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Posted Date: 12 June 2024

doi: 10.20944/preprints202406.0775.v1

Keywords: microcapsules; self-healing; thermoplastic polymers doi:10.20944/preprints202406.0775.v1

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Smart Composite Materials with Self-Healing Properties: A Review on Design and Applications

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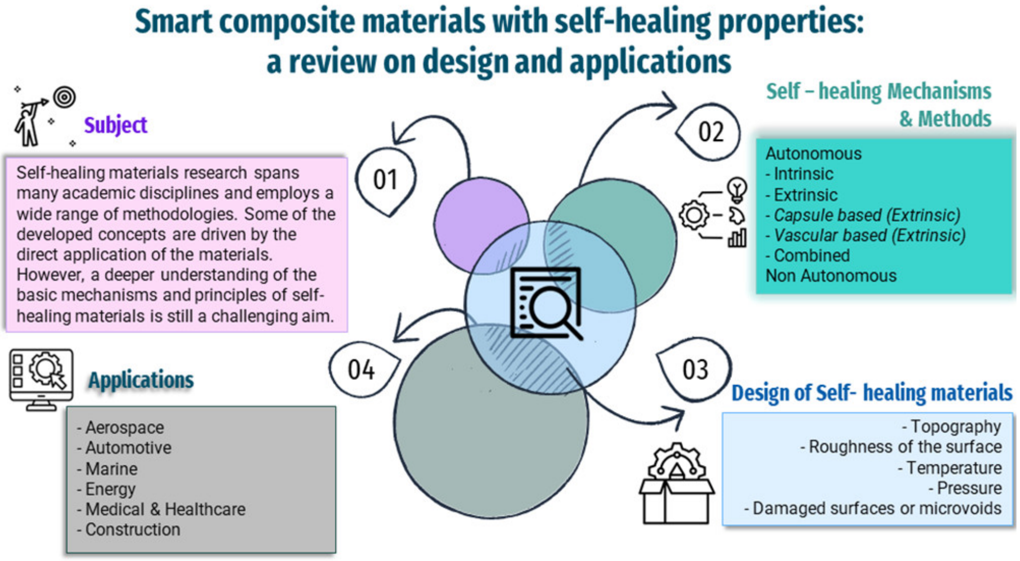
Abstract: Self-healing materials research spans many academic disciplines and employs a wide range of methodologies. Some of the developed concepts are driven by the direct application of the materials. However, a deeper understanding of the basic mechanisms and principles of self-healing materials is still a challenging aim. Nature has mostly served as an inspiration for the development of new self-healing materials, and it will undoubtedly continue to be a significant source of inspiration for the creation of novel ideas. This review encompasses the principles of self-healing mechanisms based on the concepts of autonomous and non-autonomous procedures. Studies based on smart composite materials with autonomous self-healing properties are also included and discussed from two aspects of intrinsic or extrinsic abilities, taking into consideration their components and structures as well as the design of these composites. Finally, special attention is given to the application of the materials in several fields such as aerospace, automotive, marine, energy, medical and healthcare, military, and construction.

Keywords: microcapsules; self-healing; thermoplastic polymers;



Self-healing materials research spans many academic disciplines and employs a wide range of methodologies. Some of the developed concepts are driven by the direct application of the materials. However, a deeper understanding of the basic mechanisms and principles of self-healing materials is still a challenging aim.

Autonomous
- Intrinsic
- Extrinsic
- *Capsule based (Extrinsic)*
- *Vascular based (Extrinsic)*
- Combined

Non Autonomous

- Topography
- Roughness of the surface
- Temperature
- Pressure
- Damaged surfaces or microvoids

- Aerospace
- Automotive
- Marine
- Energy
- Medical & Healthcare
- Construction

1. Introduction

Smart composite materials are also known as adaptive or intelligent composites, are characterized the advanced materials that have been produced in order to respond to environmental triggering in a useful and predictable manner [1]. The concept of intelligence has many applications, such as coating, education, agriculture, finance and cyber security. The possibility of producing materials able to perform different functions and respond to external stimuli will be an important research area for the foreseeable future. These new materials will play a crucial role, for example in additive manufacturing, since they will be designed and structured to perform specific operations and adapt autonomously to external conditions and variables, without the need for additional devices. These materials meet application demands of multi-functionality and adaptability, reducing the complexity of systems and making solutions simpler to implement. The traditional composite materials either consist of a matrix based on polymers, ceramics or metals that maintain the material together, or consist of reinforcements such as particles or fibers that provide stiffness and strength properties. The smart technologies include piezoelectric materials, magneto strictive materials, shape memory alloys, electroactive polymers carbon nanotubes and graphene and self-healing polymers [2,3].

Due to their advantages of being easily processed, lightweight, and chemically stable, polymeric materials and polymer composites are used in a wide variety of technological fields. Long-term reliability and durability become requirements for polymeric materials in structural applications. A novel technique of producing three-dimensional (3D) physical objects from three-dimensional CAD (computer-aided design) data is known as 3D printing. Due to its affordable cost, small cycle time, and user-friendly approach, fused filament fabrication (FFF), an aspect of material extrusion, is the most utilized and accessible technology. The FFF extrusion manufactures objects from 3D CAD models via thin layers of extruded thermoplastic filaments that have been semi-melted. Due to its simplicity of design, quick fabrication times, and capacity to produce lighter components with low costs and great functionality, FFF is increasingly employed for fabricating prototypes and functional replacement components using polymer materials at the design stage. The improvement of FFF-printed specimens' mechanical properties is under ongoing study that is based on factors related to filament orientation during 3D printing, layer thickness, airgaps between layers, and the process of filament solidification during extrusion. The mechanical strength of FFF-printed components, for instance, has increased due to the inclusion of reinforcement fillers such as carbon nanofibers, although there are still issues with fiber alignment in the polymer matrix, fiber-matrix debonding, and void formation. Incorporating a self-healing material system is another strategy to improve the lifetime and reliability of 3D-printed components [4–6].

