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SHAPE RECOVERY PROPERTIES OF PET-BASED 3D PRINTED SAMPLES

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Abstract: *Multimaterial fused filament fabrication can be used for producing shape memory systems. This way, the shape recovery of polyethylene terephthalate-based (PET) samples with deformation at room temperature was studied based on tensile testing and heat treatment in two deformation-recovery cycles. Two configurations were tested, one made of PET and the second made of PET and polyamide (PA). Adding PA improves the samples' shape recovery in the first deformation-recovery cycle. In the second, a major improvement in the shape recovery of pure PET was recorded. This result was assigned to the retraction effect of the PET polymeric chains due to increased elongation. Both tested configurations showed a good shape recovery effect, which can be used to repair deformed parts.*
Keywords: *Fused filament fabrication, Multi-material, Shape memory effect, Shape recovery.*

1. INTRODUCTION

Fused Filament Fabrication (FFF) is an additive manufacturing technology part of the material extrusion family. The process uses polymer-based filaments as feedstock molten in a heated zone and forced through a nozzle. Then the molten material is selectively deposited in the shape of lines to build parts [1].

The FFF can produce single or multi-material products depending on the extrusion system's build. In the last case of materials, compatibility should be considered to ensure good mechanical properties of the resulting components [2].

Multi-material FFF is used for many applications, including functional prototypes or tools, replacement parts, robotics, biomedical applications, and others [3].

Another application of FFF is the design and production of shape memory systems. They are often referred to as 4D printing. However, they are compliant mechanisms that achieve movement or shape change based on materials arrangement and their sensitivity to a stimulus (e.g., thermal, light, PH, electromagnetic) [4,5].

The Shape Memory polymers (SMP) designs can be divided into single, double, triple and multiple materials mechanisms based on the number of constituents. The number of components contained by shape memory systems is directly proportional to the number of shape changing sequences [4-7].

The shape memory cycle is characterized by permanent shape, temporary shape and shape recovery. After printing, the permanent shape results; the temporary shape is obtained by deforming the material at a temperature (T_1) above the glass transition temperature T_g, and the shape recovery is obtained by heating the SMP at the same T_1. The number of the T_g-es and programming temperatures is proportional with the number of SMP components (i.e., triple state mechanisms). The shape memory characteristics are evaluated based on the fixity ratio (1), recovery ratio (2), respectively the shape memory index (3) [4,5,7].

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \quad (1)$$

$$R_r = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \quad (2)$$

$$SMI = R_f \times R_r \quad (3)$$

where ε_m is the specimen's elongation at 100%, ε_u is the elongation after release, and ε_p is the elongation after recovery.

The shape memory behaviour of polymers has been classified into three working principles: dual state, dual component and the partial

transition mechanism. In the dual state mechanism, the permanent shape of the polymer is maintained by the covalent bonds of the polymeric chain (strong crosslinks) and the temporary shape by weak crosslinks (e.g., chain entanglement). The dual component mechanism used a hard component to retain the permanent shape and a soft one to hold the temporary shape. A mixture of materials usually represents the third mechanism to provide multiple transition phases [8-10].

Reinforcements are often used to increase functional parts' mechanical properties [11]. However, by using a softer material for the "reinforcement", effects such as increased elongation can be obtained due to the spring effect of the rubbery material [12].

This research aimed to study the shape recovery properties of dual component samples with a hard PET matrix with PA softcore and compare them with single component PET samples. The results show that the shape can be recovered even after two deforming cycles.

2. METHODS

Specimen type 5 of ASTM 638-14 was considered to evaluate the shape recovery properties. Compared to the single material sample, the dual component has a square section string reinforcement coincident with the load direction. The resulting design is presented below in figure 1.

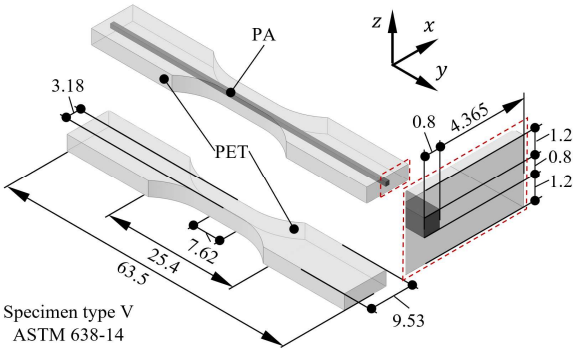

Fig. 1. CAD set up of the specimens.

