Self-healing of a high temperature cured epoxy using poly(dimethylsiloxane) chemistry

C.L. Mangun [a,*], A.C. Mader [b], N.R. Sottos [c,d], S.R. White [d,e]

[a] CU Aerospace, 2100 S. Oak St., Suite 206, Champaign, IL 61820, USA
[b] Hochschule Bremen, Neustadtswall 30, Bremen, D-28199, Germany
[c] Dept. of Materials Science and Engineering, UIUC, 1304 W. Green St., Urbana, IL 61801, USA
[d] Beckman Institute, UIUC, 405 N. Mathews Av., Urbana, IL 61801, USA
[e] Dept. of Aerospace Engineering, UIUC, 104 S. Wright St., Urbana, IL 61801, USA

ARTICLE INFO

ABSTRACT

A high temperature cured self-healing epoxy is demonstrated by incorporating microcapsules of poly (dimethylsiloxane) (PDMS) resin and separate microcapsules containing an organotin catalyst. Healing is triggered by crack propagation through the embedded microcapsules in the epoxy matrix, which releases the healing agents into the crack plane initiating crosslinking reactions. A series of tapered double-cantilever beam (TDCB) fracture tests were conducted to measure virgin and healed fracture toughness. Healing efficiencies, based on fracture toughness recovery, ranged from 11 to 51% depending on the molecular weight of PDMS resin, quantity of healing agent delivered, and use of adhesion promoters.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Advanced fiber reinforced polymeric composites are widely used in many military and commercial applications as they provide a high strength-to-weight ratio and are durable in harsh environments. However, polymers are ultimately susceptible to failure by multiple mechanisms such as thermal/mechanical fatigue, microcracking, and debonding. Self-healing polymers have potential to alleviate many of the damage mechanisms prevalent in structural composites thus greatly extending the operational lifetime and reliability of these materials. Achieving successful self-healing in structural composites require chemistries that are robust, cost-effective, environmentally stable, and provide high healing efficiencies. The first successful healing system was achieved by White et al. via a metathesis reaction of encapsulated *endo*-dicyclopentadiene (DCPD) monomer and first generation Grubbs' catalyst [1]. Although this system meets many of the characteristics desired for self-healing, stability of the catalyst phase limits the processing temperature to a maximum of ca. 40 °C unless special environmental control is maintained. For high performance structural composites, processing requirements dictate that a self-healing system must survive elevated temperature (100–200 °C) for several hours.

PDMS healing chemistries have been used previously for room temperature cured polymers such as vinyl ester, epoxy, and PDMS elastomer [2–5]. The PDMS system has several advantages as an alternative healing chemistry including stability at elevated temperatures, the components are widely available and comparatively low in cost, and encapsulation is relatively straightforward. Cho et al. [3] utilized a two-component system with silanol-terminated polydimethylsiloxane (PDMS) and the crosslinker polydiethoxysiloxane (PDES) phase separated in a vinyl ester matrix together with a microencapsulated organotin catalyst. Healing efficiency ca. 24%, based on fracture toughness recovery, was achieved after 24 h at 50 °C. Cho et al. [4] extended this research by microencapsulating both component phases (resin & catalyst) and incorporating them into either vinyl ester or epoxy coatings on steel substrates for corrosion protection.

Although the PDMS system is not capable of recovering the full fracture toughness of an epoxy, it shows surprisingly good adhesion strength that suggests that it could function well for self-sealing applications. For example, Beiermann et al. [5] demonstrated the ability to heal puncture damage using PDMS microcapsules in polymeric membranes of a polyurethane/nylon/PDMS laminate. One potential application for self-healing epoxy composites is cryogenic storage tanks, which are used as lightweight storage containers for liquid oxygen and hydrogen propellants for aerospace applications where microcracks are induced by thermal

cycling [6]. Moll et al. have investigated this application using glass fiber reinforced epoxy composites with the DCPD and Grubbs catalyst self-healing system and the results show the potential for a fully autonomic self-sealing material [7].

In this study, we incorporate the dual capsule PDMS healing system in a high temperature cured epoxy matrix and assess healing performance through fracture testing. Crack propagation through the epoxy ruptures the microcapsules releasing the healing agent and catalyst into the crack plane where they react and repair the damage automatically. Fig. 1 shows the room temperature condensation reaction of PDMS.

