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Design of SiO_2/PMHS hybrid nanocomposite for surface treatment of cement-based materials

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A B S T R A C T

A silica-based hybrid nanocomposite, SiO_2/polymethylhydrosiloxane (SiO_2/PMHS), is synthesized by a sol-gel process and used for surface treatment of hardened cement-based materials. The advantages of both normal organic and inorganic silica-based treatment agents are explored. Results revealed a covalent chemical bonding of SiO_2 and PMHS and the SiO_2/PMHS showed hydrophobicity and pozzolanic reactivity when used for surface treatment. Greater reductions of the water absorption rate and gas permeability coefficient of cement-based materials were achieved by the hybrid nanocomposite compared to its individual components, showing synergistic effects of hydrophobicity and pore refinement characteristics as proved by the measurements of the contact angle, the mineralogy, the morphology and the porosity. The results showed promising advantages of using silica-based hybrid nanocomposite for surface treatment to achieve a higher surface quality. Moreover, it can be suggested that more functionalities of the cement-based materials can be tailored through the design and use of the silica-based hybrid materials.

1. Introduction

The durability of concrete structures continues to be of great concern, especially within harsh environments [1], i.e., chloride or sulfate-rich environments. Structural concrete durability has a large impact on the sustainability of the civil infrastructure [2–13]. Various techniques, including the replacement of cement with pozzolanic materials [14–16], addition of chemical agents [17], and treatment of surfaces of concrete structures, etc. have been gaining extensive attention. As the surfaces of a concrete structure are usually the most vulnerable part, and for the relatively low cost and ease of maintenance, surface treatment of concrete with organic/inorganic agents has gained great attention to improve the durability of concrete structures [18].

Generally speaking, organic/inorganic surface treatment agents have been grouped into the impregnation and non-impregnation types, and the former takes the major part, which includes: (1) sealing agents, such as alkali silicates, which make the surface structure less porous through its in-situ pozzolanic reaction with the hydration products of cement [19]; (2) silica-based water-repelling agents, including silane- or siloxane-based water repellents which make the pores of concrete water-resistant [20]. These agents are effective in minimizing the migration of substances in and out of the surface of hardened cement-based materials as well as offer protection even when minor cracking occurs [21] due to the pore-refining and hydrophobic features [18,20]. The silica-based inorganic treatment agents are promising in anti-weathering, but the incorporation of alkali ions raises the risks of the alkali-aggregate reaction and efflorescence [22], which reduces their usage compared to the silane-/siloxane-based treatment agents.

As an inorganic nanomaterial, nanoSiO_2 has been intensively studied in cement and concrete for its high pozzolanic reactivity and ultra-fine size effect [23] to make high or ultrahigh

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performance concrete. More recently, researchers studied the effectiveness of nanoSiO_2 for surface-treatment of hardened cement-based materials. Cardnes and Struble used electrokinetic nanoparticle treatment for hardened cement paste, resulting in a reduced permeability [24]. Sanchez and his co-workers [25] studied the effects and mechanisms of using colloidal nanoSiO_2 migration for surface treatment of hardened mortar, finding efficient surface sealing and pore-refining from its in-situ pozzolanic reaction and formation of C-S-H gel. The effectiveness was further improved by using the in-situ formed nanoSiO_2 through the hydrolysis of its precursor of tetraethoxysilane (TEOS) [18], as well as the ultrafine silica oligomer [26]. All the work mentioned above suggested the effectiveness of nanoSiO_2 in improving the surface quality of concrete compared with the traditional inorganic silica-based materials, especially in reduction of water absorption rate and increase in the degree of pore-refining. However, when compared with organic silica-based impregnation agents, such as silane and siloxane, the water-resistivity is much poorer due to its intrinsic hydrophilic characteristic [18]. Considering the characteristics of the inorganic and organic agents, in this work, we synthesized a silica-based hybrid nanocomposite consisting of the organic and inorganic groups and used for surface treatment of hardened cement-based materials.

