

Characteristics of Nanosilica-Geopolymer Nanocomposites and Mixing Effect

H. Assaedi, F. U. A. Shaikh, I. M. Low

Abstract—This paper presents the effects of mixing procedures on mechanical properties of flyash-based geopolymer matrices containing nanosilica (NS) at 0.5%, 1.0%, 2.0%, and 3.0% by weight. Comparison is made with conventional mechanical dry-mixing of NS with flyash and wet-mixing of NS in alkaline solutions. Physical and mechanical properties are investigated using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). Results show that generally the addition of NS particles enhanced the microstructure and improved flexural and compressive strengths of geopolymer nanocomposites. However, samples, prepared using dry-mixing approach, demonstrate better physical and mechanical properties comparing to wet-mixing samples.

Keywords—Geopolymer, mechanical properties, nanosilica.

I. INTRODUCTION

GEOPOLYMERS are aluminosilicate inorganic polymers that are formed from polymerisation of aluminosilicates with alkaline solutions. Geopolymers have several desirable attributes, which include good mechanical properties and durability [1]. In addition, they are environmentally friendly, being derived from natural materials and because they do not emit high levels of carbon dioxide that is associated with the manufacturing of Portland cement [2], [3].

Scientists of ceramics and polymer materials have recently become interested in developing nanocomposites, which have superior physical and mechanical properties. Nanoparticles are being added to geopolymers to increase mechanical properties. For example, nano-alumina and nanosilica have been used effectively to reinforce geopolymer matrices, providing higher mechanical performance. The nanoparticles enhanced the geopolymeric reaction and acted as voids-fillers, producing matrices with higher densities [4]. In additional research, it has been found that the porosity and water absorption of geopolymer matrices have been reduced due to the addition of silica and alumina nanoparticles to geopolymer pastes [5]. A further study on the effect of addition of carbon nanotubes to fly-ash-based geopolymer has shown an increase in the mechanical and electrical properties of geopolymer nanocomposites when compared to the control paste [6]. 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 [7].

The critical benefit of the addition of nanoparticles to improve the geopolymer properties can be achieved if the nanoparticles are dispersed appropriately in geopolymer pastes. The nanoparticles dispersion is influenced significantly by mixing procedures, which influences the physical and mechanical properties of geopolymer matrices. In this study, the effect of mechanical dry mixing of NS with flyash before adding alkaline solutions and the dispersion of NS in alkaline solution are investigated. XRD analysis and SEM are used to investigate the morphology and microstructure of geopolymer nanocomposites. The effect of different nanosilica particles contents on physical and mechanical properties is also evaluated in this paper.

II. EXPERIMENTAL METHODS

A. Materials and Fabrication

Low calcium fly ash (ASTM class F), collected from the Eraring power station in NSW, and was used as the source material for the geopolymer matrix. The chemical composition of fly ash is shown in Table I. Nanosilica is obtained from Nanostructured and Amorphous Materials, Inc. of USA with average particle diameter of 18-25 nm (Fig. 1). The alkaline activator for geopolymerisation was a combination of sodium hydroxide and sodium silicate grade D solution. Sodium hydroxide flakes of 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.

TABLE I
CHEMICAL COMPOSITION OF FLY-ASH (WT%)

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

To prepare the geopolymer matrix, 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, and was prepared and combined with the sodium silicate solution one day before mixing.

The geopolymer pastes were prepared by two methods, a dry and wet process. For dry-mix process, the nanosilica was added first to the fly-ash at the dosages of 0%, 0.5%, 1.0%, 2.0% and 3.0% by weight. The fly-ash and nanosilica were dry-mixed for 5 min in a covered mixer at a low speed and then mixed for another 10 min at high speed until

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homogeneity was achieved. The alkaline solution was then added slowly to the fly-ash/nanosilica powders in the Hobart mixer at a low speed until the mixes became homogeneous, then further mixed for another 10 min on high speed.

Similar mixtures dosages were prepared to produce the wet-mix paste (Table II). However, the nanosilica powder was first

wet-mixed with the alkaline solution until the dissolution of the nanosilica powder was achieved. Then, the solutions, with different dosages of silica, were mixed with fly ash in the Hobart mixer at the same period of time of the dry-mix process.

