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Andrés Miguel Panza Uguzzoni[1], *Giovanni* Anglani[2], *Paola* Antonaci[2], and *Jean-Marc* Tulliani[1*]

[1]INSTM Research Unit PoliTO-LINCE Laboratory, Department of Applied Science and Technology (DISAT), Politecnico di Torino, 10129 Torino, Italy
[2]Department of Structural, Geotechnical and Building Engineering (DISEG), Politecnico di Torino, 10129 Torino, Italy

Abstract. Macrocapsules with an expanding mineral powder were set-up for sealing cracks into cement-based materials. The expanding mineral powder was composed of a commercial fast setting cement mortar, sodium polyacrylate and a commercial product used to produce sparkling water (based on sodium acid carbonate, malic acid and tartaric acid). An optimal proportioning of these components was determined as 10:1:1, respectively. These compounds were first mixed with polyethylene glycol and cast into cylindrical moulds. Then, the mix was heated at 230°C in an oven and the cylinders were demoulded thereafter. The obtained products could be delicately handled and were coated with an epoxy resin to produce waterproofed macrocapsules, while some uncoated cylinders were mixed with water and kept in closed containers for 14 days. Brazilian tests were performed on these hydrated cylinders to determine their indirect tensile strength. Finally, the coated macrocapsules were incorporated into mortar prisms, that were pre-cracked in three-point bending test after 14 days. The prisms were kept under water for 8 days and showed a sealing efficiency of 98.7% with a water flow of 3.8 g/min, which decreased to 3.5 g/min after 18 days of water curing. The same samples were stored 10 more days under water to reach an overall healing time of 28 days, after which they were subjected again to a three-point bending test to assess the recovery of the mechanical properties in flexion. The average recovered flexural strength was (10.6 ±4.5)%.

1 Introduction

Concrete is the most used and produced material in the world. It is characterised by a high compressive strength, but also by a limited tensile strength which makes it prone to cracking. When cracked, rebars in reinforced concrete structures can be easily corroded and the building or the infrastructure can be at risk of collapsing. Thus, in the last decades, self-healing concretes have been deeply investigated in order to increase the service life of cementitious materials and make them more sustainable. Among the different proposed solutions for autonomous healing of concrete, polymeric microcapsules (< 1 mm in diameter) and organic or inorganic macrocapsules (based on PET, PETG, PPMA or PLA, glass, cement…) were proposed [1-5]. Several healing agents based on polymers (polyurethane), inorganic solutions (silanes, sodium silicate…) or microbially induced calcite precipitation by means of bacteria were also extensively studied [1]. However, there is a concern about the effective durability of organic healing agents, considering that they could be required to remain active for decades before cracks will appear and the healing agent should be released.

Super absorbent polymers (SAPs) or hydrogels can take up a large amount of water (sometimes more than 1000 times their own weight) and entrap it in their 3D structure. When cracks occur, SAP can be exposed to humidity deriving from the environment and swell, partly sealing the fissures. After swelling, SAP particles release water to the surrounding matrix, exerting an internal curing effect. Then, further hydration products can then be formed, and calcite can also precipitate. In this way, fissures may seal completely [6]. However, SAPs alone can be subjected to erosion and removed from cracks by water or air flows when fully dried, because they withstand a reduction in size during the dehydration phase [6].

Thus, in this work, macrocapsules with an expanding mineral powder were set-up for sealing cracks and preventing water to penetrate into cement-based structural elements. Specifically, mixtures of a commercial fast setting cement mortar, as a healing agent, a commercial product used for the production of sparkling water, as an expanding agent, and sodium polyacrylate (SAP), as an internal curing agent, were investigated. In fact, the expected healing mechanism should be a combination of physical blocking because of the expansion in the cracked area of the cementitious mortar due to the production of gas by the expanding agent, in presence of water, and the formation of hydrated products promoted by the internal curing action of the SAP.

2 Materials and methods

A fast-setting mortar was used as the main component of the healing agent (Rassasie Cemento rapido, Italy,

* Corresponding author: jeanmarc.tulliani@polito.it

component A). It is made of cement type II 32.5R (cement with lime; no information on the percentage of cement replacement), quartz sand and special admixtures [7]. After water addition (23-25 wt% of mix), the pot life is 2 minutes [7]. The recommended uses are among all: quick repairs of degraded masonry, filling of cracks in plasters, setting accelerator for mortars in case of low temperature works [7]. The mortar was analysed by X-ray diffraction (Pan'Analytical X'Pert Pro, The Netherlands; CuKd anticathode) in the 2t range 5-70°. The hydrated material (50 mg) was analysed by thermogravimetric-differential thermal analysis (TG-DTA; LabSys evo, Setaram, France) under static air with a heating ramp of 10 °C/min up to 1000 °C. Its compressive strength over time is reported in Table 1.

