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Influences of nano-TiO_2 on the properties of cement-based materials: Hydration and drying shrinkage

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HIGHLIGHTS

- Nano-TiO_2 enhances the compressive strength of cement-based materials.
- Nano-TiO_2 decreases water loss of cement-based materials during drying.
- Nano-TiO_2 mitigates drying shrinkage of cement-based materials.

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ABSTRACT

To better understand the influences of nano-TiO_2 on the properties of cement-based materials, the hydration process, the compressive strength development, and the drying shrinkage of cement-based materials with the addition of nano-TiO_2 of 25 nm were investigated. Results showed that nano-TiO_2 increased the compressive strength of cement mortar through its acceleration on cement hydration and the pore-refining effect: 5 wt.% nano-TiO_2 accelerated cement hydration process for 2 h and reduced the most probable pore size by 19.4%, 48.5%, and 54.4%, respectively. In addition, the influences of the hydrophilicity of nano-TiO_2 on the water loss and volume stability of hardened cement pastes were primarily investigated and discussed in this work. For a comparison study, nano-SiO_2 of 30 nm size was also used. Results showed that the decline of the contact angle and the refining of pore structure with the addition of nano-TiO_2 slowed down the water loss of hardened cement paste, which resulted in a comparable drying shrinkage to that of the control sample at 1 month age.

1. Introduction

With the development of nanotechnology in construction and building materials, the investigations worked on the effects of nano-particles on the properties of cement-based materials were widely conducted in recent years owing to their fine particle size [1], high reactivity [2], and specific functional properties [3]. The commonly used nano-particles in cement and concrete were nano-SiO_2 [4–9], nano-Al_2O_3 [10–12], nano-TiO_2 [13–15], nano-$CaCO_3$ [16–19], etc. Hou et al. studied the effect of nano-SiO_2 on cement hydration and revealed that the early age hydration was significantly increased [20,21]. Liu et al. [16] found that the compressive strength of cement mortar with addition of 1 wt.% nano-$CaCO_3$ was increased by 111.2% and 108.6% at 7 and 28 days, respectively. The study conducted by Nazari et al. [22] suggested that the compressive strength of cement concrete was increased by 14.0% and 16.7% at 7 and 28 days when 1 wt.% nano-Al_2O_3 was introduced.

More recently, the addition of nano-TiO_2 into cement-based material has won great attention due to its chemical stability, high catalytic activity and low price [23–25]. However, the recognition of its effects on the properties of cement-based materials was far from satisfactory. Essawy et al.'s study showed that the compressive strength of cement mortar was increased by 5% when 5 wt.% nano-TiO_2 was added [26]. However, investigation conducted by Hassan [27] showed that 2 wt.% nano-TiO_2 would result in a comparable compressive strength value to that of the control sample at 28 days. Even a reduction of the strength value was reported when nano-TiO_2 was added [28]. Meng et al. ascribed the improvement of mechanical property of cement-based materials to the decrease and modification of orientation index of hydration products of cement induced by nano-TiO_2 [28], while Chen et al.'s results suggested the hydration acceleration effect on cement can be accounted for the improvement [29]. All the above results suggest that

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more work is needed to verify the effects of nano-TiO_2 on cement-based materials.

Before its real application, the influences of nano-TiO_2 on cement-based materials should be fully understood. Comparatively, it is noted that little work has been conducted on the effects of nano-TiO_2 on the volume stability of cement-based materials, which is closely related to the pore size distribution and the water vapor transport properties of cement-based materials [30]. Considering the possible influences of nano-TiO_2 on the hydration process and pore structure, together with its super-hydrophilic property, the water transport property of cement-based materials could be greatly influenced, which finally affect the volume stability of the material. In this work, based on the influences of nano-TiO_2 on the hydration properties of cement-based materials, the drying shrinkage of hardened cement paste has been investigated and discussed.

2. Materials and methods

2.1. Materials

Ordinary Portland cement complying to 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.

Commercially available colloidal nano-TiO_2 and nano-SiO_2 with the mean particle size of 25 nm and 30 nm and the solid content of 20% and 40% were used. Polycarboxylate (PC) water reducer with a solid content of 40% and a water-reducing ratio of 30% was used to achieve a flowable mortar when nano-particle was added.

2.2. Methods

2.2.1. Sample preparation

In this work, mortar samples were prepared at the W/C ratio of 0.4 and 0.6 and the cement-to-sand ratio of 1/3. River sand with a fineness modulus of 2.8 was used. All paste samples were prepared at the W/C ratio of 0.4. The samples were dry-mixed for 1 min and then wet-mixed for another 10 min before molded in 4 cm × 4 cm × 16 cm rectangular molds and covered with plastic sheet. During the mixing, nano-materials were dispersed in mixing-water before added into the sample. After 1 day curing (25 °C/60% RH), the samples were demolded and stored in curing chamber (20 ± 1 °C/RH 95%) until testing.

