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Self-Healing Composite Materials: A Review on Preceding and Perspective Research

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Abstract* — *With the need of increasing demand for enhancing the properties of composite materials to be used in different applications such as structural, aerospace, automobile, coating etc, the bio-inspired self-healing materials have been developed with the purpose of repairing themselves under damage caused by mechanical usage over time. These materials are bio-inspired (ex: healing of human skin) and designed on the basis of two different strategies: (a) release of healing agent into the cracks and (b) reversible cross links. This review paper comprehensively discusses the different methods (or approaches) of self healing mechanism in composite materials which is used to alleviate the effect of damage and to restore mechanical properties. Generally, two different self healing approaches are used (a) Extrinsic and (b) Intrinsic. Extrinsic utilizes the release of healing agents from the container (i.e. Hollow glass tubes, Capsules, micro-vascular) which ruptures once crack propagates inside the material while Intrinsic utilizes the phenomena of reverse polymerization which triggers under external stimuli such as heat, light etc. On the basis of review result, it was found that the given methods and approaches used in self-healing have the potential of restoring mechanical properties by repairing the cracks. It was concluded that HGFs and Capsule based healing mechanism are suitable for small cracks repair while vascular mechanism are more likely to be used for larger cracks. Moreover, integrating sensors and actuators into the current self-healing mechanism would enhance the healing potential and attracts a future study.

Keywords*— *Self-healing, Vascular, Capsulation, Intrinsic, Cracks

1. Introduction

The fiber reinforcement composites are widely used these days because of some important properties such as high strength to weight ratio, etc. These materials are widely applicable in aerospace and automotive industries. Despite having superior properties, concerns are associated with these materials such as crack propagation and failure under low damage velocity, impact loading. It is also important to see that once crack propagates inside the structural composites, it becomes very difficult to anticipate that cracks and rectify them. Later, these cracks provide sites for activities such as moisture swelling which further degrade material performance [1] and ultimately lead to the failure of the composite materials under applications. Traditionally damaged polymers are repaired through patching or other conventional methods which is limited to visibility of the cracks. Moreover, these methods are not autonomic and require continuous inspection. Thus, need is there to generate a mechanism which can heal or repair the cracks within the composites so that life of the composites material can be enhanced, require less maintenance, and possible reduction in the cost.

Self-healing composite materials are defined as the material which can heal or repair itself once crack propagates. The concept of self-repair is demonstrated by the fact that it contains a healing material within the structure which repairs it, analogous to the biological healing process in living organisms. As an example, human skin can heal itself once a cut appears on it. The key advantage of this mechanism over conventional repair is that no external action is required and no inspection. In self-healing, the implanted mechanism must be capable of sensing and responding to cracks or damage, restoring the material's properties without affecting the overall performance of the system. Dry [2-5] successfully developed a self-healing structure based upon biological self-healing mechanism i.e., bleeding for using it in a concrete. They stored the repair agents inside the vessels which was further distributed within the concrete specimen. The repair agents successfully repaired the cracks once vessels damaged due to crack propagation. A significant restoration of the properties was observed. A similar study was also done by White et al. [6] in which they mimic the attributes of a biological system for repairing. A typical schematic diagram of the self-healing system is shown Figure 1, consists of a three phases of healing process. Generally, three different self-healing mechanisms are identified and developed: Capsule-based, vascular, hollow glass fiber and intrinsic self-healing materials Blaiszik et al. [7-8]. In capsule-based self-healing materials, a liquid was filled inside the small capsules which are embedded inside the polymer composites. Once the crack generates due to material damage, it starts propagating which results into the rupture of the capsule.

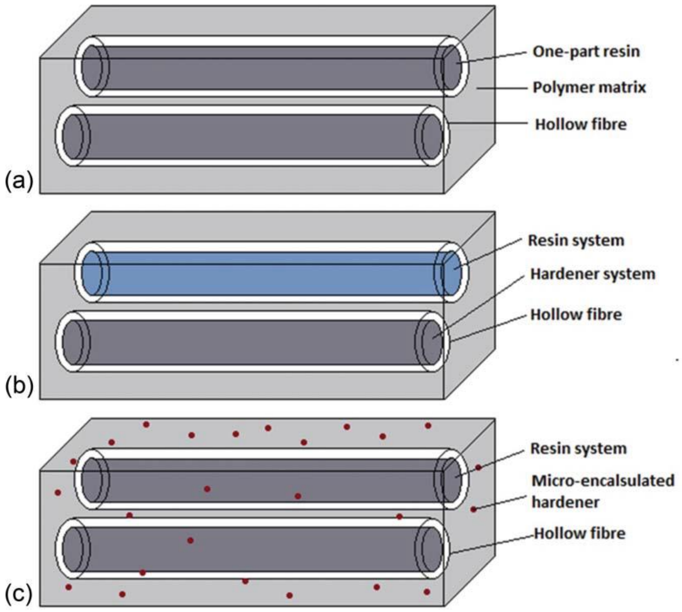


Fig. 1 Schematic diagram of Self-Healing mechanism

Thereafter, the liquid releases from the capsule and closes the crack or gap by repairing it. Vascular self-healing materials are similar in mechanism to capsule based healing system but the capsules are replaced by a vascular structure in which liquids flow in a tunnel network. These liquids work in a similar manner, fills the gap by flow once crack generates and damage the vascular network. The liquid or material which was filled inside a capsule or a vascular network is called a healing agent. The properties and behaviour of the healing agents are analogous to base material. It serves fundamental for the repair, recovery and effective restoration of mechanical properties.
Intrinsic self-healing materials heal through inherent properties of the polymer based materials such as reverse polymerization and reversibility of chemical bonding instead of using a structural design filled with healing agent as in case of capsule or vascular self-healing materials. Several authors reported work in intrinsic self-healing mechanisms and its applications such as melting and solidification of thermoplastic materials, swelling of shape memory alloy etc. [9-12]. This present review article discusses the different healing mechanisms used in self-healing materials along with critical research findings in this area. The layout of the present review article is illustrated in Figure 2.

