AUTONOMOUS SELF-HEALING FUNCTIONALITY IN ADVANCED FIBRE REINFORCED POLYMER COMPOSITE MATERIALS

T. S. Coope[1,2,*], U. F.J. Mayer[2], I. P. Bond[1], R. S. Trask[1], D. F. Wass[2]

[1] Advanced Composites Centre for Innovation and Science (ACCIS), Department of Aerospace Engineering, University of Bristol, Bristol, BS8 1TR, UK

[2] School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

* Corresponding author(Tim.Coope@bristol.ac.uk)

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Abstract

A novel Lewis acid-catalysed self-healing system is investigated for implementation in epoxy-based fibre reinforced polymer (FRP) composite materials. The catalyst, scandium(III) triflate, is selected using a qualitative approach and subsequently embedded with pre-synthesised epoxy-solvent loaded microcapsules, into an epoxy resin. Healing is initiated when microcapsules are ruptured at the onset of crack propagation. The epoxy monomer healing agent contained within, actively undergoes ring-opening polymerisation (ROP) on contact with the locally placed catalyst, forming a new polymer to bridge the two fractured crack surfaces. Self-healing performance is quantified using tapered double cantilever beam (TDCB) epoxy resin test specimens and the effects of microcapsule loading, microcapsule content and healing temperature are all independently considered. As an initial proof of concept study, results show that a material recovery value of greater than 80% fracture strength is achieved for this novel Lewis acid-catalysed self-healing epoxy resin.

1. Introduction

Self-healing materials are attracting considerable interest for their potential to undertake autonomous and in-situ repair of damage. Taking inspiration from nature, the healing function for maintaining integrity within a load-bearing structure is analogous to tissue repair in animals and plants. FRP composite materials are increasingly being used in industries such as aerospace, renewable energy, military and transport sectors, predominantly as a way to reduce excess weight. Unlike conventional structural materials, FRPs have the potential to be designed to respond to environmental stimuli by embedding addition functionalities such as self-healing [1].

Matrix microcracking, crack propagation and delamination between plies are the three major composite damage mechanisms [2] and subsequent mechanisms for release or activation of self-healing agents (SHAs). Often these failure mechanisms are difficult and expensive to detect. Current delivery systems for SHAs embedded within polymers include vascular networks [3-4], hollow glass fibres (HGFs) [5-8], and most widely exploited to date, microcapsules [9-23]. The latter comprises a monomer or polymer precursor encapsulated in a stable, thin walled, polymer shell. When ruptured during crack propagation or a damage event, the monomer actively polymerises on contact with a

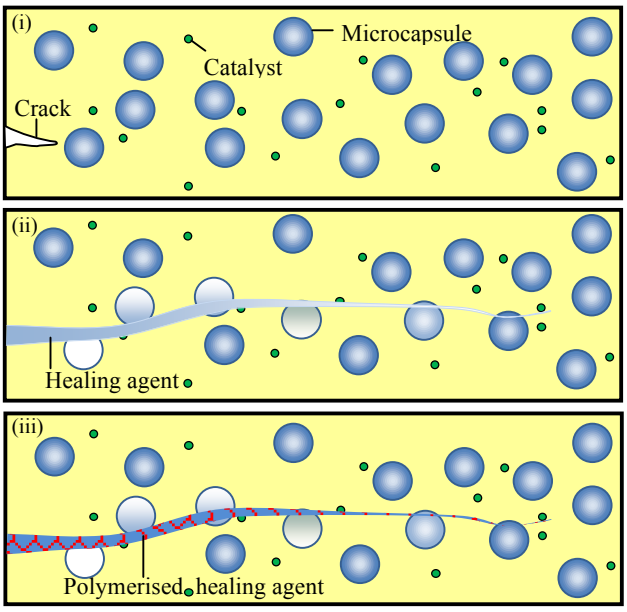

Fig.1. A self-healing polymer system concept containing epoxy-solvent loaded microcapsules and catalyst particles. (i) Crack initiation occurs from a damage event. (ii) Crack propagation releases epoxy monomer, which migrates along the crack by capillary action. (iii) Healing agent polymerises on contact with the catalyst to bridge the two exposed crack planes.

locally placed catalyst to repair the damaged region.

