A Biomimic Self-healing Shape Memory Polymer Based Syntactic Foam for Smart Structural Composites

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A BIOMIMIC SELF-HEALING SHAPE MEMORY POLYMER BASED SYNTACTIC FOAM FOR SMART STRUCTURAL COMPOSITES

A Dissertation

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 Doctor of Philosophy

in

The Department of Mechanical Engineering

By Jones Nji

B.S., ECUST, Shanghai, China, July 2005

M.E. Southern University, July 2007

May 2011
DEDICATION

To My Parents and Family
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LIST OF ABBREVIATIONS

CP: Copolyester

SMP: Shape memory polymer

PSMP: Polystyrene shape memory polymer

CP-PSMP: Copolyester/Polystyrene shape memory polymer composite

3%CP-PSMP: Copolyester/Polystyrene shape memory polymer composite with 3% copolyester content

6%CP-PSMP: Copolyester/Polystyrene shape memory polymer composite with 6% copolyester content

9%CP-PSMP: Copolyester/Polystyrene shape memory polymer composite with 9% copolyester content

CP-PSMP-SF: Copolyester/Polystyrene shape memory polymer based syntactic foam

PSMP-SF: Polystyrene shape memory polymer based syntactic foam
ABSTRACT

This study explored the development of a new self-healing Polystyrene Shape Memory Polymer (PSMP) based syntactic foam for service life extension in structural polymeric composites. The objective was to self-heal structural-length scale damage in an autonomous, efficient, timely and repeatable manner at the molecular-length scale. Self-healing is achieved through a novel two step close-then-heal (CTH) self-healing scheme, designed to mimic the natural biological process of wound healing in humans.

A new methodology to fabricate three-dimensional (3-D) fiber reinforced shape memory polymer syntactic foam for structural applications was developed. The effect of impact energy on the ability for the 3-D fiber reinforced PSMP syntactic foam (PSMP-SF) panels to seal cracks and mitigate impact was investigated in terms of the number of impacts to complete perforation. It was found that by restoring surface dents and closing internal crack, perforation was delayed (from 9 impacts to 16 impacts at 32 J impact energy) and (from 5 impacts to 7 impacts at 42 J impact energy).

A new self-healing particulate composite was developed by incorporating co-polyester thermoplastic particles (6% by volume) within the PSMP matrix. The self-healing behavior of the composite was studied on single edge notched bend (SENB) specimens through three-point bending tests. Miscibility between the PSMP and the CP was validated through differential scanning calorimetric (DSC) analysis. It was found that the composite can heal structural-length scale damage at the molecular level in 20 minutes at 150 °C. Measured in terms of fracture load, a repeatable healing efficiency of 65% was obtained.

The effect of thermoplastic content on self-healing efficiency and fracture toughness of the new self-healing particulate composite was investigated. It was found that the healing
efficiency increased with thermoplastic content. However, the fracture toughness of the composite decreased in the same direction. The healing efficiencies at 3% and 9% CP volume fraction were respectively 50% and 75%.

A new biomimetic self-healing syntactic foam was developed and shown to heal structural-length scale damage with a healing efficiency of 50% based on fracture load in three-point bending test. Repeated impact and self-healing tests revealed excellent impact tolerance and superior impact mitigation capabilities.

**Key Words:** Self-Healing, Shape Memory Polymer, Syntactic Foam.
CHAPTER 1

INTRODUCTION

This dissertation consists of six chapters. All chapters, except for the introduction and conclusion, are based on papers that have been published, are under review, or are to be submitted to peer-reviewed journals. This introductory chapter is extensive and gives a comprehensive review of pertinent literature, outlining clearly the objective of this study. Each individual chapter has a brief introduction section, which gives an overview of the research conducted in that chapter. Thus, while each chapter contributes toward achieving the final objective of this study, the work in each chapter is relatively independent. Specific research details can be found in each chapter. Some essential information may be repeated in some chapters for the completeness of each chapter. All chapters, except this introductory chapter, document the research results of the Ph.D. candidate under the direction of the candidate’s advisor as well as the dissertation committee members.

1.1 The Self-healing Concept for Polymers and Polymer Composites

Polymeric composite materials are increasingly used in industries such as the aerospace, aircraft, offshore, automobile, pipe and pressure vessel, etc, due to unique properties such as high strength-to-weight ratio and good corrosion resistance. During operation, the composites may incur damage, which may be at the microscopic or macroscopic level. Such damage may be caused during routine inspection, for example, when a tool is dropped on a composite pipe or even when an aircraft or space vehicle collides with an object (e.g, hail stones). Macroscopic damage compromises the structural functionality of the component, requiring immediate repair or replacement. Microscopic damage on the other hand, under small cyclic operating loads, could grow into macroscopic or structural-length scale damage. Replacing the damaged component or
structure could be a costly endeavor. In some applications (e.g., space vehicles) repairing or replacing the damaged component immediately following damage may not be possible if the damaged component is at a remote location (e.g., wing panel of an aircraft or space vehicle). In such a situation, continuous operation is a very risky endeavor that could lead to catastrophic failure. Thus, polymeric composite materials that can heal damage remotely, and restore degraded properties of the damaged component, would play a key role in ensuring the safe and smooth operation of systems that utilize them.

In an attempt to heal damage, restore mechanical properties and extend the service life of polymeric components and structures, the concept of self-healing damage in polymeric materials was introduced in the 1980s and has been widely investigated [1-12]. Self-healing is the ability of the polymer to repair damage and restore lost or degraded properties or performance using resources from within the polymer [13]. The development of self-healing mechanisms for polymers is greatly inspired by biological systems. By closely observing Mother Nature, researchers have synthesized and developed various mechanisms for achieving self-healing in polymers. Figure 1-1 (right half) is a schematic representation of the biological process that occurs to heal wounds in humans. The steps involved in this healing process are: inflammatory response and blood clotting to close the wound, cell proliferation, and matrix remodeling. The left half of Figure 1-1 is a synthetic self-healing route for polymers and polymer composites, which is designed by mimicking the biological wound healing process in humans. Thus a biomimic or biomimetic self-healing system is one which is designed to function by mimicking a natural or biological one. Typically, the synthetic self-healing route is designed to achieve self-healing in a shorter period of time, compared to the biological one. Healing damage in polymers through the synthetic route typically follows three steps which include: (1) actuation of self-
healing mechanism, (2) transport of healing agents/chemicals/particles to damaged site and (3) chemical/physical repair to complete self-healing. Self-healing can be autonomic (automatic without human intervention) or may require some external assistance (e.g., heat or pressure).

During the last three decades, researchers have developed several synthetic self-healing schemes in an attempt to heal damage and restore lost or degraded properties in polymeric systems. An ideal approach would possess a mechanism that can self-heal micro-length-scale as well as structural-length-scale (macro-length-scale) damage autonomously (without human intervention), efficiently (able to restore degraded properties to an acceptable extent), repeatedly (able to repeatedly restore degraded properties), timely and molecularly (at the molecular length-scale).

**Figure 1-1** Schematic representation of the biological self-healing (left) and synthetic self-healing (right) schemes [13].
Current state-of-the-art self-healing approaches in polymers and polymer composites are based on: capsule-based self-healing systems, hollow fiber self-healing systems, self-healing systems based on vascular networks, self-healing based on dispersed thermoplastic particles and intrinsic self-healing systems [13]. All classes of polymers, from thermosets through thermoplastics to elastomers, have the potential for self-healing based on any of the above approaches. These approaches differ by the mechanism used to achieve self-healing. An ideal approach would possess a mechanism that could self-heal micro to macro-length-scale damage in an efficient, timely, repeatable and autonomic manner. The sections following will examine each of the self-healing schemes in more detail.

1.2 Capsule Based Self-healing Approach

Figure 1-2 is a schematic representation of the capsule based self-healing approach [14]. In capsule based self-healing materials, liquid healing agent is encapsulated and incorporated in the polymer matrix with a pre-dispersed catalyst, as shown in Figure 1-2.

![Figure 1-2 Schematic representation of the capsule based self-healing approach [14].](image)
As such, when an approaching crack ruptures the capsule, the healing agent is released and flows into the crack by capillary action. Then a subsequent chemical reaction between the chemical and catalyst heals the material and prevents further crack growth. The ability of this mechanism to heal micro-length-scale damage autonomously in polymers and polymeric composites has been demonstrated [14, 15], with a self-healing time of 24-48 hours at ambient or elevated temperatures. A healing efficiency of 75% based on fracture toughness was reported by White et al [14] for this approach. However, immobility of healing agents at low temperatures and inability to heal multiple and repeated fractures at the same location were reported [15] as the major limitations of this approach. Also, once the healing agent is released, it leaves behind a void within the material.

![Figure 1-3 Concept of healing mechanism via hollow fibers [15].](image-url)
1.3 Hollow Fiber Self-healing Approach

Figure 1-3 is a schematic explanation of the hollow fiber self-healing approach [15] which was first pioneered by Dry and Sottos [16,17]. In the hollow fiber approach, liquid healing chemicals are stored in the fibers and released when the fibers are ruptured to repair damage. The ability of this self-healing mechanism to heal microscopic damage in polymers and polymer composites autonomously has been demonstrated [15], with a healing time of 24 hours at room temperature. Through impact testing and subsequent healing, Pang and Bond [18] achieved a healing efficiency of 93% based on flexural strength. One problem with this approach is that the fibers induce high stress concentration within the polymer, weakening its mechanical properties. Also, repeated healing of damage at the same location is not possible once the healing agent is used up. Immobility of healing agent at low temperatures is also another main limitation [15].

1.4 Vascular Self-healing Approach

Initial investigations on vascular networks were carried out by Dry and coworkers [13]. Figure 1-4 is a schematic representation of the vascular self-healing approach [19]. In this approach, healing chemicals are introduced through a main channel into a network of capillaries or hollow channels and released when the fibers are ruptured to repair damage. This ensures a continuous supply of healing agent. The fibers may be connected one dimensionally (1D), two dimensionally (2D) or three dimensionally (3D). Since there is a continuous supply of healing chemical, repeated healing is possible. The ability of this self-healing mechanism to heal damage in polymers autonomously has been demonstrated [19, 20] with healing efficiencies of 89-100 % based on mode 1 four-point bending fracture toughness, and a healing time of 48 hours at 30 °C. One main limitation of this approach is the complexity involved in designing the vascular
network systems. Another limitation is that low wettability affects the release and transport of the healing agent to the damaged site, especially at low temperatures.

**Figure 1-4** Schematic representation of the vascular self-healing approach. (a), Schematic diagram of a capillary network in the dermis layer of skin with a cut in the epidermis layer. (b), Schematic diagram of the self-healing structure composed of a microvascular substrate and a brittle epoxy coating containing embedded catalyst in a four-point bending configuration monitored with an acoustic-emission sensor [19].

### 1.5 Self-healing From Dispersed Thermoplastic Additive

Figure 1-6 is a schematic representation of self-healing using dispersed thermoplastic additives in a thermosetting polymer [15]. Self-healing occurs by the melting and subsequent re-dispersion of the thermoplastic material into the crack plane, filling the crack and bonding with the surrounding matrix material. The use of thermoplastic additive as self-healing agent for thermoset matrices was first reported by Zako and Takano [26]. By using up to 40% by volume of thermoplastic epoxy particles (average diameter of 105 µm) in a glass fiber-reinforced epoxy composite, they [26] produced tensile test specimens, reduced the stiffness of the specimens by
12.5% through tensile fatigue tests, and then recovered the stiffness completely by heating the specimens at 120 °C for 10 minutes. In another research group, the healing efficiency of an epoxy containing up to 20% by weight of polybisphenol-A-co-epichlorohydrin (PBE) thermoplastic additive was investigated at healing temperatures from 100 to 140 °C [27, 28]. Healing efficiencies of 50-70% based on compact tension fracture toughness were reported [30].

Figure 1-5 Schematic representation of self-healing using dispersed thermoplastic additives [15]
The ability of this self-healing method to heal damage repeatedly was also demonstrated [27] on glass fiber epoxy composite specimens through Charpy impact tests, with healing efficiency evaluated based on impact strength. In this scheme, self-healing is possible so long as the damaged surfaces are in close contact. But for large cracks, where the two crack surfaces pull away, self-healing by this mechanism is not possible. The two crack surfaces must be in contact for this mechanism to be effective. Also, since external heating is required to activate this self-healing mechanism, healing is not completely autonomous.

1.6 Intrinsic Self-healing Approach

In intrinsic self-healing systems, the matrix material is inherently self-healing. Current intrinsic self-healing systems can be classified according to: self-healing via molecular diffusion, self-healing polymers based on reversible reactions (thermally reversible crosslinks), ionomeric self-healing materials, self-healing based on chain rearrangement, and supramolecular self-healing materials [13, 15].

1.6.1 Self-healing Via the Molecular Diffusion Mechanism

This healing approach is applicable to thermoplastic polymers with un-crosslinked chains. Self-healing can be induced thermally, with a solvent or with light of suitable wavelength [15]. Figure 1-5 is a schematic representation of self-healing via the molecular diffusion mechanism. Self-healing via the molecular diffusion mechanism has been widely studied [15]. It has been reported [15] that when two pieces of the same polymer are brought into contact at a temperature above its glass transition temperature ($T_g$), the interface gradually disappears and the mechanical strength at the polymer–polymer interface increases as the crack heals due to molecular diffusion across the interface. To better explain the process of crack healing by this mechanism, various models have been proposed [15, 21]. In particular, [21] suggested a five
stage model to explain the crack healing process in terms of surface rearrangement, surface approaching, wetting, diffusion and randomization. Kim and Wool [6] also presented a microscopic theory for the diffusion and randomization stages. In another study [7], it was observed that the development of the mechanical strength during the crack healing process of polymers is related to inter diffusion of the molecular chains and subsequent formation of molecular entanglements. A self-healing efficiency of 120% based on the fracture toughness of thermoplastic polymer SENB specimens was achieved by Jud and Kausch [1] at 115 °C for 7-8 minutes. As demonstrated, this mechanism can heal micro to macro-length-scale damage efficiently and timely [15].

