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Self-Healing Polymers and Composite Materials

Allana Azevedo do Nascimento

Abstract

In order to overcome the challenges and limitations related to conventional maintenance and repair methods in structural composites during service, the concept of self-healing for polymeric materials has been developed in the last decades. Inspired by biological systems, ideal self-healing materials must be able to repair damages continuously during the service life of the component, recovering its performance. Several techniques have been proposed in the last years to manufacture self-healing polymers and fiber-reinforced composites to provide healing of microcracks in the composite structure without or with less intervention, extending service life and safety of the components and reducing maintenance time and cost. This book chapter proposes an overview of the most promising self-healing approaches for thermoset and polymer matrix composites developed in recent year.

Keywords: advanced materials, thermoset polymers, polymer matrix composites, self-healing, mendable resin

1. Introduction

Polymers and polymer matrix composites (PMCs) have been extensively used for a variety of structural applications due their combination of high mechanical properties and light weight savings as major benefit. During service, the operating environment often exposes these materials to severe variations in mechanical loading and environmental conditions. Such conditions induce damages and can cause the formation of microcracks. These matrix damage can lead to the coalesce and growth of larger cracks, which compromise mechanical performance and integrity of the material inside its structure, where detection and external intervention are difficult and/or impracticable. Non-destructive testing methods are generally used for inspection of components during operation. However, internal microcracks can be difficult to repair [1, 2]. To overcome the challenges related to the repair of these internal damages in thermoset matrix and FRP, self-healing materials have been proposed in the decades as an alternative to conventional repair methods.

Ideal self-healing materials are designed to present the ability repair themselves, using resources inherently available to them. The recovery of performance can be full or partial and occurs during the service life of the component with minimal or no external intervention. These materials can provide the healing of invisible

microcracks in the composite structure and can be an alternative to non-effective conventional maintenance methods to extend service life and safety of the components in addition to reducing maintenance time and cost [1, 3, 4].

Inspired by biological systems, the self-healing of synthetic materials occurs in three steps. Initially, the healing mechanism is triggered by the damage. In the second step, the healing agent, that is, the material responsible to repair the damage, is transported to the damaged area. Lastly, the repair process takes place, recovering the crack. The time and efficiency of the recovery depend on the self-healing mechanism used [5, 6].

Different types of self-healing mechanisms are described in literature for all types of materials. Polymeric materials are reported as promising for self-healing, and the self-healing ability can be introduced by chemical modification or exposure to physical or thermal conditions. The glass transition temperature (Tg), the chain mobility, and the chemical structure are important parameters to be considered during the design of the self-healing system and can influence the success of the healing ability [7].

In this scenario, self-healing polymeric materials represent a new class of materials and have attracted great attention in the past decades. Studies have been developed to better understanding of the self-healing ability, the mechanisms, and how to overcome the challenges of processing and the limitations of each system. In the last decades, a significant increase in the amount of research about self-healing polymers is reported. **Figure 1** shows the growth of the number of papers published on the topic of self-healing polymeric materials since 2000.

