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Review
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# An extensive review of the repair behavior of smart self-healing polymer matrix composites

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**Self-healing material is a material that repairs microcracks spontaneously without any external interference. Based on self-healing methods, there are two main categories for these smart materials such as intrinsic and non-intrinsic. In the intrinsic repairing system, the repair is done in the form of physical, chemical, and supermolecular reactions. In the non-intrinsic system, the factor of repair is stored inside compartments such as hollow fibers, microvascular networks, and microcapsules. The current research tries to investigate the recent developments in the field of non-intrinsic repair systems with an emphasis on their use in polymer composites, especially during the years 2009 until now. In this review, the need for composite repair, the concept of self-healing, a variety of non-intrinsic repair methods, evaluation of repair performance in various mechanical tests, and also statistical reports and evolution related to self-healing have been presented.**

## Introduction

Today, polymer matrix composites have found a very special place in various industries such as aviation, marine, transportation, and mining industries during the last decade due to their unique properties such as high strength-to-weight ratio [1–5]. These composites consist of a polymer base and one or more polymer, ceramic, or metal reinforcements [6]. Among the most widely used polymer matrix composites are fiber-reinforced composites, fiber-metal multilayers, sandwich panels, and hybrid and multi-scale structures that have found and developed a very special place in various industries [7, 8]. It is worth noting that brittle polymers and composite structures made from them are prone to microcracks in their structure when subjected to continuous thermomechanical loading [9]. In the following, these microcracks will join together and cause lamination in composite structures. Extensive studies have been done to predict the damage and the methods to fix them [10]. Generally, it is impossible to determine these microcracks at the beginning of their appearance, and it will be possible to detect them only after the progress of the crack in the structure, and at this stage, it is almost impossible to repair the damage [11, 12]. Self-healing materials were first noticed in the 1970s to evaluate and inform the behavior of elastomeric fillers used in rockets for space missions [13]. At that time, it was observed that crack growth in these elastomers can be repaired by removing the load and passing time [14–17]. Further studies in the late 1980s and early 1990s revealed the self-healing ability of thermoplastic polymers [18]. At that time, it was observed that in polymers such as polymethyl methacrylate, by increasing the temperature above the glass transition temperature, the created crack is completely repaired. Self-healing composites have a high potential to solve limiting problems such as microcracks and hidden cracks in polymer materials [19]. When the repair agent is inside the base material, the need for inspection or any external interference is minimized [20]. In Fig. 1, you can see the types of damage caused to polymer materials and polymer composites [21]. Krishnan et al. [22] extracted collagen from marine waste i.e., Sole fish skin. Their results indicated a significant interaction of all the selected variables over collagen extraction process. Scanning electron microscopy observation revealed that the extracted collagen was in the form of fibrils with irregular linkages. Sharma et al. [23] synthesized Silver nanowires using hydrothermal method. They investigated some parameters such as the effect of process temperature, $AgNO_3$ molarity, PVP, and fructose concentration influencing the synthesis of silver nanowires. Their article gives a green

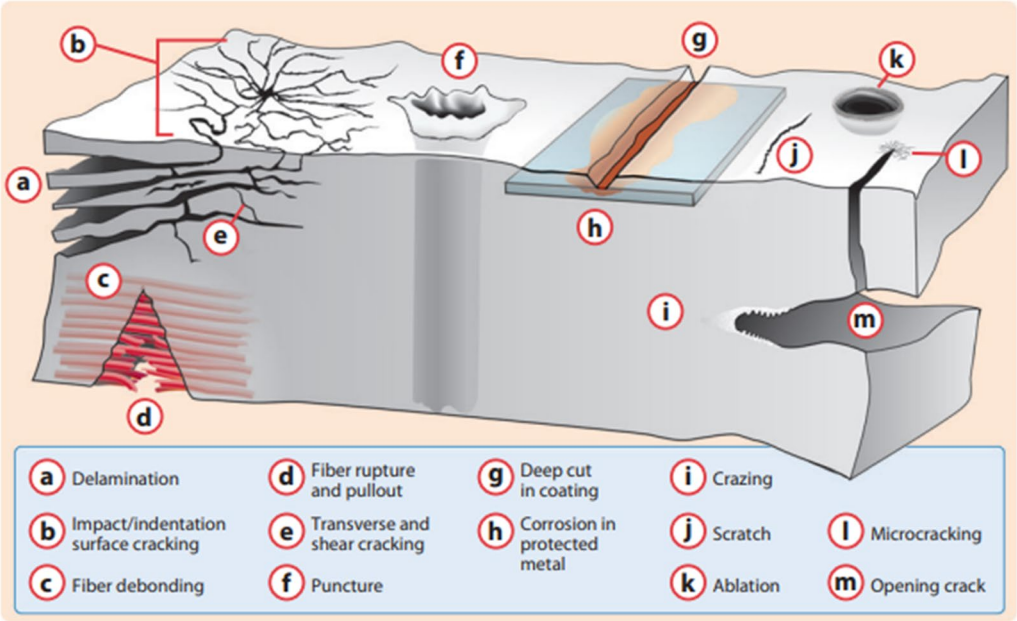


**Figure 1:** Damage modes in polymer composites and PMCs.

approach to the hydrothermal synthesis of Ag NWs using fructose with a promising antibacterial and antioxidant properties.

Therefore, increasing the lifespan and ensuring the performance of parts in the medical industry, space missions, public transport fleet, and civil facilities is very important [24]. For example, the creation of composite materials that can resist mechanical damage or corrosion and repair it in case of damage has received a lot of attention [25]. The use of self-healing materials in different branches of material science, polymer, and mechanics has been a growing trend. In such a way, they have also found industrial use [26]. Among them, self-healing coatings can be mentioned [27–31]. For example, in the automotive industry, Nissan company [21] has introduced a self-healing coating for car surfaces commercially for the first time in the world. The brand name of this product is anti-scratch coating. According to the depth of the scratch and temperature, full recovery takes 1 to 7 days [21]. Another application of self-healing materials is in medicine. Biocompatible self-healing composite is another application of self-healing materials that can increase the working life of artificial bone, artificial teeth, and other artificial components used in the body [32]. Using of self-healing materials in the manufacture of self-healing tires is also one of the commercialized applications of these smart materials [33]. Another application of these smart materials is in smart composite structures that continue to grow for commercialization in various industries, especially aerospace [34]. The search results in the available research sources show that self-healing materials and structures have occupied a large part of the world's research [35]. The diverse applications of these materials have made industrial countries make large investments in this sector. Considering that the subject of self-healing is one of the new topic and not much time has passed since the research on it, Iran can also find its place among the top countries in the world in the field of self-healing materials by having a proper program in this field. In this report, a comprehensive review of the available information in the field of non-intrinsic self-healing materials and structures in composite industries has been done. And while introducing research projects in this field comprehensively, it has been tried to investigate repair methods in polymer matrix composites. Also, research projects done on self-healing composites inside the country have been collected and analyzed to get a general overview of the progress of the self-healing science in composite structures.