Self-healing materials are a category of smart materials that have the ability to automatically repair their damage and restore their original functionality and properties after being damaged [7]. The types of self-healing materials are polymeric ceramic metallic and composite materials. Polymeric materials self-healing effect is based on microencapsulation and on intrinsic healing [8]. On microencapsulation, capsules including healing agents are loaded in the material. The damage formation, occurs the healing agent release from the capsules ruptures resulting in the repairing of the crack. The intrinsic healing is based on polymers that have reversible bonds which can be reconstructed after being broken due to an external triggering such as light, heat, or pressure. Metallic materials self-healing effect is based on self-healing alloys that alloys can undergo phase transformations allowing them to clog in cracks and reconstruct their structure and on healing via heat treatment where metals are designed to heal via procedures such as diffusion and recrystallization after heat treatment [9]. Ceramic materials self-healing effect is based on crack healing ceramics where new bonds at the crack surfaces are formed when exposed to high temperatures resulting to healing outcome [10]. The composite materials self-healing effect is based on vascular systems and on shape memory alloys [7,11]. In the vascular systems the composites contain networks of hollow tubes loaded with healing agents. When damage occurs, the healing agent is released to the damaged area. In shape memory alloys the composites utilize shape memory effects to clog cracks and reobtain functionality (Figure 1).

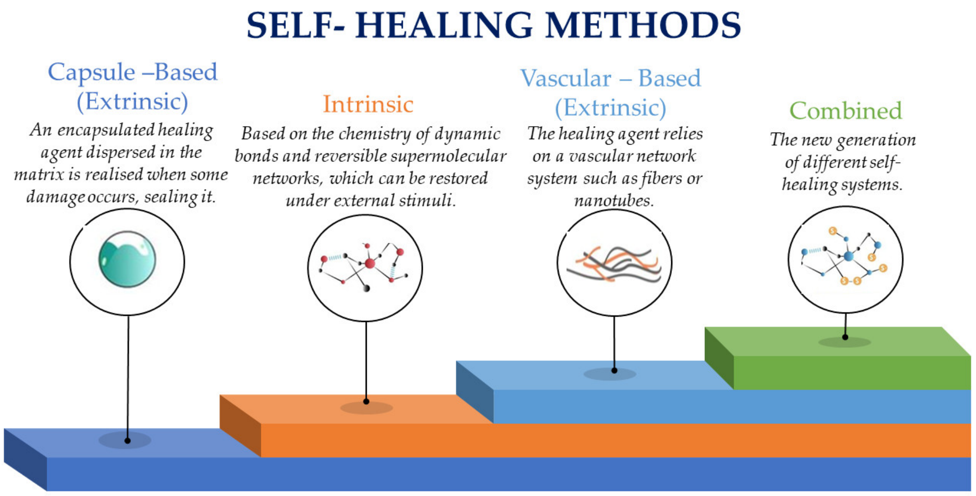


Figure 1. The self-healing methods.

In recent times, a discernible gap has emerged between capsule-based self-healing composites and intrinsic self-healing materials. Research on capsule-based systems predominantly centers on the rupture process, healing agents, mixing processes, and micro-structure manufacturing techniques. The initial focus of the work is on the three primary self-healing methodologies, addressing significant issues and challenges associated with each approach. The review encompasses a literature overview of healing agents used in recent years. This article examines recently developed discrete *(what is discrete = is this proper word)* self-healing methods, the majority of which draw their inspiration from biological systems. Here, we focus on self-healing thermoplastic polymers that are used as composite filaments [12].

2. Self-Healing Mechanisms

Self-healing is a method characterized by its ability to autonomously identify malfunctioning devices or systems, without the need for human intervention, and make necessary adjustments to restore them to their normal state [4,13]. This method is designed to detect and repair microcracks in products or systems, thereby enhancing their mechanical or functional performance. It signifies a new era of technology, significantly enhancing the crucial performance aspects of various products. Self-healing technology has been integrated into diverse applications, such as structural, electronic, medical, and aerospace products, thereby improving their overall performance (Figure 2). This approach is particularly valuable in situations where repairs or inspections are challenging, hazardous, and costly [14].

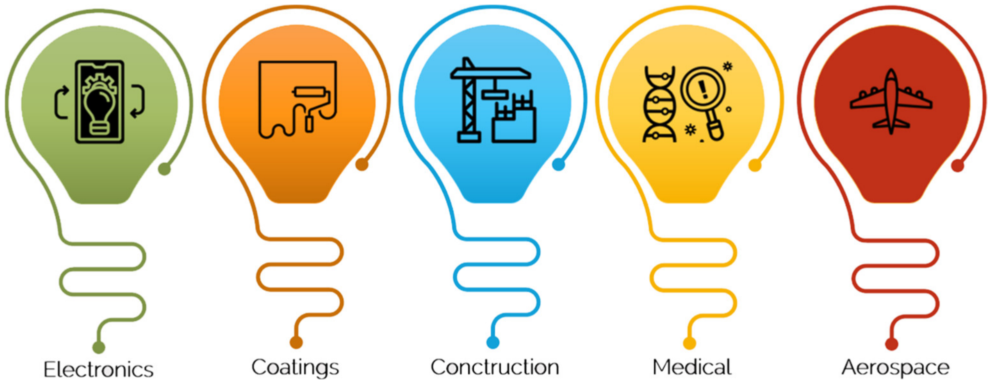


Figure 2. The self-healing technology integration into diverse applications.

2.1. *Autonomous and Non-Autonomous Self-Healing Mechanisms*

Autonomous healing systems can repair their bulk integrity or functional properties without any external physical intervention. The damage itself triggers repair processes. Coatings that aren't self-healing on their own depend on outside stimulation, usually light or heat. The healing process in these coatings can be repeated, in contrast to autonomous self-healing. Complementary corrosion-sensitive components that recognize pH changes during the early stages of corrosion can be added to these coatings to increase their response to stimuli [15]. Healing of these coatings is aided by the return of the polymer network's intrinsic chemical connections and/or physical conformation inside the coating matrix. This effect improves the chemical stability and offers the protective coating on magnesium alloy a self-healing option. As it is discussed below, the reaction mechanisms include shape memory effects and dynamic bonding [16].

