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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) ( $T_g = 59\text{ °C}$ ), Polystyrene (PS) ( $T_g = 102\text{ °C}$ ) and Poly(methyl methacrylate/n-butyl methacrylate) (P(MMA/n-BMA)) ( $T_g = 59\text{ °C}$ ). 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.

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

29

## 30 **1. Introduction**

31

32 In concrete structures, cracks often appear due to the limited tensile strength of concrete.

33 These cracks endanger the durability as aggressive substances, dissolved in fluids and

34 gasses, can easily flow inside the matrix and lead to structural failure by reinforcement

35 corrosion. Moreover, cracks are also considered undesirable for aesthetic reasons. Due

36 to regular and planned inspection rounds followed by proper treatments, maintenance

37 costs of concrete structures are quite high nowadays. It has been estimated that, in

38 Europe, around 50 % of the annual construction budget is spent on rehabilitation and

39 repair of the existing structures [1, 2].

40 Therefore, making self-healing concrete could highly reduce the maintenance costs and

41 improve the durability of concrete structures. Under control, self-healing could be taken

42 into account by designers to meet project owners' durability expectations, following the

43 'damage management concept' introduced by Van der Zwaag in opposition to the actual

44 'damage prevention principle' widely used in construction codes [3]. Consequently,

45 service life of structures would increase considerably.

46 Encapsulation of healing agents is a very effective method to obtain complete sealing of

47 the crack with chemical agents, to avoid penetration of aggressive substances and, in

48 some cases to obtain partial regain in mechanical properties which is an important

49 aspect to guarantee the performance during service life (succession of crack formations)

50 [4]. However, up to now, glass capsules have been mostly used [5-11] to store the

51 healing agent. They break upon crack appearance but they cannot resist the concrete

52 mixing process without particular protection (protection by a cement paste bar or a

53 metallic wire seem limited [12, 13], only bundling the capsules with a water soluble  
54 solution is reported to protect them while mixing in a truck [14]). This can be explained  
55 by their brittleness and their dimensions (glass tubes with a wall thickness of 2 mm are  
56 able to rupture upon crack formation, 3 mm thick tubes cannot break any more upon  
57 crack formation [15]. Survival of the concrete mixing process would facilitate the  
58 application of self-healing materials and decrease their price by reducing human work.  
59 An evolution towards polymeric encapsulation materials could be the means to adjust  
60 capsule properties more easily and to resist the mixing process (as suggested by Dry  
61 [16]). Besides glass, some natural fibres [17, 18], gelatine capsules [1], paraffin to  
62 enclose water [19], wax [20] and polyurethane [21] have been used. Ceramic, a very  
63 brittle material, has also been used by Van Tittelboom [4] who observed a better bond  
64 strength than with glass. Spherical capsules can be successfully mixed in concrete [1,  
65 20-26] but cylindrical capsules present better chances to break upon crack appearance  
66 [13] and release the healing agent more efficiently [27] even if their orientation is still a  
67 concern. Polypropylene capsules coated with wax and heated to release the capsules  
68 content [8] have been studied to produce capsules able to resist the concrete mixing  
69 process.

70 This study explores the development of polymeric capsules that are able to survive the  
71 concrete mixing process without any particular protection, and to break upon crack  
72 appearance without human intervention. The selected polymers are brittle at room  
73 temperature and have a relatively low glass transition temperature. Consequently, their  
74 ability to resist the concrete mixing process, when they were heated before mixing and  
75 mixed with heated components, was studied. The capsule breakage with crack  
76 appearance was measured by the means of three-point-bending tests performed on small  
77 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

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

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

111 A laboratory-scale inter-meshing co-rotating twin-screw extruder (MP19TC-25, APV  
112 Baker, Newcastle-under-Lyme, UK) with a length over screw diameter ratio (L/D) of  
113 25:1 was employed to extrude hollow tubes using a die with an outer hole of diameter 5  
114 mm and an inner pin of diameter 3 mm. The temperature settings used during the  
115 extrusion process to obtain a good melt without degradation, are presented in Table 1.

116

117 **Table 1:** Temperature settings (°C) at several locations in the extruder for extrusion of  
118 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

119

120 Different sizes of tubes were obtained due to different expansion ratios of the polymers.

121 Along the same tube of a length of 1 meter, the thickness and the diameter also varied.

122 Hollow tubes were cut at 5 cm length or 10 cm length for the different tests. Capsules

123 were sorted in different size ranges and their cross section area was measured by means

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

129

130 **Table 2:** Approximate dimensions of extruded capsules for the different size ranges  
 131 (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				