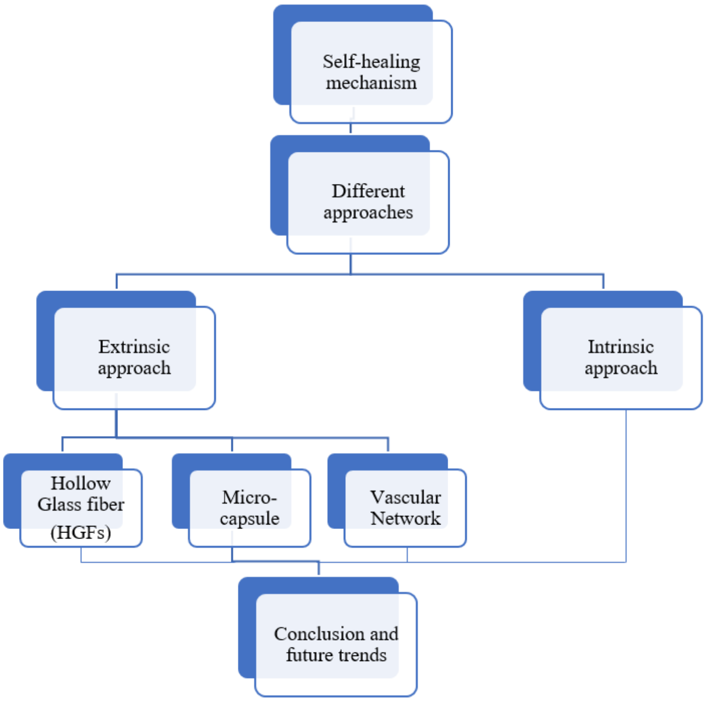


Figure 2 Schematic layout of self-healing mechanism

2. Mechanism of Self-healing

Generally, two popular techniques are utilized in developing the self-healing mechanisms: extrinsic and intrinsic self-healing mechanisms (Figure 3). The difference lies in the self-healing chemistries of the two mechanisms and behaviour of the composites under damage. In extrinsic self-healing mechanism, the damage is repaired by utilizing the healing agents from the embedded containers inside the composites. Mostly, healing action takes place at room temperature, but sometimes heating is required to enhance the healing efficiency. Unlike extrinsic, intrinsic self-healing mechanism is

obtained by the chemical bonding of the matrix material itself which has the potential to rebuild the structure after a drastic damage in the presence of external stimuli like heat, UV light, or chemicals.

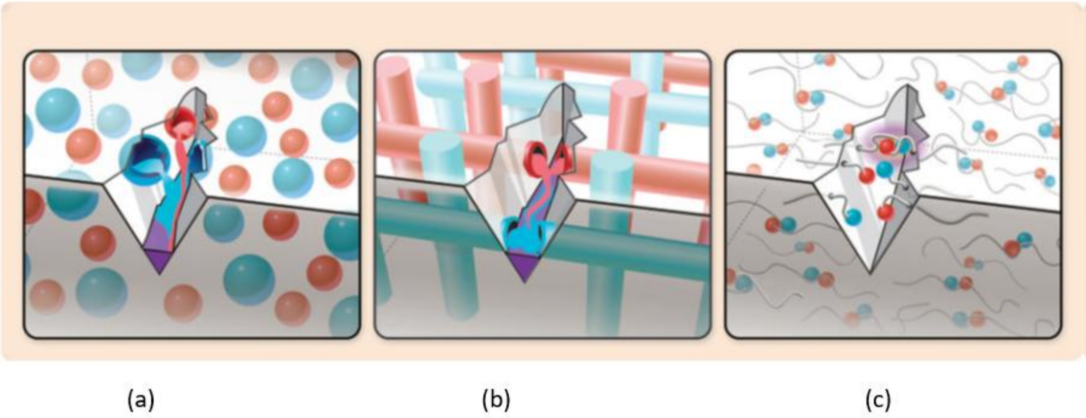


Fig. 3 Approaches to self-healing include (a) Capsule based, (b) Vascular, (c) Intrinsic

3. Extrinsic Self-healing mechanism

As defined above, extrinsic self-healing mechanism is also known as autonomous self-healing where the prefilled liquid (known as healing agent) will repair the damage or cracks. Extrinsic mechanisms can be classified into different categories based on different ways of storing healing agent inside the composite material. These are given as: (a) hollow glass tube self-healing mechanism, (b) microcapsule self-healing mechanism, and (c) vascular network self-healing mechanism. The methodology of self-healing is similar in all three categories in which crack is formed and breaks the containers. Subsequently, the healing agent is released and filled the gap which repairs the material.

3.1 Hollow Glass tube self-healing

A liquid or healing agent are filled inside the hollow glass tubes which are brittle in nature and embedded within the material which fractured during impact, allowing the healing agent to flow into the areas of damage where it subsequently cures. HGF-reinforced glass plies provide some degree of shielding under impact, absorbing energy and protecting the underlying material; they are also ideal to store self-healing functional materials. The self-healing method in hollow glass tubes majorly depends upon (a) location and extent of the damage; (b) the capabilities of the self-healing agents or repair resins; (c) environmental conditions. One such illustration of Hollow glass tubes is given in Figure 4. The self-healing fibres can be placed anywhere within the composites laminate as an additional ply at a defined distance from other plies. Hollow glass tubes can be effectively used as a repairing method only once the true or exact nature of damage is known within the composite laminate. Dry [2] was the first who developed the self-healing composites based on hollow glass tubes and suggested that it has a potential to repair the damage inside the composites. Dry et al. [4] successfully repaired a crack in the concrete by utilizing Methyl methacrylate liquid as a healing agent inside the hollow porous polypropylene fibers. Li et al. [13] also developed the self-repairing method based on hollow glass tubes and applied the mechanism to repair the cracks in cementitious composites. Ethyl cyanoacrylate was used as a repair resin which was filled inside the 500μm diameter hollow glass tubes. The resin was filled inside the tubes using capillary effect.

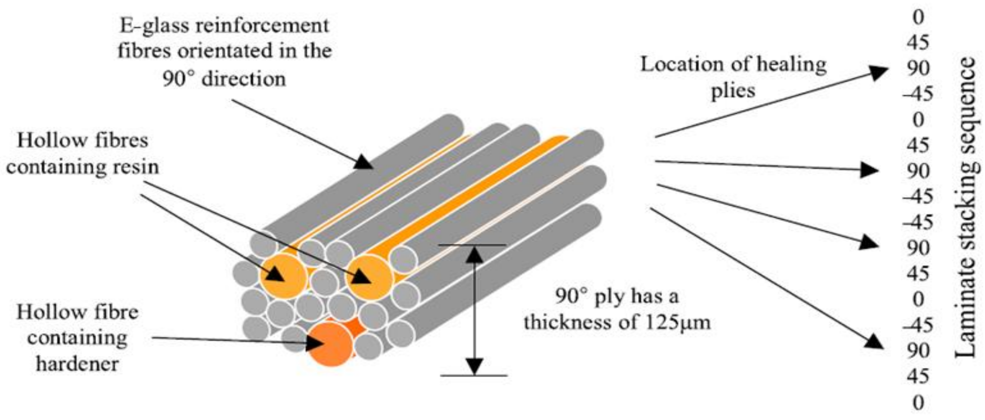


Fig. 4 Location of resin and hardener self-healing filaments in the composite laminate (Trask and Bond 2006)