In recent decades, silica-based hybrid materials have promoted numerous and extensive investigations in specialties like chromatography [27], catalysis [28,29], biochemistry [30,31] and ceramics [32] through the tailored physico-chemical properties introduced by incorporating organic components into the rigid silica framework. The present work takes advantage of both the pozzolanic reactivity of nanoSiO_2 and the hydrophobic feature of polymethylhydrosiloxane (PMHS) for surface treatment of hardened cement-based materials through the synthesized nanocomposite, i.e.,SiO_2/PMHS nanoparticles. During this work, the SiO_2/PMHS nanocomposite was first synthesized and characterized by Fourier-transform infrared analysis (FTIR), x-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). Then, the effectiveness and mechanisms involved in the use of SiO_2/PMHS nanocomposites for the surface treatment of hardened cement-based materials were assessed and investigated through thermogravimetry, x-ray diffraction (XRD), scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and nuclear magnetic resonance techniques (NMR). Greater reductions of water absorption rate and gas permeability coefficient were observed for the SiO_2/PMHS nanocomposite-treated cement-based materials compared to those treated by the individual PMHS and nanoSiO_2. The pore-refining effect resulting from the pozzolanic reaction of SiO_2/PMHS nanocomposite, and the hydrophobic characteristic of the treated-surface were obtained, showing great potential for surface-treatment of cement-based materials. This work also serves as a reference for tailoring the surface properties/functionalization of hardened cement-based materials.

2. Experimental

2.1. Materials

2.1.1. Chemicals

Polymethylhydrosiloxane (hereafter PMHS, Fig. 1 (a)) with the viscosity of 15–40 mPa s (20 °C) was supplied by Aladdin Industrial Corporation. Tetraethoxysilane (hereafter TEOS, Fig. 1 (b)) with a density of 0.931–0.934 g/cm^3 was used. Other chemical agents, i.e., tetrahydrofuran (hereafter THF), ethanol, and anhydrous ethylenediamine were used. All the chemicals were of analytical reagent (AR) grade.

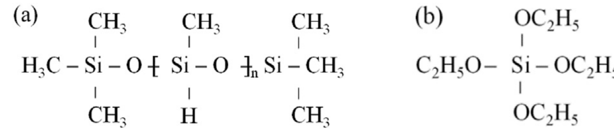

Fig. 1. The formula of (a) PMHS and (b) TEOS.

2.1.2. Cement

Ordinary Portland cement complying with 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.

2.2. Sample preparation

2.2.1. Specimens

Mortar samples with the dimension of 40 mm × 40 mm × 20 mm, cement paste samples with the dimension of 20 mm × 20 mm × 20 mm, and cement paste samples with 3 mm thickness and 35 mm diameter were investigated.

2.2.2. Synthesis of SiO_2/PMHS hybrid nanocomposite and NS

The SiO_2/PMHS hybrid nanoparticles were prepared by the following steps [33]. Firstly, 0.1 mL anhydrous ethylenediamine was added into 60 mL tetrahydrofuran (THF) solution and stirred for 0.5 h at room temperature. Then, 0.3 mL PMHS was added into the solution and stirred for another 0.5 h. An additional 2.6 mL TEOS was dropped into the solution and stirred for 12 h, after which 0.9 mL of deionized water was added and vigorously stirred for 3 h to ensure a complete hydrolysis-condensation reaction of PMHS and TEOS [34]. The final solution, designated as SiO_2/PMHS, was used for surface treatment of cement-based materials. To make comparison studies, PMHS and nanoSiO_2 (hydrolysis product of TEOS) were used for surface treatment of cement-based material, which were designated as "PMHS" and "NS". Tetrahydrofuran (THF) was taken as a comparative agent to exclude the impact of the solvent.

NanoSiO_2 (NS) was prepared by the sol-gel process [35], during which 2.6 mL of TEOS and 0.9 mL of deionized water were added into solutions, and stirred for 3 h.

The synthesized SiO_2/PMHS hybrid nanocomposite and NS were firstly centrifuged and then triple-centrifuged with ethanol. Then, the samples were dried at 60 °C for 18 h before characterization.

2.2.3. Samples preparation and curing

Mortar samples with a water-to-cement ratio (w/c) of 0.6 and the cement-to-sand ratio of 0.33 were prepared, and the fineness modulus of the sand was 2.8. Mortar samples were cast in a steel mold with dimensions of 4 cm × 4 cm × 16 cm. Two kinds of paste samples were prepared at a w/c = 0.4 in steel molds with dimensions of 2 cm × 2 cm × 2 cm and in plastic tube molds with diameters of 5 cm. Samples were demolded one day after casting and cured in a standard curing chamber (21 °C, 95% RH) for 6 months or 1 year before surface treatment.

To explore the pozzolanic reactivity of the SiO_2/PMHS hybrid nanocomposites, $Ca(OH)_2$ (CH) was mixed with SiO_2/PMHS at the mass ratio of 4:1 and the water-to-CH ratio of 2.0. Ultrasonic

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