Coaxial Electrospinning of Self-Healing Coatings

By *Jeong-Ho Park* and *Paul V. Braun**

The concept of autonomic materials, such as materials which self-repair without external intervention, is a promising alternative to damage tolerant design. Such materials have the ability to repair themselves without external intervention and recover their functionalities by using the resources inherently embedded within or available to them in the local environment. This is analogous to the biological healing process in living organisms where damage to organs and tissues can be repaired by cellular activity fueled by the nutrients available in the circulatory system. An early example of a synthetic system which self-repaired was demonstrated in 2001; this system consisted of a structural bulk epoxy which contains a microencapsulated healing agent and a suspended solid-phase catalyst.[1] Subsequently, many different types of self-healing systems have been developed including those based on microcapsule dispersions,[1–4] reversible chemistries,[5,6] particle segregation,[7] microvascular networks,[8] and hollow fibers.[9,10]

Self-healing coatings are a specific subfield of autonomic materials of particular commercial and scientific interest. There is substantial interest in coating systems that incorporate self-healing technologies to provide autonomic protection of the underlying substrate from environmental exposure after a damage event. Recently, Kumar et al. incorporated microencapsulated tung oil and spar varnish into a commercially available epoxy primer. When a coating containing these microcapsules was damaged, the capsule contents were released into the damaged region and some level of healing was observed.[11] Cho et al. employed a microcapsule-based system to formulate a siloxane-based self-healing coating that demonstrated self-repair and complete protection of the underlying substrate from corrosion, even when damaged under aqueous conditions. In this work, oligomeric reactive siloxanes and a tin catalyst were individually encapsulated and incorporated into various epoxy-based coating systems, which were subsequently coated onto cold-rolled steel. Damage to the coating released the siloxane and catalyst into the damaged region; the siloxane then cured, protecting the steel from corrosion.[12]

Here, we propose a new approach to self-healing polymer coating systems based on an electrospun coaxial healing agent and demonstrate the effectiveness of such an approach to add autonomic functionality to polymer coatings. Using this approach, liquid materials, such as a healing agent(s) or catalyst–solvent mixture(s), can be encapsulated into a core–shell bead-on-string morphology and electrospun onto a substrate. One major advantage of this process is that it utilizes purely physical forces to form the core/sheath structure, thus overcoming the rather serious limitations exhibited by methods that require a minimum emulsion stability for chemical reactions to take place and hold the capsule together.[13,14] This feature makes it suitable for processing a broader variety of materials for self-healing. Another advantage of this simple one-step coaxial electrospinning encapsulation method is the inherent flexibility in controlling the diameter of the microcapsules and connecting ligaments from the micro- to nanometer scales. Finally, electrospinning is both a high throughput and selective area technique. Thus, the self-healing functionality can be selectively added to large area substrates in a continuous process under rather mild conditions.

Figure 1a presents a schematic illustration of the system for electrospinning the self-healing coating system. It is similar to a conventional electrospinning setup except for the use of a spinneret containing two coaxial capillaries.[15] In a typical procedure, two viscous liquids are simultaneously fed through the inner and outer capillaries, respectively. If the proper combination of liquids and operation conditions are satisfied, a layered Taylor cone can be developed and a coaxial jet can be formed when a high voltage is applied to the outer metallic capillary.[13,15–17] The electro-hydro-dynamic forces smoothly stretch the fluid interface to generate coaxial fibers due to the electrostatic repulsion between the accumulated surface charges. A two-part healing agent system was electrospun in two steps onto various substrates, a steel substrate being the most useful experimentally. The electrospun fibers, randomly oriented on the surface, contained either part A or part B liquid polysiloxane precursors (Dow Corning 3-6575) encapsulated in a poly(vinylpyrrolidone) (PVP) sheath. As shown in Figure 2, the liquid healing agent is completely encapsulated in beads that are randomly distributed along polymer nanofibers. The as-spun beads exhibit a broad distribution from 2 to 10 μm (Fig. 2a). In this study, a low viscosity, two-part polysiloxane system was chosen as for self-healing chemistry due to its physical stability over a wide temperature range (-45–150 °C), fast cure at room temperature (5–24 h) and low viscosity (750 cP), which is important for electrospinning. The capsules were quite susceptible to mechanical damage as can be observed in Figure 2b, where an electrospun capsule mat was scribed with a razor blade. This is important; successful self-healing requires the capsules to rupture upon a damage event. To optically determine the presence of part A and part B siloxane precursors in the self-healing structure, fluorescent dyes were added to the encapsulated healing agents and imaged (Fig. 2c). This enabled visualization that appropriate quantities of the part A and part B system were electrospun, and that they were uniformly distributed across the substrate. The red (Rhodamine B) and green (Coumarin 6) regions correspond to encapsulated part A

