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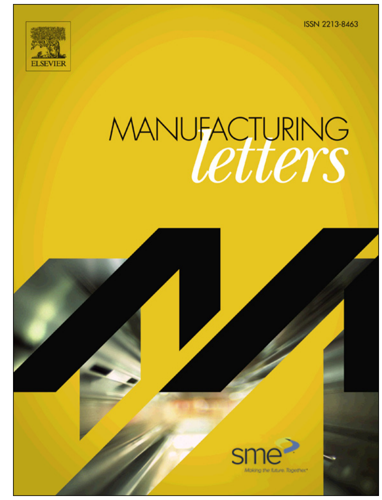

Letters

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A view into additive manufactured electro-active reinforced smart composite structures

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Abstract

Shape Memory Polymers (SMPs) and their composites (SMPCs) offer great properties, such as low cost and tailorability. Heat-activated SMPs and SMPCs are widely studied under controlled laboratory conditions, but their field applications did not receive thorough attention because manufacturing them with integrated heating elements for this use is very challenging. This work proposes and demonstrates an alternative novel solution to manufacture and activate a SMPC through resistive heating by using extrusion based additive manufacturing. Successful manufacturing of these materials can lead to broader use in strategically critical applications (biomedical stents, sports equipment, and unmanned air vehicles (UAVs)).

Keywords: Shape Memory Polymers, Additive Manufacturing, Electro-active Shape Memory Polymer Composites, 4D printing

1. Introduction

Shape Memory Materials (SMMs) have been proposed as prime candidates to substitute common mechanical actuators in many engineering applications. In contrast to mechanical actuators, these materials have the potential to reduce weight, cost and energy losses due to friction. SMMs have the ability to store a temporary shape and recover their original permanent shape upon the application of a stimulus such as temperature, uv-light exposure, pH and moisture content [1]. The phenomenon of storing a temporary shape is often referred to as the Shape Memory Effect (SME).

A temperature activated SME can be achieved in two major steps: i) Setting of the temporary shape and ii) activation of the SME. The temporary shape is set by increasing the temperature of the material above its transition temperature, sequentially applying and holding a mechanical strain and decreasing the temperature below the transition temperature. Increasing the temperature above the transition temperature can later activate the SME, i.e. the temporary shape of the material can be recalled.

Some of the most commonly used SMMs are Shape Memory Ceramics (SMCs), Alloys (SMAs) and Polymers (SMPs). Among these, SMPs often have more desirable features such as biocompatibility, recyclability, ease of manufacturing for thermoplastic SMPs, and tailorability in comparison to metallic or ceramic SMMs. Applications of SMPs have focused on strategically important applications such as morphing origami-like structures [2], self-deployable antennae for space applications [3], crawling robots [4], self-actuated hinges [5], wings for gliders and micro aerial vehicles [6]-[8] and medical devices such as stents, surgical sutures, among others [9], [10]. Other applications in the fashion industry include jewelry and textiles [11] [12].

Majority of these materials are currently being used in applications that are demonstrated in well-controlled laboratory conditions, e.g. temperature chambers. However, many of the aforementioned SMP applications require activation of the SME in the field, i.e. field activation. Activation of the SME has been attempted by inductive heating [13]-[16], embedding microvascular tubes [17], [18] and resistive heating [2], [9], [19]-[23]. Inductive heating and the use of microvascular tubes defeat the lightweight advantage of SMPs since additional mechanisms (coils and pumping system respectively) are required to activate the SME. Changing the conductivity of the material and applying a voltage across the material to provoke an increase in temperature can implement resistive heating within the SMP (a.k.a Joule heating). Conductivity of the material can be changed by the addition of conductive filler material such carbon particles and or addition of a metallic conductor to the surface of the SMP. However, the design of these Shape Memory Polymer Composites (SMPCs) requires tedious and impractical manufacturing techniques such as proper particle dispersion in solvents and additional manufacturing steps. Insertion of heating elements within the material is beneficial for field application and in addition can provide a homogenous heating of the structure.

The present work proposes an alternate manufacturing method of a SMPC that can be activated by means of resistive heating (referred as electroactive SMPs). A desktop Extrusion Based Additive Manufacturing (EBAM), commonly referred to as FDM printers, can be used to manufacture these SMPCs that can be tailored to electrically activate and increase their load bearing capabilities. A thermoplastic SMP and a conductive filler embedded polymer, e.g. a polymer matrix such as Poly-Lactic Acid (PLA) with Graphene Nano-platelet particles, can be fed into a EBAM machine to produce SMPC with simple or complex shapes. This manufacturing concept will significantly broaden the future use of SMPCs and multifunctional composites, and allow this technology to be used in many new applications.

