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Effects of partial confinement and local heating on healing efficiencies of self-healing particulate composites

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EFFECTS OF PARTIAL CONFINEMENT AND LOCAL HEATING ON HEALING EFFICIENCIES OF SELF-HEALING PARTICULATE COMPOSITES

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

in

The Department of Mechanical Engineering

by
Jonah D. Champagne
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Abstract

Shape memory polymers are smart materials that can be trained to hold a temporary shape through programming and regain their original shape upon heating. Since their discovery in the 1960s, much research has been devoted to the study of these polymers. Of particular interest in recent years is the study of self-healing shape memory polymers. In a previous study, it has been shown that in order for efficient healing to take place in self-healing shape memory polymers, confinement during healing is essential. Moreover, a two-step close-then-heal (CTH) approach to healing was suggested. It was shown that use of this CTH method on a shape memory particulate composite provided both structural (macro) and microscopic healing of the material. The present study aimed to further investigate the influence on confinement levels and local heating on healing efficiencies of a polystyrene based shape memory polymer with 6% by volume of thermoplastic particle additives (copolyester). After fabrication of the composite, the glass transition temperature was determined by DSC analysis of the material. Cylindrical specimens measuring 120 mm long and with a 10 mm diameter were used for testing. Each specimen underwent thermomechanical programming to a pre-strain level of 10%. After programming each specimen then underwent a three-point flexural test to complete failure. The broken specimens were then healed at varying levels of confinement and at varying healing stresses. In this study three levels of confinement and three healing stresses were investigated: 50 %, 75 %, 100 % and 0 MPa, 7 MPa, and 12 MPa respectively. At least two specimens were used for each test. After healing the specimens again underwent a three-point flexural test to complete failure. Comparison of the post-programming ultimate strength to the post-healing ultimate strength provided a means of calculating the healing efficiency of the material under each testing condition.
It was shown that as the level of confinement increased, so did the healing efficiency of the material. This was attributed mostly to the higher recovery stress produced by more activation of the polymer chains as more of the material is confined and heated. Also, in the case of 75 and 100\% confinement, the healing efficiency showed a steady increase as the healing stress applied increased. However, this trend was not seen in the case of 50\% confinement. The maximum average healing efficiency seen was 91.02\% and was obtained through healing at the maximum confinement level (100\%) and the maximum applied healing stress (12 MPa).
Chapter 1: Introduction

1.1 Shape Memory Polymers

Shape memory polymers (SMPs) are a special class of polymers that can be trained through a programming process to remember a shape and return to it once acted upon by a certain triggering external stimulus. After the polymers are fabricated, they assume their permanent shape. Next they can be cut into desired shapes such as cylinders for instance. Once the material is fabricated and cut into a shape, this shape is the specimen’s permanent shape (shape A). The material can then be programmed (discussed later) to another temporary shape (shape B). The material will hold this temporary shape until it is acted upon by some external triggering stimulus which signals the specimen to return to its original permanent shape (shape A). This ability or characteristic of the material reverting back from its temporary shape to its permanent shape is known as shape memory effect (SME).

The first known mention of a material exhibiting a shape memory effect was in a United States patent by L. B. Vernon in 1941 [1]. In this patent, Vernon exclaimed that a dental material composed of methacrylic acid ester resin exhibited a shape memory effect by regaining its shape upon heating. Little research was done on these materials until the 1960s when heat shrinkable tubing consisting of a shape memory material that would shrink upon heating was introduced into industry. Since then research has been increasing on these materials and in the last two decades, these SMP materials have been the subject of much research work [2].

1.2 Shape Memory Effect: The Mechanism

Indeed, the shape memory effect of a SMP is a remarkable characteristic. The driving force behind this SME is conformational entropy. In an amorphous polymer, the polymer chains take on a completely random distribution. That is, the most probable conformation of the
polymer chains is one of highest entropy which corresponds to the most thermodynamically stable state. Letting $Z$ represent the probability of a conformation, the most probable state for the polymer chains is that of highest disorder or entropy (most entangled state) and can be given by the Boltzmann equation:

$$S = k\ln Z$$  \hspace{1cm} (1)

where $k$ is the Boltzmann constant and $S$ is the entropy [3].

There are many types of external stimuli that can be incorporated into the SMP to trigger its shape memory effect. Some of the common types are light, ions, pH, pressure moisture, and temperature to name a few [4]. Once the SMP has been programmed and is thereafter exposed to its corresponding SME stimuli, it will then begin to recover its original permanent shape. The stimuli used in this study and perhaps one of the most commonly used stimuli, is temperature.

In these thermosetting SMPs, as the temperature increases, the mobility of the polymer chains also increases. Figure 1 shows the sequence involved in the SME of SMP materials. As can be seen in the first diagram, the polymer chains are initially at a state of highest entropy that is, they are very tangled. When the SMP is heated to its transition temperature ($T_{trans}$) the polymer chains become more mobile and the material can be deformed by the application of stress. If the material is deformed, the polymer chains are essentially translated to a state of lower entropy (less entropically favored state). At this point if the deformation stress is held and the material is subsequently cooled below its $T_{trans}$ then the configuration or shape will be frozen due to the immobility of the polymer chains at this temperature. This would then be the materials temporary shape. Next, the specimen could be reheated to $T_{trans}$ at which point the mobility of the polymer chains again increases and will conform back to their highest state of
Molecular Mechanism of Shape Memory Polymers

The black dots are netpoints, the blue lines are polymer chains at a temperature below $T_{trans}$, and the red lines are polymer chains at a temperature above $T_{trans}$. Adapted from [5]

entropy which is the pre-deformed conformation (original shape of the SMP). In amorphous SMPs, the $T_{trans}$ is the glass transition temperature ($T_g$) of the polymer. This is the temperature at which the polymer changes from a glassy state to an elastic, deformable state as will be discussed further section 1.4.

1.3 Shape Memory Polymer Composites

Shape memory polymer composites (SMPCs) are simply composite materials composed of shape memory polymers (as the matrix) and some type of additives. These additives can be of many different forms depending on what the objective of the SMPC is. Much of the research in recent years has been centered on self-healing composite materials. These materials are composed of a shape memory polymer matrix with healing agent as the additive. The healing
agent added to the matrix can be of various forms such as microcapsules, vascular networks, and thermoplastic particles which will all be discussed in further detail later [6].

Self-healing composites are inspired by the natural way the human body heals wounds and are therefore biomimetic. For example, when a healthy person’s skin is cut there are three basic steps that take place contributing to healing. The first is inflammatory response which causes blood clotting in the cut area, next is cell proliferation (or matrix remodeling) in which new cells traffic and congregate in the damaged area, and finally matrix remodeling, or reconstruction of the damaged area with new cells. A parallel analogy can be made with the synthetic healing mechanism intrinsic in self-healing materials. In these materials the healing process also involves three steps. The first step is actuation or triggering of the healing process by some type of external stimulus. The second step is transport and buildup of the healing agent in the wounded area and finally the last step is chemical repair of the damaged area via various chemical processes such as polymerization. A schematic representation of both the biological and synthetic healing schemes as well as the time involved for each is depicted in figure 2 [6].

Depending on the type of additive or healing scheme, the self-healing could be autonomous or non-autonomous. The autonomous self-healing materials need no external help whatsoever, the self-healing process is immediately triggered when damage is realized by the system. This is the type of self-healing process that is depicted in figure 2. The non-autonomous self-healing materials however, need some sort of external stimulus to trigger the self-healing process, such as heating. The various types of healing agents such as encapsulation, vascular networks, and thermoplastic particles will be discussed next.

1.3.1 Microencapsulation

As previously stated, there are many types of healing agents that can be incorporated into
Figure 2. Comparison of biological healing to synthetic healing and the time involved for each. Figure adapted from [6]

a self-healing material. Each of the various healing agents available has its own set of advantages and disadvantages when compared to others. The first type of healing scheme to be discussed here is microencapsulation. In this method small capsules containing healing agents and a catalyst are dispersed into the SMP matrix during fabrication [7-9]. When damage to the material occurs, such as by crack formation, these microcapsules are ruptured and healing agent and catalyst are released into the damaged region. Capillary forces suck the healing agent and catalyst into the cracks that were formed during the damaging period. Thereafter, the healing agent and catalyst react and heal the damaged area thereby, preventing further crack propagation.

