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Design of polymeric capsules for self-healing concrete

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Abstract

Up to now, glass capsules, which cannot resist the mixing process of concrete, have been mostly used in lab-scale proof-of-concept to encapsulate polymeric agents in self-healing concrete. This study presents the design of polymeric capsules which are able to resist the concrete mixing process and which can break when cracks appear. Three different polymers with a low glass transition temperature T_g have been extruded: Poly(lactic acid) (PLA) ($T_g = 59^\circ\text{C}$), Polystyrene (PS) ($T_g = 102^\circ\text{C}$) and Poly(methyl methacrylate/n-butyl methacrylate) (P(MMA/n-BMA)) ($T_g = 59^\circ\text{C}$). After heating the capsules prior to mixing with other components of the mix, to shift from a brittle state to a rubbery state, their survival ratio considerably increased. Moreover, a part of the capsules, which previously survived the concrete mixing process, broke with crack appearance. Although some optimization is still necessary concerning functional life of encapsulated adhesives, this seems to be a promising route.

Keywords: Self-healing Concrete, Polymers, Capsules, Mixing, Mortar, Cracks

1. Introduction

In concrete structures, cracks often appear due to the limited tensile strength of concrete. These cracks endanger the durability as aggressive substances, dissolved in fluids and gasses, can easily flow inside the matrix and lead to structural failure by reinforcement corrosion. Moreover, cracks are also considered undesirable for aesthetic reasons. Due to regular and planned inspection rounds followed by proper treatments, maintenance costs of concrete structures are quite high nowadays. It has been estimated that, in Europe, around 50 % of the annual construction budget is spent on rehabilitation and repair of the existing structures [1, 2].

Therefore, making self-healing concrete could highly reduce the maintenance costs and improve the durability of concrete structures. Under control, self-healing could be taken into account by designers to meet project owners' durability expectations, following the 'damage management concept' introduced by Van der Zwaag in opposition to the actual 'damage prevention principle' widely used in construction codes [3]. Consequently, service life of structures would increase considerably.

Encapsulation of healing agents is a very effective method to obtain complete sealing of the crack with chemical agents, to avoid penetration of aggressive substances and, in some cases to obtain partial regain in mechanical properties which is an important aspect to guarantee the performance during service life (succession of crack formations) [4]. However, up to now, glass capsules have been mostly used [5-11] to store the healing agent. They break upon crack appearance but they cannot resist the concrete mixing process without particular protection (protection by a cement paste bar or a

metallic wire seem limited [12, 13], only bundling the capsules with a water soluble solution is reported to protect them while mixing in a truck [14]). This can be explained by their brittleness and their dimensions (glass tubes with a wall thickness of 2 mm are able to rupture upon crack formation, 3 mm thick tubes cannot break any more upon crack formation [15]. Survival of the concrete mixing process would facilitate the application of self-healing materials and decrease their price by reducing human work. An evolution towards polymeric encapsulation materials could be the means to adjust capsule properties more easily and to resist the mixing process (as suggested by Dry [16]). Besides glass, some natural fibres [17, 18], gelatine capsules [1], paraffin to enclose water [19], wax [20] and polyurethane [21] have been used. Ceramic, a very brittle material, has also been used by Van Tittelboom [4] who observed a better bond strength than with glass. Spherical capsules can be successfully mixed in concrete [1, 20-26] but cylindrical capsules present better chances to break upon crack appearance [13] and release the healing agent more efficiently [27] even if their orientation is still a concern. Polypropylene capsules coated with wax and heated to release the capsules content [8] have been studied to produce capsules able to resist the concrete mixing process.

This study explores the development of polymeric capsules that are able to survive the concrete mixing process without any particular protection, and to break upon crack appearance without human intervention. The selected polymers are brittle at room temperature and have a relatively low glass transition temperature. Consequently, their ability to resist the concrete mixing process, when they were heated before mixing and mixed with heated components, was studied. The capsule breakage with crack appearance was measured by the means of three-point-bending tests performed on small mortar specimens.

78

79

80 **2. Materials and methods**

81 **2.1 Materials preparation**

82 **2.1.1 Extrusion of the capsules**

83 In order to be able to change easily the mechanical properties of the capsules, polymers
84 with low glass transition temperatures have been selected. Indeed, around their glass
85 transition temperature, the physical properties of polymers change considerably. At first,
86 polymers with a glass transition temperature between 35 °C and 50 °C were sought for.
87 Later, this range was extended until 100 °C to include cheaper and more common
88 materials. On the other hand, specific attention was paid to select polymeric materials
89 with a relatively brittle behaviour at room temperature (low elongation at rupture,
90 relatively high tensile strength). The permeability of the polymers was also taken into
91 account because it may influence the shelf-life of the healing agent embedded inside the
92 polymeric capsules.

93 Finally, three polymers have been selected:

94 - Poly(lactic acid) (PLA) is derived from renewable resources (sugar cane, corn, tapioca)
95 and is biodegradable. It has a low T_g (around 60 °C) and can break at limited elongation
96 (1 to 10 %). PLA is largely used in food industry to replace polystyrene but exhibits a
97 relatively high water-vapour transmission rate [28-31]. No application of PLA in
98 concrete or buildings materials is known by the authors.

99 - Polystyrene (PS) is a common plastic known for its brittleness (elongation at rupture
100 inferior to 2 %) and its good chemical resistance as it is used for food packaging. It is
101 cheap but its T_g comes close to 100 °C. Its permeation properties are relatively good and

close to the ones of PLA [32]. Expanded polystyrene is used as aggregate in place of sand and stone in lightweight concrete [33-36].

- Poly(methyl methacrylate/n-butyl methacrylate) (called P(MMA/n-BMA) in this study) with a catalogued T_g of 50 °C. It has been considered in this study because of the brittleness of Poly(Methyl Methacrylate) and the low T_g of P(MMA/n-BMA)(while T_g of pure PMMA is around 105 °C). Although pure PMMA has been compared to concrete because of its brittle behaviour [37] and has been incorporated as a waste material in asphalt mixes, no other application of P(MMA/n-BMA) in civil engineering is known by the authors [38-40].

A laboratory-scale inter-meshing co-rotating twin-screw extruder (MP19TC-25, APV Baker, Newcastle-under-Lyme, UK) with a length over screw diameter ratio (L/D) of 25:1 was employed to extrude hollow tubes using a die with an outer hole of diameter 5 mm and an inner pin of diameter 3 mm. The temperature settings used during the extrusion process to obtain a good melt without degradation, are presented in Table 1.

Table 1: Temperature settings (°C) at several locations in the extruder for extrusion of the different thermoplastics.