Bleay et al. [14] conducted self-healing studies on a composite material in which hollow glass tubes were filled with penetrating X-ray opaque colour in one and two-part curing resin systems. These were helpful in identifying the cracks easily and enhance the material ability to self-repair. It not only identifies the damaged area but also showed the action of entering of colour into the damaged zone following impact test. Results revealed that compression strength after curing enhanced by about 10 percent. The approach adopted in this study make a use of hollow fiber reinforcement with high internal volume specially developed to maximize storage capacity [15-18]. Hollow glass tubes also, at the same time, act as structural reinforcement along with storage and possibly provide a material with many other advantages [19-21]. Pang and bond et al. [22] utilized a borosilicate glass tubing of 60 µm external diameter, 50% hollow glass fiber fraction using a bespoke fiber making technique. These HGFs are then embedded along with carbon fiber or glass fiber in polymer based composite and mixed with unpreserved resin or healing agent to introduce a self-healing performance to the composites. These fibres get fractured under the application of load and recovered properties by flowing out of the damaged hollow glass tube into the damaged zone which further prevents propagation of damage. A significant increase in the restoration of the properties was observed. Trask and bond [25] examined the position of hollow glass tubes containing healing resin inside both the carbon fiber/matrix and epoxy fiber/matrix polymer laminates to diminish damage and repair mechanical strength. The hollow glass tubes are about 50 percent hollow having 30-100 µm diameters. The study showed that a substantial part of the bending strength can be restored by self-reparation of healing liquid stored in hollow fibers, once the laminates were suffering quasi-static impact damage. Pang et al. [23-24] included UV fluorescent pigment to the curing resin to observe bleeding of the restore substance in the composite as shown in Figure 5

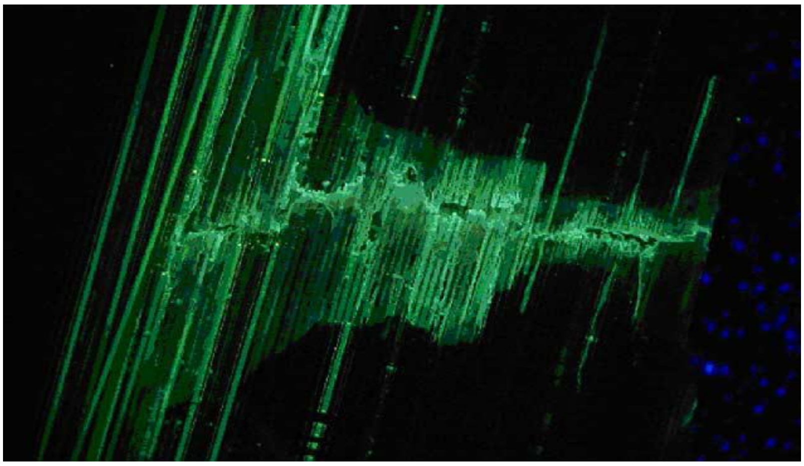
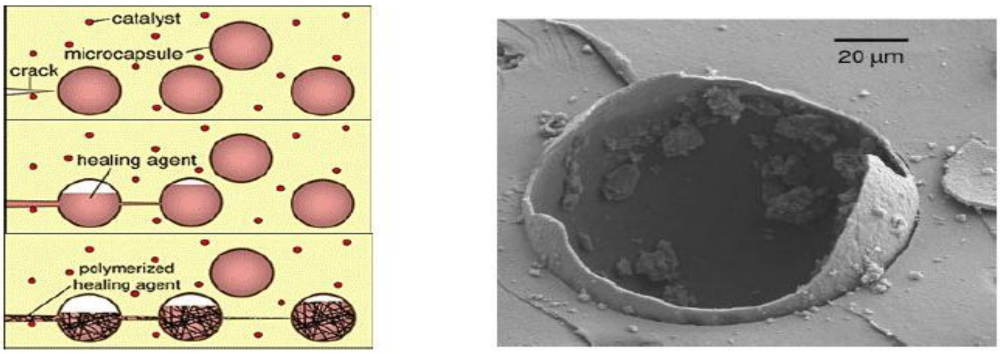


Fig. 5 visual quality of damage by using a fluorescent dye (Pang & Bond, 2005).

3.2 Capsule based Self-healing

White et al. [1] earliest presented a capsule based self-healing composite (as shown in fig.) isolated healing resin stored in the separate capsules and these capsules are diffused in the matrix or composites until burst is caused by fracture and release healing resin of capsules as shown in Figure 6. There are varieties of techniques for reactive materials encapsulation. Based on the wall formation mechanism, the process may be categorized as: (i) in-situ; (ii) coacervation; and (iii) interfacial. A thorough explanation of this process is beyond the extent of this review article; however article on agriculture, industrial, medical and food science applications contains reviews of encapsulation mechanism [26-28]. The dicyclopentadiene (DCPD) – Grubb's first generation catalyst system is an example of capsules catalyst system. This system curing procedure is accomplished by ring opening metathesis polymerization (ROMP), DCPD and Grubb's catalyst were stored in capsules and were dispersed in matrix. Once fracture or cracks initiates, the capsules are broken and DCPD is discharged into crack site. Finally, when Grubb's catalyser is in contact with DCPD, polymerization is started healing the fracture faces and restoring inherent integrity (as shown in fig.). The healing agent DCPD is micro-encapsulated in the shell of urea-formaldehyde to isolate it from being polymerized by the catalyst of Grubbs [1,14].



(a) (b)

Fig. 6 (a) shows approach used in microcapsule and (b) damage image of microcapsule (White et al, 2001)

Subsequently, Jin et al. [29] used a double cantilever width tapered beam (DCWTB) to investigate both quasi-static fracture and fatigue efficiency of the curing system on the thin laminates of epoxy adhesive, which achieve a 56 percent healing efficiency. In addition, white et al. [1], Kessler et al. [30-32], Brown et al. [33-35] used different approaches of integration of monomer resin into the matrix. These microcapsules were broken and discharged a healing resin monomer over damaged area during cracking. Earlier manual injection of the catalyst within the damaged or fractured plain of woven double cantilever beam (DCB) specimen exhibited a healing performance of about 67 percent compared to toughness of virgin fracture (without damage) [13-15,17]. Kessler et al. [31] and Brown et al. [33-35] studied the effect of catalyst concentration and its size on fracture strength. Results exhibited that developed mechanism improved the cracking and discharging of healing resin behaviour from the microcapsules. It is also concluded that the healing agent of DCPD was performing efficiently at 80°C [31] and provided a healing efficiency of greater than 70 percent [35].
To withstand harsh condition of processing such as high temperature and mechanical shear, a considerable strength of capsules is always desired. Caruso et al. [36] developed a modify encapsulating technique to manufactured a double-walled urea formaldehyde/polyurethane microcapsules. Compared with a single wall UF microcapsules, these capsules revealed good mechanical properties and thermal stability and showed that these double-walled microcapsules can resist healing temperature of more than 1200C without losing its self-healing properties [29,37,38]. Fereidoon et al. [39] integrated single-walled carbon nanotubes (SWCNTs) to improve water resistance, thermo-resistant water resistance and UF surface morphology.
The mechanical properties, activation mechanism and healing efficiency of self-healing composite material can be characterized after the capsules are incorporated into material. The bonding strength of the capsule with matrix, volume fraction and the stiffness of the capsules can affect the mechanical properties like strength, fracture, toughness and elastic modulus of the self-healing materials. The capsule size and capsule thickness directly affect the rupture and cause healing reactions. It is important to see that more healing agents are contained within the larger capsules and greater cracks can be cured. The capsule can also be more easily broken with a thinner shell wall. Most of the self-healing microcapsules were ranged from 100-200µm at a load of 10-20 wt.% [40]. Zhang et al. [40] tested a composite of embedded capsules with glass fiber-reinforced nylon and found that the elastic modulus and tensile strength was reduced. In comparison with pure epoxy, the strength of matrix fracture inserted with DCPD capsules is increased [35]. However, the toughness of fracture is decreased by adding capsules for epoxy adhesives [42]. The capsule size also affects FRC's fracture toughness and it was seen that interlaminar fracture toughness is higher with smaller capsule size. So, they preferred to use small capsule size for specific application such as adhesive and thin coating [43]. Blaiszik et al. [44] also successfully demonstrated the application of Nano capsules with average size of 220 nm as shown in figure7. Talking about various types of capsule, it has shown that the carrying capacity is almost unrelated to Young's modulus of the microcapsules [45]. Furthermore, in defining the mechanical properties of the composites, the micro-capsule shell wall did not play major part [46].

