An insight into advance self-healing composites

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Abstract

The purpose of the investigation is to review self-healing mechanisms and various advanced self-healing materials which are recently used for repairing composite materials. The manufacturing and characterization processes are studied in depth for self-healing carbon fiber reinforced composites, microcapsules, and supra-molecular elastomers. The composite structures fail due to internal cracks. These cracks are initiated due to continuous loading of structures. It is not possible to fill those cracks especially when the structures are at remote locations. Self-healing materials are designed and prepared to heal their cracks. The present review is about self-healing materials used for the fabrication of composites. It is expected that future applications are based on such advanced self-healing composite materials and thus it is needed to review advanced self-healing composite structures. A brief review of self-healing techniques and materials as well as applications are discussed in the present investigation. The efficient and effective manufacturing techniques are suggested through the article.

1. Introduction

Self-healing composites are mainly categorized into autonomic and non-autonomic methods. Furthermore, such methods are divided into the following groups such as extrinsic, intrinsic, vascular, and capsule based self-healing composites. The extrinsic self-healing is performed without any external initiation, but in intrinsic some external source will be required to initiate self-healing. In capsule-based self-healing materials, the capsules are filled with healing agents and inserted into the composite structures. Vascular network is a network of containers of self-healing materials interconnected with nodes. The cracks under the material surface are filled and healed using self-healing materials of a particular liquid. Capsules will be damaged due to cracks and thus healing agents are initiated for their actions to heal cracks at damaged locations. The capsules are mostly replaced by vascular networks with self-healing materials, in which various self-healing agents flow through networks. These materials fill gaps after cracks initiation as cracks break the network and thus, they (cracks) allow healing agents to flow inside the network. The capsules containing the healing materials will trigger the release of active healing compounds in different environments. The restoration of mechanical properties such as tensile fracture strength and its recovery is accomplished through the self-healing mechanism and using self-healing materials. Self-healing materials encompass different classes of materials such as metals, concrete, ceramics, polymer, and composites (Hager et al 2010 and Kanellopoulos et al 2011).

Healing can be achieved by two different processes such as chemical as well as physical processes. The healing action is initiated due to chemical reactions. Kinetic chemical reactions occur continuously and in sequential steps as their thermodynamics are controlled (Bond et al 2007 and Kanu et al 2019). The enthalpy and energy of reactions are mapped with chain diffusion. The internal mechanisms impact Gibbs free energy and thus contribute to healing efficiency. In Physical processes, one more factor considering the free volume in a matrix indicates the mobility of polymeric chains (Thanawala and Khanna 2016). The components such as microcapsules with some inorganic matter as well as microphase separation heal the damaged area of composites. The heterogeneous polymeric substances are prepared using a phase separation process involving shape memory composites. Various dicyclo-pentadyne (DCPD) and other polymerization techniques of
self-healing are used as chemical processes (Chen et al. 2016 and Khan et al. 2016). The matrix materials are modified with polymer chains having covalent bonds (reversible in nature). The ratio of damage rate to healing rate balances the stages of chemical processes. The chemical process was balanced by the ratio of damage rate to healing rate. The damage rate depends on the strain rate, amplitude of stress, and loading frequency. Healing rate depends upon healing materials, concentration, and temperature (Tennyson et al. 2010).

Pham et al. (2015) studied about multifunctional composite and catalysts (Grubbs catalyst and tungsten chloride). The authors noticed the stability of the healing process based on catalysts and its melting point. They studied the blend ratio, parameters of healing such as body temperature and rate of healing to assess the healing efficiency, and concluded with a revised blending mechanism (DCPD and ethylidene norbornene) to improve the effective healing rate. Jadhav et al. (2011) investigated the healed surface cracks of composites. The microcapsules filled with linseed oil were found efficient in healing surface cracks initiated after coating. The oils are oxidized in the presence of atmospheric oxygen and thus they are efficient to heal cracks in merely 80 s (Mehta and Vadher 2017). Twin capsules are used in some cases which are filled with epoxy resin and hardener and encapsulated separately and they are embedded in the composite matrix (Madara et al. 2018 and Elham et al. 2020). In some cases, they used a single capsule which contains self-healing materials and the catalysts are randomly dispersed in the composite to accelerate the healing process. In their research they used healing material and hardener in two different capsules (Liu et al. 2013 and Zhen et al. 2018). Hardener was used to accelerate the healing process and it was observed that the healing rate is influenced by catalytic inhibitors. Furthermore, self-healing efficiency was found better in a single capsule instead of twin capsules. The figure 1 shows microcapsule based self-healing approach. Microcapsules filled with healing agents are placed in different positions in composite materials. When crack was initiated and further, self-healing materials came in contact, a healing reaction was initiated in the presence of catalysts to repair the crack.

