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Self-healing composites: A review

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Abstract: Self-healing composites are composite materials capable of automatic recovery when damaged. They are inspired by biological systems such as the human skin which are naturally able to heal themselves. This paper reviews work on self-healing composites with a focus on capsule-based and vascular healing systems. Complementing previous survey articles, the paper provides an updated overview of the various self-healing concepts proposed over the past 15 years, and a comparative analysis of healing mechanisms and fabrication techniques for building capsules and vascular networks. Based on the analysis, factors that influence healing performance are presented to reveal key barriers and potential research directions.

Subjects: Aerospace Engineering; Automation Control; Composites; Materials Processing; Materials Science; Polymers & Plastics

Keywords: self-healing materials; smart repair, smart actuators; self-sensing; structural monitoring; biomimetic materials

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1. Introduction

For centuries, man has been searching for and creating tougher and more durable structural materials. However, from the perspective of other natural creatures, protection and defence are not fulfilled only by their hard coats or shells, but also adaptively as in the healing of the human skin and the regeneration of the lizard's tail. Inspired by this design, intelligent material systems defined as

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PUBLIC INTEREST STATEMENT

Lightweight, high-strength, fibre-reinforced composites are increasingly used in electric cars, aerial vehicles and wind turbines. However, the main risk in employing these new materials is that internal micro-cracks which may cause catastrophic failure are hard to detect and repair. A solution is to endow these materials with a self-healing ability so that they can repair themselves and restore their mechanical properties automatically. Research on this topic has spanned more than a decade and has produced self-healing composites able to recover properties such as interlaminar fracture toughness with over 100% efficiency. This article explains the healing mechanisms and fabrication techniques for these new materials and indicates potential research directions in this area.

self-healing composites have been developed. They are capable of automatic recovery and adaptation to environmental changes in a dynamic manner, unlike traditional tough and static composites. Through self-healing, it is expected that safety and reliability will improve, the cost of maintaining artificial composites will decrease and material life will be extended. This area has rapidly developed for more than a decade and seen a number of significant achievements.

Current self-healing composites can be categorised into three groups: capsule-based, vascular and intrinsic self-healing materials (Blaiszik et al., 2010). In capsule-based self-healing materials, small capsules containing a liquid able to fill and close cracks are embedded under the material surface. When the material is damaged, cracks cause some capsules to rupture, releasing the liquid and closing the gap. For vascular self-healing materials, the capsules are replaced by a vascular structure similar to a tunnel network, in which various functional liquids flow. These functional liquids will also fill the gap when a crack occurs and breaks the vascular network. The material contained inside a capsule or a vascular network is called a healing agent. The mechanism and behaviour of healing agents are fundamental to the recovery process and restoration of mechanical properties. Intrinsic self-healing materials heal through inherent reversibility of chemical or physical bonding instead of structure design (Chen, Wudl, Mal, Shen, & Nutt, 2003), such as the swelling of shape memory polymers (Habault, Zhang, & Zhao, 2013), the melting and solidification of thermoplastic materials (Selver, Potluri, Soutis, & Hogg, 2015), and increasing viscosities of pH-sensitive micro-gels (Zheng & Huang, 2015). Consequently, the healing mechanisms of intrinsic self-healing materials are fundamentally different from those of capsule-based and vascular self-healing composites.

Since the first review of self-healing materials in 2007 (Kessler, 2007), a number of articles have summarised and analysed this field (Aïssa, Therriault, Haddad, & Jamroz, 2012; Blaiszik et al., 2010; Frei et al., 2013; Guimard et al., 2012; Norris, Bond, & Trask, 2012; Olugebefola et al., 2010; Swait et al., 2012; Trask, H. R. Williams, & Bond, 2007; Wool, 2008; Wu, Meure, & Solomon, 2008; Yuan, 2008; Yang & Urban, 2013; Zhang & Rong, 2012). Yang and Urban (2013) and Herbst, Döhler, Michael, and Binder (2013) focused on intrinsic self-healing mechanisms. For capsule-based self-healing materials, Zhang and Rong (2012) summarised the types and properties of capsule shells, healing agents and related manufacturing methods and presented an analysis of healing performance. Some simple concepts about vascular self-healing materials and their healing mechanisms can be found in Olugebefola et al. (2010). The trends in this area were analysed by Guimard et al. (2012), who also focused on intrinsic self-healing materials. The subject of self-healing materials was covered as part of new emerging technology in Banea, da Silva, Campilho, and Sato (2014), Frei et al. (2013), Swait et al. (2012). Brief reviews are given in Aïssa et al. (2012), Norris et al. (2012) and more extensive surveys can be found in Blaiszik et al. (2010), Trask, H. R. Williams, et al. (2007), Wool (2008), Wu et al. (2008), Yuan (2008).

However, a gap has emerged between capsule-based/vascular self-healing composites and intrinsic self-healing materials in recent years. For capsule-based/vascular designs, research is generally focused not only on healing agents, but also the rupture process, mixing process and micro-structure fabrication techniques. In comparison, most research about intrinsic self-healing composites still concentrate on developing new healing mechanisms to achieve higher healing strength. This is because for both capsule-based and vascular designs, not only healing mechanisms, but also structural factors (e.g. size, shape and pattern) and dynamic factors (e.g. flow, pressure and mixing) have significant effects on healing performance. On the other hand, for intrinsic self-healing materials, the healing mechanism is purely the reversibility of the material itself. Moreover, in capsule-based/vascular self-healing composites, the development focus has shifted from healing strength to the sustainability of healing capacity. Thus, it is useful to reorganise the knowledge in the field of self-healing materials, showing both structural and dynamical effects on healing performance and mechanical properties, and to present potential developments in this fast evolving field.

This paper reviews the development of self-healing materials, especially that of self-healing composite structures. The healing and mechanical performances of the established self-healing composites

are discussed, as well as related fabrication techniques. For clarity, the review concentrates on polymer materials, but similar concepts can also be applied to other material systems, such as concrete and ceramics. The most general and simple concepts are used to make the paper readily accessible to anyone interested in the area without requiring fundamental knowledge of material science and chemistry.

The remainder of the paper is organised as follows. Mechanisms, fabrication methods, mechanical effects and healing performance for capsule-based and vascular self-healing composites are reviewed in Section 2 and Section 3, respectively. Section 4 analyses historical and future trends in self-healing composite systems, highlighting key barriers and potential solutions. Finally, conclusions are given in Section 5. The Appendix A presents some methods for quantitatively measuring healing strength.

2. Capsule-based self-healing structures

In the natural biological world, the unit that carries out self-healing is the cell, in which different liquids accomplish specific functions. Inspired by this design, artificial small capsules capable of bridging gaps when a crack occurs have been developed using encapsulation techniques.

2.1. Mechanisms

2.1.1. Ring-opening metathesis polymerisation (ROMP)

The University of Illinois at Urbana-Champaign (UIUC) presented a prototype capsule-based self-healing material (White et al., 2001), as shown in Figure 1. In the prototype, cell-like capsules containing dicyclopentadiene (DCPD) and Grubbs' catalyst were dispersed in a polymer matrix during material formulation. When the material is damaged and a crack occurs, the healing agent contained in the capsules will be released due to fracture of the poly (urea-formaldehyde) (PUF) capsule shell. The healing agent floods the crack and clots under the ROMP of DCPD catalysed by Grubbs' catalyst. ROMP is a chain growth polymerisation process where a mixture of cyclic olefin is converted to a polymeric material by opening the strained rings in monomers and reconnecting them to form long chains. As a result, almost 75% toughness can be recovered in 48 h at room temperature. This technology was later applied to fibre-reinforced composites (FRC) to produce self-healing fibre-reinforced composites

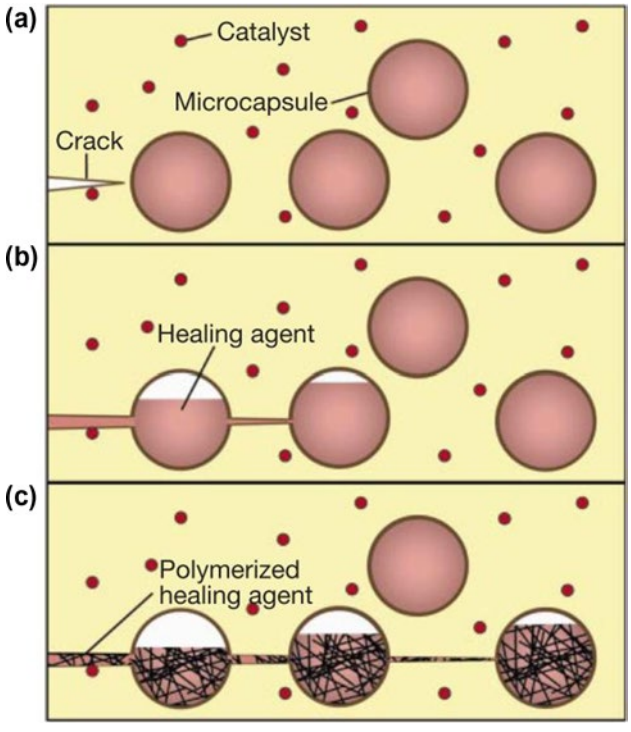


Figure 1. Prototype of capsule-based self-healing composite (White et al., 2001).