Several mechanisms are employed to obtain self-healing polymeric materials and each mechanism presents advantages, limitations, and challenges in formulation. In this review article, principles and developments in self-healing thermoset matrix and fiber reinforced polymers were presented.
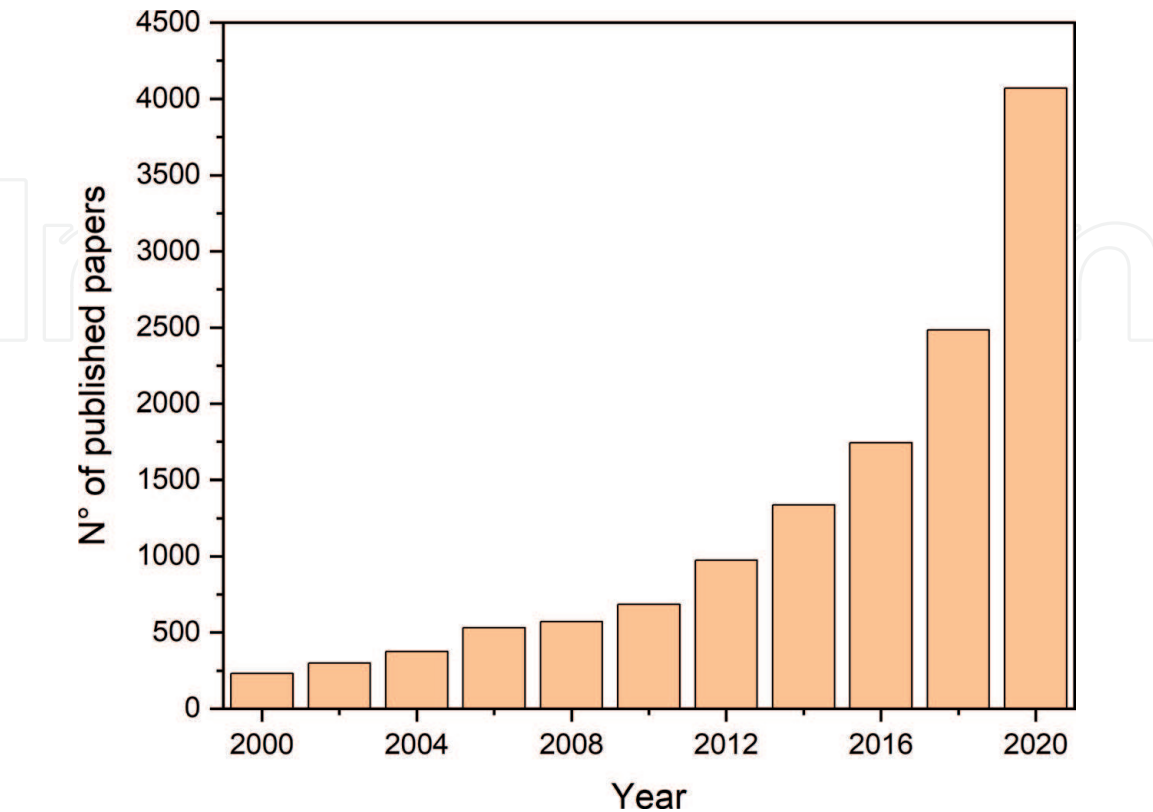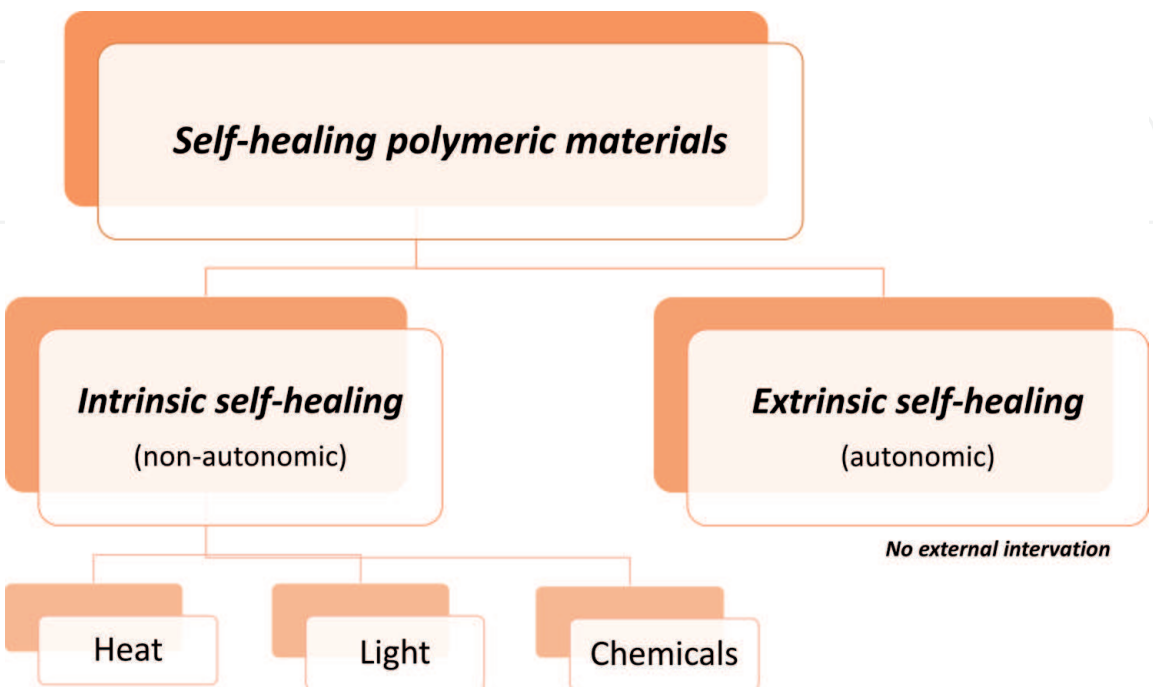

Figure 1.
Number of published papers according to science direct searched by "polymers self-healing".

