

# Elegant Design to Fill Indemnity Using Nano Partical & Self-Healing Polymers

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**Abstract**— this is an attempt to develop an innovative technique in order to recover the paints of any vehicle which has been damaged during accidents or any incident. A special preparation of paints with nanoparticles will be used for varnishing of vehicles. This will help in spreading the paint due to force on the paint which leads to scratching and its removal during any collision.

**Index Terms**— Nanoparticles , Polymers, encapsulation, healing, Dicyclopentadiene.

## I. INTRODUCTION

Although it seems hard to believe nanotechnology can help to develop: intelligent buildings that can repair themselves after an earthquake, aircraft whose structure is regenerated after a meteorite impact or cars whose paint is healed after scratching. The development of self-healing materials is attracting considerable interest in recent years, but ... what are the self-healing materials? In which applications are being used. The nature is replete with examples of materials that can repair themselves. When we suffer an injury, our body reacts to close it sending platelets. Many times, especially if the wound is small, it is not required any external coagulant substance. Something similar happens when trees are cut in the trunk or when a starfish breaks. This ability of nature to self-healing has pay the way for engineers and scientists to start to develop self-healing polymers, that is, polymers with the ability to recover most of the properties they had before breaking. Such recovery would take place without or with minimal outside help. The more interesting applications to incorporate self-healing materials are those in which a loss in the physical, chemical and mechanical properties can result in unaffordable financial or personal damage, such as aeronautics, aerospace, structural, but they are also used in electronic applications to ensure conductivity circuits. 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 the material. One area of interest is the fusion of the failed surfaces. Polymeric materials possessing selective cross-links between polymer chains that can be broken under load and then reformed by heat have been shown to offer healing efficiencies of 57% of the original fracture load. Another example is where a polymeric material hosts a second solid-state polymer phase that migrates to the damage site under the action of heat. Hayes and colleagues [Hayes et al, 2005] have developed a two-phase, solid-state repairable polymer by mixing a thermoplastic healing agent into a thermosetting epoxy matrix to produce a homogeneous matrix which contrasts with the discrete particles of uncured epoxy reported by Zako and Takano. These systems offer the capacity for self-healing, but require damage sensing, some form of higher decision-making via a feedback loop and heating requirements that are likely to be impractical in a real application. nanoparticles dispersed in polymer films to deposit at a damage site in a similar fashion to blood clotting. In this work, the nanoparticles are dispersed in polymer films within a multilayer composite and are studied by integrated computer simulations. The model comprises a brittle layer containing a nanocrack sandwiched between two polymer films with analysis suggesting a self-healing mechanism whereby nano-particles congregate at the nanocrack. The numerical models also predict load transfer from the matrix to the stiff nanoparticles. This mechanism is considered applicable to optical communications, display technologies and biomedical engineering. The authors report that mechanical properties of the composites repaired in this manner could potentially achieve 75%–100% of the undamaged material strength. Later work by Gupta and colleagues, using fluorescent nanoparticles, has shown that legends on the nanoparticles can be selected to help drive nanoparticles into a crack in a microelectronic thin film layer. No restoration of mechanical properties was investigated. The viability of this technology for use in structural composite materials is possibly limited as the target damage is on a very small scale. The third area of interest is based upon a biological 'bleeding' approach to repair, i.e. microcapsules and hollow fibers. Microencapsulation self-healing involves the use of a monomer, dicyclopentadiene (DCPD), stored in urea-formaldehyde microcapsules dispersed within a polymer matrix. When the microcapsules are ruptured by a progressing crack, the monomer is drawn along the fissure where it comes into contact with a dispersed particulate catalyst (Ruthenium based "Grubbs" catalyst), initiating polymerization and thus repair (see figure 1). The release of performance advantage. With in-situ healing, crack arrest and an improved fatigue life of up to 213% of the control specimens was demonstrated in high-cycle fatigue. Self-healing using hollow fibers embedded within an engineering structure, similar to the arteries in a natural system, has been investigated at different length scales in different engineering materials by various authors, for example, in bulk concrete, in bulk polymers and in polymeric composites at a millimeter length scale and at a micrometer length scale.

