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PROGRAMMING AND HEALING TEMPERATURE EFFECTS ON THE EFFICIENCY OF CONFINED SELF-HEALING POLYMERS

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
Yves Quentin Yougoubare
B.S., Louisiana State University, 2011
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Abstract

Shape memory polymers are smart materials capable of fixing a temporary shape and returning to their initial shape in response to an external stimulus. Since the discovery and acknowledgment of their importance in 1960s, shape memory polymers have been the subject of tremendous and continuous attention. In a previous study conducted on a biomimetic shape memory polymer (SMP), the ability of a self-healing composite to heal, and to repair and restore structural-length scale damage using a close-then-heal (CTH) self-healing mechanism was examined and validated. The present study is purposed with investigation of the effects on healing efficiencies of the variation of temperature during both thermo-mechanical programming and shape recovery under three-dimensional (3-D) confinement. The polymer considered was a polystyrene shape memory polymer with 6% by volume of thermoplastic particle additives (copolyester) dispersed in the matrix. After fabrication, and determination of their glass transition temperature using DSC, the specimens were allowed to go through a strain-controlled programming at a wide range of temperatures (20°C, 45°C, 60°C, 82°C, 100°C and 140°C), at a pre-strain level of 15%. Fracture was imposed using a three-point flexure apparatus, and was followed by shape recovery at multiple temperatures (73°C, 100°C, 122°C and 148°C). The self-healing efficiency was evaluated per flexural strength immediately after programming and following healing. The results and deductions attained were verified using EDS analysis and SEM inspection.

It is inferred from the study that the programming temperature only very slightly affects the recovered strength. Programming the specimen above its glass transition temperature provided a marginal gain in strength recovery. Shape recovery (healing) temperature, however,
was found to have a significant impact on the self-healing efficiency. A sudden “boost” was noted around the melting temperature of the thermoplastics, with a significant increase in the healing efficiency past the bonding temperature of the copolymer. It was observed that programming above the glass transition temperature of the composite and healing above the melting point of the thermoplastic additives ensured a maximum healing efficiency of up to 63% for the material considered.
Chapter 1: Introduction

1.1 Shape Memory Polymers

Shape memory polymers are smart materials that have the ability to “memorize” a permanent shape, be deformed to a “fixed” temporary shape under temperature conditions, and regain their initial (permanent) shape when subjected to thermal, electrical or some environmental settings. The functionality of shape memory polymers (SMP) is primarily based on shape memory effect, which enables to material to fix the temporary shape and return to its permanent stress-free shape after being exposed to an external stimulus. According to information collected on this topic, the first publication mentioning the term “shape-memory” was a United States patent in 1941 claiming that a dental material made of methacrylic acid exhibited “elastic memory” and could return to its original shape upon heating [1]. The important of the discovery, however, was not appreciated until the 1960s; and significant studies on shape memory effect only started in the late 1980s.

Shape memory alloys (SMA), which are also part of the family of smart materials possessing self-memory effect, happen to be the most significantly used and studied shape memory materials. The shape-memory effect in those alloys is due to their existence in two stable crystal structures – a high temperature-favored austenistic phase and a low temperature-favored martensitic phase [2]. Even though they gained popularity because of their small size and high strength, they exhibit very limited recoverable strains of less than 8%, high stiffness, high cost and complex processing. SMPs, on the other hand, are able to withstand higher deformations and recover up to 100% of compressed lengths. They are also
relatively low cost and low density materials and can undergo less demanding training conditions. In that regard, SMPs started receiving a closer look and efforts to understand and improve the behavior of SMPs have been on the rise in the last few decades.

1.2 Self-healing Shape Memory Polymers

1.2.1 Thermoplastic Polymers

Thermoplastic polymers are made of long chains of unlinked polymer molecules of high molecular weight. They mostly rely on dipole-dipole interactions, aromatic stacking ring and Van der Waals forces. Upon heating, a thermoplastic will become progressively softer until eventually melting. At those high temperatures (above melting point), damages within thermoplastic polymers can be healed, as the thermoplastic is able to flow and fill the damaged region. Healing, therefore, occurs at the molecular level through intermolecular diffusion. Self-healing in the case of thermoplastic polymers is a relatively simple process, as heating them is enough to induce damage reparation. However, due to their low stiffness and thermal instability, their use in structural and thermal applications is very limited.

1.2.2 Thermoset Polymers

SMP resin can be used as a component of a shape memory composite system. The composite acquires some SMP characteristics and can be used in a wide range of applications. SMPs that can heal macro or micro-scale length structural damage are termed self-healing shape memory polymers. The concept behind self-healing materials is inspired by biological systems in which healing occur following damage. In those systems, injury healing follows three chronological steps: inflammatory response including blood clotting, cell proliferation with matrix deposition, and matrix remodeling. The profusion of examples of biological healing
justifies and provides a basis for synthesis healing. In synthetic materials, a route similar to the biological route leads to matrix healing. Upon damage, actuation of the healing mechanism occurs. In the next step, chemicals responsible for healing are transported to the damaged location, where chemical healing takes place within hours or days [3]. Figure 1 illustrates the three-step process to healing via biological and synthetic route as well as a comparison of the response time for both processes.

Figure 1. Synthetic and biological routes to healing, and comparison of the three-step time response. Adapted from [3]

The same source emphasizes the fact that the efficacy of healing is dependent on both the rate of damage versus the rate of healing. Factors such as frequency and amplitude of loading command the rate and the intensity of damage, while rate of healing is dictated by the
healing chemical concentration and the temperature at which the healing reaction takes place. It is to note that good self-healing will occur if both damage and healing rates are balanced.

As noted previously, the shape memory self-healing composite is comprised of the self-healing material added to the SMP resin (matrix). Depending on the type of material used, the self-healing can be capsule-based, vascular or intrinsic. Capsule-based and vascular self-healing materials provide healing agent sequestration through the capsules and vascular networks, respectively [4]. During damage, the capsules containing the healing substance are broken and the healing agent is released in the damaged location. The healing reaction occurring at that location is a one-time crack repair. In clear, the self-healing at that location is not repeatable. In the case of vascular materials, the capillaries or hollow channels are fractured during damage, causing the healing agent to leak locally and heal the damaged area. The channel is subsequently refilled by a nearby undamaged vasculature or by an external source. The refilling event that occurs after healing allows and promotes repeatable healings at the same location. Intrinsic self-healing materials are free of an encased healing agent but possess a “latent self-healing functionality” triggered in an autonomic manner or through external stimulus. Self-healing in these materials mostly occur at the molecular level through reversible reactions. The repeatability in intrinsic materials is thus, possible.

1.3 Thermo-mechanical Cycle

1.3.1 Glass Transition Temperature ($T_g$)

Glass transition is a method to characterize the property of a polymeric material. The glass transition temperature is the temperature at which the modulus of the polymer drastically changes. Above this transition temperature, which can be custom-engineered, the shape
memory polymer goes from rigid (plastic state) to flexible (elastic state). Cooling it down makes it regain its rigid form again. $T_g$ is, thus, a function of polymeric chain flexibility. It occurs when the thermal energy put into the material is enough to loosen the links and create sufficient free-volume to allow sequences of 6-10 main-chain carbons to move together as a unit. This is referred to as plastic behavior. The glass transition temperature of most polymers is much lower than the melting point of the polymer. It is, in fact, one of the most important mechanical properties of the polymer as it specifies the point at which the polymer becomes soft too weak to be used in mechanical applications. For most polymers on the market, the glass transition temperature is provided by the manufacturer. However, for less common polymers, the $T_g$ can be determined using numerous methods. The most widely used method is by differential scanning calorimetry (DSC). DSC defines the glass transition temperature through the change in the heat capacity as the polymer matrix or the polymer composite goes from glassy to rubbery state. Because this is a second order endothermic transition, the graph obtained via DSC displays a step transition (instead of a peak, as obtained during melting transition). Figure 2 illustrates a typical step transition obtained by DSC.

![DSC](image.png)

Figure 2. Typical DSC plot around the glass transition
Another method commonly used for determination of the glass transition temperature is by thermal mechanical analysis (TMA). The principle under TMA involves testing the material’s dimensional change as the sample’s temperature rises. It relates the glass transition of the material in terms of coefficient of thermal expansion (CTE) during the transition, with the associated change in free molecular volume. TMA a good way for measuring the CTE of the material above and below $T_g$. However, this method may not work well with non-homogeneous mixture of two resins.

