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Capsules with evolving brittleness to resist the preparation of self-healing concrete

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ABSTRACT: Capsules for self-healing concrete have to possess multifunctional properties and it would be an enormous advantage in the valorization process when they could also be mixed in. Therefore, we aimed to develop capsules with evolving brittleness.

Capsules with high initial flexibility were prepared by adding a plasticizer to an ethyl cellulose matrix. During hardening of the concrete, the plasticizing agent should leach out to the moist environment yielding more brittle capsules which break upon crack appearance.

The tested capsules could easily be mixed in during concrete production. However, incompatibility issues between the capsule wall and the inner polymeric healing agent appeared. Moreover, the capsules became insufficiently brittle and the bond strength to the cementitious matrix was too weak.

Consequently, multilayer capsules were tested. These capsules had a high impact resistance to endure concrete mixing and were able to break upon crack formation.

KEYWORDS: Concrete; Mortar; Polymer; Durability; Mechanical properties

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RESUMEN: *Cápsulas que desarrollan gradualmente su fragilidad a fin de resistir la preparación de hormigón autoreparable*. Las cápsulas para la auto-reparación del hormigón tienen que poseer propiedades multifuncionales. Una enorme ventaja en el proceso para su valorización se obtendría si aquellas pudieran resistir con éxito el mezclado. Por lo tanto, nos propusimos desarrollar cápsulas cuya fragilidad evoluciona.

Cápsulas con una alta flexibilidad inicial se prepararon mediante la adición de un plastificante a una matriz de etil celulosa. Durante el endurecimiento del hormigón, el agente plastificante debe filtrarse hacia el medio ambiente húmedo produciendo cápsulas más frágiles que se rompen con el surgimiento de fisuras.

Las cápsulas pudieron ser fácilmente mezcladas durante la producción de hormigón. Sin embargo, aparecieron problemas de incompatibilidad entre la pared de la cápsula y el agente de curación polimérico interior. Por otra parte, las cápsulas se comportaron insuficientemente frágiles y con una baja adherencia hacia la matriz cementicia.

En consecuencia, se probaron las cápsulas multicapa. Estas cápsulas tenían una alta resistencia al impacto para sobrevivir el mezclado del hormigón y fueron capaces de romperse luego de la formación de fisuras.

PALABRAS CLAVE: Hormigón; Mortero; Polímero; Durabilidad; Propiedades mecánicas

1. INTRODUCTION

Dry et al. (1–4) were among the pioneers to study self-healing of concrete. They incorporated hollow glass fibres, filled with methyl methacrylate, epoxy or cyanoacrylate in mortar specimens. Since then, different encapsulation techniques and healing agents have been screened by different research groups. Spherical microcapsules made of urea formaldehyde (5, 6), gelatin (5, 7) and silica (due to the compatibility with the alkaline cementitious matrix) (8) have already been produced to evaluate their performance in self-healing concrete. Spherical capsules, that are well dispersed in the matrix, have the advantage that cracks can be healed simultaneously at different spots. In comparison to tubular capsules, fewer capsules break during mixing and the stress concentration around the empty capsules is lower. However, the volume of healing agent, present in a spherical microcapsule, is most often too small to obtain complete crack filling. Moreover, the adhesion between the microcapsule and the concrete must be sufficiently strong to allow the capsule to break upon cracking of the concrete. Elongated microcapsules (i.e. elliptic) (9) can possibly offer a solution to these drawbacks. In several studies, researchers could already properly mix in microcapsules in cement paste, mortar or concrete (e.g. 7, 8, 10, 11 (for micro-encapsulated bacterial spores)).

The use of tubular glass capsules was also studied by different researchers (12–14). Computer simulations performed by Mookhoek et al. (15, 16) for self-healing composites showed that tubular capsules had greater healing potential than their spherical counterparts. However, the likeliness that these stay intact during mixing is lower. Common glass tubes used in self-healing concrete have diameters of 0.8 to 3 mm and lengths between 20 and 300 mm. In addition to glass capsules, also polymeric capsules have been explored. Hilloulin et al. (17) tried to increase the resistance to concrete mixing by heating the capsules beforehand, resulting in a shift from the brittle to the rubbery state.

In the long tubing systems, a long (glass) tube is embedded in concrete and connected with an external reservoir containing healing agent (under (hydrostatic) pressure) (3, 5, 12). Upon concrete cracking, a small amount of healing agent flows into the crack and hardens. The disadvantage of these systems is that the tube can be blocked and that it is impractical for large structures. The self-repairing system developed by Nishiwaki et al. (18) uses selective heating: upon concrete cracking, the resistance of a self-diagnosis composite increases and as a consequence, a heat-sensitive pipe melts at the location of the crack and a healing agent is released. Another concept uses shrinkable polymer tendons (19): after concrete cracking, the concrete is subjected to a series of combined heating/curing regimes to activate the shrinkable polymer resulting in crack closure and promoting autogenous healing of the cementitious matrix. Also Dry (20) heated concrete to obtain crack healing by melting the coating around a porous tube which contained a healing agent. These procedures including heating are rather expensive. An approach with "porous network concrete" was investigated by Sangadji and Schlangen (21). Upon concrete cracking, the healing agent can flow (under pressure) through a porous concrete cylinder and hardens within the cracks.

Different approaches have been studied extensively. However, it is clear that suitable and practically applicable capsules for polymeric healing agents, which resist concrete mixing and casting on the one hand and break upon crack formation on the other hand, are still to be found. In the current study, the possibility is investigated to use ethyl cellulose (EC) capsules, designed to have an evolving brittleness. Plasticizing agents have been added to the EC matrix to make them more flexible at the beginning. Leaching out of the plasticizing agent during concrete hardening should make the capsules more brittle at a later stage. Moreover, because of incompatibility problems between the polymeric capsules and the healing agent, also multilayer capsules have been studied in the second stage. The capsules were composed of an inert glass layer, surrounded by a polymeric layer of EC and plasticizing agent.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Polymeric capsules

EC was chosen as material for the polymeric capsules because of its properties particularly well suited to this application. The material is used worldwide e.g. for the production of hollow tubes in industrial and pharmaceutical applications. Moreover, EC is almost insoluble in water and is chemically resistant to alkalis what is very important when it has to be added to concrete where the pore solution has a pH of ~13. EC can also be extruded and can be combined with different plasticizing agents. The EC used in this study was delivered by the Dow Chemical Company (Ethocel® FP10) and the amount of ethyl substitution varied between 48 and 49.5% w/w.

In order to obtain capsules with evolving brittleness, plasticizing agents were added. In the first stage of the study, triacetin (TAC), triethyl citrate (TEC) or dibutyl sebacate (DBS) was added to the EC in a percentage of 25% w/w. Later on, tests were also performed with polyethylene oxide (PEO), having a molecular weight of 2000 g/mol, and TAC added in a concentration of 10% w/w. TAC (ester of acetic acid and glycerine), TEC (ester of citric acid and ethanol) and PEO (polyether of ethylene glycol)

are hydrophilic plasticizing agents, while DBS (butyl ester of sebacic acid) is hydrophobic. TAC, TEC and DBS were used in liquid form and PEO in pellets. Before usage, these pellets were finely ground to powder with a mixer type IKA Yellowline A10.

In order to compare the performance of the polymeric capsules with the performance of the capsules used in earlier studies (22), glass and ceramic capsules were also tested. The glass capsules consisted of borosilicate glass (Hilgenberger, Germany) and had an inner diameter (ID) of 1.7 mm and an outer diameter (OD) of 2.3 mm. The ceramic capsules were made by VITO (Belgium) and had an ID of ~2.4 mm and an OD of ~3.0 mm. As healing agent, a polyurethane (PU) was used in this study. In order to accelerate the reaction, the healing agent was used as a two component system. One component is the precursor of Meyco® MP355 1K, the other component is composed of 10% accelerator and 90% water. The ratio of precursor to (accelerator + water) is 1:1.

