

International Journal of Advanced Manufacturing Technology
4D PRINTING: PROCESSABILITY AND MEASUREMENT OF RECOVERY FORCE IN
SHAPE MEMORY POLYMERS
 --Manuscript Draft--

Manuscript Number:	JAMT-D-16-01157R1
Full Title:	4D PRINTING: PROCESSABILITY AND MEASUREMENT OF RECOVERY FORCE IN SHAPE MEMORY POLYMERS
Article Type:	Original Research
Keywords:	4D printing; shape memory polymer, extrusion of polymers; stimuli responsive materials; additive manufacturing
Corresponding Author:	Mario Domingo Monzon Universidad of Las Palmas de Gran Canaria Las Palmas de Gran Canaria, SPAIN
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Universidad of Las Palmas de Gran Canaria
Corresponding Author's Secondary Institution:	
First Author:	Mario Domingo Monzon
First Author Secondary Information:	
Order of Authors:	Mario Domingo Monzon Rubén Paz Eujin Pei Fernando Ortega Luis A. Suárez Zaida Ortega María E. Alemán Tom Plucinski Nathan Clow
Order of Authors Secondary Information:	
Funding Information:	
Abstract:	The fourth dimension in 4D printing refers to the ability of materials to alter its form after they are produced, thereby providing additional functional capabilities and performance driven applications. Stimuli materials provide this capability through the use of shape memory polymers. For this research, the property of programming the determined shape is achieved through controlled heat under laboratory conditions. This paper shows the potential to process and experiment with thermoplastic polyurethane as a shape memory material. Taking a step further, we ascertain the properties of this material through extrusion-based additive manufacturing processes and produce parts for testing. The results show that the characteristics of the 3D printed parts successfully retain the property of the shape memory and the recovery force allows this to be utilised as a mechanical actuator. The recovery stress has been recorded to be between 0.45 MPa and 0.61 MPa (at feed rate 990 mm/min). The maximum level of recovery stress is similar to the same material being processed through conventional compression moulding. Lastly, we designed and produced a coil as an actuator to demonstrate that the same material can be extended to other applications.

[Click here to view linked References](#)

4D PRINTING: PROCESSABILITY AND MEASUREMENT OF RECOVERY FORCE IN SHAPE MEMORY POLYMERS

M.D. Monzón^{1*}, R. Paz¹, E. Pei³, F. Ortega¹, L.A. Suárez¹, Z. Ortega², M. E. Alemán²,
T. Plucinski⁴, N. Clow⁵

1 Departamento de Ingeniería Mecánica, Universidad de Las Palmas de Gran Canaria, Las Palmas de Gran Canaria, Campus de Tafira Baja, 35017, Las Palmas de Gran Canaria, Spain . * Corresponding author: mario.monzon@ulpgc.es, +34928458617

2 Departamento de Ingeniería de Procesos, Universidad de Las Palmas de Gran Canaria, Las Palmas de Gran Canaria, Campus de Tafira Baja, 35017, Las Palmas de Gran Canaria, Spain.

3 Department of Design, College of Engineering Design and Physical Sciences, Brunel University London, UB8 3PH, United Kingdom

4 BAE Systems Applied Intelligence, United Kingdom

5 Defence Science and Technology Laboratory, United Kingdom

Abstract

The fourth dimension in 4D printing refers to the ability of materials to alter its form after they are produced, thereby providing additional functional capabilities and performance driven applications. Stimuli materials provide this capability through the use of shape memory polymers. For this research, the property of programming the determined shape is achieved through controlled heat under laboratory conditions. This paper shows the potential to process and experiment with thermoplastic polyurethane as a shape memory material. Taking a step further, we ascertain the properties of this material through extrusion-based additive manufacturing processes and produce parts for testing. The results show that the characteristics of the 3D printed parts successfully retain the property of the shape memory and the recovery force allows this to be utilised as a mechanical actuator. The recovery stress has been recorded to be between 0.45 MPa and 0.61 MPa (at feed rate 990 mm/min). The maximum level of recovery stress is similar to the same material being processed through conventional

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

compression moulding. Lastly, we designed and produced a coil as an actuator to demonstrate that the same material can be extended to other applications.

Keywords: 4D printing, shape memory polymer, extrusion of polymers, stimuli responsive materials, additive manufacturing

1. Introduction

Additive Manufacturing (AM) is a solid freeform manufacturing technology that enables the direct production of bespoke parts and products in small to medium batches without resorting to the use of moulding and tooling. According to ISO/ASTM 52900:2015, AM is defined as processes of joining materials to produce objects layer upon layer from 3D model data, as opposed to subtractive manufacturing fabrication methodologies [1, 2]. The development of AM started in the 1980s [3] and significant progress has been made since then, and there is an expectation that AM can revolutionize the manufacturing industry and provide spin-off benefits to the society. Parts produced from AM have been applied in a variety of ways such as in New Product Development for visual prototypes and functional testing [4]. However, a new trend at the other far end of the technology spectrum is emerging. 4D Printing (4DP), has the economic, environmental and strategic implications of AM while providing new and unprecedented capabilities in transforming digital information of the virtual world into physical objects of the material world [5]. The fourth dimension in 4D printing refers to the ability for material objects to transform its geometry after being produced, thereby providing additional capabilities and performance-driven applications [5]. It is not about how long it takes to print a part; but rather the fact that the 3D printed object after being built, continues to evolve over time [4]. What 4D printing offers is the opportunity for objects that change and adapt in response to external stimuli. The relatively recent advancements of multi-material AM, combined with rapid developments in smart materials and active fibres mean that there are now even more opportunities and applications available for end-users [6]. The source of external stimuli could be based on physical or chemical parameters such as temperature, humidity, light or magnetic sources, etc. The response to external stimuli can be controlled through various ways such as modifying the geometrical shape as being the most common approach by other researchers. The property of programming the determined shape and the extent of the state of change when an external stimuli is applied is known as the shape memory effect (SME). All polymers with this particular characteristic are classed as Shape Memory Polymers (SMPs).

1 Conventional classes of SMPs include cross-linked PE and PE-Nylon6 graft co-
2 polymers, Trans-Polyisoprene (TPI), cross-linked Ethylenevinyl Acetate co-polymer,
3 Styrene-based polymers, Acrylate-based polymers, Polynorbornene, cross-linked
4 Polycyclooctene, Epoxy-based polymers, Thio-ene-based polymers, segmented
5 Polyurethane (PU), and segmented PU Ionomers [7]. This work focuses on the use of
6 thermal-responsive SMPs based on TPU (thermoplastic polyurethane).
7
8
9
10

11
12
13 For heat-induced (thermal-responsive) shape recovery methods, there are two main
14 types of working mechanisms [8]. This first is the dual-state mechanism (DSM). Above
15 the glass transition temperature (T_g), the polymer is in a pliable, rubbery state and soft
16 and it is easily deformed. Upon cooling to below the T_g , the polymer is in the glassy
17 state and rigid. After removal of the constraint, the deformed shape will retain the
18 programmed state and consequentially the original shape may be recovered by heating
19 over the T_g again. Here, the cross-link chains enable the component to store the
20 elastic energy which in turn, serves as the driving force for shape recovery in the later
21 stage. The second type is the dual-component mechanism (DCM) whereby two
22 components are assembled in the form of hard and soft segments within a matrix. The
23 hard segment should be elastic within the working temperature range. On the other
24 hand, the soft segment will become soft upon heating so that the material is able to
25 deform at high temperatures. Similar to DSM, after the cooling and removal of the
26 constraint, the deformed shape is retained until it is heated again to enable the soft
27 segment to become pliable for shape recovery. For this work, the selected TPU is
28 classed as a dual-state mechanism (DSM) whereby the single component is able to
29 transition into a pliable state upon reaching T_g and the original shape can be
30 recovered.
31
32
33
34
35
36
37
38
39
40
41
42
43
44

45 During the past two decades, SMPs have attracted research interest from both
46 academia and industry and real world applications have been developed for potential
47 use such as for functional textiles, smart products, active aircraft components, adaptive
48 biomedical devices and interactive electronic apparatuses [7]. Other studies have
49 focused on thermo-responsive SMPs such as PFSA, a commercial thermoplastic
50 polymer with a Polytetrafluoroethylene backbone and Perfluoroether Sulphonic acid
51 side chains [8]. The author showed the capability of using quadruple-shape memory
52 PFSA's with several programming points. Sun et al. [9] optimized the programming
53 temperature of PMMA for maximum recovery stress through good fixation points and
54 with consistent recovery. The use of Polyurethane (PU) has been popularly adapted as
55
56
57
58
59
60
61
62
63
64
65

1 an SMP where several studies have been carried out on this particular polymer either
2 as a thermoset or thermoplastic [11, 13, 19, 20, 21]. For instance, Tobushi et al [11]
3 worked with sheets of PU, studying the recovery and irrecoverable strain, whereby the
4 recoverable strain intensifies with an increasing strain-holding temperature and strain-
5 holding time above the T_g. Also, it was recorded that the higher the strain-holding
6 temperature and the longer the strain-holding time, the easier the irrecoverable strain
7 appears. A typical application of SMP parts is to serve as an actuation device within a
8 mechanism. Smith [12] designed and tested a prototype of SMP using EPON 826 as a
9 gripper for a mini robot, concluding that a 100% recovery could be observed for stored
10 angles less than 90° at ambient temperatures greater than 70.5°C. In addition, force
11 testing and static friction tests that were carried out, predicted that the SMP samples
12 used in this research could lift a maximum weight of 1.5 grams. Manzoor et al [13]
13 applied synthesized PU (SMPU) as a material for pressure bandage in medical
14 applications and it had the potential for multiple re-use.
15
16
17
18
19
20
21
22
23
24

25 In the field of AM, other authors have reported the use of SMPs as a potential material
26 for 4D printing. Some of these materials exist commercially such as experiments by
27 Dunn et al [14] who used Polyjet technology from Stratasys and Photopolymer
28 composites TangoBlack and Gray 60 were utilised. The authors also developed
29 equations to predict the behaviour of self-assembled parts by demonstrating the use of
30 foldable origami structures. In parallel, Zarek et al. [15] used a specially developed
31 photopolymer for Stereolithography (SLA) printers (Picoplus39, Asiga). Within Fused
32 Deposition Modelling (FDM), or extrusion-based AM, Yang et al. [16] presented a
33 method of using SMPs by making extruded filament from TPU pellets and measured
34 the part density, dimensional accuracy, and surface roughness of the deposited part.
35 In a different study, Raasch et al. [17] reported the behaviour of 3D printed Polyurethane-
36 based SMP specimens made by extrusion-based AM using Thermoplastic PUs in
37 commercial equipment. They carried out various annealing treatments to ascertain the
38 influence on the shape memory effect.
39
40
41
42
43
44
45
46
47
48
49

50 Our work takes a step further by exploring the use of TPU with shape memory
51 properties in a pelletized form and subjecting the material with extrusion-based AM. We
52 developed an experimental extruder and a measurement device to precisely calculate
53 the recovery force to ascertain the quality of the processed parts. We use the results of
54 the recovery force as the baseline to further improve the geometry and build
55 parameters and demonstrated the potential of this material and by producing a working
56 coil mechanism that could actuate in a vertical axis.
57
58
59
60
61
62
63
64
65

2. Materials and Methods

2.1. The SMP Material

Shape memory polymers (SMPs) are a type of polymeric materials that can be programmed to “memorize” a pre-determined shape and subsequently assumes this temporary configuration. It has the ability to revert to the memorized shape when subjected to the external stimuli [17]. The selected thermoplastic polyurethane (TPU) used for this study is a thermal-responsive SMP and the reason of selecting this TPU instead of a thermoset is the suitability of being processed by extrusion-based AM methods. In general, to be considered for use as an effective SMP, there are two factors needed to be close to 100% - the shape recovery ratio and the shape fixity ratio, which is defined as follows [18]:

$$R_r = 100\% \times (\varepsilon - \varepsilon_{rec}) / \varepsilon$$

$$R_f = 100\% \times \varepsilon / \varepsilon_{load}$$

Whereby: R_r = Shape recovery ratio; R_f = Shape fixity ratio; ε = Fixed strain after cooling and load removal; ε_{rec} = Strain after recovery; and ε_{load} = Maximum strain under load.

For this work, Desmopan[®] will be used for the investigations as it is suitable to be processed in injection moulding or extrusion processes. The material can be categorized as a high-grade thermoplastic elastomer bridging the gap between rubber and traditional thermoplastics. The MVR (melt volume-flow rate) index of this material is between 20 and 60 ml/10 min (200 °C) and the main mechanical properties are summarised in table 1. Literature review has showed that this material has not been used for AM and key to this work is to observe the behaviour of Desmopan[®] under the process of extrusion-based AM processes. Desmopan[®] is supplied in a pelletized form and needs to be dried before processing to a moisture content of ≤ 0.05 %. Such levels can be reliably reached in conventional dry air and circulating air dryers. The recommended drying temperatures are between 80 and 110 °C with drying times of between 1 to 3 hours.