Over the past 10 years, White *et al*. and co-workers have extensively researched a capsule-based healing system that proceeds on the basis of ring-opening metathesis polymerisation (ROMP) of dicyclopentadiene (DCPD) via a Grubb's catalyst [24]. While recognising the success of this approach, there remain significant barriers for commercial exploitation of such a SHA system, which is compounded by the need to use conventional FRP manufacturing techniques. Catalyst and monomer are equally critical components in achieving optimal healing performance. Grubb's catalyst is well known for its catalytic ability [25], however, it is particularly air and moisture sensitive and prohibitively expensive. High performance FRP composite materials commonly employ epoxy resins as the matrix. It is, therefore, desirable to ensure good compatibility between the epoxy host matrix and any SHA embedded within such a material.

The prerequisites above are considered when developing an alternative microcapsule-based self-healing system (Fig.1.). Microcapsules containing diglycidyl ether bisphenol A (DGEBA) epoxy monomer encapsulated in a poly(urea-formaldehyde) (pUF) shell were adopted as a desirable healing agent and delivery system [13,26].

This study selects and evaluates a low cost, robust, solid phase catalyst to initiate ring-opening polymerisation (ROP) of unreacted epoxy monomer contained within pUF microcapsules. Metal triflates (trifluoromethanesulfonate) are well documented as effective Lewis acid catalysts in contemporary organic synthesis, due to their unique reactivity and selectivity under mild conditions. The weakly coordinating triflate anion is nucleophilic resulting in a more cationic metal counter ion and a stronger Lewis acid [27]. This system is not constrained by stoichiometric mixing and can successfully propagate via chain and step-growth polymerisation mechanisms.

Initially, SHA activity and performance was qualitatively analysed to evaluate the most suitable catalyst candidates. Scandium(III) triflate ($Sc(OTf)_3$) was selected as the self-healing catalyst due to its catalytic ability, relatively low cost and toxicity, high stability and availability [28]. Additionally, a non-toxic solvent (ethyl phenyl acetate - EPA) was introduced as a co-encapsulant during *in-situ* microencapsulation of the epoxy monomer (DGEBA). This was to assist in the migration of the SHA via capillary activation through damage in the host matrix. Subsequently, monomer and solvent weight percentages (wt%) were modified to achieve a greater healing efficiency. In comparison to a pure solvent capsule system, the SHAs investigated here do not rely on excess amine cross-linker to be present in the host matrix, thus eliminating the possibility of leaching under environmental conditions [13,26].

Here, we demonstrate a self-healing epoxy resin embedded with epoxy-based microcapsules combined with $Sc(OTf)_3$ catalyst particles. The focus of this research was a proof of concept study for fracture repair in tapered double cantilever beam (TDCB) epoxy resin test specimens. As reported below, results have shown that a material recovery value of greater than 80% fracture strength was achieved for a pure epoxy resin system. Furthermore, this self-healing system has been demonstrated using a dual embedded microcapsule - hollow fibre approach in FRP composite material. Preliminary experimental data was obtained using an end-notched flexural (ENF) test arrangement.

2. Results

2.1. Self-Healing Agents

Microcapsules containing unreacted self-healing agent were prepared by *insitu* microencapsulation of DGEBA monomer and non-toxic solvent, EPA [26]. A series of pUF walled microcapsule batches containing 75, 50 and 25 wt% DGEBA monomer were successfully synthesised (D75-, D50-, D25-capsules) and contents experimentally determined by nuclear magnetic resonance (NMR).

A qualitative approach was employed to test suitable catalyst candidates. SHAs were placed in between two glass microscope slides to consider adhesion after 24 hours at room temperature. An additional study considered catalyst solubility in EPA. The two studies carried out above, highlighted $Sc(OTf)_3$ as the most suitable catalyst to explore in an epoxy-based self-healing system. This catalyst shows good catalytic ability at ambient temperature and immediate solubility in a minimum amount of EPA solvent. Complete details are presented in the experimental section.