132

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

136

### 137 2.1.2 Preparation of the mortar samples

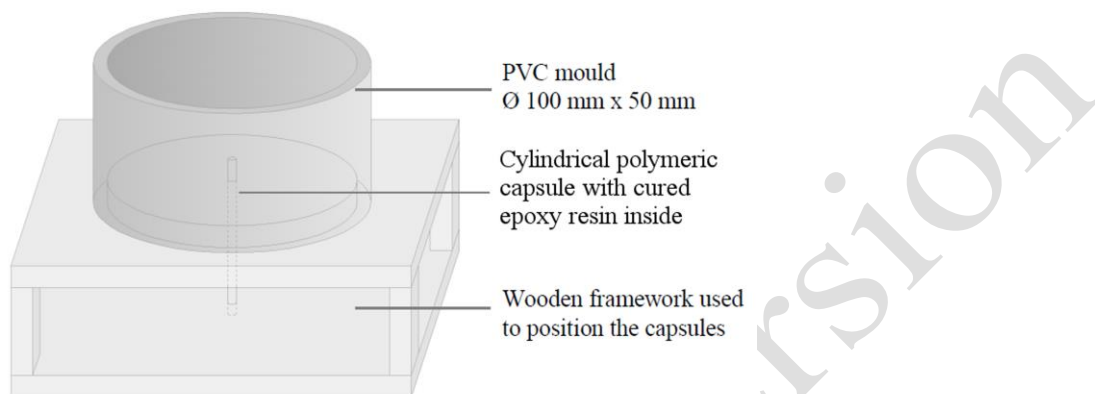
138 Bond strength test and three points bending test have been performed to show the  
 139 interest of polymeric capsules in self-healing concrete.

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

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

146 illustrated in Figure 1. After casting, the samples were stored in an air-conditioned room  
147 (20 °C, 95% RH) and demoulded after 24 hours. Subsequently, they were cured at room  
148 temperature (20 °C, 60% RH) during 14 days until testing.

149



150

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

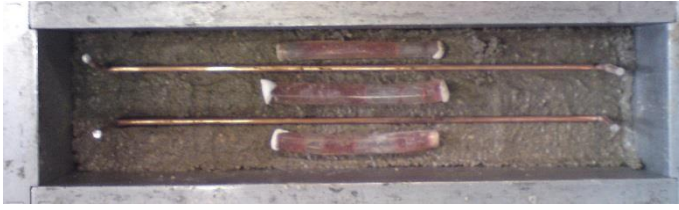
153

154 In order to quantify the ability of the capsules to break at the moment of crack formation,  
155 mortar specimens containing capsules were prepared. Mortar mixtures consisted of  
156 1350 g DIN standard sand, 450 g binder and 180 g water (W/C = 0.4). They were  
157 prepared according to the standard NBN EN 196-1 (2005).

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

163





164

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

166

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

170 **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	

171

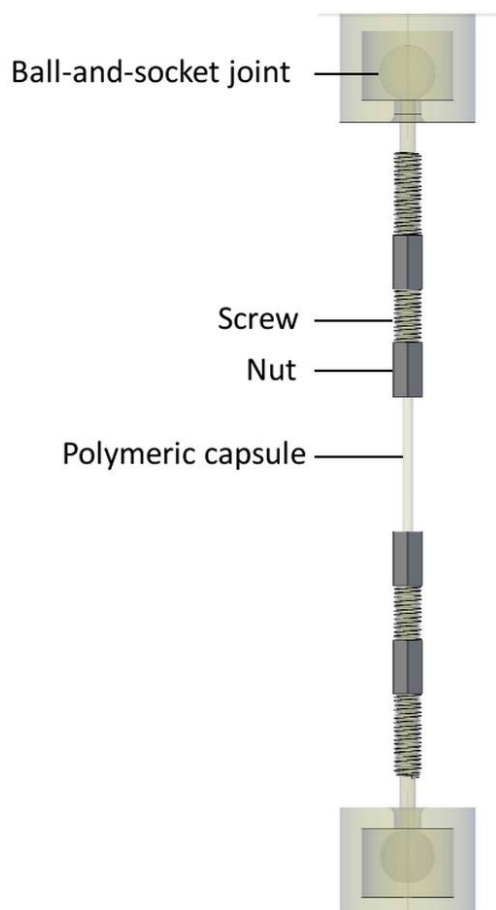
## 172 2.2 Experimental methods

### 173 2.2.1 Tensile tests and quantification of the resistance in cement slurry

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

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

183



184

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

186

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

191

192 **2.2.2 Bond strength tests**

193 Before the test, a nut was glued to the tube to one end, and the other end was 10 mm  
194 embedded into the mortar. For the test, the mortar cylinder was fixed in a metallic frame  
195 and the screw thread placed in the nut was connected to the apparatus. The loading rate  
196 was fixed at a value of 2 mm/min. For each polymer, 4 or 5 repetitions were provided.  
197 The bond strength could be calculated from the measured load according to equation 1  
198 [13, 41].

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

199 Where  $\tau$  is the bond strength [ $\text{N}/\text{mm}^2$ ],  $F_p$  is the force measured when the tube is pulled-  
200 out (or maximum force if the tube is not completely pulled-out) [N],  $d$  is the tube outer  
201 diameter [mm] and  $l$  is the embedded length of the tube [mm].

