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## Design and testing of tubular polymeric capsules for self-healing of concrete

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**Abstract.** Polymeric healing agents have proven their efficiency to heal cracks in concrete in an autonomous way. However, the bottleneck for valorisation of self-healing concrete with polymeric healing agents is their encapsulation. In the present work, the suitability of polymeric materials such as poly(methyl methacrylate) (PMMA), polystyrene (PS) and poly(lactic acid) (PLA) as carriers for healing agents in self-healing concrete has been evaluated. The durability of the polymeric capsules in different environments (demineralized water, salt water and simulated concrete pore solution) and their compatibility with various healing agents have been assessed. Next, a numerical model was used to simulate capsule rupture when intersected by a crack in concrete and validated experimentally. Finally, two real-scale self-healing concrete beams were made, containing the selected polymeric capsules (with the best properties regarding resistance to concrete mixing and breakage upon crack formation) or glass capsules and a reference beam without capsules. The self-healing efficiency was determined after crack creation by 3-point-bending tests.

### 1. Introduction

Capsules used in the context of self-healing concrete have to fulfil particular requirements namely protect the healing agent and release their content when a crack forms. Furthermore, they should survive the concrete mixing process and have a limited effect on the mechanical properties of the hardened concrete. The characteristics of the capsules needed to fulfil those requirements are sometimes contradictory: while brittleness is needed for rupturing when a crack forms, a high flexibility and impact resistance are needed to have a good survival rate when mixing. These challenging requirements may be achieved by using polymeric capsules. Research on encapsulation of healing agents for self-healing



concrete mainly focuses on the development of organic spherical microcapsules [1-4]. However, recent studies have also attempted to develop tubular polymeric capsules to carry the healing agent. Hilloulin et al. [5] investigated the potential of using brittle polymeric materials with a relatively low glass transition temperature ( $T_g$ ) as protection materials in self-healing concrete and found that the capsule survival probability could be improved if the capsules were heated (above  $T_g$ ) prior to mixing. Gruyaert et al. [6] explored the use of ethyl cellulose capsules containing different plasticizers to increase the survival of the capsules during concrete mixing. These plasticizing agents would make the capsules more flexible in an early stage and increase the resistance of the capsules during the mixing. Then, due to leaching out of the plasticizers, the capsules would become more brittle during concrete hardening and break more easily when a crack would form. The tested capsules could survive the concrete mixing, however, did not break when cracks with a width of 0.4 mm were created.

In the present work, we investigated the capability of various polymeric capsules to fulfill the aforementioned requirements. Moreover, a numerical model was used to initially evaluate the performance of the polymers regarding breakage upon crack formation. The self-sealing/healing performance of the best suited polymeric capsules was then evaluated in large concrete elements.

## 2. Materials and Methods

### 2.1. Materials

Encapsulation materials: Polystyrene (PS) was supplied by BASF AG (polystyrol VPT granule,  $M_n = 195000$  g/mol). Polylactic acid (PLA) was obtained from NatureWorks (PLA 4032D, 1.4% D-isomer). Two types of poly(methyl methacrylate) (PMMA) were tested. PMMA-1 (Plexiglas 8909,  $M_n = 38000$  g/mol) and PMMA-2 (Plexiglas 8N,  $M_n = 50000$  g/mol) were supplied by Evonik Performance Materials.

Healing agents: The healing agents used in the compatibility tests were one-component polyurethane (1-PU), two-component polyurethane (2-PU), dicyclopentadiene (DCPD) and methyl methacrylate (MMA). 1-PU was provided by De Neef Conchem, 2-PU was supplied by Reticel, DCPD was received from Sigma-aldrich and MMA-based glue was obtained from Grouttech.

The capsules used in the large scale experiments were filled with a water repellent agent (WRA). The WRA healing agent (Sikagard 750L) was supplied by Sika Belgium nv.

