Self-healing of fiber reinforced polymer composites

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SELF-HEALING OF FIBER REINFORCED POLYMER COMPOSITES

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

By
Nebiyu Fikru
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ABSTRACT

The study of self-healing materials is inspired by biological systems in which damage triggers an autonomous healing response. In recent years, this concept of autonomic healing material, where initiation of repair is integral to the material, is being considered for engineering applications. The concept offers the designer an ability to incorporate secondary functional ability of counteracting service degradation in addition to achieving the primary, usually structural integrity, requirement. Self-healing materials also have the benefit of offering lighter and optimized structures as well as reduced maintenance cost. Previous works on polymer matrix composites have shown that significant fractions of mechanical properties can be restored through self-healing in damaged materials.

The self-healing composite material developed in this study is a fiber-reinforced polymer matrix composite. The study has three major categories of self-healing composite systems. In the initial study, a single fiber polymer matrix self-healing composite system is developed and analyzed. In the latter stage of the study, multiple commercial glass fibers are used as a reinforcing material in the self-healing system. The inclusion of functionalized carbon nanotubes in the healing medium to further enhance the healing process is considered at the final stage of the study. The self-healing approach utilizes a releasable healing agent contained in a hollow fiber that is embedded in a resin system. Specimens are produced using a hollow glass fiber and epoxy resin. In addition, in the case of multiple fibers test, e-glass fibers are incorporated in the composite. When a crack is initiated and propagates through the composite breaking the hollow fiber, a liquid healing agent comes out and fills the crack gap. Polymerization of the monomer healing agent is facilitated when it contacts a catalyst that is pre-coated on the outside surface of the hollow glass fiber.
Healed, damaged and virgin specimens are tested in tension for all the different sets of composites investigated. The results demonstrate that a considerable portion of the tensile strength is recovered by the self-healing functionality of both the single fiber and fiber-reinforced polymer composites. A major advantage of this research is the fact that the healing is found to be localized allowing further multiple healing of the composite in the presence of several cracks. Incorporation of functionalized carbon nanotubes in the healing medium has provided additional efficiency in the composites compared to those without carbon nanotubes.
CHAPTER 1. INTRODUCTION

1.1 Composite Materials

Composite materials or composites are engineered materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct on a macroscopic level within the finished structure. The properties of composite materials obtained by combining the different constituent materials usually cannot be achieved by any one of the components acting alone.

1.1.1 History and Development of Composite Materials

Composite materials have been used for thousands of years in various man-made structures. The most primitive composite materials in recorded history were straw and mud combined to form bricks for building construction. Straw was used by the Israelites to strengthen mud bricks. Plywood was used by the ancient Egyptians when they realized that wood could be rearranged to achieve superior strength and resistance to thermal expansion as well as bloating caused by the absorption of moisture.

The history of modern composites however began in the late 1930’s with the invention of fiberglass. The pace of the development of composite materials accelerated during World War II and the decades following. The development of new and improved resins has also contributed to the expansion of the composites market, especially for high temperature and high corrosion resistance applications. The most advanced applications are routinely found on spacecraft in demanding environments. The most visible applications pave our roadways in the form of either steel and aggregate reinforced cement or asphalt concrete. Furthermore, composites closest to our personal hygiene form modern day shower stalls and bath tubs made of fiberglass.

Even though most composites that are used in modern engineering structures are man-
made, composites do exist in nature as well [1]. A piece of wood is a composite with long fibers of cellulose (a very complex form of starch) held together by a much weaker substance called lignin. Cellulose is also found in cotton and linen. However, the binding power of the lignin makes a piece of timber much stronger than a bundle of cotton fibers. An example of a man-made composite is concrete. It is made of cement, aggregates (such as gravel and sand), water, and chemical admixtures and is used more than any other man-made material in the world.

1.1.2 Constituents of Composites

Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials: matrix and reinforcement. At least one portion of each type is required to fabricate a composite. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination. The matrix material can be introduced to the reinforcement before or after the reinforcement material is placed into the mold cavity or onto the mold surface. The matrix material experiences a merging event, after which the part shape is essentially set. Depending upon the nature of the matrix material, this merging event can occur in various ways such as chemical polymerization or solidification from the melted state.

Most commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the applications. There are several broad categories, each with numerous variations. The most common are known as polyester, vinyl ester, epoxy, phenol, polyimide, polyamide, and polypropylene.
The reinforcement materials are often fibers but ground minerals such as metals and ceramics are used commonly. The reinforcing materials are usually strong with low densities. The principal fibers in commercial use are various types of carbon and glass, as well as aramid fibers such as Kevlar. The fiber orientation can be controlled in each layer of the laminate to create a broad range of mechanical and physical properties. Based on the type of reinforcement used, composites are often divided into fibrous composites and particulate composites.

Because of their excellent mechanical properties such as high strength, low specific weight, and impact and corrosion resistance, as well as advanced manufacturing methods and tailor ability of the lay-up, fiber-reinforced polymer matrix composites are attractive candidates for use in many performance oriented structures. Composite materials are ideal for structural applications where high strength-to-weight ratio and stiffness-to-weight ratios are important. Weight sensitive applications such as aircraft and space vehicles are the primary consumers of composites, especially fiber-reinforced polymer matrix composites. However, their use is limited due to the difficulty in damage detection and repair as well as lack of extended fatigue resistance. Several ideas have been suggested by researchers to help improve the damage detection and repair difficulty in composites, self-healing being one of them.

1.2 Self-healing Composites

Constant improvement in material quality and performance is an important parameter in the design of engineering structures. Engineering structures encompass a broad spectrum of technologies from materials development, analysis, design, testing, production and maintenance. Advances in materials science and technology have been largely responsible for major performance improvements in many engineering structures. These advances continue to be crucial in determining the reliability, performance and cost effectiveness of such structures. One
of the advancements made in materials technologies is in the field of composites which play a major role in our day to day life in the 21st century.

Microcracks in engineering materials are common and are the initial sites of failure of the structure. In composite materials, fatigue and impact damage can lead to matrix-cracking and delamination in the material structure thereby reducing the structural capability of the composite. If the damage is not detected and repaired, premature failure can occur in the material. The cracks or delaminations also provide sites for ingress of contaminants, such as micro-organisms and moisture. Such openings like moisture ingress reduce the strength of composite structures significantly over time [2]. Scientists, engineers and several research groups around the world have long sought the feasibility of autonomic healing of cracks and delaminations in composites. Therefore, a key focus of current scientific research is the development of bioinspired materials.

In the past few decades, the growing interaction between biological and material sciences is leading researchers to incorporate biomimetic features, such as sensing and self-healing into newly developed materials. Biomimetics refers to human-made processes, substances, devices, or systems that imitate nature, and has led to the development of new biologically inspired materials based on biological analogs [3]. One such remarkable property of biological materials is their ability to autonomically heal when they are damaged. This is achieved by hierarchical structuring, adjusted development instead of production, and constant amending and healing. Several key aspects need to be considered and researched for self-healing composites to acquire autonomic healing capability like biological systems. Figure 1 shows the critical parameters considered for the development of self-healing composites. The concept of self-healing composites relies on healing agent stored in a container that would break when damaged.

Analogous to biological materials, the bleeding healing agent is supposed to fill out the
damaged area. Similar to the proliferation and restructuring of building components in biological materials, the released healing agent in self-healing composites undergoes a chemical reaction or polymerization to heal the material. Even though different research groups around the world are engaged in developing self-healing materials with little success so far, the method of healing agent has garnered great success in the development of self-healing materials.

Figure 1. Critical parameters for the development of self-healing composites
The work presented in this study is the healing agent method and utilizes a releasable healing agent filled in a hollow glass fiber that is embedded in a resin system. When a crack is initiated and propagates through the composite breaking the hollow fiber, the liquid healing agent flows out and fills the crack gap. Polymerization of the monomer is facilitated when it comes in contact with a catalyst that is initially coated on the outside surface of the hollow glass fiber. The method is essentially analogous to biological materials that can autonomically heal their damaged parts via chemical balances and processes.
CHAPTER 2. LITERATURE REVIEW

In contrast to synthetic materials, naturally existing materials are greatly diverse in nature. Naturally existing materials in animals and plants have developed into highly sophisticated, integrated, hierarchical materials that commonly exhibit multipurpose behavior [4]. Mimicry of these integrated microstructures and micromechanisms offers considerable potential to engineers in the design and continual improvement of material performance in the future [5]. Besides achieving the primary structural requirement, bio-inspired concepts such as sensing and self-healing provide an ability to incorporate secondary functions in engineered materials.

Composite materials have shown tremendous improvements because of advancements made in fibers and resin materials technology. However, their use is limited due to the difficulty in damage detection and repair as well as lack of extended fatigue and impact resistance. One way to protect material degradation is through the incorporation of self-healing ability. Healing of materials, such as glass, polymers, and concrete, have been investigated in order to extend the service life of these structures [6-9]. In most of these investigations, the healing process involved human intervention and thus the materials were not able to heal autonomically.