## Definition of self-healing property

The term self-healing in material science means the spontaneous recovery of the initial properties of the material after damage by an external factor [36]. Theoretically, this term is an intelligent system that can release restorative factors under the attack of a destructive agent, in such a way that it regains its physical integrity and mechanical strength after damage [37]. The repair process depends on the rate of all three stages of setup, displacement, and repair. Therefore, the effect of restoration is achieved by the balance between the restoration rate and the damage rate, and it is equal to the total time of the three mentioned stages [38]. The damage rate for material is determined by external

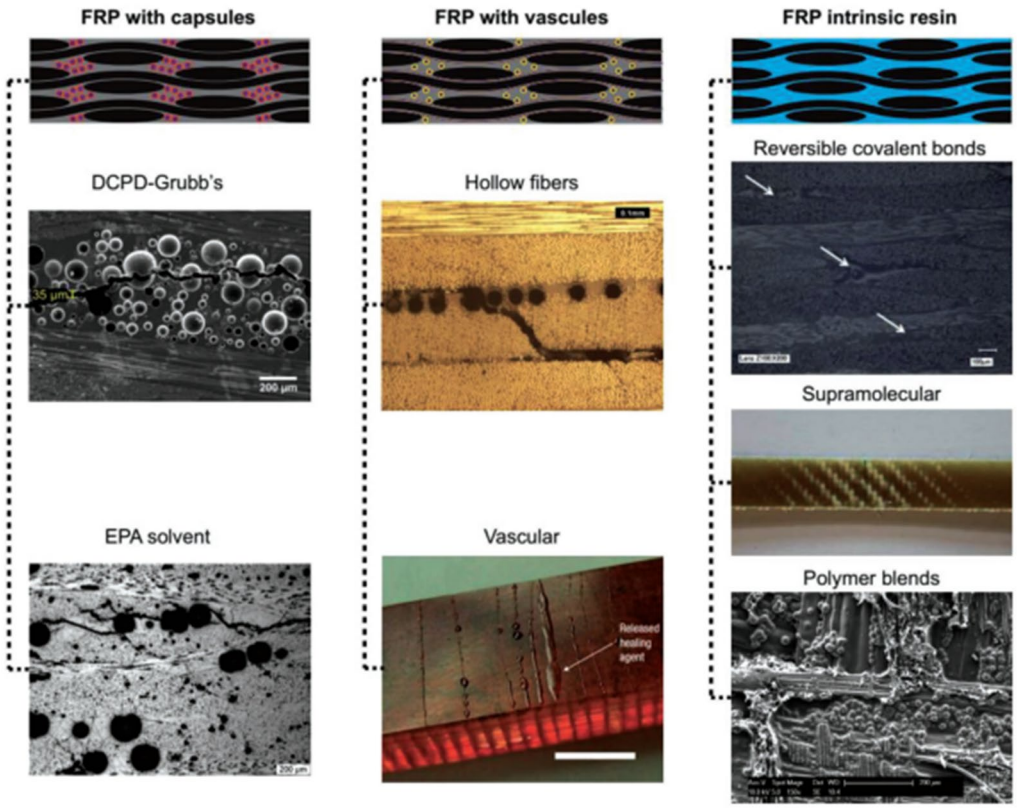


**Figure 2:** Classes of self-healing systems within structural polymer composites.

factors such as load frequency, strain rate, and stress amplitude and magnitude [39]. However, the healing rate can be adjusted for specific damage modes. The classification of self-healing polymer composites based on the mechanism of repair includes two types such as non-intrinsic self-healing [39]. The term intrinsic self-healing is based on its specific function in the ability to repair cracks spontaneously, by a specific stimulus, and without the intervention of an external factor [40]. Intrinsic self-healing method according to the dominant molecular mechanisms that are involved in the healing process is divided into two categories: methods based on physical reactions such as the distribution of thermoplastic material in the base and supramolecular materials with the ability to repair due to the application of mechanical force and methods based on chemical reactions such as reversible reactions, repair through molecular penetration, and repair due to ionic reactions [41]. In non-intrinsic self-healing methods, healing does not happen spontaneously. Rather, in this method, the repair agent is stored in a tank in such a way that after the surface damage, it can be released and can repair the damage in the vicinity of the catalyst. New research shows that the self-healing systems of polymers and polymer matrix composites can also be classified based on the form of repair, which includes intrinsic self-healing, self-healing with microcapsules, and self-healing with the use of microvessels. Figure 2 shows this classification system [42]. Self-healing polymeric materials are generally classified into two distinct groups, intrinsic and extrinsic (further classified as capsules and vascules), according to their method of incorporation. Those categories include further subcategories, which are detailed with some examples in Fig. 2.

## Evaluation of repair performance

The purpose of self-healing is to restore the desired properties that have been lost or reduced due to damage in the material [43]. The complete filling of the damage and the re-formation of the connections around the damage can restore the fracture properties of the object, and in addition to fracture properties, other material properties can be improved after repair [44]. The amount of damage depends on the loading conditions, geometry, and properties of the undamaged object. Figure 3 shows the repair efficiency and the calculated parameters for different mechanical behaviors [45]. For the successful study of the performance of a material for self-healing applications, we need to quantify this characteristic. Therefore, healing efficiency calculations are done to estimate the behavior of the material. Healing efficiency is calculated based on various ratios of the physical properties of the material after healing and before damage. The different parameters considered in calculating the