![TMA](tma.jpg)

**Figure 3.** Typical TMA curve around the glass transition

In the case where the material a made of a mixture of two or more resins, dynamic mechanical analysis (DMA) appears to be the most successful method to determine the transition temperature for secondary transitions. It is a very sensitive method used to determine several mechanical properties of the samples to be tested. The principle behind this method is the measurement of the displacement and frequency in the sample as temperature is varied with constant frequency. The dynamic mechanical properties obtained through thermal and vibrational analysis include storage modulus ($E'$), loss modulus ($E''$), loss tangent, compliance, stress relaxation, creep, and ultimately $T_g$. 
1.3.2 Shape Fixity and Shape Recovery

The shape fixity of a material can be defined as the level of deformation that can be maintained, as the deformed material is cooled down to room temperature into its temporary shape. A shape memory polymer has good shape fixity properties if it can effectively store the temporary shape acquired at higher temperature upon cooling to room temperature. Shape recovery is defined as the level of restitution obtained from temporary to final shape. It relates the initial (permanent) shape of the material, to the (permanent) shape restored after recovery. Both the shape fixity and shape recovery are parameters used to measure the performance of a SMP as it undergoes thermo-mechanical programming and recovery. They are both described in terms of strains during the thermo-mechanical cycle [5]. The shape fixity and shape recovery rates are given respectively as:

\[ R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m} \]  \[ R_r = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \]  \[ (1) \]

where \( \varepsilon_u \) is the temporary shape strain, \( \varepsilon_m \) is the ideal mechanical deformation strain, \( \varepsilon_p \) is the permanent strain and \( N \) is the number of thermo-mechanical cycles.

\[ \varepsilon_u = \frac{l_0 - l_2}{l_0}, \quad \varepsilon_m = \frac{l_0 - l_1}{l_0} \quad \text{and} \quad \varepsilon_p = \frac{l_0 - l_3}{l_0} \]  \[ (2) \]

With \( l_0, l_1, l_2 \) and \( l_3 \) being the initial length, the length after compression but before springback, the actual length after springback, and the length after recovery, respectively.

1.3.3 Thermo-mechanical Programming

In order to make the polymer smart, it is necessary for it to undergo a three-step training also called thermo-mechanical programming. A typical programming consists of the following chronological steps: loading (step (i)), cooling (step (ii)) and unloading (step (iii)). The
thermo-mechanical cycle is a combination of the thermo-mechanical programming coupled with a fourth step, recovery, which is covered in great details in the next sections. The thermo-mechanical programming for a standard SMP is shown in figure 4 below.

Figure 4. Typical thermo-mechanical cycle

The first step of the thermo-mechanical cycle is deformation. The sample is initially heated to a high constant temperature before being loaded to a desired stress $\sigma_m$ or strain $\varepsilon_m$. Typically, step (i) occurs at a temperature higher than the glass transition temperature of the material, but it is possible to deform some SMPs at lower temperature under specific conditions. In step (ii), the sample at high temperature and high stress (or strain) is allowed to cool down to a temperature lower than its glass transition temperature, while the stress (or strain) is kept constant. Fixing occurs during this stage. Step (iii) is the unloading step. The
specimen has cooled down and is unloaded. This is the step where shape fixity comes into play. Upon loading, the deformed specimen will experience springback. The desired strain $\varepsilon_m$ of the temporary shape will be reduced proportionally to the shape fixity ratio of the material.

1.3.4 Recovery

1.3.4.1 Free Recovery

After the three-step thermo-mechanical programming has occurred, the specimen is subsequently heated back up above its glass transition temperature. Step (iv) shown in figure 4 wraps up the thermo-mechanical cycle with the free recovery phase. During this step, the specimen goes from its temporary shape after springback to its permanent shape. Shape recovery, as expected, dictates the final dimensions of the programmed specimen. Shape memory polymers with good to excellent shape recovery ratios will achieve or nearly regain their original shape.

1.3.4.2 Confined Recovery / Healing

Recovery under confinement (either partial or full confinement) is an integral part of the self-healing process of a shape memory polymer. Indeed, the self-healing ability of a given SMP is due to its aptitude to recall its shape memory effect. It was demonstrate by Nettles and Li [6] that confinement during recovery was an important factor for the SMP to possess self-healing ability. It was reported that compressive programming followed by confined recovery can seal (close) macro-cracks efficiently, repeatedly and almost autonomously. It is important to note that healing in shape memory polymers refers to macroscopic crack sealing. In self-healing SMPs, healing denotes micro-scale length closure.
1.3.5 Programming and Recovery Temperature

Three of the most important parameters in a thermo-mechanical cycle are stress, strain and temperature. Stress and strain are parameters related to the degree of deformation of the specimen during programming and recovery. Temperature is also a significant factor, especially when dealing with thermally responsive shape memory polymers. Methods for activating those polymers include resistive heating, contact heating, microwave heating, infrared heating, dielectric healing and embedded heaters such as stretchy heaters and nichrome wires. The response to the application of a force on those polymers is strongly dependent on the temperature – and thus, on the type of behavior of the specimen (i.e. elastic or plastic). Elastic materials will return to their permanent shape. By contrast, materials exhibiting plastic behavior do not regain their shape as the force is removed. Instead, plastic deformation demonstrated by flow of material occurs. Most materials, however, exhibit both plastic and elastic behaviors. Most shape memory polymers are in their plastic state below their \( T_g \) region and elastic above their \( T_g \) as shown in figure 5. Based on that, the temperature of a sample during programming and during recovery can be of significance to its performance prior and post recovery.

1.3.5.1 Programming Temperature

The temporary shape of the shape memory polymer specimen is obtained in the course of programming. The modulus of a SMP is highly dependent on its temperature as shown in figure 5 above. The temperature during programming determines the amount of applied force that is needed to deform the material. Since most polymers are brittle at low temperatures, it also determines the strain limit before brittleness fracture occurs. Furthermore, the
programming temperature may prescribe the amount of springback occurring during the unloading step of the thermo-mechanical cycle, and thus influence shape fixity.

Figure 5. Storage modulus vs. temperature for a typical SMP

1.3.5.2 Recovery Temperature

The performance of a shape memory polymer is defined by its aptitude to recall shape memory effect during recovery. This effect is manifested by an increase in the segment mobility of the polymer chains [7]. Normally, shape memory polymers regain their original shape when heated up above their glass transition temperature. In cracked thermoplastic SMPs, a recovery temperature above $T_g$ is enough to trigger self-healing. In damaged composites of thermoplastic resin, recovery temperature causes crack sealing (through shape recovery) and sets the conditions for polymerization of the healing agent.
Chapter 2: Literature Survey

2.1 Literature Review

Formation of cracks and other microscopic types of damages is a persistent problem in most engineering applications. Recurrence and continuous mechanical usage can degrade the flexural strength and damage the microstructure of polymers and polymer composites over time. In that respect, smart self-healing composites possess the ability to repair structural damage and restore strength, and thus, counteract degradation due to constant use. The concept of bio-mimetic self-healing polymers was inspired from biological systems where this behavior is commonly observed, and has been extensively studied since [1-24]. Like biological systems, the self-healing mechanism of polymers can be autonomic or can require an external stimulus (usually human intervention for heating); but in either situation, the healing process is triggered by damage to and on the macro or micro level of the structure. Still following the biomimetic model, it was reported that temperature plays a critical role during wound and damage healing. It has been observed, for instance, that temperature dictates the rate of chemical and enzymatic processes occurring within the wound, and controls the metabolism of cells and tissues engaged in the repair process [25, 26]. A temperature drop of just 2°C produces a change that is sufficient enough to affect the biological healing process. A similar step change is observed in thermoplastic polymers — where the polymer changes states around its glass transition temperature ($T_g$) — a change which induces and promotes the intermolecular diffusion mechanism during polymer-polymer reactions [13, 27]. Various models have been recommended to better explain the process of crack healing by the aforementioned mechanism. Those models include the microscopic theory for diffusion proposed by Kim and
Wool [17] analyzing the motion of chains at the crack interface and providing a formula for the interpenetration distance of polymer segment as a function of molecular weight. Another model is the five-stage model suggested by Wool and O'Connor [21]. A detailed study of kinetics of craze healing in atactic polystyrene was conducted. Visual and mechanical healing was observed as nucleation times and growth rates were varied (healing temperature was held constant). Other models describing the process of interfaced crack healing such as interdiffusion of molecular chains and formation of molecular entanglements by Kausch [15], the recombination of chain ends and reversible bond formation, and photo induced healing have also been studied. Other self-healing mechanisms are often used in conjunction with thermoset polymers and are capable of effectively healing at the molecular-length scale. Such healing mechanisms involve the use of self-healing agents stored in microcapsules [4], hollow fibers [28], and microvascular networks [29, 30], intrinsic healing polymers such as ionomers [31] and thermally reversible covalent bonds [32], dispersed thermoplastic particles [33], etc.... Because these self-healing methods lack efficiency at structural-length scale, a biomimetic two-step close-then-heal (CTH) process was developed by Li and Nettles [6] and detailed by Li and Uppu [9]. The process involves the practice of two distinct steps: (1) close the crack, and then (2) heal it. The key to this method was the reduction of structure volume during programming and the application of an external rigid 3-D confinement during shape recovery (healing). Embedded confinements such as 3-D woven fabrics, integrated orthogrids and stimuli-responsive fibers were also proven to reproduce the same effect [34-38].