In summary, reversible physical or chemical polymer networks that can reduce coating flaws are essential to the non-autonomous self-healing process. However, until artificial external stimulation is applied, these flaws are left exposed to corrosive conditions. Non-autonomous (or stimuli-assisted) healing systems have the ability to repair coatings using external stimuli that are not generated from corrosion events. Heat, light, mechanical forces, chemical reactions, and pH are the most common stimuli for this type of coating because they can be easily applied in service environments. In non-autonomous smart self-healing anti-corrosion coatings, the properties of the polymer coatings are what essentially dictate their effectiveness. The polymer covering can directly repair itself when stimulated by heat or light, which greatly lessens the need for outside repair chemicals. The coating is theoretically repairable an infinite number of times. Non-autonomous healing coatings have more potential to quickly cure cracks, especially large-area cracks, than autonomous self-healing coatings. However, some protective coatings are expensive, have a narrow range of applications, could contaminate the environment, and have poor mechanical properties and weak fracture resistance.

2.2. Intrinsic and Extrinsic Self-Healing Mechanisms

Autonomous self-healing process can reported from two aspects, the intrinsic and the extrinsic type of self-healing mechanism [17]. The present review delves into the classifications of self-healing materials commonly employed for diverse applications, specifically intrinsic and extrinsic types of self-healing mechanisms. These types are further categorized into subdivisions based on various criteria such as mode of contact, healing agents, catalysts, etc., discussed in subsequent sections. Consequently, the final section of the article explores current developments and applications of self-healing materials across various domains.

Broadly, the self-repair processes of self-healing materials can be classified into two main types: extrinsic healing and intrinsic healing. Extrinsic healing encompasses features like microcapsules, microvascular networks, and nanoparticles. On the other hand, intrinsic healing is further categorized into dynamic covalent bonding, which includes reactions like Diels–Alder, disulfide formation, and dynamic non-covalent bonding, which involves hydrogen bonds, ionic interactions, and coordination [18].

A category of extrinsic healing behaviour facilitated by bacteria-assisted crystal precipitation. This approach has been successfully applied to the restoration of cementitious materials [19,20]. Also, an innovative technology of the bacteria-assisted crystal precipitation facilitates the healing of structured ceramics [21,22].

Polyurethanes and polyureas offer the potential for creating inherently recoverable polymers due to the presence of hydrogen bonds within these polymers [23–25]. These hydrogen bonds, characterized by their high dynamism can be harnessed for the design of intrinsic self-healing materials. Notably, Leibler and his research team demonstrated the self-healing effects resulting from the dynamic nature of hydrogen bonds. Moreover, the shape-memory properties of polyurethanes can be employed to augment the self-healing characteristics of polymers, a phenomenon referred to as shape-memory-assisted self-healing [26–28].

Typically, metal corrosion can trigger the release of inhibitive species present in coatings, which serve to impede the ongoing progression of corrosion [29,30]. This process can be referred to as "active protection." Essentially, active protection involves passivating the defective area with active species, allowing for the full or partial recovery of the flawed region (i.e., safeguarding the exposed metal from further corrosion). In essence, two distinct autonomous self-healing mechanisms may come into play: (1) the creation of a protective layer primarily through the oxidation of the healing agent or related reactions to fill defects, and (2) the generation of chelates/precipitates associated with corrosion inhibitors to obstruct the corrosion path [31,32]. The occurrence of mechanical damage can trigger the release of corrosion inhibitors and is frequently employed in coatings featuring autonomous self-healing mechanisms that operate through the process of filling cracks.

Cracking is a serious issue in polymer composites because a thin, brittle layer is in contact with a deformable layer. The examination of microcrack formation and propagation holds significant importance in the study of materials, particularly in their ability to withstand stress without failure during application. This is closely tied to the material's resilience. The study becomes more intricate when applied to polymer composite materials, where the distinct properties of the reinforcement and the matrix come into play. Many polymer composites experience mechanical loadings and environmental factors throughout fabrication, storage, and service. Consequently, microcracks may develop in the composites under various static, dynamic, and fatigue cyclic loading conditions, including tension, compression, and shear [33].

Exposure to fluctuating environmental conditions, such as temperature, moisture, chemicals, and radiation, can also contribute to the formation and propagation of microcracks. Polymer composites subject to the combined effects of mechanical loading and environmental exposure are generally more prone to microcrack formation and propagation. The immediate occurrence of microcracks in polymer composites results in the deterioration of thermomechanical properties. Additionally, it serves as an initiator for other types of damage, inducing delamination and fiber-matrix interfacial debonding, and causing fiber fracture. This, in turn, provides pathways for the entry of moisture, oxygen, and other corrosive liquids. Consequently, microcracks can lead to overall material degradation, significantly impacting the long-term durability of polymer composite materials [34,35].

3. Microcapsules' Synthesis Process

Various repair agents can be encapsulated to repair polymer damage. In order to facilitate failure during the repair process, the shell of the capsules must have high thermal stability and suitable mechanical properties [36,37]. Additionally, the catalyst should possess elevated thermal stability and exhibit good solubility in the repair agent. The crucial factors influencing the construction and enhancement of the self-healing performance of polymeric materials utilizing micro-capsules. The present paper aims to explore the latest advancements in intrinsic repair systems, with a specific focus on their application in polymer composites. This review covers topics such as the necessity for composite repair, the self-healing concept, diverse repair methods, assessments of repair performance in various mechanical tests, and statistical insights and trends pertaining to self-healing.

