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14. ABSTRACT The objectives of this project are to understand the constitutive behavior of shape memory polymer (SMP) fibers and bio-inspired healing-on-demand mechanisms of SMP fiber reinforced conventional thermosetting polymer composites. We have achieved and exceeded the objectives. We have (1) fabricated and characterized a new shape memory polymer fiber; (2) developed a new healing-on-demand composite with low-cost fishing line artificial muscle as crack-closing device; (3) developed a new constitutive model for amorphous shape memory polymers with physics based phase evolution law; (4) studied healing of SMP fiber reinforced composite foam subjected to					
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Report Title

Final Report: Bio-inspired Shape Memory Polymer Fiber Reinforced Thermosetting Polymer Composite for Self-healing Structural-length Scale Damage

ABSTRACT

The objectives of this project are to understand the constitutive behavior of shape memory polymer (SMP) fibers and bio-inspired healing-on-demand mechanisms of SMP fiber reinforced conventional thermosetting polymer composites. We have achieved and exceeded the objectives. We have (1) fabricated and characterized a new shape memory polymer fiber; (2) developed a new healing-on-demand composite with low-cost fishing line artificial muscle as crack-closing device; (3) developed a new constitutive model for amorphous shape memory polymers with physics based phase evolution law; (4) studied healing of SMP fiber reinforced syntactic foam subjected to tensile stress; (5) evaluated the effect of confinement level and local heating on healing efficiency; (6) conducted multiscale modeling of vibration damping response of SMP fibers; (7) investigated the one-way multi-shape memory effect and tunable two-way shape memory effect of ionomers; (8) conducted multi-scale modeling for actuation response of polymeric artificial muscles; (9) synthesized new polymeric artificial muscles based on two-way SMPs; (10) designed and synthesized a new intrinsic self-healing thermoset polymer per transesterification reaction; (11) developed a multi-mechanism model for SMPs both during programming and in service; and (12) developed a multi-scale model for the healing process of self-healing composite assisted by shape memory effect.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>	
03/08/2017	1 Amir Shojaei, Guoqiang Li. Thermomechanical Constitutive Modeling of Shape Memory Polymer Including Continuum Functional and Mechanical Damage Effects, Proc. R. Soc. A, (03 2014): 1. doi:	332,814.00
03/08/2017	18 Guoqiang Li, Anqi Wang. Cold, warm, and hot programming of shape memory polymers, Journal of Polymer Science Part B: Polymer Physics, (): 1319. doi:	1,033,089.00
03/08/2017	17 Qianxi Yang, Jizhou Fan, Guoqiang Li. Artificial muscles made of chiral two-way shape memory polymer fibers, Applied Physics Letters, (): 183701. doi:	1,033,021.00
03/08/2017	16 Lu Lu, Jizhou Fan, Guoqiang Li. Intrinsic healable and recyclable thermoset epoxy based on shape memory effect and transesterification reaction, Polymer, (): 10. doi:	1,033,020.00
03/08/2017	15 J. Fan, G. Li. High performance and tunable artificial muscle based on two-way shape memory polymer, RSC Adv., (): 1127. doi:	1,033,019.00
03/08/2017	12 Pengfei Zhang and Guoqiang Li. Fishing line artificial muscle reinforced composite for impact mitigation and on-demand damage healing, Journal of Composite Materials, (): 4235. doi:	1,016,020.00
03/08/2017	3 Qianxi Yang, Guoqiang Li. Temperature and rate dependent thermomechanical modeling of shape memory polymers with physics based phase evolution law, International Journal of Plasticity, (06 2015): 168. doi:	360,175.00
08/29/2016	5 Jonah Champagne , Su-Seng Pang, Guoqiang Li. Effect of confinement level and local heating on healing efficiency of self-healing particulate composites, Composites Part B: Engineering, (): 344. doi:	1,015,720.00
08/29/2016	6 Qianxi Yang, Guoqiang Li. A top-down multi-scale modeling for actuation response of polymeric artificial muscles, Journal of the Mechanics and Physics of Solids, (): 237. doi:	1,015,722.00
08/29/2016	7 Soodabeh Sharafi, Guoqiang Li,. Multiscale modeling of vibration damping response of shape memory polymer fibers, Composites Part B: Engineering, (): 306. doi:	1,015,723.00
08/29/2016	8 Pengfei Zhang, Guoqiang Li. Advances in healing-on-demand polymers and polymer composites, Progress in Polymer Science, (): 32. doi:	1,016,007.00
08/29/2016	9 Amir Shojaei, Guoqiang Li, P.J. Tan, Jacob Fish. Dynamic delamination in laminated fiber reinforced composites: A continuum damage mechanics approach, International Journal of Solids and Structures, (): 262. doi:	1,016,009.00
08/29/2016	10 Amir Shojaei, , Soodabeh Sharafi, Guoqiang Li. A multiscale theory of self-crack-healing with solid healing agent assisted by shape memory effect, Mechanics of Materials, (): 25. doi:	1,016,012.00

