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Healing-on-Demand Polymer Composites Based on Shape Memory Polyurethane Fibers and Polymeric Artificial Muscles

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HEALING-ON-DEMAND POLYMER COMPOSITES BASED ON SHAPE MEMORY POLYURETHANE FIBERS AND POLYMERIC ARTIFICIAL MUSCLES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Mechanical and Industrial Engineering

by

Pengfei Zhang
B.S., Wuhan Institute of Technology, 2009
M.S., University of Louisiana at Lafayette, 2011
August 2015
To my parents & sisters,

my dear wife & son,

and friends
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ABSTRACT

In this dissertation, the healing-on-demand polymer composites based on shape memory polyurethane fibers and artificial muscles are investigated, for understanding and developing a novel healing-on-demand composite so that it would be used for industrial applications that could heal structural-length scale damage and leaking autonomously, repeatedly, efficiently, timely, and molecularly. Firstly, the structural relaxation behavior of shape memory polyurethane (SMPU) fiber was studied by theoretical analysis and experimental test. Then, a self-healing composite based on cold-drawn short SMPU fiber was prepared and tested for evaluating its crack-healing performance. After that, polymer artificial muscle based healing-on-demand composite was developed and characterized. Based on the systematic research results, the study on fishing line artificial muscle reinforced composite for impact mitigation and on-demand damage healing was conducted. Future studies to grow this research area are discussed.
CHAPTER 1    INTRODUCTION

This dissertation consists of seven chapters. The chapters from second to sixth are based on papers that have been published, or are under review, or are to be submitted to peer reviewed journals. In this introduction chapter, it presents the motivation and objectives of the studies that have been carried out. Eventually, it outlines the dissertation structure. The work in each chapter is solely independent, but proceeding in an orderly way and step by step with the aim of achieving final objective of this study. All chapters, except this introductory one, document the research results of the Ph.D. candidate under the direction of the candidate’s advisor as well as his committee members.

1.1 Motivation

Polymer composite materials have been widely used in industrial areas, such as automobile industry, aerospace industry, oil & gas industry, and sport industry. Taking the example of energy storage and transportation in oil & gas industry, polymer composite materials are used in the applications of pipeline, pressure vessel, offshore oil drilling platform, riser, casing, etc., primarily due to their high specific strength/stiffness and corrosion resistance. Nevertheless, excessive pressure and accidental loading might cause the leakage of explosive gases such as natural gas. If not taking care of in situ and in time, the leaked gas may further cause violent explosion, just like the tragedy accidents such as Gulf Oil Spill [1] and natural gas pipeline explosion in San Francisco, California [2]. If the pipeline or storage tank could self-detect any leaking or damage and heal the damage autonomously through certain help, the environmental disaster, the violent explosion, and the loss of lives in the Gulf of Mexico and San Francisco would have been avoided.

1.2 Objectives

The purpose of this study is to understand and develop a novel healing-on-demand composite so that it would be used for industrial applications that would heal structural-length scale damage and leaking autonomously, repeatedly, efficiently, timely, and molecularly. With the proposed close-then-heal (CTH) scheme [3, 4], the healing-on-demand composite materials are based on shape memory polyurethane (SMPU) fibers and polymer artificial muscles.
1.3 Dissertation Outline

The study in the dissertation proceeds step by step, advancing in an orderly way by investigating structural relaxation behavior of SMPU fiber firstly, then short SMPU fiber reinforced self-healing composite, and then polymer artificial muscle based healing-on-demand composite as well as polymer artificial muscle from SMPU fibers. A brief summary of the content of each chapter is presented as follows.

In chapter 2, literatures in past decade about healing-on-demand polymers and polymer composites were surveyed from aspects of molecular behavior, modeling, and experimental achievement.

In chapter 3, the structural relaxation behavior of strain hardened shape memory polymer fibers for self-healing applications was investigated. The shape-memory polyurethane (SMPU) fibers were strain hardened by cold-drawing programming (CDP) process. The programmed fibers were experimentally studied on the physical and thermomechanical properties. Structural relaxation, which determines shape memory capability of the SMP fibers, is quantified by conformational entropy change. Based on the entanglement tube theory and reptation theory, the entropic force is derived as a “bridge” to link the stress relaxation and structural relaxation, and thus structural relaxation can be evaluated by stress relaxation.

In chapter 4, a new healing-on-demand composite based on polymer artificial muscle was prepared and characterized. The composite consists of polymer artificial muscle made of commercial fishing line, thermoset host, and thermoplastic particle. Three-point bending damage to the beam sample can be self-healed even at a constrained boundary condition upon local heating, by following the close-then-heal (CTH) procedure.

In chapter 5, a 2-D fishing line artificial muscle reinforced composite was prepared for impact mitigation and on-demand damage healing. The impact response was monitored by strain gages. Three-point bending was performed on impact/non-impact damaged samples to initiate large scale cracks. The multicracks were efficiently closed and healed by the 2-D artificial muscle grid skeleton and dispersed short thermoplastic fibers.

Chapter 6 summarizes the main achievements of the study, along with discussion on potential topics for future work.
In Appendix I, the study on a self-healing particulate composite reinforced with strain hardened short shape memory polymer fibers is added here. The work in this part is based, furthermore, on the previous work in Chapter 3. A particulate composite dispersed with thermoplastic particles and strain hardened short shape memory polymer fibers was prepared to evaluate its ability to repeatedly heal wide-opened cracks per the two-step close-then-heal (CTH) self-healing scheme. A two-step coating approach was used to enhance the shape fixity and workability of the cold-drawn programmed short polyurethane fibers. The relationship between recovery-stress and recovery-strain was experimentally determined by partially constrained shape recovery test. Notched beam specimens were prepared and fracture-healing was conducted up to five cycles.

In Appendix II and III, the copyright permissions are attached for reference.
CHAPTER 2     LITERATURE REVIEW

2.1    General

Since the discovery by Bayer and his co-workers in 1937, polyurethane (PU) has been widely used for various applications, such as biomaterials,\[5\] textiles and sensors,\[6, 7\] and coating materials.\[8\] The linear chain segmented block PU composes of soft segment and hard segment phases, similar to spider silk, \[9\] which defines its stimuli-responsive functionality. The soft segment phase contributes high ductility and elongation at break; on the other hand, the hydrogen-bonded hard segment phase plays a role in enhancing mechanical strength.\[7, 10-12\] Recently, Hu’s group has done considerable works on shape-memory polyurethane (SMPU) fibers for non-structural applications.\[6, 7, 13\] They found that the SMPU fibers exhibit a good shape memory capability with high recovery efficiency and ductility. Because of the good strain recovery ability and high ductility, the SMPU fibers have potential to close macro-cracks such as damage by impact, if their recovery stress can be improved through ways such as cold-programming.\[14, 15\] For instance, when the fibers are embedded into a host structure which is damaged by external force, constrained shape recovery of the fibers may lead to closure of the macro-cracks in the polymer matrix by thermal stimulus. Such self-healing applications in closing macro-cracks have been studied by Li’s group.\[9, 16, 17\] In a recent study,\[17\] SMPU fibers were cold-drawn to 100% strain, and 9.9% by volume of such unidirectional fibers were embedded in an epoxy matrix. The beam specimens, with length of 177.8 mm, width of 12.7 mm, and thickness of 5.0 mm, were pre-fabricated with a through thickness crack having a width of 0.15 mm. The results show that the fibers narrowed the crack to 0.02 mm by soaking at 80°C for 20 minutes. It also shows that the healing efficiency, which is defined as the tensile strength of the healed specimen over that of the original undamaged specimen, is still 54% after 7 cycles of fracture/healing. From these results obtained by Li’s group, the self-healing ability of SMPU fibers is effective even after cyclic damages. However, the previous studies were conducted in a short-time scale such as within several days of cold-drawing programming. The self-healing ability in long-time scale, such as tens of years, is unknown. This is a critical question because engineering structures are usually designed to last tens of years. It is desired to know if the SMPU fibers still possess the crack-closure capability or not after hibernation in the polymer matrix for many years.
Like bulk shape memory polymer, semi-crystalline SMPU fiber does not have shape memory capability without programming. The microstructures of SMPU fiber can be treated as in an equilibrium configuration before programming, although slight molecular orientation may exist due to melt-spinning process. Meanwhile, the molecular motion and segmental rotation are hindered by intra-molecular and inter-molecular constraints. Once cold-programmed, the fibers are deformed beyond yielding, molecular chains subsequently align and reorient along the loading axis, and so do the segments. Such a programming process leads to high strain-induced crystallinity (SIC) in the soft phase of fibers at room temperature, as well as to the reorganization of the hard segment phase.\[14, 18, 19\] The change in fiber microstructure, induced by cold-drawn programming (CDP) process, results in change in conformational entropy of the system. The critical temperature (referred to as glass transition temperature of the soft segment domain, $T_g$) of the SMPU fibers plays a key role in the stimulus of shape memory effect.\[15\] Upon heating to its transition temperature, the molecular mobility increases and the orientation of molecular chains tend to be randomness, and additionally, the less perfect crystals melt, accompanied by an increase in the conformational entropy. The increase in entropy creates the driving force for shape recovery.\[20\] It is an autonomous process for molecules to recover from non-equilibrium to equilibrium states. Consequently, the programming process is necessary to create a non-equilibrium configuration and enable them to have shape recovery capability.\[15\] However, if the SMPU fibers relax from the programming created non-equilibrium configuration to equilibrium configuration, they will lose the crack closing ability. Therefore, it is highly desired to study the structural relaxation behavior in a time scale of tens of years in order to investigate the on-demand healing ability of SMPU fibers after many years of frozen condition.

The structural relaxation mechanism has been studied for decades, see for example Li and Xu,\[15\] Narayanaswamy,\[21\] Scherer,\[22, 23\] Rekhson,\[24\] Nguyen et al.,\[25\] and Grassia and D’Amore.\[26\] The basic scenario of structural relaxation in these examples is the material’s response corresponding to a temperature jump. Phenomenologically, the evolutions of refractive index and/or volume relaxation (others may refer to the change in density with time) are two experimental methods to investigate the structural relaxation.\[21, 23, 26\] However, these methods are limited in carrying out the structural relaxation test on SMPU fibers because temperature rising may cause shape recovery of the fibers during test.
Stress relaxation has been conducted to investigate the behavior of structural relaxation of amorphous hydrogenated carbon films by Lejeune et al.[27] The study showed that the structure relaxed from a lower disorder state to a strong disorder state. At lower disorder configuration, the internal stress increased along with the structural evolution, whereas in the case of strong disorder configuration, the stress relaxed along with the structural relaxation. This study provides a smart idea to correlate the stress relaxation with structural relaxation. For SMPU fibers, the CDP process enables them to obtain high inner stress (i.e., back stress).[14] The molecular chain alignment and segmental reorientation during the CDP process reduce the conformational entropy and store back stress. Because the back stress is a growing function of energy input during programming, it is envisioned that the recovery stress, which is a portion of the back stress, depends on the way that the programming is conducted. In the case of self-healing application, the SMPU fiber is embedded in a polymer matrix, and its temporary shape is fixed by the surrounding matrix. The stored back stress undergoes stress relaxation analogous to the stress relaxation behavior with a fixed strain under lab condition.[17] Upon heating, the increase in conformational entropy provides the driving force (i.e., released back stress) for recovering the permanent shape of the SMPU fiber, thus exhibiting crack-closing effect on matrix materials. However, for most engineering structures, they are designed to last for tens of years. Therefore, the embedded SMPU fibers are required to be responsible for closing cracks anytime during service, i.e., to have long-term shape memory functionality. Because long-term shape memory is determined by structural relaxation, and structural relaxation of SMPU fibers is difficult to be determined experimentally, it is highly desired to evaluate structural relaxation in terms of stress relaxation, which is experimentally much convenient.

The Adam-Gibbs equation has been used in the analysis of structural relaxation.[22] In the expression of Adam-Gibbs equation, the structural relaxation time is a function of conformational entropy. Based on this theoretical statement, the evolution of structure is highly related to the conformational entropy change. The microstructure of programmed SMPU fibers relaxes from ordered state to disordered state, associated with increase in conformational entropy. Simon and Ploehn have developed an expression for entropic force by neglecting the intermolecular interactions under the rubber elasticity theory.[28] The expression showed that the entropic force contributes to the strand conformational entropy. In addition, they argued that the linear momentum is conserved in the strands thus obtaining a total force expression which is
zero by using entanglement tube model. The force system acting on strands includes cohesive force, entropic force, and frictional force. The cohesive force is the result of applied force on axial strands per unit area. The frictional force is linearly proportional to the velocity of the chain reptating through a junction. From a proposed reptation model,[29] the velocity of the chain reptating in the cross-linked network was derived as a function of the applied force. Because of the balance of the total force system, the entropic force is also a functional of the applied force. Thus the conformational entropy change could be expressed in a form including a term of applied force. As stated above, the structural relaxation accompanies with the conformational entropy change. Therefore, the structural relaxation could be linked with stress relaxation by a factor of conformational entropy change.

Damage-healing of polymer composite materials has been a topic of intensive research for about two decades [30-35]. Basically, healing can be divided into two categories. One is based on incorporation of external healing agent (extrinsic); the other is intrinsic healing by polymer itself. For incorporation of external healing agent, the agent can be liquid [36, 37] or solid [38, 39]. While the solid agent such as thermoplastic particles can be directly dispersed in a polymer matrix [38-41], liquid healing agent can be stored and released on-demand through various approaches such as microcapsules [42, 43], hollow fibers [44, 45], and biomimetic microvascular network [46, 47]. For intrinsic healing systems, they include polymers with thermally reversible covalent bond (TRCB) [48], ionomer [49], hydrogen bond [50], etc. Self-healing per shape memory effect of shape memory polymer matrix has also been intensively studied [20, 40, 41, 51-57]. This is a fast growing area with ample supply of literatures.

Neuser et al [58] and Kirkby et al [59, 60] proposed a very smart idea - a combination of microcapsule and shape memory alloy (SMA) wire for healing cracks in conventional polymer such as epoxy. It has been demonstrated that SMA helped the self-healing process and improved the healing efficiency. In their research, the cracks studied were in micro-length scale (about 150µm), which were introduced in tapered double cantilever beam (TDCB) specimens. Based on the description in [58-60], it is seen that the SMA wires have very low interfacial bonding strength with the epoxy matrix, as evidenced by the clamps and knots used to facilitate transfer of the recovery force from the SMA wires to the epoxy matrix.
Continuous shape memory polyurethane (SMPU) fiber has recently been applied to polymer composite for healing macroscopic damage [9, 16, 17]. The scheme of crack healing by SMPU fiber is described as following. The fiber is first programmed by cold-drawing prior to being embedded into polymer composite. The non-equilibrium structure, created by the programming method, provides potential driving force for shape recovery [15, 61]. Once the composite is damaged by external loads, crack is initiated and even propagates to a macroscopic scale. To heal the crack, the composite is heated above the glass transition temperature of the SMPU fiber, under which the shape memory effect of the reinforcing continuous SMPU fiber is activated, leading to fiber strain recovery. Because of the constraint by the surrounding matrix, the shrinkage of the embedded SMPU fiber is not free, bringing the cracked matrix to proximity. Further heating leads to melting of the incorporated thermoplastic particles. The molten thermoplastic flows into the narrowed crack by capillary force and diffuses into the fractured matrix by concentration gradient. The crack is then healed at molecular-length scale when the composite is cooled down to below the melting temperature of the thermoplastic particles. This proposed healing scheme is called close-then-heal (CTH) [3, 4]. One may argue that if the crack is wide-opened, one can directly inject adhesive into the crack, thus the CTH is not needed. This may be true for some applications but may not be the case for some others. For example, for laminated composite under low velocity impact, the damage mode may include matrix dominated damage such as matrix cracking and delamination. However, these damage modes are inside or on the back surface of the laminate, i.e., invisible and inaccessible. Therefore, directly injecting adhesive in the crack is prohibited.

In a recent study, the long-term structural behavior of strain hardened SMPU fibers has been evaluated [61]. It is found that the cold-drawing programmed fibers still exhibit good shape memory ability even after 13 years of hibernation in polymer composite. This result, theoretically, ensures the long-term performance of programmed SMPU fibers in engineering structures for self-healing applications.

There is no doubt that fibers perpendicular to the crack surface have the highest crack closing efficiency. Therefore, in our previous studies, all the fibers were aligned in the direction perpendicular to the artificially created crack [9, 16, 17]. In actual structures, however, a certain loading is unknown or unpredictable such as impact loading. Consequently, the crack location and orientation are also not known during the manufacturing process. For this type of random
cracks, aligning fibers in one direction only is not a good strategy. It is better to align fibers in three dimensions (3-D). In addition to 3-D woven fabric, short fibers are a choice. Therefore, the focus of this study is on short SMPU fibers for self-healing.

There are several challenges using short SMPU fibers. One is the low shape fixity of cold-drawn SMPU fibers. In a previous study, the shape fixity of cold-drawing programmed SMPU fibers was 33% [61]. This number is even lower than cold-compression programmed thermosetting SMPs [15]. To achieve higher shape fixity, one possible way is to coat the programmed SMPU fiber with fixing agents. Hence, some sorts of fixing agents need to be studied. The other challenge is the fabrication of programmed short SMPU fiber reinforced composite. Without a hard shell, short SMPU fibers tend to cluster and entangle together. Again, coating by a fixing agent is necessary.

One issue with the close-then-heal self-healing scheme is that, during the crack closing process, the recovery stress reduces as the recovery strain increases. Because the recovery stress is the driving force to close the crack, it is desired to know the change of the recovery stress with recovery strain. If the recovery force reduces to a value lower than the required force for narrowing a crack and maintaining the narrowed crack width, the programmed SMPU fiber will not be able to achieve the crack closing purpose. However, this type of study is rare in the open literature, particularly for cold-drawing programmed SMPU fibers coated with fixing agent.

Also, for short fiber reinforced composite, the fiber length plays an important role in mechanical properties [62-64]. However, it is not clear how the fiber length affects the self-healing efficiency.

Healing-on-demand materials are referred to materials which can heal damage induced cracks by themselves in time and in-situ. Therefore, healing-on-demand material exhibits the capability of need-based healing and recovery of functionality using resources intrinsically or extrinsically. It is noted that healing-on-demand does not mean autonomous healing. It means that with minimal external help, healing can be triggered when needed; it then proceeds in an autonomous manner. For all polymer compo-sites, the ineluctable damage and fracture can lead to serious shortening of service life. Bio-inspiration has played an important role in developing new crack-healing strategies to improve their durability during service. [33, 35, 65, 66] Healing-
on-demand polymers and polymer composites are the state-of-the-art devices smart materials as a result of the material design.

