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3D PRINTED CAPSULES FOR SELF-HEALING CONCRETE APPLICATIONS

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Abstract: This study focuses on the use of additive manufacturing techniques as a possible way to produce novel types of macro-capsules, suitable to be filled with different healing agents and subsequently embedded in cementitious materials to introduce self-healing properties and deal with the sensitivity of these materials to crack formation. Specifically, tubular macro-capsules were produced by 3D printing and filled either with an expansive polyurethane resin or with a liquid sodium silicate. The 3D-printed capsules were first characterized in terms of water tightness and shell continuity, to evaluate the eventual need for additional protective layers. Then, they were inserted into cement mortar prisms and subjected to controlled cracking by three-point-bending to experimentally investigate their bonding with the cement matrix and the ability to release their content at the crack site to promote self-healing. The actual self-healing effect was expressed in terms of recovery of load-carrying capacity under mechanical tests. Positive results were achieved, showing a good potential of the proposed capsule-based system for structural applications. Further improvements can be envisaged through the optimization of the capsule shape, for which the 3D printing technology offers virtually unlimited possibilities.

1 INTRODUCTION

Recently, a growing attention has been devoted by the international scientific community to the development of technological solutions able to introduce self-healing properties in cementitious materials, in such a way to deal with the intrinsic sensitivity of these materials to crack formation. Different strategies have been proposed so far, as extensively reviewed in [1,2]. Among all of them, the capsule-based approach appears to be one of the most promising due to its versatility. This technological approach is based on the principle that when a crack comes across a capsule, the capsule shell is broken and thus, the healing agent contained in it can be released into the crack, restoring the damage [3]. With regard to their dimension, capsules can be divided into micro- and macro-capsules, respectively presenting a maximum size smaller or larger than 1 mm. Whereas the micro-capsules [4–6] can be well

dispersed into the matrix while introducing smaller pores, the volume of carried healing agent could be too small to fill completely large cracks. Moreover, also due to their typical spherical shape, their adhesion with the surrounding matrix could be not enough to allow the shell breakage upon cracking, thus not triggering the self-healing effect.

A possible solution to these issues can be offered by tubular macro-capsules, which allow higher storage capacity and likelihood of shell breakage upon crack interception. Different encapsulation techniques have been extensively investigated and successfully used by different research groups, whether in terms of size, materials or production techniques. Examples include hollow glass tubes [7–9], ceramic tubes produced by phase-inversion spinning [7,10], cementitious capsules produced by extrusion [3,11], polymeric capsules produced by extrusion [12–15].

This study focuses on exploiting the potential offered by Additive Manufacturing (AM), also popularly known as 3D printing, as a possible way to produce novel types of macro-capsules, suitable to be filled with different healing agents and subsequently embedded in cementitious materials. In the last decade, the rapid development of AM technology allowed the fabrication of materials with increasing complex geometries [16–18] and its progressive introduction to the construction industry [19–21]. Unlike conventional manufacturing techniques that fabricate products by removing materials from a larger stock of bulk material, AM processes allow the creation of the final shape by adding materials under the control of an automated system, usually layer by layer that are built and consolidated using different techniques [22], for example the common processes of Fused Deposition Modelling (FDM), Selective Laser Sintering (SLS) or stereolithography (SLA). The technique used in this study was the FDM, which was developed and patented by S. Scott Crump in 1992 [23]. It is based on the heating and successively extrusion of thermoplastic filaments from a movable hot head that deposit the melted material in thin layers onto a substrate, which then solidify almost immediately and cold weld to the previous extruded layers [22]. The turning point for the diffusion of the FDM was the expiration in 2009 of the abovementioned patent and the widespread open-source movement which created significant cost reductions for these 3D printers, which are nowadays available on the market also with low costs (< € 1000) as not-assembled DIY (Do It Yourself) open-source printers, fully assembled open-source printers or commercial systems with proprietary software [24].

