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Multifunctional Damage Tolerant Composite Materials

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Co-continuous, thermoplastic toughened epoxy matrix composites were developed with the goal of using the thermoplastic phase as both a toughening agent and a healing system. Our strategy involved the damage-triggered release of non-toxic, solvent-based healing agents that locally swelled and flowed the thermoplastic phase to repair the cracked region. Methods were developed to incorporate this novel self-healing resin system into a unidirectional, carbon fiber/epoxy prepreg using a bench-top prepregger. We observed significant fatigue life extension of these high fiber volume fraction self-healing composites without a reduction in tensile strength.

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Multifunctional Damage Tolerant Composite Materials
Final Report – FA9550-15-1-0028

PIs: Nancy Sottos and Scott White
University of Illinois at Urbana-Champaign

1. Overview

Co-continuous, thermoplastic toughened epoxy matrix composites were developed with the goal of using the thermoplastic phase as both a toughening agent and a healing system. Our strategy, shown schematically in **Figure 1**, involved the damage-triggered release of non-toxic, solvent-based healing agents that locally swelled and flowed the thermoplastic phase to repair the cracked region. We identified a promising thermoplastic resin poly(bisphenol A-co-epichlorohydrin) (PBAE) blended with a high glass transition temperature (T_g) epoxy matrix (EPON 828: diamino diphenyl sulfone) with significant toughening and self-healing performance [1,2]. The fracture toughness of the epoxy was doubled by the addition of 20 wt % PBAE alone and tripled by the addition of both microcapsules and the thermoplastic phase. Microcapsules were coated with poly(dopamine) (PDA) to improve the thermal stability and retain the core solvent during curing at 180°C. Self-healing was achieved with up to 57% recovery of virgin fracture toughness of the toughened epoxy. Healing performance and fracture toughness of the self-healing system remained stable after aging 30 days.

We also developed methods to incorporate this novel self-healing resin system into a unidirectional, carbon fiber/epoxy prepreg using a bench-top prepregger [3,4]. We successfully manufactured high fiber volume fraction, laminated composites from this prepreg that possessed both intact microcapsules and thermoplastic phases. In the final stages of the work, we investigated the mechanical and self-healing properties of the composites under fatigue conditions [5,6]. At high volume fraction of capsules (ca. 3.7 vol%), we observe significant fatigue life extension of the self-healing composites with a reduction in tensile strength. In a recent study, the fatigue life extension was also revealed at a small volume fraction of capsules (ca. 1.1 vol%) without a reduction in tensile strength.

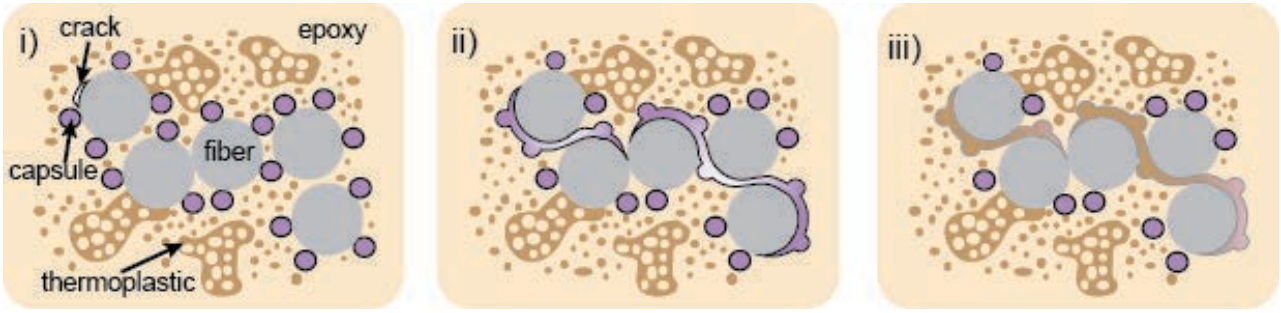

Figure 1. Schematic of proposed self-healing strategy: i) Sub-micron capsules (or microchannel) filled with a solvent based healing agent (purple) are functionalized on fibers (grey) in a co-continuous thermoplastic (brown) toughened epoxy (tan) matrix composite. (ii) Crack damage triggers the release of healing agent from the capsules, (iii) the solvent swells the matrix allowing the thermoplastic phase to flow and heal the crack.

2. Development of Multifunctional Materials for Toughening and Healing

2.1 Materials and methods

A phase separation of an epoxy (828:DDS) and thermoplastic (PBAE) was created by mixing resin and thermoplastic at elevated temperature and melt-casting. The purpose of this material is to show solvent based self-healing upon the inclusion of microcapsules. Phase morphology and mechanical properties were studied for varying mass fractions of included thermoplastic.

Inclusion of solvent (EPA) filled microcapsules was also studied. Phase interactions at the capsule surface were observed, as well as the thermal stability of the capsules during mixing and curing. The environmental stability of the capsules was then studied by exposing samples to a high-temperature, high-humidity environment.

Finally, self-healing was studied using Tapered Double Cantilever Beam (TDCB) specimen geometry with active material as an insert. The self-healing was compared to high temperature healing and healing done by deliberate injection of solvent to the crack site. The healing of thermoplastic /carbon fiber interfaces was studied using the microbond technique using solvent casting to create thermoplastic beads. Glass fibers and sized carbon were shown to preferentially bond to epoxy phase, but unsized carbon fibers can be used to have thermoplastic interfaces.

