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# Performance of modified self-healing concrete with calcium nitrate microencapsulation

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## HIGHLIGHTS

- A modification to the calcium nitrate encapsulation procedure is proposed.
- This modification targets on minimizing the concrete strength reduction
- Mortar mixes with various microcapsules concentrations were investigated.
- The compressive and flexural strengths and elastic modulus were determined.
- The results proved that the modification enhanced mortar mechanical properties.

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## ABSTRACT

This study investigates the strength reduction associated with incorporating calcium nitrate microcapsules in concrete. It also proposes modifications to the calcium nitrate micro encapsulation procedure to minimize the concrete strength reduction. These modifications consist of altering the continuous phase composition and keeping that of the aqueous phase the same. Amounts of 1%–10% of low Hydrophilic-Lipophilic Balance (HLB) emulsifier and 0.1%–1.0% of oil-soluble sulfonic acid catalyst (by weight of water in the aqueous phase) were dissolved in an organic solvent to prepare the continuous phase. The average diameter and shell thickness of the produced microcapsules were characterized using Scanning Electron Microscopy (SEM). Mortar mixes were prepared for various calcium nitrate concentrations of microcapsules that were encapsulated using the modified procedure. The compressive and flexural strengths and the elastic modulus of the mortar mixes were determined. The results show that the use of the modified encapsulation procedure resulted in a statically insignificant reduction of both compressive and flexural strengths compared to the original encapsulation method. The SEM micrographs of the fracture surface of the samples containing microcapsules showed that the strength reduction may be due to the agglomeration of the un-hydrated particles on the surface (shell) of the microcapsules. The compressive and flexural strengths of samples prepared using the proposed encapsulation procedure were enhanced compared to those prepared using previous encapsulation techniques.



## 1. Introduction

Concrete structures usually experience premature and accelerated deterioration when exposed to severe aggressive environmental conditions. Significant funds are allocated to maintenance, repair, and rehabilitation of deteriorated concrete structures [1–3]. In fact, crack propagation and water infiltration significantly accelerate the deterioration process of concrete structures and decrease their durability. ACI 201.2 R92 defines the durability of hydraulic-cement concrete as "its ability to resist weathering action, chemical attack, abrasion, or any other process of deterioration." It also defines a durable concrete as the one that "will retain its original form, quality, and serviceability when exposed to its environment". Cracking also increases concrete permeability. A permeable concrete has a high susceptibility to reinforcement corrosion due to the accelerated penetration of external aggressive agents (e.g., carbon dioxide and chloride ions). Thus, a low permeability may be the key to a better concrete durability.

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Surface deterioration (cracking) can be repaired using materials such as silicates or mortars. However, these repair techniques are time consuming and costly. Therefore, the focus has recently shifted to the use of smart materials for damage prevention and decay minimization of concrete structures. An interesting alternative to the repair and rehabilitation of deteriorated concrete elements and structures is the use of the self-healing concept using microencapsulation [4]. Self-healing concrete uses stresses and associated cracks as a stimulus for a self-healing mechanism. Microcapsules filled with healing agents are inserted in concrete during construction. After their formation, the cracks tips rupture the microcapsule shells and release the healing agents. The released healing agents interact with a catalyst to form calcium-silicate-hydrate gels that heal the cracks and prevent their propagation.

An ideal self-healing agent should be easily encapsulated and its performance and response should not be sensitive to the environmental conditions [5]. Sodium silicate, polyurethane, and cyanoacrylates were investigated in the literature as healing agents [6–8]. However, their high cost may have limited their use. Hassan et al. [9] attempted to encapsulate calcium nitrate as an alternative healing agent due to its low cost, its reactivity with the cement matrix, and its accelerated setting ability of un-hydrated cement particles. The calcium nitrate microcapsules had satisfactory healing potentials. However, they significantly reduced concrete compressive strength [10]. The adverse effect of calcium nitrate microcapsules on concrete strength needs to be investigated and resolved to take advantage of the efficiency of self-healing microcapsules without compromising concrete mechanical properties.

The comprehensive RILEM report [11] identified two healing mechanism types for cementitious materials, namely, autogenous and autonomic. Autogenous healing refers to the ability of concrete mixes with no special additives to fill and seal cracks throughout the material lifetime [11]. The formation of calcium carbonate and the hydration of un-hydrated cement particles are two potential causes for autogenous healing phenomena [12–14]. The contribution of these mechanisms to the healing process is not entirely clear and depends on many factors such as age of concrete at cracking [15,16], presence of water [17], size of cement grains[18,19], water/cement ratio [19], temperature, and crack width [20]. On the other hand, researchers attempted to develop methods to improve concrete autogenous healing capability. In recent years, researchers suggested the use of polyethylene fibers to decrease the crack widths and to enhance the effectiveness of the autogenous self-healing mechanisms [21–23]. The use of shape memory alloys (SMA) [24,25] and shape-memory polymers [26,27] were also proposed to limit crack widths. Superabsorbent polymers and nano-clays were used for improved micro-crack healing and for enhanced autogenous healing capability [28–32]. Expansive additives such as geo-materials and organic polymers were also used to improve concrete autogenous self-healing [33–35].

On the other hand, autonomic healing relies on healing agents that are not part of the normal cement composition using the following mechanics: 1) microencapsulation or direct application to the cracked areas through thin vessels [36–39] and 2) bacteria implementation [40,41]. However, the effectiveness of these mechanisms is highly dependent on the properties of the healing agent. A full review of the performance of a variety of healing agents and their activation mechanism classification can be found in Van-Tittelboom and Belie [42].

Dry [39] presented one of the first microencapsulation attempts using methyl methacrylate within polypropylene and glass fibers. Other researchers used brittle capillary tubes for agent encapsulation [8,21,43]. Yang et al. [44] used silica gel to encapsulate methyl methacrylate monomer (MMA) as the healing agent. Wang et al. [45] used urea formaldehyde to produce the microcapsules. He reported a significant decrease in the flexural and compressive strengths for microcapsules amounts larger than 3% by cement weight. Huang and Ye [46] and Pelletier et al. [7] used an encapsulated sodium silicate solution that forms calcium silicate hydrate (C-S-H) upon contact with the cement matrix calcium hydroxide. Mostavi et al. [47] used an in-situ polymerization method to develop double-walled polyurethane/urea-formaldehyde microcapsules that contain sodium silicate healing agents.