(SHFRC) by curing the host material that contained the healing agent-filled capsules. Kessler et al. developed capsules loaded with DCPD and embedded inside FRC to repair delamination and extend material life (Kessler, Sottos, & White, 2003; Kessler & White, 2001) and Brown et al. also used the same method to heal fatigue cracks in SHFRC (Brown, White, & Sottos, 2005). In addition to mixing the capsules with host materials, Blaiszik, Baginska, White, and Sottos (2010), Jones, Blaiszik, White, and Sottos (2013), and Jones, Cintora, White, and Sottos (2014) described the integration of capsules onto surfaces of reinforcement fibres, thus enabling healing of interfacial bonding between the fibres and the matrix.

Capsule-based self-healing materials can be improved in a number of respects, among which the healing mechanism is the most fundamental. In the case of capsule-based materials, this means using more advanced healing agents. For DCPD and Grubbs' catalyst, there are several drawbacks. The stability of Grubbs' catalyst is weak because of its low melting point at 153°C (Kamphaus, Rule, Moore, Sottos, & White, 2008) and its reactivity is also influenced by prolonged exposure to oxygen and moisture (Coope, Mayer, Wass, Trask, & Bond, 2011). Additionally, its application is also limited by its toxicity and high price (Billiet, Van Camp, Hillewaere, Rahier, & Du Prez, 2012). As for DCPD, it also has a low melting point and requires large amounts of catalysts for rapid reaction (Aïssa et al., 2012).

To increase the stability of the healing process, Kamphaus et al. (2008) tested tungsten chloride (WCl_6) as an alternative ROMP catalyst because of its relatively high melting point at 275°C and lower cost at the same time. In another work, (Lee, Hong, Liu, & Yoon, 2004), the DCPD healing agent was replaced by the cost-effective material 5-ethylidene-2-norbornene (ENB) which is known for much faster ROMP reaction. However, the main disadvantage of ENB is that the formed cross-link structure is less strong than the polymerised linear chain structure created using DCPD (Aïssa et al., 2012). To produce a balanced result, Liu, Lee, Yoon, and Kessler (2006) introduced a blending plan in which DCPD and ENB were both encapsulated, as DCPD reactivity built tough and reliable bonds and ENB reactivity provided immediate aid. Afterwards, Huang, Lee, and Kessler (2011) tested a number of the factors including blend ratio, healing temperature and healing time that affected healing performance and proposed an improved blending plan.

Other kinds of catalysts were also taken into consideration (Raimondo & Guadagno, 2013), such as Grubbs' second-generation catalyst (G2), Hoveyda–Grubbs' first-generation catalyst (HG1) and Hoveyda–Grubbs' second-generation catalyst (HG2). These new catalysts allow a cure temperature up to 170°C without becoming deactivated and showed high levels of healing efficiency. The establishment of alternative healing agents and catalysts provides more options in the application of ROMP reaction-based self-healing materials when higher operating temperatures and lower costs are required.

2.1.2. Polycondensation

Polycondensation is a chemical condensation to formulate a polymer by linking single or multiple kinds of monomers to form long chains and releasing water or a similar simple substance. Cho, Andersson, White, Sottos, and Braun (2006) developed a polycondensation-based mechanism using di-n-butyltin dilaurate (DBTL) as the catalyst and a mixture of hydroxyl end-functionalised poly(dimethylsiloxane) (HOPDMS) and poly(diethoxysiloxane) (PDES) as the healing agent. The new mechanism had a lower efficiency compared to that of DCPD and Grubbs' catalyst. However, it is more resistant to deactivation by air, water and the vinyl ester matrix and has a lower cost, expanding its application fields and making it more suitable for real use (Billiet et al., 2012). Self-healing coatings (Cho, White, & Braun, 2009) and woven fibre-reinforced composites (Moll, Jin, Mangun, White, & Sottos, 2013) had been developed based on this mechanism. In another work (Moll et al., 2013), it was claimed that the healing efficiency had been increased to achieve a nearly full recovery.

2.1.3. Epoxy-based system

Epoxy-based healing reactions have gained popularity. In an epoxy-hardener system (Coope et al., 2011; Yin, Rong, Zhang, & Yang, 2007; Yuan, 2008; Yuan, Liang, Xie, Li, & Guo, 2006; Yuan, Rong, & Zhang, 2008; Yuan, Rong, Zhang, Yang, & Zhao, 2011), the epoxy resin and hardener are separately encapsulated and embedded inside the composite matrix. When a crack occurs, both kinds of capsules rupture and the outflowing epoxy resin and hardener are mixed to heal the crack. In addition, solvent and epoxy-solvent capsule healing systems were also developed for polymer composites (Blaiszik et al., 2009; Caruso, Blaiszik, White, Sottos, & Moore, 2008; Caruso et al., 2007). When the encapsulated solvent is released, it locally swells and entangles the matrix across the plane and heals the crack. Epoxy resin can also be added into capsules with solvent, promoting crosslinking reaction. Epoxy-based mechanisms have become the most popular compared to ROMP reaction-based and polycondensation-based mechanisms as they are easily accessible. Capsules containing different kinds of amines for anti-corrosion of steel sheets were developed by Choi, Kim, and Park (2013). The characterisation for epoxy-based coating healing performance was analysed and summarised by Liao et al. (2011) and Liu, Zhang, Wang, Wang, and Wang (2012). More information about epoxy-amine mechanisms for self-healing can be found in the reviews by Zhang & Yang, (2014a, 2014b).

2.1.4. Others

In addition to polymeric composites, capsule-based structures have been adopted in other areas such as construction (Li, Jiang, Yang, Zhao, & Yuan, 2013; Snoeck, Van Tittelboom, Steuperaert, Dubruel, & De Belie, 2014). Dry (2000) made use of cylindrical glass capsules filled with cyanoacrylate to heal cracks in concrete and a two-part epoxy system was also used in self-healing cementitious composite materials (Xing et al., 2008). Related research to increase stability of bitumen (Su, Qiu, & Schlangen, 2013) has also evolved to a very detailed level. More information can be found in the review by Van Tittelboom and De Belie (2013).

2.2. Fabrication processes

Fabrication of capsule-based self-healing composites normally involves two processes: encapsulation of healing agents and integration of capsules with matrix materials. Existing encapsulation techniques, which have already been widely employed in the food industry and medical applications, can also be used for the encapsulation of healing agents.

Currently, *in situ* polymerisation in an oil-in-water emulsion is the most popular and effective method for developing capsules containing healing agents. With this method, the polymerisation of shell monomers is carried out on the surface of core materials. In the work of Brown, Kessler, Sottos, and White (2003), poly (urea-formaldehyde) (PUF) was used as shell material to encapsulate DCPD healing agents and the process of *in situ* polymerisation in an oil-in-water emulsion was presented in their paper in a very clear and detailed fashion. Liu, Sheng, Lee, and Kessler (2009) followed a similar method to encapsulate ENB using melamine-urea-formaldehyde (MUF) as shell materials. For two-part epoxy, PUF (Blaiszik et al., 2009; Yuan et al., 2006), poly (melamine-formaldehyde) (PMF) (Yuan et al., 2008) and poly (methyl-methacrylate) (PMMA) (Li, Siddaramaiah, Kim, Hui, & Lee, 2013; Li et al., 2013) have all been used to build shell walls by different groups around the world. During *in situ* polymerisation in an oil-in-water emulsion, agitation is critical to the size of capsules and the size of the produced capsules follows a Gaussian distribution. Zuev, Lee, Kostromin, Bronnikov, and Bhattacharyya (2013) presented a statistical analysis of the size of the produced capsules. For smaller capsules, Blaiszik, Sottos, and White (2008) used ultrasonication to assist nanocapsule generation and created nanocapsules with a diameter as small as 220 nm. In addition, Fereidoon, Ghorbanzadeh Ahangari, and Jahanshahi (2013) found a physicochemical method that can increase capsule quality: the addition of nanoparticles like single-walled carbon nanotubes or aluminium oxide nanoparticles to the shell wall can allow the diameter and roughness of capsules to be reduced.

In addition, other encapsulation techniques have also been employed to fabricate capsule-based self-healing materials to suit various material properties such as solubility and viscosity. Rule, Brown, Sottos, White, and Moore (2005) encapsulated Grubbs' catalyst with wax shell by rapidly cooling hot

and stirred wax mixed with the catalyst. Cho et al. (2006) and McIlroy et al. (2010) used interfacial polymerisation to encapsulate DBTL and amine for epoxy-based self-healing systems. Chen and Guan (2013) described the self-assembly phenomenon of poly (acrylate amide) shells, containing polystyrene as core under the principle of atom transfer radical polymerisation (ATRP). Zhang, Wang, and Yang (2014), Zhang and Yang (2013) created a fabrication method to build etched glass bubbles as healing agent containers as they would be more brittle and easy to rupture, using diluted hydrofluoric acid in a specially designed mixer. Furthermore, the shell can also be formed of more than one kind of materials. Jin et al. (2014) developed a two-layer capsule shell so that the thermal stability of the capsule can be improved without influencing the rupture performance. More information about encapsulation techniques can be found in the work of Jyothi et al. (2010).

The integration of capsules into matrix materials is another process that affects the healing quality. Sometimes, when a capsule-based material cracks, the capsules simply detach from the matrix material instead of rupturing, resulting in no healing agent outflows. Most of the recent investigations into unsatisfactory releasing of healing agents tend to investigate the influence of the encapsulation process on the quality of the capsules and the triggering of the release of healing agents. However, integration techniques and integration quality, especially mechanical properties of the interface between shells and matrix materials, are yet to be systematically studied.