2.1.2. Dip-coated glass capsules

Because of the incompatibility problems noted with the polymeric capsules in this study, multi-layer capsules were also tested. These multilayer capsules consisted of an inner inert layer, which was a glass capsule (ID 1.7 mm; OD 2.3 mm), and an outer layer of polymer. The polymer chosen was EC with as plasticizing agent PEO or DBS (20% w/w).

2.2. Methods

2.2.1. Polymeric capsules

2.2.1.1. Extrusion of polymeric capsules Before the hot-melt extrusion of the capsules, the EC was manually mixed with the plasticizing agents in the right proportion. For the extrusion, a lab-scale co-rotating twin screw extruder type MP19 TC25 (APV Baker, Newcastle-under-Lyme, UK) was used. The mixtures with liquid plasticizing agent were fed at 1.35 g/min while the mixture with PEO was fed at 1.4 g/min. The temperature profile used for the former was 80–105–115–125–125 °C (from feeding to die) while for the latter the temperature profile was adjusted to 120–130–140–150–150 °C. Hollow tubes with an ID of 3 mm and an OD of 5 mm were made. As can also be seen in Figure 1, the EC capsules with TAC and PEO could be easily extruded and their dimensions are quite constant. For the EC capsules with TEC and DBS, the outflow was not constant and also the dimensions of the tubes varied (OD between 3 and 5 mm). Nevertheless, the extrusion of the polymeric tubes was successful. The tubes were cut with a hot knife to capsules with a length of 50 mm to test their performance in self-healing concrete with polymeric healing agents.

2.2.1.2. Resistance during concrete mixing The composition of the concrete used to test the resistance of the capsules is given in Table 1.

Since crushed limestone was expected to exert a higher impact on the capsules than gravel, this aggregate was selected for the concrete mix. Capsules cut to a length of 50 mm, filled with water with red pigment and sealed with methyl-methacrylate glue were thrown in the concrete mixer (Hobart D-300) during the last 2 minutes of mixing (1 minute at 140 rotations/min and 1 minute at 285 rotations/minute). Per mix of 10 l, 10 capsules were tested and 3 batches of concrete were made for each type of capsule. After mixing, the number of intact capsules was counted and the survival ratio was determined.

2.2.1.3. Bond strength of the capsules with the cementitious matrix Breakage of the capsules at the moment of concrete cracking can only occur when the adhesion of the capsules with the cementitious matrix is good. To test the bond strength of the capsules with the cementitious matrix, capsules filled with hardened epoxy (PC 5800, TRADECC) (to prevent failure different from bond failure) were embedded in mortar cylinders (h 50 mm, diameter 100 mm) to a depth of 5 mm. A nut was glued over the capsules to make the connection with the tensile testing machine (Instron 3369). A displacement controlled tensile test was performed (loading rate of 2 mm/min). By dividing the maximum load by the circumferential area of the embedded capsule, the bond strength could be calculated.

2.2.1.4. Tensile strength of the polymeric capsules Since the tensile strength is also an important

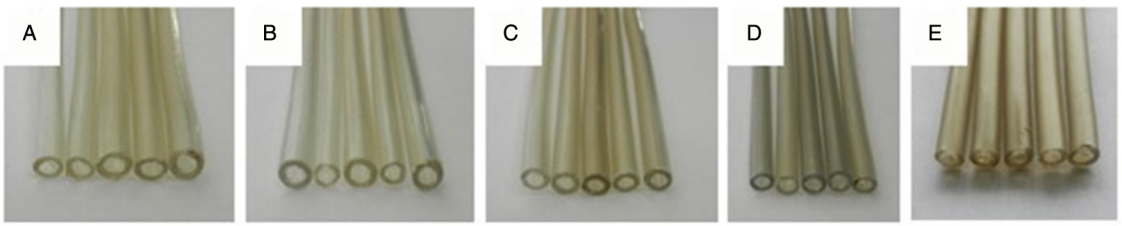

FIGURE 1. Extruded tubes of EC with plasticizing agent — (A) TEC 25% w/w – (B) DBS 25% w/w – (C) TAC 25% w/w – (D) TAC 10% w/w – (E) PEO 10% w/w.

Table 1. Concrete composition for 1 m³ concrete

Material	kg/m³ concrete
Cement CEM I 52.5 N	350
Water	165
Sand 0/4	664
Crushed limestone 2/6	450
Crushed limestone 6/20	760

parameter to evaluate the performance of the capsules in self-healing concrete, tensile strength tests were performed on capsules (length 120 mm). These capsules were filled with hardened epoxy at their ends (50 mm) and a nut was glued over the ends of the capsules in order to make the connection with the tensile testing machine (Instron 3369). A displacement controlled test (loading rate of 2 mm/min) was performed and the tensile strength was calculated as the maximum load divided by the cross-sectional area of the hollow tube.

2.2.1.5. Compatibility of the capsules with the cementitious matrix: Effect of the high pH of cementitious materials on the mechanical properties of the capsules In order to test whether the capsules are resistant to the high pH in the pore solution of concrete, polymeric capsules, sealed at their ends with epoxy, were submerged in saturated $Ca(OH)_2$ solution and embedded in cement paste. As a reference, capsules were also stored in tap water. After 1 and 4 weeks, the conditions of the capsules stored in water or saturated $Ca(OH)_2$ solution were visually inspected and a tensile test, as described in the previous paragraph, was performed to analyze the influence of the storage conditions on the mechanical properties. Capsules removed from the cement paste after 2 or 6 weeks of storage (at ~20 °C and ~60% RH), were also visually inspected and tested for tensile strength.

2.2.1.6. Compatibility of the cementitious matrix with the capsules: Effect of leaching plasticizing agents on the hydration of cement Plasticizing agents were added to the EC capsules in order to obtain capsules with evolving brittleness. Since the plasticizing agent has been added with the intention of leaching towards the cementitious matrix during hardening, the cement hydration process can possibly be disturbed. Therefore, isothermal calorimetric measurements (TAM AIR, TA instruments) were performed on reference mixes (14 g cement paste with a water-to-cement ratio of 0.4), mixes with plasticizing agent (cement paste with a water-to-cement ratio of 0.4 and an additional amount of plasticizing agent, assuming that the total amount of plasticizing agent present in a concentration of 25% w/w in a capsule with 50 mm length will leach in reality to a 1 mm thick layer of cement paste around the capsules = 2.12 g plasticizing agent vs. 11.88 g cement paste) and mixes (13.86 g cement paste with a water-to-cement ratio of 0.4) containing a capsule of 10 mm length (0.14 g). Monitoring of the heat production rate during cement hydration allows to evaluate the effect of the plasticizing agent or presence of the capsule on the hydration process.

In addition, cement paste samples containing each type of capsule have been broken at the interface with the capsule to visually inspect the effect of leaching of the plasticizing agent on the cementitious matrix. The results of the visual inspection have been compared with the results obtained from isothermal calorimetry.

2.2.1.7. Compatibility of the healing agent with the capsules : storage life of healing agents in the capsules To test the compatibility of the PU precursor and the mixture of accelerator and water with the EC capsules, capsules were filled with these materials, sealed with methyl methacrylate glue at the ends and stored for 7 days at laboratory conditions. After 2 and 7 days, the capsules were visually examined.