Due to its low cost and capability to accelerate the setting of un-hydrated cement, calcium nitrate was recently investigated as an alternate healing agent encapsulated in urea-formaldehyde shell [9]. Although their self-healing efficiency was satisfactory, calcium nitrate microcapsules causes significant reduction in concrete compressive strength [10]. Hence, it is beneficial to investigate the strength reduction and propose solutions to mitigate it. One possible solution is to propose modification to the microcapsules preparation technique that was proposed by Hassan et al. [9]. The procedure used an in-situ polymerization process under a water-in-oil emulsion and an oil-soluble sulfonic acid catalyst to prepare the continuous phase. Studies on cementitious materials such as nanocomposite cement showed a significant reduction in the compressive strength of cement mixes when sulfonic acid was used as a surfactant [48]. The effect of the sulfonic acid as a cement hydration retarder was not explicitly reported in literature. However, Singh et al. [49] studied the effect of citric acid on the hydration of Portland cement. They have concluded that a small percentage of citric acid (<0.1%) accelerates the hydration rate and a higher dosage percentage reduce it. This may be also the case with other acids such as the sulfonic acid.

Accordingly, this paper proposes a modification to the calcium nitrate microcapsule preparation procedure that was proposed by Hassan et al. [9]. This modification includes a partial replacement of the sulfonic acid catalyst with a low Hydrophilic-Lipophilic Balance (HLB) emulsifier for the preparation of the continuous phase while the aqueous phase composition is kept unaltered. The microcapsules produced using the modified procedure were then characterized using Scanning Electron Microscopy (SEM). The effect of microcapsules on concrete mechanical properties was evaluated on mortar samples first before considering full-fetched concrete testing. Finally, a suitable dosage of calcium nitrate microcapsules in concrete was recommended for future testing.

## 2. Experimental program

### 2.1. Self-healing microcapsule preparation

#### 2.1.1. Composition

Self-healing microcapsules were prepared by modifying the procedure developed by Hassan et al. [9]. The procedure, which uses an in-situ polymerization chemical process to encapsulate calcium nitrate under a water-in-oil emulsion, includes aqueous and continuous phases. The aqueous phase consists of urea, formaldehyde, resorcinol, ammonium chloride, and calcium nitrate as core materials dissolved in distilled water. The composition of the aqueous phase was designed to attain a molar ratio of formaldehyde to urea equal to 1:1.9. The continuous phase composition was modified to include an organic solvent (Hexane), a low Hydrophilic-Lipophilic Balance (HLB) emulsifier (Span 85), and a small amount of an acid catalyst soluble in oil and immiscible with water (Dodecylbenzene sulfonic acid). It is worth noting that the design of the continuous phase requires percentages of HLB emulsifier and acid catalyst to be 1.0–10.0% and 0.1–1.0% of the water weight in the aqueous phase, respectively. The water weight in the aqueous phase is equal to the distilled water weight plus the weight of formaldehyde (i.e., 37% solution) multiplied by 0.63.

#### 2.1.2. Emulsification

The continuous phase shall be subjected to high shear agitation and heated at a high temperature before the drop-wise addition of the aqueous phase over 10 min. A minimum volume ratio of 3:1 must be maintained between the continuous and dispersed phases, to maintain the desired water-in-oil emulsion. The detailed synthesis of both phases is summarized in Table 1.

**Table 1**
Modified synthesis of aqueous and continuous phases.

| Aqueous Phase | | Continuous Phase | |
|---|---|---|---|
| Component | Amount (g) | Component | Amount (g) |
| Urea | 5.0 | Organic Solvent (Hexane) | 200.0 |
| Formaldehyde (37% solution) | 12.67 | Low HLB Emulsifier (Span 85) | 5.0 |
| Resorcinol | 0.5 | Dodecylbenzene Sulfonic Acid | 0.10 |
| Ammonium Chloride | 0.5 | – | N/A |
| Calcium Nitrate | 10.0 | – | N/A |
| Distilled Water | 50.0 | | |

**Table 2**
Mortar mix design (ASTM C109 [50]).

| Material Description | | Quantity |
|---|---|---|
| Portland cement CEM I, Class 42.5 R complying with EN 197-1 (grams) | | 740 |
| Sand (Natural, Conformance to BS EN 12620) (grams) | | 2035 |
| Water (grams) | | 359 |
| Microcapsules | % by weight of cement | 0.00, 0.50, 0.75, 1.00, 1.25 |
| | grams | 0.00, 3.70, 5.55, 7.40, 9.25 |

*2.1.3. Polymerization*

Once the aqueous phase was completely added to the organic phase, the emulsion was left to react at a high shear agitation and temperature for 1–4 h to successfully form a polymer shell around the dispersed droplets. The reaction duration depends on the concentration of the sulfonic acid catalyst and the emulsion heating temperature. Once the reaction was complete, the solid microcapsules settled on the bottom and a separation occurred between them and the hydrocarbon.

The two phases were then mixed and agitated under high temperature to form the microcapsules. The aqueous phase was added to the continuous phase dropwise for a period of 10 minutes and then agitated at 1500 rpm and 40 °C for 1 h. This preparation procedure took into consideration the optimum production parameters and agitation rates recommended by Hassan et al. [9] and Milla et al. [10], respectively. The microcapsules were recovered by decanting the excess hydrocarbon and air drying the microcapsule slurry.

*2.2. Scanning electron microscopy*

The scanning electron microscope Nova NanoSEM model was used for the microcapsule characterization. The microcapsules were sprinkled on top of a double-sided tape attached to a pin stub specimen mount. The samples were then sputter-coated with platinum for four minutes before imaging them under secondary electron mode at an accelerating voltage of 20 kV.

*2.3. Mortar testing*

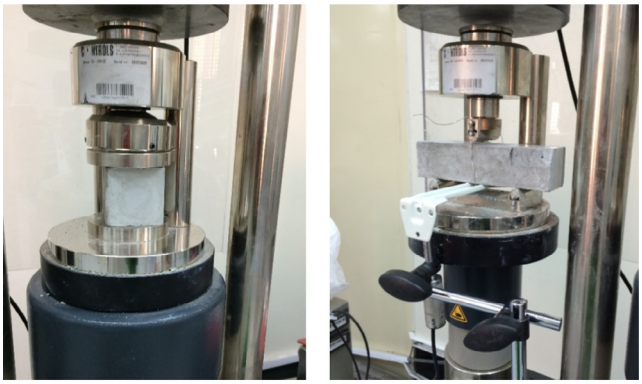
Mortar samples were prepared with various microcapsule concentrations and tested for compressive and flexural strengths according to ASTM C109 [50] and ASTM C348 [51], respectively. The load-displacement curves were also constructed to investigate the mechanical properties of the mortar samples. Future work will be directed towards investigating the self-healing efficiency of the prepared microcapsules on concrete samples. Milla et al. [10] reported that the best healing efficiency was achieved when using microcapsules with calcium nitrate concentrations of 0.50% to 1.00% (by weight of cement). Hence, four different microcapsule concentrations were investigated namely, 0.50%, 0.75%, 1.00% and 1.25% (by weight of cement) in addition to the control mix (without microcapsules). Mortar mixes were prepared as per ASTM C109 [50]. The material proportions for each mortar batch are summarized in Table 2. Because the batch volume is approximately 1.5 liters, four batches were prepared for each mortar mix.

