An Assessment of Self-Healing Fiber Reinforced Composites

Joseph G. Smith, Jr.
Langley Research Center, Hampton, Virginia
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ABSTRACT

Several reviews and books have been written concerning self-healing polymers over the last few years. These have focused primarily on the types of self-healing materials being studied, with minor emphasis given to composite properties. The purpose of this review is to assess the self-healing ability of these materials when utilized in fiber reinforced composites.

ABBREVIATIONS

CAI: compression after impact  
CFRC: carbon fiber-reinforced composite  
DCB: double cantilever beam  
DCPD: endo-dicyclopentadiene  
DETA: diethylenetriamine  
DMTA: dynamic mechanical thermal analysis  
EMAA: poly(ethylene-co-methacrylic acid)  
FRC: fiber-reinforced composite  
G\textsubscript{1C}: plane strain critical strain energy release rate  
GFRC: glass fiber-reinforced composite  
HGFs: hollow glass fibers  
IVHM: integrated health monitoring system  
K\textsubscript{1C}: plane strain critical stress intensity factor  
P\textsubscript{C}: applied load  
phr: parts per hundred resin  
rcs: residual compressive strength  
ROMP: ring-opening-metathesis-polymerization  
RT: room temperature  
SEM: scanning electron microscope  
T\textsubscript{g}: glass transition temperature  
TGA: thermogravimetric analysis  
tpi: threads per inch  
UIUC: University of Illinois at Urbana-Champaign  
WTDCB: width tapered DCB  
wt: weight  
\eta: healing efficiency

INTRODUCTION

Plants and animals possess the ability to repair damage (i.e. structural, internal, topological) through processes that have evolved over millennia. The dictionary defines healing as “1) to restore to health or soundness, cure and 2) to set right, repair”.\textsuperscript{1} Taken in the context of a polymer resin or fiber reinforced composite (FRC), healing involves the restoration of virgin material properties after incurring damage due to fatigue (e.g. microcracking) and impact damage occurring from impinging foreign objects such as rocks and dropped tools. Visible damage is easily observed, but requires an involved repair process.\textsuperscript{2} Barely visible impact damage (i.e. internal damage, microcracks, delamination, etc.) however is hard to detect, especially in its early stages when it may be easily repaired. Often this leads to rapid deterioration of material properties of the damaged part while in-service and subsequent failure. Even if detected, repairing internal damage is quite difficult. Thus it is desirable to have a material that would “heal itself” in a similar fashion as biological systems. However, this is a daunting and challenging task to replicate
with inanimate systems such as organic resins and FRCs. Additionally the type/degree of healing that one can expect depends on the service environment/mission of the vehicle. Healing in these cases is relegated to the resin and resin/fiber interface only since the technology to self-repair damaged fibers does not currently exist.

Over the last two decades, a considerable amount of research has been performed in the area of self-healing polymeric resins. This area was initiated with the pioneering work conducted by Dr. C. Dry on self-repairing concrete.\(^3\) Since that time the development of two differing self-healing methodologies referred to as intrinsic (i.e. nonautonomic) and extrinsic (i.e. autonomic) has emerged.

Intrinsic self-healing refers to the polymer/resin repairing itself usually through the application of an external stimulus such as heat or light. Materials that fall into this class include reverse Diels-Alder reaction polymers\(^4\-^7\), polyethylene-co-methacrylic acid\(^8\), and poly(\(\varepsilon\)-caprolactone)\(^9\). All of the aforementioned materials require the application of heat for healing to occur either through a chemical reaction (i.e. Diels-Alder reaction and its reverse reaction) or melting of a toughening resin to cause it to flow into the damaged area. Theoretically, these materials can be repeatedly healed based upon their respective chemistries/properties. In addition to the requirement of an external method to induce healing, an integrated health monitoring system (IVHM) would be needed to determine when damage does occur.

Conversely, extrinsic self-healing is where the material can heal itself using embedded healing agents that do not require activation by external stimuli. In this approach the healing agent is incorporated in the resin or FRC through the use of encapsulating agents: microcapsules or hollow glass fibers (HGFs). Numerous publications with respect to both encapsulant technologies have been published with a majority of the work being reported by White et al.\(^10\-^15\) (microcapsules) and Bond et al.\(^16\-^20\) (HGFs). This methodology requires the rupture of the encapsulating vessel containing the healing agent(s), interfacial mixing (i.e. static) of the healing agent(s), and reaction of the healing agent(s) with embedded catalyst, where applicable, in a reasonable time under ambient conditions. Most cures have been reported to occur at RT, typically over a period of 48 h. Faster cure is observed at elevated temperature through the application of an external heat source; however, this would necessitate an IVHM as stated above. Even though this methodology provides truly autonomous healing, it is limited to a singular event. Additionally, once the healing agent is released from the encapsulating vessel to heal a crack, a void is created where the healing agent was located. With this approach the effect of void formation on residual mechanical properties after healing has to be considered in the intended material application.

While significant recovery (>90\%) of virgin neat resin material properties has been reported using both methodologies, this is not the case with FRCs made from them. The scope of this review is concerned with self-healing FRCs prepared from self-healing resins based upon the two methodologies described above. Details of the self-healing resins will not be addressed here, but the reader is referred to several recent reviews and books on the subject.\(^21\-^33\) Currently, two US companies promoting the extrinsic self-healing approach are Autonomic Materials Inc.\(^34\) and Natural Process Design Inc.\(^35\)

**HEALINGABILITY AND HEALING EFFICIENCY (\(\eta\))**

In order to assess the recovery/restoration of a property of interest afforded by self-healing materials, researchers have coined the terms “healing ability” and “healing efficiency” that are identified as \(\eta\). Both of these terms are inter-related in that they can be defined as

\[
\text{Value of restored property of interest after self-healing} = \frac{\text{Value of virgin property of interest}}{\text{Value of virgin property of interest}}
\]

Typically \(\eta\) is reported in percent. How the material is prepared, the property measured, and the test performed to acquire the data to obtain \(\eta\) varies between research groups making direct comparisons difficult. For example, Intrinsic Self-Healing Materials assessed healing ability either through visual assessment of surface crack damage or 3 point bend tests with respect to strain energy. Extrinsic Self-Healing Materials on the other hand has reported \(\eta\) based on data obtained from double cantilever beam
(DCB), width tapered DCB, compression after impact (CAI), and 4 point bend specimens. Additionally, visual assessment of crack healing was used as a criterion similar to Intrinsic Self-Healing Materials. A very good treatise on $\eta$ is covered in a recent review.32

**INTRINSIC (NONAUTONOMIC) SELF-HEALING COMPOSITES**

Much of the work to date employing this method has been accomplished using materials based upon the Diels-Alder reaction. Following damage, the resin is able to undergo a reverse Diels-Alder reaction at elevated temperature to effect healing to recoup virgin resin properties (Figure 1). This behavior was first reported by Chen et al. for compounds containing multiple furan and maleimide groups.7 The resin $\eta$ was $\sim 80\%$ based on the virgin room temperature (RT) properties measured for modified compact tension specimens. However FRCs were not prepared from this system.