2.2.1.8. Differential scanning calorimetry to evaluate the leaching of plasticizing agent In order to evaluate whether the plasticizing agent effectively leaches out of the EC capsules, differential scanning calorimetric (DSC) measurements were performed on pieces of the capsules. If leaching of the plasticizing agent has occurred, a difference in the glass transition temperature (T_g) should be detected. Reference capsules, stored in laboratory conditions, as well as capsules stored in cement paste were thus tested. However, since other tests showed that there is also a high probability that the plasticizing agent leaches out towards the stored healing agent (instead of the cementitious matrix, to which it was aimed to leach), also capsules filled with the PU precursor and the mixture of accelerator and water were tested. All tests were performed after 8 days of storage.

2.2.1.9. Three-point bending test to evaluate breakage of capsule upon crack creation Mortar prisms (40×40×160 mm) containing two reinforcement bars of 2 mm diameter and two capsules (1 capsule filled with the PU precursor and 1 capsule filled with the mixture of accelerator and water), positioned at 10 mm from the bottom surface, were prepared. At the age of 7 days, a crack width controlled three-point bending test (loading rate of 0.001 mm/s up to a crack width of 0.4 mm) was performed (Walter + Bai DB 250/15). At maximum crack opening, the specimens were visually inspected to check leakage of healing agent and thus breakage of the capsules. Afterwards, the specimens were broken in a force-controlled test (loading rate of 0.5 kN/s) for final evaluation.

2.2.2. Multilayer capsules

2.2.2.1. Dip-coating of glass capsules Before the dip-coating process could start, the plasticizing agents were manually mixed with the EC in a concentration of 20% w/w. Via a process of solvent casting with chloroform, the polymer was subsequently brought into solution (polymer-to-solvent ratio of 25% w/v). Then, the glass capsules (filled with PU and sealed at their ends with methyl methacrylate glue) were dipped for 1 minute into the liquid coating solution. After a time, the chloroform evaporated from the liquid and a thin polymer layer was formed. The process was repeated twice to obtain a sufficiently thick coating layer on the glass capsules. Although the coating felt rough, a quite even layer of ~0.2 mm thickness was attained. The coating thickness was calculated based on the outer diameter of the dip-coated capsules, measured with sliding calipers, and the known outer diameter of the glass capsule itself.

2.2.2.2. Performance tests of the dip-coated capsules in self-healing concrete Since the multilayer capsules consist of an inner layer in glass, it is known from previous research (22) that there will be no incompatibility problems with the healing agent. Moreover, the outer layer consisting of EC and DBS or PEO will show the same performance as the pure polymeric capsules with regard to the interaction with the cement matrix. Therefore, in the second part of this study, we only focused on the two most important requirements: resistance of the dip-coated capsules during concrete mixing and breakage of the capsules upon crack formation. The test procedures applied were similar to the ones described above, except that a concrete pan mixer with a capacity of 30 l was used to test the resistance of the capsules and that two pairs of capsules, one pair consisting of one capsule filled with prepolymer and one capsule filled with accelerator and water, were provided in the mortar prisms to test breakage of the dip-coated capsules upon crack formation.

2.2.2.3. Capillary water absorption test Since the results of these tests were promising, also the self-healing efficiency of concrete specimens was tested via a capillary water absorption test. Concrete prisms (120×120×500 mm), containing two reinforcement bars of diameter 6 mm were cast. The lower layer (25 mm) was made out of self-healing concrete, thus containing randomly distributed capsules (2% v/v) which were mixed in, while the rest of the beam was cast from traditional concrete (Table 2).

The capsules were coupled (1 capsule filled with the precursor and 1 capsule filled with the mixture of accelerator and water) to increase the probability that both components are released at the same time. After a storage period of 28 days, a crack width controlled three-point bending test was performed until a crack of 0.4 mm was reached. After visual inspection of the healed crack, a prism of 120×120×40 mm, containing the healed crack, was sawn from the middle and dried in the oven at 40 °C until constant mass. Then, the side surfaces were wrapped in adhesive aluminum tape and a capillary water absorption test was performed. The samples were submerged over 10 mm and the gain in mass was recorded during 24 hours. As references, also uncracked and cracked, unhealed specimens were tested.

TABLE 2. Concrete composition for 1 m³ concrete to test the healing efficiency on realistic concrete prisms

Material	kg/m³ concrete
Cement CEM I 52.5 N	300
Water	150
Sand 0/4	670
Gravel 2/8	490
Gravel 8/16	790

3. POLYMERIC CAPSULES WITH EVOLVING BRITTLENESS – RESULTS AND DISCUSSION

3.1. Resistance of the capsules during concrete mixing

In Figure 2, the survival ratios for the different types of polymeric capsules are presented. As can be seen, 9 out of 10 capsules remain intact during mixing when 25% plasticizing agent is added to the EC capsules. This result is not surprising since these capsules were rather flexible. Even when the capsules had been squeezed between the mixer wall and blades during mixing, they sometimes remained intact (Figure 3 - A). Although, this first series of experiments was successful, decreasing the concentration of plasticizing agent to 10% had a detrimental effect on the survival ratio. Indeed, Figure 3 - B shows that several capsules were completely broken after mixing them into concrete.

3.2. Bond strength

As depicted in Figure 4, the bond strength of the EC capsules containing different types of plasticizing agents (25% w/w) differs significantly from the bond strength of ceramic capsules and glass capsules. However, there is no significant difference between the results obtained for the EC capsules with different plasticizing agents. Statistical analysis was performed by checking the homogeneity of the variances with a Levene's test (two tails and level of significance =0.05). When the variances were not homogeneous, a Dunnett's T3 Post Hoc test was performed, while a Student-Newman-Keuls test was performed when the variances were homogenous (level of significance =0.05).

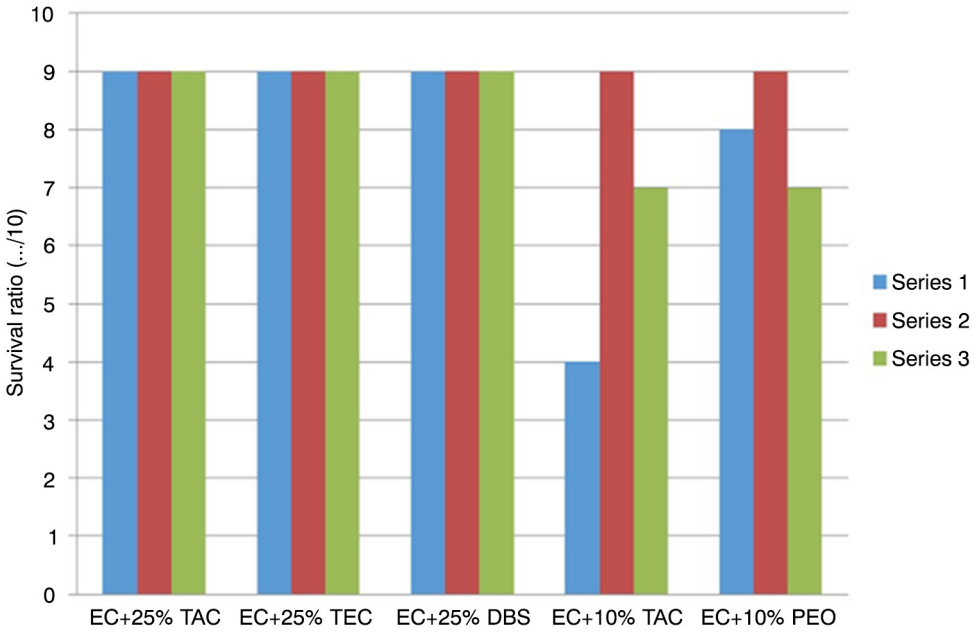

FIGURE 2. Survival ratio of EC capsules (l=50 mm).

