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The effect of adding nano-SiO_2 and nano-Al_2O_3 on properties of high calcium fly ash geopolymer cured at ambient temperature

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ABSTRACT

This article presents the effect of adding nano-SiO_2 and nano-Al_2O_3 on the properties of high calcium fly ash geopolymer pastes. Nano-particles were added to fly ash at the dosages of 0%, 1%, 2%, and 3% by weight. The sodium hydroxide concentration of 10 molars, sodium silicate to sodium hydroxide weight ratio of 2.0, the alkaline liquid/binder ratio of 0.60 and curing at ambient temperature of 23 °C were used in all mixtures. The results showed that the use of nano-SiO_2 as additive to fly ash results in the decrease of the setting time, while the addition of nano-Al_2O_3 results in only a slight reduction in setting time. Adding 1–2% nano-particles could improve compressive strength, flexural strength, and elastic modulus of pastes due to the formation of additional calcium silicate hydrate (CSH) or calcium aluminosilicate hydrate (CASH) and sodium aluminosilicate hydrate (NASH) or geopolymer gel in geopolymer matrix. In addition, the additions of both nano-SiO_2 and nano-Al_2O_3 enhances the shear bond strength between concrete substrate and geopolymer.

1. Introduction

At present, geopolymer is getting more attention as an alternative binder to normal cement binders for applications in concrete industry [1,2]. It is made from rich silica and alumina source materials such as fly ash, calcined kaolin, and blast furnace slag. In Thailand, the major source of fly ash is Mae Moh power station in the north. Approximately 3 million tons is produced annually and it is used mainly as supplementary cementitious materials to replace of Portland cement in construction industry. Many researchers have shown that it can also be used as starting material for making good geopolymer [3,4].

Geopolymeric reaction relies on the activation with alkali solutions and temperature curing at 40–75 °C [3,5]. The obtained geopolymer paste possesses similarly strength and appearance to normal Portland cement paste. However, when fly ash geopolymer material is cured at ambient temperature of around 25 °C, the strength development is rather slow and low strength is obtained [6]. Many researchers have tried to improve the strength development of fly ash geopolymers [7,8]. Khater et al. [9] and Riahi and Nazari [10] reported that the compressive strength of geopolymer depends on the type of starting material and its fineness. The fine particles induce higher leaching of silica and alumina in the alkali environment and leads to a higher strength geopolymer [3].

Recently, nanoparticle is receiving more attention as an alternative binder used for the improvement of nanostructure of building materials [9]. Nano-SiO_2 and nano-Al_2O_3 are most commonly used [11] to enhance compressive and tensile strengths of concrete by additional pozzolanic and filler effects [12]. The nano-SiO_2 particle belongs to highly pozzolanic materials because it consists essentially of SiO_2 in amorphous form with a high specific surface, therefore, exhibits great pozzolanic activity [13]. This research aims to study the properties and application of geopolymer paste made from high calcium fly ash containing nano-SiO_2 and nano-Al_2O_3. The obtained results should be very beneficial to the understanding and to the future applications of the materials.

2. Experimental details and testing analysis

2.1. Materials

The materials used in this study were high calcium fly ash (FA) from Mae Moh power plant in northern Thailand, nano-SiO_2 (S), and nano-Al_2O_3 (A). The liquid portions in the mixture were 10 M sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) with 13.89% Na_2O, 32.15% SiO_2, and 46.04% H_2O.

The chemical composition and physical properties of FA are shown in Tables 1 and 2. The FA had specific gravity, Blaine

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fineness, and average particle sizes of 2.61, 4300 cm^2/g and 8.5 μm, respectively. The average particle sizes of S and A were 12 and 13 nm with specific surface areas (BET) of 200 ± 25 and 100 ± 15 m^2/g. The properties of S and A are shown in Table 3 and the mineral compositions are shown in Fig. 1.

2.2. Mix proportion and mix detail

The nano-particles (S and A) were added to high calcium FA at the dosages of 0%, 1%, 2%, and 3% by weight. Constant liquid to binder (L/B) ratio of 0.60 and Na_2SiO_3/NaOH ratio of 2.0 were used in all mixtures. The mix proportions of geopolymer pastes are shown in Table 4. For the mixing of pastes, NaOH and Na_2SiO_3 solutions were firstly mixed together and used as the liquid solution. The FA and S or A were dry mixed until the mixture was homogenous. Right after, the liquid solution was added and the mixing of pastes was done for 5 min.

2.3. Testing

2.3.1. X-ray diffraction (XRD)

At the age of 28 days, the geopolymer cube specimens were broken and ground to fine powder. The XRD scans were performed at 5 to 60 °2theta with an increment of 0.02 degree/step and a scan speed of 0.5 s/step. The amorphous phases of geopolymer pastes at the age of 28 days were determined by quantitative XRD analysis using Bruker's TOPAS software.