Table 1. Properties of Desmopan[®]

Properties	Units	Value	Standards
Shore hardness A/D		94/	ISO R868
Stress at 100% strain	MPa	7	ISO 527
Stress at 300% strain	MPa	13	ISO 527
Tensile stress at break	MPa	40	ISO 527
Tensile strain at break	%	600	ISO 527

A thermogravimetric analysis (TGA) was carried out by dynamic analysis up to 400°C with a heat rate of 30°C/min and an air flux of 10 ml/min (Figure 1). The most relevant information that can be extracted from this TGA is that the temperature of the first endothermic phase transition (56°C). It is important not to exceed this temperature during the deformation-recovery cycles in order to achieve a suitable shape memory behaviour of the material.

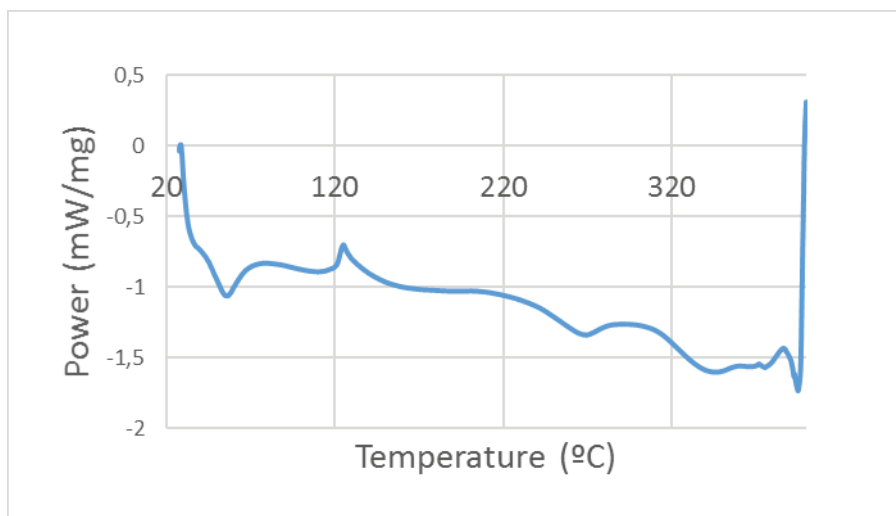
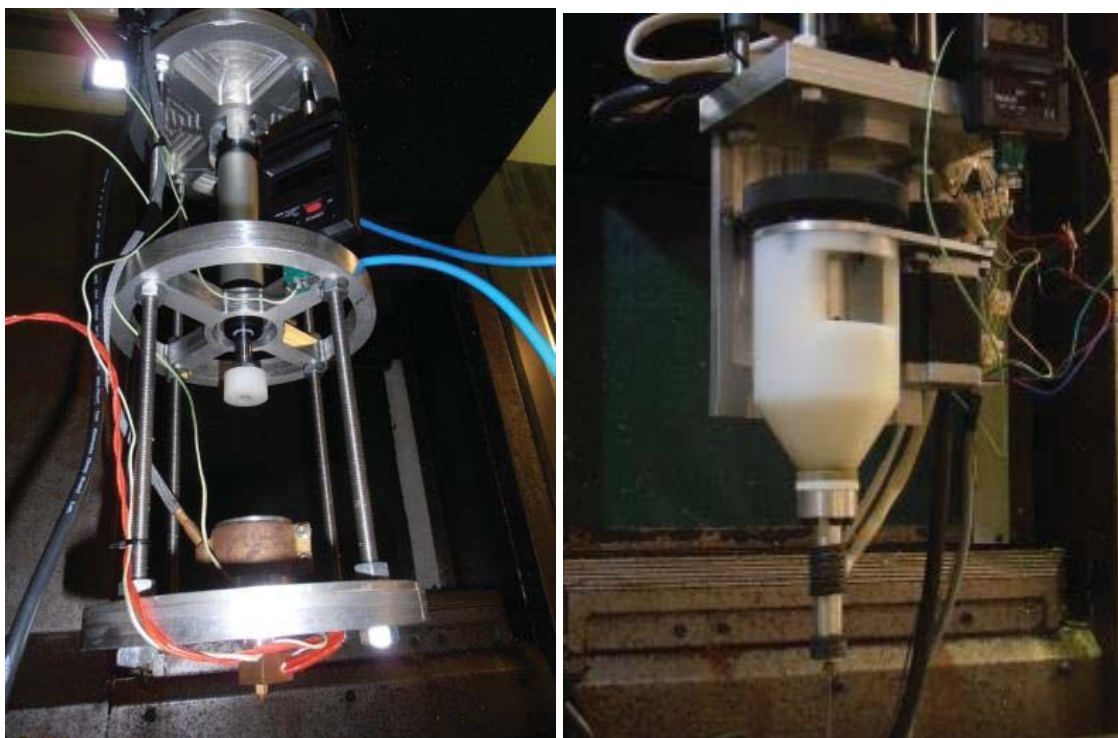


Figure 1. Calorimetric thermogram of DP2795A-SMP

2.2. The 3D extruder

As the raw material is not available as a filament on spool which is used for conventional FDM equipment, it was decided that an experimental extruder would be built, encompassing a cylinder and plunger driven by a pneumatic mechanism (Figure 2a). The cylinder would contain pellets of TPU and preheating the material under a controlled temperature. The nozzle tip would also be heated to ensure that the temperature of the TPU material would remain constant just before being deposited. To

1 avoid degradation of the material, the maximum temperature of heating was 220 °C
2 according to the specifications recommendations of the manufacturer's guide. The
3 temperature of cylinder was set to 190 °C and the temperature of the nozzle tip set at
4 210 °C. The constraint of this set up was that it would have a maximum print volume of
5 600-700 mm³. The diameter of nozzle tip was 0.4 mm and the key advantage is that
6 this particular extruder set up enabled the researchers to control and measure the
7 exact extrusion force during the process which is essential to determine the parameters
8 including material viscosity, shear rate and shear stress. The experimental extruder
9 was assembled on an industrial CNC machine and programmed by standard G code,
10 starting from STL file and obtained using the Slic3R software.
11
12
13
14
15
16



17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43 Figure 2a) (left) First version of pneumatic extruder. Figure 2b) (right) Second version
44 of feeding screw extruder
45
46
47
48
49

50 The extrusion parameters were optimised through undertaking several iterations of
51 experiments. It was observed that the relationship between the manufacturing speed
52 (axis feed rate, mm/min) and the filament output speed were co-related and it was
53 crucial for the quality of the samples being produced. It was found that the best results
54 for feed rate was between 990 and 1045mm/min. It is important to note that the
55 manufacturer's guide cautions the risk of degradation of the material under strong
56 parameters of extrusion such as heavy shear stresses (in terms of flow rate). This is the
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

main reason that the experiments had a slower speed of print as compared to other extraction based processes when using conventional materials such as ABS or PLA.

As the first extrusion device could only contain a small volume of material, a new design of an extruder based on the use of a feeding screw was developed (Figure 2b). This design would encompass a feeding chute, a 7 RPM stepper motor with a mechanical transmission, a 8mm diameter screw with a cylindrical enclosure, an electrical resistance and a nozzle tip of 0.4 mm. All of the components would be assembled onto the same CNC machine that was used for the first extruder being assembled onto the 3D printer.

2.3. Samples for recovery force tests and validation of quality

To validate the quality of parts being produced using extruded Desmopan[®], we compared the printed samples with those made from compression moulding. This processed enabled us to analyse the build quality and to establish an understanding of the recovery force. In the case of the extruded Desmopan[®], 6 samples, each with a uniform thickness of 3 mm were produced and the build settings are shown in Table 2. For the compressed parts, 30 samples were produced with 6 different configurations (Figure 3) to assess the influence of the dimensions and to compare the results with the printed parts. All the samples were produced using the same geometry and at this stage, a flat 20x10x3mm piece was produced for ease of replication and to save time and resources (Figure 4). The platen press that was used was the Collin[®] laboratory platen press P200 PM with 300°C of maximum working temperature and 125 kN of pressure capacity. The samples were processed at 230°C during 3 minutes with 10 bar of pressure exerted.

Table 2. Selected process parameters

Speed XY (mm/min)	Temperature (°C)	Area (mm ²)	N°. of Layers	Lateral pitch (mm)	Layer height (mm)	Deposition strategy, XY orientation
990	190/210	20x10	8	0.5	0.4	45°
1045	190/210	20x10	8	0.5	0.4	45°

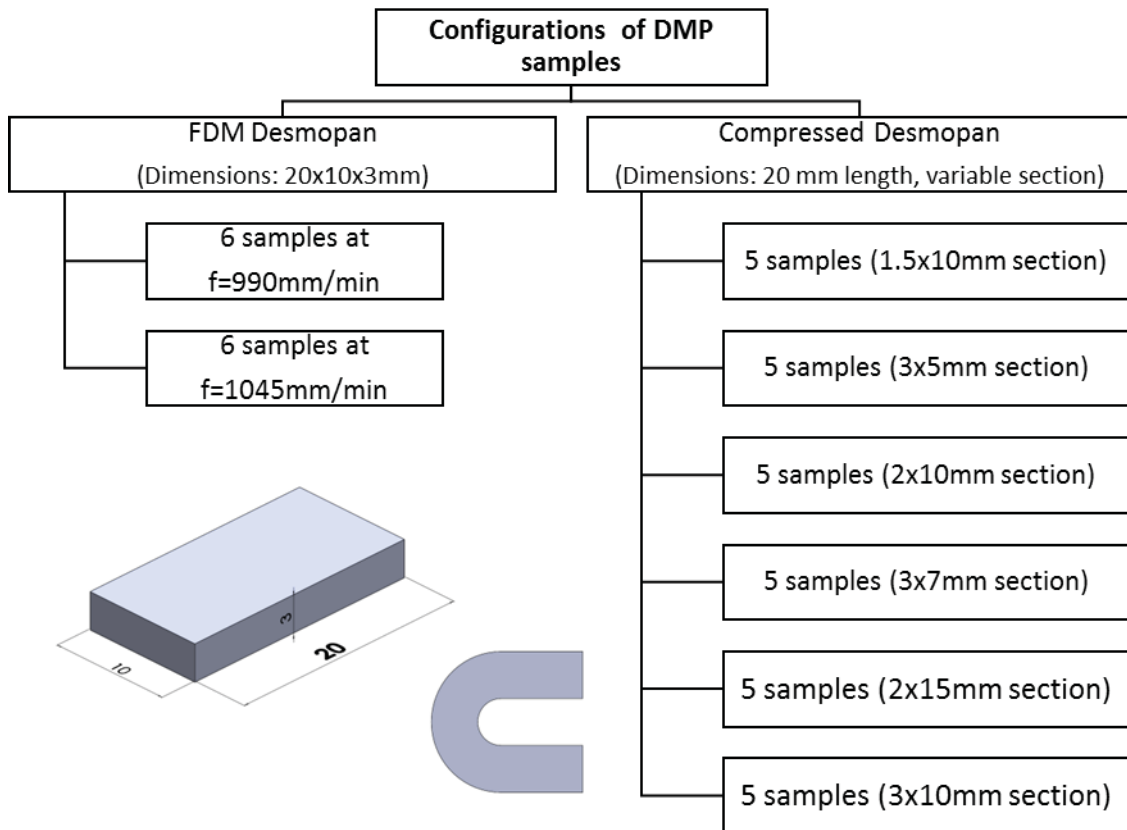


Figure 3. Characteristics of samples tested



Figure 4. Printed (left) and compressed (right) samples of Desmopan

2.4. Methodology for measurement of recovery force

1 All the samples that were produced from the summary in Figure 3 were deformed from
2 the “memorized” state to the “strained” state using the following steps below. At this
3 stage, the samples were immersed in 50°C of warm water to activate the new shape.
4 Although the use of water allow the entire component to be uniformly heated, the draw
5 back was it the process was messy and could not integrate electrical measurement
6 devices. The process is as follows:
7
8
9

- 10 1. The flat sample is immersed in water and heated to 50°C with a constant
11 temperature for 10 minutes.
- 12 2. After 10 minutes, the part is manually bent from a flat piece to a U-shape profile.
- 13 3. This newly-deformed U-shape part is left aside for another 5 minutes at 50°C
- 14 4. The U-shape part is taken out of the heated water and chilled to -18°C for 15
15 minutes
- 16 5. After 15 minutes, the part is taken out from the chiller and left at room
17 temperature for the next 10 minutes.
18
19
20
21
22
23
24

25 Next, a test bench (Figure 5) was developed in order to measure the recovery force of
26 the SMP that was produced using AM. At this stage, it was decided that heated air
27 would be used as it would enable a more effective form of measurement and with less
28 resistance than when immersed under water. The heated air would be channelled from
29 a regular flow of air that would have controlled temperature. Other requirements
30 needed for this test bench required good stability of the bench to minimise vibrations
31 during measurement, a thermocouple to enable good accuracy in measurement and
32 positioning of the static elements and providing a regular air flow with controlled
33 temperature throughout the tests. A granite bench was chosen to ensure good stability
34 of the setup and a dynamometric platform which measures the force was used. The
35 dynamometric device has an accuracy of 0.1g of force resolution. For better accuracy,
36 a sheet of a fibre-based material was used to isolate the dynamometric device and also
37 to secure the sample for the force test.
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