In this work, macro-capsules with two different sizes were produced by FDM using an open-source 3D printer and different types of thermoplastic filaments, then filled either with an expansive polyurethane resin or with a liquid sodium silicate. Their shape was tubular, with wall thickness of 200 μm, external diameter of 7.9 or 8.5 mm, and total length of 40 or 50 mm. Such simple shape settings were selected for the sake of comparison with similar macro-capsules developed and thoroughly investigated by the authors, which are made of a different material (cement paste) and produced by extrusion, filled with the same healing agents and used in the same cementitious systems [3,11,25]. The 3D-printed capsules were first characterized in terms of water tightness and shell continuity, to evaluate the eventual need for additional protective layers. Then, they were inserted into cement mortar prisms and subjected to cracking by three-point-bending, to evaluate experimentally their ability to create a stable bond with the cement matrix, to be ruptured concurrently with the formation of the fracture in the matrix and to release their content at the crack site to promote self-healing. The actual self-healing effect was expressed in terms of recovery of load-carrying capacity under mechanical tests, after reloading of the healed specimen by three-point-bending.

The purpose of this study was to assess the feasibility of this proof-of-concept self-healing system, in view of further improvements that can be envisaged through the optimization of the capsule shape, for which the 3D printing technology offers virtually unlimited possibilities.

2 3D PRINTED CAPSULES

2.1 Production of the 3D printed capsules

The open-source Prusa I3 Hephestos printer, equipped with a 0.40 mm diameter nozzle, was used to fabricate the capsules. The highest achievable print resolution by the printer is 60 µm and it can reach a maximum print speed of 80 mm/s. Figure 1 shows the printer and its main components.

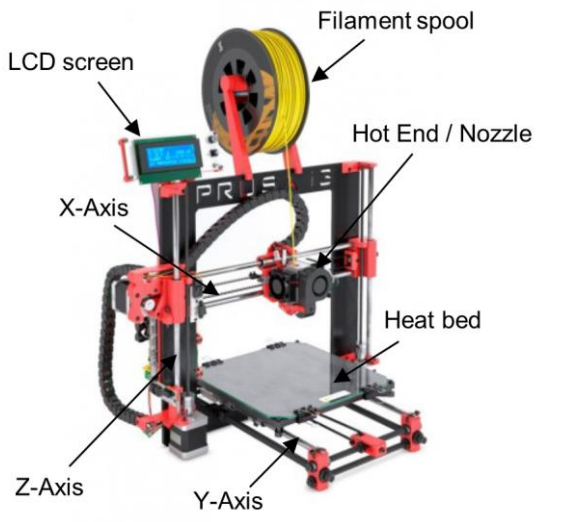

Figure 1: Prusa I3 Hephestos printer.

Nowadays, several materials are commercially available in the form of filament spools for FDM. In order to be eligible for being used as autonomous self-healing encapsulating material, several aspects should be considered, such as their melting temperature (T_m), their glass transition temperature (T_g) and their chemical resistance both to the coating and healing agent substances and towards the alkaline environment of the concrete. *Tg* of the selected material is an important feature as a relatively brittle behavior is required to trigger the encapsulated healing agent release, namely low elongation at rupture and relatively high tensile strength. Finally, low cost materials are preferable in order to produce a cost-effective self-healing system. Consequently, four different materials were selected to produce the capsules:

- Poly(lactic acid) (PLA) is derived from renewable resources such as corn or sugarcane and it is a biodegradable thermoplastic aliphatic polyester. PLA has a low T_g (around 60 °C) and limited elongation at break (<10%) [12]. It is widely used in the packaging and medical industry and it is one of the most common material for 3D printing.
- Polyethylene terephthalate (PET) is the most common thermoplastic polymer resin of the polyester family, largely used to produce beverage and food packaging, clothing and engineering resins. As a semi-crystalline polymer, PET properties depend heavily on processing conditions and its physical and chemical properties are a combination of different variables such as composition, crystallinity, orientation, etc. [26]. Due to the urgent issues connected to PET waste disposal, the use of recycled PET filaments to produce 3D printed capsules for self-healing applications could represent a possible disposal solution.
- Polyethylene terephthalate glycol-modified (PETG) is a copolyester of the pure PET prepared by partially replacing the ethylene glycol (EG) groups with 1,4-cyclohexanedimethanol (CHDM) groups in order to modify the polymer properties, such as reducing its melting temperature.
- Poly(methyl methacrylate) (PMMA), the synthetic polymer of methyl methacrylate, is a transparent thermoplastic and is a strong, tough and lightweight material, commonly used due to its properties, its ease of handling and processing and its low cost. This material was selected especially due to its brittle behavior, for which it was also compared with concrete [27].