2. Experimental Methods

A SMPC was manufactured with a SMP matrix and a conductive filler material embedded in a Polylactic Acid (PLA) polymer. Lines of the conductive material, that serve as heating elements, were placed close together within the SMP matrix by using a desktop-type EBAM 3D printer. The printer was equipped with a dual-extruder system (Ultimaker 3 ™). The two filaments were a SMP and a conductive-particle polymer (Graphene-PLA) filament with 3 mm diameters. The SMP filaments were produced in house using polyurethane based SMP pellets with a glass transition temperature (Tg) prescribed as 75°C (MM7520, SMP Technologies (Japan) [24], [25], [24]. Graphene-PLA was chosen as the conductive-particle polymer because of its lower Tg compared to the surrounding matrix (Tg at 65°C). The conductive filament was purchased form Black Magic 3D, Calverton, NY. Although PLA shows a SME in its own, filler loading impedes a complete recovery of its shape, reason why it is only used as an activation mechanism for a known high recovery percent polymer such as SMP-Polyurethane based.

Figure 1 shows a representative Gcode implemented to print the SMPC lamina (with dimensions of 15mm x 50mm x1.5mm). In the figure, the conductive material (heating elements) that is deposited in the longitudinal direction of the specimen, the adjacent SMP matrix regions, and the connecting ends are indicated. A voltage can be applied at the connecting ends to produce a change in temperature. Using the Gcode files, different types of actual samples were printed. Some of these contained a complete layer of Graphene-PLA (Figure.2.a) and some contained lines (Figure 2.b and 2.c) to reduce the conductive area and increase the contact area between materials. The sample in Figure 2.a, with a complete layer of graphene-PLA, was approximately 0.5mm in thickness representing ~33.3 w.t% of the entire composite. The sample in Figure 2.b shows the upper surface of the deposited Graphene-PLA printed lines (printed half way) and Figure 2.c represents 20 w.t % of embedded graphene lines in a SMP matrix (SMP on top and between of Graphene-PLA lines).

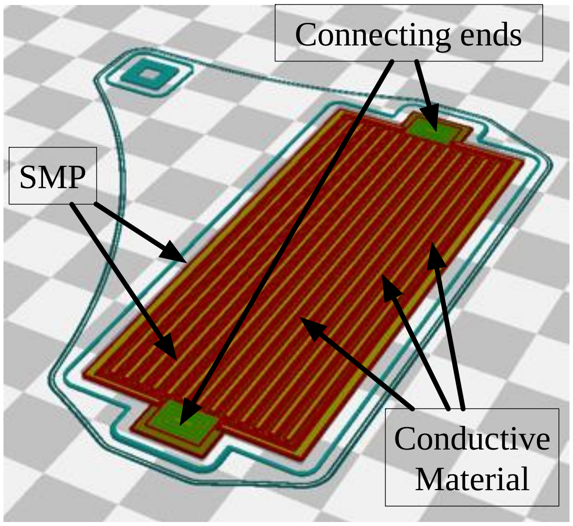


Figure 1: Gcode manufacturing of samples.

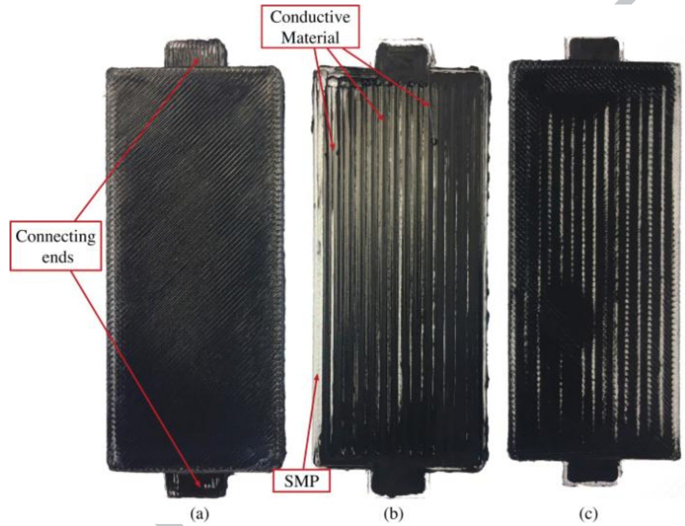


Figure 2: a) Sample with an entire layer in between representing 30 w.t% content of Graphene/PLA b) Sample showing the surface of printed Graphene/PLA layer with 20 wt.% embedded Graphene/PLA and c) Sample showing the embedded printed Graphene/PLA layer of 20 wt.% inside the SMP.