Purohit et al. (2015) studied methods for manufacturing self-healing materials and discovered that encapsulation was an effective method for developing self-healing materials. In their research, they studied the healing efficiency and curing time. Efficiency of encapsulation was almost 75%–85%, which was always greater than hollow fiber (30%–50%) and other methods. Assa et al. (2012) studied traditional methods of repairing damages in the polymeric materials and explained methods for quantification of healing efficiency in terms of strain fracture toughness. Bekas et al. (2016) have studied about cross-linking of linear polymers and found that if cross-linked polymers were used, then the healing performance could be improved significantly in the absence

![Figure 1. Schematic representation of self-healing approach](https://example.com/figure1.png)
of catalyst. Thakur et al (2011) studied organic layers of soft organic phase with dispersed nanoparticles migrating towards the surface cracks and further, heal the damage. On investigation of the structural and mechanical characteristics through simulations, results were found to be in favor of cross-linked polymers as their material properties were improved significantly. Furthermore, the healing efficiency of healed gel samples was found to be higher than 62% (Yimin et al 2020). They also studied about self-healing tests of synthesized gels at ambient temperature (Yongxi et al 2018). Recently, glass fiber, carbon nanotubes, and single-walled carbon nanotubes are used for encapsulation of healing agents to improve the healing efficiency (Lazaros et al 2019). Xiao et al (2014) studied the accelerated healing process accomplished by antimony pent-fluoride as an instant hardener of epoxy. They successfully encapsulated the healing agents and investigated on curing speed of epoxy catalyzed using Lewis acid (proportional to their acidity, SbF5 and epoxy). Pan et al (2017) studied about self-healing novel polymer/graphene oxide nanocomposite (AM–Co-DAC)/GO hydrogels. They were used as self-healing agents (Sajjad et al 2020), where, hydrogen bonds were formed due to electrostatic interactions. To improving curing time and demonstrate the temperature affects on the healing ability and hardness of the healed agents which was 93% with respect to the virgin component. Valentinii et al (2016) studied about silicone rubber graphene nano-platelets, SR/GNP composites with reversible bond thermal annealing processes. They were focused on the tensile strength of the healed structures. They recovered 87% tensile strength in the component. Zhang et al (2016) studied about graphene which was being used as a self-healing material and a Diels–Alder chemistry mechanism for the self-healing of structures. They proved that the source of temperature could affect the healing strength of components. In their research paper, IR was used as a source of temperature. Sun et al (2016) microwave is used to maintain temperature and measure stress as well as Young’s modulus. The mechanical properties of composite materials were evaluated using strain sensors integrated with Diels–Alder chemistry mechanism.

2. Fabrication and characterization of self-healing composites

Self-healing composites are fabricated by different mechanisms as listed in table 1. The mechanisms for fabrication of self-healing materials are classified on the basis of physical and chemical interactions. In the research paper, the a few techniques used for the synthesis of self-healing materials are discussed. Han et al (2017) performed the supramolecular interaction experimentation with ureidopyrimidinone terminated polyethylene glycol (PEG) as a healing substance at room temperature and found that it has 100% healing efficiency within 5 min of curing time. Dichloropentadine (DCPD) material filled capsules inserted into the composite material could yield better results, almost 78% healing efficiency. However, the partial healing is a major concern due to the limited amount of healing agent present in the capsule (Peng et al 2015).