The chosen filaments were a natural transparent PET from BasicFil and black colour PA645 (a PA6.6-based polymer) from Taulman3D. According to the filament's vendors, the PET's softening temperature starts at 60 °C and PA645's at 52 °C.

Each of the two samples' configurations was printed with five replicates using an Ultimaker 3 3D printer. The manufacturing files were generated with Cura 5.0.0 slicing tool using the process parameters described in table 1.

Table 1

Process parameters of the experimental setup.

No.	Parameter	Value
1	Layer thickness (mm)	0.15
2	Extrusion width (mm)	0.4
3	Number of walls	4/**2**
4	Top/bottom layers	11/**5**
5	Printing speed (mm/s)	30/**5**
6	First layer printing speed (mm/s)	15/**5**
7	Extrusion temperature (°C)	245/**235**
8	Maximum fan speed (%)	30/**15**
9	Bed temperature (°C)	70
10	Skin percentage overlap (%)	15
11	Z seam position	Sharpest corner
12	Brim	Yes
13	Brim width (mm)	3
14	Retraction distance (mm)	7/**8**
15	Retraction speed (mm/s)	35/**40**
16	Z hop height (mm)	1.6
17	Avoid printed parts when travelling	Yes
18	Merged meshes overlap (mm)	0.2
19	Alternate mesh removal	No
20	Enclosure	Yes
Values in bold apply to PA material.		

The testing methodology consisted of six steps as follows:

1. Measurement of the gauge length after the specimens' marking;
2. Elongation at room temperature with 100% at 1 mm/min;
3. Hold the sample at 100% elongation for 5 min;
4. Measure the elongation after release, ε_u;
5. Heat the specimens in the oven at 80 °C for 5 min;
6. Measure the elongation after recovery.

The resulting specimens were tested for a second cold deformation cycle to evaluate the shape recovery properties. The input gauge length was the ε_p from the previous testing cycle.

All specimens were tested in the same laboratory conditions with humidity of 58% at 21 °C using an Instron 4411 universal uniaxial testing machine with 5 kN load cell.

3. RESULTS AND DISCUSSION

The results include the samples' visual and numerical analysis of the shape recovery properties. A double comparison was made between the samples' materials configuration and the testing cycles.

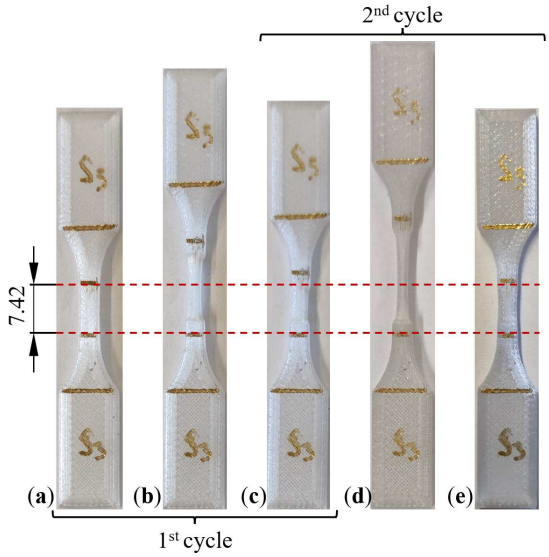

Fig. 2. Example of the methodology used to determine the shape recovery properties of the S3 sample of 100% PET with: (**a**) initial, (**b**) first deformation, (**c**) first recovery, (**d**) second deformation, (**e**) second recovery.

