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Self-healing of damage in fibre-reinforced polymer-matrix composites

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Self-healing resin systems have been discussed for over a decade and four different technologies had been proposed. However, little work on their application as composite matrices has been published although this was one of the stated aims of the earliest work in the field. This paper reports on the optimization of a solid-state self-healing resin system and its subsequent use as a matrix for high volume fraction glass fibre-reinforced composites. The resin system was optimized using Charpy impact testing and repeated healing, while the efficiency of healing in composites was determined by analysing the growth of delaminations following repeated impacts with or without a healing cycle. To act as a reference, a non-healing resin system was subjected to the same treatments and the results are compared with the healable system. The optimized resin system displays a healing efficiency of 65% after the first healing cycle, dropping to 35 and 30% after the second and third healing cycles, respectively. Correction for any healability due to further curing showed that approximately 50% healing efficiency could be achieved with the bisphenol A-based epoxy resin containing 7.5% of polybisphenol-A-*co*-epichlorohydrin. The composite, on the other hand, displays a healing efficiency of approximately 30%. It is therefore clear that the solid-state self-healing system is capable of healing transverse cracks and delaminations in a composite, but that more work is needed to optimize matrix healing within a composite and to develop a methodology for assessing recovery in performance.

Keywords: self-healing; epoxy resins; composites; impact damage; recovery

1. INTRODUCTION

Self-healing matrix systems have been under development for use in composite materials since the early 1990s, but to date much of this work has concentrated on the development of the polymer system rather than considering high volume fraction composites. Four types of self-healing system have been proposed, the earliest being that of Dry (1996) using glass capillaries to contain a liquid resin system that bled into damage sites upon fracture. This principle has been extended by other authors (Bleay *et al.* 2001; Pang & Bond 2005*a,b*) to employ hollow glass fibres, so that healing could occur under loads sufficient to cause fibre fracture. A second system employs liquid resin microencapsulated in a polymeric shell (White *et al.* 2001; Kessler *et al.* 2003; Brown *et al.* 2004). These shells release a curable resin into the matrix on fracture in the path of a propagating crack. The hardener or curing catalyst is also dispersed throughout the matrix, either as a solid or encapsulated in a soluble wax. Chen *et al.* (2003) have developed a reverse Diels–Alder polymer that has a polymerization–depolymerization equilibrium which ensures the reformation of broken bonds on heating. In

principle, perfect healing is achievable but any new resin would need to have equivalent thermomechanical properties to at least an epoxy for use as a matrix in fibre composites. To date, this is not considered to be viable for composite applications but it has directed a new way forward. Finally, Hayes & Hou (2002); Hayes & Jones (2004); Hayes *et al.* (2007) have developed a smart composite system which combines structural health monitoring with a self-healing resin. Self-sensing of micromechanical damage in the form of matrix cracks and delaminations have proved possible for carbon fibre laminates using a triangulation approach (Hayes & Hou 2002). Since the detection method employs the change in resistance in the sensed carbon fibre laminae, the sensor can also be used as a local heating element. This self-healing matrix employs a thermosetting epoxy resin into which a linear polymer is dissolved. The solubility parameters are matched so that the ‘healing agent’ remains uniformly dissolved in the matrix, without phase separation. The linear polymer should be bonded into the three-dimensional epoxy matrix through hydrogen bonding but become mobile above a particular temperature. Thus, on heating, the ‘healing agent’ can diffuse throughout the matrix bridging any closed cracks within it.

While all of these systems have been shown to be capable of causing a thermosetting polymer to recover

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One contribution of 9 to a themed supplement ‘Self-healing polymers and composites’.

