Chapter 10
Fiber-Based Self-Healing Approaches for Corrosion Protection

In this chapter in Sects. 10.1 and 10.2, corrosion protection provided by co-electrospun and emulsion-spun nanofibers (NFs), respectively, is discussed. These NFs are embedded in protective coatings, forming composite materials that are deposited on steel substrates. Upon scratching, these coatings are capable of self-healing, thus protecting the underlying metal from exposure to corrosive environments, as demonstrated by several types of corrosion testing.

10.1 Corrosion Protection Provided by Coatings with Embedded Core-Shell NFs Formed by Co-Electrospinning

Although emulsion electrospinning is among the simplest methods for fabricating core-shell NFs (cf. Sect. 4.3), the process has a significant drawback compared with co-electrospinning in its rate of core formation. The disordered formation of droplets of curing agent in the emulsion as well as the difficulties associated with material selection can interrupt the electrospinning process. Therefore, An et al. (2015) employed co-electrospinning (see Sect. 4.2) to form mats with interwoven NFs containing either resin monomer or curing agent in the cores. They prepared composites using miniscule amounts of the embedded NFs. These composites exhibited outstanding corrosion protection during corrosion tests.

Figure 10.1 illustrates the results of the corrosion test with the pristine polydimethylsiloxane (PDMS) and the self-healing core-shell NF-embedded composite (in PDMS matrix), both deposited on steel substrates. In the core-shell fibers, dimethyl siloxane (DMS) resin monomer or curing agent were in the cores, and polyacrylonitrile (PAN) was used as the shells (cf. Sects. 2.2 and 4.2). All coatings are scratched deeply with crossed lines in X shapes using a razor blade. After scratching, the specimens are left for 48 h. Then, an acetic acid solution is poured onto them.

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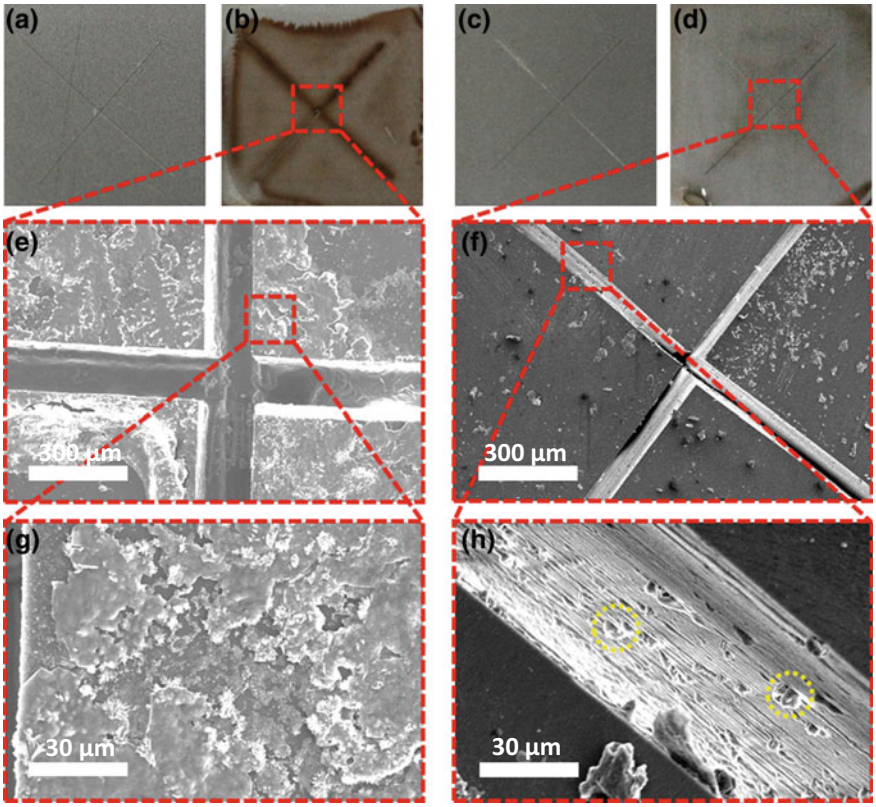