Preliminary testing on samples of the different filaments were performed in order to assess the accuracy of the technical sheets' declared values, namely Fourier-transform infrared spectroscopy (FTIR) and tensile testing. The testing confirmed the purity of the

filaments' chemical compounds and the mechanical properties typical of the selected materials.

The models for printing the capsules were realized using the open-source Ultimaker Cura software. The main printing parameters used for each material are listed in Table 1.

Table 1: Configurations of printing parameters (when configurations differ among polymers, they are reported in the following order: PLA / PET / PETG / PMMA)

Printing parameters	Configurations
Layer height (mm)	0.06
Printing temperature (°C)	211 / 235 / 235 / 240
Bed temperature (°C)	60 / 30 / 60 / 90
Filament diameter (mm)	2.85
Nozzle diameter (mm)	0.40
Printing speed (mm/s)	60
Travel speed (mm/s)	120

Two models of capsules were designed and printed. The first one (Figure 2), hereafter referred to as Model 1, were designed for the sake of comparison after the cementitious capsules developed and thoroughly investigated by the authors [3,11,25]. The shell thickness was set to 0.2 mm in order to obtain a good compromise between ease of printing, holding capacity and to guarantee the relative brittle behavior that is essential for triggering the healing agent release. Consequently, the external diameter of the capsule was set to 7.9 mm, in order to obtain a comparable internal diameter with the aforementioned cementitious capsules. For the same purpose, length was set to 40 mm, obtaining a comparable volume capacity of healing agent.

A positive aspect offered by manufacturing the capsules using FDM was the possibility of producing the sealing of the capsule ends and filling the capsules during the printing execution. The seal thickness was set to 3 mm.

The printing procedures were carried out as follows:

1. the bottom capsule end was printed, with a thickness of 3 mm;
2. the shell of the capsule was printed until reaching 40 mm height, then printing was arrested;
3. while printing procedure was on stand-by, the capsule was filled using a syringe;
4. printing was resumed and the final capsule end was sealed, with a thickness of 3 mm.

After preliminary testing aimed to assess the water tightness and the ability of the capsules to correctly store and protect the healing agents (see Section 2.2), it was considered necessary to add an external coating. The coating was made by applying an external layer of a two-component liquid epoxy resin (Plastigel, API SpA). Before coating drying, the capsules were rolled into sand in order to improve the adhesion with the surrounding mortar matrix. Figure 2 shows the manufacturing of the Model 1 capsules.

However, the preliminary testing showed that, despite their simple manufacturing and

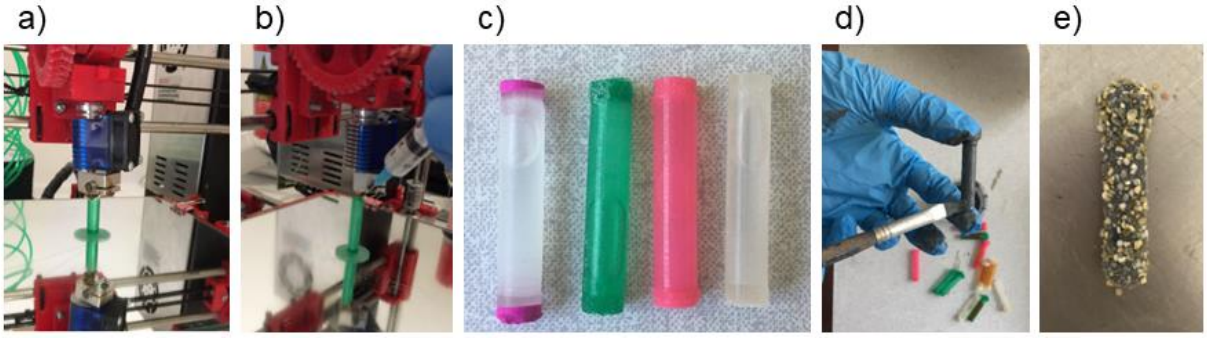

Figure 2: Model 1 capsules: a) printing of the first capsule end sealing and its shell; b) print is interrupted, capsule is filled and then print is resumed in order to realize the end sealing; c) 3D printed capsules, filled and with both ends sealed (from left to right PMMA, PET, PLA, PETG); d) coating application and e) capsule are rolled in the sand in order to improve their bonding with the cementitious matrix.