Table 1. Formulation of the epoxy resin.

ingredient	component	chemical equivalent (phr)
resin matrix	Epikote 828	100
hardener	NMA	81.2
catalyst	Capcure 3-800	30.4

greater than 60% of its original strength after fracture, there are significant differences in their operation and thus in their capabilities. The liquid resin-based systems are capable of autonomic healing, as they need no manual intervention because the mechanism of healing involves the fracture of the vessels containing the healing resins (Bleay *et al.* 2001; White *et al.* 2001). However, while autonomic healing is possible in these systems, more efficient recovery of matrix strength is observed at an elevated temperature. Thus, their advantage over the solid-state systems is somewhat reduced. The two solid-state systems share similar capabilities, in that both can heal closed cracks, but have no capability to heal open cracks. Furthermore, they both require a heating stage. However, the main advantage of the solid-state approach described by Hayes *et al.* (2007) is that it is based on conventional matrix resin technology. Therefore, the whole range of current matrix systems has the potential to be modified for healing. In addition, there is no requirement to incorporate special reinforcing fibres or microcapsules; therefore, in principle, conventional manufacturing routes can be employed.

The aim of this study was to optimize the concentration of the solid-state healing agent in a standard epoxy resin and examine the efficiency of the modified resin for healing damage in composites.

2. EXPERIMENTAL

2.1. Healable matrix

The matrix resin was chosen to be a blend of Epikote 828 (a diglycidylether of bisphenol A) cured with nadic methylene tetrahydrophthalic anhydride (NMA) and the mercaptan accelerator, Capcure 3-800. The formulation is given in table 1. This formulation was chosen for the initial studies owing to the 'liquid' state of the components which facilitated dissolution of the healing agent. The healing agent which proved to be effective in previous studies was a polybisphenol-A-*co*-epichlorohydrin (Sigma Aldrich) with $\bar{M}_w = 44\,000\text{ g mol}^{-1}$. The concentration of the healing agent was varied from 0 to 15% by weight in 2.5% intervals.

The healing agent was dissolved in Epikote 828 epoxy resin at 80°C under stirring over several hours. Stirring was continued until there was no evidence of the undissolved thermoplastic. The product was a clear viscous liquid which could be degassed at 50°C. The remaining ingredients were blended in at 80°C and further degassed. The maximum concentration of healing agent which could be added was 20% but the viscosity was too high for further handling.

2.2. Assessment of matrix healing through impact testing

The degassed resin blend was poured into pre-heated silicone rubber bar moulds to produce Charpy impact specimens. The resin was cured at 80°C for 4 h, followed by a post-cure of 130°C for 3 h. The mould dimensions were 80×10×4 mm. Specimens (50 mm long) were cut from the mouldings. The samples were lightly polished ensuring a regular rectangular shape. A notch was introduced using a broach mounted in a fly press. This cuts a BS standard notch (4 mm) in a single pass which was sharp and reproducible.

A Hounsfield Charpy Plastics Impact Tester with the appropriate hammer was used according to the instructions. The machine was not instrumented, and the instrument calibration tables were used to calculate the results. The appropriate hammer was mounted on the pivots, with sufficient pressure to hold the anvil in place, but with minimal friction. The anvil was swung, from its fixed position several times, and the friction adjusted so that a reading of zero was routinely obtained. Once this had been done, the machine was ready for testing of the resin blocks.

After testing, the samples which had broken cleanly into two pieces were further examined. The two halves were carefully aligned between two clean microscope slides using PTFE-release film and a 250 g weight. Gentle pressure of approximately 0.2 MPa was applied using the healing platform shown in figure 1. This ensured that the faces of the two halves were kept in alignment and intimate contact. The samples were healed at 130°C for 6 h or 160°C for 1 h. After cooling, they were retested to examine the effect of repeated healings on the efficiency of impact strength recovery.

2.3. Assessment of healing in composites

Composites were produced from a resin containing 7.5% by weight of the healing agent. This resin was found to have optimum healing ability in Charpy test specimens (figures 2 and 3) and a low viscosity for composite manufacture.