Polymer	T1 (breaker plate)	T2	T3	T4	T5 (entrance of the barrel)
PLA	135	148	152	150	145
P(MMA/n-BMA)	127	131	130	130	123
PS	178	171	165	160	150

Different sizes of tubes were obtained due to different expansion ratios of the polymers. Along the same tube of a length of 1 meter, the thickness and the diameter also varied. Hollow tubes were cut at 5 cm length or 10 cm length for the different tests. Capsules were sorted in different size ranges and their cross section area was measured by means

of a light microscope. The mean values of the measured sizes are presented in Table 2 (standard deviation which was relatively small (maximum 0.2 mm) is not mentioned). As PS capsules had almost all the same dimensions, they were not sorted. Rods were also extruded with dies with holes of 1.8 mm and 4.9 mm to perform dynamic mechanical analysis (DMA).

Table 2: Approximate dimensions of extruded capsules for the different size ranges (mean values of the outer diameter [mm] and the inner diameter [mm]).

Polymer	S1	S2	S3	S4	S5
PLA	1.9, 1.1	3.5, 1.8	4.0, 2.1	4.5, 2.6	5.2, 3.2
P(MMA/n-BMA)	6.0, 3.3	6.4, 3.4	6.6, 3.6	6.7, 3.8	6.8, 4.0
PS	7.2, 3.8				

PLA, P(MMA/n-BMA) and PS have been successfully extruded with a relatively wide range of temperature settings (± 5 °C in values specified in Table 1 can also lead to a successful extrusion) and no sign of degradation.

2.1.2 Preparation of the mortar samples

Bond strength test and three points bending test have been performed to show the interest of polymeric capsules in self-healing concrete.

Bond strength tests have been performed in order to ensure that the capsules would not slip in the concrete matrix during crack formation. To measure the bond strength, 5 cm long polymeric tubes filled with epoxy were partially embedded (10 mm) inside mortar samples (W/C = 0.5).

Tubes were placed in holes in wooden frames and their position was adjusted before casting of the mortar into cylindrical PVC moulds (diameter 100 mm, height 50 mm) as

illustrated in Figure 1. After casting, the samples were stored in an air-conditioned room (20 °C, 95% RH) and demoulded after 24 hours. Subsequently, they were cured at room temperature (20 °C, 60% RH) during 14 days until testing.

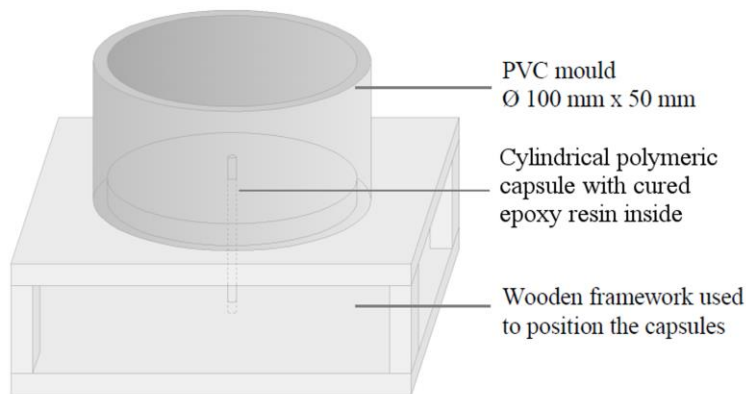


Figure 1: Moulds used to prepare the mortar samples with the embedded capsules for the bond strength tests (redrafted after [13]).

In order to quantify the ability of the capsules to break at the moment of crack formation, mortar specimens containing capsules were prepared. Mortar mixtures consisted of 1350 g DIN standard sand, 450 g binder and 180 g water ($W/C = 0.4$). They were prepared according to the standard NBN EN 196-1 (2005).

First, a layer of 10 mm mortar was poured into 40 mm x 40 mm x 160 mm moulds. Two steel reinforcing bars with a diameter of 2 mm were placed on top of the mortar layer to avoid premature failure during crack formation. Two to four capsules were positioned in the middle of the specimen where the crack was presumed to appear as illustrated in Figure 2 before filling the mould completely.



Figure 2: Preparation of mortar prisms with embedded capsules and reinforcement.

PS, PLA and P(MMA/n-BMA) capsules were placed in the mortar specimens. As illustrated in Table 3, some capsules which survived mixing were embedded, as well as ‘new’ capsules which were not mixed previously.

Table 3: Capsules embedded in mortar specimens.

Specimen	Polymer	Number of specimens	Number of capsules per specimen	Already mixed hot (MH), or cold (MC), and eventually deformed (D), or new (N)	Approximate size (range of size, cf Table 2)
PBS3MH	P(MMA/n-BMA)	2	3	MH	S3
PBS1MH	P(MMA/n-BMA)	2	3	MH	S1
PBS3MHD	P(MMA/n-BMA)	2	3	MH & D	S3
PBS3N	P(MMA/n-BMA)	2	4	N	S3,S4
PLAS3MC	PLA	1	4	MC	S3
PLAS2MH	PLA	2	4	MH	S2
PLAS1MH	PLA	2	4	MH	S1
PLAS1N	PLA	2	4	N	S1
PSN	PS	2	2	N	
PSMC	PS	2	2	MC	
PSMH	PS	2	2	MH	

2.2 Experimental methods

2.2.1 Tensile tests and quantification of the resistance in cement slurry

Tubes with a length of 10 cm were cut from the hollow tubes. They were filled with epoxy the first 4 cm from both ends in order to centralize the rupture in the 2 cm length central part. To quantify the influence of a possible degradation of the polymer capsule in a high pH environment, some tubes were immersed during 7 or 14 days in cement slurry with a water to cement ratio of 10 (pH between 12.5 and 13), before performance of the tensile tests. Then, nuts were glued at the end of the tubes with epoxy resin. The

nuts and the parts of the tubes filled with epoxy resin were covered by epoxy paste to avoid slippage. Screws were introduced into the nuts and linked to the apparatus with a ball-and-socket joint as illustrated in Figure 3.

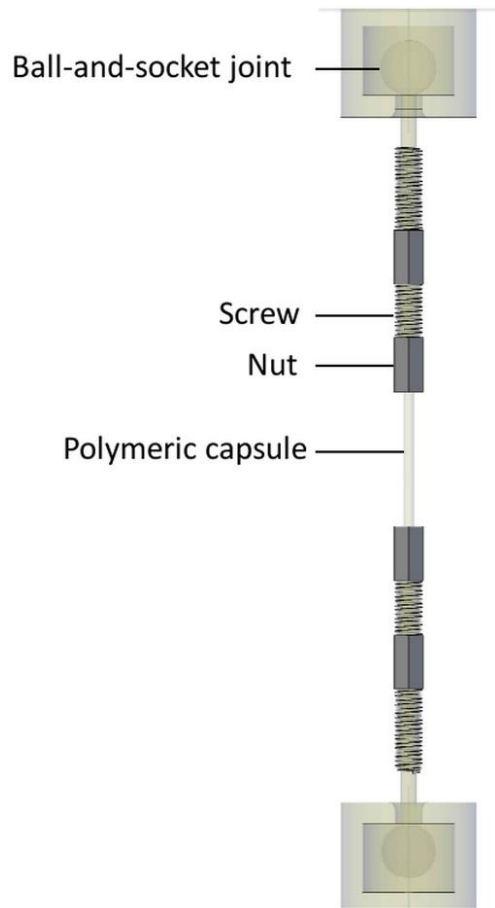


Figure 3: Test setup used to determine the tensile strength of the polymeric capsules.