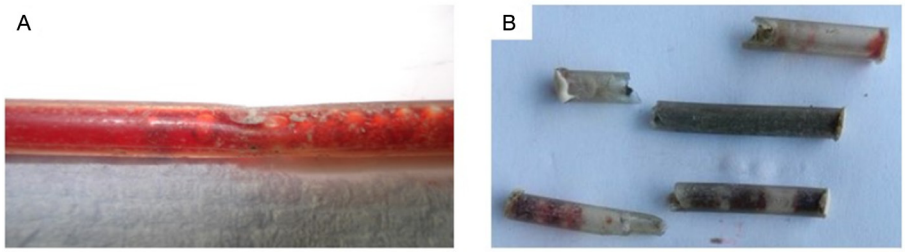

FIGURE 3. (A) Dented EC capsules with 25% TEC after mixing – (B) Damaged EC capsules with 10% TAC after mixing.

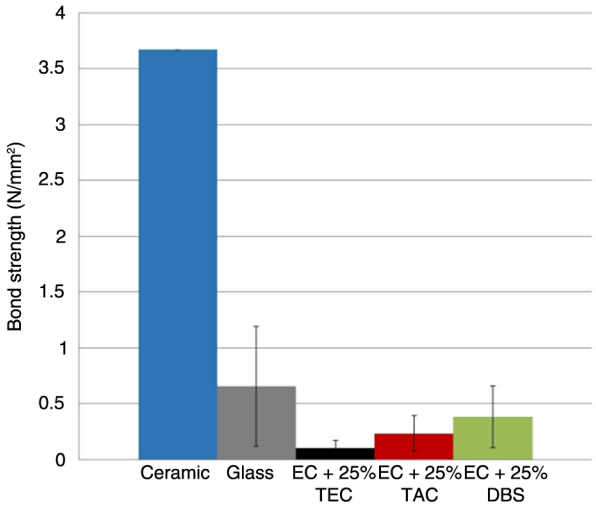

FIGURE 4. Bond strength of the capsules to the mortar matrix. No standard deviation is shown for the ceramic capsules since only one of the specimens failed due to loss of the bond.

It needs to be mentioned that during the bond strength test, for some of the ceramic and glass capsules failure was noticed in the capsules itself and not at the interface between the capsule and mortar matrix (data not shown). This means that for these capsules, the bond strength is even higher than the measured tensile strength. The fact that the bond strength of the EC capsules is very low, is probably due to leaching of the plasticizing agent towards the cementitious matrix. This can interfere with the cement hydration process, leading to a loss of adhesion. To analyze the effect of leaching of the plasticizing agents on the cement hydration, isothermal calorimetric tests were performed (Section 3.5).

3.3. Tensile strength

The tensile strength of glass (mean value of 58 N/mm²) and ceramic capsules (mean value of 40 N/mm²) is much higher than the tensile strength

of EC capsules with plasticizing agent (mean values varying between 7 and 12 N/mm²). Moreover, the strain at failure is much higher (10–20 times) for the EC capsules with 25% plasticizing agent than for the ceramic (0.006) and glass (0.005) capsules. However, a decrease in concentration of plasticizing agent induces a decrease in the strain at failure. For the EC capsules with 10% PEO, the values of the strain at failure do not significantly differ compared to the values measured for glass and ceramic capsules.

3.4. Compatibility of the capsule with the cementitious matrix: Effect of the high pH of cementitious materials on the mechanical properties of the capsules

Tensile tests performed on capsules after storage in cement paste (2–6 weeks), saturated $Ca(OH)_2$ solution (1–4 weeks) or water (1–4 weeks), show that these storage conditions do not significantly alter the tensile strength and strain at failure of the capsules. According to Rahman & Brazel (23), addition of a plasticizing agent to a polymer leads to a decrease in tensile strength and an increase of the strain at failure. Leaching of the plasticizer should thus induce an increase in tensile strength and a decrease of the strain at failure. However, such trend was not observed in the current study.

After storage of the capsules in water and saturated $Ca(OH)_2$ solution, longitudinal fissures were noted in some of the EC capsules with TAC (Figure 5) after 1 week exposure and in all EC capsules with TAC after 4 weeks exposure. Also in the EC capsules with PEO longitudinal fissures were noted, however, to a lesser extent. Capsules stored for 6 weeks in cement paste did not show this behavior, indicating that storage in pure water or saturated $Ca(OH)_2$ solution is too harsh to evaluate the compatibility of the capsules with the alkaline cementitious environment.

Measurements of the pH, clearly show that hydrolysis occurs when EC capsules with TAC, TEC and DBS are stored in saturated $Ca(OH)_2$ solution. The decrease in the pH (from 12.5 to 7 or 8.5 in 28 days) is due to the fact that the plasticizing agents, that contain ester bonds, are unstable in alkaline medium (24) and release carboxylic acids as degradation products. Thus, plasticizing agent is probably released in this case although no difference in tensile strength and strain at failure is observed.

FIGURE 5. Longitudinal fissures in EC+25% TAC capsules due to storage in water for 7 days.

3.5. Compatibility of the cementitious matrix with the capsules: Effect of leaching plasticizing agents on the hydration of cement

The effect of leaching of plasticizing agent on the hydration of cement paste is investigated by isothermal calorimetric measurements. The results are presented in Figure 6. The addition of the pure plasticizing agents has a considerable effect on the hydration of cement while the effect of adding a capsule of 10 mm length is negligible. We want to make clear from the beginning that the former can be an overestimation of the real situation due to the fact that the amount of plasticizing agent added to the mix is overdosed. However, the latter can be an underestimation as the amount of leaching plasticizing agent in relation to the cement paste mass is limited resulting in no detectable effect.

Addition of pure TAC to the mixture induces a decrease of the setting time and an acceleration of the hydration reactions. However, when the total heat production after 7 days is considered, the results are similar for mixtures with and without TAC. This accelerating effect is not completely surprising since Ray (25) added TAC to the hydraulic matrix (0.01–1% relative to the cement weight) to obtain a faster hardening process and higher strength. In contrast, addition of pure TEC hinders the hydration of the cement paste and no second hydration peak is observed. This can be clarified by the fact that in contact with water, hydrolysis occurs, leading to the formation of ethanol and citric acid. As shown by Windels et al. (26), citric acid has a negative effect on the hydration

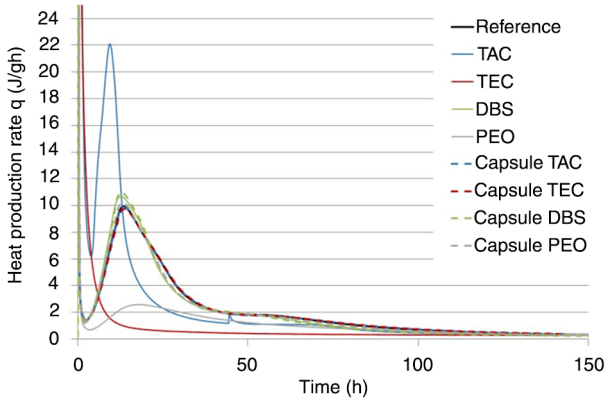

FIGURE 6. Effect of plasticizing agents on the hydration of cement – only one curve per measurement series is shown since the repetitions behave similarly.