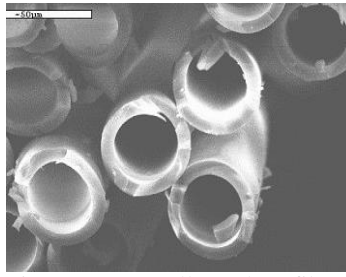


Figure 3: (a) Hollow glass fibers

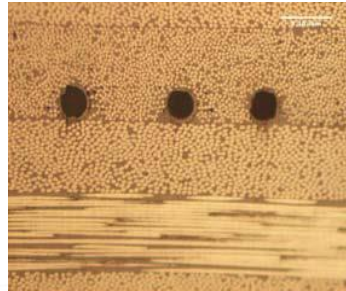


Figure 4: Hollow glass fibers embedded in carbon fiber reinforced composite laminate

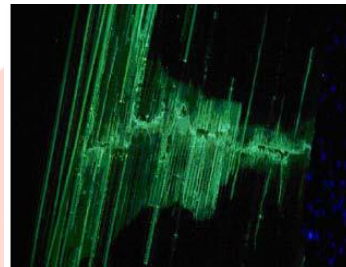


Figure 5: Damage visual enhancement in composite laminate by the bleeding action of a fluorescent dye from hollow glass fibers Multifunctional.

The first reported instance of tailoring the location of self-healing functionality in engineering to match the damage threat is by Trash *et al.* In this work the key failure interfaces were identified and then the hollow fiber self-healing network was designed for a specific composite component and operational environment, in this case a space environment. The need for self-healing in the space environment was found to put significant demands on the repair agent in terms of mechanical properties, process ability and environmental compatibility. The self-healing mechanism was found to restore 100% of the strength when compared to undamaged laminates containing healing plies. Currently there are two important technologies for developing self-healing polymeric materials. The encapsulation of healing agents is mainly used in thermo sets. It consist in the homogeneous distribution of “deposits” of healing agents in the material, so that when the crack reaches one of these deposits, the compound is released and distributed through the fracture by capillarity. Once released, the healing agent contacts the catalyst, thereby producing a chemical reaction that causes polymerization. Thus, the fracture surfaces are joined permanently. The material which acts as a repair can be incorporated into microcapsules in the form of hollow fiberglass (1), which can be broken by action of the crack itself or by external pressure. Other type of materials is able to repair themselves by an external stimulus, such as heat or light. The thermal technology uses the heating of the material with some incorporated device to repair the cracks. This technology is used mainly in thermoplastic or in thermo set material with a thermoplastic phase dispersed in them<sup>6</sup>. The heat generated raises the temperature above the melting temperature of the thermoplastic material so that it melts and flows into the damaged areas closing cracks, or raises the temperature above the of the amorphous polymer facilitating the inter diffusion of molecular chains. *Progress in Polymer Science* Other materials can heal when they are exposed to light of a certain wavelength as it is the case of PMMA or polyurethanes modified with chatoyant in which there can be a chemical reaction between chatoyant and the onetime ring. The reaction is able to repair the damage when the material is irradiated by ultraviolet light.

## II. SELF-HEALING STRATEGIES IN ENGINEERING STRUCTURE

**Bioinspired self-healing approaches** active components was clearly seen to restore a proportion of the loss in mechanical properties arising from micro cracking within a polymer matrix and results confirmed that the dispersion of microcapsules within a bulk polymer matrix material was not detrimental to stiffness.

