(96)00033-5)
4. Li B, Cao PF, Saito T, Sokolov AP. Intrinsically self-healing polymers: from Mechanistic insight to current challenges. *Chem Rev.* 2023; 123(2):701-35. <https://doi.org/10.1021/acs.chemrev.2c00575>
5. Verma A, Bhushan K, Singh H. Nanocomposites for extrinsic self-healing polymer Materials: A comprehensive review of their repair behaviour. *Results Chem.* 2025; 13:101973. <https://doi.org/10.1016/j.rechem.2024.101973>
6. White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Autonomic healing of polymer composites. *Nature.* 2001;409(6822):794-7. <http://dx.doi.org/10.1038/35057232>

7. Kardar P. Preparation of polyurethane microcapsules with different polyols component for encapsulation of isophorone diisocyanate healing agent. *Prog Org Coat.* 2015; 89:271-6. <https://www.sciencedirect.com/science/article/abs/pii/S0300944015301235>
8. Kardar P, Sadredadras F, Najafi F. synthesis of isophorene diisocyanate (core) - polyurethane (shell) microcapsules as non-catalyst healing agent in self-healing coatings. *Adv Mater New Coat.* 2023; 3(10):657-64. https://amnc.aut.ac.ir/article_69055_en.html
9. Kardar P. The effect of polyurethane-isophorone microcapsules on self-healing properties of an automotive clearcoat. *Pigm Resin Technol.* 2016; 45(2):73-8. <https://doi.org/10.1108/PRT-03-2015-0033>
10. Yin H, Li Y, Huang H. Triggering probability of self-healing mechanisms in microencapsulated self-healing composites. *Appl Math Model.* 2025; 145:116101. <https://www.sciencedirect.com/science/article/abs/pii/S0307904X25001763>
11. Zhang F, Ju P, Pan M, Zhang D, Huang Y, Li G, et al. Self-healing mechanisms in smart protective coatings: A review. *Corros Sci.* 2018; 144:74-88. <https://doi.org/10.1016/j.corsci.2018.08.005>
12. Borisova D, Akçakayiran D, Schenderlein M, Möhwald H, Shchukin DG. Nanocontainer-Based Anticorrosive Coatings: Effect of the Container Size on the Self-Healing Performance. *Adv Funct Mater.* 2013; 23(30):3799-812. <https://doi.org/10.1002/adfm.201203715>
13. Liu T, Zhang D, Zhang R, Wang J, Ma L, Keil P, et al. Self-healing and corrosion-sensing coatings based on pH-sensitive MOF-capped microcontainers for intelligent corrosion control. *Chem Eng J.* 2023; 454:140335. <https://doi.org/10.1016/j.cej.2022.140335>

14. An S, Lee MW, Yarin AL, Yoon SS. A review on corrosion-protective extrinsic self-healing: Comparison of microcapsule-based systems and those based on core-shell vascular networks. *Chem Eng J.* 2018; 344:206-20. <https://doi.org/10.1016/j.cej.2018.03.040>
15. Neuser S, Michaud V, White SR. Improving solvent-based self-healing materials through shape memory alloys. *Polymer (Guildf).* 2012; 53(2):370-8. <https://doi.org/10.1016/j.polymer.2011.12.020>
16. Caruso MM, Blaiszik BJ, White SR, Sottos NR, Moore JS. Full Recovery of Fracture Toughness Using a Nontoxic Solvent-Based Self-Healing System. *Adv Funct Mater.* 2008; 18(13):1898-904. <https://doi.org/10.1002/adfm.200800300>.
17. Zhang C, Wang H, Zhou Q. Preparation and characterization of microcapsules based self-healing coatings containing epoxy ester as healing agent. *Prog Org Coat.* 2018; 125:403-10. <https://doi.org/10.1016/j.porgcoat.2018.09.028>
18. Motuku M, Vaidya UK, Janowski GM. Parametric studies on self-repairing approaches for resin infused composites subjected to low velocity impact. *Smart Mater Struct.* 1999; 8(5):623. <https://iopscience.iop.org/article/10.1088/0964-1726/8/5/313>
19. Bleay SM, Loader CB, Hawyes VJ, Humberstone L, Curtis PT. A smart repair system for polymer matrix composites. *Compos Part A Appl Sci Manuf.* 2001; 32(12):1767-76. [https://doi.org/10.1016/S1359-835X\(01\)00020-3](https://doi.org/10.1016/S1359-835X(01)00020-3)
20. Williams G, Trask R, Bond I. A self-healing carbon fibre reinforced polymer for aerospace applications. *Compos Part A Appl Sci Manuf.* 2007; 38(6):1525-32. <https://doi.org/10.1016/j.compositesa.2007.01.013>
21. Mahmoudi R, Kardar P, Arabi AM, Amini R, Pasbakhsh P. Acid-modification and

