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A Review on the Self-Healing Property of Core Sheath Nanofibers: Applications and Recent Advances

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Abstract

Self-healing in nature is an outstanding phenomenon. The survival of animals, plants, and human beings is easier because of their ability to recover from any damage to their living organs. A review of recent advances pertinent to the self-healing performance of materials and co-electrospinning is presented in this study. Self-healing agents produced by electrospinning are one of the most promising materials for self-healing and exhibit a growing trend for a wide range of applications. The current study aims to report contributions and advances relating to the self-healing performance of materials by using co-electrospinning and the ability of nanofibers to self-heal from damage. It provides an eyesight for further progress of this promising technology. This review comprises investigations in which the self-healing nanofibers produced via the co-electrospinning process and their applications in some industries are focused. The corrosion protection of metals and damage repair in composites are addressed as well.

1 INTRODUCTION

Self-healing in nature is a fascinating phenomenon [1]. For example, scratched skin and damaged bones are rapidly healed because of the activation of the body's vascular system [2]. The survival of animals, plants, and human beings is easier because of their ability to recover [2]. Searching for the property of self-healing in engineering materials started in 2001. For engineered materials, it is satisfactory that the healing materials can be released in the damaged locations under the internal or external defect to repair and recover the damaged surface [2]. Self-healing materials have some advantages, such as life expectancy, reducing the cost of maintenance and repair, and improving the durability and reliability of an engineering system [3]. Few materials intrinsically have this property. Some of these materials are polymers, metals, ceramics, and their composites. When the so-called materials are damaged by mechanical, thermal, ballistic or other sources, they can heal and recover the material to its original properties [4]. To date, numerous studies have been done to enable self-healing in materials such as the release of healing agents, reversible cross-links, nanoparticles, and shape memory effect [3] [5]. One of the most important applications of self-healing materials is the field of corrosion protection. Polymeric coating self-healing is an important strategy to protect the metal matrix from corrosion [6]. There are two common systems for self-healing coating materials: intrinsic and capsule-based systems [7]. Intrinsic healing systems include covalent bonding, reversible hydrogen bonds, and metal-ligand bonding [6]. Capsule-based healing systems in recent years have been used for many applications [8]. In this system, healing agents are encapsulated and dispersed in a matrix. Upon damage, the capsule ruptures, and its content is released in the damaged zone [8]. Composite materials are used in many industrial applications. They have some advantages, such as high specific strength, stiffness, and lightweight. However, these advanced materials are vulnerable to impact or other mechanical loadings, especially thermosetting polymers, because of their brittle structure [9]. Self-healing in polymeric composites can prevent catastrophic failures of composites by repairing minor internal damage [10]. The rupture of containers leads to the release of healing agents into the cracks and undergoes a healing process [9]. There are various types of containers with an efficient healing system, such as microcapsules, microvascular networks, and hollow fibers [9] [11]. The microcapsules can be easily prepared and incorporated into the matrix materials [12]. But the self-healing method based on microcapsules has major disadvantages, such as an insufficient amount of healing agent for multiple healing and uncertainty of complete consumption of the healing agent [9]. Multiple healing could be achieved

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via another strategy of self-healing using tubular channels such as microvascular networks and hollow fibers due to the ability to contain a large amount of healing agents [13] [14]. Pang et al [15] developed a filled hollow fiber reinforced composite and managed to recover the flexural strength of the composite after impact damage. Electro-spun core-shell nanofibers (NFs) were first introduced as a vascular system to contain self-healing agents in 2010 [16]. Core-shell nanofibers have attracted much attention due to having several orders of magnitude smaller diameters than the microcapsule and hollow fibers and a minimum impact on polymer composite weight [9] [17]. Coaxial electrospinning is a multipurpose method to produce core-shell nanofibers [18] [19] [20] [21]. Some materials, such as Polydimethylsiloxane (PDMS), super-molecular polymers, modified rubbers, and polymeric hydrogels, have the capability of being used as healing agents [22]. Epoxy resin is the most widely accepted all-purpose material for coating applications [23]. This is because of its corrosion resistance, excellent adhesion, chemical resistance, and thermomechanical properties. In general, epoxy resins are made by the reaction of phenols with acetone or formaldehyde, and subsequently with epi-chlorohydrin followed by crosslinking with the increase of different curing agents [23]. Epoxy resin has the healing ability without the need for additional catalysts, and is a good choice as a healing agent for the fabrication of self-healing composites, usually epoxy-amine or epoxy-amide systems which are slightly alkaline [12]. In this review, the multi-functionalized applications of core-shell nanofibers in the fields of metal corrosion protection such as corrosion inhibitors, anticorrosion coating, and composite materials are summarized.

2 Fabrication of core-shell nanofibers for self-healing performance

The electrospinning process has attracted remarkable attention as an influential method for developing multifunctional micro- and nanofibrous materials from different polymers and composites [24] [25]. Electrostatic spinning is one of the methods for self-healing material preparation with some advantages such as low cost, flexibility, versatility, and easy process [6]. Nanofibers fabricated via the electrospinning method have many fascinating properties, such as a high surface-to-volume ratio, extremely small diameters along with interconnected nanostructure, high porosity, and surface functionality. Recently, they have been widely used in various applications such as tissue engineering [26], biomedical [27], drug delivery [24] [28], filtration [29], wound healing, sensors, smart textiles, composite reinforcements [30] and self-healing [31].

The electrospinning method can be carried out using single-needle electrospinning, blend electrospinning, coaxial electrospinning, modified coaxial electrospinning, and side-by-side electrospinning [24]. Coaxial electrospinning is the process of producing such structures in which two dissimilar solutions are injected separately from two different coaxial capillary channels, as shown in Figure 1 [32]. Coaxially spun hollow and core-shell nanofibers have attracted considerable attention recently [33] [34] [35] and have shown promising performance in self-healing applications. Coaxial electrospinning (co-electrospinning) is used in many research studies for the production of core-shell nanofibers. This method needs four electrospinning instruments, which makes the process complex and more difficult to control the parameters of electrospinning [9]. Also, another restriction of coaxial electrospinning is that the inner and outer polymer solutions should be immiscible to obtain a core-shell structure [36].