3. Results and Discussion

3D printed SMPC lamina, with a straight original/permanent shape, was deformed at 80°C (using an Electroforce TA Instruments thermal conditioned tensile tester) to have a bent shape (temporary shape). A total deflection of 5mm was applied at the middle of a 10 mm span of the beam. Later, the SME was activated (recovery of the original shape) by applying a voltage across the sample. Figure 3. shows a series of photographs of the activation of the SMPC lamina at different stages in time after applying a voltage of ~28V (14 V in series). The resistance obtained by the sample was ~400Ω after manufactured. After the application of the voltage, the resulting current was 0.11A. The provided voltage provoked the temperature to reach to ~100°C at steady state at the bottom surface of the sample. The figure also shows the activation steps of the sample. The sample took approximately 30mins to completely recover its shape.

The results demonstrate that an electroactive SMPC lamina can be produced in a one-step manufacturing process using EBAM. Possible improvements in resistive heating may be done by changing the percent loading of conductive material within the SMPC, that is by changing the ratio of SMP to conductive polymer. Alternatively, the conductivity of the conductive-filler material can be increased by addition of silver spheres or other nano-particles.

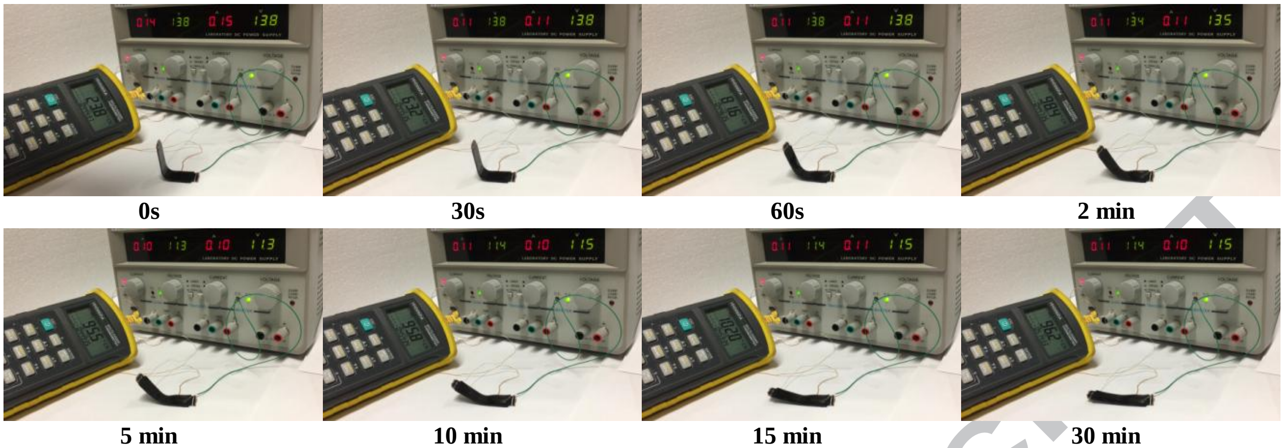


Figure 3: Recovering sequence of 3D printed SMPC laminate of size 15x50 mm

The tailorability and design of the multifunctional materials can dramatically change using this novel technique. For example, the presented manufacturing mechanism can be used to create multifunctional SMPCs by using filler material that, in addition to providing electrical activation, reinforces the matrix material. Two tailoring mechanisms may be done to find an optimal SMPC structure. The first method is by changing volume fraction of the constituents. The ratio between filler material and the surrounding matrix portrayed by the dimensions (a) and (b) in Figure 4.a can be changed to alter the volume fraction content in each lamina. The second method to tailor mechanical properties can be done by stacking laminae together at different angles (i.e. printing different laminae on top of each other to form a laminate) to further change and control the mechanical properties. Figure 4.b shows a representation of a laminate compounded of stacked laminae at different angles. These angles can be changed to improve the material's load bearing capabilities or tailor the properties of the laminate from anisotropic to orthotropic or quasi isotropic.