A displacement controlled tensile test was executed at a speed of 2 mm/min. Five repetitions were provided for each polymer type. After breakage of the tubes, the cross-section was measured for each tube end by means of a light microscope so the tensile strength σ_t and the elongation at rupture $\epsilon_{\%}$ could be calculated.

2.2.2 Bond strength tests

Before the test, a nut was glued to the tube to one end, and the other end was 10 mm embedded into the mortar. For the test, the mortar cylinder was fixed in a metallic frame and the screw thread placed in the nut was connected to the apparatus. The loading rate was fixed at a value of 2 mm/min. For each polymer, 4 or 5 repetitions were provided. The bond strength could be calculated from the measured load according to equation 1 [13, 41].

$$\tau = \frac{F_p}{\pi \times d \times l} \quad (1)$$

Where τ is the bond strength [N/mm^2], F_p is the force measured when the tube is pulled-out (or maximum force if the tube is not completely pulled-out) [N], d is the tube outer diameter [mm] and l is the embedded length of the tube [mm].

2.2.3 Differential Scanning Calorimetry

In order to determine accurately the glass transition temperature (T_g) of the polymers, differential scanning calorimetry (DSC) was performed.

2.2.4 Dynamic Mechanical Analysis

DMA was performed to investigate the evolution of the storage modulus (E'), the loss modulus (E'') and the damping (which is the ratio of E''/E') within a temperature range of 20 °C - 120 °C. Plastic rods with a diameter of 1.8 mm and 4.9 mm were extruded and placed in a Mettler-Toledo DMA/SDTA861e machine. A sinusoidal load was applied in the centre of the sample while both sides were fixed. The response is measured by a linear variable differential transformer (LVDT) and the temperature of the sample is measured by a thin metallic wire.

2.2.5 Compatibility with healing agent

As the capsules must preserve the healing agent until the appearance of cracks, the compatibility with the healing agent was investigated. After sealing the capsules at one side with fast curing MMA glue (X60, HBM, Germany), 5 capsules of each type of polymeric material were filled with a pre-polymer of polyurethane (PU) which cures in contact with water and 5 capsules were filled with water and accelerator (10% of accelerator for Meyco MP 355 1K) [4]. After sealing the other side with MMA glue, the visual aspect of the capsules was controlled regularly during 14 days: after 1, 2, 5, 10 and 14 days to observe any eventual healing agent colour change which could indicate premature hardening.

2.2.6 Mixing tests

In order to prove the efficiency of adjusting the brittleness of polymeric capsules with temperature, mixing tests have been performed to compare the resistance of capsules at room temperature and heated capsules. Hollow tubes with a length of 5 cm were used as capsules. After sealing one end with MMA (X60, HBM, Germany), capsules were filled with water mixed with red dye (in order to visualize capsule breakage), and finally sealed at the other end. For the ‘hot’ concrete mixing test, capsules were heated in an oven during 20 to 40 minutes before the mixing test. The composition of the concrete mixes is detailed in Table 4 and the mixing processes are summarized in Figure 4.

Table 4: Concrete composition for mixing tests.

Components	'Cold' mix (for 10 l of concrete)	'Hot' mix PLA or P(MMA/n-BMA)	'Hot' mix PS
Sand	6.64 kg	6.64 kg (at 80 °C)	6.64 kg (at 105 °C)
Crushed stones 2/6	4.50 kg	4.50 kg (at 80 °C)	4.50 kg (at 105 °C)
Crushed stones 6/20	7.60 kg	7.60 kg (at 80 °C)	7.60 kg (at 105 °C)
Cem I 52.5 N	3.50 kg	0 kg	0 kg
Water	1.65 l	1.65 l (at 100 °C)	1.65 l (at 100 °C)
Capsules	10	10 (at 85 °C-100 °C)	10 (at 120 °C)

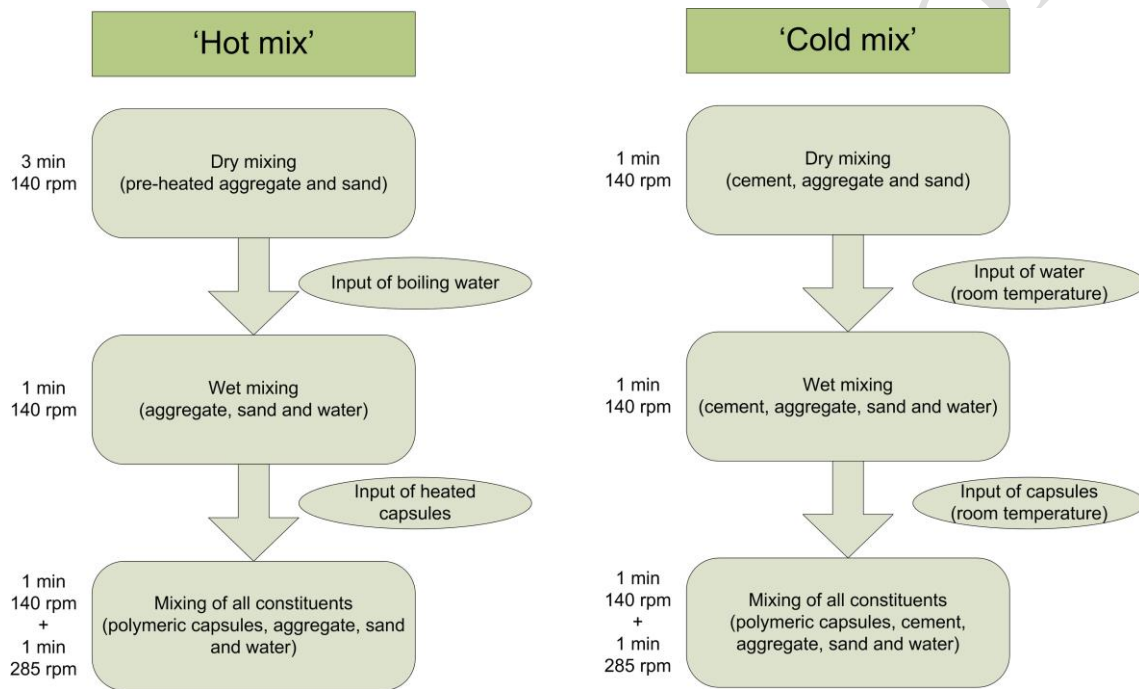


Figure 4: Mixing processes used to study the influence of the temperature on the resistance of the capsules.