Glass fibres (P84 from PPG) were wound precisely onto a square frame to obtain a preform with aligned filaments. The frame was then rotated by 90° and wound to obtain a 0°/90°/90°/0° configuration. The wound frame was heated on a hotplate, and a weighed quantity of resin was impregnated into the fibres. A vacuum bag was constructed around the panel to provide a consolidating pressure. The panel was cured at 80°C for 2 h, followed by post-curing in an oven at 130°C. Two crossply panels measuring 200×200 mm were produced. One contained the healable resin, while the other was prepared from the unmodified resin. The weight of resin applied to the fibre was kept constant to control the volume fraction. Following cure, the panels were cut into 60×60 mm squares, without visible flaws. Seven coupons of each type were obtained.

The coupons were subjected to a falling weight impact using a non-instrumented Davenport falling dart plastics tester equipped with a 10 mm diameter hemispherical tip. The impact energy was fixed at 2.6 J.

The 60 mm square coupon was supported on an annular anvil with a diameter of 50 mm. For successive impacts, care was taken to reposition the coupon so that the impact point was exactly in the same position. Following an impact, each panel was photographed to record the size of the damage. The samples were healed by heating without external restraint for 2 h at 130°C. It was anticipated that the impact damage at the edge of the damaged zone would be healed. After healing, the panel was photographed to record the morphology of post-healed damage. The whole process was repeated so that the composites had received three impact events and two healings.

The photographic record was interrogated using image analysis on a Zeiss KS400 image analysis suite. A typical example of the damage induced in a glass fibre crossply composite is given in figure 4.

3. RESULTS

3.1. Matrix healing

This study was initiated specifically to identify an optimum concentration of the healing agent. For rapid screening, Charpy testing was chosen.

Figure 2 shows the recovery in impact strength of samples tested using the Charpy impact test, containing a varying concentration of healing agent from 0 to 15% by weight. Considering the qualitative nature of the Charpy impact test, the efficiency of impact strength recovery was calculated from the relative impact energies,

$$R_E = \frac{100E_{\text{heal}}}{E_{\text{init}}}, \quad (3.1)$$

where E_{heal} and E_{init} are the post-healing and initial impact energies, respectively. R_E is the percentage recovery in impact strength. Data for three impact/heal cycles are shown to reveal the effect of multiple healing events on the healing performance.

From figure 2, it can be seen that a 25% recovery in impact strength could be observed for the unmodified (0% resin) after one healing event. This could be attributed to a slight undercure of the samples in the curing schedule. However, following further healing cycles, no more than 5% of the initial strength was recovered. For the resin blends containing 2.5, 5 and 7.5% by weight of the healing agent, significant recovery of the initial impact strength was observed after the first healing cycle. In these cases, the level of recovery builds from 48 to 52% and finally 65%, respectively. Subsequent healing cycles lead to significant recovery in impact strength although at a lower level than for the first cycle, with 23, 33 and 35% for a second healing and with 20, 23 and 33% for the third cycle. The reason for the decreased recovery after repeated impacts will be explored in future.

At higher concentrations of healing agent (10, 12.5 and 15% by weight), the capability of the system to heal is much reduced. In all the three cases, the level of recovery is approximately 30, 25 and 20% for the first, second and third cycles, respectively. For the latter cycles, the healing efficiency is still significantly higher than that of the control samples.

Figure 3 shows that healing can be accomplished in shorter periods at high temperatures. A similar optimum concentration of healing agent is required for approximately 60% recovery of impact strength. Interestingly, the unmodified resin shows some residual healing ability.

