SELF-REPAIR AND ENHANCED DAMAGE VISIBILITY IN A HOLLOW FIBRE REINFORCED PLASTIC.

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ABSTRACT

The aim of this study was to develop a novel fibre reinforced composite system which employed a biomimetic approach to undertake self-repair and visual enhancement of impact damage by a bleeding action from filled hollow fibres. The results of flexural testing have shown that for the lay-up investigated, a significant fraction of flexural strength lost after impact damage can be restored by the self-repairing effect of a resin agent stored within hollow fibres.

The release and infiltration of an UV fluorescent dye from fractured hollow fibres into damage sites within the internal structure of the composite has been successfully demonstrated. It has been correlated with respect to the ultrasonic C-scan NDT/NDE technique and shown to be an effective method of quickly and easily highlighting damage at the surface that requires further investigation. This could be of particular benefit where rapid visual inspection of large surface areas (e.g. wing skin panels) is required.

1. INTRODUCTION

The field of fibre reinforced composite materials has grown rapidly since their introduction such that over 20 million tons are now produced every year for a variety of aerospace and other applications. However, concerns remain about the structural integrity of composite materials following impact loading, as such materials are susceptible to cracks or delaminations that form deep within the structure. These cracks are extremely difficult to detect and repair by conventional methods is often impossible. In addition to compromising the material's structural properties, these cracks also provide sites for activities such as moisture swelling which further degrade material performance [1]. Low velocity impact damage can cause a substantial reduction in the undamaged structural strength of polymer matrix composites. Such damage may be caused by dropped tools, ground handling equipment and hailstones. If this damage occurs on a macroscopic level it may be easily detected and repaired, but microscopic damage such as matrix micro-cracking, fibre-matrix debonding and delamination is more insidious and may go unnoticed and unrepaired [2] giving rise to Barely Visible Impact Damage (BVID). One of the key factors limiting current design allowables is the strain at which there will be no growth of BVID. Self repairing composites offer the potential for a substantial improvement in resistance to delamination propagation, allowing the outstanding properties of fibre reinforced plastics to be more fully exploited.

The concept of self-repair is that a damaged structure is repaired by materials already contained within it, analogous to the biological healing process in living organisms. The key is that no external action is required, unlike conventional repair. The technology must sense and respond to damage, restoring the material's performance without affecting the overall properties of the system. This would make the material safer, more reliable, longer lasting, and require less maintenance and thus reduce costs.

The use of functional components stored inside composite materials to restore physical properties after damage has been advocated by several workers. Previous work [3-7] has investigated the use of stored components (e.g. uncured resin or adhesive) within a cementitious matrix which could be released after a damage event to fill cracks and gaps and inhibit crack growth. More recently, several workers [8-14] have also applied this self repairing technique to polymer matrix composites. They found that the release of active components can restore a proportion of the loss in mechanical properties arising from microcracking within a polymer matrix. They also confirmed that the storage of additional components within the matrix material was not detrimental to composite stiffness. Bleay et al. [14] attempted to develop this storage technique by using hollow fibre to store the healing resin components but were unable to procure suitable hollow glass fibre composites.

The approach investigated requires the deployment of specially developed hollow fibre reinforcement [15-18]. Hollow glass fibre is an ideal medium for storing healing components as it can simultaneously act as structural reinforcement and potentially offers many other benefits to composite materials [19-21].

During a damage event some of these hollow fibres will fracture thus initiating two processes. Firstly, the enhanced visualization of the damage site by seepage of a highly conspicuous medium (e.g. ultra-violet fluorescent dye) thus aiding the practical inspection for BVID [9] and identifying areas for permanent repair. Secondly, the recovery of properties by 'healing' whereby a repair agent passes from within any broken hollow fibres to infiltrate the damage zone and acts to ameliorate its effect on mechanical properties. This repair process will act to reduce the critical effects of matrix cracking and delamination between plies and, most importantly, prevent further damage propagation.

It is worth noting that in conventional fibre reinforced plastics, the role of a fibre is to add strength and stiffness to the polymer matrix. The introduction of fibre multi-functionality to provide addition roles is an attractive but currently unavailable option [22] and heralds the move towards ‘smarter’ materials.

