



Review

A review on corrosion-protective extrinsic self-healing: Comparison of microcapsule-based systems and those based on core-shell vascular networks

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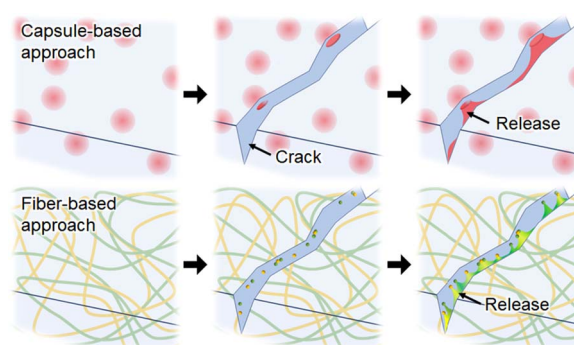
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HIGHLIGHTS

- An overview of the corrosion protection in extrinsic self-healing materials.
- The existing and recent corrosion-protection self-healing techniques are reviewed.
- Various fabrication methods of microcapsules and hollow fibers are discussed.
- Directions for the further improvements are highlighted.

GRAPHICAL ABSTRACT



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ABSTRACT

Corrosion is a natural phenomenon which significantly deteriorates metal properties. The existing corrosion protection methods are costly and require a regular replacement of sacrificial metals or inevitable use of toxic chemicals. So far, various extrinsic self-healing approaches have been attempted to prevent metal corrosion, which have facilitated the corrosion protection at a reasonable cost and non-toxicity level. Here, we review the existing and the recent novel corrosion-protective extrinsic self-healing technologies, focusing on the capsule-based and the fiber-based self-healing approaches, while looking at the pros and cons of these methods. In addition, by introducing potential ways, this review aims to provide insights for the further development of extrinsic self-healing technologies.

1. Introduction

Metals, which are strong and shiny and possess superior electrical and thermal conductivities, have been crucial materials throughout human history. In particular, since the Industrial Revolution in the 18th century, the global demand for metals as the raw materials for various

types of products and structures, including buildings, vehicles, electronic devices, pipes, and home appliances, to name a few, has increased continuously. Nevertheless, the corrosion of metals, which is a characteristic adverse phenomenon accompanying metal usage in oxygen-containing environments, remains a permanent dilemma for engineers. Metal-framed products undergo significant degradation

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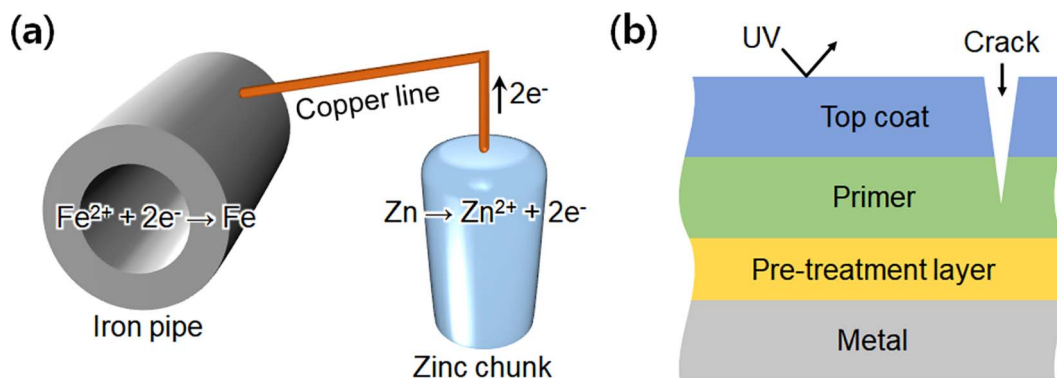


Fig. 1. Schematics for (a) the cathodic protection and (b) the multilayered coating protection.

owing to natural corrosion, resulting in metal oxides, which are more stable but highly undesirable.

For example, even though modern water supply facilities are capable of meeting the increase in the demand for clean drinking water in recent decades, rusty metal pipelines continue to be a threat to public health [1]. In addition, corrosion in buildings and bridges can cause significant strength deterioration as well as severe cracking, which can potentially result in catastrophic failure. A report by the US government puts the annual expense related to corrosion at \$276 billion [2]. To protect metal-framed structures from corrosion, the cathodic protection method as well as diverse types of coatings have been used commonly. In the cathodic protection method, which has been widely used in the industrial applications for protection of pipes, ports, piers, ships, and storage tanks, sacrificial metal (which should be connected to the protected metal) is corroded instead of the protected one by providing electrons to the protected one (cf. Fig. 1a). In other words, the sacrificial metal should be anodic to the protected metal based on the galvanic series, e.g. zinc is commonly used as the sacrificial metal for iron (Fig. 1a) [3,4]. In the case of the coating protection method, a multilayered chemical barrier protects the underlying metal, which is generally comprised of three layers: a pre-treatment layer, a primer, and a top coat (Fig. 1b) [5,6]. The pre-treatment layer contributes to adhesion between the protected metal and the primer, while the primer, which commonly consists of chromated pigments, plays the main role in the enhancement of the corrosion protection. The top coat is used to protect the underlying metal and other layers from the environmental factors such as ultra-violet radiation and high external temperature, and it is also commonly comprised of organic materials such as epoxy resin and polyurethane. However, there is an urgent need to develop alternative protection methods because the galvanic anode (or sacrificial metal) needs to be replaced regularly while in the case of coatings, the toxicity of the chemical barrier raises concerns regarding human health and the environment.

Accordingly, several self-healing techniques have been studied actively in recent years as alternative approaches for preventing corrosion, because they can aid the self-recovery of the damaged area without having to use either a galvanic anode or toxic chemical coatings. The phenomenon of self-healing can be of two types: intrinsic self-healing and extrinsic self-healing [7]. Intrinsic self-healing is based on the inherent reversibility of materials composed of chemical bonds that can be rearranged by an external stimulus [8], whereas extrinsic self-healing is activated by the release of intentionally embedded self-healing agents from an encapsulating container after damage. In recent decades, there have been significant developments in the extrinsic self-healing technique owing to advances in the fabrication and measurement techniques and the introduction of new materials. For example, dicyclopentadiene (DCPD) monomer, which is chemically stable and highly cross-linkable [9–11], has been actively used as the self-healing agent accompanied by Grubbs' catalyst [12–17], resulting in the activation of a ring-opening metathesis polymerization (ROMP, cf. Section

2). Park et al. introduced a variant of co-electrospinning method for the fabrication of the extrinsic self-healing material (cf. Section 3.2) [18]. The previously developed co-electrospinning allows one to encase healing agents inside fiber core surrounded by polymer shell [19]. The electrochemical impedance spectroscopy (EIS) and transmission electron microscopy (TEM) were employed to examine the corresponding anti-corrosion performance and the core-shell structure of co-electrospun fibers [20–22]. Accordingly, such core-shell fibers, as well as capsules have been used to form the containers needed to encapsulate the self-healing agents. The released healing agents from the containers start to coalesce and undergo cross-linking (or redox) reactions in parallel with filling and stitching cracks. Thus, a corrosion-protective barrier is formed, preventing exposure to oxidizing agents. The present review aims to provide an overview of the extrinsic self-healing methods available for corrosion protection and discuss the potential novel developments one can expect in extrinsic-self-healing-based technologies.

2. Capsule-based self-healing approaches for corrosion protection

Since White et al. [12] first introduced a capsule-based self-healing approach, there have been numerous studies on this approach in the past two decades [23]. White et al. reported a process for fabricating microcapsules and examined the self-healing effects resulting from the use of these microcapsules. In-situ polymerization method with urea-formaldehyde (UF) was used to form microcapsules with an outer diameter (OD) of 220 μm (cf. Table 1). Note that the in-situ UF polymerization method, which was used by Dietrich et al. [24], allows one to control microcapsule size by varying the agitation rate [25]. In this approach, microcapsules containing liquid dicyclopentadiene (DCPD) were dispersed in the epoxy matrix, in which Grubbs' catalyst was also embedded (Fig. 2a). When a microcrack formed and started propagating in this composite, it also penetrated through the microcapsules. This caused the liquid DCPD to be released, which subsequently wetted and infiltrated the crack (Fig. 2b). As a result, the DCPD came in contact with the Grubbs' catalyst embedded in the crack banks, triggering a ring-opening metathesis polymerization (ROMP) process, which, in turn, led to the formation of a cross-linked network (Fig. 2c). As a result, the damaged area was stitched.

Corrosion inhibitors can also be encased within microcapsules, instead of healing agents, in order to prevent corrosion [26]. When the encapsulated corrosion inhibitors are released from the capsules, they come in contact with the surrounding metal and suppress the electrochemical corrosion reactions that occur, thereby decreasing the corrosion rate. The present section surveys the literature on self-healing processes involving the use of capsules containing self-healing agents and corrosion inhibitors while focusing on the anticorrosion effects of these processes.

Table 1
Corrosion protection through self-healing based on healing-agent-containing capsules.

Fabrication method	Shell material	Capsule diameter (μm)	Healing agent [108]	Composite structure	Dispersion method	Capsule amount in composite (wt%)	Ref.
UF polymerization	UF	220 (OD)	DCPD-based, Grubbs' catalyst	Epoxy matrix	Mixing	10	[12]
UF polymerization	UF	5–100 (OD)	LO	Epoxy matrix	Slow agitating	–	[27]
UF polymerization	UF	0.75–6 (OD)	LO	Epoxy matrix	Slow agitating	5–20	[31]
UF polymerization with stabilizer	UF	48–138 (OD)	LO	Epoxy matrix	Stirring	10	[32]
UF polymerization/Interfacial polymerization	UF/PU	60 (OD, UF)/90 (OD, PU)	Siloxane-based	Epoxy matrix	Mechanic stirring with degassing	12–14	[33]
UF polymerization	UF	100 (OD)	Silyl ester-based	Epoxy matrix	Mixing and spiral bar coating	17.7	[21]
Interfacial polymerization/In situ sol-gel process	Polyurea/silica	57–328 (OD)	Isocyanate-based	Epoxy matrix	Mixing with degassing	10	[36]
Interfacial polymerization	Polyurea	88 (OD)	Isocyanate-based	Epoxy matrix	Mixing	10	[37]
Pickering emulsion polymerization	UF/TiO ₂	87–520 (OD)	Epoxy-based	Epoxy matrix	Mixing with degassing	15	[43]
Interfacial polymerization	Polyurea/PVA	96 (OD)	Isocyanate-based	Epoxy matrix	Mixing	15	[47]

UF – urea-formaldehyde, OD – outer diameter, DCPD – dicyclopentadiene, LO – linseed oil, PU – polyurethane, PVA – polyvinyl alcohol.

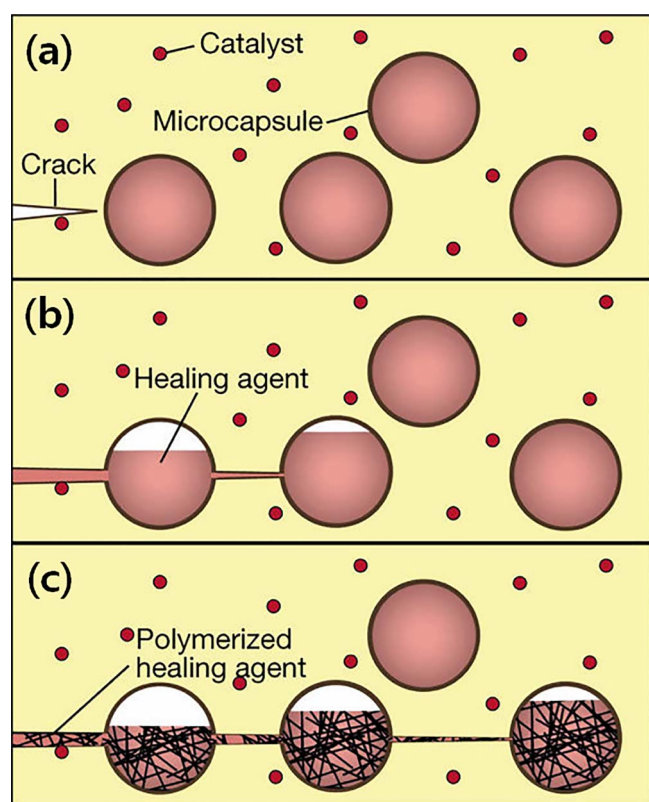


Fig. 2. Schematic showing underlying mechanism of capsule-based self-healing approach: (a) crack formation in matrix, (b) crack propagation and release of healing agent into crack, and (c) solidification of healing agent triggered by catalyst dispersed within matrix. As a result, the cross-linked network, represented by black lines in panel (c), stitches the crack banks. Reprinted with permission from [12].