202

### 203 **2.2.3 Differential Scanning Calorimetry**

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

206

### 207 **2.2.4 Dynamic Mechanical Analysis**

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

215

### 216 **2.2.5 Compatibility with healing agent**

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

226

#### 227 **2.2.6 Mixing tests**

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

236

237

238

239

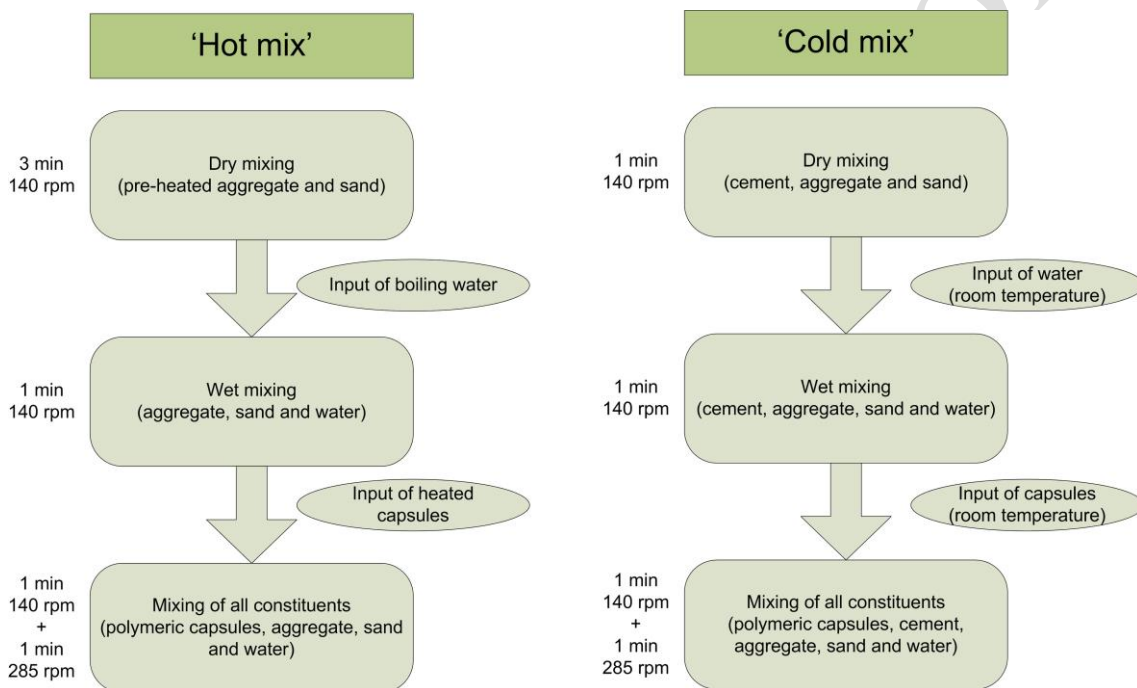
240

241 **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)

242

243



244

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

247

248 First, the dry components (aggregates, sand, cement) with a temperature of around  
 249 20 °C were mixed, in an Hobart type D-300 mixer, at a speed of 140 revolutions per  
 250 minute during 1 min for 'cold' mixing. For 'hot' mixing, pre-warmed aggregates and  
 251 sand (at a temperature decided according to the  $T_g$  of the polymeric capsule) were  
 252 mixed at a speed of 140 revolutions per minute in an initially cold mixer during

253 approximately 3 minutes (delay is due to the transportation of the heated capsules).  
254 Then, water (boiling water for hot mixes) was added and mixed for 1 minute at the same  
255 speed. Subsequently, for 'cold' and 'hot' mixes, capsules were thrown in the mix  
256 without stopping the mixer. For 'hot' mixes, the added capsules were pre-heated. Their  
257 temperature was between 85 °C and 100 °C for PLA and P(MMA/n-BMA) because  
258 they were transported in boiling water between the oven (at 85 °C) and the mixer, and  
259 around 120 °C for PS capsules which were transported in around 1 minute between the  
260 oven (at 140 °C .C) and the mixer wrapped in paper and held in heat resistant gloves.  
261 The 'hot' mix was performed without cement in order to avoid premature hardening of  
262 the cement. Capsules were mixed with the other ingredients for 1 minute at a speed of  
263 140 revolutions per minute and for 1 minute at a speed of 285 revolutions per minute.

