Influence of silica-based hybrid material on the gas permeability of hardened cement paste

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Abstract. Surface treatment is one of the most effective ways to elongate the service life of concrete. The surface treatment agents, including organic and inorganic types, have been intensively studied. In this paper, the silica-based hybrid nanocomposite, which take advantages of both organic and inorganic treatment agents, was synthesized and used for surface treatment of hardened cement-based material. The effectiveness of organic and inorganic hybrid nanocomposite was evaluated through investigations on the gas permeability of cement-based materials. The results showed that SiO_2/PMHS hybrid nanocomposite can greatly decrease the gas transport properties of hardened cement-based materials and has a great potential for surface treatment of cementitious materials.

Keywords: hybrid silica-based materials, cement-based materials, surface treatment, gas permeability

1. Introduction

Durability of concrete is of great concern in modern society [1, 2]. As the surface of the concrete is the most vulnerable part of the structure, it is the most effective way for achieving a longer service life of concrete structures by improving the surface quality [3]. There are several ways to improve the surface quality of concrete structures, and for the existing structures, surface coating is a commonly used technique [4]. In general, there are two types of coating materials that are widely used. One is the organic coating, including silane, siloxane [5], which makes the surface of the concrete structures water-repellent. The other one is the inorganic coating, like water glass, nano-SiO_2 [3, 6], which could refine the pore structure of the cement-based materials due to its in-situ pozzolanic reactivity with the hydration products of cement.

In our previous studies, nano-SiO_2 showed a good pozzolanic reactivity [7], but its reduction of water absorption rate is still far less than that of silane/siloxane-treated sample. Currently, silica-based hybrid materials bridged with organic groups has drawn particular research interests, which takes the advantages of both organic and inorganic treatment agents [8]. In this paper, a silica-based hybrid nanocomposite was synthesized and used for surface treatment of cement-based materials. Its effectiveness on the transport properties has been evaluated through gas permeability and SEM measurements. The results indicated that the hybrid materials have a good potential for surface treatment of cement-based materials.

2. Materials and methods

2.1. Materials

Commercially available Ordinary Portland cement complying with the Chinese standard GB 175-2007 was used. And its physiochemical properties are listed in table 1.

Polymethylhydrosiloxane (PMHS) was supplied by Aladdin Industrial Corporation. Tetraethoxysilane (TEOS) and other chemicals, i.e. Tetrahydrofuran (here after THF), ethanol, anhydrous ethylenediamine with the analytical reagent (AR) grade were all purchased from Tianjin Kermel Chemical Reagent Factory.

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

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

2.2. Sample preparation and surface treatment

2.2.1. Synthesis of hybrid material. The hybrid nanoparticles were synthesized by sol-gel methods. A certain amount of PMHS and TEOS was dropped into tetrahydrofuran solutions in the presence of anhydrous ethylenediamine and stirred for over 12 h to get the final product.

2.2.2. Sample cutting and surface treatment. In this work, cement pastes samples were prepared at a w/c ratio of 0.4 in centrifuge tube with the diameter of 35mm and cured for 1 year in standard curing chamber (21^{o}C, 95%RH). Before surface treatment the samples were cut into piece with the thickness of 3mm and were then oven-dried at 60 ^{o}C for 24h before been soaked with treatment agents for a certain time. After that, samples were cured in standard curing condition for 3d. Before gas permeability test, the samples were oven-dried at 60 ^{o}C for 72h to remove the moisture.

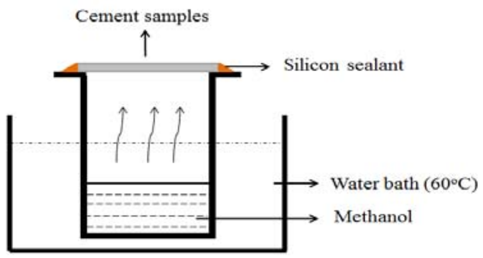

Figure 1. Schematic illustration of gas permeability test setup.

2.2.3. Gas permeability test. Gas permeability tests of cement pastes were used to evaluate the effectiveness of various surface-treatment agents in accordance with the procedures proposed by Alshamsi and Imran [9], and the set-up is shown in figure 1, a predetermined amount of methanol was kept in the cell, then cement paste samples was used to seal the cell with silicon sealant. When the silicon sealant gets dried, the mass of cell system was measured and then placed under 60 °C. The mass loss of cell was recorded at different time. The average value of three replicates was taken as the representative value.

2.2.4. SEM. Chemical grade calcium hydroxide (CH) was mixed with the hybrid material at a w/b ratio of 2.0 to simulate a cement-hybrid material system. And the morphology was observed by a field emission scanning electron microscope (SEM, QUANTA 250 FEG, FEI, America).

