

Self-healing and Progress Towards Self-sensing via Optical Waveguides in Microvascular Composites

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ABSTRACT

Internal delamination in fiber-reinforced composites is difficult to detect and nearly impossible to repair by conventional methods. Bioinspired, microvascular self-healing strategies based on sequestering reactive liquids within hollow conduits have shown promise for repairing internal damage and extending lifetimes of laminated composites. However, difficulties in achieving *in situ* mixing of two-part healing agents, polymerization times on the order of hours/days at room temperature, and propensity for flow blockages from cross-contamination are research challenges that have limited the adoption of this technology. This paper describes an interdisciplinary research effort to develop self-healing microvascular composites using a one-part, photo-reactive chemistry. The new platform employs microvascular networks for functional fluid transport combined with optical waveguides for rapid, light-activated healing. An epoxy-based, cationic photochemistry was developed to polymerize upon sub-hour exposure to visible light. The one-part cationic chemistry is able to achieve higher recovery (~75%) in mode-I fracture toughness compared to a commercial free-radical photochemistry (~55%) and two-part epoxy/amine system (~65%). In addition to providing targeted light delivery for photo-conversion, the optical waveguides are also intended to serve dual purpose as a self-sensing conduit to relate internal polymerization with mechanical self-recovery. Towards this *in situ* sensing target, Raman spectroscopy is conducted to show chemical conversion along with fracture recovery increases with increasing light exposure. This novel approach to integrated self-sensing/healing in structural composites outlines a new paradigm in multifunctional material design.

INTRODUCTION

Modern applications demand better performing and more reliable materials that can operate in a variety of environmental conditions. Fiber-reinforced polymer composites are becoming more prevalent in structural applications due to their resilience (i.e. corrosion resistance) and high strength/stiffness to weight ratio. However, these hierarchical materials are inherently susceptible to a variety of damage mechanisms. Interlaminar delamination, i.e. debonding of layered reinforcement from surrounding matrix (Figure 1), is considered the most life-limiting factor in composite design (Kim and Sham 2000).

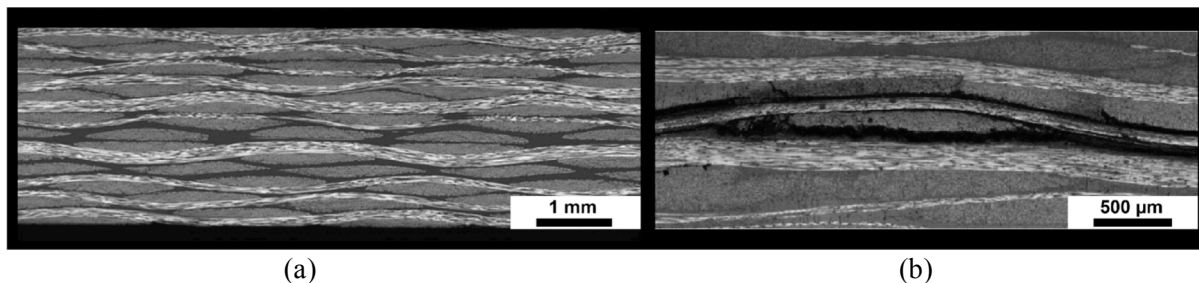


Figure 1: (a) Cross-section of a carbon-fiber reinforced composite laminate (Hayes and Gammon 2010); (b) Sub-surface interlaminar delamination (White and Sue 2012).

To combat delamination and degradation from normal in-service operation (e.g. fatigue) and inevitable overload (e.g. impact), self-healing polymers and composites have emerged (White *et al* 2001, Blaiszik *et al* 2010, Diesendruck *et al* 2015). One particularly promising route utilizes micro-channels, akin to blood vessels in animals, to sequester two-part, reactive liquid healing agents within the composite. Upon fracture/delamination the vasculature ruptures and releases reactive healing agents into the damaged region to mix, polymerize and, self-heal the crack (Patrick *et al* 2014). While this strategy possesses distinct advantages over prior approaches, namely the ability to heal larger damage volumes over multiple heal cycles (Patrick *et al* 2016), there are various challenges to realize practical self-healing with a two-part chemistry. Achieving *in situ* stoichiometric mixing requires complex vasculature and/or precise pumping protocols that are difficult to implement outside the laboratory setting. If suitable mix ratios are achieved, there is a propensity for network blockages and chemical cross-contamination. Moreover, successful demonstrations of two-part healing systems have exhibited slow polymerization times on the order of hours/days at room temperature (Diesendruck *et al* 2015, Patrick *et al* 2016). Thus, there is a need for a single-component healing agent that eliminates these issues related to delivery and reactivity for translation to real world, multi-environment applications.