264

### 265 **2.2.7 Three-point-bending test with mortar specimens containing capsules**

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

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

281

### 282 **3. Results and discussion**

#### 283 **3.1 Tensile tests and quantification of the resistance in cement slurry**

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

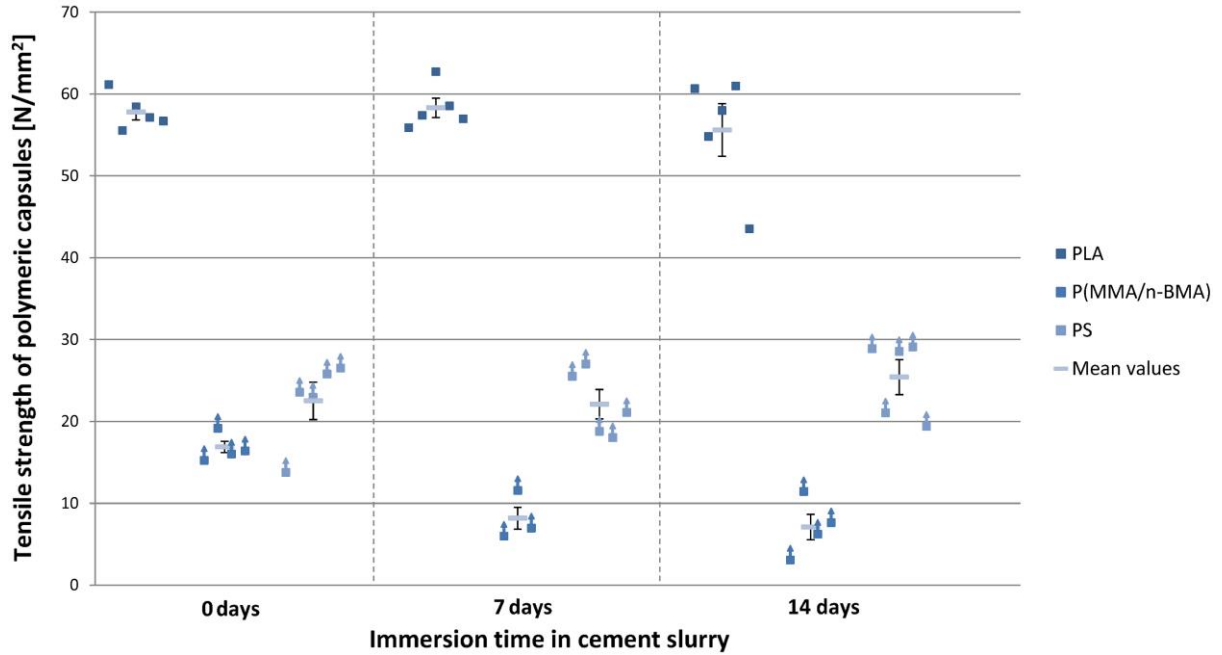
286 The measured tensile strength of PLA (around 60 N/mm<sup>2</sup>) meets the values reported in  
287 literature [28]. For PS capsules, the tensile strength is underestimated as the PS tubes  
288 broke inside the epoxy resin, which was situated between the capsule and the nut  
289 represented Fig. 3, or the epoxy resin slipped. Tabulated values of PS tensile strength  
290 are around 50 N/mm<sup>2</sup> [42] i.e. twice as high as the measured values. For P(MMA/n-  
291 BMA), breakage occurred at the interface between the epoxy resin and the tube. So the  
292 tensile strength should be higher than the obtained values. Therefore, P(MMA/n-BMA)  
293 probably has the lowest tensile strength of around 10 to 20 N/mm<sup>2</sup>.

294 For all polymers, the measured tensile strength is higher than the tensile strength of  
295 cementitious materials (5 N/mm<sup>2</sup>) and the one of PLA is close to the one reported by  
296 Van Tittelboom for glass capsules (around 60 N/mm<sup>2</sup>) [13].

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

302

303



304

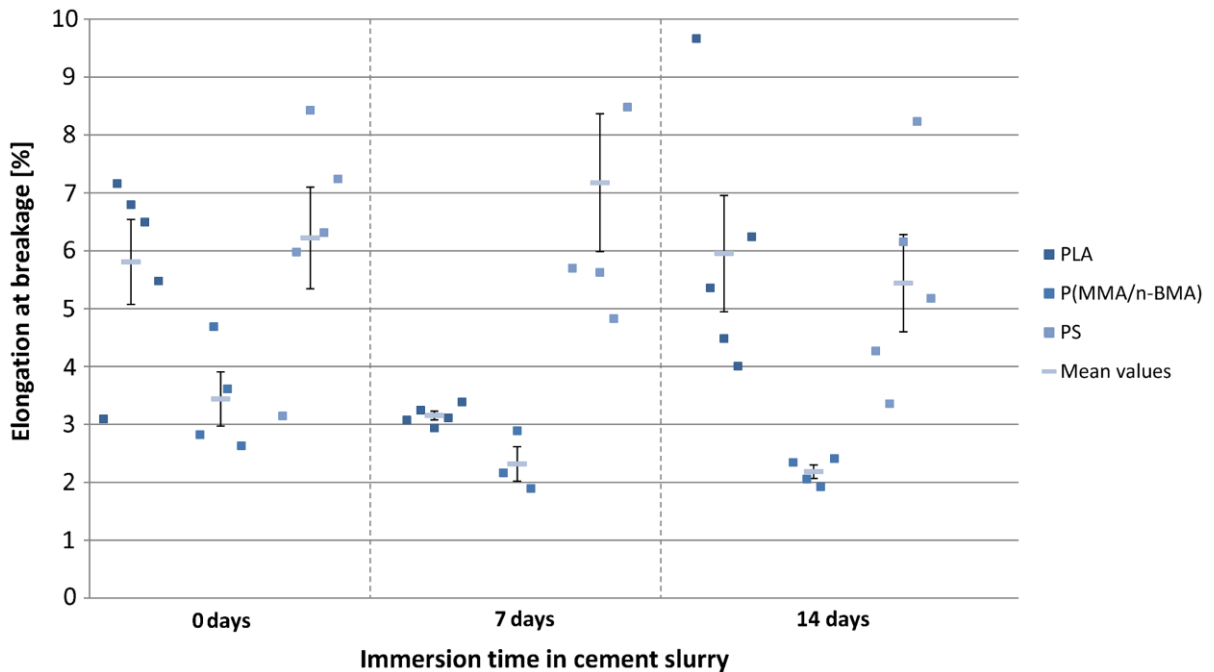
305 **Figure 5:** Individual values (squares) and mean values (horizontal lines) with standard  
306 error of the tensile strength of the polymeric capsules (upward arrows indicate that the  
307 values should be higher) versus immersion time in cement slurry.