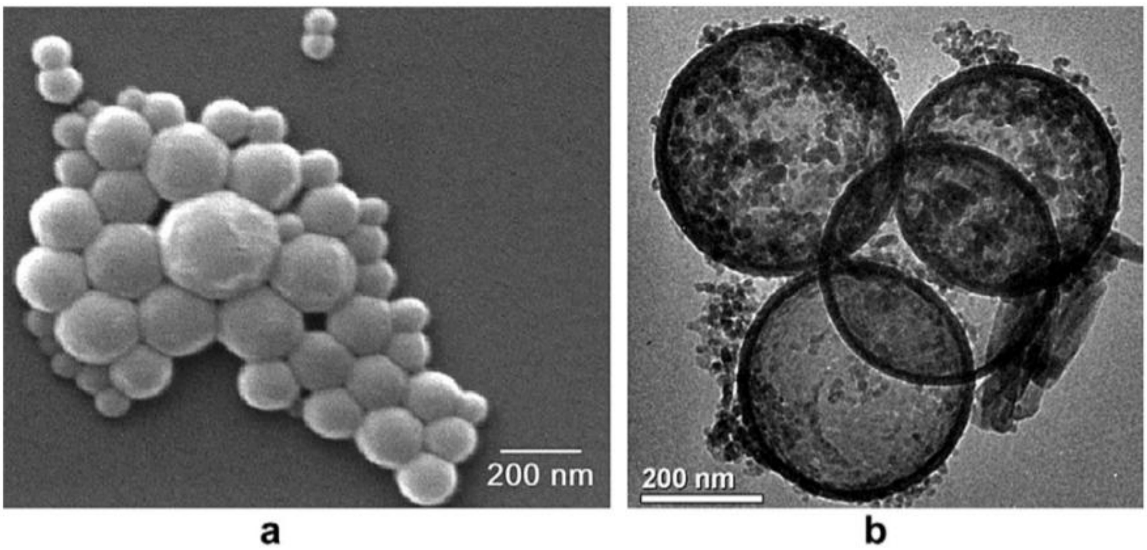


Fig. 7 (a) SEM images of Nano capsules and (b) TEM images showing the core-shell morphology of Nano capsules. (Blaiszik et al.2007)

Self-healing materials based on capsules are capable of healing minor and medium cracks in a one healing period and healing efficiency largely depend on catalyst concentration [1]. The potential of liquid healing agents also depend on how many capsules are diffused within the polymer. Usually, there will be more healing agents available with more locally diffused capsules and more effective local curing. The ratio of various components directly affects the healing efficiency of two or more components of healing agents. Yin et al. [47,48] investigated that the maximum healing efficiency was accomplished only at 10 wt.% and 2 wt.% of concentration of epoxy and hardener respectively in the epoxy + latent CuBr(2)(2-MeIm)(4) catalyst system. The healing performance of the material improves with higher pressure, increased

temperature, and more healing times. For example, the rate of healing of hydroxyl end-functionalised poly(dimethylsiloxane) (HOPDMS) and poly(diethoxysiloxane) (PDES) based healing system is 24 percent only when the specimen has 24 hours exposure to 50 ° C, as compared with 100 percent healing rate at 150 ° C and 48 hours exposure time [49]. The healing efficiency does not remain intact. For example, the effects of aging were tested by Neuser and Michaud [50-51] and the healing efficiency of samples at room temperature was decreased from 77 percent to 13 percent for fresh sample for 77 days.
There were few limitations on the catalyst of DCPD and Grubbs, since its stability was very low at 153 ° C melting point [52], long exposure to oxygen and humidity has affected its reactivity [53]. It also requires a high amount of catalyst, to execute it properly or at a rapid rate [54]. High toxicity and high pricing limit its application.

3.2 Vascular network based Self-healing

It is difficult to carry out repetitive healing in standard extrinsic auto-healing composites, since the rupture of integrated vessels with living healing agent would lead to depletion after the first injury. To solve this problem, Toohey et al. [55] provide a self-healing scheme that includes a 3D microvascular network, which can repair repetitive damage autonomously. Their job imitated human body skin design. When fluid flow from the capillary network in the dermal layer to the injury site is caused by a slice in the flesh, the coagulant would quickly form, which serve as a matrix by which proteins, cells and growth factors move because of healing. Because of its cellular nature of storage system, small crack/damage to the same region can be healed on several occasions as shown in Figure.8