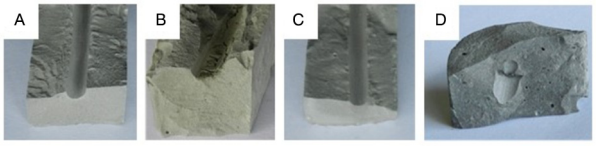

FIGURE 7. View of the cement matrix around an embedded capsule – (A) TAC 25% w/w – (B) TEC 25% w/w – (C) DBS 25% w/w – (D) PEO 10% w/w.

of cement. Moreover, as shown in Figure 7, also the cement paste around the capsules with TEC is deteriorated, which corresponds with the findings from Windels (26). DBS has no noticeable effect on the hydration of cement paste. This is probably due to the fact that this plasticizing agent has a hydrophobic character. Nevertheless, as shown in Figure 7, the cement paste around the embedded capsules is slightly discolored, indicating that hydrolysis can take place, yielding butanol and sebacic acid. Finally, it is also shown that PEO can have a negative effect on the hydration of cement. The second peak is delayed and much lower in comparison to the reference. However, visual inspection of the zone around an EC capsule with PEO shows no degradation (Figure 7). This can be due to the fact that in contact with PEO, water can hydrate and result in swelling of the PEO. In this case, no other products will be formed, but the water is no longer available for cement hydration.

3.6. Compatibility of the healing agent with the capsules: storage life of healing agents in the capsules

Visual inspection of the capsules filled with the PU precursor shows that the precursor cures within the capsule. For the capsules filled with the mixture of accelerator and water, the initial volume partly disappears. This can already be noticed after 2 days of storage, but the effect is even more clear after 7 days. In Figure 8, an example is shown for EC capsules with 25% DBS. Note that the effect is slightly reduced when the concentration of plasticizing agent is lower.

In order to clarify whether the precursor of Meyco® MP355 1K can react with the plasticizing agents (which probably also leach out towards the inner side of the capsule) or the EC, additional ^{1}H-NMR (proton nuclear magnetic resonance) spectroscopy was performed. Reference spectra of the individual components were compared to the spectra of the mixtures (precursor + plasticizing agents or EC). These results indicate that a chemical reaction can occur between the precursor and the plasticizing agents TAC (data not shown), TEC and DBS (data not shown). An example is depicted in Figure 9 (reaction between the precursor and TEC). The ^{1}H-NMR signals which can be attributed to TEC

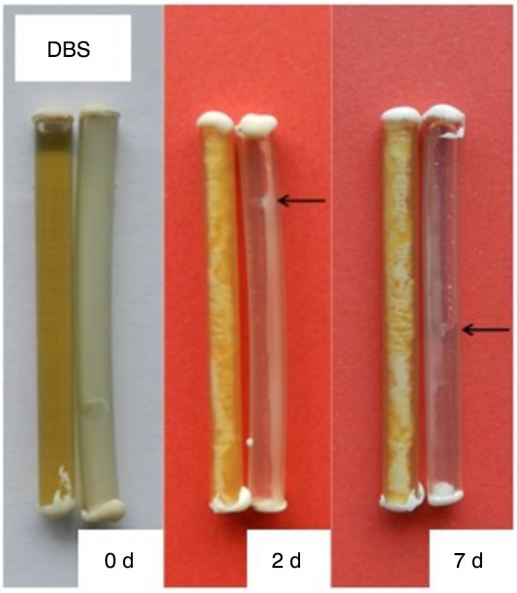

FIGURE 8. Incompatibility between the healing agent and the EC capsules with 25% DBS – left tube: Prepolymer of Meyco® MP355 1K which cures with time – right tube: mixture of accelerator and water which disappears with time.

include: 1.05 (CH_3), 2.12 (OH), 2.65 (-CH_2-C=O-), 4.05 (-CH_2-O-O=C-). A full elucidation of the ^{1}H-NMR spectrum of the PU precursor was not possible since the precise composition of the precursor was not revealed by the company. However, the following characteristic signals could be distinguished for the precursor: 0.9 to 2.2 (methyls and methylenes of diisocyanates and/or diols). When comparing the ^{1}H-NMR spectrum of the precursor with that of the combination of the precursor and TEC, a change in the number of peaks and their location in the region between 3.8 and 4 ppm can be distinguished. A complete elucidation of these signals was not possible as indicated above. However, the latter indicates that a potential reaction could have taken place between the precursor and TEC since the ^{1}H-NMR spectrum of the blend did not result in a spectrum showing all characteristic signals of the individual components being TEC and the precursor.

By ^{1}H-NMR technique, no decisive answer can be given about the possible reaction between the precursor and the EC. However, from a chemical viewpoint the PU precursor is anticipated to show cross-reactivity with the hydroxyl functionalities present in EC in case the latter is not completely substituted. Moreover, no reaction is detected between the precursor and PEO. The reason for the latter can be that the number of hydroxyl groups from PEO in the mixture is insufficient to visualize the reaction potentially taking place.

The mixture of accelerator and water has a pH of ~10. This means that esters like TAC, TEC and

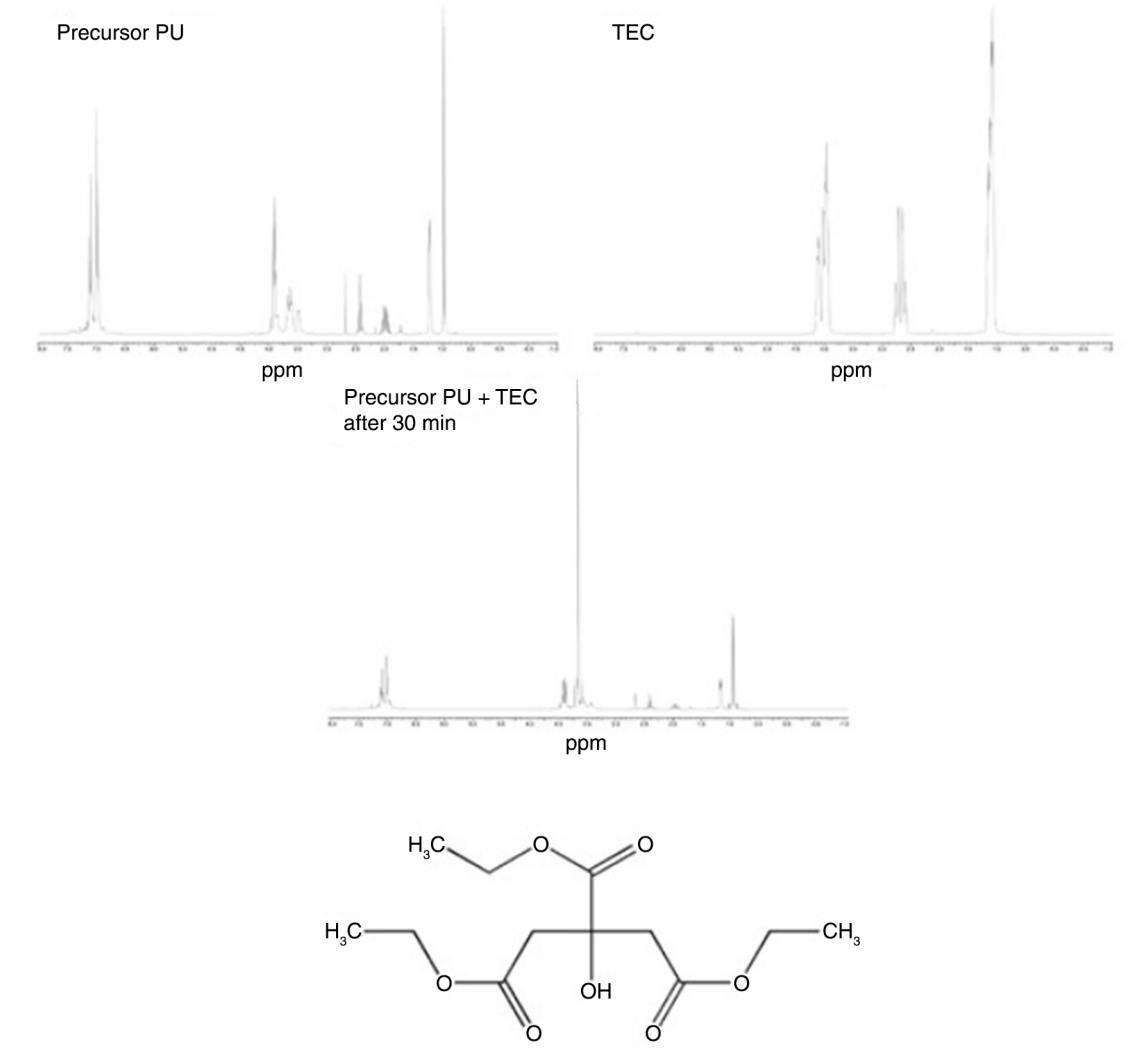

FIGURE 9. 1H-NMR spectra of pure precursor, pure TEC and a mixture of precursor and TEC. Also the structural formula of TEC is given.