Engineering polymers are designed for a specific service life. With incidental damage or degradation over time, the lifespan tends to be shortened. Inspired by biological systems on prolonging service life, the development of polymeric materials that can heal by themselves has existed for decades. Healing-on-demand polymers include ionomer [67], organometallic/metallosupero-molecular polymer [68, 69], mendomer [70-73], rubber [74-76], polymer gel [77-80], organogel [81, 82], metallo-gel [83], and hydrogel [84-90]. The approaches for triggering healing-on-demand include extrinsic stimuli such as mechanical damage, chemical stimuli, thermal treatment, pH, water, photo, sonication, and electrical treatment, as well as intrinsic stimuli like labile bonds, fusion, reversible dissociation-association, covalent bonds, host-guest interaction, and metallo/ligand complexation. In some cases, both extrinsic and intrinsic stimuli are involved.

Healing-on-demand polymer composites have recently been focused on areas from structural composites to functional coatings against degradation, damage, and failure during service. Approaches to develop smart polymer composites that can heal themselves and prolong service lifespan are inspired by biological systems, like wound healing processes in human skin. The on-demand stimulus for self-healing response may be damages from internal or external means. After the damage, repair process is triggered autonomously or partially autonomously within a timescale which depends on the type of self-healing methods used. Heretofore, the approaches for self-healing systems are capsule based [42], hollow fiber based [37], vascular based [91], shape memory based [3], and others. For the capsule based, healing agents are encapsulated into capsules and are released to cracks upon mechanical damage. While in the case of hollow fiber based, healing agents are stored in hollow fibers like hollow glass fibers or hollow polymer fibers and are released to cracks after damage. Likewise, in the case of vascular based, healing agents are stored in vasculuses and are released to crack sites after crack is created. But in the case of shape memory based, polymer composites are programmed to have shape memory ability before use and cracks are closed by constrained shape recovery upon thermal treatment. Unlike the first four methods, the fifth includes those which have not been studied systematically by scientists and engineers for healing-on-demand polymer composites. Even though the self-healing mechanisms between them are different, the common theme is that multi-
functional healing agents are incorporated into polymer composite matrix or structures. Once damage is created, the healing-on-demand behavior through embedded healing agents is activated by external stimulus, such as photo, pH, water, thermal treatment, etc.

As proposed by Li and John [20], Li and Nettles[3], and Li and Uppu [4], macrocracks due to external loading can be healed by a close-then-heal (CTH) method, inspired by surgical aspect on skin cut. The crack was first closed due to the on-demand shape memory behavior of the matrix under thermal activation. Then, at the healing temperature, the dispersed thermoplastic healing agents were melted and filled in the narrowed crack, establishing physical entanglements among molecules by diffusion and randomization. The crack was healed after the composite was cooled down to room temperature. While healing of cracks in shape memory polymer (SMP) matrix has been successful, the challenge is how to heal cracks in conventional thermosetting polymers which do not have sufficient shape memory capability or do not have any shape memory capability. One way is to add shape memory fibers to the matrix, similar to embedded sutures when doctor stitches wound in human skin [16, 17, 61, 92, 93]. However, one challenge is the low recovery force of SMP fibers, which limits the ability to heal wider cracks, particularly when the structural components are constrained in the boundary (free shape recovery is not allowed). Parallel to this SMP fiber approach, Kirkby et al. have investigated the influence of shape memory alloy (SMA) wires on the self-healing properties by combining SMA wires with polymer matrix. [59, 60] The challenge for SMA wire is the poor interfacial bonding between the metal wire and the host polymer as well as the comparatively low ductility of SMA wire, which limits its capability in crack close. Also, SMA wires face other challenges such as higher cost and poor processability.

In all animals and humans, muscle is a soft tissue that consists of a part of the musculoskeletal system; and it is the only component of the system that enables our body to move through contracting and even fast contracting. Analogous to natural muscle, polymer artificial muscle from fishing line could contract fast and deliver large strokes from inexpensive high-strength polymers fibers, such as commercial fishing lines. [94, 95] In addition, fishing lines are low cost and easily available. Also, muscles made of fishing lines are quite repeatable. If fishing line muscle is embedded in a composite, just as natural muscle in animal or human body, it will be able to close cracks in the polymer matrix, similar to the SMP fiber or SMA wire, because contacting is the fundamental requirement for embedded fibers to close wide-opened
cracks, according to the CTH scheme proposed by Li et al. [3, 20] When thermoplastic healing agent is incorporated in the polymer matrix, the system could heal any damage or degradation on-demand at molecular length scale.

Figure 2.1 shows a concept of healing-on-demand, through which the inspection and maintenance techniques have been developed to prolong service life of engineering polymer materials. In this review, we will cover different approaches for trigging the healing ability of polymers and polymer composites on-demand emerged over the past decade, especially the shape-memory based healing-on-demand approach.

![Figure 2.1 Conceptual healing-on-demand on prolonging material service life. As damage occurs, engineering polymer suffers from function degradation over service life. Lower bound of function triggers bio-inspired healing and recovers its functionality to initial status repeatedly for prolonging service life.](image)

2.2 Healing-on-demand Polymer

2.2.1 Healing-on-Demand Ionomer

The healing-on-demand ionomers have been reported either in terms of pure ionomer of poly(ethylene-co-methacrylic acid)(EMAA) or in the form of ionomer blends of EMAA and functionalized elastomers (epoxidation natural rubber (ENR) and polyisoprene (PISP)). Ionomers is a class of copolymer incorporating ionic groups, forming ionic interactions or aggregates in
their structure. Below the order-disorder transition (Ti) temperature, ionomers are solid. While upon temperature change, the structure of ionomer may rearrange itself over time due to the ionic interactions or aggregates.[49, 67, 96-98]

2.2.2 Healing-on-Demand Organometallic/Metallosupramolecular Polymer

It was reported by Williams[68] and coworkers that the organometallic polymer was successfully developed through a series of synthesis by implementing compounds formed between N-heterocyclic carbenes (NHCs) and transition metals from a molecular level. The synthesis of such polymer was challenged as pointed out in their work because of the requirement for the synthesis of appropriately functionalized multitopic NHCs poised for polymerization. Due to the transition metals and structurally dynamic equilibrium, the synthetic organometallic polymer was an electrically conductive and self-healing material. The created microcrack results in inherent electrical resistance change (i.e., high-resistance/low-current). As a result, the voltage bias generates localized heat at the microcrack site. In turn, local heat overcomes the fracture surface kinetic barriers, leading to reformation of the broken NHCs-metal bonds. Consequently, the system is electrically driven back to its original state (i.e., low-resistance/high-current) and the microcrack is healed.

2.2.3 Healing-on-Demand Mendomer

Mendomers are a group of polymers which are mendable on-demand by extrinsic or intrinsic stimulus. Park[70] and coworkers reported a mendomer 401 based on thermally reversible Diels-Alder (DA) reaction, where separated dicyclopentadiene units could be re-bonded to one unit upon thermal treatment. At the healing temperature range of 70-100°C, the fractured surface was healed within minutes. A repeatable mendomer based on thermoreversible DA reactions was reported by Syrett et al [99] Linear and star MMA polymers bearing DA adducts within their macromolecular backbone were synthesized. And the DA adduct of 9-anthracenemethanol was suggested to be incorporated, which gave the DA linkage higher thermal stability and made the DA reaction highly efficient. It was pointed out that the fractured mendomer material exhibited 83% recovery of its original strength upon heating, and such healing event could be repeated. Further, Zeng [100] and coworkers reported a bio-based furan mendomer based on room temperature reversible DA reaction, A furan polymer of poly(2,5-furandimethylene succinate)/M₂ (i.e., a bismaleimide) was prepared by DA reaction between
poly(2,5-furandimethylene succinate) and M₂. Once cracks occurred, the fractured surfaces healed well by bismaleimide solutions or solvent based on the reversible DA reaction between furan and maleimide groups at room temperature without external stimulus. Also, the healing event was repeatable.

2.2.4 Healing-on-Demand Rubber

The self-healing behavior of ENR and the corresponding unfunctionalized rubber PISP was firstly examined by Rahman et al.[74], who used the dicumyl peroxide as cross-linking agent for rubbers. Among the results from the examined rubbers, it was found that the 50 mol % epoxidized ENR exhibited the highest self-healing efficiency after treated at 60°C for half an hour, which was 70% of the virgin strength recovered from T-peel mode. The damage-induced self-healing behavior of the rubbers was also investigated in their research work. It showed that the ENR50 sample completely closed the hole at the damage site following the elastic recovery of high deformation imposed by bullet. And the hole was healed completely due to the high level of interdiffusion activated by damage-induced thermal energy. The self-healing behavior indicated that the level of epoxidation played a significant role in the healing-on-demand rubbers.

2.2.5 Healing-on-Demand Thermoset Polymer

Cross-linked nature leads to the challenge on recycling at the end of thermoset polymer life cycle. Unlike thermoplastics, the cross-linked thermosetting resins can’t be remelted or reshaped because of the decomposition and degradation of the materials at certain temperatures. Herein, Zhang[101] and coworkers reported a thermally healing-on-demand thermoset polymer in order to resolve the issue on recycling of thermosetting materials at the end of life cycle. The thermoset polymer was prepared by the Paal-Knorr reaction of the PK with furfurylamine, where the PK was used as precursor for DA reactions. When the fractured sample was heated over 110°C above its glass-transition temperature, the thermoset polymer became soft because of the opening of the DA adduct, then reactions occurred between the PK-furan and bis-maleimide leading to regeneration of the DA adduct. Upon cooling, the sample recovered its original shape, which is repeatable without any loss in mechanical properties. The uniqueness in this heal-on-demand behavior is its ultrafast self-healing response, such as 5 minutes upon heating (among 110 – 150°C) during healing event.
### 2.2.6 Healing-on-Demand Supramolecular Polymers

Supramolecular polymers are a group of polymers whose monomer repeat units are bonded together by non-covalent bonds, such as coordination, π-π interactions, and hydrogen bonding. Such a healable supramolecular polymer group can be divided into five categories, which are healing-on-demand gel, organogel, metallo-gel, hydrogel, and supramolecular elastomer. [77, 84, 89, 102-104]

### 2.3 Healing-on-demand Polymer Composites

Healing-on-demand polymer composites have recently been focused on areas from structural composites to functional coatings against degradation, damage, and failure during service. Approaches to develop smart polymer composites that can heal themselves and prolong service lifespan are inspired by biological systems, like wound healing processes. The on-demand stimulus for self-healing response initially is damages from internal or external means. After the damage, repair process is triggered autonomously or partially autonomously within a timescale which depends on the type of self-healing methods used. To date, the self-healing systems can be classified into five groups based on the on-demand methods for damage healing, i.e., capsule based, hollow fiber based, vascular based, shape memory based, and other systems, as shown in Figure 2.2. Unlike the first four groups, the fifth group includes those methods which have not been studied systematically by scientists and engineers for healing-on-demand polymer composites.

#### 2.3.1 Capsule Based Healing on-Demand Approach

In this healing-on-demand system, the polymer composites incorporate the use of capsules filled with liquid healant or liquid crosslinking hardeners, which are uniformly distributed in the matrix materials. Upon damages, the capsules are ruptured by propagating micro-cracks in the composite. Then loaded healant is released from the capsules, filling propagated micro-cracks via capillary action, and comes into contact with crosslinking hardeners; or released liquid crosslinking hardener comes into contact with embedded healant to initiate polymerization at the micro-crack site, leading to healing-on-demand events. In the following sections, microcapsule-based and nanocapsule-based healing-on-demand events will be covered from published smart polymer composite applications.
Figure 2.2 Approaches for healing-on-demand polymer composites: (1) capsule based (figure is from reference [42]): healing agents are encapsulated into capsules and are released to cracks upon mechanical damage; (2) hollow fiber based (figure is from reference [37]): healing agents are stored in hollow fibers like hollow glass fibers or hollow polymer fibers and are released to cracks after damage; (3) vascular based (figure is from reference [91]): healing agents are stored in vascules and are released to crack sites after crack is created; (4) shape memory based (reference is from [3]): polymer composites are programmed to have shape memory ability before use and cracks are closed by constrained shape recovery upon thermal treatment; (5) other healing-on-demand methods which are not studied systematically to date.

2.3.2 Hollow Fiber Based Healing on-Demand Approach

The concept of hollow fiber based technique was investigated by Bleay [37] et al. for repair of delamination in polymer composites. They explained such a concept further by three approaches, i.e., one-part liquid healing agents, two-part liquid healing agents and liquid hardener, and two-part liquid healing agents and encapsulated catalyst. After this pioneer research, a number of publications have been reported on the hollow fiber system in the healing-
on-demand applications for prolonging polymer composite service life. Based on the hollow fiber material, it can be categorized into two groups, which are hollow glass fiber (HGF) based and hollow polymer fiber (HPF) based. The following subsections will discuss HGF and HPF based healing-on-demand, respectively.

2.3.3 Vascular Based Healing on-Demand Approach

The advantage of vascular based healing-on-demand polymer composites is that it provides the self-healing ability for larger damage volume and multiple self-healing cycles. This is because of the external reservoirs containing healing agents and corresponding hardeners. The contents of the reservoir are delivered to damage sites through the embedded vascular networks. Macrovascular based smart composite could deliver more contents to the damage sites thus obtain the healing ability for macrocracks; whereas in the case of microvascular based, it has the ability for healing microcracks.

2.3.4 Shape Memory Based Healing on-Demand Approach

From the above reviews, it is seen that some healing schemes need external help, i.e., bring fractured parts in contact manually before healing occurs. While this is legitimate in lab scale specimens, it represents one of the greatest challenges in real world structures. This is because in large scale structures, fractured structural elements cannot be brought in contact manually. If they are forced together, it may create new damages. Therefore, new ideas are needed. [105-107]

It is a straightforward idea to use shape memory effect for crack closure because crack can be treated as a type of pseudo plastic deformation, and shape memory effect can restore the original shape upon external stimuli. However, the ability to close crack depends on (1) the level of programming and (2) the constraint during shape recovery. For some shape memory effect based applications such as coating, the system uses scratching, indentation, or cracking itself as \textit{ad hoc} programming. Clearly, if there is no significant barrier to resist the shape recovery, the crack can be closed if the shape recovery ratio is close to 100\%. However, if there is a significant barrier to resist free shape recovery, the crack cannot be closed. Therefore, pre-programming is usually required and is a better way for crack closure as it can be designed to consider the level of barrier to resist shape recovery and the shape recovery ratio.
In their review paper, Hu et al.[108] clearly defined two types of self-healing schemes based on shape memory effect. One is free shape recovery and the other is constrained shape recovery. Most recently, Yougoubare and Pang [109] compared the two popular shape memory effect based crack closure schemes. One is shape memory assisted self-healing (SMASH) proposed by Rodriguez et al.[55] and Luo and Mather [56], and the other is close-then-heal (CTH, firstly close the crack through confined expansion of the SMP matrix, and then heal it by embedded thermoplastic particles), which was proposed by Li et al.[20] Based on Yougoubare and Pang, the fundamental difference between SMASH and CTH is that SMASH targets non-load carrying materials, no constraint during shape recovery, no pre-programming, and usually suitable for microcracks and small indentation; on the other hand, CTH focuses on load carrying material, considers constrained shape recovery, needs pre-programming depending on the width of crack to be closed, and suitable for wide-opened crack and large indentation. It must be emphasized that shape memory effect does not heal the material. It only narrows or closes the crack. In order to heal the crack, it must be combined with other intrinsic or extrinsic healing schemes such as shape memory polymer with self-healing capability or a combination of shape memory polymer with external healing agent.

2.3.5 Other Healing on-Demand Composites

Except for the above reviewed healing-on-demand polymer composites, which were studied systematically during the past decade, some other smart polymer composites were also investigated by the research community. Even though the self-healing mechanisms between them are different, the common theme is that multi-functional healing agents are incorporated into polymer composite matrix or structures. Once damage is created, the healing-on-demand behavior through embedded healing agents is activated by external stimulus, such as photo, pH, water, thermal treatment, etc. The following topics cover those techniques for intriguing healing-on-demand abilities in smart polymer composites.[110-114].
CHAPTER 3     STRUCTURAL RELAXATION BEHAVIOR OF STRAIN HARDENED SHAPE MEMORY POLYMER FIBERS FOR SELF-HEALING APPLICATIONS†

3.1 Introduction

In this chapter, per existing models, a new model is developed to link the structural relaxation with stress relaxation. The shape memory or crack-closing capability after years of hibernation is predicted. Experimental investigation on cold-drawn programmed SMPU fibers is conducted, including mechanical behaviors, thermomechanical behavior, thermal properties by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), and molecular structures by Fourier transform infrared spectroscopy (FT-IR). Stress relaxation behavior of the SMPU fibers is studied experimentally at a series of temperatures, 8°C, 25°C, 44°C, 65°C, and 85°C. The long-term stress relaxation behavior is predicted by time-temperature superposition principal (TTSP) on such short-term stress relaxation.

3.2 Theoretical Background

3.2.1 Molecular-level Force Model

Based on a study of viscoelastic properties of coiling polymers[115], Simon and Ploehn proposed a force model to investigate the intrinsic relationship between a force system, including cohesive force, entropic force, and frictional force.[28] Molecular-level analysis on polymer chain was based on an entanglement tube model. It assumed that a polymer chain was divided into strands by entanglement junctions. In the place of the entanglement junctions, the chain motion can only undergo uniaxial reptation, whereas in the other places, the polymer chains can rotate and vibrate even move in lateral directions. The applied forces acting on the strands cause the polymer chain to slide along the entanglement tube. The reallocation of strands leads to a time-dependent viscoelastic response. In the material, the linear momentum of all strands at the place of junctions, governing the mechanical behavior, is conserved, thus the force relationship was derived

\[ \sum F = 0 \]  

In the force system, the cohesive force represents the van der Waals attraction, pulling chain segments back towards the equilibrium state. Based on a heuristic model, this force was determined by

\[
\tilde{F}^C(t) = \frac{\sigma_{zz}(t)}{n} \tilde{e}_i
\]  

(3.2)

here \(\sigma_{zz}(t)\) is the remained time-dependent uniaxial stress, \(\tilde{e}_i\) is the unit vector of the uniaxial elongation, and \(n\) is the number of axial strands per unit area, which was determined by Lin as follows [116]

\[
n = \frac{\rho N_A}{M_e} \left( C_\infty \frac{M_e}{m} r^2 \right)^{1/2}
\]  

(3.3)

where \(\rho\) is the density of polyurethane at the temperature \(T\), \(N_A\) is the Avogadro number, \(C_\infty = r^2 / (a^2 \bar{N})\) is a characteristic ratio from 5 to about 10, \((\bar{N} = Nn\) is the number of monomer in the chain, \(N\) is the number of strands in a chain and \(n\) is the number of monomer per strand, and \(a\) is the length of monomer), [117-119] \(r\) is the end-to-end distance of polymer chain, [120] \(m\) is the average mass of main chain chemical bonds, [120] and \(M_e\) is the entanglement molecular weight defined as

\[
M_e = \frac{4\rho RT}{5G_N}
\]  

(3.4)

where \(R\) is the gas constant, and \(G_N\) is the plateau modulus determined from the DMA test results.

