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A review of current strategies to induce self-healing behaviour in fibre reinforced polymer based composites.

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Abstract

While fibre reinforced composites are well known for their excellent mechanical properties and their long term stability under a wide range of mechanical/thermal/chemical conditions, even they may incur local damage. Like in other engineering materials such local damage is likely to grow and lead to macroscopic failure upon further use of the component. Self-healing strategies can be employed to mitigate the effects of local damage in order to (partially) restore the mechanical properties and to avoid premature catastrophic failure. This paper addresses the various strategies to induce self-healing behaviour in fibre reinforced polymer based composites taking into account the special architectural aspects of such structures. It distinguishes between extrinsic healing in which the healing agent is a discrete, encapsulated (liquid) entity within the polymeric matrix, at the fibre-matrix interface or within the fibrous component and intrinsic healing in which the healing action is provided by reversible (chemical or physical) bonds in the polymeric matrix. As the healing depends also on the type and extent of the damage, the self-healing ability is discussed in the context of the healing mechanism and the mode of damage creation. The conclusion is drawn that self-healing in fibre reinforced composites is possible yet unlikely to become a commercial reality in the near future.

1. Introduction

Intentionally created self-healing behaviour has become an active research topic in materials science in recent years, but in all fairness it is good to realize that self-healing behaviour has been around already for a long time. Typical examples are the Egyptian straw reinforced clay-based dwellings and the mortar holding together the old Roman building and infrastructural works. In these early examples the self-healing behaviour is based on the sequential dissolution and re-precipitation of matter in micro-cracks upon cyclic changes in the air humidity. It is very unlikely that these materials were engineered intentionally to optimise the self-healing characteristics as the self-healing behaviour more or less comes automatically with the (inorganic) chemistry of the materials themselves.

A very early example of engineered, intentional self-healing behaviour is the work of Dry,[1, 2] who included hollow glass fibres filled with a liquid adhesive in a concrete matrix prior to setting of the concrete. Upon local fracture of the concrete the glass fibres break, the liquid adhesive flows out and fills the crack, wets the crack surfaces and crosslinks. After crosslinking the load bearing capacity of the concrete is restored to some degree. The concept works and led to some restoration of properties, but the improvement was modest as the efficiency of the healing process was moderate due to various reasons: the mortar was not fully dense (leading to loss of healing agent into non-relevant pores), the fracture surfaces were rough, the crack opening was uncontrolled and sometimes too large, and there is a big difference in chemical nature between the polymeric healing agent and the inorganic concrete matrix.

A more successful and much more widely acclaimed attempt was made by the team at the Beckman Institute led by White, Sottos and Moore.[3] They mixed polymeric microcapsules filled with a crosslinkable liquid oligomer into a low viscosity epoxy matrix with dispersed Grubbs catalyst. Upon controlled fracture of the material, the crack intersects the capsules and breaks them leading to the flow of the healing agent into the crack. The healing agent wets both crack surfaces comes into contact with the dispersed catalyst particles and undergoes a crosslinking reaction leading to a significant restoration of the tensile strength of the sample. In their system a much higher healing efficiency was obtained probably due to the epoxy failing with a smooth planar surface, the fact that the crack opening distance was artificially kept low and the chemical compatibility between the healing agent and the epoxy matrix.

Very early on, it has been realised that the crack filling potential of small spherical microcapsules is intrinsically limited, and a much better ‘long distance supply’ of healing agent could be obtained by storing the healing agent in long hollow fibres. The team at Bristol led by Bond, in close cooperation with the Beckmann Institute team, was the first to show effective self-healing behaviour in fibre reinforced composites using hollow fibres.[4 ,5] The working principle of these self-healing composites is essentially the same as that for the microcapsule filled unreinforced epoxy material.

Since these three landmark contributions showing engineered self-healing behaviour in man-made materials many new healing concepts for virtually all classes of materials have been developed.[6-9] In this development process two conceptually different routes emerge: i) the *extrinsic* healing route in which the (generally liquid) healing agent is incorporated into the matrix as discrete entities not contributing to the main functionality of the base material. Given the proper capsules dimensions and capsule volumetric density, cracks with a crack opening distance of typically up to 500 μm can be healed; and ii) the *intrinsic* healing route in which the healing capability is intrinsically connected to the (chemically or compositionally tuned) matrix material. Unlike the case of extrinsic systems where the healing at a particular location can only happen once as the healing agent irreversibly loses its fluidity upon reacting, in intrinsic healing systems healing at a particular location can take place several times as no healing agents are consumed in the healing action. As the healing in intrinsic self-healing materials relies on molecular diffusion processes, only cracks more or less in contact can be healed. For intrinsic healing polymers to heal they should either be already above their Tg or a temporarily stimulus (such as temperature or moisture) to increase the molecular mobility should be applied.

While the fibre reinforced polymers (FRPs) were amongst the first materials to be developed with a self-healing functionality, the rate of development in this field has been relatively slow as the problems to be overcome are very large for a number of reasons: i) FRPs have carefully optimised internal structures not leaving much ‘space’ to bring in healing agents or more general a healing chemical action; ii) FRPs are chemically rather inhomogeneous with on the one hand highly oriented and very strong covalent carbon-carbon bonds in the reinforcing carbon fibres and far more flexible covalent or semi-covalent bonds in the polymer matrix; iii) FRPs have an extremely large number of internal interfaces of different length scale and nature (such as the interface between individual fibres and the surrounding polymer matrix and the much coarser ply-ply interface for woven or braided structures); iv) Given their structure and anisotropic properties at several length scales the fracture dimensions and topologies in composites are extremely complex to predict and can cracks can show locally large fluctuations in the crack opening distances which have somehow to be bridged. Large crack opening distances are a serious problem for any self-healing concept

It is the aim of the present review to make an inventory of the various roles the separate components in fibre reinforced polymer composites can play in creating self healing behaviour. Furthermore, examples of successful healing systems for failure after static, fatigue and impact loading are presented. . From the data presented some conclusions regarding the likelihood of self-healing fibre reinforced polymer composites entering the market in the foreseeable future are derived.

2. The role of the principal entities in fibre reinforced composites

2.1. Fibres

While the chemical nature of the carbon or polymeric reinforcing fibres used in PRP may differ, they all have a high spatial density of strong and non-reversible chemical bonds in the direction of the fibre axis leading to fibres with high stiffness and strength. Hence the chemical nature of the reinforcing fibres is such that it is intrinsically impossible to create high modulus fibres with an intrinsic healing capability as the required bond stability in the fibre axis direction will just be too high to replace it by reversible chemical bonds.

