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Introduction

Driven by the need for lighter and stronger engineering structures, fiber reinforced polymer composite materials have emerged as a new class of engineering materials for load bearing structures. From the sky to under the sea, from household products to infrastructure, from transportation vehicles to energy production, fiber reinforced polymer composites are gradually finding their way to replace traditional materials such as metal, concrete, wood, etc. This is due to the high specific strength, stiffness, and corrosion resistance of fiber reinforced polymer composites. Another advantage exists in its tailorability. Its anisotropic nature makes it work on demand, that is, optimize a design by aligning fibers along the direction that needs the highest strength and stiffness. Among the various types of fiber reinforced polymer composites, thermosetting polymer composites predominate. This is because thermosetting polymer composites are easy to manufacture using various techniques, such as resin transfer molding (RTM), vacuum assisted resin infusion molding (VARIM), filament winding, pultrusion, prepreg, or simply hand lay-up. Also, thermosetting polymer composites have better thermal and dimensional stability. However, thermosetting polymers are generally brittle and vulnerable to certain loadings, such as impact loading. Under impact loading, even under low velocity impact, severe damage such as macroscopic cracking may occur inside the composite structures, making repair a challenging task. In other words, there is an urgent need for thermosetting polymers to have self-healing capabilities. In this introductory chapter, we will briefly discuss thermosetting polymers. We will then illustrate typical fiber reinforced composite structures that use thermosetting polymer as the matrix. Then our focus will be on reviewing typical failure modes in thermosetting polymer composite structures under low velocity impact, followed by brief discussions on the repair strategies currently used in industry. Classification of self-healing systems will be the focus of the next section. Finally, we will present the organization of this book.

1.1 Thermosetting Polymers

It is well known that thermoset polymers such as epoxy, vinyl ester, polyester, phenolic, etc., are chemically or physically cross-linked polymers (chemical bonds between polymer chains, intermolecular van der Waals bonds, dipole–dipole interactions, and molecular entanglement). These cross-links serve as molecular anchorages, which prevent molecular motion of the

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polymer chains. This is how a thermoset obtains its strength, stiffness, and thermal stability and why it behaves in a brittle manner under mechanical loading. Once one chain factures, the force is transferred to its neighbors through the cross-linked network, leading to crazing, cracking, and ultimate macroscopic fracture at a relatively small strain.

Like any polymer, the physical/mechanical properties of thermosetting polymers depend on loading time (rate) and temperature. Owing to the cross-linked nature, thermosetting polymers are generally difficult to form into crystals because the cross-links prevent segments from motion and folding into lamella or spherulite. In other words, most thermosetting polymers are amorphous. Similar to thermoplastic polymers, amorphous thermosetting polymers show distinctively different behaviors at different temperatures. At temperatures below the so-called glass transition temperature (T_g), the network structure is frozen. The mobility of the segments is very low. Under external loading, stretching and rotation of the chemical bonds is the dominant deformation mode, and thus the polymer is rigid and very brittle. When the temperature is increased to the glass transition zone, we see drastic change in the mechanical properties. The stiffness may show one to two orders of decrease within a small temperature window. In this temperature range, the frozen molecules are gradually defrosted and their mobility increases dramatically so that the molecules can deform easily along the direction of loading. As a result, under the same load, the deformation in the glass transition region is significantly higher than that below T_g, leading to a considerable reduction in stiffness. Also, within this region, the viscous deformation (time dependent deformation) under dynamic loading absorbs a significant amount of energy. The deformation shows a delayed response to the dynamic loading, leading to viscoelastic behavior and vibration damping. When the temperature is above the glass transition zone, the polymer is rubbery but does not melt. Due to the cross-links, however, the ductility of the polymer is still comparatively small, even in the rubbery status. A further increase in temperature may result in decomposition and burning of the polymer. This shows a distinctive departure from thermoplastic, which becomes liquid and flows above the melting temperature and can be remolded.

The glass transition of thermosetting polymers can be explained by the free volume theory [1]. The volume in polymers consists of three parts – occupied volume, interstitial free volume, and hole free volume. The occupied volume does not change with temperature. The interstitial free volume may change linearly with temperature as it reflects the change in the interatomic distance. The hole free volume increases nonlinearly with temperature. When the temperature is increased to the glass transition region, the frozen hole free volume expands significantly, giving a free space for segmental motion of the cross-linked molecules. In other words, the mobility of the molecules increases drastically and large coordinated motion of the segments along the loading direction becomes possible. The significant increase in deformation leads to a dramatic reduction in stiffness. This is exactly what we see in the glass transition region.

Thermosetting polymers usually consist of two parts, the liquid resin and curing agent. Before mixing together, these two parts can be safely stored for months or years. When they are mixed together, the polymerization process starts, which is generally exothermic. Before it is cured into a solid, there is a time window from minutes to hours for us to work on it, such as using resin transfer molding to wet through the fibers in order to form a fiber reinforced polymer composite. The working window can be adjusted by controlling the amount of curing agent and the curing temperature. Clearly, reducing the amount of curing agent or lowering the curing temperature increases the time period before the resin hardens.

