Short Communication

AM-FFF OF OBJECTS USING COMMERCIAL PLA BASED SHAPE MEMORY POLYMER PRINTED BY AN OPEN-SOURCE 3D PRINTER

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ABSTRACT

The 4D additive manufacturing processes are considered today as the "next big thing" in R&D. The aim of this research is to provide two examples of commercial PLA based shape memory polymer (SMP) objects printed on an open-source 3D printer in order to proof the feasibility of such novel 4D printing process. To that purpose, a PLA based filament of eSUN (4D filament e4D-1white, SMP) was chosen, and two applications, a spring and a vase, were designed by 3D-printing with additive manufacturing (AM) fused filament fabrication (FFF) technique. The 4D-printed objects were successfully produced, the shape memory effect and their functionality were demonstrated by achieving the shape-memory cycle of programming, storage and recovery.

KEYWORDS: Additive manufacturing, 4D printing, Fused Filament Fabrication, Shape Memory Polymer.

1. INTRODUCTION

1.1. 4D Printing

3D printing (additive manufacturing), first developed by Charles (Chuck) Hull in 1983, is basically a technology in which complex shapes are built layer by layer. AM allows consumers to develop and create their own goods while the products can be designed without creating substantial waste. The development of "4D printing", with the fourth dimension referring to time, enables the printing of objects using specially designed materials, which change shape in a pre-programmed manner in response to external-stimuli. The AM 4D-printed structure can modify its configuration and/or property in time as a reaction to external stimuli; the shape memory polymers (SMPs) class can fix temporary shapes and revert to their permanent shapes under the action of many stimuli including thermal energy. The applications of 4D-printed structures are evident and expected across many crucial business sectors, in the medical, aerospace, space and many other industries [1], [2].

1.2. Shape Memory Polymers

As current knowledge goes, the shape memory effect term was introduced in the 1990s and was "marketed" at the conferences on Shape Memory and Superelasticity Technologies [3]. At that time, the Shape Memory Effect (SME) was mainly concentrated on some metallic materials known as shape memory alloys. SMPs are the type of polymer materials that can recover after deformation and/or apply force in response to a stimulus, e.g. heat, light, electric current, water (vapor or liquid) or other solvents [1] - [8]. Thermal energy is probably the most common stimulus. In polymer materials the SME is produced by proper programming and by the appropriate polymer structure. Typically, the thermoresponsive shape-memory cycle is achieved in three successive steps that include (Fig. 1):

- **Programming,** which consists of 4D printing to the "active/working shape", later converted through heating and deformation (by applying forces) to the "storage shape";
- **Storage,** which consists of cooling and removing force/constraints to obtain the "storage shape";
- **Recovery,** which consists of reheating to attain the "active/working shape" or "permanent shape" and/or apply the programmed/ predesigned force.

SMP is an elastic polymer network that underlies active movement. The polymer network of SMPs requires the presence of at least two different domains with different thermal transitions, therefore consisting of the molecular switching segment and net-point hard segments. The net-points determine the permanent shape of the polymer network and can be of a chemical (covalent bonds) or physical (intermolecular interactions) nature. Therefore, SMPs

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can be thermosetting or thermoplastic, respectively. The molecular switching segment can be composed, for example, of a semi-crystalline structure, presenting both crystalline domains and amorphous domains, which can be elongated and deformed upon exposure to a specific stimulus [9], [10].

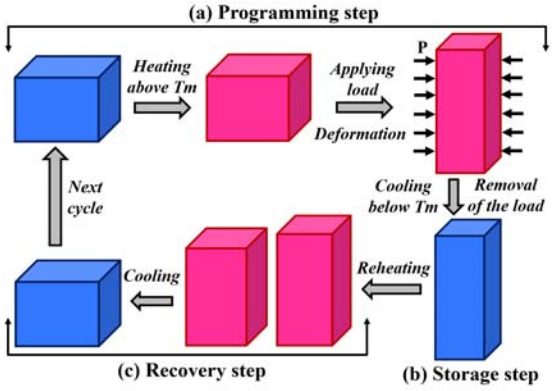

Fig. 1. The shape-memory cycle is typically achieved in three steps: a) Programming - "active/working shape"; b) Storage - "storage shape"; c) Recovery - "permanent shape"

By conventional processing, e.g. extruding or printing, the polymer is shaped into its initial, permanent form (Fig. 2a). Afterwards, in a process called 'Programming', the polymer sample is deformed and fixed into a temporary shape. This step occurs by two consecutive processes. First, the SMP is heated above its melting temperature (Tm), the crystalline region is transformed into the amorphous state and becomes soft, flexible and extendable (Fig. 2b). Then, a load is applied and the specimen of SMP extends, while it is under heat, into a temporary shape (path 1). The specimen is then cooled when it is deformed to a temperature under its Tm (path 2) and the amorphous region then changes back to the crystalline state ('Storage'). If the specimen is then heated again to a temperature above its Tm with no load on, the specimen will then recover its initial permanent shape (path 3). The speed at which this polymer returns to its original structure ('Recovery') is limited by the friction generated within the molecular structure. This cycle of programming, storage and recovery can be repeated several times, with different temporary shapes in subsequent cycles [11] - [14].