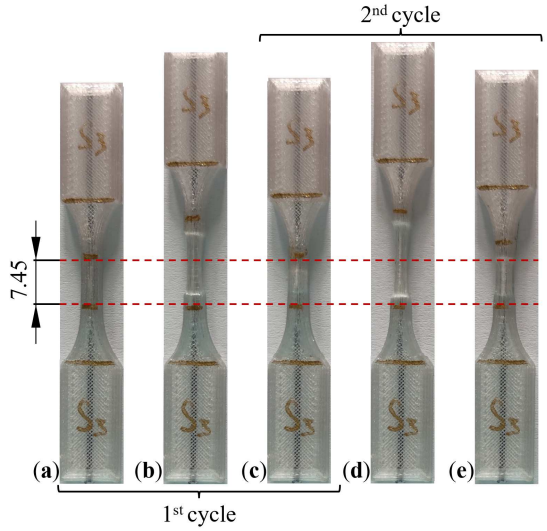

Fig. 3. Example of the methodology used to determine the shape recovery properties of the S3 sample of PET-PA645 with: (**a**) initial, (**b**) first deformation, (**c**) first recovery, (**d**) second deformation, (**e**) second recovery.

In the first deformation-recovery cycle, the samples presented a necking at the level of the gauge (see Fig. 2b, and 3b). After the heat treatment (i.e., 5 min at 80 °C), they partially recovered their shape, with the PET-PA configuration showing better results than PET (see Fig. 2c, and Fig. 3c). However, in the second deformation-recovery cycle, the PET specimens showed better recovery properties than the previous cycle and PET-PA configuration (see Fig. 2e, and Fig. 3e), even if they were elongated with the values of ε_p of the prior cycle (see Table 2).

Table 2

Shape recovery property values of the specimens subjected to deformation and recovery cycles.

Cycle	Mat.	Run no.	ε_m (mm)	ε_u (mm)	ε_p (mm)	R_f (%)	R_r (%)	*SMI* (%)	σ (MPa)
C1	PET	1	14.30	13.82	1.71	96.64	88.04	85.08	55.87
		2	14.78	14.35	1.86	97.09	87.41	84.87	55.91
		3	14.84	14.41	1.97	97.10	86.72	84.21	56.02
		4	14.78	14.37	1.82	97.22	87.68	85.25	54.65
		5	14.88	14.39	1.70	96.70	88.57	85.65	54.20
C1	PET-PA	1	14.96	14.22	0.63	95.05	95.78	91.05	52.05
		2	14.76	14.37	0.75	97.35	94.91	92.41	52.20
		3	14.9	14.41	0.78	96.71	94.76	91.64	52.03
		4	14.86	14.39	0.82	96.83	94.48	91.49	52.95
		5	14.84	14.20	0.72	95.68	95.14	91.04	52.44
C2	PET	1	17.72	16.61	-0.64	93.73	103.61	97.12	58.61
		2	18.5	17.48	-0.81	94.48	104.37	98.62	57.55
		3	18.78	17.85	-1.26	95.04	106.70	101.4	56.66
		4	18.42	17.12	-0.66	92.94	103.58	96.27	54.10
		5	18.28	17.79	-0.68	97.31	103.71	100.93	51.58
C2	PET-PA	1	16.22	16.14	0.87	99.50	94.63	94.16	38.58
		2	16.26	15.92	0.74	97.90	95.44	93.45	36.56
		3	16.46	16.08	1.15	97.69	93.013	90.86	39.10
		4	16.5	16.02	0.69	97.09	95.81	93.03	38.5
		5	16.28	16.00	0.50	98.28	96.92	95.26	37.37

The fixity ratio, R_f, measures how good a material is at "memorising" a shape, as presented in (1) by dividing ε_u at ε_m. Figure 4 shows that both PET and PET-PA specimens have good R_f as they recorded more than 90% average fixity. Interestingly, in the first deformation cycle, the PET samples showed an Rf of 96.95%; in the second cycle, it decreased to 95.79%. On the other hand, the PET-PA group presented an average R_f of 95.79% in the first cycle and increased in the second to 98.10%.

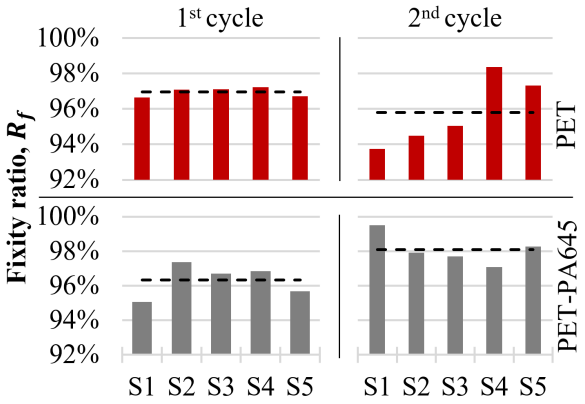

Fig. 4. Fixity ratio of the tested samples.