The authors carried out experimentation with large size capsules (>100 μm) in the resin. However, these experimentations eventually failed due to less healing efficiency, almost 28% and, further reduced strength of virgin material. Healing agent was present in hollow tubes’ network and they are linked with each other. Fabrication of the composites with grid is quite tedious and difficult but they have higher strength up to 99% due to the uninterrupted distribution of the healing agents (Banshiwal and Tripathi 2019). When dicyclopentadiene (DCPD) was made association with the Grubbs’ enzymes which was diffused in the epoxy resin, a ring like opening metathesis polymerization (ROMP) was initiated and an eminently cross-linked tough polycyclopendiene was thereafter forming which actually heals the damage (Ghosh 2009). In the research, they studied the healing efficiency and curing time of encapsulation and hollow fiber method. Efficiency of encapsulation was 75%–85% greater than hollow fiber 30%–50% (Eleonora et al 2016). During encapsulation of healing mechanisms, ring opening metathesis polymerization (ROMP) is used by most of the researchers because it yields less curing time and avoids partial healing due to polymerization (Shabani et al 2020). Through their investigation, they concluded that healing efficiency depends upon the healable systems and catalysts. Epoxy/dichloropentadine catalyst used for ROMP shows less efficiency, almost 20%, but ROMP with Grubbs catalyst yields 95% efficiency (table 1). Healing efficiency of a composite depends upon the healable system and mechanisms. In two-stage chemistry process consisting of different monomers, when the damage is triggered in the composite, the monomers initiate and perform the reaction and formation of a gel and cross-linking of two gelators (monomer reaction forming gelators) with an acid catalyst (Liberata et al 2010) and Hao-Liang et al (2020). The process of gelation is continuous until the void is filled after these second stage starts with monomer polymerization. The stage recovers the structure ability of the composite material. For two-stage chemistry method, authors performed the experimentation with 2-hydroxyethyl methacrylate used as gelators, dichloroacetic acid as a catalyst, and methyl ethyl ketone peroxide (initiator). In their experimentation, they achieved 62% healing efficiency (Ramesh et al 2020).

Thermoplastic microparticles self-repair materials are integrated with carbon fiber reinforced polymers and self-healing capacity was measured by fracture toughness testing in mode I and mode II (Naga Kumar et al 2020).
### Table 1. Self-healing mechanisms.

| Sr No. | Healing mechanism | Healable systems | Healing efficiency (%) | References |
|--------|-------------------|------------------|------------------------|------------|
| 1      | DCPD              | Grubbs catalyst (12 h at 25 °C) | 70 | Toohey et al (2009) |
| 2      | Ring opening metathesis polymerization (ROMP) | Epoxy/dichloropentadine-tunguston hexachloride catalyst | 20 | Jason et al (2007) |
| 3      | Polycondensation reaction | Polysiloxane (polydimethylsiloxane) catalyst | 100 | Cho et al (2006) |
| 4      | Epoxy/CuBr2(2methylimidazole)4 | Woven glass fabric/epoxy laminates | 68–79 | Yin et al (2009) |
| 5      | ROMP              | dichloropentadine/Poly-formaldehyde microcapsules/Grubbs catalyst | 99 | White et al (2001) |
| 6      | Curing mechanism | Epoxides/amine | 91 | Henghua et al (2012) |
| 7      | Curing mechanism | Epoxy/mercaptan | 100 | Yuan et al (2008) |
| 8      | Two-stage chemistry | 20 min to fill impact region and 3 h restore mechanical function | 62 | White et al (2014) |
| 9      | Multiple interactions | Carbon nanofibers (PNB)-borax (PB), room temperature | 95.6 | Xiaosai et al (2008) |
| 10     | Hydrogen bonding | Poly acrylic acid cross linked nanocomposite gels (PAA/CNC NC) | 91 | Xia et al (2018) |
| 11     | ROMP              | ENB 95% and DCPD 5% | 79 | Pasquale et al (2017) |
| 12     | 3D Printing       | Resin with embedded microcapsules | 87 | Sanders et al (2019) |
After fracture, the first healing cycle was performed in controlled heating conditions with the help of a heat press machine at the temperature of 130 °C for 5 h with a pressure of 15 N. After successful healing of the first cycle as shown in figure 2, the displacement was increased and the healing efficiency was reduced. Furthermore, samples after the first healing were tested for mode II self-healing activity and a fracture toughness test was performed. After impact loading, the crack was initiated further, composite was healed second time. They have shown for two continuous healing activations, indicative load (P) versus displacement (d) curves for PET–modified CFRPs was discussed (Reprinted from Athanasios and Vassilis 2020, Copyright © 2020 Elsevier Inc. All rights reserved).

Figure 2. After two successive healing cases, the outcomes of mode II experiments are depicted. According to these tests, samples did not reveal any differences when two separate healing periods were applied. Before and after two consecutive healing activations, indicative load (P) versus displacement (d) curves for PET–modified CFRPs was discussed (Reprinted from Athanasios and Vassilis 2020, Copyright © 2020 Elsevier Inc. All rights reserved).

