

# BIOMIMETIC PLANAR AND BRANCHED SELF-HEALING NETWORKS IN COMPOSITE LAMINATES

Richard S. Trask & Ian P. Bond [Richard Trask]: R.S.Trask@Bristol.ac.uk University of Bristol, Department of Aerospace Engineering, Queens Building, University Walk, Bristol, BS8 1TR, UK.

Keywords: self-healing, network, CFRP, impact, damage

## Abstract

The healing potential and repair strategies of living organisms is increasingly of interest to composite designers seeking lower mass structures with increased service life who wish to progress from a conventional damage tolerance philosophy. Naturally occurring 'materials' have evolved into highly sophisticated, integrated, hierarchical structures that commonly exhibit multifunctional behaviour (e.g. damage tolerance and self-healing). Inspiration and mimicry of these microstructures and micromechanisms offers considerable potential in the design and improvement of material performance. Most self-healing work to-date has been bioinspired and not biomimetic, although this is now changing.

This paper will present the concept of biomimetic planar and branched self-healing networks formed in carbon fibre reinforced polymer composite laminates. The actual location and housing of the healing network is instrumental to the success of this approach. The paper will also discuss the role of damage compartmentalization with self-healing attributes, the most likely short-term approach for the introduction of a self-healing concept in the safety-critical aerospace composites industry.

# **1** Introduction

The need for continual improvement in material performance is a common feature of many modern engineering endeavours. Engineering structures now encompass a wide range of technologies for materials development, analysis, design, testing, production and maintenance. Advances in these technologies have been principally responsible for major performance improvements in many engineering structures and continue to be key in determining the reliability, performance and cost effectiveness of such structures.

Lightweight, high strength, high stiffness fibre reinforced polymer composite materials are leading contenders as component materials to improve the efficiency and sustainability of many forms of transport. In addition, they offer immense scope for incorporating multifunctionality due to their hierarchical internal architecture. One limiting factor in their wider exploitation is relatively poor performance under impact loading, a critical aspect of any vehicle design, leading to a significant reduction in strength, stiffness and stability [1, 2, 3]. Their inability to plastically deform results in energy absorption via the creation of defects and damage. This damage often manifests itself internally within the material as matrix cracks and delaminations, and can thus be difficult to detect visually. Thus, a fibre reinforced polymer composite material could directly benefit from incorporating an added functionality such as self-healing.

The healing potential of living organisms and the repair strategies in natural materials is increasingly of interest to designers seeking lower mass structures with increased service life, who wish more from the conventional to progress conservative, damage tolerance philosophy. The conceptual inspiration from nature for self-healing is not new, and many other engineering approaches could be considered to have been inspired by observing natural systems. These bioinspired approaches do not typically include mimicry of the biological processes involved because in many cases they are clearly too complex. The field of selfhealing in polymer composites has seen exciting developments in recent years, for example [4, 5, 6, 7], use the inspiration of biological self-healing applied with broadly traditional engineering approaches.

## 2 Self-Healing Strategies in Polymer Composite Structures

## 2.1 Bioinspired self-healing approaches

Nature's ability to heal has inspired new ideas and new mechanisms in the engineering community. Chemists and engineers have proposed different healing concepts that offer the ability to restore the mechanical performance of polymer-based materials. A full review is beyond the scope of this paper and the reader is directed towards reference [7]. In polymer-based materials, three different selfhealing methods are under investigation, chemical fusion of the failed surfaces through the application of heat (see [8, 9]), the application of nanoparticles dispersed in polymer films to deposit at a damage site in a similar fashion to blood clotting (see [10,11]) and finally approaches based upon a biological 'bleeding' approach to repair, i.e. microcapsules [4, 5] and hollow fibres [6, 12].

The three autonomous healing approaches outlined above have been randomly distributed throughout the structure (i.e. solid-state polymers of microcapsules) or spaced evenly through the composite laminate structure. In nature the network is tailored for a specific function with the healing medium often being multifunctional. The first reported instance of tailoring the location of selfhealing functionality in engineering to match the damage threat is by Trask et al [7, 13, 14]. In this work the key failure interfaces were identified and then the hollow fibre self-healing network was designed for a specific composite component and area of application, in this case a space environment. Verberg et al [15] have computationally studied a biomimetic "leukocvte" consisting of microencapsulated nanoparticles that are released by diffusion while the microcapsule is driven along microvascular channels. The surface chemistry of the capsule and nanoparticle could be selected to enable the microcapsule to "roll" along the inner wall of the microchannel, but damage to the surface in its path would inhibit that movement until the diffusing nanoparticles aggregate at, and ideally repair, the defect thus allowing movement to recommence.