2. Methods and materials

Three different molecular weights of silanol-terminated PDMS (S21, 4200 g/mol, 90–120 cSt; S31, 26,000 g/mol, 1000 cSt; S35, 49,000 g/mol, 5000 cSt), PDES and dibutyltin dilaurate (DBTL) as the catalyst were obtained from Gelest. EPON 828 was purchased from Miller-Stephenson and diethylenetriamine (Ancamine DETA) was received from Air Products. The urethane prepolymer, Desmodur L75, was obtained from Bayer MaterialsScience. Solvents such as xylenes (a mixture of all three isomers) and hexyl acetate were purchased from Sigma–Aldrich and used as received.

2.1. Microencapsulation

PDMS microcapsules with urea-formaldehyde shells were prepared by *in situ* polymerization in an oil-in-water emulsion following a similar procedure as used by Brown et al. [8]. Stoichiometric amounts of PDMS and PDES were mixed beforehand and utilized as the core material. A full batch recipe was used with 32.0 g of S21 and 28.6 g of PDES and a mixing speed of 2000 rpm. Due to the higher molecular weight and therefore higher viscosity of the S31 and S35, the solvent xylenes was added to the core material prior to encapsulation. The minimum concentration of xylenes to produce acceptable microcapsules was used in order to maximize the quantity of healing agent delivered. All reactant quantities were decreased by 50% and an agitation speed of 1800 rpm was used. The core material of the S31 capsules consists of a mixture of 16.5 g S31, 2.5 g PDES and 9.4 g xylenes (30% by weight). For the S35 capsules, the core consisted of 11.0 g S35, 1.1 g PDES and 15.2 g xylenes (53% by weight). Finally, in an attempt to achieve good strength using a higher molecular weight PDMS but avoiding solvent, one set of capsules was produced using a blend of S31 and S21 with a core of 16.5 g S31, 5.7 g S21, and 7.6 g of PDES (no solvent). After reaction, the suspension of microcapsules was separated under vacuum with a coarse-fritted filter. The microcapsules were rinsed with deionized water at least three times, followed by a final rinse with heptane. After drying in air for 24–48 h the microcapsules were sieved and the diameters between 38 and 125 μm were kept for testing.

Since DBTL catalyst was too viscous to encapsulate directly, a 50:50 mixture of DBTL and hexyl acetate was utilized with a polyurethane shell. A 400 mL beaker was placed in a temperature-
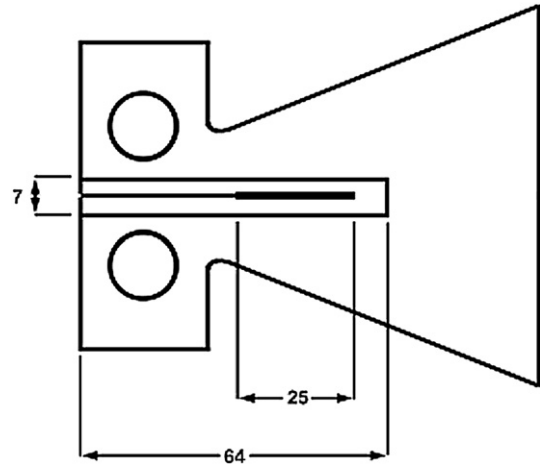

Fig. 2. Geometry of a short groove TDCB specimen (all dimensions in mm).

controlled water bath and agitated by a digital mixer with a speed of 1600 rpm 4.5 g Gum arabic was slowly dissolved in 40 mL deionized water. 10 g Hexyl acetate, 10 g DBTL and 2.5 g urethane prepolymer were mixed in a separate beaker and then poured into the agitated solution. The beaker was covered with aluminum foil and heated to 60 °C. Agitation and temperature were maintained for 1–2 h. Afterwards, the capsules were kept in a warm water bath for at least 24 h to separate as much gum arabic out of the suspension as possible. Then the capsules were filtered and air-dried for 24–48 h (no sieving was necessary).

2.2. Microcapsule characterization

Mean diameter and standard deviation were determined from multiple images taken with a Leica optical microscope interfaced with ImageJ software. A minimum of 120 measurements was made for each analysis. Images of the fracture surface were taken using a SEM (FEI/Philips XL30 ESEM FEG). Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851 using a nitrogen atmosphere and a heating rate of 10 °C/min.