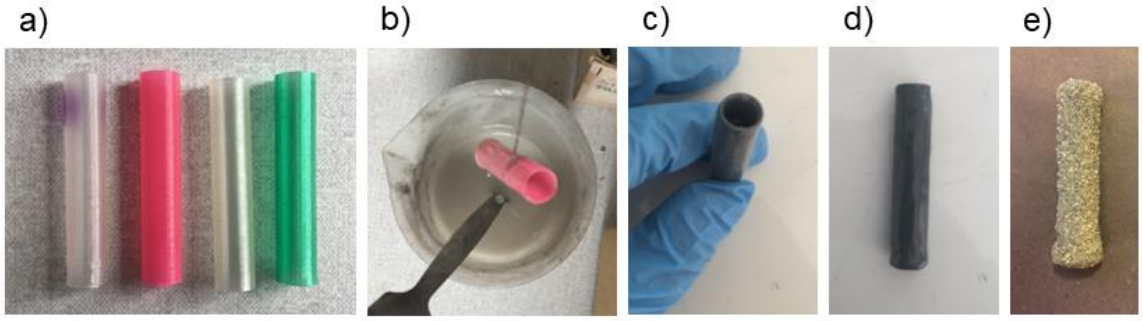

Figure 3: Model 2 capsules: a) 3D printed capsules, without capsule ends sealing (from left to right PMMA, PLA, PETG, PET); b) epoxy primer applied by immersion; c) top view of the capsule after epoxy film applied by immersion; d) lateral view of the capsule with dried epoxy coating and e) finished capsule with sealed ends, filled and rolled in the sand while epoxy was still fresh.

filling procedures and the ability to correctly encapsulate and release agents with a slow reacting mechanism, the Model 1 capsules, even after coating, were not effective in encapsulating highly reactive healing agents that are triggered for example by the contact with moisture, which require an almost perfect water/air tight condition in order to be correctly encapsulated and protected by the harsh and humid cementitious environment. Therefore, a second model was designed, hereafter referred to as Model 2 (Figure 3).

In order to provide a better protection of the healing agents, it was deemed necessary to apply a double coating, applied by immersion to have a complete coverage of the shell. Thus, to allow a correct application by immersion, only the lateral shell was printed, without end sealings that were realized later. To take into account the loss of internal volume caused by the internal coating and the application of the sealings, the capsule dimensions were slightly modified in order to obtain a comparable internal volume (i.e. volume of healing agent stored) with the Model 1. Consequently, the external diameter of the capsule was set to 8.5 mm and the length to 50 mm.

After printing, the first coating was applied by immerging the tubes in an epoxy-based two-component primer (Primer AQ, API SpA). This operation was repeated two times within 24 hours. Then, the tubes were further dip coated with a two-component liquid epoxy film (Plastigel, API SpA). The capsule ends were sealed with an epoxy-based two-component thixotropic plaster (Stucco K, API SpA), one before and one after the injection of the healing agent. A last layer of Plastigel was applied and, while it was still fresh, the capsules were rolled into sand to improve the bonding with the surrounding mortar matrix. Figure 3 shows the manufacturing of the Model 2 capsules.

Table 2 summarizes the specific features of each 3D printed capsule model configuration.

Table 2: Configurations of 3D printed capsules models

Features	Model 1	Model 2
External diameter (mm)	7.9	8.5
Length (mm)	40	50
Shell thickness (mm)	0.2	0.2
Type of sealing	3D printed	Stucco K
Type of coating	Plastigel (*ext.*)	Primer AQ Plastigel (*int.*+*ext.*)
Finishing	Sand	Sand

