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Waterproof ultra-high toughness cementitious composites containing nano reservoir silts

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- A waterproof cementitious composite was designed and fabricated.
- The toughness of cementitous composites was maintained by the dosage of nano reservoir silts upto 5%.
- The water absorption and penetration of cementitous composites were depressed essentially.
- The good material properties of waterproof cementitious composites facilitate their uses.

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ABSTRACT

The waterproof ability of cementitious composites is essentially important for the uses in the aspects of construction, decoration and repair. Here we reported a waterproof ultra-high toughness cementitious composite (WUHTCC) that has the function of seepage resistance. The waterproof effect was improved by incorporating nano reservoir silts (NRSs) into the binders of WUHTCC. The mechanical properties, microstructures and water resistances of the WUHTCCs with different loadings of NRSs were tested to assess the affecting factors. The results show that increasing the loadings of NRSs maintains and/or enhances the toughness of WUHTCCs, but decreases the compressive strength. The water absorption is decreased, and the penetration pressure and time are increased significantly with increasing the NRS content. While the incorporation of NRS particles into cementitious matrix leads to a slight increase of porosity, it shows no significant changes of micro morphology. The variations of the mechanical and waterproof properties of WUHTCCs are induced by the hydrophobic and sheet-like NRS particles that alter the surface properties and microstructures of the material substrate. The WUHTCCs with good material properties developed in this study for seepage control facilitate their applications in the fields of construction, decoration and repair.

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1. Introduction

Most cementitious materials (cement paste, mortar and concrete) have relatively low permeability, however, the problems of water seepage always occur in the roofs, bathrooms and basements of buildings, the segments of tunnels, and the stations of metros

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[\[1\]](#page--1-0). A traditional method for mitigating water seepage is to apply an organically or inorganically waterproof coating on the material surface. While this method may be effective, the high volatile organic compound level is harmful to humans and the waterproof function of this coating layer may fade rapidly under aggressive environments, such as, external loads, UV exposing, heating, wetting and drying and freezing and thawing [\[2–5\].](#page--1-0) Furthermore, an elaborate primer is generally needed for the favorable performance of a waterproof coating, which increases the costs of economy and manpower. So it is always a challenge to find an easy-to-use, manpower saving and durable way or material to control the water seepage of buildings and infrastructures. Cementitious composites modified by fibers and nano additives, like ordinary cement mortar and concrete, can adhere to most natural and man-made building materials without specifically elaborate pretreatments [\[6\]](#page--1-0), which may pave an alternative path to control the water seepage problems of buildings and infrastructures.

To date, numerous studies have been conducted to investigate the effects of clay-based nano additives on mechanical and transport properties of cementitious materials. Chang et al. [\[7\]](#page--1-0) studied the mechanical properties and water permeability of Portland cement paste with nano montmorillonite, and found that the positive effect of the nano clay was in a limited loading range. Kafi et al. [\[8\]](#page--1-0) reported the positive effect of nano montmorillonite on the mechanical properties of paste and mortar in a broader loading range. Hakamy et al. [\[9\]](#page--1-0) investigated the mechanical property and water absorption of nano clay and calcined nano clay-cement composites, and found an obvious decrease of water absorption by the nano clays. Similar studies on the enhancement of mechanical properties of cementitious materials by nano clays have been extensively reported $[10-13]$. Based on systematically experimental studies, Kuo and coworkers [\[14–17\]](#page--1-0) suggested that the design strength for normal-strength cement mortars can be attainable for up to 30% replacement of fine aggregates by surface-modified nano reservoir silt (NRS) particles that generally show layered nano structures and are mostly composed of $SiO₂$, $Al₂O₃$ and Fe₂O₃, and the permeability of the materials can be essentially decreased. The hydrophobic nano clays are expected to inhibit water from entering capillary pores and the space between the layered nano clays, and in consequence, the water permeability is lowered [\[18\]](#page--1-0).

It is noteworthy that the relatively brittle feature of ordinary Portland cement mortar and concrete, although modified by nano clays, limits their uses. Fiber-reinforced ultra-high toughness cementitious composites (UHTCCs), under rational design, can show excellent toughness, impact resistance and durability [\[19–22\]](#page--1-0) which thus provides good substrates to design and fabricate the cementitious composites with the functions of cracking and seepage controls. Hakamy et al. [\[23–25\]](#page--1-0) reported a type of NaOH treated hemp fabric and nano clay-reinforced cementitious nanocomposites with good mechanical and durability. The improvement of mechanical properties of cementitious composites by nano clays and fibers has been reported extensively $[26,27]$. Recently, Yu et al. $\lceil 2 \rceil$ reported a type of waterproof engineered cementitious composites (WECCs) containing a waterproof admixture for seepage control. It was found that the water absorption of WECCs was greatly decreased [\[2\].](#page--1-0) This thus throws fresh light on the design and fabrication of waterproof cementitious composites by incorporating surface-modified nano clays into cementitious binders to control water seepage.