While thermoplastic polymers can also find applications in load bearing structures, particularly for thermoplastic polymers that have very high melting temperatures, thermosetting polymers have dominated the application in load bearing, fiber reinforced polymer composite structures. Therefore, this book will focus on thermosetting polymer composites.

1.2 Thermosetting Polymer Composites in Structure Applications

In recent years, advanced lightweight materials have become a technological and economic driver for societies. For example, advanced lightweight materials are essential for reducing vehicle weight to boost fuel economy of modern automobiles, while maintaining safety and performance. Replacing cast iron and traditional steel components with lightweight materials such as polymer composites allows vehicles to carry advanced emission-control equipment, safety devices, and integrated electronic systems, without an associated weight penalty. Using lighter materials also reduces fuel consumption of vehicles because it takes less energy to accelerate or decelerate a lighter object [2]. Another typical example is in the aviation industry. In the Dreamliner Boeing 787, it is estimated that about 50% of the materials used was carbon fiber reinforced polymer composites. In fact, fiber reinforced thermosetting polymer composites have been widely used in almost all man-made structures, particularly in high tech and high value structures, including, but not limited to, aerospace (fixed wing aircrafts, helicopters, etc.), defense (tank, armor, etc.), energy production, storage, and transportation (wind turbine blade, pipe, on-board and off-board storage tanks for natural gas or hydrogen, etc.), vehicles (car, truck, train, etc.), electrical and electronic (rods, tubes, molded parts, electrical housings, etc.), construction (bathtubs, decks, swimming pools, utility poles, bridge decks, railings, and repair, rehabilitation, reinforcement, and reconstruction of concrete structures, etc.), marine (ship hulls, decks, bulkheads, railings, offshore oil platforms, etc.), and consumer products (golf clubs, bicycles, fishing rods, skis, tennis rackets, snowmobiles, mobile campers, etc.).

The highly cross-linked nature provides thermosetting polymers with high strength, high stiffness, high thermal stability, and good chemical resistance. The trade-off for this gain in mechanical strength is a loss in toughness and ductility, and they are prone to developing microcracks under external loading such as cyclic fatigue loading. Because microcracks are not easily detectable, the propagation and coalescence of microcracks result in macrocracks and ultimate structural failure. For some types of loading such as impact loading, cracks may be created on a macroscopic scale, leading to imminent structural failure if immediate care is not taken. Owing to various types of loadings, such as fatigue, impact, vibration, creep, earthquake, hurricane, etc., and environmental conditioning, such as corrosion, hygrothermal effects, ultraviolet radiation, fire, etc., no engineering structures last forever. Therefore, self-healing is a highly desired feature for engineering structures in general and for fiber reinforced thermosetting polymer composites in particular.

1.3 Damage in Fiber Reinforced Thermosetting Polymer Composite Structures

Fiber reinforced thermosetting polymer composites have been used in the form of laminate, sandwich, grid stiffened, stitched, Z-pinned, three-dimensional (3-D) woven fabric, and hybrid structures. In addition to carrying the designed static/dynamic loads, most composite structures experience some kind of low or high velocity impact incidents during their life cycle. A low velocity impact is not uncommon. For example, dropping a tool on to a composite structure during a routine inspection characterizes a low velocity impact incident, not to mention incidents during manufacturing, transportation, installation, and service. For armor-grade composite structures, a low to high strain rate impact or blast is the primary criterion in structural design. Although both low and high velocity impacts are of concern, a low velocity impact is more dangerous because it is often missed by visual inspection. For example, after a low velocity impact on a laminated composite, only a barely visible indentation may be identified on the impacted surface. However, significant damage may have been induced inside the laminate and on the back surface, which cannot be detected with the naked eye. As a result of the damage, the residual load carrying capacity of the structure may be considerably reduced, leading to premature and catastrophic structural failure. Therefore, low velocity impact is the focus of this section.

Low velocity impact on composite structures (laminated, sandwich, grid stiffened, 3-D woven fabric reinforced) has been a topic of research interest for years all over the world. Many researchers have experimentally and theoretically investigated the low velocity impact response and residual strength of composite structures, including instrumented low velocity impact testing, analytical modeling based on the modified Hertz contact law or conservation of energy, and finite element modeling using commercial software packages like LS-DYNA. There is no shortage of literature in this research area. These studies have greatly enhanced understanding of impact behavior, damage, the energy dissipation mechanism, and residual structural performance. As a result, more and more impact tolerance/resistance composite structures are being designed and manufactured with confidence.

1.3.1 Damage in Laminated Composites

A low velocity impact induces various types of damage in fiber reinforced laminated composite structures. In addition to the visible or barely visible indentation on the impacted surface and cracking on the back surface, the most prevalent damage inside a laminated composite includes delamination, matrix cracking, fiber/matrix interfacial debonding, and fiber fracture (see Figure 1.1) [3].

