Effect of surface roughness on the efficiency of self-healing polymers

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EFFECTS OF SURFACE ROUGHNESS ON THE EFFICIENCY OF 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
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by

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Abstract

A shape memory polymer (SMP) is a smart material capable of maintaining two distinct shapes depending on its temperature. A SMP is soft at temperatures above its glass transition temperature but hard below it. When copolyester thermoplastic additives are dispersed in a SMP, it becomes a SMP-based particulate composite capable of self-healing at both the molecular level and the structural level. This makes it very desirable for industrial applications. Upon damage to the composite, the surfaces at the damage interface have to make contact for efficient healing; the shape memory effect, coupled with a confined recovery (healing) process, ensures this. This study examined the effects of the surface roughness at the damage interface on the efficiency of the healing process. Also studied was the effect of the compressive stress at the point of contact during the healing process on the healing efficiency. The particulate composite (CP-PSMP) consisted of polystyrene shape memory polymer (PSMP) as the matrix and copolyester thermoplastic additives (CP) as the reinforcement.

Compressive programming at 10 % pre-strain was performed on the CP-PSMP, which was then tested for its pre-flexural strength. Next, the surfaces were varied using sandpapers of different embedded particle diameters, and the CP-PSMP was healed at 10 MPa using the close-then-heal (CTH) self-healing mechanism. The recovered flexural strength was then obtained and the healing efficiency computed as a fraction of the recovered flexural strength to the pre-healing flexural strength.

Healing efficiencies were found to be higher for CP-PSMP with smoother surfaces. The highest healing efficiency of 39 % was found in CP-PSMP with average and root-mean-squared roughness profile parameters, $R_a$ and $R_q$, of 0.425 and 0.617 μm respectively. Another set of tests
revealed that healing was more efficient at higher compressive stresses. Efficiencies at higher compressive stresses (20 – 80 MPa) ranged from 78 % to 118 %. Next, the effect of sanding on healing efficiency was examined by comparing the healing efficiencies of two sets of CP-PSMP with similar R_a and R_q values—one of which was treated with sandpaper. The sanded CP-PSMP samples were 24 % more efficient in healing.
Chapter 1: Introduction

1.1 Particulate Composites

1.1.1 Composite Materials

Composite materials, also called composites, are formed by combining two or more materials with different physical or chemical properties. Composites have unique properties which differ from that of each constituent. The combination of different member materials to create a composite is not a chemical process. Often, each constituent within the composite material can be easily seen. They do not dissolve or blend into each other. Natural composites exist, including mud bricks, which are composed of mud and straw; and wood, which is a combination of cellulose and lignin. Man-made composites have been in use for decades to solve industrial problems. Fiberglass, developed in the 1940s, is the first modern composite and is still the most commonly used. It is composed of plastic and fine threads or fibers of glass. Concrete is another widely used man-made composite; it consists of cement and aggregate [1].

Most composites consist of just two materials, each serving a different role – a matrix, and a reinforcement. A matrix (or binder) surrounds and binds together the reinforcement by maintaining their relative positions. The reinforcement usually possesses special mechanical and physical properties, which improve the properties of the matrix. In mud bricks, the mud acts as the matrix that holds together the straw – the reinforcement. Likewise, in fiberglass, the plastic binds the glass fibers. Composites provide beneficial properties of each of its constituent elements, which is why they are often employed in non-conventional applications not possible with either member element. For instance, the combination of the plastic and glass fibers affords fiberglass the high-tension strength of glass threads and the protection of the plastic. This makes
fiberglass light and strong which and useful for buildings, bridges, and structures such as boat hulls, surf boards, golf clubs, and car bodies.

Over decades, many new composites have been created from older ones by changing the matrix, the reinforcement or the manufacturing process used to combine them. The ability to change each of these factors provides a great amount of flexibility in creating composites. When particles are embedded in a matrix, a particulate composite is said to be formed.

1.1.2 Particulate Composites

Particulate composites consist of tiny particles of one material dispersed in a matrix. These particles can be very small (< 0.25 microns) and may include chopped glass fibers, hollow spheres or carbon nano-tubes. An example of particulate composites is syntactic foam. It is formed by mixing a resin matrix with hollow spheres. The hollow particles, also called microballoons, are dispersed in the resin. The resin matrix can either be metal, polymer or ceramic in nature. Most often, thermoset resins are used as the binder due to their ease of manufacturing rather than their specific material properties [2, 3]. Using thermoset resins also allows for a solid material after curing. The hollow particles may be of polymer, ceramic, carbon, glass or metal [4]. Since syntactic foam is essentially composed of a resin matrix, hollow glass microspheres, and entrapped air (voids), it is often regarded as a three-phase composite material [5]. A microstructure of syntactic foam is shown in Figure 1. In the figure, voids can be seen in the foam, along with microspheres and resin matrix. The voids in the foam root in the entrapped air and microsphere fracture during the specimen fabrication. Moisture absorption of foam mainly depends on the void content; especially the existence of interconnected voids which are open to the surface, leading to more moisture absorption [1].
The presence of the space (in the hollow particles) within the mixture makes it porous and classifies it as a foam. In regular foam, the pockets are filled with air, which can greatly reduce its density. However, in syntactic foam, the pockets are evenly distributed and the number of pockets is regulated by the amount of hollow particles that was used in mixing. The use of hollow particles in syntactic foam can serve various purposes. First, it can be used to enhance the mechanical characteristics of the matrix. Also, using hollow particles of lower density than the matrix allows for the creation of light-weight materials. Further, by controlling the amount of microballoons, syntactic foams of different densities and microstructures can be created through fairly easy fabrication methods [6]. It has been shown that the mechanical properties of syntactic foam are primarily guided by the density and volume fraction of constituent microballoons. Compression testing revealed that the strength and modulus of syntactic foams increase as the density of the microballoons increase [7]. Glass microballoons are the most widely used hollow particles in the creation of syntactic foam due to their high specific strength and energy.
absorption properties [8]. They are also inexpensive and offer good surface uniformity and mechanical strength [9].

Syntactic foams are just one kind of particulate composite. When the microballoons are replaced with other particles, a different kind of particulate composite is created. However, the general advantages accruable to particulate composites apply to syntactic foam and other particulate composites alike.

1.1.3 Advantages of Particulate Composites

The tailorability of particulate composites makes them adaptable for widely varying applications. Generally, particulate composites are known to possess low density, high stiffness, excellent compressive and strength, and good impact behavior [7, 10-14]. They also offer predictability in density due to their mixing ratio. This is very advantageous in applications that require products of specific density such as aerospace technology. And, since different particles may be used, particulate composites can be used in buoyancy aid materials for marine applications.

Another major advantage of particulate composites is the ease and low cost of manufacture. For instance, glass microballoons, often used as the reinforcement in syntactic foam, are inexpensive, readily available and offer good mechanical properties. They are either produced by heating dissolved water glass in a process known as ultrasonic spray pyrolysis, or as a waste product in coal-fired power stations. Used as hollow spheres, glass microballoons give syntactic foam its light weight, low thermal conductivity and resistance to compressive stress that far exceeds that of other foams [15]. It has been recommended for use in subsea environments where compressive pressures approach 45 KPa (about 15 000 ft. of water) [16]. In
lab experiments, syntactic foam (without additional fiber reinforcement) has been shown to have compressive strength exceeding 80 MPa [17], so it is useful in such environments.

1.1.4 Particulate Composite Cored Sandwich Structures

A sandwich-structured composite is a class of structure that is fabricated by attaching two thin but stiff skins to a lightweight but stiff core. The skins of a composite structure carry the bending loads thereby protecting the core from catastrophic failure. The core is to absorb impact energy in low-velocity or high-velocity situations. While the core material is often of low strength, it provides the sandwich composite with high bending stiffness. Its lightweight also provides an overall low density for the sandwich composite. A basic illustration of a sandwich composite showing the skin and the core is shown in Figure 2. Common skin materials are glass laminates, carbon fiber-reinforced thermoplastics or thermosets and sheet material.

Figure 2. Schematic of a sandwich structure showing A. complete panel, B. skins, and C. honeycomb core. [18]
The development of sandwich structures arose, among other reasons, as a solution to catastrophic structure failure due to impact. Failure of engineering structures due to impact is critical and has been well documented [19-28]. The well-known loss of Space Shuttle Columbia is an example of the implication of this failure [26]. During impact, the sandwich core of a sandwich composite is primarily responsible for absorbing impact energy in terms of “self-sacrificing” or damage, preferably in micro-length scale so that the residual strength will not be considerably compromised [29]. Therefore, the design of the core must be improved in order to enhance the impact tolerance of the sandwich.

Besides improving impact tolerance, the core plays other vital roles as part of a composite sandwich structure. Studies show that foam-cored sandwiches provide support to structures in addition to improving impact tolerance. Also, resistance to penetration, energy absorption and damage modes were shown to be a function of core stiffness, extent of filling the foam and the number of face sheet piles [30]. Gupta et al. showed that failure in syntactic foam cored sandwiches under bending loads is governed by the tensile properties of the core [31].