Inspired by the work of waterproof cement mortars by Kuo et al. [\[14–17\]](#page--1-0) and the previous studies of UHTCCs in our institute [\[28–](#page--1-0) [30\],](#page--1-0) here we reported a type of waterproof ultra-high toughness cementitious composites (WUHTCCs), where the loadings of NRS particles used are in a relatively broad range. Comprehensively experimental measurements of WUHTCCs with indepth analyses allow exploring the affecting factors and mechanisms accounting for the decrease of compressive strength, the maintenance of toughness, and the enhancement of waterproof. The findings of this research are expected to optimize the design of WUHTCCs and to pave a wild path for the uses of the materials in construction, decoration and repair with auxiliary seepage control.

2. Experimental programme

2.1. Materials and mixture design

The WUHCCs designed and fabricated in the present study are based on a UHTCC with strain hardening behaviors developed by the same research group (e.g., [\[19,20,28–30\]\)](#page--1-0). To achieve the rapid hardening of WUHTCCs, which is potentially used for emergency repair, a rapid hardening cement classified as P.II 52.5R according to the Standard of GB175-2007 (China) [\[31\]](#page--1-0) was used for fabricating the WUHTCC matrix. The binders also included active fillers (AF) that contain fly ash and silica fume. A silica sand (SS) was used as an inactive filler; see [Table 1](#page--1-0) for detailed mixture proportions. The detailed physical properties of the binders can be found elsewhere [\[2\]](#page--1-0). A very high volume of fillers (i.e., AF and SS) other than cement clinkers based on a green UHTCC mix as reported in Refs. [\[19,20,28–30\]](#page--1-0) shows beneficial effects to the reduction of steady state crack width, waterproofing and the long-term durability of a UHTCC structure. A water-to-powder ratio of 0.326 was used, and a polycarbonate super-plasticizer (SP) was added to control the rheology of flesh WUHTCCs. Discontinuous PVA fibers (K-II REC15, Kuraray Co., Ltd) in the volume fraction of 2% were used to enhance the toughness of cementitious composites. The average length, diameter, density, elastic modulus and strength of the PVA fibres are 12 mm, 39 μ m, 1.30 g/ml, 16.9 GPa and 1.28 GPa, respectively. To tune the waterproof efficiency of UHTCC, a commercial nano reservoir silt (NRS) powder (Lotos, Techome Technology Co. Ltd) was added into the binders. The main components of NRS particles are quartz (around 30%), smectite or montmorillonite (around 60%) containing $SiO₂$, $Al₂O₃$ and $Fe₂O₃$ and other phases (around 10%). A cation-exchange reaction method was used to modify the surface properties of NRS particles [\[14,15\]](#page--1-0). The NRS particles are thin warped plates with the mean diameter within 10 to 50 um and the mean thickness lower than 100 nm; see [Fig. 1](#page--1-0). The NRS-to-binder ratios of 0%, 1%, 2% and 5% were designed to obtain different WUHTCC mixes, namely, WUHTCC-0, WUHTCC-1, WUHTCC-2 and WUHTCC-5, respectively; see [Table 1.](#page--1-0)

All binders as well as NRS powders in the proportions presented in [Table 1](#page--1-0) were carefully poured into a mixer (Hobart HL200), and were mixed for 60 s to avoid the possible heterogeneity of the raw materials due to different densities. Later, the precisely weighed water was added into the mixer, and then a rapid mix lasting for 3 min was conducted. After that, the PVA fibers were added into slurries with further 3-min mixing. The mixed slurries were cast in greased steel molds with short-time vibrations. A polyethylene sheet was used to cover the surfaces exposed after the surface finishing step. This prevents the possible damages of the WUHTCC specimens induced by moisture loss. The specimens were placed in a chamber under room temperature for 24 h prior to demolding. After demolding, all specimens were cured up to 28 days in a room with the temperature and relative humidity controlled at 20 ± 2 °C and > 95%, respectively. Different specimens were prepared for different tests. Specimens in cuboid of $100 \times 100 \times 400$ mm³ were prepared for four-point bending (FPB) test. Cubic specimens with dimensions of 70 mm3 were prepared for the tests of compressive strength and water absorption. Conic specimens with upside and underside surface diameters of 70 mm and 80 mm, height of 30 mm were prepared for water penetration test. The damaged specimens from the compressive strength and FPB tests were crushed into small pieces for pore structure and microstructure tests.

2.2. Microstructural analysis

For pore structure measurement, we employed a mercury intrusion porosimetry (MIP) (Autopore IV 9510, Micromeritics Instrument Corporation, Norcross, GA, USA). The measurement of MIP can provide the pore structure and material informations of samples (e.g., porosity, mean and medium pore sizes, and pore size distribution). The mercury intrusion and extrusion were performed with the pressure from 3.7 kPa to 414 MPa with the equilibrium time for each applied pressure level of 10 s. For the evaluation of the pore size distributions of the WUHTCC samples, the contact angle between mercury and pore surface and the surface tension between vapor and liquid mercury were set as 130° and 485 N/m respectively [\[32,33\].](#page--1-0) The intrusion-extrusion hysteresis [\[34,35\]](#page--1-0) was not considered in this study.

The micro morphology of WUHTCCs was observed and analysed using an FEI Quanta FEG650 field emission environmental scanning electronic microscopy (ESEM). The samples for ESEM analysis were prepared from the crushed specimens after mechanical tests. In order to preserve the original topography of fracture surfaces, all the samples were only cut into an appropriate size without polishing the observation surfaces. The accelerating voltages within 10 kV to 20 kV were used,

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