2. EXPERIMENTAL APPROACH

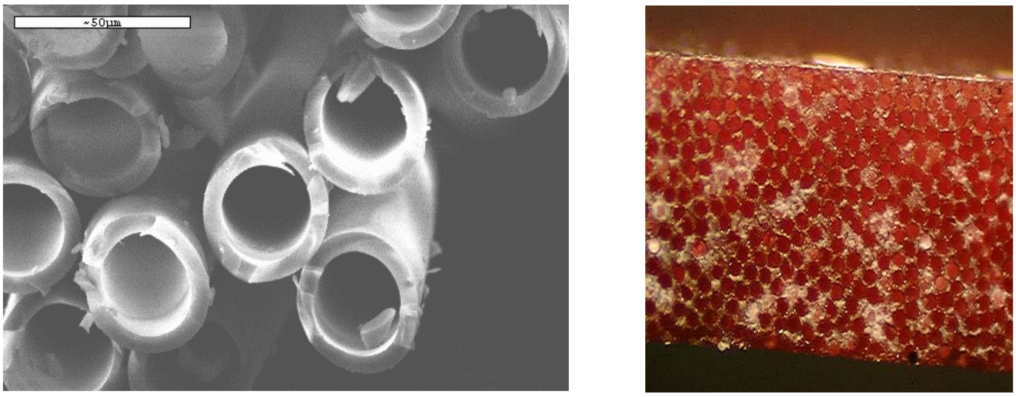
The use of hollow fibres to contain a repair medium has proved difficult to implement to date, largely due to the unavailability of high quality structural hollow fibres [14]. The in-house manufacture and application of such fibres, eliminates the need to incorporate supplementary vessels which compromise composite structural performance, disrupt fibre regularity, act as discontinuities and reduce useful fibre volume fraction. Various methodologies for imparting self-repair are possible, including one-part resins, two part resins in alternating plies, and resin in hollow fibres with the associated hardener in microcapsules dispersed within the matrix.

The aim of this study was to employ a biomimetic approach and fabricate a composite with a ‘bleeding’ ability. The material used in this study comprised unidirectional hollow glass fibres (60μm external diameter, 50% hollow fraction) in an epoxy matrix in combination with conventional E-glass/epoxy. A 0°/90° lay-up ensured that uncured resin or hardener (mixed with UV fluorescent dye) could be infiltrated into the fibre lumens without combination. Uncured epoxy resin resided within the 0° layers and hardener within the 90° layers. A series of test specimens were produced both with and without resin/dye infiltrated hollow fibre plies. A representative impact damage site was formed in the centre of each specimen and healing was allowed to take place under various 'healing' regimes to determine the efficacy of repair prior to four point bend testing.

2.1 Specimen preparation

Borosilicate glass tubing [Schott DURAN®] is drawn down into 60μm external diameter, 50% hollow fraction fibre using the bespoke fibre making facility at Bristol University. This was created through previous collaborative work with DERA Farnborough (now QinetiQ) and BAE Systems. It has the capability to draw precision solid, hollow and novel shaped glass fibres down to 10μm diameter with >50% hollowness, and processing glasses up to 1500°C.

With careful choice and control of preform dimensions, preform feed rate, fibre draw rate and furnace temperature, a highly consistent and concentric hollow fibre is produced with ± 1μm accuracy [15-18], Figure 1.



(a) (b)

Fig. 1. Optical micrographs of fibres and composites manufactured at Bristol (a) hollow glass fibres of 35μm external diameter with a hollowness of 55% and, (b) borosilicate hollow glass fibres of 60μm external diameter with a hollowness of 50% within a Hexcel 913 epoxy matrix