Due to their importance, core materials of many types have been used in fabricating sandwich cores. The core materials have been divided into categories including foam cores, web cores and hybrid foam cores. Foam cores (syntactic foam, polymeric foam, metallic foam, balsa wood, etc.) have been studied in detail in recent decades [32-34]; web cores (truss, honeycomb etc.) have also garnered attention due to their favorable mechanical properties [35, 36]. Among the different categories of sandwich cores, hybrid foam cores are the most commonly used. They are employed in structural applications. Hybrid foam cores include 3-D integrated core [37, 38], foam-filled web core [39, 30, 40], laminated composite reinforced foam core [41], grid stiffened syntactic foam core [31], etc.
1.1.5 Limitations of Syntactic Foam and Particulate Composites Cored Sandwiches in withstanding Impact and in Healing

The different types of core materials (foam core, web core, hybrid core etc.) have been studied [29] and used with limited success. Their limitations arise due to their mechanical properties. For example, the thermoset polymer matrix used in the manufacture of syntactic foam is brittle; therefore, when syntactic foam is used as the core of a sandwich structure, it absorbs impact energy primarily through macroscopic impact damage that leads to a significant decline in the residual strengths of the syntactic foam and the sandwich structure [42-45]. The nature of this damage calls for urgent repair but this is extremely difficult since the damaged syntactic foam is located within the sandwich structure. The inability to repair internal damage requires replacing the foam or rebuilding the entire structure. This effectively renders such structure singular use, which makes it hardly beneficial for many industrial applications. Therefore, there is a need to develop secondary self-sacrificing particulate composite components in sandwich structures, capable of “self-healing” (that is, damage repair that is autonomous or that does not require human intervention) for repeated use in absorbing impact energy.

1.2 Self-Healing for Micro-level Healing

1.2.1 The Need

Damages due to impact are a necessary evil in the world of engineering. Microscopic cracks are often hidden within a material where they go unnoticed. Continued use of the damaged material often leads to failure, and consequently, loss of resources and human life.

Welding and patching can be used to heal impact damage [46] but both are expensive, time consuming, and require uniquely skilled workers. Both methods only fix external damages on accessible parts of the damaged structures. In ductile materials, damages often begin as cracks at molecular levels, which grow and extend over time and could lead to structural-length cracks,
and eventually structural failure if not fixed. In brittle materials, micro-level cracks often lead to failure almost immediately with continued load application. This suggests that damage can be addressed at two levels – the micro-level (or molecular level) and the often visible macro-level (or structural-length scale).

Macro-level damage repair (welding, patching etc.) has been given a lot of consideration in the past but welding and patching address damage mostly on a macro-scale. They do not heal at the molecular level. Healing at a molecular level is possible via external assistance to the damaged material or by self-healing. Healing via external assistance is quite difficult and often too invasive in certain cases such as when the material is still in use. That leaves self-healing as the preferred option. The inspiration for self-healing is from multiple healing methods observed in biological systems.

1.2.2 Self-healing in Biological Systems – The Inspiration

Biology provides multiple self-healing systems, which guide the design of the synthetic healing process in thermoset and thermoplastic resins. Both the biological and the synthetic routes to healing are triggered by the injury to the system (i.e. both processes are automatic), and both follow the same three-step process. A pictorial comparison of both healing methods is presented in Figure 3. In biological systems, the response includes, in order, an inflammatory response (immediate), cell proliferation (secondary) and matrix remodeling (long-term). The similar, though faster, synthetic equivalent involves triggering (actuation), transport of material to the site of the damage, and a chemical repair process, which depends on the type of healing mechanism employed (e.g. polymerization, entanglement, reversible cross-linking) [47].
The rate of healing in the synthetic route is controlled by the rates of actuation, transport of materials and chemical repair. Thus, healing efficiency is regulated by the damage rate versus the healing rate. By balancing both, material stasis, and therefore, ideal healing are attained [47].

Figure 3. Synthetic and biological routes to healing [47].

1.2.3 Approaches to Self-Healing and Micro-level (or Molecular-level) Healing

What gives a material its self-healing characteristic is its ability to begin damage repair using the resources available to it. This healing resource may be a physical object within the material or an ability of the material itself. This resource, also known as healing functionality, remains dormant until triggered by damage. How this functionality is stored or hidden within the material is known as sequestration, and the type of sequestration dictates the damage volume that can be healed, the repeatability of healing, and the recovery rate for each approach. Sequestration is also useful for the classification of the self-healing material. Based on the
sequestration mechanism, self-healing materials can be classified broadly into three groups: capsule based, vascular and intrinsic [47].

Capsule-based healing uses healing agents that are sequestered in discrete capsules. Upon their damage-induced rupture, the broken capsules release the healing agents into the region of damage. This release, as well as the reaction that ensues at the region of damage, triggers the self-healing mechanism, which continues until the local healing agent is depleted, leading to only a singular local healing event. Vascular healing functions similar to capsule-based healing. In this method, the healing functionality (or healing agent) is stored in an embedded vascular network of capillaries or hollow channels that has 1D, 2D, or 3D connectivity. Upon damage to the material, the healing agent is transported to the point of damage via the network for the first delivery. The healing agent may then be replenished using an external source or an undamaged connected region of the vasculature. The ability to replenish the healing agent makes possible multiple local healing events.

In intrinsic healing, the healing functionality is not a physical agent but a latent self-healing functionality that is triggered by damage or an external stimulus. Materials in this group rely on chain mobility and entanglement, reversible polymerizations, melting of thermoplastic phases, hydrogen bonding, or ionic interactions to initiate self-healing. Because each of these reactions is reversible, multiple healing events are possible. Intrinsic healing occurs at the molecular level and is a possible solution to healing micro-level cracks which welding and patching cannot fix.

1.2.4 Intrinsic Self-healing in Thermoset Polymer Resins

Both thermoset and thermoplastics polymer resins are capable of self-healing. When heated above their melting temperature, damaged thermoplastics will achieve molecular-level
healing by flowing into the damaged region. Upon cooling, the material solidifies again, thus completing the healing process. However, thermoplastics are not very useful for structural applications because of their low stiffness and thermal instability. On the other hand, thermosets offer high strength, high stiffness and good thermal stability. Despite their favorable properties, thermoset polymer systems are brittle in nature. This makes the development of thermoset self-healing polymer systems more challenging than the development of thermoplastic polymer resins.

Synthetic healing has already been shown in thermoset polymer resins using thermoplastic glass particles as the healing agent and temperature as the external stimulus [48]. It mimicked the biological healing method in the human skin tagged the “close then heal” (CTH) method. As is the case with healing in the human skin, and shown in Figure 3, the macro-scale crack is first sealed before a self-healing mechanism is applied. The CTH method in thermoset polymer resin is capable of micro-level healing.

1.3 Macro-level Healing

As mentioned earlier, self-healing based on examples in biological systems resolve the problem of micro-level damage repair. Based on the particular healing method used, the process could be entirely autonomous or initiated by external factors such as temperature for melting of thermoplastic phases. The nature of synthetic self-healing also implies repeatability in healing if intrinsic healing method is employed.

Macro healing has also been approached in multiple ways, and one goal in the design of a solution has been to incorporate the ability of macro healing in a material that is structurally capable for industrial applications. As we saw in Section 1.1.4, sandwich composites with particulate composites at the core are structurally capable for industrial applications. Fitting such
Shape memory effect has mostly been studied in alloys. It was discovered that this effect in metals back in 1963 when a Nickel-Titanium alloy displayed shape recovery abilities [50, 51].

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Shape memory effect is the ability of a material to fix a temporal shape in response to an elastic deformation and recover the original shape after application of a stimulus. Simply put, the material remembers two different shapes and is able to switch between these shapes in response to the application of an external stimulus. This effect is not an inherent property of shape memory materials but is the result of material structure and specific functionalization techniques. Materials that exhibit the shape memory effect are not restricted to polymers (i.e. SMPs). They include metallic materials called shape memory alloys (SMA), and ceramics known as shape memory ceramics (SMC). In fact, the shape memory effect was discovered first in metals back in 1963 when a Nickel-Titanium alloy displayed shape recovery abilities [50, 51].

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A shape memory polymer (or SMP) is a smart material that can undergo deformation at high temperatures, retain the deformed shape when cooled and return to its original shape upon heating. The ability to have its shape significantly changed in a controlled fashion by an external stimulus is what makes it smart. Temperatures play a big role in the use and application of SMPs. SMPs possess two distinct phases, which are clearly separated by a transition temperature known as the glass transition temperature \( T_g \). At temperatures below the glass transition temperature \( T_g \), SMPs are rigid and are not easily deformed. However, at temperatures above \( T_g \), they are soft, rubbery, and therefore, easily deformable [49]. SMPs are polymer resin systems, but their functionality is based on the ability of these polymer resin systems to exhibit the shape memory effect.

A class of particulate composites that could serve this role is the shape memory polymer (SMP). A class of particulate composites that could serve this role is the shape memory polymer (SMP). A class of particulate composites that could serve this role is the shape memory polymer (SMP). A class of particulate composites that could serve this role is the shape memory polymer (SMP). A class of particulate composites that could serve this role is the shape memory polymer (SMP).
SMAs is due to the existence of the metals in two stable crystal structures. The first is an austenitic phase, which occurs mostly at high temperatures while the other is a low temperature-favored martensitic phase. SMAs gained popularity as stimuli responsive material due to their small size and high strength, but their disadvantages include high manufacturing costs, limited recoverable deformation and significant toxicity. On the other hand, SMPs are relatively inexpensive to produce, able to withstand higher deformations and possess high recoverable strains of up to 100% in compression and over 100% in tension. In comparison, SMAs and SMCs have very modest recoverable strain levels of just 10% and 1% respectively [52, 53]. Also, SMPs are biocompatible [54], and can be combined with other materials to form composites with shape memory effects [55, 56].

1.3.2 Shape Memory Polymers for Structural-length Scale Healing

It has been shown that the shape memory ability exhibited by shape memory polymers can be used for structural-length scale healing. For instance, in a previous study, Li and John proved that the stress-controlled programming and partially confined shape recovery of a SMP-based particulate composite is able to seal impact damage repeatedly, efficiently and almost autonomously (with heating as the only human intervention) [57]. The authors found that the key to using the shape memory effect for self-closing cracks depends on the reduction of the structure’s volume during programming and the external confinement of the structure during shape recovery. (Sections 1.4.2, 1.4.4 and 1.4.4.2 cover Programming, Shape Recovery and External Confinement in detail) This happens because after a programmed material loses volume due to damage, heating the programmed material tends it to recover its original, larger volume during the shape recovery process due to its shape memory functionality. However, if the material is unable to expand into its former shape due to an external confinement, it will be
pushed into internal spaces (such as cracks), thus self-closing on the crack. The repeatability of healing happens because each healing process does two things: self-closes on cracks, and serves as a programming step for the next healing. Both the programming and healing are accomplished by heating the material above its glass transition temperature while under external confinement [48].