After a low/high velocity impact, the residual load carrying capacity, particularly the in-plane load carrying capacity, reduces drastically. Figure 1.2 shows a laminated composite beam during an in-plane compression test after being impacted by a projectile with a mass of 7.45 g at a velocity of 390 m/s. It is clear that the damaged laminate shows global buckling and local buckling of the delaminated sublaminate. Because of the buckling, the compressive strength of the damaged laminate is reduced to below 50% of the undamaged control laminate.

1.3.2 Damage in Sandwich Composites

Catastrophic structure failure due to impact has been well documented in the literature; a well-known incident is the loss of the Space Shuttle *Columbia* [4]. A fiber reinforced polymer composite sandwich, while optimal for carrying a transverse load with a minimal weight penalty, is also vulnerable to impact damage [5–11]. Typical damage modes include indentation, face sheet cracking, core fracture, face sheet/core interfacial debonding, etc. In a sandwich construction, the two face sheets are responsible for carrying the transverse load and in-plane load, while the sandwich core is primarily responsible for fixing the skin and absorbing impact energy. Therefore, the key is to improve the core design in order to enhance impact tolerance of the sandwich. Various types of core materials have been studied such as foam core (polymeric

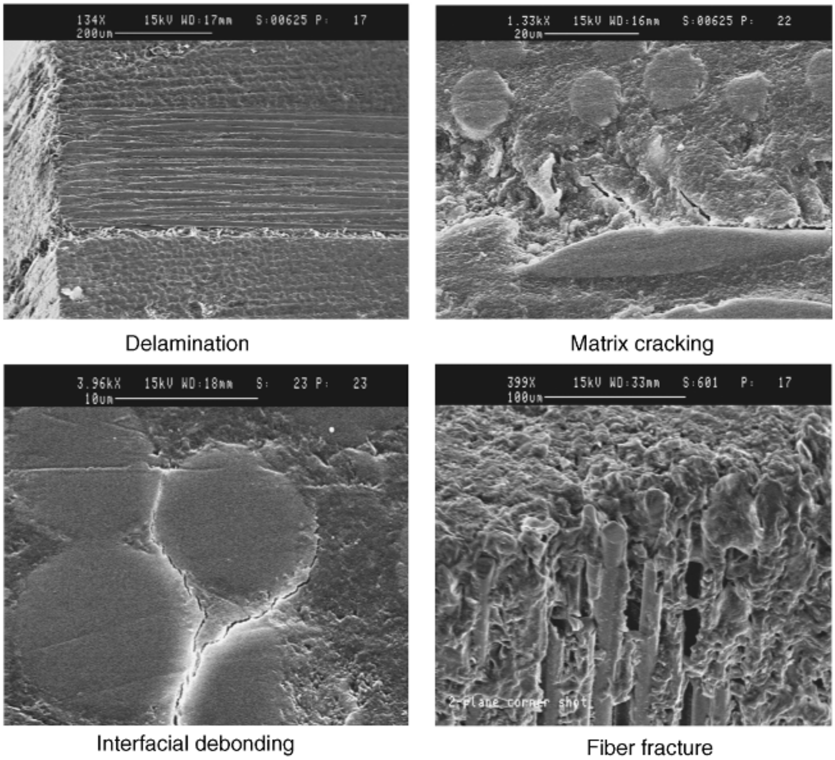

Figure 1.1 Low velocity impact damages inside a laminate. *Source:* [3] Reproduced with permission from Elsevier

Figure 1.2 Mixed global and local buckling of a laminate after a moderate velocity impact.

Figure 1.3 Low velocity impact induced indentation on the sandwich skin

foam, metallic foam, ceramic foam, balsa wood, syntactic foam, etc.) [12,13], web core (truss, honeycomb, etc.) [14], 3-D integrated core [10], foam filled web core [15], laminated composite reinforced core [9], etc. While these core materials have been used with a certain amount of success, they are limited in one way or another. For example, brittle syntactic foam cores absorb impact energy primarily through macroscopic damage, significantly sacrificing residual strength [16–20], and web cores lack bonding with the skin and also have an internal open space for easy perforation by a projectile (impact windows) [16].

Figure 1.3 shows the indentation on a sandwich beam and Figure 1.4 shows top skin delamination after a low velocity impact by a DynaTup 8250HV machine with a hammer weight of 33 kg and velocity of 3.83 m/s, which translates to an impact energy of 242 J. The tup nose has a semispherical shape with a diameter of 12.7 mm. The sandwich beam has a carbon

Figure 1.4 Low velocity impact induced delamination, debonding, and shear fracture in the laminated skin and balsa wood core

fiber reinforced epoxy skin with a thickness of 2.54 mm and a balsa wood core with a thickness of 60.0 mm. During impact, the sandwich beam of 50.8 mm wide and 254.0 mm long was simply supported and the impact was at the center of the beam on the top skin. While only a visible indentation is seen on the top skin in Figure 1.3, Figure 1.4 shows significant delamination in the top skin, debonding between the top skin and the balsa wood core, as well as shear fracture at the core. Therefore, even under a low velocity impact, damage within the sandwich beam is dramatic and urgent repair is needed.

