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Effect of nano-clay on mechanical and thermal properties of geopolymer

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ABSTRACT

The effect of nano-clay platelets (Cloisite 30B) on the mechanical and thermal properties of fly ash geopolymer has been investigated in this paper. The nano-clay platelets are added to reinforce the geopolymer at loadings of 1.0%, 2.0%, and 3.0% by weight. The phase composition and microstructure of geopolymer nano-composites are also investigated using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) techniques. Results show that the mechanical properties of geopolymer nano-composites are improved due to addition of nano-clay. It is found that the addition of 2.0 wt% nano-clay decreases the porosity and increases the nano-composite's resistance to water absorption significantly. The optimum 2.0 wt% nano-clay addition exhibited the highest flexural and compressive strengths, flexural modulus and hardness. The microstructural analysis results indicate that the nano-clay behaves not only as a filler to improve the microstructure, but also as an activator to facilitate the geopolymeric reaction. The geopolymer nano-composite also exhibited better thermal stability than its counterpart pure geopolymer.

1. Introduction

Geopolymers are synthesized by activating a solid aluminosilicate source with alkaline solutions. They are currently attracting extensive research because of their potential as a high-performance and environmentally friendly alternative to ordinary Portland cement in different applications [1,2]. It has been shown that a wide range of waste aluminosilicate materials can be converted into building materials, as they show excellent physical and chemical properties [3–7]. However, geopolymer pastes suffer from brittle failure mode under applied force. The typical values of the compressive strength of geopolymer-based ceramics are around 45 MPa [8] which are comparable to the strength of Portland cement pastes. However, geopolymer pastes show lower flexural strength ranging between 1.7 MPa and 16.8 MPa [8,9]. Improving the flexural and tensile strengths will promote the application of these materials significantly in construction and building industries.

In recent years, nanotechnology has gained attention in ceramic and polymer research, particularly in forming nano-composites which have superior physical and mechanical properties [5]. In geopolymers, various types of nanoparticles have been incorporated successfully to improve their mechanical properties. Alumina and silica nanoparticles have been used successfully as reinforcements for geopolymer pastes, giving them superior mechanical properties. Nano-alumina and nano-silica not only acted as fillers, but also enhanced the geopolymerization reaction [10]. In another study, it has been found that nano-silica and nano-alumina particles have the ability to reduce the porosity and water absorption of geopolymer matrices [11]. A further study on the effect of adding carbon nanotubes to fly-ash-based geopolymer has shown an increase in the mechanical and electrical properties of geopolymer nano-composites when compared to the control paste [12]. In another study, the addition of calcium carbonate ($CaCO_3$) nanoparticles to high-volume fly-ash concrete improved the flexural and mechanical properties, decreased the porosity and improved the concrete resistance to water absorption [13]. Recently, a study on nano-clay cement nano-composites demonstrated that the nano-clay significantly improved the mechanical and thermal properties of the cement matrix [14]. Hitherto, no research has been conducted to investigate the effect of nano-clay on thermal and mechanical properties of geopolymer. The incorporation of nano-clay in

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Table 1
Chemical composition of fly-ash (wt%).

SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	P_2O_5	SO_3	TiO_2	MnO	BaO	LOI
63.13	24.88	2.58	3.07	2.01	0.61	0.71	0.17	0.18	0.96	0.05	0.07	1.45

geopolymer paste could significantly enhance the matrix in two ways: (a) by adding more silica to the system which reacts with sodium to produce sodium aluminosilicate hydrate (geopolymer gel) [10] and (b) by producing a denser matrix through the pore filling effect [14].

The current study has examined the effect of adding different loadings of nano-clay to the geopolymer paste. Results showed that the addition of nano-clay improved the mechanical and thermal properties of geopolymer. Flexural and compressive tests have been performed to measure the various mechanical properties and thermogravimetric analysis (TGA) has been used to examine the thermal behavior of geopolymer containing nano-clay. In addition, X-ray diffraction, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques were used to characterize the phase composition and microstructure of geopolymer-nano-clay composites.