Li and Uppu [9] conducted a detailed analysis on confining tubes during programming and recovery of a self-healing syntactic foam. The confining tubes studied were double-walled
tubes with steel, nylon and rubber liners, providing rigid, intermediate and weak confinement, respectively. The thermo-mechanical behavior in terms of 2-D stress-time and temperature-time, and 3-D stress-strain-temperature was observed for each liners. Additionally, the stress recovery ratio and volume reduction due to pre-stressing were calculated for different liner type, pre-strain level and programming temperature. The following relevant conclusions were obtained. Under 3-D compression confinement, the cooling and unloading steps of the thermo-mechanical programming can be combined into a single step. The type of liner, programming temperatures and pre-strain levels used in the thermo-mechanical cycle had an influence on the stress recovery ratio and recovered stress of the sample. The study reported that the rubber liner lead to a better stress recovery ratio, while the nylon liner yielded better recovered stresses. Overall, higher pre-strain levels lead to a higher recovered stress. The study finally concluded that volume reduction during programming was key for obtaining good self-closing efficiencies for the foam based shape memory polymer. Excessive volume reduction initiated micro-balloons crushing and induced loss of shape memory capability and of the ability of the foam to seal cracks. It becomes apparent that in self-healing SMPs such as capsule-based self-healing SMPs and micro-channel self-healing SMPs, a similar problem could occur, resulting in a reduction in the performance of the self-healing polymer. In thermosets with thermoplastic additives (monomers) and in thermoplastics, volume reduction is only limited by mechanical properties like brittleness.

Njii and Li [8] conducted a similar study on a shape memory polymer based self-healing particulate composite. The composite contained thermoplastic particles (Copolyster) dispersed in a polystyrene based shape memory polymer resin. Programming, as well as recovery, was
performed in a rectangular confining mold. Self-healing was executed as described by the two-step close-then-heal (CTH) self-healing scheme. The study was purposed with the validation of the CTH method on a composite with thermoplastic particles. The sample pool, containing notched and un-notched specimens, was fractured and healed for up to five consecutive cycles. The healing performance was evaluated per the peak-bending load post programming and following healing. Healing efficiency and repeatability were key results and were analyzed. As mentioned previously, self-healing materials with intrinsic properties should be able to heal a crack at a specific location, multiple times. The analysis provided experimental proof of this fact with flexural strength healing efficiencies going as high as 65%. Molecular-length scale self-healing was a result of the diffusion of the thermoplastic copolymer into the matrix and was put in evidence by a series of elemental analyses around the crack interface. The principle behind CTH was further validated by the obtainment of a healing of structural-length scale damage.

A widely used method to trigger actuation of a shape memory polymer is through thermal stimulus. It is also a known fact that temperature plays an important role in the thermo-mechanical cycle of a polymer during programming [39]. Using a high temperature nano-indentation technique, it was determined that the instantaneous moduli of a shape memory polymer were temperature dependent. It was also determined that the surface profile of the shape memory polymer samples activated at high temperature exhibited some differences as compared to those activated at lower temperatures. A common trend was that the original shape of the SMP samples was almost fully recovered during high temperature recoveries. Due to the local nature of the micro-/nano-scale level programming, only a limited number of mechanical properties can be determined. Structural recovery is an important
aspect that has not been experimentally studied, as various temperature parameters are fluctuated.

2.2 Research Contribution

This study intends to investigate some essential mechanical properties such as the flexural strength of specimens post programming and following healing through the close-then-heal scheme, suggested by Li and Uppu [9]. For structurally rigid and efficient 3-D confinement, a method for designing, fabricating and using the full confining mold needs to be implemented. Currently, no study details how the choice and the dimensions of the 3-D mold impacts confinement during programming and healing. The present study, through finite element analysis, addresses some of the issues regarding the degree of confinement as the temperature is varied in the heating furnace.

In this study, a polystyrene shape memory polymer was considered as the matrix of the polymer composites. Thermoplastic particles were uniformly scattered into the matrix to induce healing at the molecular level (molecules entanglement). A differential scanning calorimetry (DSC) test was conducted to determine the glass transition temperature of the Polystyrene shape memory polymer, copolyester additives, and the polymer composite (CP + PSMP). Cylindrical specimens were cut, according to ISO 178 specifications, with a water jet cutting tool to reduce damage in and on the surface of the material. In order to provide rigid 3-D confinement, a low clearance, low thermal expansion mold was implemented. Three-point flexural tests were performed on un-notched cylindrical samples before programming, after programming and after healing, to evaluate the percent flexural strength recovered. A SEM-EDS
(scanning electron microscopy coupled with energy dispersive spectroscopy) provided visual and analytical images of the results, and validated the experiment.
Chapter 3: Manufacturing

3.1 Raw Materials

3.1.1 Shape Memory Polymer Composite

The shape memory polymer was synthesized using vinylbenzene, vinyl neodecanoate, and divinyl-benzene, with benzoyl peroxide as the radical initiator. Vinylbenzene (Aldrich, Reagentplus ≥ 99%); Divinyl-benzene (technical grade, 80%, mixture of isomers, (Aldrich)); Benzoyl peroxide (Luperox® A98, reagent grade, ≥ 98% (Sigma-Aldrich)); Vinyl neodecanoate (Aldrich). The thermoplastic particle was a linear copolyester (CP) made of Isophthalic acid, Terephthalic acid and 1,4-Butanediol. It was supplied by Abifor Inc., Switzerland. The particles size of the thermoplastic particles was ≤ 80 μm. The density of the thermoplastic particle was 1.3 g/cm3. The glass transition temperature, melting temperature, and bonding temperature of the copolyester were 16°C, 120°C, and 150°C, respectively.

3.1.2 Confining Mold

The material for the confining mold was comprised of two 10 cm x 10 cm x 30 cm blocks of steel alloy (0.2% carbon by weight). The mechanical and thermal properties of the steel alloy are listed in table 1 below.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus</td>
<td>200 GPa</td>
</tr>
<tr>
<td>Poisson Ratio</td>
<td>0.3</td>
</tr>
<tr>
<td>Density</td>
<td>7850 kg/m³</td>
</tr>
<tr>
<td>Linear Expansion</td>
<td>13x10⁻⁶ /°C</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>53.66 W/m K</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>490 J/kg K</td>
</tr>
</tbody>
</table>
3.2 Polymer Composite Fabrication

Vinylbenzene was added to a three-necked flask equipped with a mechanical stirrer and a thermometer. Polystyrene was dissolved in the vinylbenzene following vigorous stirring for 45 minutes using a polytetrafluoroethylene stir. An ultrasonicator (Sonic and Materials Inc, Sonic Vibra-cell, model CV334) was employed to promote the dissolution of the polystyrene. Vinyl neodecanoate and divinyl-benzene were added to the reactor followed with 10 minutes of mixing. After a clear viscous solution was obtained, thermoplastic particles (6% by volume) were added to the mixture to make the composite. For the pure shape memory polymer, this step was skipped (i.e. no thermoplastic particle was added to the mixture). After 1 hour of vigorous stirring, a homogenous solution was achieved. Benzoyl peroxide was added to the reactant as reaction thermal initiator. The reactant was further mixed at room temperature for 30 minutes. The reacting polymer was degassed in 0.1–0.2 kPa vacuum using a vacuum oven (Sargent-Welche scientific Co.ltd, Welch brand, Duo-seal, Model NO. 1402) for 30 minutes. Subsequently, the reactant was cast into a polytetrafluoroethylene coated mold, sealed using a vacuum bag sealant tape (Airtech 5 advanced materials group) and a release bag (Airtech advanced materials group) to prevent air from influencing on the reaction. The polymer was cured following the procedure: 75°C for 16 hours, then 80°C for 10 hours, and 110°C for 5 hours.