2.2 Water tightness and shell continuity

An aspect of paramount importance in the development of an effective encapsulated self-healing is the ability of the capsules to protect the healing agent from the cementitious environment and not allowing loss of agent from the capsule before rupture. In order to test this ability and assess the need of an external coating, Model 1 capsules were filled with water during printing, as explained in Section 2.1. For each material used for printing, two capsules were filled and not coated (as in Figure 2.c) and two capsules were filled and coated (as in Figure 2.e), for a

total of 16 capsules. The capsules weight was then monitored in time after exposition to air, in order to assess the mass of water loss. The permeation of water through the capsules polymeric shell and coating could be described as a Fickian diffusion process, hence linearly dependent with the square root of time [28]. Consequently, it is possible to define:

$$M_w = p \cdot t^{0.5} \quad (1)$$

where M_w (mg) is the mass loss in time attributed to the water loss, p (mg/h$^{0.5}$) is the water permeation rate and t (h) is the time of permeation. Hence, it is possible to assess the ability of protecting the healing agent by examining the reduction of the water permeation rate. Table 3 shows the water permeation rate for each tested capsule.

Table 3: Water permeation rate of the Model 1 capsules, either with or without coating

Material	#	Water permeation rate (mg/h$^{0.5}$)	
		Model 1 (no coating)	Model 1 (with coating)
PLA	1	5.13	11.38
	2	5.32	9.62
PET	1	23.07	3.28
	2	7.07	4.84
PETG	1	1.30	3.99
	2	23.13	3.25
PMMA	1	4.43	3.44
	2	5.66	3.05

Except in the case of PLA, the application of the external coating resulted in an overall reduction of the water absorption rate and an increased repeatability in the results, as in the case of the PET and PETG where the results were significantly different and most likely governed by the printing and layer adhesion defects. Consequently, even if the small number of specimens does not allow a statistically significant analysis of the results, this test provides a good indication of the importance of the external coating in providing a good protection of the healing agent and compensating the defects caused by the production of the capsules with FDM such as the interlayer adhesion. As a result of these findings, it was decided to always produce the Model 1 capsules with the external coating, as in Section 2.1.

After testing the ability of the capsules of correctly retaining the healing agents inside the capsules, it was investigated their ability of protecting them by the harsh cementitious environment. Therefore, Model 1 capsules produced with each plastic filament were filled either with the liquid sodium silicate or the moisture-reactive polyurethane precursor that would have been used as healing agent for testing the mechanical recovery after cracking (see Section 3.1) and embedded inside cement mortar prisms during casting. After 28 days of curing in water, the specimens were split in half to check the viability of the healing agents. Regardless of the plastic used for printing, the sodium silicate was still liquid and available for enabling the self-healing effect, while the polyurethane was already hardened inside the capsules (Figure 4).

Figure 4: Polyurethane hardened inside Model 1 capsules embedded in the cement mortar matrix.

In light of these findings, a more protective coating system was deemed necessary. Consequently, Model 2 capsules were designed in order to face these further requirements. The application of the double protective coating on the capsule shell before filling it, allows to reduce the possibility of moisture ingress during mortar samples curing.

The retaining ability of the Model 2 capsules was tested in the same way as Model 1, by monitoring the encapsulated water loss over time. For each material used for printing, two Model 2 capsules (as in Figure 3.e) were produced and filled, for a