08/29/2016	11	Pengfei Zhang, Babatunde Ogunmekan, Samuel Ibekwe, Dwayne Jerro, Su-Seng Pang and Guoqiang Li. Healing of shape memory polyurethane fiber-reinforced syntactic foam subjected to tensile stress, Journal of Intelligent Material Systems and Structures, (): 1792. doi: 1,016,016.00
08/29/2016	13	Pengfei Zhang, Ukeamezhim Ayaugbokor, Samuel Ibekwe, Dwayne Jerro, Su-Seng Pang, Patrick Mensah, Guoqiang Li. Healing of polymeric artificial muscle reinforced ionomer composite by resistive heating, Journal of Applied Polymer Science, (): 43660. doi: 1,016,022.00
08/29/2016	14	Lu Lu, Guoqiang Li. One-Way Multishape-Memory Effect and Tunable Two-Way Shape Memory Effect of Ionomer Poly(ethylene-co-methacrylic acid), ACS Applied Materials & Interfaces, (): 14812. doi: 1,016,024.00
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(c) Presentations

1. S. Ibekwe, G. Li, and U. Ayaugbokor. "Effect of Artificial Muscle Made from Nylon 6 Monofilament on the Healing Efficiency of Smart Composite." The 8th International Conference on Africa Materials Research Society, December 7 - 10, 2015.
2. Ibekwe, Samuel; Li, Guoqiang; Mensah, Patrick, "Ensuring Integrity of 3-D manufactured Components," Kwame Nkrumah University of Science & Technology, Kumasi, Ghana, July 2016.
- (3) P. Zhang and G. Li. Impact mitigation and on-demand damage healing by fishing line artificial muscle. GRC Multifunctional Materials Conference, Jan 31-Feb 5, 2016, Ventura, CA.
- (4) Q. Yang and G. Li. Temperature and Rate Dependent Thermomechanical Modeling of SMPs with Physics Based Phase Evolution Law. 2016 Plasticity Conference, Jan 3-9, 2016, Kona, HI.
- (5) G. Li. Bio-inspired Self-healing Composite. Presented at the ACAP 2015 Science, Engineering and Technology Seminars (SETS) and Diversity Submit, Houston, Texas, June 6-9, (2015).
- (6) G. Li. Stress Memory versus Shape Memory for Shape Memory Polymers. Presented at the ACAP 2014 Science, Engineering and Technology Seminars (SETS) and Diversity Submit, Houston, Texas, June 20-22, (2014).
- (7) G. Li and A. Shojaei. Comprehensive thermomechanical modeling of shape memory polymers including cyclic damage effects. Proceedings of Plasticity 2014, Freeport, Bahamas, January 3-8, 2014.
- (8) S. Ibekwe, H. Meng, and G. Li. Various Shape Memory Effect of Polymers. 21st International Conference on Composite or Nano Engineering, Tenerife, Spain, July 19 – 28, 2013.
- (9) G. Li, Oludayo Ajisafe, Harper Meng. Self-healing of thermosetting polymer by strain hardened shape memory polymer fibers. Proceedings of Louisiana EPSCoR RII LA-SiGMA 2013 Symposium, Baton Rouge, Louisiana, July 29, 2013.
- (10) G. Li. Bio-mimetic Self-healing Composite. Presented at the ACAP 2013 Science, Engineering and Technology Seminars (SETS) and Diversity Submit, Houston, Texas, June 13-16, (2013).

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Books

Received Book

TOTAL:

TOTAL:

Patents Submitted

Patents Awarded

Awards

1. Daniel Ferdinand-Perez (Minority Male) graduated with B.S. in Mechanical Engineering and is currently employed.
2. Mark Gabriel (Minority Male) graduated with M.S. in Mechanical Engineering and is employed by Shell Chemical Company.
3. Chidinma Imediegwu (Minority Female) graduated with M.S. in Engineering and applying for a Ph.D. program in Engineering.
4. Paula Mensah – Recipient of NASA-MURE scholarship.
5. Samuel Ibekwe received Formosa Endowed Professorship at Southern University.
6. Guoqiang Li received Major Morris S. & DeEtte A. Anderson Memorial Alumni Professorship at Louisiana State University;
7. Qianxi Yang received the 2015 Best Presentation Award in the Department of Mechanical Engineering at Louisiana State University, Baton Rouge, LA, on 04/21/2015.
8. Qianxi Yang received the 2016 Best RA Award in the Department of Mechanical Engineering at Louisiana State University, Baton Rouge, LA, on 04/23/2016.
9. Our paper “Artificial muscles made of chiral two-way shape memory polymer fibers” published in Applied Physics Letters, was reported in a couple of news release, such as https://www.eurekalert.org/pub_releases/2016-10/aio-ams103116.php; <https://phys.org/news/2016-10-artificial-muscles-flex.html>;
10. Guoqiang Li received 2015 Elsevier Reviewer Recognition Award by the journal of Polymer.
11. Guoqiang Li received 2014 Elsevier Reviewer Recognition Award by the journal of Construction and Building Materials.
12. Dursan Gokhan received ME Most Outstanding Graduate Achievement Award.
13. Paula Mensah – Renewed Recipient of NASA-MURE scholarship.