DBS, are very unstable in that environment (24) and that the plasticizing agents probably leach out towards the inner side of the capsules (instead of leaching towards the surrounding cement paste). Moreover, the fact that the volume of the accelerator with water in the capsules decreases, suggests that the capsules are not completely air and water vapour tight. Leaching of the plasticizing agents could even have a more detrimental effect on the tightness of the capsules.

Taken together, a reaction between diols and diisocyanates has to be excluded to prevent premature polymerization reactions of the precursors. Using plasticizers containing no OH-groups and ethylcellulose which is completely substituted with ethoxyl groups (and thus does not contain hydroxyl groups that can react with the PU-based healing agent) would be a good alternative. Moreover, leaching of the plasticizing agent towards the inner part of the capsule must be prevented and it has to be assured that the capsules are completely tight. Multilayer capsules with an inert material at the inner side would thus be appropriate. This is, amongst others, a rationale why, in the second stage of this study, dip-coated glass capsules were tested.

3.7. DSC to evaluate leaching of the plasticizing agent

The glass transition temperature (T_g) of pure EC varies between 129 °C and 133 °C (27). Addition of plasticizing agent clearly leads to a decrease in T_g of the EC capsules (Figure 10). For example, for EC with TAC, the T_g is ~99 °C when 10% TAC is added and ~51 °C when 25% TAC is added. This means that, when the plasticizing agent leaches out of the

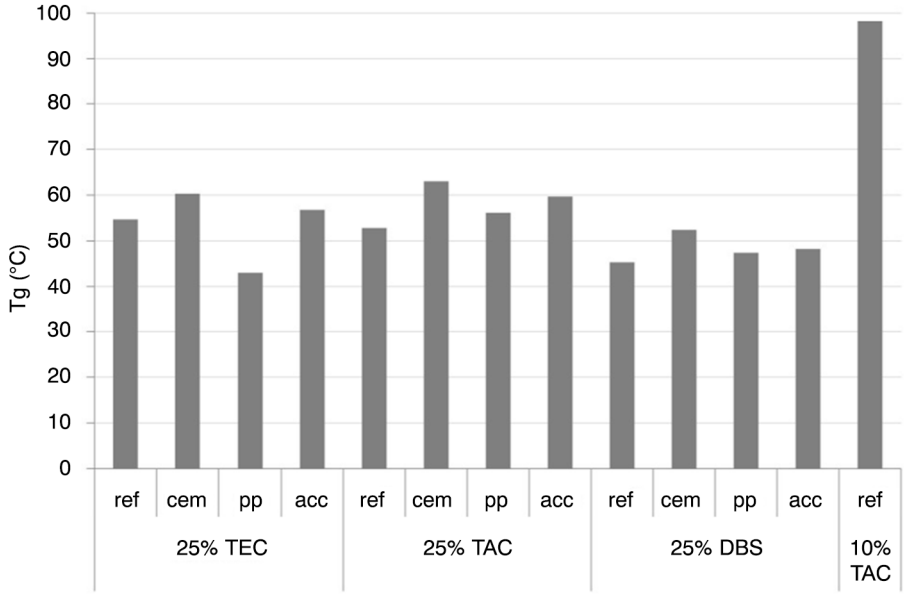

FIGURE 10. Glass transition temperature of EC capsules before (ref) and after leaching of the plasticizing agent towards the cement paste (cem), prepolymer (pp) or mixture of accelerator and water (acc). Only one measurement was performed per series.

capsules, the T_g should increase. For all EC capsules with 25% plasticizing agent stored in cement paste, a clear increase in T_g is observed in comparison to the reference values, indicating that the plasticizing agent has partly leached. However, in comparison to the measured value for the EC capsule with 10% plasticizing agent, one can conclude that only a limited amount of plasticizing agent has leached, indicating that the properties of the capsules will not have changed significantly.

Storage in air of capsules with a precursor or a mixture of accelerator and water generally also induces an increase in T_g. This can indicate that the plasticizing agent leaches out towards the inside of the capsule.

3.8. Breakage of the polymeric capsules upon crack formation

The results of the three-point bending tests are summarized in Table 3.

As can be seen, none of the capsules were broken when a crack width of 0.4 mm was reached while similar tests performed with glass and ceramic capsules, showed considerable leakage of the same healing agent out of the capsules (22). Moreover, Van Tittelboom et al. (22) could already detect breakage of the glass capsules with Acoustic Emission Analysis from a crack width less than 100 μm. Upon complete breakage of the mortar prims, all EC capsules with 25% DBS and 10% PEO were broken. However, for the other types even at complete breakage of the prisms, not all capsules were broken (Figure 11).

Visual inspection of the completely broken prisms showed that the PU precursor present in the capsules was completely cured. Consequently, even if the capsules had ruptured with the formation of the first crack, no leakage would have been detected. In addition, the volume of accelerator and water in the capsules decreased after storage for 7 days in cement paste. However, the noted decrease is lower

TABLE 3. Probability of breakage of the polymeric capsules upon crack formation

Material	# specimens where leakage of the healing agent occurred upon breakage up to 0.4 mm	# capsules with precursor, broken upon complete breakage of the specimens	# capsules with accelerator, broken upon complete breakage of the specimens
EC–25% TAC	0/3	2/3	0/3
EC–25% TEC	0/3	2/3	0/3
EC–25% DBS	0/3	3/3	3/3
EC–10% TAC	0/3	2/3	2/3
EC–10% PEO	0/3	3/3	3/3

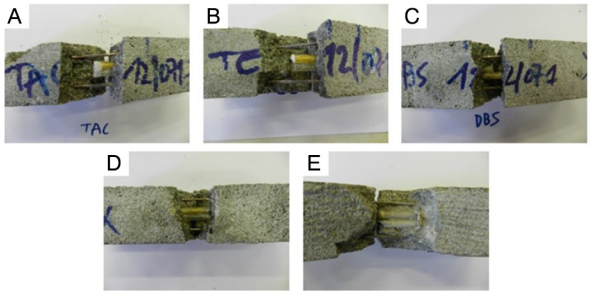

FIGURE 11. Complete breakage of the mortar specimens shows that not all capsules are broken, except for EC capsules with 25% DBS and 10% PEO. (A) TAC 25% w/w – (B) TEC 25% w/w – (C) DBS 25% w/w – (D) TAC 10% w/w – (E) PEO 10% w/w.

compared to the decrease noted upon storage under laboratory conditions.