The recovery ratio, R_r, gives information on the materials' capability to recover shape when heated above the T_g. In the figure 5 plot, it is shown that in the first cycle, the PET samples showed an average recovery of 87.69%, and in the second cycle, it increased to 104.40%. The PET-PA configuration showed a very small variation of the recovery properties between the two cycles. This way, the average R_r was 95.02% in the first, and in the second, 95.17%.

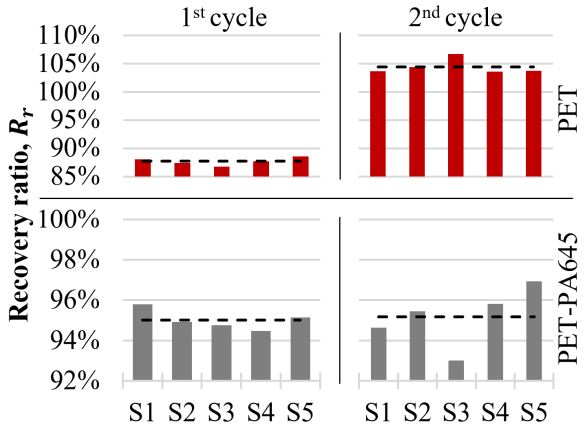

Fig. 5. Recovery ratio of the tested samples.

The shape memory index, SMI, provides information regarding materials' shape memory performance based on the previously described indexes. Figure 6 shows that the PET group's first deformation-recovery cycle averaged 85.02%. Based on these results, it can be considered that PET has poor shape memory properties. However, in the second testing cycle, the same material presented a surprisingly SMI average of 100%. For the dual component samples in the first cycle, the resulting SMI was 91.53% and 93.36% in the second. Again, an index increase can be observed, but with a smaller value.

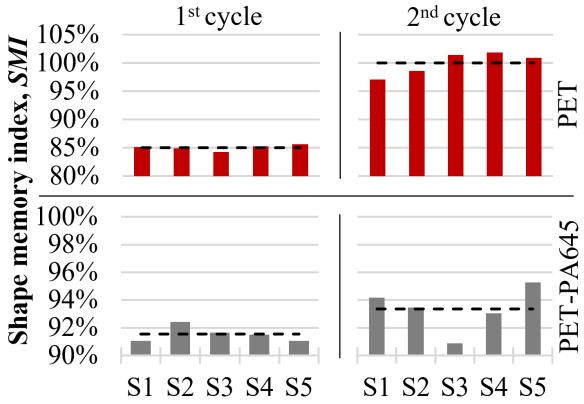

Fig. 6. Shape memory index of the tested samples.

At first sight, the above-presented results appear to be unlikely. Even so, the increase of the shape memory properties in the second deformation-recovery cycle could be explained by the polymeric chains' structure.

A thermoplastic polymer is characterized by covalent bonds (or polymeric chain chemical bonds) and physical bonds such as chain entanglement and crosslinks. During the melting phase, the polymeric chains have a low entropy, favouring their linear distribution. As they cool down, the chains tend to occupy the available volume resulting in multiple foldings and twistings of the chains (the entanglements are formed), and consequently the entropy degree increases [13]. When stretched, the chains follow the load direction, and the entanglements' capacity to align before breaking the covalent bond gives the maximum elongation (the entropy is decreasing). During the heat treatment, the chains tend to recover their natural high entropic state in which the chain's entanglements behave as a spring.

PET is a semi crystalline material having both amorphous (i.e., transparent) and crystallin (i.e., opaque) phase [14]. Based on these facts, the hypothesis is that in the first cycle, the polymeric chains were not elongated sufficiently to provide a significant recovery effect during the heating. In the second cycle, the samples were elongated with the value of ε_p from the previous cycle, which was higher than the initial ε_m. This way,

the PET chains were stretched more (they were forced to align with the load direction decreasing the entropy), which provided a way to gain more energy. This extra energy (compared to the first cycle) was released during the specimens' heating and improved the shape recovery effect (the polymeric chains recovered their high initial entropy). This assumption is based on the stress-displacement diagram from figure 7.