Three 50-mm standard cubes and three 40 mm x 40 mm x 160 mm standard prisms were prepared from each batch to be tested in compression and flexure, respectively. Table 3 summarizes the testing matrix.

The cubes and prisms were prepared as per ASTM C109 [50] and ASTM C348 [51], respectively. The specimens were kept in the molds and covered with a plastic foil for 24 h. After demolding, the samples were cured in limewater for 28 days. A universal test machine was used for compression and three point bending tests. Six specimens were tested after 7 days (2 specimens from batches 1 and 3, and one specimen from batches 2 and 4). The remaining specimens were tested after 28 days of moist curing in flexure. A Linear Variable Differential Transformer (LVDT) was fixed at the mid bottom of the sample for recording the normal displacements. Fig. 1 shows the compression and flexural test setups. The microstructures of the fractured surfaces of the samples containing microcapsules were characterized after testing using the scanning electron microscope Nova NanoSEM model. The fractured surfaces were sputtering with gold as a conductive material to increase the image resolution. The image scales were selected to capture the microcapsules and their surrounding regions. The images were obtained under secondary electron mode at an accelerating voltage of 30 kV.

**Table 3**
Testing matrix.

| Mix ID | Batch No. | Microcapsules Concentration (% by weight of cement) | No. of Samples (Compression Test) | No. of Samples (Flexural Test) |
|---|---|---|---|---|
| 0.00MC (Control) | 1 | 0.00 | 3 | 3 |
| | 2 | | 3 | 3 |
| | 3 | | 3 | 3 |
| | 4 | | 3 | 3 |
| 0.50MC | 1 | 0.50 | 3 | 3 |
| | 2 | | 3 | 3 |
| | 3 | | 3 | 3 |
| | 4 | | 3 | 3 |
| 0.75MC | 1 | 0.75 | 3 | 3 |
| | 2 | | 3 | 3 |
| | 3 | | 3 | 3 |
| | 4 | | 3 | 3 |
| 1.00MC | 1 | 1.00 | 3 | 3 |
| | 2 | | 3 | 3 |
| | 3 | | 3 | 3 |
| | 4 | | 3 | 3 |
| 1.25MC | 1 | 1.25 | 3 | 3 |
| | 2 | | 3 | 3 |
| | 3 | | 3 | 3 |
| | 4 | | 3 | 3 |



(a) (b)

**Fig. 1.** (a) Compression test setup and (b) Mortar flexural test setup.

## 3. Results and analysis

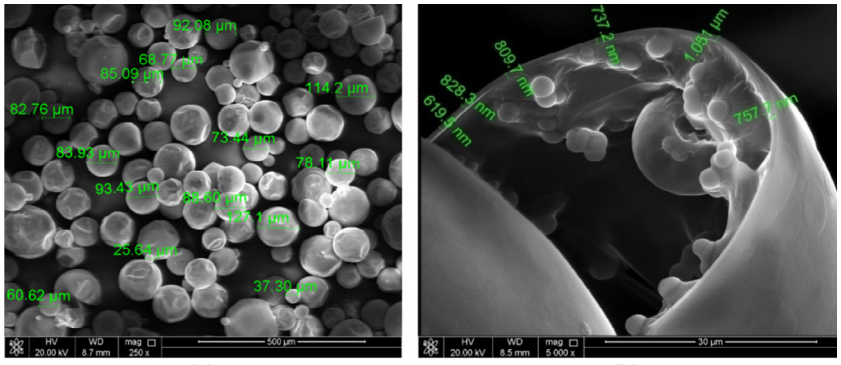
### 3.1. Microcapsule scanning electron microscopy

Fig. 2 shows a scanning electron microscope image illustrating the characteristics of the prepared microcapsules. It indicates that the average diameter of the prepared microcapsules was around 70 μm while the average shell thickness was around 0.81 μm. Using the same temperature, agitation rate and agitation time, Hassan et al. [9] have reported a microcapsule average diameter and shell thickness of around 51 μm and 0.91 μm, respectively. The authors concluded that the optimum healing efficiency could be achieved by incorporating microcapsules with an average diameter of 58.7 μm.

### 3.2. Compression and flexural strengths

Tables 4 and 5 summarize the compressive and flexural strength results, respectively. Before computing the average of the test readings, measurements were checked for outliers according to ASTM E178 [52]. No outliers were found among the test results.

Figs. 3 and 4 show the variation of compressive and flexural strengths with microcapsule concentrations, respectively. The results show that the compressive and flexural strengths decreased with increasing microcapsule concentration. However, the reduction of the 28th day compressive and flexural strengths did not exceed 10% and 17%, respectively. Milla et al. [10] reported reductions of 33% and 73% in the flexural strength of concrete beams reinforced with 1.20% and 2.00% microcapsules by weight of




(a) (b)

**Fig. 2.** Scanning electron microscope images of prepared microcapsules, (a) micro capsules diameter and (b) microcapsules shell thickness.

**Table 4**
Compressive strength test results, (MPa).

| Sample # | 0.00MC (Control) | 0.50MC | 0.75MC | 1.00MC | 1.25MC |
|---|---|---|---|---|---|
| | 7 Days | | | | |
| 1 | 28.73 | 32.14 | 24.52 | 26.74 | 30.95 |
| 2 | 24.75 | 28.00 | 28.31 | 25.42 | 18.76 |
| 3 | 27.72 | 31.99 | 24.01 | 24.28 | 24.86 |
| 4 | 32.11 | 29.23 | 23.04 | 26.34 | 27.41 |
| 5 | 26.79 | 25.05 | 30.08 | 24.75 | 24.49 |
| 6 | 29.72 | 19.30 | 32.31 | 27.30 | 25.49 |
| Average, (μ) | 28.3 | 27.6 | 27.1 | 25.8 | 25.3 |
| Stand. Dev. (σ) | 2.5 | 4.8 | 3.7 | 1.2 | 4.0 |
| % Reduction | – | 2.4 | 3.4 | 8.9 | 10.5 |
| | 28 Days | | | | |
| 1 | 34.92 | 33.73 | 31.47 | 30.00 | 28.80 |
| 2 | 31.70 | 33.79 | 31.39 | 33.21 | 34.24 |
| 3 | 30.23 | 34.13 | 30.45 | 31.24 | 31.22 |
| 4 | 39.30 | 31.03 | 33.11 | 32.59 | 29.23 |
| 5 | 35.81 | 31.73 | 33.37 | 32.29 | 33.33 |
| 6 | 39.31 | 34.16 | 35.63 | 33.78 | 34.17 |
| Average, (μ) | 35.2 | 33.1 | 32.6 | 32.2 | 31.8 |
| Stand. Dev. (σ) | 3.7 | 1.4 | 1.9 | 1.4 | 2.4 |
| % Reduction | – | 6.0 | 7.5 | 8.6 | 9.6 |