2.1. Self-healing based on use of healing-agent-containing capsules

Even though there have seen some improvements over the years in the case of capsule-based self-healing, the microcapsules used are still fabricated by the UF polymerization method [25]. However, different types of healing agents have been encased within these capsules. Suryanarayana et al. [27] studied the anticorrosion effect of linseed oil (LO) encapsulated within UF microcapsules with sizes of 5–100 μm (cf. Table 1). The presence of LO was confirmed by Fourier-transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). A corrosion test was conducted by encasing the microcapsules within the matrix of an epoxy deposited on a steel substrate and scratching the

epoxy and exposing the scratched sample to a salt-sprayed atmosphere. It was observed that the scratched epoxy layer with the embedded microcapsules completely prevented corrosion of the underlying metal because the released oil filled the cracks and formed a layer that protected the underlying metal from moisture and oxygen. On the other hand, samples in which the epoxy layer did not contain the oil-filled microcapsules rusted owing to oxidation. Note that other oils can be also used as healing agents. Drying oils such as LO and tung oil (TO) are preferable for self-healing coatings with DCPD-filled microcapsules because the former do not require a catalyst [28]. Recently, neem oils have been also introduced as the healing agent [29,30], which show great promise of eco-friendly renewable sources for self-healing materials.

Boura et al. [31] could decrease the size of the LO-containing UF capsules to less than 1 μm using ultrasonication, which facilitated the formation of fine LO droplets during the UF polymerization process (cf. Table 1). Compared to micrometer-scale capsules, these submicron-sized capsules exhibited improved anticorrosion performance during corrosion tests (Fig. 3). The finely dispersed capsules had an increased probability of coming in contact with the cracks formed, as the specific surface-to-volume ratio (S/V) of the smaller capsules was higher. It should be emphasized that a similar S/V effect has also been observed in the case of hollow-fiber-based self-healing (cf. Section 3). Recently, Lang et al. [32] reported that they were able to improve the size uniformity of LO-filled microcapsules as well as that of their distribution in the epoxy matrix. This was achieved by either adding polyvinyl alcohol (PVA) stabilizers of different molecular weights (M_w) or by varying the stirring rate during the fabrication process. The average size of the UF microcapsules decreased from 138 to 48 μm as the M_w value of the PVA stabilizer used was increased from 31 to 130 kDa (cf. Table 1). In addition, the average microcapsule size decreased from 130 to 76 μm as the stirring rate was increased from 600 to 900 rpm.

2.1.1. Modified healing agents and microcapsules

Siloxane- and silyl ester-based healing agents have also been proposed as the core healing agents to be encapsulated within UF microcapsules by Cho et al. [33] and García et al. [21], respectively. It should be emphasized that siloxane-based healing agents have been used actively in nanometer-scale hollow-fiber-based self-healing materials because of their chemical stability during the fabrication processes (cf. Section 3.2). Cho et al. [33] introduced a dual-capsule-based self-healing system involving microcapsules of two types. The first type were 60- μm UF microcapsules with an encapsulated siloxane-based healing agent, while the second were 90- μm polyurethane (PU) microcapsules that encapsulated dimethyl dinedecanoate tin (DMDNT) as a catalyst (cf. Table 1). After being embedded in an epoxy matrix,

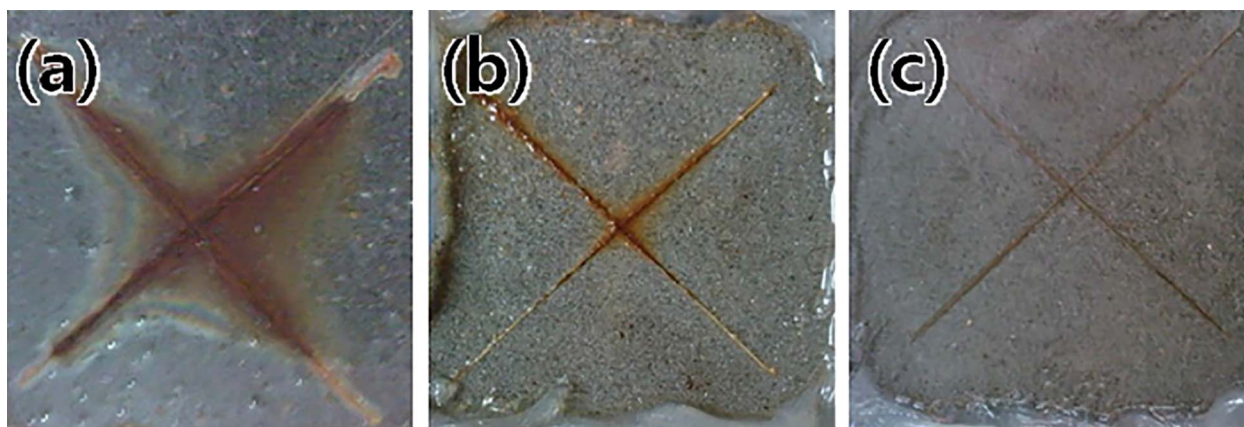


Fig. 3. Corrosion test images of scratched samples (a) without capsules and (b) with micrometer- and (c) nanometer-scale capsules. Reprinted with permission from [31].

these microcapsules formed a self-healing composite that could be coated on a steel substrate. The thus-coated and scratched samples were immersed in salt water for a corrosion test, which showed that the anticorrosion performance of the system was suitable, as determined by electrochemical measurements.

Silyl esters show good reactivity with both water and metal; this allows them to form an adhered-to-metal barrier that can prevent corrosive materials from coming in contact with the underlying metal. Similar to the case for oil-based healing agents, silyl esters do not require catalysts or cross-linking for polymerization (or solidification) because, in their case, barrier formation is based on the hydrolysis process. García et al. [21] fabricated an epoxy-matrix composite, wherein silyl-ester-filled 100- μm UF microcapsules were embedded in the epoxy (cf. Table 1). The anticorrosion performance of the composite was evaluated by electrochemical impedance spectroscopy (EIS) and the scanning vibrating electrode technique (SVET) (Fig. 4). The impedance and current density measurement results obtained in the case of the microcapsule-embedding composite confirmed that it exhibited satisfactory anticorrosion performance as compared to that of the bare samples.

The healing agents that can form a corrosion-protective barrier without catalysts or other materials (e.g., LO, TO, siloxane-, and silyl-ester-based healing agents) are called “catalyst-free one-part self-healing agent.” Among the most attractive catalyst-free one-part healing agents are water-friendly compounds with the isocyanate functional group, which facilitates both a reaction with water and the formation of an anticorrosive shield [8]. However, the water-friendly properties of the isocyanate group can cause issues during encapsulation in a shell polymer, given its high reactivity [23].

Several researchers have attempted to overcome this problem

[34–36]. For instance, Wu et al. [36] fabricated polyurea/silica hybrid microcapsules for encasing isocyanate-based healing agents by combining interfacial polymerization and an *in-situ* sol-gel process (Fig. 5). The thus-fabricated hybrid microcapsules had sizes of 57–328 μm , which could be controlled by varying the agitation rate during the fabrication process (cf. Table 1). The hybrid structure of the microcapsules not only allowed for the successful encapsulation of the isocyanate-based healing agent but also resulted in improvements in the thermal and chemical properties of the microcapsules. As a result, during a corrosion test, wherein the samples were immersed in a 10 wt % NaCl solution for 48 h, the hybrid-microcapsule-embedding epoxy resulted in a completely rust-free substrate. More recently, Sun et al. [37] fabricated 88- μm double-layered polyurea microcapsules using a similar interfacial polymerization method (cf. Table 1). Without using silica, they could successfully encase an isocyanate-based healing agent within microcapsules with shells as thick as 8 μm ; this was achieved by using a triethylenetetramine solution.

The chemical stability of catalyst-free one-part self-healing agents and the feasibility of using self-healing materials based on them on the industrial scale have also been studied. To improve the healing capabilities of these agents, heat and light sources have primarily been employed as the stimuli [38–42]. Owing to their obvious environmental and economic advantages, self-composites that use ultraviolet (UV) light and sunlight as the stimulus have also been studied. To fabricate such photoresponsive self-healing composites, Gao et al. [43] introduced UF/TiO₂ hybrid self-healing microcapsules that contained an epoxy-based healing agent and were photoabsorbent. Using the Pickering emulsion polymerization method [44–46], they embedded nanometer-scale TiO₂ particles within the microcapsule shells. The size of the microcapsules was 87–520 μm and was controlled by varying the

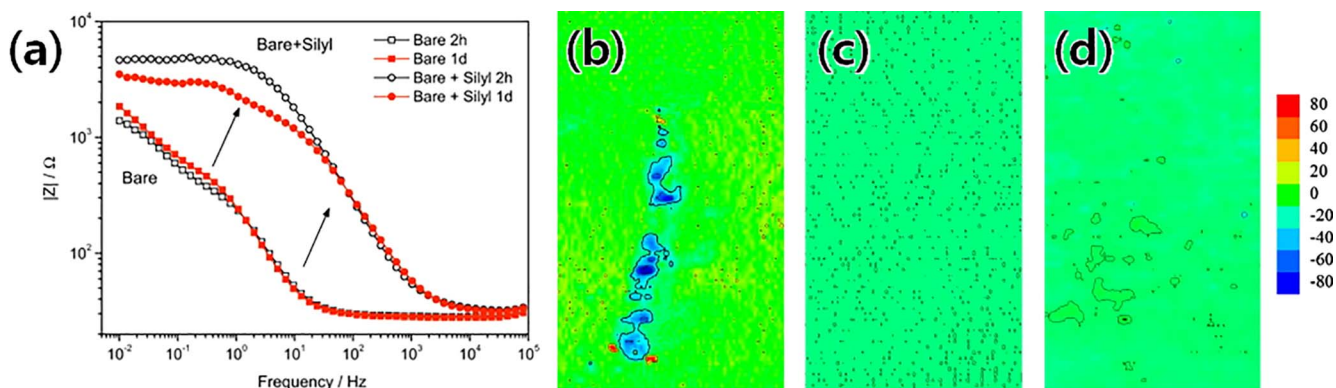


Fig. 4. (a) Impedance as function of frequency of bare and microcapsule-embedding self-healing composites after 1 and 2 days of exposure to 0.05 M NaCl solution. (b) Current density maps of intentionally damaged self-healing composite after (b) 1, (c) 24, and (d) 48 h of exposure to 0.05 M NaCl solution. Note that the composites were deposited on aluminum substrates. Reprinted with permission from [21].

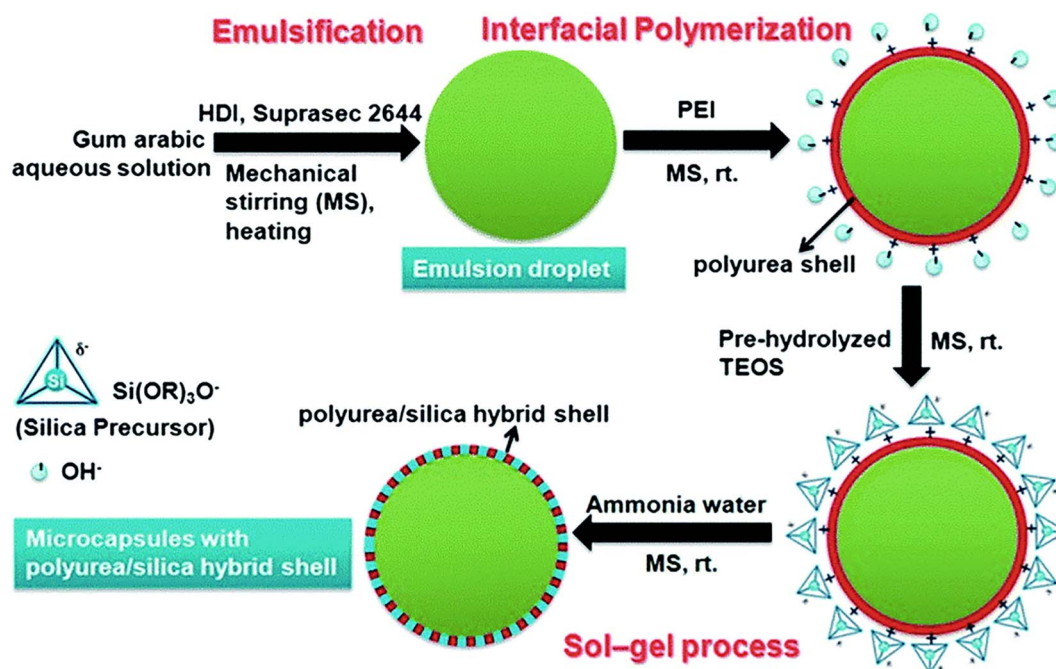


Fig. 5. Schematic of process for fabricating polyurea/silica hybrid self-healing microcapsules. Reprinted with permission from [36].

mechanical stirring speed from 1500 to 500 rpm prior to the polymerization process (cf. Table 1). Owing to the presence of the TiO_2 particles, the microcapsules could absorb UV light with a wavelength of 330 nm. The photocatalytic effect triggered by the photoabsorbing TiO_2 particles accelerated the solidification (or healing) of the epoxy-based healing agent. It should be emphasized that multicycle healing could be achieved using this photoresponsive self-healing system, as confirmed by corrosion tests.