2.2 Self-Healing Resin Results

Phase separation of the thermoplastic and epoxy system was shown to have three distinct morphologies [1]. At low thermoplastic concentration, small (ca. 1μm) regions of thermoplastic were interspersed in continuous epoxy. At high concentration, the phases were reversed and small (ca. 5μm) regions of epoxy were interspersed in thermoplastic. In middling concentrations, the two phases coexist in a bi-continuous morphology. **Figure 2** shows all three regimes. A low temperature storage modulus on the order of 3GPa was measured using Dynamic Mechanical Analysis (DMA). Additionally there was a softening of the material at ca. 80ºC attributed to thermoplastic glass transition and a system T_g around 170ºC. Interestingly, the T_g increased at the highest thermoplastic concentration (**Figure 3**), and storage modulus decreased slightly when the bi-continuous phase was present compared to lower thermoplastic concentrations. Inclusion of microcapsules (5 wt %) caused a decrease in the storage modulus and a slight decrease in T_g. The decrease in T_g remained within the experimental error for capsule free specimens.

Microcapsules were shown to attract the epoxy rich phase after ca. 45 min at high temperature (150ºC) for both PDA coated and uncoated capsules [2]. At curing temperature (180ºC) the uncoated capsules were shown to lose some structural integrity, but the PDA coating prevented this. After curing, voids appear in the capsules during cooling below 100ºC. These voids are suspected to be water. Leaving the samples at 95% relative humidity and 70ºC caused the voids to grow, suggesting water diffusion is the cause of void formation. **Figure 4** shows the void formation and thermal degradation of capsules. Samples left for the same time at ambient conditions showed no void growth indicating capsule stability under non-extreme conditions.

Healing was studied by comparing virgin and healed fracture toughness [1]. Virgin fracture toughness increased with both thermoplastic concentration and inclusion of microcapsules. Healed fracture toughness also increased with thermoplastic concentration between 15 and 20 wt % thermoplastic. Below 15 wt %, no healing was observed (**Figure 5**). Healing efficiency was shown to increase by allowing resting time up to 6 days at 30ºC to ensure full evaporation of solvent. Achieved efficiency was 57%. Also, little to no loss in healing efficiency with aging up to one month before testing was demonstrated (**Figure 6**). For interfacial healing, the thermoplastic interface was shown to be recoverable with a maximum of 80% healing efficiency. The healed interface had similar shear strength (IFSS) for all thermal treatments despite different virgin properties. For interfaces with higher virgin IFSS, healing occurred with ca 20% efficiency (**Figure 7**).

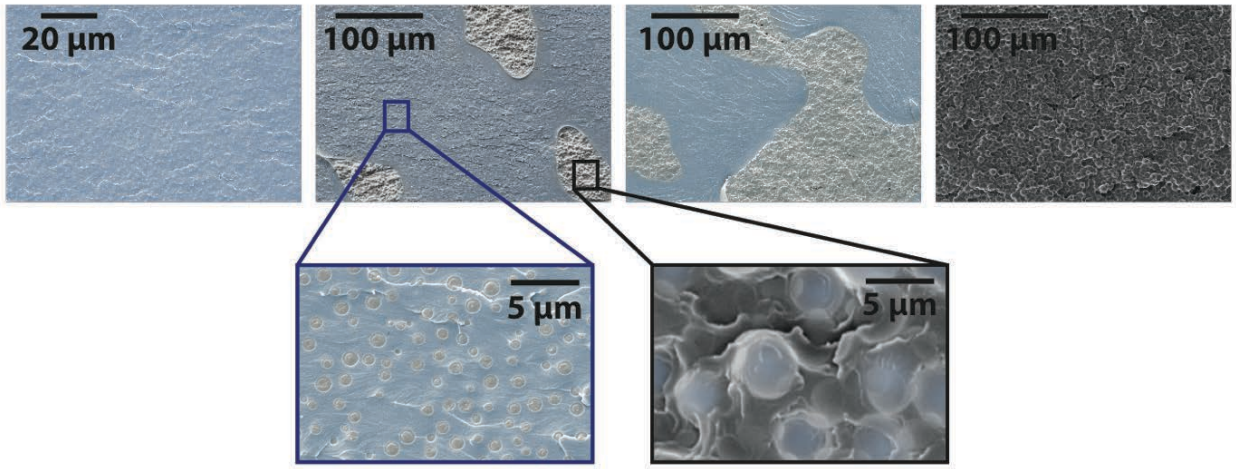

Figure 2. Phase morphology of 10, 15, 20, and 25 wt % (left to right) PBAE. The epoxy rich phase has been given artificial coloring in blue for clarity. Bi-continuous morphology can be seen at 15 and 20 wt %.

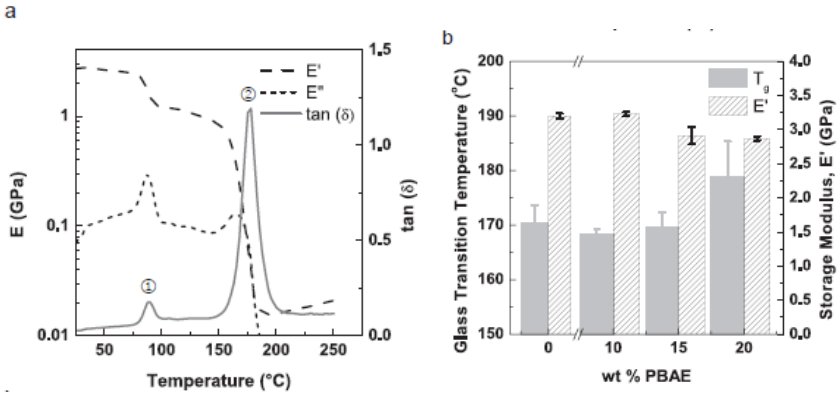

Figure 3. Left - DMA for 20 wt % PBAE showing the typical two peaks in tanδ from the softening of first thermoplastic then epoxy. Right – Property trends from increasing PBAE concentration. Error bars represent standard deviation.

