A Review of Self-Healing Mechanism as the Modern Paradigm in Structural Materials

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Abstract

In recent years, extensive research efforts have been dedicated to exploring materials with self-healing properties, both autonomously and non-autonomously. The ability of materials to autonomously repair damage offers significant advantages such as increased service life, enhanced product safety, and reduced replacement costs. This paper focuses on autonomous self-healing mechanisms achieved through the encapsulation of healing agents within polymer shells. Through an extensive review of the literature, this study presents findings on the incorporation of self-healing capsules into polymers, examining both mono and dual microcapsules. The paper also discusses the implementation of unidirectional and multidirectional vascular networks, which facilitate the distribution of healing agents throughout the material matrix. The results reported in this paper contribute to the advancement of self-healing fiber-polymer composites, with potential applications in diverse industries such as building and construction, packaging, military, and aerospace. The incorporation of self-healing mechanisms in these sectors has the potential to revolutionize material performance, leading to longer-lasting and more durable products. By harnessing the capabilities of autonomous self-healing mechanisms, materials can exhibit remarkable resilience and prolonged functionality, even in challenging environments. This paper not only highlights the promising outcomes achieved through the use of polymer-encapsulated healing agents but also provides valuable insights into the ongoing research efforts aimed at perfecting self-healing systems.

Keywords: Self-healing, Microcapsules, Encapsulation, Extrinsic, Polymer, Healing efficiency, Epoxy Resin.

1.0 INTRODUCTION

Polymeric materials fit into a wide range of applications stemming from simple household utensils, industrial packages, engineering structures, military protective gears to complex aerospace shuttles and vehicles owing to its diverse modification as polymer blends and polymer composites. Polymers serves as the major matrix in reinforcement of synthetic fibre and Natural fibre composites (Kenned *et al.*, 2020). However, polymers and polymeric composite materials are susceptible to mechanical, thermal, chemical and radiation induced damages in the form of voids, cracks, breakages and tears during service time (Khalili *et al.,* 2019; Yubin *et al.,* 2022). There are a number of methods adopted by industries for the repair of visible or detectable damages in polymer structures examples is "Hot plate welding", in this process polymers are treated above its glass transition temperature long enough for interdiffusion process across the crack face to occur thereby restoring the material strength, but the welding site is the weakest point for future damages (Daniel and Haddad, 2012)**.** However, damages incurred by materials during service time can be so deep in the material's matrix that detection and repairs at production stage are often not feasible, hence the need for smart materials (Guo *et al.,* 2019). Self-healing composites are smart materials that exhibit an automated recovery mechanism when damaged to restore material to its initial property (Idumah, 2020)**.** These materials demonstrate autonomous healing ability (with or without human interferences) to damages caused by mechanical friction or time efflux (Cuvellier *et al.,* 2018; Jagtap *et al.*, 2018). Introduction of self-healing mechanism prolong material durability, reduce cost of maintenance, improved mechanical properties and assures safety making self-healing materials to be useful in fields like aerospace, robotics and electronics, as well as building and construction. (Al-Mansoori *et al.*, 2018; Jagtap *et al.*, 2018)**.**

This pap`er is aimed at reviewing self-healing systems and its application in structural materials. To achieve this aim, self-healing mechanisms was classified, two microcapsulation method and one vascular preparation procedures was described and various applications of healing systems in polymeric material, concrete, metal, ceramics, biomedical and aerospace was discussed based on existing literature.

2.0 LITERATURE REVIEW

2.1 Classification of Self-Healing Materials

Self-healing material are materials that can partially or totally restore to its original properties autonomously or non-autonomously after damages so as to prevent mechanical degradation and ultimate failure of such material during service time (Zamal *et al.*, 2020). Self-healing composites have built-in capability to recover material's mechanical properties after damages (Idumah, 2020)**.** Self-healing is a 1980s' concept but publications by Dry and Sottos in 1993 and White and co in 2001 further inspired the world interest in extensive study of self-healing materials (Daniel and Haddad, 2012)**.** Following White *et al.,* (2001) publication, different healing mechanisms have been researched on and can be broadly categorized into intrinsic and extrinsic mechanism. In intrinsic self-healing system the cracks are healed by the polymer itself through chemical bonding while in extrinsic, healing agent are pre-embedded in the material's matrix (Yuan *et al.,* 2008b). Introduction of self-healing mechanism prolong material durability, reduce cost of maintenance, improved mechanical properties and assures safety, making self-healing materials to be useful in fields like aerospace, robotics and electronics, as well as building and construction. (Al-Mansoori *et al.*, 2018; Jagtap *et al.*, 2018)**.**

2.1.1 Intrinsic Self-Healing Mechanism

Intrinsic self-healing mechanism makes use of bond breakage and reformation in covalent or non-covalent reversible interactions, such as dynamic transesterification, reversible Diels-Alder (D-A) bonds, dynamic amine bonds and hydrogen bonds for micro-crack repair (Sheikhy *et al.*, 2015). This process is triggered by external factors such as temperature, pH, humidity, electromagnetic radiations or ionic strength (Willocq *et al.*, 2020). Thus, this healing mechanism is non-autonomous since the healing process requires external stimuli to trigger the process (Hia, *et al.*, 2016; Yuan *et al.*, 2008b). Willocq *et al.*, (2020) explained that once mechanical damage occurs in a polymer with intrinsic self-healing mechanism, there will be molecular chain cleavage resulting in formation of reactive end-groups with functional groups like COOH, OH, NH_2, Si–O, SH, S–S or B–O or even free radicals with or without conformational change. These reactive end-groups further reassemble at the damage site or oxidize to form stable products. Simultaneously on the macromolecular level, cleaved macromolecule chain will undergo conformational change resulting in network rearrangements and finally, bonds reformation take place and the network is repaired once chemico-physical condition is favoured as shown in Plate 1.