In the multiple interaction process, hybrid hydrogels were prepared using carbon nanofibers, borax, and polyvinyl alcohol (PVA). Hybrid hydrogels were prepared in five different series based on the ratio of CNB/PB (PVA-Borax). In the research, they demonstrated about the self-healing process and its ability of healing with an efficiency range of 85% to 97%. Hu et al. prepared stretchable hydrogels with the help of free radical polymerization [49]. Initial stage synthesized nanocomposite gels from Ca$_2$SiO$_5$ powder dispersed with 20 ml of water and magnetic stirring for 30 min to produce enough cross linked composite material (CNS). After the preparation of PAA/CNS NC hydrogels, tensile strength was characterized using E44 testing machine at room temperature. They recovered 91% tensile strength in the structural laminates and thus self-healing efficiency of composites was improved (Xiu et al. 2018 and Feng et al. 2020).

Fabrication of composite materials by physical and chemical processes are seen above, but encapsulation of healing agents in the capsules are of utmost importance in composite material. As per capsule arrangement, microencapsulation and microvascular network are the two major types of self-healing material preparation. Microcapsules are spaced at different locations within the composite. After initiation of the crack, they are allowed to propagate towards the capsule. and break the capsule shell, the healing material from the capsule will further fill the cracks and heal the damage. However, in some cases due to limited availability of self-healing material, the cracks are partially healed. The problem is partially solved through the microvascular network. Following the approach of microvascular network, authors prepared a structure of interconnected vessels having healing agents (Kanellopoulos et al. 2017 and Ransom et al. 2019).

When they initiated cracks within the material, the network was broken and the healing materials were allowed to fill crack and further, heal the crack. Pasquale Longo et al. experimented microencapsulation system for the fabrication of self-healing composite materials with different percentage of healing materials and polymerization reaction (Fatemeh et al. 2019). Preparation of self-healing composite was divided into three
stages. In the first stage, they took a blend of 95% 5-ethylidene-2-norbornene (ENB) and 5% dicyclopentadiene (DCPD). To improve cross-linking metathesis polymerization, DCPD was used to accelerate the healing process.

In the second stage, the synthesis of HG2 initiator was done by chemical processes. In the final stage of FTIR investigation, the self-healing efficiency of material was investigated. In the research, different polymerization reaction was performed and analyzed for the polymer contents such as polymerization of 2-norbornene (NBE) with different initiators and polymerization of 5-ethylidene-2-norbornene (ENB) with different initiators. In the research, they overcome the shortcomings related to the encapsulation system and fulfilled the requirement of structural components (Selen et al. 2019).

Authors have discussed about physical and chemical processes for self-healing mechanisms. In chemical processes, Aishwarya V Menon et al fabricated ultrafast self-healable interfaces using Diels-Alder mechanism, and microwave absorbers. Graphene oxide grafted with magnetite nanoparticles (rGO/Fe$_3$O$_4$) was covalently cross-linked to thermoplastic polyurethane using Diels-Alder chemistry and heated by microwave to achieve self-healing of materials. In the research, nanocomposites prepared using Fe$_3$O$_4$ nanoparticles of 5–10 nm size distributed uniformly on graphene oxide sheets. Researchers used different peaks of nanomaterials varying from 30.4°C to 62.8°C and successfully fabricated self-healing composite using Diels-Alder reaction. The characterization of the material was observed under FTIR spectrum. Furthermore, the material was cut into two halves and joined together by slightly applying the pressure and the waves were applied from domestic microwave operated at 900 watts for 10 min and thus, effective self-healing was accomplished. The synthesized self-healing nanocomposites were used in the coating of electronic applications (Menon et al. 2018).