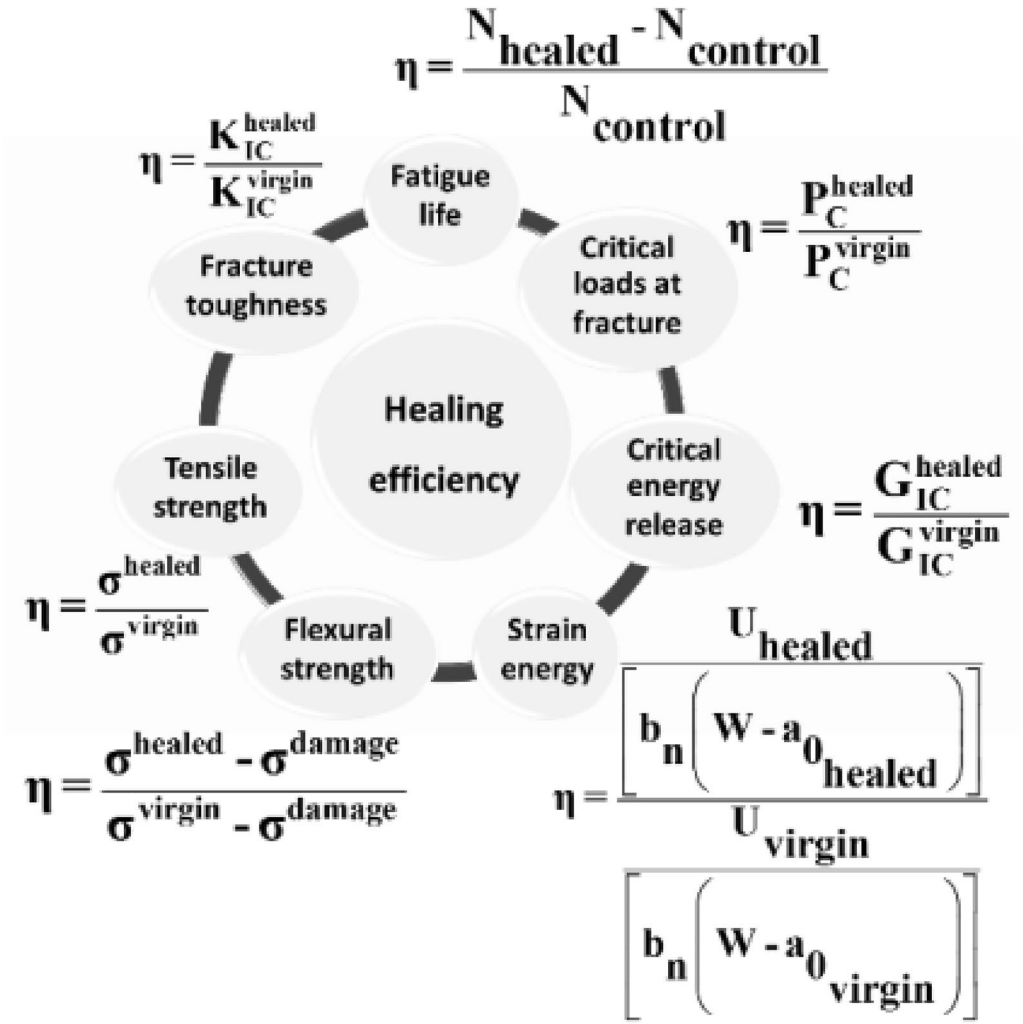


**Figure 3:** Different methods of calculation of repair efficiency.

mechanical healing efficiency are fracture toughness, fatigue life, tensile strength, etc., summarized in Fig. 3. One of the main limitations of self-healing matrix coatings is that their self-healing ability depends on temperature and might hence be ineffective inside some temperature ranges. Also there are some limitation and disadvantages for using self-healing matrices as follows:

Increased manufacturing complexity, significant degradation of baseline mechanical performance, limited damage volumes, single use at any one location, with residual voidage after rupture, and 2D/3D networks can significantly degrade baseline mechanical performance.

Table 1 shows the parameters for calculating the repair efficiency for various mechanical properties.

Table 2 provide summaries of the development of the self-healing polymers method as follows:

Figure 4 shows the overall capability of the repair methods (based on the calculation of the repair efficiency to the damage volume and the ratio of the repair rate to the damage rate) [21]. The ultimate goal of any repair method is to achieve 100% restoration efficiency. However, according to Fig. 4(a), the range of damage is different for each type of repair method [51]. Based on Fig. 4, the results of the comparison between the repair capability and efficiency of different self-healing systems show that the intrinsic systems have the lowest volume of repair because the repair is done on a molecular scale. Vascular systems can cover a larger destroyed volume, and capsular systems are placed between intrinsic and microvascular systems in terms of the level of coverage of the damaged area. Also, in all systems, the ratio of the speed of restoration to destruction is low. In an optimal repair, the speed of repair is proportional to the speed of destruction, and an acceptable volume of damaged areas can be repaired many times. Regardless of the type of self-healing system, the intelligent use of these materials in various industries can have satisfactory results in reducing costs, energy, and increasing safety.

**TABLE 1:** Introduction of parameters for calculation of repair efficiency for various mechanical properties.

| Parameters | Symbol |
|---|---|
| The fracture toughness of the repaired sample | $K_{IC}^{healed}$ |
| Fracture toughness of undamaged sample | $K_{IC}^{virgin}$ |
| Critical failure load of repaired specimen | $P_C^{healed}$ |
| The critical failure load of the specimen without damage | $P_C^{virgin}$ |
| Critical energy release rate of repaired sample | $G_{IC}^{healed}$ |
| The critical energy release rate of the sample without damage | $G_{IC}^{virgin}$ |
| Strain energy of the repaired sample | $U_{healed}$ |
| Strain energy of the sample without damage | $U_{virgin}$ |
| Distance from the load line to the end of the sample | $W$ |
| The width of the created crack surface | $b_n$ |
| The initial pre-crack length of the repaired specimen | $a_{0healed}$ |
| The strength of the repaired sample | $\sigma_{healed}$ |
| Sample strength without damage | $\sigma_{virgin}$ |
| Strength of the damaged sample | $\sigma_{damage}$ |
| Number of cycles to failure of the repaired sample | $N_{healed}$ |
| Number of cycles to sample failure without repair | $N_{Control}$ |

## Statistical reports related to self-healing

By searching among the information sources, various fields related to self-healing composites were identified. These composites include a variety of polymer bases and metal and ceramic bases. This information is based on the number of articles related to self-healing composites, ranking of countries, Active researchers, Classification of different sciences in the field of these composites, and the type of documents published in (2009–2022), which are shown in Figs. 5, 6, 7, and 8, respectively. According to Fig. 5, it can be understood that the number of published documents is growing, so it can be predicted that this growing trend will continue at a faster rate at the end of 2022. Figure 6 shows the leading countries in the field of self-healing composites, which respectively, the first to third place is assigned to the countries of China, America, and England.

Figure 6 introduces active researchers in the field of self-healing composites. According to this figure, Zhang, Rong, and Bond are the most active researchers in the field of self-healing composites.

Figure 7 shows the share of sciences associated with self-healing composites, where the fields of materials, engineering (in general), and polymer have the highest share.

In Fig. 8, you can see the type of published documents about self-healing composites. As expected, the most published document is in the form of an article.

## Types of composite structure repair methods based on non-intrinsic methods

Microcrack and crack formation and propagation are important aspects to be studied in materials. This is due to the material's capability to withstand stress without failure during application, which is highly related to it. For polymer composite material, due to the different properties of the reinforcement and the matrix, the topic of study becomes more complicated. Most polymer composites are subjected to mechanical loadings and environmental factors during fabrication, storage, and service. As a consequence, microcracks may be formed in the composites during static, dynamic, fatigue cyclic loading of different types, such as tension, compression, and shear. Exposure to variable environmental conditions such as temperature, moisture, chemicals, and radiation also causes the formation and propagation of microcracks. Polymer composites subjected to synergistic effects of mechanical loading and environmental exposure usually are more susceptible to microcrack formation and propagation. Microcracks in the polymer composites immediately instead of microcracking in the polymer composites immediately causes-deterioration of the thermomechanical properties and it also serves as initiator to other forms of damage, induces delamination and fiber-matrix interfacial debonding, and causes fiber fracture, providing pathways for entry of moisture, oxygen, and other corrosive liquid. Thus, microcracks can ultimately lead to

**TABLE 2:** Development of the self-healing polymers.

| Host matrix | Healing type | Healing method | First report of method | Best efficiency achieved | Test method | Healing conditions |
|---|---|---|---|---|---|---|
| Thermoset composites | Structural | Microencapsulation approach | 2001 | 80% [46] | Fracture toughness | 48 h at 80 °C |
| | | | | 19% [47] | Tensile strength | 24 h at Ambient then 24 h at 80 °C |
| | | Thermoplastic additives | 1999 | 100% [48] | Flexure strength | 10 min at 120 °C |
| | | | | | Tensile strength | 10 min at 120 °C |
| | | | | 30% [49] | Visual | 2 h at 130 °C |
| | | Hollow-fiber Approach | 1996 | 93% [50] | Flexure strength | 24 h at Ambient |