2. Self-healing mechanisms

Self-healing polymeric materials are capable of recovering their properties due to the repair of microcracks. Different mechanisms can be used to confer the inherent ability to self-heal to polymers. For self-healing materials, the recovery of properties can occur naturally (autonomic self-healing) or be activated after the application of an external stimulus such as heat or radiation (non-autonomic self-healing) [6, 8]. Different mechanisms of self-healing for polymer composites have been reported over the last decade. Each mechanism has limitations and aspects to be improved. Generally, self-healing mechanisms can be classified into two main groups: intrinsic and extrinsic self-healing mechanisms [9].

For extrinsic self-healing mechanisms, the healing agent is inserted into containers and incorporated into the matrix. Microcapsules and vascular network are the main extrinsic self-healing mechanisms. For encapsulated healing agents, during crack formation, the capsules are broken, releasing the healing agent within containers to fill the cracks. The polymerization of the healing agent will occur in these regions and heal the crack plane. Self-healing of polymer composites using the vascular network mechanism is developed by incorporating pipelines filled with a healing agent within a polymer composite matrix. When damage is triggered, the healing agent flows into the damage region by capillarity and polymerizes, thereby completing the process. These extrinsic mechanisms provide recovery of up to 100% of the initial fracture resistance of epoxy resins. However, despite the high recovery levels, the difficulty of processing and the inability to multiply cycles of healing in the same area are limiting factors for the application of this mechanism on a large scale [6, 8].

Intrinsic mechanisms are defined by the inherent ability to healing of the matrix, after a damage, in the presence of external stimulus such UV light, heat, or chemicals. Thermoset polymer matrices with intrinsic healing capability, also known as mendable resins, have the advantage of multiple healing cycles as long as damage to the reinforcement fibers is not excessive or highly localized. Different mechanisms have been proposed in the last decade for the production of self-healing polymer matrices [6, 8]. **Figure 2** summarizes the types of self-healing polymeric materials.

Figure 2.
Types of self-healing polymeric materials.

The healing of polymeric materials may be related to the recovery of several properties of the material, including fracture toughness, tensile strength, barrier properties and even molecular weight [1]. Then, the extent of healing can be difficult to compare, due to the range of properties that are healed in these materials. However, the majority of studies have used a basic method for describing the extent of healing in polymeric systems for a range of properties. The healing efficiency (η) is determined by the ratio of the value of the property tested after and before the healing (Eq. (1)) 5. This equation has been used as the basis for a non-property-specific method of comparing the healing efficiency of different self-healing polymeric systems [1, 3, 4].

$$Healing\ efficiency\left(\eta_p\right) = \frac{Property\ value\ healed}{Property\ value\ initial} \times 100 \qquad (1)$$

For self-healing efficiency assessment, the protocol reported on the literature involve basically three steps: (i) submit the test specimens to initial tests to promote controlled damage, (ii) healing (that can be triggered autonomically or non-autonomically), and (iii) submit the healed specimens to tests again, in order to evaluate the new properties. Usually, the first tests are carried out until a certain level of load provides damage but not the failure of the samples, while the second test is carried out until total failure. The ratio between the properties measured before and after damage is then used to quantify the healing efficiency. Nonetheless, it is not unusual to find self-healing reports that involve the visual observation of microcracks healing, without quantification of healing efficiency.

Self-healing efficiency greater than 100% have been reported for thermoset matrix in several self-healing studies. However, results of unmodified control samples are often not shown as the basis for comparison and the healing protocols are not standardized. In addition, the properties of the modified materials should be reported. Hence, although the healing efficiency equation has been extensively used for self-healing studies, a need for standardized methods for self-healing measurements still exists. In addition, when results of healing efficiencies obtained through different methods were compared it was found that healing protocols can be highly inaccurate and therefore not recommended [10, 11].

2.1 Extrinsic self-healing

Considered autonomic self-healing, extrinsic self-healing mechanisms are usually classified according to the type of the storage vessels used, although the self-healing concept is similar. Capsuled-based self-healing and vascular network self-healing are the two types of extrinsic self-healing mechanisms [6, 8].

2.1.1 Capsule-based self-healing

For capsule-based self-healing polymers, the healing agent is sequestered into microcapsules until the damage. The cracks formed are responsible for the rupture of the capsules, releasing the healing agent and healing the crack plane. This mechanism was first suggested as a self-healing technique for polymer matrix by White et al. [12]. White et al. suggested a healing system based on the ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) via Grubbs' catalyst. Microcapsules with urea-formaldehyde (UF) shell filled with DCPD were dispersed into epoxy matrix with Grubbs' catalyst and the addition of microcapsules

and catalyst increased the toughness of the epoxy [12]. This DCPD-Grubs catalyst system and the ROMP reaction were further investigated, and the healing efficiency was shown to be related to the concentration and size of the microcapsules and the catalyst [2, 13]. The low viscosity of the DCPD and the rapid polymerization at ambient conditions are strong advantages of the system, which has been extensively studied and reported as an efficient self-healing system [2, 6, 8].