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	<u>DISCIPLINE</u>
Mark Gabriel	50	Mechanical Engineering
Chidinma Imediegwu	50	Mechanical Engineering
Blessing Aluko	50	Mechanical Engineering
FTE Equivalent:	1.50	
Total Number:	3	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Harper Meng	0.80
FTE Equivalent:	0.80
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Guoqiang Li	0.10	
Samuel Ibekwe	0.10	
FTE Equivalent:	0.20	
Total Number:	2	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	<u>DISCIPLINE</u>
Mack Otis Todd	50	Mechanical Engineering
Dorlisa Robinson	50	Mechanical Engineering
Tola Anifalaje	50	Mechanical Engineering
Isoken Awanbor	50	Mechanical Engineering
Daniel Ferdinand-Perez	50	Mechanical Engineering
Chiedu Odita	50	Mechanical Engineering
Uchenna Prudensia	50	Chemistry
FTE Equivalent:	3.50	
Total Number:	7	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 7.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 3.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 1.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 1.00

Names of Personnel receiving masters degrees

<u>NAME</u>	
Mark Gabriel	
Chidinma Imediegwu	
Blessing Aluko	
Total Number:	3

Names of personnel receiving PHDs

NAME

Pengfei Zhang

Total Number:

1

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

1 a. Louisiana State University and A&M College

1 b. Office of Sponsored Programs

202 Himes Hall

Baton Rouge LA 708030001

Sub Contractor Numbers (c): 127404183

Patent Clause Number (d-1): Far 52.227

Patent Date (d-2): 12/1/07 12:00AM

Work Description (e): This is a collaborative effort including the Department of Mechanical Engineering at Sou

Sub Contract Award Date (f-1): 8/23/13 12:00AM

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1 a. Louisiana State University and A&M College

1 b. Office of Sponsored Programs

330 Thomas Boyd Hall

Baton Rouge LA 708030001

Sub Contractor Numbers (c): 127404183

Patent Clause Number (d-1): Far 52.227

Patent Date (d-2): 12/1/07 12:00AM

Work Description (e): This is a collaborative effort including the Department of Mechanical Engineering at Sou

Sub Contract Award Date (f-1): 8/23/13 12:00AM

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Inventions (DD882)

Scientific Progress

See attachment.

Technology Transfer

Scientific Progress and Accomplishments

Forward

The goal of this project is to (1) create and advance knowledge and technology in self-healing composite materials and structures and (2) enhance related research infrastructure and workforce training at Southern University (SU). The research objectives of this project are to understand the constitutive behavior of shape memory polymer (SMP) fibers and bio-inspired healing-on-demand mechanisms of SMP fiber reinforced conventional thermosetting polymer composites. In achieving the objectives, the following research tasks have been conducted: (1) fabrication and characterization of SMP fibers; (2) constitutive modeling of SMP fibers; (3) modeling and design of the self-healing composite; and (4) self-healing efficiency testing.

We have achieved and exceeded the objectives. We have (1) fabricated and characterized a new shape memory polymer fiber; (2) developed a new healing-on-demand composite with low-cost fishing line artificial muscle as crack-closing device; (3) developed a new constitutive model for amorphous shape memory polymers with physics based phase evolution law; (4) studied healing of SMP fiber reinforced syntactic foam subjected to tensile stress; (5) evaluated the effect of confinement level and local heating on healing efficiency; (6) conducted multiscale modeling of vibration damping response of SMP fibers; (7) investigated the one-way multi-shape memory effect and tunable two-way shape memory effect of ionomers; (8) conducted multi-scale modeling for actuation response of polymeric artificial muscles; (9) synthesized new polymeric artificial muscles based on two-way SMPs; (10) designed and synthesized a new intrinsic self-healing thermoset polymer per transesterification reaction; (11) developed a multi-mechanism model for SMPs both during programming and in service; and (12) developed a multi-scale model for the healing process of self-healing composite assisted by shape memory effect.

We believe that this project has resulted in new knowledge and enabling technology for engineers to design and manufacture a new generation of intelligent composite for durable, reliable, and cost-effective aircraft and other military structures.

Table of Contents

Forward.....	1
Table of Contents.....	2
Statement of the Problem Studied.....	3
Summary of the Most Important Results.....	4
(1) Fabrication and Characterization of Ionomer Fibers.....	4
(2) Healing-on-Demand Composite Based on Fishing Line Artificial Muscles.....	6
(3) Temperature and Rate Dependent Thermomechanical Modeling of Shape Memory Polymers with Physics Based Phase Evolution Law.....	7
(4) Healing of Shape Memory Polyurethane Fiber Reinforced Syntactic Foam Subjected to Tensile Stress.....	7
(5) Effect of Confinement Level and Local Heating on Healing Efficiency of Self-healing Particulate Composites.....	7
(6) Multiscale Modeling of Vibration Damping Response of Shape Memory Polymer Fibers.....	8
(7) One-way Multi-shape Memory Effect and Tunable Two-way Shape Memory Effect of Ionomer Poly(ethylene-co-methacrylic acid).....	8
(8) Multiscale Modeling of Actuation Response of Polymeric Artificial Muscles.....	8
(9) Two-Way Shape Memory Polymer Based Artificial Muscles.....	9
(10) Intrinsic Healable and Recyclable Thermoset Epoxy Based on Shape Memory Effect and Transesterification Reaction.....	10
(11) Thermomechanical Constitutive Modeling of Shape Memory Polymer Including Continuum Functional and Mechanical Damage Effects.....	10
(12) A Multiscale Theory of Self-Crack-Healing with Solid Healing Agent Assisted by Shape Memory Effect.....	11
Bibliography.....	12