**Figure 1-6** Mechanisms involved in self-healing via molecular diffusion [15].
However, damage cannot be healed autonomously since external heating is needed to trigger the self-healing mechanism. Also, for large structural-length-scale cracks where the two crack surfaces pull away from each other, self-healing by this mechanism is not possible. Some additional mechanism is required to bring the two crack surfaces together prior to self-healing.

1.6.2 Self-healing Materials Based on Reversible Reactions

Self-healing polymers and materials based on reversible reactions have components which can be reversibly transformed from the monomeric state to the crosslinked polymeric state when activated by a suitable stimulus such as heat or photo illumination. Following the application of energy, bond reformation and polymer remending occur at the damaged location. The most widely used thermally reversible reaction schemes are the Diels-Alder (DA) and retro Diels Alder (rDA) [13]. The exploration of a thermally reversible reaction such as the Diels–Alder (DA) reaction for self-healing application was pioneered by Chen et al. [22]. The ability of this self-healing scheme to heal damage efficiently and repeatedly has been demonstrated by several researchers [22-25]. Using a thermally remendable highly cross-linked polymeric material, Chen et al [22] achieved a healing efficiency of about 80% after the first healing cycle based on fracture toughness. The healing time was 6.5 hours (30 minutes at 115 °C and 6 hours at 40 °C). They reported a healing efficiency of about 78% after the second healing cycle. For healing to occur, the damaged surfaces must be in close contact. For structural-length-scale damage where the two crack surfaces pull away, some additional mechanism is needed to bring the crack surfaces back together.

1.6.3 Self-healing Based on Ionomeric Self-healing Materials

In ionomeric self-healing materials, self-healing is achieved through iononomic segments that can form clusters which act as reversible cross-links, as shown in Figure 1-7.
These clusters can be activated by external stimuli such as temperature or ultraviolet irradiation. The formation of the clusters is reversible, and so multiple local healing events are possible. Research studies by Kalista et al [29, 30], Varley and van de Zwaag [31, 32] demonstrated the ability of ionomic self-healing materials to effectively and timely self-heal projectile damage. The heat generated during the projectile damage served as the trigger for self-healing. Through pressurized burst tests, it was demonstrated [29] that strength at the puncture location can be fully restored at 130°C in less than one minute. However, for large structural length-scale damage, where the crack surfaces are far apart, this mechanism may not be very effective for self-healing damage.

![Figure 1-7 Schematic representation of the theoretical healing mechanism in ionomers [15].](image)
1.6.4 Self-healing Based on Chain Rearrangement

Self-healing in thermoset polymers can also be achieved through the rearrangement of polymer chains at ambient or elevated temperatures, as shown schematically in Figure 1.8.

![Molecular Model and Healing Stages]

<table>
<thead>
<tr>
<th>Molecular Model</th>
<th>Healing Stages</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Molecular Model" /></td>
<td><strong>Polymer Network Cut, Increasing Dangling Chains at Interface</strong></td>
</tr>
<tr>
<td><img src="image2" alt="Molecular Model" /></td>
<td><strong>Polymer Interfaces Forced Together, Dangling Chains Begin to Diffuse</strong></td>
</tr>
<tr>
<td><img src="image3" alt="Molecular Model" /></td>
<td><strong>Continued Diffusion of Polymer Chains Welds Close the Interface</strong></td>
</tr>
</tbody>
</table>

**Figure 1-8** Healing of a crosslinked network via dangling chain entanglement [15].

At ambient temperatures, self-healing occurs when polymer chains rearrange to heal cracks/scratches through the interdiffusion of dangling chains or chain slippage in the polymer network. At elevated temperatures (e.g., 150 °C), the ability of this self-healing method to heal damage repeatedly has been demonstrated through fractured epoxy resins made from diglycidyl-
ether of bisphenol-A (DGEBA), nadic methyl anhydride (NMA) and benzyl dimethylamine (BDMA) [33]. A healing efficiency of 100% based on double torsion fracture toughness was reported. Healing was attributed to Micro-Brownian motion of the polymer chains with local flow enabling good interfacial bonding and the restoration of the original surface contours. For healing to occur, the crack surfaces must be in close contact. For structural-length-scale damage where the crack surfaces pull away from each other, self-healing by this mechanism is not possible.

1.6.5 Self-healing Based on Supermolecular Self-healing Materials

In supramolecular self-healing materials, self-healing can be achieved by designing the polymer to form strong end groups and/or side group associations via multiple complementary, reversible hydrogen bonds. The repeated self-healing ability of such polymers has been demonstrated by bringing damaged pieces of the material into close contact and allowing for reformation of hydrogen bonds [34]. Healing times ranged from 5 to 180 minutes, with a healing temperature of 20 °C. For healing to occur, the crack surfaces need to be in close contact. For larger cracks where the crack surfaces pull far away from each other, self-healing by this mechanism is not possible.

1.7 Summary of Self-healing Schemes

Table 1-1 is a summary of the current state-of-the-art self-healing schemes and the ability of each one of them to heal damage autonomously, repeatedly, efficiently, molecularly, timely and structurally. From the Table 1-1, it is seen that none of the current self-healing schemes can fully satisfy all the above criteria. In this study, structural damage is considered as damage where two crack surfaces are completely separated from each other. While the capsule and hollow fiber schemes can heal damage autonomously, efficiently, molecularly and timely, they have one main
limitation in that they cannot heal damage repeatedly. The vascular scheme was developed to address this problem [13]. However, the design process is still very complicated. On the other hand, the intrinsic thermoplastic additive self-healing schemes, even though typically require an external stimulus (e.g., heat) to activate the self-healing mechanism, can heal damage repeatedly and are very easy to design and implement. Thus, so long as some mechanism can be used to bring structurally damaged surfaces together (e.g., large cracks), it would be possible to apply any of the above intrinsic schemes to heal structural-length-scale damage repeatedly.

Table 1-1 Summary of current state-of-the-Art self-healing approaches

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Autonomously</th>
<th>Repeatedly</th>
<th>Efficiently</th>
<th>Molecularly</th>
<th>timely</th>
<th>Structurally</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-capsule</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Hollow fiber</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Micro-vascular</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Thermo-plastic</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Ionomer</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Reversible reactions</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Diffusion</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Chain rearrangement</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Supermolecular</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
</tbody>
</table>

1.8 Shape Memory Polymers (SMPs)

Shape memory polymers (SMPs) are a unique class of mechanically active polymers that were first developed by CDF Chimie Company (France) in 1984 under the trade name of Polynorbene [35] and have been extensively studied recently [35, 36]. Starting from a temporary
shape, SMPs have the unique ability to return to their originally molded (memorized) shape as well as switch between two modulus states when triggered by a suitable stimulus, typically heat [37-42]. This behavior is known as the shape memory effect (SME) and was first discovered by Chang and Read [36] in 1932. When the change in shape is induced by a change in temperature, it is known as thermally induced shape-memory effect [35]. The shape memory effect is not related to a specific material property of a single polymer. Rather, it is a result of a combination of the polymer structure and the polymer morphology together with the applied processing and programming technology [35].

The permanent shape of SMPs is given either by physical or chemical crosslinks. Physically crosslinked SMPs (e.g Polyurethane SMPs) can be designed by first choosing an elastic matrix known as the soft /switching segment, whose polymer chains are able to fix a given deformation when cooled below a certain transition temperature (T_{trans}). The transition temperature (T_{trans}) can be the glass transition temperature (T_g) (for amorphous polymers) or the melting point (T_m) (for semi-crystalline polymers) of the polymer. By embedding a secondary polymer with a higher T_{trans} known as the hard segment, within the switching segment, the hard segment forms micro-clusters by phase separation, which act as functional physical net points within the switching phase, giving the polymer its fixed shape, rigidity and strength. Chemically crosslinked SMPs can be developed by the copolymerization of monofunctional monomers with low-molecular weight or oligomeric linkers, such that the chemical crosslinks serve as the netpoints [35]. Figure 1-9 is a schematic representation of the micro-mechanism of the thermally induced shape memory effect for a polymer network with T_{trans} = T_g [35]. Prior to extension and cooling, the polymer chains exhibit a random coil formation in a state of high entropy. Upon stretching the polymer above T_{trans}, the polymer chains uncoil and take a more oriented
formation. When the polymer is cooled below $T_{\text{trans}}$, the uncoiled polymer chains are “frozen” in place, giving the polymer its temporary shape.

**Figure 1-9** Schematic representation of the micro-mechanism of the thermally induced shape memory effect for a polymer network with $T_{\text{trans}} = T_g$ [35].

![Schematic representation of the micro-mechanism of the thermally induced shape memory effect](image)

**Figure 1-10** Schematic representation of macroscopic shape memory effect.

The work done in deforming the material is stored as Helmholtz free energy within the polymer. Upon reheating above $T_{\text{trans}}$, the free energy in the material is released, providing the
driving force to restore the oriented network of polymer chains back to the random coil formation, resulting in a macroscopic recovery of the original shape. The macroscopic shape memory effect is shown schematically in Figure 1-10.

Figure 1-11 Schematic graphical description of a thermo-mechanical test [35].
Storing SMPs in a temporary shape usually follows a three-step procedure known as *programming* [27], where the material is: (1) loaded and deformed elastically (e.g., in tension or compression) to a predefined strain level ($\varepsilon_m$) at a temperature ($T$) above its transition temperature ($T_{\text{trans}}$), (2) held at that strain level and cooled down below its $T_{\text{trans}}$ to fix the strain and keep the temporary shape and (3) unloaded to maintain the temporary shape. At the end of step 3, the material typically springs back slightly from the strain ($\varepsilon_m$), to a strain ($\varepsilon_u$).

By heating the polymer above its transition temperature ($T_{\text{trans}}$) to the temperature ($T$) in a fourth step known as Shape recovery, the original shape of the polymer can be restored through the thermally induced shape memory effect. This completes a thermo-mechanical cycle as shown schematically in Figure 1-11, leaving a residual strain $\varepsilon_p$. $T_{\text{trans}}$ can be melting point ($T_m$) or glass transition temperature ($T_g$). Figure 1.11 (a) is a 2-D schematic representation of the variation of strain with stress during the thermo-mechanical test. The variation of strain with temperature during the recovery step is shown in Figure 1-1 (b). Shape fixity ($R_f$) and shape recovery ($R_r$) [35] are two terms that are commonly used to describe the thermo-mechanical behavior of an SMP at a strain $\varepsilon_m$. Shape fixity is the ability of the SMP to fix and store the temporary shape while shape recovery is the ability of the material to return to its original shape upon reheating to $T$. Step 5 in Figure 1-11 corresponds to the second programming cycle. The $R_f$ and $R_r$ for the $N^{th}$ cycle can be determined from the following formula:

$$R_f = \frac{\varepsilon_u(N)}{\varepsilon_m}, \quad R_r = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)}$$  \hspace{1cm} (1.1)

Owing to their shape memory capability, some major technological applications of SMPs include: shape-recovery eye-glass frames, temperature sensitive switches, generation of stress to induce mechanical motion, heat-shrink tubing, deployable structures, microdevices, biomedical devices, etc [29, 30, 35–39]. Compared to other shape memory materials, such as shape memory
alloys, an advantage of SMPs is that they are cheap, light weight, and are easy to process. SMPs may also be biocompatible, nontoxic, and biodegradable [35, 36, 43], making them useful in medical applications.

1.9 Confined Shape Recovery for Closing Cracks

Li and John [44] demonstrated that the shape memory effect in SMPs can be employed to close structural-length-scale damage through a process known as confined shape recovery.

![Schematic explanation of confined shape recovery.](image)

**Figure 1-12** Schematic explanation of confined shape recovery.
As a first step toward addressing the issue of self-closing structural-length-scale damage, Li and John developed a shape memory polymer based syntactic foam and characterized its ability to seal damage through impact and healing tests. They found that the foam was able to close impact damage repeatedly, efficiently, and almost autonomously through a confined shape-recovery process. They self-repaired (via the closing but not healing of structural-length-scale damage) SMP based syntactic foam sandwich panels and reported about 93% recovery in compressive strength after the first healing cycle.

Figure 1-12 is a schematic explanation of the confined shape recovery process. Figure 1.12 (left half) shows a schematic of a rectangular beam made of shape memory polymer. The original length of the beam is $L$. Suppose the beam is programmed to a new length $x$, with a strain $\varepsilon_m = \delta / L$, then upon activating the shape memory effect, the beam recovers the strain $\varepsilon_m$, and returns to its original length $L$. (for simplicity, 100% recovery is assumed). In the right half of Figure 1-12, suppose the programmed beam is damaged, with a structural-length-scale crack of width $a$, (where $\delta > a$). Suppose again that the damaged beam is confined in the length direction at both ends, then upon triggering the shape memory effect, the crack of width $a$ will be recovered, as the polymer “attempts” to recover its original shape in the confined shape recovery process. Thus, so long as the both ends of the beam are confined, as shown in the figure, it is possible to utilize the shape memory effect in shape memory polymers for the purpose of closing structural-length scale cracks.