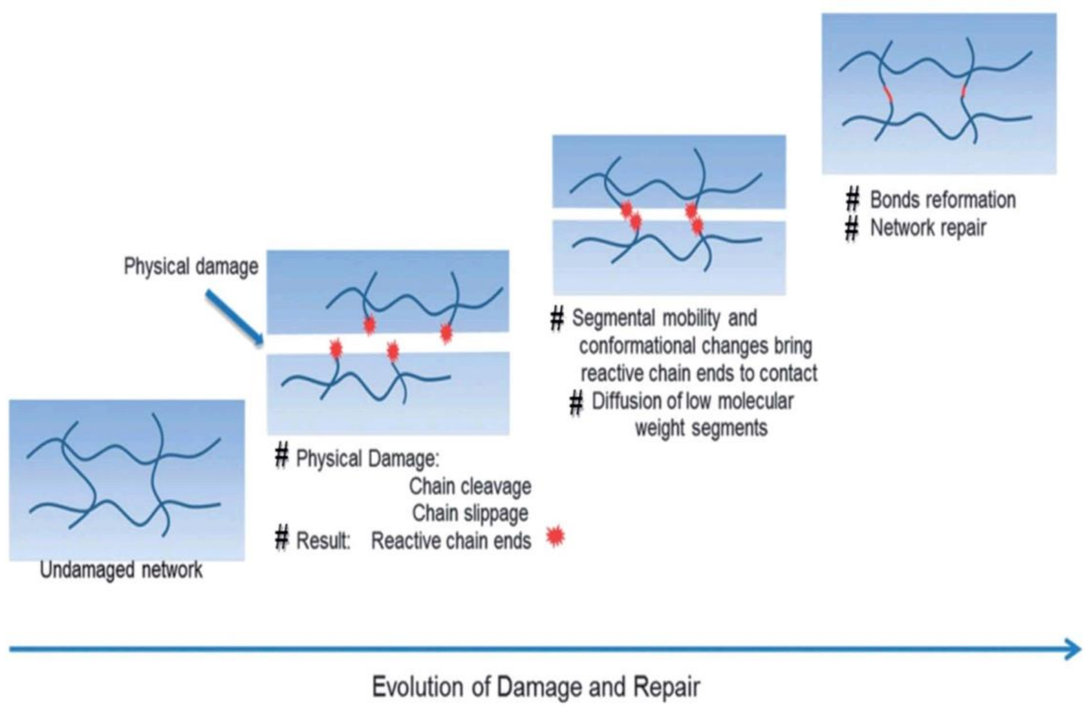


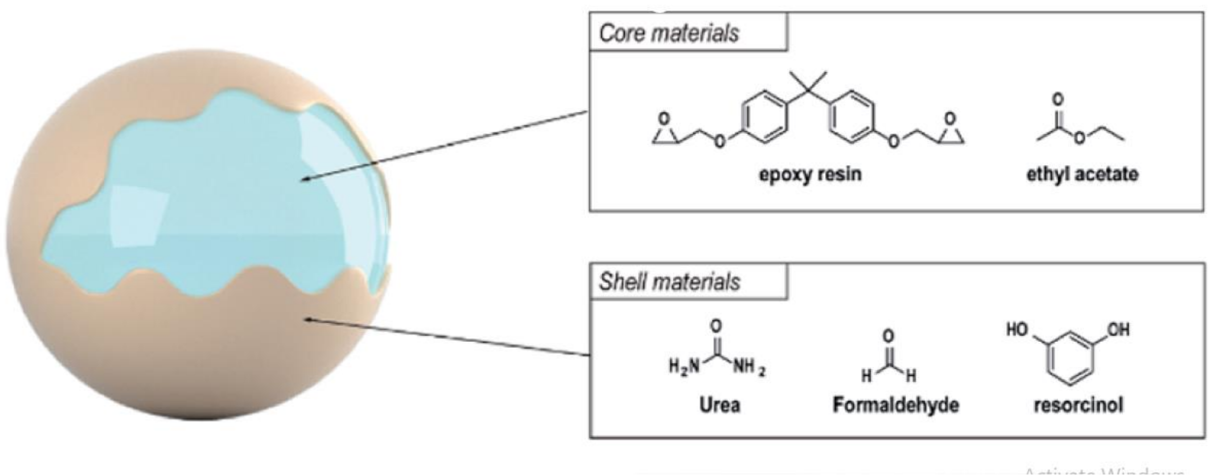
Plate 1: Self-healing concept based on intrinsic damage–repair cycle in polymers (Willocq *et al.*, 2020).

The advantage of intrinsic mechanism is that it does not require additional ingredients like microcapsules or microvascular networks, and allow multiple self-healing processes in the presence of heat to accelerate the reaction (Yubin *et al.*, 2022). However, high healing temperatures and oxidative side-reactions restrict its application as healing will be limited to surface exposed to external factor while internal cracks or thick substrate are unlikely to be healed (Binder, 2013; Hia *et al.*, 2016).

2.1.2 Extrinsic Self-Healing Mechanism

Unlike intrinsic mechanism where the material or polymer has healing properties through bonding, in extrinsic self-healing mechanism the matrix (material) does not have healing properties. Instead healing agent are encapsulated and embedded into the material matrix in advance (Yuan *et al.*, 2008). The healing agent can be encapsulated into two different containers;

microcapsule self-healing mechanism and vascular network self-healing mechanism. While material embedded with microcapsule mechanism has one time healing capability, vascular mechanism have multiple healing effect (Blaiszik *et al*., 2009; Hia *et al*., 2016). The healing concept of extrinsic mechanism irrespective of the container used is similar. the healing concept begins as soon as crack develops and eventually breaks the fragile capsules containing the healing agent, the healing agent in the microcapsule would be released into the crack planes due to capillary action and heals the cracks through polymerization as shown in Plate 2 (Hia *et al.,* 2016; Yuan *et al.,* 2008).



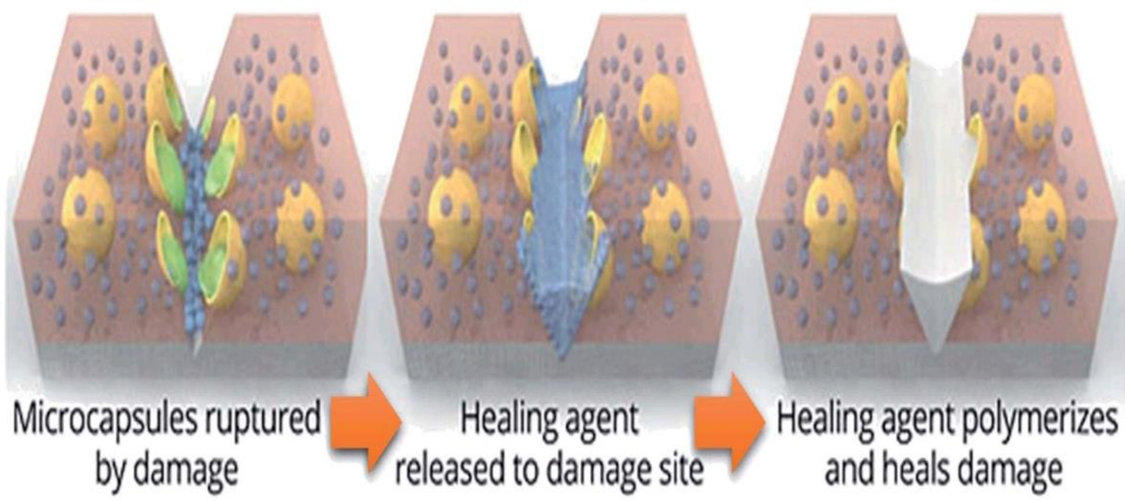


Plate 2: Self-healing concept based on microencapsulated (yellow) where the healing agent (green) is embedded in a polymer (brown) containing a catalyst (blue) capable of polymerizing the healing agent (Willocq *et al.*, 2020)

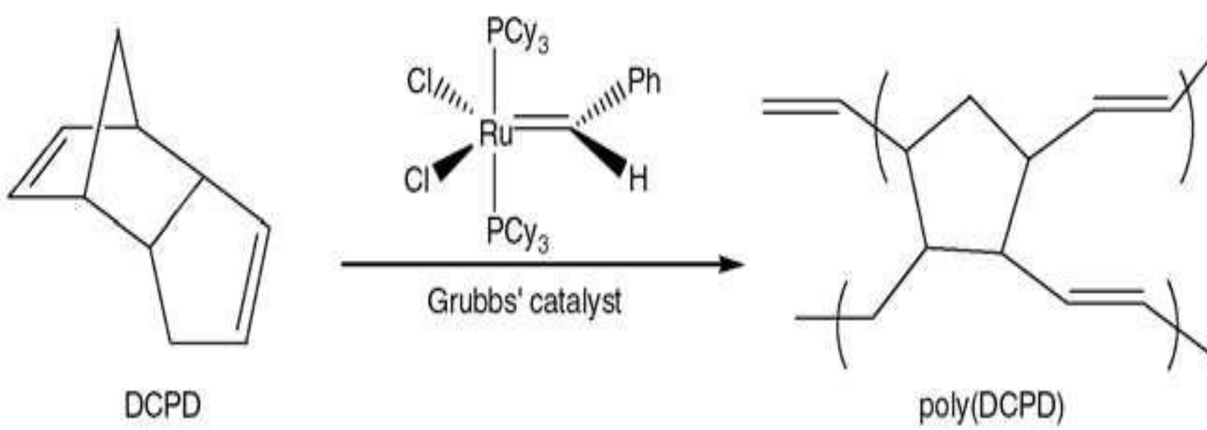
Extrinsic mechanism provides simplicity among healing system especially for novel and modification researches as it can easily be dispersed in material matrix homogeneously, it does not require external stimuli to trigger its healing process, healing agent can easily be encapsulated by

UF encapsulation method, also the healing takes place at ambient temperature (Hia *et al.*, 2016; Yuan *et al.*, 2008). But it is a single used self-healing system in encapsulation mechanism while blockage of hollow fiber may occur after healing in vascular mechanism (Binder, 2013).