2.3. Mechanical effects

Several researchers have investigated the influence of capsules on the overall mechanical properties. Zhang, Dong, and Chen (2011) tested glass fibre-reinforced nylon composite with embedded capsules and concluded that the tensile strength and elastic modulus would decrease. The fracture toughness of epoxy embedded with capsules containing DCPD was found to increase compared to that of pure epoxy (Brown, White, & Sottos, 2004). However, for epoxy adhesives, the fracture toughness is reduced by the addition of capsules (Jin et al., 2013). The size of the capsules also has effects on the fracture toughness of FRC and the interlaminar fracture toughness is higher with a smaller capsule size (Uchijo, Kuroda, Kemmochi, & Bao, 2011). Regarding the effects of different kinds of capsules, it was demonstrated numerically that the carrying capacity almost unrelated to Young's modulus of the micro-capsules (Chen, Ji, & Wang, 2013). Also, the micro-capsule shell wall material did not play any significant role in defining the mechanical properties of the composites (Tripathi, Rahamtullah, Rajagopal, & Roy, 2014).

2.4. Healing performance analysis

A summary of the main capsule-based self-healing materials and their healing performances is shown in Table 1. It is worth noting that a particular healing performance cannot be guaranteed even if the same mechanism and healing conditions are adopted due to differences in application areas, host material properties and manufacturing techniques. The point of this table is to describe the range of possible outcomes that may be achieved using a certain mechanism, and to provide a general idea of the potential of capsule-based self-healing composites.

Capsule-based self-healing materials have the ability to heal small and moderate fractures in one single healing cycle. The original ROMP reaction of DCPD facilitated by Grubbs' catalyst as the basic mechanism has a healing efficiency of 75% in 48 h (White et al., 2001). Brown, Sottos, and White (2002) explained that the healing efficiency depended largely on the concentration of catalyst. Full healing is achievable when the concentration of Grubbs' catalyst: DCPD is higher than 10:1. However, it is obvious that this will significantly increase the cost. Also, the mechanical properties of the overall composite system can be greatly affected with an increased number of capsules inside the host material. WCl_6, as an alternative to Grubbs' catalyst, has a relatively low healing efficiency at room temperature (Kamphaus et al., 2008; Li, Wang, & Liu, 2012). As for ENB, it is powerless when used alone (Lee et al., 2004), but the healing efficiency rises significantly when it is blended with DCPD (Liu et al., 2006). Increasing the temperature combined with using Hoveyda–Grubbs' catalyst will also greatly improve healing strength and save healing time (Raimondo & Guadagno, 2013).

Table 1. Summary of healing performance of capsule-based self-healing materials

Mechanism	Healing efficiency[1]	Healing time	Healing cycle	Healing Condition	Host material	References
DCPD + Grubbs	75–100%	10–48 h	1	Room Temperature (RT)	Epoxy	Brown, White, and Sottos (2006), Brown et al. (2002), Rule, Sottos, and White (2007), White et al. (2001)
DCPD + Grubbs	~30%	24 h	1	RT	Epoxy vinyl ester	Wilson, Moore, White, Sottos, and Andersson (2008)
DCPD + Grubbs	67–100% (depending on the extent of damage)	48 h	1	RT	Epoxy + CFRC	Kessler et al. (2003), Moll, White, and Sottos, (2010), Patel, Sottos, Wetzel, and White (2010)
DCPD + WCl_6	20–64.9%	24 h	1	22–50°C	Epoxy	Kamphaus et al. (2008), Li et al. (2012)
ENB + Grubbs	45 and 80%	48 h	1	RT and 80°C	Epoxy	Lee et al. (2004)
ENB/ DCPD + Grubbs	85%	48 h	1	RT	Epoxy	Liu et al. (2006)
ENB + Hoveyda Grubbs	95%	2 h	1	170°C	Epoxy	Raimondo and Guadagno (2013)
HOPDMS and PDES	24%	24 h	1	50°C	Epoxy vinyl ester	Cho et al. (2006)
HOPDMS and PDES	100%	48 h	1	150°C	Epoxy + FRC	Moll et al. (2013)
Epoxy and Solvent	82–100%	24 h	1	RT	Epoxy	Blaiszik et al. (2009), Caruso et al. (2007, 2008)
Epoxy and Solvent + scandium (III) triflate	> 80%	48 h	1	80°C	Epoxy	Coope et al. (2011)
Epoxy + CuBr(2) (2-MeIm)(4)	111%	1 h 30 min	1	130–180°C	Epoxy	Yin et al. (2007, 2008)
Epoxy + mercaptan	104%	24 h	1	20°C	Epoxy	Yuan et al. (2008)
Epoxy + MBM tetrathiol	121%	5 days	1	25°C	Epoxy	Billiet et al. (2012)
Epoxy + antimony pentafluoride	71%	15–20 s	1	RT, 0.2Mpa pressure	Epoxy	Ye et al. (2014)

[1]See Appendix A for the definition of healing efficiency.

Apart from ROMP reaction-based healing mechanisms, HOPDMS and PDES with DBTL as catalysts have demonstrated great potential when the healing temperature is high (Cho et al., 2006; Moll et al., 2013). Epoxy-solvent self-healing systems and epoxy-hardener systems have a high applicability considering their high healing efficiency and mild healing conditions. Billiet et al. (2012), Yin, Rong, and Zhang (2008), and Yuan et al. (2011) all developed epoxy-based self-healing systems able to achieve a healing efficiency higher than 100%. Ye et al. (2014) demonstrated an ultra-fast epoxy-hardener system, in which healing could be activated instantly and healing time was shortened to tens of seconds. All of these healing mechanisms have added significant diversity to this field and brought new possibilities to smart material design.

However, as seen in Table 1, the healing performance is not entirely determined by the mechanisms. The temperature and healing time play a critical role in the healing process, which is often ignored in the discussion of healing performance. These factors can be generally divided into two categories: structural factors and dynamic factors.

Structural factors:

- Capsule size, capsule shell thickness and roughness

The size of capsules and the thickness of the capsule shells directly influence rupture and the triggering of healing reactions. With larger capsule sizes, more healing agents are contained and larger cracks could be healed. Also, with a thinner shell wall, the capsule can rupture more easily. The integration quality is also related to the roughness of the capsule outer shell. In general, to secure a successful healing process, the capsule shell should be thin and rough, and the size should be suitably large to provide sufficient healing agents.

- Dispersion of capsules

The capacity of healing agents also depends on the amount of capsules dispersed inside the matrix. Generally, with more locally dispersed capsules, more healing agents will be available and local healing will be more effective.

- Ratio of different parts of a healing mechanism

For two-or-multiple-parts healing agents, the ratio of different parts directly influences the healing efficiency. For example, the maximum healing efficiency of the epoxy + latent CuBr(2)(2-MeIm)(4) catalyst system was achieved only when the concentrations of epoxy and hardener were 10 wt.% and 2 wt.%, respectively (Yin et al., 2007, 2008).

Dynamic factors:

- Temperature, pressure and healing time

With higher temperature, higher pressure and longer healing time, the healing performance will improve. For example, HOPEMS- and PDES-based healing systems can only achieve a healing efficiency of 24% when the specimen is exposed to 50°C for 24 h compared to 100% healing efficiency when the temperature is 150°C and the exposure time is 48 h.

- Ageing and fatigue

The healing performance does not stay constant. For example, Neuser and Michaud (2013, 2014) tested the effect of ageing and established that the healing efficiency reduced from 77% for fresh samples to 13% for samples aged at room temperatures for 77 days.

Structural and dynamic factors as well as healing agents decide healing performance. At the same time, there are concerns about the effects of introducing capsules on mechanical properties. If the capsule structure significantly reduces the mechanical properties of the host material and makes it no longer able to meet the mechanical requirements, then the self-healing function has no real value. The conflict between healing and mechanical performance fundamentally determines future research trends, which will be analysed in Section 4.

3. Vascular self-healing structures

If capsule-based self-healing composites mimic the natural healing process on a cellular level, then vascular self-healing materials emulate, on a macro level, healing by the vascular and circulation systems in animals. With a circulation system, the healing agent can be refilled, providing the potential for continuous healing agent delivery and flow control.

3.1. Mechanisms

In the 1990s, Dry (1996), Dry and McMillan (1996), Dry and Sottos (1993) pioneered the development of hollow glass tubes as containers preloaded with an epoxy-based healing agent. In their research, when the hollow glass tubes cracked, the loaded healing agent filled the cracked surface and solidified. These hollow fibres can be regarded as one-dimensional (1D) vessels. Bleay, Loader, Hawyes, Humberstone, and Curtis (2001) fixed hollow glass fibres with an external diameter of 15 μm and an internal diameter of 5 μm into a glass fibre-reinforced composite. It was found that negative effects on the mechanical properties of the host materials can be decreased (Trask, H. R. Williams, et al.,

2007; Yuan, 2008) by reducing the size of the vessels. Vacuum-assisted capillary action filling was used to inject the healing agent into the small fibres (Yuan, 2008). Pang and Bond (2005a, 2005b) filled 60-μm-diameter hollow glass fibres with a mixture of healing agents and UV fluorescent dye so that the "bleeding process" could be observed. These researchers constructed prototypes of 1D self-healing material structures based on hollow fibres, which are not only a healing agent container, but also a part of the reinforcing material.