First, the dry components (aggregates, sand, cement) with a temperature of around 20 °C were mixed, in an Hobart type D-300 mixer, at a speed of 140 revolutions per minute during 1 min for 'cold' mixing. For 'hot' mixing, pre-warmed aggregates and sand (at a temperature decided according to the T_g of the polymeric capsule) were mixed at a speed of 140 revolutions per minute in an initially cold mixer during

approximately 3 minutes (delay is due to the transportation of the heated capsules). Then, water (boiling water for hot mixes) was added and mixed for 1 minute at the same speed. Subsequently, for 'cold' and 'hot' mixes, capsules were thrown in the mix without stopping the mixer. For 'hot' mixes, the added capsules were pre-heated. Their temperature was between 85 °C and 100 °C for PLA and P(MMA/n-BMA) because they were transported in boiling water between the oven (at 85 °C) and the mixer, and around 120 °C for PS capsules which were transported in around 1 minute between the oven (at 140 °C .C) and the mixer wrapped in paper and held in heat resistant gloves. The 'hot' mix was performed without cement in order to avoid premature hardening of the cement. Capsules were mixed with the other ingredients for 1 minute at a speed of 140 revolutions per minute and for 1 minute at a speed of 285 revolutions per minute.

2.2.7 Three-point-bending test with mortar specimens containing capsules

To measure the crack width during the three-point-bending test a linear variable differential transformer (LVDT, Solartron AX/0.5/S) was used. This LVDT had a measurement range of $\pm 500 \mu\text{m}$ and an accuracy of $1 \mu\text{m}$. A walter + bai ag Testing machine (15 kN - 250 kN) was used to perform the three-point-bending test. Two different test methods were used. The first method was used to see if the capsules break when a crack is created and its width increases at a speed of 0.001 mm/s until 0.4 mm (measured by LVDT) after 14 days of curing. Capsule breakage was expected and some pictures were taken when leaching dye of the broken capsules was detected (water mark on the concrete surface). In the second method the mortar sample was completely broken to see whether the capsules break or whether they slip. The second method was applied 1 day after the first method in case the capsules were not broken during the first method. It consisted of a load controlled bending test (without the LVDT). The load

was increased with a speed of 0.1 kN/s. Because the rupture of a specimen was relatively fast, some pauses (30 seconds) were used to see whether the capsules were broken or not.

3. Results and discussion

3.1 Tensile tests and quantification of the resistance in cement slurry

The tensile strength of PLA seems to be the highest according to Figure 5 but results must be nuanced.

The measured tensile strength of PLA (around 60 N/mm²) meets the values reported in literature [28]. For PS capsules, the tensile strength is underestimated as the PS tubes broke inside the epoxy resin, which was situated between the capsule and the nut represented Fig. 3, or the epoxy resin slipped. Tabulated values of PS tensile strength are around 50 N/mm² [42] i.e. twice as high as the measured values. For P(MMA/n-BMA), breakage occurred at the interface between the epoxy resin and the tube. So the tensile strength should be higher than the obtained values. Therefore, P(MMA/n-BMA) probably has the lowest tensile strength of around 10 to 20 N/mm².

For all polymers, the measured tensile strength is higher than the tensile strength of cementitious materials (5 N/mm²) and the one of PLA is close to the one reported by Van Tittelboom for glass capsules (around 60 N/mm²) [13].

Exposure of the capsules to an alkaline environment for 7 or 14 days does not result in an significant difference in tensile strength for PLA and PS according to a one-way ANOVA. However there is a significant difference (significance level of 0.01) for P(MMA/n-BMA) as tensile strength of capsules placed in filtered cement slurry show a lower tensile strength.

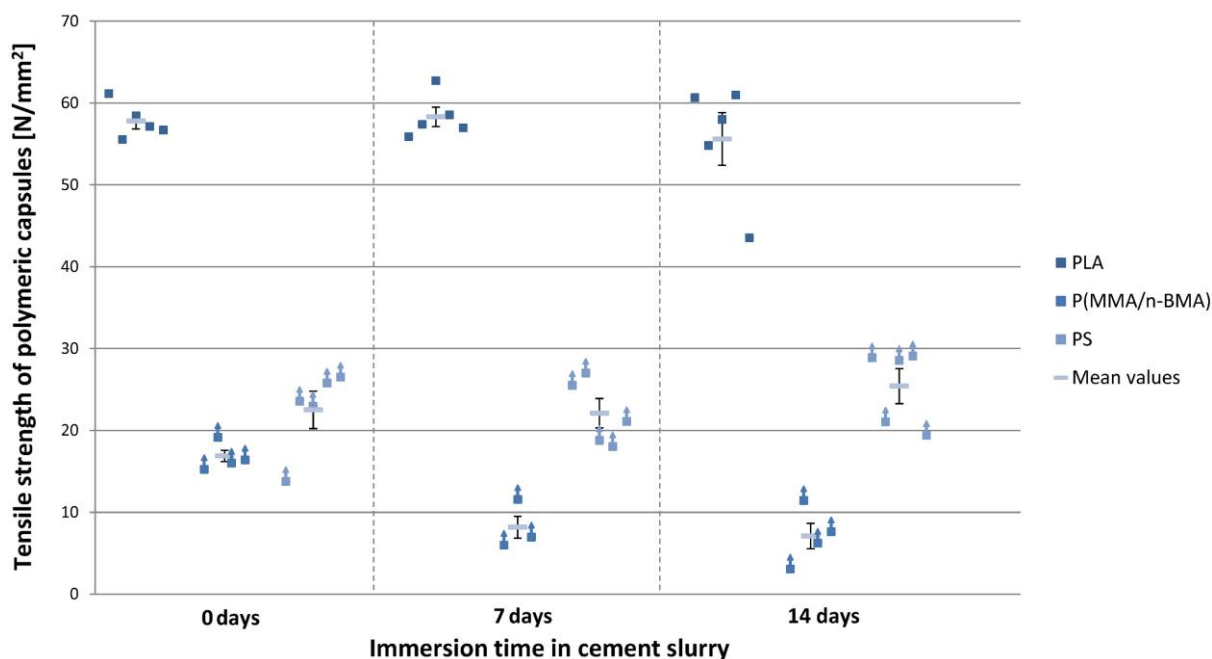


Figure 5: Individual values (squares) and mean values (horizontal lines) with standard error of the tensile strength of the polymeric capsules (upward arrows indicate that the values should be higher) versus immersion time in cement slurry.

The recorded elongation can also be analysed to compare the elongation at rupture as illustrated in Figure 6. All the elongations at rupture were between 0.5 mm and 2 mm which should represent 2.5 % to 10 % considering only that the 20 mm unfilled part of the tube can deform (but these values have to be nuanced as some breakage did not occur in the centre part and some samples have slipped in the epoxy resin). The smallest elongations have been registered for P(MMA/n-BMA) (2 % - 4 %) while PS and PLA seem to have almost the same behaviour (elongations between 4 % and 10 %). This could indicate that P(MMA/n-BMA) is the most brittle material tested among the 3 polymers. Exposure to high pH during 7 days and 14 days does not influence the brittleness of PS and P(MMA/n-BMA). For PLA, elongations are significantly lower after 7 days in filtered cement slurry (significance level of 0.05). Considering the high

value of the standard error at 14 days, no conclusion can be drawn about the influence of alkaline environment on elongation at breakage of PLA.