One of the great advantages of using this method is that the healing is autonomous; once the material is damaged, the healing agent is immediately released and the self-healing process begins. There has been much research done using this microencapsulation technique and healing
efficiencies of up to 100 % have been reported using this method [10]. There are however, a few drawbacks to using this method. First, healing can only take place once in a specified region. That is, once the capsules have been ruptured and the healing agent has been released into the damaged area, if that area gets damaged again there are no longer virgin capsules containing healing agent to repair the damage. Another drawback is that the emptied out broken capsule regions can become deformities themselves within the material which could lead to compromised strength properties [10].

1.3.2 Vascular Networks

Another method used to incorporate healing agents into a SMP is vascular networks. As is the case with many of these self-healing methods, the use of vascular networks for achieving self-healing effects can be likened to a biological system. It is well known that arteries and veins work together to circulate blood throughout the human body. However, it is very small capillaries that branch out all through the body, in the muscles, skin, organs, etc. that are responsible for delivering oxygen rich blood to these various systems of the body. Revisiting the cut example considered earlier, when the skin is cut, it is essentially the capillaries that supply or carry the blood that ultimately clots in the wound area thereby closing the cut. In much the same way, small hollow tubes have been incorporated into SMP systems for which healing agents can be added. When a crack begins to propagate or some type of damage to the system occurs, these tubes filled with healing agent are ruptured thereby releasing the healing agent in-situ [11]. Much like the microencapsulation method, the use of vascular networks for self-healing materials promotes autonomous self-healing ability. However, many of the same drawbacks also plague this method. Namely, the material can only heal once and after healing has occurred, the emptied
hollow tubes can become a source of defects within the material compromising the overall strength of the material.

1.3.3 Thermoplastic Particles

Another method used to promote self-healing in SMPCs is the incorporation of thermoplastic particles. Thermoplastics are a class of polymers that can be heated above their melting temperature (at which point they become a viscous liquid) and formed into various shapes by use of molds etc. The attractive property of these thermoplastics is that they can undergo these cycles of heating above their melting point, reforming, and cooling down into the formed shape many times without degradation of the polymer structure. It is this property that makes them ideal for use in self-healing polymer systems.

Self-healing composites that incorporate these thermoplastic particles have the ability to heal damaged areas multiple times without a large loss of strength between successive healing cycles. When the material gets damaged or cracked, it must be heated above the melting temperature ($T_m$) of the thermoplastic. At this point the thermoplastic particles become a liquid and flow into the damaged area. Further heating of the material will cause the thermoplastic particles to reach their bonding temperature ($T_b$) at which they will bond to the two sides of the cracked or damaged region. Upon cooling below the $T_m$, the thermoplastics will harden again thereby providing continuity or “gluing” between the two damaged surfaces. It should be noted that for a SMP based self-healing material using thermoplastics as the healing agent, it is required that $T_g < T_m < T_b$ [12].

1.4 Glass Transition Temperature

The glass transition temperature ($T_g$) of a polymer is perhaps one of the most important properties of the material. The glass transition temperature is the temperature at which the
polymer changes from a glassy state (hard and brittle) to an elastic or rubbery state. When a polymer is at a temperature below its $T_g$, the many monomer chains that make up the polymer are tangled and cannot easily move which causes the material to be stiff and brittle. Above the $T_g$ however, the monomer chains possess enough kinetic energy to begin moving at the molecular scale which translates to a characteristically rubbery deformable material at the macro scale.

Depending on the application, polymers can be designed to have high or low glass transition temperatures. Various elastomers, such as gaskets and O-Rings are designed to operate around their $T_g$ values which is what gives them their rubbery texture which is ideal for liquid tight seals such as are used in pumps. Other polymers such as some containers are designed to operate below their $T_g$ which makes them rather rigid and ideal for many applications. For the application of self-healing polymers, the polymers are usually designed to operate in the glassy state below their $T_g$ since healing is activated by heating above the $T_g$ of the polymer.

Most commercially available polymers have manufacturer provided values for the $T_g$. However, many SMPs and especially SMPCs do not have commercially available $T_g$ values and therefore these values must be experimentally obtained. One method commonly used to determine the $T_g$ of polymers is Differential Scanning Calorimetry (DSC). In this method a small sample of the polymeric material is placed into the DSC machine for analysis. As per the user’s specifications, the DSC will heat up and cool the sample to specified temperatures at specified rates. The heat capacity or heat flow of the sample is then plotted against the temperature. Polymeric materials have the inherent property that above their $T_g$ they have a higher heat capacity than below their $T_g$. This property causes a slight step up in the plot of the heat capacity versus temperature curve. This characteristic step up can be seen in figure 3. The $T_g$ value is then taken to be the temperature corresponding to the midpoint of the step up on the curve.
Figure 3. Characteristic step up seen on the heat capacity vs. temperature plot at the $T_g$ of the material

1.4.1 Melting Temperature

While the SMP is mostly comprised of an amorphous structure, the thermoplastic particle additives have a more semi-crystalline structure. As discussed previously, amorphous polymers exhibit a glass transition temperature that can be determined via various experimental means. The thermoplastic particles however, can exhibit both a $T_g$ and a melting temperature ($T_m$). When the thermoplastics reach their $T_m$, they become a viscous fluid that can flow.

In general, polymers are never completely amorphous or completely crystalline, and therefore may exhibit both a $T_g$ and a $T_m$ when measured experimentally. This is due to the fact that the amorphous portion will show a $T_g$ and the crystalline portion will show a $T_m$. Indeed, when the self-healing SMPC is analyzed via DSC for example, it may show both a $T_g$ and a $T_m$ value due to the fact that it is a composite composed of both semi-crystalline (thermoplastic particles) and amorphous (SMP) materials.
Much like with the $T_g$, the $T_m$ can also be found by plotting the heat capacity versus temperature of the material via DSC analysis. Just like with the $T_g$, the $T_m$ will produce a signature curve when it is reached. Figure 4 shows this characteristic curve on the heat capacity-temperature plot for the material.

![Characteristic curve](image)

Figure 4. Characteristic curve seen at melting point of polymer

Once the temperature of the polymer reaches its $T_m$, additional heat must be added to the material in order to melt the polymer. This extra heat all goes into the process of melting the polymer and not into raising the temperature. This is why there is a peak seen on the heat capacity versus temperature plot. DSC analysis of the SMPC will be performed to find the $T_g$ in chapter 5 and the characteristic curve will be seen.

1.5 Thermomechanical Cycle

The full thermomechanical cycle of a SMP consists of a 3 step programming followed by a 1 step recovery cycle. Through the completion of the thermomechanical cycle, the SMP will begin at its original permanent shape and end at (or nearly) its original permanent shape. Each of the steps and variables involved will be discussed in detail next.
1.5.1 Shape Memory Polymer Programming

For a SMP to exhibit its shape memory effect it must first go through what is known as programming. During programming the SMP is “trained” to hold a temporary shape. The programming of the SMP involves 3 basic steps: (1) high temperature loading, (2) cooling, and (3) unloading. It should be noted that the programming can be either stress or strain controlled. Before step (1) begins the specimen is heated above its $T_g$ which allows it to be deformed into a temporary shape. Step one can then begin in which case the specimen is loaded to a specified stress $\sigma_m$ (for stress controlled programming) or strain $\varepsilon_m$ (for strain controlled programming). The specimen is held at this stress or strain for a given amount of time in order to allow for relaxation of the polymer chains. Afterwards, step (2) begins in which case the specimen is cooled down below its $T_g$ while the stress or strain is held constant. Once the specimen has cooled, it is then be unloaded (step 3). It should be noted that during the unloading in step (3) springback will occur wherein the specimen will elongate by a small amount. The amount of springback that occurs depends on the shape fixity of the material which will be discussed shortly. [13]

