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Influence of SiO_2@PMHS on the Water Absorption of Cement Mortar as a Surface Treatment Agent

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ABSTRACT

In this paper, the core–shell structured SiO_2@PMHS hybrid nanoparticles were synthesized with tetraethoxysilane (TEOS) and polymethylhydrosiloxane (PMHS). And SiO_2@PMHS core–shell nanoparticles were first used as a surface treatment agent for cement-based materials. The influence of SiO_2@PMHS nanoparticles on the water absorption of hardened cement mortar with water-to-cement ratio of 0.6 was investigated. Results showed that the water absorption of cement mortar treated with SiO_2@PMHS nanoparticles was decreased by 93.47% in comparison to the control sample.

Keywords: SiO_2@PMHS, surface treatment, cement-based material, water absorption

1. INTRODUCTION

In recent years, the durability of concrete in the world is of great concern. In general, corrosion occurs first at the surface of concrete. As a carrier, water delivers the ingressive ions from surface to inner part of concrete. Surface treatment is one of the most effective ways to improve corrosion resistance of concrete, which has been the focus of investigation for quite a long time (Basheer, Basheer, Cleland, & Long, 1997). There are two kinds of coating materials for concrete protection. One is organic protective coatings, including epoxy, silane, etc. (Woo, Zhu, Chow, Leung, & Kim, 2008). Surface treatment with hydrophobic agents, such as silane, makes the pores in the concrete structure water repellent through the formation of an organic film (Cui, Liu, Chen, Li, & Shi, 2012; Guo et al., 2015). The other one is inorganic coating, like nano-SiO_2. Hou, Xin, Qian, and Zhang (2015a) found that organic TEOS was effective in making a compact microstructure of cement-based material due to the filler effect and pozzolanic reactivity of the *in situ*-formed SiO_2 nanoparticles. And nano-SiO_2 nanoparticles were potential for cement-based materials as a surface-treatment agent (Hou, Qian, Cheng, & Shah, 2015b).

To take the advantages of both organic and inorganic treatment agents on the properties of hardened cement-based material, in this paper, we studied the effectiveness of SiO_2@PMHS core–shell nanoparticle material as a surface treatment agent on hardened cement mortar. The concept of grafting the surface of inorganic surface-treatment agent of nano-SiO_2 with organic group, for example, siloxane has been studied (Rahman & Padavettan, 2012). And more recently, Collodetti, Gleize, and Monteiro (2014) used two different types of siloxane to be grafted on nano-SiO_2 particles, and then the modified nanoparticle was used as an admixture in preparing Portland cement paste, but it demonstrated that the grafted group was detrimental for the hydration of cement.

In this work, the SiO_2@PMHS core–shell nanoparticles were first synthesized. And then, the water absorption characteristics of the samples were studied and discussed.

2. MATERIALS AND METHODS

2.1 Materials

Ordinary Portland cement, complying to the Chinese standard GB 175-2007 (similar to cement prepared by co-grinding type I Portland cement clinker and supplementary materials), was used in this work, and its physiochemical properties are listed in Table 1.

Polymethylhydrosiloxane (PMHS) was purchased from Aladdin Industrial Corporation. Tetraethoxysilane (TEOS), tetrahydrofuran (THF), and ethanol were provided by Tianjin Kermel Chemical Reagent Factory. Anhydrous ethylenediamine was obtained from Nanjing Zhongshan Chemical Reagent Corporation.

Table 1. Chemical and physical properties of ordinary Portland cement.

SiO_2	Al_2O_3	Fe_2O_3	SO_3	CaO	MgO	Density (g/cm^3)	Fineness (m^2/kg)
21.1	4.7	3.5	3.3	62.9	2.8	3.1	322

2.2 Sample preparation

In this work, mortar samples were prepared at the W/C ratio of 0.6 and the cement-to-sand ratio of 1/3. River sand with a fineness modulus of 2.8 was used. Mortar samples were cast in steel mold with dimensions of 4 cm × 4 cm × 16 cm. Samples were demolded 1 day after casting and cured in standard curing chamber (21°C, 95%RH) for about 1 year.

