Core-shell nanofibers for developing self-healing materials: Recent progress and future directions

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Abstract

The knowledge of self-healing was developed to ensure more durable and reliable engineering materials. Healing agent encapsulation has shown to be one of the most promising approaches in self-healing technology. The healing agents were encapsulated within micro/nanocapsules, micro/nanofibers, and vascular-based networks. Among the methods, using core-shell nanofibers showed a compromising potential for the development of self-healing nanofibers with the minimum drawbacks and limitations. The aim of the present paper is to report the recent contributions on the recent progress of self-healing materials using core-shell nanofibers to provide insights for the further development of self-healing polymeric materials both in academic research and scalable fabrication of polymeric parts in the industries.

1. INTRODUCTION

Service life extension, maintenance cost reduction, and durable and reliable improvement, to name just a few, can be accounted as the merits that have been drawn researchers' interest toward self-healing technology. Inspired by natural biological systems, this technology has a great potential to be employed in high-tech industries, eg, aerospace, even with a higher confidence factor. Reversible cross-links, shape memory effect, nanoparticles, and healing agent release are some proposed methods for fabrications of the smart materials with self-healing ability, among which the latter has gained the most attention. Figure **1** presents the strategies for inducing self-healing ability in the polymeric materials.[1]

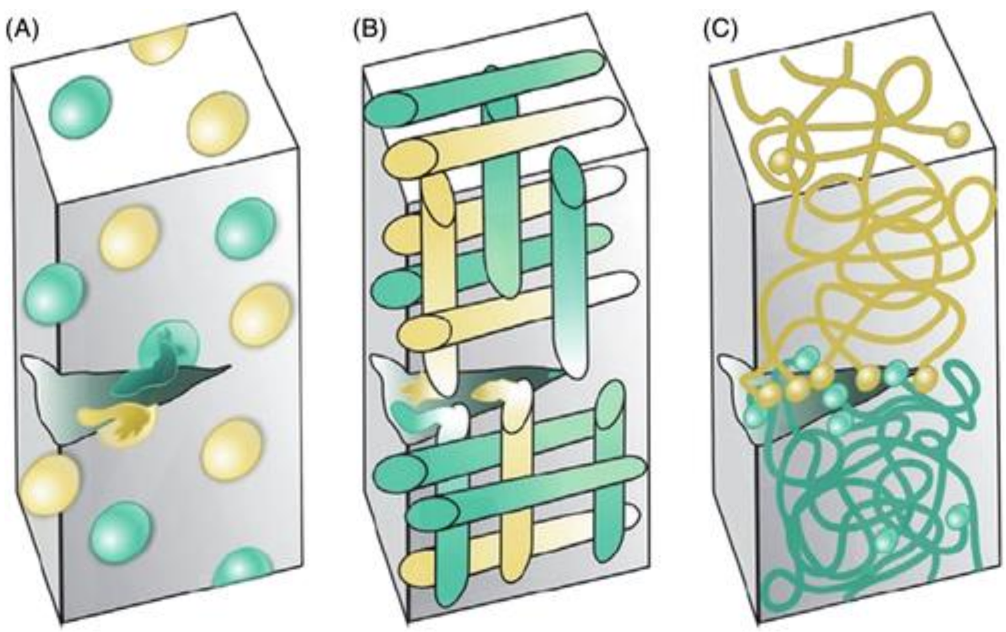

Figure 1: The strategies for the fabrication of self-healing polymeric materials. A, Capsule-based system; B, vascular-based system; and C, intrinsic method. Reprinted with permission from Döhler et al[1]