3.2. Composites healing

Seven square composite coupons prepared from the healing agent modified resin and the unmodified control was subjected to repeated impact/heal cycles. The modified resin contained the optimum 7.5% concentration of healing agent. Each coupon was subjected sequentially to a 2.6 J impact followed by a healing cycle of 2 h at 130°C. At this temperature, a shorter healing period, which is less than the post-curing time, was chosen to avoid the contribution from post-curing of the matrix, as inferred by the data in figure 2. This procedure was repeated for a total of three impact/heal cycles. Figure 5 demonstrates the effectiveness of the healing cycle in closing matrix cracks and delaminations. It also illustrates the need to improve the viscosity of the healing agent-modified resin to avoid entrapment of bubbles in the material. Future resin development will be directed towards this objective. The healing efficiency was quantified using image analysis. The damaged area for the healed coupons was normalized to the initial damage induced by the first impact event. Figure 6 shows the normalized damage areas for these glass fibre composites prepared from the healable and non-healable matrix resins. With glass fibre composites, the damaged layer can be readily measured using image analysis. The normalized damage area is defined as the calculated image analysis area for the healed system, divided the initial damage area for each coupon. Each coupon has received three successive impacts so that the relative damaged area has increased. Between each successive impact, the composite has been subjected to a healing cycle. The damage in the control system has increased in area over the experiment. While there is some indication of healing of the second impact damage, this is within the standard deviation of the data. On the other hand, the sample containing the healing agent-modified matrix shows a definite reduction in damage after each healing, despite an increase in the standard deviation in the data. We can conclude that the rate of crack growth through delamination is inhibited relative to the control by employing a healable resin with thermal cycle.

Thus, the delamination area in the composite prepared with the healable resin is shown to be reduced by 20–30% in the healing cycle. It can also be seen in figure 6 that the delamination area propagates during successive impact events, but that the normalized delamination area for the non-healable samples is always higher than that for the healable samples.

4. DISCUSSION

There are two types of solid-state approaches to self-healing or remendable polymeric resins: (i) depolymerization–polymerization equilibrium systems, e.g. retro Diels–Alder reversible cross-linked polymer

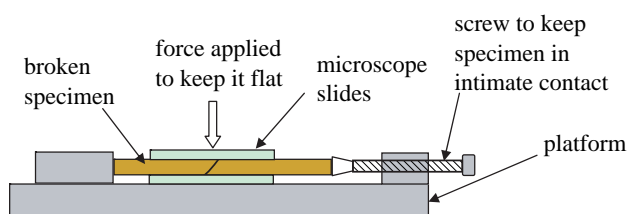


Figure 1. Schematic of the healing platform for the fractured Charpy impact specimens.

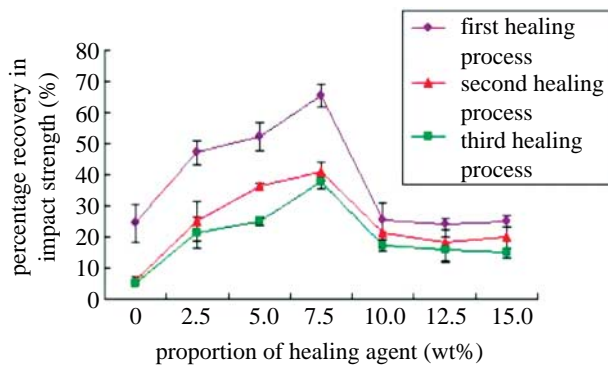


Figure 2. The percentage recovery in Charpy impact strength (R_E) as a function of the healing agent concentration from 0 to 15% by weight. Each sample has been subjected to three impact/heal cycles as shown. The healing conditions were 6 h at 130°C.

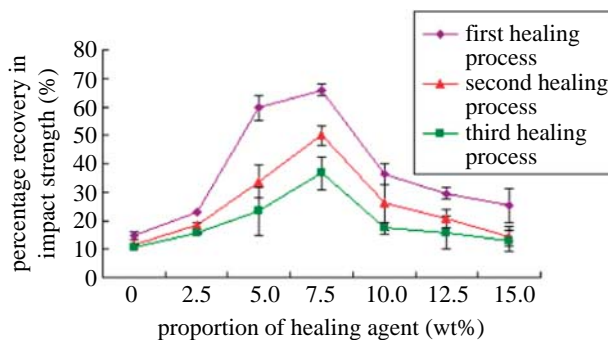


Figure 3. The percentage of recovery in Charpy impact strength (R_E) as a function of healing agent concentration. Each sample has been subjected to three impact/heal cycles. Healing was accomplished after 1 h at 160°C.