Polymer composites have been attractive candidate to introduce the autonomic healing concept into modern day engineering materials. To date, there have been significant researches in self-healing polymeric materials [10-14], and numerous studies specifically in fiber reinforced polymers [15-20]. Even though several methods have been suggested in autonomic healing materials, the concept of repair by bleeding of enclosed functional agents has garnered wide attention by the scientific community. This concept of bleeding is also being considered for commercial purposes in the aerospace industry.
2.1 Self-healing in Concrete

Based on theoretical and experimental research, Edvardsen investigated the effect of crack healing in concrete on a large scale [7]. The experimental results showed that the formation of calcite in the crack was the sole cause for the autogenous healing. Theoretical analyses of the physical/chemical processes concerned indicated that crystal growth rate is dependent on crack width and water pressure, whereas concrete composition and water hardness have no influence on autogenous healing. This notion was confirmed by experimental results.

Dry [22, 23], adapted the self-healing concept for use in concrete. Repair components were stored inside vessels dispersed within the concrete and the repair medium was released once damage occurred. This work pioneered, the use of storage vessel in a matrix material, which would be adapted to polymer composites in later studies. In a related work, Li et al. [21] also applied their concept of self-healing to concrete composites. Ethyl cyanoacrylate was used as the healing agent and was placed in hollow glass tubes. Their experiment introduced the ‘capillary action’ as a means of filling hollow short glass fibers with healing agents.

2.2 Self-healing in Glass

In the mid seventies and early eighties, Stavrinidis and Holloway [6] used a double torsion loading configuration to study crack closure and re-propagation in soda-lime-silica, borosilicate and silica glasses, and in an epoxy resin. It was found that closure and re-propagation characteristics in a given material were reproducible but depended on the environment. In some cases the strain energy release rate required to re-propagate a closed crack increased with time and heat treatment. Water from the environment appeared to play a central role in this process. Glasses are polymers in nature so the study of self-healing ability in glasses has paved the way for different kinds of polymer composites.
2.3 Self-healing in Composites

2.3.1 Self-healing in Polymer Composites

In 1982, Wool and O’Conner [8], presented crack healing in polymers through stages of healing process. The stages were surface rearrangement, surface approach, wetting, diffusion, and randomization. The recovery ratio, $R$ of mechanical properties with time was determined as a convolution product,

$$R = R_h(t) \Phi(t)$$  \hspace{1cm} (1)

where, $R_h(t)$ is an intrinsic healing function, and $\Phi(t)$ is a wetting distribution function for the crack interface or plane in the material. The repetition model of a chain in a tube was used to describe self-diffusion of interpenetrating random coil chains which formed a basis for $R_h(t)$. Applications of the theory were also described, including crack healing in amorphous polymers and melt processing of polymer resins by injection or compression molding. Relations were also developed for fracture stress, strain, and energy as a function of time, temperature, pressure, and molecular weight. Chain fracture, creep, and stress relaxation were also discussed from self-healing point of view.

The first use of self-healing for a polymer composite was in 1996 and developed by Dry [10]. Dry showed positive result in the feasibility of developing polymer matrix composites which have the ability to self-repair internal cracks due to mechanical loading. The study focused on the cracking of hollow repair fibers dispersed in a matrix and the subsequent timed release of repair chemicals which result in the sealing of matrix cracks, the restoration of strength in damaged areas and the ability to retard crack propagation. These materials, capable of passive, smart self-repair, consist of several parts:

(1) An agent of internal deterioration such as dynamic loading which induces cracking,
(2) A stimulus to release the repairing chemical such as the cracking of a fiber,

(3) A fiber,

(4) A repair chemical monomer carried inside the fiber either a part polymer or a monomer, and

(5) A method of hardening the chemical in the matrix in the case of crosslinking polymers or a method of drying the matrix in the case of a monomer.

It was found that cracking of the repair fiber and subsequent release of the repair chemicals could be achieved. By most regard, Dry’s work is considered to be a pioneer in the field of self-healing polymer composites and has paved the way for several other mechanisms of autonomic healing in composites.

Motuku and associates [15] suggested a healing concept by considering different critical parameters such as a method of storage and healing agents. In their experiment, they found that the release of a healing agent through glass was the most suitable compared to copper and aluminum tubing. Their method was able to self-repair cracks at a millimeter scale in polymer composites.

A breakthrough in the study of self-healing materials was reported in 2001 by a research group at University of Illinois. White et al. [13] first introduced the incorporation of microcapsules containing a polymer precursor into the matrix material of a non-fiber reinforced polymer composite for self-healing purposes, Figure 2. The polymer precursor was contained in microcapsules and embedded into the matrix. The matrix contained randomly dispersed catalyst that was supposed to react with the precursor flowing through any crack formed due to damage and initiate polymerization. The polymer was then supposed to bond the crack face closed.

The investigators overcame several challenges in developing microcapsules that were
weak enough to be ruptured by a crack but strong enough not to break during manufacture of the composite system. The researchers have shown that it was possible to recover up to 75% of the maximum tensile strength of the virgin composites.

Brown et al. [24] further extended the work of White et al. [13] by studying the effects of size and concentration of the catalyst and microcapsules on fracture toughness and healing efficiency. They reported that the addition of microcapsules significantly toughens the neat epoxy. Once healed, the self-healing polymer exhibits the ability to recover as much as 90% of its virgin fracture toughness.
Similar to the work by White et al. [13], Mauldin et al. [25] reported the development of self-healing materials that use the ring-opening metathesis polymerization to repair cracks. However, the novelty of their work is the introduction of exo-stereoisomer instead of the conventional epoxy resin-based self-healing system which uses commercially available endo-isomer of dicyclopentadiene. Energy to failure versus healing time of healed specimens was measured for endo- and exo-DCPD, and mixture of the two, to compare the kinetics of damage repair. Their work showed that the exo-stereoisomer has faster olefin metathesis reaction. Fracture toughness measurements were also presented as a function of healing time to compare the two systems of mixture.

Chen et al. [11] developed a reverse Diels-Alder polymer that has a polymerization-depolymerization equilibrium ensuring the reformation of broken bonds upon heating. In principle, healing is achievable but any new resin would need to have equivalent thermomechanical properties to an epoxy for use as a matrix in fiber composites.

Materials are always plagued by fatigue and associated damages with it. Jones et al. [26] demonstrated the development of self-healing polymers based on microencapsulated dicyclopentadiene and wax-protected and recrystallized Grubbs’ catalyst embedded in a polymer matrix. The material was capable of responding to propagating fatigue cracks by autonomic processes that led to higher endurance limits and life extension, or even the complete arrest of crack growth. The microcapsules ruptured by the propagating crack releasing the healing agent into the crack plane through capillary action. This led to the retardation or permanent arrest of further fatigue crack growth. They showed that the fatigue life of polymers under fast fatigue crack growth can be extended through the inclusion of periodic rest periods, effectively training the self-healing polymeric material to achieve higher endurance limits. They also showed that
the extension of the fatigue life is governed by the relation between the mechanical kinetics of crack propagation and the chemical kinetics of healing in the polymer.

Recently, Toohey et al. reported a self-healing system capable of autonomously repairing repeated damage events [27]. Their system, Figure 3, is a bio-inspired coating-substrate design that delivers healing agent to cracks in a polymer coating via a three-dimensional microvascular network embedded in the substrate. The system is composed of microvascular substrate and a brittle epoxy coating containing embedded Grubb’s catalyst. With no external pressure being required, healing agent wicks from the microchannels into the cracks through capillary action after damage occurs in the coating. This approach opens a new venue for continuous delivery of healing agents for self-repair as well as other active species for additional functionality.

Figure 3. Microvascular self-healing concept, [27]
2.3.2 Self-healing in Fiber-Reinforced Polymer Composites

The first use of hollow glass fibers embedded in a composite laminate was suggested by Bleay et al. [12]. In their study, filled hollow fibers with a resin are released into the damaged area when the fiber is fractured. A two-part epoxy resin was used as the repair medium, the two components being diluted with solvent and infiltrated into different plies of a composite based on ‘Hollex’ S2-glass fiber. Even though the method needed no manual intervention for healing damages, more efficient recovery of matrix strength was observed at elevated temperature.

More recently, several self-healing unidirectional glass fiber composites have been developed [18-20, 28, 29]. The composite systems showed considerable restoration of mechanical properties such as flexural strength, compressive strength and impact resistance through bleeding of hollow fibers that carry repair materials.

In particular, Pang and Bond [19] used glass fibers to store an uncured resin material in their self-healing composite systems. Their composite systems underwent flexural testing and they found that a significant fraction of lost flexural strength could be restored by a mixture of repair agent MY750 Ciba-Geigy and acetone placed in separate hollow fibers. They were also able to demonstrate the release and infiltration of an UV fluorescent dye from fractured hollow fibers into damage sites within the internal structure of the composite.

Trask et al. presented self-healing material that uses functional repair components stored inside hollow glass fibers [30]. Their work considered the placement of self-healing hollow glass fibers plies within both glass fiber/epoxy and carbon fiber/epoxy laminates to mitigate damage occurrence and restore mechanical strength. Their study investigated the effect of embedded hollow glass fibers on the host laminates mechanical properties and also the healing efficiency of the laminates after they were subjected to quasi-static impact damage. Results of
flexural testing were shown to confirm the self-healing efficiency.