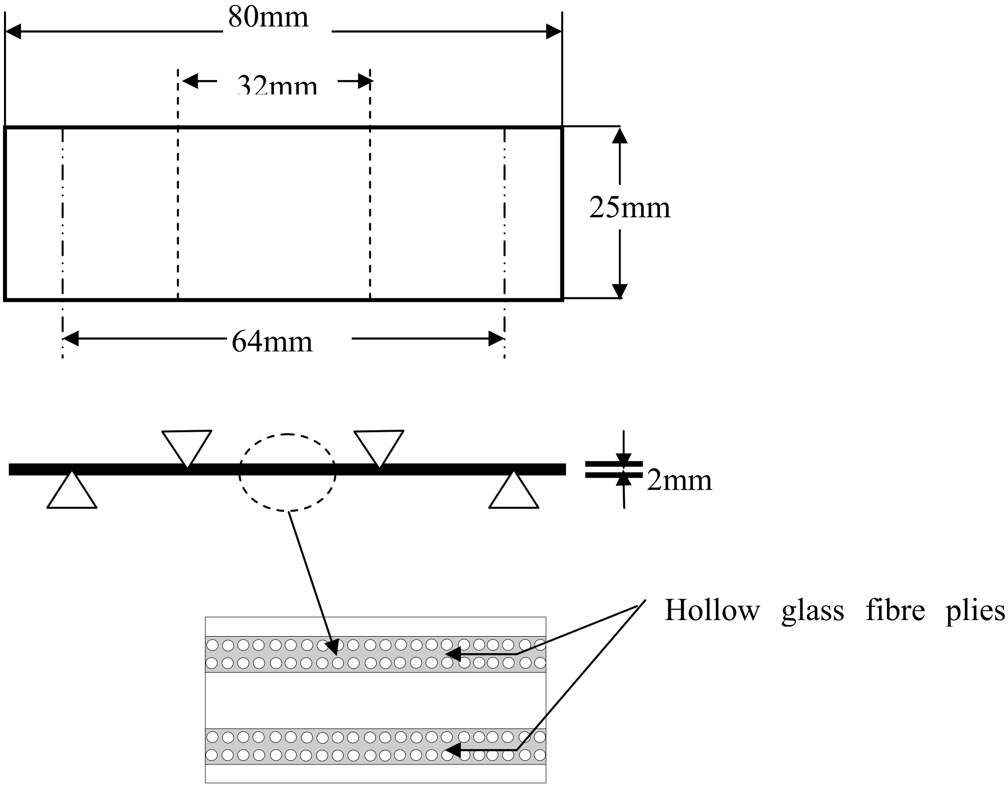


Fig. 2. Lay-up configuration and dimensions for 4-point bend flexural testing.

A resin film infusion process is used to produce hollow glass fibre/epoxy preimpregnated tape (prepreg). Hexcel 913 epoxy resin is used as the matrix material. The prepreg contained a nominal gross fibre volume fraction (V_f) of approximately 61.5%. Six laminates of 18 plies (nominal thickness 2mm) were manufactured using a hand lay-up process and cured according to manufacturers recommendations. The lay-up chosen was $\{[90°/0°]_{(solid)},[90°/0°/90°/0°]_{(hollow)},[90°/0°/90°]_{(solid)}\}_S$ to position the hollow plies in the subsurface of the laminate. A [90˚/0˚] lay up for the hollow glass plies ensures that uncured epoxy resin (plus fluorescent dye) and hardener can be infiltrated into the 0° and 90° plies respectively.

The six panels were cut into 80mm (length) x 25mm (width) x 2mm (depth) specimens (Figure 2) using a diamond saw, then a water filled ultra-sonic bath was used to remove any cutting debris from inside the hollow fibre lumens. Care was taken to fully dry specimens after this cleaning process. Four groups of specimens (B, C, D, E) had the 0° hollow plies filled with dilute epoxy resin repair agent (MY750 Ciba-Geigy + 30%/vol acetone) and the 90° plies filled with corresponding hardener. The resin and hardener weight gain per specimen was recorded and used later to normalise the flexural strength test data to an equivalence of 1%/weight for all specimens.

2.2 Mechanical Testing

Six specimen groups (A-F) were prepared in order to establish the mechanical behaviour before and after pseudo-impact damage on a self-healing hybrid solid/hollow glass fibre reinforced composite. An objective of the study was to establish the efficiency of repair after a period of time had elapsed. Thus, a series of tests were undertaken at prescribed time intervals. Four-point bend flexural testing, according to ASTM 790M-93, was chosen for simplicity.

Four specimen groups (B, C, D, E) were filled with repairing agent and two groups (A & F) were not. The latter represented undamaged and damaged states respectively. The five specimen groups (B, C, D, E, F) were subjected to impact damage by a process of indentation using a hardened steel hemi-spherical end of 4.63mm diameter with the specimen back face supported by a steel ring, as shown in Figure 3. An Instron 1341 servohydraulic machine was used for both indentation and 4-point bend testing. A PC based data acquisition system was used for all mechanical testing. Indentation was performed under load control at a crosshead displacement rate of 3mm/min to a maximum load of 1200N. This corresponds to an impact energy of approximately 0.6 Joule.

In order to ascertain the effect of time on repair efficiency, specimen groups B, C, D and E were stored in a desiccator for periods of 0, 3, 6 and 9 weeks before being subject to damage (via indentation) and flexural testing. Immediately after indentation these specimen groups were allowed to undergo a process of self-healing for 24 hours at ambient temperature as this had previously been established [23] as the most simple and effective healing regime. The four-point bend flexural testing was conducted to investigate the efficiency of a bleeding composite to effect a self-repair. Figure 2 gives a schematic of the test geometry. A displacement rate of 3.4mm/min was used for the flexural testing. The impact damaged face of the specimens was oriented such that it was subject to compressive loading.