Beyond fluid chemistry/delivery concerns, even after more than a decade of research on self-healing composites, assessment of structural repair still relies upon *ex situ*, destructive mechanical testing to quantify the extent of recovery. Structural health monitoring (SHM) approaches have been independently developed to assess stress/strain and detect damage (Boller *et al* 2009, Giurgiutiu 2016), however there is a clear gap in combining *in situ* self-sensing and self-healing to produce a truly autonomous, self-regulated system (Patrick *et al* 2016).

Here, we detail the development of a self-healing/sensing system that relies on microvasculature to deliver a one-part photochemistry in combination with optical waveguides (i.e. light conduits) to transmit necessary photonic energy for monomer conversion. The photo-polymerization reaction is rapid, occurring on the order of minutes compared to hours/days with prior two-part systems. The embedded optical waveguides are intended to be multi-purpose, also serving as a self-sensing conduit to relate internal polymerization to mechanical self-recovery (Figure 2). Based on *ex situ* healing agent characterization via Raman spectroscopy, envisioned *in situ* self-sensing will provide a remotely accessible, non-destructive technique to chemically monitor the healing reaction that can be readily correlated to mechanical status.

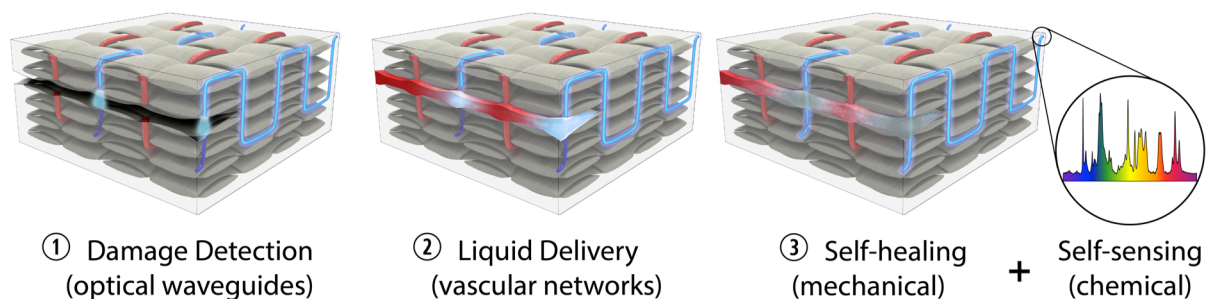


Figure 2: Multifunctional composites concept: (1) interlaminar fracture of optical waveguides (blue) releasing light; (2) simultaneous rupture of microvascular networks (red) for reactive liquid delivery; (3) photopolymerization for *in situ* structural self-healing and real-time spectroscopic self-sensing.

EXPERIMENTAL RESULTS

Photo-chemistry development

An epoxy-based, cationic photochemistry was formulated to provide superior bonding with epoxy matrix composites and mitigate cure inhibition from oxygen exposure that is typical of free-radical systems (Greene 2010). The monomer consists of a 1,4-butanediol diglycidyl ether containing a proprietary phase-separated toughening agent to enhance fracture toughness. A diphenyl iodonium salt photo-initiator and anthracene sensitizer combination is used to shift absorption into the visible spectrum (325-425 nm) for more practical photoconversion. UV-Vis spectroscopy was employed to characterize absorption spectra for various initiator/sensitizer concentrations (Figure 3a). A 4% photo-initiator and 2% sensitizer combination was selected to maximize light absorption without significantly increasing fluid viscosity, which is important for autonomous microvascular delivery. A 405 nm optical bandpass filter was paired with a broadband mercury-vapor light source to match light emission with an absorption peak (Figure 3b).