1.3.3 Damage in 3-D Woven Fabric Reinforced Composites

Delamination has been a major form of damage on a laminated composite. Therefore, enhancement in the thickness direction through stitching, Z-pinning, etc., has been widely used in laminated structures. Along the same lines is polymeric composite material reinforced with three-dimensional (3-D) fabric architecture, which has good impact tolerance [21–25]. Polymeric composite reinforced with 3-D woven fabric is an attractive candidate for use in weight sensitive industries such as aerospace, auto, and maritime where, in addition to carrying static and cyclic loads, structural components are expected to perform well under impact.

A number of studies has been conducted to understand the impact response of 3-D woven composites [26–33]. Recently, Baucom, Zikry, and Rajendran [34] investigated the effects of fabric architecture on damage propagation, perforation resistance, strength, and failure mechanisms in composite systems of comparable areal densities and fiber volume fractions, subjected to repeated impact. They found that 3-D systems survived more strikes before being perforated and absorbed more total energy compared to other systems. They reported transverse matrix cracking, fiber debonding from the matrix, fiber fracture, and fracture of *Z* direction fiber tows as failure modes in the 3-D systems. Most recent developments in the area of 3-D woven fabric composites include modeling the impact penetration of 3-D woven composite at the unit cell level [35], studying the transverse impact damage and energy absorption [36], investigating the compressive responses and energy absorption [37], and studying the effect of Z-yarns on the stiffness and strength [38]. While 3-D woven fabric reinforced composite has demonstrated considerable enhancement in terms of impact tolerance, it is still vulnerable to impact damage, in particular under repeated impact incidents. It is desired to add self-healing capacities to 3-D woven composites to further increase their impact tolerance and service life.

In order to demonstrate the damage mode in 3-D woven fabric reinforced polymer composite, a repeated impact test was conducted on a 3-D woven glass fabric reinforced thermosetting shape memory polymer composite foam [39]. The impact was conducted by the same DynaTup 8250HV impact machine with a hammer weight of 6.44 kg and velocity of 3.0 m/s. Figure 1.5 shows perforation of the 3-D woven fabric reinforced polymer composite and Figure 1.6 shows fracture of the reinforcing fiber tows, both after the ninth impact [39].

As compared to laminated composite, there is no doubt that the impact tolerance of the 3-D woven fabric reinforced polymer composite has been enhanced dramatically due to the 3-D network structure and the improved transverse shear resistance. However, it is clear that even repeated low velocity impact can cause significant damage. Therefore, like laminated composite and sandwich composite, 3-D woven fabric reinforced polymer composite also calls for self-healing capabilities.

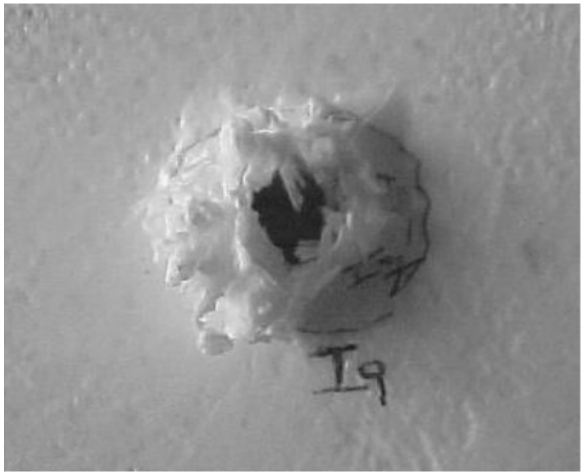

Figure 1.5 Perforation in a 3-D woven fabric reinforced polymer composite after repeated low velocity impact. *Source:* [39] Reproduced with permission from IOP Publishing

1.3.4 Damage in Grid Stiffened Composites

A basic grid structure is a latticework of rigid, interconnecting beams in two, three, or four groups and directions [40,41]. Figure 1.7 demonstrates an orthogrid structure and the terminology used to describe it. Nodes, ribs, beams, and cells are the grid structural elements. *Nodes* are the crossover points, *ribs* are the linear segments that span adjacent nodes, and *beams* are a collection of aligned ribs and nodes. *Cells* or *bays* are the spaces enclosed between ribs. Structurally related terms are center-to-center, in-plane, and out-of-plane.

Figure 1.6 Fracture of fiber tows after repeated low velocity impact. *Source:* [39] Reproduced with permission from IOP Publishing

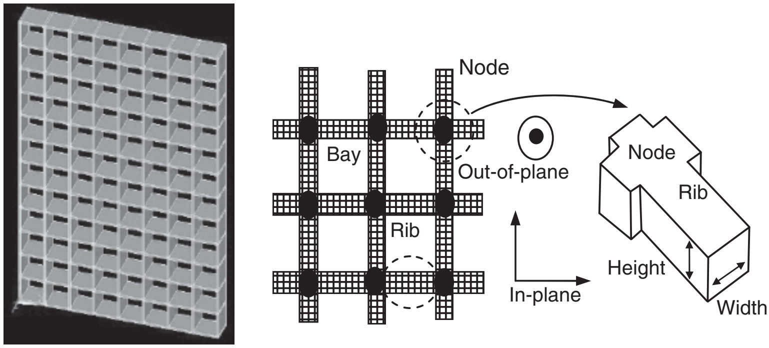

Figure 1.7 Schematic of an orthogrid.