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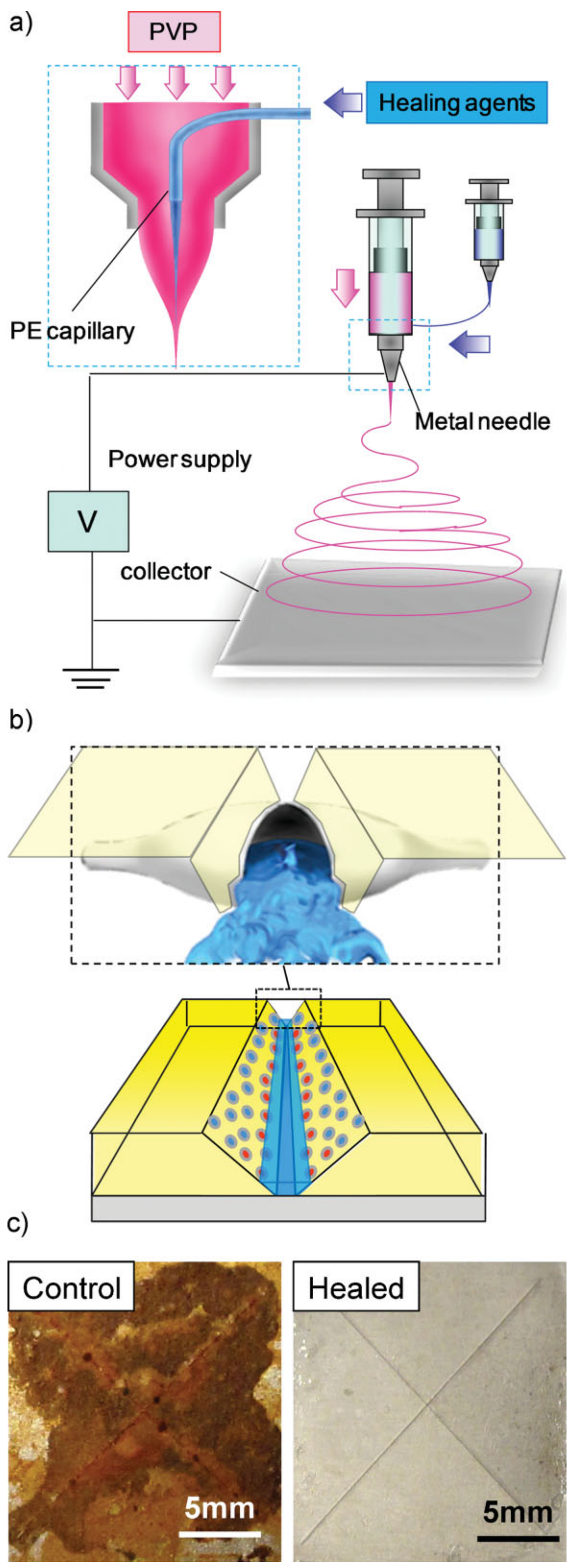

Figure 1. Illustrations of a) the coaxial electrospinneret and fiber spinning process. b) Healing agent release from mechanically ruptured capsules which consequently passivates the substrate from the environment. c) Photographs of control and self-healing coating samples that were stored under ambient conditions for 2 months after 5 days salt water immersion.

and part B siloxanes, respectively. The spinning time for each part of the siloxane system was controlled in order to satisfy the optimum mixing ratio 1:1 of two-part system. Through transmission electron microscopy (TEM) analysis, a well formed PVP shell wall and the encapsulated polysiloxane precursor could be clearly seen (Fig. 2d).