3.3 Specimen Extraction

After hardening and curing, identical specimens were cut from the cured composite slab using a water jet cutting tool.
Figure 6. Pure SMP just poured into the curing mold

Figure 7. SMP containing thermoplastic particles just poured into curing mold. The mold was divided into parts for better curing
There are several advantages of using abrasive water jet (AWJ) for cutting polymer matrix composites instead of the conventional sawing, laser beam cutting or CNC methods. Laser beam cutting induces high heat dissipation into the work-piece, causing charring, thermal cracks, surface and subsurface defects, and yielding large burr formation and dimensional inaccuracy due to thermal distortion [40]. In AWJ, burr formation has been found to be only dependent on the jet energy level at the bottom region of the cut. At high water pressures, a clean edge is formed at the bottom of the specimen, suggesting the absence of burrs in the specimen. As most shape memory polymers are very temperature sensitive, uncontrolled heat during laser cutting can also initiate the formation of heat affected zones. Sawing, likewise, can induce phenomena like delamination and fiber pull-out from a fibrous composites material. Delamination is a failure in the bonding between the layers of a laminated material during processing. It is usually to weak bonding between layers but can also be caused by repeated cyclic stresses such as in sawing. Delamination is an insidious kind of failure and may not be obvious at the surface of the material; and because it occurs at depth, it can be detrimental a polymer and especially to a self-healing material with encapsulated healing agents, hollow tubes and vascular networks. Micro-cracks resulting from such a failure can affect a polymer as early as in its thermo-mechanical programming. The saw itself can suffer from wear due to the hard and abrasive nature of the fiber/particle inside the composite. Water jet cutting, on the other hand, offers a safer alternative to polymer specimen extraction. Indeed, several parameters can be controlled to avoid damage in the machined material. For instance, the degree of initial damage of the jet at entry can be minimized with low standoff distances. Surface waviness, kerf zones, striation formation, delamination, etc, can be significantly
reduced by adjusting the machine’s parameters. Zeng developed a mathematical formula relating those parameters to the cutting quality [41].

\[
N_m = \frac{C h D^{0.618} u^{0.866}}{P_w^{1.25} m_w^{0.607} m^{0.343}}
\]  

(3)

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 equaling \(4.272 \times 10^{-4}\) for the English unit system. The expression for the transverse speed is given by:

\[
u = \left(\frac{f_a N_m P_w^{1.25} m_w^{0.607} m^{0.343}}{C h D^{0.618}}\right)^{1.15}
\]  

(4)

where \(f_a\) is the abrasive factor and \(Q\) is the quality index. \(Q\) has values from 1 to 5 and relates the AWJ settings to the final surface finish. A quality level of 1 indicates that the minimum criteria are met for separation cut, independently of surface finish. Other surface finish descriptions are summarized in the table below.

Table 2. Cut surface finish description in terms of quality index

<table>
<thead>
<tr>
<th>Quality</th>
<th>Surface Finish Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Minimum criteria are met for separation cut</td>
</tr>
<tr>
<td>2</td>
<td>Rough surface finish with striations at the lower half surface</td>
</tr>
<tr>
<td>3</td>
<td>Smooth surface with possibility of striations</td>
</tr>
<tr>
<td>4</td>
<td>Good surface finish with minimum to no striation</td>
</tr>
<tr>
<td>5</td>
<td>Excellent surface finish</td>
</tr>
</tbody>
</table>

Equations 3 and 4 above as well as the information in table 2 show the number of possible settings that can be modified to get the desired cut surface finish. In addition, water jet cutting offers a low temperature and high accuracy cut (up to 0.13 mm and 0.025 in tolerance).
Water jets have also been shown to be particularly efficacious in cutting polymer matrices and composites [40-51].

3.4 Confining Mold Fabrication

As mentioned before, confinement is a key element to the material structural restoration. For this reason, the design of the confining mold had to be carefully done in order to provide the necessary conditions for healing to take place. Parameters such as structural rigidity, uniformity and functionality were some of the design requirements observed during the conception and the fabrication of the confining mold.

3.4.1 Objectives and Design Considerations

The objective of the designing a confining mold is to provide a suitable level of confinement during the thermo-mechanical programming and the shape recovery phases. Because the overall system (consisting of the confinement and the specimen) are heated to high temperatures and are subjected to thermal effects and mechanical stresses during those phases, it is necessary to perform an analysis to determine the thermally-induced and mechanical stresses in the mold, the total mechanical and thermal strains (which defines the degree of confinement at a given temperature), the temperature distribution at the specimen-mold interface, and the dimensions of the mold. Knowledge of those parameters will ensure proper heat transfer to/from the polymer specimen, stability during programming and will limit the risks of non-uniform loading and failure during compression (as in buckling). Proper mold design will also increase the overall life of the mold.

Two shapes were initially considered: rectangular and circular cross-section. A rectangular cross-section for the confining mold prompts the manufacturing of specimens with
a rectangular cross-section, which is a major advantage as rectangle-shaped specimens are the relatively easy to construct and to analyze. A concern with rectangular cross-sections, however, is the presence of corners which would cause singularity problems in certain analyses. Asymmetric thermal shrinkage due to uneven cooling of a part and differential thermal strain due to geometry (corner) effects can cause shrinkage and warping. This will result in an inaccuracy in the specimen geometry and could even damage to the mold itself as shown in figure 8 below. Techniques consisting in redesigning the edge like rounding sharp edges and corners are solutions utilized to attenuate and remove the effects of a singularity in that region. However, the consequences of such solutions are an alteration of the desired outcome. In this case, the specimens would need to have a rectangular cross-section with round edges. This shape is clearly impractical.

Figure 8. Effects of warping at edge (sharp corner) due to additional differential strain
A cylindrical mold – and subsequently cylindrical specimens – was chosen. The advantages extend to those described for the case of a rectangular mold, in addition to a relatively easier analysis. Finite element analysis (FEA) was conducted to guarantee that the design requirements were met. Theoretical methods were also used as a mean to validate the results obtained by FEA.

A finite element analysis was conducted to determine the temperature distribution and some the effects of heat flowing inside the mold. Mechanical and thermal stresses and strains were given a particular attention. The quarter section (first quadrant) of the cross-section of the hollow cylinder used for the analysis is justified by symmetry conditions on the sides at \( x = 0 \) and at \( y = 0 \) (the origin being the center of the hollow cross-section). The mold was modeled in ANSYS as a three dimensional solid thermal mass with quadratic tetrahedral TET10 (solid 87) elements was examined. A transient thermal analysis was coupled with a structural analysis to mimic slow heating from 20\(^\circ\)C to 140\(^\circ\)C in the furnace. A series of meshes were considered. Five meshes ranging from coarse to fine were defined. Convergent tests were performed at the end of the analysis to estimate the accuracy of the results.

| Table 3. Dimensions of hollow cylinder confining mold |
|---------------------|----------------|
| **Dimensions**      | **Value**      |
| Height              | 121.50 mm      |
| Inner Diameter      | 12.70 mm       |
| Outer Diameter      | 50.05 mm       |
| Thickness           | 18.675 mm      |
3.4.2 Results

The diagrams obtained from the finite element analysis using the simulation software ANSYS are shown below. The temperature distribution inside the mold, as time is varied, provides valuable information about the holding and pre-soaking time to be used during programming and recovery. It also shows how temperature is distributed through the thickness of the hollow confining container as temperature is changing. This gives also information on the uniformity of the heat being transferred to the specimen.

The contour plots in figure 10 - 13 present some of the results of the FEA at steady-state conditions (once the temperature in the mold has reached 140°C).
Figure 10. Temperature distribution at time $t = 25$ minutes

Figure 11. Temperature on inside walls of mold as time is varied
Figure 12. Deformed (outlined) and un-deformed (shaded) quarter cross-section at steady-state conditions at 140°C

Figure 13. Von Mises thermal strain on cross-sectional area at steady-state
Radial expansion due to thermal stresses in a cylinder can be obtained using the equation:

\[ r' = r(1 + \alpha \cdot \Delta T) \]  \hspace{1cm} (5)

where \( r' \) is the new radius at the final temperature, \( r \) is the radius at room temperature, \( \alpha \) is the coefficient of thermal expansion of the material, and \( \Delta T \) denotes the difference in temperatures between the final and initial conditions.

