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INTERPENETRATING MICROVASCULAR NETWORKS FOR THERMAL ACCELERATION OF SELF-HEALING

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ABSTRACT

Self-healing polymer-matrix materials based on an embedded microcapsule design demonstrate impressive recovery of mechanical properties, yet are limited to a single heal cycle due to localized depletion of healing components [1]. In this system, a polymer matrix is embedded with dicyclopentadiene (DCPD) monomer in microcapsules and Grubbs' catalyst in the matrix, such that mechanical damage ruptures the microcapsules to release DCPD, which cures upon contact with Grubbs' catalyst to recover mechanical strength. Once a region is depleted of DCPD, the local mechanical properties will not recover if a new crack propagates through this same region.

The next generation design for self-healing material systems pursues the goal of multiple healing cycles by integrating complex three-dimensional microvascular networks. Microvascular designs provide a transport route for liquid healing chemistries to the damage region that overcomes the limited liquid volumes available via discrete encapsulated fluids. The first demonstration of this concept consisted of a biomimetic coating/microvascular substrate architecture, similar to that of the dermal skin layer supplied by underlying blood capillaries. Using the same Grubb's catalyst (coating) and DCPD monomer (microvascular liquid), the system achieved a maximum of 7 heal cycles, after which all catalyst in the crack plane was depleted [2].

Microvasculature is incorporated into structural polymers via Direct Ink Writing (DIW). In DIW of microvascular channels, a fugitive organic ink is extruded from a micro-deposition nozzle that is mounted to a 3-axis, motion-controlled positioning stage [3]. The microvascular network of interest is typically patterned by deposition of the fugitive ink in a layer-wise build sequence [3-4]. Once the 3D network is constructed, an epoxy resin infiltrates the open porosity and is cured. Finally, the fugitive ink is removed from the polymer matrix by modest heating (~80°C) and application of a light vacuum to produce a single embedded microvascular network.

We develop interpenetrating microvascular architectures to permit the use of inexpensive epoxy resins that remain sequestered in their respective networks prior to mechanical damage of the brittle coating layer. Fabrication of interpenetrating networks requires extending the capabilities of the DIW technique to include dual ink writing – to separate neighbouring networks – and vertical ink writing – to provide fluid access from the underlying networks to the surface damage region. The liquid epoxy resin and epoxy hardener retain chemical reactivity until cracking of a brittle coating layer, after which both liquid resin and hardener flow into and mix in the crack plane to restore mechanical properties. Most significantly, we find that neither healing agent is preferentially depleted, achieving up to 30 consecutive cycles (and beyond) of mechanical property recovery [5].

Here we further extend this technique by introducing a third interpenetrating network devoted to thermal control of the composite. The third microvascular network circulates a constant temperature fluid to heat the composite in regions of mechanical damage. The localized thermal profile is imaged with an infrared thermal camera, with thermal equilibrium reached within 5 to 10 minutes for circulating water temperatures of up to 70°C. The modest temperature increase to 70°C accelerates the polymerization kinetics of the epoxy healing system by over an order of magnitude, as measured by differential scanning calorimetry (DSC), oscillatory rheology, and dynamic mechanical analysis (DMA). To test recovery of mechanical properties, specimen coatings are fractured under bending, heal fluid mixes within the coating crack plane, and specimens are healed at elevated temperatures. Mechanical testing of the healed specimens demonstrate that elevated temperatures reduce the time required to match the heal strengths by an order of magnitude for 30°C specimens. Moreover, healing is first witnessed at times that correspond to the measured gel point of the epoxy systems at elevated temperatures, which are far earlier than in the previous work conducted at 48 hours. As a fully integrated system, ternary interpenetrating microvascular networks promise to effectively deliver healing fluids to damage regions and to quickly heat the polymerizing healing fluids in order to significantly decrease the time required to recover mechanical properties.

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