In 2007, three-dimensional (3D) vascular self-healing materials were developed by (Toohey, Sottos, Lewis, Moore, and White (2007). The healing mechanism was ROMP reaction of DCPD enabled by Grubbs' catalyst and the healing efficiency varied from 30 to 70% in different healing cycles. Even though the healing efficiency was lower compared to the capsule-based healing mechanisms available then, this was the first time a self-healing composite capable of multi-cycle healing was demonstrated.

Healing mechanisms for vascular self-healing composites are similar to those for capsule-based self-healing composites. For 1D vascular networks based on hollow fibres, the healing agent can be a one-part adhesive-like cyanoacrylate (Bleay et al., 2001) or a two-part epoxy resin (Trask & Bond, 2006; Trask, G. J. Williams, & Bond, 2007; G. Williams, Trask, & Bond, 2007). On the other hand, for 3D networks, ROMP reaction based on DCPD and Grubbs' catalyst was initially developed (Toohey et al., 2007). Afterwards, Toohey et al. also developed a two-part epoxy-based self-healing microvascular network (Toohey, Hansen, Lewis, White, & Sottos, 2009). They were the first to build two isolated 3D vascular networks embedded in the same host materials, each containing a different liquid. Recently, White et al. (2014) developed a two-stage chemistry, involving a gel stage for gap-filling scaffolds and a polymer stage for restoration of structural performance, so that a damaged area up to 35 mm in diameter on a PMMA specimen can be healed. To secure good fluidity and stability, the selection of healing agents is more rigorous and should consider a number of new factors such as surface wettability and viscosity (Blaiszik et al., 2010). Such a selection also in turn affects the design and development of the vascular network.

The vascular structure has been applied in developing SHFRC. William et al. have focused on embedding hollow glass fibres and forming vasculatures inside fibre-reinforced composites, especially for sandwich structures (H. R. Williams, Trask, & Bond, 2007; Williams, Trask, & Bond, 2008). Nademi et al. also carried out similar research in FRCs containing hollow glass fibres (Nademi, Mozaffari, & Farrokhabadi, 2011). Chen, Peters, and Li (2013) considered inserting vascular layers to form a sandwich-like structure as an alternative to embedding vasculatures. A two-part epoxy was also used in polymeric foam healing systems (Patrick, Sottos, & White, 2012), and for mitigation of fatigue in an epoxy matrix (Hamilton, Sottos, & White, 2012a). ROMP based on DCPD and Grubbs' catalyst was also investigated for its potential in coating technology (Toohey, Sottos, & White, 2009).

Cementitious materials with self-healing properties are another area where the vascular self-healing function is popular. Material designs have included a single vessel containing cyanoacrylate (Lark, Joseph, Isaacs, Gardner, & Jefferson, 2010; Li, Lim, & Chan, 1998) and multi-channels based on three-part MMA (Dry & McMillan, 1996). More information can be found in the review by Van Tittelboom and De Belie (2013).

3.2. Fabrication process

Even though vascular self-healing composites share similar mechanisms with capsule-based self-healing composites, research on this topic has been developing slowly due to immature fabrication techniques. As small vessel diameters, large network coverage, high vessel strength and high network interconnectivity are all required at the same time, developing suitable fabrication techniques becomes difficult. In fact, as opposed to capsule-based self-healing materials research where most of the effort has been on developing new mechanisms to improve healing efficiencies, work on vascular self-healing materials has concentrated on fabrication processes. In this section, popular fabrication methods are categorised and analysed.

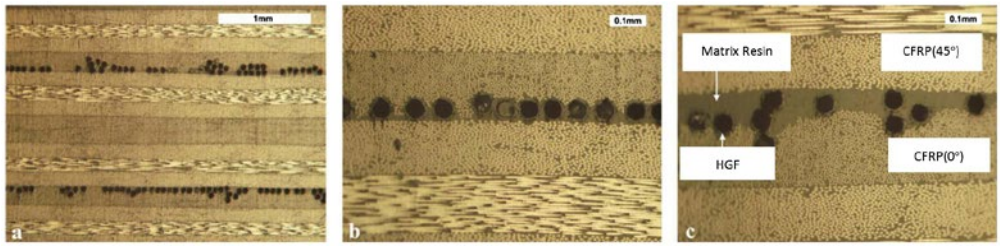


Figure 2. Composites embedded with hollow fibres (Williams, Bond, & Trask, 2009).

3.2.1. Hollow fibres

Installing tubes containing the healing agent inside is one method to fabricate vascular self-healing fibre-reinforced composites (Pang & Bond, 2005a, 2005b; Trask & Bond, 2006), as shown in Figure 2. The hollow fibres act as an isolating layer between the healing agent and the matrix. When the material is damaged, some fibres rupture and release the healing agent. The process of integrating hollow fibres with the host matrix is similar to that for a normal fibre-reinforced material (i.e. covering fibres with uncured epoxy resins followed by curing). When the hollow fibres are aligned parallel to the reinforcement fibres, the mechanical effect of the hollow fibres on the host composite is small (Kousourakis & Mouritz, 2010). However, the main drawback of using hollow fibres is that the design cannot yield interconnected networks and refilling is difficult.

3.2.2. Sacrificial fibres/scaffolds

Sacrificial fibres/scaffolds are a 3D structure formed of materials easy to remove, dissolve or degrade. Such a structure is integrated inside the polymeric host material and should be able to survive the process of curing the host material. After the polymeric system is fully cured, the sacrificial fibres/scaffolds are removed manually, or simply by increasing the temperature or changing the pH of the environment to modify the state of the embedded sacrificial materials. This leaves a hollow microvascular network inside the host material. For example, to build single-line channels, straight steel wire (Norris, Bond, & Trask, 2013) or nylon fibres (Hamilton, Sottos, & White, 2012b) were placed inside the uncured host materials. After it was fully cured, the wire or the fibre has a weak bond with the host materials and can be removed manually, leaving hollow channels. However, this method can only be used to build 1D hollow structures inside composites and the sacrificial-wire/fibre-removing process may introduce invisible damage. To build complex 3D structures, the following methods have been adopted.

(1) 3D printing of sacrificial scaffolds

A fugitive-ink 3D direct-write method to develop sacrificial microvascular networks was first developed by Lewis and Gratson (2004) and Therriault, White, and Lewis (2003) who used a robotic deposition apparatus in a layerwise scheme to print paraffin-based organic ink in three dimensions, as shown in Figure 3(a). After the integration of scaffold and polymeric host material, the system was heated up to 60°C under a light vacuum to remove the melted sacrificial materials, leaving a hollow microvascular network inside. This technique was claimed to be able to produce a scaffold with a diameter ranging from 10 to 300 μm with a root mean square (r.m.s.) surface roughness of 13.3 ± 6.5 nm. Other fugitive inks were also considered, such as a composition of 60 wt.% petroleum jelly and 40 wt.% microcrystalline wax (Toohey et al., 2007). However, it is difficult to remove the melted sacrificial materials from vascular networks and residues always exist when the diameters of vessels are small and liquids are locked inside the vessels due to viscous force.

Poly (lactic acid) (PLA) is a good option for sacrificial materials as it will turn into gas after thermal depolymerisation at high temperature. 3D-printed PLA has been used to build sacrificial structures (Guo et al., 2013). However, the high temperature during the sacrificial material-removing process may be harmful to the host material. Dong et al. (2012) discovered a catalytic reaction system based on catalysts such as tin(II) oxalate that improved the reaction rate of PLA depolymerisation from 1

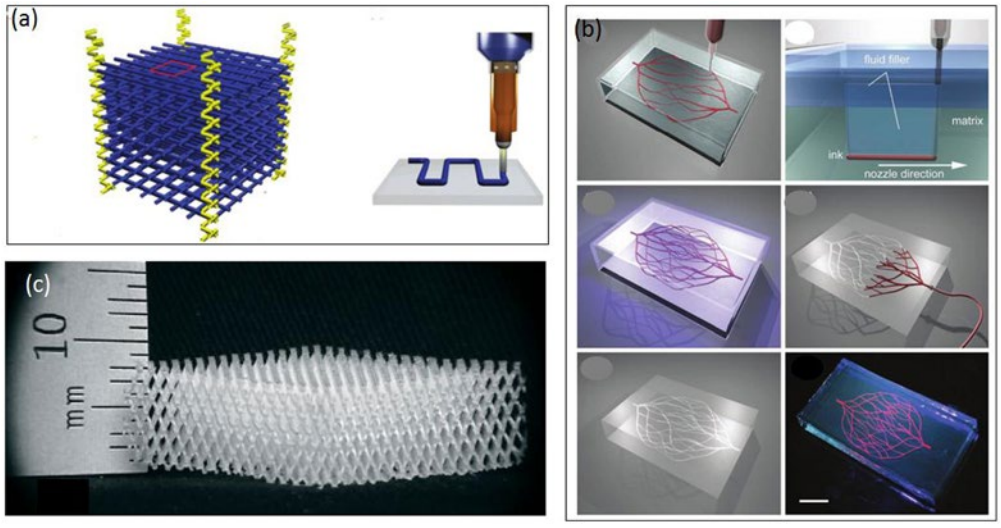


Figure 3. Fabrication of scaffolds. (a) 3D printing using nozzles (Therriault et al., 2003); (b) 3D printing of a biomimicking pattern (Wu et al., 2011); (c) self-propagated photopolymer (Jacobsen et al., 2007).

wt.%/hr (weight per cent per hour) to 25 wt.%/hr, lowering the depolymerisation temperature approximately 100°C. It is worth noting that the heat distribution on samples to remove the sacrificial PLA component must be even. Otherwise, the locally depolymerised monomers are possible to be locked inside the composites and introduce high air pressure that may damage the samples. Afterwards, the mixture of PLA and the catalyst was 3D printed to form sacrificial structures (Gergely et al., 2014). In addition, recent research has also improved the printed pattern from a simple uniform pattern to a biomimetic pattern similar to a leaf venation (Wu, DeConinck, & Lewis, 2011; Wu et al., 2010), as shown in Figure 3(b). The varying diameter of the network was achieved by changing the pressure inside the printing nozzle. To improve the printing efficiency, Hansen et al. (2013) developed a multi-nozzle array to print multiple lines simultaneously. The mechanical properties of hollow channel structures were improved by integrating halloysite nanotubes with sacrificial fibres as the nanotubes covered the inner surface of the microvascular network after dissolving the fibres and provided structural reinforcement (Olugebefola, Hamilton, Fairfield, Sottos, & White, 2014).