As a result, reinforcement fibres will not be the direct source of the healing action but they can be modified at the expense of their strength to become containers for a liquid healing agent. Bond et al. have made optimal use of this last concept, [4, 5, 10, 11] but their work also shows that the insertion of filled hollow glass fibres lowers the undamaged properties of the composites substantially as is to be expected given the large difference in specific properties of the fine yet solid carbon fibres and the relatively coarse liquid filled glass capillaries (see Fig. 1).

Furthermore, the controlled positioning of the hollow fibres at the most damage sensitive locations of the composite is by no means trivial and will increase the manufacturing costs considerably. From a manufacturing point of view the 1D systems involving filled hollow fibres seem to be the easiest to be incorporated in currently available manufacturing processes. Recent work by Norris et al. showed the importance of alignment of the channels with the local fibre orientation in the ply without disrupting the fibre architecture of adjacent plies too much.[12-15] To be successful, the distance between neighbouring channels needs to be optimized to prevent significant changes in the mechanical properties of the fibre reinforced composite material before and after introduction of the 1D vasculature. It was shown that the failure strength of $[-45/90/45/0/90]_{2s}$ carbon epoxy composites was hardly affected by the presence of 0.5 mm diameter open channels placed 10 mm apart.[12] Notwithstanding the relatively straightforward 1D healing approach almost full recovery of the mechanical properties of the impacted samples was observed in compression testing after impact.

However, the intrinsically limited healing potential of 1D filled hollow glass fibres has led to more complex 2D and 3D network systems,[16, 17] although manufacturing of such networks is hardly compatible with current large-scale production methods of fibre reinforced composite materials. An interesting new approach has recently been presented by Esser-Kahn et al. employing sacrificial polylactic fibres that are woven into 3D glass pre-forms employing a common mechanical weaving technique.[18] After curing of a thermosetting resin, the polylactic fibres are thermally decomposed to obtain a 3D microvasculature allowing infiltration with a suitable healing liquid. As with all extrinsic healing systems the healing capability is restricted to one healing action per location only.

A slightly different role for the fibres in the healing process is envisaged in the multi-encapsulate fibres produced by Mookhoek et al.[19] Instead of making long continuous capillaries they focus on the production of alginate fibres containing multiple healing agent filled discrete vacuoles all along the fibre (see Fig. 2). These fibres can be tuned to have the same mechanical properties as the epoxy. Furthermore they can be spun in diameters comparable to those of the regular reinforcing glass or carbon fibres. Insertion of such new fibres will allow multiple local release and healing events. As with the hollow continuous glass fibres, the alginate fibres will lower the specific mechanical properties of the composite, but they may be blended more easily with the reinforcing carbon fibres and their properties can be tuned to match those of the matrix.

An alternative, rather new and promising approach is the use of electrospun or solution-blown core-shell nanofibres.[20-23] Prepared as nanofibrous mats they may be easily integrated during laminate layup as thin interleaves with submicron out-of-plane dimensions hardly affecting the overall weight, strength and stiffness of its host. Yet, their presence at the interface between successive plies promises optimal dispersion of healing fluids at the relatively brittle resin-rich interface layer leading not only to the capability of micron sized damage but also potentially leading to an increase in the interface toughness at a systems level

Finally, Bor et al. and Neuser et al. have allocated yet another role to some of the fibres in FRPCs.[24, 25] They both demonstrated that the substantial contraction of metallic Shape Memory Alloy (SMA) wires upon a thermal input can be utilised to reduce the crack opening distance (provided the SMA wires are perpendicular to the crack to be healed) (see Fig. 3) . This reduction of the crack opening distance will be beneficial for the extrinsic healing systems,[25] and for intrinsic healing polymer matrices alike.[24] Of course, the insertion of such fibres will also lower the specific properties of the composite and require the availability of a power source to induce thermal wire contraction. Furthermore, the SMA fibres must show substantial delamination from the matrix to create enough fibre length to turn the local specific contraction into an absolute contraction distance comparable to the crack opening.

2.2. The fibre matrix-interface

The interface zone between fibre and polymeric matrix in a FRP plays a crucial role for load transfer from the polymeric matrix to the fibre reinforcement. Micro-cracks growing in this region due to fatigue or thermal loads ultimately cause a loss of strength and stiffness of the FRP.[26] Propagation and coalescence of such kind of cracks can also lead to large scale damage leading to catastrophic failure of the composite component. For these reasons, researchers recently start to apply self-healing methodologies also at micro-scale level in a CFRP,[6] trying to repair microscopic interface damages. Test procedures were adapted to measure the decrease and recovery of the matrix/fibre interface.[27, 30, 31]

Early research by Sanada et al. showed how the extrinsic self-healing concept based on micro or nano) capsules can be employed to heal the interface between fibre and matrix.[28] In their work, carbon fibres were coated with an epoxy based mixture containing 10 to 40 wt% urea-formaldehyde (UF) nano-capsules filled with dicyclopentadiene (DCPD) and 2.5 wt% Grubbs' catalyst dispersed in the polymeric matrix. Tensile composite specimens containing such surface modified fibres were manufactured and tested, showing a recovery of up to 19% of the original interface strength. The fact that healing took place demonstrated the validity of the approach, yet the modest level of healing also revealed the inherent limitation of small capsule sizes to heal damage of more substantial dimensions. The effects of different parameters such as capsule dimension and distribution around fibre were reported elsewhere.[29]

A similar self-healing system was studied by Blaiszik at al. using again a micro-debonding test.[30] In this research glass fibres, coated with Grubbs' catalyst and microcapsules containing a liquid healing agent (DCPD), were embedded in a commercial epoxy matrix to produce single fibre pull-out samples. A maximum average healing efficiency of 44% was measured for 1.2 wt% Grubbs' catalyst concentration and a high interfacial capsule concentration level.

Extrinsic self-healing approach based on microcapsule was also explored by Jones et al. using a single capsule solvent-based healing chemistry.[31] Prepared UF microcapsules containing EPON 862 (diglycidyl ether of bisphenol-F) dissolved in ethyl phenylacetate (EPA) solvent were dispersed on glass fibres using a dip-coat technique. Probably due to the larger capsule size and the application of an external force to close the crack, nearly full recovery of interfacial strength (86% maximum healing efficiency) was reached.