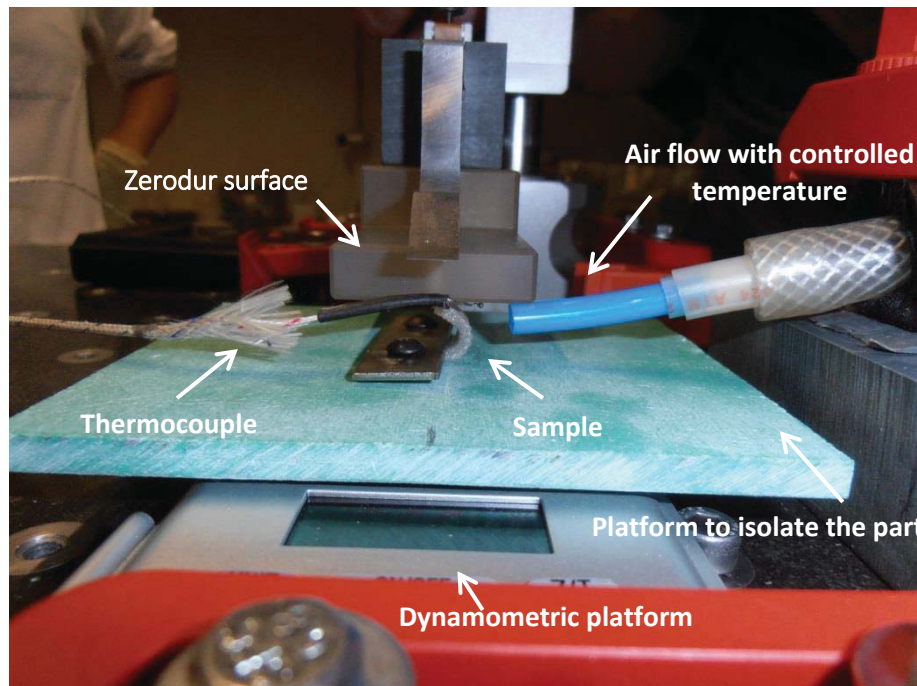


Figure 5. Equipment for measurement of recovery force

To measure the force, a ceramic glass component made of Zerodur® with a zero thermal expansion coefficient was used as a fixed wall where the U-shaped deformed sample would touch the surface during the shape recovery. The Zerodur® surface is linked to a digital measuring gauge that measures the force as the part recovers its memorized flat shape. The procedure to measure the recovery force is as follows:

- Set the temperature to a target output of 50°C with the fan switched on
- Check the temperature of the air flow with a thermocouple
- Secure the bottom of the sample on the test platform
- Lower the gauge until it touches the sample
- Direct the heated air to the sample and start the timer
- Keep the air flow constant until the sample observes a state of change
- Write down the value of the maximum force value and the time of the measurement
- Raise the gauge to allow the sample to recover to the original flat shape

From this experiment, we were able to express the unfolding moment of the sample by calculating the force exerted and the amount of distance covered (the distance from the middle of the bent area to the point of the force being applied) in the form of $\text{Moment} = \text{Force} \times \text{Distance}$. The unfolding moment enables us to calculate the maximum

recovery stress by applying the following expression commonly used in theory of elasticity:

$$\sigma_{rm} = \frac{M_r}{B \times e^2} \times 6$$

Whereby σ_{rm} : Maximum recovery stress (MPa); M_r : Maximum recovery unfolding moment (N x mm); B : Width of the sample (mm); and e : Thickness of the sample (mm)

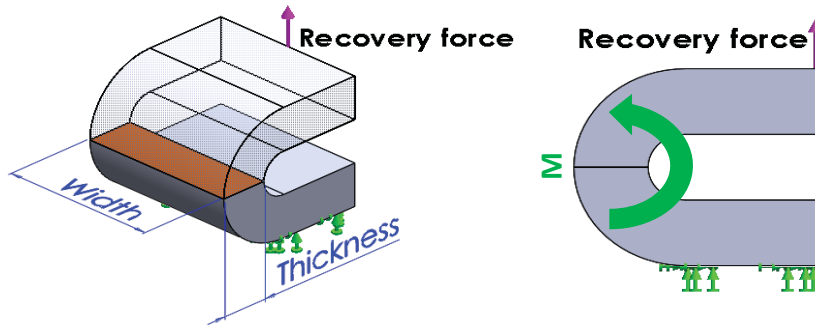


Figure 6. Recovery force and unfolding moment

We applied the theory of elasticity based on a part that transitions between two phases. In the first stage, the component becomes soft upon heating to T_g ; and in the second stage, the component is stretched until the maximum strain is achieved [7]. After cooling, the component solidifies and the deformed shape is maintained. Upon heating to soften the deformed part, the elastic energy stored in the component is released and the original shape is recovered. This hypothesis is based on a sustainable basis as demonstrated by other researchers including Smith [11] who uses SMP a T_g of 80°C and showing that the force ratio is calculated as the recovery force / force to engage was close to one (0.85 to 1). Once the recovery force was measured, the shape recovery ratio was calculated by measuring the opening angle of each sample using a Mitutoyo profile projector.

3. Results and discussion

The shape fixity ratio of the sample was 100% for all specimens made by 3D printing or compression moulding methods. In addition, the shape recovery ratio of the SMP material should be significantly high. Figure 7 summarises the results in a graphical format whereby both processes show the average value of 77% of shape recovery for the extruded samples; and 82% for compressed parts based on samples measuring $20 \times 10 \times 3$ mm. The difference could be due to the fact that compression moulded parts have a much higher density and mass as compared to the meso-structure of the

extruded parts. The results also confirm that the Desmopan® TPU is suitable for extrusion-based processes.

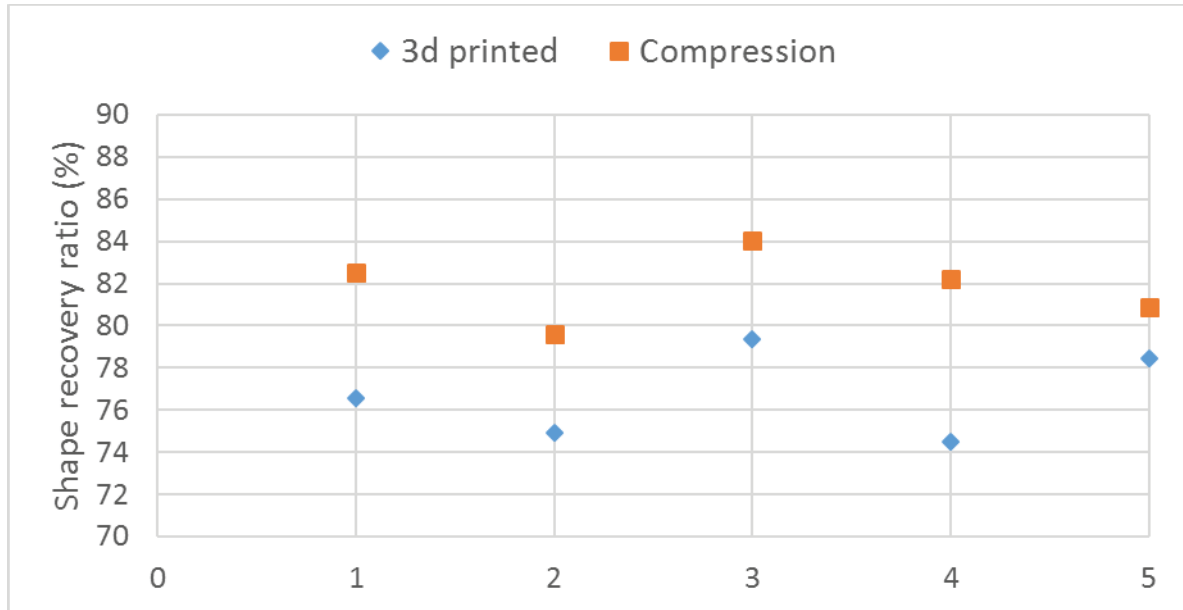


Figure 7. Shape recovery ratio in 20x10x3 mm samples

This is in line with the results of Raasch et al. [17] who printed samples from filament and also reported slightly higher shape recovery ratio for another different TPU (MM4520 SMP Technologies Inc), resulting in 85% of shape recovery ratio. Nevertheless, there is a clear difference in the maximum strain in both experiments. Raasch only developed the bending process from 180° to around 120°, but in this work, the bending process was more pronounced from a flex angle of 180° to 0°. This could explain the higher shape recovery ratio in the experiment carried out by Raasch et al. which had much less strain in terms of a higher shape recovery ratio.

3.1. Experimental test of recovery force

The recovery force test was applied in several samples manufactured with the Desmopan® TPU using both extruded and compression moulded pieces. From the results in Figure 8, it can be observed that there is a linear pattern between the recovery force and the mass of the section with shape memory effect being applied for two extruded parts manufactured at 1045mm/min and 990mm/min.

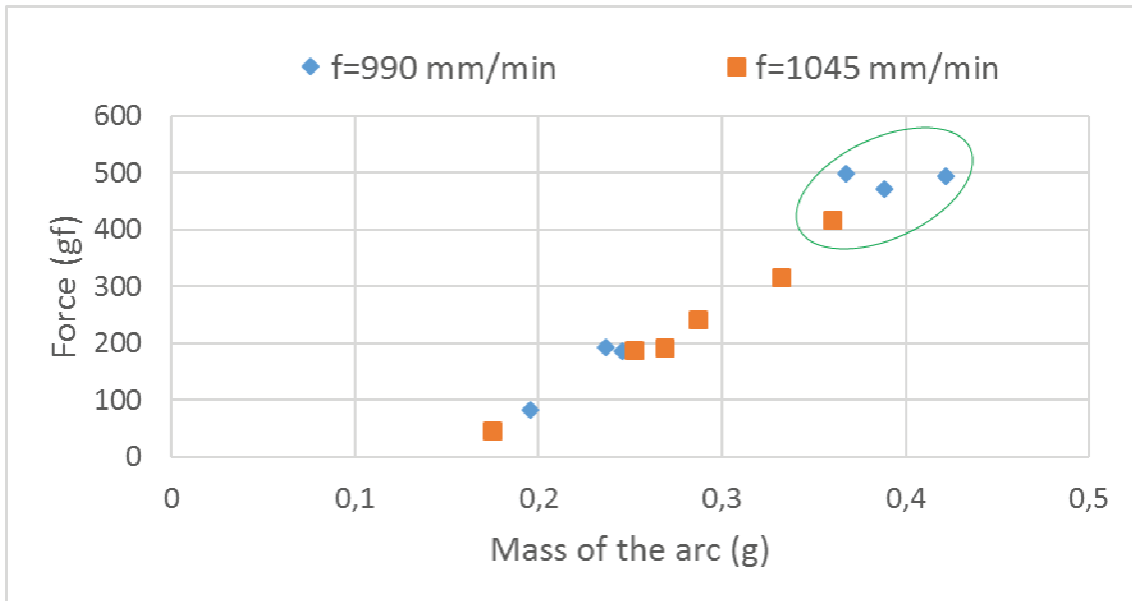


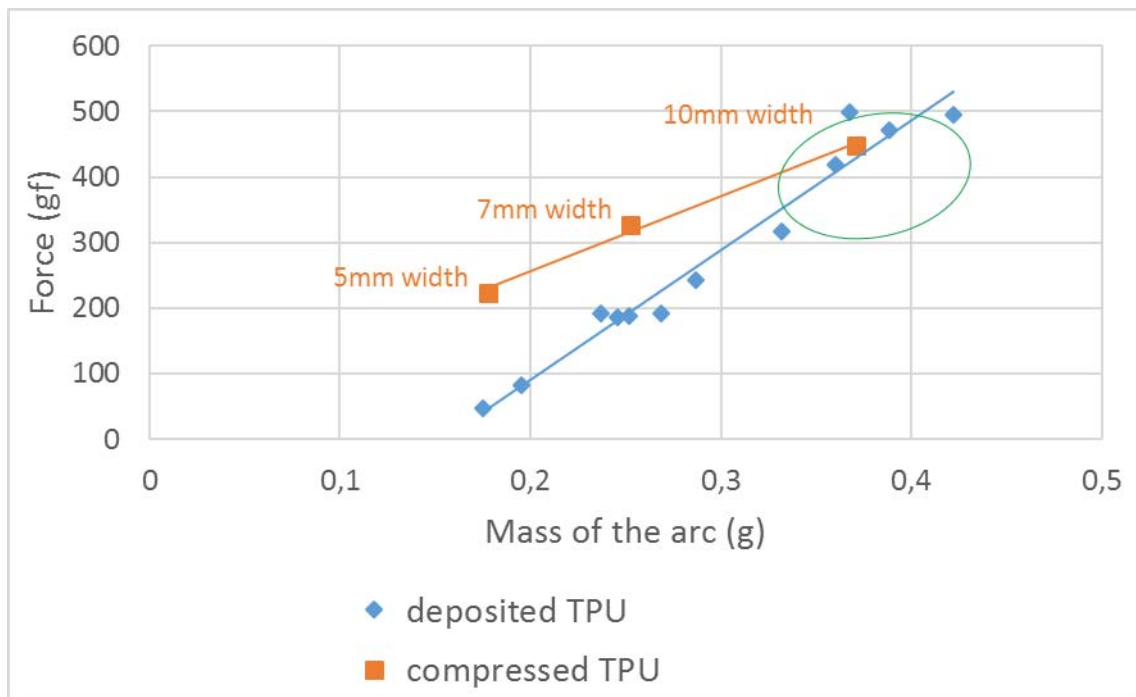
Figure 8. Recovery force and mass (of the deformed zone) for the different FDM Desmopan parts manufactured at 990mm/min and 1045mm/min.