Damages at macrolevel can easily be identified and eradicated, whereas damages at microlevel occurs very deep within the composite structure making identification and eradication neigh impossible (Idumah, 2020). For quality assurance of fibre-matrix composite, a self-healing at microlevel and nanolevel is needed (Ramesh *et al.*, 2020).

2.1.3 Single Encapsulation

In a research, the shell encapsulating epoxy resin was composed of Polymethylmethacrylate (PMMA) and scandium triflate ($Sc(OTf)_3$) to make a PMMA/$Sc(OTf)_3$-walled microcapsules. This encapsulation process was carried out through suspension polymerization resulting in 80 μm in diameter spherical microcapsules containing 30 wt% epoxy core. On evaluating the composite healing efficiency by fracture toughness recovery, the result showed healing efficiency to have increased to 57.5 and 79.1% in comparison with a composite incorporated with PMMA-walled microcapsules which showed healing efficiency of 46.7 and 55.1% when healed at 80 and 120 °C respectively (Rodriguez *et al.*, 2020). The group of White *et al.*, (2001) referred to as self-healing material pioneer systematically and successfully investigated ring opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) microencapsule in polymer matrix (White *et al.*, 2001). The research is based on the idea that once crack ruptures dispersed microcapsules embedded in the matrix, DCPD monomers are released into the crack which will then be polymerize to form poly-(dicyclopentadiene) in the presence of dispersed pre-embedded Grubbs' catalyst to speed up the reaction as shown in Equation 1. Delamination damage in glass fibre/epoxy composites was reported to be repaired by the healing agent with 99% healing efficiency (White *et al.*, 2001).

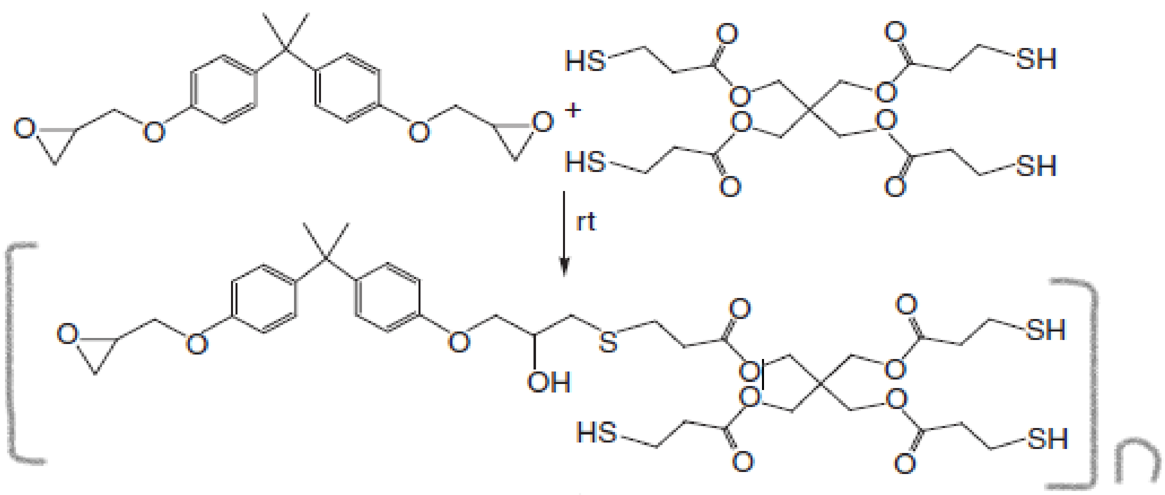


Equation 1: Ring opening metathesis polymerization of dicyclopentadiene (Yuan *et al.*, 2008)

White *et al.*, (2001) research was limited by catalyst dissolution and deactivation and use of metal catalyst, Caruso (2008) researched on solvent based autonomic system containing co-encapsulation of epoxy monomer and solvent mixture in urea formaldehyde (UF) shell which was later incorporated into epoxy matrix composites. He noted that composites embedded with epoxy monomer and solvent mixture is more superior in fracture recovery and exhibits multiple healing than those with solvent microcapsule alone. The composites has 100 % healing efficiency as capsule content in composite increases to 20 wt %. It was concluded that microcrack in the composite has led to self-healing and subsequent composite structural integrity restoration (Caruso *et al.*, 2008). In recent year, microencapsulation has found application in adverse condition such as underwater, epoxy diluted with ethyl acetate was used as healing agent in poly(urea-formaldehyde)capsule. The encapsulated diluted epoxy was embedded in fluorescent latent curing agents contained epoxy matrix. These two contents (epoxy microcapsule and fluroscent latent) serves as both self-healing and indicator for healed area. Composite specimen containing 15 wt% epoxy microcapsules and 6 wt% fluorescent latent curing agents yielded 85.6% healing efficiency at 60 ºC underwater for 4 hours and the most efficient repair indicator. This self-healing epoxy material was tested to be able to repair at temperature varying from room temperature to 100 ºC. Also, the fluorescence colour changed to yellow after repairing the cracked region (Feng *et al.,* 2020). The use of capsule and catalyst provide a simple healing concept in materials especially with epoxy-loaded capsules production that doesn't need advanced device.

2.1.4 Dual Microcapsule Self-Healing Mechanism

In a different approach to developing self-healing system, epoxy resin and mercaptan (hardener) were microencapsulated separately as two-component healing agent which are subsequently embedded in epoxy matrix. This approach is based on epoxy curing by the hardener as show in equation 2.4. The two microcapsules were prepared by in situ polymerization. It was observed that composite with 5 wt% capsules (1:1 of the two capsules) shows a healing efficiency of 104.5 % at 20 ºC after 24 hours curing duration and fracture toughness of 1.08 MPa. This approach prevents deterioration of composites healing capability during storage (Yuan *et al.*, 2008a).