5-Ethyldiene-2-norbornene (ENB) has also been investigated as a healing agent for the capsule-based self-healing mechanism due its higher ROMP reactivity when compared with DCPD. Romero-Sabat et al. [14] used ENB/DCPD microcapsules (ENB/DCPD 80:20 wt.%) and Ru-based catalysts (Hoveyda Grubbs 2nd generation and Grubbs 3rd generation) dispersed into epoxy matrix and found healing efficiency values up by 130% at low and ultra-low temperatures [14].

Although the capsule/dispersed catalyst healing system (**Figure 3a**) was first proposed, the capsule-based mechanism has been investigated also using different encapsulated agents in a dual capsule system. In this system, the monomer and the hardener are encapsulated separately and embedded into the matrix (**Figure 3b**).

Yuan et al. [15] presented the healing efficiency of a dual capsule system with a microcapsules shell made by poly(melamine-formaldehyde) (PMF) filled with epoxy prepolymer and its hardener. Diglycidyl ether of bisphenol A(DGEBA) epoxy-loaded microcapsules and microcapsules filled with hardener (2,4,6-tris (dimethylaminomethyl)phenol) were dispersed in epoxy matrix and tapered double cantilever beam (TDCB) were used to assess the self-healing efficiency of the system. For a concentration of 20 wt.% of microcapsules (10 wt.% of epoxy-loaded and 10 wt.% of hardener-loaded microcapsules), healing efficiency higher than 90% was found under 200°C [15].

Kosarli et al. [16] proposed the use of UF microcapsules filled with epoxy resin nanomodified with Multi-Wall Carbon Nanotubes (MWCNTs) as healing agent. The conductive microcapsules aimed to recover mechanical and electrical performance of the capsule-based self-healing system. 0.1 wt% of MWCNTs was dispersed into epoxy healing agent using high shear stirrer previous to the encapsulation. UF-wall microcapsules were produced using in situ emulsification polymerization. Then, the DGEBA epoxy matrix was modified with 0.5 wt.% MWCNTs, 20 wt.% produced microcapsules, and 3 wt.% of catalyst (aluminum (III) triflate $(Al(OTf)_3)$. The self-healing efficiency was assessed through fracture toughness tests and impedance spectroscopy measurements. The capsule-based self-healing polymer presented about 22% increase on mechanical properties when compared with neat matrix. In addition, a recovery rate of more than 80% of fracture toughness and electrical properties was found [16].

(a)   (b)
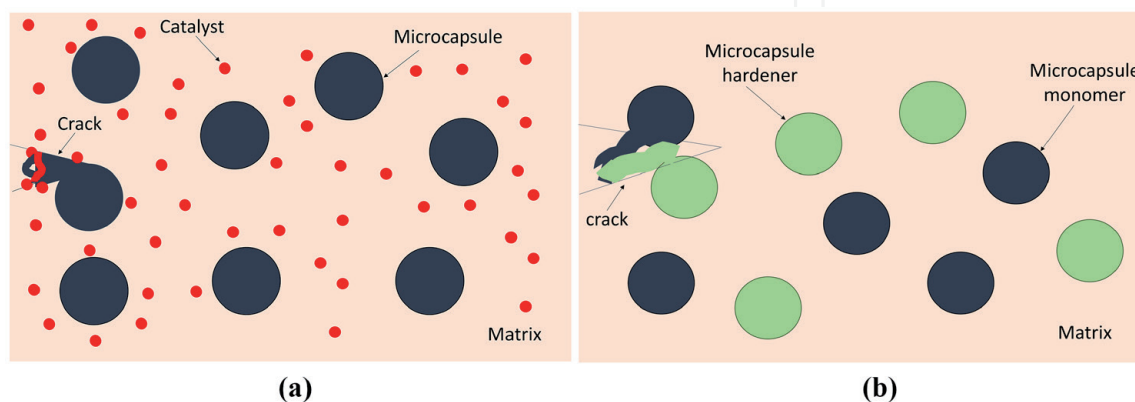
Figure 3.
Schematic of capsuled-based mechanism: a) microcapsule/disperse catalyst system and b) dual capsuled-based system.