The expanding agent was a commercial product made of a mixture of sodium bicarbonate, malic acid and tartaric acid (Idrolitina, Ristora, Italy, component B). It is a white powder, that, when in contact with water, produces an effervescent effect because sodium bicarbonate reacts with the other acids releasing CO_2, responsible for the effervescence. By measuring the volume of carbon dioxide produced by 0.5 g of this mix in presence of 50 mL of water, and using the perfect's gas law, a ratio of 1:2 was calculated for sodium bicarbonate/malic + tartaric acid.

Table 1. Fast setting mortar features after the addition of 23-25 wt% of water.

Compressive strength (MPa)	Time
9	1 h
15	3 h
25	3 days
40.5	28 days

Finally, a commercial hydrogel for agriculture was used as SAP [8] (component C). Its size was in the range 0.2-0.6 mm.

Different proportions of the three components were prepared (A:B:C = 20:2:1, 15:2:1 and 10:1:1) by manual mixing in an agate mortar with an agate pestle. 5.6 mL of each of these mixtures were put in a plastic tube (with an internal diameter of about 13 mm) and 4 mL of water were added (3 samples for each composition). After CO_2 production, the tubes were sealed for curing. These samples were then demoulded after 14 days and submitted to indirect tensile test (Brazilian test; MTS Insight 1 kN – standard length, displacement-controlled test with constant velocity of 0.015 mm/s).

Finally, the composition that led to the best results from the previous mechanical tests was selected to produce the macrocapsules to be embedded into 4 × 4 × 16 cm^3 prisms for flexural tests. To this aim, the mix was added with polypropylene glycol (PPG, about 0.3 g of PPG per gram of mix) before casting it in a tube (1 cm internal diameter) with a baking paper. Then, the filled moulds were put into an oven (Memmert UFE200, Germany) at 230 °C for 30 min and naturally cooled down to room temperature by switching off the oven. At that point, the capsules were painted with an epoxy resin (Plastigel, API SpA, Italy) by means of a brush to make them waterproof (Fig. 1). In fact, the epoxy coating is mandatory to protect cement grains from the contact with water during samples manufacturing and to prevent their undesired hydration. The selected naval epoxy resin is a commercial solvent-based product already successfully used in the past for waterproofing cementitious macrocapsules [2-4].

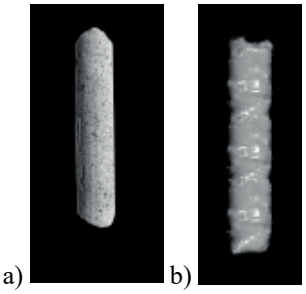


Fig. 1. Uncoated capsule: a); Epoxy coated capsule: b).

Mortar prisms were manufactured with a standardized mortar mix composition, in agreement with EN 196-1. Portland cement (CEM I 42.5 N, Buzzi Unicem S.p.A., Italy), normalized sand (grading 0–2 mm, DIN EN 196-1), and tap water were used. The water to cement ratio was equal to 0.50, and the sand to cement ratio was 3. One capsule was fixed in the center of each mold by means of a nylon wire, at about one third in height (Fig. 2). A notch was also generated in the samples by means of a removable steel element placed at the bottom of the molds. The specimens were made with a cast-in hole to allow the subsequent execution of a water flow test (Fig. 2). The longitudinal cast-in hole was produced by mounting in the mould a smooth steel bar (with a diameter of 5 mm) previously covered in demoulding oil, to remove it upon demoulding. The cast-in hole had its centre at 25 mm from the bottom side of the specimens.

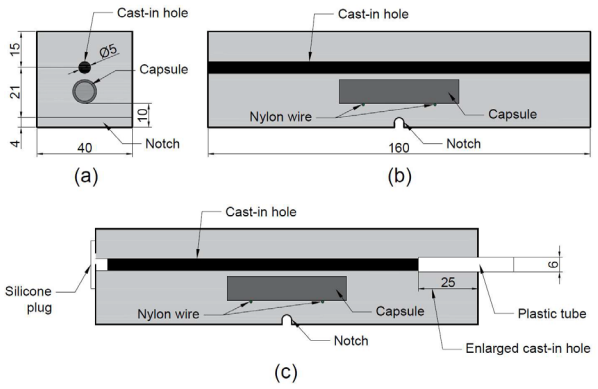


Fig. 2. Schematic cross-section of the specimens at the midpoint (a), longitudinal section after casting (b) and after the preparation for the water flow test (c) (dimensions in mm).