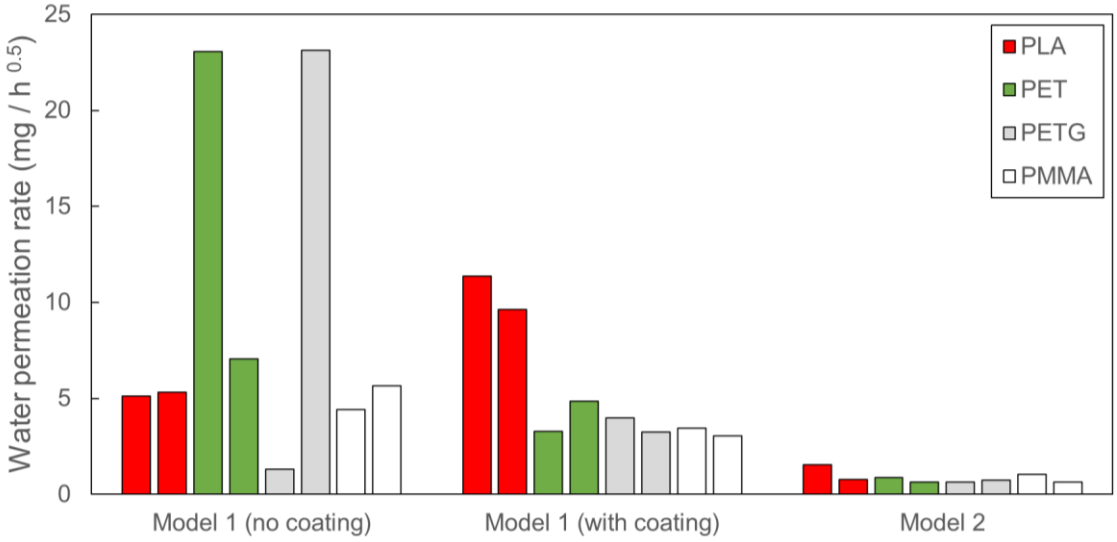

Figure 5: Water permeation rate of Model 1 capsules (with or without coating) and Model 2 capsules.

total of 8 capsules.

Figure 5 shows the comparison between the water permeation rates obtained for the Model 1 capsules (with or without coating) and the Model 2 capsules, in which it is possible to see the water loss reduction, hence a better retaining of the healing agent, when Model 2 is used. These findings about the better protection provided by the Model 2 were confirmed by filling these capsules with the polyurethane precursor and embedding it in the mortar matrix. Unlike Model 1, the Model 2 capsules were able to correctly protect the reactive healing agent during mortar samples curing and releasing it upon cracking.

The shell continuity of the capsules plays a leading role on the tightness of the capsules. In order to investigate and compare the shell continuity of the capsules printed with the four different polymers, without coating and with the double coating used in the Model 2 configuration, they were sputter coated with gold and their surfaces were analyzed using a Field Emission Scanning Electron Microscope (FE-SEM Hitachi S-4000). Figure 6 shows the 60x magnification images of the capsules printed with each material, with and without coating. It is possible to observe how the printed polymeric capsules in the absence of coatings are not able to effectively isolate the healing agent from the external environment, as they present defects due to the cohesion between the printed filaments. On the contrary, it is possible to observe the effectiveness of the double coating, which allows to obtain a shell free of defects that could cause leakage of the healing agents and vulnerability against the surrounding cementitious matrix.

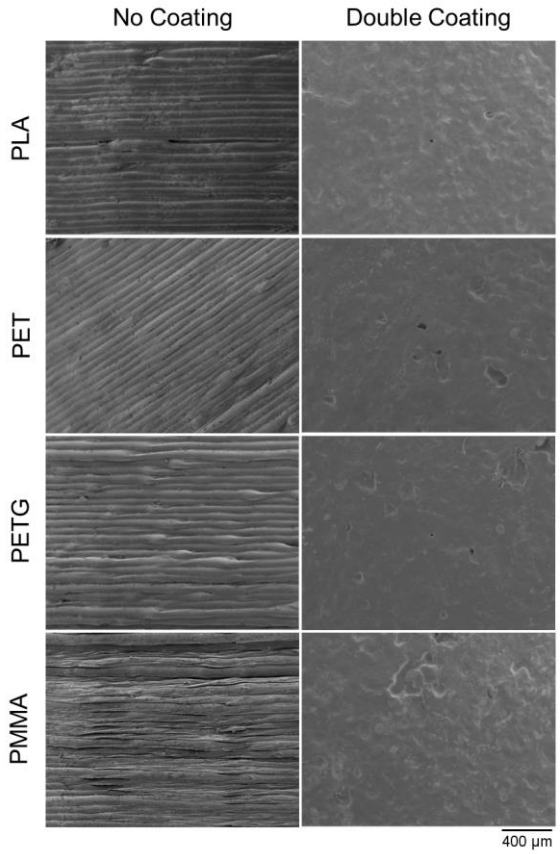

Figure 6: FE-SEM images of the capsules printed with each material, with and without coatings.

3 SELF-HEALING EFFECT

3.1 Self-healing mortar specimens

In order to realize an autonomous self-healing system, the 3D printed capsules were filled either with a liquid sodium silicate solution (Na_2O 10.6 wt%, SiO_2 26.5 wt%, and H_2O 62.9 wt%, provided by Sigma Aldrich) or an expansive polyurethane (PU) resin (CarboStop U, provided by Orica). These healing agents were selected due to the good results obtained in previous studies [3,11,25]. Since sodium silicate encapsulation does not require high protection standards due to its reaction mechanism, it was encapsulated using Model 1 capsules. Conversely, the PU precursor is very moisture-reactive and require to be encapsulated with a sufficiently water/air tight system, hence Model 2 was selected for its encapsulation.