Statement of the Problem Studied

This project has made progress in several key areas of study in shape memory polymers, artificial muscles, and self-healing composite structures. They are summarized as follows: (1) Shape memory polymer fibers (SMPFs) have been proved to close wide-opened cracks through constrained shape recovery (shrinkage) when they are embedded in a polymer matrix. However, SMPFs such as polyurethane fibers usually have higher cost, lower recovery stress, slower response to thermal actuation, and thus lower healing efficiency. The objective of the study is to manufacture SMPFs from commercially available polymers so that the cost can be lowered. (2) In addition to fabricate new SMPFs, we also searched for new fibers which have similar or better functionality than SMPFs, but at a lower cost. The objective is to investigate the healing efficiency of artificial muscles made of fishing lines in self-healing composites. (3) While the phase evolution based approach has been popular in constitutive modeling SMPs, the limitation is that the phase evolution laws usually lack physical basis. The objective of the study is to provide physical basis for the evolution of the frozen phase and active phase during the thermomechanical cycle. (4) While we have proved that SMPFs can close wide opened cracks through constrained shape recovery, it is not clear about the performance if the composite is subjected to tensile stress during the healing process. The objective of the study is to evaluate the healing efficiency of SMPF reinforced polymeric syntactic foam composite under tensile stress. (5) In the close-then-heal strategy, confinement level is a key factor determining the healing efficiency of the composite. The objective of the study is to investigate the effect of confinement levels and local heating on the healing efficiencies of the composite. (6) During impact, a portion of the impact energy is absorbed through vibration damping. However, it is not clear about the damping behavior of SMPFs. The objective of the study is to understand the vibration damping behavior of SMPFs through multiscale modeling and testing. (7) We are curious about the one-way multi-shape behavior and tunable two-way shape memory behavior of ionomer fiber. The objective of the study is to investigate the one-way multi-shape and two-way tunable shape memory behavior of commercially available ionomer. (8) While we have used fishing line artificial muscles in closing wide-opened cracks, there is currently a lack of understanding of its actuation response. The objective of the study is to develop multiscale models to understand the actuation behavior. (9) Although fishing line based artificial muscle has exhibited good actuation, the stroke is still low and the actuation temperature is too high. The objective of this study is to develop new artificial muscle based on two-way shape memory polymers. (10) The matrix that has been used in this project is conventional thermoset polymers, which need external healing agent to heal the cracks and are not recyclable. The objective of this study is to develop recyclable thermoset endowed with shape memory effect and intrinsic self-healing capability. (11) Although many phenomenological viscoplastic models have been developed in the literature for SMPs, they usually suffer from large numbers of material parameters without clear calibration methodology. Also, no damage effect is considered, which is inevitable during the thermomechanical cycle or during service. Furthermore, the existing model is SMP specific, and cannot be used for SMPs with different morphologies. The objective of the study is to develop a new constitutive model which intends to solve the above problems. (12) There is currently a lack of understanding of the healing process assisted by shape memory effect. The objective of this study is to develop a multiscale theory to understand the healing process.

Summary of the Most Important Results

(1) Fabrication and Characterization of Ionomer Fibers

DuPont™ Surlyn 8940 is a sodium ionomer thermoplastic resin; it is the DuPont trade name for advanced ethylene/methacrylic acid (E/MAA) in which the MAA acid group have been partially neutralized. It is available for use, in conventional extrusion and injection equipment to create various sheets or shapes. The maximum processing temperature for Surlyn 8940 is 285°C. Surlyn 8940 is normally processed at melt temperatures ranging from 185°-285°C. Actual processing temperatures will usually be determined by either the specific equipment or substrate or one of the other polymers in a coextrusion or coinjection.

The ionomer fiber was prepared using the One Shot Extrusion machine. The “One Shot” extrusion is a positive displacement piston type extruder. The piston is pushed onto a cylinder which contains the sample to be made into a filament. A high quality screw-jack is driven by a variable speed gear motor. This allows the operator to select speeds for producing different diameters of filament. The sample to be extruded is heated by a heating jack. Spinnerets are usually supplied containing from one to eight holes. The capillary hole diameter is usually from 0.202mm to 10.16 mm, and can be from 25.5mm to 203.2mm in length. The quenching chamber eventually distributes a flow of air across the filament as it is being extruded. A small customer-made level winder takes up the filament. The winder bobbin diameter is 4 inches, and the bobbin speed can vary from a few RPM to 3400 RPM. When the required temperature about 188 °C is set on for about an hour, the ionomer fiber is extruded out with the spinning speed of 30 rpm. The ionomer fiber has a fiber diameter of 0.26mm.