In addition to the polyurea-based microcapsules described above, other similar microcapsules have also been synthesized. He et al. [47] reported a method for fabricating polyvinyl alcohol (PVA)-based microcapsules. The shells of these microcapsules also had a polyurea layer. However, the outmost layer was of PVA. The hydrolyzed PVA layer resulted in significant improvements over polyurea-based microcapsules, namely, a robust fabrication process, higher elasticity and water resistance, and improved compatibility between the microcapsules and the epoxy matrix. Microcapsules with a size of $96\ \mu\text{m}$ were embedded in the epoxy matrix in a concentration of 15 wt% (cf. Table 1), and corrosion tests were performed, wherein the self-healing composite was coated onto steel, scratched, and the steel sample was immersed in a 10 wt% NaCl solution (Fig. 6). The epoxy layer completely protected the steel from corrosion, owing to the healing agent released from the damaged microcapsules.

2.2. Self-healing based on corrosion-inhibitor-containing capsules

Using corrosion inhibitors without encapsulating them within some type of microstructure has several disadvantages. For instance, it can lead to the degradation of or incongruities in the surrounding coating materials as well as an increase in the deactivation rate of the embedded inhibitors [48,49]. In addition, chromates, which were the mostly used corrosion inhibitors, were banned in 2007 owing to their carcinogenicity. To avoid these drawbacks, corrosion inhibitors are now usually encapsulated. For the encapsulation of corrosion inhibitors, most studies have employed polymeric micro/nanocapsules (which are surveyed in the present review), however, note that several studies have also used nanometer-scale one-dimensional (1D) inorganic clays, such as an aluminosilicate nanotube (the so-called halloysite) because the halloysite not only is economically feasible, abundant, and durable, but

also has a hollow inner space of 15 – 100 nm in diameter [50–53]. Generally, the size of corrosion-inhibitor-containing capsules is much smaller than that of healing-agent-containing ones (cf. Section 2.1). On the one hand, a small amount of the inhibitor is needed in the case of the inhibitor-embedding systems because self-healing (or corrosion protection) by the inhibitor is related to a chemical reaction. On the other hand, a large number of capsules containing the healing agent is needed to physically fill the damaged area within the sample in question, in order to block the passage of the external corrosive components (i.e., oxygen and water). Note that most studies on inhibitor-based self-healing have focused on the effect of changes in the pH on the corroded area, which is attributable to the redox reactions between the underlying metal and the corrosive materials.

To produce corrosion-inhibitor-containing nanocapsules, Zheludkevich et al. [20] used 70-nm silica nanoparticles to fabricate multilayered nanocapsules in a layer-by-layer manner, with the corrosion inhibitor layer being entrapped between the polyelectrolyte multilayers. The polyelectrolyte layer, which not only is sensitive to minor changes in the pH but also changes its permeability depending on pH [54], allowed for the controlled release of the entrapped inhibitors through the increased permeability as corrosion causes the pH near the damaged area to change. The polyelectrolyte multilayers were composed of polyethylene imine (PEI) and polystyrene sulfonate (PSS), while benzotriazole was used as the corrosion inhibitor. The layer-by-layer deposition process increased the nanocapsule size to 100 nm (cf. Table 2). Zheludkevich et al. [20] then coated the nanocapsule-embedding polymeric matrix onto an aluminum substrate and evaluated its anticorrosive performance through EIS and SVET measurements. The nanocapsule-embedding composite completely prevented corrosion, owing to the released inhibitor, which reduced the corrosion rate by preventing the cathodic reduction of oxygen.

Choi et al. [55] reported a method for fabricating 400–450-nm nanocapsules in a layer-by-layer manner by sequential emulsion polymerization (cf. Table 2). They used 100-nm latex particles as the cores for the nanocapsules. Triethanolamine (TEA), used as the corrosion inhibitor, was encapsulated by the outermost polystyrene (PS) shell. The presence of TEA within the nanocapsules was confirmed by thermogravimetric analysis (TGA) and gas chromatography-mass spectrometry (GC–MS). Encapsulating the inhibitor within the PS nanocapsules

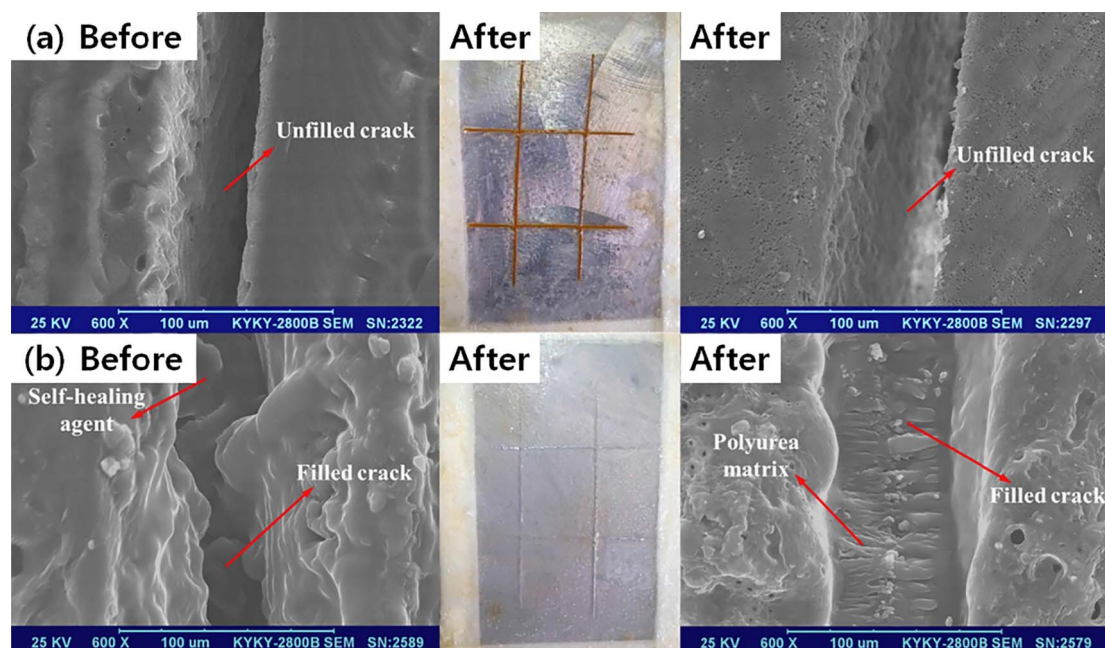


Fig. 6. Photographs and SEM images of scratched samples (a) without and (b) with microcapsules after immersion in salt solution. Reprinted with permission from [47].

increased their size from 350 to 450 nm (Fig. 7). During a corrosion test performed in NaCl solution, a change in the pH (regardless of the acidity and basicity) over the damaged area of the self-healing coating triggered the release of the inhibitor into the microgaps between the PS shell and the surrounding polymeric matrix owing to osmotic swelling. Thus, the corrosion rate of the damaged steel substrate was reduced significantly. Choi et al. [56] also studied the effects of different types of amine-based corrosion inhibitors on the anticorrosive performance of coatings. Both the encapsulation process and the osmotic swelling process were improved when an inhibitor with greater water solubility was used. In particular, linearly structured and highly water-soluble amines exhibited a faster release rate than did the other inhibitors.

Recently, 2-mercaptobenzothiazole (MBT) has also attracted significant attention as a corrosion inhibitor when encased in multilayered nanocapsules because it is a very efficient anticorrosion agent, especially for aluminum alloys. Plawecka et al. [57] fabricated 100-nm MBT-containing poly(diallyl dimethyl ammonium chloride) (PDADMAC) nanocapsules (cf. Table 2). In contrast to the previously discussed studies, they did not use a core supporter such as silica or latex nanoparticles but employed a direct encapsulation method instead. Localized EIS and SVET measurements revealed that these pH-responsive nanocapsules efficiently inhibited corrosion even at small defects on the surface.

In addition to pH-responsive capsule-based self-healing materials, other self-healing materials have also been reported. Vimalanandan et al. [58] introduced a redox-responsive capsule-based approach wherein a conducting polymer, polyaniline (PANI), and 3-nitrosalicylic acid (3-NisA) were used as the shell material and the corrosion inhibitor within the core, respectively (cf. Table 2). The conducting polymer allowed the inhibitor to be released in response to changes in the electrochemical potential at the onset of corrosion. In other words, the corrosion rate was significantly diminished not only because of the active anions stored within the capsules, which would depend on the corrosion process, but also because of the release of the inhibitor at the metal/polymer interface. To overcome the fact that the conducting polymer was unsuitable for use as an electrochemical potential change sensor, Vimalanandan et al. [58] decorated the capsules with Au nanoparticles (Fig. 8). They then investigated the changes in the electrochemical potential using a scanning Kelvin probe [59–64].

A combined method involving the mixing of a healing agent and a

corrosion inhibitor as the core materials has also been proposed. Siva et al. [65] reported 70–200-nm self-healing capsules encapsulating LO (cf. Section 2.1) and MBT as the core materials (cf. Table 2). It should be emphasized that the fabricated capsules were neither pH-responsive nor redox-responsive because their shells were composed of UF (cf. Section 2.1). The presence of the corrosion inhibitor not only allowed for the fabrication of nanometer-scale capsules despite the use of a healing agent but also resulted in improved anticorrosion performance, as determined by EIS and SVET measurements.

On the other hand, the dispersion methods for capsules and the resulting dispersed (embedded) amount of the capsules in the composite are very important because they contribute not only to the healing efficiency but also affect the rheological and mechanical properties of the corresponding composites. As listed in Tables 1 and 2, most studies on self-healing capsules have implemented mechanical mixing methods such as agitating, stirring, and attriting. All these methods employed low motion speeds, thus allowing capsules to be uniformly dispersed without being damaged. The amounts of healing agents in the composites, which seemingly had minor effects on the other property changes of the composites, ranged from 5 to 20 wt% (Table 1), whereas those of inhibitors were about 2 wt% (Table 2). Note that, in the case of the healing-agent-containing capsules, the healing agent occupied the whole volume of the capsule. However, in the case of the inhibitor-containing capsules, adding a small amount of inhibitor into the capsule was sufficient to achieve the anti-corrosion effect.

3. Fiber-based self-healing approaches for corrosion protection

Most organisms found on Earth, including human beings, can self-heal to different degrees, and this ability is maintained by the vascular system. When a minor injury occurs, a coagulation mechanism kicks in immediately, resulting in hemostasis, which reduces the scope of the injury. Such autonomous biological self-healing systems allow humans to live long and healthy lives. The demand for bioinspired technologies has increased dramatically in recent decades. As a result, vascular self-healing approaches are attracting a great deal of attention in relation to engineered self-healing materials, even since Dry introduced a hollow-tube-based self-healing technique in the 1990s [66]. Dry fabricated a thin-pipette-embedding polymeric matrix, wherein the two components of a cyanoacrylate-based adhesive had already been injected into two

Table 2
Corrosion protection through self-healing based on corrosion-inhibitor-containing capsules.

Fabrication method	Shell material	Capsule diameter (nm)	Corrosion inhibitor	Composite structure	Dispersion method	Inhibitor amount in composite	Ref.
Layer-by-layer deposition	PEI/PSS	70–100 (OD)	Benzotriazole	Sol-gel matrix	Ultrasonically agitating	0.13 wt%, 0.63 wt%	[20]
Sequential emulsion polymerization	PS	400–450 (OD)	Triethanolamine	Polymeric matrix	Mixing and bar coating	2–5 wt% in a single capsule (cf. capsules in composite = 33.3 wt%)	[55]
Multi-stage emulsion polymerization	PS	300–600 (OD)	Ethanolamine/5-Amino-1-pentanol/Diethanolamine/Triethanolamine/Propylamine/Dipropylamine	Polymeric matrix	Mixing and bar coating	0.2–2 wt%	[56]
Direct encapsulation	PDADMAC	100 (OD)	2-mercaptobenzothiazole	Epoxy matrix	Mixing and dip-coating	0.00875 g per 1 L of epoxy solution	[57]
Polymerization	PANI	< 1000 (OD)	3-Nitrosalicylic acid	Polymeric matrix	Stirring and drop casting	57 µg per 1 µL of 10 wt% PVB dissolved in ethanol	[58]
In situ emulsion polymerization	UF	70–200 (OD)	2-mercaptobenzothiazole	Epoxy matrix	Mechanical attriting	16 wt% in a single capsule (cf. capsules in composite = 10 vol%)	[65]

PEI – polyethylene imine, PSS – polystyrene sulfonate, PS – polystyrene, PANI – polyaniline, PDADMAC – poly(diallyl dimethyl ammonium chloride), PVB – poly(vinyl butyralco-vinylalcohol-co-vinyl acetate).

distinct pipettes (cf. Table 3). Cracks were formed artificially in the polymeric matrix either by impact or bending. These cracks were self-repaired by the adhesives released from the pipettes. That is to say, the two mutually jointed components of the adhesive solidified because of cross-link formation, thus preventing both crack formation and growth in the damaged polymeric matrix.