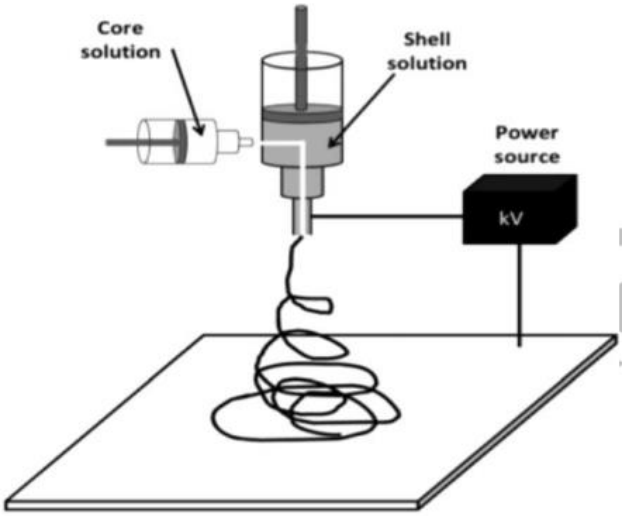

Figure 1 The traditional coaxial electrospinning setup [32]

In addition to co-electrospinning, emulsion electrospinning, and emulsion-solution blowing have also been applied to encapsulate healing agents within hollow nanofibers, where an emulsified material in a polymer solution creates the core part of hollow nanofiber, while another (matrix) material in the solution creates the shell of core–shell nanofiber [37] [38] [39]. Although there is a necessary condition that the core material should be emulsified in the polymer solution, the emulsion-based systems allow us to form core–shell nanofibers from a single nozzle, which is more appropriate compared to the co-electrospinning in which two solutions are simultaneously issued from a coaxial nozzle [40]. Sinha-Ray et al [41] fabricated hollow nanofibers with diameters of 450–1000nm by co-electrospinning, emulsion electrospinning, and emulsion-solution blowing. For co-electrospinning, a coaxial needle setup was applied, where Dicyclopentadiene (DCPD) in DMF and polyacrylonitrile (PAN) in DMF were supplied to the core and shell needles, respectively. Lee et al. [17] filled the emulsion-electrospun nanofibers and capsule-less micro droplets with a siloxane-based curing liquid and a resin monomer, respectively. They placed electrospun curing liquid (core)/PAN (shell) nanofibers on a metal substrate using a curing liquid/PAN emulsion. Consequently, they infused the resin/epoxy emulsion onto the NF-coated metal substrate; this resulted in the formation of capsule-less resin micro-droplets in the epoxy matrix. A heterogeneous matrix comprising the core-shell nanofibers and the capsule-less micro-droplets was formed (Figure 2).

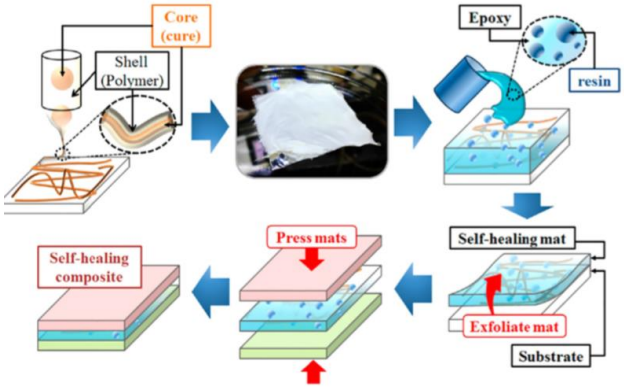

Figure 2 Schematic of fabrication of self-healing composites incorporating core-shell NFs and capsule-less micro-droplets [17]

The optimal resin-to-curing liquid ratio was found to be 10:1. To examine the anticorrosion protection afforded by the self-healing composite, they used electrochemical tests wherein they placed metal substrates with the self-healing coating as well as controls that had been scratched in salty water and acetic acid and measured the electric current across the substrates. No electric current was detected when a self-healed sample was subjected 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 [17]. Although emulsion electrospinning is one of the simplest methods for fabricating core-shell nanofibers, the process has a considerable disadvantage 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 [40]. A one–trigger component healing agent was achieved by Speraa et al. [42] by overcoming the non–spinnability of organo-silane compounds. In this research, they also implemented an adjective method for large-scale structures, spray-painting to defeat the scalability limitations for self-healing coatings.

3 Self-healing performance of nanofibers in corrosion protection

Steel corrosion in marine environments is a global concern because of its remarkable environmental effects and the economic damage that it brings. One of the main strategies for preventing the corrosion of metallic structures is based on the usage of organic coatings to prepare a barrier against the diffusion of corrosive agents [43]. These materials have some limitations, such as the propagation of micro-cracks in their structures, causing a reduction in the service life. To solve this problem, different intelligent self-healing coatings have been developed to employ the advantages of repairing the damaged area of coatings and giving an extra corrosion-protective film on steel substrates [44] [45] [46]. To reach the goal of self-healing coatings, microcapsules can be loaded in the matrix of the polymer coating to restore the micro-cracks of coatings used on metallic substrates. When the coating is disturbed, the healing agent in the microcapsules is released into the coating matrix to repair the damaged area [43].