Provided the interfacial crack faces are in some form of local contact, healing of matrix/fibre interface can also be achieved with intrinsic self-healing methodologies. Peterson et al.,[32] exploiting Diels–Alder reaction, demonstrated how maleimide-functionalized glass fibres and furan-functionalized polymer networks create a thermoreversible matrix/reinforcement interface (Fig. 4). Micro-droplet single fibre pull-out tests revealed an overall average of 41% recovery of interfacial strength upon healing for. The researchers reported multiple healing events up to 5 times where the healing efficiency dropped to about 10%. The drop in healing efficiency is not related to the loss of healing as such but reflects the detrimental effects of multiple successive local fracture events upon the crack opening distance and the decrease in topological registry across the separated interfaces.

2.3. The polymer matrix

In intrinsic healing concepts the healing process depends on the ability of the polymer matrix to locally acquire temporary mobility upon the application of an external or internal trigger such as temperature, pH or light induction and generally intrinsic healing systems are not truly autonomous.[33-35] However, they have the advantage that no external healing entities are required and multiple healing events can be obtained, albeit at the expense of their mechanical properties The general concept of intrinsic healing is depicted in Fig. 5. Three distinct polymer concepts can be employed: i) reversible covalent bonds;[36] ii) supramolecular interactions;[37] and iii) shape memory polymers.[38] Additionally, blends of conventional matrix polymers and polymers with intrinsic healing potential have been proposed to create healing capabilities while improving the mechanical properties of matrix.[39] These four approaches/concepts will now be discussed in more detail.

2.3.1. Reversible covalent bonds

Probably, the most known and widely used reversible covalent bonds in intrinsic healing are those based on Diels-Alder/retro-Diels-Alder interactions (DA/rDA). This reversible bond was first reported by Craven et al. in 1969,[40] but it was not until the beginning of the 21st century that it was used for reversible polymer matrices.[41] In this chemical reaction several di-enes and di-enophiles can be used with the furan-maleimide interaction (healing temperature range of 100-150 °C) being the one known best.[42, 43]

Polymers based on the DA-rDA reaction have already been employed in fibre reinforced composites,[44-47] as well as in self-healing hybrid nano-composites.[48]

Disulphide bonds being part of a conventional epoxy based thermoset represent an interesting reversible covalent chemistry that has nevertheless not yet been implemented into FRPs.[49, 50] Research on functional composites for thermal conduction purposes based on such polymer matrices has shown promising results even for mild healing temperatures (65-75 °C).[51, 52]

2.3.2 Supramolecular Interactions

Supramolecular interactions are by definition reversible and are ideal mechanisms to create self-healing polymer matrices.[37] Currently, hydrogen bonding is one of the most established supramolecular self-healing mechanism. A very successful approach was introduced by Sijbesma et al.[53] In their work, a strong reversible polymer system based on quadruple hydrogen bonding was developed and the concept proven. The work was successfully further developed at ESPCI in collaboration with Arkema leading to the very first commercially available intrinsic self-healing elastomer.[54, 55] Recently new chemistries have been presented using supramolecular reversible bonds as encountered in perfluoropolyethers,[56] polyethyleneimine additives in nitrile rubbers,[57] and via polydimethylsiloxane chains in traditional self-healing rubbers.[58] Due to relatively low mechanical strength, these chemistries have not yet been introduced in fibre composites although on-going research suggests that new applications will appear in the coming years.

Another type of non-covalent reversible interactions is found in ionomers. These are polymer systems containing acid groups in the form of ionic metal salts bonded to the polymer backbone creating electrostatic interactions. As a result, ionic clusters are formed within the polymer structure, which have a positive effect on the mechanical and physical properties of the material.[59] Most of the work done on self-healing ionomers has focused on autonomous healing after high speed ballistic impact,[60, 61] but stimulated self-healing after more quasi static damage production has also been demonstrated.[62, 65]

Finally, new intrinsic healing polymer systems not yet explored in FRPs may emerge in future. For example, systems based on π-π interactions were reported by Burattini et al. and there are interesting developments in the field of cellulose based nanocrystal reinforced self-healing nanocomposites.[66-68] Furthermore, a metal ligand system, which heals upon exposure to higher light fluxes, was recently reported by Burnworth et al.[69] Undoubtedly even more reversible chemical interaction systems will be developed in future.

2.3.3. Shape Memory Polymers

A third category of matrix healing processes involves Shape Memory Polymers (SMPs). These polymers have the ability to plastically deform yet to return to their original shape upon exposure to external stimuli – a phenomenon called the Shape Memory Effect (SME). In order to induce the SME, the SMP system requires both a stable polymer network and the possibility of a Reversible Switching Transition (RST). The stable polymer network determines the original shape, whereas the RST, commonly based on crystallization or vitrification, is responsible for the shape recovery.[38, 70]

Although SMPs show some potential as self-healing matrices, they have relatively low strength limiting their use in structural applications. As a possible solution, fibre reinforced SMP composites are developed improving the mechanical properties of SMPs.[71, 72] However, the additional rigidity that is supplied by the fibres lowers the SME and thereby the healing properties of the polymer matrix. Additionally, these polymer systems often need a pre-training step that determines the fixed shape, which will be difficult to realise in technical composites.[73]

As mentioned above, SMPs can be used for healing purposes although they have the intrinsic limitation that they only close the crack, yet do not restore mechanical strength across the final interface.[93] As an alternative, Li et al. proposed a close-then-heal (CTH) scheme using a SMP matrix filled with thermoplastic particles.[94] Under this concept, the material will first close the crack due to the SME and then seal due to the embedded thermoplastic particles upon heating. Li et al. reported a couple of studies on the validation and experimental testing of this concept.[95, 96] The shape memory assisted self-healing (SMASH) technique, introduced by Rodriguez et al., shows a similar approach by blending a SMP matrix with self-healing linear polymer chains.[97, 98]