The first documented research on the materials with self-repairing capability through healing agent release was referred to White et al.**2** This pioneering research opened opportunities to eager scientists looking for more reliable and durable materials. Incorporating healing agents into microcapsules and hollow fibers are known as two approaches for developing autonomous self-healable polymers. These healing-agent containers have to be dispersed within the material[3] to attain efficient healing. The critical factors in an efficient healing process are the delivery of sufficient healing agent at the damaged site and multiple repeated healing, which are things that the microcapsules lack this abilities.[4] The concept of repeated healing is attainable through incorporating surplus healing agents within the target material to ensure several healings, as proposed by Dry.[5] This group and also Motuku et al[6] used tubular channels with large diameters (in the millimeter order) to contain an excess of healing agents. However, such large-diameter hollow fibers negatively influenced on the mechanical behavior of the composite, since the size of hollow containers were significantly larger than fibrous reinforcements. To overcome such drawbacks, Trask et al[7, 8] and Williams et al[9] embedded healing agent-filled hollow glass fibers (50% hollowness) within the epoxy composites reinforced by glass fiber and carbon fiber, in which healing agent containers were substantially thinner (30-100 μm in diameter) than earlier works. This led to the fabrication of composites with recoverable initial strength. Furthermore, the inverse relationship between the size of fibrous containers and composite strength was demonstrated by Kousourakis and Mouritz.[10]

Since 2010, the massive bulk of efforts have been carried out to encapsulate healing agents into small hollow fibers, pioneering by Park and his collaborators,[11] to address the problems using microcapsules and hollow microfibers. The current paper aims to review the recent researches and advances on the fabrication of self-healing materials using core-shell fibers, in the range of 100 to 2000 nm, contacting healing agents. It would be worthy to note that the electrospinning technique is known as the easiest and most economical method for preparation of the nanofibers, which confirms a potential structure of the materials for the wide range of applications such as tissue engineering,[12] filtration applications,[13] improvements of the composite's mechanical properties,[14-17] and so on. Several parameters control the electrospinning process and affect the quality of the nanofibers and their characteristics, such as diameter and porosity. These parameters are classified as material and solution parameters (ie, viscosity, conductivity, and dielectric constant), processing parameters (ie, applied voltage, solution feed rate, and tip to needle distance), and environmental conditions (ie, temperature and humidity).[18, 19]

2. SELF-HEALING NEAT POLYMERS

To study repeated self-healing ability in an epoxy matrix, Zanjani et al employed triaxial electrospinning. Dicyclopentadiene (DCPD) and its catalyst, as well as epoxy and amine (as an epoxy curing agent), were used as healing agents. These investigations confirmed the effectiveness of nanofibrous channels incomplete or repeated healing process.[20] Self-healable polyethylene terephthalate[21] and polydimetyl siloxane[22] polymers embedded by healing agent encapsulated in core-shell fibers. In that work, the healing material was encapsulated in the fibers using the solution-blown method. Although the solution-blown technique offers a scalable method for preparation core-shell fiber, the fibers were in the range of nano and micro. The static and fatigue tests were utilized to show self-healing behavior of such systems. Recently, Cuvellier and colleagues encapsulated epoxy and amine monomer within core-shell nanofibers via coaxial electrospinning,[23] while they firstly investigated the effect of healing agent types on the healing process.[24] Their results revealed that incorporation of the prepared nanofibers within the epoxy-based matrix did not have any unfavorable impacts on the flexural properties of the epoxy matrix, while the nanofibers embedment substantially improved the Mode II delamination resistance of the epoxy and confirmed the self-healing ability of the composite via Mode I fracture assessments.[23]

3. SELF-HEALING IN POLYMERIC COATINGS

Park et al fabricated electrospun core-shell nanofibers including dimethylpolysiloxane (as a healing agent) and polyvinylpyrrolidone (PVP) (as shell material) using coaxial electrospinning and dispersed the fibrous channels in acrylated polyurethane coated on the steel panels as substrates. This group proved the effectiveness of the electrospinning technique by the healing agent encapsulation within nanoscale hollow fibers.[11] In other contributions, the self-healing coatings using core-shell nanofibers were prepared via emulsion electrospinning[25], [26] and coaxial electrospinning.[27] Self-healing properties of epoxy-based[25] and silicone-based coatings[26], [27] were studied by this group. Figure **2** schematically presents the encapsulation of healing agent via emulsion electrospinning and development of epoxy-based coating.