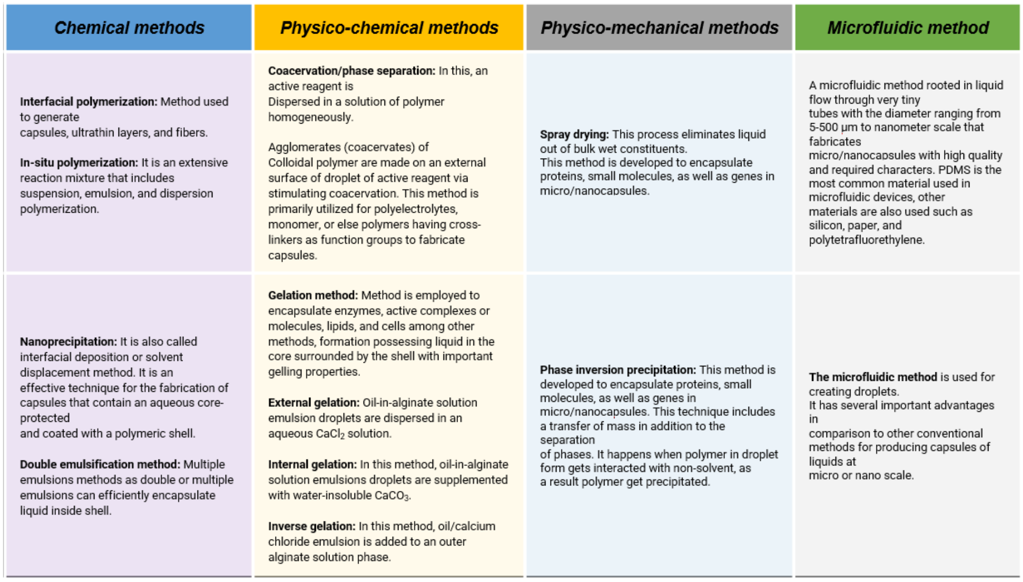
Capsule-based smart composite materials were an emerging field of research and development [38]. These materials hold great promise due to their ability to incorporate microcapsules containing functional agents within a composite material. These functional agents could be used to provide various properties or functionalities to the composite material, such as self-healing, sensing, or controlled release of substances. Extrinsic and intrinsic self-healing are the two primary divisions of self-healing polymers, which are categorized according to the type of healing. In both situations, it is necessary to have a movable phase that might fill the crack during healing. This mobile phase can be made accessible for intrinsic self-healing by the existence of reversible covalent bonds or for extrinsic self-healing by the flow of integrated catalyst or thermoplastic additives. A few sources additionally mention the addition of a secondary phase, which can give the material self-healing capabilities and affect its engineering performance, in addition to these procedures.

3.1. Micro and Nanocapsules

Nano/microcapsules are generated using various methods in a variety of structural shapes (Single-core, multi-core, multi-core, irregular), and possess a multitude of useful qualities that are useful for a variety of applications. The morphologies include (a) the shell reducing the core's reactivity, (b) the thermal stability of the dispersibility and stability of the particles is improved overall, and the particles are easily modifiable. The micro-nano/core-shell capsules have excellent interest as a result of they have remarkable qualities resulting from the combination of core and shell material and their geometrical structure. As a result, they have discovered broad application in domains such as catalysts, biology, and electrical and semiconducting materials. Furthermore, out of all morphologies, core-shell nanoparticles are the most promising and suitable for medicinal applications, such as drug delivery, gene delivery, and sensors linked to their improved dispersibility, shape, optical characteristics and bio-functionalization [39].

3.2. Encapsulation Technologies for the Fabrication of Micro/Nanocapsules

The prepared capsules demontrated diverse morphologies depending on the fabrication material, though the synthetic method also has a substantial influence on the ultimate product. Chemical methods include the fabrication of a micro/nano sphere with several polymerization reactions. Monomers or prepolymers are the preparatory materials in these methods. A chemical reaction takes place through several physical transformations for shaping capsules, called the physico-chemical method, but when we have no polymerization processes called the physico-mechanical method. Finally, a traditional microencapsulation approach has some drawbacks such as specific manipulation of morphology, distribution of size, composition, as well as porosity of developed particles, called microfluidic method (Figure 3) [40–42].



Chemical methods	*Physico-chemical methods*	*Physico-mechanical methods*	*Microfluidic method*
Interfacial polymerization: Method used to generate capsules, ultrathin layers, and fibers. **In-situ polymerization:** It is an extensive reaction mixture that includes suspension, emulsion, and dispersion polymerization.	**Coacervation/phase separation:** In this, an active reagent is Dispersed in a solution of polymer homogeneously. Agglomerates (coacervates) of Colloidal polymer are made on an external surface of droplet of active reagent via stimulating coacervation. This method is primarily utilized for polyelectrolytes, monomer, or else polymers having cross-linkers as function groups to fabricate capsules.	**Spray drying:** This process eliminates liquid out of bulk wet constituents. This method is developed to encapsulate proteins, small molecules, as well as genes in micro/nanocapsules.	A microfluidic method rooted in liquid flow through very tiny tubes with the diameter ranging from 5-500 μm to nanometer scale that fabricates micro/nanocapsules with high quality and required characters. PDMS is the most common material used in microfluidic devices, other materials are also used such as silicon, paper, and polytetrafluorethylene.
Nanoprecipitation: It is also called interfacial deposition or solvent displacement method. It is an effective technique for the fabrication of capsules that contain an aqueous core-protected and coated with a polymeric shell. **Double emulsification method:** Multiple emulsions methods as double or multiple emulsions can efficiently encapsulate liquid inside shell.	**Gelation method:** Method is employed to encapsulate enzymes, active complexes or molecules, lipids, and cells among other methods, formation possessing liquid in the core surrounded by the shell with important gelling properties. **External gelation:** Oil-in-alginate solution emulsion droplets are dispersed in an aqueous $CaCl_2$ solution. **Internal gelation:** In this method, oil-in-alginate solution emulsions droplets are supplemented with water-insoluble $CaCO_3$. **Inverse gelation:** In this method, oil/calcium chloride emulsion is added to an outer alginate solution phase.	**Phase inversion precipitation:** This method is developed to encapsulate proteins, small molecules, as well as genes in micro/nanocapsules. This technique includes a transfer of mass in addition to the separation of phases. It happens when polymer in droplet form gets interacted with non-solvent, as a result polymer get precipitated.	**The microfluidic method** is used for creating droplets. It has several important advantages in comparison to other conventional methods for producing capsules of liquids at micro or nano scale.

Figure 3. Tabulated methods for microcapsules synthesis together with active reagents encapsulation.

Double-walled microcapsules were synthesized following the general procedure of Caruso et. al. [43] which synthesizes polyurethane/poly (urea-formaldehyde) (PU-UF) microcapsules in a single batch process. The process described by Shinde et al. [44] for double shell walled microcapsule synthesis via in-situ interfacial emulsion polymerization process for preparation of EPA-filled microcapsules for FFF printing.