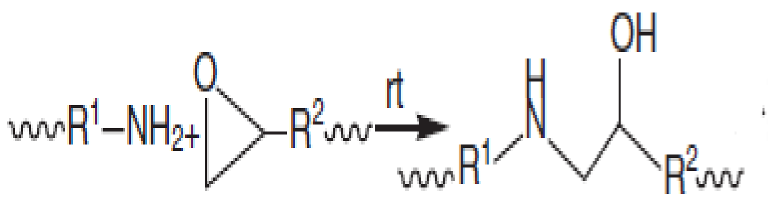


Equation 2: Curing of Epoxy resin with mercaptan (Hia *et al.,* 2016)

Dual Encapsulation making use of liquid amine as healing agents is a complicated because liquid amine is both water and organic solvent soluble making encapsulation more difficult. Dual-microcapsule epoxy-amine self-healing system serves as new approach of preparing amine microcapsules for epoxy composites. In this approach, ethylenediamine (EDA) was encapsulated in epoxy-EDA shell in water-in-oil emulsion via interfacial polymerization. The optimum synthesis condition was concluded to be 1.0:5 ratio for core to shell material weight, agitation rate to be at 200–250 rpm, reaction duration of 24 h and 1:1 compound emulsifier. Upon confirmation of the microcapsule healing ability with, differential scanning calorimetry, Fourier transform infrared, scanning electron microscope and optical microscope, 12 wt% epoxy-containing microcapsules and 8 wt% EDA-containing microcapsules were incorporated in epoxy matrix resulting 80.4 % healing efficiency. Proving that the report provides an alter preparation method of liquid amine microcapsules for epoxy-based composites development for various applications (Hu *et al.,* 2020). The greatest advantage of microencapsulation is that it can be incorporated into all kinds of polymers (thermosets, thermoplasts, and elastomers) but it is a single used self-healing system (Binder, 2013).

One Directional Vascular Network

In the search for a continuous self-repair system unlike single use microcapsule system, led to research of adding hollow fibre filled with healing agent in fibre-polymer composite. The hollow fibre was made by drawing glass fibre down to 60 µm external diameter and 50% hollowness with the use of Borosilicate glass tubing (Schott DURAN) and bespoke fibre making process respectively. The hollow fibres were filled with uncured epoxy and amine hardener using vacuum assisted liquid infiltration technique, the ends of the hollow fibres were sealed with cured epoxy putty (ITW Devcon-Magic Bond). The uncured epoxy and hardener filled hollow fibres was then reinforced at 0º and 90º respectively in epoxy matrix using hand lay–up method to manufacture six laminates of 18 plies (2 mm thickness) and cured according to Manufacturers specification. The lay-up chosen was {[90º/0º](solid), [90º/0º/90º/0º](hollow), [90º/0º/90º](solid)} which was cut into specimen using diamond saw. On breakage of the hollow fibre, the epoxy and hardener were released to cure as shown in equation 2.5 thereby healing the crack in the matrix. The flexural test on the specimens revealed that up to 90% flexural strength was restored after damage (Pang and Bond, 2005).



Equation 3: Reaction of epoxy resin with amine hardener (Binder, 2013).

Following Peng (2005) methodology, a research was aimed at mitigating damage occurrence and restoration of mechanical strength in fibre reinforced polymer (FRP). The flexural test showed that inclusion of hollow fibres in epoxy matrix led to 16% flexural strength reduction. On self-healing the damange 87% of flexural strength was restored. The study further proves that damage occurrence in fibre reinforced polymer can mitigated through restoration of mechanical strength using self-healing hollow fibre layers (a biomimetic repair) (Trask and Bond, 2006). The orientation of self-healing hollow glass fibre in polymer composites is important in the study of reinforcement capability and healing efficiency. The effect of vascular self-healing configuration at 0º, 45º and 90º healing behavior and mechanical properties was studied on epoxy/glass (50/50) composite. The hollow glass fibres (HGFs) used was 450 ± 10 µm diameter with 30–35% hollowness produced using extruder. The tensile tests showed that the composites recovered fully for all types of HGFs configurations. However, composite with 45º hollow glass fibre configuration has showed highest tensile strength while 90º configuration has the least tensile strength. Whereas in terms of healing efficiency composite incorporated with 90º orientation showed the highest efficiency (Adli *et al.*, 2019). Although unidirectional system provide multiple healing cycles in one Direction evenly, blockage of core fiber will distort the release of healing agents and hollow-fibre incorporation in composite reduces composite strength (Binder, 2013).

2.1.5 Multivascular Mechanism

Rather than a unidirectional vascular self-healing network as previous discussed, a sandwiched panel consisting of multiple layers of self-healing vascular networks system carrying two-part epoxy resin was designed and manufactured. The research was aimed at studying the compressive strength after impact of the sandwiched panel after damage. The results presented in the report shows that after damage, strength of the panel was successfully restored using a vascular self-healing system. Although, healing efficiency was not measured but the tensile strength of the material was improved proving to be a viable replacement for traditional materials with multilayers (Williams *et al.*, 2008).

In experimental study to improve microvascular mechanism dog-bone like 3D microvascular network was 3D printed as shown in Plate 3 below. The microvascular network was filled with Epoxy resin and Epichlorohydrin hardener which was incorporated into epoxy matrix to make a self-healing system. Tensile and creep behavior results shows significant healing efficiency by microvascular thereby restoring composite tensile strength due to delivery of healing agent at the damage zone. 89% healing efficiency was observed at 25 °C for tensile strength while 83% healing efficiency was obtained at 90 °C for creep rupture (Khalili *et al.*, 2019).

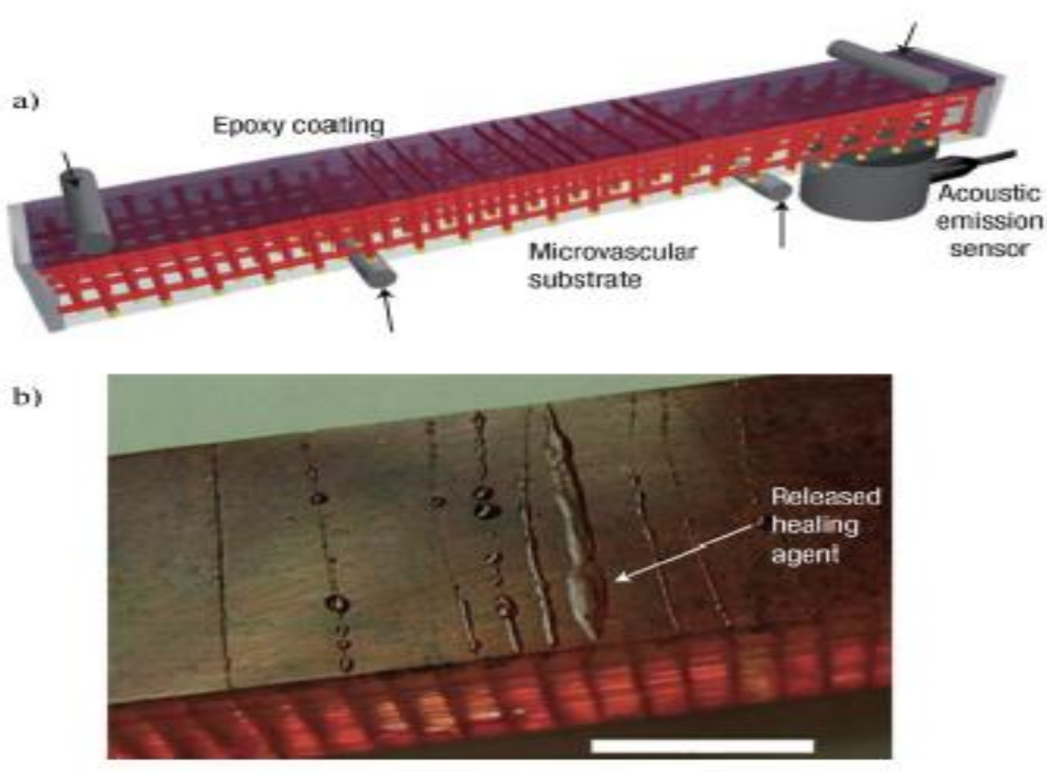


Plate Error! No text of specified style in document.**: (a) Schematic of microvascular substrate; (b) optical image of actual microvascular system after damage (Scheiner *et al.*, 2016)**

Vascular system has also being applied in composite coatings application where epoxy-PAN fibres and curing agent-PAN fibres were incorporated into HDG substrates alternatively. On waterborne polyurethane (PU) coating incorporated with core-shell healimg system was repeatedly introduced to 100 μm width scratches on the same spot. Out of all the varied composite fabricated, after three healing cycle composite coatings containing 40.4 wt % of fibres showed 93% healing efficiency because of continuous supply of healing agent interconnected electrospun fibres while other composite decreased from 99% to 50% (Xu *et al.*, 2020). Just as stated microvascular or multivascular provides healing in all direction, however blockage of hollow fiber may occur, carrier networks may mix and lastly there is complicated factors between vascular network diameter and cost to mechanical properties (Binder, 2013).