Figure 2: Preparation of core-shell nanofiber via emulsion electrospinning method for fabrication of a self-healing epoxy-based coating. Adapted with permission from Lee et al[25]

4. SELF-HEALING IN LAMINATED POLYMER MATRIX COMPOSITE

Reinforcement effects of nanofibers were reported in previous researches, upon the incorporation of nanofibers between reinforcement layers of laminated polymer matrix composites[28] and adhesives[29], [30] via a scalable, continuous roll-to-roll process. More interestingly, it has been also shown that core-shell nanofibrous mats containing healing materials can play a role as a healing agent and mechanical reinforcement in laminated composites.[31] Self-healing fiber reinforced polymer composite, using core-shell nanofibers, was firstly introduced by Sinha-Ray and his colleagues in 2012.[32] This research group employed emulsion electrospinning method to encapsulate DCPD and isophorone diisocyanate within the micro/nanofibers, in which polyacrylonitrile (PAN) was employed to form the shell of the fibers. Subsequently, the healing ability of the prepared core-shell nanofibers was assessed via embedment of the electrospun fibers between the third and fourth layers of a conventional carbon/epoxy composite. The fabricated composite was fractured and allowed to release the healing materials and cure for 24 hours. The resin-rich layer containing the nanofibers was also observed by the microscopic method to approve the healing material release and solidification.

Wu and his coworkers utilized the coaxial electrospinning to encapsulate DCPD in PAN nanofibers in 2013.[33] The nanofibers were deposited between the carbon layers of a composite, while the Grubbs' catalyst was dispersed within the epoxy matrix before the composite preparation. The composites were fabricated by vacuum-assisted resin transfer molding (VARTM) method. The three-point bending test was carried out to assess the self-healing performance of the hybrid composites. Their results revealed approximately 100% stiffness recovery after artificial damage and healing process. The fractographic assessment, by scanning electron microscopy, was also utilized to study the healing action in that interlayer, containing nanofibers, and confirmed the release of healing agent and solidification after encountering with Grubbs' catalyst.

The comprehensive researches were carried out on the development of self-healing composite using nanofibers since 2016-2018.[34-36] Figure **3**A schematically displays the concept of self-healing, and Figure **3**B presents the FESEM images of a complete healing process in a laminated-reinforced composite, including nanofiber rupture, healing agent release, and healing agent solidification. This group firstly prepared hollow PAN nanofibers including epoxy and amine-based curing agent[4] and layered them between all five interlayers of a carbon/epoxy composites. They finally assessed both mechanical properties and self-healing performance of the prepared composite. In the next contribution, epoxy and an amine-based curing agent were encapsulated into the nanofiber with poly (styrene-co-acrylonitrile) (SAN) as shell.[35] They found that, compared with PAN, SAN led to a higher encapsulation content and yield; however, the higher healing agent content did not enhance the self-healing performance. Figure **3** illustrates the morphology of the electrospun core-shell nanofibers on the surface of carbon fibers incorporated into the carbon/epoxy composites. In the later work, they employed poly(methyl methacrylate) (PMMA) shell to encapsulate epoxy resin and the amine-based curing agent. This combination demonstrated higher self-healing performance. It was reported that in the core-shell nanofiber-reinforced composites, the nanofiber diameter possesses the significant influence on enhancing the out-of-plane mechanical characteristics of the fiber reinforced composites, whereas the nanofibers' strain at break dictates the tensile properties of the composites and self-healing ability. Furthermore, they deduced that the core-shell nanofiber incorporation did not remarkably influence the impact properties of the hybrid composites.

