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Sodium silicate/polyurethane microcapsules used for self-healing in cementitious materials: Monomer optimization, characterization, and fracture behavior

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ABSTRACT

Storing healing agents in capsules is one of the most promising self-healing methods in cementitious materials. Because of the considerable advantage of microencapsulation, it has become more interested as compared to the other encapsulation methods. The sodium silicate, which has many advantages as a healing agent in cementitious materials, can be encapsulated through the interfacial polymerization of shell-forming monomer on the aqueous sodium silicate droplets. This study, which is a part of comprehensive project, aimed to produce these microcapsules by optimization of the monomer. The microcapsules were characterized by the yield, SEM, EDS, FTIR, TGA, and XRD analyses. In addition, the fracture behavior of the optimized microcapsule was examined in a cement paste matrix. It was observed that most of the microcapsules seem to be spherical shaped and free-flowing powder. Fracture behavior of optimized microcapsules revealed a sufficient shell-matrix interfacial bond strength which is essential for releasing healing agent into cracks.

1. Introduction

In many developed countries, the problems encountered in the repairing of infrastructures are important because of the fact that the repair of cracks, which are not visible or available in many cases [1], is a complex, high cost, and high labor operation work [2–4]. The repair operations in concrete bridges and tunnels can be very difficult due to the massive traffic jam. In addition, it can be dangerous in underground structures and hazardous liquid containers [5–8]. It is possible to eliminate these problems in cementitious materials through a self-healing mechanism. The service life of constructions can be increased by many passive self-healing methods with lower costs and fewer problems. The well-known autogenous self-healing mechanisms such as formations of calcium carbonate or calcium hydroxide and further hydration of the unreacted cement or cementitious materials are not long lasting mechanisms in cement-based composites [8].

There are many methods to enhance the autogenous self-healing mechanism. $Ca(OH)_2$, a product of hydrated cement, can react with SiO_2 provided by pozzolanic materials such as fly ash [9–12] and ground-granulated blast-furnace slag [12,13]. In past years, a few studies have dealt with the incorporating of silica-based microcapsules, as SiO_2 source, in cement-based composites [14–19]. Pelletier et al. [14] have introduced the idea of encapsulation of aqueous sodium silicate (SS) solution in polyurethane microcapsules through an interfacial polymerization. Colloidal silica was also used as a healing agent and a SiO_2 source in similar microcapsules [15]. In addition, Kanellopoulos et al. [19] have encapsulated SS solution in gelatin/acacia gum microcapsule through a complex coacervation technique. The self-healing mechanisms of these microcapsules are based on the rupture of their shell during the crack formation in cementitious matrix, and then the reaction of released SS or colloidal silica with $Ca(OH)_2$ to form secondary calcium-silicate-hydrate gel. Pelletier et al. [14] synthesized the SS bearing microcapsule according to the method in which the di-ammonium hydrogen phosphate was microencapsulated by Saihi et al. [20]. They emulsified the aqueous SS in toluene, which is immiscible in water, using a combination of two different surfactants. After dispersing of SS in the organic phase, the shell-forming monomer, methylene diphenyl diisocyanate (MDI), was added to initiate the interfacial reaction of MDI and water at the interface of drops of the aqueous SS [20]. Similar interfacial polymerization method was also used by Tan et al. [15] for microencapsulation of colloidal silica instead of SS.

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This study is part of comprehensive project that deals with the self-healing ability of cement-based composites. This paper has dealt with the microencapsulation of sodium silicate as healing agent in polyurethane microcapsules. Pelletier et al. [14] have used a certain amount of MDI in their synthesis procedure. However, it is well known that the amount of shell-forming monomer is a key factor in terms of the yield, shell thickness, and mechanical properties of microcapsules. In the scope of this study, various amounts of MDI were used in the synthesis of SS bearing poly(urea-urethane) microcapsules. Moreover, Pelletier et al. [14] have not characterized microcapsules in detail. Therefore, the microcapsules synthesized in this research were characterized through the microencapsulation yields, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, thermogravimetric, and Fourier transform infrared (FTIR) analyses. Besides, the fracture behavior of the optimized microcapsule was examined in a cement paste matrix.

2. Experimental

2.1. Materials

Sodium silicate solution (SS) purchased from Sigma-Aldrich (Na_2O, ~10.6% and SiO_2, ~26.5%) was used as the core material with deionized water. Shell-forming monomer, 4,4′-Methylenebis (phenyl isocyanate) 98%, and surfactants, Span 85 (Sorbitanetrioleate) and Poly(ethylene glycol) dioleate (POEDO) were also supplied from Sigma-Aldrich. In addition, Dibutyltindilaurate (95%) obtained from Sigma-Aldrich was used as catalyst. Organic phase for emulsifying of SS was Toluene (Sigma-Aldrich) that was used without further purification. CEM I 42.5 R type Portland cement and a polycarboxylic ether based superplasticizer were used for preparation of cement paste.