In addition to using nozzles, light-triggered solidification based on photopolymers can also be employed to 3D-print sacrificial components. Jacobsen, Barvosa-Carter, and Nutt (2007) and Jacobsen et al. (2010) fabricated interconnected photopolymer waveguides based on self-propagation and generated open-cellular micro-truss structures (Figure 3(c)). This technique was further developed to produce metallic vascular networks (Schaedler et al., 2011) and bicontinuous fluid networks (Roper et al., 2015).

(2) Melt-spinning and electrospinning

Melt-spinning and electrospinning generate fibres from liquids and the processes are similar to the generation of cotton candy. In fact, the original equipment for melt-spinning sacrificial fibres was simply a cotton candy machine (Bellan et al., 2009). After the sugar fibre was fabricated, it was placed in a Teflon mould. Degassed uncured PDMS mixed at a resin: hardener ratio of 10:1 was then poured over the sugar, followed by 24 h curing at room temperature. Afterwards, the devices were placed in a bath of water and ethanol at 70°C for several days to dissolve away the sugar structure, leaving a micro-channel network inside the PDMS matrix. A similar method was applied to form vascular networks inside gelatin using shellac as sacrificial fibres, as shown in Figure 4. Shellac is a kind of natural material that exhibits pH-sensitive solubility in aqueous solutions and has an appropriate melt temperature and viscosity.

Electrospinning can be used to produce similar sacrificial fibres. Gualandi, Zucchelli, Osorio, Belcari, and Focarete (2013) used pullulan as the fibre material and integrated the fibres with diameters as small as 3 μm inside an epoxy matrix. Afterwards, the pullulan degraded when heated up to 250°C. In addition, electrospinning has the potential to build core–shell structures directly as a vascular network, skipping the sacrificial fibre degradation process and healing agent injection steps. This method was proposed by Gualandi et al. (2013) and developed by Wu et al. (2013). The DCPD healing agent was contained directly inside polyacrylonitrile shells during electrospinning. With the fibres embedded, when a crack occurred, the rupture of the polyacrylonitrile shells released the DCPD healing agent to repair the damage.

The spun fibres can also be chemically or physically treated to improve the performance of the sacrificial material-removing process. As the authors mentioned, the thermal depolymerisation of the PLA impregnated can be accelerated using suitable catalysts. Dong et al. (2012) developed a technique to integrate PLA fibres with the catalyst tin(II) oxalate to lower its depolymerisation temperature, as shown in Figure 5. To build a microvascular network inside fibre-reinforced composite, PLA sacrificial fibres can be wound with reinforcement fabrics (Coppola, Thakre, Sottos, & White, 2014; Patrick et al., 2014) followed by heat treatment.

Using melt-spinning and electrospinning, the fabrication process to produce small diameter fibres is simple and fast. However, this method is only used to generate single sacrificial fibres and the installation of the fibres into a designed pattern can only be done manually. Other advanced positioning techniques have not yet established. Core–shell fibres are convenient for producing self-healing materials. However, this method cannot be used to build interconnected networks and the healing agent cannot flow inside the vessels and refilling is not possible. In this case, the material acts more like an improved capsule-based self-healing material than a vascular self-healing material.

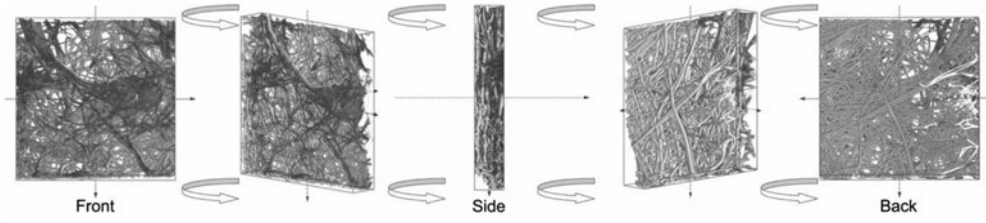


Figure 4. Vascular network formed in gelatin using sacrificial melt-spun shellac fibres (Bellan, Pearsall, Cropek, & Langer, 2012).

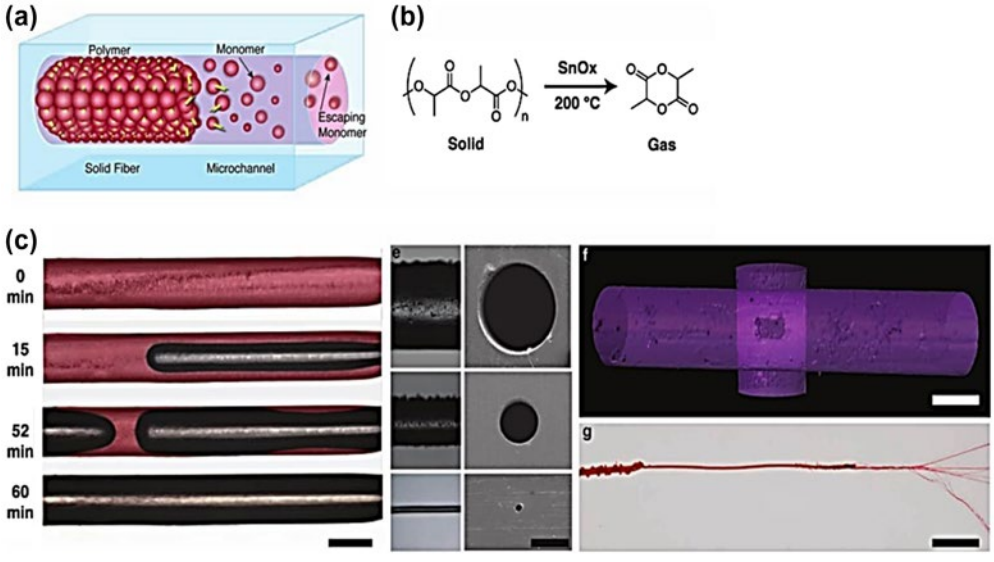


Figure 5. Decomposition of PLA fibre (Esser-Kahn et al., 2011).

(3) Replication of existing patterns

Soft lithography is a powerful tool for fabricating micro-fluidics networks (Choi et al., 2007) and a similar method can also be applied to fabricate microvascular networks for self-healing material systems. Golden and Tien (2007) described a method using gelatin as sacrificial material to form a hexagon beehive structure, as shown in Figure 6. This method started with building the pattern of a vascular network followed by replicating the pattern using a substrate made of glass or pre-oxidised PDMS, forming a "negative" version of the structure on the substrate. The gelatin then filled up the cavity in the substrate. When the gelatin became solid, it was removed from the substrate and integrated inside hydrogel, which was later heat treated. After the molten gelatin was removed, a microvascular network in the pattern was left inside the hydrogel. The diameter of the channels can be as small as 6 μm. Many natural systems also have suitable structures that can be replicated directly using PDMS. He et al. (2013) adopted a similar method to replicate the leaf venation to build interconnected vascular networks, as shown in Figure 7.

The replication of existing patterns can also be combined with other fabrication methods. Bellan et al. (2012) employed a melt-spinning technique to fabricate small diameter fibres and used soft lithography to produce primary vessels.

The replication of existing patterns is suitable for mass production as it is a fast way to copy large and complex networks precisely. However, this process is complex and inefficient when only one item is to be produced.

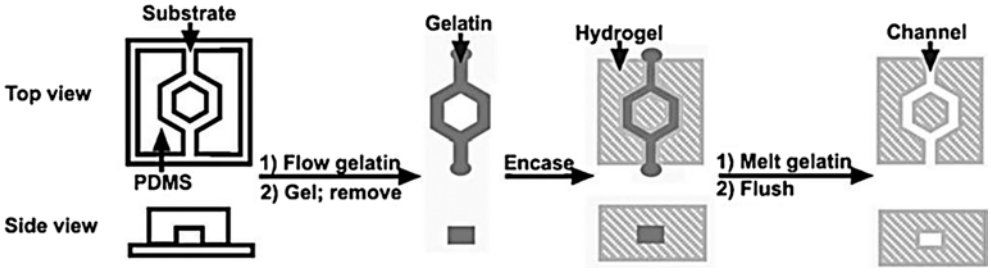


Figure 6. Soft lithography for building micro-fluidics devices (Golden & Tien, 2007).