In the work performed by Jones et al. [31], it was shown that solid-state self-healing system is capable of healing transverse cracks and delaminations in a composite. Their system involved a thermoplastic healing agent dissolved in a conventional thermosetting epoxy resin. Through Charpy impact testing, the resin system was optimized resulting in a reduced delamination area. The healing was assisted by heating the fractured samples.

Hayes et al. [32] developed a smart composite system which combines structural health monitoring with a self-healing resin. The self-healing matrix employs a thermosetting epoxy resin into which a linear polymer is dissolved. Although the system employed the conventional matrix resin technology, it was proven to heal only closed cracks while open cracks failed to heal autonomically. Furthermore, the system required a heating stage.

Woldesenbet and Williams [33] showed that, a considerable portion of the tensile strength can be restored in single fiber polymer matrix composite where the healing agent is stored in a hollow glass fiber. The releasable healing agent (DCPD) filled in a hollow glass fiber is embedded in an epoxy resin system. When a crack is initiated and propagates through the composite breaking the hollow fiber, the healing agent flows out and fills the gap. Polymerization is facilitated when the healing agent contacts the Grubb’s catalyst coated on the outside surface of the hollow glass fiber.

Despite their advantages, all approaches pose some type of problem with regard to the self-healing process. In the work by Dry and McMillan [34] and Motuku et al. [15], a dye release was added to the healing agent resulting in the inability to cure. The combination also showed no improvement in mechanical properties. In the works of Kessler and White [35], clusters of catalyst found in the matrix contribute to a decrease in virgin fracture toughness and
unstable crack propagation. Although flexural strength was restored, the method used by Pang and Bond [19] was not recommended as a permanent means to repair damage. It was also reported that the ability to self-repair deteriorated greatly over time as the repair resin degraded.

2.4 Self-healing Nanocomposites and Other Methods of Self-healing

In polymer composites, the addition of nanoparticles to enhance mechanical properties has sought tremendous progress over the past decade, [36-41]. The high strength, modulus, and large aspect ratios of CNTs combined with their unmatched electrical and thermal properties make nanotubes attractive candidates for multifunctional nanoreinforced polymer composites [42].

Lee et al. [43] showed the possibility of using nanoparticles dispersed in polymer films to deposit at a damage site in a similar fashion to blood clotting. In their work, the nanoparticles were dispersed in polymer films within a multilayer composite and were studied by integrated computer simulations. Their model comprises a brittle layer containing a nanocrack sandwiched between two polymer films. Through their analysis, it was found that the nanoparticles congregate at the nanocrack facilitating a self-healing mechanism. The numerical models also predict load transfer from the matrix to the stiff nanoparticles. Through micromechanics simulations, they evaluated the properties of these systems in the virgin, damaged, and healed states and determined optimal conditions for harnessing nanoparticles to act as responsive, self-assembled “band aids” for composite materials. Their mechanism was considered applicable to optical communications, display technologies and biomedical engineering. There were situations where the mechanical properties of the repaired composites can potentially be restored to 75%–100% of the virgin material. The work by Lee is novel in the sense that it used the nanoparticles to heal the material besides giving enhancements in its mechanical properties.
Recently, Gupta et al [44] used fluorescent nanoparticles to show that ligands on the nanoparticles can be selected to help drive nanoparticles into a crack in a microelectronic thin film polymer layer. Recently, Gupta et al [44] used fluorescent nanoparticles to show that ligands on the nanoparticles can be selected to help drive nanoparticles into a crack in a microelectronic thin film polymer layer.

Segregation of the nanoparticles to the crack depends on both the enthalpic and entropic interactions between the polymer and nanoparticles. The viability of this technology for use in structural composite materials is possibly disputed as the target damage is at a very small scale. Their work showed a simple means of fabricating systems that can heal autonomically, improving the durability of multilayered systems, and forms the basis for auto-responsive materials.

Verberg et al. [45] modeled the rolling motion of a fluid-driven, particle-filled microcapsule along a heterogeneous, adhesive substrate to determine how the release of the encapsulated nanoparticles can be utilized to repair damage on the underlying surface. They have sought the implementation of ‘synthetic leucocytes’ via microchannel delivery networks and microcapsules capable of releasing nanoparticle repair agents. Besides directing the vital components to the damaged sites, the active agents sense the state of the walls of the vasculature. Finally, the diffusion of the nanoparticles out of the microcapsules and deposition in the microchannels due to the enthalpic environment leads to an autonomic ‘repair and go’ function.

Recent work by Jeong and Kessler [46] demonstrated toughness enhancement in Norbornene-functionalized multiwalled carbon nanotube (MWNT) and poly-dicyclopentadiene (DCPD) nanocomposites. Ring-opening metathesis polymerization (ROMP) was used to prepare the DCPD/MWNT nanocomposite. They reported that tensile toughness was found to increase
by more than 900% compared to neat polyDCPD by incorporating 0.4 wt % functionalized MWNTs. Modest increase in modulus and strength were also observed with increasing nanotube loadings. By using differential scanning calorimetry, they evaluated the effect of norbornene grafted MWNTs on the polymerization kinetics of the resulting cross-linked polyDCPD network. Moreover, a decrease in damping behavior, as measured by dynamic mechanical analysis, was used to estimate the effective polymer-particle interphase thickness. Even though their work is not directly concerned about self-healing composites, the DCPD/MWNT and ROMP technique they used to show toughness enhancement are widely used in the development of self-healing composites by different research groups around the world [46].

The work by Kersey et al. [47] addressed self-healing on a molecular level by incorporating load bearing, reversible interactions onto surfaces or into covalent polymer networks. Self-healing is governed either kinetically as in the generation of new material that fills and adheres to cracks/failure sites or thermodynamically as in the regeneration of the initial state of the original molecular components (typically by annealing reversible interactions). Reversible interactions can be incorporated in a composite material with components that preserve a memory of the desired state, for example, by encasement within an exoskeleton or tethering to an endoskeleton.

Kalista and Ward [48] examined thermal effects during self-healing and investigate the link to some of the behavior observed in other self-healing systems. They showed that, a class of poly(ethylene-co-methacrylic acid), copolymers and ionomers show a unique ability to self-heal following projectile puncture. The healing process active in these materials appears to be significantly different than any of the other systems in capability and mechanism being studied elsewhere. In order to effectively design materials that can take advantage of this capability, the
mechanism by which these materials heal must still be determined. To provide further understanding of the self-healing capabilities, several new damage methods are considered, including sawing, cutting and puncture techniques.

Even though essentially different from self-healing materials, shape memory materials have found growing interest as a result of the rise of a new class of polymers. These so called shape-memory polymers by far surpass the renowned metallic shape memory alloys in their shape-memory behavior. Due to the relative ease in manufacturing and programming of shape-memory polymers, these materials represent a cheap and efficient alternative to well-established shape-memory alloys. In shape-memory polymers, the consequences of an intended or accidental deformation that is caused by an external force can be straightened out by heating the material above a defined transition temperature. This effect is usually achieved because of the given flexibility of the polymer chains. When the importance of polymeric materials in our daily life is taken into consideration, it is apparent that a very broad, additional spectrum of possible applications for intelligent polymers covers an area from minimally invasive surgery, through high-performance textiles, up to self repairing plastic components in every kind of transportation vehicles [49].

Another class of self-healing materials called supramolecular polymers have recently been developed. They are polymeric arrays of monomer units, held together by reversible and highly directional secondary interactions i.e., non-covalent bonds, such as hydrogen bonds. The resulting materials therefore maintain their polymeric properties in solution [50, 51]]. Healing of these supramolecularly based materials is accomplished by heating them and allowing the non-covalent bonds to break. Upon cooling new bonds will be formed and the material will potentially heal any damage. The approach is however in a rudimentary stage.
Despite their advantages, all approaches pose some type of problem with regard to the self-healing process. Moreover, most studies have been falling short of showing multiple or repetitive healing in their systems. Problems of localized healing and damage detection do still exist in most self-healing systems that are being suggested from different corners of the world.

The work presented in this study is novel in its kind where catalyst coated glass fibers are filled with healing agent and embedded in a resin matrix. In the event of damage, the fibers break and release the healing agent in the crack volume. Polymerization of the healing agent follows and heals the composite. Addition of nanoparticles is sought to enhance self-healing in the composites. While tensile strength is conducted to evaluate self-healing ability in the composites, microhardness test is also performed to determine healing time.
CHAPTER 3. EXPERIMENTAL

3.1 Specimen Mold Fabrication

The fabrication method used to produce self-healing composite samples is a molding process. Prior to fabricating a mold for the single fiber as well as fiber reinforced polymer matrix composite specimens, a metallic mold is first machined on a three axes machining center. The metallic mold shown in Figure 4 is fabricated from 6 mm thick steel plate. The profile of the machined part on the steel plate is exactly a negative copy of the specimens used to demonstrate self-healing in single fiber as well as fiber reinforced polymer matrix composites. The steel mold is then used to fabricate a flexible rubber mold. The rubber mold is preferred due to the ease in demolding the cured single fiber polymer matrix specimen. The rubber mold is produced using Dow Corning 3120RTV Silicon Rubber (Red Color) and Dow Corning 1 Catalyst curing agent mixed in the ratio of 10:1 by weight, respectively. Red silicone is preferred as the white glass fiber can be seen well against this background [52]. The mixture is poured into the steel mold and cured overnight at room temperature, Figure 5.