Ebrahimnezhad-Khaljiri et al. [17] used capsuled-based extrinsic mechanism to manufacture self-healing glass fiber/epoxy composites. Microcapsules with epoxy as healing agent were first dispersed into epoxy matrix in three different concentrations: 7 wt.%, 14 wt.%, and 21 wt.% using mechanical stirrer. Then, 2 wt.% of imidazole-based catalyst ($NiCl_2(imidazole)_4$) was incorporated within the matrix. 4-ply and 12-ply glass fiber/epoxy were manufactured by hand lay-up using the modified epoxy matrix. Tensile and interlaminar shear strength (ILSS) tests were used for self-healing efficiency investigation. As a result, composites with 14 wt.% of microcapsules were presented as optimum results, considering the levels of healing efficiency for tensile and shear strength [17].

Capsule-based self-healing approaches have also been investigated for coatings and corrosion protection. For these types of coatings, despite polymerizable materials, corrosion inhibitors can be encapsulated. The release of the healing agent to the damaged areas promotes the filling of the cracks of the coating, thereby creating a protective barrier. This barrier that is formed acts as a corrosion protection, protecting the metal surface from oxidizing agents [18, 19].

For the capsule-based self-healing system, the encapsulation process is one of the key factors during the processing. Several encapsulation methods as coacervation, phase separation, in situ and interfacial polymerization, layer-by-layer assembly and meltable dispersion are used for encapsulating reactive materials. However, interfacial and in situ polymerization have been largely used as an encapsulation technique for capsule-based self-healing systems [20, 21]. The synthesis of microcapsules is a complex process and must be considered a large range of parameters. The thickness of the wall and the stiffness of the capsules must ensure that the containers remain unbroken during the processing and the rupture during cracking. The capsules must have the appropriate size and amount of healing agent without leakage. In addition, the quality of the surface is also important to guarantee good adhesion with the matrix. Synthesis parameters such as temperature, stirring rate, and pH can be adjusted to influence the size and quality of microcapsules [20, 22, 23].

Besides the encapsulation process, the incorporation of the capsules into the matrix is an important step during the process and the optimization of the dispersion of the microcapsules is a challenge. The challenges faced in the processing are considered the limitations of this self-healing mechanism. In addition, the limited amount of healing available restrains the multiple healing cycles [20]. Once the microcapsule breaks and the healing agent is polymerized, the containers cannot be refilled, and repetitive repair does not occur in the same location.

2.1.2 Vascular network self-healing

The vascular self-healing system has the healing agents encapsulated into capillaries such as hollow fibers or hollow tubes. As capsule-based systems, the capillaries can be filled with healing agents, while the catalyst is dispersed within the polymer matrix and the resin and the hardener can be encapsulated separately in different capillaries. In addition, one-part resin system is also possible (**Figure 4**). The rupture of the capillaries releases the healing agent that flows to the microcrack surfaces recovering the damaged areas.

The vascular networks can be unidimensional, bidimensional, or be formed as a 3-dimensional network-like structure. 2D and 3D structures, due to the interconnected vascular network, have the advantages of repetitive healing in the same area. In addition, in addition to working as a healing agent container, the vascular networks also act as reinforcement for the polymeric matrices [5, 24].

Williams et al. [25] used hollow glass fibers (HGF) as storage vessels for the healing agent. The HGF were infused with a two-part epoxy system and inserted
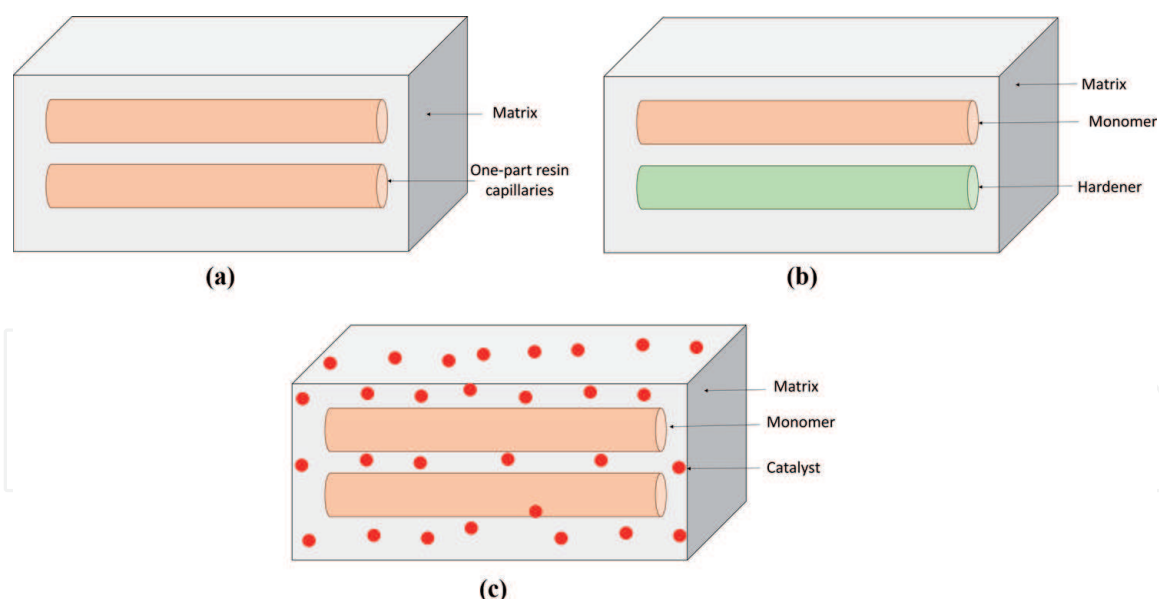
Figure 4.
a) One-part resin system, b) resin and hardener encapsulated separately and c) encapsulated resin with dispersed catalyst for vascular network self-healing system.