The frictional force resists the chain motion through entanglement junctions, thus dissipating stored strain energy to thermal energy. As assumed, this force is linearly proportional to the chain velocity \(u(t)\) reptating through the junctions

\[
F^f(t) = -\zeta u(t)
\]  

(3.5)

here \(\zeta\) is the frictional coefficient, which is defined as follows
\[ \zeta = \zeta_0 e^{bf_v} \]  

(3.6)

in which \( \zeta_0 \) and \( b \) are empirical parameters; and \( f_v = f_{v0} + \alpha_g T \) is the free-volume fraction within the entanglement junction, \( \alpha_g \) is the coefficient of thermal expansion (CTE) of polymer, and \( f_{v0} \) is the free-volume fraction at 0 K.

The force system (i.e., cohesive force \( F^C \), frictional force \( F^f \), and entropic force \( F^S \)) is balanced as given in equation (3.1), then the entropic force could be derived in the form of cohesive force and frictional force. Based on the basic thermodynamic equation

\[ dU = TdS - PdV \]  

(3.7)

the entropic force, describing the thermodynamics of polymer chains in an attempt to restoring the equilibrium configuration, can be developed in terms of strand conformational entropy at fixed end-to-end distance \( r \) as

\[ F^S = -T \left( \frac{\partial S}{\partial L} \right)_{T,V,r} \]  

(3.8)

Thus the conformational entropy could be expressed in terms of time-dependent uniaxial stress by a “bridge” of entropic force through equations (3.1), (3.2), (3.5), and (3.8)

\[ \Delta S \bigg|_{T,V,r} = \left[ \frac{\sigma_{zz}(t)}{Tn} - \frac{\zeta}{T} u(t) \right] \Delta l \]  

(3.9)

here \( \Delta l \) is the average displacement of polymer strands in the entanglement tube

\[ \Delta l = \frac{1}{N} \int u(t) dt \]  

(3.10)

### 3.2.2 Reptation Model

As pointed out by Gennes,[29] the reptation theory is useful for the problem of entanglement effects in unlinked molten polymers. The “defects” are only allowed to reptate along the chain with a velocity
\[ u(t) = \frac{dx(t)}{dt} = \frac{\mu ob^2 P(t)}{N^2 a} \]  

(3.11)

Here, \( \mu = D/(k_BT) \) is the defect mobility dependent on the diffusion coefficient \( D \) of the defects along the chain,[121] \( k_B \) is the Boltzmann’s constant,[122] \( P(t) \) is the remained time-dependent force, \( \omega = v/(na) \) is the density of defects per unit length of the extended chain with \( v \) defects within a strand, and the number of defect \( v \) is determined as[116]

\[ v = \left[ \left( C_\infty \frac{M_r r^2}{m} \right)^{0.5} / (C_\infty r) \right]^2 \]  

(3.12)

and the stored length \( b \) is determined as[117]

\[ b = 2p \]  

(3.13)

Here, \( p = C_\infty / 6 \) is the persistence length.

Through the above discussed equations, the conformational entropy change

\[ \Delta S \bigg|_{r,v,r} = \left[ \frac{\sigma_{xx}(t)}{Tn} - \frac{\zeta \mu ob^2 P(t)}{TN^2a} \right] \int \frac{\mu ob^2 P(t)}{NN^2a} \, dt \]  

(3.14)

could eventually be manipulated into a time-dependent equation in terms of material parameters and time-dependent remained stress from the experiment of stress relaxation.

### 3.2.3 Thermodynamics Model

In the scenario of thermodynamics, the entropy tends to be maximized for a system. The maximum conformational entropy[123]

\[ S_C = k_B \ln(\Omega) \]  

(3.15)

where \( \Omega \) is the number of distinguishable configurations. In an equilibrium state, the entropy achieves this maximum value.

According to the statistical mechanical treatment, the entropy of a mixing system (including components \( p \) and \( q \))[124,125]

\[ S_C = -R \left( n_p \ln X_p + n_q \ln X_q \right) \]  

(3.16)

Here, \( R = N_A k_B \) is the gas constant where \( N_A \) is the Avogadro’s number, \( n_i \) (\( i = p \) or \( q \)) represents the number of moles of the \( i \)-th component, and \( X_i \) represents the mole fraction in the mixture.
A fixed junction model of ideal rubbers was applied to derive the entropy change using the law of statistical thermodynamics.[126] In a Cartesian coordinate system, both ends of chains are fixed, allowing one end of the chain being at the origin of the coordinate system and the second end being able to move along the z-axis under an applied stress $\sigma_{zz}$. Let the uniaxial extension ratio be $\lambda$, the change in entropy resulting from the uniaxial extension is

$$\Delta S = -\frac{V\sigma_{zz}\left(\frac{2}{\lambda} + \lambda^2 - 3\right)}{2T\left(\lambda - \frac{1}{\lambda^2}\right)}$$

(3.17)

here $V$ is the volume.

In our case, suppose the configuration of the SMPU fibers after the heat treatment process is in equilibrium state.[13] Thus, due to the extension $\lambda$, the conformational entropy of SMPU fibers at the temporary shape is determined in such way, through equations (3.16) and (3.17)

$$S'_C = S_C + \Delta S$$

(3.18)

### 3.3 Experimental

#### 3.3.1 Materials

Polyurethane was synthesized by using poly(butylene adipate) (PBA, $M_n = 650$) as soft segments, 4'4'-diphenylmethane diisocyanate (MDI) and 1,4-butandiol (BDO) as hard segment. The average formula weight ratio was (MDI+BDO): PBA = 1021: 300. All the chemicals were de-moisturized prior to use. The reaction was conducted in a high-speed mixer at room temperature with nitrogen protection. The obtained polyurethane was further cured in a vacuum oven at 110°C for 12 hours. Then SMPU fiber was prepared using a modified OneShot Extrusion Machine with a spinning speed of 40 m/min. The spinning temperature is 180°C. The non-programmed SMPU fibers have a diameter 0.038 mm, as shown in Figure 3.1 (a), captured by an optical microscope (VanGuard, USA) equipped with a camera (XLI, USA).

#### 3.3.2 Cold-drawing Programming

The SMPU fibers were cyclically loaded at room temperature by using MTS (RT/5, MTS Inc., USA) equipped with a 250 N load cell. Fibers were gripped by aluminum fixtures with a gauge length of 20 mm, and stretched with a displacement rate of 400 m/ min. Fiber bundle was
cold-drawn for five loading cycles and followed by holding at a strain of 80% for half of an hour. In each cycle, the fiber bundle was stretched to 80% of strain and unloaded. In the sixth cycle, the bundle was stretched to 80% of tensile strain and held for 30 minutes (stress relaxation), and then stretched all the way to fracture, in order to determine the tensile strength of the fiber. To ensure the repeatability of the tensile test of programmed PU fibers, five fiber samples were programmed and stretched to its elongation-at-break. Here cyclic cold-drawing was used instead of one time drawing in order to ensure that the fibers have a longer time for structural relaxation so that the shape fixity can be increased. The programmed fiber has a diameter of 0.028 mm, as shown in Figure 3.1 (b). Based on the known transverse dimension and fiber length, the Poisson’s ratio can be determined as 0.33 at room temperature, which is in good agreement with reported data in the literature.

Figure 3.1 Optical microscope images of the SMPU fibers: (a) non-programmed fiber; (b) programmed fiber by 80 % strain.

### 3.3.3 Characterization

Differential scanning calorimetry (PerkinElmer DSC 4000, USA) test was conducted to investigate the thermal properties of the programmed and non-programmed fibers. Fiber samples were knotted and placed in aluminum sample pan. The samples were cooled from 30°C to -70°C at a speed of 20°C/min and scanned from -70°C to 200°C at a ramping rate of 5°C/min. The purging rate of Nitrogen is 30 ml/min. Three cooling and heating cycles were conducted on each sample. It was found that after the first heating cycle the thermal properties of the fiber samples became stabilized. The heat flow plot was derived from the second heating cycle to determine the glass transition temperature ($T_g$) and other thermal properties. Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Scientific, USA) technique was employed to study
the molecular structures of SMPU fibers. Two specimens, i.e., fibers before and after CDP process, were investigated to determine whether this physical process creates any chemical change. A bundle of fibers was prepared as a specimen with a length of 30 mm for DMA test (carried out by RSA III LN2, USA). Air was used as a purging medium. Initial and final temperatures were set as 21°C and 120°C, respectively. Heating rate was 1°C/min, and frequency was 1.0 Hz.

3.4 Results and Discussion

3.4.1 Mechanical Behavior of Programmed SMPU Fiber

Figure 3.2 shows the typical stress-strain curve of the 6th cycle of cold drawing process. From this figure, it is easy to observe that the strength of the programmed fibers has been enhanced considerably, with some sacrifices in elongation. The yield point was determined from a trial-and-error method. The fiber sample was stretched towards a designed stretch ratio and then unloaded to its initial position. In the fiber elastic region, the loading curve would match the unloading curve, whereas in the fiber plastic region the loading curve would mismatch the unloading curve. For the non-programmed fiber, the fiber was stretched to a ratio starting from 1% and unloaded back to the initial position. The second stretching was up to the ratio 1.1% (i.e., strain increment 0.1%) and unloaded.

This loading and unloading process was repeated until mismatch of the load-unloading curves. Then the maximum corresponding tensile stress was determined as yield stress for the non-programmed fibers. For the programmed fibers, it started from 81% then 81.1%, and so on. And the yield stress was obtained in the same way. The non-programmed fiber has a Young’s modulus (or stiffness) of 147 MPa and a yield stress of 5 MPa, whereas in the case of the programmed fiber, it has a Young’s modulus of 700 MPa and a corresponding yield stress of 130 MPa. As for the tensile strength, the non-programmed fiber is about 340 MPa, while the strength of the programmed fibers is as high as 618 MPa. This result is in agreement with previous study by Li and Shojaei.[16]

It is noted that the cold-drawn programmed SMPU fiber is very ductile. As shown in Figure 3.2, it will not fracture until the tensile strain is about 400%. Also, low velocity impact test (supplementary Figure 6 in Li et al.[9]) shows that the SMPU fiber is very tough. Under the same impact energy, the SMPU fiber bundle with a cross sectional area of 0.3 mm^2 did not
fracture, while the carbon fiber bundle with a cross sectional area of 2.4 mm$^2$ fractured. Therefore, the SMPU fibers embedded in thermosetting polymer matrix for closing macro crack would continue to function after the matrix cracks.

A schematic explanation on microstructure changes during cold-drawing programming are shown in Figure 3.3 according to Lee et al.[12] Hard segment is surrounded by soft segment as matrix, undergoing microphase separation and contributing to the thermodynamic incompatibility. The hypothesized microstructure morphology interprets that intermolecular sliding and segments orientation change may occur under the monotonic tension. The activated intermolecular slides result in dissipation of energy during the CDP process. Meanwhile, the alignment of the switching segments (i.e., soft segments) and reorientation of the hard segments, within the period of programming process, result in increase in the initial modulus and subsequent tensile strength.[127,128]
During the CDP process, SMPU fibers were cyclically loaded and unloaded for 5 cycles, as shown in Figure 3.4. A couple of observations can be made. (1) The fibers are strain hardened as evidenced by increase in stress and stiffness corresponding to the same strain. However, the rate of enhancement decreases as the loading cycles increase. This suggests that the strain hardening effect tends to saturate as loading cycles increase. The reason is that the enhancement in mechanical properties is due to the alignment of the molecules in segregated segments and strain induced crystallization, which saturate when they are aligned along the loading direction.

The strain induced crystallization after cold-drawing programming has been validated by small-angle X-ray scattering (SAXS) test,[16] which shows transformation of some hard segment domains to crystals, and by DSC test result,[17] which also shows stress induced crystallization in the hard segment domain. (2) The hysteresis loop in each loading-unloading cycle suggests visco-elastic and visco-plastic behavior of the fibers. The portion of energy stored in the fiber during each cyclic loading becomes back stress which will be partially recovered during the shape recovery process.

For shape-memory materials, shape fixity is a significant parameter.[20] It is given by

$$R_f = \frac{\varepsilon_i}{\varepsilon_p} \times 100$$

(3.19)

where $R_f$ is the shape fixity ratio; $\varepsilon_p$ is the pre-deformation strain, which is the strain at the end of the short-term relaxation (i.e., 30 min) after cyclic loading; $\varepsilon_i$ is the instantaneous strain after the applied load is removed.
Figure 3.5 shows that the shape fixity ratio is a function of time due to the viscoelastic response of the cold-drawing programmed fibers after removal of the external load. The stabilized shape fixity for the one-time cold-stretched SMPU fibers is 23%, whereas in the case of cyclically cold-drawing programmed fibers, it has been increased and maintains at 33%. This is why we used cyclic cold-drawing in our study, instead of one-time cold drawing programming. From the shape fixity result, it is easy to detect the effects of structural reorganization, which is in good agreement with the comments from Scherer.[23]

3.4.2 Thermal Properties

Figure 3.6 shows that the non-programmed fibers have a glass transition temperature ($T_g$) of 12.5°C and hard segment melting temperature ($T_m$) of 185°C. It is worth noting that the dominant component of this SMPU fiber is the crystalline hard segment phase with some less perfect or small sized crystals.

The cyclic loading process (i.e., CDP process) narrows the glass transition region and shifts the $T_g$ to a higher temperature. After five loading cycles, the programmed fiber exhibits a
higher $T_g$ at 28°C. Moreover, the DSC trace shows a stabilized melting temperature at 185°C for the hard segment domain.

![Graph showing shape fixity over time for programmed SMPU fibers](image)

Figure 3.5 Shape fixity for programmed SMPU fibers after one loading cycle and five loading cycles.

3.4.3 Microstructural Properties

This is necessary because the high stress involved during the CDP may cause some changes in chemical bonds such as breaking of a certain chemical bonds. Figure 3.7 presents the infrared spectrum for the non-programmed and programmed fibers which was recorded from 600 cm$^{-1}$ to 4000 cm$^{-1}$. The overall results shown in Figure 3.7 (a) are divided into three groups in Figure 3.7 (b) – (d) to have a better view. Regarding to the Figure 3.7 (a), the absorbances for both fiber samples are mainly observed in the range from 600 cm$^{-1}$ to 1600 cm$^{-1}$, which is similar to the spectra of the PCL.[129] According to Figure 3.7 (b) and (d), no changes in the ranges of 600 cm$^{-1}$ to 1700 cm$^{-1}$ and 2700 cm$^{-1}$ to 4000 cm$^{-1}$. It suggests that the bonds of C-O-C and C=O are stabilized or fixed in their conformational configuration after the CDP process as well as groups of urethane, CH$_2$, and aromatics.[130-132] However, some peaks for the programmed fibers disappear as compared to those for non-programmed fibers, as shown in Figure 3.7 (c). On the other hand, some new peaks form after the CDP process. As suggested by Wang et al.,[130] the peaks disappeared and/or created are results of NCO group vibration and carbon dioxide vibration. Therefore, it ensures that the CDP is a physical process; no chemical changes are involved.
3.4.4 Thermomechanical Behavior of Programmed SMPU Fiber

Stress recovery behavior of the programmed fibers was studied after a short-term stress relaxation process (30 min). Prior to starting the stress recovery testing, the applied load by the load cell during programming was removed, allowing the fixture head back to its original position. In order to compensate for the thermal expansion of fibers during heating process, a pre-strain on fibers was provided, ensuring that they had zero stress immediately before the stress recovery process starts. The pre-strain was determined by a trial-and-error method.[16]

The fiber was gripped by the fixture and maintained the strain constant. Then the fibers were heated from 25°C to 150°C at a rate of 0.35°C/min and the system recorded the force recovered. It is noted that the linear coefficient of thermal expansion (CTE) of the grip (i.e., aluminum) is 23.86×10^{-6}/°C. As compared with the CTE of the SMPU fiber, which is about 11.8×10^{-5}/°C,[133] the dimension change of the grip is considerably small.
Therefore, the effect of thermal expansion of the grip can be ignored. During stress recovery test, the fiber bundle was fixed by the grips in the MTS machine, and free shrinkage is not allowed. Consequently, stress develops, which is the recovery stress. As shown in Figure 3.8, a maximum recovered stress of 11.6 MPa has been obtained after a stress relaxation time of 30 minutes when temperatures are increased from 25°C to 150°C.

The stress recovery rate is distinguished at different temperatures. Technically, the stress recovery is divided into three regions based on their stress recovery rate as shown in Figure 3.8. Based on the thermal properties of the programmed SMPU fibers (Figure 3.6), it shows that the glass transition temperature of the fiber (after five loading cycles) is 28°C. Thus SMPU fibers exhibit stress recovery behavior even at room temperature. The result shows that the recovery rate reduces with time in stages I, and becomes stable in stage II followed by a stabilized stress recovery in stage III with almost zero stress recovery rate. The instantaneous stress recovery rate ($S_r$) is defined as the time derivative of stress.[134] It indicates that the stress recovery rate does not stabilize in the glass transition region, and the stabilized recovery rate is obtained above the glass transition region. It is noted that the stress recovery rate does not necessarily mean the
shape recovery rate. The reason is that the stress recovery rate is also dependent on the stiffness of the fiber at each particular temperature.

Figure 3.8 Schematic representation of stress recovery behavior for programmed SMPU fibers: (a) stress versus temperature; (b) stress versus time including three stages (i.e., I, II, and III).