2.2 Fracture Testing

Self-healing performance was assessed using a modified TDCB test specimen arrangement as developed by Beres *et al.* [29]. Similarly to previous publications [12,13], a grooved central trench (GCT) section was adopted to contain SHAs. In this study a shortened central trench (SCT), 30

mm in length, was incorporated into the TDCB test specimen and terminated with a 2 mm crack stopper (Fig. 2). This arrangement was chosen to control crack propagation and importantly crack termination in order to facilitate self-healing in fractured test specimens. Healing efficiencies (ζ) were calculated for each individual test specimen using the initial ($P_{Initial}$) and healed (P_{Healed}) fracture load values. The data presented here corresponds to average data points obtained from experimental methods.

$$\zeta = P_{Healed} / P_{Initial} \quad (1)$$

A series of SHA reagent combinations and operating conditions were considered in manual induced healing and autonomous self-healing epoxy specimens.

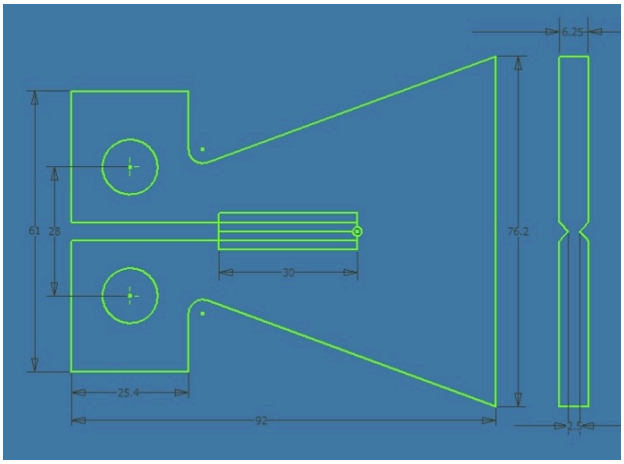

Fig.2. Tapered double cantilever beam (TDCB) geometry. Note: all dimensions in mm.

2.2.1 Manually Induced Healing

Blank Test Specimens

An initial benchmark was obtained to establish the average load failure point of a pure EPON 828/DETA resin test specimen. A series of fracture tests were performed on 10 specimens of which, 5 were suitable for manual healing. An average initial failure load and displacement value of 68.3 N and 0.58 mm were achieved for this data set.

Test specimens suitable for manual induced healing were injected with an EPA solution, containing the healing agents DGEBA monomer (20 wt%) and $Sc(OTf)_3$ (0.5 wt%), into the open crack plane. SHA loaded blank test specimens were left to heal at 45°C for 48 hours and retested to failure. Healed specimens achieved an average recovery of greater than 80% fracture strength. Average healed failure load and displacement values corresponded to 53.6 N and 0.70 mm respectively.

Microcapsule Test Specimens

An additional benchmark data set was obtained for EPON 828/DETA test specimens containing embedded D50-capsules (20 wt%). This was established to quantify the microcapsule induced toughening effect as previously documented by Brown *et al.* [26]. Average failure load and displacement values of 78 N and 0.74 mm respectively were achieved from 20 test specimens. Therefore, a marginal increase of 15% in the average peak failure load is observed in comparison with blank test specimens.

Successfully fractured specimens (10) were immediately loaded with 0.03g $Sc(OTf)_3$ after the initial fracture, to ensure microcapsule contents did not migrate out from the fractured crack planes. In total, 6 samples were healed at 45 °C and a further 4 samples were healed at 80 °C for 48 hours. Average material recovery values of 37% and 47% fracture strength were achieved at these two healing temperatures.

2.2.2 Autonomous Self-Healing

Autonomous (AUTO) self-healing test specimens contained active $Sc(OTf)_3$ catalyst particles (2.5 wt%) and DGEBA-EPA filled microcapsules (20 wt%), embedded in an EPON 828/DETA epoxy resin. The self-healing activation mechanism and the SHA mixing and delivery system were fully autonomous in nature. Therefore, no manual intervention was required to initiate self-healing, this is triggered primarily by the induced fracture event.

The healing temperatures used to evaluate manual induced healing in microcapsule samples were adopted for autonomous specimen testing. This study considers the transition from a liquid phase to a solid state healing system fully incorporated into an epoxy resin. Therefore, minimal solvent quantities were present to independently address critical healing variables. It is in AUTO test specimens that self-healing performance and efficiency was further optimised.