1.5.2 Shape Recovery

As previously discussed, to complete the full thermomechanical cycle, the SMP must undergo the 3 step programming as well as recovery. A schematic representation of the full thermomechanical cycle is shown in figure 5 and a typical thermomechanical cycle on an SMP specimen is illustrated in figure 6. Two types of recovery can be performed on the material. In the first type, the specimen is heated back up above its $T_g$ while no external strain or stress is applied, this is known as free recovery. The specimen is therefore allowed to stretch back to its original pre-programmed or permanent shape. Another type of recovery is confined recovery
Figure 5. Typical Thermomechanical cycle of a SMP: Step 1 is deformation at $T > T_g$, step 2 is cooling to $T < T_g$ while maintaining the strain level, step 3 is removal of stress, and step 4 is recovery which involves heating the material again to $T > T_g$, this time with no stress applied.

wherein the specimen is constrained to a certain level and then heated above its $T_g$. Li and Nettles [14] showed that confined recovery is needed for effective healing of self-healing SMPCs. When the material is confined and then heated above its $T_g$, the material will try to expand to its original shape but the confinement will inhibit this action. Therefore, the material is forced to expand inward which will close any cracks within the system. Li and Nettles termed this the close then heal method (CTH). As the name suggest, this is a two-step method involving (1) closing the crack by confined recovery and (2) healing. It was shown by Li and Nji [15] that use of this method in self-healing particulate composites provides both macro and micro scale
healing. The crack is healed on the macro scale when the material attempts to recover its permanent shape under confinement and it is then healed on the micro scale by melting and bonding of the thermoplastic particles along the crack surface. This method will further be discussed in section 1.7.

The shape recovery quantitatively compares the shape after thermomechanical programming and recovery, to the original permanent shape. That is it is a means by which the efficiency of the material can be measured. The shape recovery rate is given by equation 2 below.

\[
R_r(N) = \frac{\epsilon_m - \epsilon_p(N)}{\epsilon_m - \epsilon_p(N-1)}
\]  

Where \(\epsilon_m\) is the ideal mechanical deformation strain, \(\epsilon_p\) is the permanent strain, and \(N\) is the number of thermomechanical cycles the specimen has undergone. The corresponding equations...
for the ideal mechanical deformation strain and the permanent strain are given in equations 3 and 4 below.

\[ \epsilon_m = \frac{l_0 - l_1}{l_0} \]  

\[ \epsilon_p = \frac{l_0 - l_2}{l_0} \]  

Where \( l_0, l_1, \) and \( l_2 \) are the initial length, the length after compression but before springback, and the length after recovery respectively [13].

1.5.3 Shape Fixity

Whereas shape recovery compares how well the material regains its permanent shape after programming, shape fixity compares how well the material holds its programmed shape between step 2 (cooling) and step 3 (unloading). Once the specimen has cooled and begins to be unloaded, a springback effect will take place therefore changing the length or strain that was applied to the specimen during programming to some new decreased strain value. The shape fixity of the SMP is another variable that is often used to measure the efficiency of the SMP material. The shape fixity rate is given as:

\[ R_f(N) = \frac{\epsilon_u(N)}{\epsilon_m} \]  

where \( \epsilon_u \) is the temporary shape strain and is given in equation 6 below.

\[ \epsilon_u = \frac{l_0 - l_3}{l_0} \]  

Where \( l_3 \) is the actual length after springback and all other variables are as defined previously [13].

1.6 Healing Efficiency

The healing efficiency of a SMP composite is a measure of how well the material regains its pre-damaged mechanical properties after healing. As stated earlier, healing efficiencies can be
measure based on different properties of the material such as shape fixity, shape recovery, and strength recovery. Therefore, a general formula for measuring the healing efficiency of an SMP composite can be given as:

\[ \eta = \frac{f_{\text{healed}} - f_{\text{damaged}}}{f_{\text{virgin}} - f_{\text{damaged}}} \]  

where \( f \) is the property being used to measure the efficiency [13]. In this study, healing efficiency is measured via fracture strength recovery of the material after healing. As will be discussed in detail later, the specimens will undergo a 3 point flexural bending test until they completely break into two pieces. Therefore, the damaged strength is effectively zero and equation 7 can be simplified to equation 8 below.

\[ \eta_{\text{strength}} = \frac{\sigma_{\text{heal}}}{\sigma_{\text{virgin}}} \]  

Multiplying equation 8 by 100 gives the percent of strength recovery of the material.

**1.7 Close-Then-Heal Method**

**1.7.1 Close-Then-Heal Via Full Confinement**

As has been previously discussed in section 1.5.2, the CTH method can be used to provide optimum healing in thermosetting self-healing polymers. The method is a biomimetic healing process and can be likened to the healing process in many biological organisms. For example when a cut is realized in a biological organism such as the human body, the body will first close the cut by causing blood to clot the wound area. Next the body will begin healing the wounded area by building new cells in the cut region. This is the basis for the CTH method of healing. Step 1 of the CTH method involves first closing the damaged area such as a crack for example. Step 2 involves then healing the crack by use of a healing agent within the SMP matrix.

The CTH process as it pertains to the shape memory polymer particulate composite will now be discussed. The material used in this study consists of a polystyrene based shape memory
polymer (PSMP) with copolyester (CP) additives as the healing agent. The CTH method takes full advantage of the SME of SMPs. As has been discussed, after programming if the material is heated back to its $T_g$ it will begin to regain its original pre-programmed shape (permanent shape). However, if the material is confined 3-dimensionally and then heated to its $T_g$, it cannot expand outwardly due to the confinement and therefore must expand inwardly thereby structurally closing any internal cracks and damage within the material (step 1 of CTH).

![Diagram of the CTH process](image)

Figure 7. Close-Then-Heal process for shape memory polymer particulate composite. The golden color represents the shape memory polymer (PSMP) and the purple dots represent the thermoplastic particles (CP) of the composite material.

Further heating of the material to the $T_m$ of the copolyester will cause melting of the CP into liquid form. Still further heating will cause the CP to reach its $T_b$ at which point it will diffuse into the cracked region and provide bonding between the CP and PSMP thereby healing the
damaged area (step 2 of CTH). A schematic representation of this process is presented in figure 7. In previous studies [16-18] the confinement provided to perform the CTH method on the specimens was done by fully confining the specimens in a rigid confining mold. However, full confinement of the entire specimen during recovery is not necessary in order to perform healing via the CTH method.

1.7.2 Close-Then-Heal Via Partial Confinement

In the current study, specimens undergo healing under partial confinement. That is, the cylindrical specimens (discussed in section 3.2.1) are confined at varying levels along the length as is illustrated in figure 8. As the partially confining mold is heated above the $T_g$ of the material, the portion of the specimen within the mold will begin to recover. The portion of the specimen lying outside of the mold will remain relatively rigid and not recover since it is not heated above the $T_g$ of the material. Thus, the partially confining mold provides lateral confinement to the area...
of the specimen being recovered and the rigid (“cold”) portion of the specimen lying outside of the mold provides confinement in the axial direction. Thus, the portion of interest for recovery is confined 3-dimensionally and the CTH method can therefore be initiated.
Chapter 2: Literature Survey

2.1 Literature Review

Failure of mechanical components due to crack formation and propagation has plagued the engineering industry since its birth. Indeed, through continued use and cyclic loading, the flexural strength of polymers diminishes in general as well as their microstructure. This compromised strength is many times due to crack formation in the polymeric materials. The main problem is that oftentimes these cracks are difficult to detect before it is too late and failure of the component is imminent. Therefore, there is a great need for self-healing materials that can effectively seal cracks immediately when they are formed allowing no time for them to propagate. This need has been duly recognized by the engineering community and research into self-healing composite materials has rapidly increased in the last two decades [1-38].