The ability for SMPU fibers to store energy elastically and dissipate energy is presented in Figure 3.9. As indicated, the fibers in stage I have higher storage modulus and the modulus reduces gradually as temperature increases. This higher modulus leads to a higher stress recovery rate. When the temperature is about 65°C, the storage modulus stabilizes, corresponding to the stabilization of the stress recovery rate in stage II. This might be the result of the softening of the soft segment at temperatures till 65°C and completely softened at this temperature, while the hard segment is the dominant phase in the stress recovery process above the temperature of 65°C and thus results in a stabilized stress recovery rate until the melting of the crystals in the hard segment domain.

3.4.5 Viscoelastic Behavior of SMPU Fiber

SMPU fibers were prepared to investigate the stress relaxation at various temperatures. Stress relaxation testing was carried out on programmed fibers under a series of temperatures: 8°C, 25°C, 44°C, 65°C, and 85°C. The individual relaxation test time was two hours. Figure 3.10 shows the stress relaxation behavior at five different temperatures. In order to predict the long-term structural relaxation behavior of the SMPU fibers, the long-term stress relaxation behavior is needed. The long-term stress relaxation was obtained by a practical and validated time-temperature superposition principle (TTSP).[135-137]
Figure 3.9 DMA results for non-cold-drawn fibers and cold-drawn fibers including storage modulus ($E'$), loss modulus ($E''$), and loss tangent (tan $\delta$).

Figure 3.10 Test results of stress relaxation behaviors of programmed fibers at various temperatures.
Basically for a viscoelastic material with respect to a reference temperature, the stress relaxation is only dependent on time. As pointed out by Ferry,[138] data obtained from a reference temperature can be superimposed on other data taken at different temperatures by shifting along the vertical and/or horizontal axis. It allows shifting data, obtained over short-term stress relaxation process but at different temperatures, to achieve a master curve representing a long-term stress relaxation behavior at the reference temperature. The logarithm of \( \alpha_T \) (i.e., the horizontal shift factor) is determined by the WLF equation[135]

\[
\log(\alpha_T) = \frac{C_1(T - T_0)}{C_2 + T - T_0}
\]  

(3.20)

where \( C_1 \) and \( C_2 \) are constants, \( T_0 \) is the reference temperature (i.e., \( T_0 - T_s = 50^\circ \text{C} \)), and \( T \) is the testing temperature. In order to obtain a smooth master curve, the constants of \( C_1 \) and \( C_2 \) may be varied based on the experimental data at different temperatures.

Arridge discussed the consequent deduction of shift factors in the simple use of time-temperature superposition (TTS).[139] By using the theory of rubber elasticity, it assumed that the vertical shift factor is expressed in the form

\[
\beta_T = C_T \frac{T_0}{T}
\]  

(3.21)

here \( C_T = (d + \alpha_T T)^2 / d^2 \) is a constant corresponding to the thermal properties ( \( d \) is the diameter of SMPU fiber at the reference temperature \( T_0 \)). In the above equation, it indicates that the relaxed stress at temperature \( T \) is related to that at a reference temperature.

The stress relaxation behavior at various temperatures has been presented in Figure 3.10, elucidating that the stress begins relaxation after fixed at a constant stretch strain of 80%. By shifting the stress relaxation curves along vertical axis firstly and then horizontal axis (shift parameters are given in Table 3.1), the master curves are derived in Figure 3.11. It shows that the stress could be relaxed over a long-term scale in days (i.e., 4800 days, which is over 13 years). After the long-term relaxation, the remained stress is 25 % of the maximum stress (i.e., 51 MPa/203 MPa), which indicates that 25 percent of stored strain energy is still maintained in the SMPU fibers as a potential driving force for shape recovery after 13 years.[28]
Table 3.1 Vertical and horizontal shift parameters for TTS master curves.

<table>
<thead>
<tr>
<th>Factor</th>
<th>$\beta_T$</th>
<th>$C_1$</th>
<th>$C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>44 °C</td>
<td>65 °C</td>
</tr>
<tr>
<td>Values</td>
<td>4.9</td>
<td>6.9</td>
<td>9.25</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>7</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 3.11 Master curves after shifted along vertical and horizontal axis at the reference temperature (i.e., 8°C).

3.4.6 Structural Relaxation Results and Discussion

To demonstrate the structural relaxation, the conformational entropy change is theoretically derived above corresponding to the stress relaxation behavior. The experimental stress relaxation is stated in Figure 3.11, and based on the experimental data, the conformational entropy change is calculated, shown in Figure 3.12. The necessary material parameters for deriving the time-dependent entropy change are shown in Table 3.2. The result shows that the entropy change is negative at the initial stage of stress relaxation, which results in decreasing conformational entropy of fibers, as shown in Figure 3.12 (c). The decrease in conformational entropy is associated with the reorientation and alignment of polymer chains or strain-induced crystallization (SIC),[18] which may be induced by applied uniaxial stress (inertial effect). When the minimum of entropy is achieved, it indicates the highest degree of order of polymer chains is achieved. As the applied stress relaxes, the entropy start to increase from the minimum value but
the entropy change is still negative. This process indicates that the microstructure of SMPU fibers begins to relax from the non-equilibrium state (corresponding to the minimum entropy value, i.e., less disordered state) to high disordered state. The negative entropy change occurs within one hour. After that, the entropy change becomes positive, indicating conformational entropy increases accompanied with microstructure relaxation from a temporary non-equilibrium state. The evolution of the entropy change in a time-scale of tens of year shows that it is still positive and keeping propagating even after 13 years (shown in Figure 3.12 (a) and (b)), suggesting that the microstructure of the programmed SMPU fibers will still be in non-equilibrium state and still in the relaxation process. This result is qualitatively in agreement with the argument stated by Nguyen et al.,[25] which, at a given temperature, the relaxation time is finite for structure relaxing towards equilibrium. As discussed above, the non-equilibrium configuration provides the programmed SMPU fibers a driving force for shape recovering. Thus, the obtained results elucidate that the programmed fiber will still have the ability to recover its permanent shape after 13 years of relaxation.

Due to an extension ratio \( \lambda \) during cold-drawing programming, the SMPU fiber transforms from equilibrium configuration to non-equilibrium configuration, accompanied with entropy reduction. The entropy at the end of the programming is the entropy at the start of relaxation. For a long-term relaxation, the conformational entropy increases as the configuration relaxes towards equilibrium. This dynamic entropy change represents the structural relaxation behavior along with time. The average formula weight ratio for (MDI+BDO) over PBA is 1021:300. The average molecular weight of PBA is 10500 g/mol.[140] The entropy at the equilibrium configuration is calculated by equation 3.16, which is \( S_c = 5.48 \times 10^{-4} \text{ J/K} \). The entropy change due to programming is calculated through the equation 3.17, which is \( \Delta S_c = 3.13 \times 10^{-6} \text{ J/K} \). Thus the entropy for the non-equilibrium configuration, i.e., at the start of structural relaxation process, is determined as \( S'_c = 5.45 \times 10^{-4} \text{ J/K} \) through equation 3.18. The total dynamic entropy change after 13 years of relaxation is \( 2.92 \times 10^{-9} \text{ J/K} \). Comparing the entropy increase due to structural relaxation (\( 2.92 \times 10^{-9} \text{ J/K} \)) with the entropy decrease due to programming (\( 3.13 \times 10^{-6} \text{ J/K} \)), it is clear that the reduced entropy due to programming is only relaxed about 0.1% after 13 years of structural relaxation, indicating that the configuration is far away from equilibrium. This suggests that the SMPU fiber still possesses the shape memory capability. This result is again qualitatively in agreement with Nguyen et al.[25]
Table 3.2 Material parameters for determining entropy change corresponding to stress relaxation.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>25 °C</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>$k_B$</td>
<td>$1.38 \times 10^{-23} \text{ m}^2 \text{ kg} \text{ s}^{-2} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>Diffusion coefficient of the “defect” along the chain at 25 °C</td>
<td>$D$</td>
<td>$10.24 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Characteristic ratio</td>
<td>$C_\infty$</td>
<td>5~10</td>
</tr>
<tr>
<td>Expansion coefficient of PU</td>
<td>$\alpha_g$</td>
<td>$11.8 \times 10^{-5} \text{ °C}^{-1}$</td>
</tr>
<tr>
<td>Free volume fraction at 0K</td>
<td>$f_{v0}$</td>
<td>0</td>
</tr>
<tr>
<td>Characteristic frictional coefficient</td>
<td>$\zeta_0$</td>
<td>$2.0 \times 10^{-19} \text{ kg} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Length of the chain</td>
<td>$r$</td>
<td>6 nm</td>
</tr>
<tr>
<td>Gas constant</td>
<td>$R$</td>
<td>8.314 J $\text{ mol}^{-1} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>Density of the polymer at 25 °C</td>
<td>$\rho$</td>
<td>1.05 g $\text{ cm}^3$</td>
</tr>
<tr>
<td>Avogadro number</td>
<td>$N_A$</td>
<td>$6.022 \times 10^{23} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Number of strands in chain</td>
<td>$N$</td>
<td>3</td>
</tr>
<tr>
<td>Monomer per strand</td>
<td>$n$</td>
<td>6</td>
</tr>
<tr>
<td>Plateau modulus</td>
<td>$G_N$</td>
<td>$0.6 \times 10^8 \text{ Pa}$</td>
</tr>
<tr>
<td>Average mass of main chain chemical bonds</td>
<td>$m$</td>
<td>$5100 \text{ g} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Distance between monomers</td>
<td>$a$</td>
<td>0.76 nm</td>
</tr>
</tbody>
</table>

The cold-drawing programmed fiber has a maximum programming stress of about 88 MPa at room temperature (25°C) (referring to Figure 3.4), it is estimated that after almost thirteen-year hibernation in a polymer matrix at room temperature, about 22 MPa (i.e., remained stress $88 \times 25\% = 22$ MPa) stress can be stored as back stress for future shape memory behavior. For the self-healing application, the programmed fibers are embedded in matrix, undergoing a free stress state. As reported in the experimental part, the maximum recovered stress for SMPU fibers is 11.6 MPa once activated by thermal stimulus after 30-minute relaxation. From the above entropy calculation and Figure 3.12, it is seen that the entropy of the fibers after 13 years of hibernation is only increased by about 0.1%, which is negligibly small. Therefore, it is estimated that the entropy of the fiber after 13 years of relaxation is very close to that after 30 minute of relaxation. Because the recovery stress after 30 minutes of relaxation is 11.6 MPs, it is confident to predict that the recovery stress after 13 years of relaxation is still about 11.6 MPa, simply because entropy is the driving force for shape recovery. In other words, it is estimated that the SMPU fibers, after 13 years of relaxation, still possess the shape memory capability and are able to heal millimeter scale crack. [17]
3.4 Conclusions

The SMPU fibers are studied in this paper for self-healing applications. After being programmed, the physical/mechanical and thermomechanical properties are investigated experimentally. Then a theoretical analysis is performed on the conformational entropy change to analyze long-term structural relaxation behavior in terms of stress relaxation test results. Based on the results, the following conclusions are derived:

1. The CDP process is a completely physical process for SMPU fibers, such as molecular chain alignment and segments re-orientation along the loading axis. This physical process may induce formation of some crystals within the hard segment domain of the programmed fibers. The cyclic loads during the CDP process, moreover, leads to an increase in shape fixity of the programmed fibers.

2. The strength and stiffness of the programmed fibers have been improved after the CDP process. The increase in Young’s modulus of the programmed fibers is almost five times of the non-programmed fibers, the yield stress has been improved almost twenty-six times after the CDP process, and the tensile strength has doubled after the CDP process.

3. After the CDP process, the programmed fibers have a good crack-closing capability with a maximum recovered stress of 11.6 MPa and exhibit a good stress recovery behavior at the temperatures within the range of 65°C ~ 140°C.

4. After structural relaxation in the time scale of 13 years, the programmed SMPU fibers, which are “stress free” or hibernate in a polymer matrix, can still provide some recovery
force to close millimeter scale cracks in the self-healing system when triggered by thermal stimulus.
CHAPTER 4  HEALING-ON-DEMAND COMPOSITES BASED ON POLYMER ARTIFICIAL MUSCLE†

4.1 Introduction

In this chapter, we propose a new strategy by using artificial muscle to polymer composites for healing-on-demand applications, as schematically shown in Figure 4.1. Figure 4.1a shows an illustration of natural muscle contract. Physically, the contracting of muscle generates tension on both connections (i.e., tendon). As illustrated in Figure 4.1b, a healing-on-demand polymer composite, schematically, has the abilities to close or narrow macro crack and to heal it on-demand.

The objective of this study is to investigate (1) polymer artificial muscles from commercial fishing line; (2) the ability of polymer artificial muscles to repeatedly heal wide-opened cracks at a constrained condition; (3) the effect of spring index on the healing efficiency; and (4) the effect of pre-strain level of artificial muscle on the healing efficiency.

4.2 Experiment

4.2.1 Raw Materials

EPON™ Resin 862 (Momentive Specialty Chemicals Inc.) was used as the composite matrix, and the diethylenetriamine by Sigma-Aldrich was used to cure the resin for three days at 25°C. According to the supplier, the cured epoxy has an ultimate tensile strength of 28 MPa and modulus of 3700 MPa. The CAPA 6506 powder (Perstorp UK Ltd.), a high molecular weight linear polyester (composed of Isophthalic acid, Terephthalic acid, and Butane-1, 4-diol) derived from caprolactone monomer (i.e., polycaprolactone), was used here as the thermoplastic healing agent. The particle has a density of 1.1 g/cm³ at 25°C, melting temperature 58 – 60°C, and 98% of the size is smaller than 0.6 mm. Commercial fishing line is used in this study. PE fishing line (under brand name ZEBCO OMNIFLEX30LBA) has a diameter of 533 µm.

4.2.2 Differential Scanning Calorimetry (DSC) Characterization

Differential scanning calorimetry (PerkinElmer DSC 4000, USA) was used to investigate the thermal properties of CAPA 6506 and PE line. The purging rate of Nitrogen is 30 ml/min. Three effective samples were tested under the same conditions. Two cooling and heating cycles...
were conducted for each sample, and the second heating cycle was used to determine the glass transition temperature ($T_g$) and other thermal properties in order to eliminate the thermal history.

Figure 4.1 (a) Structure of nature muscle. (b) Schematic of on-demand healing process: (i) a polymer composite sample reinforced by polymer artificial muscle (light golden coiled fiber) and thermoplastic particle (light golden spheres) in a matrix (blue); (ii) crack initiated by external load during service life; (iii) crack closed by thermally activated artificial muscle and healed by the healing agent; (iv) solid wedge formed after cooled down, establishing continuity between the healing agent and the matrix.
4.2.3 Polymer Artificial Muscle Preparation

Polyethylene (PE) fishing line was twisted by a commercialized reversible rotor with bottom end fixed while the upper end attached to the rotor. The bottom end was loaded by 360 grams of load, which is 16 MPa when normalized to the PE line cross-sectional area. The polymer line was twisted by the manually controlled rotor counterclockwisely. Prior to be coiled, a steel wire was used as mandrel and wrapped by the twisted PE line in the counterclockwise direction. The mandrel (i.e., steel wire) had various diameters, which determines the coil spring index. In order to keep the bias angle constant, the wrapping rate must be the same as the twisting rate. The coiled configuration was maintained by fixing both muscle ends. Once being coiled completely, it was put into an oven and kept for at least 95 min under 80°C. The mandrel (i.e., steel wire) was removed after being cooled down to room temperature. The preparing process was repeated by using mandrel with various diameters, like 1.17 mm, 0.75mm, and 0.37 mm. After annealing, polymer artificial muscles made from PE fishing line were completed with spring index of C=3.2, C=2.4, and C=1.7, respectively.

4.2.4 Healing-on-demand Polymer Composite Fabrication

The polymer artificial muscles with pretension of 0%, 30%, and 60% were placed in an open mold as reinforcement. When fabricating the composite, the resin (EPONTM Resin 862) and 10% by volume of thermoplastic particles (CAPA 6506) were mixed firstly for 10 min. Secondly 12% by weight of curing agent (Sigma, Diethylenetriamine ReagentPlus, 99%) was mixed with the mixture for two minutes. The well mixed mixture was poured into the prepared mold. After that, the mold was kept in a chamber at 4°C for 24 hours. The first day of low temperature curing is to ensure that the curing heat be removed. The reason why keeping in low temperature has been presented in previous study [93]. The mold was then exposed to room temperature and cured for three days prior to machining into beam specimens and testing. Based on the used polymer components, sample volume, and PE line density, the volume fraction of polymer artificial muscle is 8%. In order to investigate the effect of spring index and prestrain level on the muscle behavior and healing efficiency, the muscles were fabricated with spring index C=1.7, C=2.4, and C=3.2, and before the muscles were placed into a mold for preparation of the composite, the muscles were pretensioned to 0%, 30%, and 60% prestrain, which were designated as P-0%, P-30%, and P-60%, respectively.
4.2.5 Rheology Test

The powder was heated with a Peltier device (connected with the rheometer) at 75°C. A certain pressure was loaded by using a parallel plate. After 3-4 minutes, the powder was melted. Then the temperature was cooled to room temperature quickly and the pressure was kept for 3-4 minutes. The thin film was peeled off and cut into a roundpad-shape by a scissor. The dimension of the film was 25 mm in diameter with a thickness around 1.2 mm. The prepared film was further tested by melt rheology (heated by a hot oven). The gap between the parallel plates is 1000 µm. Time sweep mode was used, and the strain was 0.1%. The frequency (shear rate) was selected to be 1 s⁻¹ and 100 s⁻¹. After the temperature reached 80°C, the sample was loaded and the data was recorded immediately.

4.2.6 Mechanical Property of Artificial Muscle Characterization

The actuation stress of artificial muscle was obtained by holding the two ends with a prestrain (pre-tension) and then heated by a heat gun periodically. The heat gun could raise the temperature to 79°C at a distance of 15 mm. Due to the contraction of polymer muscle, it generates pulse load once heated by the heat gun. And this load was collected by a 250 N load cell. The actuation stress was determined by normalizing the generated load over polymer muscle cross-sectional area.