In general, microcapsules have a large diameter and a relatively thick shell, caused by loading a limited amount of healing agents in the microcapsules, and the self-healing performance of the coating is limited. One of the drawbacks of the coatings containing microcapsules is that they can be repaired only once. Therefore, developing smart coatings containing a polymer matrix with a repeatable self-healing capability has gained great consideration. Nanofibers with interconnected network systems have attracted the attention of researchers to be applied as an alternative to microcapsules. The current section reviews investigations in which fibrous structures are encrusted into a polymeric material to manufacture a self-healing coating structure. Coatings enabling self-healing functionalities are characterized as materials of commercial and scientific concern. These novel materials are widely used to prevent corrosion on the surface of metals subjected to a corrosive environment. These types of coating are the most common method because of some advantages, such as cost-effectiveness and environmental friendliness [47].

The optimal process to enhance the performance of a self-healing coating is the control of the corrosion inhibitor release[47]. Corrosion inhibitors can slow down or hinder the corrosion process. Also, a small dosage can result in a substantial consequence [43]. In a study reported by Doan et al [7], they extended a self-healing coating polymer using electrospun core-shell nanofibers to protect the steel from corrosion (see Figure 3). In this research, core-shell nanofibers were produced using the electrospinning method. The electro-spun nanofibers containing liquid healing agents reach a crosslinking reaction of poly (dimethylsiloxane) (PDMS) to crosslinking agent poly (diethoxysiloxane) (PDES) to fill the damaged region. They investigated the performance of the self-healing coating electrochemically by applying linear polarization, in which the coating was exposed to a corrosive environment. They concluded that the corrosion inhibition efficiency of the heal coating improved by 88% in comparison to control specimens.

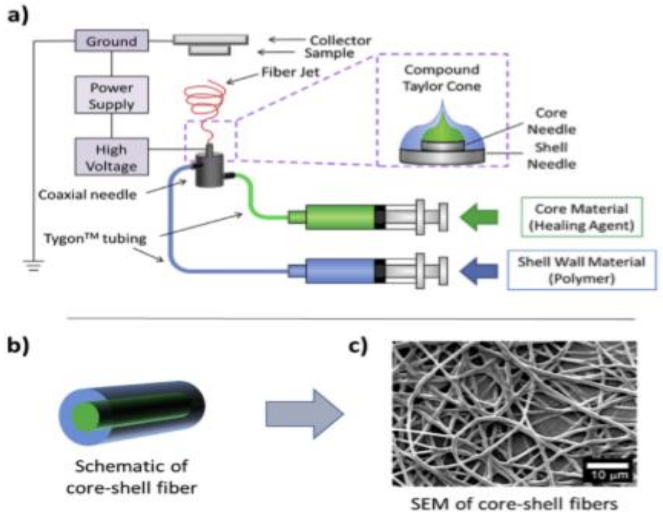

Figure 3 Fabrication of core-shell electrospun fibers: a) schematic of coaxial electrospinning setup, b) schematic of core-shell fibers of PVA (shell, shown in blue) and healing agent (core, shown in green), and c) SEM image of randomly deposited core-shell fibers [7]

Dong et al. [20] used coaxial electrospinning and examined the self–healing potential of epoxy coatings modified with coaxial core–shell nanofibers while loaded with the corrosion inhibitor 2–mercaptobenzothiazole (MBT). Polyvinylalcohol/ polyvinylidene fluoride core–shell nanofibers were produced by (Figure 4).

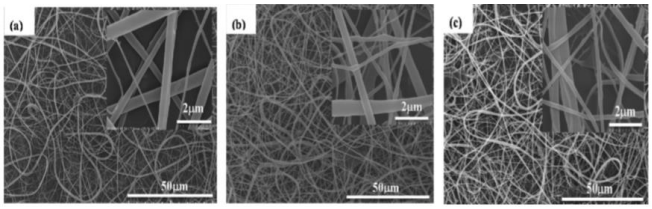

Figure 4 SEM images of coaxial electrospun nanofiber with different feed rates (inset: local magnification of the nanofiber) (a) 1.2mL/h, (b) 1.5mL/h, (c) 1.8mL/h [20]

When artificial defects were exposed to NaCl electrolyte, the MBT–loaded coaxial nanofibers could heal the corrosion and the results of the Scanning Kelvin Probe technique confirmed this healing. This study showed that adding MBT–loaded coaxial nanofibers to epoxy coatings is a proper strategy to improve the self–healing epoxy coatings [20]. Ji et al [48] could improve the performance of the coating system by synthesizing core-shell nanofibers consisting of oleic acid (OA) and 2-mercapto benzimidazole (MBI), which were encapsulated in the chitosan/poly (vinyl alcohol) (CS/PVA) after preparing a core-shell/epoxy composite coating on Q235 steel substrate. The results showed the successful preparation of the CS/PVA core-shell nanofibers loaded with corrosion inhibitors. They determined the corrosion protection performance of the composite coating by using Electrochemical impedance spectroscopy. After 10 and 20-day immersion in alkaline and acidic electrolytes, the maximum inhibition efficiency of oleic and MBI was 96.66% and 99.36%, respectively.

Lakshmi et al [49] assessed a defect-free sol-gel hybrid coating compound of cerium oxide nanofibers vis-à-vis `sol-gel coating ' for corrosion protection performance. It consisted of commercial nano-sized ceria particles as corrosion inhibitors. They verified the corrosion resistance by electrochemical impedance spectroscopy and concluded that the sol-gel matrix containing cerium oxide nanofibers, exhibiting Ce mainly in the +3 oxidation state, enhanced the performance. Dual emulsion electrospinning was introduced by Lee and colleagues [50] to fabricate core–shell nanofiber coatings with the self-healing agent dimethyl siloxane (DMS) and dimethyl-methyl hydrogen-siloxane (cure) separately in the cores. Hassim et al. [51] reported that when they examined the core-to-shell flow rate of 6.7:1, an optimal condition was attained with an encapsulation content of over 50% that was, while it did not affect the core-shell nanofibers morphology at a high core flow. Three different shell materials to evaluate the performance of self-healing coating were investigated by Xu et al. [52]. Results demonstrated that the nanofibers with PA6 as a shell material presented the best enhancement performance, which gives a greater potential for corrosion protection and long-lasting use of offshore wind turbine tower coatings.