Why does the shape memory recovery stage phenomena occur? At the programming stage ("active/working shape"), at ambient temperature, the polymer's conformational entropy is basically high. By deforming the material to the "storage shape" the "viscous-like" behaviour of the chain network (at the onset of the Tm or the glass transition temperature, Tg) is activated to the state of being disentangled, the entropic energy is lowered and stored on cooling to ambient temperature. When the polymer is reheated, the material softens, the chains' mobility increases, and the polymer returns to the initial lower state energy by releasing the stored material's entropy, i.e. by changing its shape to the ambient "active/working shape". The transition is motivated by conformational entropy due to chain entanglements and/or physical/chemical crosslinks (junction density) [8].

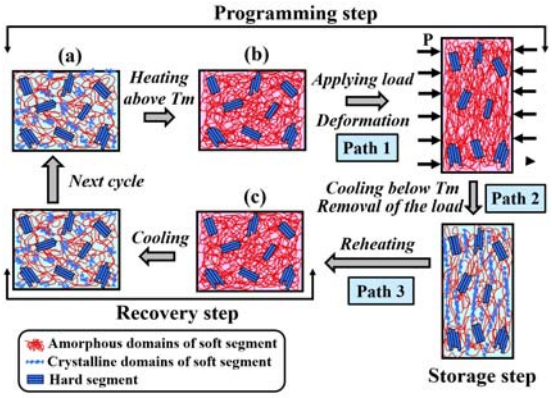

Fig. 2. The shape-memory cycle in the microscopic level: (a) the initial state (as-printed) of the SMP; and (b, c) after heating above Tm the crystalline region is transformed into an amorphous state and the material becomes soft, flexible and extendable

2. EXPERIMENTAL PART

Two applications were designed and 3D-printed by the AM-FFF technique: a) a 4D-printed spring, and b) a 4D-printed vase by using commercial polylactic acid (PLA) based SMP, as described below. To that purpose, an eSUN 4D filament e4D-1white (Esun Industrial Co., Ltd) SMP was used, with the filament diameter of 1.75 mm, and spool weight of 0.5 kg. The printing parameters of the eSUN 4D filament e4D-1 white, as recommended by the manufacturer, are shown in table 1.

Table 1. The 3D printing parameters and properties of the SUN 4D filament e4D-1 white shape memory polymer, as recommended by the manufacturer (Esun Industrial Co., Ltd)

Parameter	**Recommended value**
Density [g/cm^3]	1.23
Printing speed [mm/s]	40-90
Printing temperature [^{o}C]	190-210
Platform temperature [^{o}C]	35-50
Deformation temperature [^{o}C]	45-90
Elongation of break [%]	115
Tensile strength [%]	58
Tensile yield stress [MPa]	60.3

The spring and vase were 3D-printed by the Creality 3D® Ender-3 3D printer (Manufacturer: Creality 3D Technology Co., Ltd). The nozzle diameter was 0.4 mm, the printing temperature was 205°C, the build plate temperature was 45°C, the printing speed was 50 mm/s, and the layer height (resolution) was 0.2 mm.

2.1. Application A: The 4D-Printed Spring

The spring was designed by means of the computer aided design (CAD) SolidWorks 2019 program (Fig. 3) and was 3D printed by Ender-3 machine with a 96% infill density out of the SMP (Fig. 4).

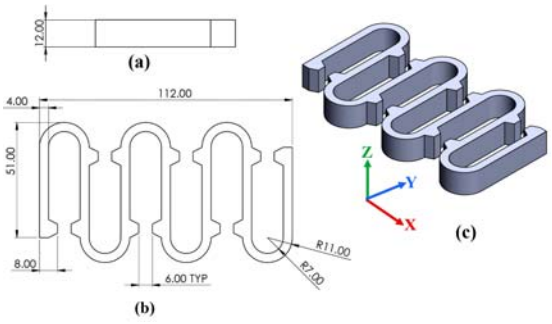

Fig. 3. The 4D-printed spring CAD model: a) side view; b) upper view; c) isometric view (designed with SolidWorks 2019)