The first objective was to test self-healing in AUTO test specimens containing catalyst and D50-capsules. A total of 24 specimens were tested to failure and 16 were suitable for self-healing studies. These specimens were split into 2 batches to evaluate healing efficiency at moderate (45 °C) and elevated (80 °C) temperatures. Retesting this dataset after healing gave healing efficiencies of 44% and 77% respectively. Therefore, a significant improvement was observed when compared to the

manual induced healing system demonstrated in microcapsule specimens. Additionally, average initial fracture and displacement values of 68.8 N and 0.62 mm were measured.

The second objective focused on monomer delivery to the damaged region, essentially the content contained within the pUF shelled microcapsules. As a result, AUTO test specimens containing catalyst and D75-capsules were manufactured and tested. Thus, microcapsules contained an increased DGEBA monomer content (75 wt%) and a reduction in EPA solvent (25 wt%).

A total of 9 test specimens were acceptable for self-healing evaluation from a batch of 17 TDCB specimens tested to failure. A healing efficiency of 49% for AUTO test specimens healed at 45 °C was obtained from 5 data points. More significantly, AUTO test specimens healed at 80 °C achieved an 87% healing efficiency, a 10% increase for that obtained using D50-capsules. Therefore, healing performance was successfully increased by increasing microcapsule monomer content. Additionally, average initial fracture and displacement values of 64.6 N and 0.64 mm were obtained from this dataset.

Subsequently, test specimens containing D25-capsules were tested at the two prescribed healing temperatures to confirm the effect of varying microcapsule content. AUTO test specimens (8) healed at 80 °C achieved 67% healing efficiency, a reduction in comparison with D50- and D75-capsule test specimens. A reduction in healing efficiency (39%) for D25-capsule test specimens (8) healed at 45 °C was also observed.

A final study addressed a truly autonomous system healed at room temperature (25 °C). AUTO test specimens containing 2.5 wt% $Sc(OTf)_3$ catalyst and 20 wt% D25-, D50- and D75-capsules were healed at 25 °C for 48 hours. Healing efficiencies were 20%, 10% and 6% respectively. Therefore this study confirms that fracture strength recovery is determined by healing temperature, microcapsule monomer content and viscosity of SHAs between the two fracture planes. Additionally, D50- and D75-capsule based test specimens were left to heal at room temperature for 7 days giving healing efficiencies of 19% and 13%.

Evaluating SHAs fully embedded in an epoxy resin clearly demonstrated that healing efficiencies could be improved significantly by optimising monomer delivery and healing temperatures, especially when compared with manually induced healing efforts.

2.3 FRP Composite Integration

Self-healing agent was successfully embedded into E-glass/epoxy FRP using conventional autoclave manufacturing methods. Cured material contained a dual microcapsule – hollow fibre delivery mechanism and was tested using an ENF test method (ASTM STP 1242). Preliminary test specimens considered manual healing via injection of blank specimens containing no HGFs and specimens containing a combination of HGFs and microcapsules (SH).

2.3.1 Preliminary results

A total of 10 test specimens were produced for each data set. Blank test specimens were tested to complete failure then EPA solutions containing SHA were manually injected into the crack plane. Specimens were then clamped and left to heal at 45°C for 48 hours. SH specimens were split into two batches to consider the microcapsule delivery mechanism and the effect of HGF. The first batch was manually injected with only a $Sc(OTf)_3$/EPA solution, utilising the microcapsules (D50) for DGEBA monomer delivery. The second batch was manually injected with separate EPA solutions of catalyst and monomer.

Initial ENF test results revealed a higher fracture load for the blank specimens, suggesting that the presence of HGF and microcapsules within a ply cut-out has a detrimental effect. However, this configuration needs optimisation to minimise this effect but does offer the potential to constrain and localise damage into pre-designated ‘self-healing regions’.

Preliminary results have shown that healing efficiency is comparable to TDCB D50 microcapsule test specimens healed at 45°C for 48 hours (Fig. 3.). In addition, specimens healed with a higher concentration of DGEBA monomer have achieved higher healing efficiencies. This system has the potential to achieve comparable or even better results than previous epoxy TDCB test data. This is primarily due to the increased available volume of DGEBA monomer from the HGFs.

2.4 Discussion

Self-healing of an EPON 828/DETA epoxy resin was achieved with a DGEBA-EPA self-healing system. This self-healing system was adopted to ensure good compatibility between the microcapsule content and the host matrix. Therefore, the healed polymer and the host matrix interfacial interactions were essentially the same material.