The analysis of hollow confining mold using finite element methods reveals that for a heat transfer coefficient of 15 W/m\(^2\)K and a final temperature of 140\(^\circ\)C, a minimum soaking time of 40 minutes is necessary for the inner walls to reach steady state conditions. At that time, the outward deflection of the inner and outer walls due to thermal stresses would be equal to 0.012 mm and 0.046 mm, respectively, according to the Von Mises criterion, and 0.011 mm if linear thermal expansion is assumed. An increase of a tenth of a millimeter in the hollowness (new radius) of the confining cylinder was judged satisfactory.

Other tools were designed to complement the confining tube and to help achieve a better programming and recovery experience. A bottom plug was implemented to provide enhanced support and prevent leakage during compression programming. A pusher was also designed to offer sturdy and stable compression at low clearance. Figure 14 below illustrates the complete confinement apparatus. Note the use of polytetrafluoroethylene (Teflon) sheet between the polymer specimen and the confining mold. Its purpose is discussed in the following sections.
Figure 14. 3-D model of confining apparatus
Chapter 4: Experimentation

4.1 Differential Scanning Calorimetry (DSC)

As discussed previously, the glass transition temperature ($T_g$) is an important parameter to know when dealing with polymers in general and shape memory polymers in particular. It gives information about when the storage modulus of the polymer is low enough to be safely compressed during compression-programming. It also determines the activation temperature at which the polymeric chains relaxation occurs as well as when the SMP starts to experience shape memory effects (during recovery). A Perkin-Elmer DSC7 differential scanning calorimeter was used for the DSC test. The purpose of this test on the Polystyrene shape memory polymer (PSMP) and on the self-healing co-polymer particulate composite (CP-PSMP) was to determine their glass transition temperature. The same test was performed on the CP to identify the $T_g$ of the particle, its melting temperature ($T_m$), and to compare those values with the specifications provided by the manufacturer. The DSC test was conducted between -70°C and 220°C at a ramp rate of 5°C/min on specimens weighing 6 mg.

Figure 15. Differential scanning calorimeter and data acquisition system
4.2 Quasi-Static Strain-Controlled Programming

A strain-controlled programming was performed the cylindrical specimens under 3-D confinement and with no confinement, with the help of a MTS 810 machine. The strain-controlled programming was preferred over the stress-controlled programming because it is easier to control strain, rather than stress, while the modulus of the material is changing inside the furnace. Strain-controlled programming also offers reasonable shape fixities. The term ‘quasi-static’ refers to the use of a fairly slow compression rate: 1.4 mm/min in this test.

The apparatus consisted of a small oven mounted around the clamps of the MTS tester. A low heating rate of 6°C/min was deemed appropriate, according to the results obtained from the finite element analysis of the confining mold. Based on the $T_g$ obtained from the DSC for the shape memory specimens, programming temperatures were chosen below, around and above the $T_g$. Several pre-strain levels were initially tested (while keep the temperature constant) to determine their effect on shape fixity and shape recovery. Note that functional shape memory polymers should display good shape fixity and shape recovery regardless of the pre-strain level used. However, it is possible that different pre-strains can have an influence on shape fixity and shape recovery parameters of the sample. Measurements of the dimensions of the specimen before and after programming (without confinement) will allow determination of the shape fixity of the material. Similarly, knowing the original length and the length of the specimen after healing will allow calculation of the shape recovery.

Next, a pre-strain level was chosen for the programming of all the specimens. The pre-strain (15%) selected was low enough to prevent and avoid the formation of structural cracks in the material during low temperature programming. The constant 15% pre-strain was applied in
the (axial) loading direction of the specimens. All the specimens programmed were held at that
pre-strain level for 60 minutes prior to being gently cooled down to room temperature.

Figure 17 shows a schematic of the complete thermo-mechanical programming under
confinement, followed by shape recovery (healing) inside the confining tube. Each of the
processes depicted is further detailed later in the analysis.
Figure 17. Thermo-mechanical programming and shape recovery under 3-D confinement

4.3 Three-Point Flexural Test

Flexural tests simulate stresses of tensile and compression on a specimen. A three-point flexural test produces a peak stress at the specimen midpoint with reduced stress everywhere else. It is therefore a great way to create at that location in brittle materials, while obtaining properties such as the modulus of elasticity and the flexural stress-strain response of the material.

Crack was initiated in the cylindrical specimens during the post-programming bending test. ISO 178 was the standard used in this experiment. Un-notched PSMP and CP-PSMP specimens of 11.5 mm diameter and 120 mm length were fractured at a rate of 0.5 mm/min on the MTS 810 machine. The specimen tested was supported by a fully adjustable three-point loading flexure fixture with roller cylinders 92 mm apart (i.e., they provided a length-to-diameter ratio of 8 to 1). It is to note that because of the brittle nature of the material, complete fracture of the specimens was expected to occur before 5% strain was reached. The
The same three-point flexural test was performed on the healed samples to check for the restoration of their structural integrity.

Figure 18. Three-point flexural test apparatus

4.4 Shape Recovery

The motivation for a 3-D confined healing was directed by the two-step close-then-heal (CTH) self-healing scheme by Li and Uppu [9]. Since the fractured surfaces were rough and exhibited some irregularities as shown in figure 19, it was possible to carefully position the alignment of the irregularities on the cracked surface in order to minimize the crack width. Due to its relatively low thermal conductivity, the steel mold delivered low heating and cooling rates to the uncased polymer, as well as a rigid confinement structure during the shape recovery process.
The basis behind the 3-D confinement shape recovery, or strain-controlled recovery, is that by constraining the specimen and bringing it to its activation temperature inside the pre-heated furnace, shape memory effects will ensue in the axial direction and thus, induce crack closure. An important factor taken into consideration during this process was the presence of the temperature dependent copolyester particles in the composite, aiding in healing. The healing temperature picked, were governed by the results obtained from the DSC test. In clear, temperature during recovery was chosen below the $T_g$ of the CP-PSMP, above the $T_g$ of the CP-PSMP and below the $T_m$ of the CP, between the $T_m$ and the bonding temperature ($T_b$) of the CP, and above the $T_b$ of the CP.
As underlined previously, the purpose of the CP additive is to provide healing at the micro-scale level. In theory, the amount of melted copolyester particles at the crack interface prescribes the recovered strength due solely to the action of the particles. In clear, the flow of melted CP particles at higher temperatures should promote a better distribution of the healing agent at the surface of the crack which, in turn, should result in improved recovered strengths. Thus, healed surface composition is dependent on programming and healing temperature. In that regard, an energy dispersive spectroscopy is sine qua non to determining the quantity of melted copolymer on the crack surface after healing. The device used was a Hitachi S-3600N VP Scanning Electron Microscope with EDS capabilities. The amount of elements (weight percent of carbon and oxygen) on five 1 mm x 1 mm areas on the crack surface of the sample was
acquired and averaged. The numbers obtained represent the averaged weight percent of carbon and oxygen over the entire healed surface.

Figure 21. Preparation of specimen before EDS

Figure 22. S-3600N VP Scanning Electron Microscope with EDS

4.6 Visual Inspection: Scanning Electron Microscope (SEM) Imaging

A visual inspection of the specimen around the healed area is necessary as it allows visual appreciation of crack closure and shape restoration in that region. A more magnified observation at the healed interface can also give information on the state or aspect of the
thermoplastic particles in that zone after healing. Therefore, a scanning electron microscopy was conducted on the samples programmed and healed at different temperatures.

Because the SMP specimens are not electrically conductive, they had to be carefully prepared before they could be observed under a SEM microscope. For the SEM microscopy, a continuous conductive surface film needs to be applied on non-conductive materials to allow incident electrons to be conducted away from the surface. An accumulation of electrons on a non-conductive surface results in a charge buildup and causes a divergence of the electron beam, which degrades the SEM image. All the samples to be scanned were sputter coated, in a 0.1 mbar vacuum, with a thin film of platinum (about 20 nm thick) by an EMS 550 Sputter Coater for 4 minutes. Coated specimens were then mounted on a plug and secured using aluminum adhesives like shown in figure 24. Subsequently, the SEM observation was conducted under a Quanter 200 SEM microscope. Images were captured at the crack interface, inside the crack at the interface and on the crack surface.