2.3 Enhancing Damage Visibility

To enhance the ‘bleeding’ process, a conspicuous medium (e.g. UV fluorescent dye) can be added to the healing resin within the hollow fibres to aid inspection for BVID. In order to investigate, validate and calibrate this enhancement of damage visibility, ultrasonic scanning (C type) was employed to compare with the proposed ultra-violet mapping technique (UVMT). Ultrasonic C-scans are widely used as a reliable non-destructive method for composite materials inspection. Thus, it is an ideal method to assess the reliability and effectiveness of the UVMT technique.

Twenty five specimens were prepared according to the manufacturing process reported above, with the exception that an UV fluorescent dye penetrant (Ardrox 985) was added to the fibres instead of repair resin or hardener. These specimens were then divided into five groups and subjected to indentation as described above. Five different indentation forces were applied to the specimens; 800N, 1000N, 1200N, 1400N and 1600N. The equivalent impact energies are shown in Table 1. Two damage sites were created on each specimen in order to provide an average result of ten damage sites for each impact energy. The damage created by the indentation process was then measured using the UVMT and then ultrasound C-scan. The former consists of recording magnified digital images of the damage site under ultra-violet illumination. Efforts were then made to measure and correlate the resulting damage maps from each specimen using the two techniques and image analysis (ImagePro®) software.

Table 1. Correlation of indentation load and impact energy.

Indentation Force (N)	Energy absorbed (J)
800	0.25
1000	0.43
1200	0.62
1400	0.80
1600	1.13

3. RESULTS & DISCUSSION

3.1 Indentation behaviour

Figure 3 shows a cross-section through an uninfiltrated specimen (group F) after indentation, illustrating interface delamination, matrix cracking and hollow fibre fracture. The majority of the impact induced damage is localised within or adjacent to the hollow fibre plies, thus creating an ideal situation for self-repair by the uncured resin within the hollow fibres. The fracture of hollow fibres in the 0° and 90° plies and the mixing of resin and hardener allows initiation of the curing process whilst simultaneously promoting infiltration of the local matrix cracks and delamination by capillary action. A key aspect of this whole self-healing process is that the impact energy must be of a sufficient threshold value to fracture hollow fibre plies. This threshold value can be tailored for any application by the constituents, number and positioning of the repair agent bearing layers within the laminate stack.

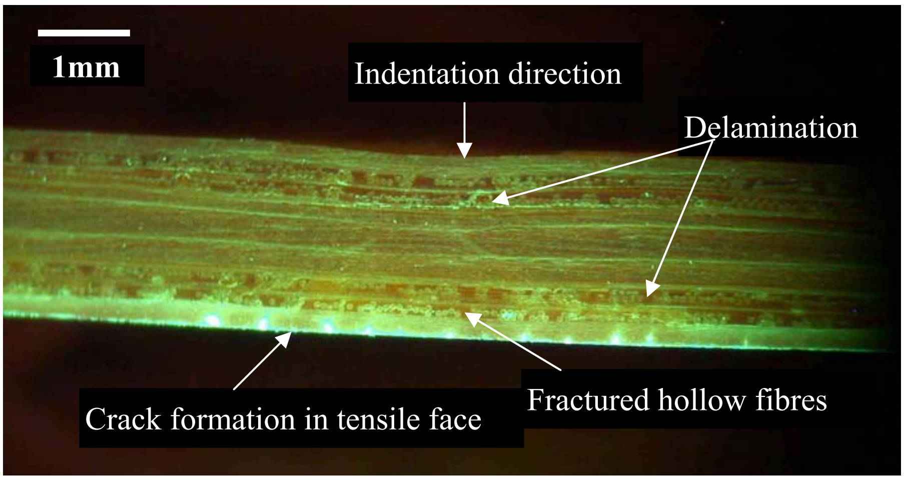


Fig. 3. Optical micrograph of cross-section through impact damaged hybrid solid glass/hollow glass/epoxy laminate.

3.2 Four-point bend flexural testing

Figure 4 and Table 2 show the results of four-point bend flexural testing for the six specimen groups. In order to provide a fairer comparison of the test data, flexural strengths for groups B-E have been normalised to a nominal 1%/weight repair resin content within the hollow fibres. This can be justified as the resin content directly affects the extent of damage repair after impact and thus the resulting flexural strength. All testing was undertaken with the damaged face of the specimen subject to compressive loading. This was because resin repair would have negligible effect on the fibre dominated tensile face.