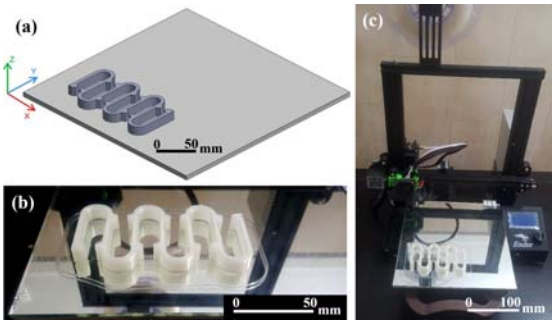

Fig. 4. The 4D-printed spring specimen produced of eSUN 4D filament e4D-1 white shape memory polymer: a) the CAD model of the spring specimen (isometric view, solidworks program); b) location on the tray; c) the spring specimen inside the 3D-priting machine

For the study of shape memory properties, three spring specimens, made of SMP, were printed (specimens 1, 2, and 3), with the programmed dimensions shown in figure 5. Next the length of each spring was measured in its initial condition after 3D-printing (25ºC) (step 1). Then each specimen was inserted into a hot water container (specimen 1 was heated to a temperature of 60ºC, specimen 2 was heated to a temperature of 70ºC, and specimen 3 was heated to a temperature of 80ºC) for 5 s (step 2). The temperature was measured by an ANENG AN8009 thermocouple, with an approximation error of ±1 ºC. Next each heated specimen was removed from the water and immediately compressed by mechanical loading (step 3). Then the specimen was cooled down below the Tg to room temperature and the storage shapes were measured again (step 4). The length of the spring was measured by digital caliber (with an accuracy of ± 0.1 mm) after steps 1, 3 and 4 (Fig. 5). The springs were reheated to temperatures of 60ºC, 70ºC and 80ºC, maintaining these temperatures for 5 s and the permanent shapes were remeasured after cooling at room temperature (step 5); and thus the entire shape-memory cycle was demonstrated.

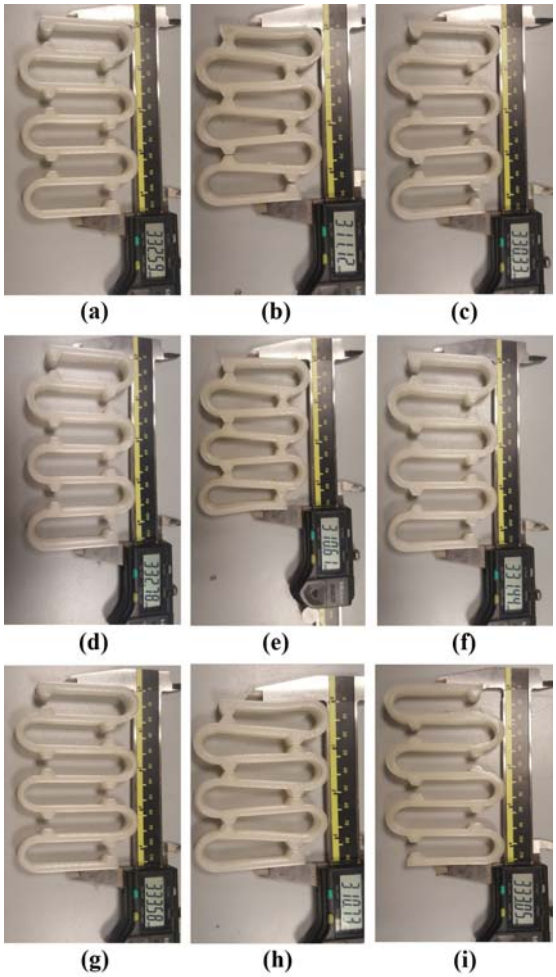

Fig. 5. The 4D-printed spring specimen, produced of eSUN 4D filament e4D-1 white shape memory polymer: (a) Specimen 1, initial length of the as-printed spring (25ºC); (b) specimen 1 after shrinking (60ºC and compression); (c) specimen 1, after reheating and cooling (25ºC); (d) specimen 2, initial length (25ºC); (e) specimen 2, after shrinking (70ºC and compression); (f) specimen 2 after reheating and cooling (25ºC); (g) specimen 3, initial length (25ºC); (h) specimen 3, after shrinking (80ºC and compression); and (i) specimen 3 after reheating and cooling (25ºC)

2.2. Application B: The 4D-Printed Vase

The vase was designed by means of the CAD program and then it was printed by an Ender-3 machine, with infill density of 100%, since only one tool path was printed (Fig. 6a). The vase was heated from room temperature to 60ºC, maintaining the temperature for 5 s, then it was compressed at this temperature and cooled down to room temperature (Fig. 6b). The vase was reheated to a temperature of 60ºC for 5 s and the permanent shape was regained (Fig. 6c), thus achieving the complete shape-memory cycle.