Center-to-center indicates the distance between the centers of adjacent parallel beams. *In-plane* actions take place within the plane of the grid. *Out-of-plane* actions occur orthogonally or transversely to the plane of the grid. Element-level terms describe the rib cross-sectional dimensions where width is an in-plane measurement and depth (thickness) is out-of-plane.

The displayed grid segment in Figure 1.7 consists of beams placed in a bidirectional pattern, giving rise to the reference term *bi-grid* [41]. A special case of the bi-grid is one in which the beams intersect orthogonally with equal spacing. In this configuration, there are two identical mechanical directions and the term orthogrid is applied. Tri-grids are formed with three beam groups and directions [41]. A special case of tri-grids is the isogrid. The isogrid has three identical mechanical directions through the uniform distribution of beams at 0°/±60° to form equilateral bays. Similar to laminated composites, the in-plane stiffness of the isogrid is quasi-isotropic.

Another grid configuration, a *quadri-grid*, uses four beam groups [41]. When equally distributed at 0°/±45°/90°, this grid has four equivalent directions. It is also quasi-isotropic in terms of in-plane stiffness, similar to an isogrid. Other grid patterns can be formed by varying these basic grid configurations. For example, in order to reduce the nodal build-up for an isogrid (three ribs cross over each other at the same point), one beam can be displaced a little so that the intersection point becomes a small triangle. Consequently, the 2-D *Kagome* grid is formed. Compared with bi-grids, the tri-grid or quadri-grid usually provides a higher in-plane shear resistance.

A number of studies have been conducted to investigate the structural behavior of grid stiffened composite structures experimentally and theoretically [40–56]. These tests and analyses show that grid stiffened structures are inherently strong and a resilient arrangement for composite materials. They are inherently resistant to impact damage, delamination and crack propagation because unidirectional composite ribs have no material mismatch. By having separate ribs, cracks do not propagate to the next ribs and may promote damage tolerance. They can achieve better performance in multiple directions by running the ribs in several directions and by finding optimal rib orientation. Also, the grids carry loads collaboratively and the overall load carrying capacity can be fully utilized because grid failure proceeds along the direction of the greatest strength. Furthermore, for the same amount of materials, grid panels are always thicker than their respective laminated composites and thus have higher flexural rigidity. Finally, other typical benefits of composite materials, such as light weight, high specific stiffness and strength, high corrosion resistance, tailorability, etc., are retained.

Recently, Li and Mathyala [16] and Li and Chakka [19] found that by filling the empty bays with lighter weight polymeric syntactic foam, the grid stiffened composite demonstrated much better impact tolerance than the laminated composite counterpart with the same fiber volume fraction. They found the following characteristics. (1) Each cell or bay is a small panel with an elastic boundary and tends to respond to impact quasi-statically. (2) The periodic grid skeleton, the primary load carrying component with 2-D continuity, is responsible for transferring the impact energy elastically and providing the in-plane strength and transverse shear resistance. (3) The extremely lightweight syntactic foam in the bay, the secondary load carrying component, is primarily responsible for absorbing impact energy through damage. If rubberized foam is used [17,18], it can also extend the impact duration. Of course, in order to ensure that the core becomes flexible during impact and stiff during regular service, the core must experience phase change such as a shape memory polymer [57]. (4) The grid skeleton and the foam develops a positive composite action; that is, the grid skeleton confines the foam to increase its strength and the foam provides lateral support to resist rib local buckling and crippling. In addition, the foam also provides additional in-plane shear strength for bi-grids such as the orthogrid. (5) The core and skin are fully bonded because the bay is fully filled, without the limitation of a honeycomb core or truss core.

However, grid stiffened composite also suffers from impact damage. Figure 1.8 shows the low velocity impact damage on an isogrid stiffened composite with impacts at different locations (rig, bay, and node) [19]. Figure 1.9 shows impact damage inside an orthogrid stiffened composite as determined by C-scan. In Figure 1.9, the pulse-echo transmission method was used to capture the signal and the color of the image changes with the strength of signal that is received by the transducer. Red color (gray color) represents an excess of 80% of the signal returning to the receiver, whereas blue color (dark color) represents the condition where 50–80% of the signal is being received by the receiver and green color (white color) indicates that less than 50% of the signal is being received. Therefore, red color (gray color) suggests composite without damage and green color (white color) means composite with some types of damage. As expected, the damage is localized primarily within the bay directly under impact. The 2-D grid skeleton does not suffer from significant damage, suggesting that the grid