Figure 4. Steel mold used for fabrication of the silicone form
Finally, the silicone form is demolded and made ready for specimen fabrication, Figure 6. This plastic mold is used for the fabrication of the single fiber polymer matrix composite specimens. However, in the case of the fiber reinforced polymer composite specimens, the steel mold is further milled to obtain the intended specimen size.

3.2 Specimen Fabrication

In this study, three types of self-healing composite systems are developed. These are, single fiber polymer matrix composite (SFPMC), fiber reinforced polymer composite (FRPMC)
and single fiber polymer matrix nanocomposite (SFPMN). However, the materials used and the fabrication technique are comparatively similar in all cases.

3.2.1 Single Fiber Composite Specimen Fabrication

3.2.1.1 Materials

Several materials are combined together to form the SFPMC specimen. The resin matrix used in is EPON Resin 828 and EPI-CURE Curing Agent 3223 from Miller-Stephenson Chemical Co. (USA). The hollow glass fiber, Figure 7, used is borosilicate glass tubing from Capillary Tube Supplies Ltd. (UK). It has an outside diameter (OD) of 125µm and degree of hollowness of 64% approximately. The healing agent used is dicyclopentadiene (DCPD) manufactured by Sigma-Aldrich (USA). The catalyst used is First Generation Grubb’s catalyst by Miller Chemical Co. (USA). Sealant used is Dow Corning Silastic Rubber 3120RTV by Sigma-Aldrich (USA). Commercial solvents such as Chloroform and Dichloromethane are also used.

![Figure 7. Borosilicate hollow glass fibers](image)

3.2.1.2 Manufacture

The specimen used in the single fiber polymer matrix composite (SFPMC) has a dimension of 42 mm x 6 mm x 2 mm. The hollow fiber has a length of 42mm where 32mm is
embedded within the resin and 5mm on both ends is free and is used to place it properly in the specimen during fabrication. Figure 8 shows the schematic diagram of the test specimen.

The procedure of fabrication starts by filling the hollow glass fiber with a repair material, dicyclopentadiene (DCPD). The DCPD is the same monomer that was used by White et al. [13]. It usually stays in solid form at room temperature and has to be heated up to 110°F in order to melt. Since the DCPD has to be in a liquid form all the time during specimen fabrication and testing, chloroform is added at a ratio of 1ml to 25ml of DCPD preventing it from solidifying at room temperature. The liquid DCPD mixture is then filled in the hollow fiber by capillary action and sealed at both ends by the silicone sealants.

As received Grubb’s catalyst is in a form of powder and must be set in a liquid form in order to coat the hollow glass fibers thoroughly. Poche and associates [53] found that mixing 10mg of Grubb’s catalyst and 1ml of dichloromethane (DCM) would enhance the Grubb’s catalyst stay in liquid form. They have also found that the Grubb’s catalyst is not affected by the DCM. The hollow glass fiber that is filled with the DCPD mixture healing agent and sealed at the ends is then placed in a dish that contains the Grubb’s catalyst and DCM mixture. The fiber is rolled in the dish so that it is coated thoroughly on the outside surface. Once the DCM evaporates, the coated glass fiber filled with the healing agent is then placed at the middle of the silicone mold to prepare the SFPMC specimen.

The EPON Resin 828 and EPI-CURE Curing Agent 3223 are mixed together at a ratio of 12:1 parts by mass. The mixed resin is poured into the silicone mold carrying the glass fiber. According to the manufacturers recommendation, the curing schedule is seven days at room temperature to obtain maximum mechanical properties. The final specimen, Figure 9, is then demolded from the silicone form and made ready for mechanical testing.
Figure 8. Schematic diagram of the single fiber polymer matrix composite specimen

Figure 9. The single fiber polymer matrix composite specimen
3.2.2 Fiber Reinforced Composite Specimen Fabrication

3.2.2.1 Materials

Most of the materials used to fabricate FRPMC specimens are the same materials used in the fabrication of SFPMC specimens. The resin matrix EPON Resin 828 with EPI-CURE Curing Agent 3223 and the borosilicate hollow glass fiber used are the same materials used in the SFPMC fabrication. In addition to the hollow fibers, solid glass fibers are used to fabricate fiber reinforced composite specimens. The solid glass fibers are commercial E-glass fibers with a diameter of 12µm and tensile strength of 2750MPa. The DCPD healing agent and the Grubb’s catalyst used are also the same materials used in SFPMC fabrication. Similarly, sealant used is Silastic rubber as used in SFPMC fabrication. Also, commercial solvents such as Chloroform and Dichloromethane are used as in SFPMC.

3.2.2.2 Manufacture

The geometry of the specimen used to demonstrate self-healing in FRPMC is rectangular with dimension of 32 mm x 3 mm x 2 mm, Figure 10. The specimen is a single layer with unidirectional hollow glass fibers (H) and solid glass fibers (S) that are placed in the matrix with a lay-up of, H/S/H/S/H/S/H, Figure 11. Both the hollow glass fiber and the solid glass fiber are entirely embedded in the matrix and have a length of 32mm. The solid fiber is a strand composed of thousands of fibers bundled together where each fiber in the strand has 12µm OD. The strand has a width of 3mm, equal to the width of the specimen. Both the solid and hollow fibers have uniform spacing between them along the cross section of the specimen.

Using Equation (2), the volume fraction of the fiber is calculated to be 18%, where over 90% of it is contributed by the solid glass fibers.

\[ V_f = \frac{V_{sf} + V_{hf}}{V_p} \]  

(2)
Figure 10. Schematic diagram of the fiber-reinforced polymer specimen

Figure 11. Cross section of specimen showing the fibers orientations
where, $V_f$ is volume fraction of the fiber, $v_{sf}$ is the volume of the solid fibers, $v_{hf}$ is the volume of the hollow fibers and $v_p$ is the volume of the specimen.

The procedure for FRPMC fabrication is highly similar to SFPMC specimen fabrication. First, solid dicyclopentadiene is heated up to 110 °F to melt. It is then mixed with chloroform at a ratio of 1ml of chloroform to 25ml of DCPD. The chloroform prevents the DCPD from solidifying at room temperature. The liquid DCPD mixture is then filled in the hollow fiber by capillary action. The DCPD filled fiber is then sealed at both ends by the Silastic sealant.

First generation Grubb’s catalyst, which comes in a form of powder, must be set in a liquid form in order to coat the outside surface of the hollow glass fibers thoroughly. Grubb’s catalyst (10mg) and DCM (1ml) are mixed to enhance the Grubb’s catalyst stay in liquid form. The filled and sealed hollow glass fibers are then rolled in a dish that contains the Grubb’s catalyst and DCM mixture. The fibers are coated thoroughly on their outside surface and the DCM evaporates very shortly.

The EPON Resin 828 and EPI-CURE Curing Agent 3223 are mixed in the ratio of 12:1 by mass and are injected into the mold while the solid and hollow glass fibers are laid-up alternatively. The specimen is let cure for seven days at room temperature. The final specimen, Figure 12, is then demolded from the silicone form and prepared for mechanical testing.

### 3.2.3 Single Fiber Nanocomposite Specimen Fabrication

#### 3.2.3.1 Materials

In the fabrication of single fiber polymer matrix nanocomposite (SFPMN) specimens, all the materials used to fabricate single fiber polymer matrix composite (SFPMC) specimens are used. These are EPON Resin 828 with EPI-CURE Curing Agent 3223, borosilicate hollow glass fibers, Dicyclopentadiene (DCPD) healing agent, Dow Corning Silastic Rubber 3120RTV, and
Chloroform and Dichloromethane. These materials are also used in the fabrication of FRPMC specimens. The catalyst used is Second Generation Grubb’s catalyst by Miller Chemical Company (USA). In addition, COOH functionalized multiwalled carbon nanotubes (COOH-MWNT) from Cheap Tubes, USA are used. Norbornenylethylidimethyl-chlorosilane from Hybrid Plastics (USA), anhydrous pyridine and anhydrous ethylene glycol from Sigma-Aldrich (USA) are also used. Reagents and solvents such as tetrahydrofuran (THF), Chloroform, Dichloromethane (DCM) and acetone are purchased from commercial suppliers and used as received.