1.10 Syntactic Foam

Syntactic foam, a class of structural materials obtained by dispersing microballoons into a polymeric or metallic matrix primarily for the purpose of weight reduction among other reasons such as good corrosion resistance, has been used increasingly in composite sandwich structures
in recent years. The history of polymeric matrix syntactic foams dates back to the mid-1950s. They were first developed as buoyancy materials for submarines, thermo insulation materials for buildings, trains, and aircraft, cushion materials for packing, etc. [45-47]. Since the 1980s, in particular the 1990s, syntactic foams have gained new momentum partly due to the increased application of foam cored composite sandwich structures in various civilian and military structures. A comprehensive and detailed survey on syntactic foams and related literature was provided by Shutov [48, 49]. The microstructure of syntactic foam is shown in Figure 1-13.

**Figure 1-13** Microstructure of syntactic foam [50]

Significant developments in polymeric syntactic foams leading up to the work of Li and John [44] include static and dynamic modeling of the constitutive behavior of syntactic foams by means of analogy to geomaterials [50] or using damage mechanics [51]; modeling of the effective elastic properties based on micromechanics, homogenization, and equivalent medium theorem [52] and [53]; toughened syntactic foam by coating microballoons with rubber latex or
adding crumb rubber particles into the polymer matrix [54-56]; and functionally graded syntactic foam by changing the volume fraction of the microballoons or changing the density of the microballoons as the spatial location changes [57,58]. It is well known that the current polymeric syntactic foam cored sandwich usually has a very low post-impact residual bearing capacity due to micro/macroscopic damage and lack of capacity for self-healing the damage [59-62]. The work of Li and John [44] on shape memory polymer based syntactic foam is a first step toward healing damage in syntactic foams. However, the sealing process does not heal the damage, and under extreme loading conditions, such as bending or tension, the foam is still vulnerable as the sealed damage may re-open and propagate through the material and cause failure. The ability of the foam to self-heal damage would be an advantage and useful in extending the service life of syntactic foam sandwich structures. One way to further improve the impact properties of the resulting self-healing syntactic foam core composite is the use three-dimensional (3-D) fibers as reinforcement.

1.11 Three-Dimensional Fibers

Three-dimensional fiber (3-D) reinforced polymeric materials have been shown to have good impact tolerance [63-68], making them attractive candidates in weight sensitive industries such as the aerospace, auto, and maritime. Such components in addition to carrying static and cyclic loads are also expected to perform well under impact. A number of studies have been conducted to understand the impact response of 3D woven composites [69-73, 74]. In particular, Baucom et al [74] investigated the effects of fabric architecture on damage progression, perforation resistance, strength, and failure mechanisms in composite systems of comparable areal densities and fiber volume fractions, subjected to repeated impact. They found that 3D 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 3D systems. Most recent developments in the area of 3D woven fabric composites include: modeling the impact penetration of 3D woven composite at the unit cell level [75], studying the transverse impact damage and energy absorption [76], investigating the compressive responses and energy absorption [77] and studying the effect of Z-yarns on the stiffness and strength [78].

1.12 Motivation and Objective of Study

Motivated by the work of Li and John [44] on shape memory polymer syntactic foams, and in an attempt to completely heal structural-length-scale damage molecularly, Li and Nettles [79] first proposed the close-then-heal (CTH) self-healing concept by mimicking human skin. This concept was further expanded by Li and Uppu [80].

![Diagram](image)

**Figure 1-14** The two-step road-map of the close-then-heal (CTH) as proposed by Li and Uppu [80].
Li and Uppu suggested that SMP can be utilized to seal cracks (step one) by confined shape recovery while thermoplastic particles can be utilized for achieving molecular-length-scale healing (step two) through the melting, diffusion and entanglement (bonding) of the thermoplastic molecular chains with SMP chains. The two-step road-map was also detailed by Li and Uppu as shown in Figure 1-14 but was not realized experimentally.

It is envisioned that by incorporating thermoplastic particles in the current shape memory polymer syntactic foam, the resulting foam core would not only be able to close structural-length-scale damage (by confined shape recovery) but will also be able to heal the damage at a molecular length scale. By reinforcing the self-healing shape memory polymer foam core with three-dimensional fibers, the resulting structural composite will not only be able to self-heal structural-length-scale damage but will also have good impact properties. Thus the objective of this study was to explore and develop this novel self-healing shape memory polymer based syntactic foam composite and utilize it to realize the two step close-then-heal (CTH) mechanism experimentally. A systematic approach was adopted toward realizing the objective of this study. A brief summary of the content of each chapter is provided in the paragraphs below.

In Chapter 2, the methodology to fabricate 3-D fiber reinforced shape memory polymer (SMP) syntactic foam for structural applications was developed. The effect of impact energy on the ability of SMP foam panels to seal damage and mitigate impact was investigated in terms of the number of impacts to complete perforation. It was found that by restoring surface dents and closing internal damage, perforation of the panels was significantly delayed.

In Chapter 3, a new self-healing particulate composite was developed by incorporating thermoplastic co-polyester (CP) particles (6% by volume) within a polystyrene shape memory polymer (PSMP) matrix. Compatibility between the two polymers was confirmed by DSC
analysis. The particulate composite was used to validate the two step close-then-heal (CTH) self-healing mechanism using single edge notched bend (SENB) specimens (with a notch width of 1mm) through three point bending tests. Healing efficiency was evaluated based on fracture load. SEM was used to evaluate healed cracks at the micro-level. Energy dispersive spectroscopy (EDS) was used to indirectly verify the diffusion of the thermoplastic copolyester molecules into the SMP matrix during self-healing.

In Chapter 4, the effect of thermoplastic content on the healing efficiency and toughness of the self-healing particulate composite (CP-PSMP) developed in chapter 3 was investigated. It was found that the healing efficiency increased with CP content. However, the fracture toughness of the composite decreased in the same direction. The effect of thermoplastic CP content on the thermo-mechanical behavior of the self-healing composite was also investigated.

In Chapter 5, the biomimetic self-healing shape memory polymer based syntactic foam was developed. The ability for the self-healing foam (CP-PSMP-SF) to close and heal structural-length-scale damage was demonstrated on SENB specimens. Impact and healing tests on 3-D fiber reinforced CP-PSMP-SF panels revealed excellent impact tolerance and good perforation resistance.

Chapter 6 summarizes the main achievements of this study, with recommendations for future work.
CHAPTER 2

IMPACT BEHAVIOR OF A 3D WOVEN FABRIC REINFORCED SHAPE MEMORY POLYMER BASED SYNTACTIC FOAM COMPOSITE

2.1 Introduction

In this chapter, 3-D woven fabric reinforced shape memory polymer based syntactic foam panels were fabricated by reinforcing shape memory polymer syntactic foam with 3-D glass fibers. The damage/perforation resistance (reported in terms of the number of impacts to perforation) and the ability for the composite to seal cracks and restore lost structural properties (such as peak impact load) was investigated at two different impact energy levels. The composite panels were programmed using a three-step strain-controlled thermo-mechanical cycle at a pre-strain level of 5% and machined to two groups of specimens (G1 and G2) with dimensions 152.4 mm × 101.6 mm × 12.7 mm. The specimens were impact tested, transversely, centrally and repeatedly with 32 and 42 J of energy. G1 specimens were healed after each impact until perforation occurred. G2 specimens were not healed after each impact and served as controls. Visual inspection, C-scan, and scanning electron microscopy techniques were used to evaluate damage, failure modes, and healing efficiency.

2.2 Materials and Methods

2.2.1 Raw Materials

The materials used in this study included: veriflex shape memory polystyrene from Corner Stone Research Group Inc. (glass transition temperature: 62 °C, tensile strength: 23 MPa, and modulus of elasticity: 1.24 GPa at room temperature); Q-cell 6014 glass microballoons from Potters Industries (bulk density: 0.08 g cm\(^{-3}\), effective density: 0.14 g cm\(^{-3}\), particle diameter

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range: 5-200 μm, average diameter: 85 μm, and crushing strength: 1.72 MPa); and 3D E-glass woven fabric from Parabeam-Netherlands (thickness: 12.7 mm, aerial density: 1.6 kgm⁻², and compressive yield strength: 3.7 MPa). A schematic of the fabric is shown in Figure 2-1.

![Figure 2-1 Schematic of 3-D woven fabric.](image)

### 2.2.2 Specimen Preparation

The composite was fabricated using a gravity assisted method by impregnating 3-D woven fabric with the shape memory polymer (SMP) based syntactic foam, which was formed by dispersing 40% by volume of microballoons into the SMP matrix as shown in Figure 2.2. three effective specimens of the SMP based syntactic foam with dimensions of 25.4 mm × 25.4 mm × 12.7 mm per ASTM C 365 to determine its mechanical properties. It was found that the peak stress was 201 ± 1.2 MPa, modulus of elasticity was 421 ± 4.1 MPa, yield strength was 17.5 ± 0.3 MPa, and yield strain was 0.07 ± 0.002 mm mm⁻¹. It was also found that the SMP based syntactic foam behaves similarly to conventional syntactic foams at room temperature [54]. The noticeable difference is that the SMP based foam remembers its original shape while conventional foam does not.
Figure 2-2 Schematic explanation of fabrication process.

The 3-D woven composite was fabricated in a steel mold. The mold was made of a 254 mm × 254 mm × 12.7 mm detachable steel frame with top and bottom plates of dimension 279 mm × 279 mm × 2.54 mm. First, one member of the frame was detached from the rest of the...
setup, put on the bottom plate and placed on a flat table. Then 3-D woven fabric with dimensions of 304.8 mm × 254 mm × 12.7 mm was placed within the frame such that 50 mm of the fabric extended out of the frame through the open end. Next, the top plate was carefully placed on top of the frame. Steel clips were then used to hold the plate and frame assembly together. The setup was placed vertically on a flat table. Once the mold was ready, the SMP based syntactic foam was poured gently into the mold from the top open end at a rate of about 8 ml/min and allowed to descend to the bottom by diffusion and gravity. This continued until the 3D woven fabric was completely filled with the SMP syntactic foam. Next, the setup was sealed and placed in an oven for curing. The material was cured as follows: 75 °C for 12 h, 90 °C for 3 h and 110 °C for 3 h. Once the panel was cured, it was de-molded. The panel was then machined down to specimens with dimensions of 152.4 mm × 101.6 mm × 12.7 mm for impact testing.

2.2.3 Specimen Programming

Prior to testing, both groups of specimens were programmed in a strain-controlled mode at a pre-strain of 5% on a CARVER Model 2697 compression molding fixture.

![Figure 2-4 Schematic explanation of specimen programming.](image)

30
Once the specimen was within the platens of the fixture, the specimen was heated to 110 °C in 20 min and left in-between the platens for another 20 min. With the help of a linear variable differential transducer (LVDT) system (Cooper Instruments LDT 200 series), the specimen was compressed to 5% strain level along the transverse (thickness) direction and held at that temperature for another 15 min, as shown schematically in Figure 2-4. After that, the heating switch on the fixture was turned off and the specimens were allowed to cool down to room temperature. Once at room temperature (about 20 °C), the load was removed. With the removal of the load at room temperature, there was a small springback. Because of the large modulus of elasticity of the specimen at room temperature and the small programming stress, the springback can be neglected. This completes the typical strain-controlled three-step thermomechanical programming.

2.3 Experimentation

2.3.1 Impact Testing and Self-healing

Low velocity impact tests were conducted using an instrumented Instron Dyntap 8250 HV drop tower testing system (Figure 2-5) with a hammer having a hemi-spherical tup nose of diameter 12.7 mm per ASTM D2444 Standard. The test was conducted at two different velocities (3 and 3.5 m/s) with the same hammer weight (6.64 kg), leading to two different energy levels (32 and 42 J). This test was conducted in order to determine the effect of impact energy on the impact response and self-healing ability of the material in terms of the number of impacts to perforation for each energy level. The first impact energy (32 J) was chosen such that it caused whitening on the rear side of the impacted specimen with no bulge. The second impact energy (42 J) was chosen such that it created a bulge less than 1 mm on the rear side of the impacted specimen. The impact was conducted at the center of the specimen.
Figure 2-5 Dynatup 8250 HV impact testing system.
Group 1 specimens were healed after each impact. The healing was performed using the same fixture as the programming. During the healing process, the impacted specimen was inserted in the fixture and the two platens were brought in contact with the bottom and top surfaces of the specimen. After that, the temperature was raised to 110 °C and kept for 30 min. Because the shape recovery was confined, i.e., the recovery in thickness was not allowed, the material was pushed into internal open space, i.e., cracks, leading to healing (sealing) of damage and recovery of indentation. This impact-healing cycle continued until the full perforation of the specimen. For the group 2 specimens, no healing was conducted. The impact continued until the complete perforation of the specimen. At least three effective specimens were used for each impact–healing test. Figure 2-6 shows a schematic of the programming and healing steps.

![Diagram](image)

**Figure 2-6** A schematic diagram of the programming ((b), (c), and (d)), damaging (e), and healing ((f), (g), and (h)) procedure. (a) Permanent shape B (below Tg), (b) heating above Tg and apply load, (c) hold the strain while cooling, (d) remove the load and fix temporary shape A (below Tg), (e) damage by cracking (below Tg), (f) apply confinement and heat above Tg, (g) cooling while hold the confinement and (h) remove confinement and return to shape A (below Tg).
2.4 Results and discussion

2.4.1 Impact Test Results

Figure 2-7 shows typical load/energy traces of a specimen impacted with 32 and 42 J of energy, respectively. The peak impact load (6.1 ± 0.15 kN) at 42 J impact energy is higher than that (5.9 ± 0.14 kN) at 32 J impact.

