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Smart releasing behavior of a chemical self-healing microcapsule in the stimulated concrete pore solution

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ABSTRACT

A novel chemical self-healing system based on microcapsule technology for cementitious composites is established. The key issue for such a system is how to release the healing agent and how to activate the healing mechanism. The present study focuses on the release behavior. The smart release behavior of the healing agent in the microcapsule is characterized by the EDTA (Ethylene Diamine Tetra-acetic Acid) titration method. The experimental results show that the release of the corrosion inhibitor covered with polystyrene resin (PS) is a function of time, and is controlled by the wall thickness of the microcapsule. Moreover, the pH value affects the release rate of the corrosion inhibitor; the release rate remarkably increases with the decreasing pH value.

1. Introduction

Concrete is a fundamental material in modern construction. Due to concrete creep, humidity changes, and non-homogeneous settlement of buildings, concrete structures may experience various types of cracking during their service periods. Such degradation of performances will affect the safety of a building and may even cause severe accidents [1]. Self-healing technology has been introduced to repair the cracks in a concrete structure automatically, resulting in the recovery of performances in concrete structures. This technology, mainly being bound up in the mechanical properties and transport properties, currently represents the major development of smart structural materials [2–5].

Several methods have been developed to imbue concrete with self-healing properties [6–8]. Solution at lower level involves incorporating alkaline-resistant (AR) glass fibers into concrete, which can control the early-age cracking due to shrinkage [9–10], yet does not have the actively healing process. Another self-healing mechanism is based on bacteria, which can produce certain type of crystals after the activation of the system. Such crystals, like biological calcium carbonate, generate the sediment layer, reducing the permeability and thus triggering the recovery of transport properties. Self-healing of cementitious composites could also be realized by means of the addition of mineral admixtures with the help of further hydration. And based on water transport theory, ion diffusion theory and thermodynamics theory, simulative analysis for self-healing efficiency under different conditions was calculated in others' papers [11–13]. However, these approaches mainly focus on mechanical property of the matrix and ions transport property by means of the physically forming the compounds to heal micro-cracks or micro-poles. Moreover, the self-healing methods above are passive healing mechanism, which denotes occurrence of healing activities lag behind the damage in the specific position or the designated direction of crack in concrete, whereas the microcapsule technology involved in this paper is an initiative self-healing method due to the distribution evenly in concrete.

Another important concern in the development of a self-healing system is the engineering feasibility, which consists of features such as easy workability, small-volume dosage and high performance. A practical engineering approach for a microcapsule based self-healing system has been developed at Shenzhen University, China. The self-healing way to improve the mechanical property and transmission performance of concrete matrix through solidification techniques based on polymer capsule was studied in previous papers (need supportive references). In addition to the further improvement of this novel approach for the crack repairing and mechanical performance recovery, its attention has been turned to the recovery of degradations induced by reinforcement corrosion, which is generally regarded as the major threatening in marine environments [14–15]. It is well known that the reinforcement

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corrosion can be initiated by means of carbonation (neutralization of alkalinity of concrete) and chloride penetration (higher concentration of chloride ion inside concrete). Therefore, it is logic to consider a self-healing system with a capacity of re-alkalization or decreasing of chloride concentration. A novel microcapsule based self-healing system aimed at the recovery of above mentioned performances has been recently proposed at Shenzhen University. The system can be chemically triggered by the given conditions, such as decreasing pH value or increasing chloride ion. After the activation of the system, healing agent will release from microcapsule depending on the different healing mechanisms. The release behavior is the major concern in this paper.

In this study, a microcapsule system with polystyrene resin (PS)/sodium monofluorophosphate (Na_2PO_3F, MFP) was fabricated and studied. Several testing method were chosen to examine and interpret the triggering mechanism of such microcapsule. Its release behavior was measured in a simulated concrete environment. Moreover, an alternative pH-value condition was designed to characterize the smart release performance of microcapsules. The effective micro-morphology of the microcapsules was also obtained to study variations in the damage pattern with different pH values.

2. Experiments

The raw materials and the formula for preparation of the microcapsules are listed in Table 1. To prepare the microcapsules, sodium monofluorophosphate and microcrystalline cellulose were mixed into Polysorbate 80. Then the small spherical particles were molded by the extrusion–spheronization method, which is able to control the diameter of a microcapsule. Finally, the spray drying method was adopted to fabricate microcapsules, spraying the liquid PS into the surface of spherical particles. In this study, three types of microcapsules with different amount of shell materials were fabricated; the mass percentages of shell materials were 10% (sample N_a in Table 1), 20% (sample N_b in Table 1) and 43% (sample N_c in Table 1). For example, 10% means the percent of increased weight of microcapsules, according to that of spherical particles mold by the extrusion–spheronization method.