With the same theoretical dimensions, the higher the deformed mass, we can expect a higher recovery force from the sample. It can also be observed that the parts produced at 990mm/min have a higher value for the average force compared to the samples produced at 1045mm/min. This can be explained whereby a slower feeding speed at 990mm/min would result in more extruded material as compared to 1045mm/min. The difference between the AM parts and the compressed ones can be noticed through the resultant average density for both samples - 1.011 g/cm³ for the AM produced part (at 990 mm/min) and 1.124 g/cm³ for the compression moulded part.

More specifically, we calculated the unfolding force whereby the average force was recorded with $M=7.76$ N·mm for the 990 mm/min sample; and $M=4.92$ N·mm for the 1045 mm/min sample. The average recovery stresses 0.45 MPa and 0.43 MPa respectively. Nevertheless, taking into account only the parts with the highest mass, the average value of the unfolding force was $M=11.56$ N·mm, representing a maximum average recovery stress of 0.61 MPa which is a value similar to those obtained from the compressed samples. The values of these recorded recovery stress could be used as a baseline measurement to determine the capacity of the Desmopan[®] SMP when employed as a working actuator in a mechanism.

In the case of compressed samples, the main difference is that this process allows us to obtain solid parts without internal cavities, whereas extrusion based parts would

1 contain internal cavities due to the meso-structure. Therefore, the idea was to compare
 2 the results and effectiveness of unfolding between both build configurations. For each
 3 different configuration shown in Figure 3, the average value of force and mass were
 4 calculated (Figure 9) both for AM and compressed parts. The best samples as
 5 indicated in the circled area in the graph (in Figure 9) have a similar recovery force to
 6 the compressed samples measuring 20x10x3 mm. From the graph, it can be seen that
 7 point of convergence shows the best manufactured samples of the AM parts do
 8 achieve a similar recovery force to those made from compression moulding.
 9
 10
 11
 12
 13



37
 38 Figure 9. Comparison of recovery force between 3D printed and compression moulded
 39 parts for the same sample thickness
 40
 41
 42
 43
 44

45 From the data, we can also deduce that the increase of mass produces an increase of
 46 recovery force. As the thickness of these parts was kept under 3mm, it can be
 47 concluded that the width and mass of the part have a linear influence on the recovery
 48 force. Apart from the earlier 3 pieces of compressed samples (3x5, 3x7 and 3x10 mm²),
 49 3 more pieces were tested (1.7x10, 2x10 and 2x15 mm²). The length of the samples
 50 was kept in 20mm in all instance. However, the thickness and width were modified to
 51 evaluate the influence of these dimensions on the recovery force. Five exact copies
 52 were manufactured for each configuration. The different configurations shown in this
 53 table were established in order to have at least 2 different configurations for
 54 approximately the same section area. For example, the first configuration has a section
 55
 56
 57
 58
 59
 60
 61
 62
 63
 64
 65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

of $1.7 \times 10 \text{ mm}^2$, which is approximately the same section area as in the second configuration ($3 \times 5 \text{ mm}^2$). Doing so enables us to compare the influence of the thickness versus the width on the recovery force (for the same mass or section area). The results of this analysis are represented in figure 10 that shows the average value of the force for each configuration.

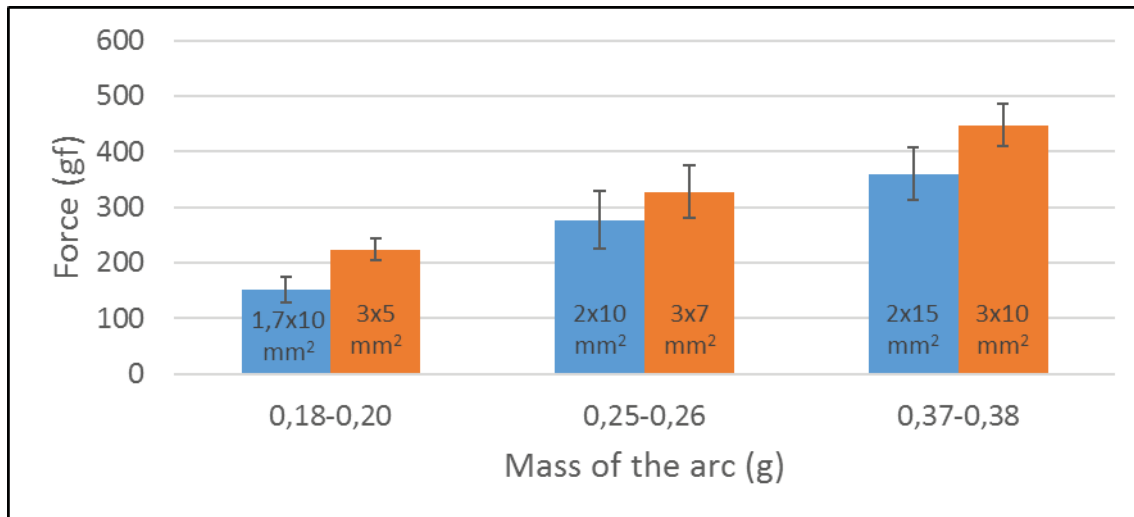


Figure 10. Comparison of recovery force among the different configurations evaluated to assess the importance of the thickness/width of the same sample section

As shown in Figure 10, for the same section area, the part with a higher thickness would achieve a higher recovery force. For example, the part measuring $1.5 \times 10 \text{ mm}^2$ had a similar cross-section as those parts measuring $3 \times 5 \text{ mm}^2$, but the recovery force is much lower because the thickness of the section becomes more critical than the width of the component. This similar pattern is also evident in the rest of the sample and it confirms that the thickness of the section is more influential in the recovery force than the width.

Figure 11 shows the results of the recovery stress for each size of compressed sample, resulting in an average rating of 0.6 MPa. The results confirmed that the sample measuring $3 \times 10 \text{ mm}^2$ with a recovery stress value of 0.61 MPa has similar performance for those being produce by AM using the same material.

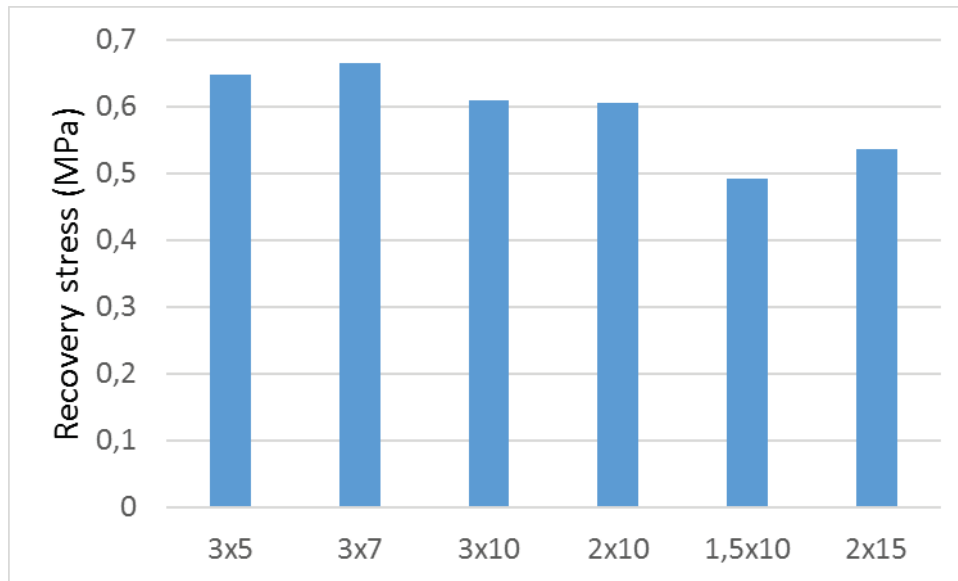


Figure 11. Experimental recovery stress (MPa) for the compressed TPU samples

Next, table 3 shows the results of other studies investigating the recovery force and recovery levels for different SMPs. Although exact comparison is not possible due to different build parameters, component size, materials and the testing process, it still provides a good response to establish the magnitude of the resultant values in this present work. Song et al [18] reported the test of different blends of TPU and PLA as a potential memory shape material where their material (DMP 385E) being used has a Tg of between 38.9°C and 34.8 °C; whereas the one chosen for this study has a Tg of about 56°C that has much better characteristics for shape memory behaviour. This is the reason for the low value of recovery force in the case of pure DMP 385E, because the memory shape property of this particular TPU is poor. The blend of using PLA with a ratio of 80:20 DMP385E/PLA in their work did improve the SMP behaviour. In addition, they tested the capacity of this material to lift a weight of 50 grams. The same authors, in other publications [19], reported the behaviour of this composition but using foam with a porous structure that could potentially decrease the recovery stress as shown in table 3.

Literature review also found that many Polyurethane-based materials are suitable to act as SMPs. Table 3 summarises associated studies by other researchers who investigated the use of either thermoset Polyurethane or thermoplastic Polyurethane [20] where the SMP property of thermoset Polyurethane is significantly better than thermoplastic Polyurethane with a recovery stress of 5.5 MPa. This is a representative value between the maximum levels of recovery stress for both types of material

1 according to the studies carried out so far [21]. In another study, Park et al [22]
 2 reported the behaviour of Poly(cyclooctene) (PCO), developing a theoretical two-phase
 3 model (rubbery and glassy) for predicting the strain and stress during the
 4 heating/cooling cycle. They compared theoretical results with experimental tensile
 5 testing as well as punching tests, obtaining for tensile test a recovery stress of 0.6
 6 MPa. All the previous experiments were done under tensile testing.
 7
 8
 9

10 Other researchers including Smith [11] investigate the area of application-based
 11 designs and applied the use of SMP as an actuator to prototype a gripping device for a
 12 robot. The material was a Diglycidyl ether of Bisphenol, an epoxy monomer (EPON
 13 825) and the curing agents used were Poly(Propylene Glycol)-bis-(2- Aminopropyl)
 14 ether (Jeffamine D230) and Decylamine (DA). The material was tested under different
 15 angles of strain observing that the recovery force was increased with the angle and the
 16 maximum recovery force (deforming about 75°) was 0.032 N. They concluded with the
 17 fact that the material was suitable and sufficiently effective to be used as a gripping
 18 actuator for mini-robots.
 19
 20
 21
 22
 23
 24
 25
 26
 27
 28
 29
 30

31 Table 3. Recovery forces and recovery stresses of different works

Reference	Material	Test	Programming Temperature (°C)	Total Recovery Force (N)	Recovery Stress (MPa)
Song et al [18]	80/20 DMP 385E /PLA	Tensile	70	0.7	0.053
Song et al [18]	DMP 385E	Tensile	70	0.19	0.015
Song et al [19]	Porous 80/20 DMP 385E /PLA	Tensile	70	0.291	0.023
Smith [11]	EPON826	Flexural Angle 75°	90	0.032	0.09

32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Park [22]	PCO	Tensile	60	-	0.6
Azra et al [20]	MP5510	Tensile	60	-	5.5
Azra et al [20]	MM5520	Tensile	60	-	1.3
Present work	Compressed DP2795A-SMP	Flexural Angle 90°	50	3.6	0.61
Present work	3D printed DP2795A-SMP	Flexural Angle 90°	50	2.9	0.45

3.2. Stabilisation time

During the experiments, the stabilisation time of recovery was also recorded. When hot air was directed onto the Desmopan® TPU sample, the recovery force automatically starts to increase gradually until achieving a maximum value after a period of time. The duration of recovery depends on the speed of heating up the component and the shape recovery effect is almost immediate if the temperature is above 50°C although the entire cross section of the component requires time to be heated up especially if hot air is being used. In the earlier experiments, the use of hot water enabled a faster recovery effect to be achieved because the entire surface area of the component would be in contact with heat. Although a heated chamber such as a convention oven could be used, it would be difficult to observe the effect in an enclosure. The air temperature in the experiments was controlled using a piped flow of air directed onto the surface of the sample. However, once the air exits from the vent, it is difficult to ensure that the surface is uniformly heated. Therefore for thermal stimuli using heated air, the rate of heating depends on the area that is being subject to heat as well as external environmental factors.