Figure 23. SMP specimens being sputter coated
Figure 24. Plug mounting and SEM loading
Chapter 5: Results and Discussion

5.1 Determination of the Glass Transition Temperature

The central focus of the DSC experiment was to identify the temperatures at which the materials to be programmed and/or healed exhibit a sudden or considerable change in viscosity. The glass transition temperature can be viewed as the most critical mechanical property for non-thermally stable polymers. The virtually abrupt change in the modulus, the thermal expansion coefficient and the specific heat of the polymer around that temperature, turn the glassy and brittle state of the material into rubber-like state. Likewise, the determination of the melting temperature for the low-melting point copolymer was imperative. The DSC test revealed a $T_g$ of ~ 89°C for the PSMP and ~ 16°C for the CP, which is consistent with the 17°C glass transition temperature indicated on the manufacturer’s specifications sheet.

The glass transition temperature of the CP-PSMP composite ($T_g = 80 – 84^\circ$C) was found to be somewhere between the glass transition of the PSMP and that of the CP, and is an indication of some compatibility between the PSMP and the CP. The intermediate $T_g$ obtained for the composite shows that me PSMP and CP copolymer influence one another to some degree. The overall $T_g$ of the CP-PSMP, however, was expected to be near that of the matrix of the composite as a consequence of the low particle-to-matrix volume ratio. The melting point of the CP copolymer ($T_m = 120^\circ$C) was also consistent with the melting temperature range ($T_m = 114 – 124^\circ$C) supplied by the manufacturer. The heat flow vs. temperature graph for the pure PSMP material is shown in figure 25 below.
5.2 Thermo-mechanical Programming

Figure 20 gives a perspective of the complete thermo-mechanical programming of a typical cylindrical specimen under confinement. The different steps of programming (I – III) can be observed on the figure. Initially, the specimen is enveloped with a few rounds of sheets made of polytetrafluoroethylene (PTFE) and loaded into the confining mold. The role of the PTFE sheet (thickness: 0.0076 mm, thermal expansion coefficient: $135 \times 10^{-6}$ K$^{-1}$, melting point: 327°C and coefficient of friction: 0.05-0.10 measured against polished steel) is to protect the specimen from thermal surface damage and to facilitate the removal of the material from the mold after programming.

The process starts with the specimen, inside the furnace, heated at a rate of 6°C/min to the final programming temperature ($T_p = 60^\circ$C, 82°C and 100°C). It then undergoes step I,
where it is loaded and compressed (at a speed of 1.4 mm/min) to the desired pre-strain level (15%) before being held there for 1 hour (step II). During that stage, both the temperature and the crosshead displacement are kept constant. As the holding time progresses, a drop in the axial stress, synonym of stress relaxation, can be observed. Step III wraps up the compression programming procedure with a slow cooling to room temperature. The specimen is subsequently unloaded and extracted from the mold.

Three other CP-PSMP specimens were programmed without confinement at 100°C (above $T_g$) at 5, 15 and 40% and were allowed to experience free recovery (i.e., no confinement) at 100°C. The shape fixities and shape recovery ratios are summarized in table #. Shape fixities of nearly 98.2% were attained for the selected 15% pre-strain level.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-strain level (%)</th>
<th>Shape fixity (%)</th>
<th>Free shape recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5</td>
<td>98.2</td>
<td>99.3</td>
</tr>
<tr>
<td>B</td>
<td>15</td>
<td>98.2</td>
<td>98.0</td>
</tr>
<tr>
<td>C</td>
<td>40</td>
<td>98.2</td>
<td>93.8</td>
</tr>
</tbody>
</table>

5.3 Three-Point Flexural Test Post-programming

Bending tests were performed (at room temperature) on the CP-PSMP samples previously programmed. The objective of this auxiliary test was to investigate the effects of the programming temperature on the flexural strength of the material, immediately following programming. Three specimens per samples (programmed at 20°C, 45°C, 60°C, 82°C, 100°C and 140°C) were used for this test. Figure 27 illustrates the results obtained for the flexural test, immediately following confined programming.
Figure 26. Typical load-deflection curve immediately after programming, for 3 selected temperatures: below $T_g$, around $T_g$ and above $T_g$.

Figure 27. Flexural strength of CP-PSMP specimens immediately after programming and after healing at 100°C for various programming temperatures.
Specimens programmed at lower temperatures exhibited a flexural strength reasonably higher than specimens programmed above $T_g$. It is also noted that flexural strength decreased as the programming temperature ($T_p$) was increased, then stabilized past the glass transition temperature ($80 - 84^\circ C$). Although the glass transition is not a phase transition in itself, considerable changes in the viscosity of the polymer around that temperature induce polymer chains mobility. Axial loading at temperatures high enough above $T_g$ allows the polymeric chains to realign in the radial direction. Conversely, axial loading at lower temperatures causes a shift and leaves the polymer chains somewhat aligned in the loading/axial direction.

5.4 Recovery

CP-PSMP specimens were healed according to the close-then-heal (CTH) scheme described previously. Steps IV and V of figure 20 illustrates the shape recovery process of the specimen (healed at $100^\circ C$) under confinement. As the confining mold containing the specimen is inserted inside the oven, an increase in the volume of the material due to thermal expansion yields to radial and axial thermal stresses inside the confinement (step IV). After a soaking time of 2 hours has elapsed, the specimen is then allowed to cool down to room temperature (step V) and to regain its temporary (programmed) shape and length.

An auxiliary test was conducted to determine the free-shape recovery ratio of the CP-PSMP samples. Three un-fractured specimens programmed at $100^\circ C$, were subjected to recovery (also at $100^\circ C$) without any confinement (step VI). The lengths of the specimens during the free-shape recovery were carefully monitored with a Cooper Instruments LDT 200 series LVDT device. It followed that close to 98% of the original (pre-programming) length of the specimens was recovered. The high free-shape recovery ratio coupled with the excellent
shape fixity obtained during programming and recovery above $T_g$, indicate a good shape
memory functionality of the polymer composite.

5.5 Three-Point Flexural Test Post Recovery

5.5.1 After Free Recovery

Two samples programmed at 60°C and 100°C were put in the furnace at 100°C to
undergo free recovery. After two hours of recovery without confinement, they were allowed to
cool down to room temperature. The cracked region was not sealed and was clearly visible with
the naked eye. The specimens were also very fragile. They would break at their midpoint upon
being picked up or being set on the three-point flexure apparatus. No flexural strength could be
recorded for these specimens.

5.5.2 After Partial (2-D) Confinement Recovery

Samples also programmed at 60°C and 100°C were allowed to recover with confinement
only in the axial direction at 100°C and 122°C. After cooling down to room temperature, all the
specimens exhibited visible indications of a crack at their midpoint, as shown in figure 28. The
trace was perfectly visible with the naked eye but could not be felt when touched with the
fingers. This is an indicated of effective crack closure. The recovered flexural strength of those
specimens, however, was very low (less than 25%) as they were not constrained in the radial
direction and the majority of them would buckle or bend during the 2-D confined recovery due
to thermal expansion (see figure 29).
5.5.3 **After Full (3-D) Confinement Recovery**

To determine the strength recovery ratio of the healed specimens, their flexural strengths directly after programming and after healing were compared. Two series of flexural tests were performed on the shape-recovered specimens in order to fully investigate the effects of programming temperature and of healing temperature. First, samples programmed
at 60°C, 82°C and 100°C (below, around and above the $T_g$ of the CP-PSMP) and healed at $T_h = 100$°C were tested. Table 5 presents the shape recovery ratios obtained (taken from figure 27).

Table 5. Flexural strength recovery for varied programming temperatures

<table>
<thead>
<tr>
<th>Constant Healing Temperature ($T_h = 100$°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_p$ (°C)</td>
</tr>
<tr>
<td>Strength Recovery (%)</td>
</tr>
</tbody>
</table>

It appears that samples programmed at and above $T_g$ displayed a strength recovery marginally greater than those programmed below $T_g$. On the other hand, gathered data from figure 26 and table 5 above, indicate that low temperature programming negatively affects healing efficiencies. The reason is that shape recovery, which is the foundation of structural-length scale healing, is better obtained at high programming and healing temperatures. In other words, better crack closures obtained at temperatures above $T_g$, are beneficial to crack healing.

Next, a batch of specimens all programmed at 100°C and healed at 73°C, 100°C, 122°C and 148°C were examined. Note that the healing temperatures were selected based on the criteria explained in section 4.4. The results obtained two selected temperatures (100°C and 122°C) are illustrated in figure 30 and the results for all four temperatures are summarized in table 6.