2.3. Sample preparation

Using the protocol established by Brown et al. [9], healing efficiency was measured by carefully controlled fracture experiments for both the virgin and healed specimens. These tests utilize a tapered double-cantilever beam (TDCB) geometry, which ensures controlled crack growth along the centerline of a brittle epoxy specimen. However, the specimens used in this work differ from those described in Brown et al. [9] in that capsules are included only in the 7 × 64 mm center section near the centerline groove as introduced by Rule et al. [10]. The specimen geometry is shown in Fig. 2.
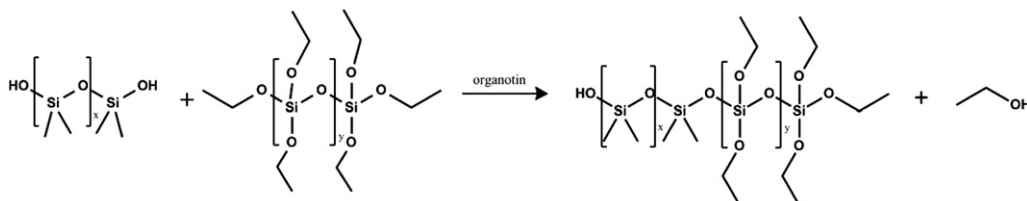

Fig. 1. Condensation reaction of silanol-terminated PDMS and its crosslinker PDES. Organotin functions as the catalyst to initiate crosslinking.
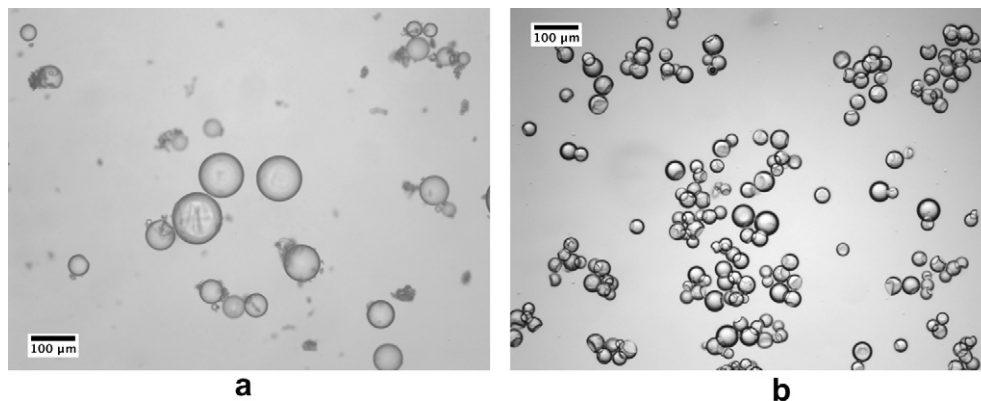
Fig. 3. Optical microscope images of (a) S31 capsules and (b) organotin capsules.

Samples for fracture testing were prepared by mixing EPON 828 and 12 pph DETA curing agent and pouring into a closed silicone rubber mold. All TDCB samples were cured for 24 h at room temperature, followed by 24 h at 35 °C and a final heat treatment at 100 °C for 1 h. Three different specimen types were investigated. The first type, designated as "reference" specimens, was conducted by manually injecting 5 μL of a pre-mixed solution, including both PDMS and catalyst in the proper ratio to mimic their respective capsules, into the crack plane. The second type, *in situ* or self-healing, were prepared using TDCB specimens with capsules that were stirred into the EPON 828:DETA matrix at various loadings by weight (1–15 wt% of PDMS capsules with corresponding 0.1–1.5 wt % DBTL capsules) and poured only into the central region of the samples. Finally, several sets of TDCB "control" samples were fabricated with 5 wt% of each type of capsule (S21, S31, or S35) and 0.5 wt% polyurethane capsules that contained only hexyl acetate (no catalyst).

The influence of adhesion promoters was also investigated by direct addition of silane coupling agents to the epoxy matrix. Three different silanes were obtained from Gelest and two combinations were tested: SIB1834.1 with a molecular formula of $C_{14}H_{36}N_2O_6Si_2$ used at 2 wt% and designated as "amino silane" while the second set was designated as "mixed silane" consisting of 1 wt% each of SIA0611.0, $C_6H_{17}NO_3Si$, and SIB1832.0, $C_{12}H_{30}O_6Si_2$.