### 2.2. Methods

*2.2.1. Durability of the encapsulation material.* Polymeric sheets with thickness of 0.5 mm were prepared from the aforementioned polymers (PS, PLA and PMMA) by compression molding using a Carver 4122 CE equipment (Carver. Inc., USA). To investigate the durability of the materials, the various polymer sheets were incubated in demi water (DI), concrete pore solution (CS) and salt solution (S) for various time intervals (1 and 6 months). The changes in molecular weight were determined by performing size-exclusion chromatography (SEC) prior and after incubation.

*2.2.2. Compatibility with healing agent.* Polymeric sheets were immersed in the different healing agents at room temperature and visually inspected at regular time intervals.

*2.2.3. Extrusion of the polymeric hollow tubes.* Hollow tubes were extruded on a Bradender extruder equipped with a single screw and a tubular die (OD: 10 mm; ID: 8 mm). The processing temperature was 225-235 °C and the screw speed was 10 min<sup>-1</sup>. The wall thickness of the tubes was controlled by adjusting the conveyor speed (0.2 – 1 m/min). The average dimensions of the capsules are shown in Table 1.

**Table 1.** Average dimensions of the capsules used.

	External diameter (mm)	Wall thickness (mm)
PLA	$7.42 \pm 0.12$	$0.44 \pm 0.11$
PMMA-1	$6.37 \pm 0.25$	$0.31 \pm 0.09$
PMMA-2	$6.14 \pm 0.09$	$0.26 \pm 0.07$
PS	$6.44 \pm 0.16$	$0.42 \pm 0.13$

**2.2.4. Capsule breakage upon crack formation: modelling and experimental testing.** A mortar block of  $30 \text{ mm} \times 30 \text{ mm} \times 30 \text{ mm}$  containing a single tubular capsule was used in the model simulations. The capsule was connected to the matrix lattice elements by bond beam elements and the bond beam elements were not allowed to break since a perfect bond is seen as a prerequisite for breakage of the capsules. A detailed description of the model used is described in [7]. To verify the model, mortar prisms ( $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$ ) with a water to cement (CEM I 52.5 N) ratio of 0.5 and a sand to cement ratio of 3 were prepared according to the standard EN 196-1. Each mortar prism contained two reinforcement bars with a diameter of 2 mm and one hollow tube with a length of 5 cm.

**2.2.5. Concrete beams with(-out capsules).** Three real-scale concrete beams ( $250 \text{ cm} \times 40 \text{ cm} \times 20 \text{ cm}$ ) were made. One of them contained PMMA-1 capsules ( $\varnothing_{\text{outer}} = 6.5 \text{ mm}$ , wall thickness =  $0.6\text{-}0.7 \text{ mm}$ , length =  $5 \text{ cm}$ ), another one contained glass capsules ( $\varnothing_{\text{outer}} = 5 \text{ mm}$ , wall thickness =  $0.8 \text{ mm}$ , length =  $5 \text{ cm}$ ), and the third one was a reference beam without capsules. All mixes had the same composition (Table 2), but for the beams with self-healing properties, PMMA-1 or glass capsules were added during the last 2 minutes of the mixing process. A vertical shaft mixer (200 L) with a rotating pan was used to mix all components. As PMMA-1 capsules tend to float due to their relatively low density, the concrete was cast in 2 layers. First, a concrete mix containing the capsules (approximately 22 capsules per liter of concrete) was prepared and poured into the mould (layer of  $12 \text{ cm}$ ). Then, another mix (without capsules) was made and placed into the mould on top of the previous layer.

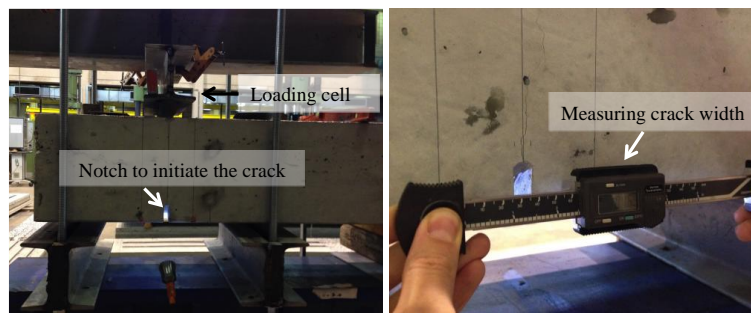
**Table 2.** Concrete mix composition used in the large-scale experiments.