Fig. 10.1 Corrosion test images evaluating RC–PAN (resin or curing agent in the cores, PAN shells) NFs in composite layers on steel substrates. Corrosion test images of (**a**, **b**) deposition time $t_{dep} = 0$ min (scratched metal with pristine PDMS coating), (**c**, **d**) $t_{dep} = 5$ min (scratched metal with NF-composite coating). Specimens shown as time passed: (**a**, **c**) 0 min and (**b**, **d**) 60 min. SEM images of the tested specimens: (**e**, **g**) $t_{dep} = 0$ min and (**f**, **h**) $t_{dep} = 5$ min. Reprinted with permission from An et al. (2015)

Unlike the pristine PDMS case, where significant corrosion occurs (Fig. 10.1b, e and g), the self-healing composite exhibits perfect anticorrosive performance, or rust prevention (Fig. 10.1d, f and h), after the coatings were damaged. Clots, as indicated by yellow dashed circles in Fig. 10.1h, are formed by the polymerization of the released resin monomer in the presence of the released curing agent, which is also evident in the SEM images of the composite in Fig. 10.2.

The results of the tests used to characterize the protective performance of the self-healing composites of Figs. 10.1 and 10.2 are shown in Figs. 10.3 and 10.4. The pristine PDMS and self-healing composites are prepared on steel substrates with different deposition times; all specimens were identically scratched, as depicted in Fig. 10.3a. After 48 h, open bottom cylinders are placed on the specimens with no gaps between the specimen support and the cylinder openings. The cylinders are

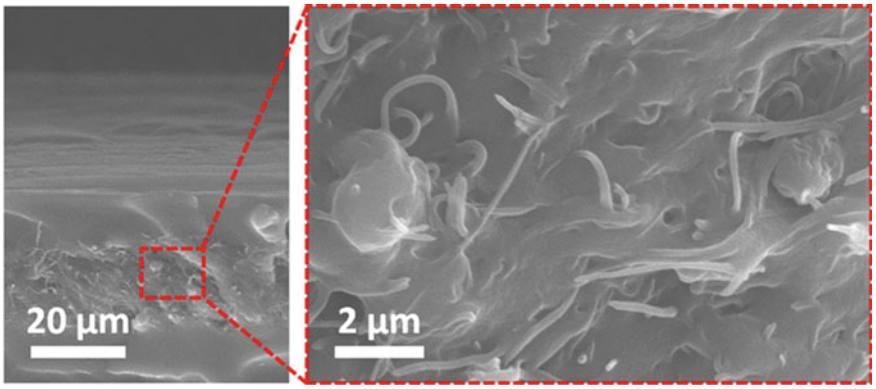

Fig. 10.2 Cross-sectional SEM images of cut composite film with healing agent release visible (NF deposition time $t_{dep} = 120$ min). Reprinted with permission from An et al. (2015)

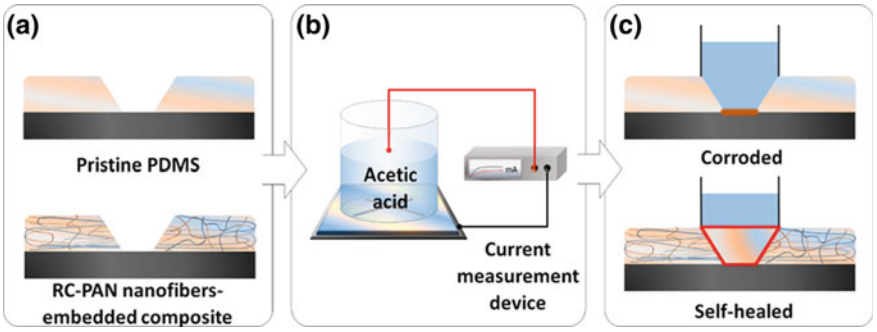

Fig. 10.3 Electrochemical test. **a** Scratched composite films on steel substrates. **b** Schematic of the electrochemical test setup. **c** The tested specimens. Reprinted with permission from An et al. (2015)

filled with acetic acid (Fig. 10.3b). Electric wires from a current-measuring device are directly connected to the electrolyte and the base of the steel substrate. As depicted in Fig. 10.3c, the self-healed specimen forms a protective layer between the steel and the electrolyte. However, the pristine PDMS does not offer this protection, as confirmed through the electrochemical testing and plotted in Fig. 10.4. The pristine PDMS ($t_{dep} = 0$ min) yields an electric current of 10–25 mA, indicating the exposure of the base steel substrate to the electrolyte because of the absence of self-healing in the damaged layer. On the other hand, perfect electrical insulation, demonstrated by the current of ~0 mA, is observed with the damaged and healed self-healing composites with $t_{dep} \geq 30$ min. A non-zero current was detected for $t_{dep} = 5$ and 10 min (not shown). This indicates that $t_{dep} \leq 10$ min is insufficient to create an intact anticorrosive coating containing such NFs, and that $t_{dep} \geq 30$ min is required to fabricate a coating with anticorrosive and electrically insulating properties.