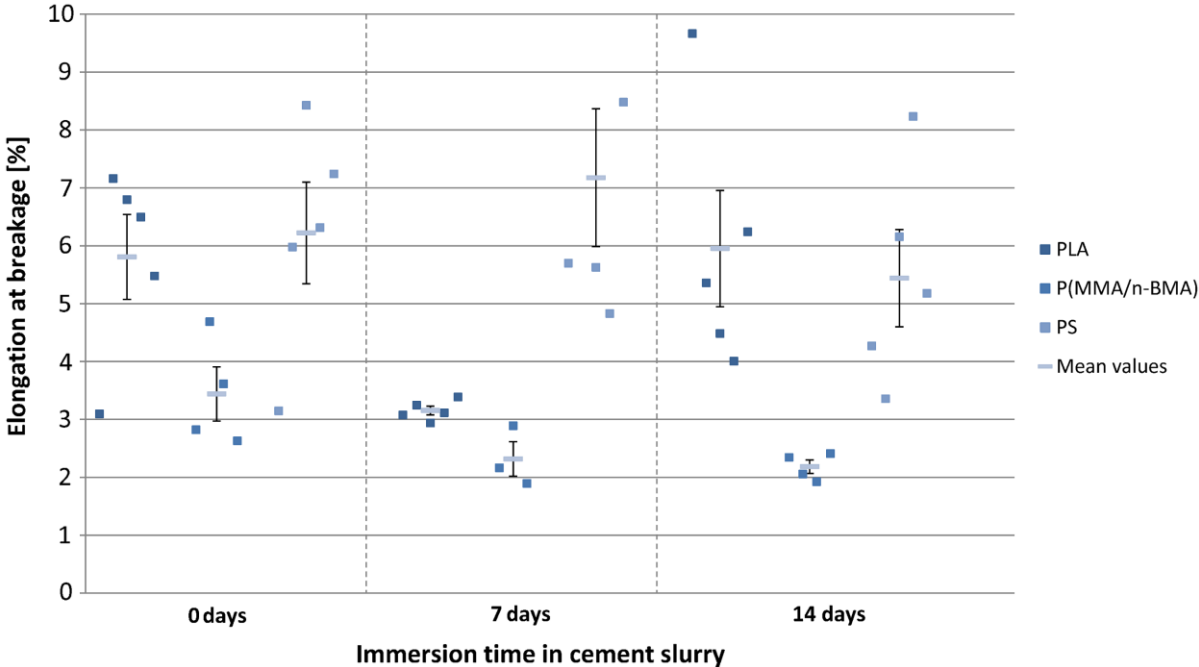


Figure 6: Individual values (squares) and mean values (horizontal lines) with standard error of the elongation at rupture of the polymeric capsules versus immersion time in cement slurry.

3.2 Bond strength tests

For several capsules (especially the ones with a small diameter and wall thickness (PLA)), failure was caused by breakage of the capsules and slippage between the epoxy (the resin holding the nut and screw thread linked to the test bench or the glue inside the capsule) and the polymeric capsules (probably after breakage of polymeric capsules). For these samples, the bond strength should be higher than the reported value. As illustrated in Figure 7, the bond strength between PS capsules and mortar is the best one with an average value around 3.5 N/mm^2 . This value is higher than the ones reported [13] for glass (between 0.2 N/mm^2 and 1 N/mm^2) and ceramic (average value around

3 N/mm²). The bond strengths between PLA or P(MMA/n-BMA) and the cementitious matrix are close to the one between glass and the cementitious matrix.

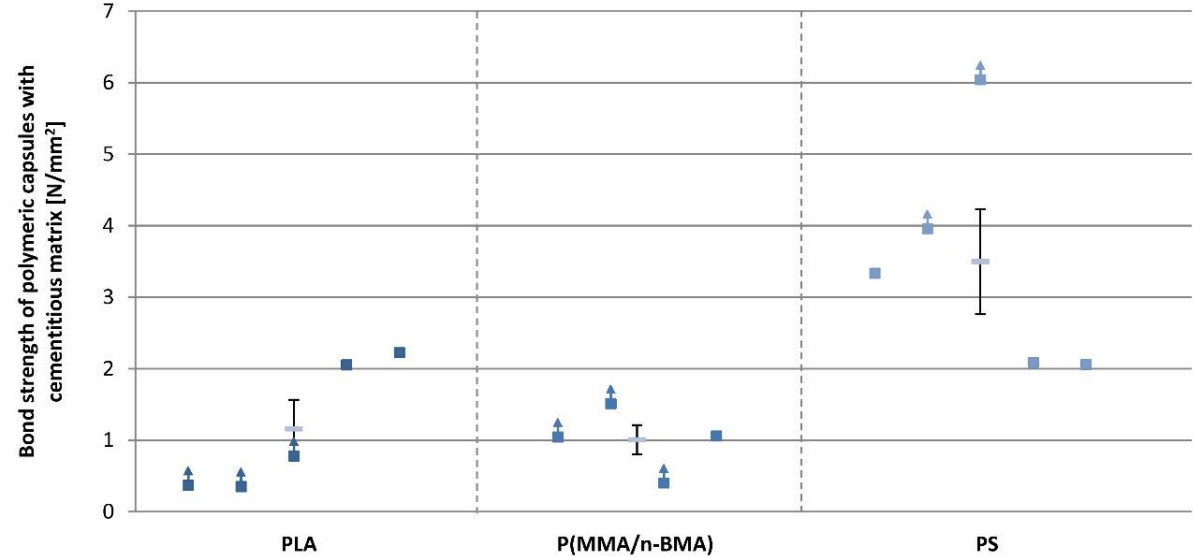


Figure 7: Individual values (squares) and mean values (horizontal lines) with standard error of bond strength between polymeric capsules and cementitious matrix (upward arrows indicate that values should be higher because failure was not caused by bond loss).

3.3. Differential Scanning Calorimetry

From the DSC measurements, it results that the T_g of PLA and P(MMA/n-BMA) is around 60 °C. Concerning P(MMA/n-BMA), this is more than the expected value of 50 °C announced by the supplier. For PS, the measured T_g is of around 102 °C. These values are relatively high compared to the initial investigated range of glass transition temperatures between 35 °C and 50 °C but are reasonable for PLA and P(MMA/n-BMA) regarding their low cost.

3.4. Dynamic Mechanical Analysis

The main interest of DMA for this study is to investigate the evolution of the mechanical behaviour of capsules with temperature. Therefore, the storage modulus (E') is the most relevant parameter as, with increasing temperature, it drops around the T_g emphasizing the transition from a brittle behaviour (with a high storage modulus) to a rubbery state (with a lower storage modulus). As illustrated in Figure 8, for the three polymers, E' drops from a value around 1000 MPa to a value around 10 MPa. For PLA the drop in E' occurs between 52 °C and 67 °C, for P(MMA/n-BMA) between 55 °C and 80 °C and for PS between 95 °C and 115 °C.