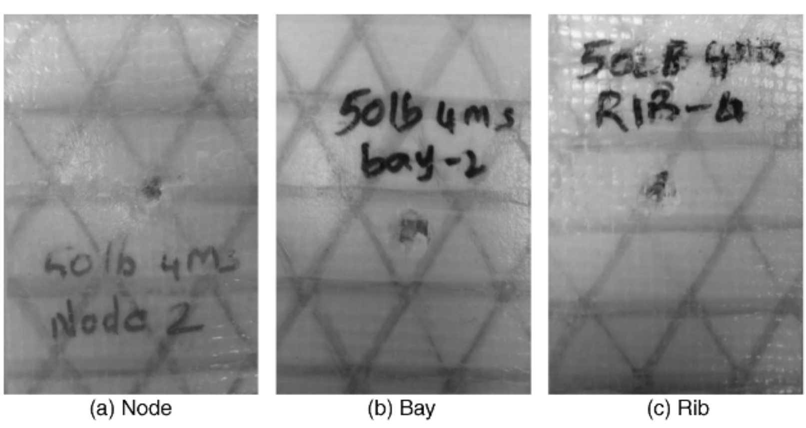

Figure 1.8 Localized damage in an isogrid stiffened composite subjected to impact energy of 193 J. *Source:* [19] Reproduced with permission from Elsevier

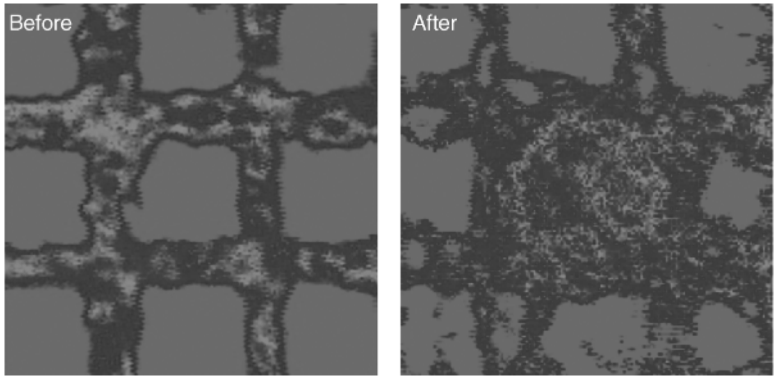

Figure 1.9 Pre- and post-impact of an orthogrid stiffened composite subjected to an impact energy of 48.8 J at the center of the bay. *Source:* [16] Reproduced with permission from Elsevier

skeleton is responsible for transferring the impact energy away from the impact point to the entire panel.

Most recently, Ji and Li [20] proved that if the brittle synthetic fibers are replaced by ductile millimeter metallic tubes, such as steel tubes or aluminum tubes, the impact tolerance of the grid stiffened composite panel can be further enhanced without a weight penalty. This is because crushing of the metallic tubes and plastic deformation of the tube wall absorb a significant amount of impact energy. Also, because the tubes are hollow, the increase in density is insignificant. It is believed that, while traditionally metals and polymer composites are competitors, this new composite construction utilizes the advantage of both polymer and metal, and may provide new opportunities for hybrid and lightweight metal/polymer composite structures.

1.4 Repair of Damage in Thermosetting Polymer Composite Structures

When polymer composites used as structural materials are damaged, there are only a few methods available to extend their functional lifetime. Ideal repair methods are those that can be executed quickly, electively, and directly on a damaged site, eliminating the need for removing a component for repair. However, the mode of damage must also be taken into consideration as repair strategies that work well for one mode might be completely useless for another. For example, matrix cracking can be repaired by sealing the crack with resin, while fiber breakage would require new fiber replacement or a fabric patch to achieve the recovery of strength.

The purpose of repair is to provide a smooth path for load transfer and/or reestablish the material's continuity, ideally not significantly changing the original stress distribution. For matrix damage, if the damage is accessible, injecting adhesive directly can restore the load carrying capacity. For fiber fracture, it is very difficult to re-establish continuity in fibers based on the current available technology. Therefore, external repair by bonding additional fiber reinforced polymer layers is essential. Currently, two techniques are available for repairing laminated composites, along with two types of repair materials [58,59]. The two techniques are scarf repair (including stepped repair) and lap (including a single or double lap) repair (see the schematics in Figure 1.10). In scarf repair, the damaged materials are removed and form a

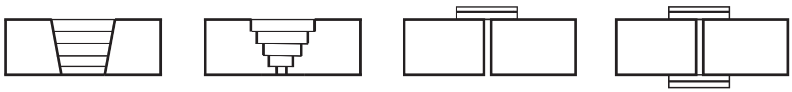

Figure 1.10 Schematic of various patch repair approaches

V-shaped space. The new repairing material is laid up layer by layer until the designed level is reached. After curing, a scarf repair is formed. The step repair is a revised version of the scarf repair. Each ply is sanded so that a flat surface is exposed, leading to a stepped finish. The advantage of scarf repair is that it provides a straighter load transfer path without increasing the structure weight. The limitation is that it needs a longer time and effort to prepare for the repair. In lap repair, the repairing layers are directly bonded to the cleaned and roughed surface of the damaged area, either on one side (single lap) or on both sides (double lap). As compared to scarf repair, the stress transfer path is disturbed and the repaired structure sees an increase in weight.