2.3.4 Polymer Blends

Despite the interesting potential of the polymers based on reversible chemistries, their application in fibre-reinforced composites may be restricted as a result of their intrinsically low mechanical properties. In order to find a better balance between base mechanical properties and some healing capability, polymer blends have been proposed. Zako and Takano reported on the inclusion of melt processable thermosetting epoxy particles in a stable and rigid polymer matrix. In case of fracture, the additives melt when heated to about 100 °C and react at the damaged site, thereby healing the material.[74] Hayes et al. developed a single phase blend by dissolving a thermoplastic linear molecules, rather than thermoplastic particles in a conventional thermoset matrix. In this case long range polymer diffusion across the interfaces of the crack may occur while the surrounding thermoset matrix remains unchanged.[75, 76] Both approaches require an external application of heat to induce healing. In an attempt to solve this issue, Swait et al. have recently proposed the use of self-sensing carbon fibre reinforced matrix systems capable of detecting barely visible impact damage by measuring changes in resistance. A combination of this matrix with a self-healing single phase blend and a self-heating mechanism could eventually result in a truly smart composite material.[77] Other single phase self-healing epoxy matrices based on mechanical interlocking and interpenetrating networks have been demonstrated successfully yet at the proof of concept level and for unreinforced bulk polymer samples.[78, 79] A fibre reinforced composite system containing a reactive thermoplastic additive (EMAA) that heals upon heating was developed by Meure et al.[80, 84] A recent study investigated the healing of these composites upon spplication of ultrasound.[85] The use of polymerization-induced phase separation to produce a poly(e-caprolactone)/epoxy blend that is capable of matrix healing by differential expansive bleeding has been proposed by Luo et al.[86] The mechanical properties of these matrices were enhanced using carbon nanofibres without loss of the self-healing properties.[87]

Supramolecular self-healing systems are also incorporated in blends in order to enhance their mechanical properties. For example, the blending of hydrogen-bonding brush polymers with a thermoplastic elastomer resulted in a polymer matrix that can heal without the requirement of external stimuli.[88] In other studies, the mechanical properties of ionomers were tuned by blending them with epoxidized natural rubbers or poly(vinyl alcohol-co-ethylene).[89-91] Additionally, Grande et al. investigated the self-healing behaviour of a pure ionomer and blended systems under different local impact conditions.[92]

3. Damage modes and reported healing efficiencies

3.1 Damage due to static (over-) loading

Quasi-static fracture tests are widely used to assess performances of self-healing FRPs. The monotonic low strain rate loading condition is generally not so relevant for real life applications, yet this mode of testing is highly controlled both for the generation of damage and a relatively straightforward and (semi-) quantitative evaluation of the restoration of properties upon healing. The most common adopted techniques are double-cantilever beam (DCB), its tapered (TDCB) or width-tapered (WTDCB) variants and end-notched flexure (ENF) tests. Other procedures, also used to evaluate global mechanical properties, include three-point and four-point bending experiments.
Kessler et al. [99, 100] studied the self-healing behaviour of both glass and carbon FRPs loaded with different DCPD/Grubbs' catalyst microcapsule systems. After mode I fracture experiments, a maximum average interlaminar fracture toughness recovery of 66% was reported for specimens healed at 80 °C for 48 h. Comparable results were obtained by Yin et al.[101] using a micro-encapsulated epoxy/latent curing agent system; after a healing cycle at 130 °C for 1 h and 24 h at room temperature, 51% fracture toughness recovery was measured.
Different systems based on a micro vascular approach (i.e. using one or two interconnected networks of hollow fibres containing one or two healing agents

respectively) were developed by Trask et al.[11]; healing efficiency of previously damaged FRPs hosting glass hollow fibres filled with a two-part epoxy healing agent were measured under flexural loads. After heating for 2 h at 100 °C were employed a strength recovery of about 80% for glass and carbon reinforced composites was reported. Following the intrinsic self-healing approach Hayes et al. employed poly(bisphenol-A-co-epichlorohydrin) as solid healing agent in a commercial epoxy resin demonstrating the ability of such system to recover up to the 70% of its fracture strength after thermal healing cycle (140 °C).[75] Other studies, revealed the potential of polyethylene-co-ethacrylic acid (EMAA) as a thermally activated thermoplastic healing agent.[84, 102] Produced carbon FRPs laminates tested under different static experiments are able to completely restore both mode I and mode II fracture toughness after a thermal cycle of 30 min at 150 °C. Melting and infusion of EMAA along the crack plane and strong EMAA-epoxy bonding are responsible for crack bridging detected during after healing fracture test (Fig. 6).

While the results of experiments aimed to demonstrate healing after quasi static loading are certainly interesting and encouraging, it should be pointed out that the test configurations are such that the crack opening distance is generally kept at a low value by careful reposition of the fracture surfaces or even the application of a minimal crack closing force In real life applications this may not always be the case or be possible.

3.2 Damage due to fatigue loading

Fatigue damage is of great relevance in FRPs and the development of self-healing systems able to operate during cyclic loading is still a relatively new challenge for researchers working in the self-healing field. Promising studies on the fatigue behaviour of microcapsule loaded epoxy matrix have been presented in the literature. Brown et al. demonstrated how a self-healing system based on a microencapsulated DCPD healing agent and Grubbs' catalyst dispersed into a commercial epoxy resin can arrest and retard fatigue crack growing.[103] As reported by the authors, fatigue life-extension, investigated using a Tapered Double Cantilever geometry, stems from the viscous flow of the healing agent in the crack plane and from its subsequent polymerization providing a short-term adhesive effect and a long term crack closure effect. It is important to underline that better results in terms of healing efficiency and life-extension were obtained in fatigue experiments with a rest period of 10 h in order to allow a complete cure of the healing agent (Fig. 7). Jones et al., using a wax-protected Grubbs' catalyst, extended the fatigue life of such system even further.[104]

Relevant results were also obtained by Yuan et al. [105]; in their research they developed an epoxy/mercaptan/tertiary amine microencapsulated healing system proving its fatigue crack retardation, arrest and healing capabilities.

Preliminary results on FRPs with intrinsic self-healing capability were presented by Pingkarawat et al. [102] In their study, a carbon fibre/epoxy laminate containing particles or fibres of an EMAA thermoplastic polymer were tested under fatigue interlaminar loading. Delaminated specimens, upon a thermal cycle at 150 °C for 30 min, partially restored their fatigue resistance demonstrating that the EMAA is an effective agent for the healing of fatigue cracks. However, researchers detected a lower healing efficiency in samples tested under fatigue loading then in those tested under static conditions.

3.3. Damage due to impact loading

Damages generated by impact events range from Barely Visible Impact Damage (BVID) to large-scale breakage like target penetration depending on projectile velocity and energy. Both scenarios are taken in account by researchers working in the self-healing field and different approaches have been developed to heal such kind of damages.