It is clear that impact has a serious effect on flexural strength, as specimen group F (damaged, uninfiltrated) shows a ≈25% reduction compared to group A (undamaged, uninfiltrated). If a process of self-repair is introduced (group B) immediately post-manufacture, it is clear that a significant proportion (93%) of flexural strength can be restored. This is probably attributable to an extensive penetration of damage crack paths (see Figure 3) by the repair resin before the viscosity rise associated with cure progression precludes this process. 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.

Specimens groups B-E were used to assess the rate of degradation of the repair resin effectiveness over time. Each group of specimens was stored for different periods (0, 3, 6 and 9 weeks) before being damaged, allowed to self-repair for 24 hours under ambient conditions and then tested in flexure. The efficiency of repair is seen to deteriorate markedly over a 9 week period (albeit with a significant degree of scatter). After a 9 week period had elapsed (group E) self-repair was no longer seen to occur. Flexural strength is then shown to be equivalent to a damaged and unrepaired material (group F). Much of this behaviour can be explained by the use of unoptimised repair resin, unsuited to being stored in an uncured state for long periods. These results indicate the importance of choosing an appropriate repair resin which offers ease of infiltration into hollow fibres, ability to infiltrate and repair damage, simple and controllable cure characteristics, and adequate mechanical properties once cured.

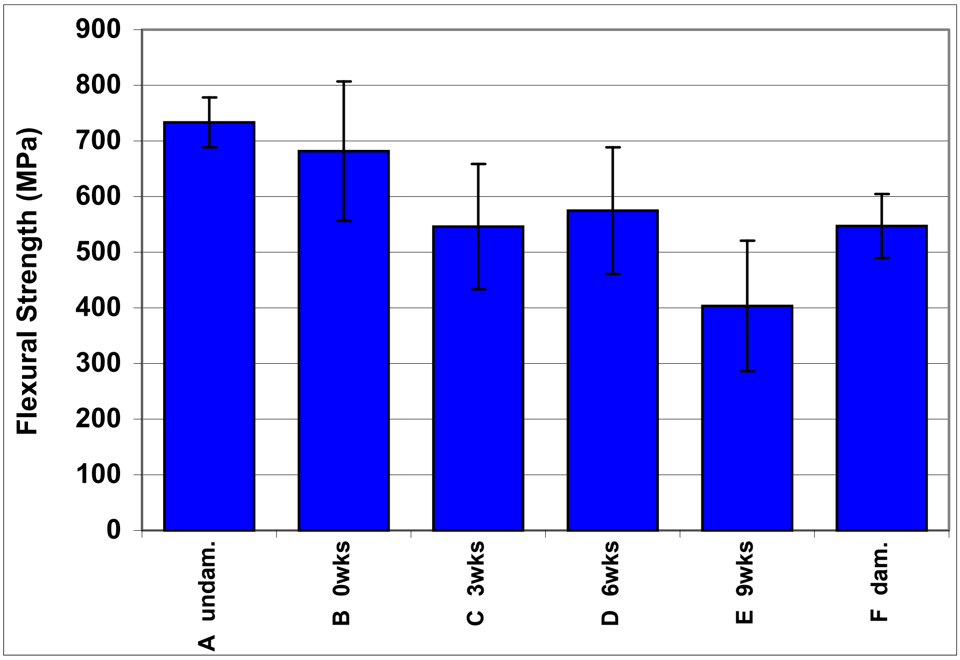


Fig.4. Results of flexural testing for damaged, undamaged and self-repaired specimens after various storage periods (bars denote standard deviation).

Table 2. Results of four-point bend flexural testing for all specimen groups.

Sample identity	Sample condition prior to testing	No. of samples	Mean flexural strength (MPa)	Standard deviation (MPa)	Percentage undamaged state (%)
A	Undamaged	14	732.90	44.87	100.0
B	Stored 0 wks, Damaged & Repaired	8	681.52	125.05	93.0
C	Stored 3 wks, Damaged & Repaired	7	546.04	112.21	74.5
D	Stored 6 wks, Damaged & Repaired	8	574.31	113.87	78.4
E	Stored 9 wks, Damaged & Repaired	8	403.54	117.34	55.1
F	Damaged	8	546.79	57.38	74.6

3.3 Visual enhancement of damage

An important aspect in the development of 'bleeding' fibre composites is to provide visual enhancement of damage, in particular BVID. The bleeding action of a highly conspicuous dye into the numerous cracks and fissures created by a damage event serves to decorate these sites, increasing their ease of detection in NDT/NDE. This could be of particular benefit where rapid visual inspection of large surface areas (e.g. wing skin panels) is required.