Component	Amount	
	kg/m <sup>3</sup>	l/m <sup>3</sup>
Sand 0/5	853	-
Gravel 2/8	370	-
Gravel 8/16	328	-
CEM I 52.5 N	300	-
Limestone filler	300	-
Water	-	165
Superplasticizer	-	2.5

#### 2.2.6. Cracking

**Mortar specimens:** At the age of 21 days, mortar prisms were cracked in a 3-point-bending test. The testing parameters used to determine the crack width at rupture can be found in [7].

**Concrete beams:** At the age of 14 days, 6 cracks with varying crack widths ( $0.3$  till  $0.5 \text{ mm}$ ) were created in each beam by means of 3-point-bending tests as shown in Fig.1. The different cracks were consecutively created (one crack per day) by moving the 3-point-bending set-up over the length of the beam. To create localized cracks, one notch was sawn at the corners of the beam in the middle of the span length ( $100 \text{ mm}$ ). After crack creation, the notches were filled with a repair mortar in order to keep the crack open. The beams were then unloaded after sufficient hardening of the repair mortar. The crack widths obtained after unloading for each beam were determined using an optical microscope. For each crack, crack width measurements were performed at 6 positions over the length of the crack.



**Figure 1.** 3-point-bending test set-up used to create cracks in the concrete beams.

*2.2.7. Evaluation of the sealing/healing efficiency in the concrete beams.* The water ingress through each crack was measured by placing the beam upside down and attaching a water basin on top of the each crack as described in [8]. Water permeability tests were also performed in uncracked zones.

### 3. Results and Discussion

#### 3.1. Durability of the encapsulation material in various solutions

Table 3 shows the molecular weight change of the PLA, PMMA and PS polymers after incubation in the different solutions. The results indicate a drop of molecular weight after 6 months for all polymers. However, this drop was more pronounced for PLA (28, 25 and 28% in DI, CS and S, respectively). This was expected since the generally accepted mechanism of degradation of PLA is the chemical hydrolysis of the ester bonds. These results suggest that PLA is more susceptible to degradation than PS and PMMA. Moreover, it should be mentioned that direct exposure of the capsules to the various solutions is quite aggressive. In real concrete, it is expected that less solution is in contact with the capsules and thus their durability is less affected by the surrounding environment.

**Table 3.** Molecular weight change of the polymers after incubation in the different solutions.

M <sub>w</sub> change (%)	Month 1			Month 6		
	DI	CS	S	DI	CS	S
PLA	+4.9	-2.4	+5.5	-28.4	-25.4	-28.4
PMMA-2	+1.1	+9.5	+5.8	-13.5	-15.0	-21.7
PS	-4.9	+1.3	+0.4	-14.8	-21.6	-8.5

#### 3.2. Compatibility with healing agent

Visual analysis of the polymer films after immersion in the various healing agents revealed that the PMMA is compatible with the healing agents used, except with MMA-based glue. PLA is compatible with 1-PU and DCPD, while PS only showed compatibility with the accelerator (second component of 2-PU). As the main component of 2-PU is the polyurethane pre-polymer (similar to 1-PU) it can be concluded that PS is not an appropriate encapsulation material for the tested healing agent.

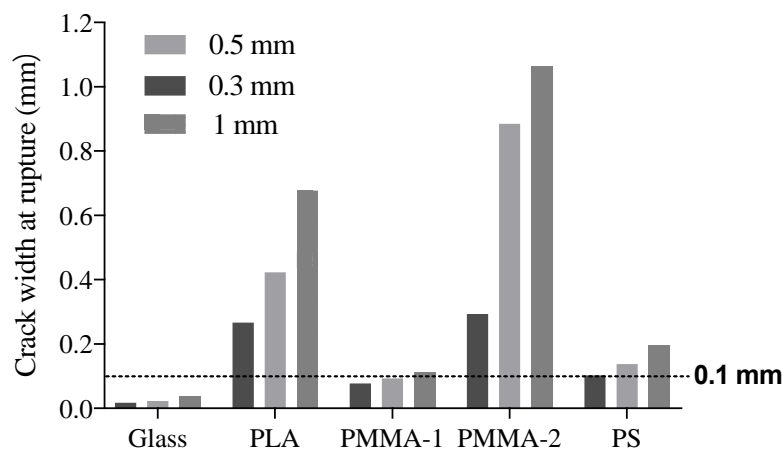
**Table 4.** Appearance of the polymer films after immersion in healing agent for 2 weeks: (+) polymer film remains unaffected; (-) polymer film becomes soft and/or dissolves partially.