![Figure 1. Self-healing Diels-Alder chemistry of furans and maleimides.]{7}

This Diels-Alder reaction approach was later extended to a new class of related materials called mendomers.4,6,36 Mendomer chemistry is based upon the dicyclopentadiene ring (Figure 2) where it was suggested that failure would occur preferentially in the bonds forming the Diels-Alder adduct regenerating the dicyclopentadiene ring. Room temperature neat resin properties of a polymer (i.e. Polymend) from a particular mendomer (mp 107°C, composition not identified) was reported to be comparable to engineering polymers such as poly(methyl methacrylate).4 Carbon FRCs (CFRCs) of Polymend were prepared by sandwiching the material between two pieces of carbon fiber fabric in a mold and heating the assembly at 120°C for 3 h under 0.55 MPa to afford a CFRC with a calculated resin volume fraction of 60%. Composite strips were placed in an Instron at RT and stretched to induce microcrack damage. After optical microscopic characterization, the cracked strips were secured between aluminum plates to simulate applied pressure (none provided) and heated in an oven at 180°C for 1 h. In order for the crack to be effectively healed, the mendomer had to be heated above its $T_g$ and the material brought close together via pressure. The crack was observed by optical microscopy to be fully healed following this process.

![Figure 2. Self-healing Diels-Alder (Mendomer) chemistry of dicyclopentadienes.]{4,6,36}
Another member of the mendomer family, mendomer 401, was used to fabricate CFRCs by placing the powder (melting point of 110°C) along all sides of two plies of AS4 fabric and heating the material in an autoclave at 150°C under 98.2 kPA vacuum for 20 h without the application of pressure. The prepared laminates were calculated to have a fiber volume fraction of ~36%. From dynamic mechanical thermal analysis (DMTA) results, the glass transition temperature \( T_g \) was 128°C. Test coupons were machined from the laminates for 3-point bend testing at RT to evaluate healing ability. The span was adjusted to induce microcracks towards the laminate center. Microcracks that formed on the coupon surface were healed through resistive heating using copper electrodes bonded to the composite surface. A temperature of 150°C was achieved which was sufficient for healing. Healing was reported to be complete in less than 15s. Healed coupons were subjected to several cycles of testing and healing. Heating ability was determined based on the virgin sample RT strain energy of 99.34 mJ up to a 14 mm deflection. Over three tests, the healed composite exhibited 92-94% of its virgin strain energy. Other mechanical properties for the composites were not reported.

A second intrinsic approach was based upon a thermoplastic dissolved in a thermoset. The hypothesis was that by heating the damaged FRC, the thermoplastic would flow into the damaged area and effectively heal the damaged resin once cooled. In this work the thermoset was a mixed epoxy system (Araldite LY1556 and GY298) cured with nadic methylene anhydride and a mercaptan terminated liquid curing agent that acted as an anhydride accelerator. The thermoplastic, poly(bisphenol A-co-epichlorohydrin) with a weight average molecular weight of 40,000 g/mol (Figure 3), was blended into the epoxy at 10 wt%. E-glass fiber composites with a [0,90,2,0] lay-up were prepared by vacuum assisted resin infusion. The cure cycle was 80°C for 4 h followed by 130°C for 3 h. The \( T_g \) of this system was not reported. To assess the healing ability, the composite was impacted with 2.7 J of energy using a Davenport falling dart with a 10 mm diameter hemispherical tup. Healing was induced by heating the damaged composite at 130°C for 1 h unrestrained in an oven. Image analysis of photographs acquired before and after healing was used to determine the efficiency of healing. It was observed that there was a >30% reduction of visible surface damage (e.g. microcracks, and delamination) after healing. Other mechanical properties (i.e. virgin or healed) of this system have not been reported.

**EXTRINSIC (AUTONOMIC) SELF-HEALING COMPOSITES**

The two prominent extrinsic approaches are based upon microcapsules and HGFs that rely upon an active matrix crack to break the encapsulating vessel to release a liquid healing resin. Microcapsules are able to release small quantities of liquid resin that can subsequently polymerize due to reaction with a catalyst distributed throughout the matrix thus healing the crack (Figure 4). HGF’s can release larger resin volumes to the damage area due to the larger size of the encapsulating vessel. The HGFs contain both a healing resin and a cure agent in separate HGFs as illustrated in Figure 5 that react together once both vessels are broken. The two approaches have demonstrated the ability to effectively heal neat resins with a recovery of up to 100% of virgin material properties. However, similar healing efficacy has not been demonstrated for FRCs utilizing these methods without manual intervention (i.e.
applied heat and pressure in some cases). Results using each approach in FRCs are described in more detail below.

Microcapsules

The FRC work involving urea–formaldehyde based microcapsules containing a liquid healing agent has been performed by two groups using two different catalytic systems distributed throughout the resin matrix to effect healing. The first reported work was by the White group located at the University of Illinois at Urbana-Champaign (UIUC), which employed a Grubb’s catalyst [bis(tricyclohexylphosphine) benzylidine ruthenium (IV) dichloride] to initiate the ring-opening-metathesis-polymerization (ROMP) of endo-dicyclopentadiene (DCPD). DCPD has a viscosity of 0.736 cP at 21°C and reacts rapidly at RT (i.e. complete within 1-5 min) when mixed with Grubb’s catalyst via a ROMP reaction affording poly(DCPD). Commercial DCPD contains 100 to 200 ppm 4-tert-butylpyrocatechol as a stabilizer which the authors state “depresses the melting point from 33°C to 15°C” thus allowing the material to remain in the liquid state at RT. The catalyst was reported to exhibit thermal decomposition above 120°C, thus placing a limit on FRC fabrication conditions.