Table 6. Flexural strength recovery for varied healing temperatures

<table>
<thead>
<tr>
<th>Constant Programming Temperature ($T_p = 100$°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_h$ (°C)</td>
</tr>
<tr>
<td>Strength Recovery (%)</td>
</tr>
</tbody>
</table>
Figure 30. Typical load-deflection curve showing the load at break for two specimens programmed at 100°C and healed at 100°C and 122°C

The action of the temperature-sensitive thermoplastic particle is put in evidence by a considerable “jump” in the recovered strength, once the melting temperature (of the CP particle) is attained. The sample is further strengthened, to a maximum of 63% of its post-programming strength, over the bonding temperature of the CP. Overall, it is observed that higher programming and healing temperatures favor strength recovery. However, it can be seen that most of the healing and strengthening occurring under confinement is due to the action of the thermoplastic particle additives.

5.5.4 Overall Shape and Strength Recovery Observations and Discussions

The proposition stating that confinement is key to self-healing was verified in the first part of this flexural test experiment. Specimens programmed above and below their $T_g$ were fractured at their midpoint during bending test. The broken surface were subsequently brought into contact and set in the furnace without any confinement for recovery. After being held
there for 2 hours at 100°C and cooled down to room temperature, the “shape-recovered” specimens obtained displayed significant fragility. Furthermore, the crack initiated during three-point bending was not sealed. The extreme breakability of these specimens is due to the fact the fractures surfaces cannot be sturdily kept in contact as a result of thermal expansion during recovery. Indeed, an increase in length of the cracked pieces during recovery can alter the stability of the cylindrical specimens by pushing them apart and preventing chemical repair. No flexural test could be conducted on those specimens healed without confinement.

Other specimens programmed under similar conditions were also submitted to shape recovery, but with only partial confinement (i.e., confinement in the axial direction only). As in the previous case, dimensional stability was also a problem. The lack of support in the radial direction induced motion in that plane as the pieces tended to expand during heating and contract during cooling. The final specimens were weakened because of recovered shape abnormalities, as shown in figure 29. It is important to note that shape deformation in during partially confined recovery is strongly dependent on the specimen’s dimensions, shape and expansion capability. For instance, shorter and wider specimens could not exhibit any deformation, while longer and thinner ones could display more significant deformations. A shape recovery ratio peak of 25% was obtained in the specimen that had the least motion instability during recovery.

The effects of programming and recovery under 3-D confinement on flexural strength recovery were finally investigated. Two series of test were conducted. First, un-notched specimens programmed at 60°C, 82°C and 100°C were cracked around their midpoint and allowed to heal under full confinement at 100°C. After healing, they were fractured at the same
location in order to determine their post-programming to post-healing strength recovery ratio. Although specimens programmed at lower temperature had an improved flexural strength following programming, they ended up have a lower strength recovery percent after 3-D healing. It can be speculated that the motion, alignment and orientation of polymer chains during programming at lower and higher temperatures offers different degrees of resistance in the radial direction, resulting in improved or reduced bending strengths. This provides a mechanical justification of the enhanced flexural strength observed in specimens programmed at lower temperatures. During recovery however, strength restoration occurring by self-healing is due to the action of the healing agents and is only slightly affected by shape recovery. A fairly constant stress is recovered after healing and shown in figure 27. Overall, it is observed that the ratio of the strength recovery after healing and immediately after programming increases as the specimen’s programming temperature is increased, and slowly stabilizes after the $T_g$ is reached.

The investigation of the effects of healing temperature on the self-healing SMP specimens was effectuated by fluctuating $T_h$ for a constant $T_p$ ($T_p = 100^\circ C$ was chosen in relation to the previous experiment). The recovered strength after healing very slowly increased for temperatures below and above the $T_g$ of the Polystyrene resin. Once the melting temperature of the copolyester particle was achieved, a substantial boost in the strength recovery was observed (from 37.4% at $100^\circ C$ to 57.4% at $122^\circ C$). The percent flexural strength recovery is further improved above the bonding point of the CP particle (63% at $148^\circ C$). The higher strength obtained beyond the $T_m$ of the CP results from the flow of self-healing melted CP and subsequent re-dispersion into the crack plane, filling the cracked zone and mechanically
interlocking with the matrix material. This statement is verified and validated using EDS, in the following section. Esthetically, the polymer specimen looks “cooked” at those high temperatures (see figure 31 below). The effects of this esthetical imperfection on the surface and chemical properties of the material were not investigated in this study.

If one’s purpose is to strengthen the flexural properties of a shape memory specimen for use in an application, while neglecting self-healing and managing the risk of buckling or cracking at low temperature, programming below $T_g$ would be a possible option. If one, however, would like to benefit from self-healing capabilities of a SMP, programming at a temperature higher than the $T_g$ of the resin and healing above the $T_m$ of the thermoplastic copolymer would provide the maximum temperature-dependent efficiency.

Figure 31. (a) CP-PSMP specimen after curing and (b) CP-PSMP specimen after high temperature 3-D confinement recovery exhibiting "cooked" appearance

5.6 Elemental Composition: EDS

The weight percent of carbon and oxygen were acquired from the crack surface using energy dispersive spectroscopy. Five distinct 1 mm x 1 mm areas on the surface were examined for carbon and oxygen composition. This test was performed on the CP-PSMP samples programmed at 100°C and healed at 73°C, 100°C, 122°C and 148°C (figure 32 and 33).
The amounts of carbon and oxygen on the crack plane of each specimen were then compared to those found in the pure PSMP and in the CP copolymer. Figure 34 and 35 were generated using the data compiled from the spectra.

The first noticeable phenomenon is a diminution in the carbon counts (alternatively, augmentation in the oxygen counts) on the crack surface starting at the melting point of the CP copolymer ($T_m \sim 120^\circ$C). A drop of about 2% in the percent weight of carbon in the CP-PSMP brings it to a more intermediate level – between that of the pure PSMP and that of the CP. The variation in the carbon and oxygen counts suggests a concentration of CP molecules onto the surface of the crack. In other terms, the enhanced flexural strength recovery obtained at higher healing temperature is due to the formation of a stratum of melted CP on the surface of the crack above the $T_m$ of the particle. As expected, the surface composition stays the same even beyond the bonding temperature. The enhanced strengthening above $T_b$ is therefore not due to an increase in the amount of CP at the crack plane, but rather, to a fortification of the molecular bonds at and above that temperature.

![Figure 32. (a) EDS spectra of pure PSMP and of (b) pure CP Copolymer](image)
Figure 33. EDS spectra of CP-PSMP programmed at 100°C and healed at (a) 73°C, (b) 100°C, (c) 122°C and (d) 148°C.

Figure 34. Weight percent of carbon at crack surface at various healing temperatures.
5.7 Scanning Electron Microscopy (SEM) Inspection

In order to confirm and validate the results extracted from the EDS spectra, the crack interface, the crack surface and the interior of the crack were observed at high magnification with a Quanter 200 SEM microscope. The purpose of the SEM microscopy is to visually compare the width of the crack track in the specimens programmed at 100°C and healed at 100°C and 122°C. The choice of those temperatures is based on the results obtained after the flexural tests and EDS analysis described in section 5.5 and 5.6 in this study. The noteworthy change in the self-healing efficiency between those healing temperatures was determined to be due to the flow and redistribution of melted thermoplastics on the crack plane during confined shape recovery. It is expected that the temperature during confined shape recovery (healing) will have some influence on the crack width after healing and the texture of the crack surface. As
discussed previously, the crack track was very hardly visible with the naked eye in both cases, as demonstrated in figure 36 below.

![Crack track on specimen programmed at 100°C and healed at 100°C, displayed by digital zoom and image sharpening](image)

Figure 36. Crack track on specimen programmed at 100°C and healed at 100°C, displayed by digital zoom and image sharpening

The thin platinum coating on the specimens analyzed permitted the inspection of the surfaces of interest at high resolution using SEM, while preserving the irregularities and roughness of the surfaces. Figure 38 shows the crack region observed at 100x under the SEM microscope for the specimens programmed at 100°C immediately after programming and after 3-D confined shape recovery at 100°C and at 122°C. The examination of the crack interface and crack interior for both specimens at higher magnifications is also illustrated below.
Figure 37. Crack interface observation at 100x superposed on load-deflection curve for specimen after programming, after confined healing below (100°C) and above (122°C) the melting temperature of the thermoplastic particle.

It is seen in both cases that the crack is closed at the structural-scale level. However, at the micro-scale, a space between the fractured pieces of the specimen can be observed. In the specimen healed at 122°C, the crack is filled with melted copolyester, which strengthens the specimen after healing. In the specimen programmed at 100°C, a relatively wider and deeper crack is observed. An observation of the cavity of the crack reveals the presence of solid copolyester aggregates.
Figure 38. SEM image (x400 magnification) around crack for specimen healed (a) below the $T_m$ of CP (100°C) and (b) above the $T_m$ of CP (122°C).