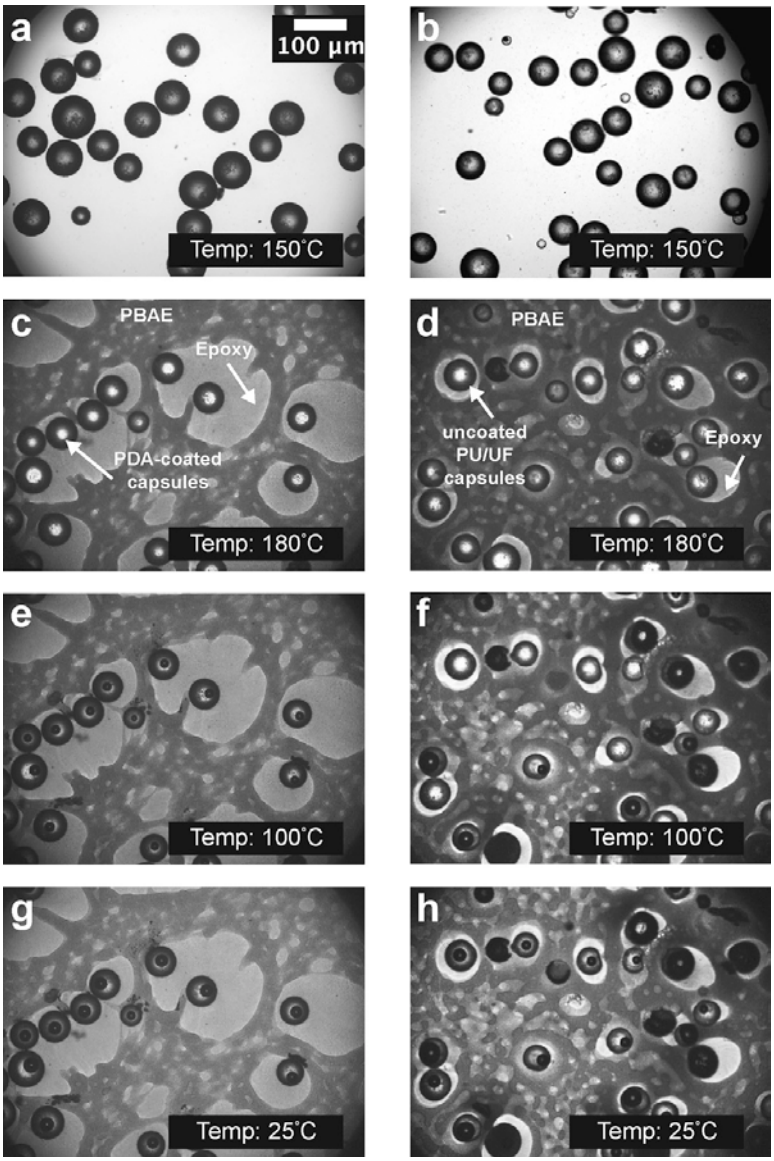

Figure 4. Thermal stability of PDA coated (left) and uncoated (right) capsules during a typical cure cycle (top to bottom). The degradation of uncoated capsules can be seen in figure (d) with slight wrinkling of most capsules and complete collapse of others indicated by the dark circles. Void formation in coated capsules can be seen in figure (e), while figure (g) shows little to no further void growth.

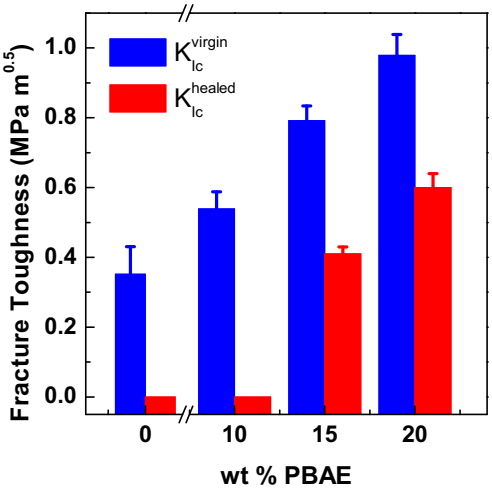

Figure 5. Effect of PBAE concentration on virgin and healed fracture toughness in reference samples. Zero healing was observed for 0 and 10 wt %.

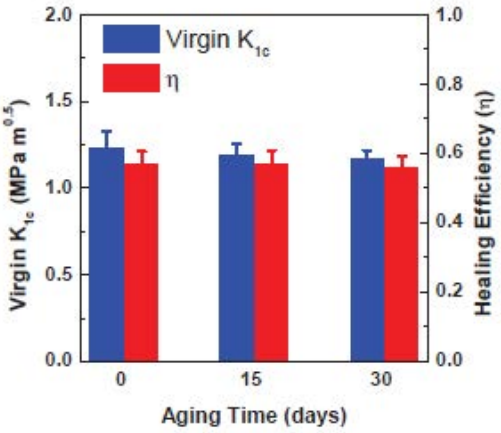

Figure 6. Healing efficiency after aging for 20 wt % PBAE. Healing efficiency and fracture toughness remained constant.

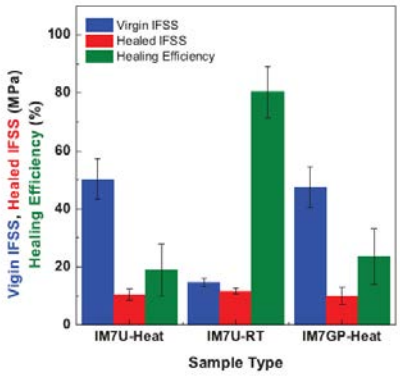

Figure 7. Healing of IFSS for PBAE. The highest healing efficiency comes for an unsized fiber with no thermal treatment. The heat treatment increased virgin IFSS, but had no effect on healed strength.