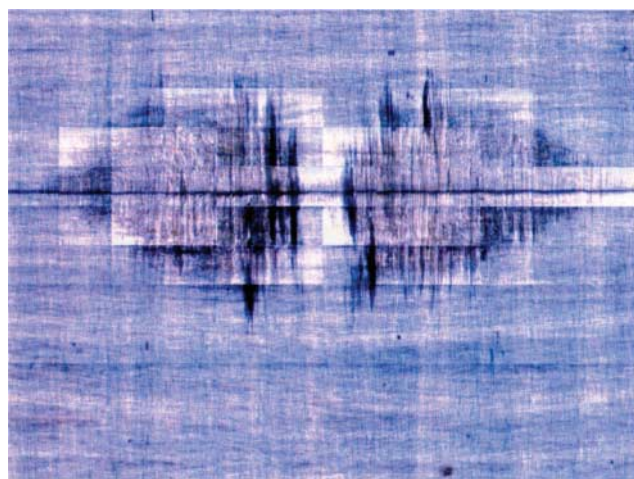


Figure 4. Typical optical micrograph of damage induced in a 0°/90°/90°/0° wound glass fibre composite (non-healable) subjected to 2.6 J impact.

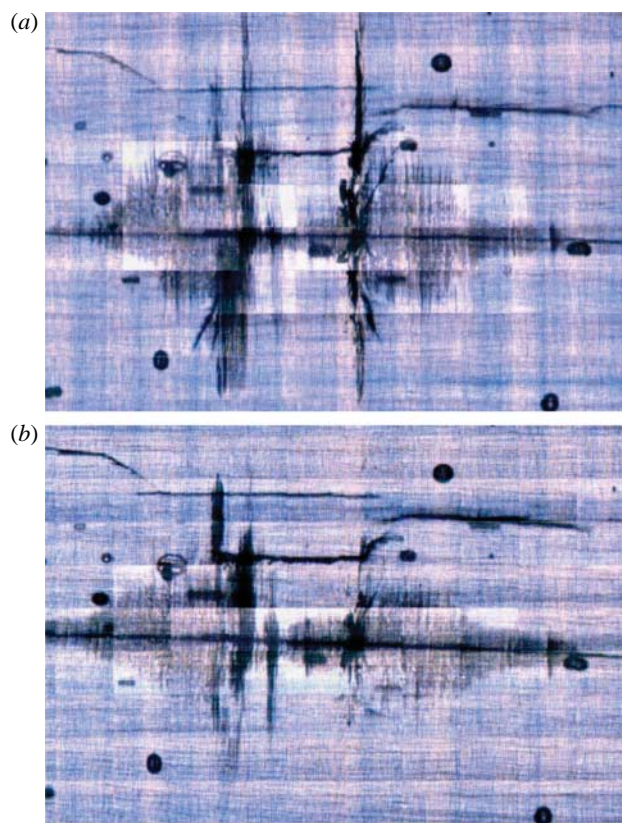


Figure 5. Optical micrographs of a glass fibre composite subjected to two impact and heal cycles showing the closure of damage in a healable matrix composite (a) non-healed and (b) after healing.

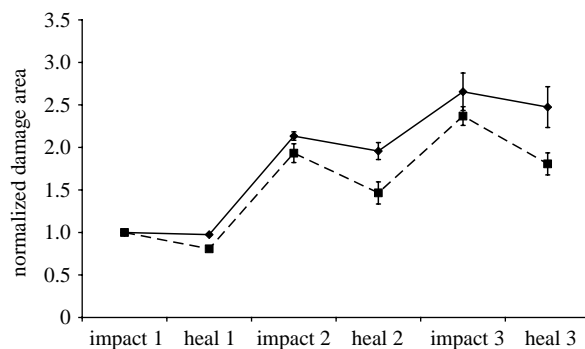


Figure 6. The effect of repeated drop weight impact and healing cycles on glass fibre composites with a heal (dashed) and non-healed (solid) matrices. The rate of growth of delamination area is lower for the system containing 7.5% of the healing agent in the matrix.