Figure 12 shows a chart that describes the samples measuring 2x10, 2x15, 3x5, 3x7 mm² with the stabilization time in the vertical axis measured in seconds, and the mass of the samples on the horizontal axis. For larger parts, the heating time is longer and

then also a longer stabilisation time of recovery force. In the first set of experiments, we immersed the SMPs under hot water and it was observed that the speed of recovery was significantly higher (a faster recovery time), but this method was not suitable to be represented in this dynamometric table.

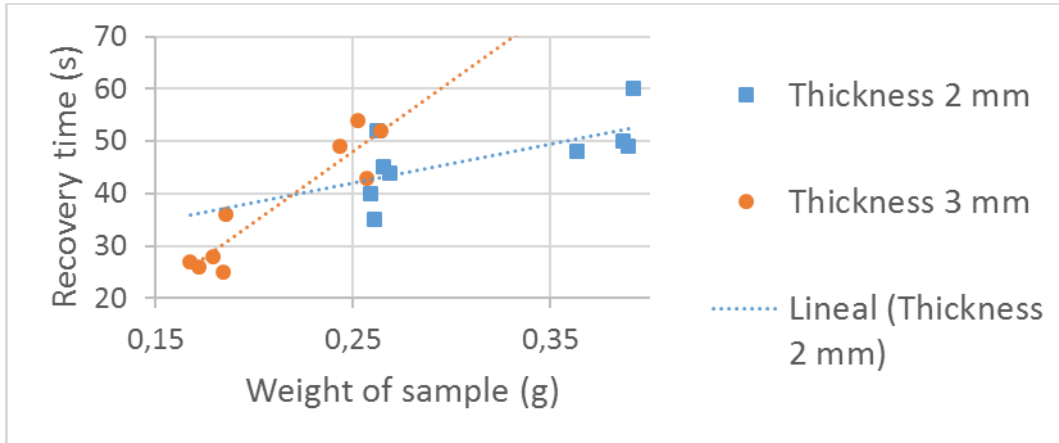


Figure 12. Stabilisation time of recovery force heated with hot air

3.3. Case study

As the Desmopan[®] TPU sample had a significant level of recovery force, there was potential for the AM parts to be used in a practical application. It was decided that the case study would utilise the SMP part as vertical actuator. A new design was developed whereby the coiled geometry as shown in Figure 13 would have a flat printed profile. The coil would be heated and at its T_g, it would be stretched vertically and programmed into a three-dimensional coil. When heated again, the coil will recover into its original flat shape. For this experiment, we subjected the test piece within an enclosed cylinder and pumped with heated air. The clear enclosure allowed us to observe the change in state as well as to ensure that the surfaces of the component would be entirely subjected to the air that is heated around it.



Figure 13 Programmed part and AM coil in its flat form

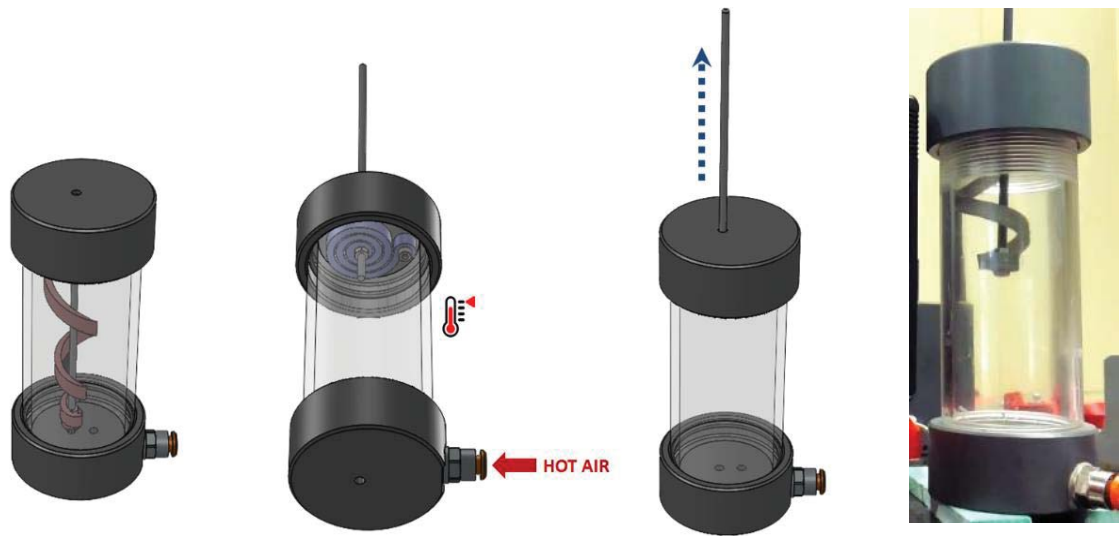


Figure 14. Chamber for heating the actuator

Conclusions

This research has showed the viability of processing the commercial thermoplastic Desmopan® Polyurethane using extrusion-based AM methods. In the experimental extruder using a pneumatic drive system, the optimal print speed was 990 mm/min which is significantly lower than those used for common materials such as ABS or PLA. However, the samples showed good behaviour as shape memory parts, either in terms of fixity ratio (100%) or recovery ratio (80%). The printed samples had similar properties than those made from compression moulding using the same material. The analysis of the results found that an increase of mass would produce an increase of recovery force, although the thickness of the section was more influential than the width of the sample. The average recovery stress was 0.6 MPa for the compressed parts and 0.41-0.61MPa for the 3Dprinted parts. Finally, to demonstrate the viability of Desmopan® Polyurethane, a coiled actuator that could expand vertically was produced. Future work will investigate exactly how the geometry affects the recovery force and how this can be optimized according to prescribed loads.

Acknowledgments

This work was supported by BAE Systems Applied Intelligence (UK) and the Defence Science and Technology Laboratory (UK) who also provided technical assistance in this work.