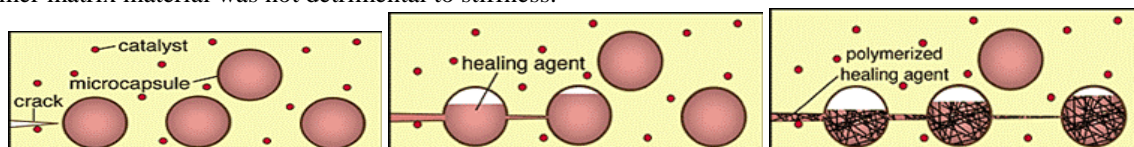


Figure 1: Basic method of the microcapsule approach

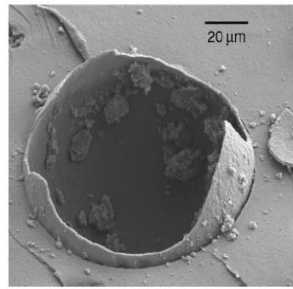


Figure 2: ESEM image showing ruptured microcapsule

A key advantage of the microencapsulation self-healing approach is the ease with which they can be incorporated within a bulk polymer material. The disadvantages are the need for microcapsule fracture and the need for the resin to encounter the catalyst prior to any repair occurring. In fiber reinforced polymer composite materials, additional problems arise due to the size of microcapsules disrupting the fiber architecture, the need for a good dispersion of the catalyst to provide uniform healing functionality, microcapsules having only limited resin volume, and the creation of a void in the wake of the crack after consumption of healing resin. Some results have indicated specific problems in terms of healing efficiency due to clumping of microcapsules into woven-roving wells whilst cracks propagate along woven-roving peaks. More recently, microcapsules have been applied to improve the fatigue life of an epoxy bulk polymer. Both manual infiltration of pre-mixed DCPD monomer and catalyst and in-situ healing using monomer filled microcapsules and dispersed catalyst have shown a The use of hollow glass fibers embedded in a composite laminate was pioneered by Belay and colleagues. In their work, commercial hollow fibers were consolidated in to lamina and then manufactured into composite laminates, i.e. the self-healing material acts as the structural fibers. The key advantages of the hollow fiber self-healing concept are that the fibers can be located to match the orientation of the surrounding reinforcing fibers thereby minimizing Poisson ratio effects. The fibers can be placed at any location within the stacking sequence to address specific failure threats (see Figure 2b), different healing resins can be used depending upon the operational requirements of the structure, different activation methods can be used to cure the resin and crucially, a significant volume of healing agent can be made be available. The disadvantages are the relatively large diameter of the fibers compared to the reinforcement, the need for fiber fracture, the need for low viscosity resin systems to facilitate fiber and damage infusion and the need for an extra processing stage for fiber infusion.

The ability to 'see' and become aware of internal damage in composite materials is as critical as in the human body. The ability to form a 'bruise' within a hollow fiber self-healing composite material was investigated by Pang and Bond. In this work they designed a damage visual enhancement method, by the bleeding action of a fluorescent dye from discrete self-healing lamina housed alongside the structural fiber lamina (see Figure 2c). This approach permitted a 'bruising' of the laminate to assist identifies regions for non-destructive evaluation. Pang and Bond also considered the rate of degradation of the repair resin effectiveness over time and correlated the infusion of an UV fluorescent dye into different damage sites with an ultrasonic C-scan NDE technique.

### III. BIOMIMETIC SELF-HEALING APPROACHES

The preceding section discussed the different bio-inspired approaches in composite materials. To date, different self-healing methods have been considered and assessed from an engineering perspective. It is only more recently that studies have begun into underlying biological methods, mechanisms and processes in order to deliver a truly biomimetic self-healing solution. 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 and will be discussed below. To date, the autonomous healing materials in engineering structures have been distributed randomly throughout the structure or spaced evenly through the composite laminate structure. In nature the network is tailored for a specific function with the healing medium often being. not been attained. Toomey *et al* utilize an interconnected micro vascular micro channel network in the coating to flow healing agent throughout an epoxy polymer block. Conversely Williams *et al* have proposed and validated a simple vascular network within a composite sandwich structure, consisting of channels approximately 1.5mm in diameter, within a polymethacrylimide (Rohacell) core capped with glass fiber reinforced epoxy skins. The generation of the network within the foam core offers a very promising delivery system for the healing of conventional sandwich structures. However, the network is only one key area for advancement, without the corresponding development of synthetic healing resins the benefits of the delivery system will be lost. Biological organisms have a highly developed, multifunctional vascular network to distribute fuel, control internal temperature and effect self-healing, among many other roles. A key feature of these systems is that they supply fluid to an area from a point reservoir, giving a branching network. Studies show that the branching and size of these vessels have evolved to minimize the power required to distribute and maintain the supporting fluid within many other constraints. The system is also reconfigurable in response to circumstances by adjusting the radius of individual vessels by vasoconstriction and dilation in mature tissue, or by growth in embryonic blood vessels. The initial steps towards this goal have been taken although a truly self-healing composite micro vascular network has still It has been estimated that the haemostatic system functions through approximately 80 coupled biochemical reactions of enzymes and platelet cells. This enormous complexity limits the degree which homeostasis can be mimicked in an engineering system. Synthetic self-healing resin systems need to be developed to duplicate the blood clotting approach found in the human body. At present, self-healing in man-made structures requires the intimate contact of two-part resin systems, whether a resin and a hardener or a resin and a catalyst. In the case of the resin and hardener approach the healing efficiency is critically dependent upon the two parts