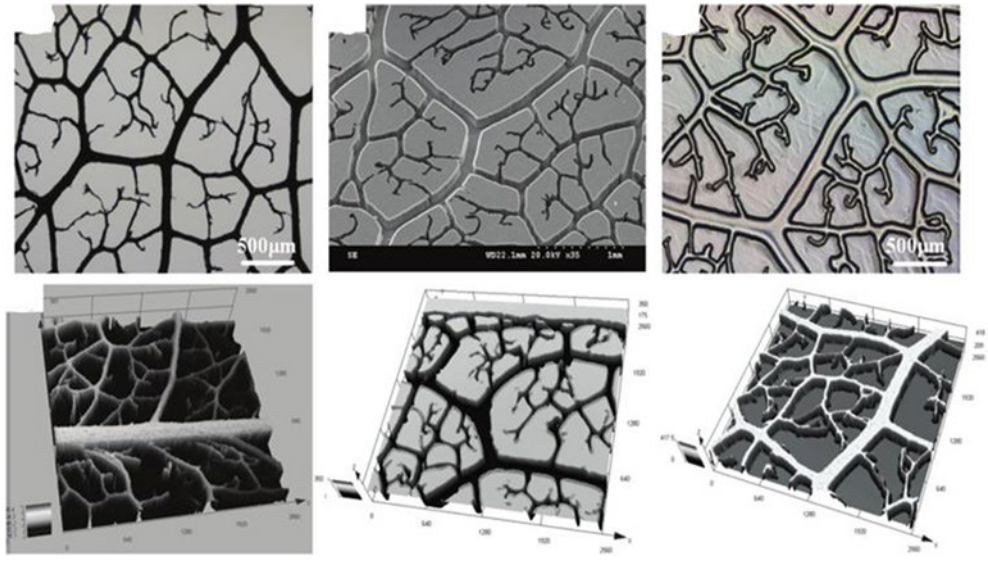


Figure 7. Replication of a leaf venation (He et al., 2013).

3.2.3. Electrostatic discharge

Electrostatic discharge is likely to be the most rapid fabrication method to build microvascular networks following natural designs (e.g. Murray's law). Huang et al. (2009) irradiated poly (methyl methacrylate) (PMMA) with an electron beam, causing electrical charges to accumulate inside the material. The specimen was then connected to the ground and a process of rapid discharge similar to lightning occurred, creating a tree-shape branched microvascular network inside the specimen block, as shown in Figure 8. Alternatively, a defect was introduced on the surface of the block prior to irradiation that became a nucleation site allowing spontaneous discharge upon exposure to the electron beam. The diameter of the vessels ranged from 10 to 500 μm.

This method is suitable for building vascular networks of any size rapidly and efficiently. However, the generated pattern is not controllable, resulting in uncertain quality of the network. Thus, this method still needs further investigation, especially as regards the performance and property of the discharge process.

3.2.4. Laser direct-write

Laser direct-write techniques have been applied to fabricate channels in micro-fluidics devices. These channels could act as vessels in vascular systems. Lim, Kamotani, Cho, Mazumder, and Takayama (2003) used high-brightness diode-pumped Nd:YAG slab laser to manufacture micro-channels on a PDMS block.

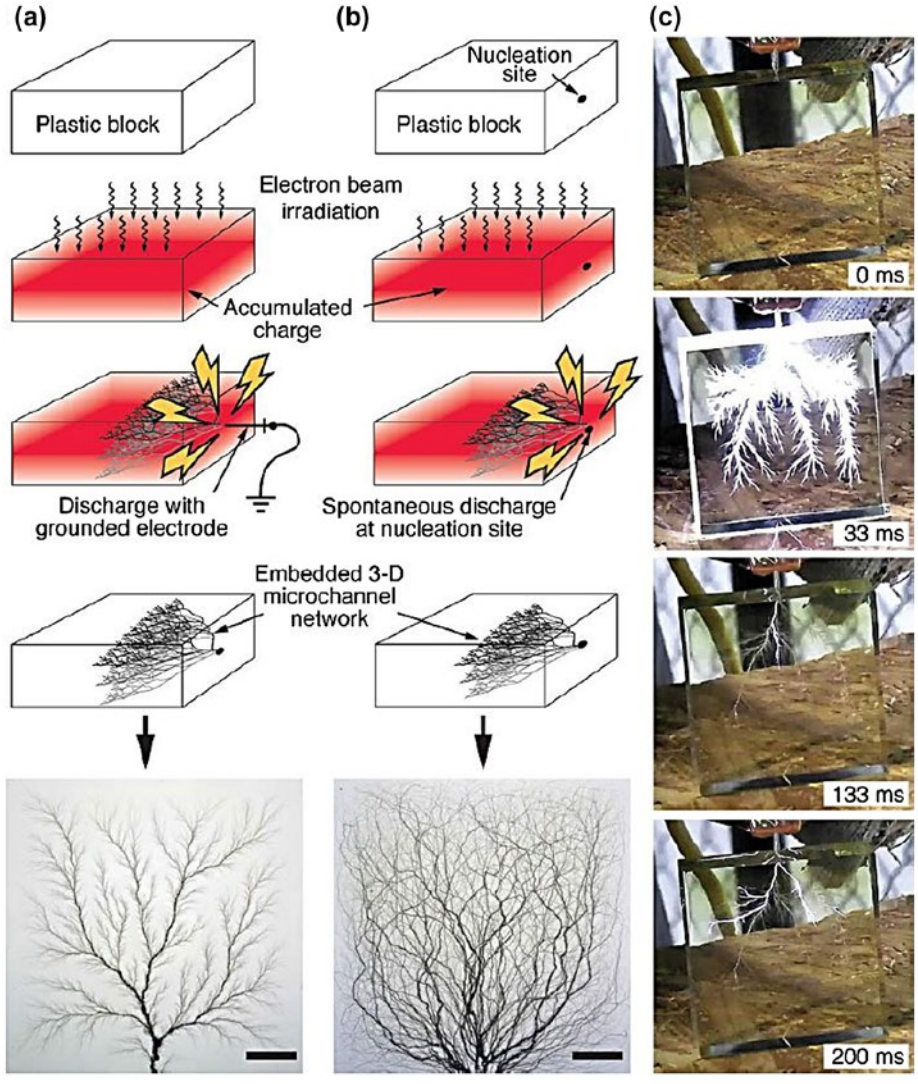


Figure 8. Electrostatic discharge to fabricate vascular patterns (Huang et al., 2009).

Lasers can be used to fabricate very complex two dimensional (2D) patterns directly on polymeric materials. However, it is difficult to produce 3D structures using lasers and more work is needed to achieve this (Table 2).

3.3. Mechanical effects

For vascular systems, Coppola et al. (2014) tested the tensile strength of fibre-reinforced composites with a wave-shaped vascular network architecture inside formed using PLA sacrificial fibres and found that vascular channels have a minimal effect on tensile behaviour when fibre alignment is unaltered and the reinforcement fibre architecture is not distorted. Zhou, Wang, and Mouritz (2010) numerically showed the influence of micro-vessels on the structural properties of laminated composites, especially on stress concentration around vessels and delamination cracking. Work by Kousourakis and Mouritz (2010) showed that hollow fibres located along the mid-thickness plane of the composite material caused no change to or a small reduction (less than a few per cent) in the in-plane elastic modulus. The tension and compression strengths did not change when hollow fibres were aligned to the loading direction, but strength decreased when the fibres were normal to the load. Nguyen and Orifici (2012) did similar work and highlighted fibre waviness angle as a key geometrical parameter for structural performance. Norris, Bond, and Trask (2011a) found the compressive strength of FRC embedded with hollow 1D vessels reduced between 13 and 70% with different vessel dimensions. Similar research has been reported by Huang, Trask, and Bond (2010).

3.4. Healing performance analysis

There are two original motivations to build vascular structures: (1) giving self-healing capability to fibre-reinforced composites, and (2) achieving multi-cycle self-healing. After approximately 10 years of development, research along these two different paths has largely converged and should be considered together and compared. A summary of the main designs in this field and their healing performances is shown in Table 3.

For vascular self-healing composites, healing efficiency is less than 80% under most circumstances. This is relatively low compared to capsule-based self-healing composites where a number of researchers have

Table 2. Features of fabrication techniques for vascular networks

	1D Hollow Fibres	Sacrificial fibres/scaffold				Electrostatic discharge	Laser direct-write
		Straight wire/fibre	3D printing	Spinning	Replication		
1D vessels	Yes	Yes	Yes	Yes	Yes	Not predictable	Yes
2D vessels	No	No	Yes	Yes	Yes	Not predictable	Yes
3D vessels	No	No	Yes	Yes	Yes	Not predictable	No
Interconnection	No	No	Yes	Yes	Yes	Yes	Yes
Refill	Possible but difficult	Possible but difficult	Easy	Possible but difficult	Easy	Easy	Easy
Size	10–500 μm	10–500 μm	10–500 μm	5–300 μm	Depends on the pattern to be replicated	20–300 μm	Depends on the size of the laser beam
Fabrication time	Short	Short	Medium	Medium	Long	Short	Short
Large-scale fabrication	Yes	Yes	Possible but inefficient	Possible but inefficient	Yes	Yes	Possible but inefficient
Possibility of damage	Low	High	Low	Low	Low	High	Low
Surface roughness	Good	Good	Good	Good	Depends on the pattern to be replicated	Good	Bad

achieved a healing efficiency higher than 100%. As seen from the table, different healing mechanisms did not make significant differences to the healing efficiency. Other structural and dynamic factors, as categorised as follows, have made a significant impact on healing performance.