![Figure 12. Fiber-reinforced polymer composite specimen](image)

3.2.3.2 Manufacture

The SFPMN specimen has a dimension of 42 mm x 6 mm x 2 mm, similar to the SFPMC specimen, Figure 8. The hollow fiber has a length of 42mm where 32mm is embedded within the resin and 5mm on both ends is free and is used to place it properly in the specimen during fabrication.
The procedure followed for norbornene functionalization of the COOH-MWNT is similar to Jeong and Kessler [46]. 1.1g of COOH-MWNT is refluxed in a thionyl chloride with a catalytic amount of N,N' Dimethylformamide (DMF) N₂ at 70 °C for 48 h. The residual SOCl₂ is removed by high vacuum distillation giving acyl chloride-functionalized MWNTs (MWNT-COCl). This MWNT-COCl is immediately reacted with 40 mL of ethylene glycol and 0.1 mL of pyridine at 120 °C for 48 h and then purified. After being cooled, the solution is filtered and rinsed with tetrahydrofuran/THF and acetone. The product is dried under vacuum at 70 °C for 24 h, giving MWNT-OH. The MWNT-OH is added in 5-norbornene-2-yl(ethyl)-chlorodimethylsilane (25 mL) solution and 0.1 mL of pyridine and refluxed for 48 h at 70 °C. The solution is filtered and washed fully with THF and dried under vacuum at 70 °C for 24 h, giving norbornene-functionalized MWNT.

Solid dicyclopentadiene is heated up to 110 °F to melt. It is them mixed with chloroform at a ratio of 1ml of chloroform to 25ml of DCPD. The chloroform prevents the DCPD from solidifying at room temperature. The product (norbornene-functionalized MWNT), is then mixed with the DCPD mixture (DCPD and chloroform as used in SFPMC specimen fabrication) using tip sonication to fully disperse the functionalized nanoparticles. The dispersion of functionalized MWNTs in a DCPD mixture is shown in Figure 13, in comparison with as supplied MWNT and DCPD mixture.

Three different loadings of functionalized MWNTs are used, 0.1, 0.3 and 0.5 wt%. The mixture is filled in the hollow glass fiber through capillary action and then sealed at both ends by Silastic sealants. Similar to SFPMC specimen fabrication, Grubb’s catalyst comes in a form of powder and must be set in a liquid form in order to coat the hollow glass fibers thoroughly. Grubb’s catalyst (10mg) and DCM (1ml) are mixed to enhance the Grubb’s catalyst stay in
liquid form. The filled and sealed hollow glass fibers are then rolled in a dish that contains the Grubb’s catalyst and DCM mixture. The fibers are coated thoroughly on their outside surface and the DCM evaporates very shortly. The coated glass fiber filled with the healing agent is then placed at the middle of the silicone mold to prepare the SFPMN specimen.

Figure 13. (Left) as supplied MWNTs in a DCPD mixture after one hour and (Right) functionalized MWNT and DCPD mixture after three days

The EPON Resin 828 and EPI-CURE Curing Agent 3223 are mixed together at a ratio of 12:1 parts by mass. The mixed resin is poured into the silicone mold which carries the filled glass fiber. The curing schedule is seven days at room temperature. The final specimen, Figure 14, is then demolded from the silicone form and made ready for mechanical testing.

3.3 Fragmentation of Fiber

In order to carry out the self-healing experiments and obtain healing efficiency, specimens need to sustain prior damage. For the hollow glass fibers, this is achieved by the application of a flexural load using a three point bending set-up, Figure 15. Prior to coating the
Grubb’s catalyst, a small surface scratch is initially made at the mid length of the hollow fiber. This small scratch is used to direct the crack when a flexural load is applied on the composite specimen. The purpose of applying a flexural load on the specimen is to break the fiber at a designated location to assist visualization of the healing process. When the fiber breaks, additional cracks are also generated in the matrix within the damage zone. In the case of FRPMC samples, damage is introduced to the solid fibers by actually breaking the solid fibers at approximately their mid-length during flexural loading. Therefore, the damaged solid fibers are two independent fibers that extend from the middle to the end of the specimen in opposite directions. However, virgin specimens also fabricated where all the fibers are not fragmented are. These specimens have undamaged solid and hollow glass fibers.

Figure 14. The single fiber polymer matrix nanocomposite specimen
Figure 15. Three-point loading of the specimen to control the crack propagation and initiate healing process
CHAPTER 4. TESTING

4.1 Microhardness Test

Microhardness test is conducted to determine the healing time and the effect of the addition of chloroform to the DCPD healing agent. The test is conducted with different ratios of DCPD and chloroform mixture with Grubb’s catalyst. The test is performed on cylindrical samples that are made in holes drilled from an aluminum bar, Figure 16. Different proportions of DCPD, chloroform mixture and Grubb’s catalyst are mixed in the holes to test their hardness. Microhardness test is also conducted for a different configuration, where functionalized MWNTs are added to the DCPD and Grubb’s catalyst. Similar to plain DCPD healing test, the test is performed on cylindrical samples that are made in holes drilled from an aluminum bar. Cylindrical samples have 0.1, 0.3 and 0.5 wt % of norbornene functionalized MWNTs in a DCPD mixture and Grubb’s catalyst. Knoop microhardness values are registered with time to determine the polymerization time and the mechanical property of the polymerized healing agent. MICROMET II Microhardness Tester is used for Knoop microhardness tests, Figure 17.

Figure 16. Mixtures of DCPD mixture and Grubb’s catalyst with different mixing ratios
4.2 Self-healing Test

4.2.1 Single Fiber Polymer Matrix Composite Tensile Test

The work presented in this study provides a foundation for the utilization of self-healing of cracks in fully integrated fiber reinforced polymer composites that are well known for their excellent properties such as tensile strength and modulus. The cracks in this experiment are transverse to the fiber orientation, and these cracks are expected to grow within the composite and cause catastrophic failure unless the healing process is successful. Similarly, the fracture toughness test performed by White et al. [13] and Chen et al. [11] used tensile load perpendicular to the crack plane to study the healing efficiency of the composite. Tensile strength is chosen as the self-healing parameter in this study in order to quantify the crack healing. The test uses four different sets of single fiber polymer matrix composite specimens tested in tension to demonstrate self-healing. They are designated as:

- Resin with undamaged fiber and catalyst (Virgin)
- Resin with undamaged fiber and no catalyst (Undamaged)
- Resin with damaged fiber and no catalyst (Damaged)
- Resin with damaged fiber and catalyst that has healed (Healed)

In each test, six samples of each set of specimen are tested in tension to predict how much of healing can be obtained in the composite. The damaged and undamaged specimens are used as control test set ups. Instron 4301 Tensile Testing Machine is used to test the specimens.

4.2.2 Fiber Reinforced Polymer Matrix Composite Tensile Test

The objective of this study is to establish the efficiency of self-repair in fiber-reinforced polymer composites which have damaged solid and hollow fibers. Since fiber-reinforced polymer composites are well known for their excellent properties such as tensile strength and modulus, autonomic recovery of these properties in damaged structures is highly desirable. Flexural load is applied to generate cracks that are transverse to the orientation of the fibers. These cracks are expected to grow within the composite and cause catastrophic failure unless the healing process retards the crack growth and heals the specimen. The test uses three different sets of fiber-reinforced polymer matrix composite specimens tested in tension to demonstrate self-healing. They are designated as:

- Lamina with undamaged fibers, where hollow fibers are catalyst coated (Virgin)
- Lamina with damaged fibers where hollow fibers are not catalyst coated (Damaged)
- Lamina with damaged fibers, where hollow fibers are catalyst coated (Healed)

In each test, six samples of each type of specimen are tested in tension to predict how much of healing can be obtained in the composite. Tensile testing is performed according to ASTM D 30309/3039M [54]. Instron 4301 Tensile Testing Machine as shown in Figure 18 is used to test specimens in tension and a computer based data acquisition system is used to acquire raw test data from the machine.
4.2.3 Single Fiber Polymer Matrix Nanocomposite Tensile Test

Three different sets of single fiber polymer matrix composites are fabricated and tested in tension to study self-healing. They are designated as

- Resin with undamaged fiber and catalyst (Virgin)
- Resin with damaged fiber and no catalyst (Damaged)
- Resin with damaged fiber and catalyst that has healed (Healed)

The healed specimen has different loadings of functionalized MWNTs. These are pure DCPD and DCPD with 0.1, 0.3 and 0.5 wt % of norbornene functionalized MWNTs dispersed in the mixture. Similar to plain SFPMC and FRPMC tests, six samples of each specimen are tested in tension to evaluate the amount of healing in the composite. Instron 4301 Tensile Testing Machine is used as in the previous test setups where a computer based data acquisition system is used to acquire raw test data from the machine.
CHAPTER 5. RESULTS AND DISCUSSION

Self healing properties in fiber reinforced composites are analyzed in this study. Three different types of self-healing systems are developed. Single fiber polymer matrix composites, fiber reinforced polymer matrix composites and single fiber polymer matrix nanocomposites.

Microhardness tests are conducted and used to understand the effect of solvent and the healing time. The results from microhardness test are further used in the self-healing (tensile) test. The tensile tests are used to determine the extent of healing obtained in the composites. While the healing process is similar in all the three different composite systems, the chemical process of healing differs slightly in the SFPMN specimens.

5.1 Healing Mechanism

When the hollow fiber breaks during damage initiation, the dicyclopentadiene healing agent is observed seeping through the fiber in the area of the crack. It can be observed from Figure 19 that the dicyclopentadiene covers the surfaces of the crack in the matrix as well as the hollow fiber and the debonded region at the interface between the matrix and the fiber. Further observation after a few hours show that the area adjacent to the healed cracked area within the hollow fiber still remains in a liquid form. Figure 20 shows the area that remained in a liquid form adjacent to the healed area demonstrating the attainment of localized healing/polymerization. Localized healing is always preferred as structures can be healed more than once in cases of repeated or multiple cracks using the remaining healing agent.