308

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



320 value of the standard error at 14 days, no conclusion can be drawn about the influence  
 321 of alkaline environment on elongation at breakage of PLA.  
 322



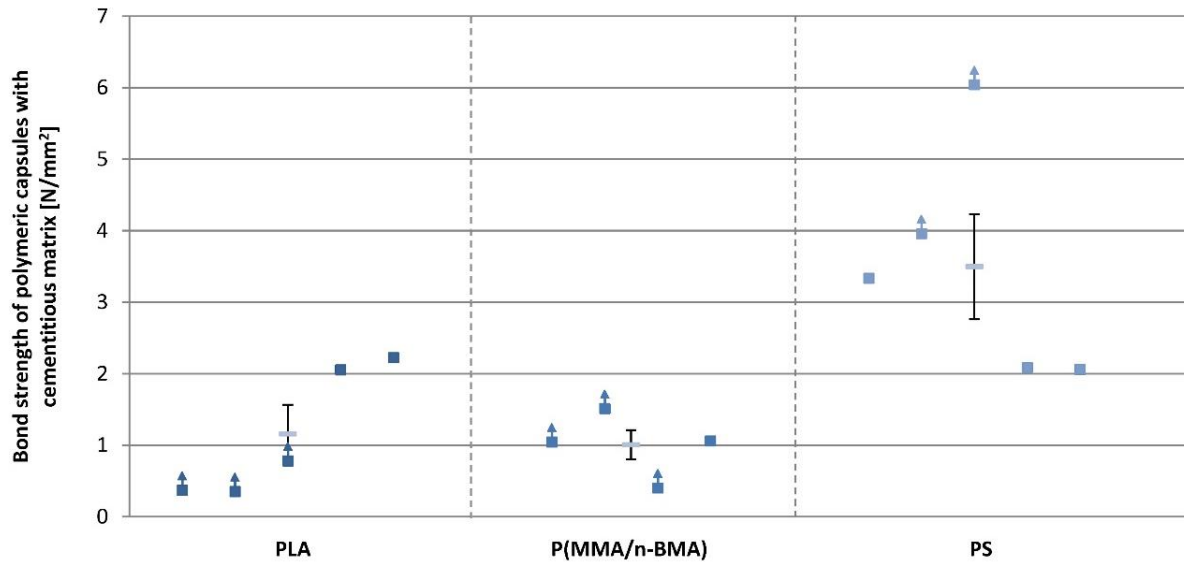
323  
 324 **Figure 6:** Individual values (squares) and mean values (horizontal lines) with standard  
 325 error of the elongation at rupture of the polymeric capsules versus immersion time in  
 326 cement slurry.

327  
 328 **3.2 Bond strength tests**

329 For several capsules (especially the ones with a small diameter and wall thickness  
 330 (PLA)), failure was caused by breakage of the capsules and slippage between the epoxy  
 331 (the resin holding the nut and screw thread linked to the test bench or the glue inside the  
 332 capsule) and the polymeric capsules (probably after breakage of polymeric capsules).  
 333 For these samples, the bond strength should be higher than the reported value. As  
 334 illustrated in Figure 7, the bond strength between PS capsules and mortar is the best one  
 335 with an average value around  $3.5 \text{ N/mm}^2$ . This value is higher than the ones reported  
 336 [13] for glass (between  $0.2 \text{ N/mm}^2$  and  $1 \text{ N/mm}^2$ ) and ceramic (average value around

337 3 N/mm<sup>2</sup>). The bond strengths between PLA or P(MMA/n-BMA) and the cementitious  
338 matrix are close to the one between glass and the cementitious matrix.