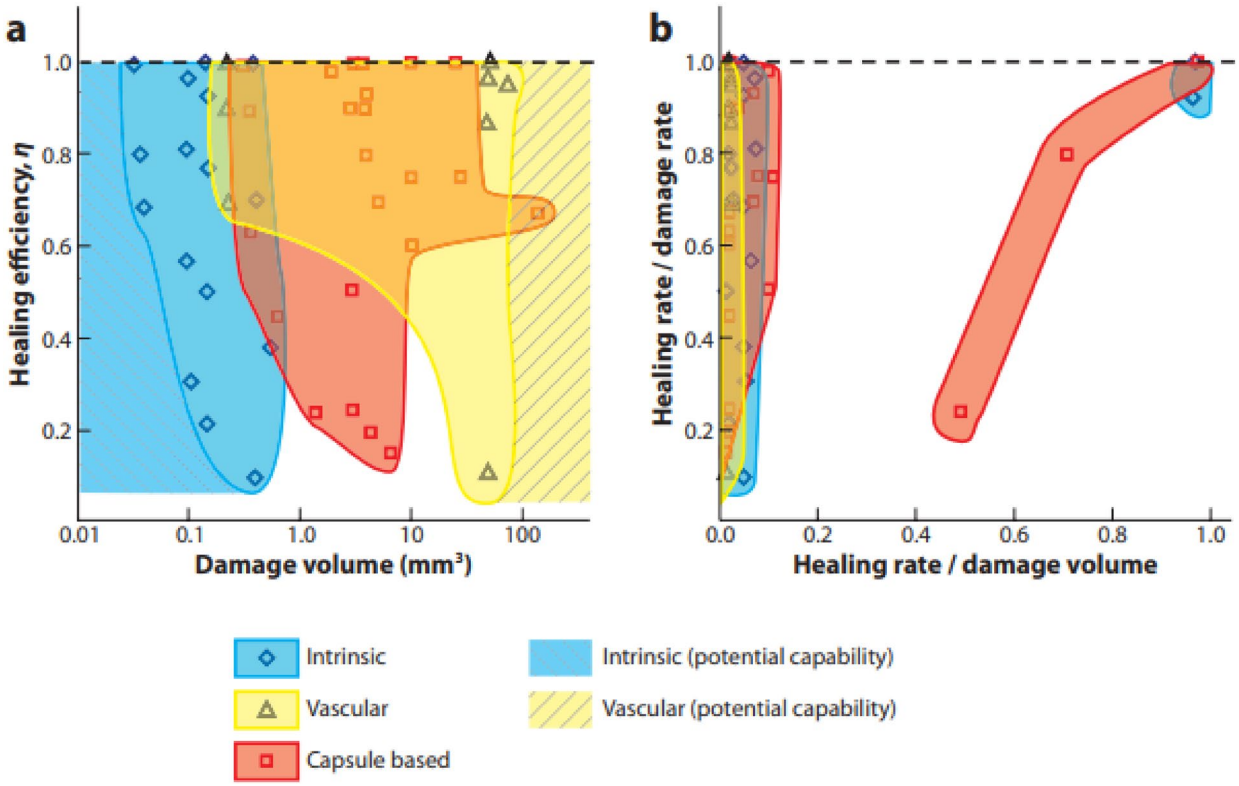


**Figure 4:** Efficiency maps for self-healing materials.

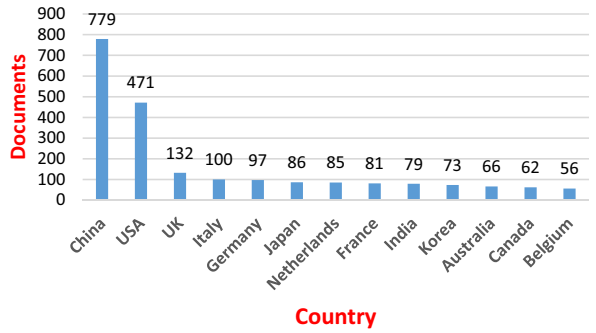


**Figure 5:** International printed papers in the field of self-healing composites by different countries.

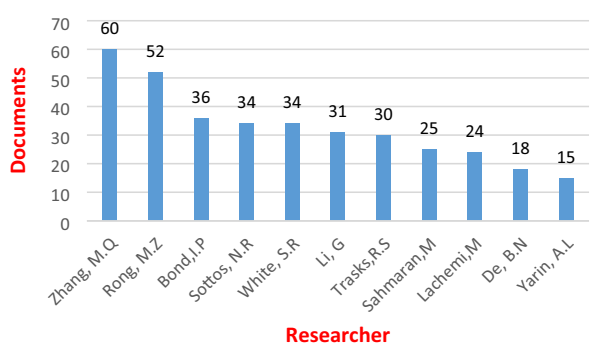


**Figure 6:** International published articles by different researchers in the area of self-healing composites.

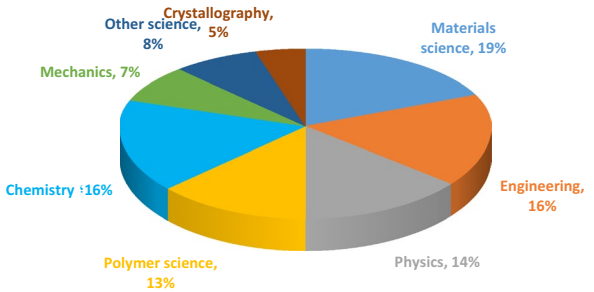


**Figure 7:** Variety of sciences associated with self-healing composites.

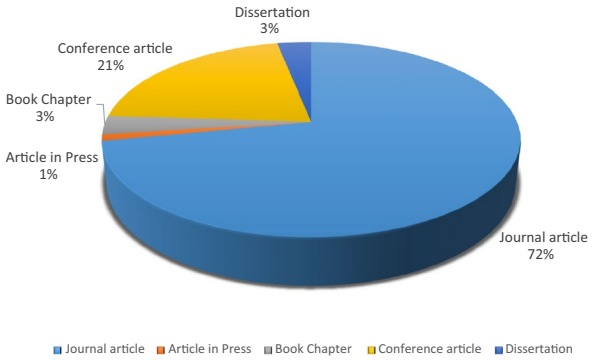


**Figure 8:** Published articles related to self-healing composites.

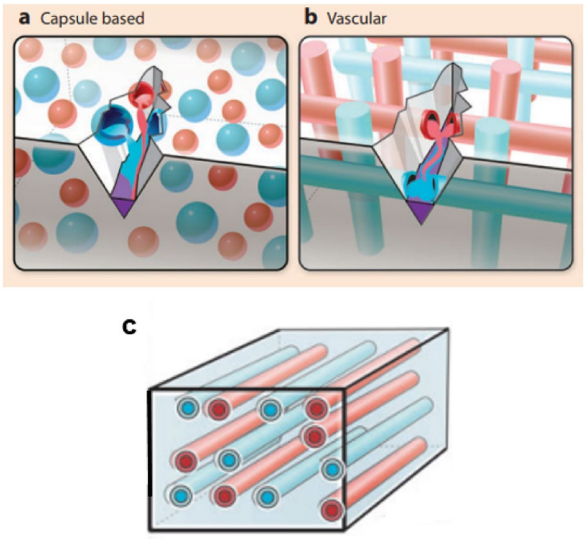


**Figure 9:** Approaches to self-healing include (a) capsule-based, (b) vascular, and (c) intrinsic methods.

overall material degradation and affect the long-term durability of the polymer composites materials.