4.2.7 Self-healing Test

A single edge notched beam (SENB) was prepared according to ASTM D 5045 standard. The three-point bending tests were carried out by the MTS (RT/5, MTS Inc., USA) system at a loading rate of 5 mm/min. The completely fractured beam specimen with a crack opening of 0.24 mm was heated by a heat gun for 10 min. Then the heat gun was removed and was cooled down to room temperature. This completed the first fracture-healing cycle. This fracture-healing continued until five cycles to evaluate the ability for repeatedly healing wide-opened cracks. During the fracture testing, the peak bending load was recorded, which was used to calculate the healing efficiency. Then, the bending tested samples were fixed by clamping both ends for evaluating healing ability at a fixed boundary condition, as shown in Figure 4.2. Once the 0.24 mm wide crack was generated, both ends of the beam were clamped to create a fixed boundary condition. The local heat was provided for 10 min. The fracture-healing continued for another five cycles. Five effective specimens were tested for each group of samples.
4.2.8 Inspection Characterization

The crack healing process was investigated by a high resolution CCD camera (Sony XCD-CR90), which is equipped with a light source and a digital interface which interlinks the computer and the camera. The CCD camera used in this test has a resolution of $3.7 \times 3.7 \mu m/pixel$. Fire-i data acquisition software was used to store the image data from the camera during testing. Specimens before healing and after healing were characterized by scanning electron microscope (SEM), Quanta 3D FEG field-emission electron microscope.

4.3 Results and Discussion

4.3.1 Thermomechanical Properties of Artificial Muscle

The artificial muscle exhibits contraction upon thermal exposure, which could be induced by either electricity, or photo, or chemical reaction, or heating. Figure 4.3 presents the fishing line has a transition temperature ($T_g$) at $74^\circ$C. Above this temperature, the polymer line undergoes negative thermal expansion (contraction) in axial direction but positive thermal expansion in radial direction [95,148]. The muscle is made of highly-oriented polymer line through twisting and coiling. The inserted twist is to increase the anisotropic properties.
specifically in thermal expansion. In this case, the thermal activation would generate a larger mismatch in axial and radial expansion than non-twisted fibers. The expansion mismatch leads to a large degree of untwisting when the muscle is heated. Once being coiled, the un-twisting (ΔT) behavior is accompanied with coil bias angle change from \( \alpha_c \) to \( \alpha_c' \), leading to torsional actuation [95,149]

\[
\Delta T = \frac{\sin(\alpha_c) \cos(\alpha_c') - \sin(\alpha_c) \cos(\alpha_c)}{\pi D'} - \frac{\sin(\alpha_c) \cos(\alpha_c)}{\pi D}
\]  

(4.1)

where D and D' are the coil diameters before and after heating. And the thermally-induced untwist results in the change in coil length

\[
\Delta L = \frac{l^2 \Delta T}{N^2}
\]  

(4.2)

where N is the number of coils and l is the fiber length in coil.

Figure 4.3 Thermal property of PE fishing line by DSC, showing a glass transition temperature (i.e., Tg) 74°C.

The working mechanism of the PE artificial muscle behind the tensile actuation is that the thermally-induced fiber untwisting decreases the fiber twist per initial fiber length, resulting in coil length reduction if the muscle is twisted and coiled in the same direction, i.e., decreases inter-coil separation. As shown in Figure 4.4a, the coils are separated by a 33-gram load at room temperature (cold), which contracts at a temperature higher than its Tg (hot). In the situation by fixing both ends at a certain prestrain (pre-tension) level, the contracting behavior generates
actuation stress. Figure 4.4b presents the actuation stress from this polymer muscle. It shows that the muscle exhibits good repeatability on tensile actuation, almost without losing any actuation ability. This is because the two fixed ends of the muscle prevent the muscle from untwisting, thus maintaining the ability in stress actuation. Furthermore, the increase in prestrain level improves the actuation stress. Owing to the coil length increase in the axial direction by prestrain, the fiber twist per initial length is increased, enabling it to have high potentiality in coil untwisting. The fixed boundary condition of the muscle converts the potentiality from length change to actuation stress change.

Figure 4.4 (a) Polymer artificial muscle from polyethylene fishing line (diameter 533 μm) that twisted and coiled with a spring index C=3.2. (b) Muscle actuation stress after thermal activation under 80°C with prestrain (pretension) 20%, 40%, and 60%, respectively.

Figure 4.5a shows the trend in the change of tensile actuation stress with spring index, when the muscle is pre-tensioned at 40% strain. The increase in spring index negatively affects the actuation stress; however, it positively affects the actuation strain, as shown in Figure 4.5b. Under a load of 33 grams, the actuation strain becomes progressively greater as spring index changes from 1.4 to 9.1. However, spring index larger than C=7.1 easily leads to coil collapse, as shown in Figure 5.6.

4.3.2 Thermal Properties of Healing Agent

The thermoplastic particle used is shown in Figure 4.7a. The particle has size smaller than 0.6 mm, approved by supplier. The thermal property is shown in Figure 4.7b, which showing a melting point around 58°C. Figure 4.7c presents the complex viscosity change at a temperature of 80°C. The complex viscosity was calculated based on storage shear modulus G'.

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loss shear modulus $G''$, and the selected frequency from the rheology test. It indicates that the healing agent becomes liquid and could flow after 80 s.

Figure 4.5 (a) Actuation stress change with spring index at a prestrain 40%. (b) Tensile actuation strain change with spring index under a load of 33 grams.

Figure 4.6 A twisted-coiled PE muscle by using 533 μm diameter PE fiber with spring index C=4.2 (Left) and C=7.1 (Right).

Figure 4.7 (a) Optical microscopic characterization of the CAPA 6506 particle. (b) Thermal property of CAPA 6506 by DSC, showing a melt point 58°C. (C) Time-dependent complex viscosity of CAPA 6506 at 80°C.
4.3.3 Crack Healing and Efficiency

In this study, the PE artificial muscle is prepared and embedded within an EPON™ Resin 862 polymer matrix, along with healing agent. The damage on sample was initiated by three point bending. The peak load for each sample was collected. Then crack healing effect was evaluated through a local heating. The heat gun could generate local heat to 79°C at a distance of 15 mm. Under this temperature, the artificial muscle has been activated, contracting upon the thermal stimulus (Figure 4.3). Meanwhile, the healing agent starts to flow after 80 s (Figure 4.7c). While maintaining the temperature at 79°C, the melted particles fill in the narrowed crack via capillary action. Molecular chain diffusion and randomization follow the crack filling process. De Gennes [29] has discussed the molecular chain diffusion and randomization by a tube model [150,151], through which the molecular chain motion was allowed reptating randomly through one-dimensional back-and-forth Brownian motion, along the randomly coiled conformational tube during a certain time period. The diffusion mechanism was also discussed by Bousmina et al. [152], who described the diffusion process by Fick’s law. They pointed out that the reptation time with complete diffusion to an equilibrium state was:

$$\tau_{rep} = \frac{\zeta N^3 b^4}{\pi^2 e^2 k_B T}$$

(4.3)

where $\zeta$ is the friction coefficient, $N$ is the number of monomers, $b$ is the effective bond length, $e$ is the segmental chain length, $k_B$ is Boltzmann’s constant, and $T$ is the absolute temperature. Obviously, the diffusion time before reaching the equilibrium state depends on the polymeric material properties and temperature. Therefore, it is necessary to have the local heating time longer than the reptation time. We kept the cracked samples under local heating for 10 min, then cooled down to room temperature, to harden the thermoplastic film.

The composite samples were first damaged and healed at free boundary condition for five cycles, and then at fixed boundary condition for another five cycles. At constrained condition, the sample ends were fixed by clamping under heat gun (Figure 4.2). Figure 5.8a to 5.8c presents the healing efficiency for the healing-on-demand composite by PE artificial muscle at a spring index C=1.7, C=2.4, and C=3.2, respectively. It shows that the spring index has no significant effect on the healing efficiency. According to Li et al [17], the contracting stress around 3 MPa.
could effectively close macro-level crack. From Figure 4.5a, all the artificial muscles have met the stress requirement. However, with the increase in the prestrain level, which translates to higher contraction force, the healing efficiency increases. This is because higher contraction force pushes the two sides of the fracture closer, reducing the film thickness of the healing agent. As reported previously, thinner adhesive layer leads to higher bonding strength. \[93, 147\]
Furthermore, larger contraction force helps diffusion of the molten thermoplastic molecules into the epoxy matrix and establishing physical entanglement. The reason is that the contraction force provided by the muscle helps overcome the diffusion barriers. Also, it is seen that the healing under fixed boundary condition is quite repeatable. Furthermore, as compared to specimens with free boundary conditions, the healing efficiency with fixed boundary condition is just reduced slightly. It is noted that, the specimens were subjected to five cycles of damage-healing with free boundary condition before they were subjected to the constrained damage-healing cycles. Otherwise, the healing efficiency should be slightly higher for the constrained damage-healing cycles.

4.3.4 Nondestructive Characterization Result

High resolution CCD camera was utilized to monitor the crack healing process at constraint condition. The advantage of the non-destructive testing is to ensure that the damaged cracks and/or healed cracks have no interruptions from unknown factors. Figure 4.9 compares crack zone before and after the healing for artificial muscle based composites at varied spring indexes. For the sample at C=1.7, the original crack gap (distance between crack boundaries) was about 0.24 mm. After heating at 79°C for 10 min, crack was narrowed completely. Similar crack close were observed for samples at C=2.4 and C=3.2.

In a previous study, the SMP fiber reinforced polymer composite beam with fixed boundary condition, which has 9.9% by volume of SMP fibers and 0%, 50%, and 100% prestrain, can repeatedly heal a 0.15 mm wide crack at an efficiency about 23%, 44%, and 53%, respectively. \[17\] For the muscle reinforced polymer composite beam with a crack opening of 0.24 mm, which has a muscle volume fraction of 8% and the same fixed boundary condition, the healing efficiency is about 54% for muscles with 60% prestrain, almost independent of the muscle spring index (1.7, 2.4, and 3.2). The reason for this is that the muscle has higher contraction force than the SMP fibers (7.1MPa for C=1.7 and 40% pretensioned muscle versus
4.8MPa for 100% pretensioned SMP fiber [17]). The fishing line muscles achieved a healing efficiency similar to SMP fibers with less muscle volume fraction (8% versus 9.9%), lower prestrain (60% versus 100%), but wider crack (0.24mm versus 0.15mm).

Figure 4.8 (a) Healing efficiency for the sample with spring index at C=1.7. (b) Healing efficiency for the sample with spring index at C=2.4. (c) Healing efficiency for the sample with spring index at C=3.2.
Figure 4.9 Microscopic inspection on samples (from artificial muscle spring index C=1.7, C=2.4, and C=3.2) before and after healing at constraint situation.

4.3.5 SEM Observation Result

By using scanning electron microscopy (SEM), the crack healing was further investigated, as shown in Figure 4.10. It presents the fractography of crack zone and healing zone, as well as damage induced crack surface. Figure 4.10b shows that the crack was healed completely, with almost no detectable separation. As compared to the smooth fracture surface (Figure 4.10c), the healed sample fracture surface was covered by a thermoplastic layer (Figure 4.10d). It is worthy to note that the thermoplastic film plays an important role in fracture surface bonding. Any of the film factors, like thickness, porous, and sharp shape, would significantly affect the healing zone strength.
Figure 4.10 SEM inspection on (a) crack zone, (b) healing zone, (c) control sample without thermoplastic film, (d) fracture surface of healed sample with thermoplastic thin film for sample at C=3.2.

4.4 Conclusions

The study on the polymer artificial muscle based healing-on-demand composite leads to the following conclusions:

1. The PE artificial muscle from commercial fishing line exhibits repeatable actuation stress upon thermal activation, without losing any actuation ability.
2. The composite based on polymer muscle could close and heal damage induced crack efficiently, even the beam is at constrained boundary condition.
3. The muscle-coil spring index has no significant effect on sample crack healing efficiency.
4. The pre-strain level of artificial muscle has a significant effect on the healing efficiency. Under allowable pre-strain level limit and constant fraction of healing agent, higher pre-strain level guarantees better crack healing efficiency.

In summary, this study has introduced a new strategy in healing-on-demand thermoset composite based on polymer artificial muscle. Excellent crack healing performance has been
demonstrated from complete constraint conditions. Due to its low cost, high efficiency healing, good compatibility, and excellent flexibility, we envision that the polymer artificial muscle will be new device in designing of next generation healing-on-demand polymer composite.
CHAPTER 5  FISHING LINE ARTIFICIAL MUSCLE REINFORCED COMPOSITE FOR IMPACT MITIGATION AND ON-DEMAND DAMAGE HEALING†

5.1 Introduction

Grid stiffened syntactic foam core was developed recently by synergizing the grid skeleton and the filled foam, aiming at improving impact tolerance and post-impact residual in-plane compressive strength. It is found that the grid stiffened structure responds to impact in a quasi-static manner because each bay is small so that the flexural waves and shear waves have sufficient time to travel to and be reflected by the boundary, making peak load, deflection, and strain more or less in phase. It is also found that the panel shows much higher residual strength as compared to laminated composite with the same fiber volume fraction. When the grid skeleton is made of SMP fibers, it proves that the composite panel also has self-healing capability. It is envisioned that, if the SMP fiber is replaced by the artificial muscle, the advantage of grid stiffed composite panels will be maintained, but with improved healing efficiency and lowered cost because the muscle is made of commercially available fishing lines or sewing threads. The purpose of this study is to investigate the impact response and healing behavior of artificial muscle grid stiffened syntactic foam composite panel.

5.2 Experiment

5.2.1 Raw Materials

EPON™ Resin 862 (Momentive Specialty Chemicals Inc.) was used as the composite matrix, and the diethylenetriamine by Sigma-Aldrich was used to cure the resin for three days at 25°C.

The CAPA 6500 (Perstorp UK Ltd.), a high molecular weight thermoplastic linear polyester derived from caprolactone monomer (i.e., polycaprolactone), was used here to make thermoplastic fibers. It has a density of 1.1 g/cm³ at 25°C and melting temperature 58 – 60°C.

Commercial fishing line, PE fishing line (533 µm diameter, under brand name ZEBCO OMNIFLEX30LBA), is used here to fabricate polymer artificial muscle.

† Zhang, P., Li, G. Fishing line artificial muscle reinforced composite for impact mitigation and on-demand damage healing. Journal of Composite Materials, 2015. (Submitted)
Glass microballoons, Q-CEL® 6014 Potters Industries, have bulk density of 0.08g/cm³, effective density of 0.14g/cm³, particle diameter range of 5 - 200μm, average diameter of 85μm, and crushing strength of 1.72MPa.

Figure 5.1 Hollow microspheres of Q-CEL® 6014.

5.2.2 Polymer Artificial Muscle Preparation

Polyethylene (PE) copolymer monofilament fishing line was twisted by a commercialized reversible rotor with bottom end fixed while the upper end attached to the rotor. The bottom end was loaded by 360 grams of load, which is 16 MPa when normalized to the PE line cross-sectional area. The polymer line was twisted by the manually controlled rotor counterclockwisely. The relationship between effective length of fishing line and twisting number is shown in Figure 5.2. It presents a slope of 0.43 /mm, which is a critical value for the line from twist to coil. For example, an effective length of 200 mm, the critical number of twisting is 86. The value larger than 86, it begins coil; otherwise, it needs more twist.

Prior to being coiled, a steel wire was used as mandrel and wrapped by the twisted PE line in the counterclockwise direction. In order to keep the bias angle constant, the wrapping rate must be the same as the twisting rate. The coiled configuration was maintained by fixing both muscle ends. Once being coiled completely, it was put into an oven and kept for at least 95 min under 80°C. The mandrel (i.e., steel wire) was removed after being cooled down to room temperature. The preparing process was repeated by using mandrel with a diameter of 0.75 mm. After annealing, polymer artificial muscle made from PE fishing line was completed with spring index of C = 2.4, as shown in Figure 5.3.
Figure 5.2 The relationship between effective length of fishing line and twisting number prior to being coiled.

Figure 5.3 Polymer artificial muscle made of PE copolymer monofilament (Spring index $C = 2.4$).
5.2.3 Microstructure of the As-Spun and Coiled PE Copolymer Fibers

The microstructure of the as-spun and coiled PE copolymer fibers before and after thermal actuation were investigated with X-ray diffractometer (XRD, EMPYREAN Cu LFF HR DK328566), operated at 45 kV and 40 mA to produce CuKα radiation (λ = 1.54 Å), to evaluate the effect of coiling and actuation on the crystal structures. The scan axis Gonio was selected with range from 15° to 70°. The diffraction intensities were measured at room temperature and at a scanning rate of 5°/min.

5.2.4 Thermoplastic Linear Polyester Fiber Preparation

The polyester fiber was fabricated by using a gravity-assisted method. The fabrication setup is shown in Figure 6.4(a). Thermoplastic polyester was added into a steel cylinder hold. It was heated up to 75°C for one hour prior to being extruded. With the help of an extruding rod, the thermoplastic fiber (TF) was formed through a die. The rate of gravity-assisted extrusion is 0.87 ml/min. The fiber diameter is 0.36 mm. Then the fiber was chopped into short fiber with average length 4 mm, as shown in Figure 6.4(b).

Figure 5.4 (a) Setup of polyester fiber fabrication; (b) Chopped thermoplastic fiber.
5.2.5 Grid Stiffened Syntactic Foam Fabrication

In this study, the effect of orthogrid bay area size and TF amount within host material was investigated. The sample design is shown in Figure 5.5, including regular sample groups and control groups. All sample groups are marked by letters and numbers, such as S1P2, S2P1, etc. with S represents sample bay area, P represents the polymer healing agent weight fraction, and the numbers represent bay area and healing agent content. The specific bay area and TF amount are elucidated in Table 5.1.

![Figure 5.5 Investigation of the bay area size effect and thermoplastic fiber amount effect; including regular sample design and control sample design.](image)

In order to fabricate orthogrid stiffened syntactic foam, orthogrid mold with mounted polymer artificial muscles was prepared first, as shown in Figure 5.6(a). By changing distance between two neighbor nails on the mold, different bay area sizes would be obtained. The chopped short TF was randomly distributed over the mold. 450 g epoxy resin was mixed with glass microballoon for one hour. 40% by volume of glass microballoon was used here to make foam. The mixing process generates a heat up to 47°C. The mixture was cooled down for 30 minutes before mixing with curing agent. After that, curing agent was added into the mixture at a ratio of 87 : 13 (resin : hardener). After mixing for three minutes, it was poured into the mold at 245 ml/min. Then the mold was taken into a vacuum chamber under a pressure of -3.1 MPa. After two minutes, it was transferred into a refrigerator and kept at 4°C for 24 hours. Room
temperature curing was followed and took the other three days for complete curing. The cured syntactic foam was cut into 220 mm × 55 mm samples (thickness 12.7 mm) according to ASTM D 790-03, as shown in Figure 5.6(b).