Slippage of the capsules occurs upon complete failure of the prisms. This can be due to the fact that the bond strength of the capsules is too low in comparison to the tensile strength of the capsules, with the hardened PU inside, in order to induce rupture of the capsules (Section 3.2 and 3.3). Moreover, this issue is probably also due to the fact that the strain at failure is too high for the polymeric capsules (no brittle failure), indicating that insufficient plasticizing agent has leached out of the capsules.

Multilayer capsules, with an inert layer at the inside, which are completely air and water vapour tight, are thus required to store polyurethane based healing agents for a longer time in self-healing concrete.

3.9. Shortcomings of the polymeric capsules to be used in combination with a PU healing agent in self-healing concrete – discussion

The EC capsules with plasticizing agent were developed to obtain "smart" capsules with evolving brittleness. This means that the capsules are at first flexible enough to withstand mixing, while later on, when the plasticizing agent has leached towards the cement matrix, they become sufficiently brittle to break upon crack formation and release the healing agent. The results of this study show that the use of EC capsules with plasticizing agent yields satisfying results during concrete mixing, but (1) the bond strength between the capsules and the cementitious matrix is too low to prevent debonding, (2) the tensile strength of the capsules is too high in comparison to the bond strength with the cementitious matrix (3) leaching of the plasticizing agent is limited and preferentially, the plasticizing agent leaches out towards the healing agent, (4) the polymeric capsules are not completely impermeable and (5) premature curing of the precursor and disappearance of the mixture of accelerator and water is noticed, already during the first days of storage. By consequence, the polymeric capsules developed here are not suitable to be used in self-healing concrete. Different polymeric materials and plasticizing agents have to be combined or multi-layer capsules have to be considered in order to combine good bond properties and tightness with flexibility of the capsules.

4. DIP-COATED GLASS CAPSULES – RESULTS AND DISCUSSION

4.1. Resistance of the dip-coated capsules during concrete mixing

The survival ratio of uncoated and dip-coated glass capsules is presented in Figure 12. As can be seen, for the glass capsules with a length of 50 mm, almost none of the capsules resist mixing. Application of a coating on the surface increases the survival ratio from 4 or 5 to 10. Since this survival ratio is not satisfying, the idea to shorten the capsules was elaborated. Thus, capsules with a length of 25 mm were thrown in the concrete mixer and the results show that the survival ratio drastically increases from 3 or 4 to 10 for the uncoated capsules and 8/10 and 9/10 for the glass capsules coated with EC+20% PEO and EC+20% DBS, respectively. This shows that the impact resistance of the glass capsules can be improved by covering them with a polymer coating. Moreover, these results are comparable to the results obtained with the polymeric capsules as discussed in section 3.1.

4.2. Breakage of the capsules upon crack formation

Visual inspection of the cracks after the three-point bending test and after complete breakage of the prisms, shows that all uncoated glass capsules (with one exception) broke upon crack formation (crack width 0.4 mm). Moreover, leakage of healing agent is clearly observed over the complete crack

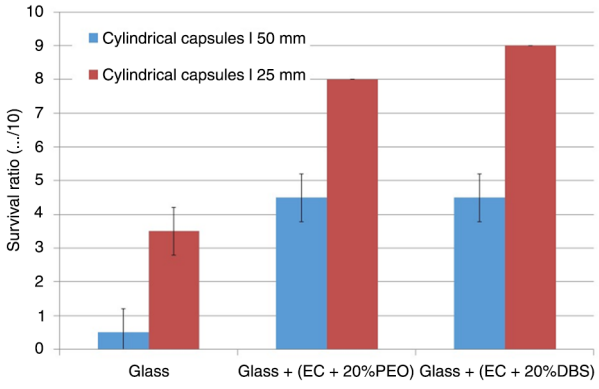

FIGURE 12. Influence of dip-coating on the survival ratio of glass capsules (l=50 mm or 25 mm).

width for the specimens containing long uncoated glass capsules (l=50 mm). For the specimens with shorter capsules, the healing agent does not cover the complete crack width at the surface of the specimens. Concerning the coated capsules, half of the capsules with EC and 20% PEO and all capsules with EC and 20% DBS ruptured upon creation of 0.4 mm wide cracks. This is true for both the short and the long capsules. However, in most cases, the crack at the surface of the specimen is only partly covered with healing agent.

4.3. Sealing efficiency

Visual inspection of the crack after the three point bending test on concrete specimens containing randomly distributed pairs of capsules shows that the crack was only partly filled with healing agent (Figure 13). Possible reasons can be that the quantity of the capsules and the volume of healing agent per capsule is too low to fill the crack completely, that the capsules do not easily break since they are now randomly oriented towards the crack or that the capsules rose above the reinforcement level during compaction.

The results of the water absorption tests show that the water tightness cannot be completely restored after self-healing. The water absorption of the specimens with healed cracks is reduced with 41% in comparison to the cracked, unhealed specimens, but it is still 38% higher than the reference samples without crack (Figure 14).

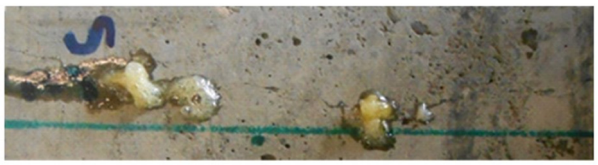

FIGURE 13. Leakage of healing agent at the underside of cracked concrete prisms.

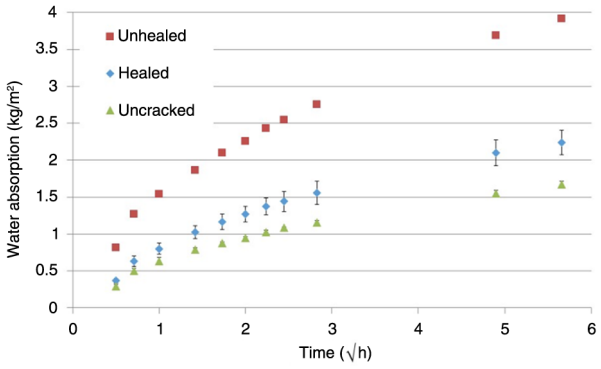

FIGURE 14. Capillary water absorption of unhealed, healed and uncracked specimens.

5. OVERALL DISCUSSION

In this study, the possibility to use EC capsules containing plasticizing agent was investigated. The hypothesis was that the plasticizing agent makes the capsules more flexible, by which they can remain intact during concrete mixing, while later on, the plasticizing agent gradually leaches out in the moist environment. By consequence, the capsules should become more brittle and break upon crack formation. For this purpose, 4 types of plasticizing agents (TAC, TEC, DBS, PEO) were combined with EC in concentrations of 25% or 10% w/w.

The results indicated that the addition of plasticizing agents helps the capsules to resist concrete mixing, however, a decrease in concentration of plasticizing agent from 25 to 10% w/w showed already a decrease in survival ratio. Nevertheless, in this respect the hypothesis appeared valid. However, incompatibility problems, mainly involving the healing agent, were encountered. Premature curing of the precursor of the healing agent and disappearance of the second component (accelerator + water) was detected. This indicates that the capsules are not completely tight and that chemical reactions between the components of the capsules and the healing agent took place. Moreover, leaching of the plasticizing agent preferably occurred towards the healing agent, and could impair its function. Finally, the fact that the capsules do not break upon crack appearance (crack width of 0.4 mm) is also a large obstacle towards application of these capsules for self-healing concrete.

Therefore, in a second stage of the study, dip-coated glass capsules were tested. These capsules have an inert layer at the inside to avoid interaction with the healing agent, but have a higher impact resistance due to the EC coating at the outside. The results showed that 80–90% of the capsules with a length of 25 mm remain intact during concrete mixing and that almost all capsules break upon crack creation. Although this technique seems to be suitable to encapsulate polymeric healing agents, further research is still needed to optimize the amount of capsules needed per m^3 concrete, the length of the capsules, the thickness of the coating, etc. Moreover, since the costs of these capsules is considerable and the risk of alkali-silica reaction is increased by adding glass to the concrete mix, research is still ongoing to develop capsules that are less expensive and do not impair the concrete quality and performance.