Initial composite work with this self-healing system examined whether neat resin self-healing was as effective in the FRC. Two different conditions were investigated using DCB specimens that involved manually injecting 1) a catalyzed healing resin (DCPD mixed with Grubb’s catalyst) into the crack (i.e. reference) and 2) healing resin (DCPD) into the crack containing embedded Grubb’s catalyst (i.e. self-activated). An illustration of these two conditions is shown in Figure 6. The reference samples were stated to provide an upper limit for η under ideal conditions and a comparison for the embedded Grubb’s catalyst specimens. The embedded catalyst in the self-activated specimens was to illustrate the retention of catalyst activity towards the ROMP reaction after FRC fabrication. The ROMP reaction would occur once the DCPD monomer would come in contact with the catalyst. Powdered Grubb’s catalyst was used as the embedded catalyst at a concentration of 1.75% by wt. For the premixed catalyzed DCPD resin, 1.38
wt% of Grubb’s catalyst was used. The DCB specimens (300 mm x 300 mm, 10-12 plies of 8H satin and plain weave E-glass fabrics) were prepared by hand lay-up followed by compression molding. The matrix resin was EPON 828 (bisphenol-A based epoxy) cured by 12 phr diethylenetriamine (DETA). Laminate cure conditions were 24 h at RT followed by a 24 h hold at 40°C. Fabrication pressure was not provided. The fabricated panels had a fiber volume fraction of 27 and 29% for the plain and satin weaves, respectively, as determined by acid digestion. Tested DCB specimens exhibited failures that were primarily interfacial debonding between the resin and fibers. Tested reference specimens had catalyzed resin injected into the crack via a syringe while DCPD was injected into the crack area of tested self-activated panels where embedded Grubb’s catalyst was present (Figure 6). Both panel types were subsequently clamped (pressure not provided) shut for 48 h at RT to allow for healing. The DCB test results are shown in Figures 7 and 8. The $\eta$ for this work was defined as $\frac{G_{IC}^{healed}}{G_{IC}^{virgin}}$ where $G_{IC}$ referred to the initiation or the plateau fracture toughness values for both conditions. The lower $G_{IC}$ values
of the self-activated plain weave FRC specimens compared to the reference shown in Figure 7 was attributed to clumping of the catalyst. Plain weave FRC reference specimens exhibited a $\eta$ of 46 and 51% for the initiation and plateau $G_{IC}$, respectively (Figure 7). The plain weave self-activated specimens had a much lower $\eta$ where the initiation and plateau $G_{IC}$s were 17 and 19%, respectively. One reason provided by the authors for the lower $\eta$ of the self-activated samples was incomplete coverage of the fracture plane by the polymerized resin, leaving it dry due to diffusion of the DCPD monomer into the matrix as a result of slow/sluggish polymerization in the crack area. Repeated healing was observed when fresh DCPD was injected into retested/reopened specimens signifying the resiliency of the catalyst. From both types of healing tests it was concluded that the interfacial bond strength between the E-glass and the DCPD healing agent was critical. Similar results were obtained for the 8H satin DCB specimens as shown in Figure 8. The lower $\eta$ of the 8H satin specimens compared to the plain weave samples was stated to be due to a lower amount of the catalyst being exposed to the DCPD monomer.

A second study was then conducted that employed lessons learned from the previous work described. One lesson was that primary amines (e.g. DETA) were observed to degrade the chemical reactivity of the Grubb’s catalyst. As a consequence, the DETA curing agent was replaced with Ancamine K54 [i.e. 2,4,6-tri(dimethylaminomethyl) phenol], a tertiary amine, and was added to EPON 828. Heloxy 71, a high molecular weight epoxy flexibilizer, was incorporated into the mix to improve matrix toughness and crack growth stability. A plain weave carbon fabric (3K, 12.5 x 12.5 tpi, 193 g/m² aerial weight) was used for composite fabrication. FRC 16-ply width tapered DCB (WTDCB) specimens were prepared by hand lay-up and cured at 25°C for 24 h under 31.7 kPa pressure followed by a post cure at 30°C for 48 h. Reference and self-activated specimens were prepared as described in the earlier study. In addition, self-healing specimens were prepared by incorporating 20 wt% DCPD containing microcapsules into the resin along with powdered Grubb’s catalyst. The microcapsules had a mean diameter of 166 $\mu$m. The Grubb’s catalyst concentration was 5 wt% for self-activated and self-healing samples. The test groups examined were: 1) reference and 2) self-activated as illustrated in Figure 6 and 3) self-healing as depicted in Figure 9. After the initial crack opening, the reference and self-activated groups were injected with the catalyst-DCPD mixture and DCPD, respectively, and subsequently clamped closed (pressure not provided) while healing occurred. The self-healing specimens were clamped closed (unspecified pressure) after testing.

Figure 8: Comparison of reference and self-activated DCB specimens for 8H Satin weave FRCs.
while the materials healed. Healing conditions for the reference group was 24 h at RT, the self-activated group was >48 h at RT, and the self-healing groups were >48 h at RT and 80°C, respectively. The 48 h cure time was chosen to ensure that full healing had occurred at RT. The $\eta$ for the WTDCB specimens was assessed as:

$$\eta = \frac{G_{IC}^{Healed}}{G_{IC}^{Virgin}} = \frac{\kappa_{IC}^{Healed}}{\kappa_{IC}^{Virgin}} = \frac{p_{C}^{Healed}}{p_{C}^{Virgin}}$$

Healed average and maximum $\eta$ were based on the ratio of the average of all healed and virgin critical load values and the ratio of maximum healed critical load to average virgin critical load. The average $\eta$ as shown in Figure 10 (i.e. healed) were as follows: reference 99%, self-activated 73%, self-healing at RT 38%, and self-healing at 80°C 66%. Maximum $\eta$ for each of the test specimens was approximately 8% higher than the average values and was attributed to varying degrees of healing inside the specimens. Reasons for the variable healing were cited as 1) uneven coverage of the crack area with healing resin and 2) variations in exposure of the DCPD to the catalyst. The difference in $\eta$ between the self-activated and reference groups was attributed to lack of interactions between the catalyst and DCPD at the fracture plane of the former. These included DCPD diffusing into the matrix due to slower polymerization resulting in incomplete coverage of the damaged area and retardation of the reaction due to a low amount of exposed Grubb’s catalyst concentration along the fracture plane as noted in the earlier study. Also, the catalyst was reported to form clumps in the matrix. These results were similar to those obtained in the prior study. The $\eta$ for self-healing specimens allowed to heal at RT was lower than either the reference or self-activated specimens. Scanning electron microscopic analysis revealed that few microcapsules were broken when the crack was located in the interfacial region between the matrix and the fiber. However, if the crack resided in the matrix numerous microcapsules were broken. As expected, when the temperature was increased to 80°C, the $\eta$ improved by almost a factor of 2 due to increased reaction rate and decreased loss of DCPD to the matrix by diffusion. In comparison to the FRC results, the neat resin was reported to have a $\eta$ of approximately 90%. The lower $\eta$ of the FRCs was contributed to a lower mass fraction of the self-healing matrix and the high thermal mass of the reinforcing fibers. This high thermal mass was thought to “result in a lower temperature in the healing region that could retard the ROMP reaction of DCPD since it is an exothermic reaction”. A retardation of approximately 20% was reported for the reaction kinetics for the FRC compared to the neat resin.

To better understand the development of $\eta$ and $K_{IC}$ at RT, a kinetic study was performed where samples were tested at nine different times from 10 min to 48 h after the virgin loading. A plot of the mean $\eta$ and $K_{IC}$ vs. the log of healing time (not shown) was a linear relationship. From this RT kinetic study, it was found that the initial cure did not commence until 0.5 h after testing with maximum cure being attained at 48 h. Times >48 h were not evaluated so it is unclear if further healing, hence an increase in $\eta$, would occur.