- praseodymium loading of halloysite nanotubes as a corrosion inhibitor. *Appl Clay Sci.* 2020; 184:105355. <https://doi.org/10.1016/j.clay.2019.105355>
22. Mahmoudi R, Kardar P, Arabi AM, Amini R, Pasbakhsh P. The active corrosion performance of silane coating treated by praseodymium encapsulated with halloysite nanotubes. *Prog Org Coat.* 2020; 138:105404. <https://doi.org/10.1016/j.porgcoat.2019.105404>
23. Vahedi V, Pasbakhsh P, Piao CS, Seng CE. A facile method for preparation of self-healing epoxy composites: using electrospun nanofibers as microchannels. *J Mater Chem A Mater.* 2015; 3(31):16005-12. <https://doi.org/10.1039/C5TA02294K>
24. Xu S, Li J, Qiu H, Xue Y, Yang J. Repeated self-healing of composite coatings with core-shell fibres. *Composit Commun.* 2020; 19:220-5. <https://doi.org/10.1016/j.coco.2020.04.007>
25. Fu X, Du W, Dou H, Fan Y, Xu J, Tian L, et al. Nanofiber composite coating with self-healing and active anticorrosive performances. *ACS Appl Mater Interf.* 2021; 13(48):57880-92. <https://doi.org/10.1021/acsami.1c16052>
26. Khramov AN, Voevodin NN, Balbyshev VN, Donley MS. Hybrid organo-ceramic corrosion protection coatings with encapsulated organic corrosion inhibitors. *Thin Solid Film.* 2004; 447-448:549-57. <https://doi.org/10.1016/j.tsf.2003.07.016>
27. Lashgari SM, Yari H, Mahdavian M, Ramezanzadeh B, Bahlakeh G, Ramezanzadeh M. Application of nanoporous cobalt-based ZIF-67 metal-organic framework (MOF) for construction of an epoxy-composite coating with superior anti-corrosion properties. *Corros Sci.* 2021; 178:109099. <https://doi.org/10.1016/j.corsci.2020.109099>.
28. Lashgari M, Yari H, Mahdavian M, Ramezanzadeh B, Bahlakeh G, Ramezanzadeh M.

- Synthesis of graphene oxide nanosheets decorated by nanoporous zeolite-imidazole (ZIF-67) based metal-organic framework with controlled-release corrosion inhibitor performance; Experimental and detailed DFT-D theoretical explorations. *J Hazard Mater.* 2020; 404:124068. <https://doi.org/10.1016/j.jhazmat.2020.124068>.
29. Lashgari SM, Yari H, Mahdavian M, Ramezanzadeh B, Bahlakeh G, Ramezanzadeh M. Synthesis of graphene oxide nanosheets decorated by nanoporous zeolite-imidazole (ZIF-67) based metal-organic framework with controlled-release corrosion inhibitor performance: Experimental and detailed DFT-D theoretical explorations. *J Hazard Mater.* 2021; 404:124068. <https://doi.org/10.1016/j.jhazmat.2020.124068>.
30. Alipanah N, Yari H, Mahdavian M, Ramezanzadeh B, Bahlakeh G. MIL-88A (Fe) filler with duplicate corrosion inhibitive/barrier effect for epoxy coatings: Electrochemical, molecular simulation, and cathodic delamination studies. *J Indust Eng Chem.* 2021; 97:200-15. <https://doi.org/10.1016/j.jiec.2021.01.035>.
31. Alipanah N, Yari H, Mahdavian M, Ramezanzadeh B, Bahlakeh G. Fabrication of MIL-88A sandwiched in graphene oxide nanocomposites using a green approach to induce active/barrier protective functioning in epoxy coatings. *J Clean Prod.* 2021; 321:128928. <https://doi.org/10.1016/j.jclepro.2021.128928>.
32. Pezeshk-Fallah H, Yari H, Mahdavian M, Ramezanzadeh B. Size/porosity-controlled zinc-based nanoporous-crystalline metal-organic frameworks for application in a high-performance self-healing epoxy coating. *Prog Org Coat.* 2023; 183:107814. <https://doi.org/10.1016/j.porgcoat.2023.107814>
33. Williams G, McMurray HN. Inhibition of filiform corrosion on polymer coated AA2024-T3 by hydrotalcite-like pigments incorporating organic anions. *Electrochem Solid-State*