Saikia et al. [53] fabricated bio-based epoxy nanocomposites by the in situ method using polyaniline nanofiber-carbon dot nano-hybrid (0.50 and 1 wt % with respect to epoxy), as the anticorrosive material. They reported that the anticorrosion study of the nanocomposites indicated excellent corrosion protection efficiency (corrosion rate: 5.8×10^{-3}mils per year) in 3.5 wt % NaCl in comparison with the pristine epoxy system.

In order to inhibit the corrosion of carbon steel, Yabuki et al. [54] developed a polymer coating with corrosion inhibitors of sodium oleate and sodium nitrate, along with a network of cellulose nanofibers (Figure 5). They measured the polarization curves of bare carbon steel in a corrosive solution containing both corrosion inhibitors. They applied multi-layer polymer coatings with both cellulose nanofibers and corrosion inhibitors to carbon steel. The electrochemical impedance of the scratched coating was monitored in a corrosive solution to evaluate the self-healing capability of different polymer coatings. The results showed that an outstanding self-healing film was formed on the scratched zone of the substrate.

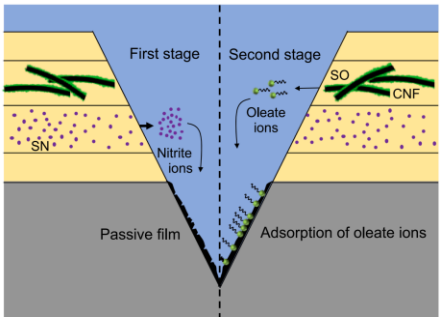

Figure 5 Mechanism for the self-healing of a scratched SO8 + CNF0.5/SN/S coating [54]

Fu and co-workers [55] developed a composite coating with accurately controllable self-healing performance by integrating lamellar graphene oxide (GO) into polycaprolactone (PCL) nanofiber loaded with 8-hydroxyquinoline (8HQ) corrosion inhibitors (Figure 6). They declared that coating imperfections can be precisely repaired under near-infrared (NIR) light irradiation in a very short time. It was reported that the accurately controllable defect recovery even within a minimal region was achieved, without causing stagnation of pristine performance in irrelevant areas [55]. This study also reported that the embedded graphene oxide could act both as an influential photothermal conversion material, and yield "labyrinth effect" to increase the passive dam against corrosive media.

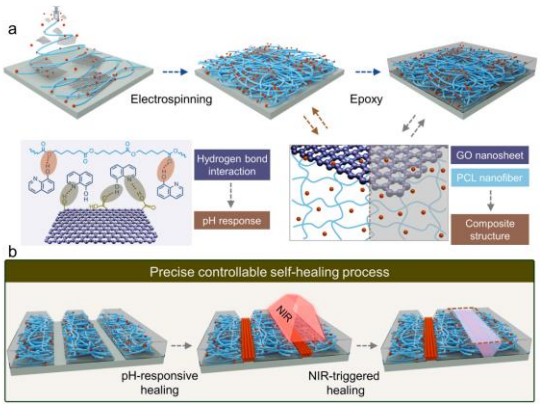

Figure 6 The schematic of the synthesis of a nanofiber composite membrane with an illustration of the interactions between GO, 8HQ molecules and PCL nanofibers. (b) The schematic of a precise controllable self-healing process [55]

In the work done by Ji et al. [56], a self-healing and self-warning core–shell fiber was synthesized in order to develop the aggregation-induced emission (AIE) material composite coating. They used a mixture of hexamethylene diisocyanate (HDI) and tetraphenylethylene (TPE) as the core constituent in the core–shell fibers, and polyacrylonitrile (PAN) was applied to construct the shell. They optimized the electrospinning procedure parameters to reach the core–shell fibers with a smooth surface. They reported that the composite coating presented an influential fluorescence in the case of cracks in a corrosive environment. The results showed that the maximum self-healing efficiency of the fiber coating was 94.8 % after soaking for 120 h [56].

In the research of Cui et al. [57], a smart protective coating with self-reporting and self-healing capabilities was developed. Polyacrylonitrile (PAN) core-shell nanofibers containing 2-amino-1,3,4-thiadiazole (2-AT) and crystal violet lactone (CVL) were embedded into an organic coating. When the prepared coating was disturbed, CVL at the damaged zone emitted bright blue fluorescence under UV light, while 2-AT adsorbed and formed a thin film on the steel surface to prevent corrosion. Moreover, the flexibility of the coating was significantly increased in comparison with the blank coating, which helped to decrease the formation of microcracks in the coating. In the research of Fu et al. [58] an accurately controllable self-healing anticorrosion composite coating was developed by the process of combining layer-specific nanofiber membranes and epoxy blockage layer, under stimulation of remote near-infrared (NIR) light. They reported that the manufactured coating gives highly precise positioning for corrosion sites, demonstrating considerable fluorescence signals by chelating with corrosion-released metal ions. The results demonstrated that accurate regional control of self-healing behavior in designated places is obtained within 30 s, with a self-healing anticorrosion efficiency of 96.32 %.

Tang et al. [59] developed a technique to prepare an anti-corrosion coating with efficient self-healing properties based on microfluidic electrospinning methods and UV-curable healing agents. The results indicated that the damaged composite coating with core–shell nanofibers completely healed within only 30 min, representing an excellent healing performance. The results also demonstrated that the corrosion current density (Icorr) of the composite coating with core–shell nanofibers was lower than that of the coating without any fibers.

