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Microstructure, characterizations, functionality and compressive strength of cement-based materials using zinc oxide nanoparticles as an additive

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ABSTRACT

Zinc oxide nanoparticles as a nanophotocatalyst has great potential for self-cleaning applications in concrete structures, its effects on the cement hydration, setting time and compressive strength are also important when using it in practice. This paper reports the effects of zinc oxide nanoparticles, as an additive material, on properties of cement-based materials. Setting time, compressive strength and porosity of mortars were investigated. Microstructure and morphology of pastes were characterized using scanning electron microscope and X-ray diffraction (XRD), respectively. Moreover, thermal gravimetric analysis (TGA) and Fourier-transform infrared spectrometer (FTIR) were also used to determine the hydration reaction. The results show that Portland cement paste with additional ZnO was found to slightly increase the water requirement while the setting time presented prolongation period than the control mix. However, compressive strength of ZnO mixes was found to be higher than that of PC mix up to 15% (at 28 days) via filler effect. Microstructure, XRD and TGA results of ZnO pastes show less hydration products before 28 days but similar at 28 days. In addition, FTIR results confirmed the retardation when ZnO was partially added in Portland cement pastes.

1. Introduction

Nanomaterials have widely attracted considerable scientific interest due to the new potential uses of particles in nanometer scale (10^{-9} m). The most active fields of nanomaterials are electronics, mechanics, medicals, biomechanics and coating. Currently, there is an increase in interest on research areas dealing with cement and concrete in understanding the hydration of cement particles and the use of nano-sized constituents. However, application and advance of nanotechnology in the construction and building materials fields have been uneven. Many researchers investigated the effects of sub-micron and nanomaterials such as silica fume, SiO_2, Fe_2O_3, Al_2O_3, ZnO_2, Cr_2O_3 and TiO_2 [1–9] on properties of Portland cement composite. Moreover, high strength properties of Portland cement and Portland cement–fly ash mortars were achieved by using multi-walled carbon nanotubes [10–12]. It was revealed that these nanomaterials could improve the strength property of Portland cement due to their ultra-fined particle properties which are not only good for hydration reaction but also its acting as filler. Thus, there are many ongoing researches on the development of a new type of nanomaterials for use with Portland cement as a way to improve its properties.

Zinc oxide nanoparticle (ZnO), a versatile semiconductor material, is an inorganic compound which can be prepared by different methods such as sol–gel method, precipitation method, hydrothermal method and pulse combustion-spray pyrolysis methods [13–18]. ZnO has been known as a representative of the photocatalyst among semiconductors which has a direct band gap (3.3 eV at room temperature), due to their high photocatalytic activity, photocatalytic degradation of organic compounds and strongly resist microorganisms [19–21]. It is widely used as an additive into numerous materials and products including plastics, ceramics, paints and glass. Similar to TiO_2 as a photocatalyst, the nano ZnO can therefore be used in self-cleaning applications in concrete structures but little is known on the fundamental understanding of nano ZnO hydration and its effect on setting time and strength.

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Previous researchers [22–27] tried to explain the effect of zinc ions on the hydration reaction of cement minerals and on the microstructure of hydration products during the use of industrial wastes in cement manufacture. Moreover, the decrement of heat of hydration was found when zinc oxide was used with Portland cement. They believed that zinc retards cement hydration via the formation of a layer of amorphous $Zn(OH)_2$ and/or crystalline $CaZn_2(OH)_6{\cdot}2H_2O$ around the anhydrous cement grains at the onset of hydration. Nano ZnO nonetheless can be used in concrete for photodegradation of pollutants and microorganisms [28]. Furthermore, Riahi [6] and Nazari [7] reported that zinc peroxide nanoparticles (ZnO_2) could improve mechanical and physical properties of concrete. Nevertheless, there are only a few reports on the utilization of ZnO together with Portland cement for structural composite application, especially of its nano size, the effects and the characterizations of this nanomaterial as a cement-based building material. Limited information on the compressive strength and characterization of ZnO nanoparticles in cement were found. Consequently, the aim of this research is to investigate the effect of zinc oxide nanoparticles on properties of cement-based materials. Portland cement–zinc oxide nanoparticles pastes were used for water requirement and setting time tests. Compressive strength and volume of permeable pore space tests were also carried out on mortar specimens. Moreover, phase characterizations and microstructure of setting behavior of Portland cement pastes with ZnO were examined using X-ray diffraction (XRD), scanning electron microscope (SEM), thermogravimetric analysis (TGA) and Furrier-transform infrared spectrometer (FTIR).

2. Experimental details

2.1. Materials

Portland cement type I (PC) was used with zinc oxide nanoparticles (ZnO) which purchased from Sigma–Aldrich, Singapore (Purity > 99%), to produce PC-ZnO pastes. Micrographs of raw materials taken from scanning electron microscope (SEM) are shown in Fig. 1a and b. Portland cement particles can be seen to be angular with the particle size of about 1–50 μm while ZnO are also angular with the particle size of approximately 100 nm. X-ray diffraction trace of Portland cement is shown in Fig. 2a. Dominant peaks of PC are shown to compose of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) as follow JCPDF files No. 310301, No. 860398, No. 381429 and No. 740803, respectively. All compositions are generally known to be main phases of Portland cement. X-ray diffraction trace of ZnO is shown in Fig. 2b where the dominant peaks are zinc oxide matches JCPDF file No. 800075.