Figure 5.6 (a) Orthogrid structure of mold design; (b) Sample cut according to ASTM D 790-03.

5.2.6 Thermal Properties Characterization

Differential scanning calorimetry (PerkinElmer DSC 4000, USA) was used to investigate the thermal properties of PE copolymer monofilament fishing line. The purging rate of Nitrogen is 30 ml/min. Three effective samples were tested under the same conditions. In order to eliminate the thermal history, two cooling and heating cycles were conducted for each sample, and the second heating cycle was used to determine the glass transition temperature (T_g) and other thermal properties.

The thermal properties of TF were characterized by thermogravimetry analysis (TGA) method. The TGA equipment (TG/DTA7300, SII Nano Technology, Japan) was used to conduct the test. TF was chopped into powder like particles, and placed in a sample hold with an amount of 27.78 mg. The sample was heated up from room temperature to 80°C at a heating rate 5°C/min. It was kept at 80°C for three hours to investigate the weight change against temperature and time. The test result gives the data on thermogravimetry (TG), differential thermal analysis (DTA), and derivative thermogravimetric (DTG). Two samples were used for the test.
5.2.7 Mechanical Damage Induced Crack Test

5.2.7.1 Low velocity impact test

Transverse low-velocity impact tests were performed on each group of beam specimens using an Instron Dynatup 8250 HV drop tower machine per ASTM D 2444. The tup nose is semi-spherical with a radius of 15.8 mm. The impact velocity was 1 m/s with a hammer weight of 2.35 kg, which results in impact energy of 1.18 J. The impact location was at the center of the beam specimen, as shown in Figure 5.7. Four effective specimens were tested for each group of specimens.

Table 5.1 Sample and test design.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Mark</th>
<th>Bay Area</th>
<th>Amount of TF (by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P1</td>
<td></td>
<td>6%</td>
</tr>
<tr>
<td>2</td>
<td>S1P2</td>
<td>11 mm × 11 mm</td>
<td>9%</td>
</tr>
<tr>
<td>3</td>
<td>S3P2</td>
<td>21 mm × 21 mm</td>
<td>9%</td>
</tr>
<tr>
<td>4</td>
<td>S2P1</td>
<td>15.8 mm × 15.8 mm</td>
<td>6%</td>
</tr>
<tr>
<td>5</td>
<td>S2P3</td>
<td>15.8 mm × 15.8 mm</td>
<td>12%</td>
</tr>
<tr>
<td>6</td>
<td>S2P2</td>
<td>15.8 mm × 15.8 mm</td>
<td>9%</td>
</tr>
</tbody>
</table>

5.2.7.2 Impact response in terms of wave propagation

Strain gages were attached to the specimens as shown in figure 1b in order to monitor the impact response. Strain gage 1 was put at 45° and 15 mm from the impact location. Strain gages 2, 3, 4 were put along the longitudinal direction but 15 mm, 40 mm, and 65 mm from the impact location. The data collection setup is shown in Figure 5.8. The signal from the strain gage conditioner was amplified with the help of an oscilloscope and the oscilloscope in turn sent signal to a Wavestar software package. Since the strain gage conditioner (Vishay Micro-measurement) is a two-channel monitor, which means it only collects signal from two strain gages during low velocity impact, the four strain gages were attached on two similar specimens, as shown in Figure 5.7.
Figure 5.7 Strain gages positions on syntactic foam samples.
5.2.7.3 Three-point bending test

Three-point bending test was conducted on the impacted specimens per ASTM D790-03. It was to verify the residual flexural strength after the low velocity impact and further propagate the impact induced crack. The span length was 192 mm. Both the loading nose and support nose had a radius of 6 mm (see Figure 5.9). To increase damage, the top surface of the beam is the impact surface and the bottom surface of the beam is the back surface of the impact. The three-point bending test was carried out by the MTS (RT/5, MTS Inc., USA) system. The loading rate was 4.84 mm/min.

![Figure 5.9 Three-point bending specimen and setup.](image-url)
5.2.8 Investigation into Damage-healing Behavior

5.2.8.1 Crack healing under free boundary condition

The impact damaged specimens were three-point tested to fracture. The fractured specimens were put into an oven for healing without any external constraints. The oven temperature was set up to 90°C with a heating rate 6°C/min and kept at this temperature for 10 minutes for crack closing and healing. The specimens were then removed from the oven and cooled to room temperature for 90 minutes. The healed specimen was again subjected to three-point bending to fracture to verify its recovered flexural strength. Then the fractured specimen was transferred into the oven for crack healing again. The damage-healing events were repeated for ten times.

5.2.8.2 Crack healing under constrained boundary condition

In real world applications, the composite panel is usually constrained at the boundary or by neighboring materials. Therefore, investigation of the healing behavior of the beam specimens under constrained boundary condition is necessary. The crack healing behavior of the syntactic foam beam under constrained boundary condition was investigated. The experiment setup is shown in Figure 5.10. After three-point bending, the fractured syntactic foam specimen was fixed at both ends by grippers, mounted in an environmental chamber. The chamber was set at a temperature of 90°C. It is worth noting that the crack width should be kept as was when preparing the constraints. The specimen was maintained at 90°C for 10 minutes; then, it was cooled down naturally and removed from the setup. At least 90 minutes later, it was bent by three-point bending again for obtaining its residual flexural strength. The damage and healing events were repeated for eight times.

5.2.9 Damage and Healing Inspection

The crack healing process was captured by a high resolution CCD camera (Sony XCD-CR90) with a resolution of \(3.7 \times 3.7 \mu m/pixel\). For free-boundary crack healing samples, the crack zone before and after thermal stimulus was captured. However, for constrained-boundary crack healing samples, the healing process was monitored from beginning (i.e., crack narrowing) until the end (i.e., crack healing) (see Figure 5.11). The advantage for using this technique is that it can snap-shot a moment during the healing process without breaking the specimens into
pieces, but having high resolution figures. The specimen was also observed by scanning electron microscope (SEM) (Quanta 3D FEG field-emission electron microscope). This technique obtains more information about crack healing as well as the specimen fracture surfaces.

![Diagram](image)

**Figure 5.10** Set-up for crack healing under constrained condition.

### 5.3 Results and Discussion

#### 5.3.1 Thermal Properties

The thermal properties for both PE copolymer fishing line and thermoplastic fiber are discussed here. The same polymer artificial muscle as previous study is used here [153]. It has a glass transition temperature at 42°C (see Figure 5.12). The artificial muscle made of PE fishing line has been well studied on its thermal actuation behavior [153-155]. The anisotropic CTE (i.e., coefficient of thermal expansion) of the coiled fishing line leads to thermal contraction along coil axial direction at a temperature above its glass transition temperature. In this study, the test temperature is 90°C, higher than the \( T_g \).
In Figure 5.11, the set-up for healing inspection under constrained condition.

Figure 5.12 DSC result of polymeric artificial muscle.

In Figure 5.13, the thermogravimetry analysis presents the thermal properties of TG, DTA, and DTG for the thermoplastic fiber. The DTA shows that the TF has a melting
temperature at 57.3°C, which is consistent with the provided T_m of 58°C. From the TG curve, it shows that the thermogravimetry keeps constant during the heating process; and the derivative thermogravimetry gives 0 mg/min, which means no weight loss at the healing temperature. It is worth noting that the TF sample was kept at the healing temperature for three hours. Since the test temperature is much higher than its melting temperature, it is necessary to make sure that the healing agent used here should be stable.

![Graph showing DTA and TG results of thermoplastic healing agents.](image)

**Figure 5.13** DTA results of thermoplastic healing agents.

### 5.3.2 Thermomechanical Actuation Property of Artificial Muscle

The artificial muscle was activated by a heat gun. The artificial muscle was stretched to 80% prestrain, analogous to the situation as a reinforcement in the syntactic foam. The actuation stress was collected by a material test system, QTEST 150. As shown in Figure 5.14, repeated actuation stress was obtained with repeated heating. It shows a maximum actuation stress at 13.8 MPa. In addition, it is repeatable without actuation scarification. This is the main difference from the shape memory polyurethane fiber [61,156,157]. The other difference is that the artificial muscle responds fast, exhibiting immediate actuation to the temperature change.
Figure 5.14 Thermomechanical response results of polymeric artificial muscle (Solid line: actuation stress; Dash line: temperature).

5.3.3 Microstructure of the As-Spun and Coiled PE Copolymer Fibers

Figure 5.15 shows X-ray diffraction (XRD) patterns from the as-spun and coiled PE copolymer fibers. The fishing lines are highly oriented copolymer fibers. The diffraction pattern shows two equatorial peaks: one is at $\theta = 20.33^\circ$ and the other is at $\theta = 23.32^\circ$. The twin peaks in the range from $15^\circ$ to $30^\circ$ are due to the symmetric diffraction peaks from the crystals whose lamellar planes are oriented along the same direction [158, 159]. The same results can be seen from the patterns of the coiled fibers. However, in the range from $35^\circ$ to $55^\circ$, the as-spun fiber has two diffraction peaks, while the muscle both before and after thermal actuation loses the peaks. The disappearance of the peaks in the muscles may be due to reorientation of the crystallites during the twisting and coiling process, similar to the semi-crystalline polymer after cold-drawing process [14]. In addition, the thermal actuation does not change the microstructure for artificial muscle because the actuation temperature is well below the melting temperature, which is about 219$^\circ$C for the muscle, indicating a good thermal stability.

5.3.4 Tensile Properties of Artificial Muscles at Various Temperatures

The tensile properties of the polymer artificial muscles are shown in Figure 5.16. Note that the artificial muscles do not have the same number of coils. Figure 5.16a presents the tensile
behavior of the polymeric artificial muscles till fracture under various temperatures, including room temperature (RT), 42°C, and 90°C. As discussed in the previous section, 42°C is the $T_g$ of the polymeric artificial muscle. It shows that the fracture behavior of the artificial muscle at $T_g$ is similar to the one at RT, but has a slight difference in fracture stress. The zigzag shapes of the stress-strain curve are due to the failure (plastic deformation) of the coils. Each drop in the stress-strain curves signals at least one coil is deformed plastically, or coil fails. Figure 5.16b is a zoomed-in portion of the stress-strain curve with lower strain. It shows that the first coil failed at about 94% strain under RT but at 88% under 42°C and at 102% under 90°C. In the previous study [153], it was concluded that higher prestrain level leads to higher actuation stress.

![Graph showing XRD results of polymeric artificial muscles under various situations.](image)

Figure 5.15 XRD results of polymeric artificial muscles under various situations.

Therefore, it is envisioned that higher prestrain is preferred during manufacturing of the muscle grid skeleton. However, the tensile behavior in figure 4 indicates that the polymeric artificial muscle with $C = 2.4$ fails if the prestrain goes up to 88%. That is why, in this study, the prestrain of the artificial muscle was chosen as 80%. Under healing temperature (i.e., 90°C), the tensile property of the artificial muscle exhibits a delectable performance. The fracture stresses as well as the stiffness are largely maintained. With this behavior, it is optimistic that the muscle
will provide sufficient strength, stiffness, and actuation force at the healing temperature (90°C in this study).

Figure 5.16 Tensile properties of polymer artificial muscles under various temperatures (room temperature (RT), 42°C, and 90°C): (a) the fracture behavior at full strain scale; (b) zoom-in at partial strain scale.

5.3.5 Impact Response

Load and energy traces for the syntactic foam beam subjected to impact energy of 1.18 J at the central bay area can be used to determine the maximum impact load, maximum impact energy, and total impact energy (see Figure 5.17). The impact deflection can also be obtained from the impact traces. The initiation energy and propagation energy can be calculated from the obtained maximum impact load, deflection, and maximum impact energy [20,53,67,160-162]. These two energies are used to evaluate the impact tolerance of the target samples. It is proposed that the initiation energy is a measurement of the capacity for the target to transfer energy elastically, while the propagation energy denotes the energy absorbed by the target for creating and propagating gross damage [141].

The calculated initiation energy and propagation energy are calculated and presented in Table 5.2. It is worth noting that higher initiation energy indicates a higher load carrying capacity while higher propagation energy implies larger damage.
Figure 5.17 Typical impact responses for syntactic foam S2P2.

From the above results, the following observations are made based on qualitative analysis:
(1) both short TF content and bay area affect syntactic foam impact behavior significantly. (2) Short TFs, as reinforcements, improve the load carrying capacity and impact damage resistance for syntactic foam. When the TF content is less than 9%, the improvement is not obvious; on the other hand, the effect is considerable once the content is larger than 9%, such as 12%. (3) Smaller bay area means better impact load carrying capacity and impact damage resistance.

Table 5.2 Impact test results of the syntactic foams subjected to an impact energy of 1.18 J.

<table>
<thead>
<tr>
<th>Sample Group</th>
<th>Investigation Factor</th>
<th>Initiation Energy (J)</th>
<th>Propagation Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Sample</td>
<td>P2 (TF content = 9%)</td>
<td>0.74±0.04</td>
<td>0.44±0.01</td>
</tr>
<tr>
<td>TF Content Change</td>
<td>S2P1 (6%)</td>
<td>0.74±0.02</td>
<td>0.44±0.03</td>
</tr>
<tr>
<td></td>
<td>S2P2 (9%)</td>
<td>0.74±0.07</td>
<td>0.44±0.01</td>
</tr>
<tr>
<td></td>
<td>S2P3 (12%)</td>
<td>0.86±0.05</td>
<td>0.32±0.03</td>
</tr>
<tr>
<td>Bay Area Change</td>
<td>S1P2 (11 mm × 11 mm)</td>
<td>0.76±0.05</td>
<td>0.42±0.02</td>
</tr>
<tr>
<td></td>
<td>S2P2 (15.8 mm × 15.8 mm)</td>
<td>0.74±0.08</td>
<td>0.44±0.01</td>
</tr>
<tr>
<td></td>
<td>S3P2 (21 mm × 21 mm)</td>
<td>0.72±0.07</td>
<td>0.46±0.02</td>
</tr>
</tbody>
</table>

After low-velocity impact, stress wave propagates along the ribs of the grid skeleton, which induces flexural deflection as electrical signals in the strain gages. Such signals were
collected by strain gages from the four positions as output voltage. The flexural strain, $\varepsilon$, is determined by

$$\varepsilon \approx \frac{4V_o}{V_i \zeta} \left(\frac{1}{1000}\right)$$

(5.1)

where $V_o$ is the output voltage with unit mV; $V_i$ is the input voltage 5.0 V; $\zeta$ is the room-temperature strain gage factor, which is 2.11. The number 4 is used here because of Quarter-Bridge circuit strain gage. It is worth noting that $\varepsilon$ is a dimensionless unit. Eq. (5.1) directly yields strain. It also can be reported as $\mu$strain. In this case, the equation should multiply by $10^6$ on its right-hand side.

The calculated flexural strain is shown in Figure 5.18. The curve for position (Pos) 1 is the waveform from 45° with respect to the longitudinal direction of the beam specimen. Pos 2, Pos 3, and Pos 4 refer to strain gages 2, 3, and 4 in Figure 5.7. Sample P2 is the control sample, which is non-grid stiffened syntactic foam. Samples of S1P2, S2P2, and S3P2 are grid stiffened but having different bay area. The following observations can be made. (1) The impact response is boundary controlled or quasi-static. Each specimen shows several rounds of back and forth of impact waves. (2) The response of the flexural strain after low velocity impact indicates that non-grid stiffened foam sample has longer impact duration while grid stiffened foam has shorter impact time. As suggested, long impact duration is associated with severe damage [163-165].

The observation after the low velocity impact shows that the non-grid stiffened foam (i.e., P2) was damaged into pieces, much severe than grid stiffened foams (S1P2, S2P2, and S3P2), which only shows small indentation on the impact surface and cracking on the back surface. (3) For the grid stiffened foam specimens, the bay area has an effect on the impact-induced flexural strain. It shows that the impact duration for S1P2 is the shortest as compared with S2P2 and S3P2, indicating the smaller the bay area, the shorter the impact duration. This is because S1P2 has the smallest bay area and thus the grid skeleton needs the shortest time to dissipate the impact energy. (4) The observation for the grid stiffened foam specimens shows that a single crack was observed on the back surface for S1P2 and S2P2, but multi-cracks for S3P2 (see Figure 5.24b). This is because S3P2 has the largest bay area and thus the bay directly under impact is stressed the longest, allowing more cracks to be produced and propagated. (5) By checking the four flexural strain traces from the strain gages, it is clear that positions 1 and 2 are basically under
compression during the entire impact event. For positions 3 and 4, the control specimen shows several rounds of tensile strain, while the grid stiffened specimens only show one round of tensile strain. This is the other evidence that the control specimen was shattered into pieces, while the grid stiffened specimens were still hold together, although with some levels of damage.

Figure 5.18 Impact response collected by strain gages at different positions.

5.3.6 Damage-Healing Ability

The healing efficiency of the crack induced by low velocity impact and three-point bending was investigated through flexural strength recovery ratio, which is determined by the recovered flexural strength over the original flexural strength. In the following subsections, the damage-healing ability under both free and constrained boundary conditions will be discussed.

5.3.6.1 Healing efficiency under free boundary condition

The flexural stresses before and after crack healing is shown in Figure 5.19. Based on those, the flexural strength recovery ratios (healing efficiencies) for specimens healed under free boundary condition are calculated and shown in Figure 5.20. The effects of the bay area and TF content on the flexural strength recovery ratio are shown in Figure 5.20a and Figure 5.20b, respectively. In addition, the crack before healing and after healing is shown in Figure 5.21.
The following observations can be made: (1) The stiffness of the healed specimens decreases as compared with the original syntactic foam specimen, except S2P3. This may be due to the partial crack healing. It in turn reduces its load bearing capacity. (2) The effect of TF content on the healing efficiency is significant (see Figure 5.20a). 6% (S2P1) and 9% (S2P2) TF contents have similar strength recovery ratio, less than 48%. However, with 12% of healing agent (S2P3), the healing efficiency is above 88% after ten damage-healing events. Obviously, this is because, when the TF content is low, there is no sufficient healing agent to fully fill in the narrowed crack volume. (3) The bay area also has an effect on the healing efficiency (see Figure 5.20b). The healing efficiency increases as the bay area increases. It is worth noting that the total
amount of polymer artificial muscle in the syntactic foam matrix is 3.5% by volume. Smaller bay area means less artificial muscle in one rib; or more artificial muscle in each rib for larger bay area. The maximum recovery force for each artificial muscle is constant. Therefore, the resultant recovery force for each group of specimens is the same. However, small bay area leads to more uniform recovery force distribution, while large bay area suggests that the force is more concentrated in several locations. For closing the same crack, concentrated force or thicker ribs is more efficient in overcoming resistance than distributed force or thinner ribs, leading to higher healing efficiency in S3P2. (4) The crack healing is improved as the number of damage-healing events increases. This is because the damage-healing event helps the distribution of molten healing agent over the fractured surface, increasing wet area, or even flowing into the crushed microballoon sites. The increase in bonding area is sure to increase the bending strength of the beam specimens. In addition, after several damage events the crushed brittle glass microballoons on the fractured surface mix with the molten healing agent. This will be elucidated by SEM results in section 5.3.7. As a result, the adhesive layer becomes a particulate reinforced healing agent, leading to increased bonding strength. Consequently, the damage-healing events improve the crack healing ability of syntactic foam specimens.