**Table 5**
Flexural strength test results, (MPa).

| Sample # | 0.00MC (Control) | 0.50MC | 0.75MC | 1.00MC | 1.25MC |
|---|---|---|---|---|---|
| | 7 Days | | | | |
| 1 | 3.92 | 4.09 | 3.47 | 3.58 | 3.53 |
| 2 | 3.67 | 4.02 | 2.97 | 3.20 | 3.52 |
| 3 | 3.69 | 3.86 | 3.99 | 3.29 | 3.29 |
| 4 | 3.90 | 3.14 | 3.35 | 4.10 | 3.09 |
| 5 | 3.34 | 4.07 | 4.61 | 3.46 | 3.71 |
| 6 | 4.51 | 3.64 | 4.19 | 3.77 | 3.64 |
| Average, (μ) | 3.84 | 3.80 | 3.76 | 3.57 | 3.46 |
| Stand. Dev. (σ) | 0.39 | 0.36 | 0.61 | 0.33 | 0.23 |
| % Reduction | – | 1.0 | 2.9 | 7.0 | 9.9 |
| | 28 Days | | | | |
| 1 | 4.65 | 3.90 | 3.51 | 3.63 | 2.86 |
| 2 | 5.30 | 5.14 | 4.67 | 3.87 | 3.10 |
| 3 | 4.15 | 4.18 | 3.98 | 4.20 | 3.27 |
| 4 | 4.09 | 4.06 | 4.26 | 3.43 | 3.96 |
| 5 | 3.93 | 4.18 | 3.14 | 3.38 | 4.27 |
| 6 | 3.62 | 4.14 | 3.52 | 3.43 | 3.89 |
| Average, (μ) | 4.29 | 4.27 | 3.85 | 3.66 | 3.56 |
| Stand. Dev. (σ) | 0.60 | 0.44 | 0.56 | 0.33 | 0.56 |
| % Reduction | – | 0.50 | 10.3 | 14.7 | 17.0 |

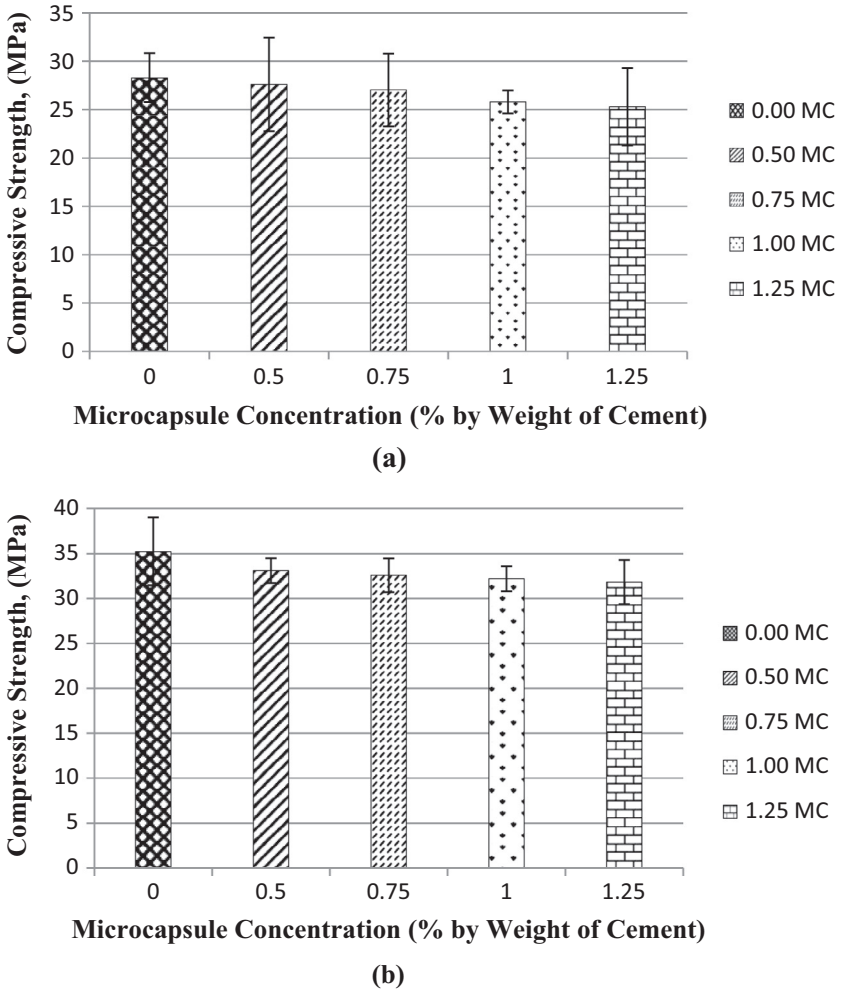



**Fig. 3.** Compressive strength versus microcapsule concentration (a) at 7 days, (b) at 28 days (Error bars = standard deviation).

cement. Thus, the strength reductions achieved in this study were lower than those reported by Milla et al. [10]. In other words, the modification to the proposed encapsulation procedure can minimize the adverse effect of microcapsules on concrete strength.

An ANOVA analysis was conducted on the obtained results to determine whether there are significant differences between the strengths of the different mixes. The null hypothesis assumed that the microcapsules had no effect on the strength results and hence