Figure 19 demonstrates the schematics of the healing process. The figure outlines the general development of healing in a single fiber composite specimen where a crack initiated at the fiber is self-healed due to the timely reaction of the DCPD mixture (DCPD and chloroform) with Grubb’s catalyst on the surface of the fiber.
Figure 19. Schematic of the healing process – a close-up (a) Unbroken/virgin fiber; (b) Initial crack in the fiber; (c) Fiber breaks; (d) Healing agent oozing out of the fiber; (e) Polymerization is initiated; and (f) Healing of the crack in the fiber and matrix.

Figure 20. Polymerization at a single place (Localized Polymerization)

5.2 Chemistry of Self-healing

Self-healing process in polymer composites relies on a suitable chemistry to polymerize the healing agent in the fracture plane. The main requirements of a self-healing system are long shelf life, low monomer viscosity and volatility, rapid polymerization at ambient conditions, and low shrinkage upon polymerization.
A chemistry that meets these requirements remarkably well is the ring opening metathesis polymerisation (ROMP) of monomers, catalyzed by a suitable catalyst. The development of the different self-healing composites presented in this document relies on this ROMP process. In the past few decades, dicyclopentadiene (DCPD) has received significant attention as a monomer for ring-opening metathesis polymerization. Dicyclopentadiene, Figure 21, is an inexpensive monomer that readily undergoes metathesis and is available as a liquid at room temperature. DCPD has low viscosity and flows easily out of its container, yet having low enough volatility to remain in the crack giving tough, highly cross-linked polymer. DCPD also has a long shelf life, owing in part to its relative insusceptibility to radical polymerization [55]. All these properties are critical for successful self-healing. DCPD exists as an endo or an exo-isomer [56]. The study in this paper makes use of endo isomer DCPD which is mostly used in ROMP processes [57-59].

The ROMP cycle in the DCPD requires a catalyst that would open up the strain rings. The catalyst relieves the ‘ring strain’, the driving force of the reaction. Grubbs' catalyst that is compatible with wide range of solvents is commonly used in the polymerization of DCPD monomer. Grubbs' catalyst, Figure 22, is a Ruthenium based transition metal carbene complex and is a relatively stable compound in air, thereby making handling very easy [60, 61].
metathesis process that produces poly(dicyclopentadiene) (polyDCPD), a highly cross-linked polymer of high toughness, Figure 23. Metathesis is a reaction in which two compounds with a similar functional group (usually a double or triple bond) exchange the components on each side of the bond to give new compounds (A-B + C-D → A-D + C-B). ROMP of DCPD is highly exothermic because of the relief of ring strain energy and is initiated by Grubb’s catalyst, [62, 63].

In ROMP, the strained norbornene-like double bond reacts nearly quantitatively, while the second, less strained cyclopentene ring opens on a fraction of the monomers to create a densely cross-linked material that is resistant to fracture. The ROMP process is quite useful
because a regular polymer with a regular amount of double bonds is formed. The resulting product can be subjected to partial or total hydrogenation or can be functionalized into more complex compounds [65].

In SFPMNC, where norbornene functionalized multi-walled carbon nanotubes are dispersed in the healing medium, there are two theories of polymerization of DCPD and funtionlized MWNT’s. The first one is the ‘Grafting to’ approach which states that first propagating linear chains of DCPD encounter the norbornene moiety on the nanotube’s surface and form covalent bonds. The other approach, which is known as the ‘Grafting from’ approach is that the norbornene moiety on the nanotube surface can be initiated by Grubbs’ catalyst resulting in catalyst-functionalized nanotubes, where the front Ruthenium catalyst subsequently reacts with surrounding DCPD to form the nanotube-polyDCPD network. With the combination of these two different mechanisms, covalent bonds between MWNTs and the polyDCPD are formed. These “tethers” between the nanotubes and the cross-linked network lead to improved interfacial stress transfer [46].

5.3 Single Fiber Polymer Matrix Composite

5.3.1 Microhardness

The microhardness test is conducted on three different mixtures of DCPD and Grubb’s catalyst in order to determine the time required for maximum healing and the effect of addition of Chloroform to DCPD. The first mixture tested is a pure DCPD and Grubbb’s catalyst at a ratio of 10:1, the second mixture is a DCPD mixture (DCPD+Chloroform) and Grubb’s catalyst at a ratio of 10:1 and the third is a DCPD mixture (DCPD+Chloroform) and Grubb’s catalyst at a ratio of 25:1 by weight. Average Knoop microhardness results are given in Table 1. The average value is calculated from tests performed at five spots on each specimen.
Table 1. The average value of Knoop Microhardness number for the different composition of the DCPD and Grubb’s catalyst

<table>
<thead>
<tr>
<th>Pure DCPD to Grubb’s catalyst ratio of 10:1 (by weight)</th>
<th>Time</th>
<th>5 min</th>
<th>20 min</th>
<th>1 hr</th>
<th>2 hrs</th>
<th>5 hrs</th>
<th>12 hrs</th>
<th>24 hrs</th>
<th>72 hrs</th>
</tr>
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<tbody>
<tr>
<td>Average Knoop Microhardness</td>
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<tr>
<td></td>
<td>40</td>
<td>61</td>
<td>94</td>
<td>120</td>
<td>154</td>
<td>187</td>
<td>187</td>
<td>187</td>
<td>188</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DCPD Mixture (DCPD and Chloroform) to Grubb’s catalyst ratio of 10:1 (by weight)</th>
<th>Time</th>
<th>5 min</th>
<th>20 min</th>
<th>1 hr</th>
<th>2 hrs</th>
<th>5 hrs</th>
<th>12 hrs</th>
<th>24 hrs</th>
<th>72hrs</th>
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<tbody>
<tr>
<td>Average Knoop Microhardness</td>
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<tr>
<td></td>
<td>36</td>
<td>60</td>
<td>91</td>
<td>121</td>
<td>150</td>
<td>187</td>
<td>188</td>
<td>188</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DCPD Mixture (DCPD and Chloroform) to Grubb’s catalyst ratio of 25:1 (by weight)</th>
<th>Time</th>
<th>5 min</th>
<th>20 min</th>
<th>1 hr</th>
<th>2 hrs</th>
<th>5 hrs</th>
<th>12 hrs</th>
<th>24 hrs</th>
<th>72hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Knoop Microhardness</td>
<td>-</td>
<td>36</td>
<td>73</td>
<td>104</td>
<td>133</td>
<td>144</td>
<td>163</td>
<td>187</td>
<td></td>
</tr>
</tbody>
</table>

The maximum standard deviation in these tests is found to be 1%.

5.3.2 Tensile

Six samples are tested in tension for each specimen type and the average of their tensile strength is obtained. It is observed during the test that, all samples broke into two sections with the fissure near or at the damage zone where healing has taken place, Figure 24. Healing
efficiency, defined as the ratio of a material parameter of the healed to virgin materials, as shown in Equation (3) is computed using the test data.

\[ \eta = \frac{P_h}{P_0} \]  

(3)

where \( P_h \) represents the material property of the ‘healed’ composite material and \( P_0 \) represents that of the ‘virgin’ composite material. The material property can be the tensile or compressive ultimate strength, yield strength, shear strength, fracture strength, deflection, or modulus. Values of healing efficiency can therefore be obtained from experiments performed to determine the material properties mentioned. In this experiment, the tensile strength of the ‘virgin’ and ‘healed’ specimens is the material property investigated.

The tensile test results from all the different specimens of single fiber polymer matrix composites are shown in Table 2 and Figure 25. The experimental results show that a significant portion (90.7%) of the tensile strength is restored due to the self-healing efficiency of the single fiber polymer matrix composite. The results indicate that structures can retain significant portion of their strength after healing and thus allow for more efficient use. The results from the tests carried out on the single fiber composite specimens with different configurations confirm that self-healing is clearly achieved. The configurations of undamaged specimens with and without catalyst show similar results, 38.2MPa and 37.9MPa tensile strength, respectively. Both specimens have unbroken and undamaged fibers. The strength of the specimen with a catalyst is slightly higher, but the difference from the specimen without catalyst is within experimental error as indicated by the standard deviation shown in Table 2. This result also proves that the catalyst does not have any deteriorating effect on the fiber-matrix interface. It should however be noted that, it is the virgin strength that is used to compute the healing efficiency of the damaged and healed specimens, not the undamaged specimen strength.
The damaged specimen is the sample that has achieved minimal or no healing. It has a broken fiber and adjacent damage zone. This specimen damaged by a flexural loading is equivalent to a single specimen with two equal size fibers extending from the middle to both ends. This damaged specimen does not represent a totally broken piece with two separate sections. The damaged specimen is found to have a tensile strength of 26.9 MPa. This value is 30% lower than the strength of the virgin specimen. The remaining strength in the damaged specimen is obtained because of the matrix strength as well as due to the stress transfer between the matrix and the two broken parts of the fiber. Unlike the damaged specimen, the healed specimen has a tensile strength of 34.6 MPa which is only 9.3% lower than the strength of the virgin specimen. In other words, the healed specimen has achieved a 90.7% healing efficiency.