Figure 5.21 Crack before healing and after healing.

5.3.6.2 Healing efficiency under constrained boundary condition

The flexural stresses before and after crack healing is shown in Supplementary Materials, Figure 5.22. Based on those, the flexural stress recovery ratios were obtained. The effect of TF content and bay area on flexural strength recovery under constrained boundary condition is
presented in Figure 5.23. And the crack healing process monitored by the high resolution camera is displayed in Figure 5.24. The following observations can be made: (1) the specimens healed under constrained boundary condition have better healing efficiency than those healed under free boundary condition. It is worth noting that, as compared to the length of the beam specimens after fracture, the syntactic foam beam healed under free boundary condition becomes shorter, while the beam healed under constrained boundary condition maintains the fractured beam length after healing. Because the muscles have 80% pre-stretch, it suggests that the muscles have a stretch less than 80% for specimens healed under free boundary condition, while they have a stretch over 80% for specimens healed under constrained boundary condition. Because the muscle strength and stiffness increase as the stretch increases, the muscles in the specimens healed under constrained condition have higher resistance to bending, leading to higher healing efficiency. (2) The healing efficiency increases as the TF volume fraction increases. The reason is the same as the specimens healed under free boundary condition, as explained in subsection 5.3.6.1. (3) The effect of bay area on the healing efficiency is insignificant. This is because under constrained boundary condition, the strength and stiffness of the muscle reinforcement dominate the bending behavior, rather than its actuation stress distribution within the crack zone.

![Flexural stresses for samples before and after 8th constrained-boundary condition healing.](image)

Figure 5.22 Flexural stresses for samples before and after 8th constrained-boundary condition healing.
Figure 5.23 Constrained boundary: (a) effect of TF content, (b) effect of bay area size.

Figure 5.24 Crack before healing and after healing.

5.3.7 Inspection of Specimens

The impact crack propagation mode is shown in Figure 5.25. For specimen having small bay area (i.e., S1P2), the low velocity impact induces a single crack on the back surface, as shown in Figure 5.25a. This is because of the shorter impact duration, see Figure 5.18. For large
bay area (i.e., S3P2), the impact induces multiple cracks on the back surface, as shown in Figure 5.25b. In addition, the adhesive layer consists of thin thermoplastic film and crushed glass microballoon shell particles (see Figure 5.25c), forming strong interfacial bonding between fractured surfaces. This layer has higher strength than the interface connection between glass microballoon-glass microballoon. As a result, it endows higher and higher healing efficiency as the impact-healing cycle increases. In Figure 5.25d, it shows the flow of the molten healing agent from melting thermoplastic fiber. The overlap indicates that the healing agent was melted first, then the artificial muscle contracted and forced the fractured surfaces into contact, spreading the molten healing agent to a larger area on the fracture surface due to the pressure by the muscles and the capillary action. The increased bonding area leads to increased healing efficiency.

Figure 5.25 (a) Impact crack mode for sample S1P2; (b) Impact crack mode for sample S3P2; (c) healed fracture surface showing thin thermoplastic film and crushed glass microballoon shell particles; (d) healed fracture surface showing flow of the molten healing agent. (In a & b, arrows show the cracks.).
5.4 Conclusions

In this study, the artificial muscle grid stiffened healing-on-demand syntactic foam composite was developed. The twisting and coiling process causes change of the microstructure of the polymer fiber. The muscle responds to thermal actuation quickly and is quite stable, even at the healing temperature. The two dimensional (2D) artificial muscle grid controls the composite panel responding to impact in a quasi-static manner. The artificial muscle grid can efficiently and repeatedly close cracks after low velocity impact and bending damage. The volume fraction of the TF healing agent has a significant effect on the flexural strength recovery for specimens healed under both free boundary condition and constrained boundary condition. The volume fraction of the TF above 9% is recommended for fabricating this type of syntactic foam composite. The bay area has a significant effect on the impact response and healing efficiency of specimens healed under free boundary condition. For specimens under constrained boundary condition, the bay area has an insignificant effect on the healing efficiency. Different from previous studies, which usually show reduced healing efficiency as the damage-healing cycle increases, the muscle reinforced syntactic foam composite shows an increased healing efficiency as the damage-healing cycle increases, probably due to the filling of the void formed by crushed microballoons with the healing agent.
CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions

In this dissertation, a literature review of the current healing-on-demand polymer and polymer composites, shape memory polyurethane (SMPU) fibers, healing-on-demand composites, and polymeric artificial muscles were first conducted in details in chapters 2, 3, 4, and 5.

In chapter 3, The SMPU fibers are studied for self-healing applications. After being programmed, the physical/mechanical and thermomechanical properties are investigated experimentally. Then a theoretical analysis is performed on the conformational entropy change to analyze its long-term structural relaxation behavior in terms of stress relaxation test results. It is found that the cyclic loads during the CDP process leads to an increase in shape fixity of the programmed fibers. The strength and stiffness of the programmed fibers have been improved by the CDP process. After the CDP process, the programmed fibers have a good crack-closing capability with a maximum recovered stress of 11.6 MPa and exhibit good stress recovery behavior at the temperatures within the range of 65°C ~ 140°C. Moreover, after structural relaxation in the time scale of 13 years, the programmed SMPU fibers, which are “stress free” or hibernate in a polymer matrix, can still provide some recovery force to close millimeter scale cracks in the self-healing system when triggered by thermal stimulus.

In chapter 4, the polymer artificial muscle based healing-on-demand composite was studied. It showed that the PE artificial muscle from commercial fishing line exhibits repeatable actuation stress upon thermal activation, without losing any actuation ability. The composite based on polymer muscle could close and heal damage induced crack efficiently, even when the beam is at constrained boundary conditions. In addition, it is found that the pre-strain level of the artificial muscle has a significant effect on the healing efficiency. Under allowable pre-strain level limit and constant volume fraction of the healing agent, higher pre-strain level guarantees better crack healing efficiency.

In chapter 5, the artificial muscle grid stiffened healing-on-demand syntactic foam composite was developed. The twisting and coiling process causes change of the microstructure of the polymer fiber. The muscle responds to thermal actuation quickly and is quite stable, even
at the healing temperature. The two dimensional (2D) artificial muscle grid controls the composite panel responding to impact in a quasi-static manner. The artificial muscle grid can efficiently and repeatedly close cracks after low velocity impact and bending damage. The volume fraction of the TF healing agent has a significant effect on the flexural strength recovery for specimens healed under both free boundary condition and constrained boundary condition. The volume fraction of the TF above 9% is recommended for fabricating this type of syntactic foam composite. The bay area has a significant effect on the impact response and healing efficiency of specimens healed under free boundary condition. For specimens under constrained boundary condition, the bay area has an insignificant effect on the healing efficiency. Different from previous studies, which usually show reduced healing efficiency as the damage-healing cycle increases, the muscle reinforced syntactic foam composite shows an increased healing efficiency as the damage-healing cycle increases, probably due to the filling of the void formed by crushed microballoons with the healing agent.

6.2 Future Works

Healing-on-demand composite could heal its damage induced cracks via the CTH strategy. The research conducted in this work shows that the polymeric artificial muscle exhibits stable actuation stress without considering structural relaxation. This makes the large scale crack be closed efficiently, timely, and repeatedly. However, the thermal actuation stress is only about 14 MPa, which limits the ability to close much wider cracks. One of the future works will be to study on how to improve the thermal actuation stress. It might need to explore new materials for polymeric artificial muscle synthesis and manufacturing. In addition, the actuation behavior of artificial muscle is activated by thermal stimulus in this work. Multi-responses such as actuation by electricity, UV, magnetic, moisture, pH, etc., may be other future works that deserve exploration.
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APPENDIX I A SELF-HEALING PARTICULATE COMPOSITE REINFORCED WITH STRAIN HARDENED SHORT SHAPE MEMORY POLYMER FIBERS AND ITS COPYRIGHT PERMISSION FROM ELSEVIER

Cold-drawing programmed short SMPU fiber reinforced composite was studied. The fibers were coated by two-layer coating agents. It showed that the two-step coating method effectively improved the shape fixity ratio of the programmed SMPU fiber from 30% to 66%. And the coated fiber had good shape memory effect (i.e., higher recovery stress). The recovery stress reduces nonlinearly with recovery strain. It is found that healing of the composite is repeatable. The healing efficiency increases as the fiber length increases for the three fiber lengths investigated due to the need of certain embedded fiber length for shear force transfer. The crack opening process is also a cold-drawing programming process for fibers bridging over the crack, which leads to springback and some closure of the crack when the external load is removed.

Experiment

Preparation, Programming, and Coating of SMPU Fibers

Polyurethane was synthesized by using poly(butylene adipate) (PBA, \(M_n = 650\)) as soft segments, 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) as hard segment. The average formula weight ratio was (MDI+BDO): PBA = 1021: 300. All the chemicals were de-moisturized prior to use. The reaction was conducted in a high-speed mixer at room temperature with nitrogen protection. The obtained polyurethane was further cured in a vacuum oven at 110\(^\circ\)C for 12 hours. Then SMPU fiber was prepared using a modified OneShot Extrusion Machine with a spinning speed of 40 m/min. The spinning temperature is 180\(^\circ\)C.

SMPU fiber bundles were programmed and stretched to a ratio 100% at room temperature by the MTS machine (RT/5, MTS Inc., USA) equipped with a 250 N load cell. A half hour structural relaxation was followed. Then acrylic conformal coating was sprayed on the programmed fibers, allowing 24-hour curing of the coating agent. As shown in Figure A1.1, the thickness of the conformal coating is much smaller than the diameter of the fiber; such a thin layer of coating could not hold the programmed fiber and thus improving its shape fixity. Hence, a two-step method was developed to improve the shape fixity of the programmed SMPU fiber. The programmed fiber was coated by acrylic conformal coating first and then by epoxy. The
reason why not use the epoxy coating only is that the curing agent for epoxy is also an organic solvent for polyurethane fiber, which would be catastrophic for the programmed fiber. Therefore, the usage of acrylic conformal coating is to protect it against the organic solvent. Then the epoxy EPON828 was sprayed after 24-hour curing of the conformal coating. Once the two-step coating was completed, one week was allowed for the curing of the epoxy. Some programmed SMPU fibers did not have the coating layer. They were used as controls.

**Partially-Fully Constrained Stress Recovery and Free Shape Recovery Tests**

In order to determine the recovery stress – recovery strain relationship, partially constrained stress recovery test was conducted on both coated and uncoated SMPU fibers which were cold-drawing programmed by 100% prestrain. In this test, one end of the fiber was clamped and the other end was loaded by a certain load, on which the stress in the fiber was based and calculated. Then the loaded fiber was heated to 80°C at 5°C/min and held for 30 minutes, and the recovered strain was recorded. By changing the load to different values and conducting the partially constrained recovery test again, a set of data points in the recovery stress-strain curve was obtained.

In addition to the partially constrained stress recovery test, fully constrained stress recovery test (zero recovery strain) and fully free shape recovery test (zero recovery stress) were conducted to obtain the two limiting data points in the recovery stress-recovery strain curve. In the fully constrained stress recovery test, both ends of the fiber were clamped by the grip of the MTS machine. During the stress recovery test, the programmed fiber became loose in the initial stage of heating, due to the thermal expansion effect. In this study, a prestrain was used in order to compensate for the thermal expansion of fibers, ensuring that they had zero stress immediately before the stress recovery process starts. The prestrain was determined by a trial-and-error method [61]. For the free shape recovery test, the programmed fiber was put in the heating chamber without applying any load. For both fully constrained and fully free recovery test, the same heating profile as the partially constrained recovery test was used.

**Material System and Composite Fabrication**

In this study, the EPON™ Resin 828 (Momentive Specialty Chemicals Inc.) was used as the composite matrix, and the diethylenetriamine by Sigma-Aldrich was used to cure the epoxy for three days at 25°C. This particular epoxy was selected due to its room temperature curing
property. Otherwise, high temperature curing would recover the programmed SMPU fibers or speed up structural relaxation, resulting in a total or partial loss of the recovery stress \[15, 25\] and the crack closing ability. According to the supplier, the cured epoxy has an ultimate tensile strength of 28 MPa and modulus of 3700 MPa. The CAPA 6506 powder (Perstorp UK Ltd.), a high molecular weight linear polyester derived from caprolactone monomer (i.e., polycaprolactone), was used as the thermoplastic healing agent. The particle has a density 1.1 g/cm\(^3\) at 25°C, melting temperature 58 – 60°C, and 98% of the size smaller than 0.6 mm.

Figure A1.1 SEM observation of the pure SMPU fibers and coated programmed SMPU fibers with a 100% stretching ratio.

The critical fiber length \(L_c\) of programmed short-SMPU fibers is a significant parameter for future tests. From an empirical theory, the critical fiber length is determined by [138]:

\[
L_c = \frac{\sigma_u f d f}{2\tau_m}
\]  
(AI.1)

here \(\sigma_u f\) is the ultimate tensile strength of the programmed SMPU fibers, \(d f\) is the programmed fiber diameter, and \(\tau_m\) is shear yield strength of the matrix. As shown in Figure A1.2, the programmed SMPU fiber at 100% prestrain has an ultimate strength of 690 MPa. After programming, the diameter of the fiber is 0.028 mm. As provided by the manufacturer, the shear
yield strength of the acrylic coating agent is 6.35 MPa. Therefore, the critical fiber length \( (L_c) \) is calculated based on Eq. (AI.1), which is 1.52 mm.

Because the fiber needs to bridge over the crack in order to close the crack, the minimum fiber length \( (L) \) is determined by \( L = \lambda L_c \), where \( \lambda \) is a length factor and \( \lambda > 1 \). The reason we need much longer fiber than \( L_c \) is that Eq. (AI.1) is the minimum fiber length for shear stress transfer with the fiber aligned along the axial loading direction. For our case, the fibers are randomly distributed in space, with most of them inclined with respect to the loading direction. Therefore, much longer fiber length is required. In this study, the coated-programmed SMPU fibers were cut into short fibers with lengths of 4 mm, 7 mm, and 10 mm, respectively. When preparing the composite, the resin and 10% by volume of thermoplastic particles (CAPA 6506) were mixed firstly for ten minutes. Secondly 13% by weight of curing agent (Sigma, Diethylenetriamine ReagentPlus, 99%) was mixed with the mixture for two minutes, then 5% by volume of short fibers were added to the mixture and mixed for three minutes. The well mixed mixture was poured into an aluminum mold. After that, the mold was kept in a chamber at 4°C for 24 hours. A thermocouple was located at the top surface center of the mold and the Yokogawa Model DC-100 was used to monitor the temperature of the mixture during the curing process. The first day of low temperature curing was to ensure that the curing heat be removed so that the embedded SMPU fibers would not be recovered. The mold was then exposed to room temperature and cured for three days prior to machining into beam specimens for testing. Composite beams without short SMPU fibers were also fabricated for comparison. For sake of convenience, the composites were denoted as Non-PUFRC and PUFRC, suggesting specimens without SMPU fiber and with SMPU fiber, respectively. Depending on the fiber length, the PUFRC was further divided into three groups, 4-PUFRC, 7-PUFRC, and 10-PUFRC, indicating specimens with 4-mm SMPU fiber, 7-mm SMPU fiber, and 10-mm SMPU fiber, respectively.

**Differential Scanning Calorimetry (DSC) Test**

Differential scanning calorimetry (PerkinElmer DSC 4000, USA) test was carried out to investigate the thermal properties of the short SMPU fiber reinforced polymer composite and also its components including thermoplastic particles, programmed SMPU fiber, and Epon matrix. It was first cooled from 30°C to -70°C at a rate of 20°C/min and scanned from -70°C to 275°C at a ramping rate of 5°C/min. The purging rate of Nitrogen is 30 ml/min. Three effective
samples were tested under the same conditions. Two cooling and heating cycles were conducted on each sample, and the second heating cycle was used to determine the glass transition temperature ($T_g$) and other thermal properties in order to eliminate the thermal history.

![stress-strain curve](image)

Figure AI.2 The room temperature stress-strain behavior of the SMPU fiber after programming by pre-stretch ratio of 100%.

**Three-Point Bending Test of Notched Beam Specimens**

Notched beam specimens with dimensions of 90 mm × 10 mm × 20 mm were fabricated per ASTM D 5045 standard, and the notch was machined by bandsaw as schematically shown in Figure AI.3. The reason of using single edge notched beam (SENB) specimens was to create structural scale crack. The three-point bending tests were carried out by the MTS (RT/5, MTS Inc., USA) system at a loading rate of 10 mm/min. The schematic setup of the test is shown in Figure AI.3.

The beam specimens were fractured completely into two halves at room temperature. Process of the bending test (i.e., crack initiation and propagation) was captured by a high resolution CCD camera (Sony XCD-CR90), which is equipped with a light source and a digital interface which interlinks the computer and the camera. The CCD camera used in this test has a
resolution of $3.7 \times 3.7 \ \mu m/pixel$. Fire-i data acquisition software was used to store the image data from the camera during testing.