![Figure 2-7 Typical load/energy traces of a specimen impacted with 32 and 42 J of energy.](image)

2.4.2 Perforation Resistance

Figure 2-8 (a) shows load/energy versus deflection graphs of a typical group 2 (control) specimen at perforation (9th impact) and a group 1 specimen at the corresponding impact number (9th impact) impacted with 32 J of energy. Figure 2-8 (b) shows load/energy versus deflection graphs of a typical group 2 (control) specimen at perforation (5th impact) and a group 1 specimen at the corresponding impact number (5th impact) impacted with 42 J of energy.
Figure 2-8 Load/energy versus deflection graphs of a typical group 2 specimen at perforation and a group 1 specimen at the same impact cycle. (a) Impact energy level I (32 J). (b) Impact energy level II (42 J).
For energy level I (32 J), it is seen that while the control specimen was perforated by the 9th impact as indicated by the significant drop in the impact load (about 80%) and total impact energy (about 50%), the group 1 specimen merely experienced a decrease (about 30%) in impact load and almost no loss in total impact energy. For energy level II (42 J), the control specimen was perforated by the 5th impact as indicated by the significant drop in impact load (about 79%) and total energy (about 55%) and the group 1 specimen merely experienced a decrease (about 29%) in impact load and almost no loss in total energy. For impact energy level I, group 1 specimens were eventually perforated at the 15th impact/healing cycle while for impact energy level II, perforation occurred at the 7th impact/healing cycle as shown in Figure 2-9.

![Load/energy versus deflection graphs of typical group 1 specimens at perforation for energy level I (32 J) and II (42 J).](image)

**Figure 2-9** Load/energy versus deflection graphs of typical group 1 specimens at perforation for energy level I (32 J) and II (42 J).
2.4.3 Variation of Energy with Impact Number

Energy transfer (mode I) and energy absorption (mode II) are two main modes of energy dissipation [81]. For mode I, the impact energy is stored in the form of elastic strain energy and kinetic energy which will be transferred back to the projectile or the environment through vibration and damping. For mode II, the impact energy is absorbed through plastic deformation (as in indentation) and damage (as in matrix cracking, fiber debonding, fiber fracture, etc). The initiation energy has been defined as the energy corresponding to the point of maximum impact force and propagation energy has been defined as the difference between the maximum energy and the initiation energy [81, 82]. Initiation energy is basically a measurement of the ability for the target to transfer energy elastically (mode I); and propagation energy is a measurement of the energy absorbed by gross damage (mode II). Figures 2.10 (a), (b), and (c) respectively show the variation of total energy, initiation energy (IE), and propagation energy (PE) with the number of impact cycles for group 1 and group 2 (control) specimens at both energy levels. It is seen that the total impact energy did not change much until the last impact for both groups 1 and 2 at both energy levels. The reason is that at the last impact, the tup perforated the specimen and thus the tup shared a portion of the available energy. At 32 J impact energy, IE of control specimens was fairly constant until the 5th impact and decreased sharply with increasing impact number, while IE of group 1 specimens was fairly constant until the 9th impact before decreasing steadily to perforation. Therefore, for group 1, the self-healing delayed the onset of energy absorption by non-healable damage until the 9th impact. The impact number where IE starts to decrease sharply indicates a decrease in energy dissipation by mode I (energy transfer) and an increase in energy dissipation by mode II (energy absorption such as by non-healable damage like fiber fracture), as seen in Figure 2-10 (c).
Figure 2-10 Variation of (a) total energy, (b) initiation energy and (c) propagation energy with impact cycles.

It is also seen that at the last impact (perforation), the PE decreased sharply, similar to the total energy, possibly due to the saturation of damage.

For impact energy level II (42 J), the initiation energy decreased faster compared to energy level I, as seen in the slope of the graph. The continuous decrease in initiation energy for energy level II indicates that energy absorption by non-healable damage started right from the
first impact. This explains why the control specimens impacted at energy level II (42 J) only lasted five rounds of impact. The self-healing mechanism delayed perforation of specimens at this energy level (42 J) by 2 rounds until the 7th impact.

### 2.4.4 Variation of Impact Load with Impact/Healing Cycle.

Figures 2-11 (a) and (b) show the variation of impact load with impact cycle for both groups 1 and 2 specimens for impact energy levels I and II, respectively. From figure 2-11 (a), the maximum load for the control specimen increased before decreasing with increasing impact cycles. This may be due to localized densification at the point of impact caused by the first impact. For group 1, the load does not vary much for the first six impacts. However a ‘step point’ was observed; there was a sharp drop in load at the seventh impact (about 28%), possibly due to some non-healable damage such as fiber fracture.

![Figure 2-11](image)

**Figure 2-11** Variation of impact load with impact number at (a) 32 J and (b) 42 J impact energy levels.

After that, the load carrying capacity continuously decreased as the impact cycle increased. However, it is clear that the drop in load carrying capacity for the group 1 specimens
is much lower than that for the group 2 specimens, as evidenced by the smaller slopes. This is a direct indication of the self-healing effect on delaying damage accumulation and perforation. From figure 2-13 (b), the same trend is found. The group 1 specimens consistently have a higher load carrying capacity and delayed onset of non-healable damage and perforation.

2.4.5 Damage Evaluation by Visual Inspection

Figure 2-12 shows photographs of a typical group 1 specimen after impact (a) and after healing (b). After healing, it is seen that the indentation was recovered. This indicates that damage in the form of dents can be recovered.

![Figure 2-12](image)

**Figure 2-12** A group 1 specimen after impact and after healing; (a) indentation before healing, (b) no dent after healing.

2.4.6 Damage and Healing Evaluation by C-scan.

Ultrasonic evaluation (C-scan, pulse echo method) was performed using an Ultrapac Ultrasonic scanning system (with Ultrasound E 2.68 software) from Physical Acoustics in order to take images, assess the internal damage caused by impact and verify the effectiveness of the self healing process. The principle of the pulse echo method is demonstrated schematically in Figure 2-13. High energy waves (frequency >20 KHz) travel from the transducer through the specimen.
If the specimen has no flaws (cracks), then the signal will be reflected at the bottom surface of the specimen and travel back to the transducer. If the specimen has flaws such as cracks, then some of the signal is lost due to reflection at the flaw surfaces. The remaining portion of the signal is further attenuated (absorbed) by the material. In general, the amplitude ($A$) of the wave signal at any point with distance $z$ from the surface of the test material is given by equation

$$A = A_0 e^{\alpha z}$$

2.1 [84], where $A_0$ is the amplitude of the original (un-attenuated signal), $\alpha$ is a material property (attenuation coefficient) and $z$ is the vertical distance from the surface of the specimen.

![Diagram of pulse echo method](image)

**Figure 2-13** Principle of the pulse echo method.

From equation 2.1, it can be seen that loss of signal strength will increase as the attenuation coefficient of the material increases.
Legend (percentage of original signal picked up by receiver)

Red = at least 80%

Blue = 50 to 80%

Green = less than 20%

Figure 2-14 C-scan images of typical specimens. (a) Impact energy level I (32 J). (b) Impact energy level II (42 J).
If specimens are made of the same material, then signal loss by attenuation and reflection at surfaces (back surface) will be the same and can be neglected. As such when there is a discontinuity (such as a crack) in the wave path, the incident wave energy will be scattered as it reaches the crack and part of it will be reflected back to the transducer from the flaw surface. The reflected signal will then represent only a percentage of the original signal. The reflected wave signal is transformed into an electrical signal by the transducer and sent to the receiver. From the signal, information about the reflector location, size, orientation etc can be determined.
Figure 2-14 shows C-scan images of typical specimens. On the C-scan images, the red color indicates that at least 80% of the signal was picked up by the receiver; blue color indicates that between 50 and 80% of the signal was received; green color means less than 20% of the signal was received. Hence, green color suggests some type of damage. For specimens impacted with energy level I, a blue or even green zone emerged in the C-scan images with increasing impact cycles as shown in Figure 2-14 (a). After healing, the blue zone or green zone has been reduced or eliminated, suggesting effective healing. For the case of energy level II in Figure 2-14 (b), it is observed that, after healing, the green color region, with reduced intensity, is still around the impact point, suggesting that the internal damage was not completely healed. Actually, some damage such as fiber fracture cannot be healed. As a result, each successive impact further increased the damage until the specimen was perforated. This is in line with the constant decrease in initiation energy that was noticed in section 2.4.3.

Post-processing of the C-scan images in Figure 2-14 was also performed by conducting cluster analysis to quantify the damage after each impact and each healing cycle. The Ultrawin 2.68 software was used. The damaged area corresponding to the C-scan images in Figure 2-14 after each impact and each healing cycle is summarized in Table 2-1. From Table 2-1, three observations can be made: (1) the damage area increases as the number of impact increases due to the accumulation of non-healable damage. However, it seems that the damage area stabilizes as the number of impact approaches perforation. Actually, the upper bound of the damage area should be an area immediately surrounding the hole perforated by the tup, which is related to the size of the tup. (2) Higher impact energy leads to early stabilization of the impact damage area because it perforates at a smaller number of impact cycles. (3) Each healing has effectively reduced or healed the impact damage.
Table 2-1 Damage area (cm$^2$) after each impact-healing cycle for the programmed specimens (group 1)

<table>
<thead>
<tr>
<th>Number of impact healing cycle</th>
<th>32 J of impact energy</th>
<th>42 J of impact energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After impact</td>
<td>After healing</td>
</tr>
<tr>
<td>1</td>
<td>0.71</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>0.90</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>2.79</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Indeed, the impact damage is fully healed up to the 5th impact–healing cycle when the impact energy is 32 J. However, the healing efficiency reduces as the impact–healing cycle increases, as evidenced by the increase in unhealed damage area. This result agrees with the impact test results.

2.4.7 Damage Evaluation by SEM

SEM images were obtained with a Hitachi 3600 scanning electron microscope (Figure 2-15) in both SEM and VPSEM modes. Figure 2-16 shows the evolution of damage starting as a ‘bulge’ on the back side of a group 2 control specimen for energy level I (32 J) by visual inspection. Figure 2-17 shows SEM images of the same group 2 specimen at the point of perforation (rear side) after the 9th impact. It is clear that, after the 9th impact, the specimen was perforated at the macro-length scale (Figure 2-17). At micro-length scale, it is seen that various types of non-healable damage such as fiber/matrix interfacial debonding, fiber fracture, etc, occurred.
Figure 2-15 Hitachi S-3600N scanning electron microscope (Materials characterization center, Louisiana State University).

Figure 2-16 Bulge growth, matrix cracking, fiber breakage and eventual perforation in a control specimen (impact energy 32 J).
**Figure 2-17** SEM images of an impact perforated group 2 control specimen showing failure modes (impact energy 32 J).
2.5 Summary

In this Chapter, the shape memory functionality of a Polystyrene based SMP has been utilized to self-repair (seal) impact damage in 3D woven fabric reinforced SMP based syntactic foam composites under repeated impact loadings. It was found that the impact energy has a significant effect on the healing efficiency. Control specimens impacted with 32 J of impact energy were perforated at the 9th impact while healed specimens lasted until the 15th impact; control specimens impacted with 42 J of impact energy were perforated at the 5th impact while healed specimens lasted until the 7th impact. This is because some unrecoverable damage, such as micro-balloon crushing and fiber fracture, increase as impact energy increases, such that non-healable damage accumulated under repeated impact events. The appearance of non-healable damage is represented by a considerable reduction in either the peak impact load or the initiation energy, or an increase in propagation energy. Perforation is signified by a sharp drop in peak load, total energy, initiation energy, and propagation energy.
CHAPTER 3

DEVELOPMENT OF A SELF-HEALING SHAPE MEMORY POLYMER BASED PARTICULATE COMPOSITE

3.1 Introduction

The objective of this chapter was to validate the close-then-heal (CTH) self-healing scheme by experimentation and mechanical testing. A particulate composite was fabricated by dispersing thermoplastic particles (Copolyester) in the Polystyrene shape memory polymer (PSMP) matrix. In this particulate composite, the confined shape recovery of the shape memory matrix was utilized for sealing (closing) cracks while molecular-length-scale healing was achieved with the thermoplastic particles. In this chapter, 6% by volume of thermoplastic particles was used. Beam specimens were prepared and programmed by compression in the longitudinal direction to a pre-strain level of 6.7%. Structural-length-scale damage was then created by producing a notch in the programmed beam specimens per ASTM D 5045. The notched beam specimens were then tested to fracture. The fractured specimens were healed per the close-then-heal mechanism and tested again to fracture. This fracture healing test lasted for 5 cycles. The healing efficiency was evaluated per the peak-bending load. Scanning electron microscopy (SEM) was used to examine healed cracks at micro-length-scale while energy dispersive spectroscopy (EDS) was used to evaluate molecular-length-scale healing.

3.2 Materials and Methods

3.2.1 Raw Materials

The materials used in this study included: veriflex polystyrene shape memory polymer (PSMP) from Corner Stone Research Group Inc. (glass transition temperature determined by

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DMA [79] 67.71°C DSC: 62 °C, tensile strength: 23 MPa, and modulus of elasticity:1.24 GPa at room temperature); a thermoplastic polymer identified as copolyester (CP) from Abifor Inc., Switzerland (particle size \( \leq 80 \) µm, density 1.3 g/cm\(^3\), glass transition temperature determined by DSC: 17 °C, melting range 114 – 124 °C, and bonding temperature range 125 – 150 °C). The Veriflex_ PSMP is a two-part resin system. Part A is composed of Styrene, Divinyl benzene and Vinyl neodecanoate. Part B is composed of Benzoyl peroxide.