BVID, usually caused by quasi-static point loading or by low velocity impacts, are characterised by intra-ply microcracking and inter-ply delaminations; a common test adopted by researchers to evaluate the various levels of impact damage and the recovery of post impact strength in a FRP laminate with self-healing ability is the Compression After Impact (CAI) protocol.

Microcapsule based self-healing systems were adopted by Yin et al. [106] and Patel et al. [107] to produce woven glass fabric composites using bisphenol-A epoxy healing agent with a latent hardener dispersed in the matrix and DCDP/Grubbs' catalyst approach, respectively. CAI experiments revealed the healing capability of such systems. However the recovery of compression strength becomes marginal for the higher impact loads, probably due to the small quantity of healing agent available given the size of the crack volume created. Micro-vascularised fibre reinforced polymer composite systems, requiring a pressure source to supply the healing agents, can potentially provide enough healing agent to fill cracks generated during high-energy low velocity impacts. Williams et al. and Norris et al. designed FRPs employing different methodologies to create a vascular system in the composite. In the first study, a resin filled hollow glass fibre system was distributed within the laminate,[108] in the second one, open channels were directly generated inside the composite during production by means of PTFE coated steel wire vascular pre-forms removed after the post-cure cycle.[15] Both studied reported a significant compression strength recovery (>90%) after impact.

High velocity impact damages typically appear in the form of perforation; these damages cannot be healed with the previously presented techniques. However, a particular class of thermoplastic materials, copolymers and ionomers based on EMAA, have shown self-healing behaviour after high velocity impacts over wide range of impact velocities.[60-65, 109, 110] Recently, it was demonstrated that the puncture healing capability of such polymeric systems is well maintained even when employed in a hybrid composite (Fig. 8).[111] The results clearly suggest that there is real potential for using self-healing thermoplastic matrix in structural composites to heal high velocity impact damage.

4. Conclusions

The rapid developments in various healing strategies over the last two decades have created the notion that incorporation of self-healing technology in fibre reinforced composite materials will seriously contribute to improve the reliability of these materials for structural applications by making them more damage resistant. Despite encouraging results on a lab scale and using well controlled samples and modest damage levels, large steps still have to be taken to bring this new technology to the right “Technology Readiness Level” where self-healable fibre reinforced products can be manufactured in an economically justifiable way on a routine basis. For the foreseeable future it may be sensible to focus on non-critical composite applications in which the mechanical properties of the starting material can be lower than the optimal properties achievable in state-of-the-art composites. We expect that in the long run solutions based on intrinsic self-healing polymer matrix concepts will dominate the market, as they leave the optimised macroscopic fibre and ply architecture required for high level mechanical properties unaffected.