Wilson et al studied the size of catalyst microspheres on healing performance with microcapsules having 34 μm and 54 μm sizes of microcapsules filled with Grubbs catalyst with additives benzoyl peroxide (BPO) and dimethylaniline (DMA) by improve the curing time. In the experimentation with three different conditions of curing agents, initially DMA was used, but there were no any significant changes in the curing time. Thus, they performed the experiment with BPO alone and combination of BPO (1 wt %) and DMA (0.1 wt %). In combination of both, the curing agent with Grubbs catalyst yielded better results compared with the first two
experiments. Afterwards, the microcapsules having 34 \(\mu\text{m}\) and 54 \(\mu\text{m}\) sizes were filled with catalyst. Two different healing agents were also considered for experimentation, i.e., endo-DCPD and exo-DCPD, and filing the self-healing agent into the urea formaldehyde microcapsule with 250 ± 31 \(\mu\text{m}\) size. After preparation of catalyst microspheres and self-healing materials, DCPD microcapsules were embedded into an epoxy vinyl ester matrix (15 wt% catalyst microspheres and 15 wt% microcapsules). Furthermore, fabrication of self-healing nanocomposites were done for fracture test for evaluation of peak load and strain energy. Finally, the self-healing efficiency for different samples were assessed and a 49% maximum efficiency was achieved with 54 \(\mu\text{m}\) size of the microcapsules and exo-DCPD self-healing samples (Wilson et al 2008 and Yong et al 2020).

Sanders et al fabricated self-healable nanocomposite structures by stereolithographic (SL) 3D printing method using combined ultraviolet (UV) curable resin embedded with solvent containing anisole/ poly-methylmethacrylate (PMMA)-filled urea-formaldehyde microcapsules as shown in figure 4. PMMA chains dissolved in anisole as shown in figure 4(a). Crack was initiated to reach upto microcapsule and rupture the capsule as shown in figure 4(b). After the rupture, the capsule released the healing material and fill the crack as shown in figure 4(c). These solvents were containing healing agents in three different quantities such as 2.5, 5, and 10 wt% capsule concentrations and self-healing was accomplished at different curing times such as 24, 72, and 120 h, respectively. Finally, mechanical testing of three samples with different curing time was done to achieve 87% self-healing efficiency for 72 h curing time and 10 wt% capsule concentration. The resin embedded with capsules were filled in the resin tank of SLA printer. As per the required structure, G code and further, .STL files were generated. The code was read by the SLA printer to fabricate self-healing composites via bottom to top approach. Finally self-healing nanocomposite materials were manufactured by 3D printing technology and successfully tested for 87% self-healing efficiency (Sanders et al 2019 and Mohammadmahdi et al 2020).

Alan Saghatelian et al (2016) prepared the microcapsule by polymerization and manufactured self-healing epoxy specimens. Initially, the microcapsule prepared by reaction mixture stirred with 10% NaOH solution at 454 rpm for average droplet size of 200 \(\mu\text{m}\). They added 37% formaldehyde and maintained the temperature at 50 °C for 2 h. Self-healing epoxy specimen prepared by mixing of epoxide with 12 parts of DCPD (dicylopentadiene). The epoxy specimen embedded with 2.5% of Grubbs catalyst and 10% of microcapsules was poured into a silicon mould to fabricate a tapered double cantilever beam (TDCB) specimens (Richard 2008). The specimen was tested with different conditions such as (1) epoxy with Grubbs catalysts, (2) epoxy with microspheres, and (3) epoxy without Grubbs catalyst and microspheres. All samples were tested and the toughness of virgin material and toughness after healing the crack were measured to evaluate the self-healing efficiency. They shown the release of the healing agent after rupture of the microsphere and when a crack approached a spherical capsule embedded in the epoxy and subjected to a tensile load perpendicular to the fracture plane. The red color dye was used to capture the perfect self-healing of the crack. Microcapsules were embedded in a red colored healing agent and they tested the samples after the initiation of crack in the epoxy composite and when it reached up to the microcapsules. Crack was propagated to the microcapsule and then healing agent was released. The healing agent was brought in contact with the catalysts and polymerization reaction was initiated. Polymerization reactions accelerated the spread of healing agents. Healing agents were used to fill the crack and mechanical properties of the self-healing material were recovered (White et al 2001 and Haddadia et al 2019).
3. Recent advances in self-healing composite