White et al. conducted the initial research on dicyclopentadiene (DCPD) as the healing agent to be encapsulated [45]. Grubbs catalyst was used to successfully demonstrate self-healing in bulk materials and coatings, but it lacks practical application due to the catalyst's poor chemical and thermal durability, poor matrix dispersion, and expensive cost. Epoxy resins, agents based on oils, and siloxanes are examples of alternative healing agents that have been studied. Due to their capacity to react with a wide range of curing agents or hardeners, such as amines and anhydrides, at various temperatures and their strong adherence to numerous substrates, epoxy resins are regarded as key core materials. Additionally, even at 200^{o}C, they maintain thermal stability and have a high thermal decomposition temperature. Commercial epoxy resins, however, typically have a high viscosity and require the use of reactive diluents to reduce it. Epoxy resins have been reported to have a self-healing effectiveness of over 90% when used in bulk materials.

After the initial healing, multiple healing is only feasible if there is an overheating agent present in the matrix. In order to achieve multiple healing in composite materials, a novel reservoir that can transport higher amounts of liquid healing agents has been created.

In another alternative self-healing system, Jung employed polyoxymethylene urea as a storage container for the self-healing agent in a polyester matrix [7]. The best healing results were obtained with a styrene-based system containing 1.3 wt% cobalt naphthenate, 1.3 wt% dimethylaniline (DMA), and 0.01 wt% paratertbutylcatechol (TBC). It was also reported that this system would have little practical use because of the limited shelf life of the healing chemicals. The rupture of the system was identified in Jung's system utilising optical techniques, including optical microscopy, SEM, and high-speed video imaging. Microcapsules, followed by the release of their contents into a crack that is about to open. Strong interfacial adhesion is established between the matrix and microspheres were crucial for even while this started the self-healing, it resulted in a reduction in the composite's durability. Compared to the fracture resistance of plain polyester resin increasing the self-healing samples at the cost of the material's rigidity.

Another variation to the traditional microencapsulation approach was patented by Skipor et al. [46] described the concept of attaching catalyst molecules to the exterior of the microcapsules filled with the healing agent and the positioning of the catalysts near the healing agent release site was claimed to potentially improve the overall healing efficiency. In this patent, proposed an improved approach that eliminated the need for a catalyst by crosslinking the healing agent directly with the damaged surfaces.

T. Yin, M. Z. Rong, M. Q. Zhang and G. C. Yang, [47] used a two-component healing system whereby UF capsules (30–70 μm diameter) filled with epoxy were distributed in a matrix that contained a latent hardener. The latent hardener consisted of a complex of CuBr2 with 2-methylimidazole, which was quite soluble and well dispersed in the epoxy composite matrix. When subjected to mechanical stress, microcracks would form and break the UF spheres, releasing the epoxy, which would then cure by contact with the embedded hardener. They observed that the self-healing epoxy with 10 wt% spheres and 2 wt% hardener achieved 111% of its original fracture toughness, and a composite with woven glass fibers achieved a healing efficiency of 68%.

Polyurethane (PU) is often used as a healing agent, with researchers reporting success in both durability and regain of mechanical properties. Maes, Van Tittelboom and De Belie, [48] studied the healing capabilities of polyurethane in macrocapsules as a potential to resist chloride environments from entering cracks. It was found that 67% of the specimens with PU resulted in almost fully regaining resistance to chloride penetration at a crack width of 0.10 mm. Whereas once the crack width is increased from 0.10 mm to 0.33 mm only 33% of specimens showed no chloride ion penetration until the glass tube, with 50% observing similar results as crack specimens (no resistance).

Anglani et al.,[49], observed more promising results when using PU as a healing agent. The author reported a healing rate of 35.9%-46.5%, in comparison to the control specimen only showing 0.1% healing. It was also found that the use of larger diameter microcapsule of 7.5 mm with epoxy external coating led to 50% regain flexural load capacity upon first reloading and 82% regain after the second reloading. The difference in regaining strength was attributed to the hardening of the PU sealing both the crack and the microcapsule. When the second unloading occurred there was unpolymerized PU which was able to be used in the second time of healing hence the increase in regained flexural strength. Ultimately, this indicates the potential of using macrocapsules with PU to improve mechanical properties after healing and potential repeat healing due to the properties of the healing agent which can protect or seal unreacted healing agents inside the capsule.

Haiyan Li et al. [50] recently provided a method for the preparation of polysulfone microcapsules containing tung oil were synthesized by a solvent evaporation method. The mean diameter and wall thickness of the synthesized microcapsules were approximately 130 m and 9 m, respectively. High thermal stability of the microcapsules with a thermal degradation onset temperature of 350°C was obtained. The multi-functional coating was fabricated by incorporating the microcapsules (10 wt%) containing tung oil into an epoxy matrix. The self-healing and self-lubricating functions were evaluated by corrosion and tribology tests. The microcapsules showed excellent anticorrosion performance in scratched coatings, which was attributed to the formation of a cross-linked polymer film after tung oil was released from the damaged microcapsules. The frictional coefficient and wear rate of the self-lubricating coating decreased significantly as compared to the neat epoxy. The formation of a transfer film from releasing tung oil and the entrapment of wear particles in the cavities left by the ruptured microcapsules were the major antifriction mechanisms.

In the work of Montemor et al. [51] epoxy-based coatings were modified with microcapsules loaded with isophorone diisocyanate and with pH-sensitive Ce tri(bis(2-ethylhexyl)phosphate ($Ce(DEHP)_3$) particles serving as inhibitor. The healing process involved multilevel protection and a synergistic effect that reinforces significantly the corrosion protection conferred by the modified epoxy coating. Graphene sheets containing porous polyhedral oligomeric silsesquioxane (POSS) framework were synthesized as nanocontainer for self-healing organic coating in the work of Ye et al. [52]. The corrosion inhibitor of benzotriazole (BTA) was loaded into the porous graphene sheets and then imbedded into epoxy coating to form composite coating. The BTA could be released from the nanocontainer to form an adsorption layer on metal surface. The physical barrier of graphene suppressed the permeation of corrosion medium.