As has been discussed, an important step in both biological and synthetic healing is closure of the cut or cracked surface prior to healing. In this regard, Li and Uppu [16] conducted a study on the level of lateral confinement influence on healing efficiencies of a self-healing syntactic foam. In the study, cylindrical specimens were enclosed in a dual material confining mold during healing. The outer wall of the confining mold was constructed of rigid steel while the inner wall material was varied. The inner wall was constructed of rubber, nylon, and steel liners which provided weak, intermediate, and rigid confinement respectively. Additionally, the effects of three different pre-strain levels during programming and two different programming temperatures on healing efficiencies were investigated. The thermomechanical behavior of the material was investigated via 3-D stress-strain-temperature as well as 2-D temperature-time and stress-time analysis for each level of confinement. The volume reduction and stress recovery ratio were also derived for each of the factors studied. Some notable results obtain from this
study are: (1) The rubber liner produced the highest stress recovery ratio, (2) the nylon liner produced the highest recovered stress, (3) the cooling and unloading steps in the typical 3 step thermomechanical programming of an SMP material can be combined into one step, and (4) the higher the pre-strain level the higher the recovered stress.

Nji and Li [15] performed a somewhat similar study on a self-healing particulate composite. The material consisted of thermoplastic particles (copolyester) dispersed in a polystyrene based shape memory polymer matrix (CP-PSMP). The object of this study was to validate the two step CTH method proposed by Li and Uppu on a self-healing particulate composite. The cured material was cut into rectangular specimens and was both programmed and healed in a rectangular mold. The notched specimens were subject to a three-point flexural bend test both after programming and after healing to determine the maximum load that could be withstood. Based off of this load the pre-damaged and post-healing strength of the material could be calculated thereby quantifying the healing efficiency. The specimens underwent 5 cycles of damage and healing and showed effective healing after each cycle. Thus, using the CTH method in conjunction with the self-healing particulate composite, repeated healing of the same damaged area could be achieved. This type of healing repeatability is an extremely sought after property of these self-healing composite materials.

Indeed, the CTH method is essential to obtaining both macro and micro scale healing of self-healing particulate composites. However, full confinement of the material is not necessary during healing. Li et al studied the effects of strain hardening of shape memory polymer fibers on healing efficiencies of thermosetting polymer composites [12]. In their study, they used continuous shape memory polymer fibers (SMPFs) in a conventional epoxy composite with thermoplastic particles dispersed in the matrix. The purpose of the study was to investigate the
effects of the strain level of the cold-drawn SMPFs on the healing efficiency of the composite material. Therefore, the SMPFs were strained to various levels before the epoxy composite was cast around them. It was found that the higher the pre-strain level of the SMPFs, the higher the recovery stress of the composite material and therefore the higher the healing efficiency. It was also demonstrated in this study, that wide open cracks can be healed in this material through local heating in the cracked region only.

2.2 Research Contribution

The present study intends to further investigate the mechanical properties of a self-healing particulate composite material via the CTH method suggested by Li and Nettles [14]. This study is purposed to investigate the healing efficiencies of the material by using the CTH method in conjunction with local heating through confinement in the local damaged area. By confining and heating varying lengths of the specimen centered at the cracked region, the healing efficiency is found as a function of the amount of the specimen that is involved in the healing process.

In this study a polystyrene based shape memory polymer (PSMP) with 6% thermoplastics (CP) by volume dispersed in it was studied. DSC analysis was conducted on the material to find the glass transition temperature. After the material was cured, a water jet cutting tool was employed to cut it into cylindrical specimens as per ISO 178 specifications. Three-point flexural tests were conducted on specimens both before and after healing in order to find the strength recovery. Lastly, SEM images were taken in order to validate crack closure under varying levels of confinement and healing stresses.
Chapter 3: Fabrication

3.1 Materials Used

3.1.1 SMP Composite

The material used in this study was a self-healing particulate composite. This material consisted of a polystyrene shape memory polymer (PSMP) with thermoplastic particle additives (CP).

Synthesis of the PSMP material was achieved by mixing vinylbenzene (Aldrich, Reagentplus ≥ 99%), vinyl neodecanoate (Aldrich), divinyl-benzene (Aldrich, technical grade, 80%, mixture of ionomers) and polystyrene-block-polybutadiene-blockpolystyrene (Sigma-Aldrich, Styrene, 30 Wt. %). Benzoyl peroxide (Sigma-Aldrich, Luperox® A98, reagent grade, ≥ 98%) was used as the radical initiator. The thermoplastic particle additive was a linear copolyester (CP) consisting of Terephthalic acid, Isothalic acid, and 1,4-Butanediol (Abifor Inc., Switzerland). Some important properties of these thermoplastics are summarized in table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>≤ 80 μm</td>
</tr>
<tr>
<td>Particle density</td>
<td>1.3 g/cm³</td>
</tr>
<tr>
<td>$T_g$</td>
<td>16 °C</td>
</tr>
<tr>
<td>$T_m$</td>
<td>114 – 124 °C</td>
</tr>
<tr>
<td>$T_b$</td>
<td>125 – 150 °C</td>
</tr>
</tbody>
</table>

3.1.2 Confining Mold

Confining molds of various sizes were fabricated in order to provide confinement to the sample during programming and healing. Each mold was constructed out of the same steel alloy
with 0.2 % carbon by weight. Table 2 lists some mechanical and thermal properties of this material.

3.1.3 Test Stand

The test stand used three different materials in its construction. The holding plates and

Table 2. Mechanical and Thermal Properties of Confining Molds

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of Elasticity</td>
<td>200 GPa</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.3</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$53.66 \text{ W/m} \cdot \text{K}$</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>$490 \text{ J/Kg} \cdot \text{K}$</td>
</tr>
<tr>
<td>Density</td>
<td>$7850 \text{ Kg/m}^3$</td>
</tr>
<tr>
<td>Linear Expansion</td>
<td>$13 \times 10^{-6}/\text{\degree C}$</td>
</tr>
</tbody>
</table>

Table 3. Mechanical and Thermal 6061 Aluminum alloy

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of Elasticity</td>
<td>75 GPa</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.33</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$180 \text{ W/m} \cdot \text{K}$</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>$896 \text{ J/Kg} \cdot \text{K}$</td>
</tr>
<tr>
<td>Density</td>
<td>$2700 \text{ Kg/m}^3$</td>
</tr>
<tr>
<td>Linear Expansion</td>
<td>$23.4 \times 10^{-6}/\text{\degree C}$</td>
</tr>
</tbody>
</table>
the heating core were constructed from 6061 Aluminum alloy. Table 3 summarizes the important properties of this material. The fasteners were simply made of standard grade 5 material. The threaded rods used were made from AISI 4140 steel alloy with material properties given in table 4.

Table 4. Mechanical and Thermal properties of AISI 4140 steel alloy

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of Elasticity</td>
<td>200 GPa</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.3</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>42.7 W/m·K</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>473 J/Kg·K</td>
</tr>
<tr>
<td>Density</td>
<td>7810 Kg/m³</td>
</tr>
<tr>
<td>Linear Expansion</td>
<td>$12.3 \times 10^{-6}$/°C</td>
</tr>
</tbody>
</table>

3.2 Fabrication

3.2.1 SMP Composite

The production of the CP-PSMP composite was achieved through a strategic mixing process followed by curing of the final material in an oven. To begin the process, vinylbenzene was added to a three-necked flask equipped with a mechanical stirrer. Next, polystyrene was added and the mixture was stirred for 30 minutes using a polytetrafluoroethylene stirrer. To that end, an ultrasonicator (Sonic and Materials Inc, Sonic Vibracell, model CV334) was employed for mixing. After 30 minutes of vigorous mixing, divinyl-benzene and vinyl neodecanoate were then added to the mixture. The mixture was again stirred for 30 minutes until it had a clear appearance. Next 6 % by volume of thermoplastic particles were added to the mixture to form
the composite material. At this point, the mixture was stirred for one hour to ensure uniform
distribution of the thermoplastic particles within the mixture. Afterwords, benzoyl peroxide was
added to the reactant to serve as reaction thermal initiator. Again, 30 minutes of mixing was
performed. The mixture was then degassed in a Sargent-Welche vacuum (Welch brand, Duo-seal, Model NO. 1402 Ac-2065) at a 0.1-0.2 KPa vacuum for 30 minutes. After degassing, the mixture was poured into rectangular curing molds constructed from polytetrafluoroethylene. The material was cured as per the following scheme: 16 hours at 75 °C, 10 hours at 80 °C, and 5 hours at 110 °C. After curing the composite was allowed to cool to room temperature after which it was then demolded.

