Supplementary

Post-Print Thermal Annealing: A Simple and Effective Strategy for Enhancing Adhesion in FDM-Based SMA-PLA Composites

Contents

Design of the experimental study

It was decided to plan an experimental campaign in order to research an effective method for embedding SMA wires within 3D-printed material, paying particular attention to the results regarding the adhesion of such wires to the plastic material and consequently its resistance to being extracted afterwards.

Planning began with the choice of materials to be used and the conceptualization of the various alternatives to be explored, in terms of the geometry of the printed specimen and of the parameters used for printing. These alternatives are divided into two large subgroups: specimens made without stopping the printing process, with the SMA wire inserted at the end of the print, and specimens made by stopping the printing at a predefined layer, inserting the thread and then letting the process continue until its end.

Materials inventory

A 0.5 mm diameter SMA wire was used throughout the experimentation.

As for the material used for 3D printing, two filaments from the manufacturer BASF were used, marking two distinct phases of the experimentation: in the first phase, PET Ultrafuse was used, and in the second, PLA PRO1.

The following materials were also used:

- CRIMP: TE Connectivity Insulated loop terminal, maximum wire size 0.2 mm^2;
- SLEEVE: RS PRO cable sheath made of PTFE, sleeve (inner) diameter 0.71mm;

Fabrication of specimens: PET

1. Adhesion test with sleeve

The first tests focused on methods to insert a SMA wire in the 3D-printed material with the protection of an outer sheath. This solution was designed for contexts in which one wants to minimize the contact of the wire with the printed material and not expose it in any way to the high temperatures due to the proximity of the extruder.

Therefore, the choice was made to design the specimen to encase the sheath by pausing the print and to insert the SMA wire inside the sheath only later, after the printing process was completed and at room temperature, to avoid unnecessary overheating.

Materials:

- SMA wire 0.5 mm
- RS PRO cable sheath made of PTFE: sleeve diameter (inside) 0.71 mm; wall thickness 0.25 mm

We can then calculate the outer diameter of the sleeve, which tells us the minimum diameter of the hole to be made inside the specimen:

$$0.71\ mm + 2 \times 0.25\ mm = 1.21\ mm$$

To find the hole diameter that would bring the best results, three cubes were printed with square-section pits of different side lengths:

A. Ø 1.2 mm – *right, gray*

B. Ø 1.4 mm – *middle, light blue*

C. Ø 1.6 mm – *left, blue*

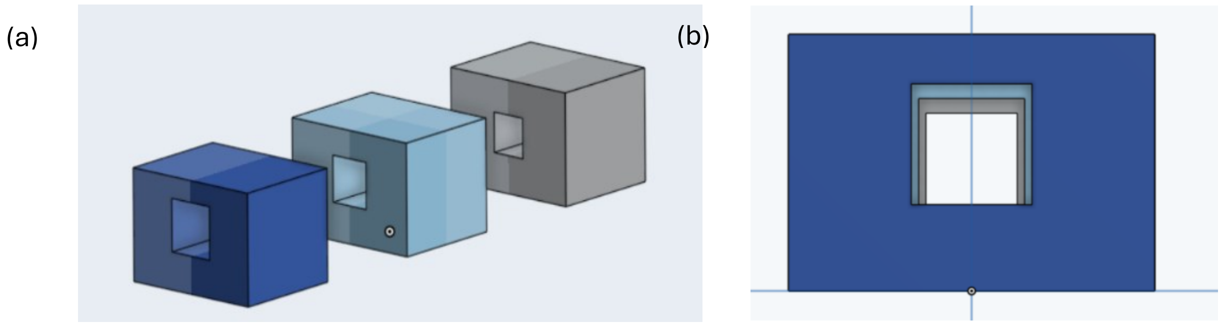

Figure 1 – 3D model of the three printed cubes, general view (a) and front view (b)

The pits of different sizes were aligned at their lower side so that the pause of the printing could be made at that level and the sleeve would be placed flat on it. Through the software, layer 24 was identified as the layer at which to stop printing, it is in fact the last layer made before the closing of the smaller side hole occurs, still allowing the sheathing to be inserted. By selecting layer 24, printing stops at the end of the fabrication of that layer.