into carbon fiber reinforced plastic (CFRP) prior to the hand lay-up lamination. The CFRP showed the ability to restore compressive strength after low velocity impact damage [25].

Mohammadi et al. [26] investigated the self-healing efficiency of a glass fiber/ epoxy composite containing microvascular channels. The one-dimensional vascular network was fabricated with the assistance of polymide wires. The polymeric wires were used as re-tractable preforms and positioned between the glass fiber during the resin impregnation via hand lay-up. The wires were covered with silicone and pulled out after the curing. The hollow channels were then filled with the healing agent. A three-part healing agent consisting of epoxy resin, maleic anhydride hardener, and CuBr2 (2-Methylimidazole) accelerator was used to fill the microvascular channels. After damage, the healing was activated by heating at 130°C for 30 min. Healing efficiencies above 50% were reported under tensile and flexural loadings [26].

The DCPD/Grubbs' catalysts system is also largely used as a healing agent for hollow fiber/capillaries vascular networks. Radovic et al. [27] investigated the influence of the solvent on the stability of the Grubbs' catalyst and the healing efficiency of the glass fiber/epoxy composites with embedded filled glass capillaries. Dichloromethane (DCM) and toluene (TO) were used for the dissolution of the Grubbs' catalyst. A two-parts glass capillaries system was used: monomer and catalyst encapsulated in different capillaries. The monomer was a solution of 10 wt.% DCPD in dimethylformamamide 99.8% (DMF) and the catalyst was a solution of 1 wt.% of Grubbs catalyst dissolved in two different solvents (DCM e TO) for comparison. Controlled energy impact tests showed that samples with DCM solvent presented 60% of recovery of impact strength after healing, while samples with TO solvent exhibited 51% of recovery. In addition, results showed that the filled capillaries for healing purpose also are suitable as reinforcement for the composite during loading [27].

Extrinsic self-healing mechanisms have attracted attention and been extensively studied through the last decades. The main advantage of this type of mechanism is that it does not require external stimulus, it being a totally autonomic self-healing mechanism. However, repeatable healing is limited due to the limited amount of healing agent available.

2.2 Intrinsic self-healing

The concept of intrinsic self-healing mechanism is considered more competitive in terms of manufacturing and applications because the intrinsic healing ability is conferred to the polymer matrix. Thermoset polymer matrices with intrinsic healing capability have the advantage of multiple healing cycles as long as damage to the reinforcement fibers is not excessive or highly localized. Different mechanisms have been proposed in the last decade for the production of self-healing polymer matrices. The healing capability is achieved through the modification of the polymeric matrix to contain intrinsic functionality or healing agent [28, 29].

Intrinsic self-healing systems are obtained through the modification of the structure of polymeric matrix (crosslinking density, aromatic chains, crystallinity, for instance) or by the modification of the polymeric matrix through the addition of a thermoplastic modifier, obtained by a miscible or immiscible thermoplastic/thermoset blend [28].

2.2.1 Reversible polymer networks self-healing system

For this intrinsic mechanism, the polymeric matrix is chemically modified with functional groups that experience reversible reactions in the presence of external stimulus. Then, the healing is achieved due to the resulting conformation changes of the dynamic dissociation and re-association of stress-bearing bonds. Different types of dynamic covalent bonds and non-covalent bonds (referred to a supramolecular interactions) have been investigated for self-healing purposes such as Diels-Alder, disulfide exchange reactions, hydrogen bonds, and poly(dimethylsiloxane) reactions. The healing is usually initiated by temperature, although studies showing pH changes, chemical additives and irradiation as stimulus for the healing activation can be found [29, 30].