From the reviewed literature it is observed that self-healing of polymeric material with both intrinsic and extrinsic mechanism has been widely researched on and its incorporation into synthetic fibre reinforced polymer has been reported as well. However, there is no report on incorporation of self-healing systems in natural fibre reinforced polymers which provide a more suiting advantages to synthetic fibres.

3.0 RESULTS AND DISCUSSION

3.1 Application of Self-Healing In Structural Material

3.1.1 Application of Self-healing in Anticorrosion Coating

Corrosion is natural process that is estimated globally to cost $300 billion per year to manage (Mobaraki *et al.,* 2020). Corrosion protection ability of self-healing materials is a crucial application that is targeted at increasing materials' service life and reduce cost of corrosion (Choudhury *et al.,* 2021; Mobaraki *et al.,* 2020). Behzadnasab *et al.,* (2017) researched on green corrosion by encapsulating Linseed oil in urea-formaldehyde (UF) shell. In the research, varied microcapsules sizes were synthesized by agitating the medium at different agitating speed.

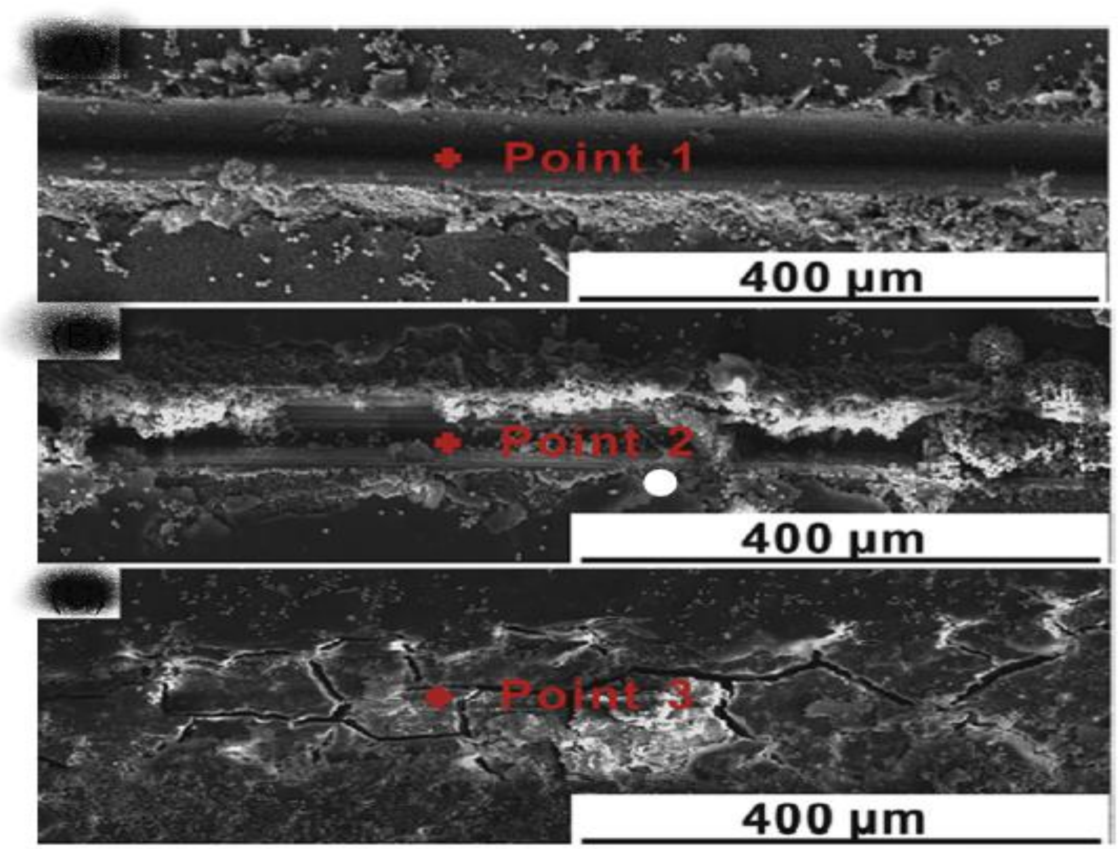


Plate 4: Represent micrograph of 0, 24, and 96 h Self-healing process of microarc oxidation/polymethyltrimethoxysilane composite (Cui *et al.*, 2017).

The synthesized microcapsules were later incorporated in epoxy-based coating and subjected to corrosion assessment. The research concluded that the all microcapsules have direct effect on corrosion. However, large microcapsules exhibited a better corrosion inhibition via self-healing than smaller microcapsule which was explained to be as a result of ease rupture of larger microcapsule (Behzadnasab *et al.,* 2017). Nanocapsules composing of *Azadirachta indica* as a healing agent, urea-formaldehyde as shell and dispersed in epoxy-polyamide matrix were developed as inhibition coating. It was observed that thermal stability and healing ability of the samples were improved and the coating has the potential as corrosion protection. (Bagale *et al.*, 2018). Magnesium alloy AZ31 was protected from corrosion by coating polymethyl-trimethoxysilane composite on its surface Cui *et al.*, (2017). It was observed that thick coating layer of significantly decreased corrosion process. Figure 2.8 illustrates the self-healing process of polymethyltrimethoxysilane composite.

Mobaraki *et al.,* (2020a) also researched on hybrid nanocomposite as anticorrosive coating. The nanocomposite was composed of epoxy resin incorporated with (3-glycidoxypropyl) trimethoxysilane (GPTMS) modified nanosilica and three different healing agents microcapsule (ethanolamine, perfluorooctyl triethoxysilane (POT), and diethanolamine). It was that samples containing GPTMS-modified silica (3 wt%) and POT microcapsules (10 wt%) showed the greatest corrosion inhibitory properties and best self-healing performance. In another hybrid composite research, Mahmoudian *et al.*, (2018) studied hybrid self-healing coatings on copper metal substrate. Poly(urea-formaldehyde) shell and linseed oil based nanocapsules were synthesized. To enhance the self-healing and anticorrosion properties, benzotriazole and potassium ethyl xanthate were embedded into the coating which significantly increased corrosion resistance of the coatings. After 7 days, the crack in the samples was completed filled linseed oil and anticorrosion agents for polymerization of healing agents. Coating containing 1.7 wt% zeolitic imidazole framework (ZIF) nanoparticles was developed and assessed in acid medium for self-healing anticorrosion coatings. The nanoparticle enhance the carbon steel corrosion resistivity (Yang, *et al.,* 2018c)**.**

3.1.2 Application of Self-Healing in Polymer Composite

Fiber-reinforced composites of aramid fiber, polyethylene (PE) fiber, glass fiber, and carbon fiber are attracting Researchers and production companies' attention due to increasing public demand for lightweight materials and structures for various application (Lee *et al.*, 2014). The global market for fibre-polymer materials is estimated to grow to $113.6 billion by 2024 from $90 billion in 2019. This growth in global market is as a result of fibre-polymer application in automobiles, sporting equipment, and protective equipment (Joshi, 2019)**.** Aside lightweight, fibre-polymer composites offers other unique properties like flexibility, lightness, easy to process, and environmental friendly (Habault *et al.*, 2013; Thakur *et al.*, 2014).