(McElhanon *et al.* 2002; Chen *et al.* 2003) and (ii) thermal diffusion of a healing agent. In this paper, we describe a system based on type (ii).

4.1. Healable solid-state resins

The requirements for solid-state healing of a thermoset resin, which used the thermal diffusion of a healing agent, are as follows:

- The healing agent should be reversibly bonded (e.g. through hydrogen bonding) to the cross-linked network of the cured resin below the

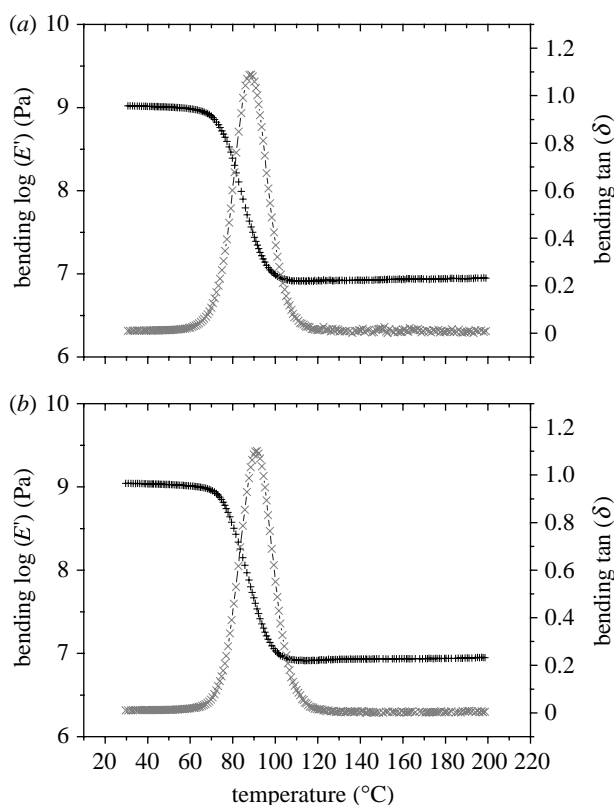


Figure 7. Dynamical mechanical thermal analysis (DMTA) traces for the NMA-cured bisphenol A epoxy resin (a) unmodified and (b) containing 7.5% by weight of poly-bisphenol-A-co-epichlorohydrin healing agent.

minimum healing temperature to limit its effect on thermomechanical properties.

- (ii) The healing agent should become mobile above this minimum healing temperature so that it can diffuse across a hairline crack, such as a transverse crack, to provide a recovery in strength.
- (iii) The addition of the linear chain molecule should not significantly reduce the thermomechanical properties of the resin matrix.

The glass transition temperature (T_g) for the linear polybisphenol-A-co-epichlorohydrin healing agent was found by differential scanning calorimetry (DSC) to be 88°C. We also estimated using group interaction modelling (Gumen *et al.* 2001) that on reactive branching its T_g would increase to 152°C. The dynamic mechanical thermal analysis (DMTA) curve in figure 7b does not exhibit a peak at this temperature, indicating that phase separation has not occurred. The data from the dynamic mechanical thermal analyses for the healable resin are compared with the control in table 2. It is seen that 7.5% addition of the modifier has a minimal effect on the thermomechanical properties. Thus, criterion (iii) is met by this system.