The chemical structure of each component is shown in Figure 3.1 (a). The thermoplastic Copolyester is composed of Isopthalic acid, Terephthalic acid and Butane-1, 4-diol. The chemical structure of each component is shown in Figure 3.1 (b).
3.2.2 Fabrication Method

To produce the composite, PSMP was preheated for two hours at 75 °C just before the thickening and curing process began. This was done in order to prevent the denser CP particles from settling to the bottom of the SMP matrix. After that, copolyester (CP) particles (3 % by volume) were dispersed in a beaker containing the pre-heated SMP matrix. The mixture was mixed to uniformity and poured in a steel mold with dimensions 300 mm × 300 mm × 12.5 mm. The mold was sealed and the material was cured in an oven as follows: 75 °C for 12 hours, 90 °C for 3 hours and 112 °C for 3 hours. Once the curing procedure was complete, the setup was cooled down and de-molded.

![Figure 3-2 Beakers showing polystyrene shape memory polymer and copolyester particles.](image)

3.2.3 Beam Specimen Preparation

Beam specimens with dimensions of 120 mm × 25 mm × 12.5 mm were fabricated by machining the cured composite slab and programmed in compression to 6.7% pre-strain in the length direction in an adjustable metal frame on a CARVER Model 2697 compression molding...
fixture. Figure 3-3 is a schematic explanation of the specimen preparation, programming, and notching process. After programming, single edge notched bend (SENB) specimens were fabricated per ASTM D 5045 standard as shown in Figure 3-3. The purpose of using SENB specimens was to artificially create structural-length scale damage.

![Figure 3-3 Schematic explanation of the specimen preparation process](image)

3.2.4 Close-Then-Heal (CTH) Self-healing

Following the two-step self-healing scheme proposed by Li and Uppu [80], fractured specimens were placed in the adjustable rectangular steel frame as shown in Figure 3.4 at room temperature. Once the specimen was fitted into the frame, the frame was placed on the
compression-molding fixture which was pre-heated to 150 °C. It is noted that the steel frame provided confinement in the length and width directions during heating (in-plane confinement). The top surface of the framed specimen was close to the top heating plate but not in direct contact. This facilitated uniform heating of the specimen without applying confinement in the thickness direction. Therefore, only 2-D in-plane confinement was used during healing. The specimens were kept within the pre-heated fixture for 20 min. During this time period, the temperature within the specimen was gradually increased; first pass its T_g, which caused shape recovery or closing of the fractured surface and the pre-notch, and then through the T_m of the CP (between 114 °C and 150 °C) causing melting of the CP, and finally to the bonding temperature of the CP (between 125 °C and 150 °C), so that the CP molecules diffused and bonded with the PSMP molecules. After 20 min, the heating plates were turned off and cooled down to room temperature. This completed the two-step self-healing scheme. Subsequent healing after fracture was done in a similar manner.

\[
\text{Total crack to be healed} = \text{pre-notch} + \text{fracture crack}
\]

Figure 3-4 Schematic of a fractured specimen in the steel frame ready for healing.

3.3 Experimentation

3.3.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (TA Instruments, Q100) test was performed in order to investigate the compatibility between the PSMP and CP. The glass transition temperatures of the
pure PSMP, pure CP, and their CP-PSMP composite were investigated. The sample size was 6.5 mg and the test was conducted from 0 °C to 130 °C at a ramping rate of 5 °C /min. Three effective specimens were tested to obtain an average glass transition temperature value.

3.3.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was performed (Rheometric Scientific RSA III, Figure 3-5) at a frequency of 1 Hz on CP-PSMP specimens in order to determine the glass transition temperature of the composite. Rectangular tension specimens with dimensions of 36 mm × 11.5 mm × 2 mm were used. The temperature was increased at a rate of 5 °C /min.

Figure 3-5 RSA III DMA machine
3.3.3 **Thermo-mechanical Behavior**

The thermo-mechanical behavior (programming and recovery) of the composite was investigated on specimens with dimensions of $25 \text{ mm} \times 25 \text{ mm} \times 12.5 \text{ mm}$ using an MTS QTEST 150 testing machine (Figure 3-7) equipped with a heating furnace (ATS heating chamber) in order to evaluate the effect of CP particles on the shape memory functionality of the CP-PSMP composite.

![Setup showing a specimen just before a free recovery test.](image)

**Figure 3-6** Setup showing a specimen just before a free recovery test.

3.3.4 **Three-point Bending Test**

Three-point bending tests were performed on a universal MTS 810 testing system with a span length of 100 mm (Figure 3-8) and at a loading rate of 10 mm/min per ASTM D 5045 standard to determine the load carrying capacity of the composite using the SENB specimens. The specimens were tested and fractured completely into two halves.
Figure 3-7 MTS QTEST 150 testing machine (Materials Testing Lab, Southern University, Baton Rouge LA).
3.3.5 SEM Observation

SEM observation was conducted (Hitachi S-3600N scanning electron microscope) in order to (1) verify that the copolyester particles melted during the healing process and (2) visually verify the crack closing by examining a cracked specimen before healing and after healing.

3.3.6 EDS Analysis

In order to verify molecular-length scale healing, energy dispersive spectroscopy (EDS, 15 kV, super ultra-thin window (SUTW)-Saphire detector, AMPT: 25.6) analysis was conducted using a Hitachi 3600 N scanning electron microscope equipped with an EDAX genesis detector (Figure 3-9). The rationale was that if the CP molecules diffused into the PSMP matrix, the chemical composition near the interface will show a certain gradient. In this study, a specially
prepared EDS specimen was used. To prepare the EDS specimen, a SENB specimen made of pure PSMP was fractured and a very thin layer of copolyester was placed in-between the fractured surfaces. Next, the EDS specimen was healed as described in Section 3.2.4. EDS analysis was conducted at and around the healed interface of the EDS specimen.

![Figure 3-9 Hitachi S-3600 N SEM with EDAX Genesis detector](image)

**Figure 3-9** Hitachi S-3600 N SEM with EDAX Genesis detector (*Materials Characterization center, Louisiana State University, Baton Rouge LA*).

3.4 Results and Discussion

3.4.1 DSC Test Results

In order to investigate the compatibility of the two polymers (PSMP and CP) within the composite, the single glass transition criterion [84] was adopted. Based on this criterion, PSMP and CP are compatible if the composite shows a single glass transition temperature which is in-between the glass transition temperatures of the pure PSMP and CP.
Figure 3-10 Typical DSC thermograms of CP, PSMP and CP-PSMP.

Figure 3-10 shows the DSC thermograms of PSMP, CP and CP-PSMP. The PSMP shows a single glass transition temperature ($T_1 = 62 ^\circ C$). The CP, on the other hand, shows two glass transition temperatures ($T_1' = 17 ^\circ C$ and $T_2' = 70 ^\circ C$) and a melting temperature $T_m (118 ^\circ C)$, which is within the melting range of the CP (114-124 °C provided by the manufacturer). Obviously, the CP used in this study is a copolymer as provided by the manufacturer. Between $T_1$ and $T_1'$, a single glass transition temperature $T_{g1} (50 ^\circ C)$ is observed for the CP-PSMP composite. This indicates some degree of compatibility between the PSMP and one component of the CP copolymer. The CP-PSMP composite also shows a second glass transition temperature $T_{g2} = 72 ^\circ C$. This should be an indication of the effect of the other component of the CP
copolymer. Because the PSMP does not have the corresponding second glass transition temperature, the PSMP does not have compatibility with the second component of the CP copolymer. Therefore, it is concluded that the PSMP and CP only has partial compatibility. However, as will be shown in the DMA test results, the concentration of the second component in the CP copolymer may be very small. Therefore, the PSMP has a certain compatibility with the major component of the CP copolymer.

3.4.2 DMA Results

Figure 3-11 shows typical storage modulus (E’)/loss modulus (E’’') - temperature plots of the CP-PSMP composite.

![Figure 3-11](image)

**Figure 3-11** E’/E’’ - temperature plots of CP-PSMP (a) and E’ - temperature plots of PSMP, CP-PSMP and CP (b).

It was found that the CP-PSMP composite shows a single T_g at 54 °C. No other transition was observed above 54 °C, indicating that the component causing T_g2 (72 °C) that was observed...
through the DSC test, which is an indication of the existence of the second component in the CP copolymer, may only have a small concentration. In other words, the major component of the CP copolymer has a certain compatibility with the PSMP. It is noted that the $T_g$ (54 °C) from the DMA test is 4 °C higher than $T_{g1}$ (50 °C) from the DSC test. This trend has been reported before [79]. Based on the $T_g$ (54 °C), the programming temperature was taken as 80 °C, which was well above the $T_g$ (54 °C) of the composite.

3.4.3 Thermo-mechanical Behavior

Figure 3-12 shows a typical 3-D plot of stress, strain, and temperature for this composite (CP-PSMP) with graphs of the programming (ABCD), 1-D confined recovery (DEF) and free recovery (DG) processes.

![Figure 3-12](image)

**Figure 3-12** A typical strain-temperature-stress plot with graphs showing the behavior of CP-PSMP during programming (ABCD), confined recovery (DEF) and free recovery (DG).
Figure 3-13 Typical 2-D plots showing (a) variation of programming stress with time at 80 °C, (b) variation of confined recovery stress with time and (c) variation of strain with time.

Specimens were heated to 80 °C (at point A), compressed (strain controlled mode) in the thickness direction to 10% pre-strain level (point B, loading rate: 1.3 mm/min), held at 80 °C for 1 h to stabilize the stress (point C) and cooled down to room temperature (CD). While confined in the thickness direction, the specimens were heated back to 80 °C at an average rate of 0.5 °C /min in order to determine the recovery stress of the composite (DEF). The specimens were held at 80 °C for 1 h to stabilize the stress (point F). Free-shape recovery was also conducted. Programmed specimens were re-heated to 80 °C (0.18 °C /min) in an oven without applying any
stress to determine the free shape recovery ability of the composite by measuring displacement in the thickness direction with change in temperature (DG). A linear variable differential transducer (Cooper Instruments LDT 200 series LVDT) was used to measure the displacement while the temperature was measured and recorded with a thermocouple instrument (Yokogawa Model DC-100). The average programming stress (at point C) was found to be (74 ± 2 kPa) while the average recovery stress (point F) was (45 ± 1 kPa). The shape fixity from the programming curve was found to be 98% while the shape recovery based on the free shape recovery test was over 98%, indicating good shape memory functionality of the composite. Two-dimensional (2-D) plots showing (a) the variation of programming stress with time at 80 °C (BC), (b) the variation of confined recovery stress with time (DEF), and (c) the variation of strain with time during free recovery (DG), are presented in Figure 3-13.

### 3.4.4 Three-point Bending Test Results

Figure 3-14 (a) shows typical load-deflection plots of the un-notched, notched, and healed (after the first fracture-healing cycle) pure PSMP specimens while (b) shows typical load-deflection plots of the un-notched, notched, and healed (after the first fracture-healing cycle) CP-PSMP composite specimens. The peak loads (average of three specimens) of the originally un-notched PSMP and CP-PSMP specimens were 1385 ± 4 N and 1060 ± 3 N respectively.

The maximum loads (average of three specimens) of the notched PSMP and notched CP-PSMP specimens were (358 ± 2 N) and (230 ± 2 N) respectively. This shows that the structural-length scale damage (notch) significantly reduced the load carrying capacity of both the pure PSMP and the CP-PSMP composite. The maximum loads of the healed PSMP and CP-PSMP specimens were (250 ±3 N) and (693 ± 3 N) respectively. Several observations can be made: (1) using crack sealing by confined shape recovery only (step 1) in the pure PSMP, the peak bending
load of the resulting “healed” specimen is lower than the peak bending load of the notched specimen, indicating that the pre-crack (notch) and newly created crack (complete fracture of the notched beam during bending test) could not be healed by this step alone as shown in Figure 3-14 (a).

**Figure 3-14** Typical load-deflection curves of original and healed specimens after the first healing cycle; (a) PSMP, (b) CP-PSMP.
The reason is that the shape recovery can only narrow or close the crack, but not heal it at molecular-length scale. Therefore, under bending load, a very low healing efficiency is obtained. It is noted that in previous studies, it was found that confined shape recovery can effectively recover the lost structural capacity [44, 85]. The reason is that the previous healing efficiency was evaluated in terms of compressive strength, which was not very sensitive to the existence of cracks. (2) With the two-step CTH healing, as shown in Figure 3-14 (b), about 65% of the peak bending load was recovered.

![Graph](image)

**Figure 3-15** Variation of peak load with healing cycle.

As compared to the notched specimen, the increase in the peak bending load in the healed specimen is about 300%. It is believed that by changing either the concentration of the thermoplastic particles or the pre-strain level during programming, the healing efficiency could be further increased and optimized. Figure 3-14 (b) shows typical plots of the peak bending load with fracture/healing cycle for the CP-PSMP composite. From Figure 3-15, it can be seen that
for five fracture/healing cycles, the proposed healing mechanism as tested through CP-PSMP specimens is reasonably repeatable.

3.4.5 Damage Evaluation by Visual Inspection

Figure 3-16 (a) shows pictures of a specimen with structural-length-scale damage before and after healing.

![Figure 3-16](image)

**Figure 3-16** Pictures of typical specimens with structural-length-scale damage before healing (left) and after healing (right).