Diels-Alder and hydrogen binding active groups are extensively investigated to produce polymer networks with self-healing ability due to thermally reversible properties. In these networks, the bonds reconnection that allow the repair, can occur under different temperatures and conditions. The introduced functional groups are decisive for the healing event and the ratio between these groups can control the conditions necessary for the healing activation; that is, the levels of energy necessary to trigger the reversible interactions [31]. In addition, the introduced functional groups are decisive for the healing efficiency, as characteristics such as association and flexibility and architecture of the molecule have to be considered and they can influence the success of healing [29].

Ehrhardt et al. synthesized a UV-cured reversible poly(methacrylate) network capable of healing damage at ambient conditions. Reversibility is introduced by Diels-Alder bonds formed through the reaction between maleimide and furan. UV-cured polymer films were ground into a powder, which was further compressed in a mold in order to bring off particles into close contact. Compressed samples were healed for 7 days at 1 bar and 20°C. As result, the network was healed in the fully vitrified state [32].

Grande et al. [33] investigated the healing behavior of aromatic disulphide-based poly(urea-urethane) (PUU). Different combinations of disulphide and polyurethane pre-polymers were used to obtain different crosslink densities with the same number of reversible covalent bonds. Then, the effect of the polymer structure was investigated. Dynamical mechanical thermal analysis (DMTA), tensile tests and single edge notch tensile (SENT) fracture tests were carried out to assess the self-healing efficiency at room temperature. Results suggested that the

structure of the network interferes with the levels of recovery after damage. The addition of high contents of difunctional units resulted in polymers with low tensile strength but high viscoelastic properties and healing efficiency [33].

Supramolecular interactions easily dissociate under mechanical loading due the weak nature of the interactions. Nevertheless, these bonds can re-associate with minimal external trigger. Intrinsic self-healing systems based on supramolecular interactions present as major benefit the ability to self-heal at low temperatures, near to room temperature [34]. However, the dynamic nature of the reversible bonds implies in temperature-dependent behavior, and the long-term mechanical stability is an issue. Polymers network with covalent reversible bonds, on the other hand, potentially are able to operate in a higher temperature range, presenting more mechanical properties stability, but require higher temperatures for healing activation. In addition, the design of reversible polymer networks can involve long, expensive, and complex synthesis steps [33, 34].

2.2.2 Thermoplastic/thermoset blends self-healing system

The addition of thermoplastic modifiers is considered promising as an intrinsic healing mechanism proposed for thermoset resin. This mechanism is based on the incorporation of a solid-state thermoplastic healing agent in the thermoset matrix. During heating, the movement of these molecules promotes the flow of the healing agent into the damaged regions, filling the crack and providing the healing of the thermoset matrix [8, 35].

Three properties of thermoplastics are considered critical for the use of these polymers as the healing agent: fluidity, reactivity of functional groups, and adhesive properties. The thermoplastic must have a melting point and viscosity that provide flow inside the cracks besides being chemically reactive functional groups with the groups of the thermoset matrix. The thermoplastic must also have good adhesive properties, providing strong bonding with the matrix during crack repair [8].

In addition, as for this mechanism, the external activation to promote the healing is necessary, selecting the optimal parameters to promote the flow of the thermoplastic healing agent as an important step. Temperature and pressure are usually applied to enable the healing. In terms of temperature, the activation temperature has to be enough to provide the flow of the thermoplastic, the temperature being above its melting point. In practice, is also suggested that the activation of the healing occurs at temperatures above the glass transition of the matrix. The mobility of the crosslink matrix can increase the diffusion between thermoplastic and matrix and facilitate the adhesion of the healing agent to the matrix networks [35, 36].

Considering these requirements, some thermoplastic polymers have been suggested as possible healing agents for epoxy resin. Poly bisphenol-A-co-epichlorohydrin, polycaprolactone (PCL), poly (methyl methacrylate) (PMMA), poly (ethylene-co-methyl acrylate) (EMA), poly (ethylene-co-methacrylic acid) (EMAA), and poly (ethylene glycidyl methacrylate) (EGMA) are examples of thermoplastic polymers studied as healing agents for epoxy resin [6, 8].

Varley et al. [35] investigated the healing efficiency of six different thermoplastic modifiers dispersed into epoxy amine network. Ethylene vinyl acetate (EVA), poly(vinyl-butyral) (PVB), styrene-ethylene-butadiene copolymer (SEBS), poly(ethylene-co-glycidyl)-methacrylate (PEGMA), polyethylene-co-methacrylic acid (EMAA), and acrylonitrile-butadiene-styrene (ABS) were used. The healing agents were cryogenically ground and the particles (with size distribution between 149 and 295 μm) were blended within epoxy resin. The healing efficiency was assessed through single end notched beam (SENB) tests and four healing

cycles were performed in order to investigate the ability for repetitive healing. All healing agents presented load recovery after the first healing cycle. However, ABS, SEBS, and PVB showed lower repeatability of healing. EMAA, PEGMA, and EVA presented high levels of mendable behavior, especially after further healing cycles [35].