Song et al. [60] synthesized a novel poly (vinyl alcohol) grafted phytic acid (PVA-PA) electrospinning solution (Figure 7). In this paper, a sandwich-like microvascular network (SMN) was prepared by the coaxial electrospinning technique. PVA-PA solution was applied as the shell material, and epoxy resin 51 (E51), tetraphenylethylene (TPE), and polyamide resin were applied as the core materials. It was reported that because of the high porosity of SMN, epoxy resin could be directly spin-coated on it to form a composite coating (PVA-PA/SMN/EP). It was also reported that owing to the strong chelation and coordination interaction between PA and mild steel, the pull-out adhesion of the PVA-PA/SMN/EP composite coating on mild steel was enhanced by 0.92 MPa.

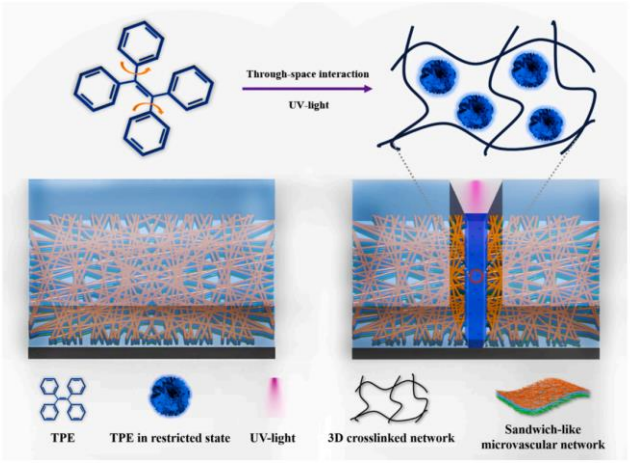

Figure 7 Schematic diagram of the self-healing and self-reporting mechanism of PVA-PA/SMN/EP composite coating [60]

In the research of Wang et al. [61], a smart epoxy based on a nanofiber network combination of active anticorrosion and self-healing functions for carbon steel protection was designed. The structural characterization techniques in this research revealed a successfully synthesized PVA/ CS@LO/8-HQ nanofiber network. Moreover, DFT calculations showed a strong intermolecular interaction between LO and 8-HQ by forming a hydrogen bond interaction. In addition, the Tafel polarization curves also indicated that the compound corrosion inhibitor presented a high corrosion inhibition performance of 90.31% at pH = 7.

Xu et al. [62] investigated three promising shell materials to optimize the performance of the self-healing coating. They prepared self-healing core-shell nanofibers with various shell materials using coaxial electrospinning. The prepared nanofibers were applied to fabricate a self-healing corrosion-resistant coating. The tensile test indicated a considerable increase in the tensile strength of PA6 core-shell nanofiber epoxy composite coatings in comparison with the epoxy coating, showing an increase of 26.92%. An electrochemical impedance spectroscopy (EIS) test was applied to evaluate the self-healing and anti-corrosion performance of composites. The results showed that all three coatings presented excellent self-healing efficiencies exceeding 90%.

In the work done by Zhao et al. [63] in order to enhance the adhesion between electro-spun nanofibers, metal substrate, and surface coating, the nanofibrous membrane was electro-spun between two layers of epoxy resin to form a sandwich structure, thereby enhancing the adhesion to the substrate.

3-1 Application of Polyaniline (PANI) Nanofibers in self-healing performance

In modern decades, the use of conductive polymers (CPs) in anticorrosive coatings has gained increasing consideration [60]. Numerous conductive polymers have been used to advance the anti-corrosion performance, including polyaniline (PANI) [61] [62] [63], polypyrrole (PPY) [64], polythiophene [65], and polybenzoxazine [66]. PANI-based coatings are increasingly employed and considered to be the best choice for metal corrosion protection. PANIs protect the substrates by inhibiting the penetration of the etchant and

shaping the passivation oxide layer on the surface of the metal structure, as reported by Yao et al. [60]. In this work, the corrosion protection performance of 2-hydroxyphosphonocarboxylic acid doped polyaniline (HPA-PANI)/epoxy composite was determined after coating on a low-carbon steel. Qiu et al synthesized the self-doped sulfonated polyaniline (SPANi) nanofiber by the copolymerization of 2- aminobenzenesulfonic acid (ASA) and aniline by applying a rapid mixing polymerization process [67].

Scanning electron microscope (SEM) evidence demonstrated that the as-prepared SPANi nanofibers had 45 nm average diameter and a length up to 750 nm. Excellent aqueous solubility, reversible redox activity, and good conductivity (0.11 S/cm) of the self-doped SPANi nanofiber made it suitable as a corrosion inhibitor for waterborne coatings. They also worked on the passivation influence of SPANi nanofibers and the corrosion products beneath the epoxy coating plunged in 3.5% NaCl solution as a function of time. Zhao et al. [68] studied the mechanical properties of composite coatings by using polyacrylonitrile nanofibers (PAN-NFs) filled with benzotriazole (BTA) as an inhibitor created by the coaxial electrospinning method (Figure 7). They applied tensile testing to evaluate the crack growth versus the strength of samples (Figure 8). They immersed it 15 days and found that the inhibition efficiency of the PAN-NFs/BTA/EP coating process was 91.0% after this time duration.