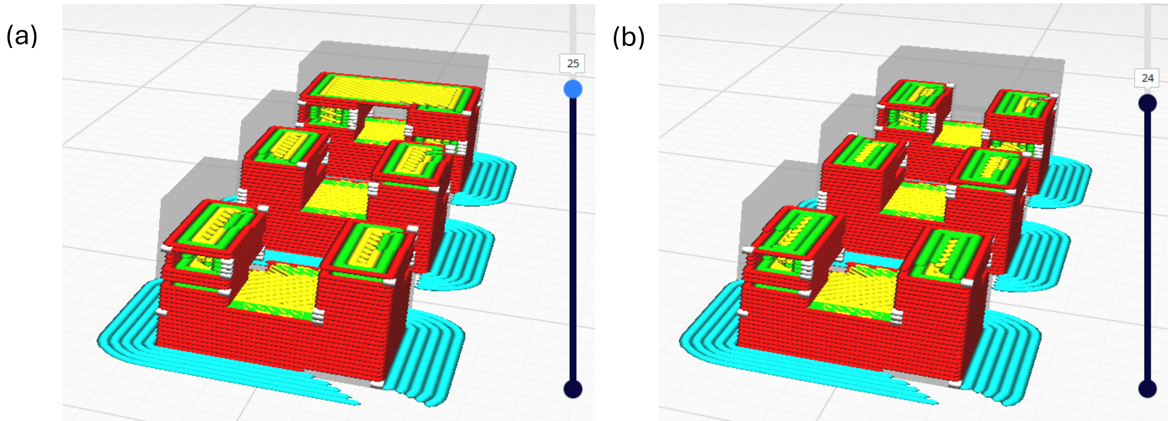

Figure 2 – visualization in the slicer of layer 25 (a) and layer 24 (b)

At the end of printing, a manual sheath pull-out test was performed to analyze its adhesion to the specimen: the wires inside the cubes with holes of 1.6 and 1.4 mm were pulled out immediately, while the one with a hole of 0.2 mm put up more resistance, and then pulled out as well. Another problem encountered in this print test is the fact that holes are spotted in the first few layers after the pause; it is hypothesized that this may be caused by the fact that the sheath after insertion exerts upward pressure while making the first few layers.

It is then decided to change the height of the bridge (upper bridge that closes the hole) by increasing it to 1.3 to try to reduce the formation of post-pause holes, and the problem of adhesion is addressed by acting not on the height but rather on the length of the specimen: it is hypothesized that the resistance to extraction may improve if the friction surface is increased by printing a 30-mm-long specimen. To test the effectiveness of both changes made, we choose to raise the height to 1.3 mm only for the first centimeter and leave it at 1.2 mm for the remaining 2 cm: thus, we can observe the change in terms of the holes present while maintaining a greater grip in most of the specimen.

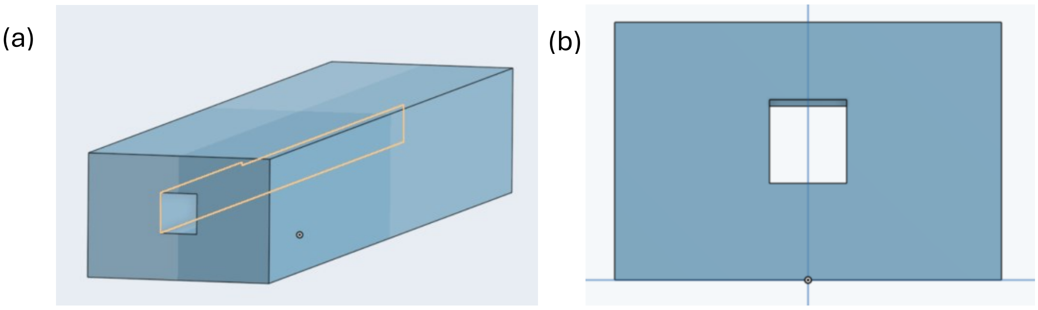

Figure 3 – 3D model of the test specimen with height variation, general view (a) and front view (b)

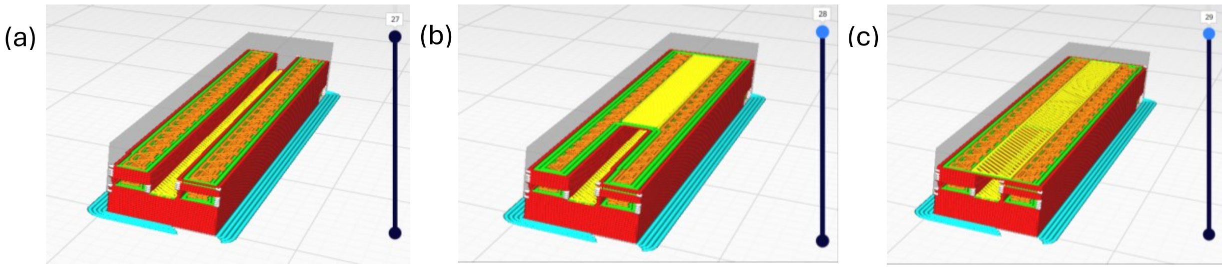

Figure 4 – display of layer 27 (a), 28 (b) and 29 (c) in the slicer, with progressive closure of the hole

The outcome after printing is displayed below, it can be seen that the holes in the layer after printing are still visible but present to such a small extent that they do not affect the integrity of the specimen. Adhesion is good, and the sheath offers a fair amount of resistance to being pulled out, to the point that manual removal without tools proves difficult.

