Self-sealing cementitious composites by gelation in-situ: an experimental and modelling study

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Abstract. Healable crack widths of cementitious composites are still at micro scale currently, even after specific self-healing agents like bacteria are incorporated. To enlarge the size of healable cracks to macro scale (> 1 mm), in-situ gelation strategy was adopted to develop self-sealing concrete herein. This strategy was achieved by encapsulating sodium alginate which could be released then react with calcium ions to in-situ generate calcium alginate hydrogels within cracks. The characteristics of capsules were investigated, and results revealed that these capsules could endure shear stress during mixing of cementitious composites, rupture when composite cracked and subsequently induce in-situ gelation. Owing to the characteristics of capsules, mortar specimens with the capsules obtained self-sealing capacity for macro cracks. The crack sealing of cementitious composites with capsules was further simulated based on the volume growth kinetics of hydrogels and stereology. The simulation results were generally consistent with the experimental results in this study. To sum up, the experimental and modelling explorations suggested a great potential of macro-scale self-sealing of cracks in cementitious composites via in-situ gelation.

1 Introduction

As the most widely used materials in construction, concrete may crack due to overloading and volume instability resulted from shrinkage, thermal expansion, alkali-silica reaction [1], etc. After cracking, mechanical properties and durability of cementitious composites can be declined [2-5], which can be severer under the ingress of aggressive ions, such as chloride [6] and sulphate ions [7]. Hence, repairing of cracks in cementitious composites is essential to improve durability of cementitious composites and hence prolong their service life. However, crack repairing will cause high labour cost and associated carbon emissions [8-10]. Additionally, it can be hardly applied in inaccessible cracks, such as those underwater or underground. These limitations lead to the development of self-healing concrete which can repair itself without labour.

Normal cementitious composites have certain self-healing capacity due to further hydration and carbonation [11-12], but the capacity was restricted to cracks with limited sizes. To enhance the capacity, innovative agents, such as shape memory polymers [13], bacteria [14] and minerals [15], have been incorporated into cementitious composites for autonomous healing.

The desired autonomous healing ought to be an expansive process, meaning healing product volume will be higher than healing agent volume after self-healing, thereby sealing cracks with the increased volume. To achieve this objective, several approaches have been developed for cementitious composites. The first approach is using expansive minerals including MgO [16], CaO [17] and calcium sulphaaluminate cement [18]. After the minerals are exposed to cracks, they can conduct hydration then seal cracks. However, ratios of hydration product volume to initial mineral volume are in a range of 1.9-2.4 [19], which was relatively low. Additionally, hydration products could cover on surfaces of minerals, suppressing further dissolution and full hydration of minerals.

The second approach is by carbonation of calcium or magnesium-based materials, such as portlandite and brucite. The volume increase by carbonation of portlandite was around 1.17 times to its initial solid volume, whilst higher volume enlargement could be obtained by carbonation of brucite, of which carbonation product volume was 1.69 and 3.04 times approximately to brucite volume when hydromagnesite and nesquehonite were generated respectively [20]. If initial healing agents were CaO or MgO, the calculated volume increase in terms of their volume can be even higher. Nevertheless, carbonation mainly happens at crack surfaces due to limited transport of CO₂ to crack interior under restrictions from water and sealing at crack mouths [21], indicating only crack mouths could be effectively sealed via carbonation.

Different from volume increase after generations of solid products, another approach for volume increase is through formation of semisolid phase by using superabsorbent polymers (SAPs). Due to high absorption capacity, superabsorbent polymers could absorb much water then swell up to hundreds of times to initial volume in deionized water [22-23], suggesting the potential of sealing large cracks. However, sorption capacity of superabsorbent polymers will be dramatically reduced to below 100 g/ (g SAP) in
Concrete environments, due to high pH and cations, such as Na⁺, K⁺ and Ca²⁺ [24-25]. Moreover, as SAP were incorporated in particle shapes, final crack sealing capacity will be dependent on swelling capacity of individual particles [26]. These limitations resulted in the maximum crack widths by SAP swelling were generally below 500 μm [23], which was far below expected.

To further increase volume increment potential and thus seal larger cracks, a novel approach of self-sealing by gelation in-situ is proposed herein. After the gelation, hydrogels as one semisolid phase can be generated and water will be entrapped in the crosslinking network, thereby achieving exceptional volume increase. To attain the in-situ gelation, one capsule with encapsulated sodium alginate powders and embedded calcium sulphaaluminate cementitious materials was designed. By using the capsules in cementitious composites, alginate and calcium could leach from capsules after cracking, thus calcium alginate crosslinking [27-28] would be generated in-situ to seal cracks. Crack-sealing performance was evaluated by crack width reductions. A mathematical model to simulate crack sealing due to hydrogel generations was proposed and modelling results were validated with experimental outcomes.