In order to increase the survival ratio of capsules during mixing, one has to heat the capsules at least around the temperature corresponding to the end of the drop of storage modulus: 67 °C for PLA, 80 °C for P(MMA/n-BMA) and 115 °C for PS.

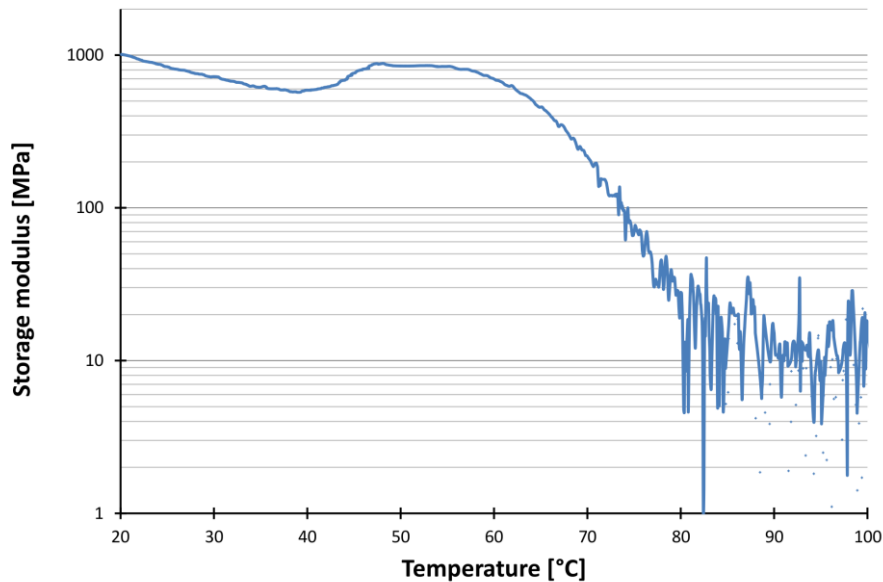


Figure 8: Evolution of the storage modulus of P(MMA/n-BMA) between 20 °C and 100 °C.

3.5. Compatibility with healing agent

Pictures of the capsules, taken regularly during 14 days after injection of the healing agent, revealed that the polyurethane pre-polymer hardens in the polymeric capsules. However, the speed of hardening seems different for the 3 polymers. First hardening signs have been observed after 5 days for P(MMA/n-BMA) capsules and after 4 days for PLA capsules, while hardening started after 10 days in PS capsules (and no white deposits were observed, only a global change in colour was noticeable). Even after 3 weeks PU was not completely hard in PS capsules when 2 capsules were cut. This curing of the pre-polymer is probably due to a lack of permeability of the studied polymeric capsules or a possible reaction between the pre-polymer and the capsule. All these times of curing are still much too fast to be applicable in self-healing concrete and the shelf-life of the capsules must be increased.

3.6. Mixing tests

At the end of the mixing test, entire capsules and parts of capsules were found in the concrete mix. The survival ratios are reported in Figure 9.

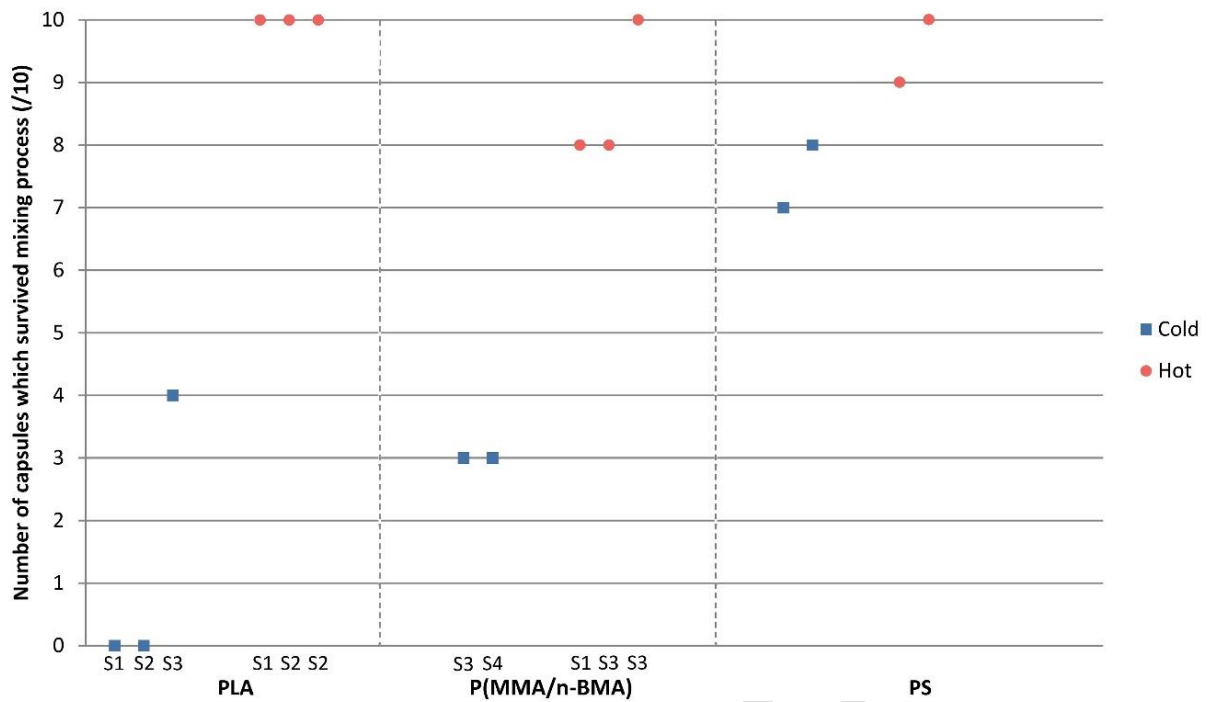


Figure 9: Survival ratio of polymeric capsules during cold and hot concrete mixing process.

The improvement in survival ratio after hot mixing is assumed to be caused by the more flexible behaviour of the capsules above their T_g . For PLA, all the capsules survived the hot mixing process, even the very small ones with a wall thickness around 0.4 - 0.5 mm (S1 see Table 5) whereas none survived the cold mixing process. For P(MMA/n-BMA), capsules had bigger dimensions so that could explain the slightly higher cold survival ratio. The capsules heated during 1 hour were flat and the wall thickness a little bit smaller maybe due to thermal expansion before mixing (as illustrated in Figure 10, the capsule is larger close to the sealing MMA glue) inducing a different resistance due to their new shape whereas the capsules heated only 30 minutes conserved their cylindrical shape and all survived the mixing test. PS capsules were initially the ones with the biggest diameter and wall thickness. Therefore it is supposed that this is the reason why they survived the cold mixing process rather well. The improvement between the cold

and hot mixing process for PS capsules is noticeable even if it is not sure the capsules temperature remained above their T_g (102 °C) during all the mixing process as the final temperature of the ‘hot concrete’ mix has been measured to be around 70 °C.