In close, impact-induced damage can be addressed at two distinct levels – micro (or molecular level) and the macro (or structural-scale) level. One way to heal structural-scale impact damage is through the use of SMP-based particulate composite. A way to heal at the molecular level is by applying the CTH method. This method is possible in thermally activated SMPs when thermoplastic additives are used as the reinforcement for the resin matrix. Each method has been independently tested with success over the years. Li and Nji showed that combining both the CTH and SMP methods can yield successful molecular and structural level healing [58].

1.4 Thermomechanical Cycle

The ability of a SMP to exhibit shape memory effect enables it to remember two distinct shapes, which it is able to alter between based on its temperature. The SMP exists in one of these shapes, the **permanent shape**, at temperatures below $T_g$, while it exists in its **temporary shape** at temperatures above $T_g$. The process of transitioning from its permanent shape to its temporary shape, and back to its permanent shape is called a thermomechanical cycle [59, 60]. The process of transitioning from its permanent shape to its temporary shape is known as **programming**, while the transition back to its temporary shape is known as **shape recovery**.

A typical thermomechanical cycle is composed of four sequential steps: (1) High temperature loading, (2) cooling, (3) unloading, and (4) recovery. Each of these steps requires a
temperature or range of temperatures, as well as stress and strain. 2D stress-strain plot and 3D stress-strain-temperature plots in Figure 4 illustrate a typical thermodynamic cycle below. In this figure, the $T_g$, is shown as $T_{\text{trans}}$.

Figure 4. A compressive thermomechanical cycle for a SMP [61].

Figure 5. A typical thermomechanical cycle for a SMP illustrated with (a) 2D, and (b) 3D plots with 1-D tensile stress ($\sigma$), tensile strain ($\varepsilon$) and temperature ($T$) [65].

1.4.1 Glass Transition Temperature

SMPs are useful for shape memory because they can memorize and take two distinct shapes upon the application of heat. These two separate memorized shapes occur at two different
temperature ranges which are separated by a unique temperature known as the glass transition temperature, often represented, $T_g$. $T_g$ is a significant identifier of any polymer. At temperatures below $T_g$, a SMP is in a plastic state (i.e. hard and rigid) or its permanent shape. At temperatures below $T_g$, the SMP exists in its elastic state (soft and rubbery) or in its temporary shape. The quasi-change in its physical states occurs whenever the polymer changes temperature across $T_g$.

SMP is an amorphous polymer. Amorphous polymers are those in which the polymer chains are not in an orderly fashion. Illustratively, the rubbery state of a SMP (as with that of all amorphous polymers) may be regarded as the situation in which entanglements restrict the motion of complete chains with respect to each other. Only the coiled sections of the chains lying between entanglements are moving which is why the polymer seems ‘rubbery’. This is illustrated in Figure 6. At higher temperatures, the entanglements are resolved, and the polymer behaves like a viscous liquid. As the temperature is lowered below $T_g$, many of a SMP’s properties change. Significant changes occur to the elastic moduli and damping and it becomes brittle [63].

![Figure 6: Mechanism for shape recovery in SMPs. Adapted from [55]](image-url)
Most polymers on the market come with $T_g$ values specified by the manufacturer, but $T_g$ can also be evaluated using experimental methods. These methods are based on the molecular behavior of SMPs at the glass transition temperature. While the viscosity of a material changes slowly around the glass transition temperature, some properties like thermal expansion, heat flux, heat capacity and dielectric constant experience a sudden change at the glass transition temperature [64]. The sudden change occurs because the SMP undergoes a second-order phase transition. In second-order phase transitions, there is no change in phase whereas first-order reactions predicate a change of phase. Thus, a comparison of heat flux with time (as seen in Figure 7) displays a step transition at $T_g$ instead of a peak transition as a melting transition would [64]. By increasing the temperature of a SMP sample across $T_g$ while noting its properties, the temperature where this change occurs can be noted. This is the glass transition temperature.

Dilatometry is the use of the thermal expansion response of a polymer to find its glass transition temperature. A more common method, however, is differential scanning calorimetry (DSC) which uses the response of its heat capacity to find its glass transition temperature.

![Figure 7](image.png)

Figure 7. A typical DSC result showing how to extrapolate the glass transition temperature, $T_g$. [64]
Thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) are two other methods that can be used to measure the glass transition temperature of a polymer. TMA measures the change in dimension (i.e. expansion in two directions) of the polymer as it is subjected to a heat regimen. It defines the glass transition in terms of the change in the coefficient of thermal expansion (CTE) as the polymer goes from glass to rubber state with the associated change in free molecular volume [65]. In DMA, a sinusoidal stress is applied to a polymer and the corresponding strain is recorded. Using this information, the complex modulus – the ratio of stress to strain under vibratory conditions – can be computed. When the temperature of the sample is varied while the DMA is run at low constant frequency, the complex modulus varies, and the pattern of variation of the complex modulus can be used to locate the glass transition temperature.

While DSC is the main method employed in calculating $T_g$, TMA allows for easier testing of the $T_g$ in polymers with a very large coefficient of thermal expansion above the glass transition than DSC does. However, DMA is the best method for finding the $T_g$ in materials that are a mixture of resins. Using DMA (as described above), multiple transitions in a polymer blend can be found. In fact, DMA can be used to show separate transitions for semi-crystalline polymers (mixtures of crystalline and amorphous polymers) [66].

1.4.2 Programming

Programming covers the first three steps of the four-step thermomechanical cycle. A SMP becomes smart (that is, is able to change shapes upon the application of heat) after it has gone through the programming process. There are three stages in programming: (1) High temperature loading, (2) cooling, and (3) unloading.
The first step involves deformation at a temperature above the glass transition temperature of the SMP. The SMP is heated to a temperature $T > T_g$, and then it is compressed until it attains a desired (or ideal) mechanical strain, $\varepsilon_m$, at a stress, $\sigma_m$. Next, the sample is cooled to a temperature below $T_g$ while keeping either its stress constant (for stress-controlled programming) or its strain constant (for strain-controlled programming). After the sample has cooled, the load is removed or the sample is unconstrained, depending on which kind of constraint was employed. At this point, the sample may expand as it relaxes to a lower strain level, $\varepsilon_u$. This measurable relaxation in strain level is known as springback. $\varepsilon_u$ is now the strain value for the temporary shape which the programmed sample is in.

1.4.3 Shape Fixity and Shape Recovery

Shape fixity and shape recovery are the main thermomechanical properties of a SMP. Shape fixity measures how close the cooled fixed shape of the SMP is to the deformed shape of the SMP. In short, it is a ratio of the shape strain before and after unloading. What causes the shape of the SMP to differ at both these points is springback which occurs after unloading - the third and final step in programming. If a SMP has zero springback, it will have 100% shape fixity.

The shape fixity for $N$ cycles, $R_f(N)$, can be found using the formula,

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m}$$

(1)
where \( \varepsilon_m \) is the ideal mechanical deformation strain and \( \varepsilon_u \) is the temporary (or ‘fixed’) strain for the Nth cycle.

Shape recovery takes a broader look at the SMP in the thermomechanical cycle. After the programming stage, a SMP undergoes recovery which is the fourth and final step in the thermomechanical cycle. The recovery process restores the SMP to a shape (denoted by the strain, \( \varepsilon_p \), also called the **permanent strain**) which is similar to the shape it had before the current thermomechanical cycle (or any deformation therein) took place. The shape recovery measures how well the permanent shape is restored or recovered. In measuring the value of the shape recovery, the programmed sample is allowed to undergo free recovery. (More on Free Recovery in Section 1.4.4.1)

The shape recovery for N cycles, \( R_r(N) \), is calculated as

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

where \( \varepsilon_m \) is the ideal mechanical deformation strain and \( \varepsilon_p(N) \) is the permanent strain obtained at the end of the Nth thermomechanical cycle.

Since the initial permanent shape is strain-free, for the case of the first cycle, \( \varepsilon_p(N - 1) \) is zero and the equation can be reduced to Equation 3 [67].

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

(3)
1.4.4 Recovery

The last step in the thermomechanical cycle involves heating the programmed SMP in order that it recovers its permanent shape. For this, the SMP needs to be heat up to a temperature higher than its glass transition temperature, $T_g$. In terms of strain, the recovery takes a SMP goes from the temporary strain, $\varepsilon_u$, to a permanent strain, $\varepsilon_p$. There are two types of recovery – free recovery and confined recovery.

1.4.4.1 Free Recovery

When a SMP undergoes shape recovery without physical boundary constraints, it is said to undergo free recovery. Free recovery is useful, amongst other reasons, for computing the value of shape recovery. Experiments have shown that in free recovery, a SMP without thermoplastic additives is often able to close relatively small cracks, but is not very efficient at healing the damaged region because while the cracks may be closed, molecular-level healing is lacking.

1.4.4.2 Confined Recovery

In the confined recovery process, physical boundary constraints are placed on the SMP as it is heated up. The main goal of confining a SMP in the recovery process is to ensure that cracks within the specimen are closed and that surfaces at the damage interface are in contact so that molecular-based healing can occur (i.e. close-then-heal). Nettles and Li showed that confinement during recovery was one of the necessary prerequisites for self-healing in a SMP [64].

If compressive programming is followed by confined recovery, the SMP is forced to close in on cracks and possibly create stress at the regions of new contact which may facilitate micro-scale healing.
1.5 Surface Roughness

Surface roughness, or roughness, is one of the three measurements used to characterize a surface. The overall characteristics of a surface are summed up in the term, surface finish, which is made up of lay, surface roughness and waviness [72].

