SHAPE MEMORY ASSISTED SELF-HEALING COATINGS

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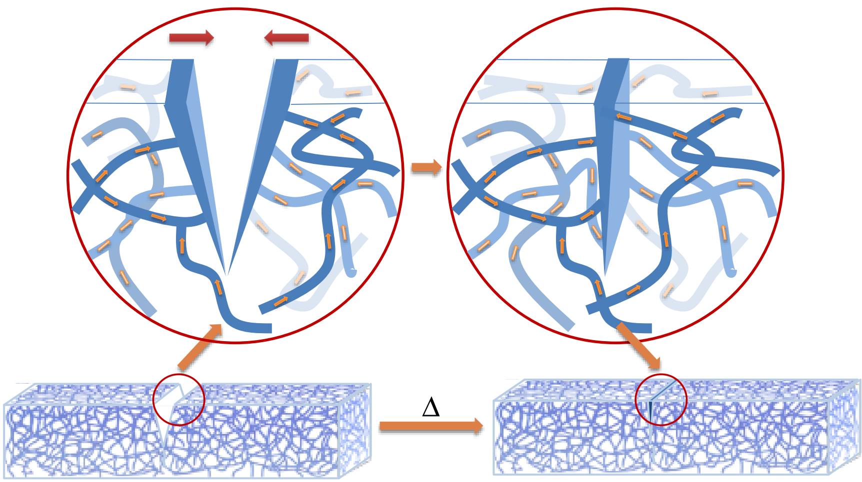
Keywords: Self-healing, shape memory, electrospinning, coating, corrosion resistance

ABSTRACT

Most self-healing coatings reported to date feature a passive, "crack-filling" mechanism. One downside of this mechanism is the fact that the crack never closes, limiting the healability of large cracks and structural defects. The primary objective of this study, therefore, was to develop new self-healing coatings that are capable of simultaneously closing and re-bonding cracks.

To achieve this, we utilized shape memory assisted self-healing (SMASH), a strategy demonstrated previously in bulk self-healing polymer systems [1]. The overall concept of shape memory assisted self-healing coatings is illustrated in Scheme 1. Structurally, the coating is composed of low-melting thermoplastic microfibers randomly distributed in a shape memory polymer (SMP) matrix. Self-healing is initiated by heating a damaged coating to a temperature that is higher than both the melting temperature (T_m) of the fibers as well as the transition temperature (either T_m or T_g) of the SMP matrix. Two events are triggered simultaneously: (1) recovery of the SMP matrix that releases the stored strain energy in the plastic zone surrounding the crack to close the crack, and (2) melting and microscopic flow of the thermoplastic to re-bond the crack. The most significant advantage of this design is that the shape memory induced crack closure brings the crack surfaces in spatial proximity, minimizing the healing agent needed for re-bonding the crack. Therefore cracks could be healed regardless of their sizes.



Scheme 1. Schematic illustration of the shape memory assisted self-healing mechanism.

Experimentally, the coatings were prepared using a two-step process. In the first step, poly(ε-caprolactone) (PCL; T_m ~ 60 °C) was electrospun directly onto a steel substrate. This led to a uniform, fibrous coating covering the entire substrate surface (Figure 1a). The second step involved spin coating of a liquid epoxy SMP [2] onto the PCL coating. The epoxy could easily wet PCL due to favourable surface energetics, but does not dissolve or swell PCL. In other words the fiber structure of PCL is not affected by this step. The coating was fully cured at room temperature for 72 h then 40 °C for 24 h.

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Self-healing of the prepared coatings was characterized in terms of both structural healing (recovery of plastic deformation) and functional healing (restoration of coating functions, in our case the corrosion resistance). The former can be seen from Figure 1b, which shows the full recovery of damage (introduced by scribing the coating through its thickness with a sharp razor blade) upon heating to 80 °C (above the transition temperature of shape memory epoxy). The crack closed completely, allowing the self-healing agent – molten PCL – to re-bond the crack surfaces. As a result, the corrosion resistance of the coating was restored. Linear sweep voltammetry results (Figure 1c) reveal a significant difference between the damaged and self-healed coatings. The damaged coating exhibits relatively large electrical currents, indicating active corrosion of the exposed substrate. In contrast, very little electrical current was detected for the self-healed coating. Visual inspection of the two samples confirms the drastic difference in rust formation, and further proves the effectiveness of self-healing.

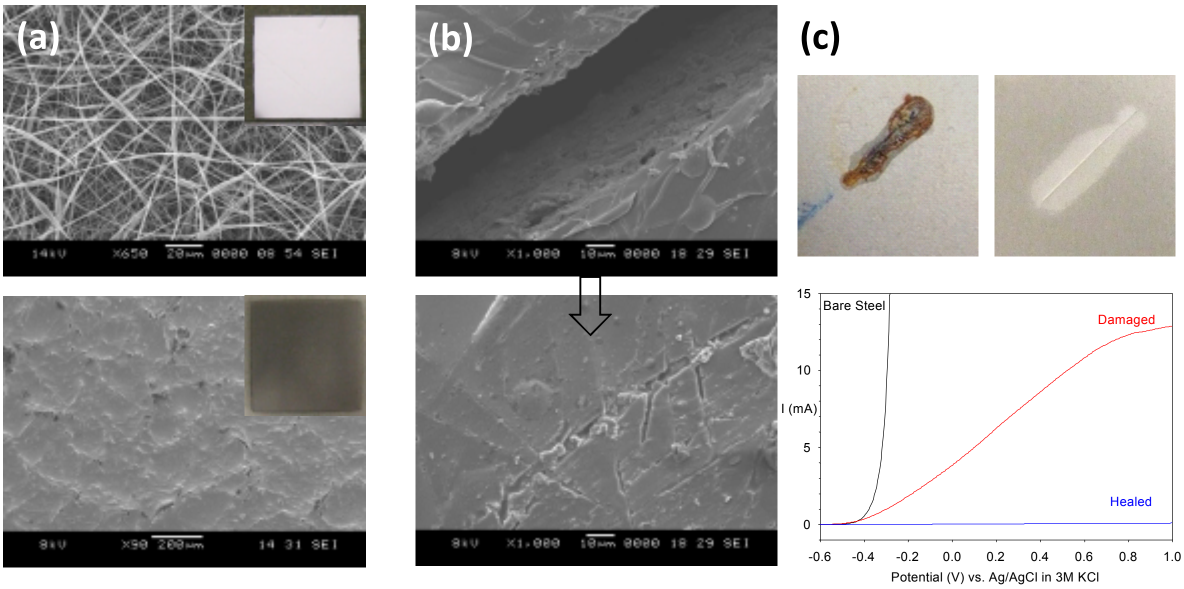

Figure 1. (a) Scanning electron microscopy (SEM) images showing the PCL fiber coating (top) and fully cured epoxy/PCL self-healing coating (bottom). The insets are macroscopic photos of the coatings. (b) SEM images showing the as-damaged crack (top) and a self-healed crack by heating to 80 °C (bottom). (c) Linear sweep voltammetry results of bare steel, damaged coating and self-healed coating, along with photos of the specimens after the testing (left: damaged; right: self-healed).

Ongoing studies include transparent SMASH coatings used for scratch resistant optical applications and/or where transparent coatings are needed. Here, we use an amorphous thermosetting formulation to form both the network and thermoplastic to achieve the shape memory assisted self healing effect. Coatings are applied on glass substrates with crack closure and healing being observed using stereo microcopy. Other studies also include the use of spectrometric analysis to observe light properties as a function of virgin, damaged and healed scratches on the coatings.

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