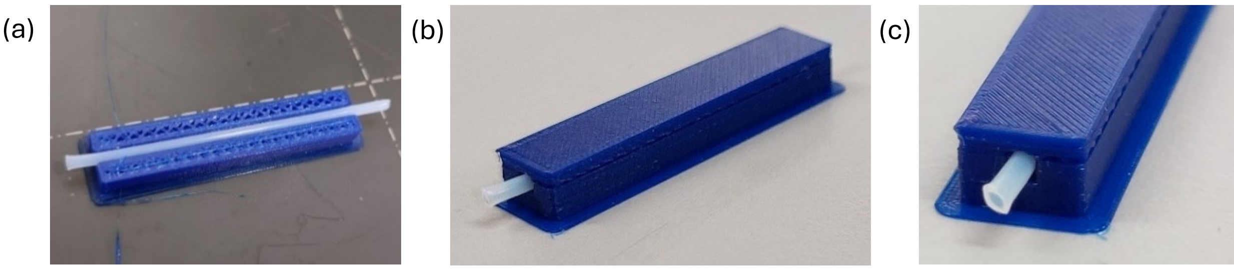

Figure 5 – printed specimen, during the print pause (a), after printing (b) e close-up (c)

The result of the test is therefore deemed satisfactory, it's important to keep in mind that the choice of this option implies the subsequent insertion of the SMA wire inside the sleeve: the wire will be free to move inside the sleeve. For this reason, it is considered the preferable solution in the case of drives where the wire has to slide inside the object that encases it or where the protection requirements of the SMA wire are clearly prioritized.

2. Adhesion test with simple SMA wire

The previous experimental procedure is repeated by calibrating it to the size of the wire used and no longer to the size of the sheath, for practical cases where it is necessary for the SMA wire to be firmly secured and adhered to the printed specimen. Since the chosen SMA wire has a diameter of 0.5 mm, a series of cubes with hole sizes 0.4, 0.5, 0.6 and 0.7 mm are designed.

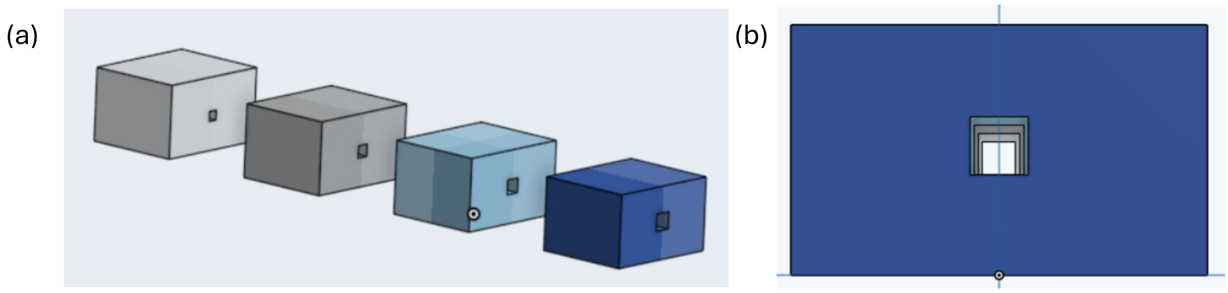

Figure 6 1 – 3D model of the four printed cubes, general view (a) and frontal view (b)