2.4. Fracture testing

In this protocol, healing efficiency is defined as the ability to recover mode-I fracture toughness, K_{Ic}. During the initial virgin loading cycle, the self-healing specimen is loaded until the crack propagates through the insert groove section of the sample where the microcapsules reside. Prior to testing, a pre-crack was initiated with a razor blade into the groove of the sample. TDCB specimens were pin-loaded and tested to failure using an Instron load frame under displacement control at a rate of 5 μm/s. The samples were unloaded, allowing the crack faces to come back into contact, and then allowed to heal for 24 h at room temperature (without any external intervention, e.g. no applied heat or pressure) before again being loaded to failure. Average healing efficiencies are reported

Table 1
Microcapsule average diameters with standard deviation.

Capsule Type	Diameter (μm)
S21	37 ± 13
S31	72 ± 35
S35	66 ± 29
S21/S31	58 ± 24
Catalyst	33 ± 7.1

based on sets of 3–5 samples. The tapered geometry is designed so that the resulting fracture toughness measurement is independent of crack length, and healing efficiency (η_s) is expressed simply as a ratio of the peak loads (P_c) of the healed and virgin samples.

$$\eta_s = \frac{K_{Ic \text{ healed}}}{K_{Ic \text{ virigin}}} = \frac{P_{c \text{ healed}}}{P_{c \text{ virigin}}} \tag{1}$$

3. Results and discussion

3.1. Microcapsule characterization

A representative image of the PDMS microcapsules is shown in Fig. 3a for the S31 system.

In general, the S21 was the best capsules in terms of shape and free-flowing nature with little debris. Whereas the higher viscosity S31 or S35 resulted in microcapsules that were less uniform in shape with more debris and a tendency to cluster. Although the same range of capsules (38–125 μm) were sieved, the average diameter of each batch varied greatly and the standard deviation was quite large (Table 1).

TGA experiments (Fig. 4a) showed that the thermal stability of the S31 and S35 was greatly influenced by both the inclusion of xylenes and to some extent, poorer capsule quality (note that the first drop in mass loss occurred for the S35 before the S31). However, both S21 and the S21/S31 capsules showed practically no mass loss until at least 200 °C and an appreciable decline does not occur until 250 °C when the PDES component is most likely boiling away. At higher temperatures, the remaining PDMS starts to char as the mass steadily decreases with temperature.

The catalyst capsules were of uniform shape with no debris (Fig. 3b) and a fairly narrow size distribution with an average diameter of 33 μm (Table 1). Although they tended to agglomerate after drying (probably due to remnants of the gum arabic), they would readily break apart and disperse evenly when stirred into epoxy. TGA curves of the catalyst capsules along with the corresponding core materials of 50:50 DBTL and hexyl acetate are shown in Fig. 4b. The hexyl acetate in the solution evaporates rapidly at ca. 120 °C. When this core material was encapsulated, the thermal stability doubles to almost 250 °C. After the capsule shells rupture, the core content is quickly liberated near 300 °C.

3.2. Control samples

Multiple sets of TDCB samples were made as controls with 5 wt% of each type of capsule (S21, S31, or S35) and 0.5 wt% polyurethane capsules that contained only hexyl acetate (no catalyst).
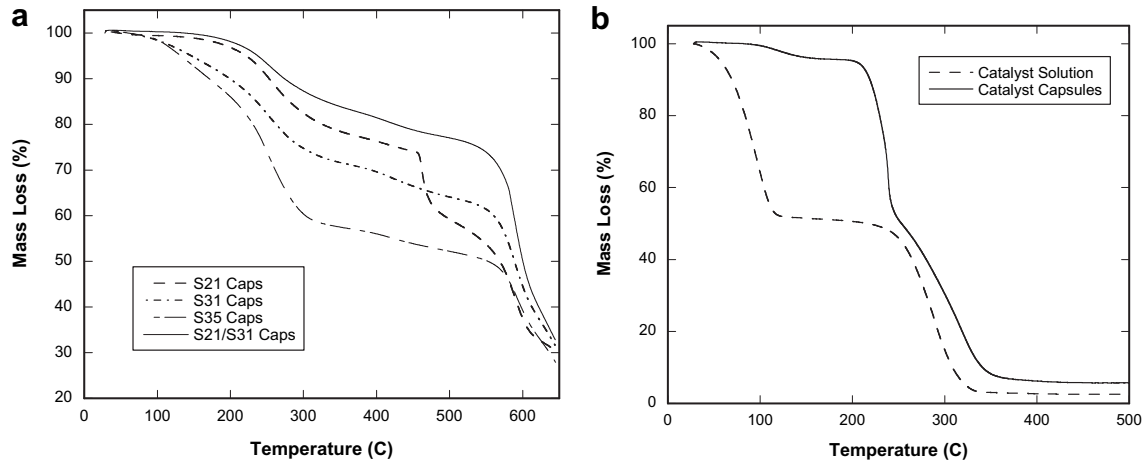
Fig. 4. TGA plots of (a) the different PDMS capsules and (b) the catalyst solution (DBTL plus hexyl acetate) with corresponding capsules.