3. Processing and Characterization of Toughened Self-Healing Composites

3.1 Material and methods

A unidirectional carbon fiber/thermoplastic-toughened epoxy prepreg with EPA-filled microcapsules (ca. 2.8 μm) was fabricated using a bench-top prepregger. The prepregger consisted of a carbon fiber bobbin (AS4C-3k, Hexcel), a self-inking sizing drum, a resin-impregnator, and a take-up drum (**Figure 8.**). During the prepreg fabrication, a carbon tow was coated with a sizing agent containing microcapsules, impregnated with epoxy/thermoplastic blend resin, and wound onto a take-up drum. The sizing agent consisted of a mixture of microcapsules and butanone (MEK) solvent and was consistently supplied to a sizing drum from a vortex mixer. The sizing drum delivered a sizing agent to the carbon tow as it traveled below the drum. Drying process was not required after fiber-sizing because the resin impregnation process also contained MEK solvent. The capsule-sized tow was then impregnated with a mixture of epoxy (EPON 828, DDS), thermoplastic (PBAE), and MEK solvent. A take-up drum continuously wound this resin-impregnated tow side-by-side to create the unidirectional prepreg fabric. The residual MEK solvent within the prepreg fabric was removed at 80 °C under vacuum for 45 min.

Self-healing laminated composites were fabricated from the prepreg fabrics. A stack of prepreg was hot-pressed at 120 °C under 0.3 MPa for 3 hours, followed by 180 °C under 0.3 MPa for 1 hour. The vacuum was applied at room temperature and held until the temperature reached 120 °C. Confocal fluorescent microscopy was used to visualize the microcapsules within a composite and scanning electron microscopy was used to examine the fracture surface and morphology of the microcapsules and phase-separated thermoplastic.

3.2 Composite Processing Results

The sizing drum successfully separated the tow fibers and delivered the capsules into the interior region of the tow. Intact microcapsules were found to reside in the interstitial spaces of fibers in prepreg as shown in **Figure 9**. The tow was then successfully impregnated with resin after evaporating the MEK solvent. The final microcapsule concentration of the prepreg was proportional to the capsule concentration of sizing agent. The fiber volume fraction of the prepreg was controlled by the solvent concentration in the resin. MEK solvent reduced the viscosity of the resin, facilitating flow during the tow impregnation process. Too much solvent (ca. > 130 pph), however, led to an insufficient amount of resin in the prepreg. The prepreg obtained capsule volume fraction (V_c) of 0.024, and fiber volume fraction (V_f) of 0.43 corresponding to a sizing agent containing 2 wt% capsules and a prepreg resin with 60 pph MEK. The deviation of fiber volume and capsule volume was < 10 % across the width of prepreg.

The prepreg was then processed into composite laminates with V_f = 0.62 and V_c = 0.031. A confocal fluorescent image of the consolidated composite (**Figure 10**) reveals intact EPA filled microcapsules in the interstitial spaces between fibers and thermoplastic phase. **Figure 11** contains an optical image of a polished cross-section of the composite that reveals good consolidation and minimal void content (ca. 0.007).

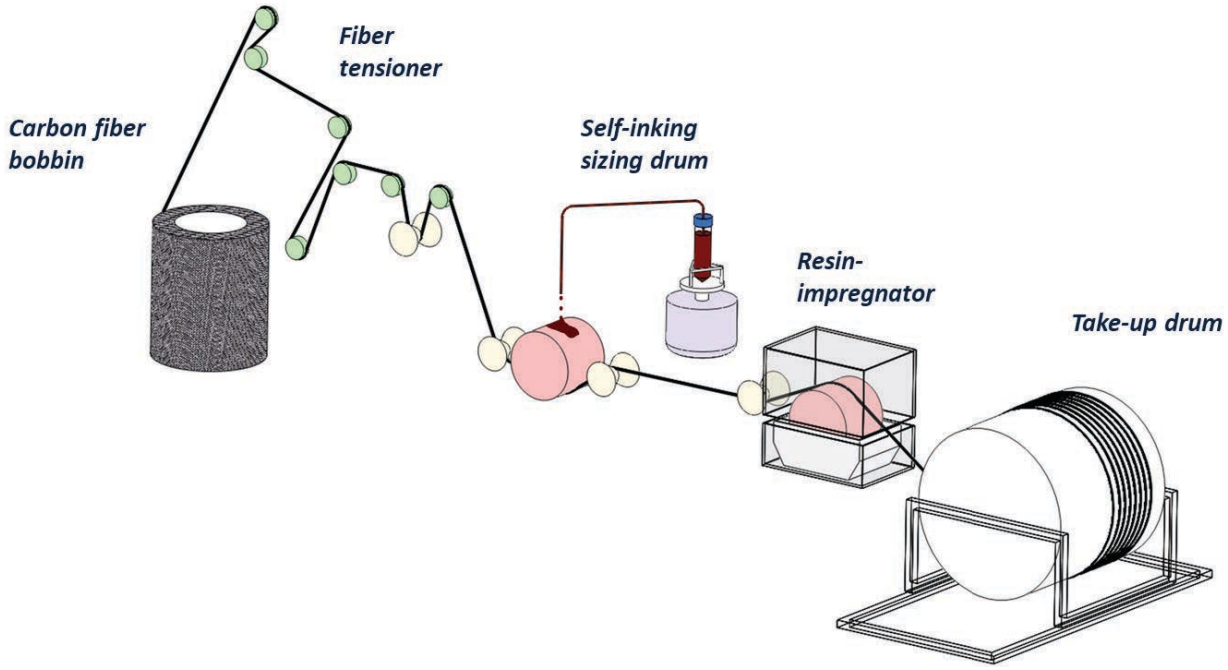

Figure 8. Schematic of bench-top prepregger.