In the study of Chen et al. [53] TiO_2 nanotubes were synthesized using a hydrothermal method and act as nanocontainers for molybdate corrosion inhibitors. The molybdate-loaded TiO_2 nanotubes were pH-sensitive and the fabricated PPy/TiO_2@Mo coating exhibited superior corrosion resistance and electroactivity. The improvement in the anti-corrosion performance of the coating was assigned to the superior anodic protection, physical barrier and the corrosion inhibitors that were efficiently released from TiO_2 nanotubes. The group of Shchukin et al. [54] investigated the corrosion-protection ability of developed coating based on a combination of passive and active parts loaded with nano- and microcontainers. The active part was presented by the incorporation of polyurethane microcontainers loaded with alkoxysilanes possessing a long hydrophobic tail. The results revealed improved corrosion protection of the formatted film. The development of a stimulus responsive smart self -healing anticorrosion coating based on acrylic resin, incorporated with Dendrimer like Mesoporous Silica Nanoparticles (DMSN) loaded inside with 8-hydroxyquinoline inhibitor was evaluated in the work of Sathiyanarayanan et al. [55]. The electrochemical characterizations confirmed the corrosion-resistant and self-healing properties of the produced coating.

4. Design of Self-Healing Materials

How to induce or design for self-healing is a significant problem for rigid materials below their glass temperature (T_g) value, such as composite matrices. This is crucial for glassy amorphous polymers, semicrystalline materials, and thermosetting composite matrices, which are often extensively cross-linked. The research team of C.M.Dry [56] created multiple patents based on these cutting-edge materials because there was interest in the self-healing properties of fiber filled composites, which may be used in concrete and polymer matrices. A system of hollow fibers that contained a reactive fluid that, when subjected to mechanical shock, was discharged and then responded to seal the area's fissures.

On polymer matrices with various fibers, Dry et al. [57] conducted several intriguing self-repair tests. On polymer samples with a continuous metal fiber inserted and two self-repair fibers nearby, one of which contained an epoxy monomer and the other of which had a diamine cross-linking agent, experiments were conducted. In a fiber-pullout test, they first mechanically unbonded the metal fiber without disrupting the fibers that self-repair. At this time, the metal fiber had little to no adherence to the matrix and was easily and gently removable. They then applied sub-critical loads to the composite, which allowed the fluids in the fibers to self-repair. The fluids blended and diffused to the polymer-metal interface and repaired the damage to the interface, leading to a significant gain of the fiber pullout stress. This approach to self-repair is very flexible with regard to the design of fiber, number of fibers, healing fluid, fiber construction, fiber coating and so forth. Matrix solvents could also be used to promote solvent bonding in micro-voids. Thermally induced healing can also be induced by exothermic reactions of the self-repair fluid, either with itself or with components of the composite [58].

It should be taken into account the topography or roughness of the surface and how it varies with time, temperature, and pressure following contact with the healing fluid when the recently damaged surfaces or microvoids are produced in fracture or fatigue. The rate of crack healing in fractured polymers is influenced by changes in fibrillar shape as well as other variables. Chain-end distributions near the surface can change as molecules diffuse back into the bulk. If the chain ends are required for the fluid interaction, they might be made to preferentially migrate to the surface by tilizing moieties with lower surface tension. The molecular weight distribution can also shift spatially, for instance when low molecular weight species migrate to the surface more frequently. Nanoparticles in the bulk could preferentially migrate into nanovoids. In time-release solvents or adhesives, surface rearrangement is affected by the polymer–solvent interaction. Chemical reactions, for example, oxidation and cross-linking can occur on the surface and complicate the dynamics of diffusion. Solvents used in the passive healing experiments could also cause additional damage for example, by causing crazes and microvoids to swell and allow them to propagate further [59]. The critical entanglement molecular weight Mc will also be changed with surface polymer concentration φ in the good solvent as:

$$M_c(\varphi) = M_c(1)\varphi^{-5/4} \tag{1}$$

where $M_c(1)$ is the unperturbed M_c value with $\varphi = 1$. This means that when a compatible healing fluid interacts with the polymer surfaces, the entanglement molecular weight increases.

For polymer–solid interfaces as commonly encountered in composites, surface restructuring dominates the mechanism of adhesion between the polymer and the solid. When a mole fraction of sticker groups f(X) is used to bond the polymer to the surface, an optimal sticker group concentration f*(X) is needed to maximize adhesion while minimizing cohesive failure in the boundary layer adjacent to the solid [60]. When $f < f^*$, adhesive failure dominates, the fracture energy G1c ~ f and the solid separates cleanly from the polymer. When $f > f^*$, cohesive failure occurs in a polymer layer adjacent to the surface and G1c ~ 1/f. The f* value is determined from the entanglement percolation theory to be:

$$f^* = 4j\left(\frac{M_j}{M_c}\right) \tag{2}$$

where M_j is the molecular weight per bond of a random walk chain.

Crack surfaces that are brought together to mend either on their own or with the assistance of the healing fluid are treated using the surface technique. In order to construct the interface at this stage of healing, the various surfaces′ time-dependent contact is taken into account. In composites, where damage may impact the polymer matrix, fibres, and the matrix-fiber interface, the surface approach may be particularly crucial. Healing will be minimal or nonexistent if the fluid that promotes healing only adheres to one surface. The pressure of swelling may also press the surfaces together during the healing process.

5. Damage and Healing Theories

By examining the damage mechanisms, materials can teach us about their own healing processes. Figure 4 illustrates a practical method for calculating the fracture energy G_{1c} of an A-B polymer healing interface [61]. In the double cantilever beam (DCB) system, a crack first forms at the crack tip and then spreads through the interface region. The J-integral approach can be used to calculate the fracture energy for cohesive failure, where G_{1c} is the integral of the traction stresses with crack opening displacements δ, in the cohesive zone after yielding at a local yield or craze stress σ_Y . At a maximum stress value, the cohesive zone at the fracture tip disintegrates by a percolation process (at a maximum stress value, $\sigma_m > \sigma_Y$). The yield stress dominates the fracture process for non-crazing matrices such as thermosets and this is determined by the twinkling fractal theory (TFT). Both σ_m and δ are rate dependent and in the simplest case, the fracture energy is determined by:

$$G_{1c} = \sigma_m \, \delta_m \quad (3)$$

where δ_m is the critical crack opening displacement. Both σ_m and δ_m depend on the damage zone structure and the microscopic deformation mechanisms controlling the percolation fracture process via disentanglement and bond rupture.