These controls verified if the healing was due to the catalyzed reaction of the PDMS and not other factors (e.g. the inherent tackiness of PDMS). Fig. 5 shows representative load-displacement curves for the S35 control along with its corresponding *in situ* self-healing sample. Note the distinct difference in the two plots: the healed curve has the same stiffness of the virgin material until the PDMS starts to tear away from the crack plane, leading to a distinctive healed peak. After the healed material debonds, the curve loads up along the same line as the last segment of the virgin test. For the control sample in the second plot, the curve immediately lines up with the end of the virgin test thus indicating that no healing has taken place.

3.3. Reference and in-situ samples

A summary of the TDCB healing efficiencies for the PDMS capsules is shown in Fig. 6. In addition, several sets of reference samples were prepared of the matrix polymer alone and healed manually by injecting a pre-mixed solution of the appropriate healing system as described in Methods section (data is represented as solid lines in Fig. 6).

In order to give a more straightforward comparison of the *in situ* healing data versus each capsule type (since the capsule size and mass fraction of resin in the core varied), the results were plotted against the amount of PDMS delivered (mg/cm^2). The mass of

healing agent delivered to the crack plane was calculated with the equation developed by Rule et al. [10] as:

$$M_{\text{Resin}} = \rho_s \varphi D_c \xi \qquad (2)$$

where ρ_s is the density of the matrix, φ is the mass fraction of microcapsules in the epoxy matrix and D_c is the mean diameter of the microcapsules. In this study, the quantity ξ represents the weight fraction of PDMS resin in the core (e.g. this value would 1 for S21, 0.7 for S31, etc.). In addition, several SEM images were taken of the fracture surface that clearly indicate ruptured microcapsules where the PDMS resin has reacted with the catalyst to form an extensive healed film (Fig. 7).

The reference healing efficiencies followed the expected trend, as the molecular weight increased, the strength of the polymerized PDMS resin increased. The blend of S21/S31 healing mixture fell between the results for S21 and S31 in almost exactly the calculated value based on the proportions of each component. The *in situ* healing efficiencies from Fig. 6 exhibit the same trend as observed for the reference samples. Although quite close for the S21 sample, the *in situ* values are higher for the higher viscosity PDMS samples when compared to the reference. Typically, TDCB reference tests are utilized as an indicator of the maximum η_s that can be achieved for an encapsulated system. This decrease in healing efficiency is attributed to difficulty of injecting the viscous healing agents into the crack plane. Self-healing samples, however, have uniform
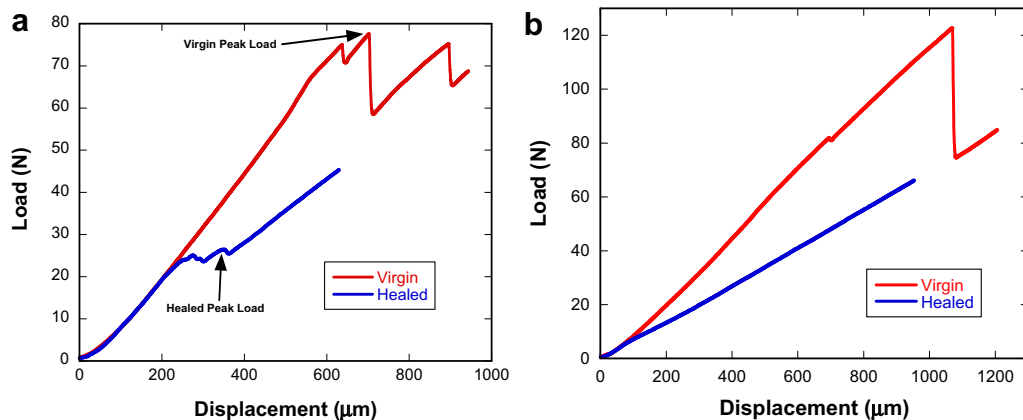