	PLA	PMMA-2	PS
Accelerator (2-PU)	-	+	+
1-PU	+	+	-
DCPD	+	+	-
MMA	-	-	-

From these results, it can be concluded that PMMA is the most suitable polymeric material to use as carrier in self-healing concrete as it is compatible with the most commonly used healing agents.

### 3.3. Capsules breakage upon crack formation

In this work, a numerical model was used to simulate breakage of capsules when intersected by a crack in concrete and validated with experimental methods. Fig. 2 shows the results obtained from the numerical model considering capsules with a 5 mm outer diameter and varying wall thickness. The results revealed that only PMMA-1 and PS capsules are suitable if one considers that capsules should rupture for crack sizes below 100  $\mu\text{m}$ .



**Figure 2.** Model output for capsules with an external diameter of 5 mm and varying wall thickness (0.3 – 0.5 or 1 mm).

In table 5, the crack size at breakage determined experimentally for the various types of capsules is presented. It can be seen that the crack sizes at rupture obtained for both PMMA-1 and PMMA-2 are comparable with the results predicted by the model. The model could not be validated for the PLA capsules since no rupture was detected when 400  $\mu\text{m}$  wide cracks were created (experimental settings) and the model suggested rupture at a crack size of approximately 550  $\mu\text{m}$ . For PS it was observed that 2 out of the 3 capsules did not break during testing although the model output indicated rupture at a crack opening of 136  $\mu\text{m}$ . Since in the numerical simulations the capsule was connected to the matrix and the bond beam elements were not allowed to break, the obtained differences might be related to a reduced adhesion between the PS capsule and the mortar matrix or the mechanical properties of PS may have been altered during the extrusion process.

It should also be mentioned that although in these experiments hollow tubes were used, the presence of healing agent inside the tubes is not expected to have an effect on the obtained results since the healing agent should be compatible with the capsule and should not alter its properties.



**Table 5.** Average crack width at rupture, n=3 (experimental versus model).

	Crack width at rupture ( $\mu\text{m}$ )	
	Experimental	Model
PLA	$> 400 \mu\text{m}$	547
PMMA-1	$69 \pm 22$	96
PS	246*	138
PMMA-2	$360 \pm 45$	395

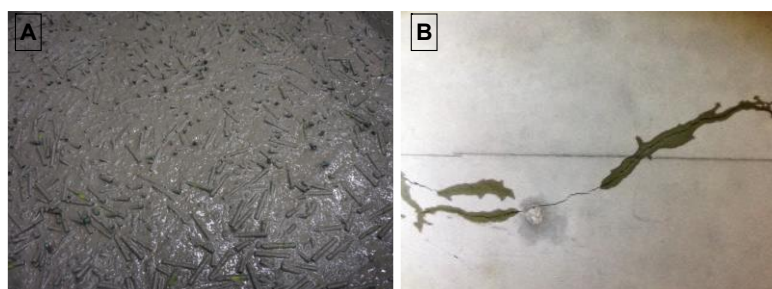
\* 2 out of 3 samples did not rupture before  $400 \mu\text{m}$ .

### 3.4. Self-healing efficiency of large concrete elements

Poly(methyl methacrylate) with a low molecular weight (PMMA-1) was selected as the polymeric encapsulation material to test in real-scale concrete elements based on the aforementioned results and survival tests [9].