Despite the nascent nature of the idea of non-intrinsic self-healing polymer composites, various methods have been introduced to create these composites [52]. The repair methods used in polymer matrix composites in a non-intrinsic way are very similar to the methods used in the repair of polymers. In all these methods, the repair agent is stored in a tank in such a way it can be discharged in the form of microcracks after the damage, so that it can repair the composite damage directly or with the help of a catalyst [27, 28, 53]. In general, non-intrinsic repair methods in self-healing composites can be classified in the form of methods of encapsulating the repair agent, using hollow fibers, and creating microvascular networks (Fig. 9) [21]. In the encapsulation method, the repair agent is placed in a ceramic coating such as silica or a polymer such as urea–formaldehyde. In the hollow fiber method, the repair agent is injected into hollow fibers made of polymer, ceramic, or metal [54]. Investigations show that in the microvascular network method, both of the above methods can be used to fill the repair agent. For example, by using a 3D printer, a microvascular network is first made of hollow fibers and then filled with a repair agent. While in the manufacturing method by electrospinning, the repair agent along with another polymer is continuously discharged from a syringe with a micron diameter and due to the evaporation of the solvent, the polymer is placed on the surface of the repair agent as a polymer coating. Finally, the micro-anode network is obtained in the form of microfibers containing the repair agent [55, 56]. Finally, the microvascular network will be appearing in the form of microfibers containing the repair agent. To examine more precisely and express the characteristics and differences of each of the mentioned methods, in the following, the evolution of the research conducted on various non-intrinsic self-healing methods has been examined [57]. Each of the self-healing methods, including intrinsic and non-intrinsic, has advantages and disadvantages, therefore choosing which method is better depends on various factors. In general, the advantage of the intrinsic method is that it does not require separate agents, and for this reason, it makes the repair process easier, but depending on the type of materials and the repair mechanism, it will not always be possible. The formation of chemical bonds (primary or secondary) and physical interactions between crack surfaces (adhesion, moisture) are successful examples of spontaneous repair in this way, provided that the crack width is less than a certain value. Based on Fig. 4, the intrinsic systems have the smallest volume of repair, because the repair is done on a molecular scale. Also, the speed of repair is higher in non-intrinsic systems.

## The evolution of the hollow fiber repair method

For the first time in 1991, Dry [58] investigated the repair of damage to building components using a chemical repair agent stored in hollow fibers. At first, He used this method only in cement materials, crack repair, and erosion prevention and as a sensor. But later, the use of this method in polymer materials was also developed. In 1999, Motuku et al. [59] investigated the response of self-healing composite sheets under low-speed impact. The studied composite samples included hollow fibers (as a self-healing reservoir) in two different types of epoxy and vinyl ester substrates. In this research, the effect of various factors such as the type of hollow fibers (glass, aluminum, and copper fibers), the number and spatial distribution of these fibers, and the type of repair agent were investigated. Among the types of hollow fibers examined, glass fibers showed better performance than aluminum and copper fibers for two reasons. Placing hollow glass fibers in the polymer base does not have a negative effect on the mechanical strength of the sheet. Also, glass fibers break at lower energy levels than other materials and by creating very small cracks in the sheet. The results showed that the amount and spatial allocation of hollow fibers affect the microstructure and mechanical reaction of self-healing layers. Motuku et al. [59] stated that increasing the distance between hollow fibers and using fibers with a smaller diameter can partially prevent the creation of cavities between fibers during the production process. During 2005–2009, research continued on the production of self-healing composites based on hollow fibers. The researchers suggested that hollow fibers containing an epoxy-based self-healing agent and ultraviolet detector dye can be used simultaneously to strengthen the composite structure, self-repair, and identify the location of

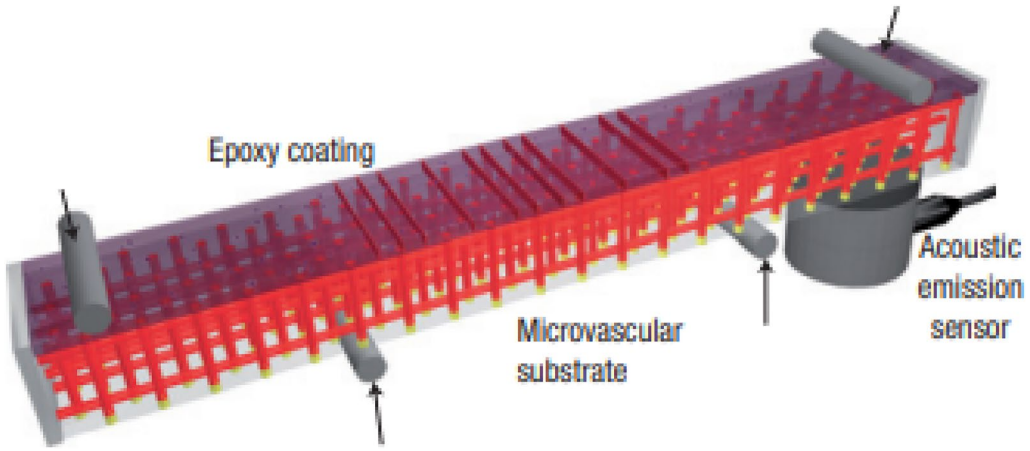


**Figure 10:** Schematic diagram of the self-healing structure composed of a microvascular substrate.

damage to the unit. The idea presented in this research is the feasibility of using self-healing systems for specific engineering applications (such as aerospace applications) by changing the chemistry of the self-healing agent and the number and location of hollow fibers among the composite layers. In another study, Pang and Bond [50] used hollow glass fibers with an external diameter of 60 μm and 50% empty space to store the self-healing material. Unidirectional hollow glass fibers were embedded in an epoxy/E-type glass fiber sheet. Epoxy resin and hardener were also used as restoration materials. Hollow fibers filled with these two materials were placed in the composite with 0 and 90 degrees angles. A 4-point bending test was used to check the restoration behavior. The reported results showed a 93% recovery of flexural strength. In 2010, Kousourakis and Mouritz [60] conducted a laboratory evaluation of the effect of hollow glass fibers on the mechanical properties of epoxy-carbon fiber composites. In this research, the aim was to design and improve the properties of hollow fibers in the composite for use in self-healing applications. Therefore, the hollow fibers were not filled with the repair agent, but the effect of the diameter of the fibers and the orientation of the fibers on the mechanical properties of the composite was investigated. The results of their research showed that the tensile and compressive properties of the composite do not change much in the case where the loading direction is parallel to the fibers. But in the case of loading in the direction perpendicular to the fibers with a large diameter (more than 200 μm), the strength of the parts decreases to some extent. The preliminary results showed that the presence of hollow glass fibers reduced the bending strength by 16% compared to the sample without hollow glass fibers. In this research, the repair efficiency was reported for restoring flexural strength to be 87%. In 2008, Tomizuka [61] investigated the feasibility of using epoxy-based composite sheets containing crushed glass fibers containing an epoxy repair agent in the manufacture of aircraft parts. Different types of glass fibers with different placements and different types of two-component repair agents were investigated in this research. The composite sheets were subjected to the autoclave process, which is a common process in the manufacture of aircraft composite components. The efficiency of self-healing was investigated using the impact test and the bending strength test. The results showed the 85% efficiency of the repair system in recovering bending strength and performing the repair process in less than 1 min. In 2014, Kling and Czigány [62] studied about self-healing in epoxy-based composites reinforced with hollow glass fibers. H-type glass fibers with an outer diameter of 10–12 μm and an inner diameter of 5–6 μm were filled with polyester resin repair agent. In addition to the repair agent, a type of UV detector dye was also stored in the hollow fibers. The efficiency of the self-healing system was evaluated using the impact test, and the results of the bending test after the repair showed a 20% improvement in properties compared to the undamaged sample.

## The evolution of the microvascular network repair method

In 2007, Toohey et al. [63] designed the first microvascular system. In this system, they used dicyclopentadiene as a repairing agent and Grubbs as a catalyst. The system consisted of applying a 700-micron catalytic coating on the microvessel substrate, and its 200-micron channels were filled and sealed with a repair agent. Figure 10 [63] shows the system designed by these researchers including the epoxy-microvascular network.