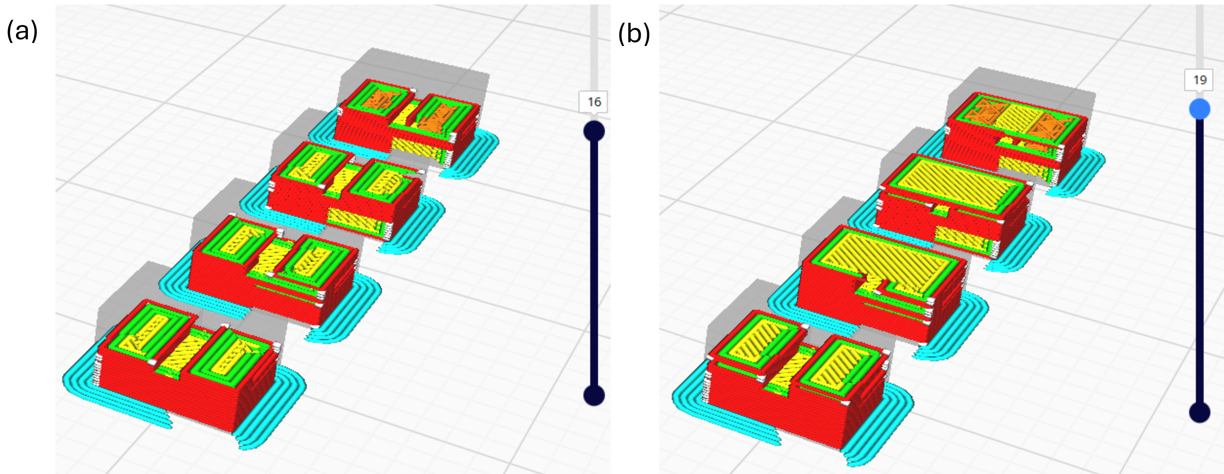

Figure 7 2 – display of layer 16 (a) and 19 (b) in the slicer, with progressive closure of the hole

A 30-degree chamfer is also added in the upper left corner of the hole to keep the wire locked on the underside of the channel, in its absence it is observed that the wire lifts up and out of the hole immediately as the printing starts again.

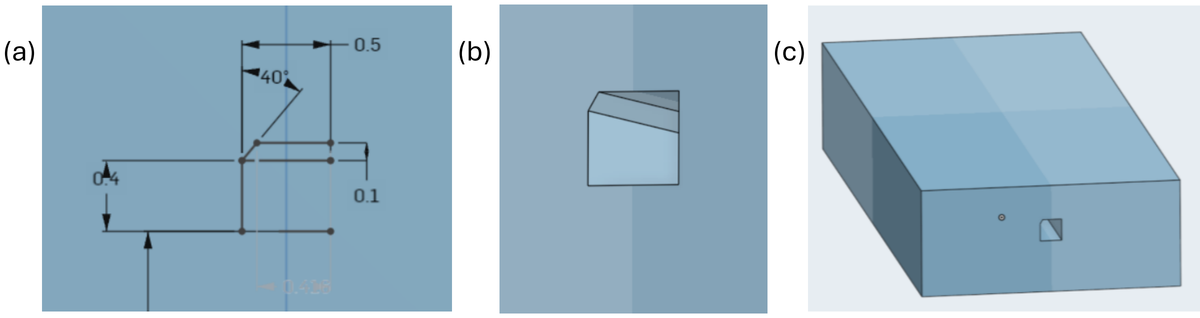

Figure 8 3 – 3D model of specimen with chamfer, detailed dimensions (a), close-up (b) and general view (c)

The specimen exhibits good adhesion to the wire; to further improve the quality of the print, we choose to increase the extrusion temperature to 220°C for the first layer after the printing pause. This is done to increase the adhesion of that layer to the one immediately below it: the last layer prior to the pause has most likely cooled during the time required for insertion, and resuming printing without temperature changes would make the connection between these two layers more fragile than the rest of the object.

A higher extrusion temperature, however, increases the amount of material lost during the pause. To limit the negative effects this may have on the quality of the print, in addition to changing the Coasting Volume, a cube near the specimen was added, choosing its position so that it would be printed before the specimen once the layer began. In this way, even when the volume of filament lost during the pause is significant, the negative effect is exhausted in the printing of the cube and the nominal flow is already restored once the printing of the specimen is reached.

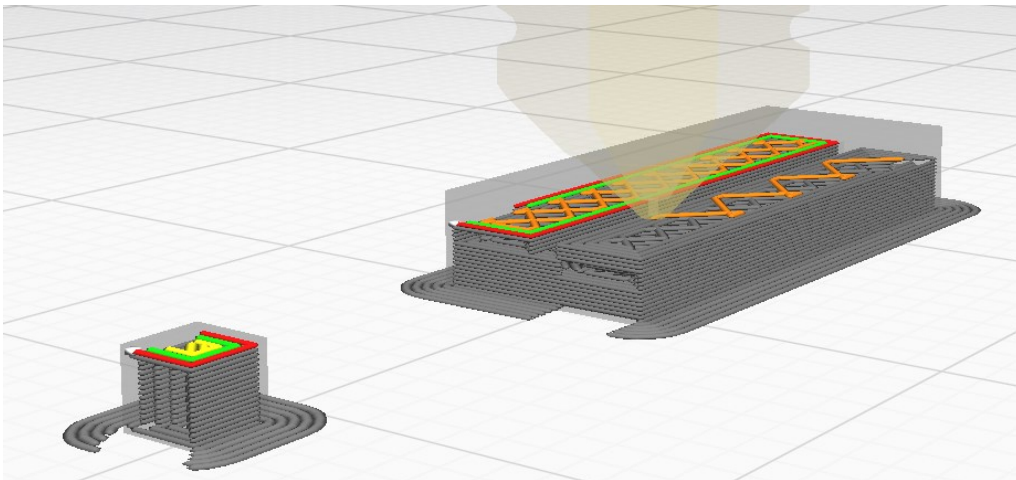

Figure 9 – display of extruder movement when printing a layer with an auxiliary cube

In this way, a good printing result is achieved: the SMA wire is not completely blocked but has good adhesion and resistance to being pull-out.