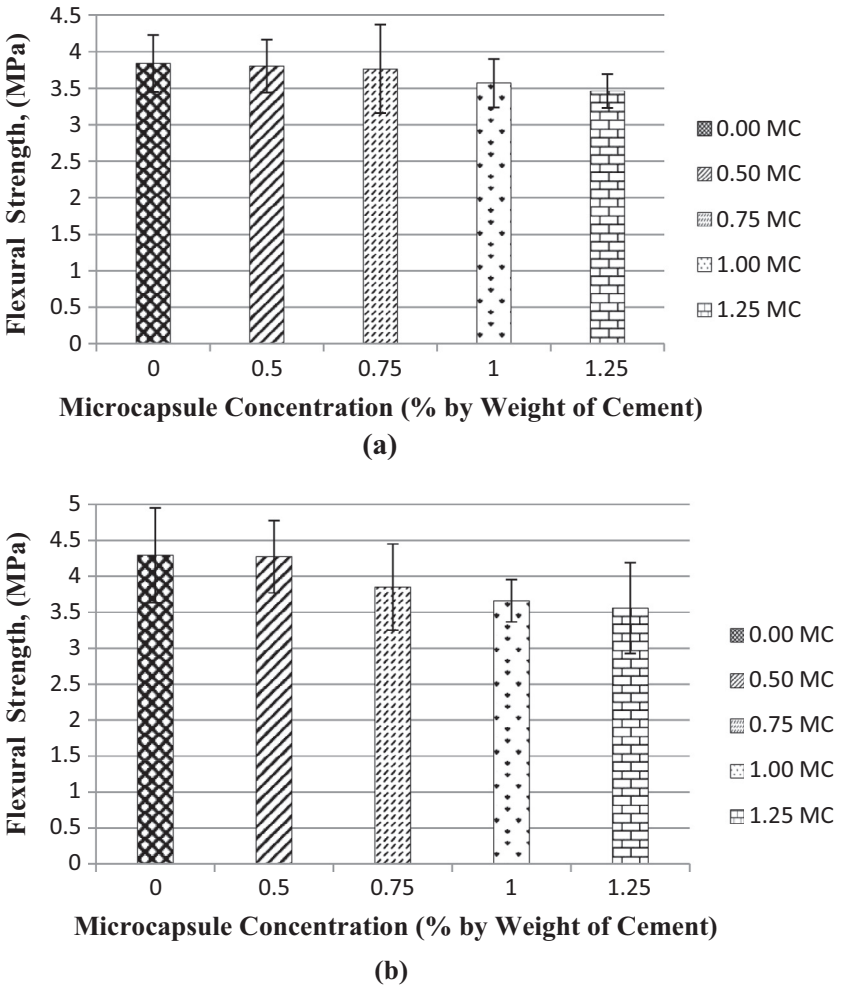



**Fig. 4.** Mortar flexural strength versus microcapsule concentration (a) at 7 days, (b) at 28 days (Error bars = standard deviation).

the average strength values of the mixes containing microcapsules did not significantly differ from those of the control mix. The degrees of freedom between and within the mixes were considered as $df_1 = 5$ and $df_2 = 25$ respectively. Considering a significance level of 0.05 ($\alpha = 0.05$), the F critical value is equal to 2.76. The null hypothesis is rejected if the F-statistic is more than or equal to the critical F value. Rejecting the null hypothesis implies a statistically significant evidence that there is a difference between the group means. Tables 6 and 7 summarize the ANOVA analysis of the compressive and flexural test results for all mixes.

Tables 6 and 7 show that the null hypothesis (no statistical significant difference between means of all mixes) cannot be rejected as the F values are less than the critical F value obtained from the F distribution (i.e. 2.76). This indicates that the integration of microcapsules (prepared using the modified encapsulation procedure), up to the concentrations investigated in this work, would not have a statistically significant adverse effect on the mix compressive and flexural strengths.

### 3.3. Characterization of mortar microstructure

Fig. 5 shows three fracture surface SEM micrographs of samples containing microcapsules. Fig. 5(a) shows that few microcapsules were ruptured due to their location on the crack plane. It is worth

**Table 6**
ANOVA analysis of the compressive strength results at 7 and 28 days.

| Source of Variation | 7 Days | | | |
|---|---|---|---|---|
| | Sum of Squares (SS) | Degrees of Freedom (df) | Mean Squares (MS) | F-value |
| Between Mixes | 36.91 | 4 | 9.23 | 0.75 |
| Within Mix (Error) | 307.28 | 25 | 12.29 | |
| Total | 344.19 | 29 | | |
| | 28 Days | | | |
| | Sum of Squares (SS) | Degrees of Freedom (df) | Mean Squares (MS) | F-value |
| Between Mixes | 42.57 | 4 | 10.64 | 1.94 |
| Within Mix (Error) | 137.08 | 25 | 5.48 | |
| Total | 179.65 | 29 | | |

**Table 7**
ANOVA analysis of the flexural strength results at 7 and 28 days.

| Source of Variation | 7 Days | | | |
|---|---|---|---|---|
| | Sum of Squares (SS) | Degrees of Freedom (df) | Mean Squares (MS) | F-value |
| Between Mixes | 0.64 | 4 | 0.16 | 0.98 |
| Within Mix (Error) | 4.07 | 25 | 0.16 | |
| Total | 4.71 | 29 | | |
| | 28 Days | | | |
| | Sum of Squares (SS) | Degrees of Freedom (df) | Mean Squares (MS) | F-value |
| Between Mixes | 2.76 | 4 | 0.69 | 2.67 |
| Within Mix (Error) | 6.46 | 25 | 0.26 | |
| Total | 9.22 | 29 | | |

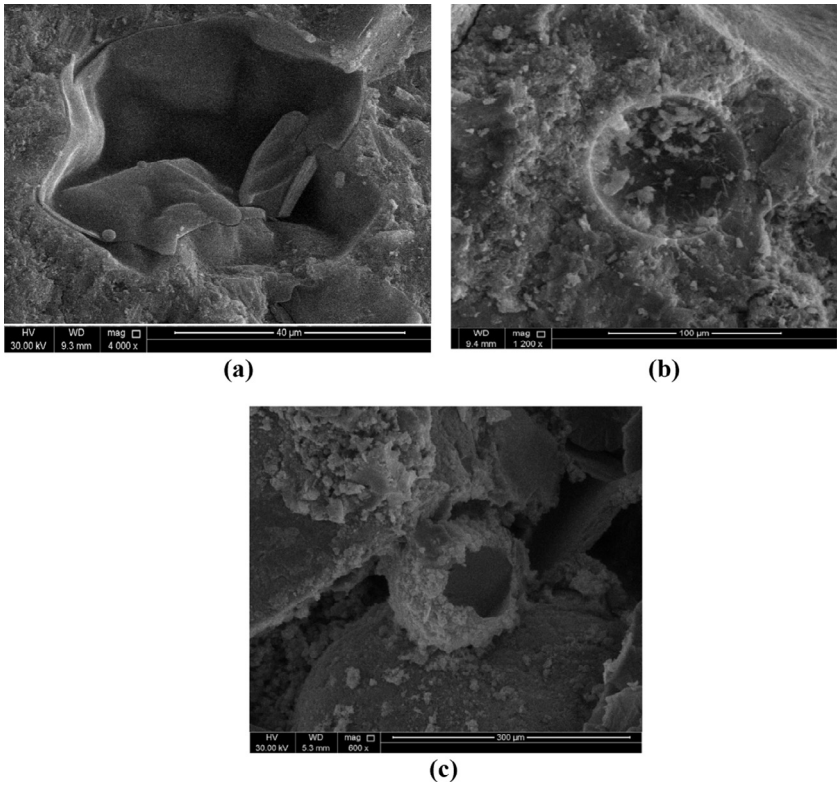



**Fig. 5.** SEM micrographs of fracture surface region of mortar containing microcapsules (a) ruptured microcapsule, (b) and (c) agglomerated un-hydrated cement particles on the microcapsule shell.