After the SMP composite was cured into the mold, it then needed to be removed and cut into a shape and size that was optimal for testing. As already alluded to, the final shape desired for testing purposes were cylindrical specimens. These shapes were obtained by employing an abrasive water jet (AWJ) cutting tool. There are a host of advantages to using a water jet for cutting over conventional methods such as laser, saw, or CNC machines. For instance, laser cutting methods involve high heat dissipation into the material, which can cause thermal cracks, charring, surface and subsurface defects, as well as burr formation and thermal
distortion [39]. Also, heat affected zones within the material can also be induced by the high heat used in laser cutting methods. Alternatively, abrasive water jet is a low heat cutting method which eliminates the presence of thermal distortion, charring, heat affected zones, and thermal cracks. This is especially important because of the thermo sensitivity of the SMP composite. Also, in AWJ burr formation is only dependent on the jet energy level, and a clean cut edge at the bottom of the specimen being cut evidences an absence of burrs within it. Another advantage is the surface cuts produced using this method are smooth. Use of saws for cutting also inflicts unwanted damage to the sample. The repeated cyclic stresses caused by sawing can induce delamination within the material which is failure of the bonding between the layers of a laminated material. Delamination can be especially troublesome because it may not be detected on the surface of the material, however it could be present within the material. Also, depending on the type of healing mechanism (capsule, vascular networks, ect.) delamination can cause damage to the imbedded healing mechanisms. AWJ on the other hand, does not cause delamination.

Another great advantage of AWJ is that the various cutting parameters can be easily controlled. Many types of damage such as kerf zones, surface waviness, delamination, striation formation ect. can be reduced through careful adjustment of the machines parameters. Equation 9 was developed by Zeng and relates such parameters to the cutting quality [40].

$$N_m = \frac{ChD^{0.618}u^{0.866}}{P_w^{1.25}m_w^{0.687}m^{0.343}}$$  \hspace{1cm} (9)

Where h is the depth of the cut, D is the focusing nozzle diameter, u is the traverse speed, $P_w$ is the water pressure, $m_w$ is the water flow rate, m is the abrasive flow rate, and C is a constant equal to $4.272 \times 10^{-4}$ in the English unit system. The transvers speed can be given by equation 10.
In equation 10, \( f_a \) is the abrasive factor and \( Q \) is the quality index which relates the AWJ settings to quality of the surface finish. \( Q \) takes on integer values ranging from 1 to 5 which are summarized in table 5. Use of equations 9 and 10 in conjunction with table 5, a desired surface finish can be obtained. In addition to the already mentioned advantages of AWJ, it also provides high cutting accuracy with tolerances up to 0.13 mm [39-50].

### 3.2.2 Confining Molds and Complementing Tools

Three confining molds were constructed to provide varying levels of confinement to the specimens during programming and healing. As previously mentioned, Uppu [16] used a double walled circular steel confining mold to provide rigid confinement to the specimen during programming and recovery. Additionally, Yougoubare [17] and Okoro [18] used similar confining molds in their research. Therefore, circular confining molds were deemed appropriate for use in the current study. Yougoubare conducted a Finite Element model of a hollow confining mold having a heat transfer coefficient of 15 \( W/m^2K \) and a final temperature of 140 °C. The dimensions of the mold were 121.50 mm height, 12.70 mm inner diameter, and a
50.05 mm outer diameter. Based off his analysis, a minimum soaking time of 40 minutes is necessary for the inner walls of the confining mold to reach a constant temperature. Based off of his analysis, soaking times of 1 hour are used in the present study which will be discussed more in the appropriate sections. The radial expansion of the confining molds due to thermal stresses can be calculated via equation 11.

\[ r' = r(1 + \alpha \cdot \Delta T) \]  

(11)

In equation 11, \( r' \) is the radius at the final temperature, \( r \) is the initial radius at room temperature, and \( \Delta T \) is the value for the change in temperature from the initial temperature to the final temperature. Use of this equation under the assumption of linear thermal expansion produces a deflection of 0.008 mm of the inner walls of the confining tubes which was deemed satisfactory. The dimensions of the confining molds are summarized in table 6 and the molds are pictured in figure 12. In addition, two test plugs were constructed to aid in the programming and healing of specimens under full confinement. These plugs are depicted in figure 13.

<table>
<thead>
<tr>
<th>Table 6. Confining Mold Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mold</strong></td>
</tr>
<tr>
<td>-------------------------------</td>
</tr>
<tr>
<td><strong>100% Confinement</strong></td>
</tr>
<tr>
<td><strong>75% Confinement</strong></td>
</tr>
<tr>
<td><strong>50% Confinement</strong></td>
</tr>
</tbody>
</table>

3.2.3 Test Stand

In order to facilitate the partially confined healing process, a test stand was constructed. The test stand consisted of four all-thread rods, two holding plates, and one base plate as can be
Figure 12. Pictured from left to right: 100, 75, and 50 % confining molds

Figure 13. Test plugs used in conjunction with the fully confining mold during programming and healing

seen in figure 14. The sole purpose of the test stand was to provide a method of holding the different sized confinement containers during healing. The confining tubes would be placed between the two top plates depicted in figure 14.
3.2.4 Heating Jacket

XtremeFLEX BSO Silicone Rubber Heating tape (BriskHeat) was used in the heating process during healing. The tape was first wrapped around the confining mold with the remaining length wrapped around an aluminum jacket. This setup can be seen in figure 15. Using

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Density</td>
<td>0.007 watts/mm²</td>
</tr>
<tr>
<td>Current Source</td>
<td>120 VAC</td>
</tr>
<tr>
<td>Maximum Exposure Temperature</td>
<td>232 °C</td>
</tr>
<tr>
<td>Length</td>
<td>1.83 m</td>
</tr>
<tr>
<td>Width</td>
<td>12.7 mm</td>
</tr>
</tbody>
</table>
this type of setup made it possible to purchase only one length of tape and use it for each of the different sized confining molds. It also provided ample heating capabilities. The manufacturer supplied properties of the heating tape are summarized in table 7.

Figure 15. Outer heating jacket surrounding one-half confinement mold
Chapter 4: Experimentation

4.1 Differential Scanning Calimetry (DSC) Analysis

The $T_g$ of the SMP composite was found via differential scanning calorimetry analysis. A 6.20 mg sample of the SMP composite was placed on the sample pan in the DSC machine. Figure 16, shows a schematic of the DSC sample and reference pan orientation. The material was first held at 30 °C for one minute before it was cooled to -70 °C at a rate of 20 °C/min. The sample was then held for 30 minutes at -70 °C after which it was heated to 230 °C at a rate of 10 °C/min. It was then held at 230 °C for one minute before again being cooled to -70 °C at a rate of 20 °C/min. This heating and cooling cycle was performed two times and the curve produced from the second heating cycle was used for the analysis of the thermal properties of the SMP composite.

4.2 Strain Controlled Programming

The thermomechanical programming of the SMP composite sample was performed under
strain control. As the sample is heated up during programming, its modulus of elasticity is constantly changing which makes controlling the applied stress very difficult. For this reason, strain controlled programming was preferred over stress controlled programming. The programming was performed using a QTEST/150 MTS machine equipped with a furnace. A picture of this setup can be seen in figure 17. The programming was performed under full confinement using the fully confining mold described previously. Once the desired strain level of 10% was reached, the furnace was then switched off and the sample was allowed to cool for one hour with the strain held constant throughout. After one hour elapsed, the sample was then removed from the confining mold and the programming was then complete. The sample was then at its temporary shape and ready to begin testing.