2.2. Synthesis of microcapsules

The synthesis of microcapsules was performed in a 100 mL beaker by using a magnetic cylindrical stirrer bar. As mentioned earlier, the synthesis process was based on the in situ interfacial polymerization method introduced by Saihi et al. [20]. However, some necessary modifications were performed in the process. This method has two main steps as follows: 1) dispersion of the aqueous solution SS in organic phase, 2) addition of shell-forming solution. It must be noted that many preliminary tests were carried out to find out the material ratios and stirring rates. Three solutions were prepared in the synthesis process as follows: 1) S1 is a solution of surfactants, which are Span 85 (2 g) and POEDO (1 g), in 45 mL of toluene, 2) S2 is a solution of shell-forming substances, which are MDI and a few droplets of catalyst, in 7.5 mL of S1 and 12.5 mL of additional toluene, 3) S3 is solution of SS (7.5 g) in 7.5 mL of deionized water.

In the microencapsulation procedure, S3 was emulsified in S1 (37.5 mL) solution at a speed of 1000 rpm for 20 min. After dispersion and stabilization of aqueous SS micro droplets in organic phase, S2 solution was added to the primary emulsion. Based on the preliminary test results, various amounts of MDI were used in this study to determine the effect of diisocyanate monomer on the properties of the microcapsules. Therefore, four different mixtures (hereafter called MDI-1, MDI-2, MDI-3, and MDI-4) were prepared by using 7.5, 10, 12.5, and 15 g of MDI, respectively. It must be noted that shell-forming monomer to core material ratios of MDI-1, MDI-2, MDI-3, and MDI-4 mixtures are 0.50, 0.67, 0.83, and 1.00, respectively.

The mixture was stirred at a speed of 900 rpm for 20 min at room temperature to form the primary membrane [20]. Then, temperature was gradually increased to 63 °C, while the stirring speed was reduced to 800 rpm. The stirring was continued at 63 °C and 800 rpm for 4 h to grow the membrane. The microcapsules were vacuum filtered, and then washed with toluene for removal of MDI residue and ethanol/water for removal of surfactant residue and non-encapsulated SS. The microcapsules were dried at room temperature for 48 h, and then weighed for yield calculation.

2.3. FTIR analysis

FTIR-ATR analyses of the samples were made by using Fourier transform infrared spectrometer (Perkin Elmer Spectrum BX) in the range 4.000–650 cm^{-1}.

2.4. TG analysis (TGA)

Thermal stability of microcapsules was analyzed by TGA using a DTG-60/60 Simultaneous Thermogravimetry/Differential Thermal Analyzer (Shimadzu). The analyses were carried out at a heating rate of 10 °C/min from room temperature to 800 °C under nitrogen atmosphere.

2.5. XRD analysis

The crystallographic properties of MDI samples were examined by X-ray diffractometer (RIGAKU, D-Max 2200 PC with Cu K_α radiation (λ = 1.54 Å).

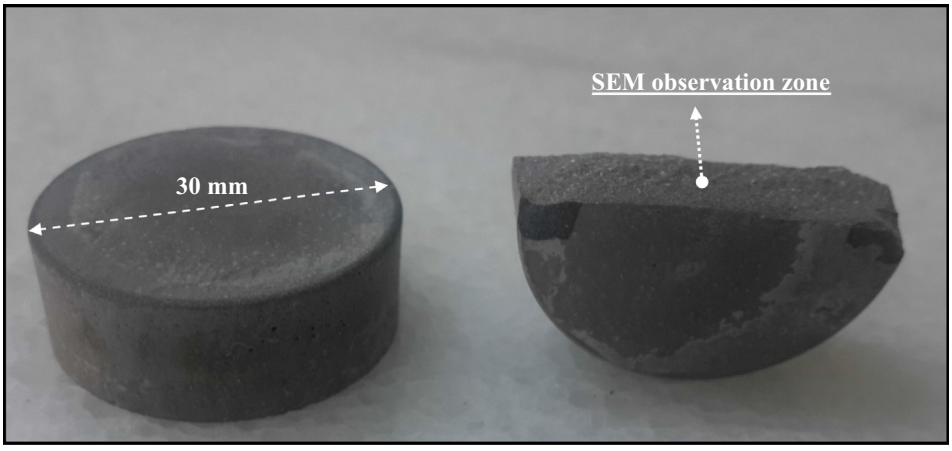

Fig. 1. Disk-shaped specimen.