3.1.3 Application of Self-Healing in Concrete and Asphalt

Capsule based healing have been reported to be an effective method in concrete healing. In this method, healing agent is entrapped in microcapsules and is released when a crack forms. Microcapsules should survive the concrete mixing process. In addition, this method, generally, does not have negative effects on the mechanical properties of the hardened concrete (Mobaraki *et al.,* 2020a). For example, poly(methyl methacrylate) shell was identified by Arau´jo *et al.*, (2017) to be a better choice in encapsulation of healing agent to be incorporated in concrete as compared with polystyrene shell. This observation was made after subjected the caosules to parameters like durability in diverse conditions as well as the shell compatibility with healing agents. In another research Water-repellant was chosen as healing agent and encapsulated in poly(methyl methacrylate). The capsule survival was assess through concrete mixing and it was observed that sample incorporated with 0.7 mm thickness capsule shows better adhesion enhancement (Arau´jo *et al.*, 2017). A novel strategy was used in order to obtain self-healing properties by Kanellopoulos *et al.*, (2017) researched on a novel strategy in concrete healing. Sodium silicate was encapsulated in gelatin shell was stable in 190 ºC and showed a switchable mechanical properties of soft and stiff when hydrated and dried respectively. The healing process follows the usual trend in extrinsic mechanism where creak in the concrete lead to release of healing agent on microcapsule rupture. In a more interesting aim, Dong *et al.,* (2018) aimed at protecting rebar used in concrete from corrosion. The research made use of ethyl cellulose as shell, encapsulating sodium nitrite and sodium monofluorophosphate (healing agent) (Plate 5).

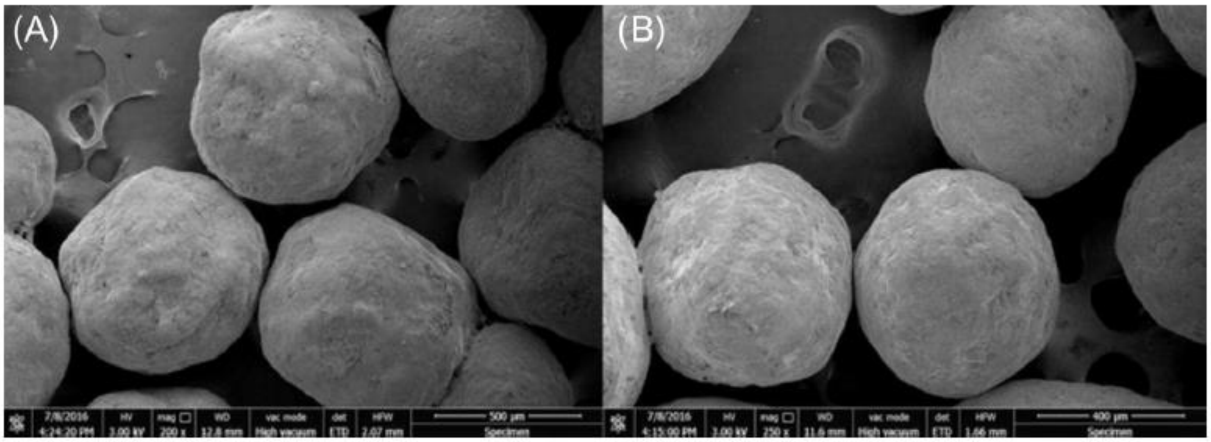


Plate 5: Represent the Emission scanning electron microscopy images of sodium nitrite (A) and sodium monofluorophosphate (B) (Dong *et al.,* 2018).

The healing system was activated by change in pH, protective layer was observed to be formed on rebar surface confirming corrosion protection. Aside concrete, self-healing has found application in asphalt commonly used for paving roads. Rejuvenator in Melamine ureaformaldehyde (MUF) microcapsules was used to study asphalt fatigue behavior. The samples were found to be stable through Thermogravimetric analysis and sample with 3 wt % microcapsule was observed to have the ability to double the fatigue life of the asphalt sample thereby solving asphalt aging problem (Sun *et al.,* 2018). Sunflower oil has also been utilized as healing agent. This system healing effect is found to depend on the oil content and temperature of the system (Al Mansoori *et al.,* 2018)**.**

3.1.4 Application of Self-healing in Aerospace Expeditions

Impact resistance and dynamic damage have been reported to be repaired via self-healing polymer composite. Xu and Chen (2017) researched on fabrication of polyurethane/attapulgite nanocomposites incorporated with self-healing. Aside attapulgite self-healing in the composite, the mechanical properties of the fabricated nanocomposites sample with 3 wt % of attapulgite was observed to have improved. Carbon fibre-polymer composites are usually utilize in aerospace structural application for high mechanical loading due to its strength and stiffness. Zhang *et al.,* (2018) experimented on carbon fiber-polymer reinforcement in isocyanurate-oxazolidone as polymer matrix for self-healing application. The designed material recovered 85% of its initial strength after healing and 285 ^{o}C glass transition temperature (Plate 6).

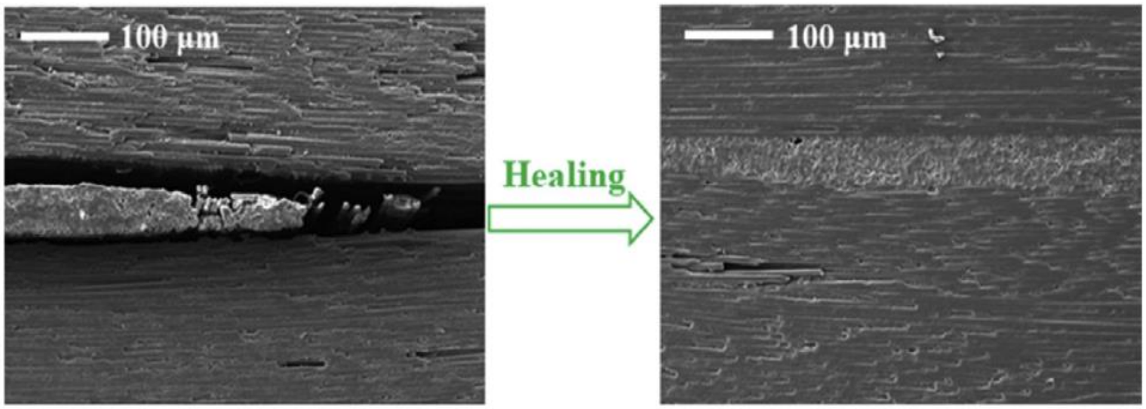


Plate 6: Shows micrograph comparison between before and after sample damage (Zhang *et al.*, 2018)