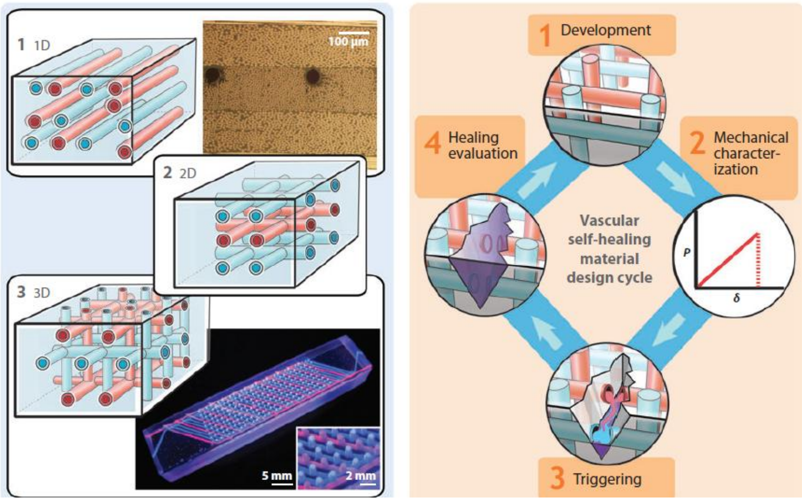


Fig. 8 The design cycle for vascular self-healing materials

In contrast to capsule-based structure, the healing agents are inserted in the vascular materials after the network is incorporated in the matrix. Thus viscosity, chemical reactivity and surface wettability are some characteristic that determine selection of healing agents. Undesired wetting and/or high viscosity characteristic discourage effective network filling, while chemical inconsistency threatens the system long term stability. These characteristics influence the structure of the vascular network, particularly the diameter of the vessel as viscosity and wettability impact the discharge and transfer of the healing agent(s).
The rigidity of the network wall, the connection between matrix and the network, the fraction of the network quantity and the allocation and homogeneity of the channels influence the physical features of an integrated network matrix. It validates the triggering processes and the healing efficiency is described in a way comparable to capsule-based processes. Basically, access to a big supply of healing units and the capacity to refill the network allow frequent healing of subsequent damage occurrences, for vascular healing systems.
The healing nature of this system used ROMP (ring opening metathesis polymerization) of DCPD resin by Grubbs' catalyser. The healing agents encounter the catalyst in the fracture region to start polymerization in the composite, autonomously re-bonding of fracture site take place. The damage site was cured and coating's structural integrity was recovered after optimal span of time. The process of healing was reiterated, as cracks surfaced under successive loading. The coating/substrate samples showed an average healing effectiveness of 49% and a maximum of seven healing cycles, with the four-point bending setup supervised with an acoustic emission detector [56]. Previous studies have shown the limit of small healing rate due to deficiency of catalyst [56].
To integrate a two-part epoxy resin and hardener layer into the 3D microvascular network in independent self-healing coatings system, Hansen et al. [57] introduced comparable assembly techniques, however, with a double- ink extraction and a vertical ink drawing capabilities. The above interlinked dual 3D network allowing separate infiltration of resin monomer and hardener. When a four-point bending, experiment was carried out, the materials was damaged and continuous periodic bending loading were exposed to enhanced liquid blending in the damaged zone before healing. Healing effectiveness as elevated as 100 percent was obtained after 30 healing cycles and at least 50 percent of the toughness of the fracture was retained.

Huang et al. [58] explore that stainless metal cables were integrated into the composite laminate rather than using HGF. The vascular were created by a polytetrafluoroethylene (PTFE) covered stainless steel cable with high melting point temperature and high stiffness. These cables were placed into the middle layer of the laminate and separated manually after the laminate was healed. Coop et al. [59] then further examined the cure performance of CRPF composites materials comprising integrated scandium (iii) triflate catalyst and microvascular channels produced using the above-mentioned method [56]. The double cantilever beam (DCB) samples were discovered to have been healed up to five times with healing effectiveness of up to 108 %.

The microvascular network requires resupply of multiple healing agents within the architectures that make it least reliable but this problem can be controlled by expanding this strategy to incorporate pump pumps and inner tanks and by introducing fresh functionalities through flow of molecular signals, coolant or other entities including self-diagnosis or self-cooling. Providing theoretical insights on how to vascularize composite self-healing products so that supporting liquid is reaching all the fracture locations which can happen by random means. The network setup Bejan et al. [60-62] researched that can supply the fastest liquid to all fracture. By implementing an appropriate pumping approach through the blending method of viscous fluids, it is feasible to increase healing effectiveness from 50 percent to nearly 100 percent as shown in Figure 9 (Hamilton et al. [63]).

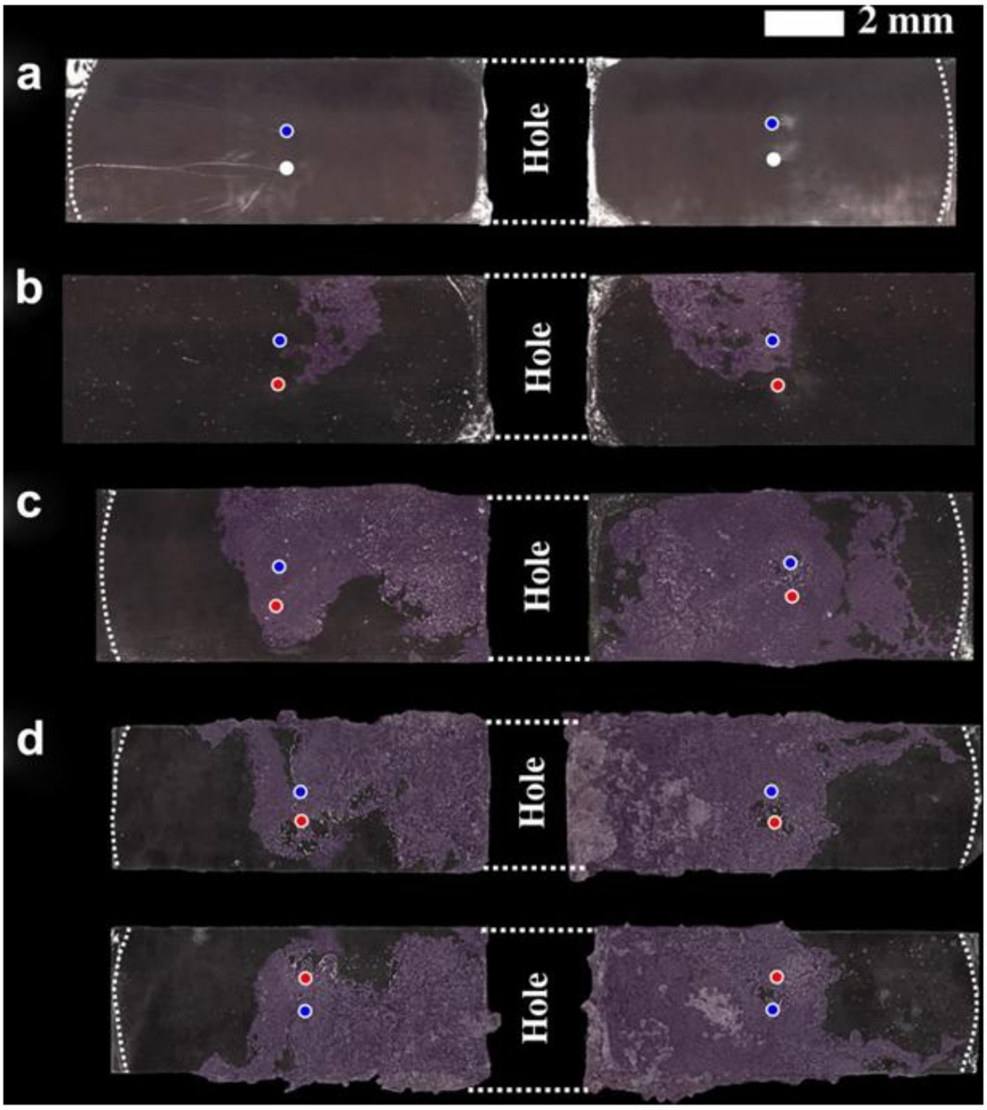


Fig. 9 Fracture surfaces of specimens loaded to Kmax ¼ 0.73KIC with (a) a single healing agent delivered to the cracks, (b) both healing agents delivered at a low pumping rate), (c) both healing agents delivered at 4 mL/h,(d) both healing agents delivered at 7 mL/ h. Healed material is highlighted in false purple colouring. Microchannel are highlighted with solid circles coloured red for those containing Part A, blue for those containing Part B, or white for empty channels. (Hamilton et al. 2012)