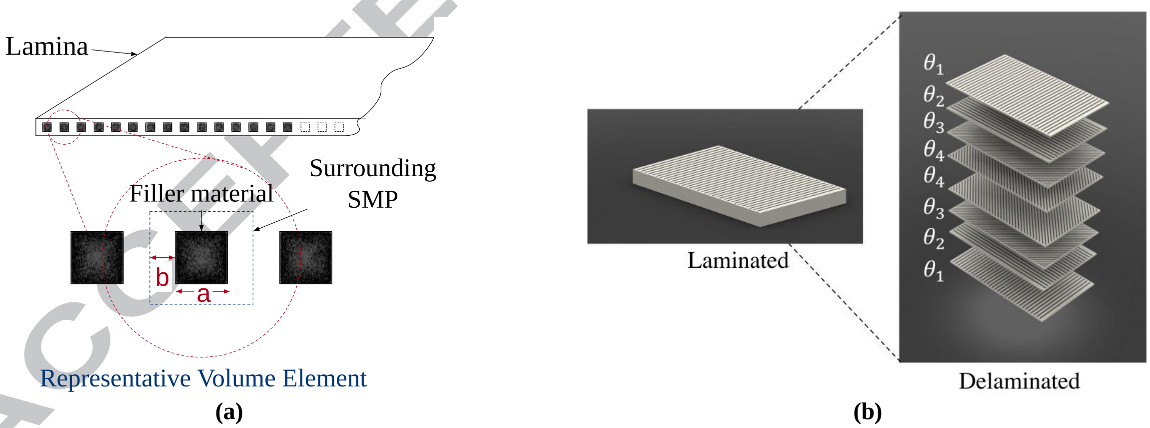
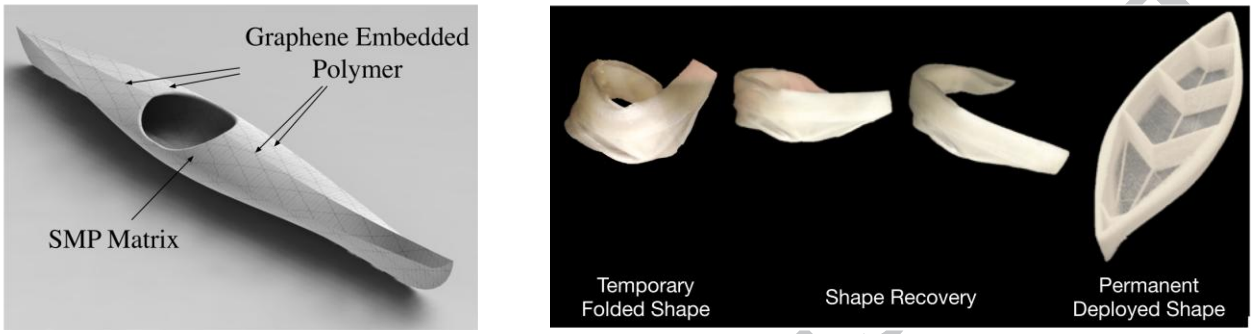


Figure 4: a) Lamina showing a detail of the embedded Graphene-PLA lines showing an alteration of volume fraction by changing ratio between distances a and b. b) Laminate showing exploded delaminated view compounded of different angle oriented laminae.

The presented technology can be scaled up in size, from desktop printers to large-scale printers and larger production quantities. An example of the potentially novel applications is the production of a SMPC Kayak using SMP matrix and conductive and reinforcing fillers in a large scale EBAM machine, as illustrated in Figure 5 a. As proof of concept a prototype of a 3D printed kayak of SMP has been manufactured and is portrayed in Figure 5 b.The 3D printed Kayak can be folded and stored away using the SME of the SMPC by connecting it to a power source in site, such as a vehicle's power outlet. There are high end Kayak's available in the market manufactured of military grade polyurethane that can be assembled and disassembled using many parts and fasteners and are currently quite costly. The proposed idea can change the way such sports equipment is designed, manufactured, and utilized.



(a) **(b)**

Figure 5: (a) concept of a 3D printed Kayak with graphene embedded polymer on a SMP matrix. CAD adapted from [25], (b) Printed prototype of a kayak made of SMP deploying.

4. Conclusions

The present study proposes an innovative, low cost methodology of manufacturing SMPCs by using Extrusion Based Additive Manufacturing. Resistive heating can be used to electrically activate SMPCs. A SMPC can be manufactured to improve the mechanical properties of raw SMPs. The proposed manufacturing mechanism obtains a SMPC that can be activated in the field and have high load bearing capabilities.

In this work a SMP-Polyurethane based was the base material used for this study. Additionally, Graphene-PLA polymer was investigated as possible conductive filler material. Both materials were 3D printed next to each other to form a lamina like structure. The mechanical properties of SMPC can be tailored by changing the volume fraction percent content of conductive/reinforce material and by printing laminae stacked together at different angles to form a laminate like structure, much like what is seen in the aviation industry with the use of fiber reinforced composites.

The present work will propel SMPs and SMPCs into the consumer industry by contributing with an alternate, low cost manufacturing technique. The method includes an activation procedure of the SME and a reinforcing mechanism of the raw SMP material. The present technology may redefine the way sports equipment like a kayak is transported and utilized. This work is part of a much bigger investigation related to SMPCs and the manufacturing of electro-active shape memory polymer composite smart laminated structures.

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