3.1.5 Application of Self-Healing in Biomedical

In tissue engineering construct, based on poly(ethylene glycol) diacrylate and dithiothreitol with borax as a glucose-sensitive motif in self-healing hydrogel was fabricated. Hydrogels have the ability to self-heal and the mechanical property to house branched tubular structure (Tseng *et al.,* 2017). Hsieh *et al.,* (2017) synthesized chitosan-fibrin based self-healing hydrogel for vascular endothelial cells. The hydrogel in this research was all injectable and biodegradability at degradation rate of 70% in 2 weeks. Self-healing hydrogel has also found application in wound healing promotion. Based on quaternized chitosan-g-polyaniline, self-healing hydrogel was designed for cutaneous wound healing. The designed self-healed hydrogel exhibited a good vivo blood clotting ability thereby improving healing process in vivo wound. Self-healing hydrogel exhibited other properties like biocompatibility, electroactivity, adhesiveness, antibacterial activity, conductivity and free radical scavenging capacity (Zhao *et al.*, 2017). For drug and cell delivery vehicles. Qu *et al.,* (2017) utilizes Michael base reactions to design injectable self-healing hydrogels with polysaccharide as matrix. In the research N-carboxyethyl chitosan hydrogels was used for doxorubicin (Dox) delivery as anticancer drug. In addition to pH-response and rapid self-healing, the healing process was initiated without external stimulus. Other researches by Jing *et al.*, (2017), and Ye *et al.,* (2017) designed hydrogel for tissue engineering, injectable drug delivery systems, and regenerative medicine. Aside polymer, concrete and asphalt, self-healing sytems are also incorporated in ceramics, metals and their composites. In metal, Atomic bonding hinders the flow of healing agent in metal matrix resulting in high energy requirement in metal healing process. Elevated temperature has been identified to promote lattice diffusion of the solutes (An *et al.,* 2021).

4.0 CONCLUSION

In conclusion, self-healing mechanisms has found application in all structural materials utilized in road and building constructions, household polymeric wares, biomedical and aerospace expeditions. The size, healing agents, shell material, synthesis method and mode of healing are dependent on healing systems final application. It was also observed that incorporation of healing systems in structural materials has not only lengthen the material's service time but also improve tensile strength, flexural and other mechanical properties. However, most researches utilizes synthetic components like glass fibre, carbon fibre, synthetic polymers and so on while research on eco-friendly natural materials are few.

References

Adli, A., Shelesh-nezhad, K., and Azar, M. K. (2019). The effect of vascular self-healing pattern on mechanical behaviour and healing performance of epoxy / glass composite. Plastics, Rubber and Composites, 0(0), 1–12. https://doi.org/10.1080/14658011.2019.1706278

Al-Mansoori, T., Norambuena-Contreras, J., Micaelo, R., Garcia, A., (2018). Self-healing of asphalt mastic by the action of polymeric capsules containing rejuvenators. Construction and Building Material,161:330-9.

An, S., Yoon, S. S., and Lee, M. W. (2021). Self-Healing Structural Materials. Polymers, 13(2297), 1–11.

Arau´jo M *et al.*, (2017). Design and testing of tubular polymeric capsules for self-healing of concrete. In: IOP conference series: materials science and engineering;1,12003.

Araujo M, *et al.*, (2018). Poly (methyl methacrylate) capsules as an alternative to the proof-of concept glass capsules used in self-healing concrete. Cement and Concrete Composite, 89:260-71.

Bagale, U.D., Sonawane, S.H., Bhanvase, B.A., Kulkarni, R.D., Gogate, P.R. (2018). Green synthesis of nanocapsules for self-healing anticorrosion coating using ultrasound-assisted approach. Green Process Synthesis,7(2):147-59.

Behzadnasab, M., Mirabedini, S.M., Esfandeh, M., Farnood, R.R. (2017). Evaluation of corrosion performance of a self-healing epoxy-based coating containing linseed oil-filled microcapsules via electrochemical impedance spectroscopy. Progress in Organic Coatings, 105:212_24.

Binder, W. H. (2013). Self-Healing Polymers from Principles to App (W. H. Binder (ed.)). Wiley-VCH Verlag GmbH.

Blaiszik, B. J., Caruso, M. M., Mcilroy, D. A., Moore, J. S., White, S. R., and Sottos, N. R. (2009). Microcapsules filled with reactive solutions for self-healing materials. Polymer, 50, 990–997. https://doi.org/10.1016/j.polymer.2008.12.040

Caruso, B. M. M., Blaiszik, B. J., White, S. R., Sottos, N. R., and Moore, J. S. (2008). Full Recovery of Fracture Toughness Using a Nontoxic Solvent-Based Self-Healing System. Advanced Functional Material, 18, 1898–1904. https://doi.org/10.1002/adfm.200800300

Cho, S.H., White, S.R., Braun, P.V. (2009). Self-healing polymer coatings. Advance Material. 21(6):645-9.

Cui L-Y, *et al.*, (2017). Corrosion resistance of a self-healing micro-arc oxidation/polymethyltrimethoxysilane composite coating on magnesium alloy AZ31. Corrosion Science, 118:84_95.

Daniel, T., and Haddad, E. (2012). Self-Healing Materials Systems : Overview of Major Approaches and Recent Self-Healing Materials Systems : Overview of Major. February. https://doi.org/10.1155/2012/854203

Dong B, *et al.*, (2018). Chemical self-healing system with novel microcapsules for corrosion inhibition of rebar in concrete. Cement and Concrete Composite, 85:83-91.

Feng, H., Yu, F., Zhou, Y., Li, M., Xiao, L., and Ao, Y. (2020). Fabrication of Microcapsule-type Composites with the Capability of Underwater Self-healing and Damage Visualization. Royal Society of Chemistry Advances, 10, 33675–33682. https://doi.org/10.1039/d0ra03197f

Guo, M., He, Y., Wang, J., Zhang, X., and Li, W. (2019). Microencapsulation of oil soluble polyaspartic acid ester and isophorone diisocyanate and their application in self-healing anticorrosive epoxy resin. Journal of Applied Polymer and Science, 1–14. https://doi.org/10.1002/app.48478

Habault D, Zhang H, Zhao Y (2013). Light-triggered self-healing and shape-memory polymers. Chemical Society Review, 42(17):7244-56.

Hia, I. L., Vahedi, V., and Pasbakhsh, P. (2016). Self-Healing Polymer Composites : Prospects , Challenges , and Applications. Polymer Reviews, 56(2), 225–261.

https://doi.org/10.1080/15583724.2015.1106555

Hsieh, F-Y., Tao, L., Wei Y., Hsu, S., (2017). A novel biodegradable self-healing hydrogel to induce blood capillary formation. NPG Asia Material, 9(3):363.

Hu, H., Zhang, L., Yu, R., Yuan, L., Yang, Y., He, X., Wang, J., and Li, Z. (2020). Microencapsulation of ethylenediamine and its application in binary self- healing system using dual-microcapsule. Materials and Design, 189, 108535. https://doi.org/10.1016/j.matdes.2020.108535

Idumah, C. I. (2020). Recent advancements in self-healing polymers , polymer blends , and nanocomposites. 1–13. https://doi.org/10.1177/0967391120910882

Jagtap, S., Patil, V., and Suresh, K. (2018). Functionalized carbon nanotube reinforced polymer nanocomposite microcapsules with enhanced stiffness. Colloids Surf, 550, 82–89.

Jing, X., Mi, H-Y., Napiwocki, B.N., Peng, X-F., Turng, L-S. (2017). Mussel-inspired electroactive chitosan/graphene oxide composite hydrogel with rapid self-healing and recovery behavior for tissue engineering. Carbon NY, 125:557-70.

Joshi, L.N.A.P. (2019). Composites Market-Global Forecast to 2024; Lucintel: Dallas, TX, USA.

Judit, T., Abdul, S., and Gyo¨ngyi, V., (2018). Micro/nanocapsules for anticorrosion coatings. Fundamentals of nanoparticles. Elsevier; 2018. p. 521_51.

Kanellopoulos, A., Giannaros, P., Palmer, D., Kerr, A., Al-Tabbaa, A., (2017). Polymeric microcapsules with switchable mechanical properties for self-healing concrete: synthesis, characterization and proof of concept. Smart Material Structure, 26(4):45025.