Lay is a rough measure of the direction of the predominant machining pattern on the surface. A lay pattern is the repeated pattern produced on the surface by a specific machining operation. Often, it is measured perpendicular to the plan of the lay pattern. Figure 8 shows a surface with a vertical lay pattern.

Surface roughness and waviness are both measures of the texture of a surface, but the sampling lengths used in calculating waviness are more than the sample lengths used in calculating surface roughness. An illustration of this is given in Figure 8.

![Figure 8: Illustration of Surface Finish measurements][73]

1.5.1 Quantification of Surface Roughness

A surface can be quantified numerically. This value can be obtained by measuring a profile (line) or a surface (area). 3D roughness measurement is relatively new. R_i and S_i are
generic parameters used to denote line and surface parameters respectively. The subscript, $i$ in this case, refers to the specific type of parameter in use. Common parameters and their corresponding subscript include the arithmetic average of absolute values, $a$ (or $aa$), the root-mean-squared, $q$ (or $rms$), the skewness, $sk$, the maximum profile height, $t$, the maximum valley depth, $v$, and the kurtosis, $ku$. Of the quantification methods, profile roughness parameters ($R_a$, $R_q$,...) are more common. Furthermore, among the profile roughness parameters, $R_a$ is, by far, the most common. It is measured in units of micrometers or microinches.

1.5.2 Measurement of Surface Roughness

A profilometer is a device used to measure a surface’s profile. Profilometers are generally classified into contact and non-contact. In contact profilometry, a diamond stylus is moved vertically in contact with a sample and then moved laterally across the sample for a specified distance and specified contact force. As the stylus moves, the profilometer measures small surface variations in the stylus displacement as a function of its position. Non-contact profilometry employs the use of non-contact methods (e.g. optical methods) to provide the same information. While non-contact profilometry offers higher speeds and better reliability, contact profilometry have more widely accepted results because most of the engineering standards for surface profiling are designed for contact methods. Also, contact profilometry has better resolution and eliminates error due to the presence of surface contaminants [74].

The height measurements obtained with a profilometer can be plotted to reveal the total profile of the measured surface. This measurements includes errors in geometric form. When the roughness heights are attenuated, the waviness profile of the surface is obtained. Further attenuation (of the waviness height) leaves the roughness profile. This is shown in Figure 9.
1.5.3 Sandpaper

During the healing step in the thermomechanical cycle, the surfaces at the crack interface will be in forced contact, and the effects of these varied surfaces on the healing efficiency obtained will be investigated. Different types of sandpaper were used to vary the crack surfaces. The grit sizes of these sandpaper were also noted. Grit sizes refer to the size of the particles embedded in the sandpaper, and they follow several standards. The two most common standards employed are the United States CAMI (Coated Abrasive Manufacturers Institute) and the European FEPA (Federation of European Producers of Abrasives) "P" grade. For lower grit sizes (i.e. rougher sandpaper), the CAMI and FEPA designations are similar, i.e. the average particle diamters are very close. In this study, the CAMI grit size designation was employed. Based on their grit sizes, sandpaper can be broadly classified into two categories – macrogrits and microgrits. Macrogrits are further classified into coarse, medium, fine and very fine. Likewise, microgrits can be further classified into very fine, extra-fine, super-fine and ultra-fine. Based on the sources used, the very fine categories of both the macrogrits and microgrits overlapped. [76 -78] For the purpose of this study, the very fine category will be considered as a median of the macrogrits and microgrits. This allows for the evaluation of seven separate classifications as shown in Table 1.
Table 1. CAMI grit designation of sandpaper [76]

<table>
<thead>
<tr>
<th>Grit Category</th>
<th>CAMI Grit Size</th>
<th>Avg. Particle Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Macrogrits</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Medium</td>
<td></td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
</tr>
<tr>
<td>Fine</td>
<td></td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
</tr>
<tr>
<td></td>
<td></td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280</td>
</tr>
<tr>
<td>Very fine</td>
<td></td>
<td>320</td>
</tr>
<tr>
<td></td>
<td></td>
<td>360</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
</tr>
<tr>
<td>Extra-fine</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
</tr>
<tr>
<td>Microgrits</td>
<td></td>
<td>800</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1200</td>
</tr>
<tr>
<td>Ultra-fine</td>
<td></td>
<td>1500</td>
</tr>
</tbody>
</table>

1.6 Scope and Objectives of Research

So far, it has been shown that SMP-based particulate composites cored sandwiches with self-healing capabilities are able to heal cracks on both a structural scale and a micro-level, autonomously, efficiently and repeatedly [57].

This goal of this research is to build on previous scholarly works in the study of SMP characteristics that affect its healing capabilities. One such important study was by Li and Nji which proved that CTH (for structural healing) and thermoplastic additives (for micro-healing) can be combined effectively in a single material. In the study, a composite comprising of
thermoplastic particles and SMP-based particulate composite was used. The thermoplastic particles comprised 6% of the mixture by volume. Also, the compression programming level was limited to 6.7% [58]. The study concluded that over 65% of the peak beginning loads could be repeatedly recovered and that structural-length scale damages were healed at molecular-length scales. Yougoubare went further to study the effects of programming and healing temperatures on this same composite [68]. He found only a slight effect of programming temperature on the healing of the composites, but the temperature at which healing occurred significantly affected the recovered healing especially at temperatures around the melting point of the thermoplastic particles.

As with both mentioned studies, many others on SMP have focused on healing efficiency. But, defining healing efficiency has been quite arbitrary over the years because it can be done in various ways. For instance, a material can be tested for a certain property after programming (i.e. before healing) and then after healing in order to see how much of that property is recovered during the healing process, or the properties of a material before programming and after healing can be tested and compared. Blasizik at al. drew on the former idea to define healing efficiency (\(\eta\)) using the formula:

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

(4)

where \(f\) is the property of interest [47].

In both Nji’s and Yougoubare’s separate studies, 3-point bending tests for flexural strength measurement were performed on the composite after programming. Then, the specimens were healed using confined recovery, and then tested for strength afterwards. The healing efficiency employed in these cases appear to be a simple ratio,
\[ \eta = \frac{f_{heated}}{f_{virgin}} \]  

(5)

where \( f \) is the property of interest, which in this case, is the flexural strength [58, 68].

As this research builds on Nji’s and Yougoubare’s studies, the materials used here will be the same as used in both studies, as will the definition for healing efficiency.

Both studies employed 3-point bending tests to damage the composite specimens and confined recovery to heal them. Before healing the damaged specimens, the broken pieces – roughly halves – were forced together as best as the researchers could based on simple eye examinations of the surfaces at the damage interface. The effect of the roughness of these surfaces was not investigated at the time. That is the main goal of this research. The experiments will be repeated on samples with all factors (programming and healing temperatures, pre-strain etc.) kept constant while the roughness of the fractured surfaces will be altered before confined recovery is initiated.

The initial hypothesis is that surfaces with smoother fracture interfaces (prior to healing) will heal more efficiently than surfaces with rougher fracture surfaces because the smoother surfaces will allow for better contact, and thus, better dispersion of the healing agent during the healing process. For a control, some samples will be healed without their surfaces sanded. It is also expected that these samples which are healed without any sandpaper treatment will heal efficiently since they preserve their original pre-fracture orientation.
2.1 Raw Materials

As discussed in Section 1, this study will incorporate the use of SMP-based particulate composites for structural-scale healing and thermoplastic particles for micro-scale healing. This chapter details how a SMP-based particulate composite was fabricated, along with the materials used in the process. The fabrication of the testing mold is also included.

2.1.1 Particulate Composite (CP-PSMP)

The particulate composite (CP-PSMP) consists of the polystyrene shape memory polymer (PSMP) and the thermoplastic additives (CP). First, the PSMP was synthesized using vinyl benzene, vinyl neodecanoate, and divinyl-benzene, and polystyrene-block-polybutadiene-block-polystyrene. Benzoyl peroxide served as the radical initiator. The vinylbenzene (Reagentplus ≥ 99%), divinyl-benzene (technical grade, 80%, mixture of isomers) and vinyl neodecanoate were supplied by Aldrich. Sigma-Aldrich supplied both Polystyrene-block-polybutadiene-block-polystyrene (styrene, 30 wt. %) and Benzoyl peroxide (Luperox® A98, reagent grade, ≥ 98%).

The thermoplastic additives were not created in the lab. They were obtained from Abifor Inc., Switzerland. The thermoplastic particle was a linear copolyester (CP) made of Isophthalic acid, Terephthalic acid and 1, 4-Butanediol. The listed particle size of the thermoplastic particles was ≤ 80 μm. The listed density of the thermoplastic particles was 1.3 g/cm³. The glass transition temperature, melting temperature, and bonding temperature of the copolyester were listed as 16 °C, 120 °C, and 150 °C, respectively.
2.1.2 Confining Mold

The confining mold was cut out of AISI 1018 steel with the properties listed below. The thermal properties were useful for computing the time for even heat distribution during programming and healing [68].