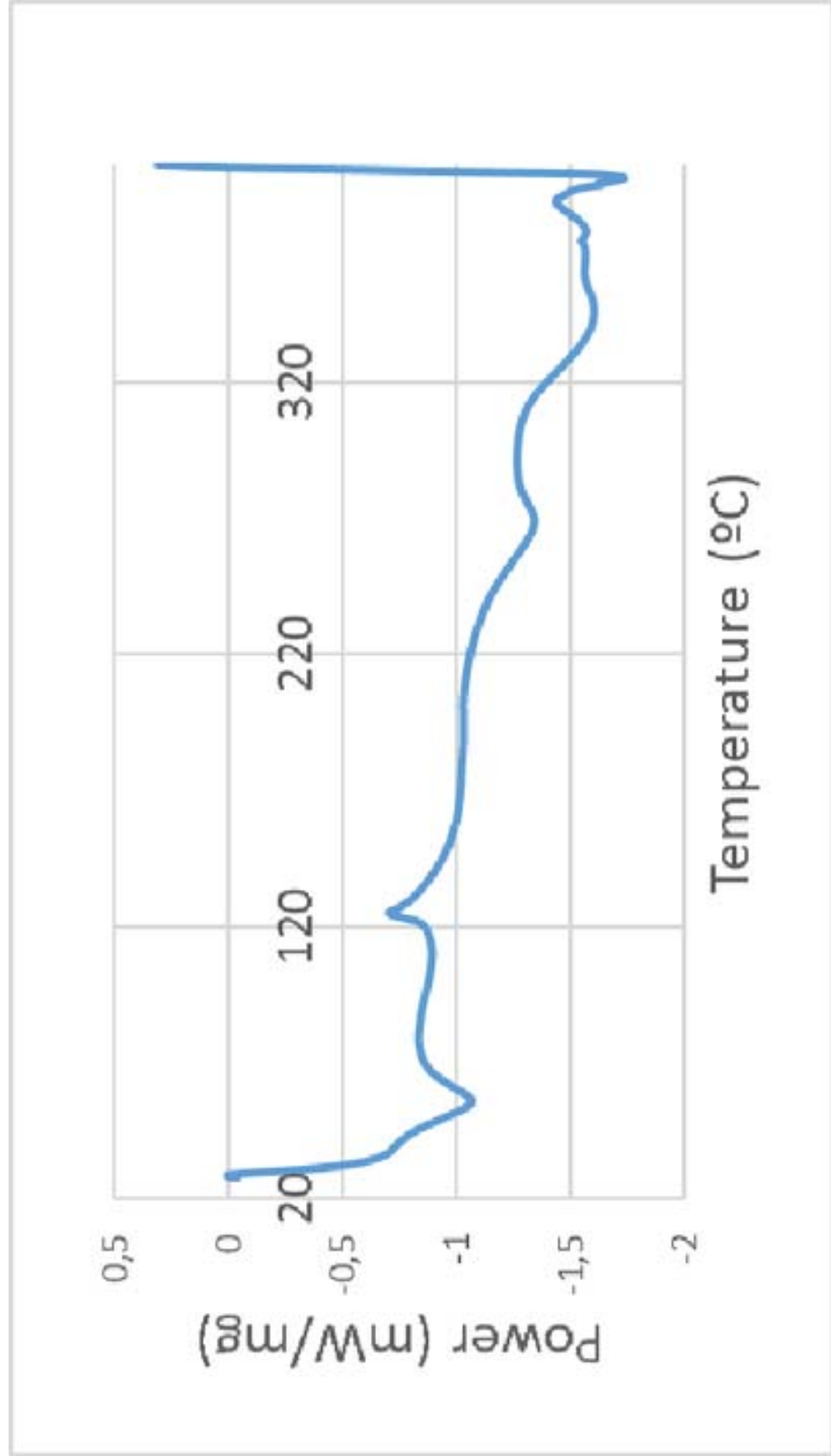
References

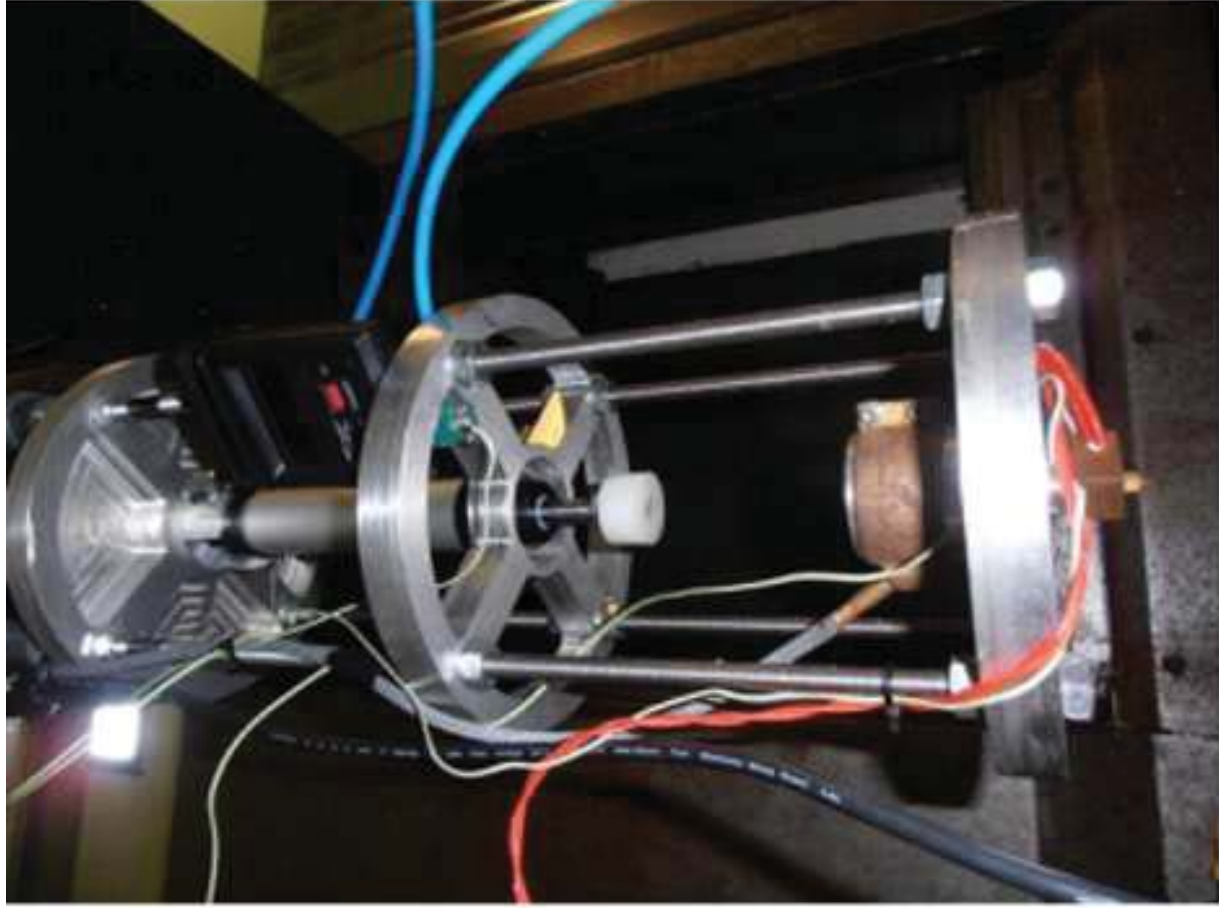
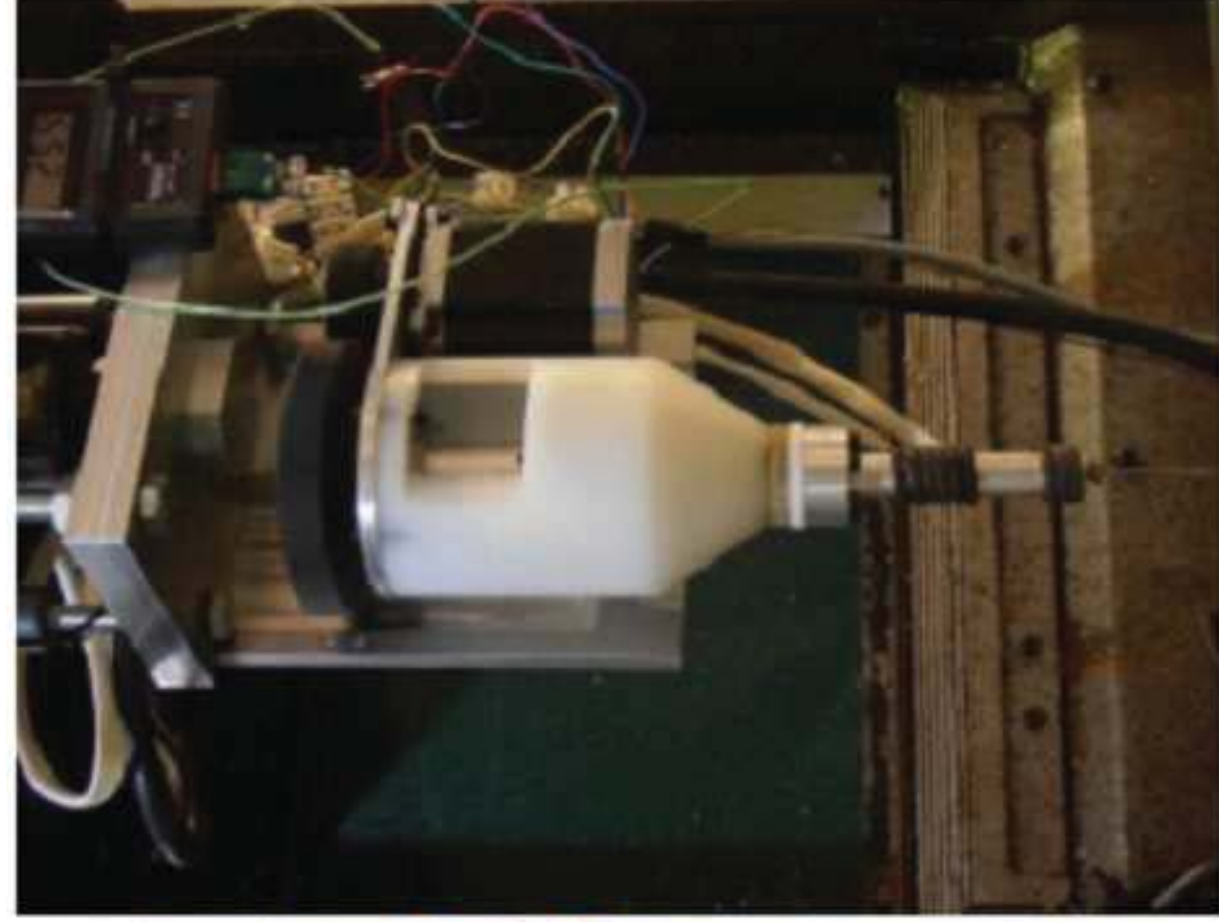
- 1
2 [1] Monzon MD, Ortega Z, Martínez A, Ortega F (2015) Standardization in additive
3 manufacturing: activities carried out by international organizations and projects. *Int J*
4 *Adv Manuf Technol* 76:1111-1121
5
6
7
8 [2] ISO/ASTM (2015) ISO/ASTM 52900:2015 Additive manufacturing - General
9 principles - Terminology.
10
11
12 [3] Huang S H, Liu P, Mokasdar A, Hou L (2013) Additive manufacturing and its
13 societal impact: a literature review. *Int J Adv Manuf Technol* 67:1191–1203
14
15
16 [4] Pei E (2014) 4D printing – revolution or fad?. *Assembly Automation* 34:123 - 127
17
18
19 [5] Campbell TA, Tibbits S, Garrett B The next wave: 4D printing programming the
20 material world. Atlantic council.
21
22 [http://www.atlanticcouncil.org/images/publications/The_Next_Wave_4D_Printing_Programm](http://www.atlanticcouncil.org/images/publications/The_Next_Wave_4D_Printing_Programming_the_Material_World.pdf)
23 [ing_the_Material_World.pdf](http://www.atlanticcouncil.org/images/publications/The_Next_Wave_4D_Printing_Programming_the_Material_World.pdf). Accessed 4 January 2016
24
25
26 [6] Pei E (2014) 4D Printing: dawn of an emerging technology cycle. *Assembly*
27 *Automation* 34: 310 – 314
28
29
30
31 [7] Hu J, Zhu Y, Huang H, Lu J (2012) Recent advances in shape–memory polymers:
32 Structure, mechanism, functionality, modeling and applications. *Progress in Polymer*
33 *Science* 37: 1720– 1763
34
35
36
37 [8] Yang WG , Lu H, Huang WM, Qi HQ ,Wu XL, Sun KY (2014) Advanced Shape
38 Memory Technology to Reshape Product Design, Manufacturing and Recycling.
39 *Polymers* 6: 2287-2308
40
41
42
43 [9] Xie T (2010) Tunable polymer multi-shape memory effect. *Nature* 464: 267-270
44
45
46 [10] Sun L, Huang WM, Wang CC, Zhao Y, Ding Z, Purnawali H (2011) Optimization of
47 the Shape Memory Effect in Shape Memory Polymers. *Journal of Polymer Science*
48 *Part A: Polymer Chemistry* 49: 3574–3581
49
50
51 [11] Tobushi H, Hayashi S, Hoshio K, Ejiri Y (2008) Shape recovery and irrecoverable
52 strain control in polyurethane shape-memory polymer. *IOP Publishing Sci. Technol.*
53 *Adv. Mater.* <http://iopscience.iop.org/article/10.1088/1468-6996/9/1/015009/pdf>.
54
55
56
57 Accessed 4 January 2016
58
59
60
61
62
63
64
65

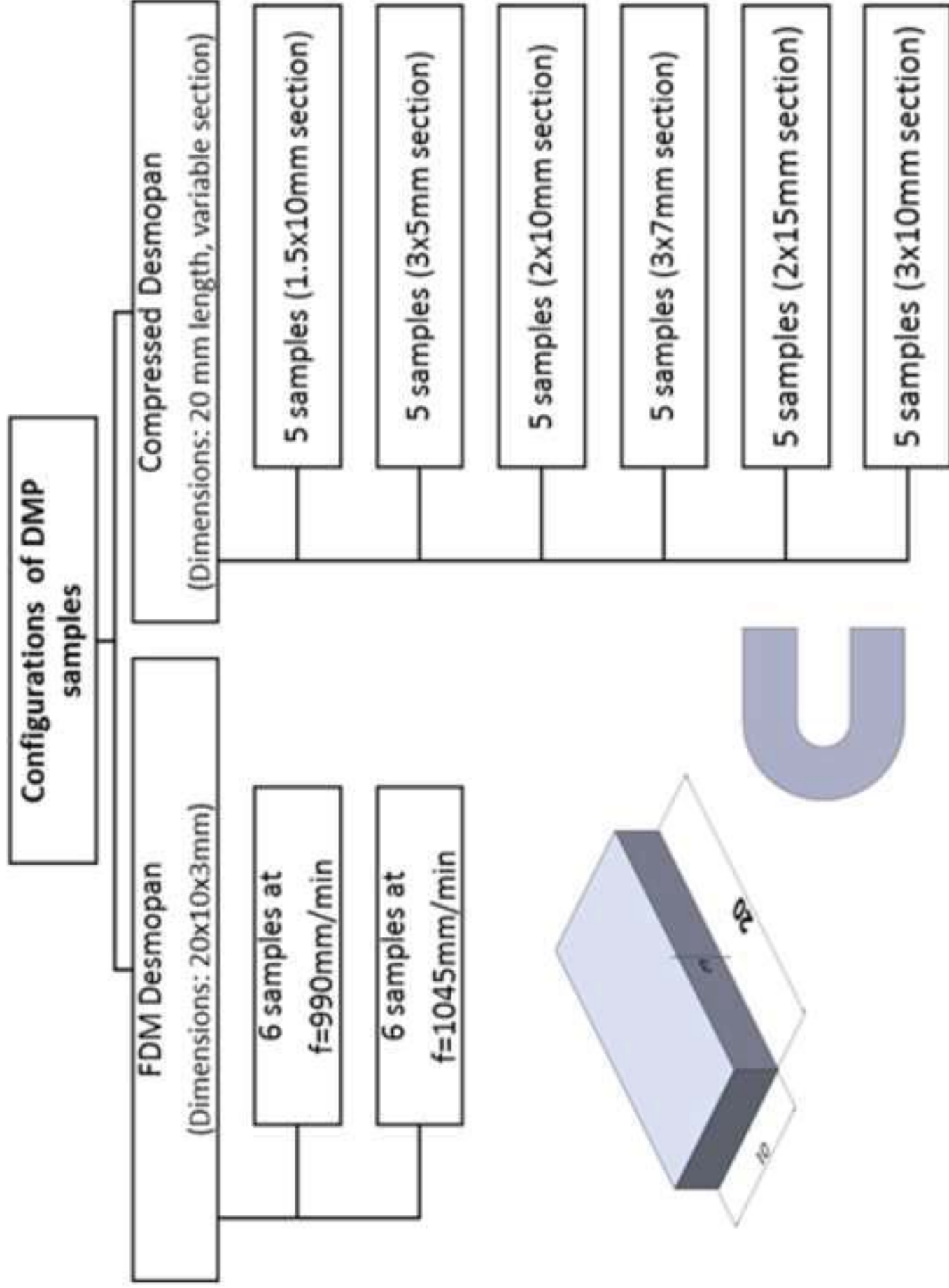
- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- [12] Smith JL Material testing of shape memory polymers for modular robotics applications and development of a prototype SMP gripper for mini-PR2 robot. NSF Summer Undergraduate Fellowship in Sensor Technologies. <http://www.seas.upenn.edu/sunfest/docs/papers/SmithJennifer10.pdf>. Accessed 4 January 2016
- [13] Ahmad M, Luo J, Mirafteb M (2012) Feasibility study of polyurethane shape-memory polymer actuators for pressure bandage application. IOP Publishing Sci. Technol. Adv. Mater. <http://iopscience.iop.org/article/10.1088/1468-6996/13/1/015006/meta>. Accessed 4 January 2016
- [14] Ge Q, Dunn CK, Qi HJ, Dunn ML (2014) Active origami by 4D printing. IOP Publishing Smart Mater. Struct. <http://iopscience.iop.org/0964-1726/23/9/094007/media>. Accessed January 2016
- [15] Zarek M , Layani M , Cooperstein I , Sachyani E , Cohn D , Magdassi S (2015) 3D Printing of Shape Memory Polymers for Flexible Electronic Devices. Adv. Mater. DOI: 10.1002/adma.201503132
- [16] Yang Y, Chen Y, Wei Y, Li Y (2015) 3D printing of shape memory polymer for functional part fabrication. Int J Adv Manuf Technol DOI: 10.1007/s00170-015-7843-2
- [17] Raasch J, Ivey JM, Aldrich D, Nobes DS, Ayranci C (2015) Characterization of polyurethane shape memory polymer processed by material extrusion additive manufacturing. Additive Manufacturing 8: 132–141
- [18] Lendlein A, Kelch S (2002) Shape-memory polymers. Angewandte Chemie-International 41:2034-2057
- [19] Song JJ, Chang HH, Naguib HE (2015) Biocompatible shape memory polymer actuators with high force capabilities. European Polymer Journal 67: 186-198
- [120] Song JJ, Chang HH, Naguib HE (2014) Design and characterization of biocompatible shape memory polymer (SMP) blend foams with a dynamic porous structure. Polymer 56:82-92
- [21] Azra C, Plummer CJG, Manson JAE (2011) Isothermal recovery rates in shape memory polyurethanes. IOP Publishing Smart Mater. Struct. doi:10.1088/0964-1726/20/8/082002