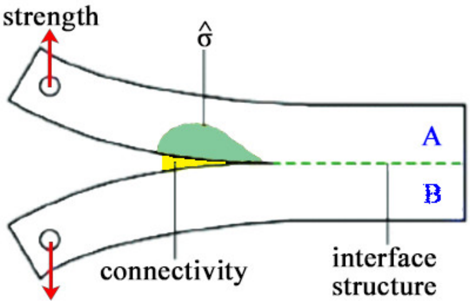


Figure 4. The microscopic entanglement structure [61].

This experiment can be used to understand fracture and healing on any 2D or 3D lattice subject to random bond fracture and with starting tensile modulus E. Microvoids are created by random bond scission, which then grow into larger voids and help a macroscopic break spread across the net at the percolation threshold. The stored elastic strain energy density U, (energy per unit volume), in the lattice due to an applied uniaxial stress σ is determined by:

$$U = \frac{\sigma^2}{2E} \quad (4)$$

In a few recent papers, Boiko et al. [62] examined the connecting of the virgin rather than fragmented surfaces to identify the healing at the PET and PS interfaces. It was demonstrated that even after 15 hours of treatment at 18°C above their T_g, virgin PET/PET and PET/PS joints only suffered minimal adhesion. Yang F et al. [63], studied interfacial healing of carbon-reinforced polyether–ether–ketone (PEEK) and polyether–ketone–ketone (PEKK) under nonisothermal conditions. After different processing times, the strength of the thermally bonded plates was compared with their ultimate shear strength. All of the systems tested reached 100% efficiency and a model was proposed for the non-isothermal healing of the thermoplastic surfaces, but this model appears to be more applicable to polymer processing than repair. Takeda et al. [64], have demonstrated that various technical thermoplastics made through condensation processes, such as polybutylene (PB), polycarbonate (PC), polyether-ketone (PEK), polybutyl terephthalate (PBT), and PEEK, can be treated with a quick response that the chain scission is reversed. The authors observed that the self-healing reaction of this polymer did occur in the solid state, and a series of events was identified prior to and during the healing process. These events include (i) occurrence of chain cleavage due to degradation; (ii) diffusion of oxygen into the polymer materials; (iii) re-combination of the cleaved chain ends by the catalytic redox reaction under oxygen atmosphere and in the presence of copper/amine catalyst; and (iv) water discharge as a result of the self-healing reaction.

Additionally, it was found that when reaction time increases, the speed of the healing response slows down due to a decrease in the mobility of the polymer chain the reaction progresses with an increasing molecular weight and a progressive drop in the amount of hydroxyl (OH) available end groups as the recombination process consumes them.

Several techniques were employed to clarify the self-healing mechanism. These included peel tests, controlled projectile tests, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and a pressurised burst test to measure the healing response.

A common strategy used to observe self-healing by numerous researchers is to observe the healing of crack width [65]. Several works in the technical literature show that crack size is one of the most important factors when dealing with autogenous healing. It was reported in more recent research that larger crack widths of 0.40 mm wide could not be healed, rather incomplete were observed in specimens with 0.40 mm crack width [66]. Thus, as the crack width increases self-healing by autogenous mechanism becomes less effective and complete healing may not be achievable. Despite this, even at narrower crack widths, the healing process can only be partially exploited [67]. Indeed, crack widths within 0.138 mm-0.150 mm were reported to be only partially healed.

The challenge in the design of sel”-healing materials is to create a new composite material with an autonomous or externally stimulated damage-healing capability in order to extend the performance lifetime of the newly developed material or product. Thermal or electrochemical degradation can also be included under this definition. Therefore, it is essential to keep an eye on those changes in order to gauge how well the new composite material will perform. These modifications can also be used to describe the healing process qualitatively or statistically. The new material’s qualities will, in the best case, be on par with or better than those of the original. In order to evaluate the performance of the improved self-healing material, the researcher or engineer should compare it to the virgin, unmodified material [68].

Most of the self-healing systems that are reported in the literature consist of a polymeric matrix and self-healing agents. The most frequently used characterization techniques for these materials are Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). DMA is a widely used technique for materials characterization and it is mostly used to determine the glass transition temperature of the constituent materials and the viscoelastic properties in terms of storage and loss moduli. TGA is commonly used to determine selected characteristics of materials that exhibit either mass gain or loss. Other techniques that are employed in self-healing materials characterization include Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR) and RAMAN spectroscopy. These techniques are widely used for monitoring the self-healing process and will be further discussed in later sections [69–71].

The self-healing concept has also been implemented and achieved for materials with electrical functionality. Such materials are able to recover conduction paths at different scales and most investigations of conductivity recovery in the literature deal with the healing of such conductive paths. In self-healing studies, the Wheatstone bridge setup was employed by Blaiszik et al. [72] to in situ monitor a four-point bending test on samples of microencapsulated metal dispersed in a dielectric medium. On the Wheatstone bridge circuit, the specimen serves as one resistor. Throughout the four-point bend test, the circuit is observed using a Wheatstone bridge with the specimen serving as one of the bridge arms. The performance of the circuit is evaluated by measuring the normalized bridge voltage:

$$V_{norm} = \frac{(V_h - V_\infty)}{(V_o - V_\infty)} \tag{5}$$

where V_o is the bridge voltage before the damage, V_∞ is the bridge voltage measured for a fully broken circuit, and V_h is the instantaneous bridge voltage of the circuit. The value of V_{norm} ranges from zero for a specimen with no electrical conductance to one for a fully conductive specimen. The efficiency of conductivity restoration, ηc, is defined for each specimen as V_{norm} after fracture.