Other variable such as humidity and oxygen can also affect the healing process. The impacts of environmental variables on capsule-based healing processes have been regarded by several scientists. These variables should also apply to composites that heal themselves from the vascular system but that is still to be shown. Like capsule-based materials, healing efficiency is determined by structural and dynamic parameters as well as healing agents. However, the impacts of vascular based structure on mechanical efficiency may be more important opposed to those of capsule-based structure.

3.4 Intrinsic Self-healing Composites:

Intrinsic self-healing mechanism is characterized by reversible reactions of polymer matrix which is activated by external source like heat, light, or pressure. Bergman & Wudl [64] successfully provided detailed information regarding intrinsic self-healing method in materials which can be done by thermally reversible reactions, dispersion of melt able thermoplastic phase, or molecular diffusion and hydrogen bonding within the polymer matrix as shown in figure 10. Wool et al. [65] built up a microscopic model which demonstrates that protensive diffusion is responsible for the healing of the crack in composite materials and gives a theory of damage extracting from the area of polymer-polymer interfaces. In comparison to micro vascular and capsule based self-healing mechanism, no healing agents are required which makes the structure of intrinsic self-healing more simple and it also avoids the problem of integrating designs with matrix. A detailed review on recent development in self-healing composite materials is also given by Rajput et al. [66] in which different self-healing approaches were discussed.

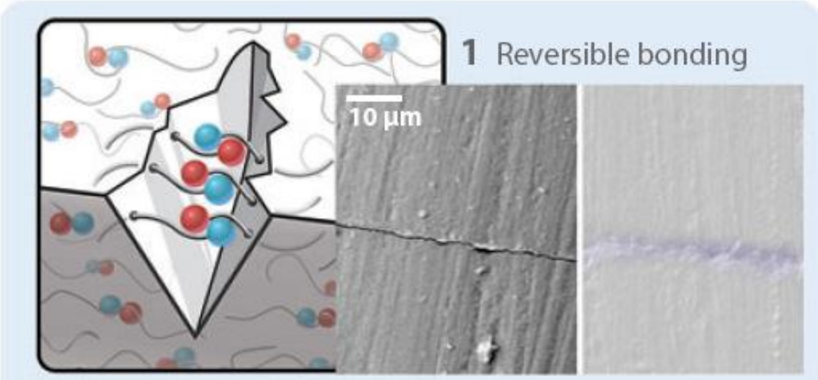


Fig. 10 (a) reversible bonding as observed in Diels-Alder–retro-Diels-Alder healing system (Blaiszik et al.2010)

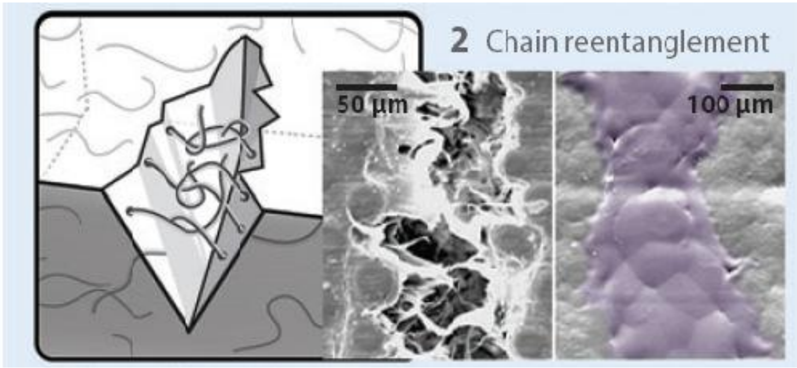


Fig. 10 (b) chain entanglement spanning crack surface (Blaiszik et al.2010)

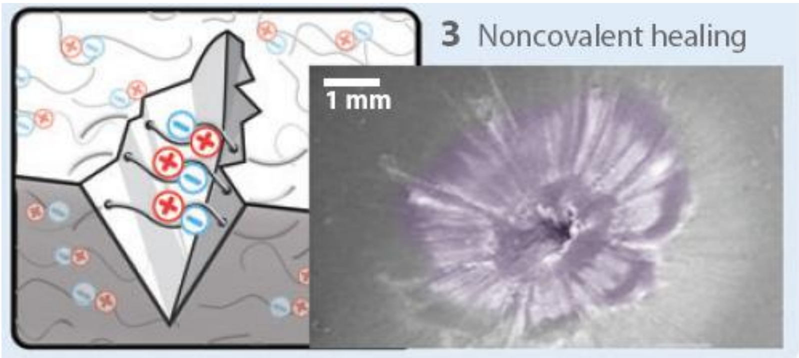


Fig. 10. (c) Noncovalent bonding accomplished by reversible hydrogen bonding (Blaiszik et al.2010).

CONCLUSIONS AND FUTURE STUDY

The present article reviews the recent developments made in the field of self-healing composites. A discussion on different self-healing approaches was done to comprehend the process in a more detailed manner. On the basis of present review, the major conclusions drawn are given underneath:

- Self-healing is known to be a proven technology for enhancing the life of structural composite materials.
- Hollow glass tubes capable of providing the structural strength to the material.

- Capsule based self-healing system has exhibited better improvements over the past decade in terms of its robustness and types.
- HGFs and Capsule based healing mechanism are suitable for small cracks repair while Vascular mechanism are more likely to be used for larger cracks.
- Vascular networks provide multiple channels for releasing healing agents at discrete location, providing multiple healing events per crack when compared to hollow glass tubes and micro-capsules where healing events are limited to one event per crack

However, recent studies done by several researchers were focused majorly on the design and fabrication of self-healing composites for specific purposes and to comprehend the self-healing mechanism. Very rarely, the concept is being utilized for commercialization. The future aspects in this area can be seen by integrating sensing system and smart actuators within the composites to identify the cracks more rapidly and to enhance the process capability.