The healed specimens are tested 12 hours after going through initial damage that causes the bleeding of the healing agent. This is in accordance to the test results of the microhardness test that clearly showed that maximum healing or maximum mechanical property is attained at least 12 hours after the sample is damaged and let heal.
Table 2. Average tensile strength, standard deviation and healing efficiency for the single damage/single healing of SFPMC specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>Healing Efficiency, $\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>38.2</td>
<td>0.45</td>
<td>100</td>
</tr>
<tr>
<td>Undamaged</td>
<td>37.9</td>
<td>0.44</td>
<td>99.2</td>
</tr>
<tr>
<td>Damaged</td>
<td>26.9</td>
<td>0.81</td>
<td>70.5</td>
</tr>
<tr>
<td>Healed</td>
<td>34.6</td>
<td>0.6</td>
<td>90.7</td>
</tr>
</tbody>
</table>

Figure 25. The stress versus strain diagram of the single damage SFPMC specimens

The self-healing efficiency (90.7%) obtained from the test is substantial; however the damage on the specimens is only at a single place. Multiple damages may occur on structures and therefore the self-healing efficiency has to be determined for cases when several cracks occur. Thus a test is conducted on single fiber polymer composite specimens that are damaged.
at two places. A similar process of fabrication and testing is followed as in for a single damage specimen. However, there is no need to test undamaged samples with multiple breaks because the previous (single damage) test has already confirmed that the Grubb’s catalyst has no detrimental effect on the mechanical property of the composite. The tensile test results for the multiple damages test are shown in Table 3 and Figure 26.

The healed specimens that are broken at two locations (at one third of the fiber length from both ends) have recovered 80.4% of the virgin strength. In comparison with the result from the previous test (single damage), the tensile strength of the healed specimen (with multiple damages) is lower than that of the healed specimen (with single damage). This is expected as each damage does not completely heal and therefore contributes to the larger reduction in strength for multiple damages. However, it should still be considered that significant self-healing has been achieved since the damaged specimen with no healing agent has only a tensile strength of 21.7MPa, i.e., 56.8% of the virgin specimen’s strength. This value is not small as compared to the 27.8MPa for the healed specimen, i.e., equivalent to 80.4% of the virgin specimen’s strength.

Table 3. Average tensile strength, standard deviation and healing efficiency for the multiple damage/multiple healing of SPMC specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>Healing Efficiency, $\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>38.2</td>
<td>0.45</td>
<td>100</td>
</tr>
<tr>
<td>Damaged</td>
<td>21.7</td>
<td>0.93</td>
<td>56.8</td>
</tr>
<tr>
<td>Healed</td>
<td>27.8</td>
<td>0.68</td>
<td>80.4</td>
</tr>
</tbody>
</table>
Figure 26. The stress versus strain diagram of the multiple damage SFPMC specimens

5.4 Fiber Reinforced Polymer Matrix Composite

Six samples are tested in tension for each specimen type in all tests and the average of their tensile strength is calculated. Healing efficiency, defined as the ratio of a material parameter of the healed specimen to the virgin specimen, as defined previously in Equation (3) is computed using the test data. In computing the healing efficiency of the FRPMC specimens, the material property can be the tensile or compressive ultimate strength, yield strength, shear strength, fracture strength, deflection, or modulus as previously stated in SFPMC testing. Values of healing efficiency can therefore be obtained from experiments that can determine the different material properties. In this experiment, the tensile strengths of the ‘virgin’, ‘damaged’ and ‘healed’ specimens are the material properties used to determine the healing efficiency.

The tensile test results of all the different specimens of fiber-reinforced polymer matrix composites are shown in Table 4 and Figure 27. The experimental results demonstrate that a considerable portion (76.55%) of the tensile strength is restored due to the self-healing ability of
the fiber-reinforced polymer matrix composite. The standard deviation is calculated for the six samples in each type of specimen tested and is within 1% deviation from the average strength. The results indicate that the specimens can retain significant portion of their strength after healing. Self-healing is achieved in the composites suggesting the idea that structures made of these materials are damage tolerant that allow for more efficient use.

Table 4. Average tensile strength, standard deviation and healing efficiency of FRPMC specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>Healing Efficiency, η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>264.1</td>
<td>2.58</td>
<td>100</td>
</tr>
<tr>
<td>Damaged</td>
<td>171.7</td>
<td>1.12</td>
<td>65.01</td>
</tr>
<tr>
<td>Healed</td>
<td>202.16</td>
<td>1.93</td>
<td>76.55</td>
</tr>
</tbody>
</table>

Figure 27. The stress versus strain diagram of FRPMC specimens
Similar to SFPMC, the damaged specimen is the sample that has achieved minimal or no healing. It has broken hollow and solid fibers and an adjacent matrix damage zone. This specimen, with in-situ damaged solid fibers and flexurally damaged hollow fibers, is equivalent to specimen with fibers extending from the middle to opposite ends. This damaged specimen does not represent a completely broken piece with two separate sections. The damaged specimen is found to have a tensile strength of 171.7 MPa. This value is 35% lower than the strength of the virgin specimen. The remaining strength in the damaged specimen is obtained because of the matrix strength as well as due to the stress transfer between the matrix and the broken hollow and solid fibers. The healed specimen has a tensile strength of 202.16 MPa which is 18% increment of strength from the damaged specimen. The self-healed specimen has achieved a 76.55% healing efficiency. The healed specimens are tested 12 hours after going through initial damage causing the bleeding of the healing agent in accordance with the results from SFPMC tests. It can be observed from Figure 28, that failure in all samples begins at the mid-length of the specimen, where healing occurs and propagates throughout the specimen.

Figure 28. Healed specimen after going through tensile test
5.5 Single Fiber Polymer Matrix Nanocomposite

5.5.1 Microhardness

Microhardness test is conducted in order to determine the time required for maximum healing and the hardness behavior of functionalized MWNT dispersed DCPD mixture. The microhardness test is conducted on four different samples of functionalized MWNTs, DCPD mixture and Grubb’s catalyst. The first sample is a pure DCPD mixture (DCPD and chloroform) with excess Grubb’s catalyst while the rest have 0.1, 0.3 and 0.5 wt % norbornene MWNT added to the DCPD mixture and excess Grubb’s catalyst. Average Knoop microhardness results are shown in Table 5.

It is observed from Table 5 that the highest value of hardness is found for the sample with the highest concentration of functionalized MWNT, 0.5wt% and is 195. From Table 5, it can be also observed that the highest hardness values are obtained after 12 hours for the samples with 0.1, 0.3 and 0.5 wt% functionalized MWNT. Thus any additional time does not provide any advantage to the healing process as shown by the microhardness value at 24 hrs. Therefore, it is concluded to run the self-healing test after 12 hours.

The results also show that the higher the functionalized MWNTs used, the higher the hardness value gets. Table 5 indicates that the addition of norbornene functionalized MWNTs enhanced the hardness value of the polymerized healing agent. It can also be observed from the table that the difference between the hardness values after 5 minutes and after 12 hours is smaller for higher loadings of functionalized MWNTs than the lower loadings.

5.5.2 Tensile

Six samples are tested in tension for each specimen type and the average of their tensile strength is calculated. The tensile test results of all the different specimens of single fiber
polymer matrix composites are shown in Table 6 and Figure 29. It can be observed from Table 2 and Figure 28, that a significant portion (92.6%) of the tensile strength is restored due to the self-healing process. The results indicate that structures can retain their significant portion of their strength after healing and thus allow for more efficient use.

Table 5. The average value of Knoop Microhardness number for the different composition of DCPD and MWNT’s with Grubb’s catalyst

<table>
<thead>
<tr>
<th>Time</th>
<th>5 min</th>
<th>15 min</th>
<th>30 min</th>
<th>1 hr</th>
<th>2 hrs</th>
<th>12 hrs</th>
<th>24 hrs</th>
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<tr>
<td>Pure DCPD Mixture</td>
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<td></td>
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<tr>
<td>Average Knoop Microhardness</td>
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<td>174</td>
<td>179</td>
<td>182</td>
<td>185</td>
<td>187</td>
<td>187</td>
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</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>5 min</th>
<th>20 min</th>
<th>1 hr</th>
<th>2 hrs</th>
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<tr>
<td>0.1 wt % Norbornene MWNT added to DCPD Mixture</td>
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<tr>
<td>Average Knoop Microhardness</td>
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<table>
<thead>
<tr>
<th>Time</th>
<th>5 min</th>
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<tr>
<td>0.3 wt % Norbornene MWNT added to DCPD Mixture</td>
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<tr>
<td>Average Knoop Microhardness</td>
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<table>
<thead>
<tr>
<th>Time</th>
<th>5 min</th>
<th>20 min</th>
<th>1 hr</th>
<th>2 hrs</th>
<th>5 hrs</th>
<th>12 hrs</th>
<th>24 hrs</th>
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<tr>
<td>0.5 wt % Norbornene MWNT added to DCPD Mixture</td>
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<td></td>
</tr>
<tr>
<td>Average Knoop Microhardness</td>
<td>183</td>
<td>187</td>
<td>190</td>
<td>191</td>
<td>193</td>
<td>195</td>
<td>195</td>
</tr>
</tbody>
</table>
Table 6. Average tensile strength, standard deviation and healing efficiency of SFPMN specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tensile Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>Healing Efficiency, $\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>38.2</td>
<td>0.45</td>
<td>100</td>
</tr>
<tr>
<td>Damaged</td>
<td>26.9</td>
<td>0.81</td>
<td>70.4</td>
</tr>
<tr>
<td>Healed (Pure DCPD)</td>
<td>34.6</td>
<td>0.6</td>
<td>90.6</td>
</tr>
<tr>
<td>Healed (0.1%wt MWNT)</td>
<td>35</td>
<td>0.38</td>
<td>91.6</td>
</tr>
<tr>
<td>Healed (0.3%wt MWNT)</td>
<td>35.2</td>
<td>0.41</td>
<td>92.1</td>
</tr>
<tr>
<td>Healed (0.5%wt MWNT)</td>
<td>35.4</td>
<td>0.48</td>
<td>92.6</td>
</tr>
</tbody>
</table>