To alleviate catalyst clumping, a subsequent study was performed where the Grubb’s catalyst was encased within paraffin wax microspheres at a concentration of 10 wt%. In this study a qualitative
Figure 10: Effect of healing condition upon $K_{IC}$ and $\eta$ for WTDCB specimens.\textsuperscript{39}

Visual assessment of crack reduction was made for panels subjected to low velocity impact damage. The original EPON 828/DETA (4:1 weight ratio) was evaluated along with a new resin system: EPON 862.
(bisphenol-F based epoxy) cured with Epi-cure 3274 (a moderately reactive aliphatic amine) in a 100:40 weight ratio. FRCs were prepared using 4 plies of 810 g/m² 5 x 5 yarns-per-inch plain weave S2 glass fabric and the appropriate resin and healing system. For EPON 828/DETA, 35 μm microcapsules containing DCPD and 270 μm wax microspheres containing 10 wt% Grubb’s catalyst were used. The DCPD microcapsules and Grubb’s catalyst wax microspheres were present at 10 and 3 wt%, respectively. For the EPON 862/Epi-cure 3274 system, a 2:1 ratio of 35 and 180 μm microcapsules containing DCPD and 135 μm wax microspheres of Grubb’s catalyst were employed. The DCPD microcapsules and Grubb’s catalyst wax microspheres were present at 7 and 2 wt%, respectively. FRC fabrication was by hand lay-up with the panels being cured at RT for 24 h under a pressure of 93 kPa. The EPON 828 and 862 systems were then post-cured without applied pressure at 35°C for 24 and 48 h, respectively. Control panels for both resin systems contained the same quantity of microcapsules and wax microspheres as the self-healing panels except that no catalyst was present in the microspheres. The fiber volume was estimated at approximately 30 based on the areal density of the fabric and panel thickness. FRC panels of the EPON 828 and 862 systems were then subjected to impact energies of 81 and 44 J, respectively. The lower impact energy used for the EPON 862 system was due to the panels being more prone to damage. After impact, all panels were allowed to heal unrestrained for 48 h prior to retesting. Both resin/healing FRC systems were compared to control panels. Self-healing EPON 828 FRCs exhibited healed microcracks compared to the control panel based on total crack length per imaged edge. Crack healing though was not as anticipated with only regions along the cracks being healed as determined by optical microscopy and SEM. Subsequent analysis showed patchy regions of the DCPD healing resin located around the microspheres containing the Grubb’s catalyst after healing. This was attributed to some inactivated catalyst and poor microsphere dispersion in the FRC during panel fabrication. These problems were addressed using the EPON 862 system and a mixture of two different sizes of microcapsules containing the DCPD monomer. The two microcapsule sizes were utilized so as to deliver more healing resin to the cracks. After impact testing, the self-healed EPON 862 FRCs showed a 51% reduction in crack length compared to the control as confirmed by optical microscopy and SEM which indicated predominantly healed delaminated areas with minor unfilled areas. Unfilled surface cracks and transverse cracks where no healing materials were present were also identified. Comparison of crack length per imaged edge results of EPON 862 FRC panels containing 1) no microcapsules or wax microspheres, 2) microcapsules only, and 3) microspheres and unfilled wax microspheres revealed that unfilled wax microsphere incorporation had a deleterious effect upon damage resistance whereas microcapsules alone had a negligible effect. Reasons put forth by the authors focused on the unfilled wax microspheres plasticizing the FRC, reducing interlaminar shear properties, or acting as voids.

Compression after impact (CAI) testing was performed on a series of EPON 862/Epi-cure 3274 FRC panels to assess self-healing performance by comparison to two controls. Control (C-I) FRC panels contained no DCPD filled microcapsules and wax microspheres filled with Grubb’s catalyst. The second control, designated C-III, contained DCPD filled microcapsules, 35 and 125 μm, and unfilled 135 μm wax microspheres. The two different microcapsule sizes were to 1) allow for even distribution of the microcapsules within the FRC, 2) delivery of a large volume of healing resin (i.e. 125 μm microcapsules) to the damage area, and 3) delivery of healing resin to restricted locations (i.e. 35 μm microcapsules). Self healing FRC panels (SH) contained DCPD filled microcapsules, 35 and 125 μm, and 135 μm wax microspheres filled with 10 wt% Grubb’s catalyst. The microcapsules were incorporated at a 2:1 ratio of 35 μm:125 μm in the respective panels. The weight percent loading of the microcapsules, wax microspheres, and active catalyst in the SH panels was 7.4, 2.3, and 0.23, respectively. Impact energies ranged from 13.3 to 45.1 J delivered using a spherically shaped impact head. After impact the SH panels were allowed to heal unrestrained under ambient conditions for 48 h. The compressive strength for pristine (i.e. impact energy 0 J) FRC panels of C-I and C-III were comparable, approximately 80 MPa, implying no effect due to microcapsule and wax microsphere incorporation. The residual compressive strength (rcs) for SH and C-III were comparable (i.e. within 2%), approximately 56 MPa, after impact with 45.1 J of energy. C-I though had a rcs of 72 MPa when impacted with 45.1 J that was approximately 29% higher than the rcs for the SH and C-III FRC panels and was attributed to wax microsphere
incorporation. A comparison of SH to C-III after an impact with 17.8 J showed an approximate 16% higher rcs (i.e. 79 vs. 68 MPa, respectively) that can be attributed to healing. The higher rcs for the SH FRC panels compared to C-III FRC panels decreased with increasing impact energy to approximately 2% for an impact energy of 45.1 J as shown in Figure 11. Optical microscopy of C-III FRC panels showed delamination separations of approximately 35 to 100 μm for impact energies of 17.8 and 45.1 J, respectively. By calculating the theoretical volume of released healing agent, the authors determined that separations of approximately 100 μm or greater would not be filled or healed whereas at the lower impact energy there was sufficient healing agent present to completely fill the damage area. The authors concluded that for increasing impact energies the damage separations would increase resulting in a decrease of rcs recovery. Application of 1077 kPa pressure during healing to SH FRC panels that were impacted with 45.1 J resulted in the rcs increasing to 64 MPa compared to SH panels healed without applied pressure (56 MPa). C-III FRC panels subjected to the same conditions saw no improvements in rcs (54 vs 55 MPa, respectively).