The moulds were filled in two layers, each one compacted on a jolting table by 60 jolts. In addition, the moulds were covered with plastic foils prior to demolding, the day after casting. To conclude samples preparation, the samples were cured for 14 days under water at room temperature. Four samples were made without any capsule (as a reference) and four others contained one capsule each.

The specimens were cracked in a three-point bending test with a span of 100 mm by means of a 250 kN closed-loop servo-controlled MTS hydraulic press. The target maximum crack mouth opening displacement (CMOD) under loading conditions was fixed at 600 µm (Fig. 3).

Fig. 3. Sample during the pre-cracking step; on the right side, the tube for the water flow test is visible.

The load recovery index (*LRI(%)*) was evaluated after the re-loading stage in accordance to equation 1:

$$LRI(\%) = 100.\frac{P_1 - P_u}{P_p - P_u} \qquad (1)$$

Where P_1 is the peak load measured during the re-loading stage, P_p is the peak load attained during the pre-loading stage (i.e., when the crack is created in the intact material) and P_u is the residual load, corresponding to the specimen load-bearing capacity upon reaching the target value of 600 µm during the first loading stage.

After cracking, the samples were kept under water at room temperature for 8 days to allow them to repair autonomously. The water permeability of the cracked/repaired specimens was measured using a water flow test (Fig. 4) [9, 10].

The specimens were first submerged in demineralised water for 24–48 h to limit water absorption by the cementitious matrix on the water flow test results. Afterwards, the specimens were removed from the water and surface-dried with a sheet of paper. On one side, before cracking, the cast-in hole was enlarged to a diameter of 6 mm over a length of (25 ± 5) mm by drilling. In this way, it was possible to insert a short plastic tube (length of ~ 60 mm, internal and external diameters = 4 and 6 mm, respectively) into the cast-in hole over a fixed portion. The plastic tube was then glued using silicone, to prevent possible leakages during the water flow test. The other side of the cast-in hole was clogged with a silicone plug. Finally, the lateral faces of the crack were sealed by means of silicone before the sample saturation to ensure that the water could leak out of the specimen only through the crack mouth (Fig. 2).

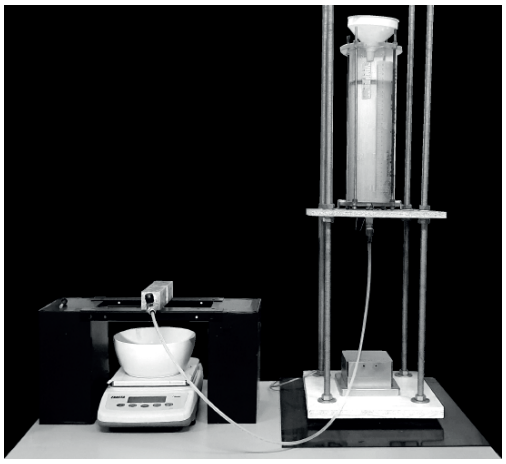


Fig. 4. Sample during the water flow test.

During the water flow test, the plastic tube was connected to an open water reservoir. The water head, measured from the centre of the cast-in hole up to the upper water level, was kept constant during the measurements at (50 ± 0.5) cm by constantly refilling the tank with demineralised water. Thus, the pressure was kept constant at ~ 0.05 bar.. A PC connected to a balance (Exacta Optech 7000, Germany) allowed to record the water flow. The data recorded during the first 60 s of water leakage were discarded, in order to let water bubbles go out of the system and have a regular flow. Subsequently, the weight of the water permeating through the crack was recorded for at least 6 min. The water flow (g/min) was then expressed as in equation 2:

$$WF = \frac{\Delta_m}{\Delta_t} \qquad (2)$$

Finally, the sealing efficiency (*SE(%)*) was defined according to equation 3:

$$SE(\%) = 100.\frac{WF_{ref} - WF_{caps}}{WF_{ref}} \qquad (3)$$

Where WF_{ref} is the average water flow determined for reference samples, while WF_{caps} is the water flow measured on each sample containing a capsule. The tests were performed after 8 and 18 days of water curing.