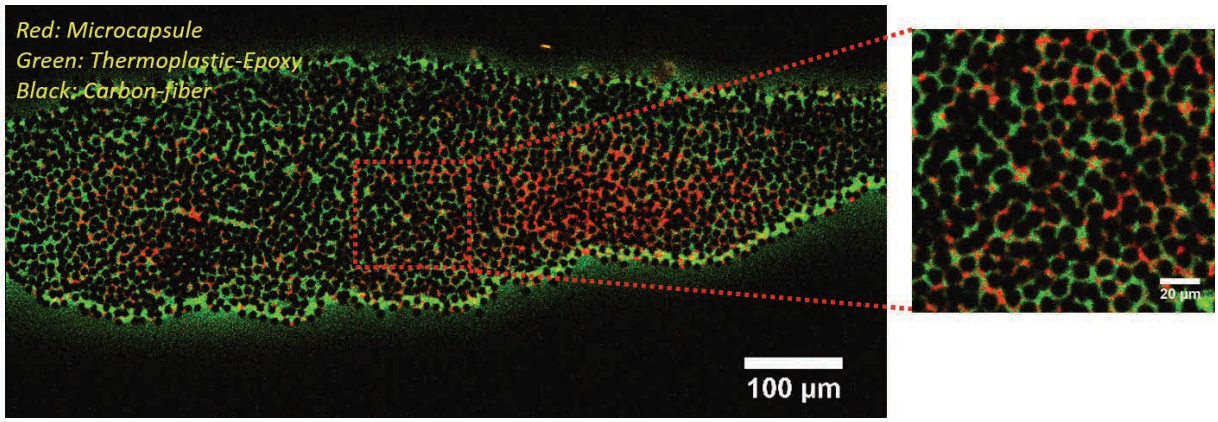

Figure 9. Confocal fluorescent microscopy of a carbon fiber tow within a prepreg, revealing intact microcapsules containing a fluorescent red dye in EPA solvent.

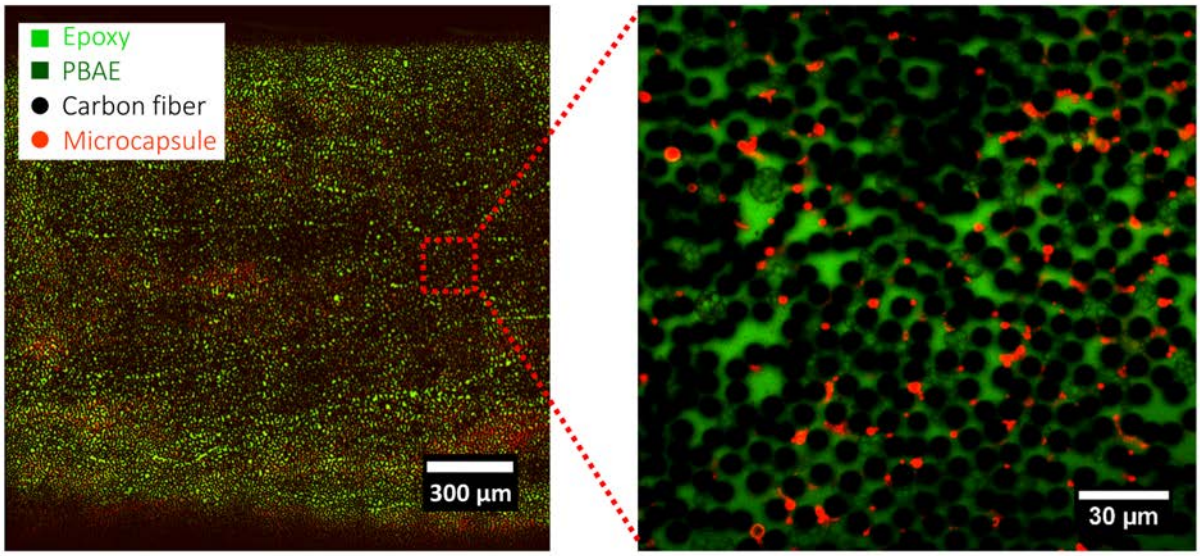

Figure 10. Confocal fluorescent image of a self-healing laminated composite demonstrates the presence of intact microcapsules and thermoplastic phase within the matrix.

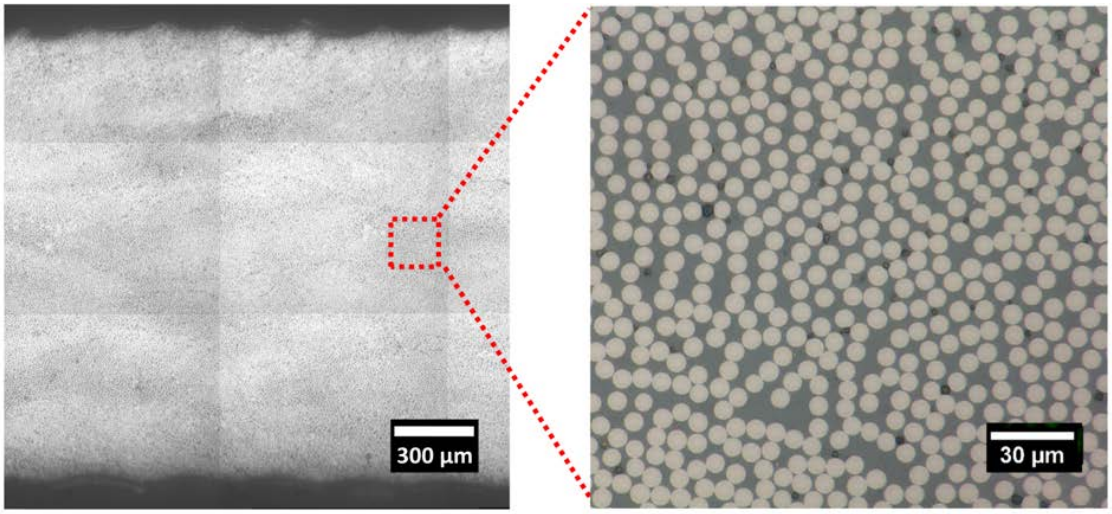

Figure 11. Optical microscope image of a self-healing composite shows the cross-section of fiber (white pixels) and microcapsules (black pixels) without the presence of voids.