![Diagram of specimen and three-point bending test set-up](image)

**Figure A1.3** Schematic explanation of the specimen and three-point bending test set-up.

**Close-then-heal (CTH) Self-healing**

Unlike using an external confinement in the two-step self-healing process [4] or clamped ends in the CTH process [17], the fractured specimens in the experiment underwent free recovery under thermal stimulus. The scheme of the close-then-heal program is elucidated in Figure A1.4. It is seen that, while complete fracture of the notched beam might cause fiber pull-out, fibers bridging over the crack were not fractured because of the high ductility of the SMPU fibers, which were the fibers leading to closure of the crack per the CTH scheme. The completely fractured beam specimen was transferred into an oven. For the control beam without the programmed short SMPU fibers, the separated two half beams were put together manually, fitting along the crack. The oven chamber was heated up from room temperature (about 21°C) to 80°C at a rate of 5°C/min. The specimen was held inside the chamber at 80°C for 30 minutes. At this moment, the shape recovery effect of the programmed short SMPU fibers were activated thus closing the crack automatically to micro-scale. Because of the melting and diffusion of the polyester CAPA, the thermoplastic particles filled the narrowed crack and diffused into the fractured EPON matrix. Cooling leads to hardening of the thermoplastic film and healing of the fractured beam. This completed the first fracture-healing cycle. This fracture-healing continued until five cycles to evaluate the ability for repeatedly healing wide-opened cracks. During the
fracture testing, the peak bending load was recorded, which was used to calculate the healing efficiency. At least three effective specimens were tested for each group of samples.

![Figure AI.4 Schematic of the two-step healing process (i.e., close-then-heal (CTH)) on a fractured short-SMPU-fiber-reinforced beam specimen.](image)

**Non-Destructive Testing**

The crack was measured by UNICO zoom stereo microscope, equipped with an optional digital camera (AmScope MD35). Also, the healed crack was investigated by an optical microscope (VanGuard, USA) equipped with a camera (XLI, USA). The advantage of the non-destructive testing is to ensure that the damaged cracks and/or healed cracks have no interruption from some unknown factors.

**SEM Fractography**

The fractured surfaces for specimens before healing and after healing were characterized by scanning electron microscope (SEM), Quanta 3D FEG field-emission electron microscope. This is to investigate crack interface, where a bonding layer was formed by melted thermoplastic particles as an adhesive for bonding the two fractured surfaces.
Results and Discussion

Coated Programmed SMPU Fiber Properties

Shape fixity (i.e., strain fixity) ratio is one of the important parameters for describing shape-memory effect, indicating the ability to fix a temporary shape [61]. It is determined by

\[ R_f = \frac{\varepsilon_i}{\varepsilon_p} \times 100\% \]  

(AI.2)

here \( R_f \) is the shape fixity ratio, \( \varepsilon_i \) is the instantaneous strain of the programmed SMPU fibers after removal of the applied load, and \( \varepsilon_p \) is the predeformation strain at the end of the programming process (i.e., 100% in this case). As shown in Figure AI.5, the shape fixity of the programmed SMPU fibers has been significantly improved by the coating agent from 30% to 66%. It also shows that the shape fixity of uncoated programmed SMPU fiber relaxes fast at the first three minutes and becomes stabilized within five minutes. The reason for this phenomenon has been emphasized and discussed in a previous study by Zhang and Li [61]. This is due to the fast structural relaxation at the early stage after the removal of the stretching load. However, in the case of coated programmed SMPU fiber, it keeps relaxing and is still un-stabilized even after 30 minutes. This can be explained as follows. The removal of the stretching load leads to large springback and viscoelastic rebound in the first few minutes. However, due to the layer of coated fixing agent, free springback of the fiber is not allowed, leading to slower structural relaxation of the fiber. Based on the shape fixity information, the coated programmed SMPU fibers were cut into short fibers and mixed with resin after 30 minutes of the removal of the programming stretching load.

In addition, the stress recovery behavior of the coated-programmed and uncoated-programmed SMPU fibers was investigated, as shown in Figure AI.6. It was soaked at 80°C for three hours to obtain stabilized recovery stress. The linear coefficient of thermal expansion (CTE) of the aluminum grip device is 23.86×10^{-6} °C, while the CTE of the SMPU fiber is 11.8×10^{-5} °C. Obviously, the dimension change of the grip due to heating to 80°C is considerably small as compared with that of the fiber. Thus, the effect of thermal expansion of the grip is ignored in this study. As shown in Figure AI.6, the stabilized recovery stress for coated-programmed SMPU fiber is 25 MPa; while in the case of uncoated-programmed SMPU fiber, the recovery stress is 13.2 MPa. The difference between the recovery stresses for coated-
and uncoated programmed SMPU fibers is due to their different shape fixity ratios. The higher shape fixity ratio of the coated fiber leads to a larger conformational entropy change and a better alignment of the molecules along the fiber direction [61,126]. Such a change would lead to a higher potential driving force for shape recovery under thermal stimulus and thus a higher recovery stress.

Figure AI.5 Shape fixity for uncoated and coated programmed SMPU fibers at room temperature (about 21°C).

Figure AI.6 Stress recovery behavior of coated programmed SMPU fiber under temperatures from room temperature (about 21°C) to 80°C.
Partially Constrained Shape Recovery Behavior

Based on the maximum recovery stress (see Figure AI.6), the maximum recovery load for a bundle of 24 SMPU fibers is 0.4 N. In this study, five groups of fiber bundles were used to perform the partially constrained shape recovery test. The first group was heated to 80°C at a stress-free condition (i.e., without clamping at any end or zero stress). The second group was recovered with one end clamped and the other end loaded by 0.1 N load. The third and fourth groups were recovered under 0.2 N and 0.3 N loads, respectively. For groups 1 to 4, the stabilized fiber bundle length was measured to determine the stabilized recovery strain. For the fifth group, both ends were clamped (i.e., fully constrained test or zero recovery strain, as compared with the terminology of partially constrained test). The results were averaged out from three bundles in each group. This yields five points in the recovery stress and recovery strain curves, as shown in Figure AI.7, presenting that the recovery stress reduces as the recovery strain increases. This suggests that, in the application to self-healing composite, the recovery force of the SMPU fibers will decrease as the crack narrows.

![Figure AI.7](image)

Figure AI.7 Recovery stress - recovery strain behavior of the coated and uncoated SMPU fibers recovered at 80°C with varying level of constraints.

From Figure AI.7, the coated programmed fiber exhibits a maximum recovery strain of 52%, which means 48% of its deformation is permanent at the temperature 80°C. The reason for this is due to the coated epoxy. As shown in Figure AI.8, the glass transition temperature of the epoxy is above 100°C, indicating that the fixing agent is still in glassy state at the recovery temperature of 80°C and resists free shape recovery of the coated SMPU fiber. Also, the
recovery stress of the coated fiber reduces faster with recovery strain than that of uncoated fiber. In the case of uncoated programmed fiber, it shows an almost fully shape recovery, 98.6% recovery strain. Using curve fitting, the relationship between the recovery stress (σ) and recovery strain (ε) are obtained in Figure AI.7. Based on the obtained σ-ε expression, the recovery force could be calculated at a certain crack width. In comparison with uncoated SMPU fiber, the coated SMPU fiber has higher recovery stress when the recovery strain is smaller than 24%. Therefore, when the recovery strain is lower than 24%, the coated fiber has larger recovery force to close crack, i.e., higher crack-closing efficiency. When the recovery strain is higher than 24%, on the contrary, the uncoated fiber has larger recovery stress and should be more effective. In practice, however, due to the resistance to crack closing by the un-fractured matrix or by constrained boundary, very high recovery strain is unlikely because of the equilibrium requirement between the recovery force and resistance force. Of course, this also suggests that the crack width that can be closed by the SMPU fibers is limited. A very rough estimation between the recovery stress and crack width has been given in [17].

![Figure AI.8](image-url)

**Figure AI.8** Thermal properties from DSC results: (a) programmed short SMPU-fiber reinforced composite; (b) programmed SMPU fiber only; (c) plastic particle only; (d) EPON matrix only.
Thermal Properties of SMPU Fiber Reinforced Composite

The thermal properties of the composite and its components were studied by DSC method. In Figure AI.8(a), it shows a peak around 58°C which is the melting point of the thermoplastic particles, and a step change around 103°C which indicates the glass transition temperature ($T_g$) of the composite. The programmed SMPU fiber has a $T_g$ of 45°C, as shown in Figure AI.8(b). As concluded from previous study, the cold-drawn programming shifts the $T_g$ of the SMPU fiber to a higher temperature [61]. Thus the $T_g$ of the coated programmed fiber exhibits a higher temperature than its non-programmed counterpart, which is around 12°C [61]. However, the heat flux released by the programmed fiber is not clearly shown in Figure AI.8(a). The reason is that only 5% by volume of SMPU fibers were incorporated in the composite, which is a small amount as compared with the other components in the test composite sample. As shown in Figure AI.8(c) and (d), the pure thermoplastic particle has a melting temperature of 58°C, and the composite matrix (i.e., EPON resin) exhibits a glass transition temperature of 103°C. Clearly, the transition temperatures of the composite in Figure AI.8(a) are good reflections of the two components – epoxy matrix and thermoplastic particles.

Temperature Evolution during Curing of the Composite

As discussed in section AI.2.4, a special approach was used to fabricate the composite in order to avoid overheating. Since the chemical reaction between the resin and the curing agent releases a large amount of heat during the curing process of the composite, the SMPU fibers would likely to be overheated, i.e., above the glass transition temperature, if the heat were not removed effectively. As shown in Figure AI.8(b), the programmed SMPU fiber has a $T_g$ of 45°C, indicating that any temperature higher than 45°C will activate its shape recovery ability, thus sacrificing its crack closing ability. In order to solve this challenge, one solution suggested by Meng and Li [66] is to use a SMP fiber that has a high thermal resistance temperature. However, in this study, the solution is to put the mold in a chamber under 4°C for 24 hours. As shown in Figure 4.9, the composite started fast curing after two hours of adding the curing agent, and slowed down in two and half hours. The maximum recorded temperature was 26°C, which means the reinforced SMPU fibers were not recovered in the matrix. Once stimulated by thermal energy, the fibers are still able to recover their shape thus closing cracks.
Figure AI.9 Heat released during the process of the curing of Epon resin with Diethylenetriamine.

**Three-point Bending Test**

Typical load-deflection curves of the different groups (i.e., 10-PUFRC notched beam, Non-PUFRC notched beam, healed 10-PUFRC beam, and healed Non-PUFRC beam) are shown in Figure AI.10. It is seen that the PUFRC notched beam has higher toughness and strength than the Non-PUFRC notched beam; and healed 10-PUFRC beam has good toughness and strength properties even after being fractured. However, the healed Non-PUFRC beam exhibits a very small peak load (shown in the upper-right corner of Figure AI.10), which could be neglected. In other words, the healing efficiency of the notched beam without SMPU fibers can be neglected. The improvement in toughness and strength is due to the advantages of the programmed short SMPU fiber reinforcement [142-145]. The difference between the healed beams without and with the SMPU fibers would be elucidated by Figure AI.11. Without SMPU fibers, the healing agent (i.e., thermoplastic particles) melted and flowed into the wide-opened crack at 80°C, leaving porous interface when cooled down to room temperature, which created a weak bonding interface, as shown in Figure AI.11(a). As a result, the Non-PUFRC beam has poor crack healing ability even though the crack was closed manually. However, for the PUFRC beam with SMPU fibers, the shape memory effect of the reinforcing SMPU fibers was activated when heated, and the constrained shrinkage of the SMPU fibers bridging over the crack narrowed the crack. As shown in Figure AI.6, the maximum recovery stress is 25 MPa, indicating that the crack could be continuously narrowed until an equilibrium between the force exerted by the fiber and resistance to crack closing (such as by the uneven fractured surface) was achieved. It is noted that as the crack narrows, the force exerted by the fiber reduces. Therefore, the crack cannot be fully closed.
unless the resistance to crack closing can be neglected. A recent study by Okoro indicates that the healing efficiency increases when the fractured surfaces become smoother [146]. Meanwhile, the healing agent melted, flowed into the narrowing crack, and diffused into the fractured matrix. Under the exertion of the sustained recovery force by the SMPU fibers, the healing agent may become a thin film. Of course, the ability for the thin film to resist crack initiation and propagation increases as the film thickness (crack width) reduces [147], leading to higher healing efficiency. Also, with the sustained recovery force, there are fewer defects in the film, as schematically shown in Figure AI.11(b).

![Figure AI.10 Typical load-deflection curves of notched and healed (after first CTH program) specimens.](image)

![Figure AI.11 Healed crack interfaces for beams (a) without SMPU fiber reinforcement and (b) with SMPU fiber reinforcement (F(x) is the recovered force exerted by the programmed short SMPU fiber reinforcement).](image)
The ability for repeatedly healing cracks was evaluated by cyclic fracture-healing test per the three-point bending approach. As shown in Figure AI.12, the self-healing ability of the PUFRC beams with various fiber lengths was investigated for up to five fracture/healing cycles. It indicates that the close-then-heal ability is repeatable for programmed short SMPU fiber reinforced composite. From Figure AI.12, the peak bending loads for all three groups decrease with fracture-healing cycles. In other words, the healing efficiency reduces as the fracture-healing cycle increases. It is noted that, from the results of the peak load, fibers with longer length leads to higher peak load value. The reason might be that the critical fiber length as determined by Eq. (AI.1) is the shortest fiber length required for effective shear force transfer. Because of the 3-D dispersion of the fibers, even for those fibers that bridge over the crack, the fiber length within one side of the fractured matrix may be smaller than that required for the shear-force transfer, although the other side might be sufficient. Therefore, the actual fiber length required for effective stress transfer may be much longer than the critical fiber length. Therefore, the peak load increases as fiber length increases. However, it is believed that this increase will gradually approach that by continuous fibers such as in [17]. As pointed out by Takao and Taya [63] and Sato et al [142], the increase in short-fiber length within a certain range would improve the stress distribution along the interface between fiber and matrix. Because of this, the fibers with longer length exert larger recovery force to the cracked matrix and lead to thinner thermoplastic film and thus higher bending load.

Figure AI.12 Peak bending load with healing cycles for short programmed SMPU fiber reinforced composite beam with different fiber length.
The healing efficiency \((\eta)\) is defined as the ratio of the peak load \((P_h)\) of the healed PUFRC beam over the peak load \((P_{non})\) of the original Non-PUFRC beam. It is given by

\[
\eta = \frac{P_h}{P_{non}} \times 100\%
\]

Using Eq. (AI.3), the healing efficiencies after five fracture-healing cycles for the 4-PUFRC, 7-PUFRC, 10-PUFRC are 42\%, 52\%, and 61\%, respectively. Consequently, it is believed that the two-step CTH healing is repeatable for programmed short SMPU fiber reinforced particulate composite.

**Non-destructive Observation Results**

With the help of the high resolution optical microscope, the bending crack and the effect of CTH are captured in Figure AI.13 and Figure AI.14. The advantage of using optical microscope rather than electron microscope is that it allows the scanned sample to be intact without additional damage. Accordingly, the scanned results keep consistent and repeatable. As shown in Figure AI.13, the bending crack width was 1.8 mm at the peak bending load, and because of the springback of the SMPU fibers, the crack was narrowed to 0.7 mm, 0.6 mm, and 0.32 mm in 4-PUFRC, 7-PUFRC, and 10-PUFRC beams, respectively, after the removal of bending loads at room temperature. Therefore, the closure of the crack under two-step CTH is initiated by the springback of the programmed short SMPU fibers. It is interesting to investigate why springback occurred as the springback due to programming has been allowed before fabricating specimens. This is because the crack opening process during bending test is also a cold-drawing process for fibers bridging over the crack. For longer fibers, they have longer length embedded in the matrix and thus store higher energy. Once the bending load is removed, the longer fibers springback more and lead to narrower crack. As shown in Figure AI.14, the bending damaged PUFRC beams were healed effectively under two-step CTH. It also shows that the healed crack width reduces from 37 \(\mu\)m to 26 \(\mu\)m as the length of the SMPU fibers increases from 4 mm to 10 mm, which is in agreement with the healing efficiency test results.

The healed crack interface is also investigated, as shown in Figure AI.15. It shows that the narrowed cracks are filled in with healing agent (i.e., thermoplastic).
Crack narrowing due to springback of the SMPU fibers bridging over the crack immediately before and after removal of the bending load as captured by the CCD camera.

**SEM Observation Results**

The fractography of three-point bending induced crack surface was investigated by field-emission SEM. In Figure A1.16, it shows that the beam crack surface fractured after the first fracture (A) and (B) and the fifth fracture (C)-(F). From Figure A1.16 (A) and (B), the spherical objects observed are thermoplastic particles. It is also seen that the coating layer on the fibers were broken during the crack opening process in the bending test. This is because the fibers are ductile while the coating epoxy is brittle. The large strain on the fiber during crack opening fractured the coating layer, but not the fibers. This is in agreement with the above discussion that
the bridging fibers springback once the bending load is removed and narrow the crack to a certain level. In addition, the directions of fibers on the crack surface are multi-orientations, indicating 3-D dispersion of the coated SMPU short fibers. Therefore, the SMPU fibers can close crack in any orientations, not limited to the notched direction in this study. This is the major advantage of using short-fiber reinforcement. After the fifth fracture, a layer of bonding interface can still be observed on the fractured surface as shown in Figure AI.16 (C) to (F). From (C) to (F), the microscope focused on the same area but in an increasing magnification. With increasing magnification, it is clearly seen the flowing traces and branching of the flow of the molten thermoplastic, an indication of rough fractured surface.

Figure AI.14 Effect of crack initiation and healing on short programmed SMPU fiber reinforced composite.
Conclusions

Based on the studies on cold-drawing programmed short SMPU fiber reinforced composite, in which the fibers were coated by two-layer coating agents, the following conclusions are obtained:

(1) The two-step coating method effectively improves the shape fixity ratio of the programmed SMPU fiber from 30% to 66%. And the coated fiber has good shape memory effect (i.e., higher recovery stress).

(2) The recovery stress reduces nonlinearly with recovery strain. The crack closing force applied to the cracked matrix reduces as the crack narrows. The coated fiber is more effective in closing cracks than the uncoated fiber when the recovery strain is within a certain range, which is 24% in this study.

(3) The fabrication method proposed in this study is able to avoid the loss of shape memory effect of the programmed short SMPU fibers by curing the composite at low temperature in the first 24 hours of curing.

(4) Healing of the composite is repeatable. The healing efficiency increases as the fiber length increases for the three fiber lengths investigated due to the need of certain embedded fiber length for shear force transfer.

The crack opening process is also a cold-drawing programming process for fibers bridging over the crack, which leads to springback and some closure of the crack when the external load is removed.
Figure AI.1 The SEM fractography for three-point bending damaged beam after first fracture (A) and (B) and after fifth fracture (C), (D), (E), and (F).
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VITA

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