4.3 Three-Point Bend Test

In order to quantify the specimen’s strength value, it was subjected to a three-point flexural bend test to complete fracture. This test was performed both after programming and after healing and provided a way for the healed strength recovery of the specimen to be compared to the pre-damaged strength of the specimen via equation 8. The three-point bend test was performed using the QTEST/150 MTS machine in conjunction with a fully adjustable three-point bend fixture. The rollers on the fixture were set to a span of 86 mm which provided at least an 8 to 1 length to diameter ratio for each specimen as per ISO 178 standards. The un-notched specimens measuring 120 mm in length and 10 mm in diameter were loaded to complete fracture at a rate of 0.5 mm/min. The setup for this test can be seen in figure 18.

4.4 Healing

4.4.1 Fully Confined Healing

The completely fractured specimens were healed under varying levels of confinement.
Figure 17. MTS and heating furnace setup for sample programming

Figure 18. Three-point bend test apparatus setup
Figure 19 shows an example of the rough edges of a completely fractured specimen. These rough edges were carefully aligned and brought together before wrapping in a Teflon sheet. Next, the specimen was placed into the fully confining mold for healing. The mold was wrapped with XtremeFLEX BSO Silicone Rubber Heating tape (BriskHeat) and placed onto the test stand. The QTEST/150 MTS machine was then used to compress the specimen to a desired healing stress level (0, 7, or 12 MPa). The healing stress was applied at a rate of 1.3 mm/min in the case of the 7 and 12 MPa healing stress. For the case of 0 healing stress, the MTS clips were brought into contact with the specimen before the next step began. Once the desired stress level was reached (or the clips were brought into contact with the specimen in the case of 0 MPa applied stress), the confining mold was then heated to the healing temperature of 135 °C. This temperature was chosen as the healing temperature because it lies above the \( T_m \) of the thermoplastic (114 -124 °C) and in the range of the \( T_h \) (125 -150 °C). Once the temperature of the mold reached 135 °C, 30 minutes was allowed for the enclosed specimen to reach the equilibrium
temperature. After the 30 minutes had elapsed, the heat was removed and the mold and specimen were allowed to cool to room temperature at which point the specimen was removed from the mold. At this state the specimen was ready to undergo a post-healing three-point flexural strength test.

4.4.2 Partially Confined Healing

Specimens were also healed under three-fourths and one-half confinement. In these cases, the fractured surfaces of the specimen were again carefully aligned and brought together. Next a piece of Teflon sheet the length of the confining mold (82.5 mm and 55 mm respectively) was wrapped around the center of the specimen to be healed. The specimen was then placed into the selected confining mold by carefully centering the cracked region at the center of the mold. In this way the crack was confined an equal amount on either side. The mold was then wrapped with XtremeFLEX BSO Silicone Rubber Heating tape (Briskheat). The healing was again performed in a stress controlled manner under varying levels of applied stress (0, 7, and 12 MPa). The stress was applied to the specimen at a rate of 1.3 mm/min in the case of the 7 and 12 MPa healing stress. For the case of 0 healing stress, the MTS clips were brought into contact with the specimen before the next step began. Once the desired stress level was reached (or the clips were brought into contact with the specimen in the case of 0 MPa applied stress), the selected mold was heated to the healing temperature of 135 °C. Again, 30 minutes was allowed for healing and for the specimen to reach the healing temperature once the mold reached the healing temperature of 135 °C.

4.5 Scanning Electron Microscope (SEM) Imaging

As discussed, the key to effective healing in self-healing materials is first closing the opened crack and then sealing it with healing agent (in this study thermoplastic particles). To
evaluate crack closure and thermoplastic deposition in crack regions after healing at varying levels of confinement and healing stress, a Hitachi S-3600N Scanning Electron Microscope was employed. Images were taken of samples healed under 50 % confinement at 0 MPa applied healing stress, and specimens healed under 100 % confinement at 7 MPa healing stress.

In order for a material to be observed using SEM analysis, it must be conductive. Because the CP-PSMP material is not inherently conductive, it had to first be coated with a conductive layer before observing with SEM. This was done by sputter coating the specimens with a thin (~ 20nm thick) layer of platinum in a 0.1 mbar vacuum using a EMS 550 sputter coater for 4 minutes. After coating, the specimens were secured to the sample holder with aluminum tape and then loaded into the SEM machine.

Figure 20. Specimens being sputter coated in EMS 550 sputter coater
Figure 21. Specimens placed on test stand and being loaded into SEM for imaging
Chapter 5: Results and Discussion

5.1 Glass Transition Temperature ($T_g$)

Differential Scanning Calimetry (DSC) was employed to find the $T_g$ of the CP-PSMP composite material. Knowledge of the $T_g$ of the material was imperative in order to know what temperatures could be used for programming purposes. A 6.20 mg sample was loaded into Figure 22. Differential Scanning Calimetry results for CP-PSMP composite the DSC and analysis was performed as per the method described in section 4.1. The linear copolymer’s $T_g$ value supplied by the manufacture was 16 °C and the $T_g$ of the pure PSMP was determined to be ~ 89 °C in [17]. Analysis of the curve produced by the DSC analysis (shown in figure 22) suggests two values for the $T_g$ of the material; one at 12.74 °C and one at 85.33 °C. Because the material primarily consists of the PSMP (94 % by volume), the $T_g$ of the composite
is mostly influenced by the $T_g$ of the pure PSMP. Therefore, it is expected that the $T_g$ of the composite be close to the $T_g$ of the pure PSMP. This is indeed the case as can be seen in figure 22. The composite material shows two values for the $T_g$, however. The smaller value is likely due to the presence of the CP which has a $T_g$ value close to the first one in the figure. Therefore, the larger value of 85.33 °C was taken as the value of the $T_g$ for the CP-PSMP material.

### 5.2 Thermomechanical Programming

As previously mentioned, the specimens underwent fully confined thermomechanical programming to a 10 % pre-strain level. Steps I-III of figure 23 outline the programming process for a typical CP-PSMP specimen programmed under full confinement. To begin programming, the sample was first carefully wrapped with a piece of polytetrafluoroethylene (PTFE, common

![Figure 23. Typical thermomechanical cycle for CP-PSMP [17].](image-url)
name Teflon) sheet. Some properties of the sheet are as follows: thickness: $7.6 \times 10^{-6} \text{ m}$, thermal expansion coefficient: $135 \times 10^{-6} \text{ K}^{-1}$, melting point: 327 °C and coefficient of friction: $0.5 - 1.0$ as measured against polished steel. Due to the low coefficient of friction of the Teflon sheet, it facilitated easy removal of the sample from the confining mold after programming was complete. Next the Teflon wrapped sample was placed into the confinement mold which was then placed inside the furnace as pictured in figure 17. The furnace was then heated from room temperature (20 – 25 °C) to the programming temperature of 100 °C at a ramp rate of 6 °C/min. Once the interior of the furnace reached the desired temperature of 100 °C, one hour was allowed for the SMP composite specimen to reach an equilibrium temperature.

5.3 Three-Point Bend Test Post Programming

After the specimens were programmed, they were subject to a three-point flexural bend test to complete fracture. The test was performed at room temperature on un-notched specimens. After the test was complete, the maximum load required to break the specimens was recorded and then used to calculate the post programming fracture strength of the specimens.

5.4 Three-Point Bend Test Post Healing

After the specimens were healed via the various means discussed, they were then subject to post-healing three point flexural test to complete failure. Comparison of the post-programming three-point bend test to the post-healing three-point bend test allowed for calculation of the healing efficiency of the CP-PSMP material specimens.

5.5 Healing

As discussed previously, after the post programming three point bending test was complete, the specimens were then healed under varying levels of confinement. This was done to test what type of relationship there is between confinement level and healing efficiency. It has
been shown in other studies [12, 16] that the healing efficiency of a CP-PSMP material increases with increased recovery stress. This is due to the higher recovery stress causing more complete closure of the crack thereby providing better healing to the damaged material. It has also been suggested that higher recovery stress can aid in the diffusion of the thermoplastic particles by pressure assisted diffusion which could also increase healing efficiency [12].