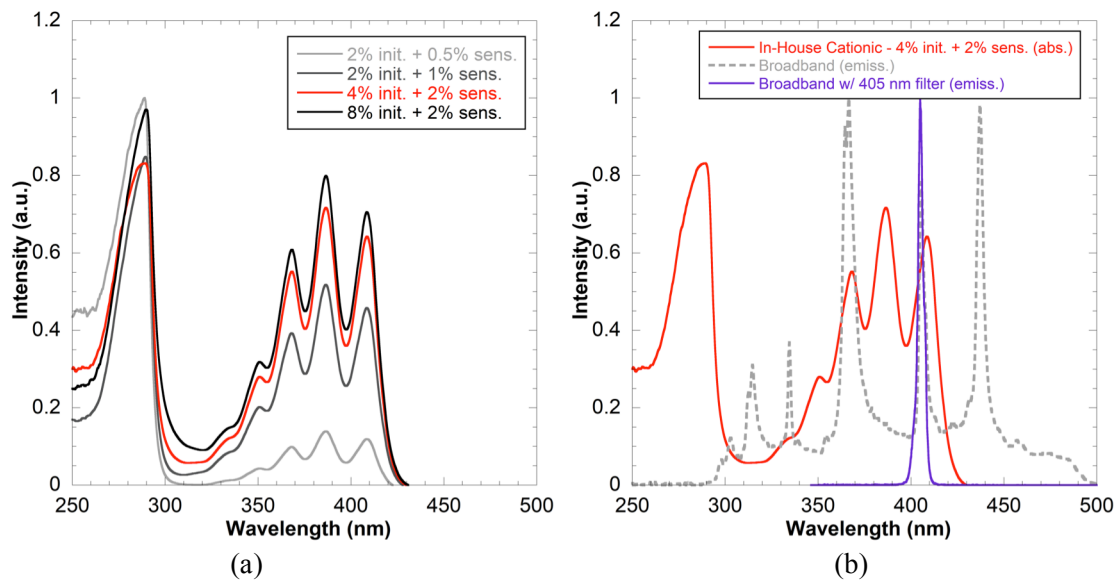


Figure 3: (a) UV-Vis absorption for cationic chemistry at varying concentrations of photo-initiator (init.) and sensitizer (sens.). (b) UV-Vis for in-house cationic chemistry (4% photo-initiator + 2% sensitizer) overlaid with the emission profile for the broadband light with a 405 nm bandpass filter.

Self-healing fracture evaluation

The tapered double cantilever beam (TDCB) was selected to assess mode-I fracture recovery, i.e. healing efficiency (Brown *et al* 2002). This sample geometry exhibits fracture toughness (K_{IC}) that is independent of crack length and merely a function of the critical applied load (P_c) and geometric constant (α), which reduces analysis complexity, equation 1.

$$K_{IC} = \alpha P_c \quad (1)$$

Based on contact angle and capillary height surface energy characterization of the liquid cationic chemistry, 220 μm diameter micro-channels were created within the TDCB geometry using a sacrificial precursor technique (Figure 4a). Samples containing micro-channels did not exhibit statistically different virgin fracture toughness than those without ($K_{IC} = 0.62 \pm 0.06 \text{ MPa}\cdot\text{m}^{1/2}$). *Ex situ* self-healing studies were conducted by first pre-cracking the TDCB, then filling the micro-channels with liquid healing agent, followed by fracturing the specimen under quasi-static displacement-controlled loading (5 $\mu\text{m/s}$), and

then unloading to allow the liquid chemistry to fill the entire crack plane. Samples containing one-part photo-chemistry were then exposed to prescribed light doses (irradiance \times time) within the test fixture before the “healed” TDCBs were re-tested to failure. For reference to previous studies, a pre-mixed two-part, epoxy-amine system (Patrick *et al* 2014) was autonomically delivered via fractured microchannels and cured in an oven for 48 h at 30°C prior to re-testing. Figure 4b compares self-healing results for the in-house, cationic photo-chemistry at varying light doses to the two-part, epoxy/amine reference system and a commercial, free-radical acrylated/urethane photo-chemistry. Healing efficiencies (η) were determined from the ratio of healed to virgin peak loads (White *et al* 2001), equation 2.