339



340

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

345

### 346 3.3. Differential Scanning Calorimetry

347 From the DSC measurements, it results that the  $T_g$  of PLA and P(MMA/n-BMA) is  
348 around 60 °C. Concerning P(MMA/n-BMA), this is more than the expected value of  
349 50 °C announced by the supplier. For PS, the measured  $T_g$  is of around 102 °C. These  
350 values are relatively high compared to the initial investigated range of glass transition  
351 temperatures between 35 °C and 50 °C but are reasonable for PLA and P(MMA/n-BMA)  
352 regarding their low cost.

353

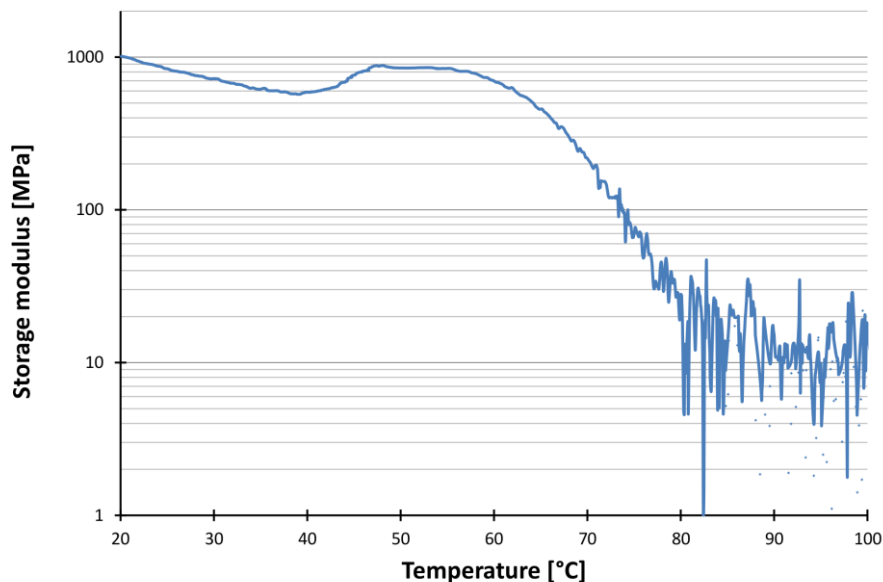
354

### 355 3.4. Dynamic Mechanical Analysis

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

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

367



368

369 **Figure 8:** Evolution of the storage modulus of P(MMA/n-BMA) between 20 °C and  
370 100 °C.

371

### 372 **3.5. Compatibility with healing agent**

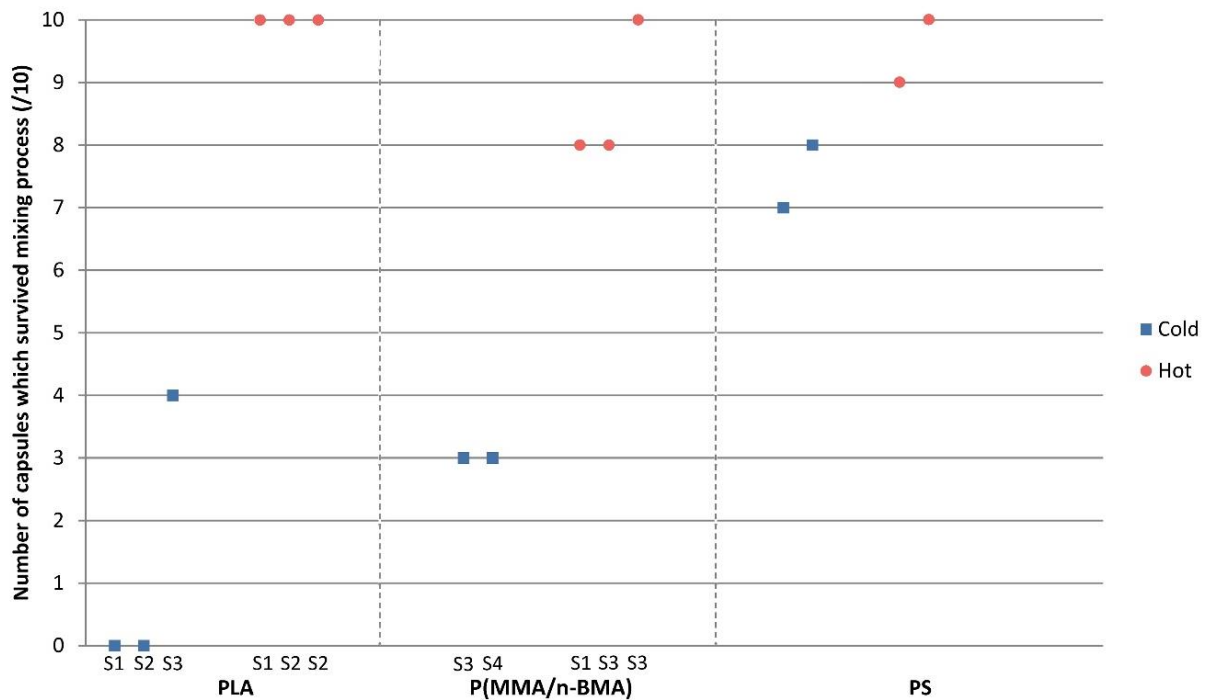
373 Pictures of the capsules, taken regularly during 14 days after injection of the healing  
374 agent, revealed that the polyurethane pre-polymer hardens in the polymeric capsules.  
375 However, the speed of hardening seems different for the 3 polymers. First hardening  
376 signs have been observed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