The release behavior of the microcapsule was studied by the EDTA titration method. Since Ca^{2+} reacts with PO_3F^{2-} released from the sodium monofluorophosphate inside the microcapsules to form $Ca_5(PO_4)_3F$ and CaF_2, the amount of consumed Ca^{2+} can be used to calculate the amount of released sodium monofluorophosphate according to the following equation:

$$m = \frac{3\times10^{-3} - 0.05\times V\times10^{-3}}{2}\times 144\times\frac{400}{25}g$$
$$= 1.152\times(3 - 0.05V)g \qquad (1)$$

where m is the released amount of sodium monofluorophosphate, and V is the consumed volume (mL) of EDTA, which corresponds to the Ca^{2+} consumption.

Table 1
Raw materials and the formulation used for microcapsule fabrication.

Ingredients	Capsule core materials	N_a	N_b	N_c
Sodium monofluorophosphate (g)	500	0	0	0
Microcrystalline cellulose (g)	500	0	0	0
Polysorbate 80 (g)	50	0	0	0
Talc powder (g)	0	35	70	146
Polystyrene resin (g)	0	50	100	150
Chloroform (mL)	0	500	1000	1500
Pure water (g)	50	50	50	50

The micro-morphology of the microcapsule samples was obtained by Scanning Electronic Microscopy (SEM) (SU-70; Hitachi, Japan) and the particle size distribution of the microcapsule samples was measured by a Laser Particle Analyzer (S3500; Microtrac, USA).

3. Results and discussion

The macro- and micro-morphology for the microcapsule samples can be seen in Fig. 1. The microcapsules appear basically spheroidal, having sizes on the order of hundreds of micrometers. The particle size distribution shown in Fig. 2 is consistent with a normal distribution; capsule diameter generally lies in the range between 400 μm and 1200 μm. As the amount of shell materials increases, the mean diameter of microcapsules increases too. It is because the increased the amount of shell materials would result in a shell with increased thickness. Based on the size distribution results, the average shell thickness of microcapsules with different formulae can be calculated as shown in Table 2.

To pinpoint the effectiveness of such a self-healing system based microcapsule in concrete structures, one of the important steps is to fully understand the release behavior of healing agent in a microcapsule. In this study, $Ca(OH)_2$ solutions with different pH levels were adopted to simulate a cementitious environment. Different dosages of microcapsules were then added to the $Ca(OH)_2$ solutions. The involved chemical reactions are as following:

$$Na_2PO_3F \rightarrow 2Na^{+} + PO_3F^{2-} \qquad (2)$$

$$3PO_3F^{2-} + 6Ca(OH)_{2(\text{crystalline})} \leftrightarrow Ca_5(PO_4)_3F_{(\text{amorphous})} + CaF_{2(\text{crystalline})} + 6OH^{-} + 3H_2O \qquad (3)$$

As the test passing, the microcapsules triggered by the pH condition result in either being punched pores or being tore cracks, even being peeled. The main core material, sodium monofluorophosphate, ionizing PO_3F^{2-} and Na^{+}, as the reaction (1) and, PO_3F^{2-} proceeds to reacts with hydration product of cementitious materials in light of the equilibrium (3). Such programs produce an increase in OH ion activity in the medium as well as the pH 12.4 of the calcium hydroxide suspension increases to 13.5 after the release of aqueous MFP in microcapsules.

It is expected that release behavior, which is a function of the shell thickness of microcapsules, can be controlled by the amount of used shell materials. Fig. 3 shows the total mass of sodium monofluorophosphate released from the microcapsules in the simulated cementitious environment ($pH = 13$) for various releasing times. The released amount of healing agent was found to increase monotonically with time. It was also noticed that the total released amount of healing agent decreases as the shell thickness increases. This implies that the release rate of healing agent inside the microcapsules could be effectively controlled by controlling the shell thickness of microcapsules.

The influence of pH on the release behavior of the microcapsule is shown in the Fig. 4. The curves show that release rate is at the maximum for a pH value of 7, and reduces with the pH increases. It is well know that polystyrene resin swells in the presence of water; which could cause micro cracking or pinholes on the surface of the microcapsules. In addition, microcrystalline cellulose has strong capability to absorb water, and Na_2PO_3F can be easily dissolved in water. Moreover, a concentration gradient of healing agent exists between inside and outside of microcapsules. Therefore, the healing agent in microcapsules can be diffusively released through micro-cracks or pinholes as soon as water is available, even only in a small amount. At the beginning, the release rate should be slow since there is little damage on the surface of the microcapsules. Later on, the number and size of