1 [22] Hu J, Zhu Y, Huang H, Lu J (2012) Recent advances in shape-memory polymers:
2 Structure, mechanism, functionality, modeling and applications. Progress in Polymer
3 Science 37: 1720– 1763
4

5 [23] Park H, Harrison P, Guoc Z, Leed MG, Yua WR (2016) Three-dimensional
6 constitutive model for shape memory polymers using multiplicative decomposition of
7 the deformation gradient and shape memory strains. Mechanics of Materials 93: 43-62
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65









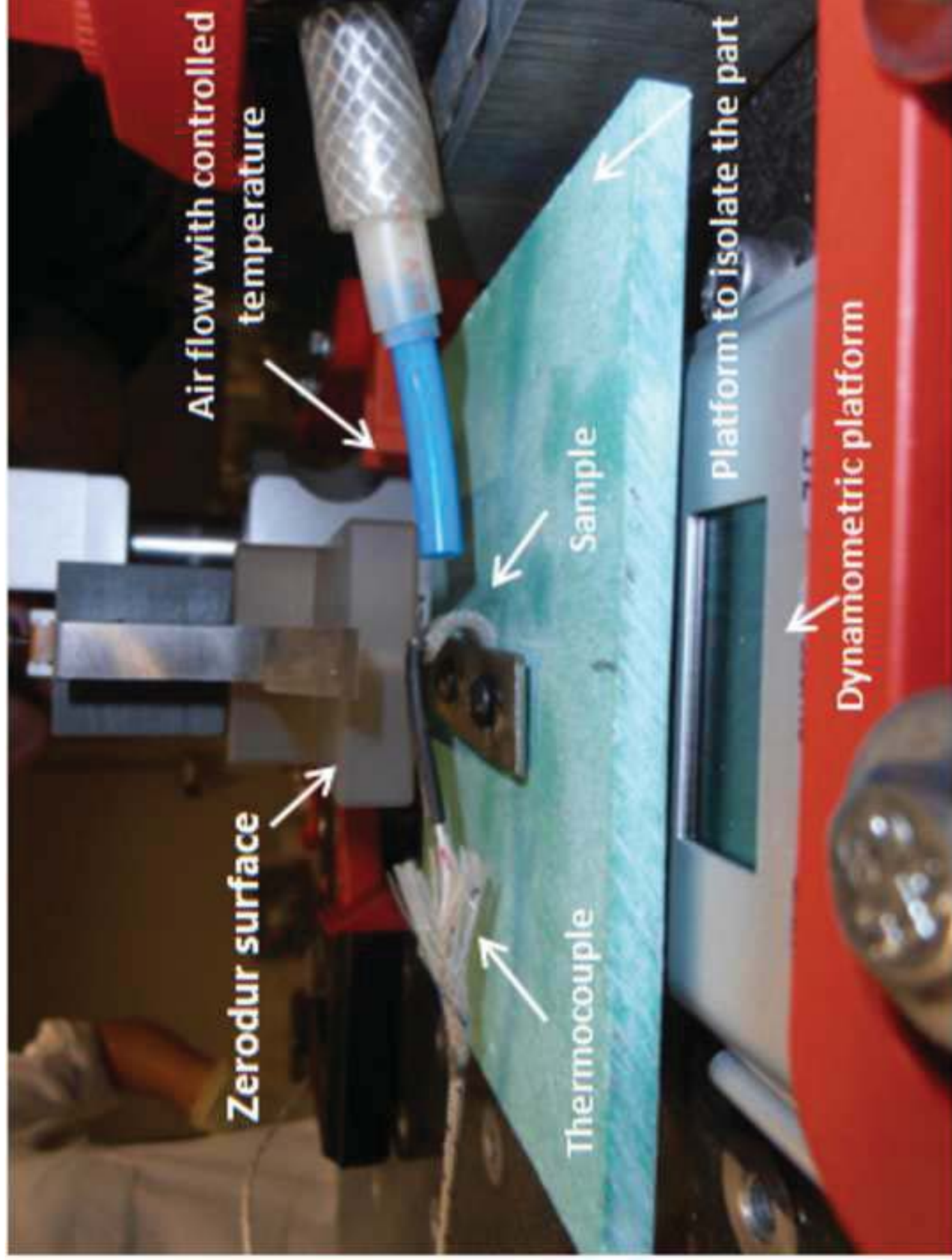
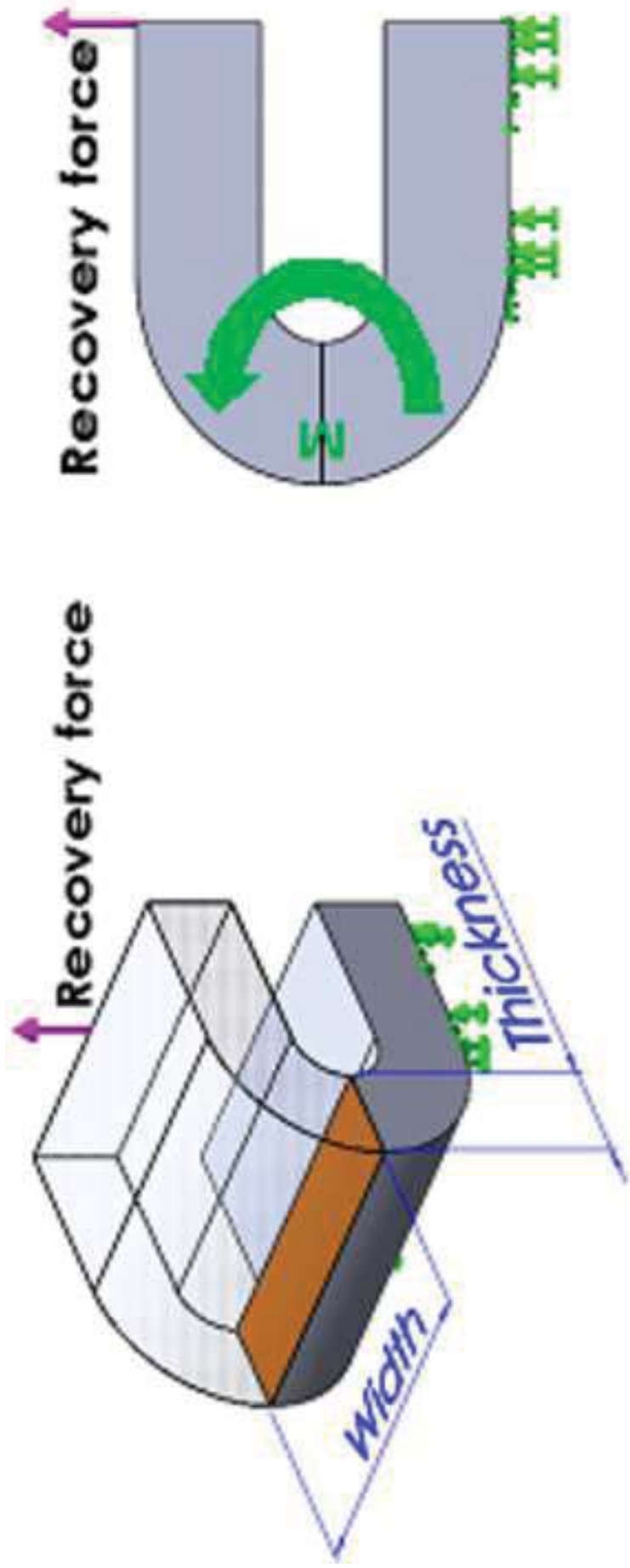
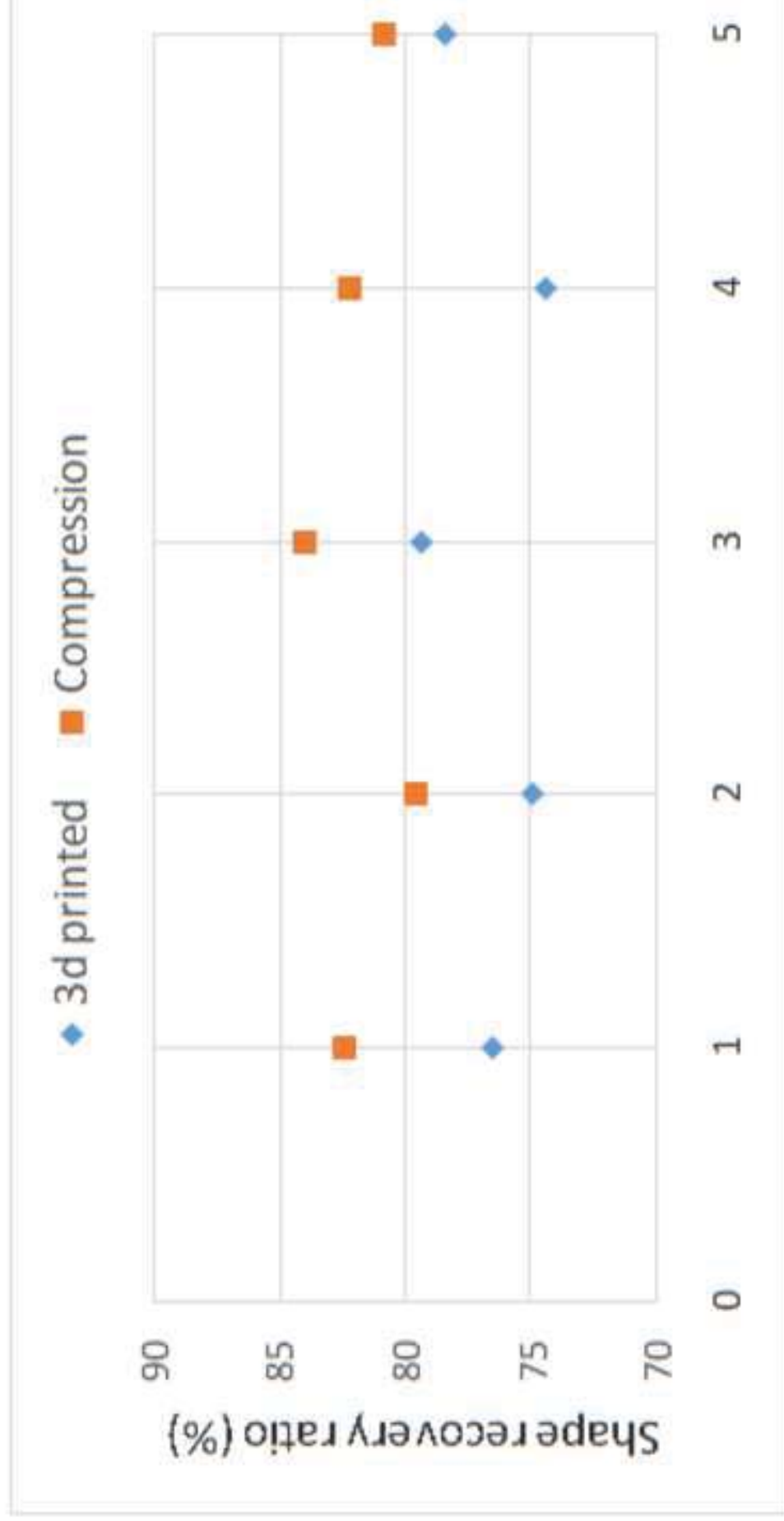