Mortar prisms (40 mm x 40 mm x 160 mm) were made by using ordinary Portland cement CEM I 52.5 N, tap water (water to cement ratio of 0.5) and normalized sand (sand to cement ratio of 3), in accordance with the standard UNI EN 196-1. Mortar is often chosen instead of concrete as cementitious material reference for testing the efficiency of the self-healing systems. In addition to the fact that mortar is more homogenous than concrete, the main reason for using mortar is the often high production cost of the self-healing systems in the prototype phase, thus it is very useful to do a fast screening of their effectiveness in mortar before upscaling them for the use in concrete [29].

The capsules were manually embedded in the middle of the mortar specimens during casting. For each plastic filament, two specimens containing one Model 1 capsule filled with sodium silicate and two specimens containing one Model 2 capsule filled with PU resin were produced for testing the correct capsule breakage and consequent mechanical recovery, for a total of 16 specimens.

After 24 hours covered with plastic foils, the specimens were demolded and then stored in water for 28 days. This curing condition was chosen in order to obtain sufficiently developed properties and allow a high degree of hydration of the matrix, hence limiting the effect of autogenous healing due to unhydrated cement particle and thus being able to attribute the healing efficiency to the contribution of the capsule system.

3.2 Self-healing effect evaluation

At an age of 28 days from casting, the specimens were pre-cracked via a crack-width controlled three-point bending test with a span of 10 cm, using a 100 kN closed-loop servo-controlled MTS hydraulic press. The target maximum crack mouth opening displacement (CMOD) during loading was set at 800 µm, in order to test the ability of the system to heal large cracks and in order to reduce the influence of the autogenous healing. A U-shaped notch was created by saw cutting a day before the pre-cracking procedure, measuring 4 mm in width and 5 mm in height. Figure 7 shows the setup for the pre-cracking phase.

Figure 7: Specimen during the pre-cracking phase.

During the pre-cracking phase, it was possible to observe the leakage of the healing agent up to the external surfaces of the specimens, which denoted the correct breakage of the capsules, thus the triggering of the autonomous healing mechanism. The leakage of the sodium silicate was visible due to the wetting of the crack sides, while for the PU resin it was possible to clearly observe the expansion of the yellow closed-cell foam.

The specimens were stored in air in the laboratory environment for a time well beyond the curing time of both the healing agents, so as to allow the full curing of the healing agents and avoid that water could promote autogenous healing or cause the foaming of the unpolymerized polyurethane that could have remained in the capsules. In order to maintain the condition as close as possible to the crack formation phase, thus better simulating the real healing condition of a damaged structure, the specimens were placed on two supports with a span of 10 cm with the crack mouth pointing downward.

After complete curing of the healing agent and before evaluating the strength regain, a visual inspection of the crack filling was performed. While the PU resin filling was visible to the naked eyes due to its yellow color and the presence of foam above the crack, in order to observe the sodium silicate, a 40x magnification microscope was used. Figure 8 shows the crack on the lateral face of one specimen, filled with the sodium silicate.

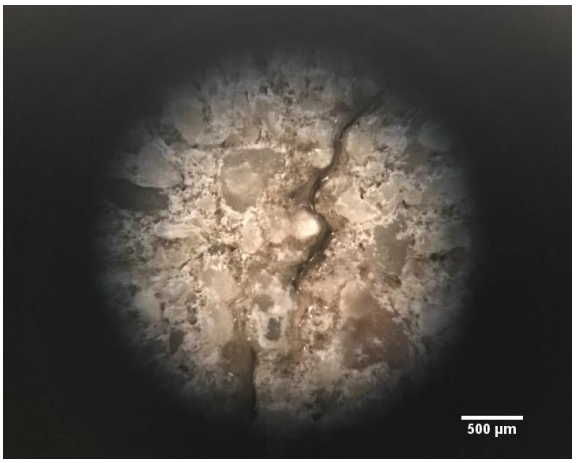

Figure 8: Filling of the crack by the sodium silicate (lateral face of the specimen).