3. Results and discussion

3.1 Gas permeability

The variations in the mass loss of methanol with time are shown in figure 2. All the cement paste samples within or without surface treatment have comparable trends, i.e., the loss of methanol increase with time. In comparison to that of control samples, the samples treated by hybrid material have less mass loss. It indicates that the cement paste samples could be densified by treated with hybrid material, and this could be attributed to the pozzolanic reactivity of the hybrid material that hydrolysized from TEOS. As proposed by Taylor that reaction between hydrous silica and CH in aqueous suspension at ordinary temperature gives a product called C-S-H (I). In this case, the silica-based hybrid materials have a reaction with CH which was products of cement hydration, and form additional C-S-H gel to refine the pore structure of cementitious materials, leading to a reduced methanol loss at 60 °C.

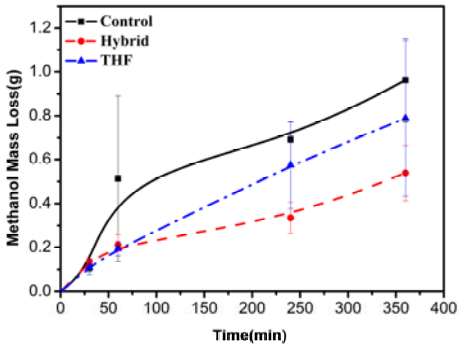

Figure 2. Mass loss vs. time of samples with and without surface treatment.

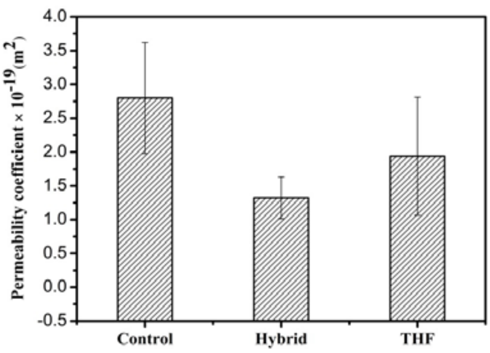

Figure 3. Gas permeability coefficient of samples.

The gas permeability coefficient k (m^2) was calculated using the equations mentioned by Han [10]. As shown in figure 3, the hybrid material provides a good protection from gas penetration, the reduction of gas permeability of cement paste treated by hybrid material is about 36.5% compared to that of control samples, which indicates a highly impermeable, dense microstructure of the hybrid materials treated surface. It suggests that the dense of the cement paste could be attributing to the pozzolanic reactivity of hybrid material, which will be discussed next.

3.2 SEM

The imagines of dried-calcium hydroxide powder before and after mixed with hybrid materials (cured for 3 d with the w/b=2) are demonstrated in figure 4(a-b) and the influence of hybrid material on the morphology of CH can be observed. It can be seen in the control sample that there are a lot of sharp hexagonal plates, which were calcium hydroxide. Meanwhile, the hexagonal plates can be hardly found in hybrid material-treated sample. It clearly shows that the hybrid material can react with calcium hydroxide and densify the surface structure of hardened cement-based materials.

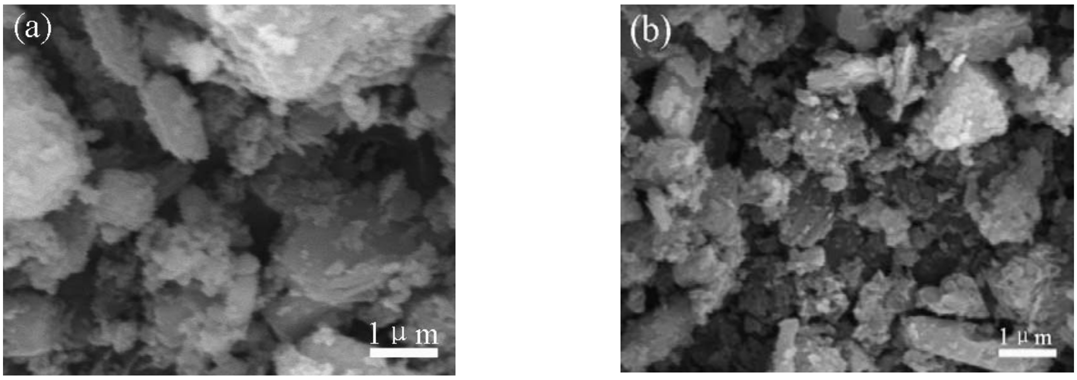

Figure 4. (a) Images of CH (w/c=0.4) before and after hybrid material treated.

4. Conclusions

- The silica-based hybrid materials are effective in decreasing the gas permeability of cement-based materials.
- The silica-based hybrid material could densify the cementitious materials.
- The silica-based hybrid material has the potential to be used for surface treatment of cement-based materials.

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