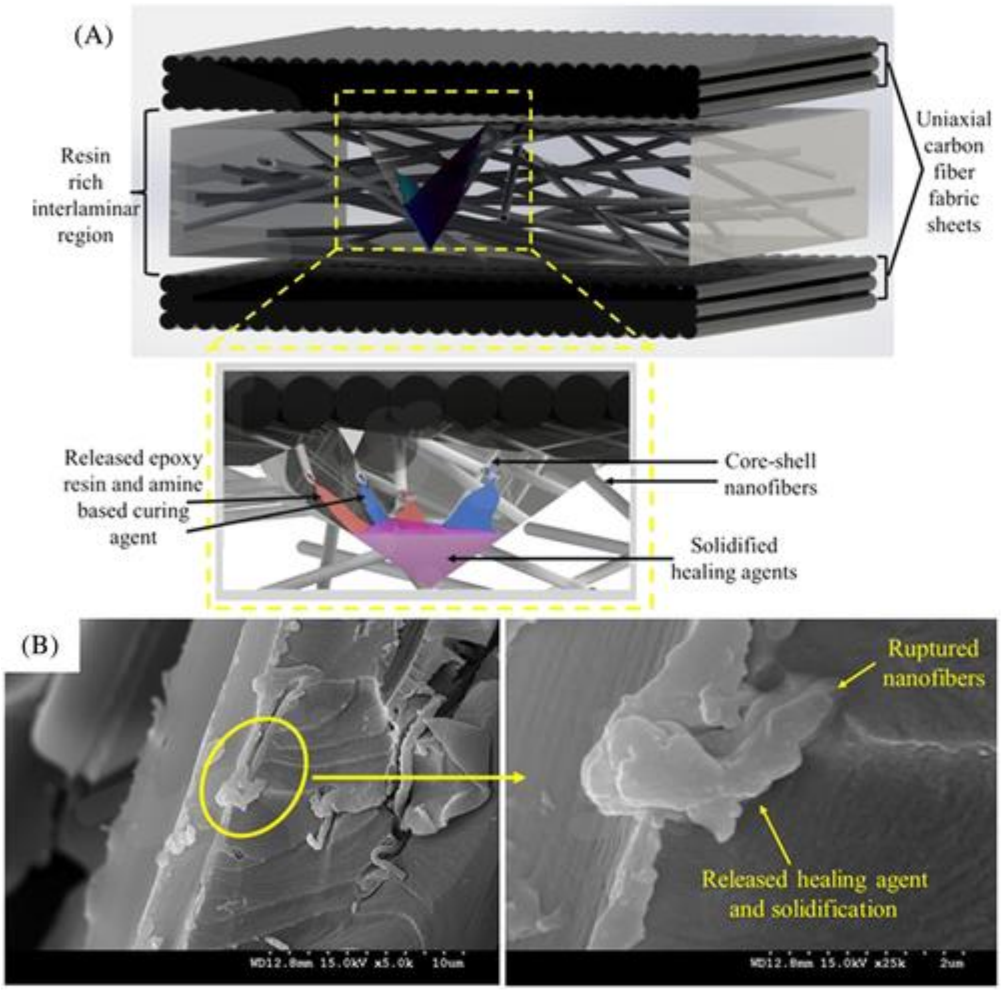

Figure 3: A, Core-shell nanofiber role for inducing self-healing ability in the laminated composites. B, FESEM images of releasing healing agent from ruptured core-shell nanofiber in a carbon/epoxy composite. Adapted with permission from Neisiany et al[36]

Zanjani et al**37** developed a self-healing glass fiber/epoxy composite by interleaving core-shell nanofibers containing healing agent between the glass fiber layers. They also utilized epoxy resin as a healing material and PMMA as the outer shell. Using the inner shell extended the healing lifetime functionality. In order to examine the self-healing performance of the prepared composites, these researchers utilized flexural tests besides the fractographical analyses. The results proved the increase in self-healing and mechanical performances upon the incorporation of triaxial nanofibers into the glass fibers/epoxy composites.

5. CONCLUSIONS AND INSIGHT FOR FUTURE

Encapsulating healing agent into core-shell fibers with a diameter in the range of 200 to 2000 nm via emulsion and coaxial electrospinning and solution-blown technique offers several benefits when compared with previous encapsulation methods. Furthermore, due to the cost-efficiency of these methods, they can be employed in the scalable fabrication of self-healing polymeric material. However, there is still a lot of work to extend the self-healing knowledge to materials such as hydrogels and aerogels, self-healing biomedical materials, and even concrete. In the case of polymeric coatings in which capsule-based healing agent systems are more efficient, the door is still open to working on the fabrication of nanocapsules containing healing agents, through manipulating processing parameters.

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CONFLICT OF INTEREST
The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS
All the authors are involved in the conceptualization, ideation, and visualization of the paper. All the authors contributed to the writing and editing of the manuscript.

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