3. Adhesion test with crimped SMA wire

In the context of some use cases, the SMA wire can be presented already crimped, i.e., following the addition of two crimps at its ends, used in some applications to secure the wire externally to the specimen (a TE Connectivity Insulated Loop Terminal was used here).

The effectiveness of different fastening systems was then tested, starting with the solution that contemplates making pits inside the specimen, following the geometry of the crimps.

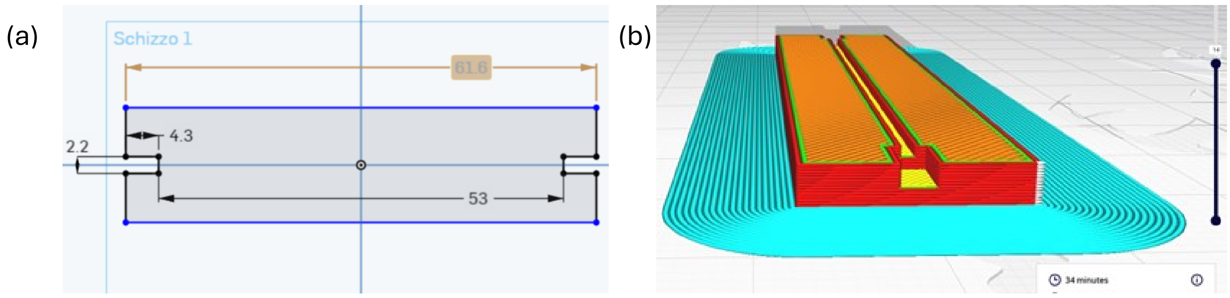

Figure 10 – specimen dimensions (a) and display of the specimen section in the slicer (b)

For the same reasons followed during the experimentation with the plain wire, it was chosen to add a 30° chamfer to the hole.

This solution proved inconclusive, however, since from the very first print test it could be seen that the height of the part of the crimp on which the pit was modeled was too prominent compared to the height of the layer. Increasing the height of the pit would necessarily have increased the height of the channel containing the SMA wire, resulting in too great a distance between the wire and the upper bridge and too little adhesion between the two surfaces; on the other hand, maintaining the original height causes a certain impact between crimp and nozzle and consequent wire breakage, as well as the possibility of damage to the printer itself.

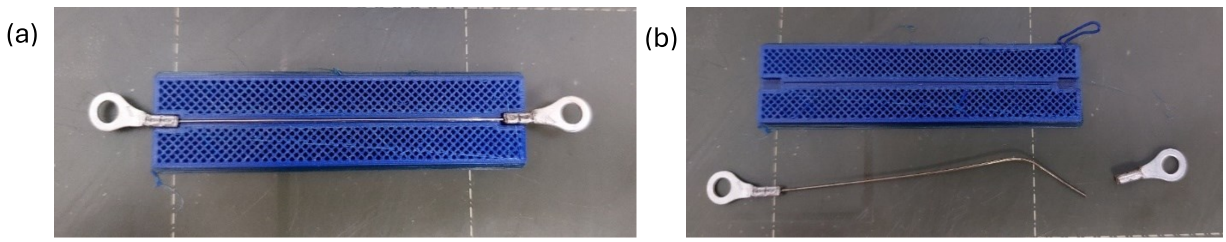

Figure 11 4 – specimen after wire insertion during the pause (a) and wire breaking following impact with the nozzle (b)

Therefore, having discarded this first hypothesis, we moved on to the design of the cylinder fastening system, i.e., the realization of cylinders that are external to the specimen but molded integral with it, which can be inserted into the crimp holes while keeping the wire clamped.

Two types of cylinders are designed for different functions: solid cylinders for the realization of a self-contained and movable fastening system, and hollow cylinders that can be joined to an underlying plane (auxiliary fastening system) by means of nails or the like, to subject the specimen to further processing such as oven cure.