The healing agent was chosen to have the same solubility parameter as the thermoset matrix so as to meet criteria (i) and (ii). The solubility parameters of the healing agent and a model of the NMA-cured diglycidylether of bisphenol A were calculated using the group contribution methodology of Hoy (1970). The

Table 2. The effect of the healing agent modification on the dynamic thermomechanical properties of the epoxy resin.

concentration of healing agent (%)	onset of modulus drop (°C)	$\log(E')$ (Pa)	$\tan \delta$ peak (°C)
0	76.2	8.98	88.7
2.5	75.6	8.97	89.5
5	74.1	8.99	89.9
7.5	74.2	8.97	91.4
10	74.1	9.03	90.2
12.5	73.7	8.99	91.3
15	73.5	8.98	90.6

respective values are 22.1 and 24 MPa^{1/2}. Linear epoxy resins also have a hydroxyl group within the repeat unit to provide the mechanism of hydrogen bonding. Figure 7 shows the DMTA curves for the unmodified and modified resins. The traces are essentially identical demonstrating the solubility of the healing agent although the data in table 2 do indicate some broadening of the peak. Figure 2 confirms that by closely matching the linear molecule to the cross-linked network, diffusional healing can be achieved. Figure 3 also shows that the process of healing is an activation process since raising the temperature for healing to 160°C enables the healing to occur more rapidly. Interestingly, the control sample exhibited a significantly lower level of healing. This would imply that the additional curing attributed to the healing effect at 130°C occurs before diffusional healing can occur. Thus, the activation energy for diffusion differs from that for post-curing. A full detailed kinetic study is required in future studies.

Both figures 2 and 3 show that a healing agent concentration of 2.5% has a limited effect which decreases on repeated healing. We know that at 160°C, the rate of hydroxyl group reaction with the epoxy groups to form ether groups becomes significant in the later stages of cure. It is therefore possible that the healing agent can be chemically reacted to the network when post-curing occurs in the healing stage, reducing its mobility.

Figure 2 shows that the control resin can be thermally healed to a limited extent after 6 h at 130°C. The implication is that there is some post-cure over this extended period despite an initial post-curing schedule of 3 h at 130°C. To compensate for this, the resin healing efficiency (H_E) has been re-estimated from equation (4.1). Thus, H_E contribution to healing from the addition of the healing agent can be examined.

$$H_E = R_E - R_E^0. \quad (4.1)$$

Table 3 shows the healing efficiency across the range of concentrations of the healing agent. A maximum healing efficiency of 43–50% was observed independent of the healing temperature.

An optimum healing agent concentration of approximately 7.5% is observed in both sets of data in figures 2 and 3. However, in the preliminary studies reported elsewhere (Hayes *et al.* 2007), healing agent concentrations up to 20% were effective. The difference appears to lie in the testing procedure. In the preliminary work, we

Table 3. Corrected healing efficiency (H_E) of the NMA-cured DGEBA resin obtained from Charpy impact data in figures 2 and 3.

concentration of healing agent (%)	healing (%)					
	R_E^0		R_E		H_E	
	healing temperature (°C)					
	130	160	130	160	130	160
0	25	16				
2.5	—	—	49	23	24	7
5	—	—	54	60	29	44
7.5	—	—	68	66	43	50
10	—	—	25	36	0	20
12.5	—	—	25	29	0	13
15	—	—	25	25	0	9

used compact tension tests to identify the temperature dependence of the healing phenomenon. In this case, both the strain energy release rate (G_I) and the mode 1 stress intensity factor (K_I) recovered by approximately 65% at 140°C. For the current programme, we needed a test regime requiring smaller quantities of resin and thinner samples which could be used to screen the phenomenon. The preparation of compact tension specimens is particularly time consuming and suffer from potential degassing and exotherm issues. On the other hand, the Charpy impact test has a complex loading arrangement. While it is relevant to impact loads on composites where damage healing is important, it has many disadvantages. For this project, we need to reregister the fracture surfaces for healing. From the thermomechanical data in table 2, we can expect that at concentrations of healing agent greater than 10%, there may be some plasticity in the fracture surface making precise registration of the fracture surface difficult to achieve. We therefore attribute the optimum healing agent concentration to a facet of the test arrangement and the plasticizing effect of the linear polymer. An alternative explanation could be that the healing agent is not completely dissolved in the thermosetting matrix at high concentrations. Further study is required to establish the fundamentals of healing. However, under the impact test conditions for the composite, we have identified a concentration of 7.5%.