Table 2. Mechanical and Thermal Properties of Steel Mold

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>7870 kg/m$^3$</td>
</tr>
<tr>
<td>Ultimate Tensile Strength</td>
<td>450 MPa</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>200 GPa</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.29</td>
</tr>
<tr>
<td>Linear CTE</td>
<td>11.5 $\mu$m/m°C</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>51.9 W/m-K</td>
</tr>
</tbody>
</table>

2.2 Polymer Composite Fabrication

2.2.1 Mixing

Vinylbenzene was poured into a three-necked flask equipped with a mechanical stirrer and a thermometer and polystyrene was added in. The mixture was stirred for 45 minutes with a stirrer made of polytetrafluoroethylene. An ultrasonicator (Sonic and Materials Inc, Sonic Vibra-cell, model CV334) was used in the stirring process. Next, divinyl-benzene and vinyl neodecanoate were added to the mixture followed by additional stirring for about 10 minutes until the mixture was clear to the human eye. At this point, thermoplastic particles (6% by volume) were added to the mixture to make the composite. Then stirring resumed for another hour.
Benzoyl peroxide was added as reaction thermal initiator and further stirring ensued for about 30 minutes. The mixture was degassed in 0.1–0.2 KPa vacuum using a Sargent-Welche vacuum (Welch brand, Duo-seal, Model NO. 1402) for 30 minutes. At this time, the mixture was cast in a rectangular mold coated with polytetrafluoroethylene and sealed using a vacuum bag (both, Airtech Advanced Materials Group) to keep air out from the mixture.

2.2.2 Curing

The mixture was cured thus:

- 16 hours at 75 °C,
- 10 hours at 80 °C, and
- 5 hours at 110 °C.

The cured sample was a rectangular slab roughly 15 mm thick. Following curing, the polymer was left to cool to room temperature after which it was demolded.

Figure 10. Pure SMP before curing [68].
2.3 Polymer Cutting

2.3.1 Cutting Method

The cured composite was then cut to the required sample size. While many options (using a saw, laser beam, CNC machine, lathe machine etc.) are available for cutting the cured composite, the use of abrasive water jet offers several advantages over the other methods [69]. For instance, laser beam cutting induces high heat dissipation into the composite sample, causing charring, thermal cracks, surface and subsurface defects, and yielding large burr formation and dimensional inaccuracy due to thermal distortion. On the other hand, using abrasive water method does not always lead to burr formation depending on the energy level of the water jet. The absence of burr formation, characterized by a clean edge at the bottom of the specimen, results whenever high water pressure is used in the employment abrasive water jet. Also, the heat
from laser beams could induce the existence of heat affected zones at different spots on the specimen where heat concentration occurs. The heat localization could also cause unintended and non-uniform programming of the sample during cutting. In contrast, water jet cuts at low temperatures.

Sawing is not beneficial because it can lead to delamination and wanton fiber extraction from fiber-reinforced composites. A delaminated material has bonding failure between its layers. It could arise from the cyclic process of sawing. The main danger of delamination is that it has far-reaching problems, literally. A delaminated composite could experience failure within a material but not on its surface. In a self-healing material, this deep damage could disrupt the sequestration method (capsule, vascular or intrinsic) embedded within the material. Saws used in cutting polymers could also suffer damage. Diamond saws are capable of producing clean-cut composite polymer pieces but a halt midway through the sawing process could allow for the polymer to self-heal around the blade and entrap it. In contrast, water jet cutting can be controlled in order to prevent damage to the composite material.

2.3.2 Cutting Speed

The following mathematical formula can be used to compute the ideal cutting speed [71].

$$N_m = \frac{ChD^{618}u^{866}}{P_w^{1.25}m_w^{687}m^{343}}$$

(6)

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. Equation 6 can be used to compute the transverse speed, \(u\).

\[
u = \left( \frac{f_a N_m P_w^{1.25} m_w^{0.687} m^{3.43}}{QC D^{0.618} u^{0.866}} \right)^{1.15}
\]

In Equation 7, \(f_a\) is the abrasive factor and \(Q\) is the quality index. \(Q\) has values from 1 to 5 and relates the abrasive water jet settings to the final surface finish as shown in Table 3. In addition to controllability, water jet cutting offers a reasonable tolerance of 0.13 mm.

<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>

2.3.3 Polymer Shape

Since the sample would be heated up to a specific temperature, it was necessary that a cross-section with the least number of edges be used. Realistically, the only shapes available were circular, triangular and rectangular (square). Next, for ideal heat distribution, the heat absorption by the sample should be uniform on all sides/edges. Also, cross-sections with sharp edges may cause warping on the edge of the sample. This rules out the triangular- and square-edged samples. Thus, a circular cross-section was chosen for the composite samples. In addition to the concerns about heat, shapes with sharp edges often entertain singularities during stress test.
This is not the case with shapes which have rounded edges. Thus, a circular cross-section is preferable for both thermal and stress-related reasons.

![Cured specimen cut using an abrasive water jet.](image)

**Figure 12.** A cured specimen cut using an abrasive water jet.

### 2.3.4 Sample Dimensions

Determining the final dimensions of the sample was based on both the requirements for 3-point flexural strength testing as per ISO 178 standards, and designing against buckling. Bucking calculation were performed using known stress values from prior experiments with self-healing SMP-based particulate composites. Each of the final samples was 10 mm in diameter and 120 mm long.
2.4 Confining Mold Fabrication

A double-walled confining tube (practically, a hollow steel cylinder) was employed in both by both Uppu [48] and Yougoubare [68] as a restraint for polymers during programming and healing. The goal of the confining mold was to maintain the roughly constant diameter of the composite sample during both programming and healing such that the volume reduction required during programming would be dependent only on the height of the specimen. That way, the axial strain on the sample would be the only parameter needed to compute the change in the volume (or ‘shape’) of the sample.

The shape of the confining mold was determined by the shape of the sample used. A cylindrical sample necessitated the need for a hollow mold with a cylindrical groove. For the same reason of heating uniformity as given in Section 2.3.3, a circular cross-section was picked for the outer circumference of the cylindrical mold.

To compress the cylindrical sample along its length while it was within the steel mold, **end plugs** were made for either end of the confining mold as shown in Figure 11. The plugs were made of the same AISI 1018 steel as the confining mold.

Surfaces in contact during the heating process (i.e. programming and healing) were separated with a polytetrafluoroethylene sheet. This was to allow for easy extraction of the sample after each heating step. The dimensions of the cylindrical mold used are given in Table 4.

<table>
<thead>
<tr>
<th>Element</th>
<th>Value (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>142mm</td>
</tr>
<tr>
<td>Inner Diameter</td>
<td>10.7 mm</td>
</tr>
<tr>
<td>Outer Diameter</td>
<td>50 mm</td>
</tr>
</tbody>
</table>
Figure 13. (a) Confining mold with end plugs, (b) an end plug (alone), and (b) the confining mold (alone) showing polytetrafluoroethylene sheet around a sample
Since the mold would be the source of heat transmission to the sample, it was necessary to perform a heat analysis on the mold based on its geometry and both its mechanical and thermal properties. A detailed structural and transient thermal finite element analysis (FEA) was performed by Yougoubare [68] using ANSYS software. The goal of the FEA was to determine the temperature distribution and some of the effects of heat flow within the mold. The analyses mimicked heating at a slow rate from 20 °C to 140 °C. The results of this study showed that for a hollow cylinder of height, 121.50 mm, inner diameter, 12.70 mm, outer diameter 50.05 mm and a heat transfer coefficient of 15 W m\(^{-2}\) K\(^{-1}\), a minimum soaking time of 40 minutes was necessary for the inner walls to reach steady state conditions. The maximum deflection of the inner and
outer walls due to thermal stresses was found to be 0.012 mm and 0.046 mm respectively according to the Von Mises criterion, and 0.011 mm if linear thermal expansion was assumed. The overall deflection of the mold corresponded to 0.24 % of the diameter of the sample, and so should be relatively insignificant. Moreover, the inward push from the mold should resist the sample’s expansion during heating.
Chapter 3: Experimentation

3.1 Differential Scanning Calorimetry

Differential scanning calorimetry is one possible method of determining the glass transition temperature ($T_g$) of the polymer sample. This temperature is useful for designing a thermomechanical cycle for the composite sample because thermomechanical cycle depends on $T_g$. At temperatures below $T_g$, the SMP is hard and brittle, but it is elastic and ductile at temperatures above $T_g$. Therefore, knowing $T_g$ can reveal when the polymer will be soft enough to compress during programming; it can also tell when healing will occur during heating. A Perkin-Elmer differential scanning calorimeter was used to test composite samples weighing about 7 mg.

Figure 14. Differential scanning calorimeter and a computer with PYREX™ software for data acquisition [68]
3.2 Thermomechanical Programming

After being cut to the desired shape, the composite sample was ready for programming. Compressive programming was employed in this study, as was described in Section 1.4.2. The type of programming employed in this study was strain-controlled. Strain-controlled programming was selected over stress-controlled programming because the strain is more easily managed (i.e. through compression) than the stress. Also, the heating process could alter the mechanical properties of the sample, which could affect the stress even while the crosshead of the MTS machine is held steady (i.e. at constant strain). Programming was performed on a Universal QTEST/150 MTS machine fitted with a Eurotherm heating chamber and an attached temperature controller (shown in Figure 15) that was used to monitor the temperature within the chamber. All samples were programmed under the same conditions. A pre-strain level of 10% was chosen. This low pre-strain value will ensure that the samples are not cracked during programming but ensure that volume reduction necessary for healing takes place. Also, a programming temperature of 100 °C was used. The sample was heated at 6 °C/min from room temperature to the programming temperature. This heating rate was deemed appropriate based on the results obtained from the structural and thermal FEA performed [68]. The choice of the compression rate (how quickly the composite sample is strained) is not a trivial one for the programming process. Strain-controlled programming should be a ‘quasi-static’ process. Ideally, the compression should occur in infinitesimal increments over infinitesimal time periods. Therefore, a slow compression rate of 1.4 mm/min was chosen. Similar values has been used in previous results with useful results [48, 68]. Figure 16 schematically illustrates the programming process.
Figure 15. Programming Set-up

Figure 16. Schematic illustration of the specimen programming. Adapted from [58].
3.3 Three-Point Flexural Strength Bending Test

Three-point bending tests were performed as per ISO 178 standards on a universal MTS 810 testing system with a span length of 80 mm and at a loading rate of 10 mm/min to determine the flexural strength of programmed and healed samples. Un-notched programmed and healed specimens with diameter of 10 mm were used in this experiment. The span-to-diameter ratio was 8 to 1. The equipment was set up as is shown in Figure 18. Also, as per ISO 178 standards, force application continued until the sample broke into halves. Flexural strength tests were performed after programming and after healing.
3.4 Sanding

The goal of this study was to investigate the effect of surface roughness on the healing efficiency of the composite samples. Therefore, the surface roughness at the damage interface of the sample needed to be varied. This was accomplished by sanding the fracture surfaces with sandpaper of different grades. The CAMI grits used were 40, 80, 120, 220, 320, 600 and 1200. Two kinds of control were employed: Control A samples were not sanded (i.e. untreated) at the crack interface, while the samples in Control B were shaved using a water jet. The samples in Control A were fit as close as possible to their pre-fracture form before the healing process was begun. In all cases, the extensions and grooves compatibility at the crack interface matched the pre-fracture form. The water jet was employed as another control because the water jetting process avoids force application normally to the crack interface.
To improve consistency in sanding and compatibility in alignment during the healing process, the sanding process was accomplished with the use of a DEWALT D26441K 2.4-AMP Orbital 1/4-Sheet Sander. The orbital sander moved the sandpaper in small, quick circular motions. By holding the surface to be grinded directly onto the sandpaper, grinding in circular motion was accomplished. For each CAMI grit sandpaper, three samples were used. Likewise, three samples were used for each control group.