References

[1] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, Brown EN, Viswanatham S. Autonomic healing of polymer composites. Nature 2001;409(6822):794-797.
[2] Dry C. Alteration of matrix permeability, pore and crack structure by the time release of internal chemicals. In Proceedings: Advance in Cementitious Materials, American Ceramic Society, Gaithersbury, Maryland, 729-68, 1990.
[3] Dry C. Matrix cracking repair and filling using active and passive modes for smart timed release of chemicals from fibres into cement matrices. Smart Matls. & Structs. 1994;3(2):118–123.
[4] Dry C and McMillan W. Three-part methylmethacrylate adhesive system as an internal delivery system for smart responsive concrete. Smart Matls. & Structs. 1996;5(3):297–300.
[5] Dry C. Three design for the internal release of sealants, adhesives and waterproofing chemical into concrete to release. Cem. and Conc. Res. 2000; 30:1969–1977.
[6] White, S.R., Sottos, N.R., Geubelle, PH., Moore, J.S., Kessler, M.R., Sriram, S.R., Brown, E.N., and Viswanathan, S., "Autonomic Healing of Polymer Composites," Nature, 409, 794-797 (2001).
[7] Blaiszik, B. J., Kramer, S. L. B., Olugebefola, S. C., Moore, J. S., Sottos, N. R., & White, S. R. (2010). Self-healing polymers and composites. Annual Review of Materials Research, 40, 179–211. doi:10.1146/annurev-matsci-070909-104532
[8] Blaiszik, B. J., Baginska, M., White, S. R., & Sottos, N. R. (2010). Autonomic recovery of fiber/matrix interfacial bond strength in a model composite. Advanced Functional Materials, 20, 3547–3554. doi:10.1002/adfm.2010007.
[9] Chen X. X., Wudl F., Mal A.K., Shen H.B. and Nutt S.R.(2003). New thermally remendable highly cross-linked polymeric materials. Macromolecules, 36, 1802-1807. Doi:/10.102/Ma0210675
[10] Habault, D., Zhang, H., & Zhao, Y. (2013). Light-triggered selfhealing and shape-memory polymers. Chemical Society Reviews, 42, 7244–7256. doi:10.1039/C3CS35489 J
[11] Selver, E., Potluri, P., Soutis, C., & Hogg, P. (2015). Healing potential of hybrid materials for structural composites. Composite Structures, 122, 57–66.
[12] Zheng, C., & Huang, Z. (2015). Microgel reinforced composite hydrogels with pH-responsive, self-healing properties. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 468, 327–332. doi:10.1016/j.colsurfa.2014.12.060.
[13] Li VC, Lim YM, Chan YW. Feasibility of a passive smart self-healing cementitious composite. Composites B 1998;29B:819-827.
[14] Bleay SM, Loader CB, Hawyes VJ, Humberstone L, Curtis PT. A smart repair system for polymer matrix composites. Composites A 2001;32:1767-1776.
[15] Hucker MJ, Bond I, Bleay S, Haq S. Experimental evaluation of unidirectional hollow glass fibre/epoxy composites under compressive loading. Composites A 2003;34(10):927-932.
[16] Hucker MJ, Bond I, Bleay S, Haq S. Investigation into the behaviour of hollow glass fibre bundles under compressive loading. Composites A 2003;34(11):1045-1052.
[17] Hucker MJ, Bond IP, Haq S, Bleay S, Foreman A. Influence of manufacturing parameters on the tensile strengths of hollow and solid glass fibres. J. Mat. Sci. 2002;37(2):309-315.
[18] Hucker M, Bond I, Foreman A, Hudd J. Optimisation of hollow glass fibres and their composites. Adv Comp. Lett. 1999; 8(4):181-189.
[19] Burgman JA. Hollow Glass Fibers. Symposium on Polymers and Plastics in Construction Presented before the Division of Petroleum Chemistry, American Chemistry Society, September 12-17 1965: A97-A112
[20] Rosen BW, Hollow glass fibre reinforced laminates. Final Report 15 June 1963–15 August 1964, US Navy, Bureau of Naval Weapons, Contract No.: NOW-63-0674-C, GE Missile & Space Division, GE Company, Philadelphia, Pa., 1964
[21] Rosen BW, Ketler AE, Hashin Z. Hollow glass fibre reinforced plastics. Final Report, US Navy, Bureau of Naval Weapons, Contract No.: NOW-61-0613-D, GE Missile & Space Division, GE company, Philadelphia, Pa., 1962