![Figure 11: Residual Compressive Strength vs. Impact Energy.](image)

Similar to the work conducted by White et al., the Zhang group from Zhongshan University in the People’s Republic of China employed a complex of copper (II) bromide and 2-methylimidazole [CuBr$_2$(2-MeIm)$_4$] as a pre-dissolved latent hardener in a bisphenol-A epoxy matrix (type E-51). The healing agent was contained in microcapsules (30-70 μm in diameter) distributed throughout the matrix and was the same as the epoxy matrix used to prepare the composite. (The authors noted that this system requires the manual application of heat to effect healing. Thus it is not truly extrinsic.) FRCs were fabricated from 16 x 14 plain weave 400 g/m$^2$ E-glass. The matrix resin was type E-51 epoxy cured with a mixture of tetraethylenepentamine and acrylonitrile (1:2:1 wt:wt) at a wt ratio of epoxy to curing agent of 100:30. The CuBr$_2$(2-MeIm)$_4$ and microcapsules containing type E-51 epoxy were added at 10 and 2 wt%, respectively, to the matrix resin. Four plies of prepreg containing the healing agents were placed in the center of a twelve-ply panel during hand lay-up of the composite. In the middle of the composite was a Teflon film used to initiate a delamination crack. The FRC was cured at 80°C for 4 h followed by 100°C for 2 h. Compaction pressure was not provided. Fiber volume was 27% based on thermogravimetric
analysis (TGA). DCB laminates were subsequently machined from the FRC and tested at RT. Once tested, the specimens were healed at 130°C for 1 h and then retested. It is assumed that the laminates were unrestrained during healing since no clamp pressure was provided. The \( \eta \) was determined in a similar manner to that of the White group using

\[
\eta_{\text{laminates}} = \frac{K_{\text{IC}}}{K_{\text{IC}}} = \sqrt{\frac{G_{\text{IC}}}{G_{\text{IC}}'}}
\]

where \( \theta \) and \( \theta' \) denote virgin and healed material properties, respectively. The \( \eta \) for this system was 68%. This was comparable to the \( \eta \) of 66% obtained for self-healed WTDCB specimens heated at 80°C reported by the White group and calculated in the same manner.\(^{39}\)

The Zhang group also evaluated the effect of microcapsule and catalyst loading upon tensile and interlaminar fracture toughness properties and \( \eta \) in three small studies.\(^{44}\) DCB and tensile specimens were fabricated using 13 x 12 plain weave C-glass (0/90, 1000 tows, 200 g/m²) and cured at RT for 7 h unrestrained and then compression molded (pressure not provided) at 60, 80, and 100°C for 2 h at each temperature. The estimated fiber volume for both types of specimens was approximately 27%. The low fiber volume was desired by the authors so as to have a high concentration of the healing agent in the composite and to avoid microcapsule damage during manufacture. The microcapsule diameter ranged from 37 to 42 \( \mu \)m and contained bisphenol-A epoxy (type E-51) as the healing agent. The catalyst/hardener was CuBr₂(2-MeIm)_4. Testing and subsequent healing (with the added step of a 24 h rest at RT prior to retesting) of the composites was performed as described in their previous work above. The first part of this study investigated the effect of microcapsule loading upon virgin RT tensile strength and Young’s modulus. The catalyst loading was 2 wt%. A negligible decrease in properties was observed in the stress vs. strain graph for a sample containing only 2 wt% catalyst compared to one not containing catalyst or microcapsules. The addition of microcapsules resulted in decreased tensile strength and Young’s modulus with increasing microcapsule loading with the largest decrease occurring for a 30 wt% loading (Figure 12). Composite porosity was found to increase with increasing microcapsule loading with a 30 wt% microcapsule loading having the highest porosity.

![Figure 12: Effect of microcapsule loading upon composite properties.\(^{44}\)](image)

The second part of the study investigated the effect upon virgin \( G_{\text{IC}} \) properties and \( \eta \) by varying the catalyst loading (i.e. 0.5 to 3 wt%) for DCB specimens containing 20 wt% microcapsules with the results shown in Figure 13. The \( \eta \) was determined as previously defined.\(^{39,43}\) The virgin \( G_{\text{IC}} \) was observed to be
comparable regardless of the catalyst concentration. Healed (average) and maximum $\eta$ were based on the ratio of the average of all healed and virgin $G_{IC}$ values and the ratio of maximum healed $G_{IC}$ to average virgin $G_{IC}$. Samples that were tested, healed, and retested saw an increase in the $\eta$ from 39 to 71% for the average and healed maximum $G_{IC}$, respectively, when the catalyst concentration increased from 0.5 to 2 wt% with a slight decrease at a 3 wt% catalyst loading. However, the $\eta$ for the healed $G_{IC}$ leveled off for catalyst loadings $\geq$1 wt%. The third part of the study varied microcapsule loading in DCB specimens (i.e. 10, 30, and 35 wt%) while holding the catalyst concentration at 2 and 3 wt%, respectively. The results for specimens containing 2 wt% catalyst and 20 wt% microcapsule loadings were included. In Figure 14 are shown the results for the 2 wt% catalyst loading. The virgin $G_{IC}$ was observed to minimally decrease.

Figure 13: Effect of catalyst concentration upon $G_{IC}$ and $\eta$ at a microcapsule loading of 20 wt%.

Figure 14: Effect of microcapsule loading upon $G_{IC}$ and $\eta$ at a catalyst concentration of 2 wt%.

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(approximately 2%) for a microcapsule loading of 20 wt% compared to one containing 10 wt% microcapsules for a catalyst loading of 2 wt%. Increasing the microcapsule loading to 30 and 35 wt% saw further reductions in virgin G\textsubscript{IC} by 13 and 17%, respectively. A similar trend in virgin G\textsubscript{IC} was observed for specimens containing a catalyst loading of 3 wt%. For a catalyst loading of 2 wt% the \eta was observed to increase from 37 to 47% for microcapsule loadings of 10 to 20 wt%, respectively. Smaller improvements in \eta (i.e. increase of 2 to 4%) were observed for healed G\textsubscript{IC} specimens containing higher microcapsule concentrations (i.e. 30 and 35 wt%, respectively) compared to the 20 wt% microcapsule loading. The \eta for the healed maximum G\textsubscript{IC} was seen to increase up to a 30 wt% microcapsule loading prior to decreasing at the higher loading. Similar results in \eta were observed for a catalyst loading of 3 wt%. From these small studies the authors found that a) high microcapsule loading is required for delivering sufficient healing agent to damaged areas so as to obtain high \eta and b) increasing microcapsule loading led to a reduction in tensile properties. 44 The authors stated that “… a balance between strength and toughness restoration should be considered when manufacturing self-healing composites for practical applications.” 44