2.2.2. Setting time and fluidity

ASTM C191 [31] was followed and a manual Vicat apparatus was used to determine the initial and final setting times of pastes with a W/C ratio of 0.4: the penetration of the Vicat needle into cement paste at 25 mm and 0.5 mm were determined as the initial and final setting, respectively.

The fluidity of mortars with the W/C ratio of 0.4 and 0.6 were measured using a flow table by following ASTM C230 [32].

2.2.3. Compressive strength

The influences of nano-TiO_2 on the mechanical property of cement mortars with the W/C ratio of 0.4 and 0.6 were evaluated by measuring the 3-, 7- and 28-day compressive strength at a loading speed of 2.5 kN/s. The average value of six replicates was taken as the representative value.

2.2.4. XRD

X-ray diffractometry (Bruker D8 Advance, Germany) was used to qualitatively evaluate the influences on cement hydration. The accelerate voltage, accelerate current, step size and dwelling time of the tests were 40 kV, 20 mA, 0.05°, and 1 s, respectively.

2.2.5. MIP

Mercury intrusion porosimetry (MIP, Quantachrome, PM60GT-18, USA) technique was used to quantitatively evaluate the pore structures of the samples with or without the addition of nano-particles. A pressure of more than 400 MPa can be achieved by the machine and this pressure allows the mercury to penetrate pores as fine as 0.003 μm diameter. After curing, samples were vacuum-dried at 60 °C for 24 h before MIP tests. About 0.6 g sample was used for each test.

2.2.6. Calorimetric measurements

A conduction calorimeter (TAM Air C80, Thermometric, Sweden) operating at 25 °C was used to determine the hydration heat flow. During the tests, a W/C = 0.5 was used and no water-reducer was added. The heat flow was recorded every 44 s for 48 h.

2.2.7. Contact angle test

Contact angle meter (OCA40) was used to evaluate the hydrophilicity of the cement past samples with different additions of nano-TiO_2. Before testing, samples with the W/C ratio of 0.4 were sliced into pieces of 1 mm height by 2.5 mm diameter. The newly-cut surface of the sample was polished using silicon carbide paper of gradation 6.5 μm for 5 min. Samples were stored in 60% RH environment for 2 h before contact angle measurement. During the measurement, 2 s elapsed before the capture of the shape of the droplet on the sample surface and then the contact angle was recorded. The average value of three tests was taken as the representative value.

2.2.8. Drying shrinkage

Cement paste (W/C = 0.4) sample with dimension of 25 mm × 25 mm × 280 mm was used for drying shrinkage measurement. Samples were demolded 1 day after casting. Immediately after demolding, the initial length of the sample was recorded before removed into a chamber of 25 °C and 60% RH. Sample length and weight were recorded every 24 h for the first 2 weeks and then every other day for the next 2 weeks. The average of three samples was taken as the representative value.

Unless otherwise stated, only one test of the sample was conducted due to their generally good repeatability.

3. Results and discussions

3.1. Mortar fluidity

One of the shortages of introducing nano-particle into cementitious material is the reduction of the workability due to its high specific surface area [33,34]. Influences of nano-TiO_2 on the fluidity of cement mortar were evaluated on samples with W/C of 0.4 and 0.6, and the results are shown in Fig. 1.

It can be seen in Fig. 1 that the fluidity of cement mortar greatly decreases by nano-TiO_2, and the greater amount of nano-TiO_2, the greater reduction of fluidity: the reduction of the slump flow of 2.8%, 19.8%, and 20.8% were resulted when 1%, 3%, and 5% nano-TiO_2 were added into the W/C = 0.6 mortar. For the W/C = 0.4 mortar, it shows that the addition of superplasticizer of 1%, 1.3%, 2.2% and 2.7% were needed when 0%, 1%, 3%, and 5% nano-TiO_2 were added to achieve a slump flow of about 165 mm.

The increase of the amount of water needed when nano-particle is added could be due to its small size and great surface area, which will absorb more water on the surface [35,36].

3.2. Setting time

The influences of nano-TiO_2 on the hardening process of cement pastes were evaluated by measuring the setting time and the results are presented in Fig. 2.

It shows in Fig. 2 that the initial setting time was shortened by 37.9%, 63.4%, 76.5%, and the finial setting time decreased by 15.7%, 37.4%, 46.2% when 1%, 3% and 5% nano-TiO_2 were added. It has been widely accepted that cement hydration is a dissolution and precipitation process [37,38]. The acceleration effect of nano-TiO_2 on cement hydration can be ascribed to the seeding effect:

Table 1
Physiochemical properties of cement.

SiO_2	Al_2O_3	Fe_2O_3	SO_3	CaO	MgO	LOI	Total	Density (g/cm^3)	Fineness (m^2/kg)	28-Day compressive strength (MPa)
21.1	4.7	3.5	3.3	62.9	2.8	1.1	99.4	3.1	390	50.1