[22] Pang J W C and Bond I P 2004 Self-Repair and enhanced damage visibility in a hollow fibre reinforced plastic Proc.11th European Conf. on Composite Materials (Rhodes, May–June 2004) Paper BO13
[23] Pang J W C and Bond I P 2005 'Bleeding composites'—damage detection and self-repair using a biomimetic approach Composites A 36 183–8
[24] Pang J W C and Bond I P 2005 A hollow fibre reinforced polymer composite encompassing self-healing and enhancd damage visibility Compos. Sci. Technol. 65 1791–9
[25] Trask R S, Bond I P and Semprimoschnig C 2005 Self-healing composite structures in a space environment ICCM-15: 15th Int. Conf. on Composite Materials (Durban, SA, June–July 2005)
[26] Kond¯o A,Van Valkenburg JW. 1979. Microcapsule Processing and Technology. New York: Marcel Dekker
[27] Benita S, ed. 2006. Microencapsulation: Methods and Industrial Applications. Boca Raton, FL: CRC/Taylor & Francis
[28] Ghosh SK, ed. 2006. Functional Coatings: By Polymer Microencapsulation. Weinheim:Wiley-VCH
[29] Jin, H.; Miller, G. M.; Sottos, N. R.; White, S. R. "Fracture and fatigue response of a self-healing epoxy adhesive", Polymer 2011, 52, 1628–1634.
[30] Kessler MR, White SR. Self-activated healing of delamination damage in woven composites. Composites A 2001;32(5):683-699.
[31] Kessler MR, White SR, Sottos NR. Self healing of composites using embedded microcapsules: repair of delamination damage in woven composites. 10th European Conference on Composite Materials (ECCM-10) 3-7 June 2002, Bruges, Belgium.
[32] Kessler MR, Sottos NR, White SR; Self-healing structural composite materials. Composites A 2003;34(8):743-753.
[33] Brown EN, Sottos NR, White SR. Fracture testing of a self-healing polymer composite. Exptl. Mech. 2002;42(4):372-379.
[34] Brown EN, Kessler M, Sottos N, White S. In situ polu(urea-formaldehyde) microencapsulation of dicyclopentadiene. J. Microencapsulation 2003;20(6):719–730.
[35] Brown EN, White SR, Sottos NR. Microcapsule induced toughening in a self-healing polymer composite. J. Mat. Sci. 2004; 39:1703-1710.
[36] Caruso, M. M.; Blaiszik, B. J.; Jin, H.; Schelkopf, S. R.; Stradley, D. S.; Sottos, N. R.; White, S. R.; Moore, J. S. "Robust, double-walled microcapsules for self-healing polymeric materials", ACS Applied Materials & Interfaces 2010, 2, 1195–1199.
[37] Jin, H.; Mangun, C. L.; Griffin, A. S.; Moore, J. S.; Sottos, N. R.; White, S. R. "Thermally stable autonomic healing in epoxy using a dual-microcapsule system", Adv. Mater. 2014, 26, 282–287.
[38] Di Credico, B.; Levi, M.; Turri, S. "An efficient method for the output of new self-repairing materials through a reactive isocyanate encapsulation", Eur. Polym. J. 2013, 49, 2467–2476.
[39] Fereidoon, A.; Ghorbanzadeh Ahangari, M.; Jahanshahi, M. "Effect of nanoparticles on the morphology and thermal properties of self-healing poly(urea-formaldehyde) microcapsules", Journal of Polymer Research 2013, 20, 1–8.
[40] Rule, J. D.; Sottos, N. R.; White, S. R. "Effect of microcapsule size on the performance of self-healing polymers", Polymer 2007, 48, 3520–3529.
[41] Zhang, L., Dong, X. P., & Chen, H. (2011). Study on the effects of the self-healing microcapsules on the tensile properties of polymer composite. Materials and Manufacturing, Pts 1 and 2, 299–300, 460–465. doi: 10.4028/www.scientific. net/AMR.299-300.460
[42] Jin, H., Miller, G. M., Pety, S. J., Griffin, A. S., Stradley, D. S., Roach, D., … White, S. R. (2013). Fracture behavior of a self-healing, toughened epoxy adhesive. International Journal of Adhesion and Adhesives, 44, 157–165. doi: 10.1016/j.ijadhadh.2013.02.015
[43] Uchijo, C., Kuroda, Y., Kemmochi, K., & Bao, L. M. (2011). Research on FRP composite structures with self-healing function—Effect of filler on FRP interlaminar fracture toughness. Advanced Textile Materials, Pts 1–3, 31–34. doi: 10.4028/www.scientific.net/AMR.332-334.31
[44] Blaiszik, B.; Sottos, N.; White, S. "Nanocapsules for self-healing materials", Compos. Sci. Technol. 2008, 68, 978–986.
[45] Chen, C., Ji, H. W., & Wang, H. W. (2013). Damage properties simulations of self-healing composites. Journal of Nanoscience and Nanotechnology, 13, 6679–6686. doi:10.1166/jnn.2013.7780
[46] Tripathi, M., Rahamtullah, K. D., Rajagopal, C., & Roy, P. K. (2014). Influence of microcapsule shell material on the mechanical behaviour of epoxy composites for self-healing applications. Journal of Applied Polymer Science, 131, Article ID: 40572. doi:10.1002/App.40572
[47] Yin, T., Rong, M. Z., Zhang, M. Q., & Yang, G. C. (2007). Self-healing epoxy composites—Preparation and effect ofthe healant consisting of microencapsulated epoxy and latent curing agent. Composites Science and Technology, 67, 201–212. doi: 10.1016/j.compscitech.2006.07.028
[48] Yin, T., Rong, M. Z., & Zhang, M. Q. (2008). Self-healing of cracks in epoxy composites. Multi-Functional Materials and Structures, Pts 1 and 2, 47–50, 282–285.
[49] Moll, J. L., Jin, H., Mangun, C. L., White, S. R., & Sottos, N. R. (2013). Self-sealing of mechanical damage in a fully cured structural composite. Composites Science and Technology, 79, 15–20. doi: 10.1016/j.compscitech.2013.02.006

[50] Neuser, S., & Michaud, V. (2013). Effect of aging on the performance of solvent-based self-healing materials. Polymer Chemistry, 4, 4993. doi:10.1039/c3py00064h
[51] Neuser, S., & Michaud, V. (2014). Fatigue response of solvent based self-healing smart materials. Experimental Mechanics, 54, 293–304. doi:10.1007/s11340-013-9787-5
[52] Kamphaus, J.M., Rule, J.D., Moore, J.S., Sottos, N.R. and White, S.R. (2008) A new selfhealing epoxy with tungsten (VI) chloride catalyst, Journal of the Royal Society Interface, Vol. 5, Pp. 95–103.
[53] Coope, T.S., Mayer, U.F.J., Wass, D.F., Trask, R.S. and Bond, I.P. (2011) Self-healing of an epoxy resin using Scandium(III) Triflate as a catalytic curing agent. Advanced Functional Materials, Vol. 21, Pp. 4624–4631.
[54] Billiet, S., Van Camp, W., Hillewaere, X.K.D., Rahier, H. and Du Prez, F.E. (2012) Development of optimized autonomous self-healing systems for epoxy materials based on maleimide chemistry, Polymer, 53, Pp. 2320–2326.
[55] Toohey, K. S.; Sottos, N. R.; Lewis, J. A.; Moore, J. S.; White, S. R. "Self-healing materials with microvascular networks", Nature Materials 2007, 6, 581–585.
[56] Toohey, K.; Sottos, N.; White, S. "Characterization of microvascular-based self-healing coatings", Experimental Mechanics 2009, 49, 707–717.
[57] Hansen, C. J.; Wu, W.; Toohey, K. S.; Sottos, N. R.; White, S. R.; Lewis, J. A. "Self-healing materials with interpenetrating microvascular networks", Adv. Mater. 2009, 21, 4143–4147.
[58] Huang, C.-Y.; Trask, R.; Bond, I. "Characterization and analysis of carbon fiber-reinforced polymer composite laminates with embedded circular vasculature", Journal of The Royal Society Interface 2010, 7, 1229–1241.
[59] Coope, T.; Wass, D.; Trask, R.; Bond, I. "Repeated self-healing of microvascular carbon fiber reinforced polymer composites", Smart Mater. Struct. 2014, 23, 115002.
[60] Bejan, A., & Lorente, S. (2008). Vascularized multi-functional materials and structures. Multi-Functional Materials and Structures, Pts 1 and 2, 47–50, 511–514
[61] Bejan, A., Lorente, S., & Wang, K. M. (2006). Networks of channels for self-healing composite materials. Journal of Applied Physics, 100, 033528. doi:10.1063/1.2218768
[62] Lorente, S., & Bejan, A. (2009). Vascularized smart materials: Designed porous media for self-healing and self-cooling. Journal of Porous Media, 12(1), 1–18.
[63] Hamilton, A. R., Sottos, N. R., & White, S. R. (2012b). Mitigation of fatigue damage in self-healing vascular materials. Polymer, 53, 5575–5581. doi:10.1016/j. polymer.2012.09.050
[64] Bergman, S.D. and Wudl, F. (2008) Mendable polymers. Journal of material chemistry, 18(1), Pp. 41–62.
[65] Wool, R. P. and O Connor, K. M. (1981) A theory of crack healing in polymers. Journal of applied physics, 52, Pp.5953.
[66] Rajput, V; Goud, Mudimallana & Samir, S. (2017). A review of developments in the self-healing approaches of composite materials. International Journal of Mechanical Engineering and Technology. 8. 1699-1709.