Many recent studies on fiber-based encapsulation for self-healing have used similar healing-agent-embedding hollow fibers. Such systems are known as “vascular self-healing structures,” given the similarity between the hollow fibers and blood vessels [67]. Depending on the fabrication method and type of healing agents used as well as the end purpose, the diameter of the one-dimensional (1D) hollow fibers used in such structures can be made to range from hundreds of nanometers to hundreds of micrometers. Hence, the present section surveys the existing literature on fiber-based self-healing materials by subdividing them into the micrometer scale and the nanometer scale.

3.1. Self-healing based on micrometer-scale hollow fibers

Before we discuss self-healing systems based on micrometer-scale hollow fibers, it should be noted that such fibers were reported before the more recently developed nanometer-scale ones (NFs). Accordingly, most studies on self-healing hollow microfibers (MFs) were reported in the early 2000s, whereas those on hollow NFs have only started appearing in recent years. It should also be noted that there have been no reports on MF-based self-healing systems that protect against chemical corrosion. Accordingly, this section only deals with micromechanically rooted self-healing.

Motoku et al. [68] developed a vacuum-assisted resin transfer molding process for fabricating microtube-embedding composites (or laminates). They also parametrically investigated the self-healing performance of these composites as functions of the type of tube used, number of tubes embedded in the composite, spatial distribution of the tubes, type of healing agent injected in the tubes, and composite thickness. Among the various types of tubes and healing agents investigated, 1.15-mm glass micropipettes containing the vinyl ester (VE) resin C50 as the curing agent (cf. Table 3) showed the best performance during impact tests.

Bleay et al. [69] used hollow MFs not only as healing-agent containers but also as structural reinforcement materials for a fiber-embedding polymeric matrix composite. Based on the assumption that fibers with a larger diameter could lead to the inadvertent failure of the composite, they used thinner hollow fibers, whose inner and outer diameters were 5 and 15 µm, respectively (cf. Table 3). In addition, they employed solvent-mixed epoxy resins to reduce the viscosity; this facilitated the rapid release of the resin into the damaged regions. They also used heating to accelerate the solidification of the released resin. These processes dramatically enhanced the self-healing effect and thus have been explored extensively by other researchers as well. Bleay et al. [69] also proposed a method involving the use of both hollow fibers and microcapsules in the polymeric matrix. This method was demonstrated later by Lee et al. [70].

Fiber-embedding epoxy composites composed of 60-µm hollow glass fibers as 50% of the total volume were fabricated by Pang and Bond [71,72] (Fig. 9 and cf. Table 3). The hollow MFs were filled with an uncured amine-based epoxy resin and a hardener along with a UV fluorescent dye. The dye allowed for improved detection of “bleeding” from the broken hollow MFs into the polymeric composite. They also employed ultrasonic C-scanning and the UV mapping technique (UVMT) to observe barely visible impact damage, as shown in Fig. 9. These techniques are effective for ascertaining the scope of microscopic damage within fiber-embedding composites.

In the case of large-scale macrocracks, a sufficiently long period would be required for the healing agents to harden once they have fully filled the damaged spaces. Otherwise, unhealed microscopic gaps can result, leading to continuous crack propagation. Large-scale macrocrack

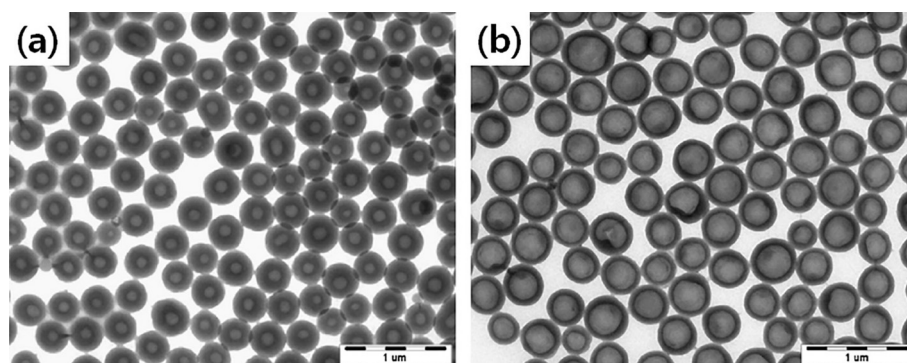


Fig. 7. Transmission electron microscopy (TEM) images of self-healing nanocapsules: (a) without and (b) with corrosion inhibitor. Reprinted with permission from [55].

healing was investigated by White et al. [73] using a two-stage polymer chemistry approach: the gelation stage required that the macrocracks be filled to a suitable degree. This was followed by the polymerization stage, which was necessary for the solidification of the filled crack. White et al. [73] carefully adjusted the component proportions in the self-healing agent used to ensure that the macrocracks were filled by the agent to a sufficiently high degree resulting in subsequent solidification. They found that a macrocrack 35 mm in diameter could be recovered completely by the two steps involved, namely, filling and solidification, whose durations were several minutes and a few hours, respectively (cf. Table 3).

3.1.1. Hollow fibers for self-healing

Multicycle healing was investigated by Toohey et al. [74], who also evaluated its healing efficiency. They fabricated 200-μm 3D polymeric microchannels in a rectangular epoxy matrix. The dicyclopentadiene (DCPD) monomer was forced to infiltrate into the microchannels and Grubb's catalyst particles were embedded in the surrounding epoxy matrix (cf. Table 3). The self-healing process was attributable to the DCPD monomer being released from the microchannels once damaged by a propagating crack and coming in contact with the Grubb's catalyst in the matrix. The continuous release of the self-healing agent from the 3D vascular microstructure and the subsequent ring-opening metathesis polymerization (ROMP) reaction resulted in repeatable self-healing, with the healing efficiency during each cycle being 30–70%. This repeatable self-healing process could be repeated for up to 7 cycles; in contrast, microcapsule-based self-healing is a one-time process [75]. Hamilton et al. reported that, when a vascular system consisting of 230-μm microchannels embedded in an epoxy matrix was subjected to active pressurization using external pumps, it exhibited satisfactory healing efficiency up to 15 cycles [76,77] (cf. Table 3).

Multicycle self-healing was also studied by Patrick et al. [78], who evaluated the self-healing efficiency of 300-μm stitch-like and parallel microchannels (Fig. 10 and cf. Table 3). The self-healing efficiency of the herring-bone-like stitch-patterned microchannels increased to more than 100% as the number of cycles was increased, whereas that of the parallel microchannels remained at 35–85%.

3.1.2. Scaling-up of hollow-fiber-based self-healing

Based on the use of different types of structural elements, self-healing materials can be employed in various industrial fields, ranging from vehicles, which correspond to a scale of a few meters, to buildings, which have a characteristic scale of a few hundred meters. Williams et al. [79–81] studied the effects of a vascular self-healing system on sandwich-structured composites using 1.5-mm polyvinyl chloride (PVC) tubes (cf. Table 4). They showed that, when embedded in a composite, this vascular network, which consisted of tubes filled with either a premixed amine-epoxy resin or an unmixed amine-epoxy resin and hardener (separate tubes), resulted in complete healing after flexural failure tests.

Kousourakis et al. [82] evaluated the vascular self-healing efficiency of carbon-epoxy-based composite panels. They explored the effects of changing the direction of the hollow fibers used, which had outer diameters of 170, 320, 430, and 680 μm, from parallel to the load direction to normal to it (cf. Table 3). They also conducted mechanical tests in the absence of a self-healing agent, in order to examine the changes induced in the mechanical properties solely owing to the presence of hollow MFs for reference. While the overall mechanical durability was not affected adversely when the hollow MFs were aligned parallel to the external load, it was reduced significantly when the MFs were oriented normal to the external load.

Patrick et al. [83] used polyurethane (PUR) foam as an encasing

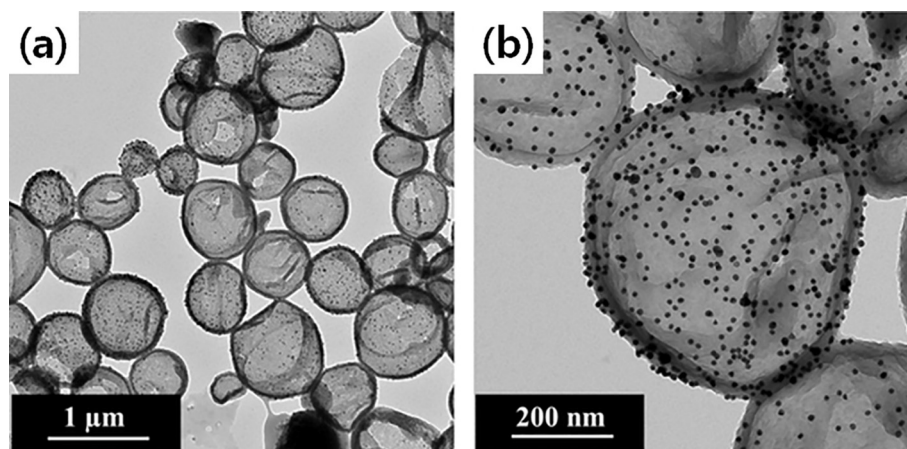


Fig. 8. TEM images of redox-responsive PANI capsules decorated with Au nanoparticles. Reprinted with permission from [58].

Table 3

Corrosion protection through self-healing based on micrometer-scale hollow fibers (self-healing efficiency was evaluated through mechanical tests).

Fiber type	Composite structure	Fiber diameter (μm)	Healing agent [108]	Self-healing efficiency (%)	Cycles	Ref.
Thin pipette	Polymeric matrix	Hundreds	Cyanoacrylate -based	Healed	–	[66]
Glass tube	Laminate	1150 (ID)	Vinyl ester -based	Healed	–	[68]
Glass fiber	Polymeric matrix	5 (ID)	Cyanoacrylate-based	Healed	–	[69]
Glass fiber	Polymeric matrix	60 (OD)	Amine-epoxy-based	97	–	[71,72]
Microchannel	Polymeric matrix	330 (ID)	Acyhydrazine/methacrylate-based	Healed	–	[73]
Microchannel	Epoxy matrix	200 (OD)	DCPD-based, Grubbs' catalyst	70 (at 2nd cycle)	7	[74,75]
Microchannel	Epoxy matrix	230 (ID)	Amine-epoxy-based	100 (at 5th cycle)	15	[76,77]
Microchannel	Epoxy matrix	300 (ID)	Amine-epoxy-based	> 100 (at 3rd cycle)	3	[78]
PVC tube	Sandwich structure	1500 (ID)	Amine-epoxy-based	Healed	–	[79–81]
Glass fiber	Carbon epoxy matrix	170–680 (ID)	–	Healed	–	[82]
Microchannel	PUR foam	970 (ID)	Isocyanate-based	> 100	4	[83]
Microchannel	FRP laminate	250, 500 (ID)	Amine-epoxy-based	99	–	[85–87]

ID – inner diameter, OD – outer diameter, DCPD – dicyclopentadiene, PVC – Polyvinyl chloride, PUR – polyurethane, FRP – fiber-reinforced polymer.

composite material to encapsulate isocyanate-based healing agents (cf. Table 3). During mechanical tests performed to evaluate the self-healing efficiency of the material, they observed that it allowed for the complete recovery of the mechanical properties of the healed material and could be used for four-cycle self-healing. The microscale porosity of the foam allowed the healing agents to be dispersed rapidly due to the pore wettability and solidify (heal) readily. The microchannels were large in this case (diameter of 970 μm). The healing agents were filled into the microchannels using an external pumping system (Fig. 11).

Fiber-reinforced polymer (FRP) composites have attracted attention because of their outstanding mechanical strength and stiffness. Such composites also show great durability against mechanical cracking and chemical corrosion [84]. Accordingly, FRP composites are used widely in the aerospace industry. Norris et al. [85–87] studied a vascular self-healing system based on aerospace-grade carbon-based FRP laminates, wherein a steel wire with an outer diameter of 500 μm was used to make microchannels in the laminated composite. The microchannels were filled with thiol-epoxy-based healing agents (cf. Table 3). They investigated the ability of the system to heal using microchannels

having different sizes and placed at different locations. When delamination occurred in the laminated composite due to external impacts, the self-healing agents were released into the delaminated area, resulting in self-healing, with the efficiency being greater than 96% for all the tests conducted.