The MTS Q-TEST 150 machine was used to conduct the tensile test of the ionomer fibers. A 250N load cell and the MTS fiber test fixture were used. The loading rate was 10 mm/min and the test was conducted at room temperature. The fiber was tensioned until fracture. During this process, the MTS software (TestWork4) captured all the important data. The stress was recalculated using the Excel before plotting the stress-strain graph.

It is found that the stress increased linearly as the strain increased, then shows non-linear behavior until the yield points (22MPa). After that the fiber shows a strain softening, followed by strain hardening and plastic flow. The fracture stress is about 37MPa and the fracture strain is about 700%, indicating huge ductility. Obviously, this fiber is too soft to be directly used in self-healing. Programming through cyclic strain hardening is required.

DMA measures the storage and loss modulus and $\text{Tan}\delta$ of the material. Storage modulus is the material ability to store energy applied to it for future use or spring back when the force is removed after deformation. Loss modulus is the material's ability to dissipate energy that is applied to it. $\text{Tan}\delta$ is the ratio of the loss modulus to storage modulus. Together, they represent the materials viscoelastic response to stress, temperature and frequency. TA Q-800 DMA machine was used to conduct the test. The temperature scan test was from 25°C to 85°C at a frequency of 1Hz. The fiber bundle length was 16.78mm, which consists of 8 filaments. Using the peak of $\text{Tan}\delta$ to determine the glass transition temperature (T_g) of the fiber, it is found that

the T_g is about 57°C. The peak of $\text{Tan}\delta$ is about 0.1. From 25°C to 80°C, the drop in storage modulus is about 10 times. Usually, two orders of drop in storage modulus is expected for a polymer to demonstrate good shape memory. Therefore, the ionomer fiber only has weak shape memory capability.

Differential scanning calorimeter (DSC) test was carried out on the fiber to determine its glass transition temperature (T_g) and melting temperatures (T_m) using PerkinElmer DSC 4000. The fiber sample was placed in an aluminum container and placed in the DSC chamber for testing. The sample with an average weight of 4.37 mg was thermally scanned using two cycles. The purge rate of nitrogen gas was 20.0ml/min. The scanning was first cooled from 30 °C to -70 °C at a cooling rate of 10.0 °C/min. The sample was then held isothermally for 10 min at -70°C and heated from -70 °C to 200 °C with the same scanning rate of 10.0 °C/min and held for 5 min at 200 °C; the second cycle repeated the first cycle. The first cycle was used to eliminate the thermal stress history of the samples and the second cycle was used to determine the glass transition and melting temperatures. It is found that the T_g and T_m of the ionomer fiber are 57°C and 90°C, respectively. It is noted that although the melting temperature is 90°C, a higher temperature of 188°C was used to fabricate the fibers, in order to reduce the viscosity.

Tensile programming was conducted on the ionomer fibers. Hot programming was used to determine the shape recovery ratio and cold programming was used to determine the stress recovery capability. In hot tension programming, the temperature used include 50°C, 55°C, 60°C, and 65 °C. For each temperature, the prestrain level was 200%, 300%, 450%, and 550%. For cold tension programming, the temperature was 25°C, and the prestrain levels were 200%, 450%, and 550%, respectively.

After the hot programming process, the fibers was brought to an oven to heat up to 65°C and held for 30minutes. The shape fixity ratio is from 65% - 95%, while the shape recovery ratio is from 22% - 44%. As compared to other shape memory polymers, ionomer has limited shape recovery ratio. Therefore, ionomer can be treated as a polymer with weak shape memory capability. Even with this limited shape memory capability, we believe that ionomer fiber is a new addition to the shape memory polymer fiber family and can be used in self-healing applications.

For the cold tension programmed ionomer fibers, fully constrained shape recovery test, or stress recovery test was conducted. The recovery temperature was 65°C. It is noted that, an initial tensile strain about 10% was applied before the stress recovery test starts. The stabilized recovery stress corresponding to the programming strain of 200%, 450%, and 550% is 8MPa, 20MPa, and 22MPa, respectively.

In summary, we prepared ionomer fibers and characterized its physical and thermomechanical behavior. We found that ionomer has weak shape memory behavior but has comparable stress recovery ability to polyurethane fibers. It is thus expected that ionomer fiber would have similar crack closing capability in self-healing composites. Owing to its lower cost as compared to polyurethane, we envision that ionomer fiber would be a viable alternative for polyurethane fibers in self-healing applications.