Fig. 5. Representative load-displacement curves for TDCB fracture specimens of (a) *in situ* 5 wt% S35 capsules displaying ca. 33% healing efficiency and (b) an S35 control (no healing).
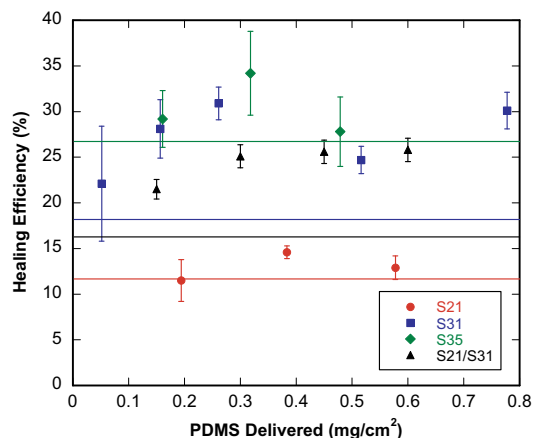
Fig. 6. Summary of *in situ* healing efficiencies for PDMS capsules. Error bars represent one standard deviation. Solid lines indicate the corresponding value for reference samples.

delivery across the crack plane from fractured microcapsules. For the S21 specimens, η_s is fairly constant over the entire range of mass delivered. The S21/S31 shows a modest increase in η_s with a plateau reached around 0.3 mg/cm^2 (which corresponds to the volume of healing agent needed to fill the crack in a short groove TDCB). For the two PDMS capsules containing solvent, S31 and S35, there is again a peak around 0.3 mg/cm^2 but η_s tends to fall as the amount delivered increases. This decrease could be due to the much larger volume of xylenes released at higher capsule loadings that could interfere with PDMS condensation reaction and/or causes swelling of the reacted polymer if it does not evaporate. However, the S35 system yields the best η_s value of ca. 35% although the standard deviations are the largest of all samples. Variability is likely due to the poorer capsule quality (i.e. lower thermal stability, non-spherical) and the presence of debris, either from reactants not incorporated into shell walls or broken microcapsules. Based on the reference values, one would expect the S35 to achieve an even higher η_s than 35%. Hence, there is a trade-off when using a higher molecular weight PDMS, which increases the viscosity of the core thus necessitating solvent and degrades capsule quality and thermal stability. Finally, it is interesting to note that the samples with ca. 0.05 mg/cm^2 of S31 (equivalent to only 0.9 wt% capsules) achieve a η_s of 22%. Fewer capsules are therefore needed to render the matrix self-healing, facilitating integration into a composite matrix.
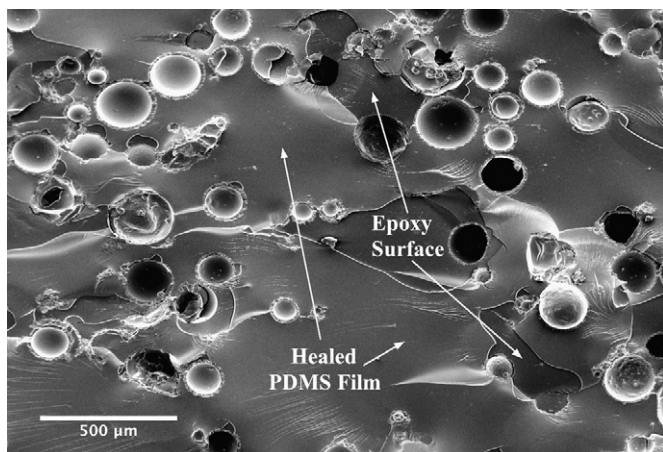

Fig. 7. Representative SEM image of a TDCB fracture surface, the specimen contains 15 wt% S31 capsules and 1.5 wt% catalyst capsules.

Table 2
Summary of adhesion promoter results using a constant 0.3 mg/cm^2 PDMS delivered *in situ*.