It is the possibility of self-healing a damaged structure that is increasingly of interest to composite designers seeking lower mass structures with increased service life, who wish to progress from the more conventional conservative, damage tolerance philosophy. A more recent advance is the detailed study of natural healing to allow true biomimetic self-healing. The tailored placement of healing components and the adoption of biomimetic vascular networks for self-healing are very attractive solutions to the composite engineer where the baseline materials are very susceptible to low velocity impact damage. The challenge for the future is the evolution of 'engineering self-healing' towards a biomimetic solution. To date, this work is still in its infancy but mimicry of blood clotting, tissue bruising and tailoring healing networks to address damage formation are all being considered.

# **3** Biomimetic Self-Healing

# 3.1 Vascular Networks

Biological organisms have a highly developed multifunctional vascular network to distribute fuel, remove waste, control internal temperature and effect self-healing, among many other roles. These attributes are achieved via fluid distribution and collection systems supplying all body tissues from a point reservoir via a branching, hierarchical network. This branching configuration allows easy access for the fluid to all tissues. Studies show that the branching and size of these vessels have evolved to minimise the power required to distribute and maintain the supporting fluid within many other constraints [16]. The system is also reconfigurable in response to environment by adjusting the radius of individual vessels, by vasoconstriction and dilation in mature tissue, or by growth in embryonic blood vessels [17].

The future of the self-healing concept for composite materials relies on the development of a continuous healing network embedded within a composite laminate that delivers healing agent from a reservoir to regions of damage. Existing liquidbased self-healing approaches such as microcapsules and hollow fibres have a limited volume of healing agent available. This volume cannot be replenished or renewed during the life of the structure. Biological vascular networks have a similar need to widely distribute significant volumes of liquid around an organism and like a vascular composite, perform this role without disrupting the primary structural performance. A vascular composite material would permit the repair of all types of composite failure modes at any point in a structure. It must restore the matrix material properties and restore the structural efficiency of fractured fibres. Both a passive (open-loop) vascular network and a

fully circulating configuration could be considered for self-healing. The former offers the advantage of simplicity but practical difficulties in ensuring complete removal of entrained gases from the system. New and novel approaches must be found to ensure that the healing agent can be replenished and renewed during the life of the structure; a circulating system provides this possibility. Circulating flow in a biological system also plays a role in limiting blood clotting to the area of damage; this offers an avenue for investigating novel approaches for a healing agent. A circulatory self-healing system integrated within a composite material could also perform additional functions such as thermal control. like those in a biological network. Redundancy in biological networks is usually approached via localised duplicated supply routes, whereas wholly independent duplicate systems are the conventional engineering approach. The former could offer a simpler system, but for high performance, safety critical engineering applications duplicate systems would normally be preferred. At a detailed level, in both engineering and biological vascular networks it is necessary to minimise the power required to deliver the fluid; biological principles such as Murray's law [16] offer a biomimetic route to achieve this by selection of appropriate vessel diameters for each section of the network.

## 3.1 Flow Architecture

Bejan *et al* [18] has undertaken a fundamental study to vascularize a self-healing composite material such that the healing fluid reaches all the crack sites that may occur randomly through the material. The problem is assessed using Constructal Theory, which regards the generation of flow configuration as a natural (physics) phenomenon [18]. When a structure is damaged and a crack forms fluid flows from the network into the crack. This is an area-to-point flow, where the crack site is the point and the area is the structure.

The function of flow architecture is to provide flow access between a volume of structure (in the case of this work a structural composite material) loaded with healing liquid and one or more sites where cracks may develop. The damage formation in a composite material occurs at number of length scales and this will significantly influence the flow architecture. The initial damage mechanism active in an advanced composite structure is matrix cracking. These tend to form in the polymer matrix transverse to the loading direction and tend to be on the micron length scale and usually occur between the structural fibres. As the load increases the length and frequency of the matrix cracks increases until the crack starts to debond individual fibres from the matrix. These cracks (which are now referred to as delaminations and can occur over the millimetre length scale) start to run along the axis of the structural fibres. Ultimately, the delaminations increase to such a number that individual reinforcing fibres are no longer supported by the surrounding matrix and then individual fibre fracture occurs. After a threshold level of localised failures is reached, total catastrophic failure of the composite will ensue. Clearly the design of the flow architecture will depend upon which of these failure modes needs to be addressed by healing. Whilst fibre fracture represents irrecoverable failure in the structure, in composite engineering it is the delaminations which are considered the most critical since they can initiate at very low energy impact events and grow undetected under static and fatigue loading. Unlike other engineering materials, growth of delamination damage occurs in preferential directions depending upon the fibre mismatch angle and hence at predictable locations within the fibre stacking sequence. Butler et al [19] has reported experimental methods for the coalescence of impact induced delamination damage to a single critical failure path under compressive fatigue loading. In essence, polymeric composite materials are not damage resistant (due to their brittle nature) but are damage tolerant to the growth and propagation of critical delaminations.