They found that by increasing the amount of catalyst, it is possible to achieve more regeneration cycles so that for the sample containing 10% catalyst, they achieved 7 regeneration cycles. But this increase in the amount of catalyst does not have much

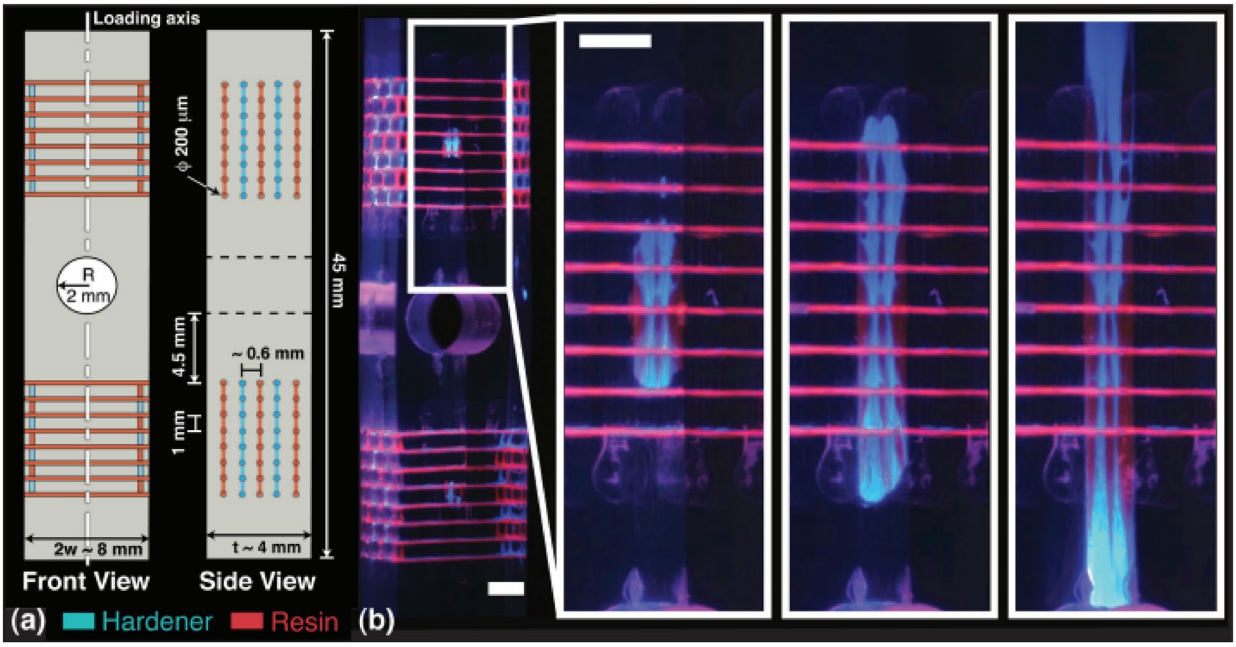


**Figure 11:** (a) Microvascular double cleavage drilled compression specimen, (b) evolution of healing agents released into the crack plane of a fractured double cleavage drilled compression specimen.

effect on the recovery efficiency of a sample during multiple cycles. On the other hand, they found that by increasing the percentage of the catalyst, a larger fraction of the damage site is covered by the repair agent, and after repeating the repair cycles, the crack edges are completely covered. And, the coarser the catalyst particles are, the greater the surface coverage of the damaged area. The maximum restoration efficiency of this system is reported to be around 70%. Following the previous research, Toohey et al. [63] performed self-healing tests based on a microvascular network. The basis of the design of the microvascular network used in this research was to increase the possibility of the repair agent reaching the damage site compared to the previous research so that the repair agent inside the microvascular network and the catalyst agent were distributed directly in the composite field. In the research conducted by Hamilton et al. [64], epoxy resin restoration samples containing channels with a diameter of 200 microns were tested. These channels were fed separately with epoxy resin and curing agent. In this research, the capability of multiple repairs of the designed system was investigated, which is introduced as the number of repair cycles. The prepared samples were subjected to the tensile test of two split ends, and with the progress of the crack and the failure of the microchannels, the repair agent flowed into the damaged area, which is well shown in Fig. 11 [64] using fluorescent colors. In the research conducted, the evaluation of the repair behavior was considered in terms of the fracture toughness of the sample after repair, so that in the first repair cycle, the average repair efficiency was 86% and its maximum value was 120%. In this research, surface viscosity was an important parameter that was investigated in the gradual closing of microchannels, which resulted in the lack of complete surface coverage by the repair agent. In research conducted by Fifo et al. [65] on the composite with glass fibers, the self-healing behavior of this composite was investigated under three-point bending loading. In this research, a microvascular network with a diameter of 400 microns was designed based on preventing the reduction of the effective volume of the composite and increasing the effect of fiber reinforcement. To create damage and evaluate the repair efficiency, initial damage was created in the form of a groove on the samples, and the samples were subjected to a three-point bending test. Upon reaching a 30% reduction in the load–displacement curve, the test was stopped and the samples were kept at ambient temperature for 24 h to be repaired by the polyester agent and its catalyst as a repair agent. The results of the restoration showed an 84% recovery in flexural strength.

One of the goals of this research was to investigate the effect of reducing the viscosity of the repair agent, which increased the penetration of the repair agent to the damage site and decreased the strength of the bonds. On the other hand, breaking glass fibers during loading were an inevitable thing, which caused a decrease in repair efficiency (due to lack of complete connection after the repair process). In a research done by Coope [66], a study was done on the effect of the amount of solvent and catalyst at different temperatures. In this research, epoxy resin and ethyl phenylacetate solvent along with glass fibers were used as composite ingredients. Various metal catalysts were also