Kenned, J. J., Sankaranarayanasamy, K., and Kumar, C. S. (2020). Chemical, biological, and nanoclay treatments for natural plant fiberreinforced polymer composites: A review. Polymer and Polymer Matrix.

Khalili, S. M. R., Khademoltoliati, A., and Saeedi, A. (2019). Tensile and creep behavior of microvascular based self-healing composites : Experimental study Tensile and creep behavior of microvascular based self-healing composites : Mechanics of Advanced Materials and Structures, 0(0), 1–7. https://doi.org/10.1080/15376494.2019.1567882

Lee, M.W. An, S. Lee, C. Liou, M. Yarin, A.L. Yoon, S.S. (2014). Hybrid self-healing matrix using core-shell nanofibers and capsuleless microdroplets. ACS Application of Material Interfaces, 6;10461–10468.

Mahmoudian, M., Nozad E., Kochameshki, M.G., Enayati, M., (2018). Preparation and investigation of hybrid self-healing coatings containing linseed oil loaded nanocapsules, potassium ethyl xanthate and benzotriazole on copper surface. Progress Organic Coating, 120:167-78.

Mobaraki, M., Ghaffari, M., and Mozafari, M. (2020a). Potential self-healing functionality in a composite structure: methodology and applications. In Self-Healing Composite Materials. Elsevier Inc. https://doi.org/10.1016/B978-0-12-817354-1.00004-1

Mobaraki, M., Ghaffari, M., and Mozafari, M. (2020b). Self-healing polymers for composite structural applications. In Self-Healing Composite Materials (pp. 33–52). Elsevier Inc. https://doi.org/10.1016/B978-0-12-817354-1.00003-X

Pang, J. W. C., and Bond, I. P. (2005). A hollow fibre reinforced polymer composite encompassing self-healing and enhanced damage visibility. Composites Science and Technology, 65, 1791–1799. https://doi.org/10.1016/j.compscitech.2005.03.008

Qu, J., Zhao, X., Ma, P.X., Guo, B., (2017). pH-responsive self-healing injectable hydrogel based on N-carboxyethyl chitosan for hepatocellular carcinoma therapy. Acta Biomaterialia, 58:168-80.

Ramesh, M., Kumar, L. R., Khan, A., and Asiri, A. M. (2020). Self-healing polymer composites and its chemistry. In Self-healing composite materials (pp. 415–428). Elsevier Inc. https://doi.org/10.1016/B978-0-12-817354-1.00022-3

Rodriguez, R., Kosarli, M., Paipetis, A. S., Bekas, D. G., and Fl, S. (2020). Development of self-contained microcapsules for optimised catalyst position in self-healing materials. Polymer, 18(December 2019), 1–7. https://doi.org/10.1016/j.polymer.2019.122084

Scheiner, M., Dickens, T. J., and Okol, O. (2016). Progress towards self-healing polymers for composite structural applications. Polymer, 83, 260–282.

Sheikhy, H., Ramezanzadeh, M., and Shahidzadeh, B. (2015). An evaluation of the mechanical and adhesion properties of a hydroxyl-terminated polybutadiene (HTPB) -based adhesive including different kinds of chain extenders. Polymer Bulletin, 72, 755–777. https://doi.org/10.1007/s00289-015-1303-x

Sun, D., Li, B., Ye, F., Zhu, X., Lu, T., Tian Y., (2018) Fatigue behavior of microcapsule-induced self-healing asphalt concrete. Journal of Clean Production,188:466-76.

Thakur, V.K., Thakur, M.K., Raghavan, P., Kessler M.R., (2014). Progress in green polymer composites from lignin for multifunctional applications: a review. ACS Sustain Chemical Engineering 2(5):1072-92.

Trask, R. S., and Bond, I. P. (2006). Biomimetic self-healing of advanced composite structures using hollow glass fibres. Smart Materials and Structures, 15, 704–710. https://doi.org/10.1088/0964-1726/15/3/005

Tseng, T-C., Hsieh, F-Y., Theato, P., Wei, Y., Hsu, S., (2017). Glucose-sensitive self-healing hydrogel as sacrificial materials to fabricate vascularized constructs. Biomaterials, 133:20-8.

White, S. R., Sottos, N. R., Bollinger, J., Britton, J., Gisin, N., Knight, P., Kwiat, P., and Percival, I. (2001). Autonomic healing of polymer composites. *Nature*, *409*(6822), 794 – 797.

Williams, H. R., Trask, R. S., and Bond, I. P. (2008). Self-healing sandwich panels : Restoration of compressive strength after impact. Composites Science and Technology, 68(15–16), 3171–3177. https://doi.org/10.1016/j.compscitech.2008.07.016

Willocq, B., Odent, J., Dubois, P., and Raquez, J.-M. (2020). Advances in intrinsic self-healing polyurethanesand related composites. Royal Society of Chemistry Advances, 10(C), 13766–13782. https://doi.org/10.1039/d0ra01394c

Xu, S., Li, J., Qiu, H., Xue, Y., and Yang, J. (2020). Repeated self-healing of composite coatings with core-shell fibres. Composites Communications, 19(February), 220–225. https://doi.org/10.1016/j.coco.2020.04.007

Xu, Y., and Chen, D. (2017). Self-healing polyurethane/attapulgite nanocomposites based on disulfide bonds and shape memory effect. Materials Chemistry and Physics, 195:40-8.

Yang S, et al (2018). pH-responsive zeolitic imidazole framework nanoparticles with high active inhibitor content for self-healing anticorrosion coatings. Colloids Surfaces A Physicochem Eng Asp, 555(4):18-26.

Ye, X., Li, X., Shen, Y., Chang, G., Yang, J., Gu, Z. (2017). Self-healing pH-sensitive cytosine-and guanosine-modified hyaluronic acid hydrogels via hydrogen bonding. Polymer, 108:348-60.

Yuan, Y. C., Yin, T., Rong, M. Z., and Zhang, M. Q. (2008a). Self-Healing Polymeric Materials Using Epoxy / Mercaptan as the Healant. Macromolecules, 41, 5197–5202.

Yuan, Y. C., Yin, T., Rong, M. Z., and Zhang, M. Q. (2008b). Self healing in polymers and polymer composites . Concepts , realization and outlook : A review. EXPRESS Polymer Letters, 2(4), 238–250. https://doi.org/10.3144/expresspolymlett.2008.29

Yubin, L. I., Zheng, W., Liping, P. A. N., Zhijian, Y., Weixin, W., Lingang, L. A. N., and Ii,

M. (2022). Preparation and damage healing behavior of intrinsic self-repairing polymeric bonded explosives. 35(8), 2023–2031.

Zamal, H. H., Barba, D., Aïssa, B., Haddad, E., and Rosei, F. (2020). Recovery of electro-mechanical properties inside self- healing composites through microencapsulation of carbon nanotubes. Scientic Reports, 10, 1–13. https://doi.org/10.1038/s41598-020-59725-6

Zhang, L., Tian, X., Malakooti, M,H., Sodano, H.A., (2018). Novel self-healing CFRP composites with high glass transition temperatures. Composite Science and Technology, 168:96-103.

Zhao, X., Wu, H., Guo, B., Dong, R., Qiu, Y., Ma, P.X., (2017). Antibacterial anti-oxidant electroactive injectable hydrogel as self-healing wound dressing with hemostasis and adhesiveness for cutaneous wound healing. Biomaterials, 122:34-47.