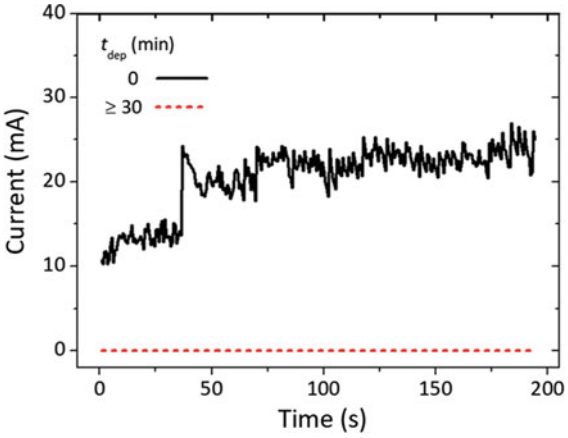

Fig. 10.4 Results of electrochemical test with RC-PAN NF-embedded composite film with different deposition times t_{dep} on steel substrates (the electric current $I \rightarrow 0$ mA for $t_{dep} \geq 30$ min, for which all straight lines are overlaid, indicating complete electrical insulation achieved with the self-healed materials). Reprinted with permission from An et al. (2015)

Park and Braun (2010) fabricated bead-on-the-string NFs using co-electrospinning (cf. Sect. 4.2) with the healing agents (resin monomer and curing agent) encapsulated primarily within capsule-like beads with outer diameter of 2–10 μm. A coating containing these fibers was deposited on cold-rolled steel sheet specimens. To examine the anticorrosion performance of the NF-embedded coating, they pre-notched cracks on the specimen coatings and let them heal for 24 h. Then, they immersed the specimens in salt water for hundreds of hours and analyzed the formation of rust. Significant corrosion had occurred in the control specimen with no self-healing coating. On the other hand, no corrosion was observed in the NF-containing specimen, as the damaged cracks were healed successfully, which protected the underlying metal substrate from the salt water.

10.2 Corrosion Protection Provided by Coatings with Embedded Core-Shell NFs Formed by Emulsion Spinning

Lee et al. (2014a) used the dual-emulsion electrospinning method to simultaneously encapsulate a siloxane-based resin and its curing agent as healing agents within the NF cores (cf. Sect. 4.3). The NF shell was PAN; the self-healing NFs were embedded in a PDMS matrix. The surfaces of steel specimens are coated with the self-healing NF mat. The coatings are then cut with X-shaped scratches (see Fig. 10.5) with a paper knife. The bare steel specimens used as controls are also scratched with X marks. The performance of the self-healing mat is evaluated by the corrosion testing in either 4 wt% NaCl solution (modeling sea water) or acetic acid. The scratched specimens (both coated and unprotected) are submerged into the corrosive media.