3.5 Roughness Measurement

Profile measurements for the different samples were taken using a WYKONT1000 Optical Profilometer, with a computer equipped with SURFPAK-SV software. 15125 data points were measured over a distance of 3.025 mm. The specified range was 800 µm, and the stylus speed was 0.2 mm/s. The measurement distance of 3.025 mm was radial, symmetrical coincided with the geometrical center of the treated surface. The choice of this measurement orientation and distance (a third of the diameter) is necessary to ensure that the profile would be obtained from regions of the treated surfaces that would definitely make contact during the healing process. For this reason, the outer parts of the treated surfaces were avoided.

Two samples for each grit size were measured, and each sample was measured three times to obtain the profile parameters using Equations (8) and (9),

$$R_a = \frac{1}{n} \sum_{i=1}^{n} |y_i|$$

(8)
\[ R_q = \sqrt{\frac{1}{n} \sum_{i=1}^{n} y_i^2} \]  

Where \( R_a \) is the **arithmetic average of absolute values profile roughness parameter**, \( R_q \) is the **root mean squared profile roughness parameter** and \( y_i \) is the vertical distance from the mean line to the \( i^{th} \) data point, and \( n \) is the number of points measured.

Figure 19. Profilometer and a computer with SURFPACK-SV software
3.6 Shape Recovery / Healing

Following the two-step self-healing scheme proposed by Li and Uppu [48], sanded specimens were placed in the steel confining mold as shown in Figure 13 at room temperature. Once the specimen was set appropriately, the compression-molding fixture was pre-heated to 60 °C at a heating rate of 6 °C/min. It is noted that the confining mold provided confinement in the radial (2D) plane while the MTS compressed along the sample along its length and provided confinement in the axial plane. The ends of both of both steel plugs were in direct contact with the sample so that 3D confinement was achieved during healing. The specimens were kept within the pre-heated fixture for 20 minutes. Then, the temperature within the specimen was gradually increased, first past its T_g, which caused shape recovery or closing of the fractured surface and the milled holes, and then through the T_m of the copolymer (about 120 °C) till the CP melting temperature of 150 °C. This was used as the healing temperature. After an hour, the healed sample and the mold were removed from the heating chamber and cooled to room temperature. This completed the two-step self-healing scheme.

3.7 Scanning Electron Microscopy Observation

The healing process is promoted by the shape memory effect of the SMP for structural-scale healing, as well as the melting of the copolyester particles (CP) at the crack interface for micro-scale healing. The flow of the thermal additives (copolyester particles) at high temperatures should promote a better distribution of the healing agent at the surface of the crack, which should translate to improved recovered strengths.

Scanning Electron Microscopy (SEM) observation was conducted using a Hitachi S-3600N Scanning Electron Microscope in order to verify that the copolyester particles were not removed during the sanding process and that the CP melted during the healing process. To that
end, SEM was performed on the surfaces at the damage interface before the sanding process, after the sanding process and after the healing process.

Since CP-PSMP are not electrically conductive, they had to be specially prepared for viewing under the SEM microscope. This preparation involves the continuous application of a conductive surface film (usually a metal film) in a process known as sputter-coating. For this observation, a platinum film was used. Before coating, the CP-PSMP were mounted on a plug and secured using aluminum adhesives as shown in Figure 20 (a). A conductive coating is needed to prevent charging of a specimen with an electron beam in conventional SEM mode (high vacuum, high voltage). Samples which underwent SEM observation were sputter-coated in 0.1 mbar vacuum, with about 20 nm of platinum using an EMS 550 Sputter Coater. The coating time was 4 minutes for each sample.

Figure 20. CP-PSMP specimens (a) before sputter-coating, (b) placed in sputter-coater, and (c) after (sputter-coating)
Figure 21. (a) Sputter-coated CP-PSMP being loaded into the scanning electron microscope, and (b) the scanning electron microscope
Chapter 4. Results and Discussion

4.1 DSC Test Results

The DSC was used to find the glass transition temperature of the CP-PSMP (composite sample). It was also to find the melting temperatures, as well as if there was any compatibility between the PSMP and the CP. Using this method, the PSMP and CP are compatible if the CP-PSMP has a $T_g$ within the glass temperatures registered by either the CP and the PSMP.

4.1.1 $T_g$ of the CP

The $T_g$ of the CP was given as 16 °C by the manufacturer. Previous DSC tests have confirmed this value to be accurate [58]. Also confirmed is that the CP has another $T_g$ value at 70 °C. Having two $T_g$ values means that there are likely two components within the CP. The major component would be that which is more than the other. The other component, called the minor component, would exist in a relatively small amount. Even though the CP registers two different $T_g$ values, only the $T_g$ of the major component would influence the $T_g$ of the composite sample (CP-PSMP).

4.1.2 $T_g$ of the PSMP

Other DSC results showed the $T_g$ of the pure PSMP to be ~ 89 °C. Knowing the $T_g$ of the PSMP proved useful in determining which of the two $T_g$ values of the CP was for the dominant component.

4.1.3 $T_g$ of the CP-PSMP

The DSC data, as shown in Figure 22 indicates that the CP-PSMP has two values of $T_g$: $T_g^1 \approx 5$ °C, and $T_g^2 \approx 73$ °C. This means that both components of the CP had an impacts on the DSC result. However, the $T_g$ value of the PSMP makes it an obvious choice which is the true
value. Since the PSMP has a $T_g$ of roughly 89 °C and is the larger portion (94% by volume) of the CP-PSMP composite, its $T_g$ value would have more effect on the $T_g$ of the overall CP-PSMP composite than the CP would. Therefore, the $T_g$ of the CP-PSMP composite is taken as $T_g^2$, which is 73 °C. Though the $T_g$ is 73 °C, the presence of $T_g^1$ suggests that there is another component in the CP, which was hypothesized in Section 4.1.1, but, that component probably exists in very small quantity and is the minor component.

![Figure 22. DSC results of the CP-PSMP](image)

4.2 Thermomechanical Programming

A typical 3D plot of stress, strain and temperature for this composite (CP-PCMP) is shown in Figure 23 with graphs of the programing (ABCD), confined recovery (DEF) and free recovery (DG) processes. The programming steps were taken as described in Section 1.4.2. First, specimens were heated to 100 °C (at point A), then compressed with strain-control along the axial direction to the specified 10 % pre-strain level (point B, loading rate: 1.4 mm/min), and
held at 100 °C for an hour to stabilize the stress (point C). The soak time for the programming process, determined from the analysis mentioned in Section 2.4.2, also serves as the soak time for the healing process—i.e. how long it would take for the temperatures across the mold and the specimen to stabilize inside the heating chamber. Next, the specimen and confining mold were cooled to room temperature. The specimen was then removed from the mold.

Before being placed into the confining mold, the composite samples were wrapped in polytetrafluoroethylene (PFTE) sheets (thickness: 7.6 X 10^{-6} m, thermal expansion coefficient: 135 X 10^{-6} K^{-1}, melting point: 327 °C and coefficient of friction: 0.5 – 1.0 as measured against polished steel). Using the sheets allowed for easy extraction of the sample from the confining mold.

Figure 23. A typical strain-temperature-stress plot with graphs showing the behavior of CP-PSMP during programming (ABCD), confined recovery (DEF) and free recovery (DG). Adapted from [58].
4.3 Three-Point Bending (Pre-Healing) Test Results

One goal of this study was to determine the effects of surface roughness on the healing efficiency of CP-PSMP. The samples expended towards that goal underwent two sets of three-point bending tests. The first round of three-point bending test was pre-healing and this occurred right after programming. At this point, no parameter had been varied in the preparation and thermomechanical treatment of the samples so the flexural strengths were expected to be similar. The average flexural strength of the CP-PSMP was found to be 34.87 ± 3.40 MPa. There were no controls for this stage. Each sample was tested until fracture, leaving two separate halves.

4.4 Sanding

The fracture surfaces at the crack interface were sanded using sandpaper from each of the seven categories (as listed in Table 1 in Section 1.5.3). The grit sizes used were 40, 80, 120, 220, 320, 600, and 1200. As mentioned in Section 3.4, an orbital sander was used to ensure that the sanding process was consistently done in circular fashion. Thus, before healing, there was no need for special alignment during healing. The (visual) distinction between a pre-sanded fracture surface of a sample and a sanded fracture surface is shown in Figure 24.