3 Results and discussion

3.1 Mortar characterisation and indirect tensile test results on capsules

Fig. 5 reports the X-ray diffraction (XRD) pattern of the used mortar. Calcium carbonate (calcite, JCPDF card n° 05-0586) was the main phase, while dicalcium silicate ($2CaO.SiO_2$, C_2S, JCPDF card n° 20-0237) and tricalcium silicate ($3CaO.SiO_2$, C_3S, JCPDF card n° 42-0551) were minor phases. Neither gypsum, nor anhydrite were detected, probably because this is a fast-setting mortar. More surprisingly, quartz was not visible too (main peak at 26.64° in 2theta, JCPDF card n°46-1045).

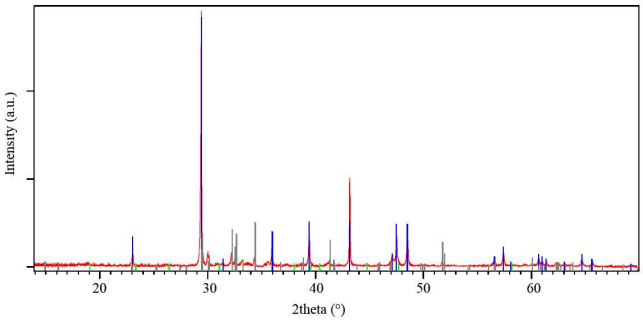


Fig. 5. XRD pattern of the commercial mortar used as the healing agent (blu=calcite, grey=C_3S, green=C_2S).

The TG-DTA curve of the hydrated mortar (Fig. 6) showed three exothermic peaks at 115.6, 449.3 and 842.6 °C.

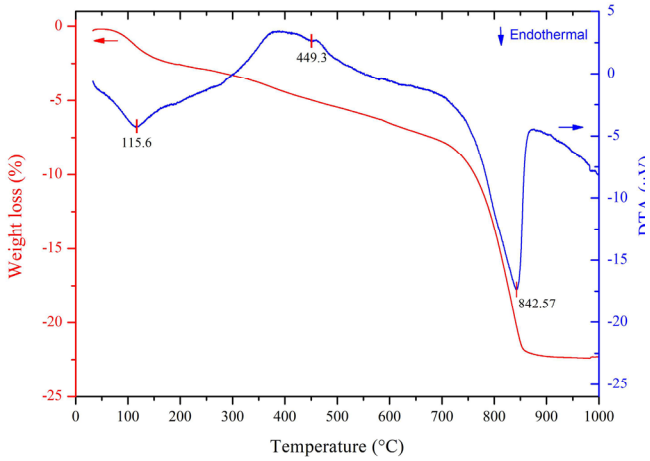


Fig. 6. TG-DTA curve of the commercial mortar used as the healing agent (blu=calcite, grey=C_3S, green=C_2S).

The first peak is due to thermal decomposition of calcium silicate hydrates (C-S-H), the second peak is due to portlandite dehydration ($Ca(OH)_2$), while the last peak is related to the decarbonation of calcite. These results agree with XRD ones. The mass loss, in the temperature range from 695 °C to 930 °C, was 14.6%. Considering the theoretical mass loss in a pure lime sample, the calcite content in the sample was estimated to be about 33.2%.

The indirect tensile tests results are reported in Table 2. The composition 10:1:1 (mortar:expanding agent:SAP) gave the best results, which was rather surprising as this mix contained the lowest amount of mortar. However, the other mixtures contained a higher amount of expanding agent and were probably more porous.

The mixtures prepared with polypropylene glycol were first selected based on the possibility to handle them in order to coat them by brushing with the epoxy resin. Then, the tensile strength determined on the hydrated mixtures was chosen as a criterion considering the stresses that the capsules must withstand when handling before casting and during flexural tests.

Table 2. Brazilian tests results.

Sample	Tensile strength (MPa)
10:1:1	0.64 ± 0.26
15:2:1	0.42 ± 0.08
20:2:1	0.32 ± 0.20

3.2 Tests on prisms

Figure 7 depicts an example of a load vs CMOD curve resulting from pre-loading and re-loading stages for a prism with a coated capsule. The load recovery indexes determined as per equation 1 were quite low and equal to 10.4% on average.