Figure 5





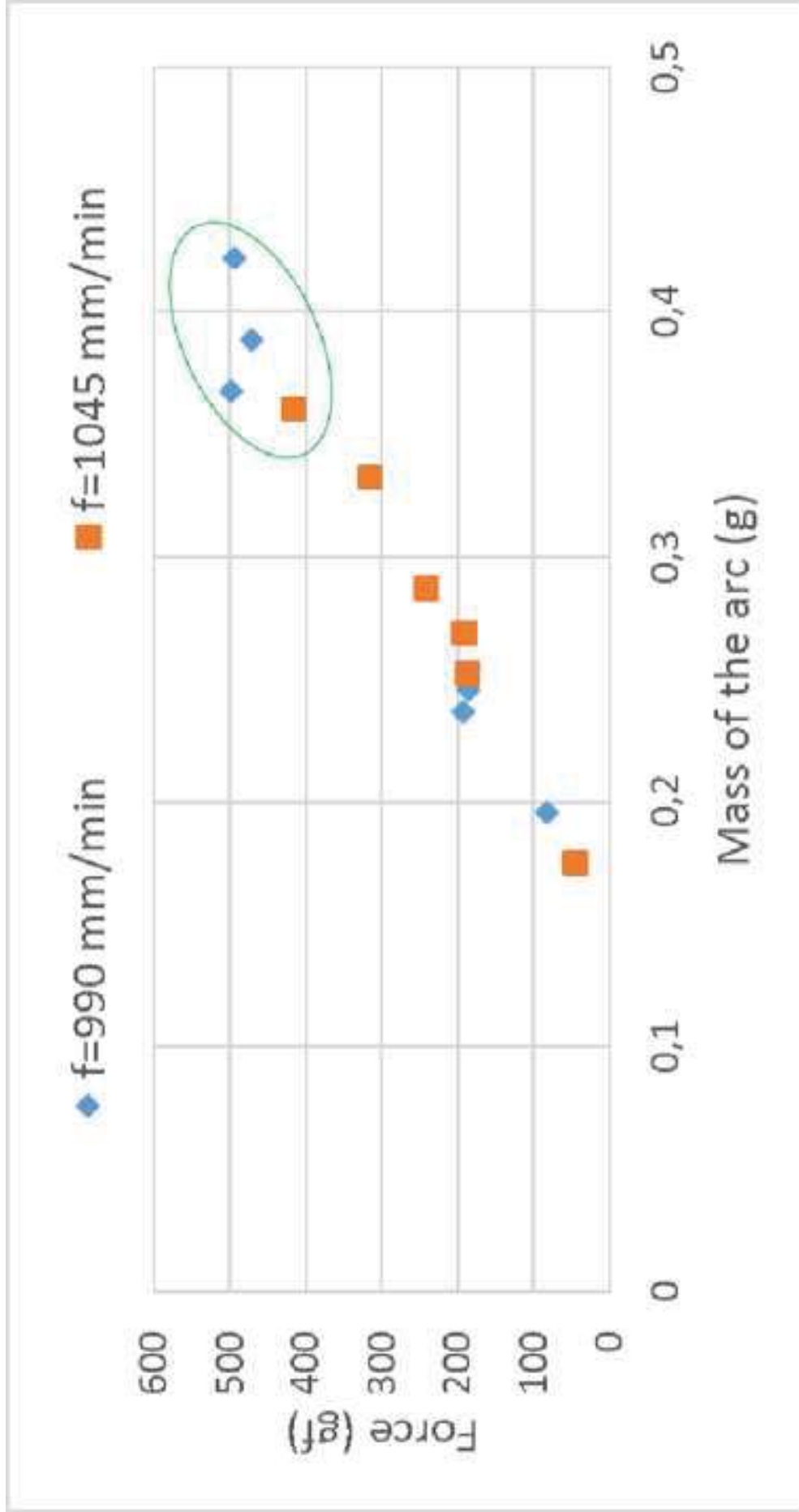
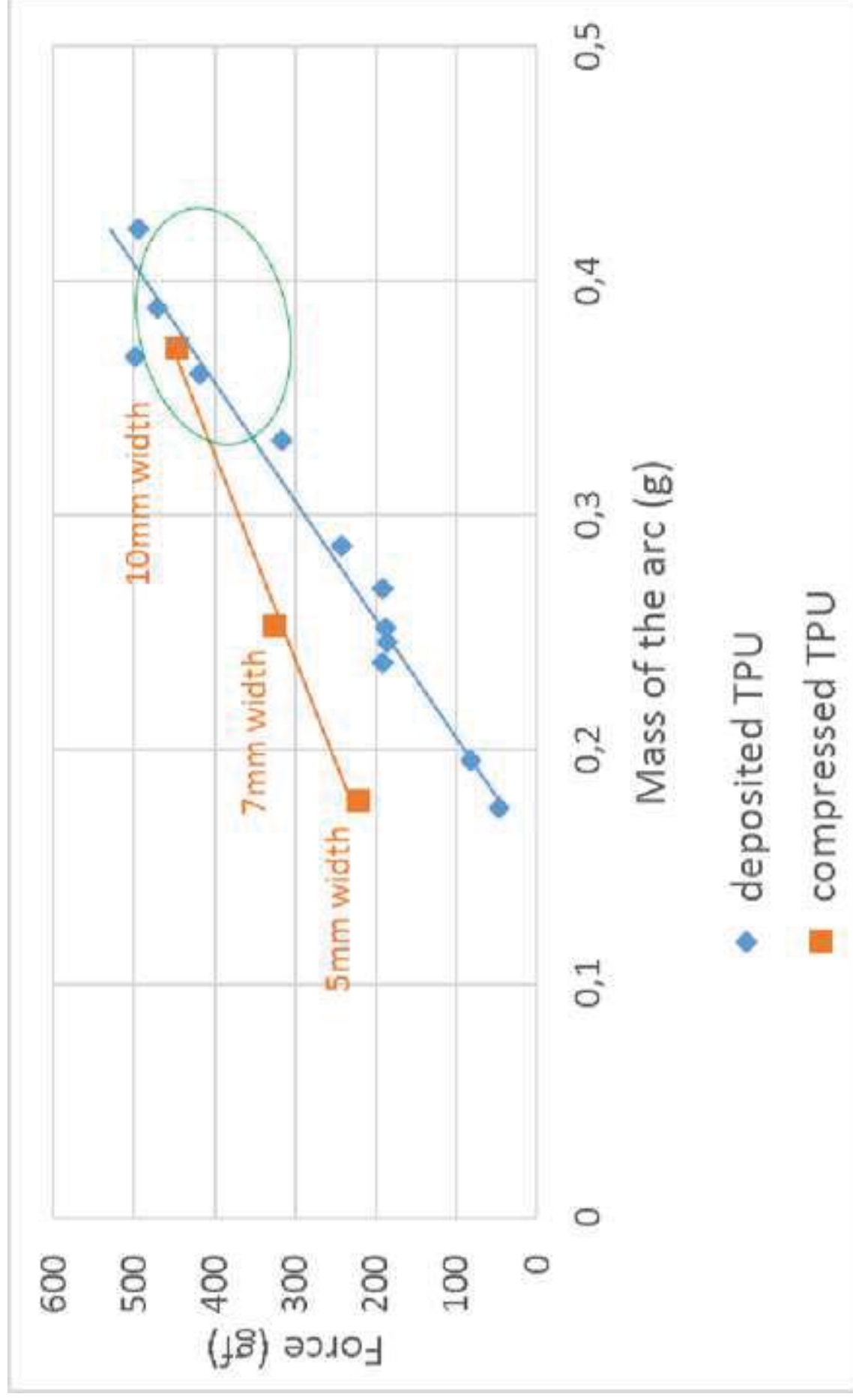
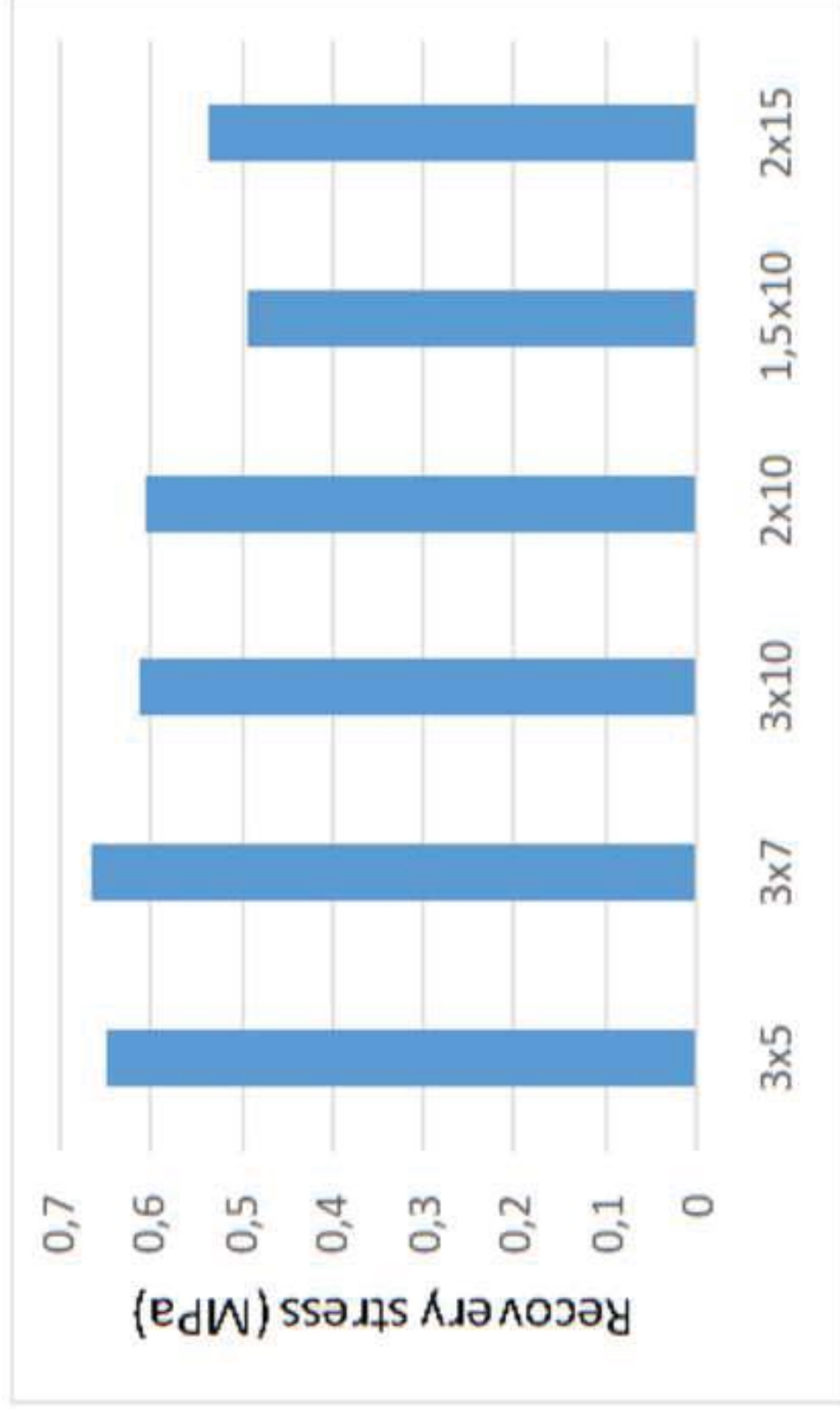
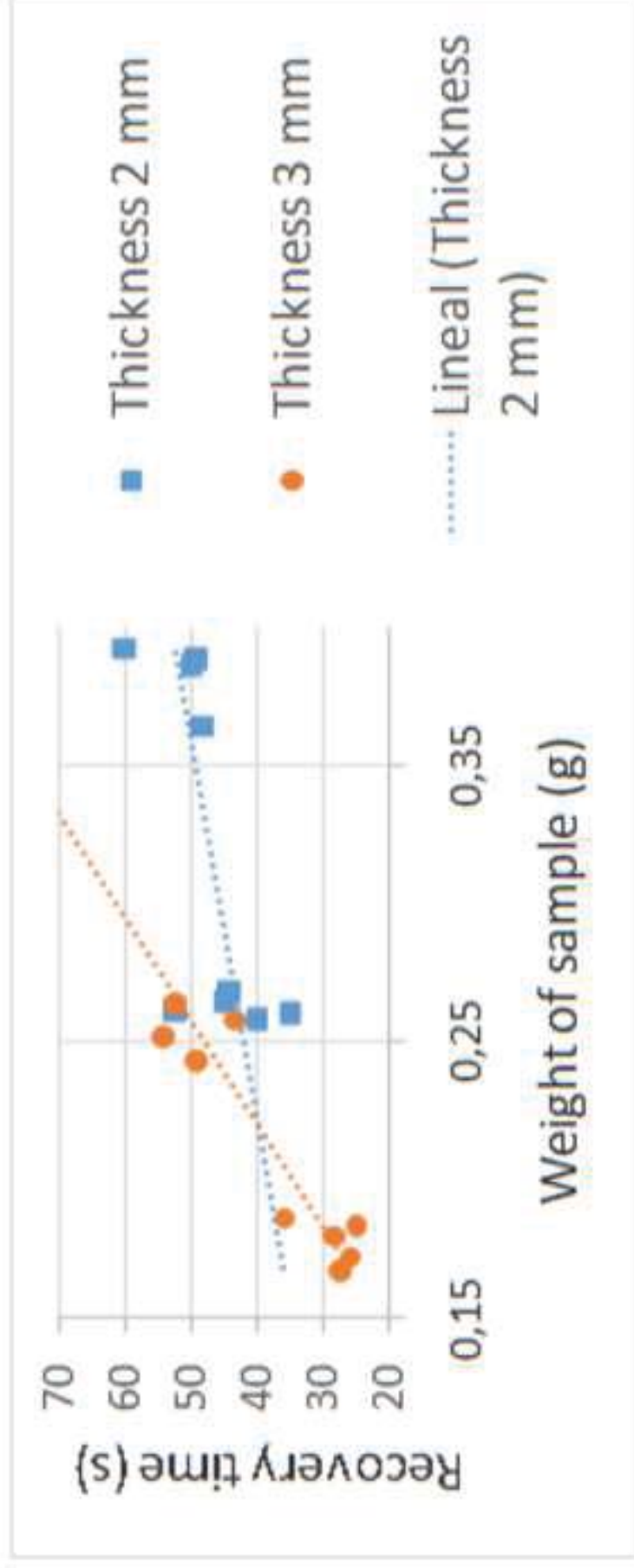


Figure 8











Programmed part
COIL ACTUATOR