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Figures

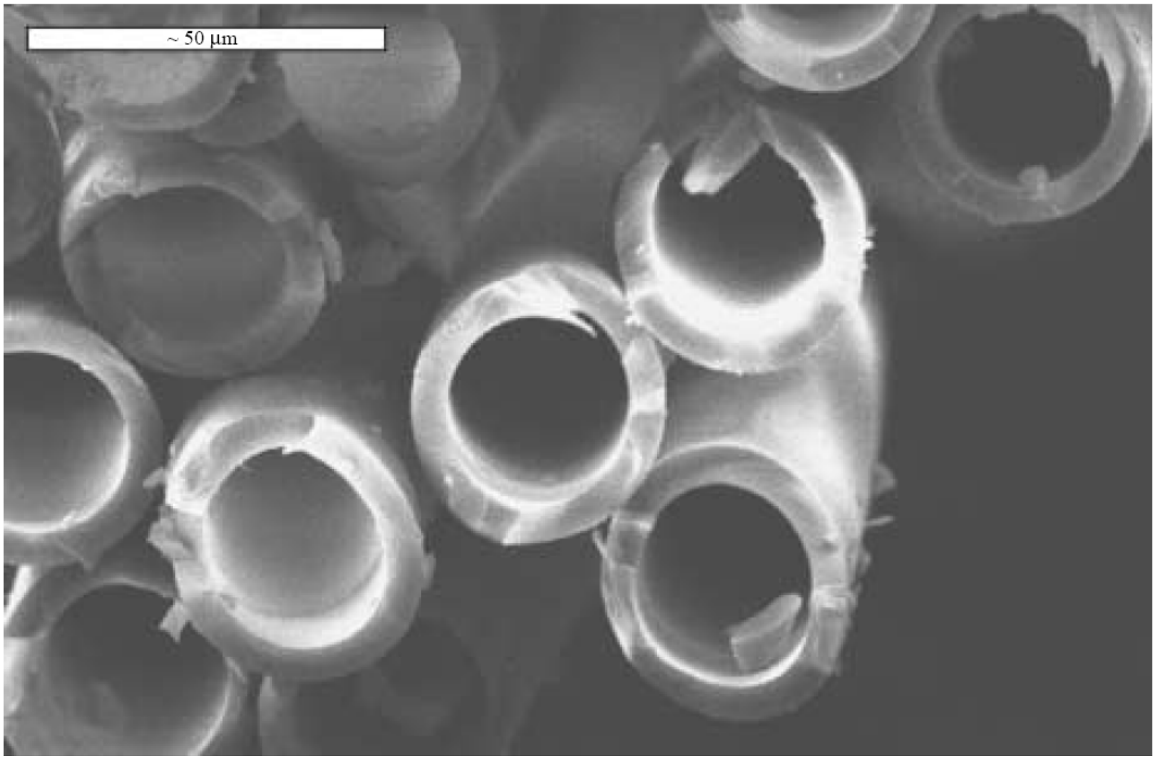
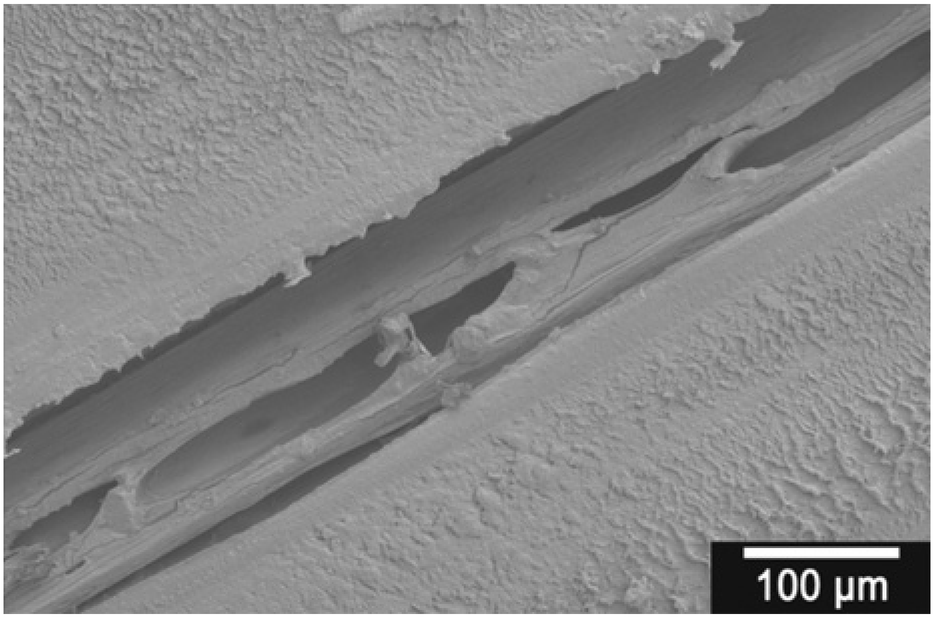
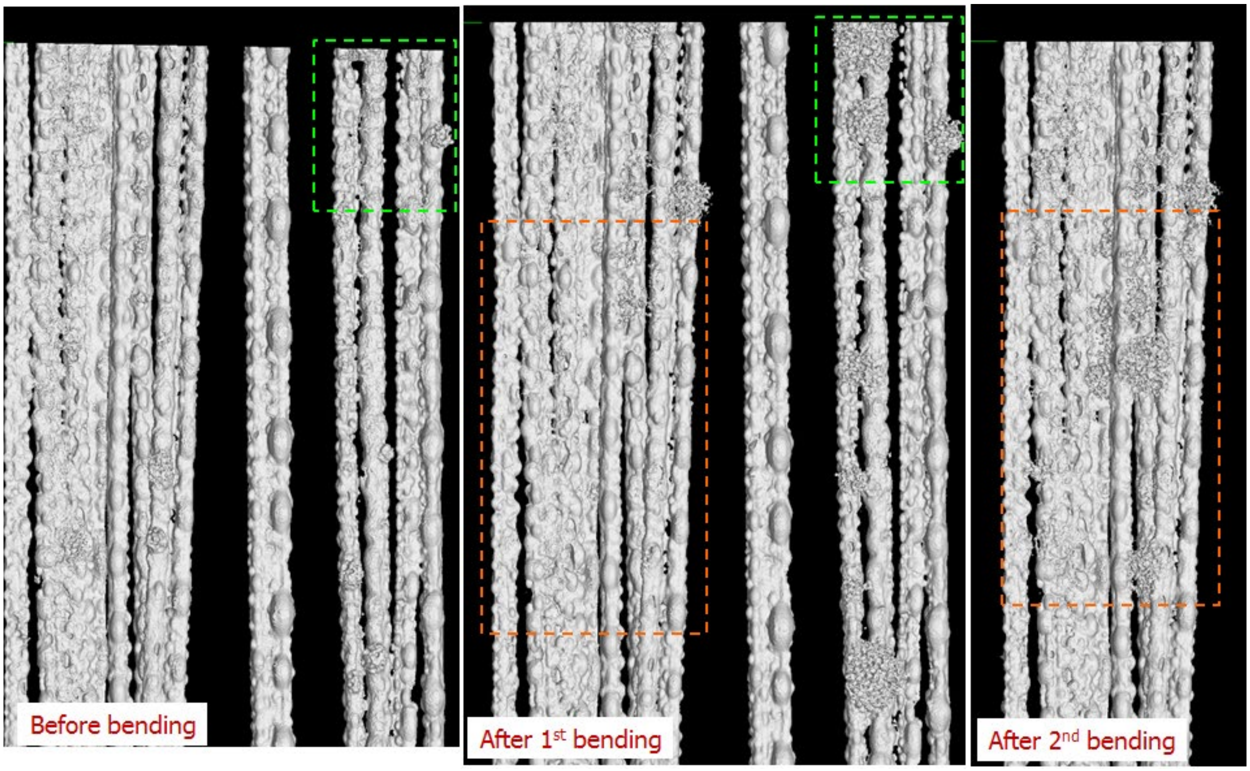


Fig. 1: SEM micrograph of hollow glass fibre to be used in a Carbon fibre epoxy composite. [11]



a)



b)

Fig. 2: a) SEM micrograph of a cross-section of a fibre containing multiple vacuoles and b) the tomographic image of a set of PMMA embedded multi-vacuole fibres in the unloaded as-produced state, after a first sample bending and after a second bending. The sites where release of the healing agent took place have a cauliflower like appearance. The progressive release is clearly visibly when comparing the images.