The two repair materials are a wet lay-up material, which is cured at room temperature, and a prepreg material, which is cured at an elevated temperature. However, the currently used repair materials have limitations. The wet lay-up material usually requires three to seven days for complete curing of the resin. In many applications, however, a seven-day wait is unacceptable. A heat activated curing prepreg can reduce the repair time to several hours. However, these materials generally require freezer storage and have a limited shelf life. Heat and pressure are required to cure the adhesive and patch material in order to obtain a uniform, nonporous adhesive layer. The most common heating method for field repairs requires heat blankets that are controlled by a programmable temperature controller. The heat blankets are a series of electrical resistance wires embedded in silicone rubber. There are several disadvantages to this heating method. First, prepreg curing requires a curing temperature with a narrow tolerance. However, due to thermally complex structures, achieving curing temperatures within the required range is often difficult. Second, heating large areas using heat blankets requires large amounts of energy that can easily exceed available power sources. Third, for structures with complicated geometries, the required curing pressure is generally difficult to apply. Finally, the time required for field level repair is still too long. This is because the curing cycle includes heating the blanket to the curing temperature, followed by soaking and cooling down to the ambient temperature, which may take several hours. Li *et al.* [60] used fiber reinforced ultraviolet (UV) curing resin composite to repair a low velocity impact damaged laminated composite beam. Hybrid scarf repair and patch (single lap) repair were used. Because of the fast curing of the UV curing resin, it has been found that fiber reinforced UV curing resin is a fast, strong, durable, and cost effective method to repair low velocity impact damaged composite laminates. This fast curing resin has also been used to repair damaged concrete structures [61,62] and to join composite pipes [63]. However, one limitation of such a repair strategy is the large volume change during the curing process of UV curing resins.

It should be pointed out that none of these methods of repair is an ideal solution to damage in load carrying structures. These methods are temporary solutions to extend the service time of the material, and each of these repair strategies requires monitoring of the damage and manual intervention to enact the repair. Also, all these repair methods require an interruption to the service. This is unacceptable for some structures, such as aircraft during flight, where immediate and in-service care is needed to avoid a catastrophic incident. Therefore, self-healing strategies are urgently needed.

1.5 Classification of Self-Healing Schemes

Because of the need for self-healing in thermosetting polymer composite materials, various self-healing approaches have been explored and have been published in the form of papers, books, and patents. Therefore, it is time to classify self-healing approaches so that engineers can utilize the results in design and researchers can plan new research topics. It is noted that, due to the vast body of literature in the area of self-healing, this book is by no means a comprehensive review of all the existing literature on self-healing. Rather, this section aims to provide a brief overview of the literature and to focus on the classifications. Detailed reviews can be found in recent review papers [64–93] and books [94–100].

Based on the characteristics of healing – healing by the polymer itself or healing by an externally added healing agent – self-healing can be broadly divided into two categories: intrinsic self-healing and extrinsic self-healing. Intrinsic self-healing can be further categorized into physical healing or chemical healing. For physical healing, molecules with high mobility at temperature above the glass transition or melting temperature entangle each other at the fractured surface by segmental interdiffusion or reptation, which is driven by the thermodynamic force and forms physical cross-linking, such as healing of thermoplastic polymers [101]. For chemical healing, chemical bonds such as the covalent bond, ionic bond, hydrogen bond, etc., are reestablished at the interface through various means, such as a thermosetting epoxy with unreacted epoxide [102], ionic attraction in ionomers [103], polymers with thermally reversible cross-links [104], supramolecule chemistry (hydrogen bonds, metal–ligand coordination, π–π stacking interactions) [90,105], dynamic covalent bond exchange [106], etc. Extrinsic self-healing can also be divided into chemical or physical healing. For a liquid healing agent contained in microcapsules [107], hollow fibers or hollow channels [108,109], and microvascular networks [110], the healing is through in situ polymerization of the contained monomers when contacting with the embedded catalyst. This healing mechanism is chemical, with the formation of covalent bonds at the interface. For a solid healing agent such as thermoplastic healing agents, the healing is through diffusion of molten thermoplastic molecules into the fractured matrix, leading to molecule entanglement and thus physical healing [111,112]. The bio-inspired close-then-heal (CTH) self-healing scheme, which aims at healing wide-opened, millimeter scale cracks and is the focus of this book, belongs to this category of extrinsic physical healing. Figure 1.11 shows a schematic of the categorization of self-healing schemes. Classification of self-healing can also be based on other functional or compositional criteria. For example, based on the repeatability of healing, some self-healing can be categorized as healing only one time, while others can heal more than once. For instance, most of covalent bonded healing chemistry can only heal one time, unless a reversible covalent bond or dynamic covalent bond exchange is used, while most physical based healing is repeatable.