many examples of Nature has flow architecture, the tree-shaped (dendritic) flow structure being the most apparent offering maximum access from the area to a point (see Figure 1(a)). In engineering we tend to think and operate in networks and grids, obvious examples being road design for city traffic (see Figure 1(b) for a map of New York, USA which confirms to the general principal of grids and networks). The objective of a network design is to optimise the geometrical constants (i.e. shape and channel size) such that the permeability of the network/grid is maximised. The network shape could be formed by a square, triangular or hexagonal loop. Conversely, a second way to morph the flow configuration is to follow nature's example and scale the network's diameter according to Murray's law, i.e. where the vessels sub-divide, the sum of the cubes of the daughter vessel radii  $(r_1 \text{ and } r_2)$  should equal the cube of the parent vessel radius  $r_0$  for minimum power input. This approach offers the minimum power requirement for the system but if the lowest resistance is required then the largest vessel diameter should be chosen for all points.



Fig. 1. Flow architecture (a) Dendritic; (b) Grid/ road network – New York, USA http://maps.google.com/maps

The choice between dendritic flow and grid flow architecture for composite materials is an interesting discussion point. According to Bejan et al [18] the choice between the dendritic and grid system is dependent upon whether the position of the crack is known. He argues that if the crack position is not known, and that several cracks may form at different sites simultaneously, then a grid structure and not dendritic flow architecture is required. However, as indicated before the critical failure interfaces for damage propagation are known in the design phase. Furthermore, since a number of delaminations and transverse matrix cracks migrate under load to the preferential failure path it is possible to utilise both a dendritic and grid network flow architecture (located within the failure path) to intercept a propagating crack and initiate the healing process. This is clearly not possible in all engineering materials but in the context of developing a self-healing ability in composite materials it is their lamina construction and fibre orientation that permits different flow architectures to be considered.

#### **3.2 Damage Tolerant Composite Structures**

At present the composite materials community has developed highly damage tolerant structures via the selection of materials that are capable of absorbing extensive energy without fracture. This could be obtained through the selection of a material with a fracture toughness threshold above the impact damage threshold, the selection of a material that fails in a controlled but highly energy demanding manner, or the selection of a design philosophy that generates a crashworthiness approach by damage compartmentalisation. By comparison, nature (especially plants) combine the role of damage tolerance with self-healing. For example, palm (*Chamaerops humilis*) petiole has a structure which exhibits a uniform distribution of vascular bundles and parenchyma cells (Fig. 2). The regions of differing density offer a unique method of obtaining both stiffness and damage absorption.



Fig. 2. (a) Micrograph of Palm (Chamaerops humilis) petiole showing uniform distribution of vascular bundles and parenchyma cells; (b) vascular bundles at higher magnification [20]

In the interim it is this type of flow architecture, coupled with a damage tolerance philosophy, which will be more acceptable to the engineering community.





Bio-inspired nano-materials with open hole structures (see Fig. 3) tailored to protect the surrounding structural composite and introduced at key failure interfaces offer an interesting alternative to the dendritic and grid flow architectures. These porous solids, which are typically defined as having pore sizes greater than 100 nm [21], offer a viable route towards the manufacture of a damage tolerant self-healing layer that could be readily included within existing aerospace composite processing routes. Clearly, there are concerns about the permeability of the network's architecture and whether it is sufficient to ensure efficient crack filling. Physical concerns about how the network can be connected to the resin delivery system and whether the available healing volume is sufficient to heal delamination damage also have to be addressed.

A number of flow architectures for inclusion within a composite laminate and hybrid composite laminates are now under evaluation at the University of Bristol (see Fig. 4 and Fig. 5).