It can be seen that the two crack surfaces are not in contact. After the specimen is healed, per the STH mechanism, the crack is closed and healed. Figure 3.16 (b) shows a group of
specimens that were completely fractured and then healed. It can be seen that cracks were completely closed and healed, indicating the effectiveness of this mechanism to heal structural-length-scale damage.

### 3.4.6 SEM Observation

Figure 3-17 shows SEM pictures (fractured surface) of a typical specimen (a) after initial fracture and (b) after the first healing cycle.

![SEM pictures showing fractured surfaces of a typical specimen after initial fracture (a) and after the first healing cycle (b).](image-url)
Figure 3-18 Top surface view SEM pictures of a typical specimen after initial fracture (a) and healing (b).
Solid copolyester particles are clearly visible in Figure 3-17 (a). In Figure 3-17 (b), solid particles are not seen but traces of melted, deformed and debonded copolyester are identified. Also, the surface in Figure 3-17 (b) is smoother as compared to that in Figure 3-17 (a). This is due to the compressive stress exerted on the surface during the crack sealing process (step one), resulting from the shape memory effect. This was necessary in order to keep both crack surfaces in intimate contact during the subsequent crack healing process (step two) via the melting, penetration, diffusion and bonding of copolyester across the crack interface. Figure 3.18 shows top surface view of SEM pictures of a typical specimen (a) after initial fracture and (b) after healing. In Figure 3-18 (a), a crack originating from the end of the pre-notch is clearly visible. In Figure 3-18 (b), the notch and the crack disappear after the two-step healing. The zoomed-in SEM picture shows good interfacial bonding.

3.4.7 EDS Analysis

Figure 3-19 shows EDS spectra of (a) pure PSMP and (b) pure CP with percentage counts of Carbon and Oxygen. The spectra were obtained to serve as baseline data. Top surface view SEM pictures showing the healed interface of the EDS specimen are presented in Figure 3.20. EDS analysis was performed at three points: directly at the interface, 0.1 mm away from the center of the interface and 0.3 mm away from the center of the interface. EDS spectra corresponding to the analyzed points were recorded as shown in Figure 3-20. Figure 3-21 shows the variation of Carbon and Oxygen counts in terms of weight percent with distance away from the interface. It was observed that the carbon count increased away from the interface (pure CP) while the oxygen count reduced in that same direction as the material approached pure PSMP. From Figures 3-19 (b) and 3-20, the oxygen and carbon counts at the interface are slightly different from the pure CP. The reason is that the counts obtained from the box immediately
above the CP interlayer in the composite specimen were an average from an interaction volume, which includes the CP interlayer and may also include a small portion of the neighboring PSMP matrix. However, the interaction volume did not affect the composition in the box 0.1 mm and box 0.3 mm away from the interface. Based on Potts [86], the width of the interaction volume

Figure 3-19 EDS spectra of (a) PSMP and (b) CP.
Figure 3-20 Top surface view SEM pictures (left) of the EDS specimen showing a healed interface, three analysis points ((a) at the center of the interface, (b) 0.1 mm left of interface and (c) 0.3 mm left of interface) and respective EDS spectra (right).
Figure 3-21 Variation of component count with distance away from the healed interface.

was about 3.4 mm. This suggests that the interaction volume for the box 0.1 mm and 0.3 mm away from the interface did not include the CP interlayer. In other words, the counts in the two boxes were due to the diffusion of the CP molecules into the PSMP matrix.

3.5 Summary

In this chapter, a self-healing particulate composite (CP-PSMP) was developed by dispersing 6% by volume of copolyester particles in a polystyrene shape memory polymer matrix in order to realize and validate the two-step close-then-heal (CTH) self-healing mechanism for healing structural-length-scale damage. Based on the test results, it was found that:

(1) The healing efficiency is 65% and is repeatable.
(2) The two-step scheme leads to molecular-length-scale self-healing as evidenced by the EDS test results.

(3) The two-step self-healing is achieved by holding the temperature at 150 °C for 20 min. Therefore, the self-healing should be treated as timely.

(4) Because the notched specimens were fractured completely, the two-step self-healing scheme as validated by this study should be treated as being able to heal structural-length scale damage.

Further studies such as changing the volume fraction of the thermoplastic particles, changing the pre-strain levels during programming, etc., may serve to further increase the healing efficiency.
CHAPTER 4

EFFECT OF THERMOPLASTIC CONTENT ON HEALING EFFICIENCY AND FRACTURE TOUGHNESS

4.1 Introduction

In the previous chapter, a self-healing particulate composite (CP-PSMP) was fabricated by dispersing 6% by volume of copolyester (CP) thermoplastic particles in a Veriflex polystyrene shape memory polymer (PSMP) matrix. Beam specimens of the CP-PSMP composite were used to validate the close-then-heal (CTH) self-healing scheme through three-point bending tests. A healing efficiency of 65% was achieved and shown to be repeatable for the first five fracture/healing cycles. This chapter investigates the effect of thermoplastic content on the healing efficiency of the CP-PSMP composite. To that end, two additional groups of the CP-PSMP composite were fabricated, with CP contents of 3% and 9% respectively. The effect of CP content on fracture toughness and thermo-mechanical behavior of the composite was also investigated.

4.2 Materials and Methods

4.2.1 Raw Materials

The same materials that were used in section 3.2.1 in the previous chapter were used in this chapter.

4.2.2 Fabrication Method

The fabrication procedure is the same as that described in section in the previous chapter.

4.2.3 Beam Specimen Preparation

Single edge notched beam (SENB) specimens were prepared as described in the previous chapter.
4.2.4 Specimen Healing

Fractured specimens were healed as described in the previous chapter.

4.3 Experimentation

4.3.1 Dynamic Mechanical Analysis (DMA)

In addition to determining the effect of CP content on $T_g$ using the methods described in the previous chapter, the effect of repeated programming on $T_g$ was studied on a 6%CP-PSMP specimen for up to five programming cycles.

4.3.2 Thermo-mechanical Behavior

The thermo-mechanical behavior of the composites was investigated as described in the previous chapter to determine the effect of CP content on the shape memory functionality the composite.

4.3.3 Three-point Bending Test

Three point bending tests were performed on SENB specimens as described in the previous chapter in order to determine the effect of the CP content on fracture toughness of the composite. This test was also used to determine the peak bending load of un-notched (control) specimens and healed specimens in order to determine the healing efficiency.

4.3.4 Compression Tests

Compression tests were conducted on specimens with dimensions of 25mm $\times$ 25mm $\times$12.5mm per ASTM D 5045 standard using the MTS 810 testing system (loading rate 10 mm/min) in order to determine the compressive yield strength of the composites. The yield strength is required to determine the fracture toughness of the CP-PSMP composite in terms of critical stress intensity factor ($K_{IC}$).
4.3.5 Indentation Tests

Indentation tests were performed on CP-PSMP specimens (MTS Qtest 150 testing system, loading rate 10 mm/min) per ASTM D 5045 standard in order to obtain load-deflection plots. A Schematic diagram of the indentation test is shown in Figure 4-1. The plots were used to determine the fracture toughness of the CP-PSMP composite in terms of critical energy release rate \( (G_{IC}) \). Un-notched specimens with dimensions of 120 mm × 25 mm × 12.5 mm were used.

4.3.6 SEM Observation

To better understand the effect of the CP content on healing efficiency, SEM (Hitachi S-3600N scanning electron microscope) was used to examine fracture surfaces of typical 3%CP-PSMP and 9%CP-PSMP specimens.

4.4 Results and Discussion

4.4.1 DMA Results

Figure 4-2 shows typical plots of storage modulus and loss modulus with temperature for the 3%CP-PSMP and 9%CP-PSMP composites. In the previous chapter, we showed that the CP polymer has some degree of compatibility with the PSMP matrix. The glass transition temperature was taken as the temperature corresponding to the peak of the loss modulus curve. It can be seen that the glass transition temperature of the composite reduces with increasing CP
content. Based on this result, a programming temperature of 80 °C was selected, which is well above the glass transition temperatures of the composites. From Figure 4-2, it can also be seen that at 30 °C, the storage modulus decreases with increasing CP content. This is consistent with the rule of mixtures [87]. The glass transition temperature and the storage modulus at 30 °C are 56°C and 650MPa, 54°C and 600MPa [from chapter 3], and 52°C and 480MPa, when the CP contents are 3%, 6%, and 9%, respectively.

**Figure 4-2** Typical plots of storage modulus (E') and loss modulus (E'') with temperature.

Figure 4-3 shows typical plots of storage modulus and loss modulus with temperature for a 6%CP-PSMP composite specimen with glass transition temperatures \( T_g^0 \), \( T_g^3 \) and \( T_g^5 \) corresponding to the zero (un-programmed), third and fifth programming cycles, respectively. From the graph, it is seen that the glass transition temperature of the composite increased slightly with programming cycle. The \( T_g \) values were respectively \( T_g^0 = 54°C, T_g^3 = 56°C \) and \( T_g^5 = 57 °C \). This result shows that for up to five programming cycles, \( T_g^5 = 57°C \) is still well below the programming temperature of 80°C. Using this result as a guide, we deduce that the increase in
$T_g$ for the 3%CP-PSMP and 9%CP-PSMP composites for the first 5 repeated programming cycles is also very small. Thus, the programming temperature of 80°C was used for all the specimens in this study.

![Figure 4-3](image)

**Figure 4-3** Typical plots of storage modulus and loss modulus with temperature for a 6%CP-PSMP composite specimen showing variation of $T_g$ with programming cycle.

### 4.4.2 Thermo-mechanical Behavior

Figure 4-4 shows typical 3D thermo-mechanical plots of 3%CP-PSMP and 9%CP-PSMP. The programming, confined recovery and free recovery procedures were detailed in the previous chapter. The stabilized programming stress (SPS) is the stress at point C. The stabilized confined recovery stress (SCRS) is the stress at point F. Stress recovery is defined as the ratio of the SCRS at point F to the SPS at point C. A high value of SCRS is an indication of good capability of closing cracks during confined shape recovery of the damaged composite. The stress recovery ratios are 66%, 60%, and 44% when the CP contents are 3%, 6%, and 9%, respectively. Therefore, the stress recovery functionality of the CP-PSMP composite reduces with increasing CP content.
Figure 4-4 Typical 3D thermo-mechanical plots of (a) 3\%CP-PSMP and (b) 9\%CP-PSMP.
Since the pressure required to seal cracks and keep crack surfaces in close contact during healing comes from the confined recovery stress, this result indicates that with increasing CP content, the stress exerted to keep the crack surfaces together reduces.

Figure 4-5 shows a 2D plot of the recovery strain with time for the composite with CP contents of 3%, 6% [from chapter 3] and 9%.

![2D plot of recovery strain with time](image)

**Figure 4-5** Typical 2D plots of recovery strain with time.

The shape recovery (ability for the composite to recover the strain at point D) as seen in Figure 4-5, is larger than 98 % for all three groups, indicating that the CP-PSMP composite retained its shape recovery ability and shape memory functionality with a variation in CP content. However, it can be seen (Figure 4-5) that after the “lift off” point L, 3% CP shows a steeper and sharper slope of recovery (higher recovery rate) compared to the other two
specimens. This indicates that the speed of recovery or shape recovery rate reduces with increasing CP content. For instance, when the time equals 3.5 hours, the 3%CP composite has already recovered 86% of the strain while the 6% and 9% specimens have only recovered 77% and 71% of the same property, respectively.

4.4.3 Three-point Bending Test Results and the Effect of CP Content on Healing Efficiency

Figure 4-6 shows typical load deflection curves of (a) 3% CP-PSMP and (b) 9% CP-PSMP.

![Figure 4-6 Typical load deflection curves of (a) 3% CP-PSMP and (b) 9% CP-PSMP.](image)

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For the 3%CP specimen, the average peak bending loads for the un-notched, notched and healed specimens were respectively 1260 ± 4 N, 321 ± 3 N, and 645 ± 2 N. For the 9%CP specimen, the average peak bending load for the corresponding specimens were respectively 847 ± 3 N, 220 ± 2 N, and 631 ± 3 N. Figure 4-7 shows the variation of the peak bending load with CP content for the un-notched and healed specimens.