2.3.2. Scanning electron microscopy (SEM)

The geopolymer cube samples at the age of 28 days were broken and the middle portions were used for the SEM analyses. The specimen was placed on a brass stub sample holder with double stick carbon tape. The specimen was dried using infrared light for 5 min and then coated with a layer of gold approximately 20–25A thick using a blazer sputtering coater. The micrographs were recorded at 15 kV and 1000× magnification.

2.3.3. Setting time

The setting time of geopolymer pastes were tested in accordance with ASTM: C191.

2.3.4. Compressive strength and modulus of elasticity

The 50 × 50 × 50 mm cube specimens were used for compressive strength test in accordance with the ASTM: C109. The 25 mm diameter and 50 mm height cylindrical specimens were used for the determination of modulus of elasticity as described in ASTM: C469. The specimens were demolded at the age of 1 day and immediately wrapped with vinyl sheet to protect moisture loss and kept in the 23 °C controlled room. The compressive strength and modulus of elasticity were measured at the ages of 7, 28, and 90 days. The reported results were the average of three samples.

2.3.5. Flexural strength

The flexural strength of geopolymer pastes were obtained from modulus of rupture tests using 40 × 40 × 160 mm prisms in accordance with the ASTM: C293. The specimens were tested in deflection controlled with loading rate of 0.05 mm/min [14]. The flexural strength was measured at the ages of 7, 28, and 90 days. The reported results were the average of three samples.

Table 1
Chemical composition of FA (by weight).

Materials	Chemical composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
FA	29.32	12.96	15.64	25.79	2.94	2.93	2.83	7.29	0.30

2.3.6. Shear bond strength between concrete substrate and geopolymer pastes

The adhesion strength or shear bond strength was evaluated using the slant shear test as described in ASTM: C882 of geopolymer and concrete. The concrete specimens were cured in water for 28 days and then they were wrapped with vinyl sheet to protect moisture loss for 60 days. This long curing period was chosen to provide advanced concrete hydration as in the old concretes in field of construction [15]. The properties of concrete substrate are shown in Table 5. The slant shear 50 × 50 × 125 mm prisms with the interface line at 45° to the vertical as shown in Fig. 2 were used [2,16]. For casting of specimens, the paste was placed into a mold with concrete substrate in two equal layers. Each layer was tamped 25 times and then vibrated for 45 s to obtain good compaction. After the casting of samples, they were covered with vinyl sheet to protect moisture loss and kept in the 23 °C controlled room until the testing ages. The shear bond strength was the ratio of maximum load at failure and the bond area, and the specimens were tested in constant loading rate of 0.30 MPa/s. The shear bond strength was measured at the ages of 7, 28 and 90 days, and the reported results were the average of five samples.

3. Results and discussions

3.1. XRD analysis

The XRD patterns of fly ash and geopolymer pastes containing nano-SiO_2 are shown in Fig. 3. The as-received FA consisted of a glassy matrix as shown by the hump at 25–35 °2theta and crystalline phases of quartz (SiO_2), magnesioferrite ($MgFe_2O_4$) and calcium carbonate ($CaCO_3$). The XRD patterns of the geopolymer pastes containing nano-SiO_2 (Control, S1, S2, and S3) are similar with that of FA, with the presence of a larger amount of quartz and some magnesioferrite and the disappearance of calcium carbonate. The increase in the intensity of quartz is due to the presence of additional SiO_2 in the system. However, the amorphous phases were easily detected as broad hump around 25–38 °2theta due to transformation of the amorphous component in the geopolymer matrix [9], which was also reflected in a small shift of this hump compared with that of FA [17,18]. The presence of CSH phase could be confirmed by the presence of peaks at 29.5 and 32.05 °2theta [19]. The CSH co-existed with the geopolymer products and enhanced the strength of the geopolymer [20].

The XRD patterns of FA and geopolymer pastes containing nano-Al_2O_3 are shown in Fig. 4. The trends of XRD patterns of geopolymer pastes containing nano-Al_2O_3 were also similar to those of control and nano-SiO_2 pastes. The lower peak of quartz compared with that containing nano-SiO_2 was evident. The broad hump of amorphous gel was very significant indicating the advanced degree of reaction to form NASH gel.

3.2. SEM analysis

The SEM photos of geopolymer pastes are shown in Fig. 5. The control paste contained less dense matrix with a larger number of non-reacted and/or partially reacted fly ash particles embedded in a continuous matrix (Fig. 5a). For the 1–2% nano-SiO_2 (Fig. 5b and c) and nano-Al_2O_3 (Fig. 5e and f), less number of fly ash particles were observed, and the matrix appeared denser than that of the control paste. The high magnification (3000×) of 1% nano-SiO_2 (Fig. 5h) and nano-Al_2O_3 (Fig. 5i) showed the denser matrices compared with that of control paste. The uses of nano-SiO_2 and