$$\eta = \frac{K_{Ic}^{healed}}{K_{Ic}^{virgin}} \equiv \frac{P_c^{healed}}{P_c^{virgin}} \quad (2)$$

The in-house, epoxy-based cationic photo-chemistry achieved the highest healing efficiency \sim 75%, followed by the two-part epoxy/amine system at \sim 65% and the commercial, free-radical chemistry at \sim 55%. In contrast to the 48 hours polymerization time for the two-part system, development of mechanical integrity is drastically reduced to seconds/minutes with the one-part photo-chemistries. While the in-house photo-chemistry resulted in the highest healing efficiency, it required more photonic energy (i.e. dose) than the commercial system to reach a fracture toughness plateau.

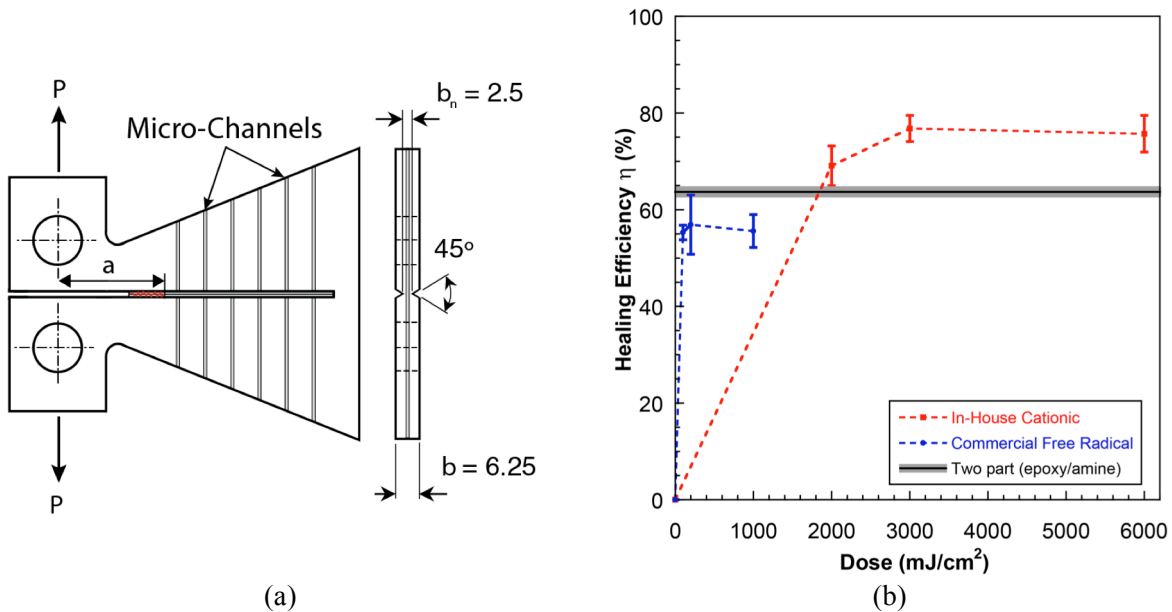


Figure 4: (a) Tapered Double Cantilever Beam (TDCB) specimen with 220 μ m diameter micro-channels for liquid healing agent delivery, (b) *Ex situ* self-healing results.

Towards self-sensing Raman spectroscopy

Raman spectroscopy was employed to investigate the relationship of photo-chemical conversion (i.e. sensing) for the cationic system to mechanical recovery (i.e. healing). Thin films (\sim 40 μ m) of liquid photo-chemistry were drop cast between polydimethylsiloxane (PDMS) substrates and exposed to varying light doses using the broadband source equipped with the 405 nm bandpass filter. The films were subsequently removed and *ex situ* Raman scattering spectra were acquired using a HORIBA XplorRa Plus confocal system with a 785 nm near-infrared (NIR) laser source. Spectrophotometer studies confirmed the NIR excitation wavelength does not exhibit spectral overlap with the absorbance profile of the photo-