4. Fatigue Performance of Self-Healing Composites

4.1 Material and methods

Self-healing composites (V_f = 0.62, V_c = 0.037) were fabricated with a high volume fraction of microcapsules – capsule fraction of 10 vol% in matrix alone. Epoxy composites (V_f = 0.71) and toughened-epoxy composites (V_f = 0.66) were also fabricated from the process identical to self-healing composites except for the presence of thermoplastic/microcapsules or microcapsules, respectively.

Composite specimens were prepared as a cross-ply [0/90$_3$/0] scheme and subjected a tension-tension cyclic loading at 10 Hz with a load ratio R (S_{max}/S_{min}) = 10 and 80 % of ultimate tensile strength (UTS) for S_{max} as shown in **Figure 12**. The UTS of composite specimens were measured prior to the fatigue tests by quasi-static tensile loading at 0.6 mm/min. The cycle numbers at the fatigue failure were plotted into a two-parameter Weibull cumulative distribution curve, using a least square method, and the value of 95 percentile in the curve was used to represent the fatigue life.

Two types of fatigue test protocols were performed to demonstrate the effect of self-healing on composites' fatigue life. A continuous test applied cyclic loading to specimens until the ultimate failure. On the other hand, an intermittent test applied cyclic loading to specimens until 100 cycles and a resting period of 5 days was given to promote thermoplastic flow and liberation of healing agent. After the resting period, the specimens underwent to the subsequent cyclic loading until the ultimate failure.

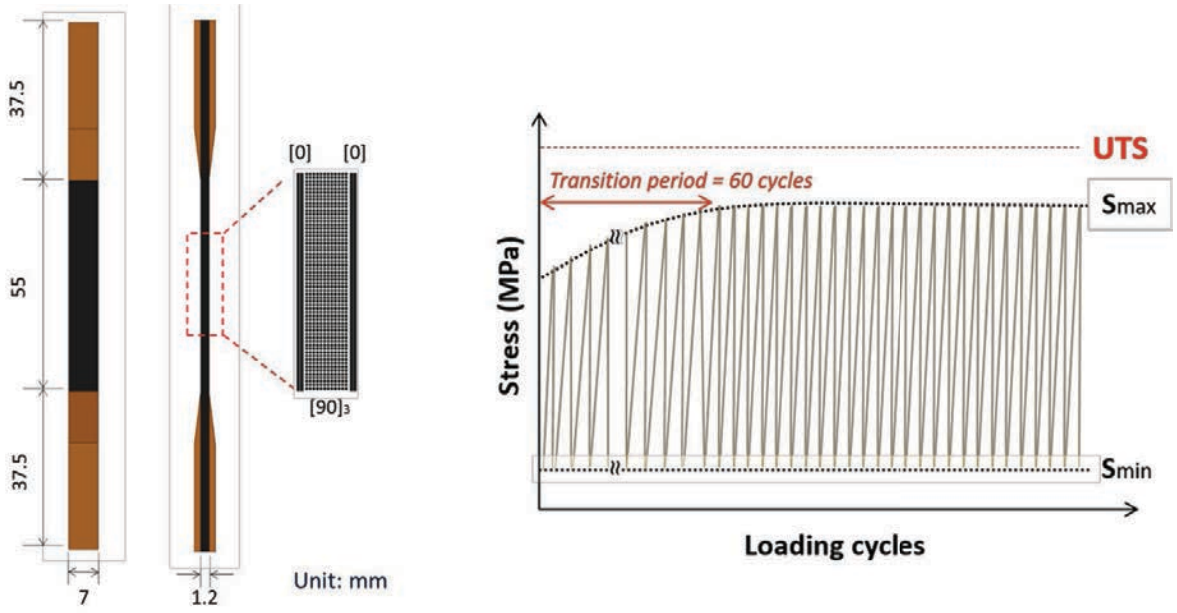

Figure 12. Schematic of test specimen (left) and fatigue loading conditions (right).

4.2 Self-Healing Composite Results

Ultimate tensile strength (UTS) of self-healing composites was 667.3 ± 19.2 MPa slightly reduced value compared to epoxy (703.5 ± 22.3 MPa) and toughened-epoxy (716.2 ± 46.3 MPa) composite. This drop in UTS is supposedly due to a combined effect of high loading of microcapsules (ca. 0.037) and low fiber volume fraction (0.62 vs. 0.66 or 0.71) in self-healing composites.

Measurement of secant modulus reveals the progressive damage in a cross-ply [0/90$_3$/0] laminated composite during a fatigue test (**Figure 13**). At the beginning of fatigue test, the secant modulus was exponentially decayed due to the transverse cracking in 90 plies and plateaued as the cracks saturate. Optical micrograph of the cross-sectional surface shows these transverse cracks are matrix-dominant damage which can be repaired by the self-healing mechanism (**Figure 14**). Soon after the crack saturation, a composite specimen exhibits the abrupt modulus reduction indicating the delamination or fiber breakage and further fatigue loads led to the catastrophic failure.

Fatigue life extension due to self-healing was demonstrated when a resting period is given to promote thermoplastic flow and liberation of the healing agent (**Figure 15**). All of the continuous test specimens failed before reaching 1,000 cycles while intermittent test specimens survived up to 4,000 cycles. Weibull cumulative distribution curve reveals that the fatigue life was extended by 410 % (963 vs. 3901) due to self-healing. Confocal imaging of a self-healing specimen also reveals that the microcapsules along the crack are ruptured implying the release of healing agent to crack planes (**Figure 16**).

Self-healing composites with low capsule volume (ca. 1.1 vol%) exhibited equivalent UTS with thermoplastic-toughened epoxy composites (**Figure 17**). Additionally, fatigue testing of these composites revealed the extension of the fatigue life due to self-healing (**Figure 18**), thus high-performance applications of these self-healing composites are feasible. Therefore, future work will focus on the self-healing performance depending on the stacking sequence and environmental fatigue.