Table 5: Three-point-bending test results concerning capsule breakage.

Name of specimen	Number of broken capsules	Crack width when breakage [mm]	Dye visible
PBS3MH	2	0.142, 0.347	No
PBS1MH	1	0.300	Yes
PBS3MHD	5	0.080, 0.120, 0.270, 0.158, 0.320	Yes
PBS3N	0		
PLAS3MC, PLAS2MH, PLAS1MH, PLAS1N	0		
PSN, PSMC, PSMH	0		

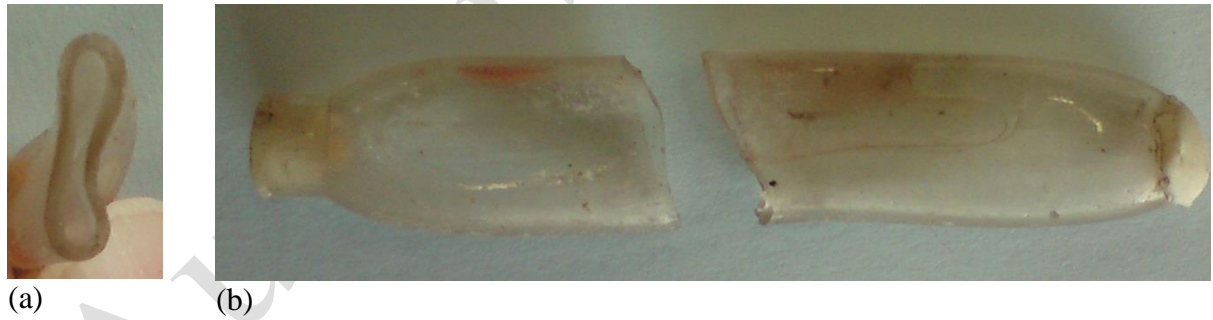


Figure 10: Deformed P(MMA/n-BMA) caused by excessive heating time ((a) cross-section with wall thickness smaller than for straight capsules, (b) side view with visible thermal expansion).

3.7. Three-point-bending tests with mortar specimens containing capsules

The results of the first test for all the capsules are presented in Table 5 with the codes presented in Table 3.

3.7.1. Polystyrene and Poly(lactic acid) capsules

None of the PS and PLA capsules broke when cracks with a width of 0.4 mm were created. No drops were observed on the load curves and no water marks were observed. During the second test, the PS capsules broke without visible slippage when the specimens were completely broken. The fact that PS capsules only broke when the two parts of the specimen were disconnected can be explained by the wall thickness of the capsules. Breakage of the capsules occurred suddenly. Consequently, the brittle behaviour of PS capsules is confirmed. Also the good bond strength of PS capsules with the cementitious matrix is verified as the capsules were not pulled out even if the load was around 6 kN.

PLA capsules also broke during the second test, but most of them broke just before specimen failure at loads of around 5.5 kN. A white colour caused by plastic deformation of the capsules was observed. This explains why the capsules did not break during the first test even though the wall thickness was small (around 0.4 mm for the smallest ones). Moreover, some small capsules (PLAS1N and PLAS3MC) were pulled out when the two parts of the specimens were disconnected. This indicates that there is unsufficient bond between these PLA capsules and the cementitious matrix.

3.7.2. Poly(methyl methacrylate/n-butyl methacrylate) capsules

Some P(MMA/n-BMA) capsules broke with crack appearance. For the two specimens with incorporated deformed capsules, which previously survived the hot mixing process, some capsules broke and released the water they initially contained as illustrated in Figure 11. For two other specimens with capsules which previously resisted the concrete mixing process but were not deformed, breakage of capsules was observed.

445



446

447 **Figure 11:** Water released because of capsule breakage in the specimen PBS3MHD.

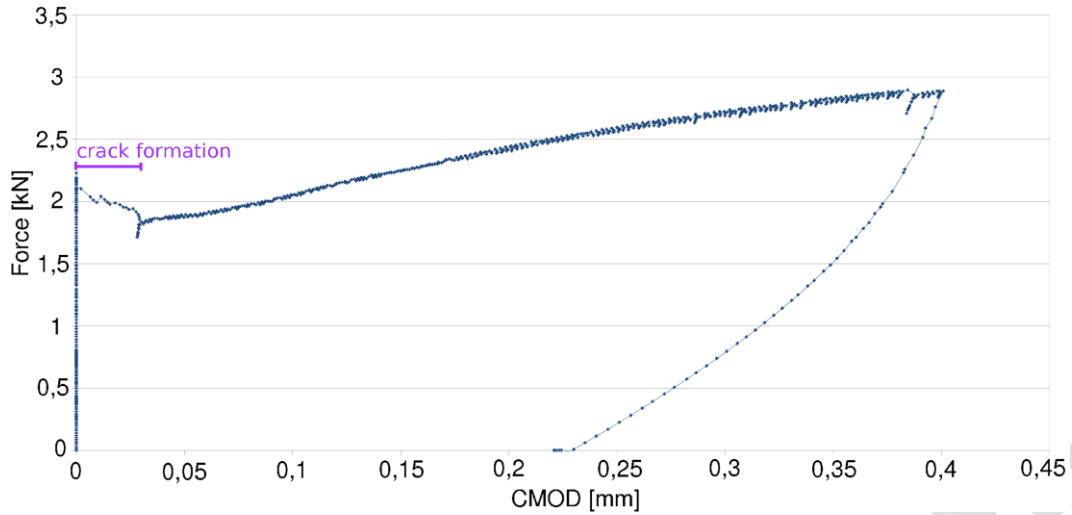
448

449 The crack width at which the capsules broke was deduced from the graphs representing
450 the load in function of the crack width measured by the LVDT. When a sudden drop in
451 the curve was observed (as illustrated in Figure 12) and the sound of capsule breakage
452 was heard, the capsules were supposed to be broken.