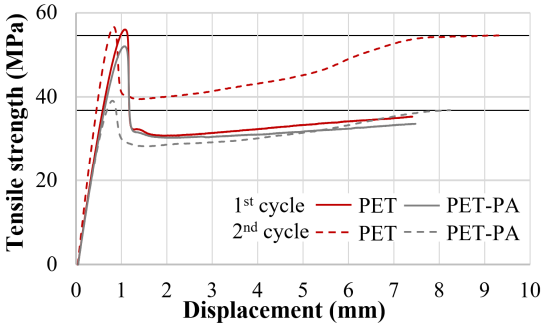

Fig. 7. Stress-displacement diagrams of the S3 samples for first and second deformation cycles.

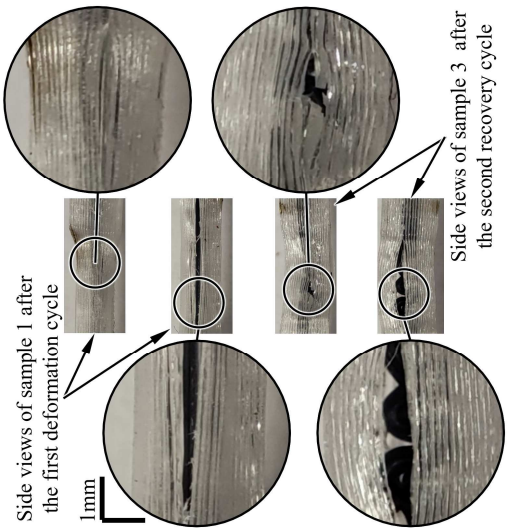

Fig. 8. Failure mode of S1 and S3 samples at different deformation recovery cycles.

In the second cycle, the S3 PET sample obtained maximum stress similar to the first. After surpassing the 2 mm displacement, the sample's stress increased, reaching a new peak (54.65 MPa) after 8 mm stretching, close to the initial one of 56.66 MPa. A similar behavior can be observed for the PET-PA S3 specimen in the second cycle but with a decrease in the load capacity referred to the first. Comparable results were obtained for all tested samples.

The shape recovery effect of the PET-based specimens is possible even after the initial deformation at cold. Even so, in the case of PET-PA samples, the elongation at room temperature can lead to the samples' delamination. As shown in figure 8, the first and third samples presented delamination of the PET shell in the yz plane (see Fig. 1). This effect can result from improper bonding of materials lines during the printing process or inconsistent areas of the PET matrix's cross-section along the y direction.

4. CONCLUSIONS

PET is a polymeric material widely used in industry due to its good mechanical properties and processability.

Adding PA reinforcement strings was considered to improve the shape recovery properties of pure PET samples after elongation at room temperature. In the first deformation-recovery cycle, the PET-PA group of specimens showed a good shape memory effect compared to “pure” PET. Even so, in the second deformation-recovery cycle, due to the increased deformation, the polymeric chains of PET specimens elongated more, resulting in a higher spring effect during the recovery cycle. This effect significantly improved the shape recovery properties of the PET samples.

The combination of PET-PA materials shows good shape recovery properties but with some limitations regarding the samples' integrity. At the same time, for “pure” PET, elongations exceeding 100% of the gauge improve the recovery effect.

Using relatively soft PA as a reinforcement for functional parts made of PET can be a viable solution for repairing deformed parts by simply heat treating them, as long as the PET matrix's cross-section area has no inconsistencies.