6. Potential Applications of self-Healing Polymer Composites

All materials, whether organic or manufactured, sustain a decrease during use. If the total amount of damage in the area rises above a certain threshold, a component will fail, and the device’s functionality will be lost. Self-healing materials, on the other hand, have the capacity to stop the progression of damage, several times, or even multiple times. As a result, they significantly increase the lifetime and reliability of the material and, by extension, the device (damage management). Such new levels of performance are particularly relevant to materials employed in fields where men have no or limited access, such as medicine and the engineering of the civil, aerospace, automotive, and power sectors. Costs could be greatly reduced by eliminating monitoring and regulating measures if self-healing of damage induced by manufacture or during application can significantly extend the effective lifetime and reliability of future new materials. Additionally, a significant reduction in the previously required safety margins for the constructive geometry of mechanically, thermally, and corrosion-exposed components in practically all technical domains might be expected to result in significant resource and energy savings. Self-healing materials would significantly increase material dependability and change component design and manufacture. Moreover, extending the lifespan of essential components could significantly improve economic efficiency. For instance, the lifespan of stents could be extended, which could significantly lower therapy costs. Other examples of where this could happen include constructions for alternative energy production (wind energy, photovoltaic, solar heat), new lighting applications (e.g., LEDs), or medical implants. In aerospace and automotive engineering, optimized lightweight design combined with higher structural reliability could lower energy costs as well as environmental impact. The enormous application potential of these materials is further demonstrated by Arkema's start-up production of self-healing elastomers and self-healing coatings.

Spacecraft commonly utilize composite materials composed of a polymer matrix reinforced with fibers, including fiber-reinforced plastics (FRPs) reinforced with glass fibers (GFRPs), FRPs reinforced with carbon fibers, and carbon-epoxy fiber-reinforced plastic (CFRP) composites, such as thermosetting epoxy reinforced with high-performance fibers [73]. *Other* matrix composites applied in this context include ceramic matrix composites (CMCs), metal matrix composites (MMCs), and E-glass-epoxy composites (EGCs) [74]. However, these composite materials are susceptible to deterioration caused by impact loads. The impact damage initiates at the microscopic level with the formation of voids, leading to deep microcracking and delamination within the structure. In previous methods, damage repair involved using resin patches, injection, and thermal plate techniques. However, these methods had several drawbacks, including their inefficiency in addressing invisible damages, the need for continuous damage monitoring, and their limited applicability during construction operations. Additionally, the resulting material often differed from the individual components and lacked a proven track record. Consequently, the use of composites in aircraft components was restricted due to their demanding maintenance requirements.

Since they have been a subject for almost ten years, self-healing materials research spans many academic disciplines and employs a wide range of methodologies. Some of the concepts developed are driven by the direct application of the materials. However, to gain a deeper understanding of the basic mechanisms and principles of self-healing materials is still a challenging aim. Nature has mostly served as an inspiration for the development of new self-healing materials, and it will undoubtedly continue to be a significant source of inspiration for the creation of novel ideas. The intrinsic nature of engineered materials must be considered while reproducing the model, though [75–77]. Following the repair or restoration of mechanical damages, the mechanical qualities are (partially) recovered. However, there are still obstacles to overcome, such as the need to create self-healing materials that can recover from mechanical damage and other adverse influences like intense light and heat while also regaining conductivity and color. The well-established microcapsule concept could be successfully used to release a charge-transfer salt as a "healing agent" to restore conductivity [78]. Nanostructured systems, such as photonic nanomaterials and metamaterials, also face difficulties. These systems' high surface area concerning volume makes them especially vulnerable to damage.

In addition to the hollow fiber and microencapsulation techniques that have received the most research, technologies that use thermally triggered healing (such as molecular thermally reversible crosslinks, interdiffusion, and thermoplastic additives) offer a new route for the development of self-healing polymers among other people. These innovations have a bigger potential to offer numerous healing capabilities. Current developments are moving towards the development and optimization of microvascular healing agent delivery networks and healing agent-filled capsules that may be used in conjunction with these microvascular networks. In reviewing recent developments of self-healing polymeric materials, it is evident that significant advancements have been made toward the production of genuinely self-healing materials suitable for structural and other commercial applications.

The adaptability of polymeric materials allows them to serve as self-healing agents across a wide range of applications, from rigid to flexible uses. Various forms of polymeric materials, including pure polymers, polymer composites, and hydrogels, can be harnessed for self-healing purposes. The self-healing mechanism has demonstrated significant enhancements in crack properties. Nonetheless, there remain challenges in developing an ideal self-healing system. Future advancements are anticipated to explore emerging polymeric materials and various self-healing mechanisms for the efficient development of self-healing materials. Future developments in the field of self-healing will probably consider biomimetic materials, especially those having complex molecular aggregates made of amino acid sequences. Large ensembles of these supramolecular protein-like structures that interact with one another will be able to respond to external stress in a way that lessens the trauma and then self-assemble back to the original form. It should be feasible to work with novel materials made of folded proteins, for example, which would partially unfold as a way of collecting mechanical energy and then refold and self-heal, just like in the case of self-healing nanobeams.

7. Conclusions

In this review, the classification of repair systems based on recent advancements in self-healing science, with a particular focus on self-healing in composite structures is reported. Two main perspectives exist for classifying self-healing systems. The first viewpoint is based on the classification of intrinsic and non-intrinsic repair. The second classification is centred on the repair method, categorizing self-healing into three major types: microcapsules, vascular network, and intrinsic. Subsequently, an attempt is performed to assess repair performance across various mechanical properties, including repair capability and efficiency.

Additionally, the review investigates the growing trend of research in self-healing materials, examining the number of international documents published in this field, active researchers, and the role of different scientific disciplines in the development of self-healing technologies. The primary objective of this research is to delve into recent advances with a specific emphasis on the application of self-healing materials in polymer-based composites.

In all three methods mentioned, the repair agent is housed within a compartment inside the composite structure. When a crack reaches this area, the compartment breaks, releasing the repair agent and facilitating repair at the crack tip. Each method has unique characteristics and advantages. Microcapsule-based self-healing stands out for its uniform distribution and ease of design in composite structures compared to the other non-intrinsic methods.

The review also investigates factors influencing the performance of each healing system and the choice of system type. Regarding the encapsulation method commonly uses formaldehyde-based polymers such as urea–formaldehyde as the repair agent, while various materials have been employed, research indicates that, in many cases, using the base polymer as a repair agent is more suitable than other materials for repairing the base.

Author Contributions: All authors have read and agreed to the published version of the manuscript.

Funding: “This research received no external funding”.

Conflicts of Interest: The authors declare no conflicts of interest.

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