3.2. Self-healing based on nanometer-scale hollow fibers

In most studies on vascular self-healing using hollow MFs, only the effects on the mechanical properties were analyzed when evaluating the healing efficiency (cf. Section 3.1). However, a few recent studies based on hollow NFs have also analyzed the corrosion protection accorded by self-healing systems. This is important for improving the sustainability of the industrially relevant materials incorporated within metal-framed structures such as vehicles and buildings under humid conditions (cf. Section 1). It should be emphasized that the recovery of the mechanical properties owing to self-healing based on hollow NFs has also been studied previously [88–94]. Further, it was also reviewed recently by Lee et al. [95]. In the current review, we focus only on the corrosion

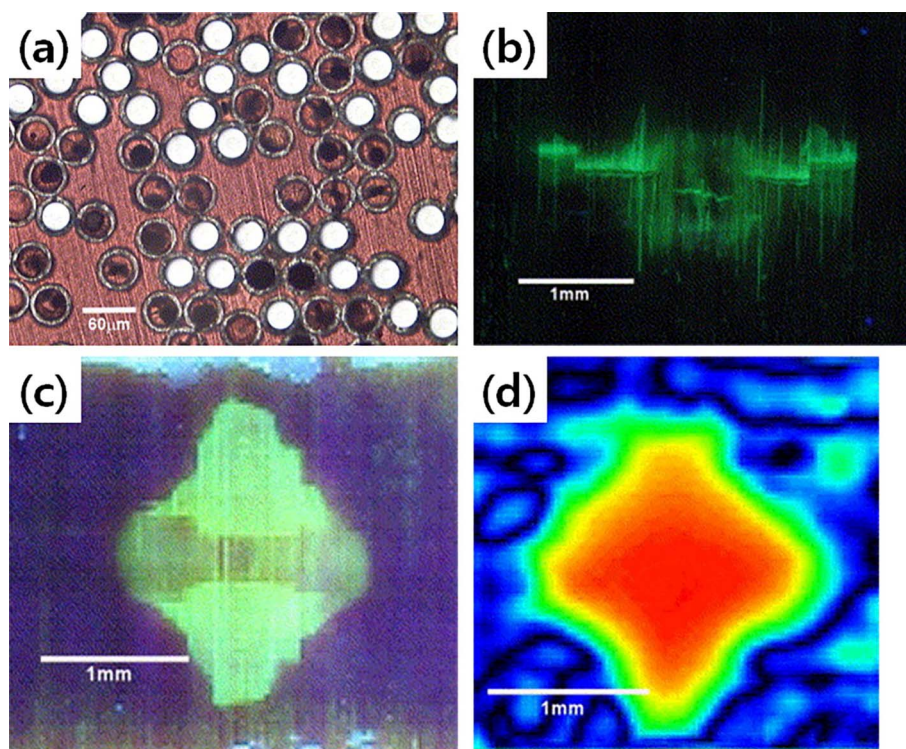


Fig. 9. (a) Optical microscopy image of hollow-fiber-embedding composite containing hollow microfibers (MFs) in volume fraction of 50%. Epoxy-based healing agent was encased within 60- μm MFs. (b) Front and (c) rear images of composite obtained using UVMT. (d) C-scan image of composite. Reprinted with permission from [72].

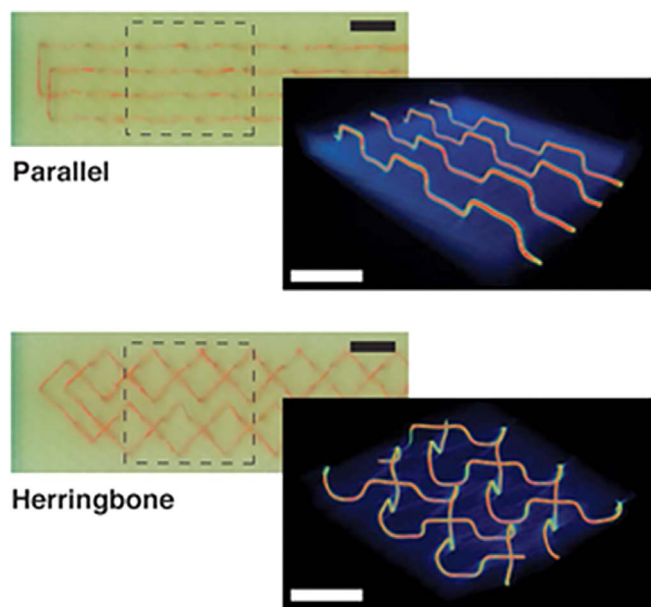


Fig. 10. Photographs of parallel and herring-bone-like stitched microchannels embedded within composite (left), and X-ray computed microtomographic images of stitch-like patterned microchannels (right). Reprinted with permission from [78].

protection provided by self-healing based on hollow NFs.

Park et al. [18] used electrospinning to fabricate self-healing core-shell-structured NFs. They employed a two-coaxial nozzle system for co-electrospinning, as shown in Fig. 12 [19,96]. The core was filled with either part A (resin) or part B (hardener) of a siloxane-based healing agent while a polyvinylpyrrolidone (PVP) solution, produced using dimethylformamide (DMF), was used to form the shell (cf. Table 4). The co-electrospun NFs were then embedded within a polymeric matrix to form a composite. It is known that beads are formed on electrospun NFs when the electrical conductivity of the solution is too low to allow for the stretching of the polymer jet [97,98]. Thus, Park et al. [18] were able to fabricate bead-on-string NFs, such that the outer diameters of the NFs and beads were of the order of hundreds of nanometers and several micrometers, respectively. As a result, the healing agent was primarily present within the capsule-like beads with an outer diameter of 2–10 μm . For this reason, the approach used by Park et al. [18] is similar to capsule-based self-healing. To examine the anticorrosion performance of the self-healing agent-embedding hollow NFs, they pre-notched cracks on the sample coatings and let them heal for 24 h. They then immersed the samples in salt water for hundreds of hours and analyzed the formation of rust. They found that significant corrosion had occurred in the control sample, which did not have a self-healing coating. On the other hand, no corrosion was observed in the NF-embedding sample, as the damaged cracks were healed successfully, owing to which the underlying metal substrate was protected from the

salt water.

3.2.1. Fabrication of core-shell nanometer-scale fibers for self-healing

In addition to co-electrospinning, emulsion electrospinning and emulsion-solution blowing have also been used to encapsulate healing agents within hollow NFs, where an emulsified material in a polymer solution forms the core part of hollow NF, whereas another (matrix) material in the solution forms the shell of core-shell ('hollow') NF [99–101]. Even though there is a necessary condition that the potential core material should be emulsified in the polymer solution, the emulsion-based methods allow one to form core-shell-structured NFs from a single nozzle, which is more convenient compared to the co-electrospinning where two solutions should be simultaneously issued from a co-axial nozzle. Sinha-Ray et al. [15] fabricated hollow NFs with diameters of 450–1000 nm by co-electrospinning, emulsion electrospinning, and emulsion-solution blowing (Fig. 13 and Table 4). For co-electrospinning, they used a co-axial needle setup, wherein DCPD in DMF and polyacrylonitrile (PAN) in DMF were supplied to the core and shell needles, respectively. For emulsion electrospinning and emulsion-solution blowing, PAN/DCPD in DMF and PAN/isophorone diisocyanate in DMF were used to form the emulsions. They were able to form uniform electrospun and solution-blown core-shell NFs. Further, the presence of the core materials was confirmed using optical microscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). In addition, they employed a self-sustaining diffusion method [102–104] to intercalate a self-healing agent into empty carbon nanotubes (CNTs) with an inner diameter of a few nanometers. They blended a CNT powder with a DCPD or isophorone diisocyanate solution (dissolved in benzene) and subjected the dispersion to sonication to ensure the self-sustaining diffusion of the healing agent into the CNTs; the process was driven by solvent (benzene) evaporation.

Furthermore, Lee et al. [105] recently introduced a dual-emulsion electrospinning method to simultaneously encapsulate a siloxane-based resin and its curing liquid as healing agents within the NF cores. The resin monomer liquid was mixed with *n*-hexane to reduce its viscosity while the curing liquid was emulsified using a PAN/DMF solution. The two emulsions were then electrospun simultaneously from two different nozzles to obtain core-shell self-healing NFs containing either the resin or the curing liquid within the fiber core; the shell of the NFs was formed of PAN. The electrospun NFs had an average outer diameter of 444 nm. Further, the presence of the resin/curing liquid in the core was confirmed by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) (cf. Table 4). The dual-emulsion electrospinning process was performed using a rotating drum collector, thus allowing for the fabrication of large-scale samples. The electrospun NF mats were intercalated with polydimethylsiloxane (PDMS) in order to form a composite. The solidification of the PDMS increased the transmittance of the composite by up to 90% when the amount of the NFs in the composite (controlled by the electrospinning time) was reduced. During subsequent corrosion tests, samples of this transparent self-healing composite with pre-notched and healed cracks were immersed into salt

Table 4
Corrosion protection through self-healing based on nanometer-scale hollow fibers.

Fabrication method	Shell material	Composite structure	Fiber diameter (nm)	Healing agent	Ref.
Co-electrospinning	PVP	Polymeric matrix	Hundreds (OD, NFs)/Thousands (OD, beads)	Siloxane-based	[18]
Co-electrospinning/emulsion-electrospinning/emulsion-solution blowing	PAN	–	1000–2000 (OD), /450–1000 (ID)	DCPD-based or Isocyanate-based	[15]
Self-sustained diffusion method	CNT		100 (OD), 40 (ID)		
Emulsion-electrospinning	PAN	Epoxy matrix	444 (OD)	Siloxane-based	[105]
Emulsion-electrospinning	PAN	Epoxy matrix	200–300 (OD, NFs), /600–1000 (OD, beads)	Siloxane-based	[70]
Co-electrospinning	PAN	Epoxy matrix	300–360 (OD)/190–200 (ID)	Siloxane-based	[22]

PVP – polyvinyl pyrrolidone, NFs – nanofibers, PAN – polyacrylonitrile, CNT – carbon nanotube, PDMS – polydimethylsiloxane.

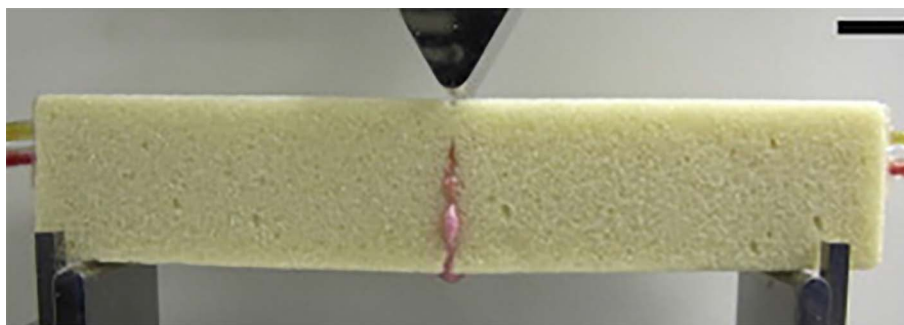


Fig. 11. Photograph of vascular self-healing systems for the foam-structured composites after impact damage. It can be seen that the two healing agents (pink color) were released at damage sites. Reprinted with permission from [83].

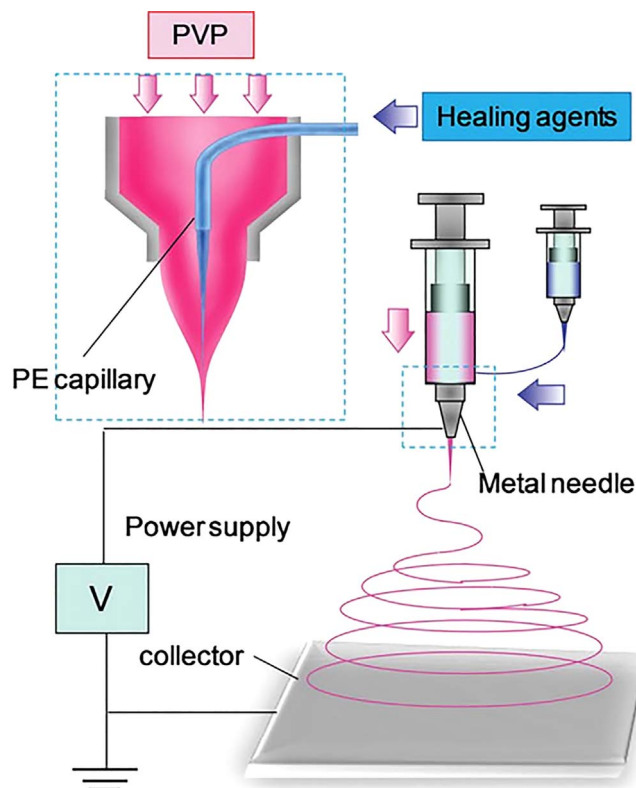


Fig. 12. Schematic of coaxial electrospinning process. Reprinted with permission from [18].

water and acid solutions. It was observed that the composite exhibited perfect anticorrosion performance.