![Figure 24. Pre-sanded rough crack surface before sanding, and a smooth post-sanding surface](image-url)
The choice of 1200 over higher grit sandpaper (e.g. 2000 or 5000) is because the composite was quite hard, and sandpaper of much finer sanding quality would barely make alter the surface of the sample. Also, there was very little variation in the average particle diameter in the ultra-fine region (1 – 12.2 µm) compared with other regions, e.g. coarse (351 – 715 µm) and fine (93 – 116 µm).

4.5 Roughness

The sanded samples were ranked based on the following:

1. The average particle diameter of the sandpaper used.
2. The Ra value obtained from the sanded surface.
3. The Rq value obtained from the sanded surface.

The results of the profilometer measurements are given in Table 5.

<table>
<thead>
<tr>
<th>CAMI Grit Size</th>
<th>Paper Finish (µm)</th>
<th>Ra (µm)</th>
<th>Rq (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>425</td>
<td>1.77</td>
<td>2.224</td>
</tr>
<tr>
<td>80</td>
<td>190</td>
<td>1.415</td>
<td>1.918</td>
</tr>
<tr>
<td>120</td>
<td>115</td>
<td>1.336</td>
<td>1.77</td>
</tr>
<tr>
<td>220</td>
<td>68</td>
<td>0.854</td>
<td>0.991</td>
</tr>
<tr>
<td>320</td>
<td>36</td>
<td>0.425</td>
<td>0.617</td>
</tr>
<tr>
<td>600</td>
<td>16</td>
<td>0.298</td>
<td>0.439</td>
</tr>
<tr>
<td>1200</td>
<td>6.5</td>
<td>0.192</td>
<td>0.37</td>
</tr>
<tr>
<td>No treatment (Control A)</td>
<td>NA</td>
<td>1.677</td>
<td>2.237</td>
</tr>
<tr>
<td>Water jet (Control B)</td>
<td>NA</td>
<td>0.825</td>
<td>1.005</td>
</tr>
</tbody>
</table>
As is seen in Table 5, the surface of the composite sample was clearly affected by the different particles sizes of the sandpapers. As was expected, using finer sandpaper produced smoother surfaces. The Ra and Rq values also reduced accordingly. This is similarly evident in the roughness profiles of 40, 220 and 1200 grit sandpapers shown in Figure 25 (a), (b) and (c) respectively. The surfaces become smoother as the particle diameter of the sandpaper used increases. Likewise, it can be seen in Figures 25 (d) that the untreated sample (Control A) appears the roughest of the samples, which is to be expected. Figure 25 (e), the roughness profile of a surface, which was shaved off with a water jet, appears rough; but it appears more even than the untreated surface. A summary of the average roughness values obtained are given in Table 6.

Table 6. Average roughness profiles

<table>
<thead>
<tr>
<th></th>
<th>Avg. Ra (µm)</th>
<th>Avg. Rq (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sanded samples</td>
<td>0.898</td>
<td>1.190</td>
</tr>
<tr>
<td>No treatment (Control A)</td>
<td>1.677</td>
<td>2.237</td>
</tr>
<tr>
<td>Water jet (Control B)</td>
<td>0.825</td>
<td>1.005</td>
</tr>
</tbody>
</table>

It is noteworthy to mention that the un-sanded specimens (Control A) yielded roughness values that were relatively high; only the samples treated with CAMI grit size 40—the roughest sandpaper used—offered higher roughness values. However, the samples that were cut with a water jet parallel to the fracture surface (Control B) were within 5% of the roughness values of the sample sanded with CAMI grit 220 sandpaper. Based on its roughness values, Control B would have fallen within the very fine category.
CAMI Grit 40, Ra = 1.636 μm, Rq = 2.027 μm

CAMI Grit 220, Ra = 0.725 μm, Rq = 0.917 μm

CAMI Grit 1200, Ra = 0.229 μm, Rq = 0.338 μm
The relationship between the size of the sandpaper particles and the roughness profiles of the sanded composite was investigated. The results are shown in Figure 26. The points on the graph are respectively coarse, medium, fine, very fine, extra-fine, super-fine and ultra-fine. There is a near-linear relationship sandpaper particle size and the roughness profile in the microgrit region, but the proportionality weakens when macrogrit sandpaper is used. But, there is an overall increase in the roughness parameters as coarser sandpaper is employed on the fracture interfaces to be healed.
Figure 26. Sandpaper particle size vs. roughness profiles of the composite samples

4.6 Recovery/Healing

Healing of the CP-PSMP was carried out according to the close-then-heal (CTH) method described by Li and Uppu. During healing, the CP-PSMP is compressed then heated through $T_g$ until 150 °C. The healing temperature was selected in order to sufficiently surpass the melting temperature of the thermoplastic copolyester additives (120 °C) during healing. This would ensure that effective healing took place in accordance with the methods outlined by Li and Nji. To ensure surface contact during the healing process, the sanded specimens were compressed to 10 MPa and held there for 1 hour (greater than the calculated soak time of 40 minutes). 10 MPa was used as the compressive stress for healing.

Most of the samples experienced reductions in both their lengths and volumes ranging from 0.1 % to 8 %. This was expected for the sanded specimens as the sanded surfaces were not
perfectly aligned. Most of the healed samples had a visible line at the crack interface after healing. This crack boundary line is shown in Figure 27.

![Figure 27. Healed CP-PSMP showing the crack boundary line (compressive healing stress of 10 MPa)](image)

**4.7 Three-Point Bending (Post-Healing) Test Results**

After sanding and healing, three-point bending tests were repeated on the samples. The flexural strengths obtained pre-healing and post-healing were used to compute the healing efficiency using Equation 5. A comparison with the control specimens is given in Table 6.

**4.7.1 General Observations and Discussion**

Overall, the efficiencies obtained from the sanded samples varied between 0.263 and 0.386. The average efficiency was $0.312 \pm 0.043$. Samples sanded with CAMI grit 320 sandpaper had the highest healing efficiency of 0.386 while CAMI grit 80 yielded the least efficiency (0.263) among the sanded specimens. The efficiencies can be expressed as percentages by multiplying by 100%.
Table 7. Comparing healing efficiency with roughness

<table>
<thead>
<tr>
<th>CAMI Grit Size</th>
<th>Paper Particle Size (µm)</th>
<th>Ra (µm)</th>
<th>Rq (µm)</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>425</td>
<td>1.770</td>
<td>2.224</td>
<td>0.320 ± 0.056</td>
</tr>
<tr>
<td>80</td>
<td>190</td>
<td>1.415</td>
<td>1.918</td>
<td>0.263 ± 0.014</td>
</tr>
<tr>
<td>120</td>
<td>115</td>
<td>1.336</td>
<td>1.770</td>
<td>0.278 ± 0.014</td>
</tr>
<tr>
<td>220</td>
<td>68</td>
<td>0.854</td>
<td>0.991</td>
<td>0.355 ± 0.058</td>
</tr>
<tr>
<td>320</td>
<td>36</td>
<td>0.425</td>
<td>0.617</td>
<td>0.386 ± 0.058</td>
</tr>
<tr>
<td>600</td>
<td>16</td>
<td>0.298</td>
<td>0.439</td>
<td>0.264 ± 0.000</td>
</tr>
<tr>
<td>1200</td>
<td>6.5</td>
<td>0.192</td>
<td>0.370</td>
<td>0.321 ± 0.082</td>
</tr>
<tr>
<td>No treatment (Control A)</td>
<td>NA</td>
<td>1.677</td>
<td>2.237</td>
<td>0.271 ± 0.027</td>
</tr>
<tr>
<td>Water jet (Control B)</td>
<td>NA</td>
<td>0.825</td>
<td>1.005</td>
<td>0.214 ± 0.027</td>
</tr>
</tbody>
</table>

The healing efficiencies obtained were compared with the sandpaper size used and both the Ra and Rq values as shown in Figures 28 through 30.

Figure 28. Sandpaper particle size vs. efficiency
Figure 29. Ra vs. efficiency

Figure 30. Rq vs. efficiency
4.7.2 Macrogrit vs. Microgrit in Healing Efficiency

First, the roughness profiles shown in Figure 25 (a) through (c) confirm that using finer sandpaper on the fracture surfaces yielded smoother surfaces, i.e. microgrit-treated samples produced smoother pre-healing surfaces than macrogrit-treated samples. Such surfaces also had lower $R_a$ and $R_q$ values as shown in Table 7. Tables 7 and 8 show that, on average, samples with smoother pre-healing surfaces healed more efficiently than samples with rougher pre-healing interfaces. This is likely because the smoother surfaces (treated with microgrit sandpaper) made more contact during healing than the rougher surfaces, which were macrogrit-treated. This confirms the hypothesis offered in Section 1.6.

Table 8. Summarized comparison of sanded samples with control samples

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macrogrit sandpaper</td>
<td>0.287 ± 0.024</td>
</tr>
<tr>
<td>Very fine sandpaper</td>
<td>0.355 ± 0.058</td>
</tr>
<tr>
<td>Microgrit sandpaper</td>
<td>0.324 ± 0.050</td>
</tr>
<tr>
<td>Sanded samples (All)</td>
<td>0.312 ± 0.043</td>
</tr>
<tr>
<td>No Treatment (Control A)</td>
<td>0.271 ± 0.027</td>
</tr>
<tr>
<td>Water Jet (Control B)</td>
<td>0.214 ± 0.027</td>
</tr>
</tbody>
</table>

4.7.3 Sanded vs. Control Samples

As was stated earlier, two kinds of controls (A and B) were employed. Control A samples were left untreated after fracture and they were aligned for healing as close to their orientation prior to fracture. This was easy since the asperities (“stalactites” and “stalagmites”) matched up. It was hypothesized that this alignment advantage would allow for a relatively high healing efficiency compared to samples that were sanded. However, it is seen in Table 6 that the average efficiency of the sanded samples is higher than that of the untreated samples (Control A) by
about 13 %. The perceived advantage of having an unaltered fracture interface did not translate into an improved healing efficiency.