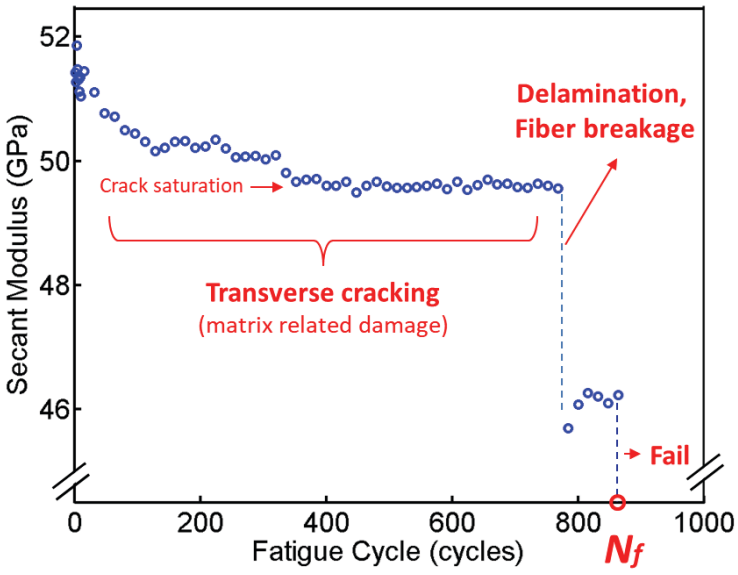

Figure 13. Secant modulus of self-healing composite as a function of fatigue cycles.

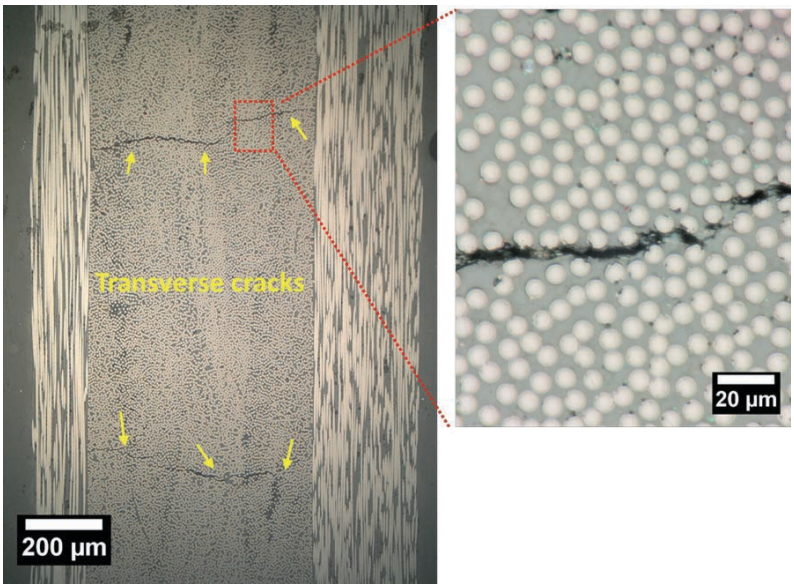

Figure 14. Optical cross-sectional image of a self-healing composite with transverse cracks due to a fatigue loading.

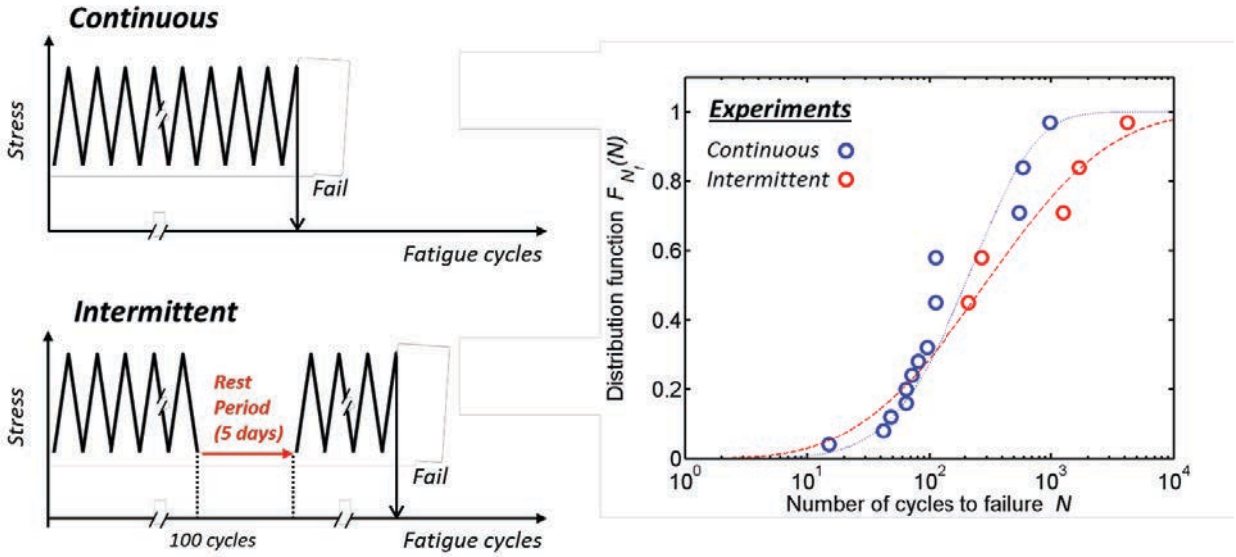

Figure 15. Weibull cumulative distribution curve for the fatigue life of self-healing composites at high capsule volume (ca. 3.7 vol%). Fatigue life (0.95) of self-healing composites is increased from 963 to 3901 cycles with a resting period.