(2) **Healing-on-Demand Composite Based on Fishing Line Artificial Muscles**

In this study, a new polymer artificial muscle based healing-on-demand composite 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 healed even at a constrained boundary condition upon local heating, undergoing a close-then-heal procedure. The fractured beams were heated locally by a heat gun for 10 min. The healing efficiency was investigated at both free boundary condition and fixed boundary condition. The fast contraction of artificial muscle brings the fractured surfaces in spatial proximity; simultaneously, the melting thermoplastic agent fills the crack via capillary action and bonds the two fracture surfaces. With 60% prestrain of the reinforcing polymer artificial muscles (8% volume fraction), over 60% of healing efficiency was achieved at free boundary condition and 54% at fixed boundary condition after repeated damage-healing events. Due to its low cost, high healing efficiency, good compatibility, and excellent flexibility, we envision that the polymer artificial muscle will be a new device in designing next generation healing-on-demand polymer composite. Details of this study can be found in [1].

In another study, a fishing line artificial muscle reinforced syntactic foam composite was investigated. About 3.5 vol.% of polymer artificial muscle was woven into a two-dimensional grid skeleton and embedded into a syntactic foam matrix. The grid-stiffened syntactic foam composite was designed to be able to repeatedly heal cracks on-demand. Short thermoplastic fibers were also dispersed into the foam matrix both as reinforcement and as a healing agent. The composite panel was repeatedly impacted, bending fractured, and healed as per the biomimetic close-then-heal strategy. It is found that the composite panel responds to impact quasi-statically. The impact- and bending-induced macroscopic cracks can be repeatedly healed with high healing efficiency, under both free and clamped boundary conditions. Contrary to most healing systems, the healing efficiency within the damage-healing cycles in this study increases as the damage-healing cycle increases. Because the artificial muscle is made of low-cost and high-strength fishing line, it is envisioned that the composite panel developed in this study may be a viable alternative core for healable lightweight composite sandwich structures at competitive cost. Details of this study can be found in [2].

In the third study, structural-scale crack healing of artificial muscle reinforced ionomer composite was investigated following the close-then-heal (CTH) healing strategy. Structural-scale crack of 3 mm deep and 1 mm wide in notched beam specimens was first closed by actuation of the embedded polymeric artificial muscles made of fishing lines, followed by intrinsic healing of the ionomer matrix. The healing process was triggered by resistive heating of embedded carbon fibers by DC power. It is found that, with 0.7% by volume of polymeric artificial muscles, the wide-opened cracks are effectively closed, and the closed cracks in the ionomer composite are effectively and repeatedly healed, with a healing efficiency of over 80%. Details of this study can be found in [3].

(3) Temperature and Rate Dependent Thermomechanical Modeling of Shape Memory Polymers with Physics based Phase Evolution Law

The thermomechanical constitutive models are critical for shape memory polymers (SMPs) in analyzing their shape memory behaviors under different conditions. Recently, the phase evolution modeling approach has been extended and widely used due to its simplicity and generality. However, the lack of physical explanation has become its major limitation. In this study, a phase evolution law was proposed from the physics perspective. The shape memory polymer was then treated as a frozen-phase matrix with active-phase inclusions embedded in it and the Mori-Tanaka approach was used to predict the effective mechanical properties. The theoretical predictions were compared with available experimental results and reasonable agreement was found. The influence of the intrinsic material structures and the thermomechanical conditions on the shape memory behavior were evaluated by parametric studies. Details of this study can be found in [4].

(4) Healing of Shape Memory Polyurethane Fiber Reinforced Syntactic Foam Subjected to Tensile Stress

In this study, healing of conventional non-shape memory syntactic foam embedded with shape memory polyurethane fibers was investigated per the biomimetic close-then-heal strategy. The syntactic foam was made of epoxy matrix dispersed with 30% by volume of glass microballoons, 5% by volume of shape memory polyurethane fibers, and three levels of thermoplastic healing agent (5%, 10%, and 15% by volume). Notched beam specimens were prepared and fractured by tension to create macroscopic cracks. Three levels of tensile stresses (26.5, 24.5, and 22.5 kPa) were applied to the fractured beam specimens during healing, in order to evaluate the healing capability of the composite under in-service conditions. It is found that the tensile stress level and healing agent content have a significant effect on the healing efficiency. Subjected to 22.5 kPa of tensile stress, the healing efficiency determined by peak tensile load is as high as 90%. Details of this study can be found in [5].

(5) Effect of Confinement Level and Local Heating on Healing Efficiency of Self-healing Particulate Composites

Shape memory polymer based self-healing materials are a special class of materials that have been the subject of much research over the past decade and many impactful discoveries have been made thus far. In a previous study it was shown that in order for efficient healing, confinement during healing is essential. It was also shown that use of a two-step close-then-heal (CTH) method during healing of damaged shape memory particulate composites provided molecular scale healing. The present study further investigates the influence of confinement levels and local heating on the healing efficiencies of a polystyrene based shape memory polymer with 6% by volume of thermoplastic particle additives (copolyester as solid healing agent). The healing process was conducted by locally heating fractured cylindrical specimens at three levels of lateral (radial) confinements and axial constraints, and varying heating times. It is found that, lateral confinement levels, axial constraints, and heating times all control the healing efficiency. Almost complete strength recovery is obtained with 100% lateral confinement, 12 MPa axial constraint stress, and 60 min of heating time. Details of this study can be found in [6].