The strength regain was evaluated, after re-loading the healed specimens via a crack-width controlled three-point bending test as in the crack creation phase, through a load recovery index (LRI) [2,3,25]. The load recovery index was defined as:

$$LRI(\%) = (P_r - P_u)/(P_p - P_u)\cdot 100 \qquad (2)$$

where P_r is the peak load obtained during the re-loading stage, P_p is the peak load reached during the pre-cracking stage and P_u is the residual load obtained at the moment of unloading preceding the re-loading stage. Table 4 summarizes the LRI obtained for each tested specimen.

Table 4: Load Recovery Indexes of the self-healing system realized with 3D printed capsules

Material	#	Load Recovery Index (%)	
		Sodium silicate (Model 1)	PU resin (Model 2)
PLA	1	33	22
	2	57	49
PET	1	27	36
	2	18	65
PETG	1	31	35
	2	45	12
PMMA	1	16	46
	2	24	18

On average, both the healing agents showed a good recovery of mechanical properties, with an average LRI of (31 ± 14) % for the sodium silicate and of (35 ± 18) % for the PU resin. The best results for the sodium silicate were obtained when PLA was used as printing material, while in the case of the PU resin the best printing material was PET.

After completion of the mechanical recovery testing, the samples were split at the location of the crack in order to visually evaluate the spreading of the healing agent on the crack faces, in order to gain a qualitative information about the filling of the crack. Figure 9 shows an example of the spreading of the sodium silicate and the PU resin that highlights in both cases a large covered area, hence a good bridging of the crack faces.

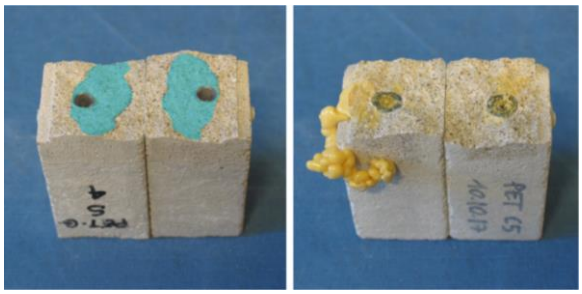

Figure 9: Spreading of the liquid sodium silicate (left) and the PU foam (right) on the crack faces. The area covered by the sodium silicate was colored in cyan in order to highlight its spreading region.

4 CONCLUSIONS AND FUTURE PERSPECTIVES

In this work, Fusion Deposition Modelling was used to produce novel macro-capsules to be used in self-healing cementitious systems. Four different types of thermoplastic filaments were selected, based on characteristics that make them suitable for the requirements of a functioning autonomous self-healing system.

Two types of tubular capsules were produced, namely Model 1 and Model 2 capsules, with slightly different shapes and different sealing and coating configurations. The two models were characterized in terms of water tightness and shell continuity, which proved them effective to be used to encapsulate liquid healing agents and highlighted their unique features. The Model 1 capsule presents simple manufacturing, filling and coating procedures and was proved suitable for the encapsulation of healing agents that does not require a perfect air and water tight encapsulation system, such as liquid silicates. However, it is not suitable for reactive healing agents, which require on the contrary a better protection from the humid cementitious environment, such as polyurethane precursors. To overcome this limit, the Model 2 capsule was designed in order to guarantee high performances in terms of tightness at the cost of a slightly more complex sealing, coating and filling procedure. Both models, when filled with the healing agents suitable for their characteristic features, showed satisfactory results in terms of mechanical recovery and spreading of the healing agent on the crack faces. This last feature suggests a good self-sealing ability, which is very important for preventing the ingress of harmful substances inside the fractured matrix. This aspect will be further investigated through tests aimed to assess self-sealing and durability-related features, such as water permeability and absorption tests.

These positive results show a good potential of the proposed capsule-based system for structural applications. This work served as proof of concept of the use of Additive Manufacturing to produce self-healing encapsulated system, by using simple tubular capsules for the sake of comparison of extensively investigated system. Further improvements can be envisaged through the optimization of the capsule shape, for which the 3D printing technology offers virtually unlimited tailoring possibilities.

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