A total of three separate healing mechanisms were investigated. An initial healing study acted as a proof of concept using epoxy only TDCB test specimens. This study used SHA in an EPA solution that was subsequently manually injected into an open fracture plane. A homogeneous liquid healing solution containing epoxy monomer and catalyst is fully optimised in terms of a delivery system. Therefore, a high healing efficiency is easily achievable using significantly lower loadings (wt%) of catalyst and reactive monomer. This clearly demonstrates the potential, but application of this liquid-based system is not directly applicable to a fully autonomous solution.

An autonomous-based self-healing was the predominant focus after identification of a viable SHA/catalyst combination. Healing efficiency was optimised to achieve recovery of fracture strength close to initial pristine values. A direct correlation between healing efficiency was independently observed with increased monomer content and healing temperature. Healing at a higher temperature produced a much stronger polymer, which is analogous to a post-cure step used for generic room temperature cured epoxy materials. It could be concluded that an increased crack pinning effect was likely to have been present, bridging the two crack surfaces much more effectively to achieve a successfully self-healed epoxy material.

The various parameters that contribute to self-healing performance were chosen initially to demonstrate and compare healing efficiencies with previously reported self-healing systems for epoxy materials [10,13]. Therefore, the healing temperature, duration and catalyst loading were limited to 25 °C, 45 °C and 80 °C, 48 hours and 2.5 wt% respectively. A microcapsule loading of 20 wt% was selected for preliminary studies using D50-capsules to ensure sufficient DGEBA monomer was delivered to facilitate self-healing functionality. This microcapsule loading remained constant to evaluate the effect of increasing DGEBA content and decreasing EPA content contained within the pUF-walled microcapsules. Essentially, the catalyst and microcapsule loading is high, however, the actual quantity present on the crack plane and available for healing is significantly lower than this in practice. Additionally, failure points for self-healed test specimens were considered conservative by considering the first major failure load.

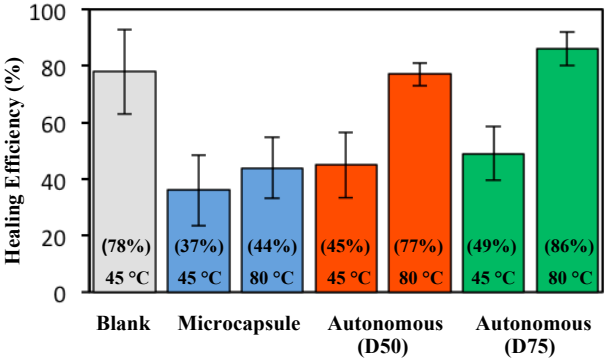

Fig.3. Comparison of healing efficiencies (%) for blank, microcapsule and autonomous TDCB test specimens healed at 45 °C and 80 °C for 48 hours.

3. Conclusions

Epoxy resin (EPON 828/DETA) was embedded with DGEBA-EPA microcapsules (ca. 100-250 μm diameter) and $Sc(OTf)_3$ catalyst particles. A marginal toughening effect was observed for autonomous test specimens containing SHAs. Healing was demonstrated using modified epoxy resin TDCB test specimens to accurately quantify healing efficiencies and fracture behaviour. The epoxy monomer SHA was encapsulated using an *in-situ* microencapsulation method and healing performance was considered over a fixed time period (48 hours) and independently considered microcapsule content, microcapsule loading and healing temperature.

Blank EPON 828/DETA test specimens manually healed at 45 °C achieved a maximum average healing efficiency of 80%, demonstrating SHA proof of concept. An autonomous delivery mechanism was the desired approach. The highest healing efficiency was obtaining using D75-capsules (20 wt%) and $Sc(OTf)_3$ particles healed at 80 °C for 48 hours. A material recovery value of greater than 80% fracture strength was achieved for this configuration.

Additionally, achieved healing performances are comparable to the significantly more expensive and less stable Grubbs' DCPD-capsule system. With further developments our self-healing system shows the potential for incorporation into a variety of commercial applications to provide lightweight multifunctional composite materials. As demonstrated in ENF test specimens, this self-healing system is not limited to a specific single delivery system. Therefore by utilising a dual embedded microcapsule - hollow fibre approach, small and large-scale damage such as microcracking and delamination, can be addressed to provide effective recovery of mechanical properties.