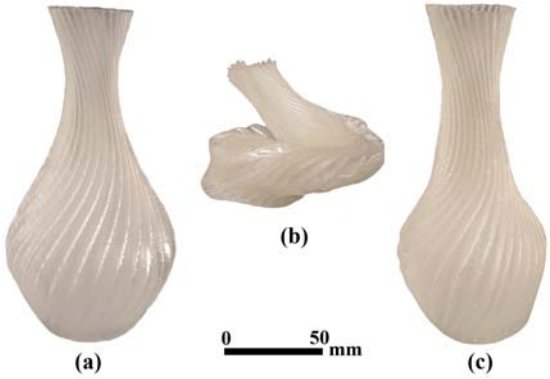

Fig. 6. The 4D-printed vase specimen, produced of eSUN 4D filament e4D-1 white shape memory polymer: a) the initial shape of the as-printed vase (25ºC); b) the vase after shrinking (60ºC and compression) and release of the load (25ºC); c) return from the storage shape (deformed state) to the permanent (programmed) shape

3. RESULTS AND DISCUSSION

The PLA based (eSUN 4D filament e4D-1white) glassy polymer objects (spring, Figs. 4, 5 and vase, Fig. 6) were heated above their Tg (about 60°C) and then deformed in the rubbery state ('Programming'). The switch characteristic to these polymers is usually a direct change in temperature which is based on the *T*g, for amorphous polymers, or on the Tm, for semicrystalline polymers. In our case, the soft segments in the polymer and its viscoelastic properties exhibit mobility above the Tg, and as a result allow for considerable changes in shape. Upon elastic deformation, elongation of the random polymer coils will occur, and they will align along the direction of the applied stress. Therefore, different shapes can be obtained at each cycle, while each shape results in reducing the number of possible configurations, and thus also reduces the entropy relative to its initial shape.

On cooling, the objects return to the glassy state and the molecular motion is frozen; after the employed constraint is removed, both objects essentially maintain the less favorable deformed shape from an entropic point of view, while storing the energy related to the deformation ('Storage'). After programming and storage, the objects were reheated into the rubbery state and the SME was detected ('Recovery'). The objects' shape recovery occurs only when the polymer is reheated to its rubbery state. This triggers the soft polymer chain motion, while the net-point hard segments force the material to revert to its entropically favourable original shape, which exhibits the most coiled conformation. We can presume that the SME was obtained by utilizing the PLA based material's glass transition; as there are two phases (the rubbery and the glassy one) the mechanism is often called a dual-state mechanism (DSM) [4], [5].

The structure of the polymer greatly affects its properties and the trigger which will activate its shape memory cycle. This should be taken into account depending on the application required. For example, one of the factors influencing the performance of a SMP is crosslink density. This indicates a balance occurring between brittle, heavily crosslinked polymers with improved shape recovery properties, and flexible, less crosslinked polymers with slightly less shape recovery [15]. Moreover, programming and recovery cycles can usually be applied multiple times. However, while literature usually refers to three cycles for the characterization of the shape-memory behaviour, no theoretical limit exists prior to the occurrence of material fatigue [16].

3.1. Application A

The dimension of the spring samples (1) after printing, (2) after applying force and (3) after reheating the SM polymer are shown in table 2. The results demonstrate the ability of the eSUN 4D filament e4D-1white polymer to return from the storage shape (deformed state) to the permanent (programmed) shape, on applying the external heat stimulus (Fig. 5).

3.2. Application B

The visualization of the SM polymer's ability to return from the storage shape (deformed state) to the permanent (programmed) shape was demonstrated by utilizing a thin walled vase as shown in figure 6.

4. SUMMARY

This study shows the feasibility of producing objects out of commercial PLA based SMP, using an open source FFF machine. For that purpose, two applications made of PLA based SMP, a spring, and a vase, were designed and manufactured by the FFF AM technology. The SME was positively demonstrated by the use of plastic deformation linked to a heating and cooling cycle. The shape memory effect, of shape changes of deformable materials under external stimulus conditions was shown by

completing the shape-memory cycle of programming, storage and recovery.

We can presume that the SME was obtained by utilizing the PLA based material's glass transition; since there are two phases (rubbery and glassy), the SME mechanism is often called a dual-state mechanism [4], [5].

While engineering applications of SMPs are currently being considered and the basic modelling principles are still in preliminary research, the 4D examples included in the paper may accelerate the usage of SMPs in the AM industry.

Table 2. The length of: the as-print spring samples (=A), the samples after applying load and deformation (=B), and the samples after reheating and cooling (=C).

Sample no.	Temperature [^{o}C]	Length [mm]			D [mm]		
		A	B	C	A-B	C-B	A-C
1	60	332.6±0.1	311.1±0.1	330.3±0.1	21.5±0.1	19.2±0.1	2.3±0.1
2	70	332.8±0.1	310.6±0.1	331.4±0.1	22.2±0.1	20.8±0.1	1.4±0.1
3	80	333.6±0.1	310.7±0.1	333.1±0.1	22.9±0.1	22.4±0.1	0.5±0.1

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