A similar evaluation to that conducted by White’s group 41 was performed to assess the self-healing ability of this FRC system by evaluating impact damage and CAI. 45 FRC panels containing microcapsules were prepared by hand lay-up using epoxy type E-51, 2-ethyl-4-methylimidazole (2 wt%) as the curing agent, and 13 x 12 plain weave C-glass (1000 tows, 200 g/m\textsuperscript{2}). The cure conditions were 80, 120, and 140\degree C for 2 h at each temperature. No mold pressure was cited. The main focus of the study evaluated loading effect of 40 \mu m microcapsules (i.e. 10 and 20 wt%) upon \eta. A secondary study evaluated the effect of microcapsule size (i.e. 40, 65, and 140 \mu m) upon \eta at a 10 wt% loading. The larger microcapsule size was anticipated to deliver more healing agent to the damaged area. The CuBr\textsubscript{2}(2-MeIm)\textsubscript{4} was pre-dispersed in the matrix at a 2 wt% loading for both studies. The fiber volume of the cured FRCs was 30% as determined by TGA. Impact tests were conducted at 30\degree C at 1.5, 2.0, 2.5, and 3.5 J, representing energies that would cause matrix cracking transitioning to fiber fracture, using a hemispherical tip. The impacted panels were then healed at 140\degree C for 0.5 h unrestrained in an oven or under pressure (i.e. 60 or 240 kPa, 0.6 or 2.4 atm) in a heated press. The \eta was determined by

$$\eta = \left[ \left( \frac{\sigma_{\text{healed}} - \sigma_{\text{impact}}}{\sigma_{\text{virgin}} - \sigma_{\text{impact}}} \right) \right] \times 100\%$$

where \sigma_{\text{healed}} is the compressive strength after healing, \sigma_{\text{virgin}} is the compressive strength of the pristine FRC, and \sigma_{\text{impact}} is the compressive strength of the impacted panel. Similar to the results reported by White et al. 41, as the impact energy increased from 1.5 to 3.5 J the \eta decreased from 95 to 18% for FRCs healed unrestrained. The decrease in \eta was attributed to a change in the impact damage progressing from matrix cracking to delamination and fiber breakage as impact energy increased thus making healing less effective. Healing conducted at 60 kPa pressure afforded an approximate 10 and 20% improvement in \eta for FRCs impacted at 2.5 to 3.5 J, respectively, compared to the unrestrained panels. This was attributed to the pressure bringing the cracks closer together to promote more effective healing. A negligible improvement was seen for the FRCs that were impacted with 2.0 J. From this result the authors stated “It can thus be concluded that applying pressure on the specimens during healing is necessary for the composites with severe damages to improve the efficiency of repairing.” 48 Increasing the pressure to 240 kPa during healing showed no increase in \eta over the 60 kPa results. FRCs containing 20 wt% microcapsules and impacted at 1.5 J showed an approximate 5% increase in \eta for panels healed unrestrained and under 60 kPa of pressure compared to ones containing 10 wt% microcapsules. This improvement was attributed to a larger volume of healing agent present for the 20 wt% loading compared to the 10 wt%. When impacted at 2.5 J, this improvement was 13 to 20% for FRCs healed unrestrained and under 60 kPa, respectively, and was also attributed to the larger amount of healing agent present. It was observed that increasing microcapsule size had a negligible effect upon \eta for FRCs impacted at the same energy level (i.e. 1.5 and 2.5 J).


Hollow Glass Fibers (HGFs)

The earliest work using HGFs to repair polymeric matrix composites was by Dry. It was a proof-of-concept using HGFs filled with a cyanoacrylate adhesive in a resin matrix composed of 2.7 parts by wt EPON 871 (i.e. an aliphatic epoxy ester resin) and 2.0 parts by wt EPON 828 (i.e. a difunctional epoxy based on bisphenol A and epichlorohydrin) and cured with 1.0 part by wt PACEM (unknown, not defined by author) at RT for 1 week. Panels containing several filled HGFs were impacted at RT and allowed to heal unrestrained at RT for approximately 8 months prior to retesting. No mechanical properties were provided, however, the adhesive reportedly healed the matrix cracks.

Building upon this early demonstration was the work by Bleay et al. The η in this study was not determined in the same manner as the microcapsule work or described in the beginning of this review. Rather it was assessed by comparison of CAI results of control and self-healing FRCs. The FRCs were fabricated using unidirectional prepreg of “Hollex” fiber (Owens-Corning, S2-glass based, 5 and 15 μm inner and outer diameter, respectively) and HTM40U epoxy resin with the following lay-ups: [(0°/90°)12], and [(±45°/0°/90°)c]. The FRCs were cured at 180°C for 2 h affording a cured Tg of 185°C. The processing pressure and fiber volume of the FRCs were not provided. Several one- (cyanoacrylate resins) and two-part (epoxy resins) healing system candidates exhibiting a range of cure times and viscosities were evaluated before deciding upon Ciba MY750 based on its apparent viscosity. Even though Ciba MY750 possessed a low viscosity, it still had to be diluted with acetone to further reduce the viscosity of the healing resin so as to properly fill the HGFs in the panels. An acetone solution (approximately 40% by volume) of this two-part epoxy system (i.e. Ciba-Geigy MY750) was utilized as the healing agent and incorporated into the post-fabricated FRC via a vacuum assisted capillary action filling technique. An illustration of a parallel HGF configuration with resin and hardener is shown in Figure 15.

Figure 15. Illustration of HGF self-healing approach.

panels were allowed to stand (temperature and time not provided) for solvent evaporation. The curing agent (hardener and accelerator, neither identified) filled HGFs in the 0° direction whereas the epoxy resin filled HGFs in the 90° and ±45° directions. After filling the HGFs, the weight of the FRCs increased approximately 1%. FRCs were impacted with 80 J of energy from a hemispherical loading head. Four different healing conditions were applied to post-impacted panels. These were 1) no treatment (control), 2) heated to 60°C and held for 1 h, 3) vacuum (presumably at RT), and 4) heated to 60°C and then a vacuum applied (presumably for 1 h). The lay-up for the FRCs tested and reported was not provided, but is assumed to be [(±45°/0°/90°)c]. The CAI results were comparable for filled (i.e. healed, approximately 180 MPa) and unfilled HGFs (i.e. 185 MPa) in FRCs impacted at 80 J for all healing conditions except for condition 4 where an approximate 10% increase in CAI strength (i.e. 201 MPa) was observed. The result for condition 4 implied limited healing. The CAI strength for all healed FRCs though was significantly lower than virgin FRCs, 430-663 MPa.

The work by Bleay et al. was then continued by Bond et al. using HGFs that were custom fabricated at a fiber fabrication facility located at the University of Bristol. The HGFs had an external diameter of 60 μm with a 50% hollow fraction. Hexcel 913/HGF prepreg with a fiber volume of approximately 61.5% was prepared by a resin infusion process. FRCs with a 0°/90° lay-up were fabricated from Hexcel 913/E-glass (12 μm diameter fiber) prepreg and the Hexcel 913/HGF prepreg for 4 point bend flexural
specimens to assess healing. Panel lay-up was \{[0°/90°]_{solid}, [90°/0°/90°/0°]_{HGF}, [0°/90°]_{solid}\} with the FRCs being cured following manufacturer conditions. The HGFs in the cured FRC were subsequently filled with an acetone solution (30 volume %) of uncured MY750 epoxy in the 0° direction and the hardener (not identified) in the 90° direction by a vacuum assisted liquid infiltration technique. Acetone (30% volume) was used to reduce the resin viscosity for HGF infiltration and was not allowed to evaporate as in the Bleay study. The retention of acetone in the mix was to aid in the dispersal of the resin during repair.\textsuperscript{17} To assess the stability and effectiveness of the healing agents, filled FRCs (B-E) were aged for 0, 3, 6, and 9 weeks after fabrication and prior to being damaged.\textsuperscript{16} The aged FRCs were then damaged, healed, and retested with the results compared to pristine (A) and damaged (F) unfilled control FRCs. Damage was induced by an indentation of the FRC by an Instron with a hemispherical tip to a maximum load of 1200 N corresponding to approximately 0.6 J. Prior to retesting, the impacted filled panels were allowed to self-heal for 24 h at RT unrestrained. The \(\eta\) was not determined in this work as defined earlier in this review, but was inferred from comparing the flexural strength of the aged healed damaged filled panels to that of the pristine unfilled panel.