Structural factors:

- Vessel size and roughness.

The vessel size and the roughness of the vessel's inner surface determine the efficiency of liquid flow inside the vascular system (Cho, Lee, Kim, & Bejan, 2010). A large-size vessel is able to efficiently provide adequate healing agents when a large-scale crack occurs (Norris et al., 2011a, 2011b, 2013).

- Vascular network pattern.

The healing behaviour is triggered by the rupture of the vascular network. Thus, in order to create a high possibility of releasing the healing agent, the pattern of the network should have a high coverage. However, a large volume of hollow structures inside composites brings uncertain impact on mechanical properties. Thus, a balance between acceptable pattern coverage and a compact pattern structure is required (Aragón et al., 2013; Bejan & Lorente, 2008; Bejan, Lorente, & Wang, 2006; Lorente & Bejan, 2009).

Dynamic factors:

- Temperature and healing time.

For two-part epoxy systems, suitably high temperatures and long healing time normally result in high healing efficiency. For example, given the same healing time, Hansen, White, Sottos, and Lewis (2011) found that healing efficiency increased to 74% from 24% as the temperature increased to 70°C from 30°C. Temperature is a common factor for both capsule-based healing systems and vascular healing systems.

- Hydraulic pressure and mixing process.

The applied hydraulic pressure inside the vascular network not only determines the amount of healing agents outflow, but also the mixing quality of the multiple-parts healing agents. With a

Table 3. Summary of healing performance of vascular self-healing materials

Mechanism	Healing efficiency (%)	Healing condition	Healing cycle	Host material	References
DCPD + Grubbs' catalyst	70	12 h25°C	7	Epoxy	Toohey et al.(2007), Toohey, Sottos, et al. (2009)
Epoxy resin + Hardener	60–90	48 h30°C	30	Epoxy	Hansen et al. (2009), Toohey, Hansen, et al. (2009)
Epoxy resin + Hardener	74 and 27	6 h70 and 30°C	1	Epoxy	Hansen et al. (2011)
Epoxy resin + Hardener	87–100	Normally higher than RT	1	FRC	Norris, Meadway, O'Sullivan, Bond, and Trask (2011), Norris et al. (2011a, 2011b, 2012, 2013), Pang and Bond (2005a, 2005b), Patrick et al. (2014), Trask and Bond (2006), Trask, G. J. Williams, et al. (2007), G. Williams et al. (2007), H. R. Williams et al. (2007)
Two-stage chemistry	62	20 min to fill impacted regions, 3 h to restore mechanical function, 125°C	1	PMMA	White et al. (2014)

suitably high hydraulic pressure inside vessels, continuous delivery of healing agent to the crack location is possible. More importantly, when two-part epoxy healing agents are applied and epoxy resin and hardener contact at the crack location, the mixing only takes place at the interfaces of those two viscous liquids and the mixing ratio of the different parts is hard to control. By applying a suitable pumping strategy according to the mixing process of viscous liquids, it is possible to enhance healing efficiency from 50% to almost 100% (Hamilton et al., 2012b).

- Other environmental factors.

Other factors like moisture and oxygen can also influence the healing performance. A number of researchers have considered the effects of the environmental factors on capsule-based healing systems. These factors should also be valid for vascular self-healing composites, but this is yet to be demonstrated.

As with capsule-based materials, structural and dynamic factors as well as healing agents determine healing performance. However, the effects of vessels on mechanical performance could be more significant compared to those of capsule-based structures. Such concerns fundamentally determine future trends, which will be analysed in Section 4.

4. Trends

4.1. Shift in development focus and new opportunities

Although researchers may claim to have greatly improved the healing performance of self-healing composites, these products have yet to be used in practical applications owing to uncertainties in their performances. Some self-healing composites heal well only when conditions are favourable and the damage is minor. For self-healing products to be practically useful, it is essential that the material is able to achieve "sustainable healing". This means that healing can effectively carry on regardless of environmental conditions and the size of the damage.

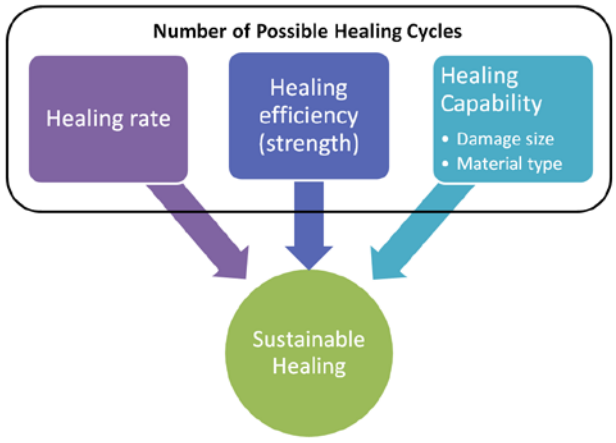
Sustainable healing consists of three main aspects: healing efficiency (healing strength), healing rate and healing capability, as shown in Figure 9. Healing rate and efficiency represent the rate of curing and the strength of the repaired material, respectively. Healing capability relates to the size of the damaged area and the range of materials that can be healed. For example, vascular self-healing composites have a larger healing capability than capsule-based self-healing composites, as vascular systems can heal larger areas, although the types of healable materials are similar in both cases. In addition, sustainable healing implies the ability to undergo multiple healing cycles and, ideally, means that the healing rate, healing efficiency and healing capability remain unchanged throughout.

The past 10 years have seen great improvements in healing efficiency (strength). Whether in capsule-based or vascular healing systems, when the size of the damage is small or moderate and appropriate healing conditions are adopted, healing efficiencies of more than 60% and sometimes even higher than 100% can be achieved. Thus, healing strength is no longer an issue. By comparison, advances in healing rate and capability are less obvious. To achieve sustainable healing, the healing rate must be controllable and the healing capability must be improved to ensure that large damage sizes and a wide variety of types of materials can be healed. Hence, the research focus will shift from healing efficiency to healing rate and healing capability, as they have become the key barriers to sustainable healing. New research opportunities are discussed below.

4.1.1. Healing rate

There are potentially a number of methods to increase healing rate, such as employing advanced healing agents, increasing the healing temperature and adopting better mixing strategies. On the other hand, the healing rate cannot be too high in some applications. For example, one-part healing agents must have a medium healing rate to avoid solidifying inside vascular networks. Fundamentally,

Figure 9. Sustainable healing.



once the type of healing mechanism has been confirmed, the healing rate in a particular environment is intrinsically determined as well. For sustainable healing, the healing rate must be controllable and kept in an appropriate range regardless of environmental conditions. However, this has yet to be achieved.

Having a controllable healing rate means that the healing rate can be accelerated or decelerated according to the situation. This will be a significant step towards sustainable healing. As the healing rate is fundamentally determined by the energy provided, it becomes controllable as long as a suitable energy delivery component able to supply energy to healing agents is available. Chu, Zhang, Liu, and Leng (2014) and Zhang, Chu, Wang, Liu, and Leng (2013) developed a carbon nanotube paper for de-icing that is able to heat up a composite surface from −22 to 150°C, which is an ideal temperature for accelerating reaction in two-part epoxy systems. Fehrman and Korde (2013) developed a method to deliver acoustic energy to certain target defect locations. All of these techniques have the potential to provide energy in self-healing composites. Vascular systems can be more easily actuated by controlling the pressure and temperature of the liquids inside the network. Research on this topic will be strongly related to studies of the characteristics and the design of vascular networks.

However, to achieve a controllable healing rate, it is not enough to have an energy delivery component. A sensing system is also necessary. The sensing system is particularly critical to the application of structural materials working in extreme environments.

The devices studied include Brillouin distributed fibre sensors (Galindez-Jamioy & López-Higuera, 2012), Fibre Bragg Gratings (FBG), inkjet-printed sensors (Yun et al., 2014), carbon nanotube-based sensors (Thostenson & Chou, 2006) and acoustic emission sensors (Ranachowski, Jozwiak-Niedzwiedzka, Brandt, & Debowski, 2012). Some of these sensing systems have been adopted for detection of cracks in self-healing materials (Aïssa et al., 2012; Kirkby, de Oliveira, Michaud, & Månson, 2011; Trask, Norris, & Bond, 2014). For example, Hong and Su (2012) designed a multifunctional healing and monitoring system based on the vascular model by introducing conductive carbon powders and metallic micro-wires inside micro-tubes. However, researchers have mainly focused on gathering crack information and the feedback loop has not been built to guide healing process in real time.

Overall, through combining energy delivery control and sensing, it is possible to achieve a controllable healing rate. The former is to ensure that the rate is in an appropriate range, while the latter is to obtain crack and environmental information to determine the appropriate energy control strategy.

4.1.2. Healing capability

There have been two significant improvements regarding the healing scale: the establishment of vascular self-healing composites to achieve multi-cycle healing and moderate-scale healing (Toohey

et al., 2007), and the development of multi-phase healing mechanisms for large-scale healing (White et al., 2014). The authors believe that, ultimately, the healing size would be infinite which means the damage can be healed regardless of its size. This situation might be referred to as self-regeneration, a process similar to the regeneration of a lizard's tail which has yet to be artificially accomplished.