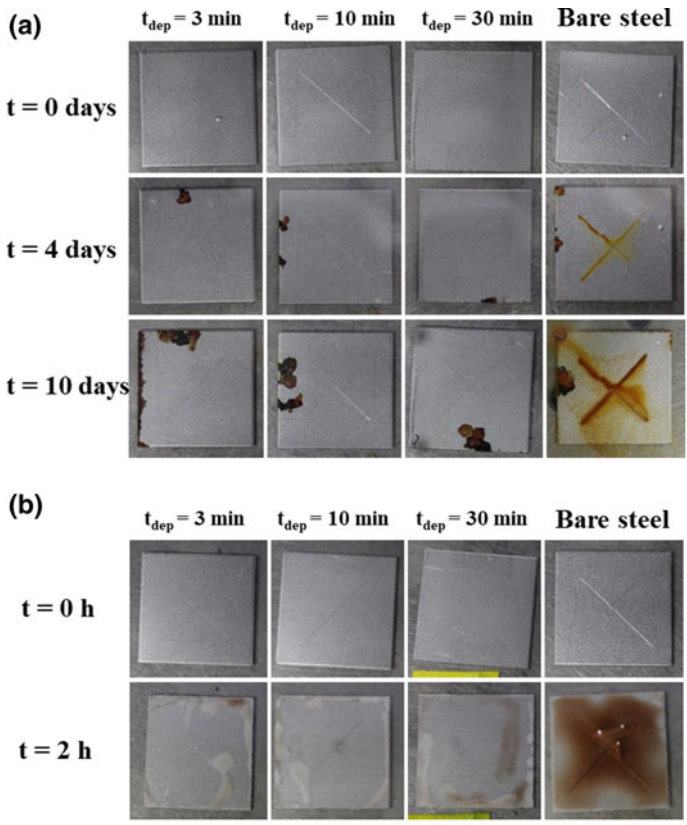

Fig. 10.5 Corrosion testing in **a** NaCl 4 wt% aqueous solution; **b** acetic acid. Reprinted with permission from Lee et al. (2014a)

Figure 10.5a shows the results of the corrosion test in the 4 wt% NaCl solution. In this case the corrosion time scale is a few days. Meanwhile, Fig. 10.5b shows the results of the corrosion tests in acetic acid with the corrosion time scale of a few hours. After the damaged specimens are immersed in the corrosive solutions, the corrosion processes are monitored. The self-healing mats used herein are fabricated with the deposition times of $t_{dep} = 3$, 10, and 30 min. As is seen in Fig. 10.5, none of the self-healing specimens are corroded near the X- shaped cuts; see the photographs in the first three columns of the figure. The corrosion observed near the edges of the substrate arises from the imperfection of the protective mat at the specimen edges. The damaged X-shaped regions show no corrosion, indicating the rapid self-healing provided by the NF mat. All three mats with different deposition times (i.e., $t_{dep} = 3$, 10, and 30 min) completely prevent corrosion. This indicates that exceedingly thick coatings with such self-healing NFs may be unnecessary to protect the steel surface;

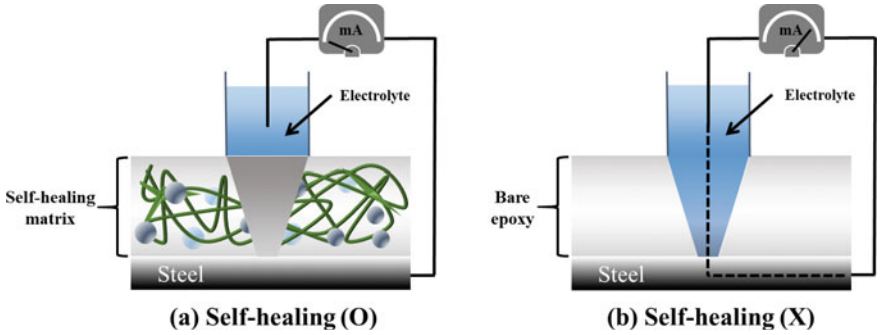

Fig. 10.6 Schematic of electrochemical test. **a** Steel protected by self-healing epoxy coating (with embedded NFs containing curing agent in the cores, and embedded microdroplets with resin monomer). **b** Steel without self-healing coating, the control case. This experiment is an electrochemical analog of SVET. Reprinted with permission from Lee et al. (2014b)

a thin core-shell self-healing mat with $t_{dep} = 3$ min is sufficient for protecting the steel surface from corrosion.

Lee et al. (2014b) employed a slightly different approach to fabricate self-healing core-shell NF-embedded composites. They formed a hybrid epoxy-matrix composite with embedded core-shell NFs with curing agent in the fiber cores and DMS resin monomer in microdroplets embedded in the epoxy matrix (cf. Sect. 4.3). To analyze the corrosion protection provided by such a self-healing composite, they performed electrochemical tests. They placed scratched metal substrates with and without the self-healing coatings in salt water or acetic acid and measured the electric currents across the substrates.

To test the self-healing performance of such a hybrid composite, an electrochemical device depicted in Fig. 10.6 is used; it is an electrochemical analog of the scanning vibrating electrode technique (SVET).