Samples in Control B had their surfaces at the fracture interface shaved off using a water jet with a stream perpendicular to the fracture interface. It was noticed from the profilometry results that Control B samples had very similar roughness parameters (within 5 %) to the samples treated with CAMI grit 220. However Control B showed much lower efficiency, by about 24 %. Therefore, it may be postulated that there may be one or more aspect(s) of the sanding process which affect the healing efficiency, but which is not reflected in the roughness value.

Also, Control B had the lowest efficiencies at 0.214. There are two possible reasons for this low efficiency: absence of sanding, and the disregard for orientation in alignment during the healing process. Since the samples in Control B were shaved off perpendicularly to the fracture interface, there was no orientation of preference during healing unlike in the other samples.

4.8 Investigation of the Effect of Compressive Stresses during Healing on the Healing Efficiency

Healing in CP-PSMP has shown up to 63 % recovery in flexural stress after healing [68] and up to 65 % recovery in peak loads after healing [58]. In this study however, the maximum healing obtained in flexural stress was 38.6 %. One possible cause of this low efficiency is the low compressive stress of 10 MPa employed during healing. Thus, a test to examine the effect of compressive stresses during healing was carried out.

Programmed and fractured samples which were sanded with CAMI 220 sandpaper were healed at different compressive stresses—20, 35, 50, 65 and 85 MPa—and then tested for recovered flexural strength. Two samples were used for each healing stress. Next, SEM was
performed as described in Section 3.7 on a sample after pre-healing fracture, after sanding, and after healing. The sample used for the SEM analysis was healed at 30 MPa.

### 4.8.1 General Observations and Discussion

The symbols used are defined thus:

- **P1**: pre-healing flexural stress peak load
- **P2**: post-healing flexural stress peak load
- **σ_h**: compressive stress for healing
- **σ_f1**: pre-healing flexural stress
- **σ_f2**: post-healing flexural stress
- **η**: efficiency, obtained using Equation (5)

The results obtained are given in Tables 9 (a) — (c), and in Figures 31 (a) — (c).

Table 9. Results of varying healing stress on (a) peak load in 3-point bending flexural stress test, (b) 3pt flexural stress, and (c) efficiency, η

<table>
<thead>
<tr>
<th>σ_h (MPa)</th>
<th>P1 (N)</th>
<th>P2 (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>140.42 ± 16.09</td>
<td>119.11 ± 37.81</td>
</tr>
<tr>
<td>35</td>
<td>120.20 ± 11.73</td>
<td>151.95 ± 20.82</td>
</tr>
<tr>
<td>50</td>
<td>127.31 ± 6.79</td>
<td>158.60 ± 23.00</td>
</tr>
<tr>
<td>65</td>
<td>140.45 ± 16.05</td>
<td>119.48 ± 2.87</td>
</tr>
<tr>
<td>80</td>
<td>127.38 ± 19.74</td>
<td>155.53 ± 8.99</td>
</tr>
</tbody>
</table>

(a)
Noteworthy are the healing efficiencies which exceeded 100%. Blaiszik used a performance map to show that intrinsic self-healing polymers could attain healing efficiencies up to 100% in peak fracture loads at low damage volumes (< 1 mm³) [47]. Similar studies on capsule-based and vascular-based self-healing polymers have also yielded efficiencies of 100% or more when the healing measure used was peak fracture load [73] or fracture toughness [74-79]. The reported healing is greater than 100% because the flexural stress in the post-healing case is greater than in the pre-healing case. The low damage volume was easily attained in the thermomechanical process since the damage surfaces were sanded and made as flat as possible. Also, by increasing the compressive force required for confined healing, volume reduction was likely improved.
4.8.2 SEM Images

SEM Images were taken of a sample healed at 30 MPa at the following three stages:

1. Pre-healing fracture
2. Post-sanding
3. Post-healing fracture

For each stage, two SEM images were stage—one at a low magnification of X 25 and another at a high magnification of X 1500.
Figure 3.2. SEM Images at X 25 magnification of a CP-PSMP damaged surface (a) after programming (pre-healing), (b) after sanding, and (c) after healing

Figure 3.3. SEM Images at X 1500 magnification of a CP-PSMP damaged surface (a) after programming (pre-healing), (b) after sanding, and (c) after healing

The effect of the sanding can be seen in Figure 3.2 (b). Magnified SEM images of the surface in Figures 3.3 (a), (b) and (c) show the presence of thermoplastic particles after programming, after sanding and after healing. The thermoplastic particles appear significantly more after programming (i.e. before sanding) in Figure 3.3 (a) as may be expected. However, it is still present, albeit in smaller quantities, after the sanding process as shown in Figures 3.1 (b) as well as after healing and re-fracture process as shown in Figures 3.1 (c). This shows that the sanding process did not rid the CP-PSMP of the thermoplastic plastic particles needed for molecular-scale healing.
The efficiencies obtained varied from 0.75 to 1.18 (i.e. 75 % to 118 %) with three of the five healing stresses showing healing efficiencies above 100 %. The maximum healing efficiency was found at the healing stress was obtained at 50 MPa while 65 MPa yielded the minimum healing efficiency. It is remarkable that the healing efficiencies exceed those obtained at a healing stress of 10 MPa (max of 38.6 %), which the previous tests were done at. Thus, higher compressive forces were required for efficient healing.
5.1 Conclusions

In this study, the effects of the surface roughness of post-fracture interfaces on the efficiency of self-healing CP-PSMP polymers were investigated. The polymer composite used was developed by dispersing 6% by volume of copolyester (CP) particles in a polystyrene shape memory polymer (PSMP). Self-healing was achieved using the validated bio-mimicking two-fold close-then-heal (CTH) mechanism for healing the composite. Using this method, composite samples (CP-PSMP) are healed both at the structural-scale and the micro-scale. The cured CP-PSMP mold was cut into cylindrical specimens, which were thermomechanically programmed to 10% pre-strain and tested for flexural strength using three-point bending method. Next, the surfaces were varied using sandpaper of different particle diameters (6.5 to 425 μm), and the roughness profile parameters, $R_a$ and $R_q$, were measured. The $R_a$ and $R_q$ values ranged from 0.192 to 1.770 μm and from 0.370 to 2.224 μm respectively. The sandpapers used were classified based on grit size into seven categories: coarse, medium, fine, very fine, extra-fine, super-fine and ultra-fine. Next, the CP-PSMP was healed using the close-then-heal (CTH) self-healing mechanism, and the recovered strength was obtained using another three point bending test. The healing efficiency was obtained as the fraction of the recovered flexural strength to the pre-healing flexural strength. The relationship between the average particle diameter of the sandpaper used and the roughness profile parameters of the sanded composite surface was investigated. The healing efficiencies were then computed and compared against the roughness profile parameters as well as the particle diameter of the sandpaper used.
Also, the effects of compressive stresses during healing on efficiency was investigated by comparing the efficiencies obtained from separate CP-PSMP samples sanded with very fine sand paper (of particle diameter 68 μm). Based on the test results, it is found that:

1. As was expected, the roughness profile parameters of the sanded surface increased as the average particle diameters of the sandpaper used decreased. The rate of proportionality was higher for microgrit sandpaper (i.e. average particle diameter less than 53 μm) than for macrogrit sandpaper (average particle diameter greater than 68 μm).

2. Samples with smoother pre-healing surfaces healed more efficiently than samples with rougher pre-healing surfaces. Overall, the samples treated with microgrit sandpaper healed more efficiently than the samples treated with macrogrit sandpaper.

3. The highest healing efficiencies of about 39 % were obtained in samples treated with very fine and extra-fine sandpaper.

4. Sanding likely has an effect on the healing efficiency in ways that are beyond characterization by the roughness parameter profiles, $R_a$ and $R_q$. Two groups of specimens with similar $R_a$ and $R_q$ values – some treated with sandpaper, others not – were tested and compared. The sanded specimens had about 24 % better efficiency than their untreated counterparts. The advantage of achieving a near-perfect pre-fracture orientation during healing was overcome by the absence of sanding.

5. Shaving off the edges at a crack interface using a water jet reduces the efficiency since the specimens cannot be aligned in any orientation that resembles their pre-fracture state.

6. High compressive stresses generally allow for more efficient healing.
5.2 Future Recommendations

Due to the nature of thermomechanical characterization, many parameters have to be set including pre-strain level, programming temperature, healing temperature etc. Changing just one of these factors could affect the mechanical properties of the programmed sample. For a more detailed understanding of the CP-PSMP sample, it is paramount that these studies be repeated while varying as many parameters as possible in the thermomechanical process. Ways to improve the flexural strength of the CP-PSMP should be sought because, presently, the polymer loses as much as 72% of its pre-healing flexural strength upon the addition of CP. More recommendations specific to this study include:

1. Other mechanical properties (such as toughness) could be tested to see the impact that surface roughness could have.

2. This study could be expanded to find the effects of other roughness profile parameters ($R_t$, $R_v$, $R_{sk}$ etc.) or roughness surface parameters ($S_a$, $S_q$, $S_{sk}$, $S_t$, etc) or even 3D roughness parameters on healing efficiency. Also, other parameters such as waviness and lay could be varied to find their effects on healing. New methods of varying such parameters would have to be devised.

3. This study could be performed at different programming and healing temperatures in order to see the combined effect of temperature and surface roughness on the efficiency of self-healing.

If an analytical model for CP-PSMP could be created that would vary these factors, fewer physical tests may be required and more data could be obtained for deeper understanding of the composite.

4. These tests could be repeated for materials that are programmed in tension.
5. A more detailed study of the effects of compressive stresses during healing on efficiency can be attempted. This could extend to samples treated with sandpaper and sample left untreated. This could also be varied with programming and healing temperatures.
References


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