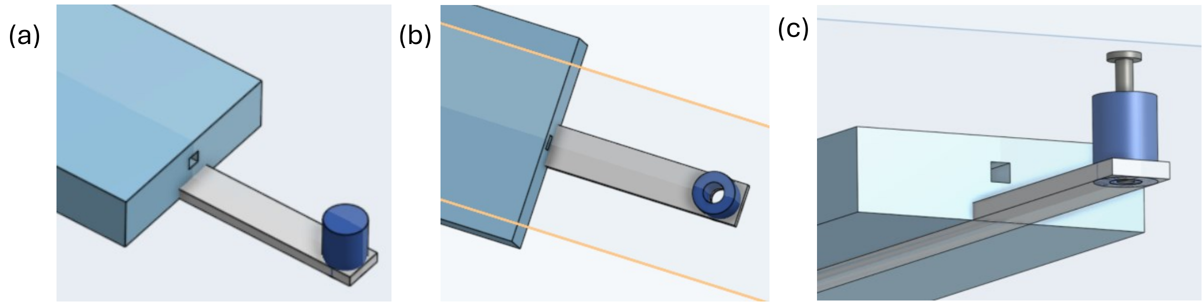

Figure 12 – 3D model of the fastening system with solid cylinder (a), hollow cylinder (b) and hollow cylinder fixed with nail (c)

To improve the robustness of the assembly each cylinder was surrounded with a concentrically shaped protection system that closes over the crimp following inclusion, so that the system is more robust and less sensitive to impact. The design requires special attention to the ends of the crimp: it is essential to leave the ends free so as not to run into the problems typical of the solution with pits.

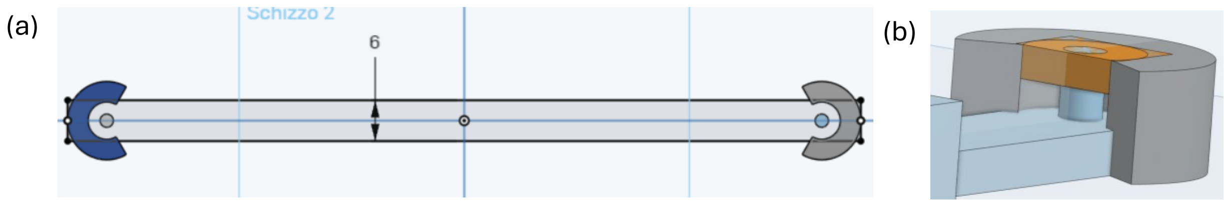

Figure 13 – protection system, top view drawing (a) and close-up of the enclosed 3D model (b)

The result obtained is very firm; the major criticality of this solution is the great attention required for measurements at the design stage, since the successful inclusion for the entire system relies on the accuracy with which the actual dimensions of the wire are reproduced; an accuracy of about 0.5 mm is estimated as necessary.

This solution also requires the use of crimps with a minimum diameter of 3 mm, as smaller crimps do not have adequate dimensions to support the forces involved.

(a) (b)

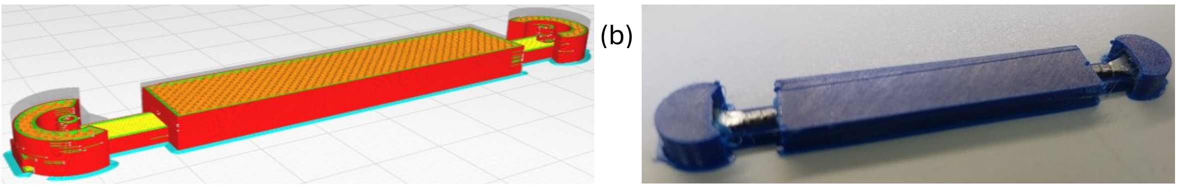

Figure 14 – 3D model of specimen with protection system (a) and implementation including crimped wire (b)

Fabrication of specimens with oven cure: PLA PRO1

The second part of this experimental study focused on how the PLA PRO1 filament is cured in the oven and the effects that crystallization and annealing have on the successful inclusion of the SMA filament.

Crystallization leads to increased material strength and hardness but also to increased brittleness. At the macroscopic level, a change in transparency (the crystallized material is more opaque than the original filament) and volumetric reduction can be seen.

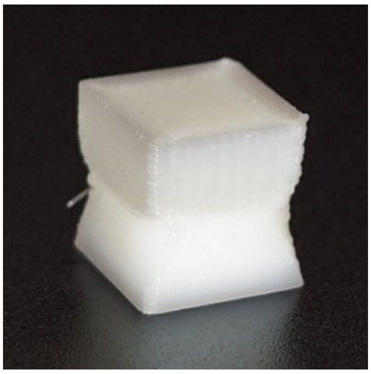

Figure 15 – close-up of printed cube with obvious shrinking effects

To make sure that the material does not crystallize during printing, it is necessary to moderate the extrusion temperature so that it does not exceed a certain threshold and simultaneously act to have rapid cooling. High fan action and low printing temperatures, however, can negatively impact the adhesion between layers and other characteristics of the mold, so many tests have been done to find the best compromise between the various requirements so that the filament solidifies with the best properties without crystallizing.