Regarding the types of materials able to self-heal, there have been no obvious advances since the establishment of capsule-based self-healing composites. In any composite formed of more than one substance, different parts have different functions. Once a certain component in a composite has failed and cannot be healed, the corresponding functions disappear. For example, the recovery in self-healing fibre-reinforced composites can only be effective when the structures of the reinforcement fibres remain intact. To restore all functions, it is essential that all types of materials can be repaired or replaced by newly generated parts that are able to fulfil the same functions. However, this is still not achievable at the moment. A new opportunity is to develop mechanisms for healing reinforcement fibres and other materials used in composite systems.

4.1.3. Other opportunities

Carbon nanotubes also present other promising properties in addition to heating and sensing. The potential of carbon nanotubes as containers was highlighted when they were successfully filled with materials such as hydrogen (Lee, Frauenheim, Elstner, Hwang, & Lee, 2000; Lee & Lee, 2000; Liu et al., 1999). In 2009, Lanzara, Yoon, Liu, Peng, and Lee (2009) investigated the possibility of inserting healing agents into carbon nanotubes, and obtained simulation results theoretically to indicate that a carbon nanotube released healing agents upon rupture. Moreover, carbon nanotubes show intrinsic self-repairing of their walls on a small scale (Börrnert et al., 2010). However, inserting healing agents into nanotubes as small as 2–3 nm in diameter is still a difficult task. In summary, carbon nanotubes can potentially enhance the mechanical properties of the host materials (as mentioned in Sections 3 and 5), contain and release healing agents, detect strain cracks and temperature, and self-heal at the same time.

4.2. Comparison of and future trends in capsule-based and vascular structures

As mentioned previously, the two main topics in the area of self-healing composites are healing performance and mechanical properties. As for healing performance, in most cases, a capsule-based self-healing composite can only cope with very small cracks due to the limited amount of healing agent contained inside the capsules. So this is especially suitable for dealing with delamination and other kinds of damage on the micro level, which is a common issue when using layered composites. Even though capsule-based structures can provide higher healing strength compared to vascular structures, thanks to the dispersion of capsules providing wide coverage, the key advantages of the vascular structure are its capability for multi-cycle healing and large area healing, both of which are essential to sustainable healing. As for large-scale damage, capsule-based self-healing structures become powerless, while vascular self-healing composites can heal relatively large gaps when healing agent refill and multi-phase healing are effective (White et al., 2014). A multi-phase healing mechanism can build a semi-solidified surface for later epoxy curing or solid healing, just like the multi-phase healing behaviour in biological systems. Figure 10 shows the performance of multi-cycle healing, comparing vascular networks with micro-capsules. Considering that the sustainability of healing behaviour becomes increasingly important, the development of vascular structures is likely to be the focus of research in the future.

Regarding the mechanical properties of capsule-based and vascular structures, the size of the capsule and vessel makes a large difference to the mechanical properties of the overall composite. Smaller sizes tend to introduce less effect on the host material. On the other hand, smaller containers generally cannot provide adequate amounts of healing agents. In order to minimise the mechanical effects of capsules and optimise the capacity of healing agents, the crack location can be predicted (Knipprath, McCombe, Trask, & Bond, 2012; Williams, Trask, & Bond, 2011) from the

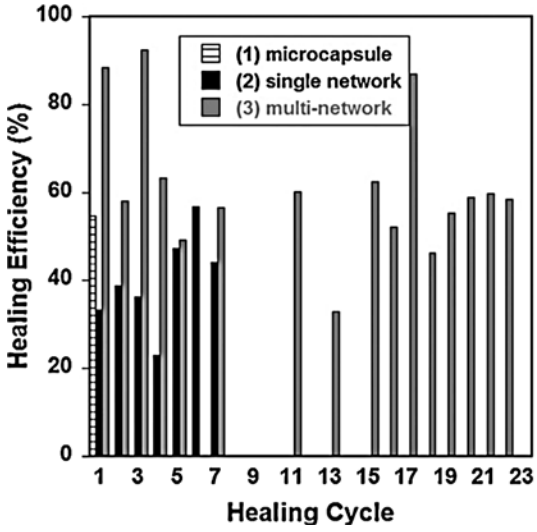


Figure 10. Healing potential for multi-cycle healing (Toohey, Hansen, et al., 2009).

perspective of structural optimisation and the location and number of capsules can be designed and planned instead of being random. However, an upper limit of the capacity of healing agents still exists and the conflict between having enough healing agent and satisfying mechanical performance requests remains for capsule-based structure. The potential to refill a vascular structure makes this problem solvable, and also makes vascular structure more competitive in this regard.

Even though a vascular structure has more advantages, it still cannot totally replace capsule-based structure. Actually, in biological systems, healing is fulfilled by both cells and vascular networks in combination. As the capsule-based structure is more suitable for healing small crack and the vascular structure is more suitable for healing medium and large crack, these two structures can be combined and used simultaneously to develop sustainable healing systems to cope with all kinds of damage conditions.

5. Conclusion

Main developments in self-healing materials in the past 15 years have been reviewed in this paper. Capsule-based and vascular self-healing structures are the main routes to building autonomous self-healing structures. Healing mechanisms, healing performance and fabrication techniques for producing capsules and building vascular networks have been summarised and analysed. Capsule-based self-healing materials are able to heal small cracks, while vascular systems are more suitable for healing larger damaged areas. The healing performance varies from 24 to 121% depending on the types of healing agents, different healing and damage conditions.

Future work in this area will still follow historical trends: (i) *improvement of healing performance* and (ii) *investigation of effects on mechanical properties*. However, the development focus has been shifting from healing strength to the sustainability of healing ability. With the development of smart material technology and composite materials, the boundaries between structural materials and functional materials will be less clear. Potential approaches to improving this technology have been discussed which involve introducing sensing systems and smart actuators to build a controllable healing system. Vascular self-healing composites are highly promising and their development is likely to attract more research effort in the future.

List of abbreviations and symbols

ATRP—Atom transfer radical polymerisation

DBTL—Di-n-butyltin dilaurate

DCPD—Dicyclopentadiene

ENB—5-ethylidene-2-norbornene

FBG—Fibre Bragg Gratings

FRC—Fibre-reinforced composite

G2—Grubbs' second-generation catalyst

HG1—Hoveyda–Grubbs' first-generation catalyst

HG2—Hoveyda–Grubbs' second-generation catalyst

HOPDMS—Hydroxyl end-functionalised poly (dimethylsiloxane)

MMA—Methylmethacrylate

MUF—Melamine-urea-formaldehyde

ROMP—Ring-opening metathesis polymerisation

PUF—Poly (urea formaldehyde)

PDES—Poly (diethoxysiloxane)

PDMS—Poly (dimethylsiloxane)

PLA—Poly (lactic acid)

PMF—Poly (melamineformaldehyde)

PMMA—Poly (methylmethacrylate)

SH—Self-healing

SHFRC—Self-healing fibre-reinforced composite

WCl_6—Tungsten chloride

η—Healing efficiency

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Appendix A

Quantification of healing strength

Healing performance can be measured from a number of aspects, among which healing efficiency as defined in Equation 1 is the most widely recognised.

$$\eta = \frac{f_{Healed} - f_{damaged}}{f_{virgin} - f_{damaged}} \times 100\% \quad (1)$$

where f refers to the property of interest (Blaiszik et al., 2010), such as flexural strength or tear strength.

Healing efficiency entirely represents the quality of the final healed wound, neglecting the differences in healing processes and damage conditions. For structural use, healing efficiency can also be defined as healing strength, in which fracture toughness, tear strength, fatigue response, impact response and tensile strength are emphasised. However, standards for strength measurements would not be suitable for other properties such as electrical conductivity in a self-healing circuit (Palleau, Reece, Desai, Smith, & Dickey, 2013).

Fracture toughness and fatigue response

Three-point bending, four-point bending, compact tension (CT) test, double-cantilever beam (DCB) test, tapered double-cantilever beam (TDCB) test and double-cleavage drilled compression (DCDC) are common methods to test fracture toughness and fatigue response. Three-point bending and four-point bending are the most general methods for testing flexural properties. CT tests, DCB tests and TDCB tests explore delamination in materials and are especially suitable for layered and fabric-reinforced composites. DCDC testing aims to study the effects of uneven composite structures such as hollow bubbles and hollow channels which lead to damage propagates because of stress concentration. Normally, fracture testing begins with adding loads to a virgin specimen until failure. Afterwards, the load is removed and certain healing conditions such as high temperature and suitably long healing time are given in the healing process. Then, the healed specimen is loaded until failure again. The loads withstood by the original specimen and that by the healed specimen are used to calculate healing efficiency as in Equation 1. This process can be repeated for multi-cycles. Fatigue response is difficult to measure because instead of just the load, other factors should also be considered, such as the applied stress intensity range, the loading frequency, the ratio of applied stress intensity and the rest periods employed (Aïssa et al., 2012; Brown et al., 2005). Fatigue response is usually measured by comparing the lifetime of the material with and without healing functions under the same loading and operating conditions. The ratio of life extension represents the healing performance.

Impact response

Most studies concerning the impact response of self-healing composite materials have been concentrated on low-speed impact response. The commonly used compression-after-impact (CAI) test is employed to obtain the compression strength before and after impact. Previously introduced mechanical testing methods such as DCDC and four-point bending can also be used to study impact response. High-speed impact response (e.g. ballistic puncture) has also been investigated, but only for intrinsic self-healing materials, such as poly (ethylene-co-methacrylic acid) copolymers and ionomers (EMAA) (Kalista, 2007; Kalista, Pflug, & Varley, 2013).

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