The poly (ethylene-co-methacrylic acid) (EMAA) has been extensively studied as a healing agent for epoxy resin and FRP, presenting high healing efficiency. In the case of EMAA, the thermoplastic is incorporated to the thermoset matrix and remains insoluble. When used as a healing agent in high concentrations (concentrations above 5 wt.% are usually reported), EMAA is considered effective in healing the cracks in both epoxy resin and carbon fiber epoxy composites [37]. EMAA was first suggested as a healing agent for epoxy networks by Meure et al. [38]. EMAA particles with concentration of 15 wt.% were incorporated into epoxy resin and the healing efficiency was assessed by TDCB and SENB tests. As a result, a strong recovery due to the thermal expansion of the EMAA and the formation of an adhesive layers between adjacent damaged surfaces was found. Further studies [39, 40] showed that strong chemical interactions between EMAA and epoxy networks are responsible for the healing mechanism [38–40].

EMAA was also reported as an efficient self-healing agent for CFRC, exhibiting more than 100% recovery of properties [41, 42]. For FRC, the self-healing efficiency of the system is a result of the plastic deformation of the EMAA during the heating, which gets transformed into thin ligaments, which bridge the crack. These thermoplastic ligaments are able to transfer the applied tension through the crack, increasing the interlaminar resistance of the system [43].

Even though temperature is highly used to activate EMAA as a healing agent, Hargou et al. [44] showed that ultrasonic welding can be used to activate the healing mechanism for carbon fiber/epoxy systems. The ultrasonic vibration generated the temperature to activate the healing [44].

Miscible blends of epoxy cured with 4,4′-diaminodiphenylsulfone(DDS) and PCL as thermoplastic healing agent have also been investigated. Cohades et al. [45] used epoxy-PCL blends with 25 vol.% of PCL to manufacture glass fiber reinforced composites and the self-healing ability was assessed through compression after impact (CAI) tests. Results showed that even though epoxy-PCL composites presented a lower resistance to crack propagation when compared with pure epoxy composites, the PCL modified composites presented a recovery rate of 22 to 96% of compressive residual strength after low-velocity impact damage. Low levels of recovery were ascribed to fiber damage, which cannot be healed by the self-healing mechanism focused on the healing of matrix microcracking [45].

Kong et al. [46] incorporated fusible thermoplastic polystyrene (PS) as a healing agent into a shape of memory polyimide matrix. Shapes of memory polymers (SMPs) have the ability to return to the original shapes under external stimuli such as heat and light. Then, the combination of self-healing performance with the shape of memory effect through self-healing SMPs have been studied. In their study, Kong et al. incorporated 8% of PS into the shape of memory polyimide matrix and showed that the combined effect can heal damages such as cracks, pierced holes, and cuts at 243°C [46].

Intrinsic self-healing mechanisms have as its main advantage the indefinite repeatability, since repair is inherent to the chemical structure of the polymer. However, the need for some external activation can be considered a limitation of this repair mechanism and the design of the requirements for healing activation is specific for each system [47]. In addition, due to the need of modification of the matrix network, synthesizing intrinsic self-healing polymers to obtain high healing efficiency without mechanical strength loss is a challenge.

3. Conclusion

Self-healing materials are able to heal themselves when damaged, restoring initial properties fully or partially. Inspired by natural mechanisms, self-healing mechanisms have been explored for all types of materials, including metals, polymers, ceramics, and composites.

In the last decades, great progress has been made in the design and development of self-healing polymeric materials and the existing self-healing polymers are considered smart materials able to recover their properties autonomically or non-autonomically. These materials have been suggested for a series of applications such as water membranes, lithium batteries, energy transducers, biomedical devices, flexible electronics, and soft robotics [48].

Ideal self-healing polymers cannot significantly decrease the initial properties of the virgin material. In addition, the methods to assess the healing agent efficiency still need to be better standardized.

Self-healing materials are a new class of smart materials and have attracted a significant interest for research. Several self-healing techniques have been developed and investigated in the last decades. All techniques developed are reported as promising but they also presented with limitations and downsides. Adjustments are still necessary in order to apply the techniques to industrial scale production. Thus, further investigations and research are still necessary.

Conflict of interest

The authors declare no conflict of interest.

Author details

Allana Azevedo do Nascimento
Department of Materials Science and Engineering, Federal University of Rio Grande do Norte, Natal, Brazil

*Address all correspondence to: allanaazevedon@hotmail.com

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