Lee et al. [70] employed a slightly different approach to fabricate self-healing core-shell NF-embedding composites. They filled the emulsion-electrospun NFs and capsule-less microdroplets with a siloxane-based curing liquid and a resin monomer, respectively (cf. Table 4). First, they electrospun curing liquid (core)/PAN (shell) NFs on a metal substrate using a curing liquid/PAN emulsion. Next, they poured the resin/epoxy emulsion onto the NF-coated metal substrate; this resulted in the formation of capsule-less resin microdroplets within the epoxy matrix. That is to say, a heterogeneous matrix consisting of the core-shell NFs and the capsule-less microdroplets was formed (Fig. 14). The optimal resin-to-curing liquid ratio was found to be 10:1. Note that this was not the case in a previous study [105], because, in that study, the electrospinning conditions for the curing-liquid- and resin-containing NFs were almost similar. However, in a subsequent work, the ratio could be improved by embedding capsule-less resin microdroplets within the matrix instead of using core-shell NFs. To analyze the anticorrosion protection afforded by the self-healing composite, they

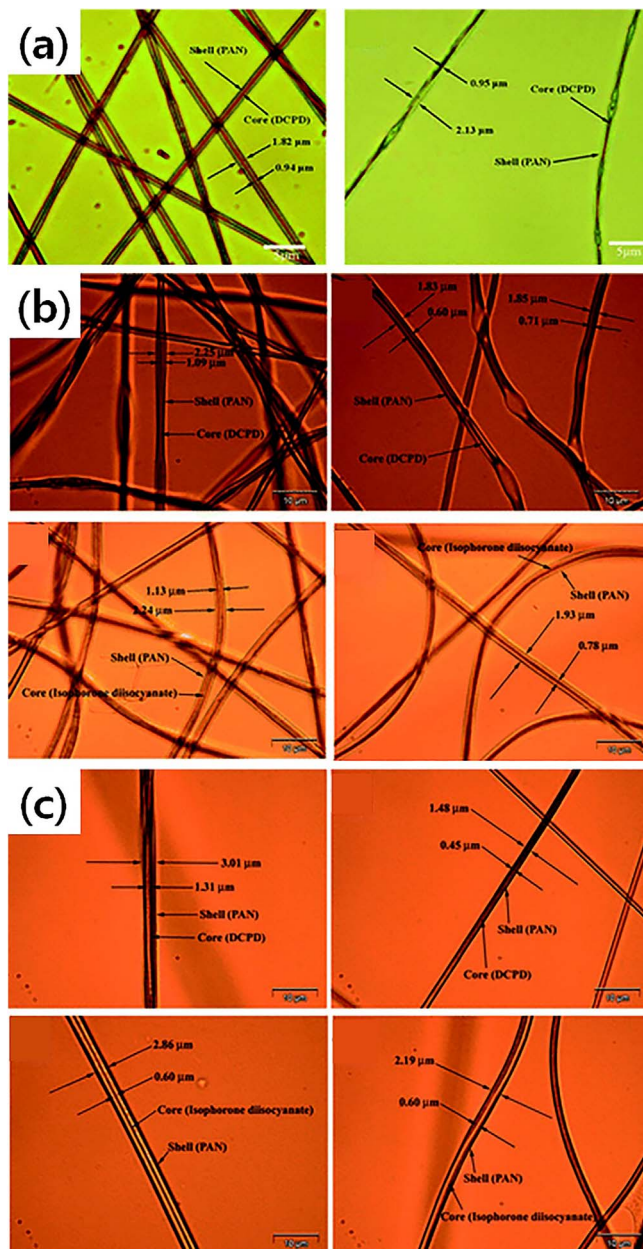


Fig. 13. Optical images of hollow NFs formed by: (a) co-electrospinning, (b) emulsion electrospinning, and (c) emulsion-solution blowing. Reprinted with permission from [15].

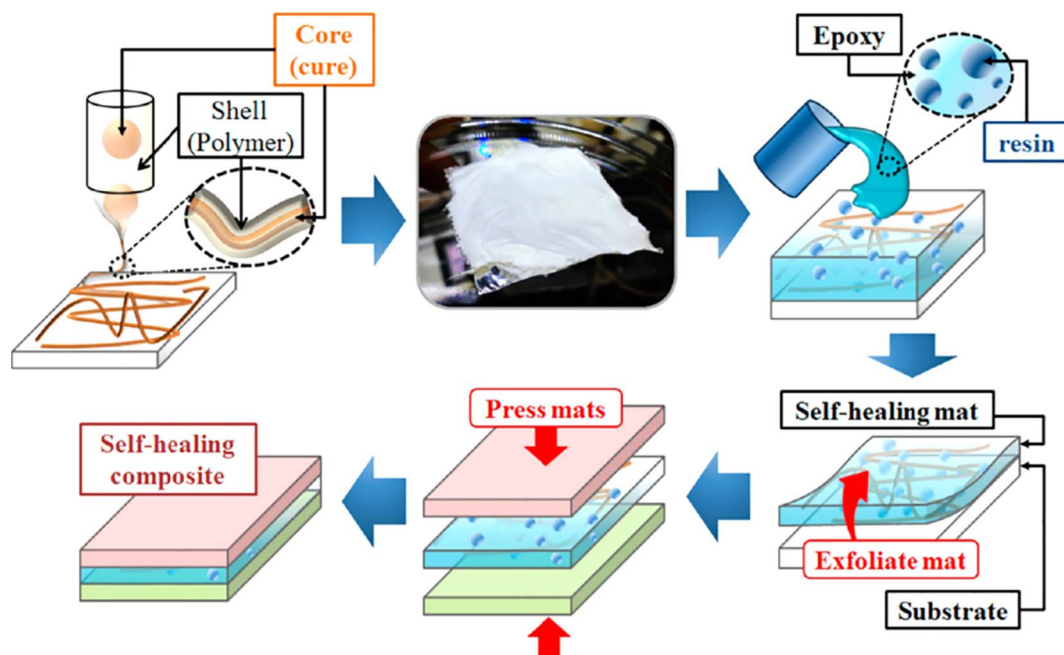


Fig. 14. Schematic of fabrication of self-healing composites incorporating core-shell NFs and capsule-less microdroplets. Reprinted with permission from [70]. Copyright 2014 American Chemical Society.

performed electrochemical tests wherein they placed metal substrates with the self-healing coating as well as controls that had been scratched in salt water and acetic acid and measured the electric current across the substrates. No electric current was detected when a self-healed sample was exposed to the electrolytes because the healed coating was nonconductive. In contrast, a significant electric current was observed when the sample with the non-healed coating was exposed to the electrolytes.

3.2.2. Scaling-up of core-shell nanometer-scale fiber networks

Even though emulsion electrospinning is one of the simplest methods for fabricating core-shell NFs, the process has a significant drawback in that the rate of core formation is low. The disordered formation of the droplets of the healing agent in the emulsion as well as the difficulties associated with material selection interrupts the electrospinning process. To ensure that the core formation process is robust and to prevent the formation of beads on the fibers, An et al. [22] analyzed the effect of the ratio of the radii of the inner core and the outer shell nozzles and found that a ratio of 0.4 improved process robustness. They found that this ratio resulted in an almost perfect core-shell structure, as identified by SEM, transmission electron microscopy (TEM), TGA, and DTG (cf. Fig. 15). The characterization

results showed that the siloxane-based resin and curing liquid were encased within the cores, which were covered by shells of solidified PAN. Note that TEM was used in this work only to observe the core-shell structure of the self-healing NFs. The self-healing composite fabricated for an electrospinning period of 5 min was highly transparent, with the transparency being as high as 93%. Finally, even though only a miniscule amount of the NFs was used, the composited exhibited outstanding anticorrosion performance during corrosion tests.

4. Future perspectives

Even though numerous self-healing materials have been developed and several industries are currently researching and investing in self-healing techniques, especially for self-healable electronics [106,107], it remains unclear whether the methods proposed for fabricating these materials are economically feasible and scalable to the industrial level. For example, capsule-based self-healing methods have several disadvantages such as low uniformity of the dispersed capsules and complicated fabrication processes (cf. Fig. 16). To overcome these drawbacks, several fiber-based self-healing approaches have been introduced recently. Nevertheless, the range of materials that can be used as the shell for encasing the core materials in these core-shell NFs is highly

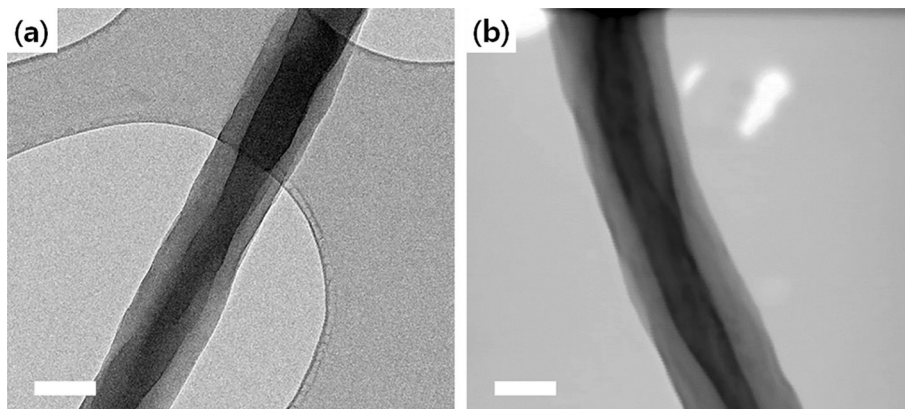


Fig. 15. TEM images of (a) resin-infused core-shell NFs and (b) curing-liquid-infused core-shell NFs. Reprinted with permission from Ref. [22].

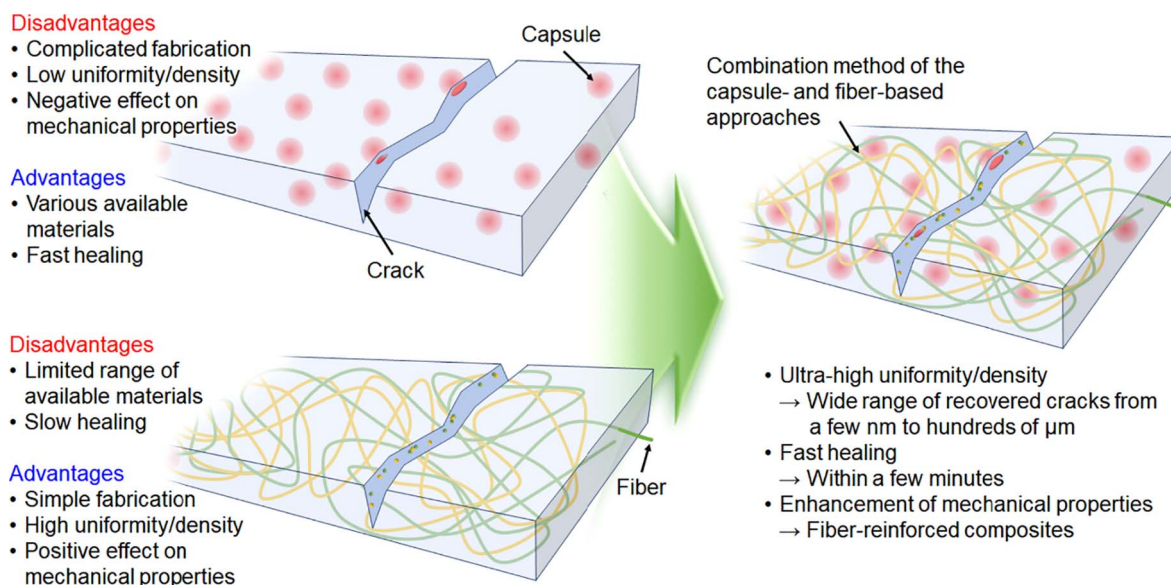


Fig. 16. Schematics for the capsule-based, fiber-based, and hybrid self-healing approaches and the corresponding advantages and disadvantages of each method.

limited (cf. Fig. 16). On the other hand, the capsule-based methods allow for the use of a wider range of materials within their limitations.

It should be emphasized that several additional goals must be pursued in future studies. First, it would be highly desirable to decrease the outer diameter of the shells from the micrometer scale to the nanometer scale, in order to enhance the self-healing performance by increasing the specific surface-to-volume ratio (S/V). Second, the development of core materials with shorter healing times, of the order of a few hours, is essential. The core and shell materials that can currently be used for the fiber-based approach have healing times of the order of tens of hours. Third, fabrication processes that are industrially scalable and economically viable need to be developed so that self-healing techniques find greater use in the automotive and construction industries. The recent development of multi-nozzle coating systems and roll-to-roll devices for the fabrication of NFs is encouraging and should help in overcoming the scalability challenge.

At the same time, hybrid methods incorporating both the capsule-based approach and the fiber-based approach should also be developed further to maximize the advantages of both these approaches. For example, as illustrated in Fig. 16, self-healing composites consisting of both rapidly healing capsules and miniscule self-healing core-shell NFs could be used for the damage recovery of a wide range of cracks, such as those from a few nanometers in size (owing to the NFs) to those hundreds of nanometers wide (owing to the capsules). In addition, such a hybrid approach would not exhibit the limitations related to slow healing, given the use of the capsules, and low uniformity, owing to the presence of the NFs. Finally, adding a corrosion inhibitor or using pH- and redox-responsive polymers would lead to additional improvements in the self-healing performance.