(a)

Second phase sacrificial channel-forming material introduced within the composite laminate



After post processing of the laminate an internal network







(c)

Fig. 4. Branched networks (a) Flow architecture inspiration; (b) Flow architecture manufacturing route; (c) CFRP composite laminates with flow architecture (branch diameter of 0.25mm)



(a)



(b)



(c)

Fig. 5. Natural cellular structures; (b) Gold template sea urchin skeletal plates; (c) CFRP composite interleaved laminates offering the potential for direction flow architecture

The network of choice must satisfy a number of key requirements, namely;

- alignment with surrounding fibre orientations;
- no initiation of any new damage modes or lowering of damage threshold for the primary fracture path;
- network architecture must have permeability to ensure efficient crack-filling; and,
- network must be tailored to the damage sensitivity of the surrounding structure, i.e. the network can expand or contract to match the damage threat, without influencing the mechanical or physical properties of the system.

In essence, the healing network would have to work alongside or within the current damage tolerance philosophy.

### 4 Concluding remarks

Advanced aerospace composite laminates are manufactured by stacking individual lamina of preferred orientation. The lamina configuration, the

brittle nature of the resin system and the complex fracture paths result in a damage tolerant material rather than a damage resistant material. It is precisely the lamina configuration and damage tolerant nature of the material that permits the introduction of both dendritic and grid based flow architectures as a means of imparting a method of repeated self-healing. Whether the flow architecture is embedded within the composite lamina or introduced as a new lamina within the stack sequence is still to be evaluated. The work at Bristol is still in its early stages and further work is ongoing to characterise the flow architecture and network location upon the structural performance (toughness, stiffness, strength and damage tolerance) of the laminate before networks with dendritic or grid structures will be acceptable as a viable method for the self-repair of composite structures.

#### **5** Acknowledgements

The authors would like to acknowledge Dr Julie Etches for constructive advice offered in the preparation of this paper and the UK Engineering and Physical Sciences Research Council for funding this work under Grant No. GR/T17984

#### **6** References

- Dorey G 1987 in Proc 6<sup>th</sup> Int. Conf. Comp Mat comb 2<sup>nd</sup> European Conf Comp Mat, London, 3.1-3.26
- [2] Richardson M O W and Wisheart M J 1996 Composite Part A 27A 1123-1131
- [3] Abrate S 1997 Applied Mechanics Reviews 50 69-82
- [4] White S R, Sottos N R, Geubelle P H, Moore J S, Kessler M R, Sriram S R, Brown E N and Viswanatham S 2001 Nature 409 (6822) 794
- [5] Brown E N, White S R and Sottos N R 2005 Composites Science and Technology 65 2474-2480
- [6] Pang J W C and Bond I P 2005 Composites Part A 36183-188
- Trask R S, Williams GW and Bond I P 2007 J. Roy. Soc. Interface – Special Issue: Self Healing Materials 4(13) 257-271 (doi: 10.1098/rsif.2006.0189)
- [8] Zako M and Takano N 1999 J Int Mat Sys & Struc 10(10) 836-841
- [9] Hayes S A, Jones F R, Marhiya K, Zhang W 2005 Proc 15<sup>th</sup> ICCM, Durban, South Africa, 27 June-01 July 2005
- [10] Lee J Y, Buxton G A and Balazs A C 2004 J CHEM PHYS 121 (11) 5531-5540
- [11] Gutpa S, Zhang Q, Emrick T, Balazs A C and Russell T P 2006. Nature Materials 5 229-233.

- [12] Pang J W C and Bond I P 2005 Composites Science and Technology 65 1791-1799
- [13] Trask R S and Bond I P 2006 Smart Mat. & Struct. 15 704-710
- [14] Trask R S, Bond I P and Semprimoschnig C O A 2006a ESA Technical Note, Materials Report Number 4476
- [15] Verberg R, Alexeev A, Balazs A C 2006 Fifteenth United States National Congress of Theoretical and Applied Mechanics 25th-31st June 2006, Boulder, Colorado, USA
- [16] Murray, C D 1926 United States of America. 12 207-214
- [17] Taber L A, Ng S, Quesnel A M, Whatman J and Carmen C J 2001 Journal of Biomechanics 34 121-124
- [18] Bejan A, Lorente S & Wang K-M 2006 Journal of Applied Physics 100 033528
- [19] Butler R, Almond D P, Hunt G W, Hu B & Gathercole N 2007 Composites Part A 38(4) 1211-1215
- [20] Gibson L.J, Ashby M.F, Karam G.N., Wegst U. & Shercliff H.R 1995 Proc. R. Soc. Lond. A 450 141-162
- [21] Yue W, Park RJ, Kulak AN & Meldrum FC 2006 Journal of Crystal Growth 294 69–77