At a fixed volumetric flow rate of the sheath PVP polymer solution, $F_{\mathrm{PVP}} = 5.0\,\mu\mathrm{L\,min}^{-1}$, thermo gravimetric analysis (TGA) and the morphology of electrospun beads on fiber structures was investigated as a function of the feed rate of polysiloxane, part A ($F_{\mathrm{Si}} = 1.5$, 3.5, and $5.0\,\mu\mathrm{L\,min}^{-1}$). As expected, the amount of healing agent inside the PVP capsules increases as the feed rate of the healing agent increases. Perhaps surprisingly, no significant change in the bead diameter as a function of feeding ratio was observed. Rather, larger number of beads and a shorter average bead-to-bead distance along the fiber was observed as F_{Si} increased from 0.5 to $3.5\,\mu\mathrm{L\,min}^{-1}$ (Supporting Information, Fig. S2).

Next, a polymer matrix was spun-cast into the electrospun fiber mat, and cured (Supporting Information, Fig. S1). In this study an acrylated polyurethane UV curing resin, NOA (Noland optical adhesive 73) was chosen as the polymer matrix due to its simple chemistry and fast UV initiated curing process. Upon damage to the coating, liquid healing agents from the mechanically ruptured capsules are released and flow into the scribed region. Passivation of substrate is complete once the healing agents crosslink at room temperature (Fig. 1b).

Visualization of self-healing was obtained through scanning electron microscopy (SEM); imaging of a mechanically damaged region of the self-healing coating. Prior to SEM analysis, all damaged films were allowed to heal at room temperature for 24 h. In Figure 3a, the ruptured microcapsules can be seen as black dots, the damage in the substrate as a dark groove, and the polysiloxane healing agent as the material now present within the scribe. A top view of the damaged region also shows polymerized healing agent in the crack plane (Fig. 3b). Figure 3c shows a cross-sectional tear surface of a self-healed and re-torn film along the scribe after it was detached from the steel substrate. The rough surface in the bottom half of the sample is indicative of crosslinked polysiloxane healing agent, evidence that the two liquids are efficiently released into the crack plane and mix in the vicinity of the interface between the coating and substrate where they polymerize. An image of an empty micro-void left by the polysiloxane healing agents droplet embedded in the UV cured NOA matrix is shown in inset Figure 3c. Figure 3d presents a self-healing coating was prepared on a Si wafer. The crosslinked siloxane polymer fills the scribe despite its large crack width (the large crack width is due to poor adhesion of NOA on the Si substrate). The silicon substrate both enables high resolution imaging, due to its non-magnetic nature, and demonstrations the generality of the coaxially electrospun self-healing coating system.

Electrochemical evaluation of self-healing was investigated by linear sweep voltammetry (Fig. 4) and chronoamperometry (Supporting Information, Fig. S3a) in a conventional three-electrode electrochemical cell.[18,19] For the scribed self-healing sample, no current was detected (detection limit ~100 nA). On the other hand, the control sample, a scribed NOA polymer coated steel substrate, exhibits a significant current flow on the order of 4 mA at a slightly positive bias versus

Ag/AgCl, and the bare substrate a very high current at a similar bias. The dramatically different electrochemical behavior of the self-healing and control samples is a clear demonstration of the effectiveness of the electrospun-based self-healing coating system. Visual evidence for self-healing was provided by salt water (5 wt % NaCl) immersion testing[12] (Supporting Information, Fig. S3b). After salt water immersion for 120 h, no rust formation was observed on the self-healing sample while a control sample rapidly corrodes in the scribed region. The long term viability of the self-healing system was evaluated by storing the control and healing two samples in an ambient environment for 3 months after immersion in the salt water for 120 h (Fig. 1c). No rust was observed on the self-healing sample, while the control sample exhibited extensive corrosion.