Figure 5 compares three typical views of a damaged (0.8J) specimen identical to those described previously, but containing a UV fluorescent dye (Ardrox 985) within the hollow fibres. Figures 5a and 5b show the respective front (side of impact) and back face views under UV illumination, while Figure 5c shows an ultrasonic C-scan of the same damage site . It is clear that the use of a UV dye is very effective in highlighting a damage site. Also, it appears from Figures 5b and 5c that the damage shown using UVMT correlates very well with that from C-scan. This is further verified by Figure 6 which attempts to quantify and compare the damage areas after various impact energies, measured using UVMT and C-scan. Measurement of damage on the back face using UVMT closely correlates to C-scan, with a reasonably uniform discrepancy of approximately 25%, for the impact energies investigated. Measurement of damage area from the front face using UVMT is less distinctive. However, it is useful in finding and marking a damage site on the surface, offering a rapid and easy technique for highlighting suspect areas for further NDT/NDE.

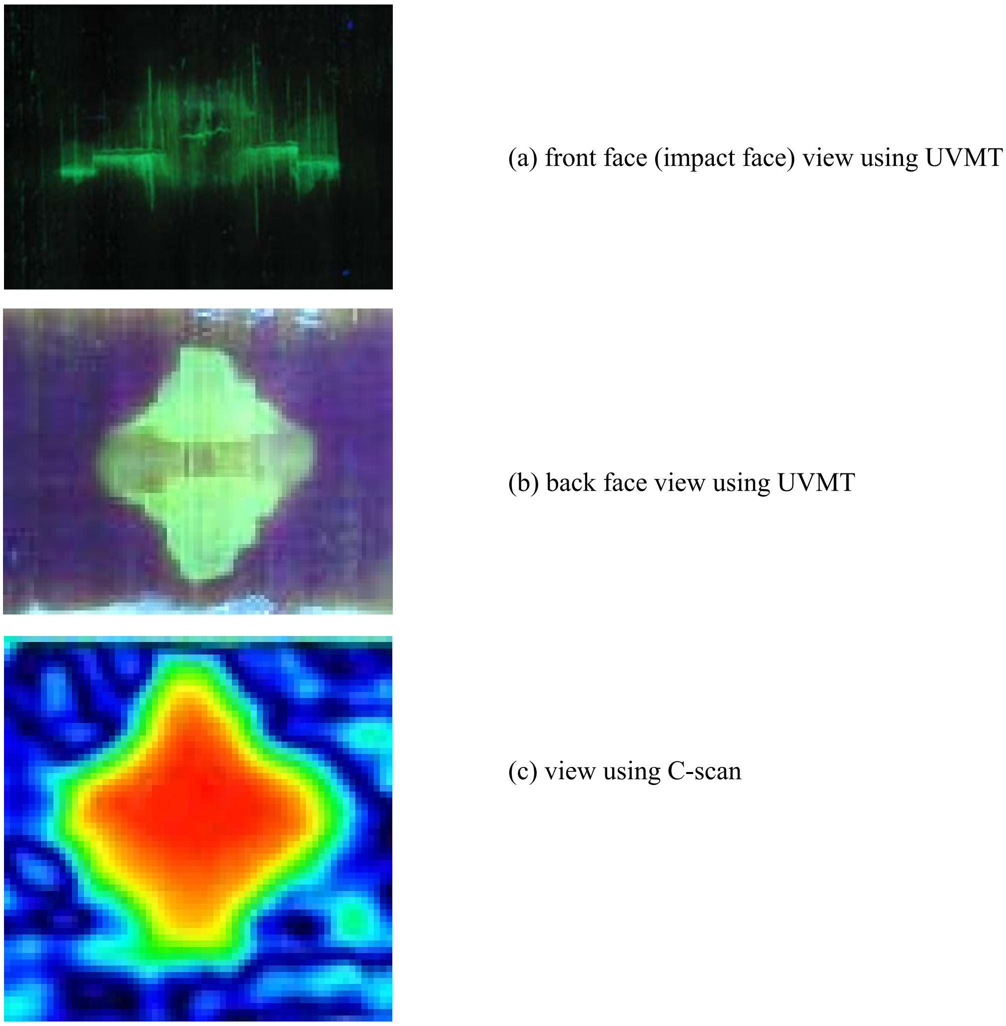


Fig. 5. Comparison of Ultra-Violet Mapping Technique (UMVT) viewed from (a) front and (b) back faces of specimen and (c) Ultrasonic C-scan after impact damage of 0.8J (i.e. indentation @ 1400N). (Note: images not to scale)

