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Effects of nano-SiO_2 particles on the mechanical and microstructural properties of ultra-high performance cementitious composites

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ABSTRACT

In this research the effects of nano-SiO_2 particles on the mechanical performance, hydration process and microstructure evolution of ultra-high performance cementitious composites were investigated by different methods. The results showed that the compressive and flexural strength increased with the increase of the nano-SiO_2 content up to 3% and due to agglomeration of nano-SiO_2 particles, the mechanical properties decreased slightly when the nano-SiO_2 content was more than 3%. The hydration process was accelerated by the addition of nano-SiO_2. The porosity and the average pore diameter decreased with the increase of the nano-SiO_2 content and aging. The microstructure was more homogenous and dense for nano-SiO_2 specimens as compared to the control specimen. All of these improvements could be mainly attributed to the pozzolanic and filler effects of nano-SiO_2.

1. Introduction

In recent years, the performance of concrete has been significantly increased. Ultra-high performance cementitious composites (UHPCC) are a new type of composite materials made primarily from hydraulic cements, fine aggregates and discrete reinforcing fibers with outstanding material properties. UHPCC has been used extensively throughout the whole world due to its ultra-high mechanical properties, dense structure, low capillary porosity and excellent durability [1–5].

The use of nanotechnology in cement and concrete has been increasing in recent years in order to obtain higher performance. Using nano-particles can lead to novel properties in concrete. It causes an improvement in the mechanical properties and durability of concrete [6–8]. A lot of research has been carried out over the last years in order to understand the influence of nanoparticles on cement and concrete properties [9–12]. The most commonly used nanoparticles in concrete are SiO_2, $CaCO_3$, TiO_2, ZnO_2, Al_2O_3, Fe_2O_3 and other nanofibers [13–15]. Among them, nano-SiO_2 has been studied intensively. It has been widely reported that nano-SiO_2 addition can greatly improve the mechanical properties and durability of concrete and also reduce the permeability of hardened concrete [16]. Li et al. [17] showed that the mechanical performance of concrete can be enhanced by incorporating nano-SiO_2. The experimental studies by Ji [18], He and Shi [19] showed that the addition of nano-SiO_2 improves the durability of concrete. Ghafari et al. [20] studied the effect of nano-SiO_2 on the flowability, strength and transport properties of ultra high performance concrete. They focused on the pozzolanic reactivitiy of nano-SiO_2 and silicon fume in cement pastes, mechanical properties and microstructure of the composites. The whole process of hydration and hydration products were not discussed deeply. These effects are caused by the pozzolanic reaction which results in a finer hydrates phase and the nano-filler effects which densify the microstructure of cementitious composites. However, so far the effects of nano-SiO_2 on the hydration process and microstructure evolution of UHPCC are rarely explored in literature due to its special characteristics like higher cement content and strength grade, lower water–binder ratio and the introduction of different types of mineral admixtures to partly replace the Portland cement. Accordingly, the hydration process and microstructure evolution of UHPCC may demonstrate significant differences as compared to ordinary concretes. In addition, at low water–binder ratio (w/b), cement cannot hydrate completely, implying that the problems are induced by nano-SiO_2 during the pozzolanic reaction at early or later age. For the above reasons, this research program was initiated to investigate the influence of nano-SiO_2 on the mechanical and microstructural properties of UHPCC via different analysis and testing methods.

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2. Experiments

2.1. Materials

Three types of cementitious materials were used in the research, including Portland cement, ultra-fine fly ash (FA) and nano-SiO_2 particles. The cement was P·II52.5 in accordance with the relevant Chinese standard. The compositions of the cement and FA are shown in Table 1. The nan-SiO_2 was manufactured by HangZhou WanJing New Materials Co., Ltd, P.R China. FA used in this paper was from NanJing Thermal Power Company, P.R China. The average particle size of nano-SiO_2 was 20 nm and the purity was no less than 99.5%. The amorphous structure of nano-SiO_2 is revealed by the XRD pattern (illustrated in Fig. 1) and the spherical shape of nano-SiO_2 can be observed in Fig. 2. According to former research [21,22], FA was added as a partial replacement of cement at a level of 35% by weight of the total cementitious materials. The proportion was chosen based on a large amount of experiments which can get a homogeneous gradient of fine and coarse particles in the mixture and also considering the workability of the composites. The water reducing ratio of the superplasticizer was no less than 35%. For mortar mixes, commercial river sand with a maximum size of 2.5 mm was used as aggregate in the mortar. The specific gravity and the fineness modulus of the sand were 2.6 and 2.26, respectively.