1. Curing test with square section specimens

The first set of specimens to be tested in the oven has a horizontally developed parallelepiped shape, measuring $25.4\ mm \times 6\ mm\ \times 6\ mm$ (length of 25.4 mm corresponding to the standard size of 1 inch). Two specimens were initially made from the same print, so as to minimize external variables and make them as similar as possible, they were then simultaneously subjected to the annealing process for 45 minutes at 110°C.

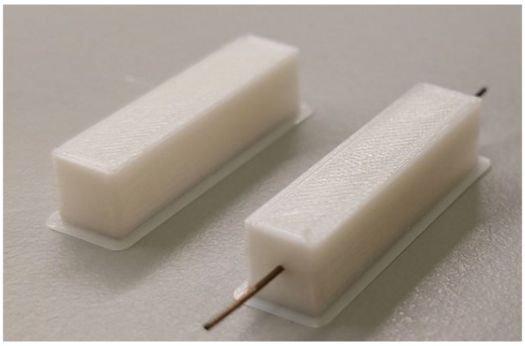

Figure 16 – printed specimens, with and without SMA wire insertion

In order to have a restriction of the hole containing the SMA wire, one would want a volume reduction in height and width, so as to compress the channel; however, it is observed that in the experiment carried out, the height even increased, while the shrinkage occurred on the length. Thus, it was deduced that the desired volumetric shrinkage due to crystallization occurs in the plane parallel to the printing of the layers, balanced by an expansion in the vertical growth direction of the printing.

For this reason, horizontal specimens were abandoned in favor of a geometry that grows in height, opting in favor of a circular cross-section. This way, the inner hole wall can better adhere to the cylindrical geometry of the SMA wire and the smoothness of the extrusion motion is favored, allowing the printing of concentric circular crowns that minimize the creation of holes within the material.

2. Curing test with circular section specimens

Initially, several cylinders were molded with holes of varying diameters to determine the minimum diameter that would allow for a cold insertion of the SMA wire, maintaining the previously chosen temperatures of extrusion temperature 210°C, plate temperature 60°C, and fan at 60 (also below as T

210-60, f 60). Several tests were then carried out to find the optimum inner diameter for inserting the SMA wire, which turns out to be 0.55 mm, on a specimen with a height of 20 mm and an outer diameter of 5.5 mm.

Two specimens are printed, one for control (CC) and one to be annealed for 15 minutes at 110°C (C0). It is necessary in this situation to avoid printing one single cylinder at a time, since given the concentric geometry and small size of the test specimens the extruder would remain fixed on the same surface for too long, causing the material to overheat and the resulting in a poor solidification of the layers. Therefore, it is always necessary to print the specimens at least two at a time, possibly in distant positions of the printing plate, so that the movement of the nozzle from one cylinder to the other during layer printing can provide enough time for the underlying layer to solidify.

Both specimens were subjected to a tensile test to see indicatively if any differences were present in the wire's resistance to being pulled out; the results are shown below.

PRE-ANNEALING:

C0: $h\ 20.20\ mm\ \ \emptyset 5.70\ mm$

CC: $h\ 20.15\ mm\ \ \emptyset 5.40\ mm$

POST-ANNEALING:

C0: $h\ 20.30\ mm\ \ \emptyset 5.33\ mm$

An increase in height of +0.15 mm and a shrinkage in the outer diameter of the specimen of -0.07 mm, as desired, can be observed. The pull-out tests to which these preliminary specimens were subjected also proved consistent with the initial hypothesis: the C0 specimen subjected to annealing exhibited a peak tensile strength of 12N, twice that of the control specimen CC (6N).