The self-healing composite coatings are prepared on stainless steel substrates. The substrate and coating are in contact with an electrolyte layer and thus included in the electric circuit; cf. Fig. 10.6. However, for an intact coating, no electric current should pass through the circuit, because the coating is an insulator. Once a cut is introduced to the coating, the stainless steel at the bottom is exposed to the electrolyte and an electric current passes through the circuit. Simultaneously, the resin monomer and curing agent liquids are released from the fractured droplets and NF cores embedded in the damaged area of the composite. Once the resin and curing agent come in contact, the resin crosslinks and solidifies (see Sect. 2.2), which manifests the self-healing of the coating and stops the current again.

The coatings are cut by a razor and left for a 48 h resting time to allow crosslinking and polymerization of the resin and curing agent. Then the electric current is measured, as described above in conjunction with Fig. 10.6. Figure 10.7 shows the measured electric current versus time. For the non-self-healing coatings (i.e., epoxy matrix with only resin droplets being embedded), an electric current of approxi-

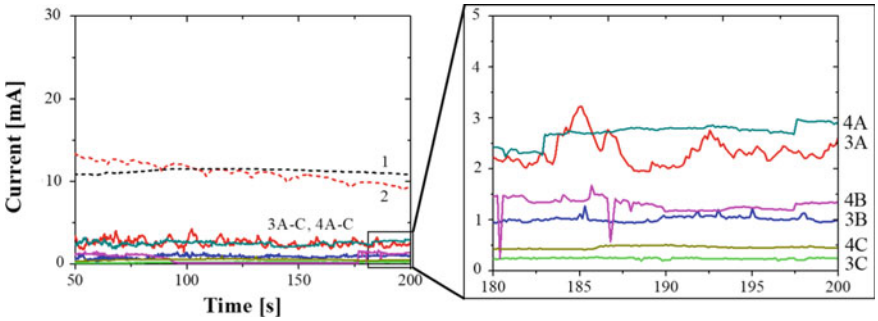

Fig. 10.7 Electric current. 1: Epoxy (non-self-healing). 2: Resin–epoxy (5 wt%) (no self-healing). 3A: curing agent NF mat with $t_{dep} = 3$ min, matrix-5. 3B: curing agent NF mat with $t_{dep} = 3$ min, matrix-10, 3C: curing agent NF mat with $t_{dep} = 3$ min, matrix-20. 4A: curing agent NF mat with $t_{dep} = 10$ min, matrix-5. 4B: curing agent NF mat with $t_{dep} = 10$ min, matrix-10. 4C: curing agent NF mat with $t_{dep} = 10$ min, matrix-20. The epoxy matrices containing 5, 10, and 20 wt% resin emulsion with respect to the weight of epoxy are denoted as matrix-5, -10 and -20, respectively. Time is counted from the moment when measurements are started. Reprinted with permission from Lee et al. (2014b)

mately 10 mA is measured for 200 s. This clearly shows that these coatings have not self-healed, as expected. On the other hand, the self-healing coatings (i.e., epoxy matrices-5, -10, and -20 with the embedded NFs deposited for $t_{dep} = 3$ and 10 min, in addition to the embedded microdroplets containing resin monomer) show electric currents below 2.5 mA (comparable to the noise level) demonstrating insulating properties. This means that these coatings undergo self-healing, which occurs with the coatings containing fibers deposited either for $t_{dep} = 3$ or 10 min, indicating that the deposition time does not significantly affect self-healing performance. This means that long deposition times for curing agent-containing NFs are not necessary, which is favorable from a manufacturing perspective. The signals below the noise level also do not allow a reliable distinction of the effects of the resin contents (i.e., the matrix-5 versus matrix-20 cases), but imply that larger resin contents relative to the amount of curing agent are preferable to maximize the self-healing performance.

References

An S, Liou M, Song KY, Jo HS, Lee MW, Al-Deyab SS, Yarin AL, Yoon SS (2015) Highly flexible transparent self-healing composite based on electrospun core–shell nanofibers produced by coaxial electrospinning for anti-corrosion and electrical insulation. Nanoscale 7:17778–17785

Lee MW, An S, Lee C, Liou M, Yarin AL, Yoon SS (2014a) Self-healing transparent core–shell nanofiber coatings for anti-corrosive protection. J Mater Chem A 2:7045–7053

Lee MW, An S, Lee C, Liou M, Yarin AL, Yoon SS (2014b) Hybrid self-healing matrix using core–shell nanofibers and capsuleless microdroplets. ACS Appl Mater Interfaces 6:10461–10468

Park JH, Braun PV (2010) Coaxial electrospinning of self-healing coatings. Adv Mater 22:496–499