**Table 8**
Mix average maximum flexural loads and displacements.

| Mix ID | Average Maximum Flexural Load, kN | Average Maximum Displacement, μm |
|---|---|---|
| 0.00MC (Control) | 2.37 | 89.8 |
| 0.50MC | 2.29 | 131.8 |
| 0.75MC | 2.12 | 124.9 |
| 1.00MC | 2.01 | 205.4 |
| 1.25MC | 2.03 | 197.6 |

noting that part of the sulfonic acid used during the encapsulation of the calcium nitrate healing agent may stick on the microcapsules shell (surface). Hence, the acidity of the microcapsules surface increases with the concentration of the sulfonic acid and microcapsules. The surface acidity prevents the hydration of the particles around the shell as the acidic medium is not suitable for cement hydration. As a result, the mixture strength is reduced. Fig. 5(b and c) supports this finding by showing the agglomeration

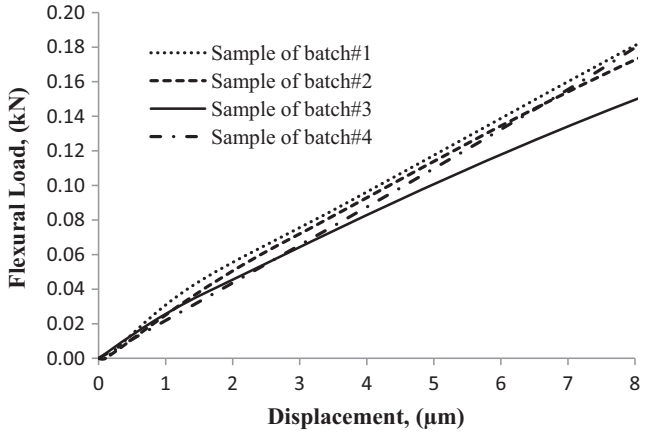



**Fig. 6.** First region flexural load-displacement curves (four batches from one mix).

**Table 9**
Flexural (elastic) modulus test results.

| Mix ID | Average Flexural (Elastic) Modulus, GPa (% Reduction) | Standard Deviation |
|---|---|---|
| 0.00MC(Control) | 11.20 (–) | 1.31 |
| 0.50MC | 6.95 (37.95) | 1.28 |
| 0.75MC | 6.80 (39.29) | 0.48 |
| 1.00MC | 3.80 (66.07) | 0.24 |
| 1.25MC | 3.02 (73.04) | 0.73 |

of the un-hydrated cement particles on the surface (shell) of the microcapsules. Accordingly, the proposed encapsulation procedure enhances concrete strength results because it significantly reduces the amount of sulfonic acid needed for encapsulation.

### 3.4. Load-displacement curves/flexural (elastic) modulus

Four samples (i.e., one from each batch) were selected to study the effect of microcapsule on the flexural load-displacement behavior. During the flexural testing, an LVDT was fixed at the middle of each specimen to measure the normal displacements. Table 8 shows the average maximum flexural load and displacement for each concrete mix. It could be noted in Table 8 that the mortar mixes containing microcapsules exhibited higher displacement. This is an indication that the microcapsules decreased the mortar stiffness. Fig. 6 shows the first region of the flexural load-displacement curves of four batches from one mix.

In order to quantify the aforementioned observations, the average flexural (bending) modulus was computed for each mix. The initial slope of the load-displacement curve was used to calculate the flexural modulus using the following equation [53]:

$$E_{flex} = (mL^3)/(4bh^3) \quad (1)$$

where $E_{flex}$ = flexural modulus of elasticity (MPa); L = support span (mm); b = tested beam width (mm); h = tested beam depth (mm); m = slope of the initial straight-line portion of the load-displacement curve obtained from the three point bending test, (P/δ) (N/mm); and δ = maximum mid-span deflection of the tested beam (mm). It is worth noting that the behavior of mortar samples under flexure is supposed to be linear. However, some nonlinearity may arise due to the incorporation of microcapsules. Hence, the initial slope (m) was taken equal to the slope of the best fit linear regression over the flexural load range of 2.00–2.10 kN.

Given that $\delta = (PL^3)/(48EI)$ and $I = bh^3/12$, the flexural elastic modulus ($E_{flex}$) is equivalent to the elastic modulus of elasticity (E) [54]. Table 9 summarizes the average flexural elastic modulus for all mixes. Table 9 shows that adding the microcapsules to the mortar mixes reduced their stiffness considerably before healing took place. The higher is the microcapsule concentration; the lower is the mix elastic modulus. This preliminary observation needs to be thoroughly investigated when testing the self-healing mechanism in concrete beams as part of the modulus recovered after healing [10].

The ANOVA analysis of the elastic modulus means for all mixes is shown in Table 10. The degrees of freedom between and within the mixes are $df_1$. = 5 and $df_2$ = 15, respectively and the significance level is set equal to 0.05 (α = 0.05). The F critical value is equal to 3.06.

**Table 10**
ANOVA analysis of elastic modulus results.

| Source of Variation | Sum of Squares (SS) | Degrees of Freedom (df) | Mean Squares (MS) | F-value |
|---|---|---|---|---|
| Between Mixes | 168.33 | 4 | 42.08 | 50.62 |
| Within Mix (Error) | 12.47 | 15 | 0.83 | |
| Total | 180.80 | 19 | | |

**Table 11**
Tukey's scores for all possible pairs from different mixes.

| | 1.25MC | 1.00MC | 0.75MC | 0.50MC |
|---|---|---|---|---|
| 0.00MC (Control) | 17.94 | 16.23 | 9.65 | 9.32 |
| 0.50MC | 8.62 | 6.91 | 0.33 | |
| 0.75MC | 8.29 | 6.58 | | |
| 1.00MC | 1.71 | | | |

As the F value (i.e. 50.62) is more than the critical F value obtained from the F distribution (i.e. 3.06), the null hypotheses was rejected. Hence, there is a statistically significant difference between the mean elastic modulus of all mixes. To explore the means that are significantly different from each other, a post hoc Tukey's HSD test was performed. Considering 5 mixes (treatments) and 15 degrees of freedom within the mix, the q value (Tukey's probability/critical value) at a significance level of 0.05 (α = 0.05) is equal to 4.37. The following formula was used to calculate the Tukey's score for each mean comparison:

$$\text{Tukey's score} = (\mu_1 - \mu_2)/\sqrt{(MSE/n)} \quad (2)$$

where $\mu_1, \mu_2$ = means to be compared; MSE = mean square within mix (error); n = number of samples in a mix.

Table 11 shows the Tukey's scores for all possible pairs of different means.

Comparing the Tukey's scores shown in Table 11 to the critical value (i.e., 4.37), it is worth noting that the differences between all pairs of mixes is statically significant except that between the mixes with 0.5% and 0.75% microcapsules and that between the mixes with 1.0% and 1.25% microcapsules. This supports the results shown in Table 9 which indicate that the mixtures with 0.5% and 0.75% microcapsules are very similar as well as those with 1.0% and 1.25% microcapsules. However, the elastic modulus of the mixtures with 1.0% and 1.25% microcapsules are almost half of that of the mixtures with 0.5% and 0.75% microcapsules. Accordingly, increasing the microcapsules concentration to more than 0.75% (by weight of cement) is not recommended in order to limit the reduction in the elastic modulus before healing. However, it is worth noting that part of the modulus will be recovered after healing as reported by Milla et al. [10].

