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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.