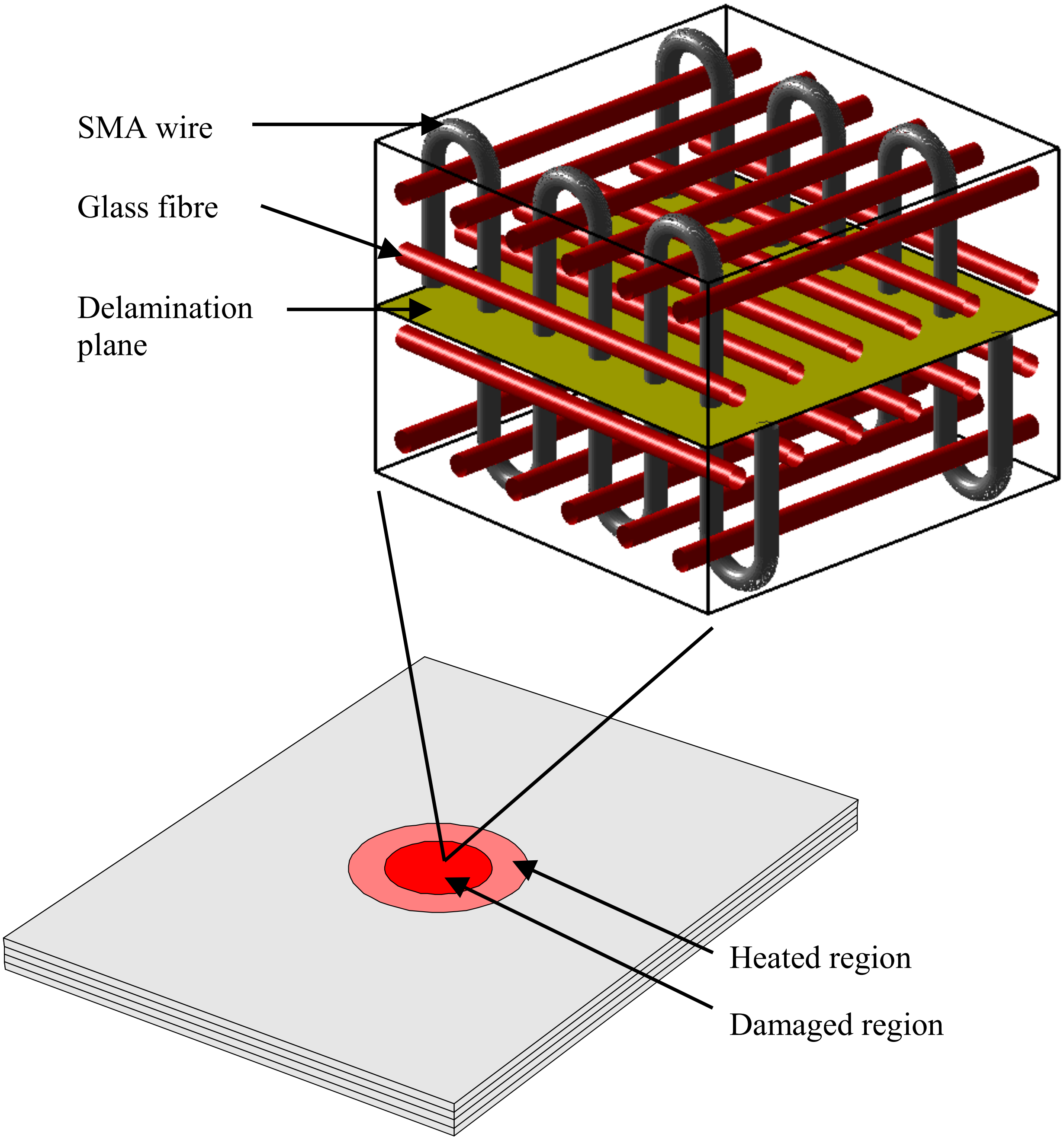


Fig. 3: Schematic diagram of a self-healing composite using woven SMA fibres to reduce the crack opening distance for glass fibre reinforced polymer composites.

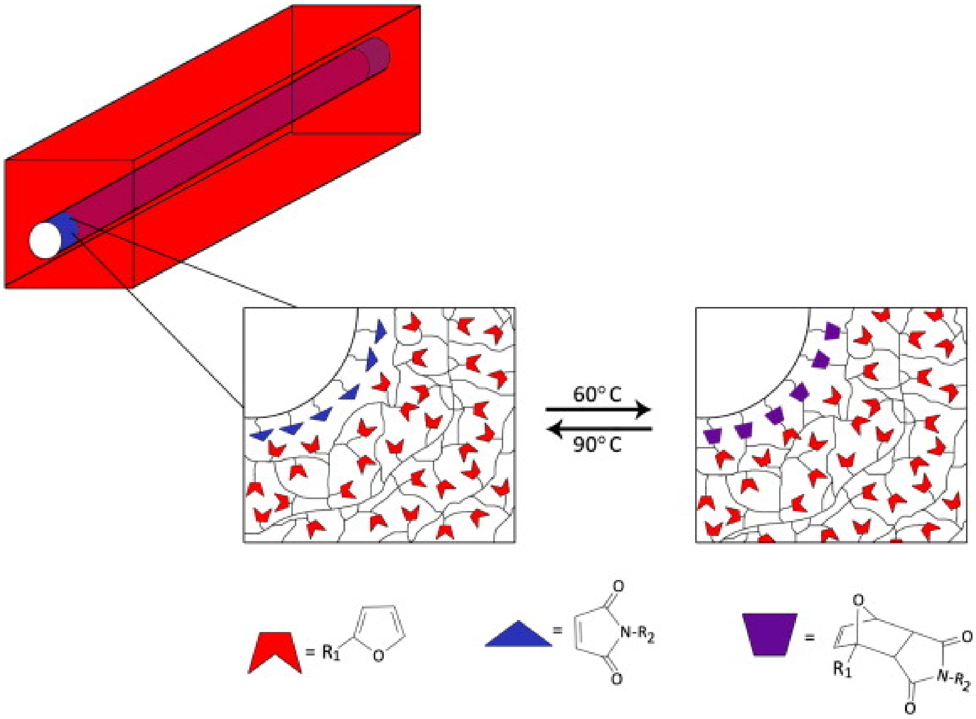


Fig. 4: Intrinsic interfacial healing concept based on Diels–Alder reaction. Failed bonds between furans and maleimides are restored after a thermal cycle. Reproduced from [32] with permission from Elsevier.