6. CONCLUSION

EC capsules containing plasticizing agents (25% w/w) were able to resist concrete mixing, but due to incompatibility problems (mainly premature curing of the precursor) and the fact that the capsules do

not break upon crack appearance, these capsules are not suitable for self-healing concrete. The idea of using plasticizing agents remains however very interesting and final solutions can probably be found by using more brittle basic materials as matrix for the capsules and an appropriate ratio of plasticizing agent/polymer matrix. Moreover, no chemical reactions may occur between the precursor and the capsule material in order to guarantee a long storage life of the precursor.

Using dip-coated glass capsules solves the problems arising with the EC capsules, but these multilayer capsules are quite expensive and the use of glass is not desirable in concrete (because of ASR). Searching for alternative materials for the inner layer could lead to a solution.

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REFERENCES

1. Dry, C. (1994) Smart multiphase composite materials that repair themselves by a release of liquids that become solids, in: Proceedings SPIE 2189, Smart Structures and Materials 1994: Smart Materials, 62–70. http://dx.doi.org/10.1117/12.174085.
2. Dry, C.; McMillan, W. (1996) Three-part methylmethacrylate adhesive system as an internal delivery system for smart responsive concrete. *Smart Materials and Structures* 5, 297–300. http://dx.doi.org/10.1088/0964-1726/5/3/007.
3. Dry, C. (2000) Three designs for the internal release of sealants, adhesives, and waterproofing chemicals into concrete to reduce permeability. *Cem. Concr. Res*. 30, 1969–1977. http://dx.doi.org/10.1016/S0008-8846(00)00415-4.
4. Dry, C.; Corsaw, M. (2003) A comparison of bending strength between adhesive and steel reinforced concrete with steel only reinforced concrete. *Cem. Concr. Res* 33, 1723–1727. http://dx.doi.org/10.1016/S0008-8846(03)00102-9.
5. Mihasi, H.; Kaneko, Y.; Nishiwaki T.; Otsuka K. (2000) Fundamental study on development of intelligent concrete characterized by self-healing capability for strength. *Transactions of the Japan Concrete Institute* 22, 441–450. http://doi.org/10.3151/crt1990.11.2_21.
6. Zhang, M.; Han, N.; Xing, F.; Wang, X.; Schlangen, E. (2013) Design of microcapsule system used for self-healing cementitious material, in: N. De Belie, S. van der Zwaag, E. Gruyaert, K. Van Tittelboom, B. Debbaut (Eds.) Fourth international conference on self-healing materials, Ghent, Belgium, 109.
7. Cailleux, E.; Pollet, V. (2009) Investigations on the development of self-healing properties in protective coatings for concrete and repair mortars, in: Second International Conference on Self Healing Materials, 120.
8. Kaltzakorta, I.; Erkizial, E. (2011) Silica microcapsules encapsulating epoxy compounds for self-healing cementitious materials, in: I. Bond, R. Varley (Eds.) Third international conference self-healing materials, Bath, United Kingdom, 271–272.
9. Li, W.; Buhrow, J.W.; Calle, L.M. (2011) Synthesis of elongated microcapsules, in: I. Bond, R. Varley (Eds.) Third international conference self-healing materials, Bath, United Kingdom, 273–274.
10. Yang, Z.; Hollar, J.; He, X.; Shi, X. (2011) A self-healing cementitious composite using oil core/silica gel shell microcapsules. *Cem. Concr. Comp.* 33, 506–512. http://dx.doi.org/10.1016/j.cemconcomp.2011.01.010.
11. Wang, J.; Soens, H.; Verstraete, W.; De Belie, N. (2014) Self-healing concrete by use of microencapsulated bacterial spores, *Cem. Concr. Res.* 56, 139–152. http://dx.doi.org/10.1016/j.cemconres.2013.11.009.
12. Joseph, C.; Jefferson, A.D.; Canoni, M.B. (2007) Issues relating to the autonomic healing of cementitious materials, in: First International Conference on Self-healing Materials, 1–8.
13. Li, V.C.; Lim, Y.M.; Chan Y.-W. (1998) Feasibility study of a passive smart self-healing cementitious composite. *Compos. Part B: Eng.* 29, 819–827. http://dx.doi.org/10.1016/S1359-8368(98)00034-1.
14. Thao, T.D.P.; Johnson, T.J.S.; Tong, Q.S.; Dai, P.S. (2009) Implementation of self healing in concrete - Proof of concept. *The IES Journal Part A: Civil & Structural Engineering* 2, 116–125. http://dx.doi.org/10.1080/19373260902843506.
15. Mookhoek, S.D.; Fischer, H.R.; van der Zwaag, S. (2009) A numerical study into the effects of elongated capsules on the healing efficiency of liquid-based systems. *Comp. Mater. Sci.* 47, 506–511. http://dx.doi.org/10.1016/j.commatsci.2009.09.017.
16. Mookhoek, S.D. (2010) Novel routes to liquid-based self-healing polymer systems, PhD, Technische Universiteit Delft, Delft.
17. Hilloulin, B.; Van Tittelboom, K.; Gruyaert, E.; De Belie, N.; Loukili, A. (2015) Design of polymeric capsules for self-healing concrete. *Cem. Concr. Comp* 55, 298–307. http://dx.doi.org/10.1016/j.cemconcomp.2014.09.022.
18. Nishiwaki, T.; Oohira, A.; Pareek, S. (2011) An experimental study on the application of self-repairing system to RC structures using selective heating, in: I. Bond, R. Varley (Eds.) Third international conference self-healing materials, Bath, United Kingdom, 320–321.
19. Isaacs, B.; Lark, R.J.; Jefferson, A.D.; Gardner, D.; Dunn, S. (2011) Enhancement of self-healing in cementitious materials, in: I. Bond, R. Varley (Eds.) Third international conference self-healing materials, Bath, United Kingdom, 119–120.
20. Dry, C.; Corsaw, M.; Bayer, E. (2003) A comparison of internal self-repair with resin injection in repair of concrete. *J. Adhes. Sci. Technol.* 17, 79–89. http://dx.doi.org/10.1163/15685610360472457.
21. Sangadji, S.; Schlangen, E. (2011) Porous network concrete: a new approach to make concrete structures self-healing using prefabricated porous layer, in: I. Bond, R. Varley (Eds.) Third international conference self-healing materials, Bath, United Kingdom, 291–292.
22. Van Tittelboom, K. (2012) Self-healing concrete through incorporation of encapsulated bacteria- or polymer-based healing agents, PhD, Ghent University, Ghent.
23. Rahman, M.; Brazel, C.S. (2004) The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. *Prog. Polym. Sci.* 29, 1223–1248. http://dx.doi.org/10.1016/j.progpolymsci.2004.10.001.
24. Bruneel, D; Dirinck, P. (2007) Organische Chemie Deel 1 (in Dutch), Kaho Sint-Lieven.
25. Ray, J.A. (1978) Hydraulic cement mixes and process for improving hydraulic cement mixes (US4089696).
26. Windels, C. (2010) Optimale samenstelling en duurzaamheid van volledig recycleerbaar beton (in Dutch), Master thesis at Ghent University, Ghent.
27. Rowe, R.C.; Sheskey, P.J.; Owen, S.C. (2006) Handbook of Pharmaceutical Excipients (fifth edition), Washington D.C.