384

### 385 **3.6. Mixing tests**

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

388



389

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

392

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

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

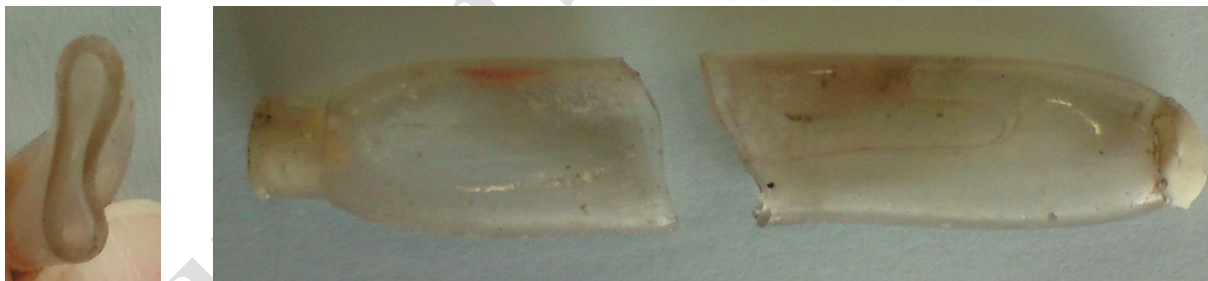
408

409 **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		

410

411



(a)

(b)

412

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

416

### 417 3.7. Three-point-bending tests with mortar specimens containing capsules

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

420

### 421 **3.7.1. Polystyrene and Poly(lactic acid) capsules**

422 None of the PS and PLA capsules broke when cracks with a width of 0.4 mm were  
423 created. No drops were observed on the load curves and no water marks were observed.

424 During the second test, the PS capsules broke without visible slippage when the  
425 specimens were completely broken. The fact that PS capsules only broke when the two  
426 parts of the specimen were disconnected can be explained by the wall thickness of the  
427 capsules. Breakage of the capsules occurred suddenly. Consequently, the brittle  
428 behaviour of PS capsules is confirmed. Also the good bond strength of PS capsules with  
429 the cementitious matrix is verified as the capsules were not pulled out even if the load  
430 was around 6 kN.

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

438

### 439 **3.7.2. Poly(methyl methacrylate/n-butyl methacrylate) capsules**

440 Some P(MMA/n-BMA) capsules broke with crack appearance. For the two specimens  
441 with incorporated deformed capsules, which previously survived the hot mixing process,  
442 some capsules broke and released the water they initially contained as illustrated in  
443 Figure 11. For two other specimens with capsules which previously resisted the  
444 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

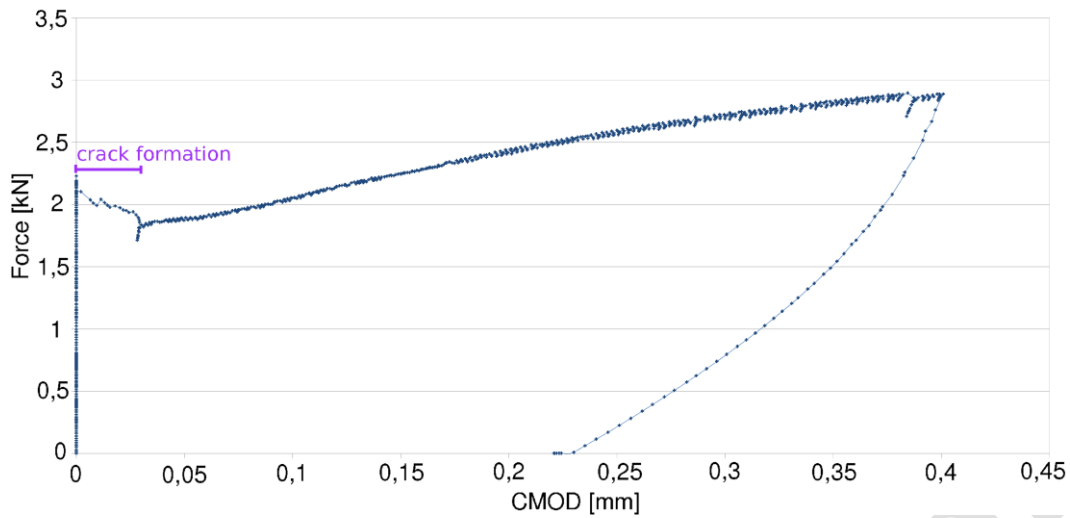
449 The crack width at which the capsules broke was deduced from the graphs representing  
450 the load in function of the crack width measured by the LVDT. When a sudden drop in  
451 the curve was observed (as illustrated in Figure 12) and the sound of capsule breakage  
452 was heard, the capsules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