2.3 Synthesis of SiO_2@PMHS

SiO_2@PMHS core–shell nanoparticles were synthesized following the two-step method. First, 0.1-mL anhydrous ethylenediamine was added into 60-mL tetrahydrofuran solution and stirred for 0.5 h at room temperature. After that, 0.3-mL PMHS was dipped into the solution by stirring for 0.5 h. Then, 2.6-mL TEOS was added into the system and continuously stirred for 12 h. After that, 0.3-mL H_2O was dipped into the system and vigorously stirred for 3 h to ensure the occurrence of hydrolysis–condensation reaction between PMHS and TEOS. Figure 1 shows the synthesis procedure of SiO_2@PMHS core–shell nanoparticles.

2.4 Sample cutting and surface treatment

Samples used for the measurement of water absorption were cut into pieces with dimensions of 4 cm × 4 cm × 2 cm by using a water-cooled saw. Sectioned samples were vacuum dried at 60°C for 18 h before being soaked in surface-treatment solutions (water, SiO_2@PMHS, TEOS, and PMHS) for 6 h. After soaking, samples were removed from the solutions and cured in standard conditions (21°C, 95%RH) for another 3 days to ensure a full reaction of the treatment agent with the superficial components and the evaporation of the residual agent.

2.5 Water absorption ratio

Before measuring the water absorption ratio, samples were vacuum dried at 60°C for 18 h. Then, a similar process to the ASTMC1585-13 Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes was used, one face (4 cm × 4 cm) of the treated sample was left uncovered, while the other five faces were sealed with two-component epoxy as did in Dang et al. (2014) (see Figure 2). The uncovered face of the sample was immersed into water for a certain time, and sample mass after various soaking times was recorded in the saturated-dry condition by using a precise scale with a resolution of 0.01 g. The mass increase was ascribed to the water intake by the capillary pore effect. The water absorption ratio was calculated by dividing the mass increase (milligrams) by the surface area (square centimeters) of the sample. For each test, the water absorption ratios of three replicates at 10 min, 20 min, 40 min, and 90 min water-soaking time were tested and averaged to be taken as the representative value. Based on the water absorption ratio results, the initial water absorption coefficient, i.e., slope of water absorption ratio vs. square root of time (seconds) at the beginning of water absorption described in Khatib and Mangat (1995) was adopted to reflect the water transport properties, by which the pore structure characteristics can be reflected to some extent.

3. RESULTS AND DISCUSSIONS

3.1 Water absorption ratio and the initial water absorption coefficient

Two main reaction mechanisms of SiO_2@PMHS nanoparticles may exert on the surface of hardened cement mortar. On the one hand, SiO_2 nanoparticle

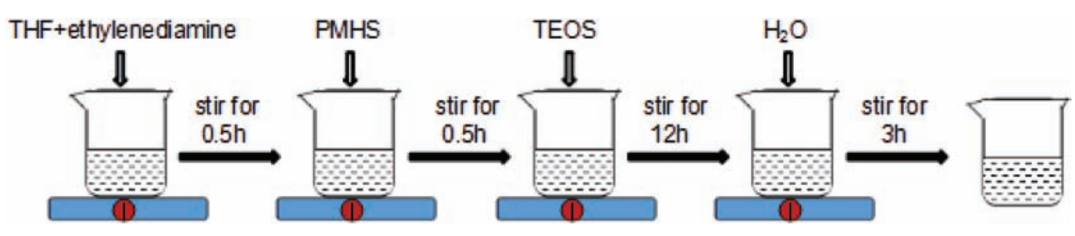

Figure 1. Synthesis procedure of SiO_2@PMHS core–shell nanoparticles.

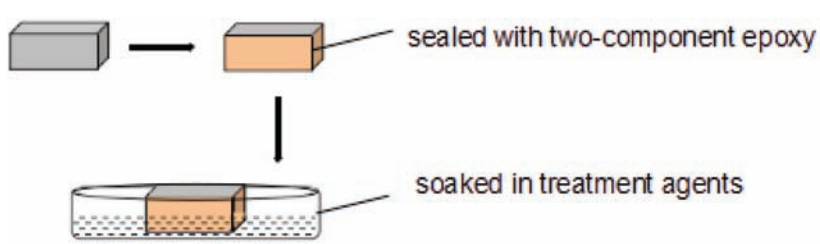

Figure 2. The procedure of cement pastes treatment for water absorption test.

may penetrate into the pores and react with the hydration product of calcium hydroxide forming calcium silicate hydrate (C–S–H gel), which could physically and chemically block the transportation root of aggressive agent. On the other hand, PMHS would form a hydrophobic membrane on the surface of concrete, thus leading to a reduction of water absorption. The water absorption characteristics of cement mortar with different treatment agents are shown in Figure 3. It can be seen in Figure 4 that the water absorption ratio of cement mortar treated by SiO_2@PMHS has been significantly reduced. Results showed that the water absorption of cement paste treated with SiO_2@PMHS nanoparticles decreased by 93.47% in comparison to the control sample. In order to exclude the effect of solvent on the results, THF was used as an agent for surface treatment of the samples. Results show that THF has a negative impact on the water absorption, i.e., increasing the water absorption ratio of the sample.