## 4. Conclusions

Based on the results of the experimental study, the following conclusions can be drawn:

- The use of the microcapsules prepared using the modified procedure resulted in a lower reduction of both compressive and flexural strengths as compared to the original encapsulation method. The reduction in the 28-day strengths did not exceed 10% in compression and 17% in flexure.
- According to the statistical ANOVA analysis, the microcapsules prepared using the modified encapsulation procedure would not have a statistically significant adverse effect on the mix strength. However, the differences between the elastic modulus means for all different mixes were found statistically significant except the differences between the mixes with 0.5% and 0.75% microcapsules and those between the mixes with 1.0% and 1.25% microcapsules.
- The SEM micrographs of the fracture surface of samples containing microcapsules showed that the reduction in strength may be due to the agglomeration of un-hydrated particles on the surface (shell) of the microcapsules. The modification on

the encapsulation procedure presented herein enhanced mortar strength results because it significantly reduced the amount of sulfonic acid needed for the encapsulation.

- The stiffness of mortar mixes containing microcapsules was found to be less than that of the control mix. The reduction in the elastic modulus (before healing took place) was more significant for high microcapsule concentrations.
- The study showed that the integration of calcium nitrate microcapsules prepared using the modified procedure does not have a statistically significant impact on the strength. However, the strength results show that in order to achieve a strength reduction less than or equal to 10% the optimal microcapsule concentration by weight of cement should be selected in the range of 0.75% and 1.00%. On the other hand, the results of the elastic modulus showed that increasing the microcapsules concentrations to more than 0.75% (by weight of cement) was associated with a reduction of the elastic modulus to almost half. Hence, in order to achieve both acceptable strength and elastic modulus, it is recommended to use microcapsule concentration of 0.75% by cement weight.

## 5. Future work

The effect of calcium nitrate microcapsule self-healing on concrete mechanical properties should be investigated using the same preparation parameters (i.e., 1500 rpm, 40 °C temperature, and 1 hour agitation time). Microcapsule concentration of 0.75% by cement weight may be considered so that the reductions in concrete strength and stiffness associated with the microcapsules may not be significant.

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## References

[1] Vision 2020: A vision for the concrete repair protection and strengthening industry, The Strategic Development Council (SDC), 2006.
[2] E. Cailleux, V. Pollet, 2009. Investigations on the development of self-healing properties in protective coatings for concrete and repair mortars, in: Proceedings of the 2nd International Conference on Self-Healing Materials, Chicago, IL, USA, 2009.
[3] E. Schlangen, S. Sangadji, Addressing infrastructure durability and sustainability by self-healing mechanisms - recent advances in self-healingconcrete and asphalt, Proc. Eng. 54 (2013) 39–57.
[4] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, S. Viswanathan, Autonomic healing of polymer composites, Nature 409 (2001) 794–797.
[5] D.Y. Wu, S. Meure, D. Solomon, Self-healing polymeric materials: a review of recent developments, Prog. Polym. Sci. 33 (2008) 479–522.
[6] M. Kaes, K. Van-Tittelboom, N. De-Belie, The efficiency of self-healing cementitious materials by means of encapsulated polyurethane in chloride containing environments, Constr. Build. Mater. 71 (2014) 528–537.
[7] M. Pelletier, R. Brown, A. Shukla, A. Bose, Self-healing concrete with a microencapsulated healing agent, Available online: http://energetics.chm.uri.edu/system/files/ Self healing concrete-7-11.pdf. (accessed May 2015).
[8] K. Van-Tittelboom, N. De-Belie, D. Van-Loo, P. Jacobs, Self-healing efficiency of cementitious materials containing tubular capsules filled with healing agent, Cement Concr. Compos. 33 (2011) 497–505.
[9] M. Hassan, J. Milla, T. Rupnow, M. Al-Ansari, B. Daly, 2016. Micro-Encapsulation of Calcium Nitrate for Concrete Applications, Paper # 16–0421, submitted to the 95th Transportation Research Board Annual meeting, Washington, D.C., 2016.
[10] J. Milla, M. Hassan, T. Rupnow, M. Al-Ansari, G. Arce, 2016. Evaluation of the Effect of Self-Healing Calcium Nitrate Microcapsules on Concrete Properties. Paper # 16–0422, submitted to the 95th Transportation Research Board Annual meeting, Washington, D.C., 2016.
[11] Self-Healing Phenomena in Cement-Based Materials: State-of-the-Art Report of Rilem Technical Committee 221-SHC, RILEM, New York, 2013.
[12] C. Edvardsen, Water permeability and autogenous healing of cracks in concrete, ACI Mater. J. 96 (1999) 448–454.
[13] W. Ramm, M. Biscoping, Autogenous healing and reinforcement corrosion of water-penetrated separation cracks in reinforced concrete, Nucl. Eng. Des. 179 (1998) 191–200.
[14] M. Wu, A review: self-healing in cementitious materials and engineered cementitious composite as a self-healing material, Constr. Build. Mater. 28 (2012) 571–583.
[15] A. Neville, Autogenous healing: a concrete miracle?, Concr Int. 24 (2002) 76–82.
[16] N. TerHeide, E. Schlangen, 2007. Self-Healing of Early Age Cracks in Concrete. First International Conference on Self Healing Materials, Dordrecht, 2007.
[17] C.A. Clear, Effects of Autogenous Healing Upon the Leakage of Water Through Cracks in Concrete, Technical Report – Cement and Concrete Association, 1985.
[18] K. Van-Breugel, Noordwijkaan Zee, 2007, Is There a Market for Self-Healing Cement-Based Materials? First International Conference on Self Healing Materials, Noordwijk aan Zee, The Netherlands, 2007.
[19] K. Van-Tittelboom, E. Gruyaert, H. Rahier, N. De-Belie, Influence of mix composition on the extent of autogenous crack healing by continued hydration or calcium carbonate formation, Constr. Build. Mater. 37 (2012) 349–359.
[20] H.W. Reinhardt, M. Jooss, Permeability and self-healing of cracked concrete as a function of temperature and crack width, Cem. Concr. Res. 33 (2003) 981–985.
[21] V.C. Li, Y.M. Lim, Y.W. Chan, Feasibility study of a passive smart self-healing cementitious composite, Compos. B Eng. 29 (1998) 819–827.
[22] Y. Yang, M.D. Lepech, E.H. Yang, V.C. Li, Autogenous healing of engineered cementitious composites under wet-dry cycles, Cem. Concr. Res. 39 (2009) 382–390.
[23] Y.Y.E.H. Yang, Autogenous healing of engineered cementitious composites at early age, Cem. Concr. Res. 41 (2011) 176–183.
[24] Y. Kuang, J. Ou, Self-repairing performance of concrete beams strengthened using superelastic SMA wires in combination with adhesives released from hollow fibers, Smart Mater. Struct. 17 (2008).
[25] Y. Kuang, J. Ou, Passive smart self-repairing concrete beams by using shape memory alloy wires and fibers containing adhesives, J. Central South Univ. Technol. (English Ed.) 15 (2008) 411–417.
[26] A.D. Jefferson, C. Joseph, R.J. Lark, B. Isaacs, S.C. Dunn, B. Weager, A new system for crack closure of cementitious materials using shrinkable polymers, Cem. Concr. Res. 40 (2010) 795–801.
[27] B. Isaacs, R.J. Lark, A.D. Jefferson, R. Davies, S.C. Dunn, Crack healing of cementitious materials using shrinkable polymer tendons, Struct. Concr. 14 (2013) 138–147.
[28] H.X.D. Lee, H.S. Wong, N.R. Buenfeld, Potential of superabsorbent polymer for self-sealing cracks in concrete, Adv. Appl. Ceram. 109 (2010) 296–302.
[29] S.Z. Qian, J. Zhou, E. Schlangen, Influence of curing condition and pre-cracking time on the self-healing behavior of engineered cementitious composites, Cement Concr. Compos. 32 (2010) 686–693.
[30] P. Dejonghe, N. De-Belie, S. Steuperaert, D. Snoeck, 2011, The Behavior of Superabsorbing Polymers as a Sealing Agent in Concrete: Absorption Kinetics, Degradation and Water Permeability, 3rd International Conference on Self-Healing Materials, Bath, UK, 2011.
[31] J.S. Kim, E. Schlangen, 2011, Self-Healing in ECC Stimulated by SAP under Flexural Cyclic Load, in: Proceedings of 3rd International Conference on Self Healing Materials, Bath, UK, 2011.
[32] D. Snoeck, K. Van-Tittelboom, N. De-Belie, S. Steuperaert, P. Dubruel, The Use of Superabsorbent Polymers as a Crack Sealing and Crack Healing Mechanism in Cementitious Materials, In: Concrete Repair, Rehabilitation and Retrofitting III-Proceedings of the 3rd International Conference on Concrete Repair, Rehabilitation and Retrofitting, ICCRRR, Cape Town, South Africa, 2012, pp. 152–157.
[33] M. Abd-Elmoaty, Self-Healing of Polymer Modified Concrete Alexandria Engineering Journal, 50, 171–178.
[34] T.H. Ahn, T. Kishi, The Effect of Geo-Materials on the Autogenous Healing Behavior of Cracked Concrete, Concrete Repair, Rehabilitation and Retrofitting II, Cape Town, South Africa, 2008, pp. 125–126.
[35] K. Sisomphon, O. Copuroglu, 2011, Self Healing Mortars by Using Different Cementitious Materials, International Conference on Advances in Construction Materials through Science and Engineering, Hong Kong, China, 2011.
[36] S. Sangadji, E. Schlangen, Mimicking Bone Healing Process to Self Repair Concrete Structure Novel Approach Using Porous Network Concrete, Procedia Engineering, the 2nd International Conference on Rehabilitation and Maintenance in Civil Engineering (ICRMCE), 54 (2013) 315–326.
[37] C. Joseph, A.D. Jefferson, B. Isaacs, R.J. Lark, D. Gardner, Experimental investigation of adhesive-based self-healing of cementitious materials, Magaz. Concr. Res. 62 (2010) 831–843.
[38] C. Dry, W. McMillan, Three-part methylmethacrylate adhesive system as an internal delivery system for smart responsive concrete, Smart Mater. Struct. 5 (1996) 297–300.
[39] C. Dry, Matrix cracking repair and filling using active and passive modes for smart timed release of chemicals from fibers into cement matrices, Smart Mater. Struct. 3 (1994) 118–123.
[40] J. Wang, K. Van-Tittelboom, W. Verstraete, Use of silica gel or polyurethane immobilized bacteria for self-healing concrete, Constr. Build. Mater. 26 (2012) 532–540.
[41] H.M. Jonkers, Bacteria-based self-healing concrete, Heron 56 (2011) 5–16.