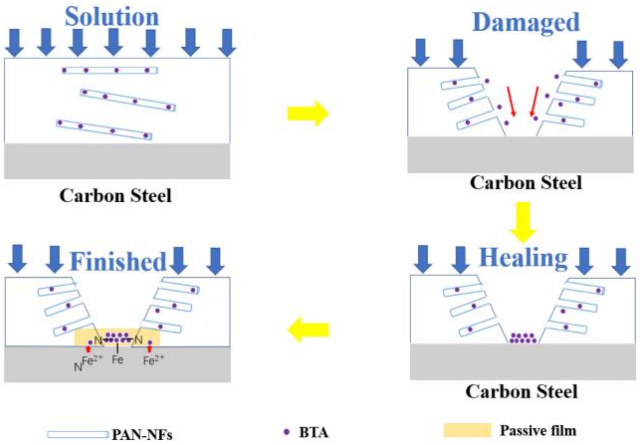

Figure 8 Inhibition mechanism of epoxy coating containing PAN-NFs/BTA [72]

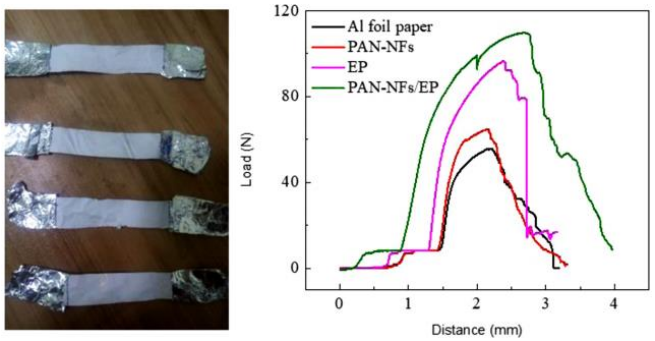

Figure 9 Tensile testing of different samples (a) test samples (b) tensile results [72]

3-2 Self-healing performance of graphene oxide incorporated nanofibers in corrosion protection

Carbon-based nanomaterials such as graphene oxide can be employed to create an excellent anti-corrosion system [73] [74]. The anticorrosion performance of polyaniline nanofibers (PANI) modified graphene oxide (GO) in epoxy resin was investigated by Hayatgheib et al. [74] for the corrosion protection of soft steel. In this research, PANI nanofibers were functionalized with GO sheets by three different methods. In the first method, polymerization of aniline on GO was performed in the presence of an initiator (ammonium persulfate). In the second method, polymerization of aniline on GO was performed in the presence of surfactant (sodium-dodecyl sulfate) and initiator. In the third method, the polymerization process was done in the absence of both initiator and surfactant. GO-modified epoxy and GO-PANI-modified epoxy nanocomposites were constructed through a wet transfer method. Results showed that the epoxy coating containing GO-PANI synthesized by the first method shows the best results because of the formation of the emeraldine salt (ES) form of PANI on the GO sheets.

3-3 Self-healing cellulose nanofiber in corrosion protection

A bio mimic network structure is useful for the expansion of the self-healing coatings because it provides many more healing agents [75] [76] [77] network can be reached from a biodegradable polymer such as cellulose nanofiber, because of the flexibility and the environmental appeal [47]. Cellulose is one of the most promising nature-derived nanomaterials owing to its supernatural mechanical properties incorporated with its sustainable nature [78]. The abundance of OH groups on the surface of cellulose aids the formation of hydrogen bonds, causing the cellulose chains to assemble in highly ordered structures, which in turn results in its extraordinary mechanical properties [76]. Studies have shown that using this system, the cellulose nanofiber networks acted well as a pathway to releasing the corrosion inhibitor [80]. Vijayan et al. [78] investigated the self-healing capability of the cellulose nanofibers. In this research, epoxy monomer and amine curing agents were immobilized on cellulose nanofibers (CNF). The electron microscopy (SEM) images Obtained of the epoxy-immobilized CNF (EiCNF) and amine curing agent immobilized CNF (AiCNF). The likely mechanism and nature of interaction between the EiCNF and AiCNF was explored in this study. They found that only physical interaction exists between epoxy monomer and CNF. That was while chemical interaction was observed between the amine curing agent and CNF. The self-healing ability of epoxy coating incorporated in both EiCNF and AiCNF was demonstrated via a preliminary investigation. The self-healing mechanism designed by Vijayan and co-workers is shown in Figure 9.

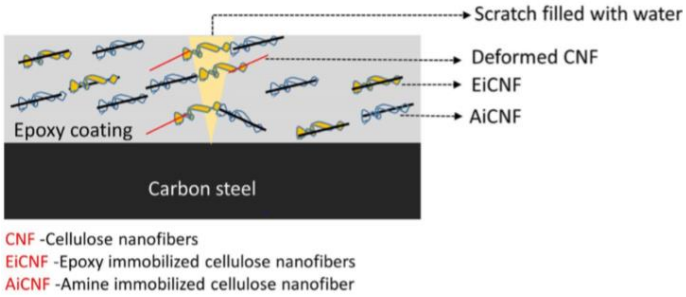

Figure 10 Schematic diagram showing the self-healing mechanism in epoxy/EiCNF/AiCNF coating [78]

They concluded that the dual healing agents supported by CNF can improve the self-healing ability of epoxy coatings. The electro-spinning method was used to fabricate cellulose acetate (CA) nanofibers and depositing on stainless steel plates [81]. In this research, dip-coating was used for coating the composite of hydroxyapatite (HAP) nanoparticles and chitosan (CHI). Biocompatible CA/HAP/CHI-coated metallic implants can be very influential in the long-term stability of biomedical applications. Deposition of cellulose acetate films doped with amoxicillin on the surface of AA2024-T3 aluminum alloy is another reported work in this area [82]. The corrosion protection in 0.05 M NaCl was assessed, and the results showed that the doping of the cellulose acetate film with amoxicillin yielded a remarkable increase in the high-frequency resistance and a reduction in the capacitance of the material. Another study introduced a novel self-healing coating with intrinsic properties in both super-hydrophobicity and pH-responsibility [83]. Oleic acid and epoxy resin were encapsulated in cellulose acetate nanofibers using an electrospinning process, followed by a layer of epoxy coating modified with both polydimethylsiloxane and SiO_2 nanoparticles. They reported that the prepared core-shell fibers/epoxy coating had a static contact angle of 157.3 ± 3◦ with sliding angle of 3.5 ± 0.5◦. It was concluded from the electrochemical impedance spectroscopy that the self-healing rate of the scratched core-shell fibers/epoxy coating was 55.65 and 87.10 $k\Omega cm^2\ d^{-1}$ after 4 and 12 days soaking in the 3.5 wt% NaCl solution with pH = 12.0 and 4.0, respectively.