![Graph showing variation of peak bending load with CP content](image)

**Figure 4-7** Variation of the peak bending load with CP content for the un-notched and healed specimens

From Figures 4-6 and 4-7, several observations can be made: (1) By introducing 3% of CP particles into the PSMP matrix, there is a drop in load of -125 N for the un-notched specimen (Figure 4-7). However, once the specimen is healed, the gain in load is +395 N, which is greater than the drop in load for the un-notched specimen. This is a positive trend since the load gained in the healed 3%CP-PSMP specimen is greater than the load sacrificed in the un-notched
specimen. To be consistent with the previous chapter, the healing efficiency in this study was obtained by comparing the peak bending load of the healed specimen to that of the original un-notched specimen with the same CP content. Thus at 3% CP content, the healing efficiency is 51.2%. Also, the increase in the peak bending load for the healed specimen, as compared to the notched specimen, is 200.1% (Figure 4.6). (2) At 6% CP content, the total drop in peak load for the un-notched specimen, compared to the pure PSMP matrix is -325 N, with a total gain in load of +441 N after the specimen is healed (Figure 4-7). This again is a positive trend. The healing efficiency was 65% and the increase in peak bending load in the healed specimen was over 300%. (3) By further increasing the CP content to 9%, a healing efficiency of 75% was obtained. However, the drop in peak bending load (-543 N) is greater than the total gain in load (+381 N) after the specimen is healed, indicating a negative trend. The increase in the peak bending load in the healed specimen was 280%. In section 4.4.2 it was noted that the confined recovery stress reduces with increasing CP content. Thus, it is possible that the negative trend observed at 9%CP content is due to a low confined recovery stress during the healing procedure, such that physical contact between the two crack surfaces was not maximized during the healing procedure. In a control experiment, a group of SENB specimens with 9% CP content was prepared and programmed to 10% pre-strain level so as to increase the confined recovery stress. By testing to fracture and then healing as described earlier, almost identical peak bending load results in the healed specimen were obtained. This indicates that further increasing the pre-strain level has no effect on the healing efficiency. Thus, the drop in the recovery load in the 9%CP specimen is a result of saturation of the PSMP matrix with CP as will be revealed by SEM observation. This is also an indication that a large amount of thermoplastic adversely affects the structural capacity of the thermosetting polymer based particulate composite.
4.4.4 Fracture Toughness

Fracture toughness values of the CP-PSMP composites in terms of critical stress intensity factor ($K_{IC}$) were determined using Equation (1) per ASTM D 5045 standard:

$$K = \left( \frac{P}{BW^{1/2}} \right) f(x)$$

...............................................................................................................(4.1)

where ($0 < x < 1$)

$$f(x) = (6x^{1/2}) \left[ \frac{1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)}{(1+2x)(1-x)^{3/2}} \right]$$

In Eq. (1), $a$ is the total crack length (pre-notch and induced crack), $W$ is the specimen width, $B$ is the specimen thickness and $x$ is the ratio of $a$ to $W$. The value of $K$ becomes $K_{IC}$ when the condition in Eq. (2) is satisfied.

$$a,B,(W-a) > 2.5 * (K/\sigma_y)^2$$

...............................................................................................................(4.2)

where $\sigma_y$ is the tensile yield strength or 0.7 times the compressive yield strength.

![Figure 4-8 Typical compressive stress-strain plots of the CP-PSMP composites.](image)
Typical compressive stress-strain curves of the CP-PSMP composite are shown in Figure 4-8. The average compressive yield strength for the 3%CP, 6% CP and 9% CP specimens were respectively 36 ± 2MPa, 31 ± 1MPa and 28 ± 1MPa.

Fracture toughness values of the CP-PSMP composites in terms of energy release rate ($G_{IC}$) were determined according to Eq. (3) per the ASTM D 5045 standard:

$$G = \frac{U}{BW\phi}$$

where $\phi$ is a parameter taken as 0.246 for $x = 0.5$, and $U$ is the corrected energy obtained by subtracting area A2 (ABEA) from area A1 (ACDA) in Figure 4-9.

![Figure 4-9 Load-deflection co- plots of SENB specimens and indentation specimens.](image)
The area $A_1$ represents the energy required to fracture the SENB specimen during the three-point bending test. In order to correct the effect of system compliance, load pin penetration into the specimen, and compression of the specimen during the bending test, the area $A_2$ below the indentation curve is subtracted from $A_1$ to obtain the corrected energy $U$.

The $K_{IC}$ and $G_{IC}$ values for 3%, 6% and 9% CP content were respectively $1.7334 \text{ MPa.m}^{1/2}$ and $1968 \text{ J/m}^2$, $1.2420 \text{ MPa.m}^{1/2}$ and $1421 \text{ J/m}^2$, and $1.1826 \text{ MPa.m}^{1/2}$ and $1267 \text{ J/m}^2$. The results are plotted in Figure 4-10.

![Figure 4-10](image)

**Figure 4-10** Variation of fracture toughness with CP content.

It is seen that the fracture toughness reduces very sharply when the CP content is less than 6%. Above 6% CP content, the fracture toughness reduces very slowly and almost levels off.
In actual composites, there are three factors controlling the selection of the CP content, which must be balanced. These include absolute peak bending load, toughness, and healing efficiency. Thus, it is seen that for applications where a higher fracture toughness and load carrying capacity are desirable over healing efficiency, CP contents of less than 6% would be appropriate (Figure 4-10). In the case where healing efficiency is desirable over fracture toughness and peak bending load, a CP content greater than 6% may be used.

4.4.5 Effects of CP Content on Healing Repeatability

Figure 4-11 shows graphs of peak bending load (with error bars) with healing cycle for the CP-PSMP composite at different CP contents. For the first five healing cycles, the peak bending load did not vary much for all the three groups, indicating good healing repeatability.
4.4.6 SEM Observation

Figure 4-12 shows typical SEM images of the fractured surfaces of (a) a 3% CP specimen and (b) a 9% CP specimen, after first healing and fracture cycle.

![SEM images of fractured surfaces](image)

**Figure 4-12** Typical SEM images with fracture surfaces of (a) a 3% CP specimen and (b) a 9% CP specimen, after healing and re-fracture.

In Figure 4-12 (b), heavy traces of CP were seen on the fractured surface. This suggests that at the interface, there was more CP-CP bonding compared to the desired CP-PSMP bonding with increasing CP content. This explains the drop in peak bending for the healed 9%CP specimen (as seen in Figure 6).

4.5 Summary

Based on the test results in this chapter, it was found that:

- The healing efficiency of the CP-PSMP composite increases with increasing CP content (up to 9%). However, the fracture toughness and the absolute recovered peak bending load of the composite decreases as the CP content increases.
• For applications where higher healing efficiency is desired, a CP content of at least 6% is suggested.

• As compared to the existing self-healing schemes incorporating thermoplastics, a higher healing efficiency is achieved with a smaller amount of thermoplastic in this study, due to the two-step self-healing scheme used.

• The glass transition temperature and storage modulus decrease as the CP content increases. Repeated programming-healing cycles slightly increase the glass transition temperature of the composite.

• Shape recovery ratio reduces with increasing CP content.
CHAPTER 5
A BIOMIMIC SELF-HEALING SHAPE MEMORY POLYMER BASED SYNTACTIC FOAM FOR 3D WOVEN FABRIC REINFORCED COMPOSITES

5.1 Introduction

In the previous chapter, the effect of thermoplastic copolyester (CP) content on the healing efficiency of the newly developed self-healing particulate composite (CP-PSMP) was investigated for three CP contents (3%, 6% and 9%, by volume). It was found that the healing efficiency increased with increasing CP content while the fracture toughness of the composite decreased in the same direction. This chapter focuses on the development of the proposed biomimetic self-healing syntactic foam. To produce the new self-healing syntactic foam, glass micro-balloons were incorporated into the 9%CP-PSMP particulate composite. In order to strengthen and improve the structural performance of the composite, the self-healing syntactic foam (CP-PSMP-SF) was reinforced with 3-D glass fibers. The ability of the CP-PSMP-SF to heal structural-length-scale damage was investigated using single edge notched bend (SENB) specimens as described in chapter 3. The impact behavior of the composite was investigated on 3-D glass fiber reinforced CP-PSMP-SF panels.

5.2 Materials and Methods

5.2.1 Raw Materials

The same materials that were used in Chapters 2 to 4 were used in this chapter.

5.2.2 Fabrication of CP-PSMP Syntactic Foam

To produce the CP-PSMP syntactic foam, copolyester (CP) particles (9 % by volume) were dispersed in a beaker containing the SMP matrix and mixed to uniformity. Next, glass micro-balloons (GMB), 40% by volume, were dispersed into the CP-PSMP mixture to form a
GMB/CP-PSMP consistency. The GMB/CP-PSMP mixture was then mixed to uniformity and poured in a steel mold with dimensions 300 mm × 300 mm × 12.5 mm. The mold was sealed and the material was cured in an oven as follows: 75 °C for 12 hours, 90 °C for 3 hours and 120 °C for 3 hours. Once the curing procedure was complete, the setup was cooled down and de-molded.

5.2.3 Beam Specimen Preparation

Single edge notched bend (SENB) specimens of the CP-PSMP-SF composite were prepared as described in Chapter 3.

5.2.4 Specimen Healing

Fractured specimens of the CP-PSMP-SF composite were healed as described in Chapter 3.

5.2.5 Fabrication of 3D Fiber Reinforced CP-PSMP Syntactic Foam Composite

The 3-D fiber reinforced CP-PSMP syntactic foam composite was fabricated in a steel mold using the gravity assisted method that was described in Chapter 2. The 3-D woven fabric was impregnating with the GMB/CP-PSMP consistency from section 5.2.2 as shown schematically in Figure 5-1.

![Figure 5-1 Schematic explanation of fabrication process.](image-url)
The material was cured as follows: 75 °C for 12 h, 90 °C for 3 h and 120 °C for 3 h. Once the panel was cured, it was de-molded. The panel was then machined down to specimens with dimensions of 152.4 mm × 101.6 mm × 12.7 mm for impact testing.

5.2.6 Programming of 3-D Fiber Reinforced CP-PSMP-SF

Prior to testing, the 3-D fiber reinforced CP-PSMP-SF specimens were programmed in a strain-controlled mode at a pre-strain of 5% on a CARVER Model 2697 compression molding fixture as described in Chapter 2. The energy stored in the specimen during the programming was later used to heal surface dents and damage resulting from impact.

5.3 Experimentation

5.3.1 Dynamic Mechanical Analysis (DMA) of CP-PSMP-SF

The glass transition temperature of the CP-PSMP-SF was determined using specimens with dimensions of 36 mm × 11.5 mm × 2 mm. The same procedure described in Chapter 2 was used.

5.3.2 Thermo-mechanical Behavior CP-PSMP-SF

The thermo-mechanical behavior of the CP-PSMP-SF composite was investigated using the same procedure that was used in Chapter 3.

5.3.3 Three-point Bending Test

Three-point bending tests were performed on CP-PSMP-SF composite specimens as described in Chapter 3.

5.3.4 Compression Test

Compression tests (MTS QTEST 150, loading rate: 1.3 mm/min) were conducted on CP-PSMP-SF specimens with dimensions of 25mm × 25mm ×12.5mm in order to determine the strength of the CP-PSMP-SF composite.
5.3.5 SEM Observation

SEM was used to observe the distribution of the CP particles and the glass micro-balloons within the PSMP matrix. SEM was also used to study healed and re-fractured surfaces of the CP-PSMP-SF in order to understand the healing behavior of the material.

5.3.6 Impact testing and self-healing of 3D fiber reinforced CP-PSMP-SF

Low velocity impact tests were conducted as described in Chapter 2. The impact energy was 42 J. This test was conducted in order to determine the impact response and self-healing ability of the material in terms of the number of impacts to perforation. The impact tests were conducted at the center of the specimen. Two groups of test specimens were produced. Group 1 (G1) specimens were healed after each impact. Healing was performed using the same fixture that was used during programming. During the healing process, the impacted specimen was inserted in the fixture and the two pre-heated (150 °C) platens were brought in contact with the bottom and top surfaces of the specimen. The specimen was kept within the platens for 20 min to heal dents and damage per the two-step Close-Then-Heal (CTH) mechanism that was described in Chapter 1. This impact-healing cycle continued until full perforation of the specimen. For the group 2 (G2) specimens, no healing was conducted. Three effective specimens per group were used for each impact-healing test.

5.4 Results and Discussion

5.4.1 DMA Results of CP-PSMP-SF

Figure 5-2 shows typical plots of storage modulus and loss modulus with temperature of the CP-PSMP-SF syntactic foam composite. The glass transition temperature was taken as the temperature corresponding to the peak of the loss modulus curve. The glass transition temperature was found to be 49 °C. Based on this result, the programming temperature of 80 °C
used in the previous chapters was maintained, which is well above the glass transition temperatures of the composites. Compared to 9%CP-PSMP from the previous chapter, it can also be seen that at 30 °C, the storage modulus increased with the incorporation of glass micro-balloons (from 480 MPa for 9%CP-PSMP to 720 MPa for CP-PSMP-SF). This is consistent with the rule of mixtures [87].

### 5.4.2 Thermo-mechanical Behavior of CP-PSMP-SF

Figure 5.3 shows typical 3-D thermo-mechanical plots of the CP-PSMP-SF composite. The programming, confined recovery and free recovery procedures were detailed in Chapter 3.

![Typical plots of storage modulus (E') and loss modulus (E'') with temperature of CP-PSMP-SF](image)

**Figure 5-2** Typical plots of storage modulus (E’) and loss modulus (E’’’) with temperature of CP-PSMP-SF.

The stabilized programming stress (SPS) is the stress at point C. The stabilized confined recovery stress (SCRS) is the stress at point F. Stress recovery ratio is defined as the ratio of the SCRS at point F to the SPS at point C. A high value of SCRS is an indication of good capability
of closing cracks during confined shape recovery of the damaged composite. Based on Figure 5-3 the stress recovery ratio of the composite was found to be 60%.

Figure 5-4 shows a 2-D plot of the recovery strain with time for the CP-PSMP-SF syntactic foam composite. The shape recovery (ability of the composite to recover the strain at point D) as seen in Figure 5.4, is larger than 98 %, indicating that the CP-PSMP syntactic foam composite retained its shape recovery ability and shape memory functionality. However, it can be seen (Figure 5-4) that the strain of CP-PSMP-SF starts taking off earlier (around the 1 hour mark) compared to that of 9%CP-PSMP (around 1-5 hour mark). This is reasonable since CP-PSMP-SF has a lower $T_g$.