[42] K. Van-Tittelboom, N.D. Belie, Self-Healing in cementitious materials-a review, Materials 6 (2013) 2182–2217.
[43] H. Mihashi, Y. Kaneko, T. Nishiwaki, K. Otsuka, Fundamental study on development of intelligent concrete characterized by self-healing capability for strength, Trans. Japan Concr. Inst. 22 (2000) 441–450.
[44] Z. Yang, J. Hollar, X. He, X. Shi, A self-healing cementitious composite using oil core/silica gel shell microcapsules, Cement Concr. Compos. 33 (2011) 506–512.
[45] X. Wang, F. Xing, M. Zhang, N. Han, Z. Qian, Experimental study on cementitious composites embedded with organic microcapsules, Materials 6 (2013) 4064–4081.
[46] H. Huang, G. Ye, Application of Sodium Silicate Solution as Self-Healing Agent in Cementitious Materials, in: Proceedings of International RILEM Conference on Advances in Construction Materials Through Science and Engineering, Hong Kong, 2011, pp. 530–536.
[47] E. Mostavi, S. Asadi, M. Hassan, M. Alansari, Evaluation of self-healing mechanisms in concrete with double-walled sodium silicate microcapsules, J. Mater. Civ. Eng. 27 (2015).
[48] A. Sobolkina, V. Mechtcherine, V. Khavrus, D. Maier, M. Mende, M. Ritschel, A. Leonhardt, Dispersion of carbon nanotubes and its influence on the mechanical properties of the cement matrix, Cement Concr. Compos. 34 (2012) 1104–1113.
[49] N.B. Singh, A.K. Singh, S. Prabha-Singh, Effect of citric acid on the hydration of portland cement, Cem. Concr. Res. 16 (1986) 911–920.
[50] ASTM C109/C109M-16a, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens), ASTM International, West Conshohocken, PA, 2016. 10 pp..
[51] ASTM C348-14, Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars, ASTM International, West Conshohocken, PA, 2014. 6 pp..
[52] ASTM E178-08, Standard Practice for Dealing With Outlying Observations, ASTM International, West Conshohocken, PA, 2008. 18 pp..
[53] Three point flexural test Wikipedia: The Free Encyclopedia. Wikipedia: The Free Encyclopedia, Wikimedia Foundation, Inc., 24 June. 2016, Web. 17 July. 2016. https://en.wikipedia.org/wiki/Three_point_flexural_test.
[54] Flexural modulus. Wikipedia: The Free Encyclopedia, Wikimedia Foundation, Inc., 13 July. 2016, Web. 17 July. 2016. https://en.wikipedia.org/wiki/Flexural_modulus.