2.2. Preparation of pastes

In this research, ZnO was used as an additive material at 0, 1, 2 and 5 wt% of PC which was abbreviated by PC, 1Z, 2Z and 5Z, respectively. Water requirement for normal consistency and time of setting of these pastes was tested with the following of ASTM C187 [29] and ASTM C191 [30] standards, respectively.

For paste characterization, ZnO was firstly ultra-sonicated with water in a basin for 15 min at ambient temperature for homogeneous mixing. Portland cement was then added to the mixture with a constant water to cement ratio (w/c) of 0.5. Paste was cast into the cylinder molds which the size of 15 mm (diameter) and 20 mm (high) and then wrapped with plastic film. For PC sample, it was demolded after 24 h casting and then cured in saturated lime water for another 2 days, 6 days and 23 days. For ZnO samples (2Z mix), the samples were demolded after holding in the mold for 2 days to ensure samples are hardened. These samples were then cured for another 1, 5 and 23 days in saturated lime water (for 3, 7 and 28 days test). After these periods, the paste samples were soaked in acetone for 24 h to stop hydration reaction and then dried in 60 °C oven for 24 h. Dried samples were crushed for microstructure analysis using field emission scanning electron microscopy (FE-SEM; JEOL JSM-840A). Moreover, crushed samples were ground for X-ray diffraction (XRD; Philips PW-3040) and thermal gravimetric analysis (Mettler Toledo TG/SDTA 851^e). For thermal analysis condition, the samples were heated from room temperature to 1000 °C with a scanning rate of 10 °C min^{-1} under nitrogen atmosphere condition. Furrier-transform infrared spectrometer (FTIR) was also used and was recorded in the region of 4000–400 cm^{-1} with a FTIR model FT-710 of Horiba Company, Japan. A constant sample (1 mg) and potassium bromide (KBr) of 99 mg were ground together and then pressed into a sample holder of 7 mm diameter. Normal 10 time scans with a resolution of 2.5 cm^{-1} were carried out.

2.3. Preparation of mortars

Mortar samples were prepared for compressive strength analysis using water: cement: sand ratio at 0.5:1:2.5. Mix proportion of Portland cement mortars blended with ZnO nanoparticles as additive materials at 0, 1, 2 and 5 wt% of PC is shown in Table 2. Compressive strength test was conducted at 3, 7, 28 and 90 days of each 3 samples which presented by the average values. After mixing, mortar was cast in the cube mold (50 mm × 50 mm × 50 mm), compacted and then wrapped with plastic film. Mortar samples of PC mix were demolded after casting in the mold at 24 h while ZnO mix were demolded after 3 days (for 3 days test) and after 5 days (for 7, 28 and 90 days test). All mortars were cured in saturated lime water until tested times. Moreover, porosity of mortars was tested using the volume of permeable pore space following the standard of ASTM C642 [31] and then calculated following Eq. (1).

$$V\ (\%) = \left(\frac{W_B - W_A}{W_B - W_C}\right) \times 100 \quad (1)$$

where:

V = volume of permeable pore space (%).
W_A = mass of oven-dried sample in air (g).
W_B = mass of surface-dry sample in air after immersion and boiling (g).
W_C = apparent mass of sample in water after immersion and boiling (g).

3. Results and discussion

3.1. Normal consistency and setting time of pastes

The water requirements for normal consistency of Portland cement paste with 0, 1, 2 and 5 wt% of ZnO were tested according to ASTM C187 standard, as given in Table 1. It was found that the water demand of ZnO mixes was slightly increased (up to 28.4%) when compared with PC mix (26.2%), calculated from water to binder ratio. It can be explained that particle size of ZnO was smaller

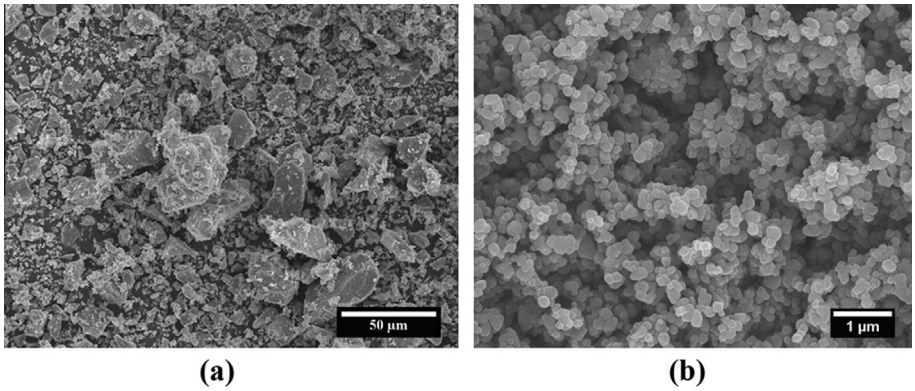

Fig. 1. SEM micrographs of raw materials (a) Portland cement and (b) zinc oxide.