2. Experimental procedure

2.1. Materials

Low-calcium fly-ash (ASTM class F), obtained from the Eraring power station in NSW, was used to prepare the geopolymeric nano-composites. The chemical composition of fly-ash is shown in Table 1. The alkaline activator for geopolymerization was a combination of sodium hydroxide solution and sodium silicate grade D solution. Sodium hydroxide flakes with 98% purity were used to prepare the solution. The chemical composition of sodium silicate used was 14.7% Na_2O, 29.4% SiO_2 and 55.9% water by mass. The nano-clay (Cloisite 30B) used in this investigation was based on natural montmorillonite clay which has composition of $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$. Cloisite 30B is a natural montmorillonite modified with a quaternary ammonium salt, which was supplied by Southern Clay Products, USA. The specification and physical properties of Cloisite 30B are outlined in Table 2 [15].

2.2. Preparation of geopolymer nano-composites

To prepare the geopolymer pastes, an alkaline solution to fly ash ratio of 0.75 was used and the ratio of sodium silicate solution to sodium hydroxide solution was fixed at 2.5. The concentration of sodium hydroxide solution was 8 M, which is prepared and combined with the sodium silicate solution one day before mixing.

The nano-clay was added to the fly-ash at the loadings of 1.0%, 2.0% and 3.0% by weight. The fly-ash and nano-clay were first dry mixed for 5 min in a Hobart mixer at a low speed and then mixed for another 10 min at high speed until a uniform mixture was achieved.

Table 2
Physical properties of the nano-clay platelets (Cloisite 30B) [13].

Color	Off white
Density (g/cm^3)	1.98
d-Spacing (0 0 1) (nm)	1.85
Aspect ratio	200–1000
Surface area (m^2/g)	750
Typical dry particle sizes	90% volume < 13 μm 50% volume < 6 μm 10% volume < 2 μm

The alkaline solution was then added slowly to the fly-ash and nano-clay in the mixer at a low speed until the mix became homogeneous, then further mixed for another 10 min on high speed. The resultant mixture was then poured into wooden molds. The wooden molds were then placed on a vibration table for 2 min before they were covered with a plastic film and cured at 80 °C for 24 h in an oven before demolding. They were then cured under ambient conditions for 28 days. The pure geopolymer, and nano-composites containing 1.0%, 2.0% and 3.0% nano-clay were labeled GP, GPNC-1, GPNC-2 and GPNC-3, respectively. The formulation of samples is given in Table 3.

2.3. Physical properties

Measurements of bulk density and porosity were conducted to define the quality of geopolymer nano-composite. Density of samples (ρ) with volume (V) and dry mass (m_d) was calculated using Eq. (1):

$$\rho = \frac{m_d}{V} \quad (1)$$

The value of apparent porosity (P_a) was determined using Archimedes' principle in accordance with the ASTM Standard (C-20) [16]. Pure geopolymer and nano-composite samples were immersed in clean water, and the apparent porosity (P_a) was calculated using Eq. (2) [17]:

$$P_a = \frac{m_a - m_d}{m_a - m_w} \times 100 \quad (2)$$

where m_a is mass of the saturated samples in air, and m_w is mass of the saturated samples in water.

For the water absorption test, samples of pure geopolymer and geopolymer nano-composites were dried at a temperature of 80 °C until reaching stable mass (m_o). The samples were then submerged in clean water at a temperature of 20 °C for 48 h. After the desired absorption period, the samples were removed and the mass was weighed (m_1) immediately. The water absorption (W_A) of samples was calculated using the equation [18]:

$$W_A = \frac{m_1 - m_0}{m_0} \times 100 \quad (3)$$

2.4. Mechanical properties

A LLOYD Material Testing Machine (50 kN capacity) with a displacement rate of 0.5 mm/min was used to perform the mechanical tests. Rectangular bars of 60 mm × 18 mm × 15 mm were cut from the fully cured samples for three-point bend test with a span of 40 mm to evaluate the flexural strength. Five samples of each group were used to evaluate the flexural strength and flexural modulus of geopolymer composites. The values were recorded and analyzed with the machine software (NEXYGENPlus) and average values

Table 3
Formulation of samples.

Sample	Fly-ash (g)	NaOH solution (g)	Na_2SiO_3 solution (g)	Nano-clay (g)
GP	1000	214.5	535.5	0
GPNC-1	1000	214.5	535.5	10
GPNC-2	1000	214.5	535.5	20
GPNC-3	1000	214.5	535.5	30