![Figure 5-3 Typical 3-D thermo-mechanical plots CP-PSMP-SF.](image-url)
Figure 5.4.3 Three-point Bending Test Results

Figure 5-5 shows typical load deflection curves of the CP-PSMP-SF composite. The average peak bending loads for the un-notched, notched and healed CP-PSMP-SF specimens were respectively 650 ± 2N, 170 ± 3N, and 350 ± 2 N. For ease of comparison, the peak bending loads for the un-notched, notched and healed specimens of 9%CP-PSMP from the previous chapter are presented; the values are 847 ± 3N, 220 ± 2N, and 631 ± 3 N respectively. By comparing the peak loads of the healed CP-PSMP-SF specimens to those of the Notched and un-notched CP-PSMP-SF specimens, it can be seen that about 185 % of the load in the fractured specimen was recovered after healing, which corresponds to about 50% of the peak load in the undamaged specimen.
For both the un-notched and notched specimens, the peak load values of the CP-PSMP-SF are 25% lower than those of the 9%CP-PSMP. Also, the healing efficiency of the composite is only 50%, compared to 75% that was obtained for 9%CP-PSMP in the previous chapter. This may be due to the presence of glass micro-balloons in the crack plane during the healing process, which take up space and reduce or minimize contact between the PSMP and CP chains during the healing process. This will be further studied by SEM observation in section 5.4.6. Glass micro-balloons may serve as discontinuities at the crack interface, preventing polymer chains from both crack surfaces to come in contact and entangle during the healing process.

![Typical load deflection curves of CP-PSMP-SF composite.](image)

**Figure 5-5** Typical load deflection curves of CP-PSMP-SF composite.
5.4.4 Compression Test Results

Figure 5-6 shows typical compressive stress-strain plots of the CP-PSMP-SF. The average yield strength of the foam was found to be $15 \pm 0.5$ MPa, which is slightly lower than that of the PSMP-SF.

![Graph of compressive stress-strain plots](image)

**Figure 5-6** Typical compressive stress-strain plots of the CP-PSMP-SF.

5.4.5 Variation of Healing Efficiency with Healing Cycle

Figure 5-7 shows a graph of peak bending load (with error bars) with healing cycle for the CP-PSMP-SF composite. For the first five healing cycles, the peak bending load was seen to decrease from 350 N to 225 N as shown in Figure 5-7.
Thus the healing efficiency based on peak bending load at the 5th healing cycle was 37.5%. As compared to CP-PSMP, the healing efficiency decreases much faster as fracture-healing cycle increases. The reason is that, in the fractured surface CP-PSMP-SF specimens, the glass microballoons (some of them may have also been fractured) occupy a certain area, which prevent the molten the CP molecules from diffusing into the fracture PSMP matrix. Consequently, molecular-length scale healing is not achieved for this occupied area.

5.4.6 SEM Observation

Figure 5-8 (a) shows a spherical glass microballoon (GMB) within copolyester (CP) thermoplastic particles at room temperature. Figure 5-8 (b) shows a typical SEM image of the fractured surface of a CP-PSMP-SF specimen after the first fracture. The CP particles, shown in Figure 5-8 (a), could not be clearly identified in Figure 5-8 (b). The final curing temperature for the CP-PSMP-SF was 120 °C, which is within the melting range of the CP particles. Thus it is possible that the particles melted during the curing process.
Figure 5-8 SEM pictures showing (a) a glass micro-balloon within CP particles at room temperature (b) distribution of glass micro-balloons within CP-PSMP Matrix.
Figure 5-9  Typical SEM pictures of a CP-PSMP-SF specimen after initial fracture (a) and after the first healing cycle (b).
Figure 5-9 shows typical SEM pictures of a CP-PSMP-SF specimen after initial fracture (a) and after the first healing cycle (b). It is seen that the crack was closed and healed. Figure 5-10 shows a typical re-fractured surface of CP-PSMP-SF after the first healing cycle, with glass micro-balloons clearly seen on the surface. The glass micro-balloons in the crack plane hinder and block PSMP and CP polymer chains from coming together and bonding during the healing process. This results in a reduction in the total surface area available for bonding the CP and PSMP chains across the crack interface, as reflected by the drop in healing efficiency that was observed earlier. The glass micro-balloons may also serve as discontinuities in the crack plane, facilitating the initiation and propagation of cracks.

Figure 5-10 A typical re-fractured surface of CP-PSMP-SF after the first healing cycle showing glass microballoon on the surface.
5.4.7 Variation of Impact Load with Impact Cycle

Figure 5-11 shows the variation of impact load with impact cycle for G1 and G2 specimens of the CP-PSMP-SF. The average peak impact load was found to be $5.3 \pm 0.1$ kN. The average deflection after the first impact was found to be $12 \pm 0.2$ mm.

**Figure 5-11** Variation of impact load with impact number for both G1 and G2.

Comparing the CP-PSMP-SF to the PSMP-SF from Chapter 2, the following observations are made: (1) it is seen that the incorporation of CP slightly reduces the peak impact load (from 6 kN in PSMP-SF to 5.3 kN in CP-PSMP-SF). However, the impact and perforation resistance of the foam is significantly increased (requiring up to 16 impacts to perforate the CP-PSMP-SF compared to only 5 impacts for PSMP-SF); (2) the close-then-heal (CTH) mechanism delays perforation in the G1 specimens of CP-PSMP-SF by up to five (5) impacts to a total of 21 impacts. For the PSMP-SF (Chapter 2), perforation was delayed by only two impacts to a total of
seven (7) impacts. The first impact causes local densification around the impact region for the G2 specimen, as reflected by the sudden rise in peak load at the second impact cycle (Figure 5.11). This trend was observed before in the PSMP-SF specimens (Chapter 2). For the G2 specimens, it is seen that the load reduces very slowly for the first 12 impacts, before reducing more rapidly from the 13th impact to perforation at the 16th impact. This indicates that major unhealable damage was inflicted in the 3D fibers at the point of impact at the 13th impact cycle. For the G1 specimen, the sudden rise in peak load at the second impact was not observed. Since the G1 specimens were healed after each impact, the infliction of major damage in the material was delayed. For example, at the 13th impact, while the average peak impact load of the G2 specimen has already dropped to about 3.6 kN, the peak load of the G1 specimen is still up at 4.6 kN. Figure 5.12 shows a representative load-deflection curve of G1 specimens at perforation (21st impact).

![Figure 5-12 Representative load-deflection curve of G1 specimens at perforation (21st impact).]
5.4.8 Variation of Energy with Impact Number

As was seen in Chapter 2, when a specimen is impacted, it can dissipate energy in two modes: energy transfer (mode I) and energy absorption (mode II). For mode I, the impact energy is stored in the form of elastic strain energy and kinetic energy which is later transferred back to the projectile or the environment through vibration and damping. For mode II, the impact energy is absorbed through plastic deformation (as in indentation) and damage (as in matrix cracking, fiber debonding, fiber breakage, etc). The initiation energy has been defined as the energy corresponding to the point of maximum impact force and is basically a measurement of the ability for the target to transfer energy elastically (mode I).

![Total energy and Initiation energy graph](image)

**Figure 5-13** Variation of energy with impact number for both G1 and G2.

Propagation energy (the difference between the maximum energy and the initiation energy) is a measurement of the energy absorbed by gross damage (mode II). Figure 5.13 shows
the variation of total energy and initiation energy (IE) with the number of impact cycles for the G1 and G2 (control) CP-PSMP-SF specimens. It is seen that the total impact energy did not change much until the last few impacts for both G1 and G2. The reason is that toward the last few impacts, the tup begins to perforate the specimen and thus (the tub) shares a portion of the available energy. The IE of control specimens was fairly constant until the 13th impact and decreased sharply with increasing impact number, while IE of G1 specimens was fairly constant until the 18th impact before decreasing steadily to perforation. Therefore, for G1, the self-healing delayed the onset of energy absorption by non-healable damage until the 18th impact. The impact number where IE starts to decrease sharply indicates a decrease in energy dissipation by mode I (energy transfer) and an increase in energy dissipation by mode II (energy absorption such as by non-healable damage like fiber fracture), as seen in Figure 5.13.

![Variation of deflection with impact number.](image)

**Figure 5-14** Variation of deflection with impact number.
5.4.9 Variation of Deflection with Impact Cycle

The variation of deflection with impact number for both G1 and G2 specimens of CP-PSMP-SF is shown in Figure 5-17. From the Figure, it can be seen that the deflection of G2 increased faster than that of G1. This suggests that the self-healing process reduced the rate of degradation in stiffness in and around the impact region in G1 specimens.

5.5 Summary

In this chapter, the biomimetic self-healing shape memory polymer based syntactic foam (CP-PSMP-SF) was developed and its ability to heal structural length-scale damage was evaluated through crack sensitive three-point bending tests. The healing efficiency after the first healing cycle was 50%. SEM revealed the presence of glass micro-balloons in the crack plane which reduced the total surface area available to bond the thermoplastic copolyester and polystyrene shape memory polymer during healing. Impact tests results on 3-D fiber reinforced CP-PSMP-SF panels revealed excellent impact properties at 42 J impact energy. Sixteen (16) impacts (without healing) were required to perforate the panels, indicating good impact tolerance. The self-healing scheme delayed the perforation of the panels by 5 impacts to a total of 21 impacts.
CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions

In this dissertation, a novel two-step biomimic close-then-heal (CTH) self-healing mechanism for polymer composite materials was realized experimentally, and its ability to heal structural-length-scale damage molecularly in an autonomic, efficient, repeatable, and timely manner was evaluated. Such a mechanism is useful for extending the service life of polymeric composites, such as syntactic foam, which is increasingly used in weight sensitive applications. A systematic approach was adopted to realize and validate this novel scheme for self-healing structural-length-scale damage in structural polymeric syntactic foam composites.

In the second chapter of this dissertation, the methodology to fabricate 3-D fiber reinforced shape memory polymer syntactic foam for structural applications was developed. The effect of impact energy on the ability of SMP foam panels to seal damage and mitigate impact was investigated in terms of the number of impacts to complete perforation. It was found that by healing surface dents and closing internal damage, perforation was delayed (from 9 impacts to 16 impacts at 32 J impact energy and from 5 impacts to 7 impacts at 42 joules impact energy).

In the third chapter of this dissertation, a new self-healing particulate composite was developed by incorporating co-polyester thermoplastic particles (6% by volume) within a polystyrene shape memory polymer matrix. Compatibility between the two polymers was confirmed by DSC analysis. The particulate composite was used to validate the two-step close-then-heal (CTH) self-healing mechanism using single edge notched bend (SENB) specimens (with a notch width of 1mm) through three-point bending tests. SEM showed that the notch was completely closed and healed during the healing process, indicating that the CTH scheme was
successfully used to close and heal structural-length-scale damage. Energy dispersive spectroscopy (EDS) was used to indirectly verify the diffusion of the thermoplastic copolyester molecules into the SMP matrix during self-healing, indicating that healing occurred at the molecular level. Self-healing was achieved in 20 minutes, at 150 °C. Thus the self-healing process can be treated as timely. A repeatable healing efficiency of 65% was obtained. Human assistance was required to confine and heat the specimens during the healing process. However, once the healing mechanism was activated, healing took place autonomously.

In the fourth chapter of this dissertation, the effect of thermoplastic content on self-healing efficiency was investigated. CP-PSMP composites with CP contents of 3% and 9% were fabricated and the effect of CP content on healing efficiency was studied. It was found that the healing efficiency increased with CP content. The healing efficiencies at 3% and 9% CP volume fraction were respectively 50% and 75%. However, the fracture toughness of the composite decreased in the same direction.

In the fifth chapter of this dissertation, the self-healing shape memory polymer based syntactic foam proposed in this dissertation was developed. The ability for the foam to close and heal structural-length-scale damage was demonstrated on SENB specimens. Through three-point bending tests, a healing efficiency of 50 % based on fracture load was achieved. The healing efficiency was seen to reduce with healing cycle for the first five healing cycles. SEM revealed that glass-micro-balloons in the crack plane shared the total area available for bonding between the SMP matrix and thermoplastic particles. Impact tests on 3-D fiber reinforced CP-PSMP-SF panels revealed good impact properties. Compared to the PSMP-SF in Chapter two (5 impact to perforation, at 42 J impact energy), the CP-PSMP-SF was perforated at the 16th round of impact. Self-healing damage after each impact delayed perforation by five more rounds to the 21st
impact. The self-healing scheme restored the stiffness around the impact area, as revealed by the variation of deflection with impact number.

Thus, it is seen that the STH self-healing scheme as validated on CP-PSMP-SF can heal structural-length-scale damage timely (20 minutes at 150 °C). Based on the EDS analysis in Chapter 3, it can be inferred that self-healing occurred at the molecular level. Human assistance was required to trigger self-healing (by thermal activation), but once the self-healing mechanism was activated, healing occurred autonomously.

6.2 Future Work

The healing efficiency of the CP-PSMP-SF obtained in this study is 50%. The challenge for future work is to improve the healing efficiency of the self-healing syntactic foam.

![Diagram](image)

**Figure 6-1** Schematic diagram showing the distribution of glass micro-balloons and thermoplastic particles within a crack plane.
One suggestion is to use glass micro-balloons with a smaller average diameter compared to the thermoplastic particles so as to maximize contact between the shape memory polymer chains and the CP chains during the self-healing process. Figure 6-1 is a schematic diagram showing the distribution of glass micro-balloons and thermoplastic particles within a crack plane. In Figure 6-1 (a), the glass micro-balloons are larger than the thermoplastic particles. In Figure 6-1 (b) the thermoplastic particles are larger than the glass micro-balloons. Thus per Figure 6-1 (b, it is envisioned that there would be better contact between the thermoplastic particles and the shape memory polymer matrix during the self-healing process, leading to an increase in healing efficiency as well as repeatability. Also, good bonding between the thermoplastic and microballoons could also increase the healing efficiency.
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