Optimization of the healing process and developing new self-healing systems improves the healing cycle time and efficiency. To develop some advanced systems which heal the material multiple times are recent research areas for study (Li et al. 2018). Hydrogels showed self-healing ability and improved mechanical properties. Recently experiments were conducted as shown in figure 5(a) for hydrogels connected with electrodes (inserted into rabbit’s body) and the signals were measured to check the hydrogels behavior at the time of troubling situations. Figure 5(b) shows signals detected by intramuscular electrodes. Hydrogels were used as self-healing materials and they are fabricated by using grape pomace waste after making red wine. Crushed grape extraction with ethanol was dried in a vacuum oven at 60°C and processed with different chemical processes to generate crystalline cellulose (Siva et al. 2019 and Qichao et al. 2020). Composite material reinforced with borax, glycerol, and cellulose nanocrystals (CNCs) was evaluated after initiation of cracks. Components of healing agents were reacted with each other and hydrogels were generated to show polymerization reaction of CNCs. The crystalline cellulose was mixed with deep eutectic solvent in a mechanical stirrer. Afterwards, the achieved cellulose nanocrystals (CNC) were taken in paste form for their utilization as self-healing materials. Characterized results of self-healing hydrogels were observed and it was found that they have improved self-healing ability with 90% of recovered tensile strength and improved mechanical properties with stress and starning being 0.95 MPa and 170%, respectively (Selên et al. 2019). The research shows an environmental friendly concept to extract CNS from grape waste and fabricate self-healing nanocomposites. Figure 6 shows cotton-FRCs (type E) laminates and woven carbon-FRCs (type C) laminates. Figure 6(a) shows E1 random-discontinuous cotton string laminates and E2 random-discontinuous cotton string laminates embedded with porous CNT layer. Figure 6(b) shows C1-woven carbon fibre laminates and C2-porous CNT ply with woven carbon fibers (Wang et al. 2016).

Synthesis of physically cross-linked nanocomposite hydrogels based on the super molecular networks between hydrogen bonds and dual metal carboxylate is discussed in detail. In self-healing experimentation, these cross-links between hydrogen bonds could improve mechanical properties and demonstrate the self-healing efficiency. Healing was achieved at room temperature without any external or human intervention and almost 90% of healing efficiency claimed thereafter (Changyou et al. 2017).

Ability of self-healing and mechanical properties were studied in-depth and found that the aramid/boron nitride nano sheet (BNNS) self-healing nanocomposite would have improved tensile strength around 42.20 - 560.25 MPa in addition to sustainable self-healing performance. In their research, they explained the preparation of 1 mm thick aramid/BNNS self-healable nanocomposites and successfully tested the micro topography of such nanocomposites and dielectric constant for stability (stable between 3.8 and 4) (Lixin et al. 2017). Self-healing ability of material was tested with experimentation on virgin material, i.e., sample of 4 mm which was cut centrally and finally due to internal bonding, the structures heal themselves. Orientation method was used for composite manufacturing, as it was found to improve self-healing ability. Cross ply stacking method was done to manufacture the composite material reinforced with polyethylene terephthalate (PET) particles (mixed in 7% volume of epoxy resin and fabricated using hand laying process) (Konwar et al. 2016).

During the fabrication of the composite, 13 μm sheets placed at the middle surface of the composite laminate,
and afterwards, post curing for 10 h at 60 °C was done. After fabrication of self-healing, composites, their characterization for improved mechanical properties remain as an essential task. Thus, they performed inspection to assess the composites quality via 3-point bending test, impact compression, and dynamic mechanical analysis test. They observed improvement in healing toughness of nearly 56% (previously 40%). Furthermore, the difference in tensile stresses were due to differences in blend of self-healing materials; the tensile stresses varied in the range between 31 MPa and 39 MPa (Mohammadmahdi et al. 2020).

Figure 7(a) shows temperatures of the samples which varies due to change in voltage, were maintained in the range 15 °C–80 °C for voltage range 10–16 V. Figure 7(b) shows thermal distribution in CNS which was sufficient for enable healing process in 20–24 h. Figure 7(c) shows frozen and de-iced area of composite material and efficiency of carbon nanotube sheet (CNS) (Wang et al. 2016). Feng Xu et al prepared self-healable hydrogels with different molar concentrations of 0.25 mol % to 1.25 mol % and measured the mechanical properties, stress, strain, and toughness. After assessment of the mechanical properties, they compared the healing efficiency at different molar percentage. Cellulose nanofibers (CNF), in colloidal solutions of concentration of 1.2 wt %, are used to prepare poly acrylic acid (PAA)-CNF iron ion (Fe^{3+}) hydrogels via polymerization after the successful preparation of hydrogels (physical hydrogels with varying percentage of Fe^{3+} moles). The authors prepared six different samples and measured their mechanical properties (Liangjiu et al. 2019 and Xinxin et al. 2020). In figure 8(a), the stress versus strain curves of different samples were plotted to state that 1% molar percentage could yield better results as compared to other molar percentage. In figure 8(b) the they discssed for higher toughness of component (11 MJ m⁻³ and 0.53 MPa) at same 1% molar percentage. In their research, they also measured the self-healing efficiency at different time intervals. As the efficiency was measured at a regular interval of three hours after initiation of crack, in the first 12 h, 78% of the material properties were regained, and after 24 h the efficiency reached up to 82%. At the end of 48 h, the final efficiency was measured and afterwards there was no change in efficiency after it reached up to 90% (Madara et al. 2018).