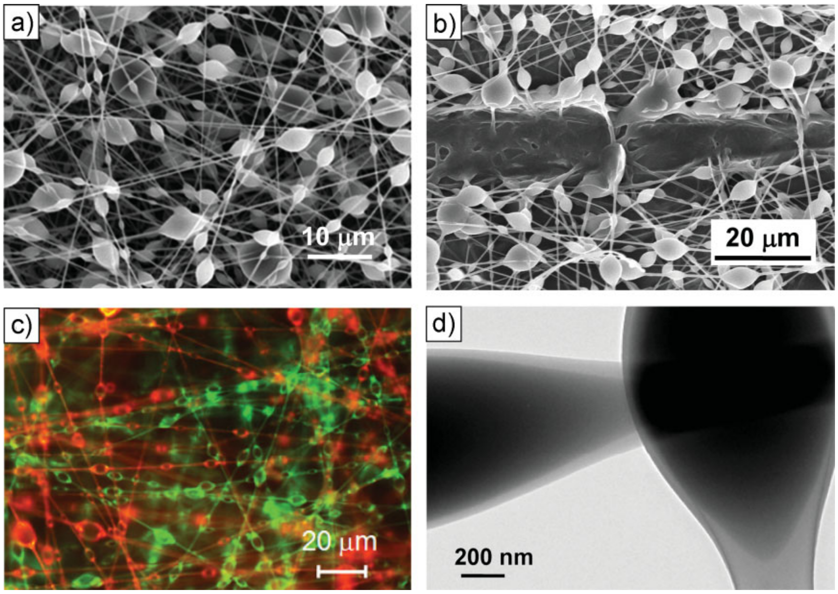

Figure 2. SEM images of a) the as-spun core–shell bead-on-string morphology and b) healing agent released from the capsules when ruptured by mechanical scribing. c) Fluorescent optical microscopic image of sequentially spun Rhodamine B (red) doped part A polysiloxane precursor capsules and Coumarin 6 (green) doped part B capsules. d) TEM image of as-spun bean-on-fiber

The concept of a coaxial electrospun self-healing polymer coating system was demonstrated for polysiloxane-based healing agents and an acrylate matrix. Electrospinning offers a number of unique opportunities. Perhaps most significantly, the location and concentration of the healing component can be spatially varied; this is in contrast to a capsule-based system, where the capsules are mixed into the matrix precursors before it is applied to the substrate. Furthermore, the fibers are electrospun before the matrix is applied, reducing a number of issues with chemical incompatibilities between various matrices and healing agents that are present when capsules are dispersed in the matrix precursors.

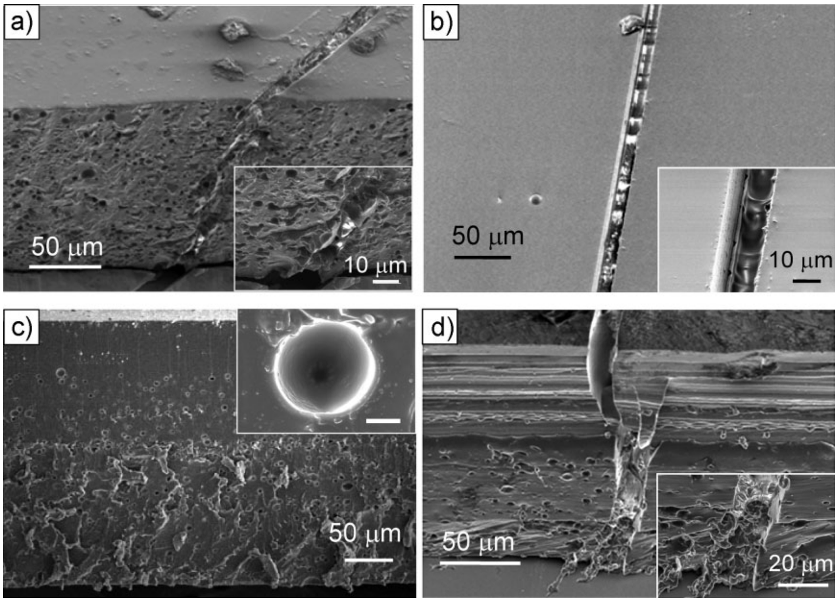

Figure 3. SEM images of scribed region of the self-healing sample after healing a) 45° cross-section and b) top view of the scribed region on a steel substrate. Insets are higher magnification views. c) SEM image of the cross-section of a torn self-healing coating. The inset shows an empty bead-on-string microcapsule (scale bar 2 μm). d) SEM cross-section of a scribed self-healing coating on a Si substrate. In the inset, the PDMS healing agent can be seen at the substrate-coating interface. All samples healed at room temperature for 24 h before imaging.