Yoshimoto et al. [81] developed a polymer coating binding alginates and multivalent cations. The studied coating used cellulose nanofibers (CNF) of 1% to create pathways for the corrosion inhibitors sodium alginate (Alg) and calcium nitrite (CN). The mentioned pathways allowed the release of Alg and calcium nitrite into the damaged areas for corrosion protection. The results showed that the combination of calcium nitride and cellulose nanofiber layer formed a coating of 8% CN layer and 5% Alg layer with CNF that presented fascinating self-healing properties.

Cellulose nanofibers (CNFs) were used for the stimulation of self-healing behaviour of Ultra High-Performance Concretes (UHPCs) [88]. To evaluate the mechanical recovery after self-healing, the flexural test on 4-point bending on 30 mm-thick and 100 mm wide beam specimens was performed. They also carried out a double-edge wedge Splitting test to identify the tensile stress crack-opening response. The presence of cellulose nanofibers enhanced the self-healing efficiency of Ultra-High-Performance Concretes, since for the same crack width value and same healing period (1, 3, or 6 months), the specimens with cellulose nanofibers reached higher crack sealing rates in comparison with those without nano-additives. Double network ionic hydrogels were concurrently introduced by Abouzeid et al. [89]. The results demonstrated that the incorporation of borax provided a superabsorbent combination to the polyacrylamide/ dicarboxylic cellulose nanofiber hydrogels (without borax), with the equilibrium water absorption rate enhanced from 552 to 1800% after 42 h. A technique for stabilizing liquid metal emulsions applying cationic cellulose nanofibers (CCNFs) to encapsulate liquid metal droplets via strong electrostatic attraction with liquid metal was developed by Wu et al. [90].

A hierarchically core–shell structure construction method was proposed by Cao et al. [89] to increase the capacitance storage of cellulose-based electrodes using the homogeneous carbon nanotubes scattering in 2,2,6,6-tetramethylpiperidin-1-yloxy-oxidized cellulose nanofibers and an easygoing in-place polymerization of manganese dioxide (MnO2) and polyaniline (PANI).

The research of Liu et al. [91] developed a technique for preparing a dual cross-linked hydrogel network by combining chemical and physical procedures. In this research, carboxylated cellulose nanofibers (CNF-C) and tannic acid (TA) were gathered into a borax-polyvinyl alcohol (PVA) matrix, followed by the incorporation of metal cations (Al3+) to prepare PVA/CNF-C composite hydrogel. The results demonstrated that The PVA-TA@CNF-C-Borax-Al3+ hydrogel builds a multi-crosslinked 3D network through dynamic borate ester bonds between PVA and borax, coordination bonds between TA and Al3+, and hydrogen bonds from CNF, endowing the hydrogel with superior mechanical properties.

In the work done by Xiong et al. [92], a photothermal self-healing DN-M-P hydrogel presenting excellent toughness and superior antifouling performance was fabricated. In this research, polyhexamethylene-biguanide (PHMB) and MXene are introduced into the carboxylated cellulose nanofibers (CNF) reinforced polyvinyl alcohol (PVA) hydrogel to reach an ultra-high toughness antifouling hydrogel with self-healing properties. The results demonstrated that the prepared hydrogel blends the bactericidal influence of MXene and PHMB as well as the anti-adhesion performance brought by hydrophilicity, rendering superior antifouling capability, with 0.03 % adhesion rates of viable bacteria and 0 % adhesion rates of both algae and protein.

By incorporating waterborne polyurethane with thiol-functionalized cellulose nanofiber, Zhu et al. [93] synthesized a novel 3D printable, eco-friendly waterborne polyurethane composite (CSPU). The prepared CSPU composite samples demonstrated outstanding mechanical strength and ductility, indicating an elongation at break of up to 1300 % and a stress of 5.5 MPa. Moreover, the composite achieves efficient self-healing after UV irradiation, with both strain and stress recovery reaching nearly 100 % within 1.5 h.

4 Self-healing performance of nanofibers in polymeric composite materials

4-1 Co--electrospinning nanofiber for self-healing composites

After over four decades of intensive research, advanced composites made of high-modulus fibers in the compliant polymeric matrix have appeared as lightweight structural materials of choice for many aerospace and aeronautical applications because of their extraordinary advantages superior to traditional metallic materials, including the high specific strength and stiffness, high processability, and corrosion resistance [90]. To date, much research in composite materials has been focused on further exploitation of the existing properties to satisfy the ever-growing demands in aggressive structural applications. A few works have concentrated on the exploration of innovative material functions, including damage self-repairing and stiffness/strength self-recovery in these engineering materials. Self-healing systems are capable of healing damaged epoxy composites and could increase the lifetime of the structural materials. Many researchers have focused on the encapsulation of epoxy resin and its curing agent in dual capsule healing systems[94] [95] [96] [97] [98] [99]. Mitchell and Keller [100] fabricated electrospun core-shell fibers suitable for self-healing of composites by changing process parameters such as interfacial tension and viscosity. Coaxial solution spinning was applied for the incorporation of epoxy into a poly (vinyl alcohol) (PVA) shell which was associated with beaded morphology. Based on experimental results, a concentration of 8.5% w/w PVA in a combined ethanol and water solution (water: EtOH = 1:0.15) yielded a PVA solution that had the suitable interfacial tension and viscosity characteristics for coaxial solution spinning. Park et al [31] applied electrospinning to fabricate the self-healing core-shell nanofibers. They used a two-coaxial nozzle system for co-electrospinning. The core was filled with either part A (resin) or part B (hardener) of a siloxane-based healing agent and, a polyvinylpyrrolidone (PVP) solution, produced using dimethylformamide (DMF), used to form the shell. The co-electrospun nanofibers were embedded within a polymeric matrix to form a composite.