The observations made during the SEM inspection confirm and validate the results obtained by EDS analysis. The presence of melted CP on the crack surface after healing above the $T_m$ of the CP (122°C) could be observed at high magnification and was responsible for healing and sealing the crack at the micro-length scale. In the case of the specimen healed at 100°C, the width and depth of the crack was relatively bigger and randomly distributed copolyester aggregates could be observed inside the crack. This is consistent with our proposition, stating that molten CP distributed across the surface of the crack was responsible for strength restoration.
Figure 39. View of the interior of the crack for the specimen healed at (a) 100°C and at (b) 122°C.

Figure 40. SEM illustration of the cracked surface of the PSMP with 6% wt. CP.
Chapter 6: Conclusion

This dissertation presents a literature survey along with an extensive background on self-healing shape memory polymers. It was determined from the literature review that in order to effectively activate healing in a self-healing shape memory polymer, a close-then-heal (CTH) procedure has to be followed. This procedure recommends that the crack in a specimen be sealed (by activation of the shape memory effect), before it is healed. It was also determined from the literature review that temperature during programming and healing could have an influence on the efficiency of a self-healing polymer.

In order to thoroughly investigate the effects of programming and healing temperature on the efficiency of the self-healing particulate composite used in this study, the work was allocated into chapters. The research was introduced and explained in the first two chapters. Chapter 3 dealt mostly with the polymer composite manufacture, specimens extraction and confining container fabrication. The importance of using good cutting techniques for extracting the polymer samples was underlined in that chapter. Since 3-D (full) confinement was an important component of the system used during programming and recovery, a way to design it to ensure a structurally rigid confinement and an appropriate at higher temperatures had to be implemented. A finite element analysis using ANSYS was performed to generate a simulation of the heat distribution inside the confining mold, as well as the strains due to thermal stresses at a temperature of 140°C. The results obtained were validated by hand calculations and confirmed a good design of the 3-D confinement mold.

In chapter 4, experiments were conducted in order to determine the effects of programming and healing temperature on the self-healing efficiency of the polystyrene based
resin with 6% by volume of copolyester (CP-PSMP) composite. First, the glass transition temperatures of the pure PSMP, CP particles and CP-PSMP composite were determined using differential scanning calorimetry (DSC). The \( T_g \) and \( T_m \) of the CP were found to be consistent with the specifications provided by the manufacturer (\( T_g = 17^\circ C \) and \( T_m = 120^\circ C \)). The \( T_g \) of the PSMP was found to around 89\(^\circ C\). The \( T_g \) of the CP-PSMP was 80 – 84\(^\circ C\) (between that of the CP and of the PSMP) and is an indication of some compatibility between the PSMP and the CP.

Next, a quasi-static strain-controlled programming was conducted without confinement, with partial (2-D axial) confinement and with full (3-D axial and lateral/radial) confinement. The results showed that the absence of axial and/or lateral confinement is detrimental to effective healing. Shape fixity was also observed for different pre-strain levels of 5%, 15% and 40%. An excellent value 98.2% was obtained for each of the cases. For the particular case of programming under 3-D confinement, six temperatures were considered at \( T_p = 20^\circ C, 45^\circ C, 60^\circ C, 82^\circ C, 100^\circ C \) and 140\(^\circ C\), with special attention to 60\(^\circ C\) (below \( T_g \)), 82\(^\circ C\) (around \( T_g \)) and 100\(^\circ C\) (above \( T_g \)). It was observed that the flexural strength of the specimen was decreased at temperature increased, immediately after programming (before healing). This was found to be due to the position and alignment of the polymer chains during programming. However, the strength recovered after healing at 100\(^\circ C\) was increased as \( T_p \) was increased. The resultant healing efficiency obtained was relatively lower below \( T_g \) (~34.4% at 60\(^\circ C\)) and slightly increased and stabilized above \( T_g \) (~36.9% at 82\(^\circ C\) and 37.4% at 100\(^\circ C\)). The influence of the programming temperature on the healing efficiency was apparent but very marginal. The effects of recovery temperature on the self-healing efficiency were, then, examined. Four specimens programmed at 100\(^\circ C\) and fractured by the means of a flexural test, were healed at 73\(^\circ C\), 100\(^\circ C\), 122\(^\circ C\) and
148°C. A substantial “jump” in the healing efficiency was observed past the melting temperature of the thermoplastic particles. The strength recovery percent went from 37.4% to 57.4% between 100°C and 122°C, suggesting the importance of the action of melted thermoplastics. An EDS analysis revealed that the elemental composition (in terms of carbon and oxygen) on the surface of the crack changed between the two temperatures. It was determined that the reduction in the amount of carbon (alternatively, augmentation in the amount of oxygen) was due to the flow and the redistribution of the particles when healed above their melting point. The surface composition stayed the same above the bonding point of the CP. The increase in the strength recovery ratio beyond that point was due to better temperature conditions for chains entanglement. A scanning electron microscopy technique was finally used to observe the crack interface and the crack interior for those two specimens (programmed at 100°C) and healed at 100°C and 122°C. Although the crack track was invisible to the naked eye for the specimens programmed at both temperatures, a scanning electron microscopy revealed a wider and deeper microscopic crack on the interface of the specimen programmed at 100°C. A look at higher magnifications showed some CP aggregates in the interior of the crack of that specimen. In the case of the specimen programmed at 122°C, however, the crack was mostly sealed by the molten CP. Traces of melted CP could be clearly observed under the SEM microscope. The results of the EDS analysis and the observation made via SEM validated the deductions made after the three-point flexural tests.
Chapter 7: Recommendations and Future Work

The study presented some evidence that better self-healing efficiency could be obtained by choosing adequate programming and healing temperatures. One of the key factors for self-healing to occur was determined to be the use of a full (3-D) confinement as suggested in previous studies. The confining container was therefore designed to offer a structurally rigid and low clearance confinement, even at high temperatures (140°C, in this case). The 0.122 mm radial clearance obtained at that temperature was judged to be small enough to deliver "enough confinement." A previous study conducted by Li and Uppu [9] showed that different types of confinement induce different volumes reduction as well as different compression stress recovery ratios on a shape memory polymer based self-healing syntactic foam. A similar study could be conducted to investigate the effects of clearance level on the flexural strength recovery of the shape memory polymer based particulate composite.

Figure 40 illustrates a high magnification view of the crack surface following the three-point flexural test: the crack surface exhibits some roughness and irregularities. As discussed extensively in this study, the redistribution of thermoplastic particles during recovery is responsible for higher self-healing efficiencies. Hence, the surface condition of the crack post fracture could have some effects on the flow and dispersion of molten thermoplastics on the cracked surface. In this experiment, the broken pieces were carefully put together to minimize the crack width prior to healing. This process can be tedious or even impossible to achieve in specimens that display smoother surfaces. If the surface of the fractured piece was to be gently polished, the healing efficiency during recovery could be affected. A good avenue to pursue in this regard is to polish or gring the surface of the broken piece with different grit sizes and
abrasives in order to alter the surface roughness and the surface finish of the workpiece, resulting in a reduction of the crack width before healing.

Another way to promote crack closure could be with the usage of shape memory fibers. The fibers could be programmed (stretched) so that they regain their final shape (unstretched) during programming. The advantages of using such fibers could be multiple. First, the use of the fibers would strengthen the material as a whole. Second, the fiber could be used, in conjunction with the shape memory polymer, to help seal the crack during recovery. Finally, the fibers could act as a three-dimensional confinement by bringing and holding the fractured surfaces together. The human intervention during the self-healing process would, thus, be significantly reduced.
References


Appendix: Supplementary Notes

All finite element analysis (FEA) simulations and contour plots were done using ANSYS, Release 13.0, ANSYS, Inc., November 2010.

The 3-D model in figure 14 was created using Photoview 360 in SolidWorks 2010.
Vita

Quentin Yougoubare was born in February 1989 in Abidjan, Cote d'Ivoire (Ivory Coast). He obtained in Bachelor of Science in Mechanical Engineering from Louisiana State University in May 2011. He joined the NASA EPSCoR program, working on smart composite materials under the supervision of Dr. Su-Seng Pang. He is a candidate for a Master of Science in Mechanical Engineering to be awarded in December 2012.