Considering the trend of the load vs CMOD curve reported in Fig. 7, it is easy to infer that the capsule broke in the range of crack width from 0.2 to 0.4 mm where a certain instability of the load due to the control action of the testing machine is visible. On the contrary, the softening part of the curve in the samples without capsules was continuously decreasing after the peak load and showed no mechanical regain in the subsequent re-loading stage. Neither pull-out, nor debonding of the capsules from the mortar matrix were ever observed in the tested prisms.

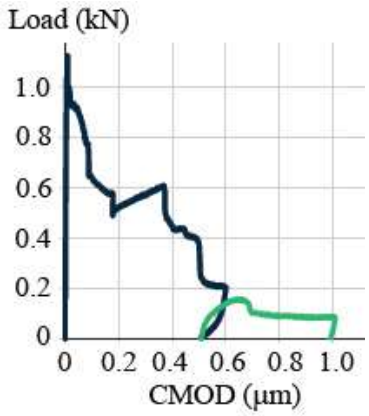
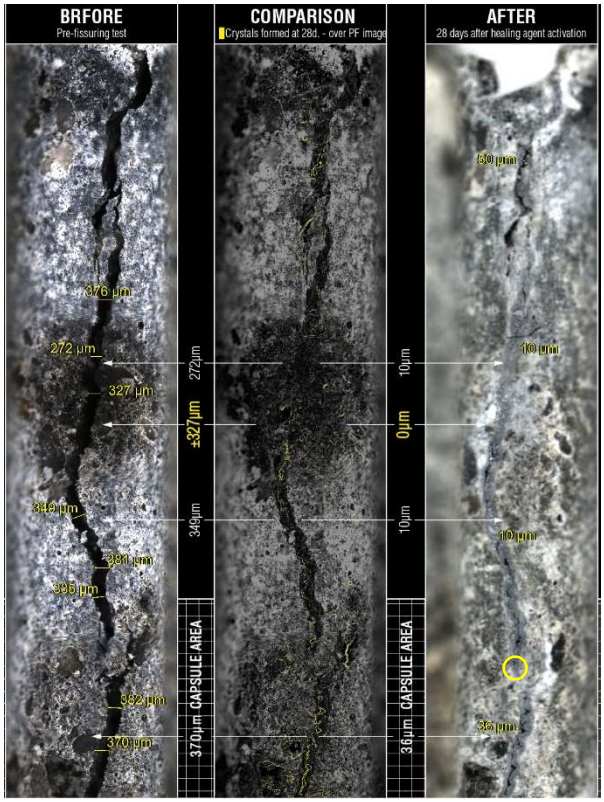


Fig. 7. Example of a load vs CMOD curve resulting from pre-loading (black curve) and re-loading (green curve) stages for a sample with a coated capsule.

Conversely, the sealing efficiency calculated in accordance with equation 3 after 8 days was already very high (98.7% ± 2.2%) and remained almost constant after 18 days (98.8% ± 2.3%). These values are even higher than those obtained using extruded cementitious capsules containing different healing agents [11]. The average water flow values were equal to 3.8 g/min and 3.5 g/min, respectively after 8 and 18 days of curing. For the sake of comparison, the average water flow value was 292.1 g/min for the reference samples. These very good results could be ascribed to the combined effect of the expanded healing mortar in the cracks and the use of SAPs.

The samples were also observed by means of a stereomicroscope (SMZ18, Nikon Corporation, Japan) after cracking and repairing (Fig. 8). The partial closure of the crack is evident and can explain the mechanical, as well as the water flow tests results (Fig. 9). In fact, the average crack aperture on 8 measurements was equal to (346 ± 10) μm after cracking, while after repairing, it decreased to (26.5 ± 19.9) μm.



a) b) c)

Fig. 8. Optical micrographs of: as-cracked a); comparison after cracking and repair b); repaired c) sample. The circled area corresponds to the magnification shown in Fig. 9.

Fig. 9. Optical micrographs of a detail of a repaired zone.

4 Conclusions

A new healing agent based on a mix of a commercial fast setting mortar, a mineral expanding agent and SAPs was successfully proposed. Among the different investigated compositions, the mixture 10:1:1 (mortar:expanding agent:SAP) gave the best results during indirect tensile tests on capsules.

Three-point bending tests showed limited load recovery indexes, around 10%, after 8 days of healing. However, the sealing efficiency was very high (close to 99%) respect to reference samples.

These preliminary results indicate that the proposed solution is promising but needs further development. One key point of the system is probably the setting rate of the mortar which should be investigated with other binders with different setting time. Specifically, the binder should allow water to permeate through the cracks and the complete expansion of the mix before setting, to fill in as much as possible the damaged area.

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