Self-healing efficiency also depends upon the surrounding conditions, and maintaining the surrounding environmental factor is essential for sustainable self-healing (Ding et al. 2018). They show that self-healing laminates can heal themselves through sustainable way as efficiently as 100% at a temperature around – 60 °C. The self-healing mechanism occurs in the presence of catalytic agents, similar to the case of living species at normal body temperature. Two types of FRC laminates (E and C) are embedded with CNT ply. Testing was
performed at 20 °C–25 °C and keeping the voltage range from 10–16 V. The authors stated that the laminate with CNS, has an average efficiency of 96.22% in terms of peak load. In the results and discussion, authors compared the results of two different samples with CNS and CFS and performed mechanical testing on samples to evaluate the efficiency by measuring the peak load and strain energy as shown in figures (a) and (b) and, further compared load with respect to displacement under one plot via curves of original, damaged and healed materials with or without CNS (Wang et al 2016).
4. Applications of self-healing

Injured tissues of the human’s body repair themselves without any external intervention. Thus, researchers are trying to make such man-made self-healable smart material in different sections. Various applications of self-healing materials in biomedical sector, anticorrosion coatings, concrete and asphalt, composite materials, aerospace, and marine equipment (Rong et al 2001 and Reddy et al 2020) are listed in table 2. Automatic self-healing materials and hydrogels are used in the biomedical sector for contact lenses, biosensors, and tissue engineering. Self-healing materials are used to fabricate anticancer self-healing double network films (Chao et al 2013). Hydrogels are used in number of research papers for biomedical and dental applications (Mostafa et al 2020). In anticorrosion coatings self-healing materials are used to respond mechanical and chemical damage of the material and heal the surface cracks and make an anticorrosive coating (Sina and Bahram 2020), some cases linseed oil, potassium ethyl xanthate, and other anti-corrosive agents are embedded into the coatings and enhance the anticorrosive properties of material. In the healing of concrete and asphalt cracks are healed by sodium nitrite, sunflower oil, and other healing agents, cases, 3% wt of microcapsules inserted into the asphalt double the fatigue life of asphalt (Peng et al 2015). Self-healing epoxy materials may improve the properties of nanocomposite materials (SIAG). These materials are replacing the metal parts with composite material in aerial vehicles and reduce its weight and economical. Aviation industries face problems with internal cracks in the composite and it is very difficult to detect internal cracks. Due to this internal crack, serious accidents happened in past. After combining a shape memory polymer with cross-ply (0/90/90/0) carbon fabric and carbon nanotubes (CNTs), self-healing CFRP laminates are fabricated using a high-pressure molding mechanism (Thanawala et al 2014). It is reported to have improved fatigue resistance and therefore, it is used as an aerospace material. Some autonomic self-healing hydrogels are used as a biomedical application biosensor cells in tissue engineering and drug delivery (Mobarak et al 2020).

5. Future scope

The reality is that self-healing materials have a future in smart materials and innovative product development. Today, researchers are trying to improve the properties of material and recover the material properties after the damage. There is also substantial scope in the development of self-healing composite materials for space applications and aircrafts to recover micro cracks and damages during operation in space. However, there are some limitations to understanding the healing process and stability in the process. Detection of internal cracks and further efficient healing are major challenges in self-healing process (Blaiszik et al 2008 and Eleonora et al 2016).