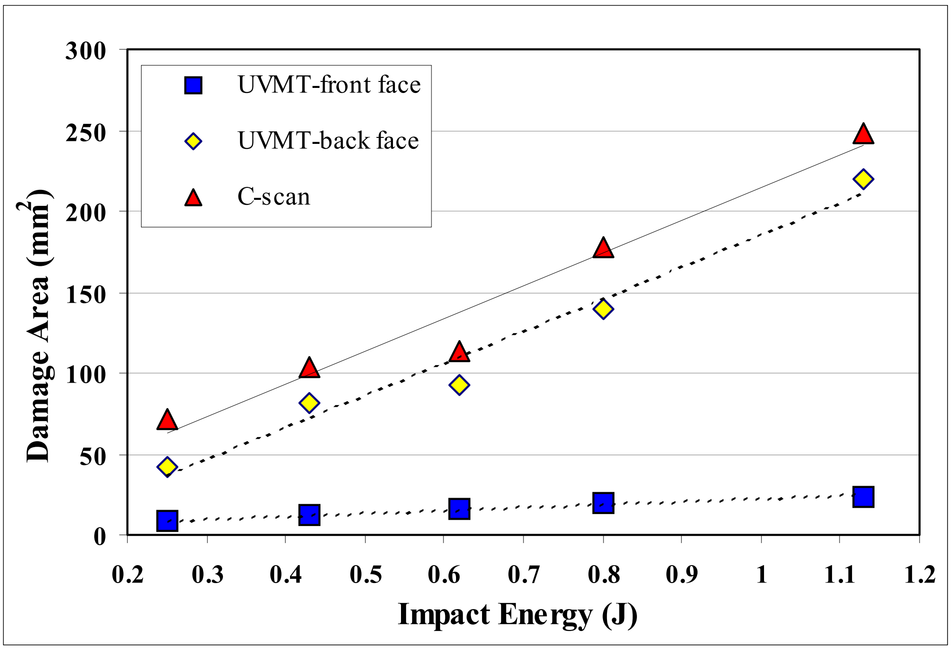


Fig. 6. Correlation of damaged area measured by UVMT (from front and back faces) and C-scan.

4. CONCLUSIONS

A biomimetic approach has been used to develop and demonstrate a self-repairing, enhanced damage visibility, 'bleeding' composite which provides an effective way to recover mechanical strength and highlight concealed damage after an impact damage event .

The results of flexural testing have shown that for the lay-up investigated, a significant fraction of lost flexural strength can be restored by the self-repairing effect of a repair agent stored within hollow fibres. The 'self-repair' is dependent upon uncured resin (in the 0° plies) combining with the hardener (in the 90° plies) as a result of fibre fracture in both these layers. 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.
The ability of self-repair has been shown to deteriorate significantly over time as the repair resin degrades.
Further work is needed to optimise the repair resin used within the fibres to provide increased environmental stability and effective service life.

The release and infiltration of an UV fluorescent dye from fractured hollow fibres into damage sites within the internal structure of the composite has been successfully demonstrated. It has been correlated with respect to the ultrasonic C-scan NDT/NDE technique and shown to be an effective method of quickly and easily highlighting damage at the surface that requires further investigation. This could be of particular benefit where rapid visual inspection of large surface areas (e.g. wing skin panels) is required.

Further work is currently ongoing to refine both the self-repairing and damage enhancement processes by the use of tailored resins and dyes which provide improved repair properties, damage enhancement and environmental stability/longevity.