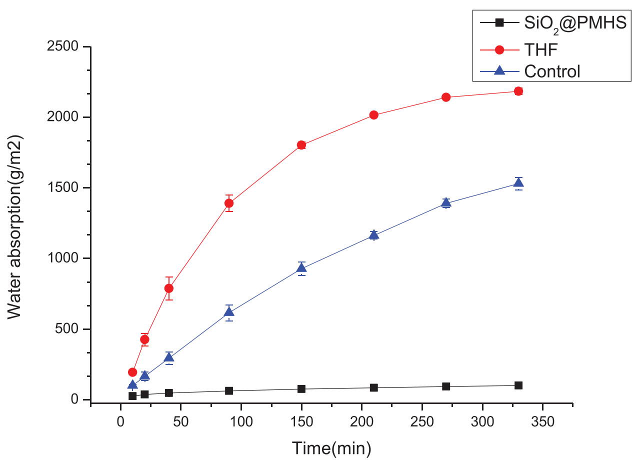

Figure 3. Effect of surface treatment of cement paste with SiO_2@ PMHS and THF on the water absorption ratios.

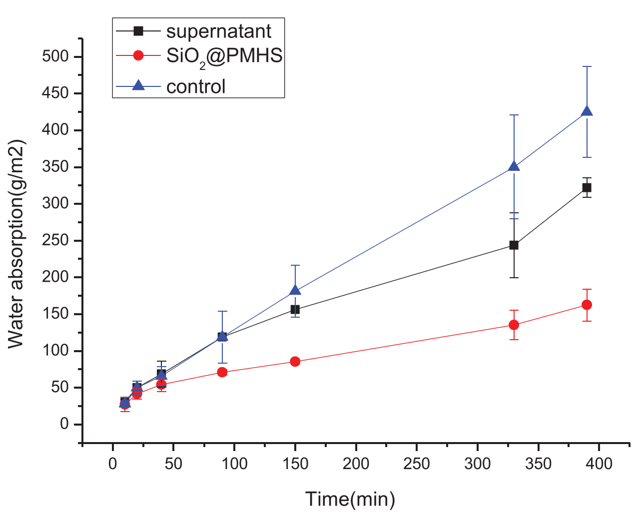

Figure 4. Effect of surface treatment of cement paste with SiO_2@ PMHS and supernatant on the water absorption ratios.

To distinguish the effect of SiO_2@PMHS and TEOS in the solvent which has not been hydrolyzed completely, the SiO_2@PMHS was centrifuged from the solvent. The supernatant was used as a surface treatment agent to treatment cement mortar samples. The result of water absorption ratio was shown in Figure 4. From the comparison of the results, it can be seen that SiO_2@PMHS is more prolific in decreasing the water absorption ratio, reflecting that it is more effective in densifying the superficial capillary pore structure of the samples.

The initial water absorption coefficients of samples treated with water, THF, and SiO_2@PMHS are exhibited in Table 2. Results show that the water absorption rate of the sample decreases when supernatant and SiO_2@PMHS treatments were applied. Similar to the water absorption ratio results, a greater reduction of the water absorption rate can be found in SiO_2@PMHS-treatment sample. It demonstrated that SiO_2@PMHS nanoparticles were effective in reducing the water absorption of cement mortar.

Table 2. Initial water absorption coefficients of cement pastes before and after treatment ($mg/cm^2 \times s^{1/2}$).

W/C	Control	Supernatant	SiO_2@PMHS
0.6	7.12 (100%)	5.4 (75.8%)	2.72 (38.2%)

4. CONCLUSION

(1) The SiO_2@PMHS core–shell nanoparticles have the potential to be used for surface treatment of cement-based materials.

(2) The SiO_2@PMHS core–shell nanoparticles are effective in decreasing the water absorption of cement-based materials.

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