In the review, it is not possible to ignore encapsulation techniques and self-healing hydrogels for biomedical applications. The importance of DCPD and its blend with various materials affects the curing time. Thus, healing percentage, healing efficiency, and mechanical properties of a component after healing are the key sides...
Table 2. Applications of self-healing materials.

| Self-healing Mechanism                  | Material                                      | Self-healing Condition                           | Healing Efficiency | Applications                      | References       |
|----------------------------------------|-----------------------------------------------|--------------------------------------------------|--------------------|------------------------------------|------------------|
| Hydrogen bonding                       | Poly acrylic acid cross linked nano composite gels (PAA/CNC NC) | Room temperature and 30 min magnetic stirrer      | 91                 | Robotics                          | Assa et al (2012) |
| ROMP                                   | ENB DCPD                                      | Room temperature                                 | 79%                | Structural composite application   | Pasquale et al (2017) |
| Ionic binding                         | PAA-GO-Fe3+ Hydrogel                          | Contact and immersed in FeCl3/HCl                | 100%               | Robotics                          | Therriault et al (2003) |
| Reversible bonds                       | SR/GNP composite                              | Thermal annealing                                 | 87% of Tensile Strength | Fluid mechanics and machine tool control System | Valentini et al (2016) |
| Hydrogen bonds, electrostatic interaction | P(AM-co-DAC)/GO hydrogels                    | Drop water                                        | >92% of tensile strength | —                                | Pan et al (2017) |
| Diels-Alder chemistry                  | Graphene/PU                                    | IR                                               | 96%                | Flexible electronics              | Wu et al (2017)  |
| Diels-Alder chemistry                  | RFGO/PU composites                            | Microwaves                                       | 93%                | Strain sensors                    | Li et al (2016)  |
| π-π stacking, hydrogen bonds           | Chitosan/GO hydrogel                          | Contact (room temperature)                       | -                  | Electroactive tissue engineering applications | Jing et al (2017) |
to follow and thus understanding of these aspects is critical for the development of self-healing laminates (Thakur and Kessler 2015 and Yu et al 2020).

The review promotes researchers to investigate application-based self-healing materials and more focus on self-healing hydrogels for different structural applications. Carbon fiber composites need to be used in aerospace applications. Research progress of self-healing composites is reviewed to motivate researchers towards sustainable self-healing at low temperatures in composites. Study of efficient self-healing thermo-reversible elastomer (HBN-GO) through stress-strain curves (Haili et al 2019). CNS nanotube composite materials can self-heal cracks effectively (Hart et al 2019 and Idumah and Odera 2020). Wang et al (2016) have achieved healing efficiency 96.22% in peak load in FRCs and 100% in fracture energy at −60 °C temperature. Some self-healing materials are used for store energy mechanically and electrically (Luzhi et al 2019 and Sangbaek et al 2018).

6. Conclusion

The review article discusses about the physical and chemical processes of self-healing and parameters such as catalysts, temperature, healing type, melting point, capsule size, shape and orientation, and curing time; affecting self-healing performance. In physical processes, the movement of chains is required for healing the cracks. The movements are continued and controlled by thermodynamics and kinetics. Cross-linking of linear polymers have been extensively studied and found that if cross-linked polymers are used then healing process could be efficiently repeated without addition of chemical agents. In the present review, various techniques used for the synthesis of self-healing materials and physical interactions, hydrogen bond, hydrophobic interaction, and chemical interactions are discussed. The advantages and disadvantages of self-healing techniques are reviewed in-depth and discussed for their implementation. Chemical fabrication methods are more efficient but also they are not easy to initiate for a controlled healing with respect to physical processes. In addition to that they take more curing time. It is found that self-healable nanocomposite structures could be fabricated by stereolithographic (SL), a 3D printing method by combining ultraviolet (UV) curable resin embedded with a solvent containing anisole/poly-methylmethacrylate (PMMA)-filled urea-formaldehyde microcapsule. Self-healing hydrogels and supramolecular networks between hydrogen bonds are the key elements of the medical field. In self-healing experimentation, the cross-links between hydrogen bonds improve mechanical properties and demonstrate the self-healing. The applications of self-healing structures could be so many and are not limited to aerospace, biomedical, robotics, fluid mechanics, flexible electronics, and tissue engineering. It is reported about self-healing structures that they have improved fatigue resistance, and therefore, they are used as aerospace materials. Some autonomic self-healing hydrogels are also discussed herewith. Primary used as biomedical application biosensors, cells in tissue engineering and drug delivery. In the review, it is not possible to ignore encapsulation techniques and self-healing hydrogels for biomedical applications. The importance of DCPD and its blend with various materials affects the curing time. Thus, the healing percentage, healing efficiency, and mechanical properties of the component after healing are two different situations. Therefore, maintaining a balance between these is still a challenging task. The review promotes researchers to investigate application-based self-healing materials and more focus on self-healing hydrogels for different structural applications. Carbon fiber self-healing composites need to be used in aerospace applications.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

The authors declare that there are no conflicts of interest.

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