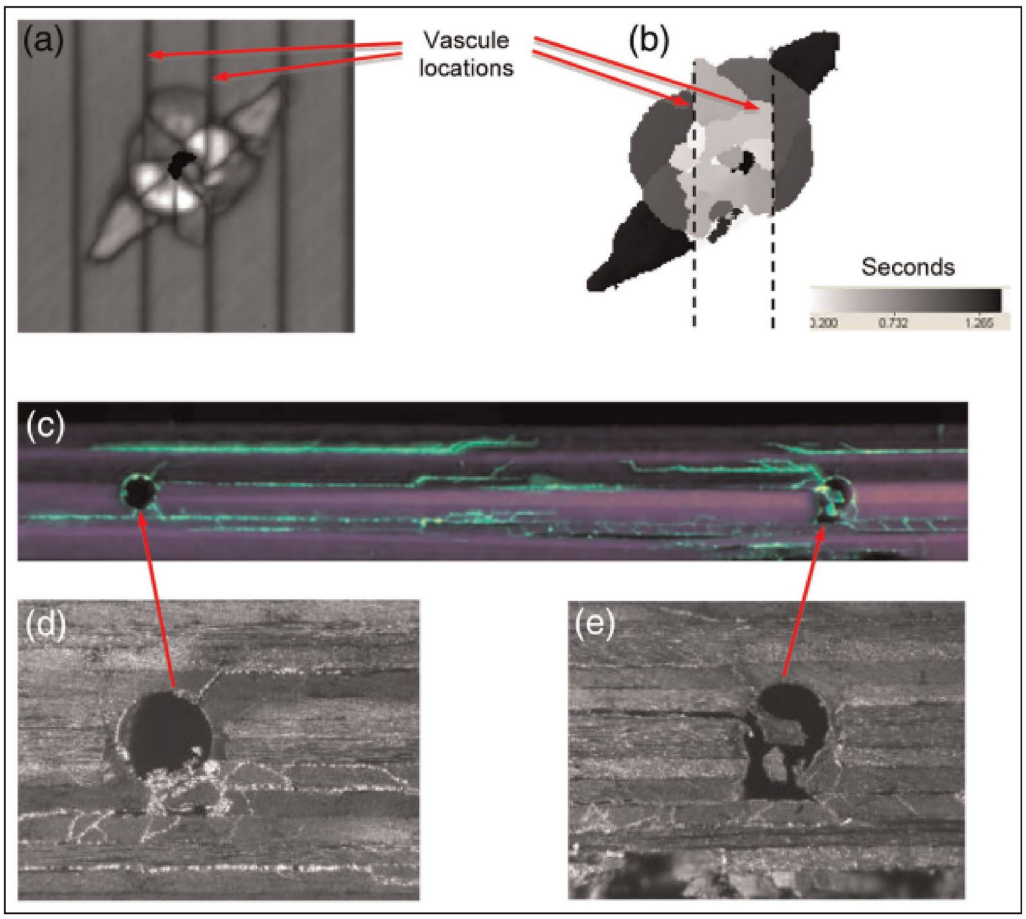


**Figure 12:** Impact damage characterization, (a) ultrasonic scan image of the vascular network and damage profile, (b) ultrasonic scan image of the damage site, (c) optical microscopy under UV illumination illustrating the infusion paths through the damage site, (d) and (e) optical microscopy at higher magnification illustrating the impact damage–vascular interaction.

tested for investigation. The microvascular network used in this research had a diameter of 500 microns, which were created in the direction of the fibers inside the composite. The results of this research indicated that assuming a constant amount of catalyst and increasing the amount of solvent, the starting temperature of composite curing decreased. Figure 12 [67] shows the location of the vascular network, the way damage is caused by impact and the penetration of the repair agent to the damage site. The intended goals of this experiment were to investigate the effect of the diameter of the network and its location in the composite, in such a way that two diameters of 250 and 500 microns were used for the microvascular network between the fibers and in the form of a nest in the direction of the fibers. On the other hand, the location of the network was symmetrical and asymmetrical. The results of this research indicated that with the increase in the diameter of the microvascular network, due to the increase in the contact surface of the network with the fibers and the increase in the possibility of damage to the channels, the repair efficiency has increased. On the other hand, by increasing the diameter of the channel, the necessary force for the removal of the repair material and its penetration into the damaged area was provided.

Increasing the diameter of the channel had a significant effect on repairing damaged areas. In examining the network position in the composite, it was found that the samples with the microvascular network in the center performed a better healing behavior. Because by placing it in the center, the probability of damage to the network increases, and the repair efficiency increases. The average repair efficiency in this research was reported to be more than 96%, which indicates the effective fluidity of the repair agent to reach and penetrate the damaged area and the proper connection of the damage and the microvascular network. In another study of the same research group, the independent release of the repair agent was done by three different methods. Carbon fiber-reinforced composite and RT151 restorative agent were used, and the vascular network was created by pulling out a metal wire with a diameter of 500 microns. To create damage and investigate the repair behavior in this research, a pressure test after impact test was used. This research aimed to investigate the process of repair and damage in the sample at the

same time. For this purpose, two separate methods were used. In the first method, the repair agent was injected inside the vessels and the pressure of the input and output of the vessel was measured by the device. The decrease in output pressure indicated the rupture of the vessel and the injection of the repair agent to the crack site. By using a pressure reduction and repair agent containing epoxy paint, the location and size of the damage in the structure were determined. In the second method, the repair agent was continuously flowing inside the microvessels, and the amount of damage and the repair process were identified by the ultrasonic scanning method. After causing damage, to evaluate the repair efficiency, the samples were placed at ambient temperature for 24 h. The results showed that in the first method, the average repair efficiency was 94%, and in the second method, it was 100%. The reason for the better result of the second method is the effect of the constant circulation of the repair agent on the damage formation and the better penetration of the repair agent. On the other hand, according to numerical studies, repairing 30% of the damaged areas was enough to achieve 90% efficiency.

## The evolution of the microcapsule repair method

In the capsule repair method, reactive liquid agents such as monomers, pigments, catalysts, and hardeners are placed inside a polymer coating using in situ polymerization, interfacial polymerization, and solvent evaporation methods. Then these microcapsules are distributed in polymer or polymer matrix composite to create self-healing properties in them. These broken capsules and reactive (repair) agents penetrate the cracks by capillary forces, and in the presence of pre-dispersed catalysts, the polymerization reaction takes place for repair. Crack expansion is the main driving force for this process. To create self-healing properties, the synthesized microcapsules must have the following conditions [43, 68]:

1. Having enough strength so as not to be damaged during the process of polymer matrix production.
2. Being able to break in piece easily at the time of creating the crack.
3. Being able to release the repair agent or catalyst into the crack.
4. Having the least destructive effect on the properties of pure polymer resin or reinforced composite.

Brown et al. [69] in 2002 showed that microcapsules with a shell thickness of 160–220 nm are suitable for use in self-healing systems because while having enough strength to remain intact during the polymer production process, when microcracks are formed in the epoxy-microcapsule composite, they are easily broken and release the repair agent. It was observed that during the production of microcapsules, the surface of microcapsule became rough by settling urea–formaldehyde nanoparticles on the surface. An increase can appear in adhesion to the polymer by increasing the roughness of the microcapsule surface so, a way to prevent the deposit of urea–formaldehyde nanoparticles on the microcapsules is to increase the contact surface of the water and the dicyclopentadiene core. Just after production and drying, elemental analysis of the microcapsules showed 83–93% by weight of dicyclopentadiene and 6–12% by weight of urea–formaldehyde are in microcapsules. It was found that after thirty days in ambient conditions, the amount of dicyclopentadiene in microcapsules decreased to 3.2% by weight. The reason was probably dicyclopentadiene leakage from the wall of microcapsules. Another study is needed to determine the reduction range of contents of microcapsules under operating conditions of the self-healing sample. This proposed study can include examining parameters such as wall thickness or microcapsule wall material. Brown et al. in 2003 [70] proposed another method that reduced the need for a catalyst by creating a bond between the repair agent and the damaged surface. Limited laboratory data were reported for both methods, and the efficiency of the restoration system has not been published. In 2005, Rule et al. [71] proposed encapsulating Grubbs catalyst to solve the problem of deactivation of catalysts. This was done by using a type of encapsulation process used in pharmaceuticals. The average diameter of catalyst capsules was in the range of 50–150 μm. In 2006, Jones et al. [72] found that the structure of Grubbs catalyst affects its dissolution form, thermal stability, and its opposition to deactivation. They showed that smaller catalyst crystals have a faster liquidation in dicyclopentadiene monomer but smaller crystals do not have a higher repair efficiency than larger crystals. Rule et al. [73] in 2007 examined the effect of the size of microcapsules on self-healing efficiency. In this research, three samples with different capsule sizes were tested under the same conditions. Based on the obtained results, in a fixed volume fraction, the larger the size of the capsules, the higher the absorbed energy for failure. The reason was reported the more amount of repair agent in the capsule, and by more releasing of this factor, the better repair was done. In 2011, Jin et al. [74] investigated fracture and fatigue in epoxy-microcapsule composites containing dicyclopentadiene remedial agents. In this research, capsules containing dicyclopentadiene monomers were used as repair materials and Grubbs particles as catalysts. After conducting static and dynamic fracture tests and comparing with epoxy without capsule, the obtained results indicated the improvement of these properties. For a better investigation, the repair agents were directly introduced into the damaged area. The obtained results showed 56% recovery in static failure mode. Also, due to the low frequency of fatigue force, complete elimination of fatigue crack was observed. SEM images also showed the polymerization of dicyclopentadiene at the fracture surface. In 2012, Zhao et al. [75] prepared nanocapsules containing self-healing substances. Since most of

