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Nano boron nitride modified reactive powder concrete

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HIGHLIGHTS

- Nano boron nitride (nano-BN) is used to reinforce reactive powder concrete (RPC).
- Effects of nano-BN size and content on strength and durability of RPC are studied.
- Properties of nano-BN reinforced RPC with water and heat curing are compared.
- Low dosage nano-BN can obviously improve strength, toughness and durability.
- Nano-BN reinforcing effects are due to its properties and RPC structure improvement.

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ABSTRACT

This paper aims to investigate the effects of particle size and content of nano boron nitride (nano-BN) as well as curing method on the strength and durability of reactive powder concrete (RPC). The enhancing mechanisms are analyzed through performance, X-ray diffraction, nuclear magnetic resonance, thermogravimetry and scanning electron microscope tests. The flexural strength and compressive strength of RPC containing 0.5 wt% of 120 nm nano-BN achieve an increase of 2.65 MPa/15.7% and 11.61 MPa/12.96% at standard curing age of 28 d, respectively. Furthermore, heat curing for 2 d causes the increasing compressive strength of 120 nm nano-BN filled RPC, compared to standard curing for 28 d. For the durability performance, the introduction of 0.5 wt% of 120 nm nano-BN enhances the resistance of RPC with standard curing and heat curing maximally by 55.56% and 34.96%, respectively. The chloride penetration resistance of RPC containing appropriate amount of 120 nm nano-BN is improved by 100%. Experimental results show that the strengthening mechanisms of nano-BN on RPC performances are multifaceted, and can be attributed to small size, nucleation, filling, bridging, lubrication and layered blocking effects.

1. Introduction

Reactive powder concrete (RPC) is a high performance cementitious material with high strength and outstanding durability. The high properties of RPC are mainly attributed to its optimized particle size, lower porosity and improved microstructure [1,2]. The combination of RPC and nano boron nitride (nano-BN) with excellent properties is of great interests for developing a new type of concrete with (ultra)high strength and durability. Moreover, nano-sized boron nitride particles can fill the pores of RPC at nanoscale, making the microstructure more compact. It is expected that RPC has a better composition effect with nano-BN compared to traditional concrete. Therefore, RPC was selected as the matrix of nano-BN reinforced cementitious composites.

As an emerging nanomaterial, nano-BN has been widely studied and applied in recent years. Similar to the structure of graphene [3], nano-BN is a two-dimensional crystal material with a layered structure. Due to its high mechanical strength [4–6,8–11], high thermal conductivity [4,7], high resistivity [12], excellent heat resistance [13], lubricity [5], corrosion resistance [14], low friction coefficient and low expansion coefficient [13,15], nano-BN has greater potential in the fields of machining, electronics, aerospace as well as reinforced composites. However, the reinforcing effect of nano-BN on cementitious composites has less been researched. In 2013, Rafiee et al. studied the cementitious composites incorporating nano-BN and nano graphite oxide (nano-GO). Experimental results indicated that concrete containing 1 wt% nano-BN reached an enhancement of 64% in compressive strength and 200% in

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toughness. Also, the compressive strength and toughness of nano-BN filled cement were increased by 89% and 85% compared to pure cement, respectively [16]. In 2015, He reported that the introduction of 1 wt% of 5 μm nano-BN and 1 wt% of 0.5 μm nano-BN improved the compressive strength of concrete by 4.27 MPa/8.6% and 6.59 MPa/13.26%, respectively. Moreover, concrete with 1 wt% of 5 μm nano-BN obtained a higher compressive strength when soaked in a 20 wt% of NaCl solution, compared to concrete without nano-BN [17]. In 2018, Wang et al. studied the exfoliation and dispersion of nano-BN and its enhancing effect on strength of cement paste. They reported that cement paste with 0.003 wt% nano-BN gained a rise of 13% and 8% in compressive and tensile strength at 7 d, respectively [18]. To sum up, fewer researches about the application of nano-BN in civil engineering were conducted, and the research of nano-BN filled cementitious composite principally focused on the strength. A comprehensive study on the mechanical properties, durability and reinforcing mechanisms of nano-BN cementitious composite is necessary.

This paper aims to fabricate a new type of concrete with (ultra) high strength and durability by combining nano-BN and RPC. The influences of 1 wt%, 3 wt% and 5 wt% nano-BN on the flexural strength and compressive strength of RPC were researched. Nano-BN with particle sizes of 120 nm, 500 nm and 1 μm were used. Then 120 nm nano-BN with better modifying effect was selected as a filler to further study its effect on mechanical strength, abrasion resistance and chloride permeability of RPC. Moreover, the effects of standard curing and heat curing methods on RPC composites were compared. Finally, the enhancing mechanisms of nano-BN on RPC were analyzed by thermogravimetry (TG), X-ray diffraction (XRD), ^{29}Si nuclear magnetic resonance (NMR) and scanning electron microscope (SEM) tests.