4. Experimental Section

4.1 Materials

Ethyl phenylacetate (EPA), urea (NH_2CONH_2), poly(ethylene-*alt*-maleic anhydride) (EMA, M_w 100,000-500,000); used in 2.5 wt% aqueous surfactant solution, resorcinol (C_6H_4-1,3-$(OH)_2$), formaldehyde (37 wt% in H_2O), diglycidyl ether bisphenol A (DGEBA), diethylenetriamine (DETA, $(NH_2CH_2CH_2)_2NH$) and scandium(III) triflate ($Sc(OTf)_3$) were purchased from Sigma-Aldrich and used as received. Ammonium chloride (NH_4Cl) and sodium hydroxide (NaOH) were purchased from Fischer Scientific. EPON® 828 was purchased from Polysciences, Inc.. E-glass/epoxy pre-impregnated tape was purchased from Hexcel.

4.2 Microencapsulation method

Microcapsules containing DGEBA-EPA, at weight percentages of 75, 50 and 25, were prepared using the *insitu* urea-formaldehyde (UF) encapsulation procedure as described by Blaiszik *et al*. [26] DGEBA was dissolved in EPA prior to addition to the reaction mixture. A 30 mL solution of approximately 2.5% (wt/vol) ethylene-maleic anhydride copolymer (EMA), urea (2.5 g), resorcinol (0.25 g) and ammonium chloride (0.25 g) was stirred for 10 min before adding the DGEBA-EPA solution (60 mL). The pH was adjusted by addition of NaOH solution from approximately 2.7 to 3.5. The beaker was placed on a temperature controlled water bath equipped with a mechanical stirring blade. The solution was stirred at an agitation rate of 700 RPM for 10 minutes. Next, formalin (6.33 g) was added and the temperature increased to 55 °C. The reaction proceeded under continuous agitation with the temperature held at 55 °C for 4 hours. The fully formed microcapsules were recovered by filtration and subsequent air-drying after allowing the bath to cool for at least 6 hr after completion of the reaction.

Microcapsule contents (to within ±1%) was determined by proton (^1H) nuclear magnetic resonance (NMR) in deuterated chloroform ($CDCl_3$) using a Jeol ECP(Eclipse) 400.

4.3 Catalyst Selection

Selected catalyst candidates were evaluated using a qualitative approach. Pre-synthesised microcapsules (pea-sized amount) were placed in the centre of a glass microscope slide. A dusting of solid catalyst particles was carefully placed on top of the microcapsules. An additional microscope slide was placed on top of the first microscope slide in order to crush the microcapsules and release the epoxy monomer contained within. This configuration was clamped and left at room temperature for 24 hr. Specimens were then checked for adhesion and left for a further 24 hr if there was any evidence of adhesion. Selected catalysts capable of polymer initiation and subsequent microscope slide adhesion within 48 hr at room temperature were considered viable candidates. Microcapsules containing 50 wt% DGEBA monomer were chosen to assist in SHA migration in between the two microscope slides.

Suitable catalysts were dissolved in EPA to consider their solubility. A quantifiable catalyst mass and EPA volume was recorded to identify the most soluble catalyst. Solutions were left for 24 hr to determine if certain candidates were soluble over a long time period.

4.3 Self-healing agent testing

Self-healing agents were evaluated using a modified TDCB geometry [29] to include a grooved central trench (GCT) exclusively to contain the desired SHA. All TDCB test specimens were prepared by mixing 100 parts EPON 828 with 12 parts curing agent DETA. The mixture was degassed, cast into closed silicon moulds and left to cure for 24 hr at room temperature and 24 hr at 35 °C. Main TDCB microcapsule and autonomous samples were prepared using precast GCT sections, cured at room temperature for 24 hr, containing embedded DGEBA-EPA microcapsules (20 wt%) and $Sc(OTf)_3$ particles (2.5 wt%). 'Healed' blank and microcapsule reference samples were injected with an EPA solution of DGEBA and $Sc(OTf)_3$ and a $Sc(OTf)_3$/EPA solution respectively. A sharp razor blade was used to precrack cured samples prior to being pin-loaded on an Instron 3343 1 kN load cell at a displacement rate of 5 μm s^{-1}. Test specimens were cracked along the complete GCT length, left to heal either manually or autonomously and retested after a specified time period and temperature.