the capsule productions are on scales higher than microns, in this review, the goal was to produce nanocapsules for thin self-healing materials or microelectronic coatings. Nanocapsules were prepared using high-speed mixing or ultrasonic mixing and then deposition evaporation and their size was checked by transmission electron microscope. This method is widely used in measuring mechanical properties on a micro-scale. In this research, microcapsules containing epoxy as a hardening agent and coated with poly melamine–formaldehyde were prepared. Investigation of micromechanical properties showed that poly melamine–formaldehyde wall exhibits viscoelastic-plastic behavior. In 2013, Zhu et al. [76] developed an analytical model for the number of capsules used in self-healing materials. In terms of the geometry of the damaged area and using the integral concept, this research was done to develop and determine theoretical solutions about the required amount of repair agent to repair the crack. Based on a general fact, the capsule is randomly scattered in the matrix and the crack is formed independently in the matrix. In this research, based on the volume of the restoration, the volume fraction of the required capsules was predicted. In 2013, Li et al. [77] investigated the effect of different parameters on microcapsules used in self-healing materials. In this research, polyetheramine was used as the material inside the capsule core and polymethyl methacrylate was used as the coating material. The morphology and thickness of the capsule wall, the amount of suitable curing agent, and the life and size distribution of the microcapsules were studied. In this research, polymethyl methacrylate microcapsules containing polyethylamine were produced in oil–water emulsion, and the effect of different parameters was investigated. As a result of this research, the appropriate temperature for solvent evaporation reaction and microcapsule formation was reported to be 40 °C. At this temperature, the external surface of the capsules was smooth, while at higher temperatures, a porous surface was obtained, and at lower temperatures, an uneven and rough surface was obtained. The thickness of the capsule wall was mostly dependent on the core-wall weight ratio, and the appropriate ratio was reported between 2 and 4. In higher and lower ratios, capsule disintegration or wrinkling was seen. The size and size distribution of microcapsules was controlled by mixing speed and concentration of emulsifying agent, and proper stability was reported for these microcapsules. The impact strength of epoxy containing 5% by weight of microcapsules increased by 20% compared to pure epoxy. The highest self-healing efficiency in epoxy containing 15% by weight of microcapsules was reported as 93.5%. In 2013, Jones et al. [78] observed the complete recovery of the interfacial strength of glass fiber-reinforced epoxy composite by microcapsules. In this research, after completely breaking the interface bonds, the bonds were restored using microcapsules containing restorative substances. Microcapsules around glass fibers and containing different concentrations of epoxy resin and ethyl phenylacetate solution were prepared and used. (Fig. 13) [78]. Using a ratio of 70:30 solution to epoxy resin, 100% recovery of interface shear stress was observed, while in the use of dicyclopentadiene, the recovery of about 44% was reported. Tripathi et al. [79] were able to encapsulate the epoxy-based amine hardener with a self-epoxy shell. The best ratio of epoxy matrix to amine hardener to achieve 100% repair efficiency was reported to be 10 to 2.3. The science of encapsulation and restoration of polymer composite structures is new, and there are many ideas and creativity to achieve better and more optimal restoration. Making microcapsules containing benzyl peroxide, reaching the structure of nanocapsules, making microcapsules containing polydimethylsiloxane, microcapsules containing palm oil to repair the epoxy base, making microcapsules containing linseed oil and the effect of silane agent on microcapsules and Multi-core microcapsule are among the latest research field in the field of improving self-healing behavior. These research projects still need improvement and optimization for their use in composite structures.

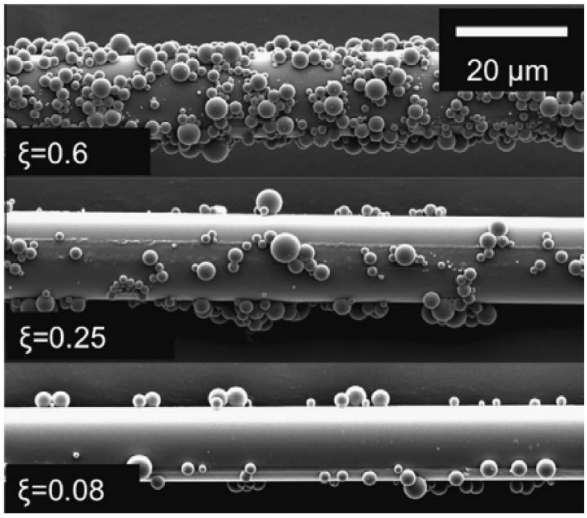


**Figure 13:** SEM micrographs of glass fibers with varying capsule coverage.

## Conclusion

In this review research, at first, the types of repair systems and their classification were examined based on recent developments in the field of self-healing science, especially self-healing in composite structures. There are two general views on the classification of self-healing systems. The first point of view is the classification base on the intrinsic and non-intrinsic repair. The second classification is based on the repair method, which is divided into three major categories of self-healing, based on microcapsules, vascular, network, and intrinsic. In the next step, it was tried to evaluate the repair performance in various mechanical properties, and repair

capability and efficiency. Also, in this review research, the growing trend of research in the field of self-healing materials, the number of international documents published in this field, active researchers, active countries, and the role of different fields of science in the development of self-healing were studied. Since the main goal of this research was to investigate the recent advances in non-intrinsic self-healing with emphasis on the use of self-healing materials in polymer-based composites, the evolutionary course of non-intrinsic self-healing based on hollow glass fibers, microvascular networks, and microcapsule was investigated. In all the three mentioned methods, the repair agent is kept in a compartment inside the composite structure, and as soon as the crack reaches that area, this compartment is broken and by releasing the repair agent, repair takes place in the area of the crack tip. Each of the mentioned methods has its own characteristics and advantages. For example, in the repair system based on a microvascular network, it is possible to repair multiple structures. The most important feature of self-healing based on microcapsules is the uniform distribution and ease of designing composite structures compared to the other two non-natural methods. In the self-healing methods based on hollow fibers, these fibers can perform the role of reinforcement and repair agent at the same time. Also, in this review research, it was tried to investigate the factors influencing the performance of each of the healing systems. The type of placement of the repair agent chamber in the structure, the type of catalyst, the solvent, the penetration speed of the repair agent are among the factors that have a great influence on the choice of system type and repair efficiency. According to the stated contents, the most important materials for the construction of the holding chamber for the repair of non-intrinsic processes in the hollow fiber method include hollow fibers of glass and polypropylene. In the microvascular network method, polymers used in 3D printers, such as petrochemical jelly, microcrystalline wax, and polylactic acid, are used to make the storage compartment for the repair agent. In the method of encapsulating the repair agent, it is very common to use formaldehyde-based polymers such as urea–formaldehyde. In relation to the type of repair agent, many different materials have been used, but research has shown that in many cases, the use of base polymer as a repair agent is more suitable than other materials to repair the base.

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## Data availability

Data required to reproduce these findings have been given in the text.

## Declarations

**Conflict of interest** No conflict of interest exists in the submission of this article.

## Consent to participate

Not applicable.

## Consent to publish

The article is approved by all authors for publication.

## Ethical approval

Not applicable.

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