5. REFERENCES

[1] Singh, S., Singh, G., Prakash, C., Ramakrishna, S. *Current status and future directions of fused filament fabrication*. J Manuf Process, 55, 288-306, 2020, https://doi.org/10.1016/j.jmapro.2020.04.049

[2] Popescu, D., Zapciu, A., Amza, C., Baciu, F., Marinescu, R. *FDM process parameters influence the mechanical properties of polymer specimens: A review*. Polymer Testing, 69, 157-66, 2018, https://doi.org/10.1016/j.polymertesting.2018.05.020

[3] Hasanov, S., Alkunte, S., Rajeshirke, M., Gupta, A., Huseynov, O., Fidan, I., Alifui-Segbaya, F., Rennie, A. *Review on Additive Manufacturing of Multi-Material Parts: Progress and Challenges*. J Manuf Mater Process, 6(1), 4, 2022, https://doi.org/10.3390/jmmp6010004

[4] Valvez, S., Reis, P.N.B., Susmel, L., Berto, F. *Fused Filament Fabrication-4D-Printed Shape Memory Polymers: A Review*. Polymers, 13(5), 701, 2021, https://doi.org/ 10.3390/polym13050701

[5] Rafiee, M., Farahani, R.D., Therriault, D. *Multi-Material 3D and 4D Printing: A Survey*. Adv Sci, 7, 1902307, 2020, https://doi.org/10.1002/advs.201902307

[6] Carrell, J., Gruss, G., Gomez, E. *Four-dimensional printing using fused-deposition modeling: a review*. Rapid Prototyp J, 26(5), 855-69, 2020,https://doi.org/10.1108/RPJ-12-2018-0305

[7] Scalet, G. *Two-Way and Multiple-Way Shape Memory Polymers for Soft Robotics: An Overview*. Actuators, 9(10), 2020, https://doi.org/10.3390/act9010010

[8] Hu, J., Zhu, Y., Huang, H., Lu, J. *Recent advances in shape–memory polymers: Structure, mechanism, functionality, modeling and applications*. Prog Polym Sci, 37(12), 1720-63, 2012, https://doi.org/10. 1016/j.progpolymsci.2012.06.001

[9] Biswas, M.C., Chakraborty, S., Bhattacharjee, A., Mohammed, Z. *4D Printing of Shape Memory Materials for Textiles: Mechanism, Mathematical Modeling, and Challenges*. Adv Funct Mater, 31, 2100257, 2021, https://doi.org/10.1002 /adfm.202100257

[10] Quiñonez, P.A., Ugarte-Sanchez, L., Bermudez, D., Chinolla, P., Dueck, R., Cavender-Word, T.J., Roberson, D.A. *Design of Shape Memory Thermoplastic Material Systems for FDM-Type Additive Manufacturing*. Materials, 14, 4254, 2021, https://doi.org /10.3390/ma14154254

[11] Mittal, G., Rhee, Y.K., Mišković-Stanković, V., Hui, D. *Reinforcements in multi-scale polymer composites: Processing, properties, and applications.* Compos. B. Eng., 138, 122-39, 2018, https://doi.org/ 10.1016/j.compositesb.2017.11.028

[12] Ermolai, V., Sover, A., Nagîț, G. *Strength characterisation of dissimilar material samples produced via Fused Filament Fabrication*. Nonconventional Technologies Review, 26(1), 2022.

[13] Ehrenstein, G.W. *Structure of Polymeric Materials*, In: Polymeric materials, Hanser, Ohio, ISBN 1-569900-310-7, 61-141, 2001.

[14] Ehrenstein, G.W. *Overview of Selected Polymeric Materials*, In: Polymeric materials, Hanser, Ohio, ISBN 1-569900-310-7, 241-259, 2001, https://doi.org/10.3139/9783446434134.008.

CAPACITĂȚILE DE RECUPERARE A FORMEI REPERELOR DIN PET PRINTATE 3D

Această lucrare abordează proprietățile de recuperare a formei pentru epruvete printate 3D pe bază de polietilen tereftalat (PET). Caracteristicile de recuperare a formei au fost evaluate prin deformare la rece și revenire la cald. Astfel au fost testate două grupuri de epruvete, unul din PET și cel de-al doilea din același material, ranforsat cu un cordon de poliamidă (PA). În primul ciclu de alungire-revenire rezultatele arată că ranforsarea cu PA contribuie la o recuperare mai bună a formei. În cel de-al doilea, a fost obținută a îmbunătățire semnificativă a capacității de recuperare a formei pentru epruvetele din PET. Aceste rezultate au fost puse pe baza tensionării mari a lanțurilor polimerice de PET în urma alungirii crescute. Ambele configurații de materiale testate prezintă proprietăți bune de recuperare a formei.

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