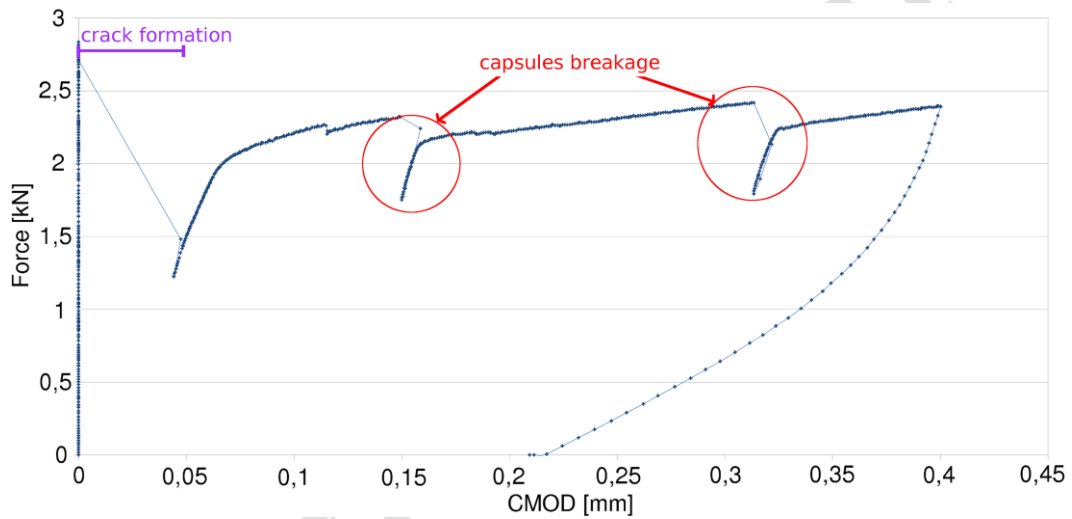
453

454 Almost all the capsules which were mixed in while heated and which deformed, broke
455 during the three-point-bending test (5/6): 3 capsules broke when the crack width was
456 around 0.15 mm, which corresponds to a relatively small crack. Therefore, if the healing
457 agent could be encapsulated by these capsules, healing of cracks with a width of around
458 0.15 mm could be possible. 2 other capsules broke while the crack width was around
459 0.30 mm. None of the P(MMA/n-BMA) capsules which had not been mixed previously,
460 broke during the three-point-bending test.

461



(a)



(b)

Figure 12: Loading curves obtained during the three-point-bending test, (a) without capsules breakage, (b) with capsules breakage (specimen PBS3MHD2)

The second test confirmed that all the capsules were broken during the first test for one of the two specimens (PBS3MHD) as the capsules were empty. For the other specimen (PBS3MHD) containing deformed capsules, one capsule broke when the load was around 4 kN releasing the water it was containing. For the straight P(MMA/n-BMA) capsules which survived the hot mixing process, all the capsules which did not break

during the first test, broke during the second test before specimen failure at loads around 3.5 - 4.5 kN (pauses were made every 1 kN to check if water marks appeared). For the P(MMA/n- BMA) capsules which had not been mixed with concrete, breakage occurred at higher loads around 5 kN and even sometimes at the moment of complete specimen failure. These results demonstrate that the chance of capsules breakage is higher when the capsules have been previously mixed in (and probably damaged, as, in certain cases visible precracking was noticed).

The results obtained during the three-point-bending test confirmed the first trends observed with the tensile and bond strength tests:

- The P(MMA/n-BMA) capsules are the most brittle ones and they can break when they are subjected to relatively small deformations as in the case when a crack appears,
- The bond of all the capsules with the cementitious matrix, except the smallest PLA capsules, seems sufficient to avoid pull out of the capsules. Therefore, the majority of the capsules broke during the three-point-bending test (at least during the second test).

The P(MMA/n-BMA) capsules are the only ones which broke at the moment of crack appearance. This indicates that the brittleness of the polymeric capsules has to be as high as possible. PS is known for its brittleness, but the capsules extruded in this study were probably too thick to break. Therefore, besides the brittleness, the shape of the capsules plays an important role. After complete breakage of the specimens, the thickness of the broken P(MMA/n-BMA) capsules was measured. It revealed what was expected after the mixing test: the wall thickness of the deformed capsules is lower than the thickness of the straight capsules. This difference in thickness of the capsules which survived the mixing process is probably the cause of the better breakage efficiency of the deformed capsules.

499

500 **4. Conclusions and perspectives**

501 The use of polymeric capsules to obtain self-healing properties in concrete seems
502 promising. In this study, it was investigated whether brittle thermoplastics can resist the
503 concrete mixing process through heating, and break with crack appearance at room
504 temperature. The selected polymers P(MMA/n-BMA), PLA and PS show a brittle
505 behaviour at room temperature with an elongation at rupture lower than 10 %. Their
506 glass transition temperatures, measured by DSC is relatively low: respectively 59 °C,
507 ≈ 59 °C and ≈ 102 °C. Tensile strength tests ensured that the tensile strength of these
508 polymeric capsules (10 to 80 N/mm²) is higher than the tensile strength of concrete
509 (5 N/mm²). Bond strength tests revealed that polymeric capsules can have similar bond
510 strength with concrete as glass capsules (around 1 N/mm²). Therefore, it is expected that
511 these capsules will not lower the mechanical properties of concrete when they are
512 embedded inside the matrix. The dynamic mechanical analysis showed a drop in the
513 storage modulus around the T_g of the 3 polymers. This drop emphasizes an important
514 loss of rigidity occurring along small temperature ranges: between 52 °C and 67 °C for
515 PLA, between 55 °C and 80 °C for P(MMA/n-BMA) and between 95 °C and 115 °C for
516 PS. Therefore, it is possible to adjust accurately the temperature at which capsules have
517 to be heated to obtain the desirable softness and increase the chance to survive the
518 concrete mixing process. The compatibility between polymeric capsules and the two-
519 component polyurethane-based healing agent needs to be improved. The prepolymer of
520 this healing agent starts to harden in the capsules probably because of the air and
521 moisture permeability of the polymers. A combination of glass to protect moisture
522 sensitive healing agent, and thermoplastic to protect glass against mixing could be a
523 possible solution to this problem. The mixing of concrete with incorporated capsules

demonstrated the interest to heat the capsules beforehand. When capsules were mixed at room temperature with aggregates, sand, cement and water, only the ones with an important wall thickness (around 1.6 mm for PS capsules) resisted the process, exhibiting a high survival ratio (over 8/10). The majority of the capsules with a wall thickness between 0.4 mm (PLA S1) and 1.5 mm (P(MMA/n-BMA S3) did not resist the mixing process at room temperature. However, when capsules were heated in a small oven at temperatures above their T_g (90 °C for PLA and P(MMA/n-BMA), 140 °C for PS) and were mixed with heated aggregates and sand (80 °C for PLA and P(MMA/n-BMA), 105 °C for PS) and boiling water, almost all the capsules resisted the hot mixing process, even the smallest ones. Some P(MMA/n-BMA) capsules, which previously survived the concrete mixing process, broke with crack appearance during the three-point-bending test. The probability of breakage is linked to the wall thickness of the capsules, their shape and, probably, the damage they suffered during the mixing process because none of the P(MMA/n-BMA) which had not previously mixed in, broke with crack appearance.

Although heating capsules prior to mixing seems complicated from an industrial point of view, a deeper characterisation of the polymer degradation over time (increase of the brittleness due to aging) supports the development of time-evolution capsules for industrial applications in the future. The authors believe that polymeric capsules will be useful to replace glass capsules to carry polymeric healing agent for self-healing concrete because they can resist the concrete mixing process. Therefore, the global cost of self-healing concrete will decrease, and the solution could be extended to industry in large-scale concrete structural elements.

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