Figure 29. The stress versus strain diagram of SFPMN specimens
The results from the tests carried out on the single fiber composite specimens with different configurations confirm that self-healing is clearly achieved. The virgin sample is found to have a tensile strength of 38.2 MPa. The norbornene functionalized MWNT added to the DCPD healing agent has enhanced the self-healing efficiency as compared to specimens without MWNTs. Pure DCPD has 90.6% healing efficiency whereas 0.5 wt% MWNT has 92.6% healing efficiency.

Similar to SFMPC and FRPMC, the damaged specimen is the one that has achieved minimal or no healing. The single fiber specimen after being damaged by three-point loading is equivalent to a specimen with two equal size fibers extending from the middle to each end of the specimen. However, the specimen is not completely broken. The damaged specimen can be assumed to have healed an insignificant amount based on a few minutes it takes for setting up the specimen on the Instron machine to carry out the tensile test. Looking at the microhardness values from Table 5, this is a valid assumption because it takes approximately 5 minutes for the tensile test set up for each specimen. The damaged specimen is found to have a tensile strength of 26.9 MPa. This value is 30% lower than the virgin specimen. The remaining strength in the damaged specimen is obtained because of the matrix strength or the small amount of healing that may take place during tensile test set up as well as due to the stress transfer between the matrix and the two broken parts of the fiber.

The healed specimen for pure DCPD has a 90.6% healing efficiency, i.e., it has retained 34.6 MPa strength of the virgin specimen. Healing efficiency increases as the functionalized MWNT loading increases in the specimen reaching a high 92.6% value for the specimen with 0.5 wt% loading. The 0.1% and 0.3 % wt% loadings of functionalized MWNT have also shown healing efficiency values of 91.6% and 92.1% respectively. All the healed specimens are tested
12 hours after flexural loading that extended the initial surface scratch/crack on the surface of the hollow fiber and release of the healing agent. If there is no healing taking place during any of these tests, it can be considered that the final specimen will be broken and obviously end up with no or zero strength.

5.6 Fiber Reinforced Polymer Matrix Composite Optical Microscopy

Analysis of damage within fiber-reinforced composites is a complicated task because the actual damage event is not easily detectable. In this study, optical microscope images of the top surface of the specimen are taken to help understand the healing process. Figure 30a shows the virgin sample with hollow fibers that are not damaged. When the hollow fiber breaks during damage initiation, the dicyclopentadiene healing agent is observed seeping through the fiber in the area of the crack. It can be observed from Figure 30b that the dicyclopentadiene covers the surfaces of the crack in the matrix as well as the hollow and solid fibers and the debonded region at the interface between the matrix and the fibers. Figure 30c shows the dicyclopentadiene starting polymerization when it contacts the catalyst. Finally, the dicyclopentadiene is fully polymerized in the damage zone, bonding the crack plane as depicted in Figure 30d.
Figure 30. Optical images of multiple fiber healing, (a) Hollow fiber not damaged, (b) Fiber breaks releasing healing agent in the damage zone, (c) Healing agent starts to polymerize when it contacts the pre-coated catalyst, (d) Fully polymerized healing agent bonding crack plane.
CHAPTER 6. CONCLUSIONS

The self-healing composite material developed in this study is fiber-reinforced polymer matrix composite. The study has three major categories of self-healing composite systems. Single fiber polymer matrix composites, fiber reinforced polymer matrix composites and single fiber polymer matrix nanocomposites. All the three composites are organized in a different manner showing different healing efficiencies accordingly.

6.1 Self-healing in Single Fiber Polymer Matrix Composites

The SFPMC experiments show that self-healing is achieved in a single fiber polymer matrix composite with high (90.7%) degree of restoration of the original tensile strength. The self-healing composite includes a healing agent, a catalyst, a hollow fiber, and resin. The catalyst is placed on the outer surface of the hollow fiber to avoid untimely polymerization. When the hollow fiber breaks due to the propagation of cracks, the healing agent, a DCPD mixture (DCPD and chloroform) is released. The healing agent then fills the gap in the fiber and matrix damage zone. Healing of the crack takes place after the healing agent polymerizes when it comes in contact with the Grubb’s catalyst on the surface of the fiber. Other configurations of the single fiber polymer matrix composite are also tested in order to characterize the effect of the catalyst and damage on the composite. The catalyst is found to have no deteriorating effect on the fiber-matrix interface. Unhealed or damaged specimen that contains a broken fiber with no healing has produced a much lower tensile strength. The presence of the healing agent, a DCPD mixture, the Grubb’s catalyst, and their appropriate placement in a single fiber polymer composite confirms the possibility of self-healing in fully integrated structural fiber reinforced composites with a DCPD mixture. When the specimen is subjected to damage at two places, a healing efficiency of 80.4% is obtained, showing that multiple damages as well can be healed.
significantly. Localized healing is achieved allowing the remaining healing agent to remain in a liquid form for further healing of cracks.

6.2 Self-healing in Fiber Reinforced Polymer Matrix Composites

In FRPMC, the experiments show that self-healing is achieved with considerable (76.55%) degree of restoration of the original tensile strength of the composite. The self-healing composite includes a healing agent, a catalyst, hollow glass fibers, e-glass solid fibers and resin. The hollow and solid glass fibers are stacked sequentially within the resin. Unhealed or damaged specimen that contains broken fibers with no healing has produced a much lower tensile strength. The presence of the healing agent, a DCPD mixture, Grubb’s catalyst, and their appropriate placement in fiber-reinforced polymer composite confirms the possibility of self-healing in fully integrated structural fiber reinforced composites with a DCPD mixture. Structures designed out of these materials have the potential of transcending the conventional damage tolerant structures.

6.3 Self-healing in Single Fiber Polymer Matrix Nanocomposite

In SFPMN, the effect of functionalized carbon nanotubes on the self-healing behavior of single fiber polymer matrix composites is studied. The experiments show that self-healing is achieved in a single fiber test with high (92.6%) degree of restoration of the original tensile strength. The self-healing composite includes a healing agent, a catalyst, a hollow fiber, resin and norbornene functionalized MWNT. The composite system is similar to the SFPMC except the addition of the functionalized MWNT in the healing agent. When the hollow fiber breaks due to the propagation of cracks, the healing agent (DCPD and norbornene functionalized MWNT) is released and fills the gap in the fiber and matrix crack volume providing a better polymerization. It is found that norbornene functionalized MWNTs can be dispersed in a liquid
DCPD and enhances the healing efficiency of the composite. Contrary to the damaged specimen, the presence of the healing agent with MWNTs, a DCPD mixture, the Grubbs’s catalyst, and their appropriate placement confirms the ability of self-healing in fiber reinforced composites with a DCPD mixture.

6.4 Future Works

The study presented in this document clearly demonstrates that self-healing fiber-reinforced polymer composites can be produced. Addition of functionalized carbon nanotubes also helps boost the healing efficiency of single fiber polymer composites. These experimental results should be confirmed through analytical and finite element modeling of the system. Therefore, modeling will be part of the future work.

The study paves the way for the development of a fully integrated fiber-reinforced composite laminate. Since self-healing is achieved in a single layer that contains stacks of hollow and solid glass fibers, the development of laminate composites should encompass the newly developed functionalized MWNT dispersed healing agent and catalyst coated hollow glass fibers alongside the conventional fiber-resin technology.
REFERENCES


VITA

Nebiyu Fikru was born in Addis Ababa, Ethiopia, in the year 1979. He graduated high school in 1997 from St. Joseph School, Addis Ababa, Ethiopia. His interest in mechanical systems and proclivity towards mechanics led him to join Mechanical Engineering Department at Addis Ababa University, Faculty of Technology, and earned a Bachelor of Science Degree in Mechanical Engineering in the year 2003. After graduation, he worked in a structural engineering company for four years in Addis Ababa, Ethiopia. He then decided to pursue higher education in the United States of America and enrolled in the master’s program at Louisiana State University, Baton Rouge, in fall 2007. He will be graduating in August 2009 with Master of Science Degree in Mechanical Engineering.