Comparison of the HGF containing FRCs (A-F) illustrating the effect of aging upon healing is shown in Figure 16. The flexural strength of the unfilled pristine panel (A) was 733 MPa while that of the damaged unfilled panel (F) was 547 MPa; 75% that of panel A. An unaged (0 weeks, B) self-healed panel had a flexural strength of 682 MPa; 93% that of the flexural strength of panel A. The improvement of 18% in the flexural strength of panel B compared to panel F can be attributed to healing. Based on this result the authors stated

\textit{“This self-repairing mechanism is not proposed as a permanent measure to eradicate the effects of damage within a composite but to provide a means to inhibit further damage propagation.”}\textsuperscript{16}

Filled FRCs aged 3 (C) and 6 weeks (D) had flexural strengths of 546 and 574 MPa, respectively. Compared to the flexural strength of 547 MPa for the unfilled damaged panel, panel C showed no improvement due to healing while panel D afforded a minimal improvement of 3%. The flexural strength for panel E after 9 weeks of aging was 55% (i.e. 404 MPa) of panel A whereas the control panel F exhibited 75% of the flexural strength of panel A. The reason for the reduction of the self-healing ability, as stated by the authors, was attributed to several factors, including the unoptimized healing resin and its
modification with acetone. No reason was provided for the significant reduction of the flexural strength of panel E compared panel F.

A second part of this study evaluated the effect of time and temperature upon healing ability (Figure 17). Damage was induced to 4 point flexural specimens by an Instron with a hemispherical tip to a maximum load of 1200 N corresponding to an impact energy of approximately 0.55 J. The unfilled damaged panel (panel A) exhibited approximately 88%, (i.e. 548 MPa) of the flexural strength of the pristine unfilled panel (i.e. panel B, 624 MPa). Damaged filled panels were allowed to heal for 1) 24 h at RT (panel C) or 2) 1.5 h at 40°C (panel D). For condition 1 the self-healed panels (C) had a flexural strength of 604 MPa (97% of the flexural strength of panel B) that was 10% greater than that of panel A that was attributed to healing. Panel D, condition 2, exhibited a flexural strength of 555 MPa that was comparable to panel A. The reason for the poor self-healing ability at elevated temperature was attributed to insufficient filling of the cracks by the healing resin due to a much faster cure reaction of the healing resin.

Bond et al. then evaluated the healing ability of CFRCs using Hexcel T300/914 prepreg where HGFs contained Cytec Cycom® 823 RTM (a RT cure two-part epoxy) as the “healing resin”. This work however was a proof-of-concept to attain the highest possible η since the HGFs were infiltrated with a premixed healing resin prior to FRC testing. Also, the healing process was aided by the addition of external heat to help reduce the viscosity of the healing resin for improved flow and subsequently speed up the cure (hours instead of a week at RT) after damage was incurred. The authors stated that “Cycom® 823 is not designated a 'healing agent' and was chosen as the best available commercial system to fulfill this role. In fact, no epoxy resin system currently exists which is specifically designed for this type of application (i.e., low viscosity, insensitivity to mix ratio, rapid cure under ambient conditions and unlimited shelf-life).”

The HGFs had external and internal diameters of 60 and 42 µm, respectively, providing a 50% hollow fraction. The CFRCs (plain and containing HGFs spaced either 70 or 200 µm apart) for 4-point bend flexural testing were fabricated by hand lay-up and cured per manufacturer instructions. The HGFs were wound directly onto uncured CRFP prepreg prior to fabrication. A quasi-isotropic lay-up [16 ply (-45°/90°/45°/0°)2s] was used to fabric test specimens. At a 70 µm spacing the fibers were said to be...
effectively next to one another while a 200 μm spacing separated the HGFs by three fiber diameters. The reasoning for these spacings was to balance the self-healing properties provided by the HGFs (i.e. sufficient volume of healing resin) while minimizing the disruption caused by the HGFs upon laminate properties. The two HGF spacings, 70 and 200 μm, were incorporated directly into the prepreg affording a 3 and 1% volume fraction, respectively, that could hold 197 and 69 mm³, respectively, of the healing resin. The HGFs were located at two 0°/-45° ply interfaces in the 0° direction per the following lay-up:

(-45°/90°/45°/0°/HGF/-45°/90°/45°/0°/45°/90°/-45°/HGF/0°/45°/90°/-45°).

The healing resin, Cycom® 823 (a two-part epoxy resin), was premixed in a 4:1 ratio (other component not identified) and infiltrated into the HGFs via a vacuum assist technique prior to testing. The samples were indented with peak loads of 1700 or 2000 N using a spherical tup to create quasi-static impact damage that the authors stated could be related to Barely Visible Impact Damage. Once indented, the CFRCs were heated at 70°C for 0.75 h to reduce the healing resin viscosity for better filling of the damage sites. The panels were then heated at 125°C for 1.25 h to cure the healing resin. The healed CFRCs were then tested with the results compared to the damaged and undamaged samples to assess healing. The results are shown in Figure 18. For the pristine CFRC it was found that the incorporation of the HGFs resulted in a 2 to 8% reduction (200 and 70 μm spacing, respectively) in flexural strength (i.e. 569 and 535 MPa, respectively) compared to the plain CFRC, 584 MPa. HGFs spaced 70 μm apart in the CFRCs exhibited better damage tolerance after an indentation of 2000 N compared to the 200 μm spacing even though the 70 μm spacing had a lower initial strength. After healing, the CFRCs with HGFs at a 70 μm spacing exhibited a 14% improvement in the flexural strength (i.e. 97% of the undamaged panel flexural strength) for samples indented at 2000 N compared to the 200 μm spacing even though the 70 μm spacing had a lower initial strength. After heating, the CFRCs with HGFs at a 70 μm spacing exhibited a 14% improvement in the flexural strength (i.e. 97% of the undamaged panel flexural strength) for samples indented at 2000 N compared to the flexural strength of the damaged CRFC panel containing HGFs spaced at 70 μm. Samples with HGFs spaced at 70 μm and indented at 1700 N exhibited little change in flexural strength compared to the damaged panel and hence no healing was observed. This was attributed to the better damage tolerance afforded by this spacing compared to the 200 μm spacing. CRFCs containing HGFs that were spaced 200 μm apart exhibited 86 and 70% of the flexural strength of the undamaged panel containing HGFs at a 200 μm spacing when indented with 1700

![Figure 18: Comparison of pristine and HGF containing FRCs.](image)
and 2000 N, respectively. After healing, the flexural strength of the two 200 μm HGF spacing indented panels (1700 and 2000 N) increased to 92 and 82%, respectively, of the undamaged CFRC. This increase in flexural strength (i.e. 6 and 12%, respectively), compared to the flexural strength of the unhealed damaged panels containing HGFs spaced at 200 μm can be attributed to healing. These results indicated that the initial flexural strength was unaffected by the HGF incorporation at a 200 μm spacing, but a better recoup of the pristine properties after healing was achieved at the 70 μm HGF spacing.