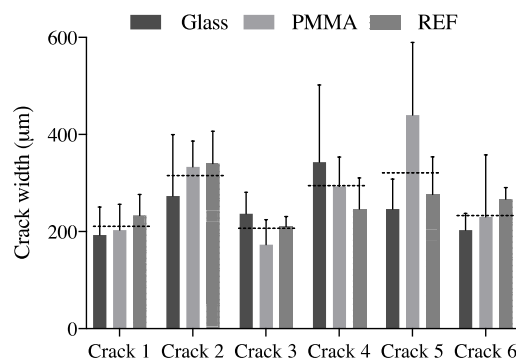
Positive results with regard to strength regain and regain in liquid-tightness using encapsulated one-component polyurethane were obtained previously in lab-scale proof-of-concept tests [10]. Since compatibility tests showed that PMMA capsules are compatible with 1-PU, this healing agent seemed to be the preferential choice. However, when capsules were filled with 1-PU, it was noticed that the healing agent cured prematurely inside the capsules within a few days. Moreover, since the main component of 2-PU healing agent is also a polyurethane pre-polymer, which polymerizes in the presence of moisture/air, this healing agent will also cure prematurely inside the capsules. The DCPD healing agent was compatible with the capsules, however, the polymerization of this healing agent requires the use of a catalyst (which is often very expensive), which would imply the use of coupled capsules to store both components. Furthermore, the healing efficiency of this 2-component system depends on the mix ratio of both components. Therefore, as curing of the healing agent could have an influence on the ability of the capsules to break upon cracking (and thus on the self-healing efficiency) and this, together with an investigation on the survival of the capsules during concrete mixing, were the main aims of these large-scale tests, a water repellent agent (which reduced also the chloride ingress) was selected as healing agent for these experiments.

As anticipated [9], the capsules (both polymeric and glass) survived the mixing process (Fig. 3A) and broke upon crack appearance as leaching out of healing agent was detected (Fig. 3B). The latter was more noticeable for glass capsules (leaching of WRA was visible for all cracks).

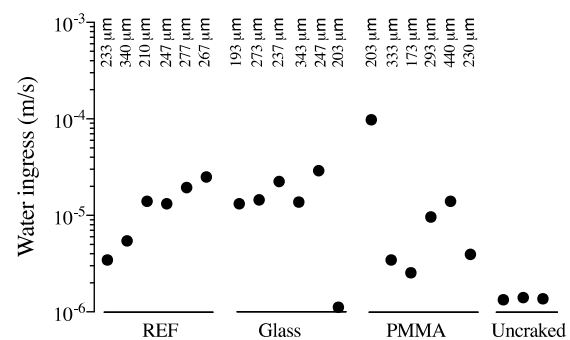


**Figure 3.** Concrete with dispersed PMMA capsules (A) and WRA agent visible at the crack during loading (B).

For all beams, cracks with similar widths were aimed for since the healing efficiency depends on the crack width. In Fig. 4, the average crack widths obtained after unloading for each beam are shown.



**Figure 4.** Average crack width measured for each beam. Dashed line indicates the targeted crack width.



**Figure 5.** Water ingress via each crack for the different beams.

Water ingress measurements were performed for each crack and the results obtained are presented in Fig.5. The average crack width measured for each crack at the top of the beam is also indicated in Fig.5. It can be seen that the water ingress via the (treated) cracks is higher compared to the water ingress obtained in the uncracked zones. When comparing glass and REF, it can also be noticed that the values obtained for glass are comparable with the values obtained for REF. This is somewhat unexpected since leaching of WRA was clearly visible at crack faces during loading. The water ingress values obtained for PMMA are slightly lower compared to the values found for REF. It should be mentioned that during these permeability tests, leakage of water through the nearby cracks (parallel micro cracks) was observed for some of the cracks, which made it difficult to perform these tests. Therefore, it is difficult to draw clear conclusions from these tests.

#### 4. Conclusions

In the present work, the potential of using polymeric materials (PLA, PMMA and PS) as carriers of healing agent in self-healing of concrete has been investigated. The experimental results showed that capsules made with PMMA-1 have favorable properties to be used as encapsulation material. Real-scale tests revealed that PMMA-1 capsules could survive the concrete mixing process and break upon crack creation.

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