References

1. **White, S.R., Sottos, N.R., Geubelle, P.H., Moore, J.S., Kessler, M.R., Sriram, S.R., Brown, E.N., Viswanatham, S.**, "Autonomic healing of polymer composites." *Nature,* **409**/6822 (2001), 794-797.
2. **Motuku, M., Vaidya, U.K., Janowski, G.M.**, Parametric studies on self-repairing approaches for resin infused composites subjected to low velocity impact. *Smart Matls. & Structs.*, **8** (1999), 623-638.
3. **Dry, C.**, "Alteration of matrix permeability, pore and crack structure by the time release of internal chemicals. *Proc. Advances in Cementitious Materials*, American Ceramic Society, Gaithersbury, Maryland, (1990), 729-68.
4. **Dry, C.**, "Matrix cracking repair and filling using active and passive modes for smart timed release of chemicals from fibres into cement matrices." *Smart Matls. & Structs.,* **3**/2 (1994), 118-123.
5. **Dry, C., McMillan, W.**, "Three-part methylmethacrylate adhesive system as an internal delivery system for smart responsive concrete." *Smart Matls. & Structs.,* **5**/3 (1996), 297-300
6. **Dry, C.**, "Three designs for the internal release of sealants, adhesives and waterproofing chemicals into concrete." *Cement & Concrete Research*, **30** (2000) 1969-1977.
7. **Li, V.C., Lim, Y.M., Chan, Y.W.**, "Feasibility of a passive smart self-healing cementitious composite." *Composites B*, **29B** (1998), 819-827.
8. **Dry, C., Sottos, N.**, "Passive smart self-repair in polymer matrix composite materials." Smart Matls. & Structs., ed. K. Varadian. *Proc. SPIE 1916* (1993), 438-444.
9. **Dry, C., McMillan, W.**, "A novel method to detect crack location and volume in opaque and semi-opaque brittle materials." *Smart Matls. & Structs.*, **6**/1 (1997), 35-39.
10. **Dry, C.**, "Procedure developed for self-repair of polymer matrix composite materials." *Comp. Structs*, **35**/3 (1996), 263-269.
11. **Zako, M., Takano, N.**, "Intelligent material systems using epoxy particles to repair microcracks and delamination damage in GFRP." *J. Int. Mat. Sys. & Struc.,* **10**/10 (1999) 836-841.
12. **Kessler, M.R., White, S.R.**, "Self-activated healing of delamination damage in woven composites." *Composites A*. **32**/5 (2001), 683-699.
13. **Kessler, M.R., White, S.R., Sottos, N.R.**, "Self healing of composites using embedded microcapsules: repair of delamination damage in woven composites." *10th European Conference on Composite Materials (ECCM-10)* 3-7 June 2002, Bruges, Belgium (2002)

14. **Bleay, S.M., Loader, C.B., Hawyes, V.J., Humberstone, L., Curtis, P.T.**, "A smart repair system for polymer matrix composites." *Composites A*, **32** (2001), 1767-1776.
15. **Hucker, M.J., Bond, I., Bleay, S., Haq, S.**, "Experimental evaluation of unidirectional hollow glass fibre/epoxy composites under compressive loading." *Composites A,* **34**/10 (2003), 927-932.
16. **Hucker M.J., Bond I., Bleay S., Haq S.,** "Investigation into the behaviour of hollow glass fibre bundles under compressive loading." *Composites A*, **34**/11 (2003), 1045-1052.
17. **Hucker M.J., Bond I.P., Haq S., Bleay S., Foreman A.,** "Influence of manufacturing parameters on the tensile strengths of hollow and solid glass fibres." *J.Mat.Sci.* **37**/2 (2002), 309-315.
18. **Hucker, M., Bond, I., Foreman, A., Hudd, J.**, "Optimisation of hollow glass fibres and their composites." *Adv.Comp.Lett.,* **8**/4 (1999), 181-189.
19. **Burgman, J.A.**, "Hollow Glass Fibers." *Symposium on Polymers and Plastics in Construction Presented before the Division of Petroleum Chemistry*, American Chemistry Society, September 12-17, (1965), A97-A112
20. **Rosen, B.W.**, "Hollow glass fibre reinforced laminates." *Final Report 15 June 1963–15 August 1964, US Navy, Bureau of Naval Weapons, Contract No.: NOW-63-0674-C*, GE Missile & Space Division, GE Company, Philadelphia, Pa., 1964
21. **Rosen, B.W., Ketler, A.E., Hashin, Z.**, "Hollow glass fibre reinforced plastics." *Final Report, US Navy, Bureau of Naval Weapons, Contract No.: NOW-61-0613-D*, GE Missile & Space Division, GE company, Philadelphia, Pa., 1962
22. **Curtis, P.T.**, "Multifunctional polymer composites." *Adv.Perf. Mater.* **3** (1996), 279-293.
23. **Pang, J., Bond, I.**, "'Bleeding Composites' - Damage Detection And Self-Repair Using A Biomimetic Approach." *Composites A* (In Press - October 2003)