- Lett. 2004; 7(5):B13. <https://doi.org/10.1149/1.1691529>.
34. Yang H, Van Ooij WJ. Plasma-treated triazole as a novel organic slow-release paint pigment for corrosion control of AA2024-T3. *Prog Org Coat*. 2004; 50(3):149-61. <https://doi.org/10.1016/j.porgcoat.2003.10.006>.
35. Shchukin DG, Zheludkevich M, Yasakau K, Lamaka S, Ferreira MGS, Möhwald H. Layer-by-layer assembled nanocontainers for self-healing corrosion protection. *Adv Mater*. 2006; 18(13):1672-8. <https://doi.org/10.1002/adma.200502053>.
36. Ramezanzadeh B, Kardar P, Bahlakeh G, Hayatgheib Y, Mahdavian M. Fabrication of a highly tunable graphene oxide composite through layer-by-layer assembly of highly crystalline polyaniline nanofibers and green corrosion inhibitors: complementary experimental and first-principles quantum-mechanics modeling approaches. *J Phys Chem C*. 2017; 121(37):20433-50. <https://doi.org/10.1021/acs.jpcc.7b04323>.
37. Hayatgheib Y, Ramezanzadeh B, Kardar P, Mahdavian M. A comparative study on fabrication of a highly effective corrosion protective system based on graphene oxide-polyaniline nanofibers/epoxy composite. *Corros Sci*. 2018 ;133:358-73. <https://doi.org/10.1016/j.corsci.2018.01.046>.
38. Dahlke J, Zechel S, Hager MD, Schubert US. How to design a self-healing polymer: general concepts of dynamic covalent bonds and their application for intrinsic healable materials. *Adv Mater Interf*. 2018; 5(17):1800051. <https://doi.org/10.1002/admi.201800051>
39. Zheng N, Xu Y, Zhao Q, Xie T. Dynamic covalent polymer networks: a molecular platform for designing functions beyond chemical recycling and self-healing. *Chem Rev*. 2021; 121(3):1716-45. <https://doi.org/10.1021/acs.chemrev.0c00938>

40. Kuhl N, Bode S, Hager MD, Schubert US. Self-healing polymers based on reversible covalent bonds. in: *Advances in Polymer Science* Springer, Cham; 2015. p. 1-58.
https://link.springer.com/chapter/10.1007/12_2015_336
41. Tanasi P, Hernández Santana M, Carretero-González J, Verdejo R, López-Manchado MA. Thermo-reversible crosslinked natural rubber: A Diels-Alder route for reuse and self-healing properties in elastomers. *Polymer*. 2019; 175:15-24.
<https://doi.org/10.1016/j.polymer.2019.04.059>
42. Chen X, Dam MA, Ono K, Mal A, Shen H, Nutt SR, et al. A thermally re-mendable cross-linked polymeric material. *Science* (1979). 2002; 295(5560):1698-702.
<https://doi.org/10.1126/science.1065879>
43. Chang JY, Do SK, Han MJ. A sol–gel reaction of vinyl polymers based on thermally reversible urea linkages. *Polymer (Guildf)*. 2001; 42(18):7589-94.
[https://doi.org/10.1016/S0032-3861\(01\)00270-1](https://doi.org/10.1016/S0032-3861(01)00270-1)
44. Postiglione G, Turri S, Levi M. Effect of the plasticizer on the self-healing properties of a polymer coating based on the thermoreversible Diels–Alder reaction. *Prog Org Coat* 2015;78:526-31. <https://doi.org/10.1016/j.porgcoat.2014.05.022>
45. Wang J, Seidi F, Shi X, Li C, Huang Y, Xiao H. Lignin self-healing coatings based on thermo-reversible Diels-Alder reaction for anticorrosion applications. *Prog Org Coat*. 2024; 191:108428. <https://doi.org/10.1016/j.porgcoat.2024.108428>
46. Ke R, Lin Z, Zhang H, Zhou S. Research Progress in Intrinsic Self-healing Polyurethane Materials Based on Dynamic Reversible Non-covalent Bonds. *J Phys Conf Ser*. 2022; 2324(1):012007. <https://doi.org/10.1088/1742-6596/2324/1/012007>
47. Buaksuntear K, Limarun P, Suethao S, Smitthipong W. Non-covalent interaction on the