2.2. Mix proportion of UHPCC

Four mixes were studied in this paper. The recipe of the UHPCC matrices is listed in Table 2. Cement was replaced by FA and nano-SiO_2, and the dosages of nano-SiO_2 varied from 0% to 1%, 3% and 5% by mass of the cementitious materials. The w/b and sand-binder ratios were 0.2 and 1.2, respectively.

2.3. Methods

To prepare the UHPCC containing nano-SiO_2, the superplasticizer was dissolved in water and then the nano-SiO_2 was added and mixed using an ultrasonic mixer for 3 min. The cement, FA and sand were put into a mortar mixer together and mixed for 3 min. After that, the sonicated mixture was added and mixed for another 3 min to homogenize the mixture. Afterwards, the fresh mixtures were cast into steel moulds and compacted via a standard vibrating table. The specimens were demoulded after 24 h and cured under standard conditions (20 °C ± 2 °C, RH > 90%) for designated ages (3 days, 7 days, 28 days and 90 days) before testing.

Specimens for static mechanical strength were 40 mm by 40 mm by 160 mm prisms. Flexural strength and compressive strength were tested according to BS EN 196-1. At first, the three-point bending test was performed to obtain flexural strength. After bending test, the broken two parts were used to conduct compressive test. Three samples were tested for each mix. The average value was served as the final flexural strength and compressive strength.

Heat of hydration was measured under isothermal conditions (20 °C ± 0.1 °C) using an isothermal calorimeter produced by TAM instrument. The model of the instrument was TAM Air, which is well-suited for measuring the heat release during the hydration of cement. TAM Air is an 8-channel isothermal heat conduction calorimeter for heat flow measurements in the milliwatt range. All calorimetric channels are of twin type, consisting of a sample and a reference vessel. Each test consisted of a 15-g sample which was placed into the calorimeter cup. The cup was then put into the calorimeter and held for 5–6 h to attain temperature equilibrium. An data acquisition system was initiated at the same time to record the output voltage from which the heat flow in the system could be calculated. The reproducibility of the results was checked. Duplicate tests showed that total heat measurements were within ± 5%. Rate of heat evolution did vary somewhat in the first few minutes but after 30 min the rates were essentially identical. All tests were carried out for 72 h to observe later reactions.

For X-ray diffraction quantitative analysis, the specimens were soaked in absolute alcohol for 48 h to stop hydration and then milled to particles that could pass the 80 μm sieve. After that,

Table 1
Chemical composition of cement and fly ash (mass%).

Type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	N_2O	L.O.I
Cement	20.4	4.70	3.38	64.7	0.87	1.89	0.49	0.33	3.24
FA	53.98	28.84	6.49	4.77	1.31	1.16	1.61	1.03	0.72

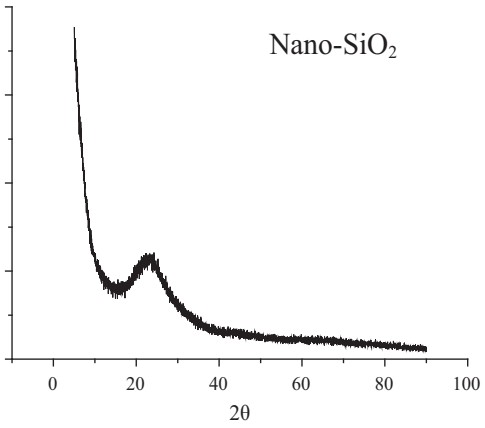

Fig. 1. XRD analysis of nano-SiO_2.

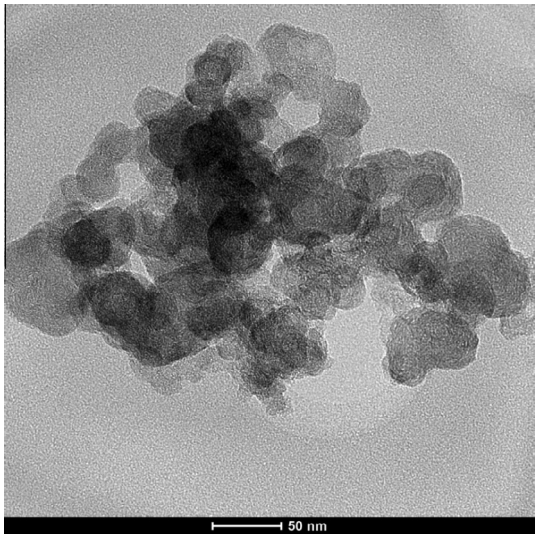

Fig. 2. TEM micrograph of nano-SiO_2.

Table 2
Mix proportions of UHPCC matrix.

Type	Cement (%)	FA (%)	Nano-SiO_2 (%)	w/b	Superplasticizer (%)
N0	65	35	0	0.2	2
NS1	64	35	1	0.2	2
NS3	62	35	3	0.2	2
NS5	60	35	5	0.2	2