5. Conclusion

Recent studies of corrosion-protective extrinsic self-healing have been reviewed. It can be concluded that the capsule-based self-healing approaches have a wide choice of the inner healing agent materials. On the other hand, such approaches involve complicated fabrication processes and revealed a low uniformity of the dispersed capsules in composites. In contrast, fiber-based self-healing approaches involve simple fabrication processes and revealed a high uniformity in composites. On the other hand, the fiber-based self-healing approaches have a narrow choice of the inner healing agent materials. For these reasons, future works in this field will aim at the following goals: (i) decreasing

the overall size of the outer shell, (ii) reducing the healing time, and (iii) developing high-yield fabrication processes. In addition, hybrid methods integrating the capsule-based and the fiber-based approaches, as well as the corrosion inhibitors and stimuli-responsive materials are also expected to overcome the existing disadvantages.

Acknowledgements

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References

- [1] A.C.M. Silva, A.D. Moghadam, P. Singh, P.K. Rohatgi, Self-healing composite coatings based on in situ micro-nanoencapsulation process for corrosion protection, *J. Coat. Technol. Res.* 1–29 (2017).
- [2] G.H. Koch, M.P.H. Brongers, N.G. Thompson, Y.P. Virmani, J.H. Payer, Corrosion cost and preventive strategies in the United States, 2002.
- [3] W. von Baekmann, W. Schwenk, W. Prinz, *Handbook of Cathodic Corrosion Protection*, Gulf Professional Publishing, Houston, TX, 1997.
- [4] V. Cicek, *Cathodic Protection: Industrial Solutions for Protecting against Corrosion*, John Wiley & Sons, New Jersey, 2013.
- [5] R. Twite, G. Bierwagen, Review of alternatives to chromate for corrosion protection of aluminum aerospace alloys, *Prog. Org. Coat.* 33 (1998) 91–100.
- [6] H. Wei, Y. Wang, J. Guo, N.Z. Shen, D. Jiang, X. Zhang, X. Yan, J. Zhu, Q. Wang, L. Shao, Advanced micro/nanocapsules for self-healing smart anticorrosion coatings, *J. Mater. Chem. A* 3 (2015) 469–480.
- [7] M.D. Hager, P. Greil, C. Leyens, S. van der Zwaag, U.S. Schubert, Self-healing materials, *Adv. Mater.* 22 (2010) 5424–5430.
- [8] W.H. Binder, *Self-healing Polymers: from Principles to Applications*, Wiley-VCH Verlag GmbH, Weinheim, 2013.
- [9] S. Zwaag, *Self Healing Materials: An Alternative Approach to 20 Centuries of Materials Science*, Springer, Dordrecht, 2007.
- [10] M. Perring, T.R. Long, N.B. Bowden, Epoxidation of the surface of polydicyclopentadiene for the self-assembly of organic monolayers, *J. Mater. Chem.* 20 (2010) 8679–8685.
- [11] J.M. Lenhardt, S.H. Kim, A.J. Nelson, P. Singhal, T.F. Baumann, J.H. Satcher Jr, Increasing the oxidative stability of poly (dicyclopentadiene) aerogels by-hydrogenation, *Polym.* 54 (2013) 542–547.
- [12] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, Autonomic healing of polymer composites, *Nature* 409 (2001) 794.
- [13] E.N. Brown, S.R. White, N.R. Sottos, Microcapsule induced toughening in a self-healing polymer composite, *J. Mater. Sci.* 39 (2004) 1703–1710.
- [14] T.C. Mauldin, J.D. Rule, N.R. Sottos, S.R. White, J.S. Moore, Self-healing kinetics and the stereoisomers of dicyclopentadiene, *J. R. Soc. Interface* 4 (2007) 389–393.

- [15] S. Sinha-Ray, D.D. Pelot, Z.P. Zhou, A. Rahman, X.-F. Wu, A.L. Yarin, Encapsulation of self-healing materials by coelectrospinning, emulsion electrospinning, solution blowing and intercalation, *J. Mater. Chem.* 22 (2012) 9138–9146.
- [16] X.F. Wu, A. Rahman, Z. Zhou, D.D. Pelot, S. Sinha-Ray, B. Chen, S. Payne, A.L. Yarin, Electrospinning core-shell nanofibers for interfacial toughening and self-healing of carbon-fiber/epoxy composites, *J. Appl. Polym. Sci.* 129 (2013) 1383–1393.
- [17] O. Yerro, V. Radojevic, I. Radovic, M. Petrovic, P. Uskokovic, D. Stojanovic, R. Aleksic, Thermoplastic acrylic resin with self-healing properties, *Polym. Eng. Sci.* 56 (2016) 251–257.
- [18] J.H. Park, P.V. Braun, Coaxial electrospinning of self-healing coatings, *Adv. Mater.* 22 (2010) 496–499.
- [19] Z. Sun, E. Zussman, A.L. Yarin, J.H. Wendorff, A. Greiner, Compound core-shell polymer nanofibers by co-electrospinning, *Adv. Mater.* 15 (2003) 1929–1932.
- [20] M.L. Zheludkevich, D.G. Shchukin, K.A. Yasakau, H. Möhwald, M.G.S. Ferreira, Anticorrosion coatings with self-healing effect based on nanocontainers impregnated with corrosion inhibitor, *Chem. Mater.* 19 (2007) 402–411.
- [21] S.J. García, H.R. Fischer, P.A. White, J. Mardel, Y. González-García, A.J.M.C. Mol, A.E. Hughes, Self-healing anticorrosive organic coating based on an encapsulated water reactive silyl ester: synthesis and proof of concept, *Prog. Org. Coat.* 70 (2011) 142–149.
- [22] S. An, M. Liou, K.Y. Song, H.S. Jo, M.W. Lee, S.S. Al-Deyab, A.L. Yarin, S.S. Yoon, Highly flexible transparent self-healing composite based on electrospun core-shell nanofibers produced by coaxial electrospinning for anti-corrosion and electrical insulation, *Nanoscale* 7 (2015) 17778–17785.
- [23] H. Ullah, K.A.M. Azizli, Z.B. Man, M.B.C. Ismail, M.I. Khan, The potential of microencapsulated self-healing materials for microcracks recovery in self-healing composite systems: a review, *Polym. Rev.* 56 (2016) 429–485.
- [24] K. Dietrich, H. Herma, R. Nastke, E. Bonatz, W. Teige, Amino resin microcapsules. I. Literature and patent review, *Acta Polym.* 40 (1989) 243–251.
- [25] E.N. Brown, M.R. Kessler, N.R. Sottos, S.R. White, In situ poly (urea-formaldehyde) microencapsulation of dicyclopentadiene, *J. Microencapsulation* 20 (2003) 719–730.
- [26] Sybrand van der Zwaag, Martin D. Hager, Ulrich S. Schubert, *Self-healing Materials*, Springer International Publishing, Switzerland, 2016.
- [27] C.V. Suryanarayana, K.C. Rao, D. Kumar, Preparation and characterization of microcapsules containing linseed oil and its use in self-healing coatings, *Prog. Org. Coat.* 63 (2008) 72–78.
- [28] M. Samadzadeh, S.H. Boura, M. Peikari, A. Ashrafi, M. Kasiriha, Tung oil: an autonomous repairing agent for self-healing epoxy coatings, *Prog. Org. Coat.* 70 (2011) 383–387.
- [29] A.B. Chaudhari, P.D. Tatiya, R.K. Hedaoo, R.D. Kulkarni, V.V. Gite, Polyurethane prepared from neem oil polyesteramides for self-healing anticorrosion coatings, *Ind. Eng. Chem. Res.* 52 (2013) 10189–10197.
- [30] R. Marathe, P. Tatiya, A. Chaudhari, J. Lee, P. Mahulikar, D. Sohn, V. Gite, Neem acetylated polyester polyol—Renewable source based smart PU coatings containing quinoline (corrosion inhibitor) encapsulated polyurea microcapsules for enhance anticorrosive property, *Ind. Crops Prod.* 77 (2015) 239–250.
- [31] S.H. Boura, M. Peikari, A. Ashrafi, M. Samadzadeh, Self-healing ability and adhesion strength of capsule embedded coatings—Micro and nano sized capsules containing linseed oil, *Prog. Org. Coat.* 75 (2012) 292–300.
- [32] S. Lang, Q. Zhou, Synthesis and characterization of poly (urea-formaldehyde) microcapsules containing linseed oil for self-healing coating development, *Prog. Org. Coat.* 105 (2017) 99–110.
- [33] S.H. Cho, S.R. White, P.V. Braun, Self-healing polymer coatings, *Adv. Mater.* 21 (2009) 645–649.
- [34] J. Yang, M.W. Keller, J.S. Moore, S.R. White, N.R. Sottos, Microencapsulation of isocyanates for self-healing polymers, *Macromol.* 41 (2008) 9650–9655.
- [35] M. Huang, J. Yang, Facile microencapsulation of HDI for self-healing anticorrosion coatings, *J. Mater. Chem.* 21 (2011) 11123–11130.
- [36] G. Wu, J. An, D. Sun, X. Tang, Y. Xiang, J. Yang, Robust microcapsules with polyurea/silica hybrid shell for one-part self-healing anticorrosion coatings, *J. Mater. Chem. A* 2 (2014) 11614–11620.
- [37] D. Sun, J. An, G. Wu, J. Yang, Double-layered reactive microcapsules with excellent thermal and non-polar solvent resistance for self-healing coatings, *J. Mater. Chem. A* 3 (2015) 4435–4444.
- [38] B. Ghosh, M.W. Urban, Self-repairing oxetane-substituted chitosan polyurethane networks, *Sci.* 323 (2009) 1458–1460.
- [39] H.M. Klukovich, Z.S. Kean, S.T. Iacono, S.L. Craig, Mechanically induced scission and subsequent thermal remending of perfluorocyclobutane polymers, *J. Am. Chem. Soc.* 133 (2011) 17882–17888.
- [40] J. Ling, M.Z. Rong, M.Q. Zhang, Photo-stimulated self-healing polyurethane containing dihydroxyl coumarin derivatives, *Polymer* 53 (2012) 2691–2698.
- [41] Y.-K. Song, Y.-H. Jo, Y.-J. Lim, S.-Y. Cho, H.-C. Yu, B.-C. Ryu, S.-I. Lee, C.-M. Chung, Sunlight-induced self-healing of a microcapsule-type protective coating, *ACS Appl. Mater. Interfaces* 5 (2013) 1378–1384.
- [42] B. Kiskan, Y. Yagci, Self-healing of poly (propylene oxide)-polybenzoxazine thermosets by photoinduced coumarin dimerization, *J. Polym. Sci., Part A: Polym. Chem.* 52 (2014) 2911–2918.
- [43] L. Gao, J. He, J. Hu, C. Wang, Photoresponsive self-healing polymer composite with photoabsorbing hybrid microcapsules, *ACS Appl. Mater. Interfaces* 7 (2015) 25546–25552.
- [44] S. Stiller, H. Gers-Barlag, M. Lergenmueller, F. Pflücker, J. Schulz, K.P. Wittern, R. Daniels, Investigation of the stability in emulsions stabilized with different surface modified titanium dioxides, *Colloids Surf., A* 232 (2004) 261–267.
- [45] T. Chen, P.J. Colver, S.A.F. Bon, Organic-inorganic hybrid hollow spheres prepared from TiO₂-stabilized pickering emulsion polymerization, *Adv. Mater.* 19 (2007) 2286–2289.
- [46] Y. Chevalier, M.-A. Bolzinger, Emulsions stabilized with solid nanoparticles: pickering emulsions, *Colloids Surf., A* 439 (2013) 23–34.
- [47] Z. He, S. Jiang, Q. Li, J. Wang, Y. Zhao, M. Kang, Facile and cost-effective synthesis of isocyanate microcapsules via polyvinyl alcohol-mediated interfacial polymerization and their application in self-healing materials, *Compos. Sci. Technol.* 138 (2017) 15–23.
- [48] N.N. Voevodin, N.T. Grebasch, W.S. Soto, F.E. Arnold, M.S. Donley, Potentiodynamic evaluation of sol-gel coatings with inorganic inhibitors, *Surf. Coat. Technol.* 140 (2001) 24–28.
- [49] M. Garcia-Heras, A. Jimenez-Morales, B. Casal, J.C. Galvan, S.S. Radzki, M.A. Villegas, Preparation and electrochemical study of cerium-silica sol-gel thin films, *J. Alloys Compd.* 380 (2004) 219–224.
- [50] Y.M. Lvov, D.G. Shchukin, H. Mohwald, R.R. Price, Halloysite clay nanotubes for controlled release of protective agents, *ACS Nano* 2 (2008) 814–820.
- [51] D. Fix, D.V. Andreeva, Y.M. Lvov, D.G. Shchukin, H. Möhwald, Application of inhibitor-loaded halloysite nanotubes in active anti-corrosive coatings, *Adv. Funct. Mater.* 19 (2009) 1720–1727.
- [52] G.L. Li, Z. Zheng, H. Möhwald, D.G. Shchukin, Silica/polymer double-walled hybrid nanotubes: synthesis and application as stimuli-responsive nanocontainers in self-healing coatings, *ACS Nano* 7 (2013) 2470–2478.
- [53] E. Abdullayev, V. Abbasov, A. Tursunbayeva, V. Portnov, H. Ibrahimov, G. Mukhtarova, Y. Lvov, Self-healing coatings based on halloysite clay polymer composites for protection of copper alloys, *ACS Appl. Mater. Interfaces* 5 (2013) 4464–4471.
- [54] A.A. Antipov, G.B. Sukhorukov, Polyelectrolyte multilayer capsules as vehicles with tunable permeability, *Adv. Colloid Interface Sci.* 111 (2004) 49–61.
- [55] H. Choi, Y.K. Song, K.Y. Kim, J.M. Park, Encapsulation of triethanolamine as organic corrosion inhibitor into nanoparticles and its active corrosion protection for steel sheets, *Surf. Coat. Technol.* 206 (2012) 2354–2362.
- [56] H. Choi, K.Y. Kim, J.M. Park, Encapsulation of aliphatic amines into nanoparticles for self-healing corrosion protection of steel sheets, *Prog. Org. Coat.* 76 (2013) 1316–1324.
- [57] M. Plawecka, D. Snihirova, B. Martins, K. Szczepanowicz, P. Warszynski, M.F. Montemor, Self healing ability of inhibitor-containing nanocapsules loaded in epoxy coatings applied on aluminium 5083 and galvanneal substrates, *Electrochim. Acta* 140 (2014) 282–293.
- [58] A. Vimalanandan, L.P. Lv, T.H. Tran, K. Landfester, D. Crespy, M. Rohwerder, Redox-responsive self-healing for corrosion protection, *Adv. Mater.* 25 (2013) 6980–6984.
- [59] M. Stratmann, The investigation of the corrosion properties of metals, covered with adsorbed electrolyte layers—a new experimental technique, *Corros. Sci.* 27 (1987) 869–872.
- [60] M. Stratmann, H. Streckel, On the atmospheric corrosion of metals which are covered with thin electrolyte layers—I. verification of the experimental technique, *Corros. Sci.* 30 (1990) 681–696.
- [61] M. Stratmann, A. Leng, W. Fürbeth, H. Streckel, H.G. Gehmecker, K.-H. Große-Brinkhaus, The scanning Kelvin probe: a new technique for the in situ analysis of the delamination of organic coatings, *Prog. Org. Coat.* 27 (1996) 261–267.
- [62] W. Fürbeth, M. Stratmann, The delamination of polymeric coatings from electrogalvanised steel—a mechanistic approach.: Part 1: delamination from a defect with intact zinc layer, *Corros. Sci.* 43 (2001) 207–227.
- [63] G.S. Frankel, M. Stratmann, M. Rohwerder, A. Michalik, B. Maier, J. Dora, M. Wicinski, Potential control under thin aqueous layers using a Kelvin Probe, *Corros. Sci.* 49 (2007) 2021–2036.
- [64] J. Umeda, N. Nakanishi, K. Kondoh, H. Imai, Surface potential analysis on initial galvanic corrosion of Ti/Mg-Al dissimilar material, *Mater. Chem. Phys.* 179 (2016) 5–9.
- [65] T. Siva, S. Sathiyarayanan, Self healing coatings containing dual active agent loaded urea formaldehyde (UF) microcapsules, *Prog. Org. Coat.* 82 (2015) 57–67.
- [66] C. Dry, Procedures developed for self-repair of polymer matrix composite materials, *Compos. Struct.* 35 (1996) 263–269.
- [67] Y. Wang, D.T. Pham, C. Ji, Self-healing composites: a review, *Cogent. Eng.* 2 (2015) 1075686.
- [68] M. Motuku, U. Vaidya, G.M. Janowski, Parametric studies on self-repairing approaches for resin infused composites subjected to low velocity impact, *Smart Mater. Struct.* 8 (1999) 623.
- [69] S.M. Bleay, C.B. Loader, V.J. Hawyes, L. Humberstone, P.T. Curtis, A smart repair system for polymer matrix composites, *Composites, Part A* 32 (2001) 1767–1776.
- [70] M.W. Lee, S. An, C. Lee, M. Liou, A.L. Yarin, S.S. Yoon, Hybrid self-healing matrix using core-shell nanofibers and capsuleless microdroplets, *ACS Appl. Mater. Interfaces* 6 (2014) 10461–10468.
- [71] J.W.C. Pang, I.P. Bond, ‘Bleeding composites’—damage detection and self-repair using a biomimetic approach, *Composites, Part A* 36 (2005) 183–188.
- [72] J.W.C. Pang, I.P. Bond, A hollow fibre reinforced polymer composite encompassing self-healing and enhanced damage visibility, *Compos. Sci. Technol.* 65 (2005) 1791–1799.
- [73] S.R. White, J.S. Moore, N.R. Sottos, B.P. Krull, W.A. Santa Cruz, R.C.R. Gergely, Restoration of large damage volumes in polymers, *Sci.* 344 (2014) 620–623.
- [74] K.S. Toohey, N.R. Sottos, J.A. Lewis, J.S. Moore, S.R. White, Self-healing materials with microvascular networks, *Nat. Mater.* 6 (2007) 581–585.
- [75] K.S. Toohey, N.R. Sottos, S.R. White, Characterization of microvascular-based self-healing coatings, *Exp. Mech.* 49 (2009) 707–717.
- [76] A.R. Hamilton, N.R. Sottos, S.R. White, Pressurized vascular systems for self-