5.5.1 Influence of Confinement Level on Strength Recovery

After the post-programming three point flexural tests was complete, the specimens were then healed (recovered) at varying levels of confinement. To begin the healing process, the two broken halves of each specimen were carefully aligned before being wrapped in a PTFE sheet.

Figure 24. Example of flexural strength after programming and after healing for specimens healed at 7 MPa healing stress
Thereafter the specimen was placed in a 50, 75, or 100 % confinement container which was wrapped with XtremeFLEX BSO Silicone Rubber Heating tape (BriskHeat). A healing stress of 0, 7, or 12 MPa was then applied to the ends of the specimen (more on this in the next section). Once the healing stress was applied, heating of the specimen began. Each specimen was heated to a constant healing temperature of 135 °C and allowed to remain at this temperature for 30 minutes before cooling began. After 30 minutes, the heat was turned off and the mold and specimen were allowed to cool to room temperature. Once at room temperature, the healed specimen was removed from the mold and ready to undergo a post-healing flexural test.

Figure 25. Strength recovery increase with increasing confinement for specimens healed at 0 MPa applied healing stress. In each case the specimens were allowed to heal under their own recovery stress.
Varying the level of confinement proved to influence the strength recovery of the CP-PSMP specimens. In each case, the healing efficiency showed a trend of increasing with increasing confinement level. Figure 25 shows a typical trend for the strength recovery increase with increasing confinement for specimens healed at 0 MPa applied healing stress. To further investigate healing under partial confinement, specimens were healed at varying levels of applied compressive stress (healing stress). As can be seen in figures 26 and 27, the overall healing efficiency of the specimens tested at 0, 7, and 12 MPa increase as confinement level increases. The maximum average healing efficiency of 91.02% was attained through healing under 100% confinement at an applied healing stress of 12 MPa. This trend agrees with results obtained by Okoro [18] for CP-PSMP specimens healed under 100% confinement at increasing healing stress levels.

Figure 26. Healing efficiency versus healing stress for varying levels of confinement
It can also be seen in figure 26 that for specimens healed at 75 and 100 % confinement the strength recovery steadily increases as the healing stress increases. However, for specimens healed under 50 % confinement this is not the case. As will be discussed in more detail in section 5.6, there exist a heat affected zone at the area of the specimen that lies just outside of the confining mold in the case of 50 and 75 % confinement. Through radiation of heat from the confining mold and conduction within the specimen, this small area that lies outside of any confinement reaches a temperature near or above the $T_g$ of the material. Because this area is not confined, it is weak and easily deformable. In the case of 50 % confinement, 25 % of the total length of the specimen lies outside (above and below) the confinement container (see figure 8). Therefore, high levels of applied stress (12 MPa) can cause the specimen to buckle at the heat affected zone thereby not transferring the applied healing stress levels internally through the

![Diagram](image.png)

Figure 27. Strength recovery as a function of confinement for varying levels of healing stress
specimen to provide closure of the internal crack. Therefore, in the case of 50 % confinement, there is a healing stress level threshold that if exceeded, will decrease healing efficiency. In the case of 75 % confinement, this threshold is not seen. This is because only 12.5 % of the specimen lies outside (above and below) the confining mold. Therefore, it is more resistant to buckling. It is expected that if higher healing stress levels were investigated for 75 % confinement, a healing stress level threshold would arise as it did for 50 % confinement.

5.5.2 Influence of Confinement Level on Recovery Stress

Recovery stress, defined as the stress the specimen exhibits during recovery (or attempt at recovery) to its original shape, was also investigated. It was found that as the confinement level increased, so did the recovery stress. In fact, the increase was almost perfectly linear. This

![Figure 28](image.png)

Figure 28. Recovery stress versus time for specimens healed under 50 and 100% confinement. The recovery stress peaks around the Tg of the specimen and then decrease as the temperature is increased
was due to more of the polymer chains in the specimen trying to regain their original conformation during recovery. Figure 29 shows the recovery stress of specimens recovered at varying levels of confinement. As can be seen in figure 29, the larger the level of confinement, the larger the recovery stress. Figure 25 suggests that the higher the level of confinement, the higher the healing efficiency. Therefore, there exists a direct correlation between the level of confinement and the healing efficiency; namely, the healing efficiency increases with increasing confinement. The reason for this is that when 50 % of the specimen is confined (and heated above $T_g$), only this 50 % of the specimen is activated and trying to recover its original shape. Therefore, there is less recovery stress when 50 % of the specimen is heated than when 75 % of it is heated. Likewise, there is less recovery stress when 75 % of the specimen is heated than when 100 % is heated. This translates to less force closing in on the internal crack during recovery for less confined specimens which leads to smaller values of strength recovery. This is
apparent in figure 25 where there was no external healing stress applied, the only stress involved in structurally closing the internal crack was the recovery stress produced by the specimen itself. Indeed, this increase in recovery stress with increasing confinement is one major reason better healing efficiencies are obtained with higher levels of confinement.

Table 8. Summary of Results

<table>
<thead>
<tr>
<th>Confinement (%)</th>
<th>Peak Recovery Stress (MPa)</th>
<th>Applied Stress (MPa)</th>
<th>Healing Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.75 ± 0.01</td>
<td>--</td>
<td>48.84 ± 1.07</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>7.0</td>
<td>75.58 ± 8.38</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>12.0</td>
<td>71.84 ± 7.60</td>
</tr>
<tr>
<td>75</td>
<td>1.11 ± 0.07</td>
<td>--</td>
<td>56.30 ± 3.94</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>7.0</td>
<td>77.73 ± 11.6</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>12.0</td>
<td>81.12 ± 0.87</td>
</tr>
<tr>
<td>100</td>
<td>1.67 ± 0.02</td>
<td>--</td>
<td>69.42 ± 5.03</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>7.0</td>
<td>82.97 ± 2.19</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>12.0</td>
<td>91.02 ± 10.58</td>
</tr>
</tbody>
</table>

5.6 Visual Inspection

5.6.1 Crack Inspection

After healing, the specimens were visually analyzed for any apparent cracks or deformities. Specimens healed under no applied healing stress exhibited visible cracks after healing at each level of confinement. Figure 30 shows an example of one of these visible cracks seen in specimens healed under no applied healing stress. This confirms that the recovery stress of the specimen (at any level of confinement) is not enough to provide efficient and complete closure of the crack. This is why the specimens healed under no applied healing stress showed relatively lower healing efficiencies compared to those healed under 7 and 12 MPa healing stress. In those specimens healed at 7 and 12 MPa healing stress no crack was visible to the naked eye after healing.
5.6.2 Deformities

Visual inspection of the healed CP-PSMP specimens showed that when the specimens were healed under partial lateral confinement (at 7 and 12 MPa), they possessed deformities near the edge of the healed area. This indicated that there is a heat affected zone along the portion of the specimen that lies just outside of the confinement container. That is, the temperature of the
specimen outside of the confining mold, but near to the edge of the confining mold attains a temperature around the $T_g$ of the material during healing. This is evident in the bulge that is seen at this area. The healing stress applied to the specimen forces the specimen to expand inward as it recovers therefore closing any internal cracks on the macro scale. However, in the case of partial confinement, the heat affected zone cannot withstand this stress and therefore deforms.

![Small Bulge](image1.png) ![Large Bulge](image2.png)

Figure 32. Bulge seen in specimen healed under 75% confinement at 7 MPa healing stress.

Thus, the amount of healing stress applied to the specimen is not completely transferred to the internal crack. Also, as the healing stress applied is increased, the size of the bulge also increases. This bulge caused no noticeable strength reduction or structural impairment. However, in real world application, this bulged area could potentially cause problems and further research into eliminating it could be useful.