(6) Multiscale Modeling of Vibration Damping Response of Shape Memory Polymer Fibers

Health of a structure under vibration loads is highly related to the damping characteristics of the system. This work explores an engineered smart Shape Memory Polymer Fiber (SMPF) system that is capable of adjusting its damping capabilities based on applied load frequency and temperatures. A SMPF based structure with smart vibration/damping capability is of interest to many industries including aerospace, automotive and biomedical sectors. SMPFs enable structure engineers to incorporate smart functionality into their design through programming or training of SMPFs. While SMPF structural applications in the case of static loadings have been studied, the application of SMPFs in mitigating vibration responses of a structure has not been fully addressed in the research arena. The vibration damping response of a SMPF material system is studied with a goal to design damping response of smart structures that can mitigate severe vibrations. In this work vibration damping response of a SMPF bundle is experimentally studied through Dynamic Mechanical Analyzer (DMA) machine, and a numerical model is developed to correlate the loss/storage moduli to the damping/stiffness characteristics of the SMPF system. The model is then applied to study forced vibration responses of SMPFs. DMA data are utilized to verify the performance of the proposed model. The presented experimental data and the numerical model provide insight into vibration damping application of SMPFs in smart structures. Details of this study can be found in [7].

(7) One-way Multi-shape Memory Effect and Tunable Two-way Shape Memory Effect of Ionomer Poly(ethylene-co-methacrylic acid)

Reversible elongation by cooling and contraction by heating, without the need for repeated programming, is well-known as the two-way shape-memory effect (2W-SME). This behavior is contrary to the common physics—contraction when cooling and expansion when heating. Materials with such behavior may find many applications in real life, such as self-sufficient grippers, fastening devices, optical gratings, soft actuators, and sealant. Here, it is shown that ionomer Surllyn 8940, a 50-year old polymer, exhibits both one-way multishape-memory effects and tunable two-way reversible actuation. The required external tensile stress to trigger the tunable 2W-SME is very low when randomly jumping the temperatures within the melting transition window. With a proper one-time programming, “true” 2W-SME (i.e., 2W-SME without the need for an external tensile load) is also achieved. A long training process is not needed to trigger the tunable 2W-SME. Instead, a proper one-time tensile programming is sufficient to trigger repeated and tunable 2W-SME. Because the 2W-SME of the ionomer Surllyn is driven by the thermally reversible network, here crystallization and melting transitions of the semicrystalline poly(ethylene-co-methacrylic acid), it is believed that a class of thermally reversible polymers should also exhibit tunable 2W-SMEs. Details of this study can be found in [8].

(8) Multiscale Modeling of Actuation Response of Polymeric Artificial Muscles

Artificial muscles are emerging materials in the field of smart materials with applications in aerospace, robotic, and biomedical industries. Despite extensive experimental investigations in this field, there is a need for numerical modeling techniques that facilitate cutting edge research

and development. This work aims at studying an artificial muscle made of twisted Nylon 6.6 fibers that are highly cold-drawn. A computationally efficient phenomenological thermo-mechanical constitutive model is developed in which several physical properties of the artificial muscles are incorporated to minimize the trial-and-error numerical curve fitting processes. Two types of molecular chains are considered at the micro-scale level that control training and actuation processes *viz.* (a) helically oriented chains which are structural switches that store a twisted shape in their low temperature phase and restore their random configuration during the thermal actuation process, and (b) entropic chains which are highly drawn chains that could actuate as soon as the muscle heats up, and saturates when coil contact temperature is reached. The thermal actuation response of the muscle over working temperatures has been elaborated in the Modeling section. The performance of the model is validated by available experiments in the literature. The model may provide a design platform for future artificial muscle developments. Details of this study can be found in [9].

(9) Two-Way Shape Memory Polymer Based Artificial Muscles

In this work, we demonstrate the unusual improvement of the tensile actuation of hierarchically chiral structured artificial muscle made of two-way shape memory polymer (2W-SMP) fiber. Experimental results show that the chemically cross-linked poly(ethylene-co-vinyl acetate) 2W-SMP fibers possess an average negative coefficient of thermal expansion (NCTE) that is at least one order higher than that of the polyethylene fiber used previously. As expected, the increase in axial thermal contraction of the precursor fiber leads to an increase in the recovered torque (4.4 Nmm) of the chiral fiber and eventually in the tensile actuation of the twisted-then-coiled artificial muscle ($67.81 \pm 1.82\%$). A mechanical model based on Castigliano's second theorem is proposed, and the calculated result is consistent with the experimental result (64.17% tensile stroke). The model proves the significance of the NCTE and the recovered torque on tensile actuation of the artificial muscle and can be used as a guidance for the future design. Details of this study can be found in [10].