- self-healing of mechanical properties in supramolecular polymers. *Intern J Mol Sci.* 2022; 23(13):6902. <https://doi.org/10.3390/ijms23136902>
48. Yari H, Mohseni M, Messori M. A scratch resistant yet healable automotive clearcoat containing hyperbranched polymer and POSS nanostructures. *RSC Adv.* 2016; 6(79):76028-41. <https://doi.org/10.1039/C6RA07824A>
49. Yari H, Mohseni M, Messori M. Toughened acrylic/melamine thermosetting clear coats using POSS molecules: Mechanical and morphological studies. *Polymer (Guildf).* 2015; 63:19-29. <https://doi.org/10.1016/j.polymer.2015.02.040>
50. Mirabedini SM, Alizadegan F. Ionomers as self-healing materials. *Self-Healing Polymer-Based Systems.* 2020; 279-91. <https://doi.org/10.1016/B978-0-12-818450-9.00011-8>
51. Varley RJ, Shen S, van der Zwaag S. The effect of cluster plasticisation on the self healing behaviour of ionomers. *Polymer.* 2010; 51(3):679-86. <https://doi.org/10.1016/j.polymer.2009.12.025>
52. Meurer J, Hniopek J, Dahlke J, Schmitt M, Popp J, Zechel S, et al. Novel biobased self-healing ionomers derived from itaconic acid derivatives. *Macromol Rapid Commun.* 2021; 42(8): 2000636. <https://doi.org/10.1002/marc.202000636>
53. Luo G, Pang B, Luo X, Zeng X, Wang Y, Zhao L. Self-healing and enhanced anticorrosion coatings based on graphene-reinforced brominated butyl rubber ionomer. *Prog Org Coat.* 2023; 174:107245. <https://doi.org/10.1016/j.porgcoat.2022.107245>
54. Reuther JF, Scanga RA, Shahrokhinia A, Biswas P. Self-healing materials utilizing supramolecular interactions. *Self-Healing Polymer-Based Systems.* 2020; 293-367. <https://doi.org/10.1016/B978-0-12-818450-9.00012-X>
55. Beijer FH, Sijbesma RP, Kooijman H, Spek AL, Meijer EW. Strong dimerization of

- ureidopyrimidones via quadruple hydrogen bonding. *J Am Chem Soc* 1998; 120(27):6761-9. <https://doi.org/10.1021/ja974112a>
56. Oya N, Ikezaki T, Yoshie N. A crystalline supramolecular polymer with self-healing capability at room temperature. *Polym J*. 2013; 45(9):955-61. <https://doi.org/10.1038/pj.2012.230>
57. Bazzicalupi C, Bianchi A, García-España E, Delgado-Pinar E. Metals in supramolecular chemistry. *Inorg Chim Acta*. 2014; 417:3-26. <https://doi.org/10.1016/j.ica.2014.03.001>
58. Liu Q, Urban MW. Stimulus-responsive macromolecules in polymeric coatings. *Polymer Rev*. 2023; 63(2):289-323. <https://doi.org/10.1080/15583724.2022.2065299>
59. New Self-Healing Coating Fixes Car Scratches in Only 30 Minutes In The Sun. 2025. <https://www.intelligentliving.co/new-self-healing-coating-fixes-car-scratches-in-only-30-minutes-in-the-sun/>
60. Rana Sohel, Fanguero Raul. Advanced composite materials for aerospace engineering : processing, properties and applications. 2016; https://books.google.com/books/about/Advanced_Composite_Materials_for_Aerospace.html?id=QauSBgAAQBAJ
61. What If Airplanes Could Repair Their Own Damage?-USC Viterbi School of Engineering. <https://viterbischool.usc.edu/news/2020/03/what-if-airplanes-could-repair-their-own-damage/>
62. Cui J, Li X, Pei Z, Pei Y. A long-term stable and environmental friendly self-healing coating with polyaniline/sodium alginate microcapsule structure for corrosion protection of water-delivery pipelines. *Chem Eng J*. 2019; 358:379-88. <https://doi.org/10.1016/j.cej.2018.10.062>

63. Ma X, Wang T, Gong B, Hou J, Ji S, Cao H. Enhanced corrosion resistance of an eco-friendly MXene composite coating with self-healing performance. *Green Chem.* 2025; 27(16):4369-84. <https://doi.org/10.1039/D4GC06219A>
64. Zhou G, Zhou Y, Zhang X, Lei Z, Wang X. High-strength, self-healable, transparent castor-oil-based waterborne polyurethane barrier coatings enabled by a dynamic acylhydrazone co-monomer. *Green Chem.* 2025; 27(8):2220-9. <https://doi.org/10.1039/D4GC06103A>
65. Self Healing Coatings Market Size, Share, Industry Forecast 2032. <https://www.sphericalinsights.com/reports/self-healing-coatings-market>
66. Self Healing Coatings Market Size, Share, Industry Forecast 2032. <https://www.sphericalinsights.com/request-sample/2083>