chemistry, resulting in no additional polymerization, and thus providing an orthogonal sensing modality. Cure kinetics for the cationic chemistry is established in a similar manner to a prior self-healing study by calculating reactive to invariant peak ratios (Hardis *et al* 2013, Patrick *et al* 2014). Upon light exposure and absorbance, the oxirane molecule reacts with a photo-generated acid and as a result decreases in intensity (1256 cm^{-1}) whereas the phenyl ring peak (1609 cm^{-1}) remains reaction invariant (Figure 5a). The initial (un-exposed) oxirane/phenyl ratio is roughly 1.6, where a statistical plateau in normalized peak ratio of approximately 0.6 indicates complete epoxy monomer conversion (Figure 5b). The observed Raman peak ratio plateau in films was also confirmed on a healed TDCB and correlates well with recovery in fracture toughness (Figure 4b), thus providing a molecular measure and promising pathway for *in situ* self-sensing of mechanical recovery.

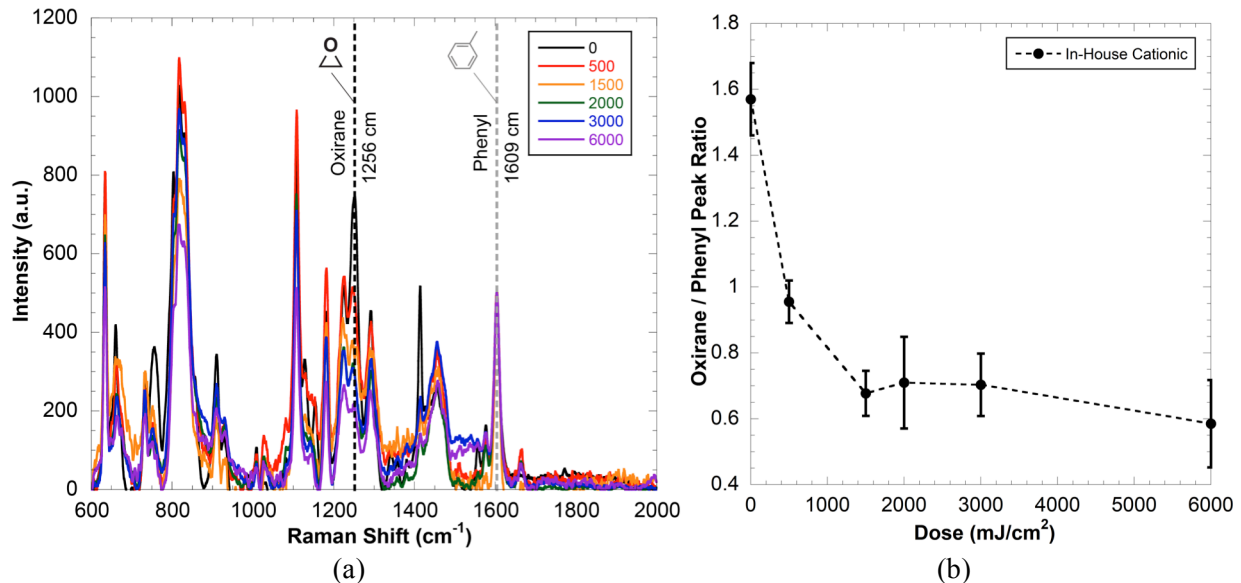


Figure 5: (a) Raman spectra of in-house, cationic photochemistry showing decrease in epoxide (oxirane) peak relative to invariant (phenyl) band as 405 nm light dose increases. (b) *Ex situ* Raman evolution where complete polymerization is achieved when the reactive/invariant peak ratio plateaus.

CONCLUSION

Microvascular materials that overcome current self-healing limitations with the added benefit of self-sensing eliminate the need for recurring inspection and costly repair. Similar to liquid delivery through hollow channels, embedded optical waveguides will serve as a light conduit for photonic energy delivery to achieve both *in situ* photo-chemical conversion (healing) and spectroscopic characterization (sensing). While the foundations for this novel approach have been established, further development is needed to combine the modalities and attain *in situ* functionality in a fiber-reinforced composite. The envisioned multifunctional platform has the potential to significantly reduce weight, size, and other overdesign costs while improving performance, reliability, and extending useful lifetime.

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