It is known that beads are created on electrospun nanofibers when the electrical conductivity of the solution is too low to allow for the stretching of the polymer jet [101] [102]. Thus, Park et al were able to fabricate bead-on-string nanofibers, such that the outer diameters of the nanofibers and beads were of the order of hundreds of nanometers and several micrometers, respectively [31]. Muruzabal et al. [103] developed a nano-vascular network using electrospun sacrificial nanofibers for self-healing properties (Figure 10). They examined the flexural properties of a bulk material produced by this system. The flexural properties of the nanocomposite are compared with those of the neat matrix. Epoxy resins with nano-vascular networks had a volume fraction of nanochannels of 6-9 vol%. The diameter of channels ranged from 250-830nm. The results show a significant improvement in mechanical properties compared with the micro-capsules containing the same amount of healing agent.

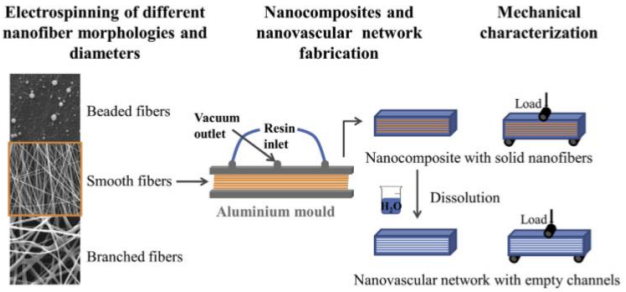

Figure 11 Schematic drawing of the methodology, including the optimization of the electrospinning process, the fabrication of the nanocomposite and the nano-vascular network, and the flexural testing on the nanocomposite and the nano-vascular network [103].

Yoon et al [104] fabricated bulk PAN and core-shell (PAN-resin) nanofiber mats to study the crack propagation, initiated from an initial notch into a self-healing material under tensile test. These mats were encased into a polydimethylsiloxane matrix to form a composite structure and investigated the inter-laminar fracture toughness properties in case of crack propagation behavior. Based on experimental results, core-shell mats showed lower crack propagation speed (by 10%), but they were not able to be healed and stop the crack growth because of the lack of heat and time. Composite specimens showed more stable crack propagation. A nanofibre network was fabricated via coaxial electrospinning by embedding the healing agent dicyclopentadiene (DCPD) in polyacrylonitrile (PAN) fibers in a study reported by Vintila et al. [105]. They reported that in comparison with other encapsulation systems, filling of anofibres with a healing agent will provide a larger healing area while having no effect on the mechanical properties of the matrix. They added carbon nanotubes as nanofillers to improve the reactivity between DCPD and the epoxydic matrix. Flexural tests revealed that after 48 h, the epoxy resin recovered 84% of its flexural strength, and the composite material recovered 93%.

Investigation conducted by Mao et al. [106] showed that incorporating electro-spun polyacrylonitrile core–shell nanofibers between the layers of carbon fiber reinforced polymer composites enhanced the damage healing ability of samples after being subjected to low-velocity impact up to 80%. A self-warning and self-healing core–shell fiber for developing aggregation-induced emission composite coatings was synthesized by Ji et al. [107]. They reported that the composite coating indicated effective fluorescence in case of cracks in a corrosive environment and the maximum self-healing efficiency of the fiber coating was 94.8 % after soaking for 120 h. Luo et al. [108] prepared a composite with self-healing capabilities, and dye through synergistic hydrogen bonding between oxidized natural rubber (ONR) and cellulose nanofibers (CNFs). They reported that the composite samples indicated improved compatibility with the CNFs filler because of the oxidation of the natural rubber (NR) matrix. The results also showed that in comparison with the ONR, the mechanical strength and toughness of the ONR/CNFs-5 and NR/CNFs-5 composites were enhanced by 37 % and 58 %, and 125.64 % and 48.88 %, respectively. Hassim et al. [109] developed a composite by interlayering core–shell poly(lactic) acid (PLA) nanofibers between the

flax fibers as a preventive and reactive mechanism to matrix damages in the resin-rich zone. They reported that by interlayering the flax fiber laminates with self-healing core–shell nanofibers, the flexural modulus enhanced by 31%. Yu et al. [110] developed a high-performance natural rubber (NR) composite reinforced with redispersed TEMPO-oxidized cellulose nanofibers (TOCN) in combination with sodium lignosulfonate(LS).

5 Summary and future trends

In the current review, the self-healing performance of core-shell electrospun nanofibers by the coaxial method is reviewed and presented according to the applied technology. Most of the reported works have mainly focused on self-healing of polymeric composites and coating structures. Furthermore, most studies apply self-healing agents in core-shell form made by the coaxial electrospinning process. Fabrication of core-shell nanofibers for self-healing performance, and its applications in corrosion protection, application of Polyaniline (PANI) nanofibers in self-healing performance, application of graphene oxide and cellulose nanofibers in corrosion protection, and self-healing performance of nanofibers in polymeric composite materials are the different parts of this review. This study shows how a self-healing composite can be completely recovered by the self-healing nanofiber interlayers after a pre-damage failure. In future works, using piezoelectric components such as PVDF and PAN nanofibers in the bulk of composites can provide the chance of monitoring the healing procedure by signal processing, since it enables the system to act as energy harvesting by generating electricity. Nanofiber-based self-healing approaches involve simple fabrication processes and help the recovery performance and corrosion protection in composites to a large extent. Hence, further study for developing new materials is of prime interest. These studies have shown the merits of nanofiber-based self-healing approaches as an inner healing agent in composite materials.

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