5.7 SEM Inspection

To further validate the results of this study, images were taken of the CP-PSMP surface using a scanning electron microscope. As previously discussed, in order for effective healing of
cracks and damage, the cracks must first be effectively closed. Once the cracks have been closed through confined recovery at a temperature above the $T_g$ of the material, further heating will cause melting of the thermoplastic additives which will then be sucked into the cracks by capillary forces. However, insufficient recovery stress leads to the presence of unclosed cracks.

![Figure 33](image1.png)

(a) shows the crack at 500X magnification and (b) shows the outlined region of the crack at 5000X magnification.

**Figure 33.** Crack seen on surface of CP-PSMP sample healed under 50% confinement with zero applied stress. (a) shows the crack at 500X magnification and (b) shows the outlined region of the crack at 5000X magnification.

![Figure 34](image2.png)

(a) shows the sealed crack at 500X magnification and (b) shows the outlined region in (a) at 5000X magnification further revealing the sealed crack.

**Figure 34.** Effectively sealed crack seen on surface of CP-PSMP specimen healed under 100% confinement at 7 MPa healing stress. (a) Shows the sealed crack at 500X magnification and (b) shows the outlined region in (a) at 5000X magnification further revealing the sealed crack.
within the material during healing which ultimately leads to limited healing efficiency.

Figure 32 shows a typical healed crack seen on the surface of the CP-PSMP specimen after healing under 50% confinement at 0 MPa applied healing stress. As can be seen in the figure, the crack is not completely closed suggesting that the recovery stress of the material healed under 50% confinement is not enough to fully close cracks during healing. Inspection of image (b) of figure 32 further validates this claim. In this image, it is seen that the thermoplastic particles have melted into the crack; however, it seems the crack may not have been closed enough for effective “gluing” of the two cracked surfaces by the thermoplastics. In contrast, figure 33 shows a healed surface crack seen on the surface of a specimen healed under 100% confinement at 7 MPa healing stress. In image (a) of figure 33, it can be seen that the healed crack is completely closed suggesting that full confinement coupled with a relatively high healing stress of 7 MPa produces effective closure of cracks within the specimen. Further magnification of the region seen in image (b) validates this claim. As can be seen in the image, the crack has been completely closed with only the outline remaining as evidence of its existence. Therefore, it is seen that the low healing stress produced during recovery of the material under 50% confinement (0.75 MPa) is not sufficient for effective closure of small cracks within the sample. This is why the average strength recovery of the sample was relatively low (48.84%). Alternatively, it is seen that 100% confinement coupled with a higher applied healing stress of 7 MPa is sufficient to effectively close and heal damage within the specimen producing relatively high average healing efficiencies of 91.02%.
Chapter 6: Conclusions

In this study the effects of partial confinement and local heating (around the damaged area) on healing efficiency were investigated for a self-healing particulate composite. The particulate composite used in this study was a polystyrene shape memory polymer (PSMP) with 6% by volume of thermoplastics (CP) dispersed in it. Three levels of confinement were employed in order to further investigate the close-then-heal (CTH) method suggested by Li and Nettles. This was achieved through fabrication of three confining molds that provided 50, 75, and 100% confinement to the specimen (as measured against the length of the specimens).

During healing only the confining mold (which was centered at the cracked region of the specimen) was heated to the healing temperature of 135 °C. Thus, the confining mold provided lateral confinement and the specimen lying outside of the confining mold (at a temperature below $T_g$) provided axial confinement. At each level of confinement, three healing stresses were investigated: 0, 7, and 12 MPa. Specimens healed under 0 MPa applied healing stress were allowed to heal under their own recovery stress. It was found that as the level of confinement increased, the recovery stress produced by the material also increased. The maximum average recovery stress of 1.67 MPa was obtained under 100% confined recovery. At 50% confinement, the maximum average recovery stress was 0.75 MPa. Therefore, there was over 2 times as much peak recovery stress produced by specimens healed under full confinement compared to specimens healed under 50% confinement. Thus, higher confinement levels were found to produce higher recovery stress due to more of the specimen recovering as the whole specimen is heated and recovery is activated. Thus, the internal crack within the specimen was pushed in more by specimens healed under higher levels of confinement due to the higher recovery stress. This was further validated by the healing efficiency of specimens healed under varying levels of
confinement under their own recovery stress. Specimens healed under 50, 75, and 100% confinement at 0 MPa applied healing stress exhibited a average healing efficiencies of 48.84, 56.30, and 69.42% respectively.

The applied healing stress during recovery was also investigated for each level of confinement. The healing stresses studied were 0, 7, and 12 MPa. At 0 MPa as just discussed, the specimen was allowed to heal under its own recovery stress with no external healing stress applied. For 7 and 12 MPa healing stress, the specimens were compressed to the specified healing stress before healing commenced. It was found that for both 75 and 100% confinement, the healing efficiency increased with increasing applied healing stress. This is due to better structural closing of the internal crack during healing. However, this trend was not seen in the case of specimens healed under 50% confinement. At 50% confinement the healing efficiency increased as the applied healing stress increased up to 7 MPa applied healing stress. However, when the healing stress was increased to 12 MPa, the healing efficiency dropped. It was concluded that this is due to the heat affected zone that exists on the area of the specimen that lies directly out of the confining mold during healing. It was apparent that this area reached temperatures around the $T_g$ of the CP-PSMP as evidenced by bulges in the area seen in specimens healed under 50 and 75% confinement. Because this area is not completely rigid, it could not withstand the full 12 MPa of applied healing stress and buckled somewhat thereby not transferring the total 12 MPa through the specimen to close the crack. Therefore, there is a threshold for the healing stress that can be applied at each level of partial confinement above which, the healing efficiency will drop.

To further validate the results of this study, SEM images of the surface of specimens were taken after healing under varied conditions. The surface of specimens healed under 50%
confinement with no applied healing stress and specimens healed under full confinement at 7 MPa healing stress were examined. It was found that many small cracks were present in the specimens healed at 50% confinement and no applied stress. This suggests what was already concluded; that is that the recovery stress of specimens healed under 50% confinement is not high enough to effectively close surface cracks. On the other hand, the surfaces of the specimens healed under full confinement at 7 MPa healing stress showed effective closure of cracks within the specimen. This further validates the results that higher levels of confinement and higher healing stress (to a certain extent) provides better structural and microscopic closure and healing of cracks which ultimately increases the healing efficiency of the material.
Chapter 7: Recommendations for Future Work

Although much research has been conducted on self-healing material, there is still much to be done. In the present study it was shown that increasing confinement level effectively increases the healing efficiency of self-healing particulate composites. However, there are many parameters that could still be studied related to this research. The following list presents ideas for future work that have arisen from the current research:

1. Research into elimination of the heat affected zone seen in specimens healed under partial confinement. Perhaps one way this could be done is by addition of a thermal barrier on the ends of the confining container with a non-conductive confining plate. This would provide confinement and heat to the area around the crack while eliminating the bulge which should cause even higher levels of healing efficiency.

2. Variance in the programming strain level and the healing temperature could also be studied. In the current study one pre-strain level and one healing temperature were used but varying these parameters could prove to affect the healing efficiency.

3. A simple analytical formula could be derived for the amount of the specimen that needs to be confined in order to provide effective closure to varying sized cracks. As eluded to, the shape recovery and recovery stress are dependent on how much of the specimen is thermally activated. Therefore, a mathematical formula could be derived to relate the amount of the specimen that should be confined and heated in order to close cracks based on: size of the cracks, programming stain, shape recovery of material ect. This could prove to be very useful.
References


[19] SolidWorks 2010


Vita

Jonah Champagne was born in December 1987 in Thibodaux Louisiana. He obtained a bachelor of science in mathematics from Nicholls State University in December 2009. He began working on his Master degree in mechanical engineering in August 2011 and joined the NASA ESPCoR program in August 2012 working on self-healing composite materials under the direction of Dr. Su-Seng Pang. He is a candidate for the degree of Master of Science in Mechanical Engineering to be awarded in December 2013.