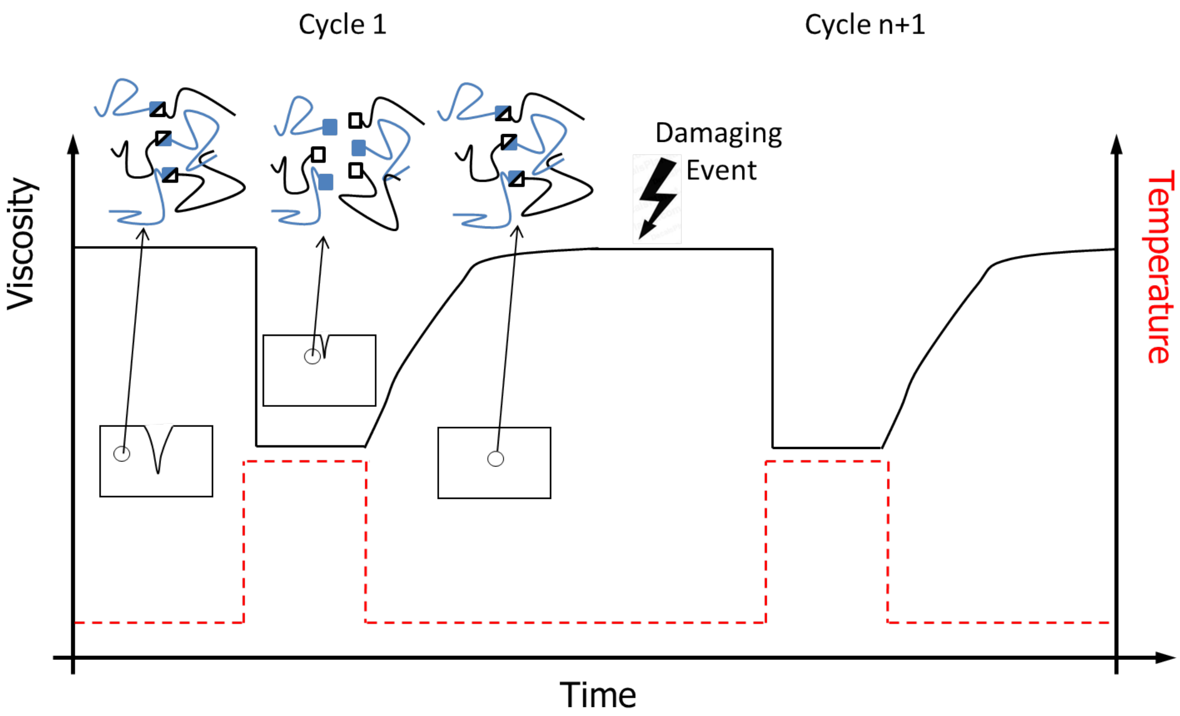


Fig. 5: General concept of matrix healing using intrinsic healing concepts. Figure shows a sudden drop in viscosity upon heating linked to local temporary network mobility necessary for flow and damage repair. Upon cooling the local properties (e.g. viscosity) are restored to initial values so the material can be further used. Figure also shows the multiple healing events possible with intrinsic healing concepts.

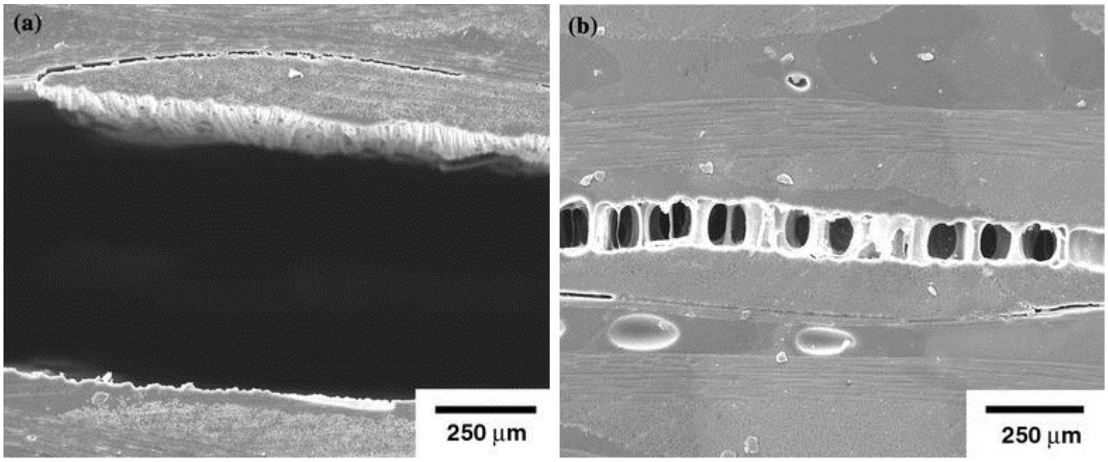


Fig. 6: Crack path during static mode I fracture test for virgin (a) and healed (b) sample (Reproduced from Reference [102] with permission from Springer).

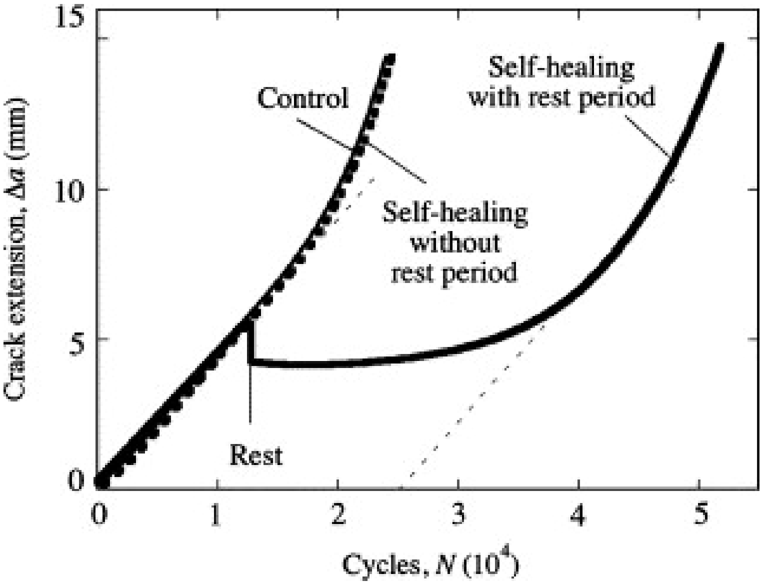
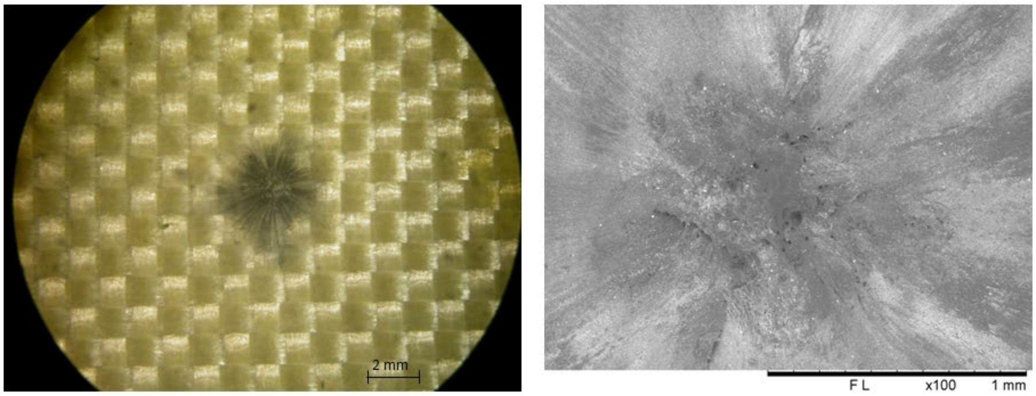


Fig. 7: Evolution of crack length under fatigue loading with and without rest period (reproduced from Reference [103] with permission from Elsevier).



(a) (b)

Fig. 8: Optical (a) and SEM (b) micrographs of damaged areas of EMAA/aramid fabric multilayer composite impacted at 700 m/s with a 5.65 pointed projectile.