2 Materials and experiments

2.1 Materials

Polyethylene glycol (PEG) with an average molecular weight of 1000 was used. Other components of capsules included sodium alginate (W201502, Sigma-Aldrich), epoxy resin (M02, Kunshan Chemical Co., Ltd) and calcium sulphaaluminate cement (LSAC 42.5, Dengdian Cement Co., Ltd) with a particle size range of 10-200 μm.

In cementitious composites, raw materials were Portland cement I 52.5, ISO standard sand, tap water and polyethylene fibers with a length of 18 mm and a diameter of 26 μm in addition to capsules.

2.2 Experimental methodology

PEG at 60 °C and sodium alginate powders were mixed at a mass ratio of 1:2: 1 then solidified at 23 °C for around 6 hours before fabricated to 3×3×3 mm cubes. The cubes were further covered with epoxy resin and calcium sulphaaluminate for two times to form a protective shell on the cubic particles. Thereafter, the capsules in the sizes of 4.75-9.5 mm were sieved out for further usage. Apparent density of the capsules was tested according to ASTM C127.

To understand generations of hydrogels by using capsules, volume growth of hydrogels from capsules were measured. 10 g capsules were split by using a sharp knife then immersed in 100 ml deionized water. After submersion for 1 day, 2 days, 3 days, 5 days and 7 days, volume of hydrogels with capsules was tested by using a gas pycnometer (UltrapyC 5000, Anton Paar) under helium flow at 25 °C. Three replications were carried out in each testing.

Cementitious composites with capsules were prepared for self-sealing experiments. The mix design is shown in Table 1. Mass of cement, water and sand was kept at a ratio of 1: 0.45: 2. Polyethylene fibers were added by 0.25% of the total volume. Volume fractions of capsules in mixture SS5C and SS10C were 5% and 10% respectively. During mixing, solid ingredients were mixed at low speed for 3 mins before fibers were gradually loaded in 60 s. After that, the mixture was kept mixing at medium speed for 2 mins then high speed for another 3 mins. After mixing, the composites were cast into 40×40×160 mm prism molds then vibrated to eliminate entrained air and subsequently covered with plastic sheet to avoid evaporation. After 1 day, specimens were demolished and cured in air (23±2 °C, 75±3% RH) for 28 days.

Table 1. Mix design of mortar specimens (kg/m³)

<table>
<thead>
<tr>
<th>Mix group</th>
<th>C</th>
<th>S</th>
<th>Ca</th>
<th>W</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>671</td>
<td>1342</td>
<td>0</td>
<td>302</td>
<td>2.45</td>
</tr>
<tr>
<td>SS5C</td>
<td>637</td>
<td>1274</td>
<td>80</td>
<td>287</td>
<td>2.45</td>
</tr>
<tr>
<td>SS10C</td>
<td>604</td>
<td>1208</td>
<td>160</td>
<td>272</td>
<td>2.45</td>
</tr>
</tbody>
</table>

Notes: The density of capsules was 1600 kg/m³. C denotes cement; S denotes sand; Ca denotes capsules; W denotes water and P denotes polyethylene fibers.

After curing, the specimens were cracked by center-point loading at a displacement rate of 0.5 mm/min until crack openings reached 1-4 mm approximately. The cracked mortar samples were submerged in water at 23 ±2 °C for self-sealing.

Cracks were observed before and after self-sealing for 1 day, 3 days, 5 days and 7 days by using a stereo microscope (SMZ745T, Nikon). After cracking, 3-5 positions along each crack of mortars specimens without healing were marked to ensure that observations were conducted at same positions after various healing durations.

3 Experimental results and discussions

The images of crack mouths of SS, SS5C and SS10C mixture after healing for 1 day, 3 days, 5 days and 7 days are shown in Figure 1. For control mortar specimens without capsules, no obvious healing products could be found on crack mouths, as shown in Figure. 1a, thus crack widths were not reduced after autogenous healing.

Conversely, macro cracks of mortar samples with capsules were sealed by in-situ generated hydrogels, as illustrated in Figure 1b-c. The hydrogels were formed after healing for only 1 day, indicating the rapid sealing of cracks. After healing for 1 day, no significant volume change of the hydrogels within cracks was observed, suggesting the stability of self-sealing by hydrogels. Hence, in-situ generation of hydrogels was effective in sealing macro cracks of cementitious composites.
Crack sealing by in-situ generated cracked was modelled using crack widths, capsule properties including its density, diameter, breakage ratio and dosages in cementitious composites, hydrogel properties including volume growth of hydrogels upon gelation. With these inputs, crack sealing was estimated by volume of in-situ generated hydrogels from capsules that were random, uniform and isotropic distributed in matrix with a randomly intersected plane as the crack.