Artificial muscles, a class of bio-inspired actuators, have been investigated for decades. Recently, a remarkable breakthrough in artificial muscles was achieved by twisting then coiling polymeric fishing lines or sewing threads. Driven by the negative coefficient of thermal expansion (NCTE), the tensile actuation strain, which was about 4% in the precursor nylon 6,6 fiber, was magnified to about 34% in the muscle. However, the muscle is limited by its higher actuation temperature (up to 160 °C). Also, some applications such as soft robots require even larger actuation strain to maintain locomotion. In another study, chemically cross-linked poly(ethylene-co-vinyl acetate) (cPEVA) two-way shape memory polymer (2W-SMP) was synthesized, characterized, and processed into precursor fibers based on a solid solution approach. Artificial muscles were manufactured through twist insertion in the precursor fibers. It was found that the 2W-SMP fibers contract upon heating and expand upon cooling, similar to polymeric fibers with NCTE, but with lower actuation temperature and higher actuation strain. The cPEVA fiber, which has about 18% contraction when the temperature is increased from 20 °C to 67 °C, exhibits an actuation strain up to 68% in the muscle. It was also found that the muscle actuation is tunable, *i.e.*, independent of its actuation history. Details of this study can be found in [11].

(10) Intrinsic Healable and Recyclable Thermoset Epoxy Based on Shape Memory Effect and Transesterification Reaction

A shape memory and healable epoxy was prepared based on esterification between diglycidyl ether of bisphenol A and tricarballic acid. The healing was achieved through transesterification at the fracture surface between two epoxy blocks in a confined space assisted by shape recovery force. The shape recovery of the compression programmed epoxy at elevated temperature tightly closed the gap between the two epoxy blocks, whose fracture surfaces are saw-cut and not perfectly matched during healing, which is the worst case scenario for the healing test. A healing efficiency of ~60% was achieved. This suggests that, for naturally cracked surfaces, which have smoother fracture surfaces and better surface alignments during healing, higher healing efficiencies could be expected. We believe that the combination of shape memory and intrinsic healing capability within one network will broaden the applications of thermosets and enable recycling. Details of this study can be found in [12].

(11) Thermomechanical Constitutive Modeling of Shape Memory Polymer Including Continuum Functional and Mechanical Damage Effects

In this work, a multi-mechanism based model, which is suitable for Finite Element Analysis (FEA) implementation, is developed within the finite deformation kinematics framework for simulating the thermomechanical cycles of shape memory polymer (SMPs) both during programming and in service. The developed model takes into account several distinctive deformation mechanisms involved in the thermomechanical cycle of SMPs, including glass transition loss event, thermal expansion effect, temperature dependent material properties, stress relaxation, shape recovery transient response, and cyclic damage effects. Particularly, the damage mechanisms in SMPs are studied in which they are classified into mechanical or physical damage mainly during service condition, and functional damage primarily during thermomechanical, viz. programming and recovery cycle, within the Continuum Damage Mechanics (CDM) framework. A viscoplastic constitutive model is also developed in this work to capture the rate and the temperature dependent stress-strain response of SMPs under mechanical loading conditions. The model is based upon physical descriptions of the deformation mechanisms involved in the inelastic responses of SMPs including polymeric chain conformational rotations and the chain stretching process. The statistical mechanics is incorporated to describe the initiation and saturation of these deformation mechanisms. The main advantage of the presented viscoplastic model, compared to existing counterparts, is its simplicity and capability to simulate the non-linear stress-strain behavior of amorphous, crystalline and semicrystalline polymers. The developed viscoplastic theory incorporates only a few material parameters to capture the post-yield strain hardening effect through a Gaussian statistical approach in which only the center and the band width of the non-linearity is required to simulate the complex hardening response. Also effort is made to minimize the number of material parameters in the developed framework and to provide a clear method for material parameter identification. Furthermore, the model is designed in such a way that most of the material parameters are directly obtained from macroscopic experimental data rather than cumbersome numerical calibration techniques. The established model correlates well with the experimental results and its FEA implementation capability may provide the material designers

with a powerful design tool for future SMP applications. Details of this study can be found in [13].

(12) A Multiscale Theory of Self-Crack-Healing with Solid Healing Agent Assisted by Shape Memory Effect

Solid healing agents, such as thermoplastic particles, have been widely used in molecular healing of thermosetting polymers, including conventional thermosetting polymers such as epoxy and thermosetting shape memory polymers (SMPs) such as polystyrene. Despite extensive experimental developments in this field, there is an urgent need for healing theories with the ability to correlate molecular level healing events to the bulk scale recovered material properties. A multiscale healing constitutive theory is developed in this manuscript for self-crack-healing composites with embedded solid healing agents. It is assumed that the matrix is made of SMP; and the model accounts for several microscopic healing processes including: (a) rearrangement of free crack surfaces, (b) surface approaching due to shape memory effect, (c) wetting the free surfaces by the molten solid healing agent, (d) diffusion of the solid healing agent, which has been molten upon heating, into the crack surfaces, and (e) randomization. The Continuum Damage Healing Mechanics (CDHM) is utilized to bridge the microscopic and bulk scales. The healing parameters correlate the microscopic level descriptions of the healing to the recovery of bulk material properties. The model is then introduced into the ABAQUS, through user-defined coding, and it is shown that it correlates well with the experimental observations. The developed physically consistent multiscale theory provides material designers with the ability to optimize their self-healing systems via computer aided simulations. Details of this study can be found in [14].

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