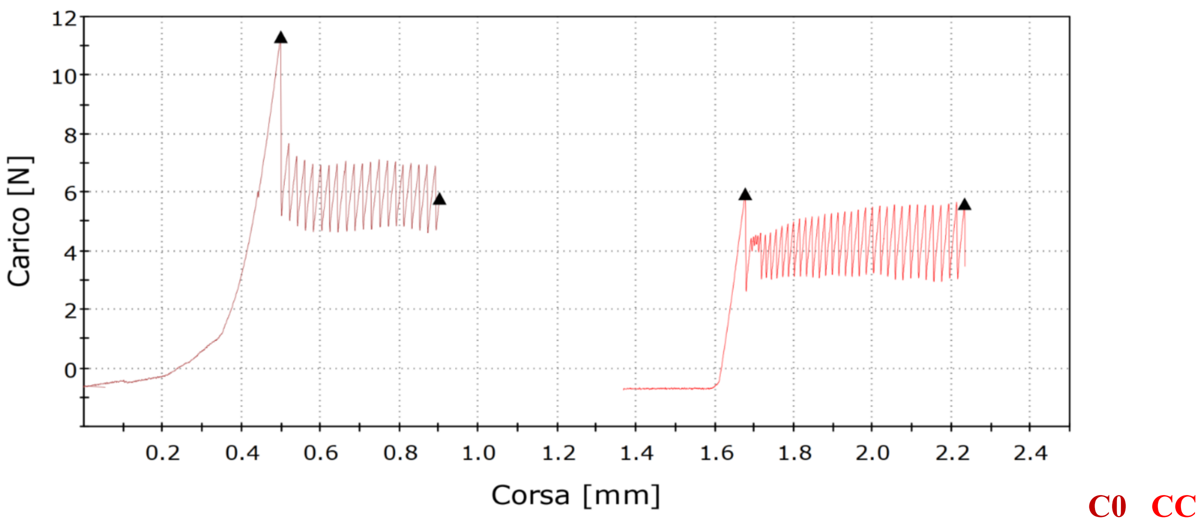

Figure 17 – Results of the pull-out test carried out on C0 (left) and CC (right)

Through some trial and error the printing parameters were optimized as follows:

- *Infill Density* = 100%;
- *Extrusion Temperature* = 200°C (210°C for the first layer), *Bed Temperature* = 30°C;
- *Wall Line Count* = 20, amount equal to the total number of concentric circles in each layer, to create a uniform structure with no difference between the wall and the inner part;

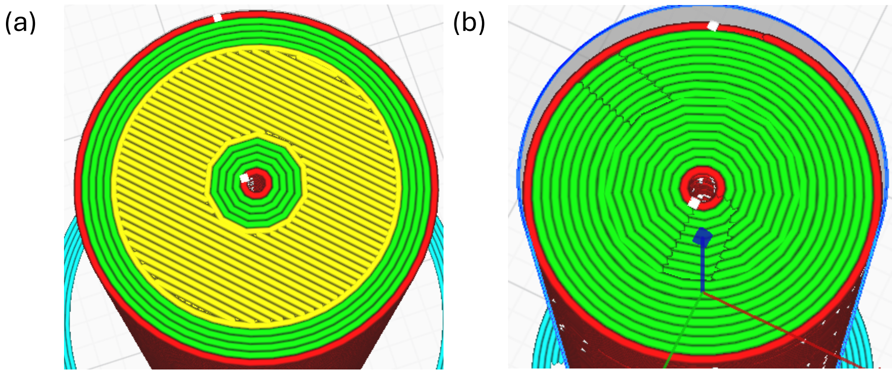

Figure 18 – difference between specimen with five walls (a) and specimen consisting entirely of walls (b)

- *Minimum Polygon Circumference* = 0.4 mm, necessary to correctly print a hole of 0.5 mm;
- *Hole Horizontal Expansion* $= 0.145\ mm$ and *Wall Line Width* $= 0.256\ mm$, optimal values to have an internal hole with diamater 6.45 mm (the minimum value to insert a 0.5 mm wire) without compromizing the internal structure of the specimen;
- *All At Once,* this way the extruder moves from one cylinder to the other, giving enough time to each layer to solidify before printing the next one;
- *Outer Before Inner,* so that the printing of the outer walls does not generate pressure on the inner walls, reducing the diameter of the hole;
- *Optimize Wall Printing Order,* to limit the movements of the extruder and reduce *stringing*;
- *Maximum Deviation* = 0.05 (minimum value possible), to obtain the best possible approximation of the circumference;
- *Coasting Volume* = $0.03\ mm^3$ and *Retraction Distance* = 3 mm*,* to reduce *stringing;*
- *Small Features:* the most delicate part of the printing process is the printing of the internal hole, so it's useful to change the parameters of just that part by making it fall into the category of "Small Features". We redefine the Small Features as all the features with a

diameter < 2 mm, so *Small Feature Max Length* = 6.5 mm (the corresponding circumference, rounded up). Now it's possible to reduce the speed of the printing process in correspondence to the hole, to obtain a better printing quality: *Small Feature Speed* = 50% and *Small Feature Initial Layer Speed* = 50% ;

- *Build Plate Adhesion: Raft*, *Raft Air Gap* = 0.05 mm, *Initial Layer Z Overlap* = $0.2\ mm$, to have the best Build Plate Adhesion and stability of the specimen during the rest of printing process.