In the crack, mass of broken capsules per area can be determined by:

\[ m_c = b \times N_c \times m_o \]  

(1)

Where \( m_c \) denotes the mass of broken capsules per area of cracks; \( b \) denotes the breakage ratio of capsules within cracks; \( N_c \) denotes capsule numbers per area of crack; \( m_o \) denotes mass of one capsule.

The number of capsules at unit area of crack (\( N_c \)) was calculated according to stereology [29-30], as expressed in equation (2-3):

\[ N_c = N_V \times d_c \]  

(2)

\[ N_V = D / m_o \]  

(3)

Where \( N_V \) denotes number of capsules at unit volume of the composite; \( d_c \) denotes capsule diameter; \( D \) represents dosages of capsules in cementitious composites.

After determining the mass of broken capsules per area of crack using equations (1-3), crack sealing could be estimated in terms of volume growth of generated hydrogels from the broken capsules, as given by:

\[ C_s = \frac{m_c (V_i(t) - 1)}{C_w} \]  

(4)

Where \( C_s \) denotes crack healing ratios; \( \rho_c \) denotes the density of capsules before cracking; \( V_i(t) \) denotes volume ratios of capsules with in-situ generated hydrogels to capsules before gelation after \( t \)-day healing; \( C_w \) denotes crack widths.

Volume evolution of hydrogels generated from broken capsules was measured as expressed in section 2.2 and the experimental results were fitted by exponential decay function \( (R^2=0.997) \) to obtain a relationship between time and volume of in-situ generated hydrogels with capsules. By combining the relationship with equation (4), crack sealing evolutions with time was obtained. The modelling results are presented in Figure 2.

Fig. 1. Images of crack mouths of (a) control mortar specimens, (b) mortar specimens with 5% capsules and (c) mortar samples with 10% capsules after self-healing for 1 day, 3 days, 5 days and 7 days.

4 Modelling of the crack self-sealing by in-situ generated hydrogels
Fig. 2. Modelling results of crack healing by in-situ generated hydrogels within cracks. (a) Healing ratios of cementitious composites with 5% capsules; (b) crack healing ratios of cementitious composites with 10% capsules. Colormaps at bottom surfaces of (a) or (b) are the projections of the corresponding space curves.

According to the modelling results, increase in capsule dosages could improve crack healing ratios. For cementitious composites with 5% capsules as illustrated in Figure 2a, the maximum healable crack width was about 1 mm, while it reached over 2 mm when 10% capsules were incorporated, as shown in Figure 2b. Self-sealing by in-situ generated hydrogels was relatively rapid, as macro cracks of specimens with both 5% and 10% capsules could be potentially sealed after healing for only 1 day, while no obvious healing was obtained in plain mortar specimens without capsules. Hence, in-situ generated hydrogels were able to seal macro cracks rapidly by incorporating the designed capsules with proper dosages. Mathematical modelling was established based on stereology. With capsule properties, cracking information, and experimental results of hydrogel volume growth upon crosslinking, crack healing by generated hydrogels in cracks was successfully simulated and simulation results were generally consistent with the experimental observations. The cementitious composites with designed capsules could be applied in engineering underwater or at wet environments.

In the future, effects of crack sealing by in-situ generated hydrogels on recovery of durability, such as water and chloride permeability resistance, could be investigated. Additionally, compatibility of the capsules with cementitious composites deserves extensive explorations.

5 Conclusions and prospects

In this study, rapid self-sealing of macro cracks in cementitious composites was achieved by in-situ generated calcium alginate hydrogels from capsules with encapsulated sodium alginate and embedded calcium sulphoaluminate cementitious materials. The capsules were incorporated into mortar with volume fractions of 5% and 10%. After incorporations of the capsules, cracks over 1 mm were effectively sealed by generated hydrogels after healing for only 1 day, while no obvious healing was obtained in plain mortar specimens without capsules. Hence, in-situ generated hydrogels were able to seal macro cracks rapidly by incorporating the designed capsules with proper dosages. Mathematical modelling was established based on stereology. With capsule properties, cracking information, and experimental results of hydrogel volume growth upon crosslinking, crack healing by generated hydrogels in cracks was successfully simulated and simulation results were generally consistent with the experimental observations. The cementitious composites with designed capsules could be applied in engineering underwater or at wet environments.

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