This work was then continued with CAI tests being conducted. The prepreg, HGFs, and healing systems used were the same as described above. An optimized FRC lay-up was

\[-45°/90°/45°/HGF(70)/0°/HGF(70)/-45°/90°/45°/HGF(70)/0°/0°/HGF(140)/-45°/90°/45°/HGF(140)/45°/90°/-45°\]

where 70 and 140 referred to the HGF spacing in μm. This stacking sequence afforded two different HGF distributions within the laminate at 5 different interfaces. The 140 μm HGFs were situated two interfaces above the center line while the 70 μm HGFs were below located three interfaces below the center line. This configuration was expected to deliver more healing resin to large delaminations occurring near the back face while providing enough material to be delivered to the front face where a lower amount of damage would be expected. A hemispherical tup was used to generate an impact energy of 3 J to simulate low velocity impact damage. After impact, the panels were heated to allow for healing according to the cycle previously described. The FRCs were retested with the results shown in Figure 19. The strength of the undamaged (i.e. pristine) HGF containing FRC was comparable to the plain undamaged FRC. After testing, the CAI strength of the unhealed HGF panel was 63% of the undamaged HGF containing FRC. The CAI strength improved to 90% of the undamaged HGF containing FRC after healing. The approximate 30% increase in strength can be attributed to healing of the FRC. However, this test was not realistic due to the premixing of the healing resin and heating of the FRC to achieve the best properties.

![Figure 19: Comparison of pristine and HGF containing FRCs.](image)

The work by Bond et al. continued with the fabrication of a 16 ply Glass FRC (GFRC) for flexural strength evaluation from E-glass/913 epoxy prepreg and in-house prepared HGF/913 prepreg. The lay-up for the panel was \([0°/+45°/90°/-45°]_2\) with the HGF/913 prepreg plies at the \(0°/45°\) damage critical ply interfaces as previously described. The HGFs had an external and internal diameter of 60 and 40 μm, respectively, affording a hollow fraction of 55%. The healing agent was Cycom® 823 as used in the
previous study\textsuperscript{18,19} Unlike the prior study where the healing resin was infiltrated into the HGFs following FRC panel fabrication and prior to testing, the HGFs were filled with the two unmixed components (i.e. resin and curing agent) of Cycom\textsuperscript{®} 823 prior to panel fabrication. The authors stated that the two components of Cycom\textsuperscript{®} 823 were robust enough to survive the GRFC fabrication temperature of 120°C for 1 h per manufacturer’s guidelines.\textsuperscript{48} Prior to 4-point bend flexural strength testing, low velocity impact damage was simulated using a spherical tup at a peak load of 2500 N in a 3-point bend quasi-static indentation. Damaged panels were then healed by heating in an oven for 2 h at 100°C and then retested. The results are shown in Figure 20. As previously observed\textsuperscript{18,19}, the incorporation of the HGFs in the composite decreased the flexural strength compared to a panel containing no HGFs. In this case the HGF panel flexural strength was 84\% of that of the plain baseline panel. Once damaged, the flexural strength of the FRC panel was 72\% of the pristine GFRC. The HGF containing panel, prior to self-healing was more robust and retained 88\% of the pristine HGF containing GFRC flexural strength. After healing the damaged FRC panel containing HGFs at elevated temperature, it was found that the flexural strength increased to 103\% that of the pristine HGF containing GFRC. Compared to the unhealed damaged FRC panel containing HGFs, this was an increase of approximately 15\% that could be attributed to healing.

![Figure 20: Comparison of pristine and HGF containing FRCs.\textsuperscript{48}](image)

Currently, the Bond et al. research is being conducted under a program entitled “CRack Arrest and Self-Healing in COMposite Structures (CRASHCOMPS)”. This is a 4-year program awarded in 2009 and funded at £1.2 million by the Engineering and Physical Sciences Research Council and the Defence Science and Technology Laboratory.\textsuperscript{49} The program goals are to “to develop methods to arrest, redirect and self-heal compression fracture in composite structures”.\textsuperscript{49}

CONCLUSIONS

Self-healing resins have, in many cases, been able to restore >90\% of the virgin neat resin material properties after healing. However, attempts at producing self-healing FRCs from these self-healing resins with comparable reclamation of virgin FRC properties after healing have met with limited success. The lack of translation of self-healing efficacy into FRCs has been attributed to lower quantities of the self-healing resin in the FRC to close “wide cracks/delaminations” and thermal loss of the healing reaction to the reinforcing fibers. This is in spite of significantly lower fiber volumes and thus greater resin content.
used in some studies, compared to conventional FRCs. The application of external pressure and stimuli (i.e. heat in most cases) tended to improve the FRC healing ability but requires an IVHM to alert one to the damage. If the FRC is heated for healing to occur (as with intrinsic resins), then dimensional stability of the structure/part may become a concern. Extrinsic materials are desirable; however, there are a number of concerns including, but not limited to, healing resin stability over the FRC service life, reaction rate of the healing resin, quantity of healing resin available, and void formation due to resin flowing from encapsulating vessels. Besides certification issues regardless of the methodology, two critical questions arise: “When would healing of the FRC occur?” and “How fast can healing occur to restore virgin FRC properties?” Regarding the first question, in-service or out-of-service healing environments could afford very different outcomes. The answer to this question would be dependent upon the vehicle mission/use. The second question concerning healing rate might mean the difference between catastrophic failure and survivability.

Further work in this area needs to address the development of appropriate resins that possess properties such as stability over the FRC lifetime; ability to react quickly once activated, and ability to survive FRC and final part fabrication. Additionally, determination of self-healing FRC properties under applicable test conditions (e.g. low and elevated temperatures, cyclic loading, etc.) needs to be performed to assess the effect of the environmental conditions.

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Several reviews and books have been written concerning self-healing polymers over the last few years. These have focused primarily on the types of self-healing materials being studied, with minor emphasis given to composite properties. The purpose of this review is to assess the self-healing ability of these materials when utilized in fiber reinforced composites.