4.4 Composite manufacture

E-glass/epoxy (Hexply 913, Hexcel Composites) uni-directional (UD) plates (275 mm x 160 mm x 3 mm) were manufactured using hand lay-up [24 ply]. Cure was undertaken at reduced temperature (80 °C), pressure (15 psi) and extended cycle (16 hr). HGFs [17] (ca. 200 μm in diameter) were placed transverse to the fibre direction in a 30 mm ply cut out (2 central plies) from the centre line (ca. 500 μm HGF pitch). Microcapsules (D50) were placed between the HGF. Release film was placed from the self-healing edge to the laminate edge in the centre of the laminate. Cured composite plates were cut into ten samples using a water-cooled diamond grit saw (140 mm x 25 mm x 3 mm).

4.5 Composite testing

End-notched flexural testing was carried out according to ASTM STP 1242 at a displacement rate of 1 mm/min. Specimens were placed on a 3-point bend flexural bending ring with a span (2L) measurement of 110 mm. The ratio for crack length to half span, *a/L*, was 0.45. All specimens were tested to failure and healed by manual injection of separate DGEBA-EPA and $Sc(OTf)_3$-EPA solutions (Ratio of 8:1, 50 wt% EPA). Healed specimens were left at 50°C for 48 hr and then retested to failure.

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References

[1] R. F. Gibson "A review of recent research on mechanics of multifunctional composite materials and structures". *Composite Structures*, Vol. 92, pp 2793-2810, 2010.

[2] J. A. Nairn, "Matrix microcracking in composites". *Comprehensive Composite Materials,* Vol. 2, pp 403-432, 2003.

[3] K. S. Toohey, N. R. Sottos, J. A. Lewis, J. S. Moore, S. R. White "Self-healing materials with microvascular networks". *Nature Materials*, Vol. 6, pp 581-585, 2007.

[4] C. J. Hansen, W. Wu, K. S. Toohey, N. R. Sottos, S. R. White, J. A. Lewis "Self-healing materials with