It deserves mentioning that most of the existing self-healing schemes can only heal microscopic cracks because almost all the healing mechanisms need to bring the fractured surfaces in contact before healing occurs. Of course, this is not an issue at all in lab testing as the fractured pieces can be manually brought into contact easily. However, in real world applications, this simple operation represents a grand challenge for application of the

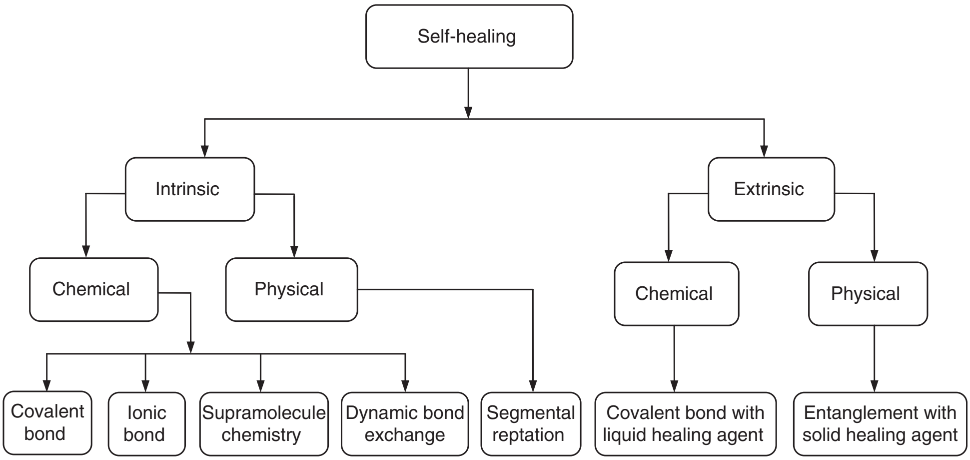

Figure 1.11 Schematic classification of self-healing schemes

self-healing schemes in engineering structures. In full-scale structures, almost all the structural components are subjected to a certain constraint by their neighboring components. In other words, the boundary conditions of the structural components are not free. The cracks cannot be brought into contact manually. This is why we propose to use the shape memory effect to bring the fractured matrix into contact before the self-healing scheme takes effect.

1.6 Organization of This Book

With the fast advancement in materials science and engineering, as well as an understanding of self-healing mechanisms and modeling capability, self-healing is evolving towards engineering practice instead of engineering dream. Self-healing is gradually changing the paradigm of structural design. While the literature related to self-healing of thermosetting polymer composites is growing quickly and in vast volume, most examples are based on either a liquid healing agent encased in microcapsules, hollow fibers, and microvascular networks or a solid healing agent such as thermoplastic particles dispersed in a thermosetting polymer matrix. The challenge facing liquid healing and solid healing agents is the difficulty in healing macroscopic or structural length scale damage. The author's research group has been working on shape memory polymer (SMP) based healing systems, which has demonstrated the ability to heal structural length scale damage, such as impact damage, repeatedly, efficiently, and molecularly. Therefore, the purpose of this book is to summarize systematically the experimental and theoretical advancement made in our lab and discuss future endeavors needed to enhance this area of study.

The book is organized as follows. Chapter 1 has introduced some basics on damage in various composite structures and classifications for self-healing. Chapter 2 will focus on the introduction of self-healing in biological systems, which inspired the self-healing scheme in this book. Chapter 3 will focus on the thermomechanical behavior of thermosetting SMPs and SMP based syntactic foam. Chapter 4 will provide some basics on solid mechanics modeling and discuss the two popular strategies to model SMPs – thermodynamic based and stress/structural relaxation based approaches. Modeling on both thermosetting SMP and SMP based syntactic foam will be reported. Chapter 5 will focus on testing and modeling of polyurethane SMP fibers, including physical, mechanical, thermomechanical, damping, and microstructure characterization. Viscoplasticity theory will be presented to model the effect of strain hardening by cold-drawing programming on stress recovery. The underlying mechanisms controlling the difference in strain memory and stress memory will be discussed and new definitions of stress fixity and stress recovery ratios will be given. Chapter 6 will deal with the self-healing of SMP matrix based composite structures. Self-healing of notched beam, sandwich, grid stiffened, and 3-D woven fabric reinforced SMP polymer composite structures will be discussed in detail. Chapter 7 will focus on self-healing of conventional thermosetting polymer by embedding SMP fibers and thermoplastic particles. SMP fiber reinforcement in the form of 1-D, 2-D, and 3-D will be presented. Chapter 8 will briefly discuss modeling of damage–healing by revising the reptation model. An evaluation of healing efficiency using the adhesively bonded configuration will also be discussed. Healing efficiency in terms of Mode I, Mode II, and Mixed Mode I&II fracture modes will be formulated. Chapter 9 will give some future perspectives on this topic.

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