4.2. Healing in crossply glass fibre composites

Figure 5 shows that the healing of delaminations is also possible using this modified matrix resin. Optically, the impact damaged area can be seen to have been reduced by approximately 30% in a heating cycle of 2 h at 130°C. Figure 6 attempts to quantify the healing response after successive 2.6 J impacts and thermal healing cycles. Of note is that although the damaged area for the healable composite remains less than that in the control, under a third impact the change in area is larger for the healable system. This demonstrates that the propagation of impact damage appears to be higher in the healed resin.

The experiment was repeated with different coupons taken from the same laminates. In this case, the control

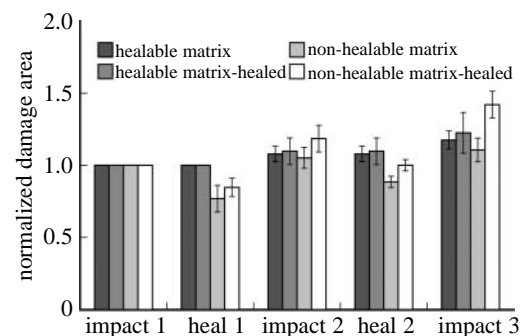


Figure 8. The rate of growth of delamination under impact in healed and non-healed composite specimens prepared from healable or non-healable resin. ‘Healable matrix’ refers to a composite laminate prepared from the modified resin subjected to successive impacts but without a thermal healing. The ‘healable matrix-healed’ referred to a similar experiment but with two thermal healing events. ‘Non-healable matrix’ and ‘non-healable matrix-healed’ refer to the analogous experiments with the non-modified control resin.

laminates (with and without healing agent—healable matrix and non-healable matrix) were subjected to successive impact events so that the damage progression (in the absence of heal) could be compared to the overall damage progression with intermittent healing cycles. Figure 8 shows that after three impacts, both laminates without a healing step had similar damaged areas. For this set of experiments, the healed system appeared to exhibit less damage after three impacts than that shown in figure 6. More importantly, it was also less than that in either of the controls. The non-healable matrix composite subjected to thermal healing (non-healable matrix-healed) cycles exhibited more damage than the equivalent materials without these two healing cycles. This shows that the additional thermal cycles given to the composite prepared from the unmodified resin tend to embrittle the matrix leading to a larger damaged region after three successive impacts of 2.6 J. The healable system (healable matrix-healed), however, exhibited more damage tolerance than its non-thermally cycled (healed) equivalent.

5. CONCLUSIONS

We have attempted to quantify the healing efficiency in a laminate by comparing the areas of damage for a fixed impact energy. We estimate that the healing efficiencies similar to the resin alone are achievable, but there is a need for more detailed experiment.

The addition of a soluble linear polymer to a thermosetting epoxy resin has been shown to be an effective means of inducing self-healing. These resins are intended for use as matrices in carbon fibre and glass fibre composites. Healing of cracks without significant opening can be achieved by a simple heating stage. Coupled to a carbon fibre reinforcement which can be used as a sensor or local heating source, a smart composite system has been identified. In this paper, we have used a glass fibre composite with crossply configuration, which can be probed using optical microscopy, to demonstrate significant multiple healing of composite materials.

An optimum concentration of 7.5% by weight of the healing agent, polybisphenol-A-*co*-epichlorohydrin, appears to exist. However, in a previous study, higher concentrations were more effective. This demonstrates that the testing methodology for demonstrating healability of resins needs to be defined more precisely in future. It was also possible to remove the contribution of further cure during the healing cycle using control samples. A healing efficiency of 43–50% was identified. At this concentration, effective healing of composites transverse cracks and delamination has been demonstrated.

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