2. Materials and experimental method

2.1. Materials

The nano-BN with a thickness of 5–10 nm is produced by Shanghai Xiang Tian Nano Materials Co., Ltd. in China. The properties of nano-BN are shown in Table 1, and their morphologies under transmission electron microscope (TEM) are shown in Fig. 1. It should be noted that TEM observation only gives the image in a local area. Actually, the average particle sizes are 120 nm, 500 nm and 1 μm for three types of nano-BN, respectively.

As listed in Table 1, the contact angles between nano-BN particles and water are all less than 90°, indicating that nano-BN is hydrophilic [19]. This ensures the solubility of nano-BN in water. Moreover, the wettability of nano-BN is enhanced with the increase of its particle size. The zeta potential, also known as electric potential, is an important indicator of the stability of colloidal dispersion. The smaller the dispersed particles, the higher the zeta potential (positive or negative), i.e., the more stable the dispersion system. Conversely, the lower the zeta potential (positive or negative), the easier to condense or agglomerate for nano-BN [20]. It is confirmed that when zeta potential is between 0 and ±5mV, the colloid in solvent is unstable and tends to coagulate and agglomerate. Obviously, the zeta potentials of nano-BN particles listed in Table 1 manifest that nano-BN can easily agglomerate in water. The water adsorption and desorption isotherms of nano-BN along with pressure under room temperature are diagramed in Fig. 2. With the increase of particle size, the surface area of nano-BN reduces, resulting in the decline of adsorption capacity per gram of nano-BN. This means that the workability of nano-BN filled RPC does not reduce with the rise of nano particle size.

The Portland cement (P·O 42.5R) provided by Dalian Onoda Cement Co. Ltd. in China was used as a binder. The mineral admixtures include fly ash produced by Dalian Daokete Building Materials Co. Ltd. in China, and silica fume produced by Elkem Materials Ltd. in Shanghai, China. The properties of silica fume and fly ash are listed in Tables 2 and 3. The particle size of quartz sand is 0.12–0.83 mm and its SiO_2 content is >99%. RHEOPLUS411 (BASF411), a polycarboxylate superplasticizer (SP), was used to adjust the workability of concrete. Its solid concentration was 45%.

2.2. Preparation

Nano-BN with average particle sizes of 120 nm, 500 nm and 1 μm were used. The dosages of nano-BN for each size are designed as 1 wt%, 3 wt% and 5 wt% of cement weight. The water to cement ratio of RPC was fixed at 0.38 for all mixtures. The dosage of SP was adjusted according to the workability of concrete and represented as a percentage of cement weight. The mix proportion of RPC containing nano-BN with different particle sizes is listed in Table 3. Besides, the mix ratio of raw materials for RPC used in this experiment was referenced to that proposed by Richard [21]. Specimens were numbered according to the rule of 'Nano particle size - Dosage'. For example, '120-1' represents RPC blending 1 wt% of 120 nm nano-BN.

The above experimental results indicated the addition of 120 nm nano-BN at lower content had better reinforcing effects on the strength of RPC. Therefore, 120 nm nano-BN was adopted in the following experiments. The ratios of 120 nm nano-BN were adjusted to 0.5 wt%, 1 wt% and 1.5 wt% of cement weight, and the dosage of SP is fixed at 0.8% of cement weight. Besides, the proportion of other materials was the same with Table 4. Samples were numbered following the method of 'BN + dosage'. For instance, 'BN05' represents RPC with 5 wt% of 120 nm nano-BN.

The specimen sizes for strength test is 40 mm × 40 mm×160 mm, for abrasion resistance test is 150 mm × 150 mm×150 mm and for rapid chloride migration (RCM) test is Φ100mm×h50mm. The process of fabricating nano-BN filled RPC is as follows: (1) Water, nano-BN and water reducer were mixed in a mixing pot and stirred for 20 s at low speed. (2) Then silica fume was added and stirred for 60 s at low speed. (3) Cement and fly ash were put into the mixing pot and stirred at low speed for 2 min firstly and then at high speed for 2 min. (4) Finally, quartz sand was added and stirred at low speed for 1 min and then at high speed for 4 min. Nano-BN with sheet-like structure exhibits lubricated effect during mechanical stirring. As a result, the inclusion of nano-BN has no obvious effect on the workability unlike other nano fillers (e.g., carbon nanotubes, nano-SiO_2, nano-TiO_2 or nano-ZrO_2) [22–27]. The mixture was poured into the oiled mold in two layers and each layer was compacted. Then the mold was vibrated in the table vibrator for 60 s to eliminate bubbles. All

Table 1
Properties of nano-BN.

Average particle size	Specific surface area (m^2/g)	Bulk density (g/cm^3)	Density (m^3)	Pure (%)	Crystal form	Contact angle (°)	Zeta potential (mV)	Adsorption capacity (mg/g)
120 nm	19	0.30	2.30	99.9	Hexagon	40.7	−4.89	58.1
500 nm	9.16	0.45	2.30	99.9	Hexagon	37.9	−4.58	47.3
1 μm	9	1.6	2.30	99.9	Hexagon	30.3	−6.3	43.3