- healing materials, *J. R. Soc. Interface* (2011) 1–9.
- [77] A.R. Hamilton, N.R. Sottos, S.R. White, Mitigation of fatigue damage in self-healing vascular materials, *Polymer* 53 (2012) 5575–5581.
- [78] J.F. Patrick, K.R. Hart, B.P. Krull, C.E. Diesendruck, J.S. Moore, S.R. White, N.R. Sottos, Continuous self-healing life cycle in vascularized structural composites, *Adv. Mater.* 26 (2014) 4302–4308.
- [79] H.R. Williams, R.S. Trask, I.P. Bond, Self-healing composite sandwich structures, *Smart Mater. Struct.* 16 (2007) 1198.
- [80] H.R. Williams, R.S. Trask, P.M. Weaver, I.P. Bond, Minimum mass vascular networks in multifunctional materials, *J. R. Soc Interface* 5 (2008) 55–65.
- [81] H.R. Williams, R.S. Trask, I.P. Bond, Self-healing sandwich panels: restoration of compressive strength after impact, *Compos. Sci. Technol.* 68 (2008) 3171–3177.
- [82] A. Kousourakis, A.P. Mouritz, The effect of self-healing hollow fibres on the mechanical properties of polymer composites, *Smart Mater. Struct.* 19 (2010) 085021.
- [83] J.F. Patrick, N.R. Sottos, S.R. White, Microvascular based self-healing polymeric foam, *Polymer* 53 (2012) 4231–4240.
- [84] H. Ku, H. Wang, N. Pattarachaiyakoo, M. Trada, A review on the tensile properties of natural fiber reinforced polymer composites, *Composites, Part B* 42 (2011) 856–873.
- [85] C.J. Norris, G.J. Meadway, M.J. O'Sullivan, I.P. Bond, R.S. Trask, Self-healing fibre reinforced composites via a bioinspired vasculature, *Adv. Funct. Mater.* 21 (2011) 3624–3633.
- [86] C.J. Norris, J.A.P. White, G. McCombe, P. Chatterjee, I.P. Bond, R.S. Trask, Autonomous stimulus triggered self-healing in smart structural composites, *Smart Mater. Struct.* 21 (2012) 094027.
- [87] C.J. Norris, I.P. Bond, R.S. Trask, Healing of low-velocity impact damage in vascularised composites, *Composites, Part A* 44 (2013) 78–85.
- [88] M.W. Lee, S. An, H.S. Jo, S.S. Yoon, A.L. Yarin, Self-healing nanofiber-reinforced polymer composites. 1. Tensile testing and recovery of mechanical properties, *ACS Appl. Mater. Interfaces* 7 (2015) 19546–19554.
- [89] M.W. Lee, S. An, H.S. Jo, S.S. Yoon, A.L. Yarin, Self-healing nanofiber-reinforced polymer composites. 2. Delamination/debonding and adhesive and cohesive properties, *ACS Appl. Mater. Interfaces* 7 (2015) 19555–19561.
- [90] M.W. Lee, S.S. Yoon, A.L. Yarin, Solution-blown core-shell self-healing nano-and microfibers, *ACS Appl. Mater. Interfaces* 8 (2016) 4955–4962.
- [91] M.W. Lee, S. Sett, S.S. Yoon, A.L. Yarin, Fatigue of self-healing nanofiber-based composites: static test and subcritical crack propagation, *ACS Appl. Mater. Interfaces* 8 (2016) 18462–18470.
- [92] M.W. Lee, S. Sett, S.S. Yoon, A.L. Yarin, Self-healing of nanofiber-based composites in the course of stretching, *Polymer* 103 (2016) 180–188.
- [93] M.W. Lee, S.S. Yoon, A.L. Yarin, Release of self-healing agents in a material: what happens next? *ACS Appl. Mater. Interfaces* 9 (2017) 17449–17455.
- [94] M.W. Lee, S. Sett, S. An, S.S. Yoon, A.L. Yarin, Self-healing nanotextured vascular-like materials: Mode I crack propagation, *ACS Appl. Mater. Interfaces* 9 (2017) 27223–27231.
- [95] M.W. Lee, S. An, S.S. Yoon, A.L. Yarin, Advances in self-healing materials based on vascular networks with mechanical self-repair characteristics, *Adv. Colloid Interface Sci.* 252 (2018) 21–37.
- [96] A.L. Yarin, B. Pourdeyhi, S. Ramakrishna, *Fundamentals and Applications of Micro-and Nanofibers*, Cambridge University Press, Cambridge, 2014.
- [97] D.H. Reneker, A.L. Yarin, E. Zussman, H. Xu, Electrospinning of nanofibers from polymer solutions and melts, *Adv. Appl. Mech.* 41 (2007) 43–195.
- [98] M.W. Lee, S. An, B. Joshi, S.S. Lathe, S.S. Yoon, Highly efficient wettability control via three-dimensional (3D) suspension of titania nanoparticles in polystyrene nanofibers, *ACS Appl. Mater. Interfaces* 5 (2013) 1232–1239.
- [99] X. Xu, L. Yang, X. Xu, X. Wang, X. Chen, Q. Liang, J. Zeng, X. Jing, Ultrafine medicated fibers electrospun from W/O emulsions, *J. Controlled Release* 108 (2005) 33–42.
- [100] X. Xu, X. Zhuang, X. Chen, X. Wang, L. Yang, X. Jing, Preparation of core-sheath composite nanofibers by emulsion electrospinning, *Macromol. Rapid Commun.* 27 (2006) 1637–1642.
- [101] A.V. Bazilevsky, A.L. Yarin, C.M. Megaridis, Co-electrospinning of core-shell fibers using a single-nozzle technique, *Langmuir* 23 (2007) 2311–2314.
- [102] A.V. Bazilevsky, K. Sun, A.L. Yarin, C.M. Megaridis, Selective intercalation of polymers in carbon nanotubes, *Langmuir* 23 (2007) 7451–7455.
- [103] A.V. Bazilevsky, K. Sun, A.L. Yarin, C.M. Megaridis, Room-temperature, open-air, wet intercalation of liquids, surfactants, polymers and nanoparticles within nanotubes and microchannels, *J. Mater. Chem.* 18 (2008) 696–702.
- [104] S. Sinha-Ray, R.P. Sahu, A.L. Yarin, Nano-encapsulated smart tunable phase change materials, *Soft Matter* 7 (2011) 8823–8827.
- [105] M.W. Lee, S. An, C. Lee, M. Liou, A.L. Yarin, S.S. Yoon, Self-healing transparent core-shell nanofiber coatings for anti-corrosive protection, *J. Mater. Chem. A* 2 (2014) 7045–7053.
- [106] A.S.S. Olson, Self-healing polymer compositions, US Patent US7108914B2, 2006.
- [107] B.-W. Ahn, Sealant compositions, methods of preparing sealant compositions and display panel including sealants, US Patent US9752065B2, 2017.
- [108] X.K. Hillewaere, F.E. Du Prez, Fifteen chemistries for autonomous external self-healing polymers and composites, *Prog. Polym. Sci.* 49 (2015) 121–153.