becoming successfully 'mixed' at the point of contact, i.e. molecular transfer across the liquid resin/hardener boundary. Conversely, in the case of the resin and catalyst approach, the contact between the two will ensure the chemical reaction occurs within the damage site and beyond it, using up the resin supply in one repair episode. In mammals this is not observed. In blood clotting the once inactive blood cells are triggered when the endothelial cells are breached. This only occurs locally to the damage site, remote from the damage the clotting sequence is stable and inhibited. It is desirable to develop a resin system that can mimic this in order to allow multiple, localized repair events. The rapid reaction of blood clotting is dependent on a series of reactions activated by a very small input. The biological solution is to use a continuous fluid flow and active inhibition away from the damage site to prevent this initial impetus propagating below a certain threshold. Both one and two part healing agent systems are usually initiated by the presence of an introduced second 'part', either chemical or physical. A key inspiration from homeostasis is to have the reaction initiated by the absence of an inhibitor. Anaerobic resin systems could be considered to function in this way. Other biomimetic approaches would be to use aqueous based reactions where achieving strength and stiffness comparable with epoxy resins would be a challenge. The notable mechanical property of the fibrin in blood clots is extensibility and this could offer an alternative avenue for investigation.

#### IV. HEALING AGENT

Mammalian blood clotting has evolved around the chemical reactions of a series of active enzymes and their inactive precursors known as clotting factors. The intrinsic system takes the form of an enzyme "cascade" or "waterfall" of reactions involving clotting factors. It was first proposed by Macfarlane and Davie and Runoff. It is initiated by damage that breaches the endothelial cells that line the blood vessels and culminates in the production of fibrin, a fibrous polymer. Recent research has shown that fibrin fibers are notable amongst protein fibers for their large extensibility: 300% primarily elastic extension has been demonstrated. One of the most notable features of the haemostatic system is that despite the rapid response to injury, system malfunction. This is achieved by the rapid removal of the activated enzymes upon the production of fibrin, and the action of endothelial cells. Endothelial cells initiate a series of reactions that break down fibrin, such that any fibrin produced in a region of injury and carried away by blood flow is broken down in undamaged areas of the circulation so as not to clot in healthy blood vessels. Biomimetic hollow fiber self-healing mimic's mammalian self-heal in that a liquid healing agent leaks from a region of mechanical damage that has resulted in the fracture of an enclosed conduit. An important difference is that the primary reason for the relatively rapid haemostatic response in mammals is the need to arrest bleeding; the actual tissue and skin healing is a more lengthy process during which time the tissue could not necessarily be expected to carry a "service load". In biomimetic self-healing, a reasonably rapid response is required to restore some degree of structural integrity or prevent crack propagation since, for example, an aircraft in flight could potentially experience a limit load at any time after a damage event.

To date, self-healing in fiber reinforced composite materials has been primarily focused on the potential offered by the polymer matrices because typical impact damage is primarily in the matrix. However, the reinforcing phase provides the majority of the strength and stiffness within any composite material, and it is this component that would benefit significantly from a self-healing capability for other failure modes. The healing potential of fractured bone in the human body is influenced by a variety of biochemical, biomechanical, cellular hormonal and pathological mechanisms. The healing process is a continuous state of bone deposition, desorption, and remodeling. The natural process of bone healing is a complicated process involving blood clotting, the formation of collagen fibers, the subsequent mineralization (stiffening) and transformation of the collagen matrix into bone. This initial 'woven' bone, which can be considered as randomly arranged collagen bundles, is remodeled and replaced by mature 'lamellar' bone. The remodeling process can take up to 18 months to complete in which the healing bone is restored to its original shape, structure and mechanical strength. This process can be accelerated through the application of an axial load to the fracture site. This loading promotes the formation of bone to align with the primary load path and the redistribution of bone where it is not required. The problem with this approach is the timescales required for growth, which are unlikely to be realistic for engineering applications.

#### V. ACKNOWLEDGMENT

During the last decades, constant improvements have been made on composite materials, manufacturing processes and structural design. Nevertheless, the problem of damage initiation, propagation and tolerance has limited the acceptance of composite materials in all engineering disciplines. Conversely, after billions of years of evolution, nature has developed materials that have healing potential and repair strategies ensuring their survival. 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. Self-healing approaches applied.

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