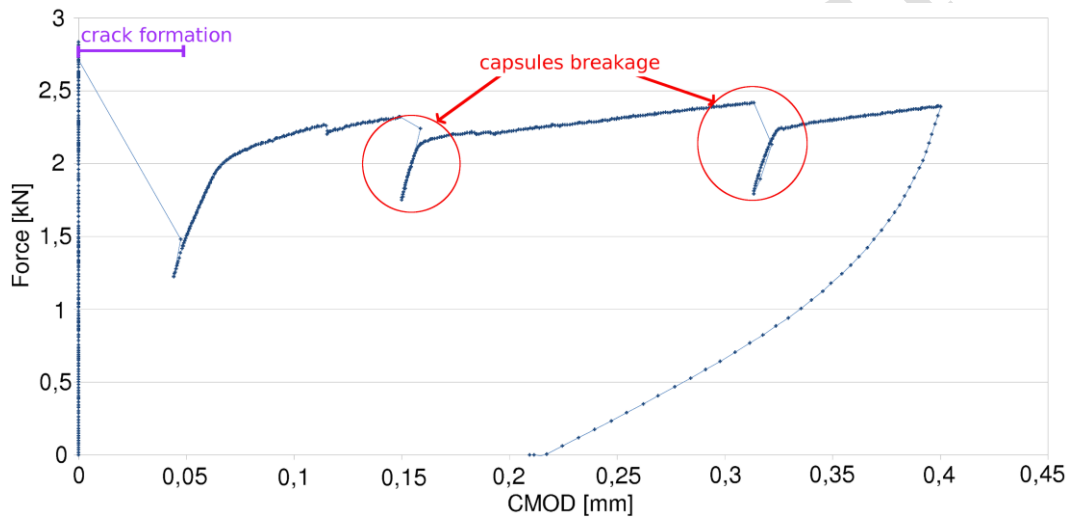
461





462

463 (a)



464

465 (b)

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

468

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

474 during the first test, broke during the second test before specimen failure at loads around  
475 3.5 - 4.5 kN (pauses were made every 1 kN to check if water marks appeared). For the  
476 P(MMA/n- BMA) capsules which had not been mixed with concrete, breakage occurred  
477 at higher loads around 5 kN and even sometimes at the moment of complete specimen  
478 failure. These results demonstrate that the chance of capsules breakage is higher when  
479 the capsules have been previously mixed in (and probably damaged, as, in certain cases  
480 visible precracking was noticed).

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

483 - The P(MMA/n-BMA) capsules are the most brittle ones and they can break when they  
484 are subjected to relatively small deformations as in the case when a crack appears,

485 - The bond of all the capsules with the cementitious matrix, except the smallest PLA  
486 capsules, seems sufficient to avoid pull out of the capsules. Therefore, the majority of  
487 the capsules broke during the three-point-bending test (at least during the second test).

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

498

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  $\approx 59$  °C and  $\approx 102$  °C. Tensile strength tests ensured that the tensile strength of these  
508 polymeric capsules (10 to 80 N/mm<sup>2</sup>) is higher than the tensile strength of concrete  
509 (5 N/mm<sup>2</sup>). Bond strength tests revealed that polymeric capsules can have similar bond  
510 strength with concrete as glass capsules (around 1 N/mm<sup>2</sup>). 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

524 demonstrated the interest to heat the capsules beforehand. When capsules were mixed at  
525 room temperature with aggregates, sand, cement and water, only the ones with an  
526 important wall thickness (around 1.6 mm for PS capsules) resisted the process,  
527 exhibiting a high survival ratio (over 8/10). The majority of the capsules with a wall  
528 thickness between 0.4 mm (PLA S1) and 1.5 mm (P(MMA/n-BMA S3) did not resist  
529 the mixing process at room temperature. However, when capsules were heated in a  
530 small oven at temperatures above their  $T_g$  (90 °C for PLA and P(MMA/n-BMA),  
531 140 °C for PS) and were mixed with heated aggregates and sand (80 °C for PLA and  
532 P(MMA/n-BMA), 105 °C for PS) and boiling water, almost all the capsules resisted the  
533 hot mixing process, even the smallest ones. Some P(MMA/n-BMA) capsules, which  
534 previously survived the concrete mixing process, broke with crack appearance during  
535 the three-point-bending test. The probability of breakage is linked to the wall thickness  
536 of the capsules, their shape and, probably, the damage they suffered during the mixing  
537 process because none of the P(MMA/n-BMA) which had not previously mixed in,  
538 broke with crack appearance.

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

547

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551

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