Capsule Type	Adhesion promoter	Avg healing efficiency (%)
S21/S31	–	25.1 ± 1.1
S21/S31	Amino silane	33.4 ± 3.4
S21/S31	Mixed silane	45.1 ± 2.3
S35	–	34.2 ± 4.6
S35	Amino silane	44.6 ± 2.4
S35	Mixed silane	51.7 ± 3.5

3.4. Effect of adhesion promoters

From observation of the PDMS healing film on the TDCB samples, it was apparent that in all cases, the failure was mainly adhesive in nature (i.e. the polymerized PDMS would only be present on one side of the fracture surface in any given area). Therefore two sets of adhesion promoters, based upon silane coupling agents, were examined by directly mixing with epoxy matrix. The first (designed as "amino silane") contained two primary amine groups to bond with the epoxy matrix and three methoxy groups on each end to react with the silanol-terminated PDMS. The second was a mixture of two coupling agents (designated as "mixed silane") and contained equal amounts of an amine/methoxy compound and one that had no amine functional groups but just the three methoxy groups on each end. The self-healing results from several *in situ* specimens are shown in Table 2 (a constant value of 0.3 mg/cm^2 PDMS delivered was used for easier comparison). In all cases, the use of silane coupling agents had a positive effect on η_s with the mixed silane yielding the best results. For example, the η_s for S21/S31 sample increased from 25.1 to 33.4% for the amino silane and up to 45.1% for the mixed silane, an almost 80% improvement. Similar results were obtained for the S35 capsules, which also generated the highest η_s of 51.7% using the mixed silane.

3.5. High temperature treatment

An additional set of *in situ* S21/S31 specimens with mixed silane coupling agents was prepared with a higher temperature post-treatment of 4 h at 177 °C (i.e. typical final cure temperature for a commercial structural epoxy composite) to evaluate the thermal stability of the encapsulated healing agents. This system was chosen as it had the best stability according to TGA (i.e. no solvent) in combination with a high η_s of 45.1 ± 2.3 (Table 2). The fracture tests resulted in a η_s of 28.0 ± 3.3, which is over 60% retention of self-healing efficiency when compared to the standard cure cycle for this resin system. Since the coupling agents should be stable in this temperature range, the loss of η_s could be due to leakage of the microcapsules and/or degradation of the PDMS components. The TGA data indicates the capsules are stable at this temperature range thus it seems likely that some auto-polymerization has taken place. Regardless, this data is quite encouraging for future development of high performance structural composites that require high temperature fabrication techniques.

4. Conclusions

A self-healing system in a fully cured epoxy matrix was achieved by incorporating urea-formaldehyde encapsulated PDMS resin and urethane encapsulated organotin catalyst. The thermal stability of these microcapsules was measured with TGA and found to be at least 100 °C and up to 200 °C when no solvent was used in the core. TDCB specimens were fabricated and tested to determine healing

efficiency, based on fracture toughness recovery. The healing efficiencies ranged from 11 to 35% and increased as the molecular weight of the PDMS resin increased. Examination of the healing film showed only adhesive failure, thus the use of silane coupling agents was explored. Use of these adhesion promoters resulted in at least 30% and up to 80% improvement in healing efficiency with the highest value of 51% obtained. In addition, this is the first demonstration of self-healing, based on encapsulated healing agents, for high temperature (177 °C) cure conditions. This allows for the possibility of fabricating high performance composites that have viable self-healing components even after high temperature post-treatments. This healing system could be quite practical for applications such as self-sealing (e.g. cryogenic storage tanks) and current research is examining this functionality using the optimal systems as determined by this TDCB study.

References

[1] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Nature 2001;409:794–7.
[2] Keller MK, White SR, Sottos NR. Advanced Functional Materials 2007; 17:2399–404.
[3] Cho SH, Andersson HM, White SR, Sottos NR, Braun PV. Advanced Materials 2006;18:997–1000.
[4] Cho SH, White SR, Braun PV. Advanced Materials 2009;21:645–9.
[5] Beiermann B, Keller MW, Sottos NR. Smart Materials and Structures 2009;18:085001.
[6] Heydenreich R. Cryogenics 1998;38:125–30.
[7] Moll JL, White SR, Sottos NR. Journal of Composite Materials; 2010. doi: 10.177/0021998306356605.
[8] Brown EN, Kessler MR, Sottos NR, White SR. Journal of Microencapsulation 2003;20(6):719–30.
[9] Brown EN, Sottos NR, White SR. Experimental Mechanics 2002;42(4):372–9.
[10] Rule JD, Sottos NR, White SR. Polymer 2007;48:3520–9.