Experimental

In a typical coaxial electro-spinning, 20 wt % PVP (Aldrich, $M_w = 1.3 \times 10^6$) solution in dimethylformamide was added to the syringe connected to the metallic needle, and one component of the polydimethylsiloxane healing agent (Dow corning, 3-6576 dielectric kit) was added to another syringe connected to the inner polyethylene capillary (Polymicro Technologies) as a healing agent. These two liquids were fed at a constant rate through syringe pumps (KDScientific). The feed rate for the PVP solution was typically fixed at 5.0 μL min^{-1}. The polysiloxane feed rate was varied from 1.5 to 5.0 μL min^{-1}. The metallic needle was connected to a 30 kV high-voltage power supply (RHR30PN10, Spellman). The collector, a copper wire mesh with a diameter 10 cm, was placed 9 cm below the tip of the metallic needle. The spinneret nozzle was made by inserting the polyethylene capillary tube (inner diameter 280 μm, outer diameter 610 μm) into the stainless steel needle (inner diameter 840 μm). The polyethylene capillary penetrated the plastic syringe wall and was connected to another plastic syringe (Fig. 1a) [15]. All connections were sealed with epoxy resin. The typical voltage range for electrospinning was 5–7 kV. The part A and part B polysiloxane encapsulated PVP fibers were sequentially spun on the 1 × 1 inch cold-rolled steel sheets for 3 min. The spin-cast polymer matrix resin, NOA 76 was cured by UV illumination for 5 min.

For fluorescent microscopic images, the polysiloxane healing agents were doped with Rhodamine B

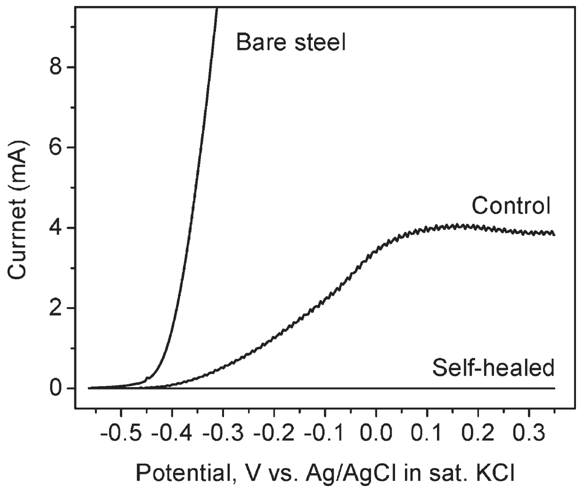

Figure 4. Electrochemical testing of self-healing coating on the cold-rolled steel substrate. *I* versus *V* characteristics using linear sweep voltammetry for the bare substrate, the scribed control and scribed self-healed sample.

(part A), Coumarin 6 (part B). Fluorescence images of each dye were captured and overlapped (Fig. 2c).

Electrochemical evaluation (linear sweep voltammetry and chronoamperometry) was performed using a computer controlled potentiostat in a conventional a three-electrode electrochemical cell equipped with a Pt counter electrode, a Ag/AgCl in saturated KCl aqueous solution as a reference electrode, and the control or self-healing polymer coated steel substrate as working electrode, respectively. The scribed region on the sample was exposed to 1 M NaCl aqueous electrolyte (inset Fig. 4a). Linear sweep voltammetry was performed from −600 mV to +1100 mV at a rate of 20 mV s^{-1} and a chronoamperometric curve was measured at 0.3 V for 200 s.

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