interpenetrating microvascular networks". *Advanced Materials*, Vol. 21, pp 1-5, 2009.
[5] J. W. C. Pang, I. P. Bond "Bleeding composites'-damage detection and self-repair using a biomimetic approach". *Compos. Pt. A – Appl. Sci. Manuf.,* pp 183-188, 2005.
[6] R. S. Trask, G. J. Williams, I. P. Bond "Bioinspired self-healing of advanced composite structures using hollow glass fibres". *J. Royal Soc. Interface*, Vol. 4, pp 363-371, 2007.
[7] G. Williams, R. Trask, I. Bond "A self-healing carbon fibre reinforced polymer for aerospace applications". *Compos. Pt. A – Appl. Sci. Manuf.*, Vol. 38, pp 1525-1532, 2007.
[8] H. R. Williams, R. S. Trask, I. P. Bond "Self-healing sandwich panels: Restoration of compressive strength after impact". *Compos. Sci. Technol.*, Vol. 68, pp 3171-3177, 2008.
[9] S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N. Brown, S. Viswanathan "Autonomic healing of polymer composites". *Nature*, Vol. 409, pp 794-797, 2001.
[10] E. N. Brown, N. R. Sottos, S. R. White "Fracture testing of a self-healing polymer composite". *Exp. Mech.*, Vol. 42, pp 372-379, 2002.
[11] E. N. Brown, S. R. White, N. R. Sottos "Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite—Part II: In situ self-healing". *Compos. Sci. Technol.*, Vol. 65, pp 2474-2480, 2005.
[12] J. D. Rule, N. R. Sottos, S. R. White "Effect of microcapsule size on the performance of self-healing polymers". *Polymer*, Vol. 48, pp 3520-3529, 2007.
[13] M. M. Caruso, B. J. Blaiszik, S. R. White, N. R. Sottos, J. S. Moore "Full Recovery of Fracture Toughness Using a Nontoxic Solvent-Based Self-Healing System". *Adv. Funct. Mater.*, Vol. 18, pp 1898-1904, 2008.
[14] E. L. Kirkby, J. D. Rule, V. L. Michaud, N. R. Sottos, S. R. White, J. A. E. Manson "Embedded Shape-Memory Alloy Wires for Improved Performance of Self-Healing Polymers". *Adv. Funct. Mater.*, Vol. 18, pp 2253-2260, 2008.
[15] D. S. Xiao, Y. C. Yuan, M. Z. Rong, M. Q. Zhang "Self-healing epoxy based on cationic chain polymerization". *Polymer*, Vol. 50, pp 2967-2975, 2009.
[16] Y. C. Yuan, M. Z. Rong, M. Q. Zhang, J. Chen, G. C. Yang, X. M. Li "Self-Healing Polymeric Materials Using Epoxy/Mercaptan as the Healant". *Macromolecules*, Vol. 41, pp 5197-5202, 2008.
[17] S. H. Cho, H. M. Andersson, S. R. White, N. R. Sottos, P. V. Braun "Polydimethylsiloxane-Based Self-Healing Materials". *Adv. Mater.*, Vol. 18, pp 997-1000, 2006.
[18] M. R. Kessler, S. R. White "Self-activated healing of delamination damage in woven composites". *Compos. Pt. A – Appl. Sci. Manuf.*, Vol. 32, pp 683-699, 2001.
[19] J. L. Moll, S. R. White, N. R. Sottos "A Self-Sealing Fiber-reinforced Composite". *J. Compos. Mater.*, Vol. 44, pp 2573-2585, 2010.
[20] A. J. Patel, N. R. Sottos, E. D. Wetzel, S. R. White "Autonomic healing of low-velocity impact damage in fiber-reinforced composites". *Compos. Pt. A – Appl. Sci. Manuf.*, Vol. 41, 360-368, 2010.
[21] K. Sanada, I. Yasuda, Y. Shindo "Transverse tensile strength of unidirectional fibre-reinforced polymers and self-healing of interfacial debonding". *Plast. Rubber Compos.*, Vol. 35, pp 67-72, 2006.
[22] T. Yin, L. Zhou, M. Z. Rong, M. Q. Zhang "Self-healing woven glass fabric/epoxy composites with the healant consisting of micro-encapsulated epoxy and latent curing agent". *Smart Mater. Struct.*, Vol. 17, pp 015019, 2008.
[23] M. W. Keller, S. R. White, N. R. Sottos "A Self-Healing Poly(Dimethyl Siloxane) Elastomer". *Adv. Funct. Mater.*, Vol. 17, 2399-2404, 2007.
[24] B. J. Blaiszik, S. L. B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, S. R. White "Self-Healing Polymers and Composites". *Annu. Rev. Mater. Res.*, Vol. 40, pp 179-211, 2010.
[25] P. Schwab, R. H. Grubbs, J. W. Ziller "Synthesis and Applications of $RuCl_2(=CHR')(PR_3)_2$: The Influence of the Alkylidene Moiety on Metathesis Activity". *J. Am. Chem. Soc.*, Vol. 118, pp 100-110, 1996.
[26] B. J. Blasizik, M. M. Caruso, D. A. McIlroy, J. S. Moore, S. R. Moore, N. R. Sottos "Microcapsules filled with reactive solutions for self-healing materials". *Polymer*, Vol. 50, No. 4, pp 990-997, 2009.
[27] C. Hertweck "Copper(II) Triflate in Organic Synthesis". *J. Prakt. Chem*, Vol. 342, pp 316-321, 2000.
[28] J. S. Yadav, V. Naveen Kumar, R. Srinivasa Rao, A. Diana Priyadarshini, P. Purushothama Rao, B. V. S. Reddy, K. Nagaiah "Sc(OTf)3 catalyzed highly rapid and efficient synthesis of β-enamino compounds under solvent-free conditions". *J. Molecular Catalysis A: Chemical*, Vol. 256, pp 234-237, 2006.
[29] W. Beres, A. K. Koul, R. Thamburaj "A tapered Double-Cantilever-Beam Specimen Designed for Constant-*K* Testing at Elevated Temperatures". *Journal of testing and Evaluation,* JTEVA, Vol. 25, No. 6, pp 536-542, 1997.