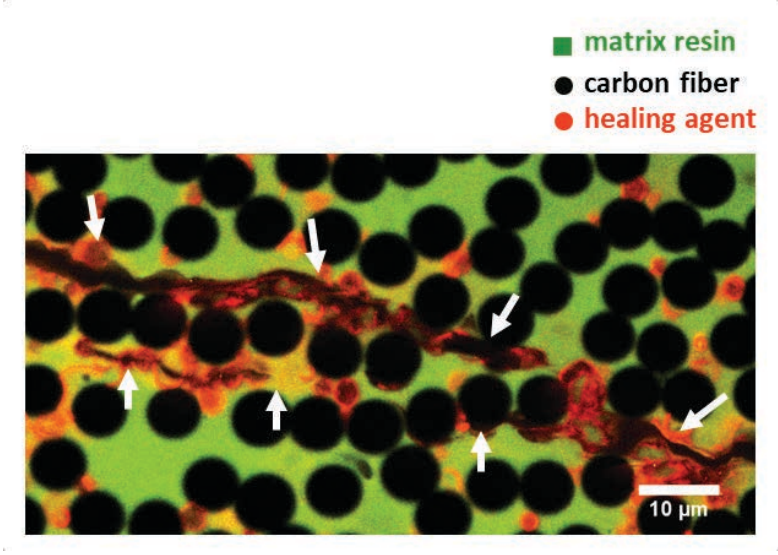

Figure 16. Confocal cross-sectional image of transverse crack in self-healing composite show ruptured microcapsules, implying the release of healing agent to crack plane.

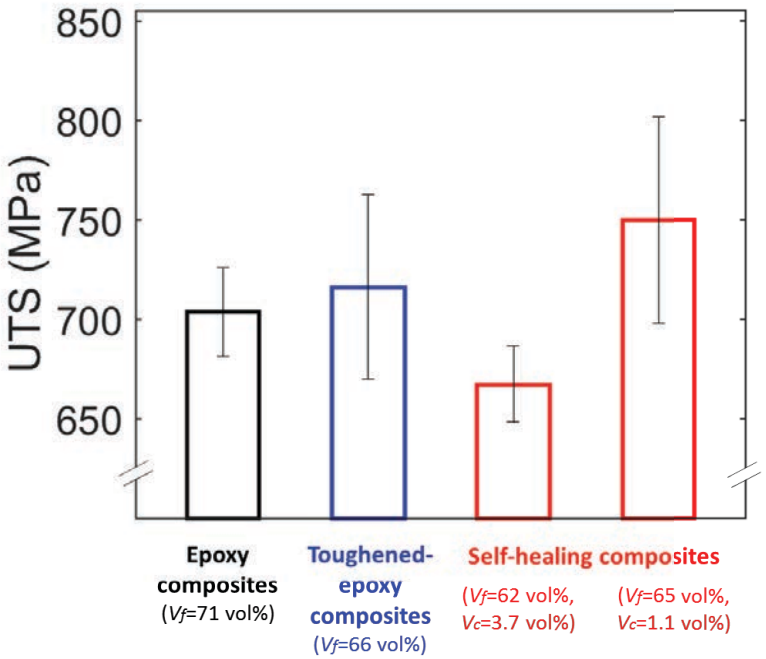

Figure 17. Ultimate tensile strength of laminated composites.

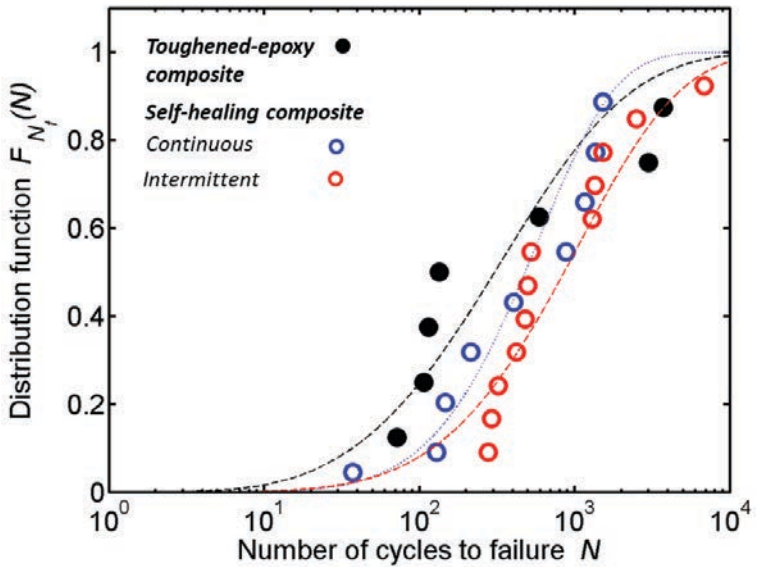

Figure 18. Weibull cumulative distribution of fatigue life for self-healing composites at low capsule volume fraction (ca. 1.1 vol%). Fatigue life (0.95) of self-healing composites increased from 2264 to 6621 cycles with a rest period, while the toughened-epoxy composite reached 3558 cycles.

5. Summary and Conclusions

The thermoplastic/solvent healing chemistry has been shown to overcome limitations of other self-healing for high T_g, high cure temperature epoxies. The microcapsules were thermally stable when coated in PDA with the exception of the formation of small voids that had negligible effect on core retention and healing. Thermoplastic and microcapsules both served to increase virgin toughness of the epoxy, and self-healing toughness was comparable to reference injection tests. Aging for up to 30 days did not cause deterioration in healing performance.

A unidirectional carbon fiber/thermoplastic-toughened epoxy prepreg with EPA-filled microcapsules was successfully fabricated using a bench-top prepregger. Processing parameters were varied to control the fiber volume fraction and capsule concentration of the prepreg. A sizing agent containing microcapsules and MEK solvent aided the direct resin-impregnation without a fiber drying process. A high fiber volume fraction self-healing laminated composite was fabricated from this prepreg by hot-pressing. This laminated composite possessed both intact microcapsules and thermoplastic phases. Fatigue life extension of 300% was demonstrated in self-healing composites at high capsule volume (ca. 3.7 vol%) with some reduction in the ultimate tensile strength. Remarkably, at lower capsule fractions (ca. 1.1%), a fatigue life extension of over 200% is achieved with no loss in tensile strength.

6. References

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