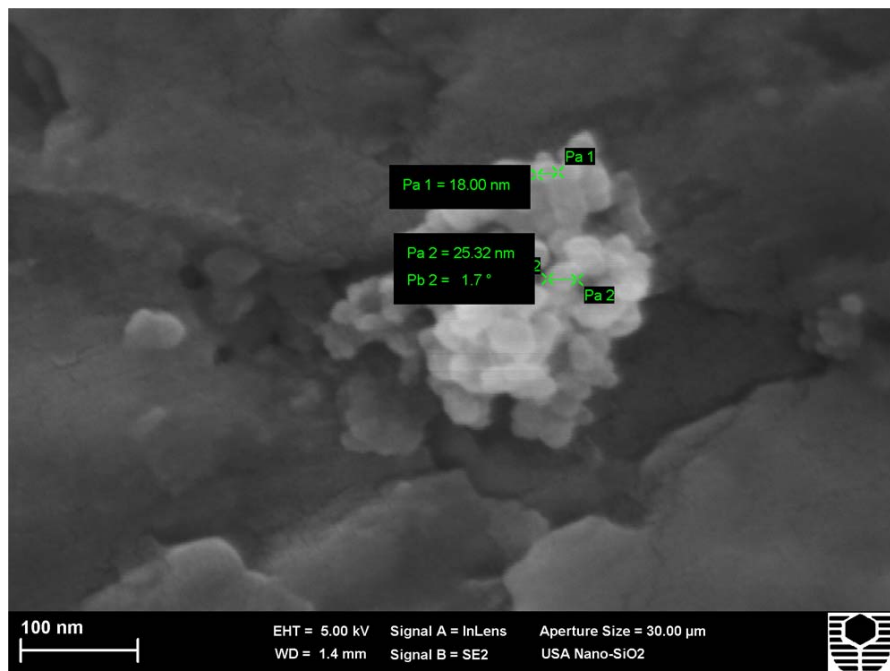


Fig. 1 SEM image of nanosilica

The resultant mixtures, dry/wet-mixes, were then poured into wooden moulds and placed on a vibration table for two minutes to remove any entrapped air inside the pastes. All samples were covered with plastic film and cured at 80°C for 24 hours in an oven before demoulding. They were then dried under ambient conditions for 28 days.

TABLE II
FORMULATION OF SAMPLES

| Sample | Flyash(g) | NaOH (g) | Na ₂ SiO ₃ (g) | Nano-SiO ₂ (g) | Mixing |
|-----------|-----------|----------|--------------------------------------|---------------------------|--------|
| GP | 1000 | 214.5 | 535.5 | 0 | – |
| GPDNS-0.5 | 1000 | 214.5 | 535.5 | 5 | Dry |
| GPDNS-1 | 1000 | 214.5 | 535.5 | 10 | Dry |
| GPDNS-2 | 1000 | 214.5 | 535.5 | 20 | Dry |
| GPDNS-3 | 1000 | 214.5 | 535.5 | 30 | Dry |
| GPWNS-0.5 | 1000 | 214.5 | 535.5 | 5 | Wet |
| GPWNS-1 | 1000 | 214.5 | 535.5 | 10 | Wet |
| GPWNS-2 | 1000 | 214.5 | 535.5 | 20 | Wet |
| GPWNS-3 | 1000 | 214.5 | 535.5 | 30 | Wet |

B. Characterization

The samples were measured on a D8 Advance Diffractometer (Bruker-AXS) using copper radiation and a LynxEye position sensitive detector. The diffractometer were scanned from 7° to 60° (2θ) in steps of 0.015° using a scanning rate of 0.5°/min. XRD patterns were obtained by

using Cu Kα lines (k = 1.5406 Å). An FTIR spectrum was performed on a Perkin Elmer Spectrum 100 FTIR spectrometer in the range of 4000–500 cm⁻¹ at room temperature. The spectrum was an average of 10 scans at a resolution of 2 cm⁻¹, corrected for background. The microstructures of geopolymer composites were examined using a Zeiss Evo (40XVP) scanning electron microscope, equipped with energy dispersive spectroscopy (EDS). Quantitative EDS analysis was undertaken using Oxford Instruments Inca analyser software package calibrated to a copper standard. Samples were polished to 1 mm and coated with platinum to prevent charging before the observation.

C. Density

Measurements of bulk density were conducted to define the quality of geopolymer nanocomposite. Density of samples (ρ) with volume (V) and dry mass (m) was calculated using the relation:

$$\rho = \frac{m}{V}$$

D. Flexural and Compressive Strengths

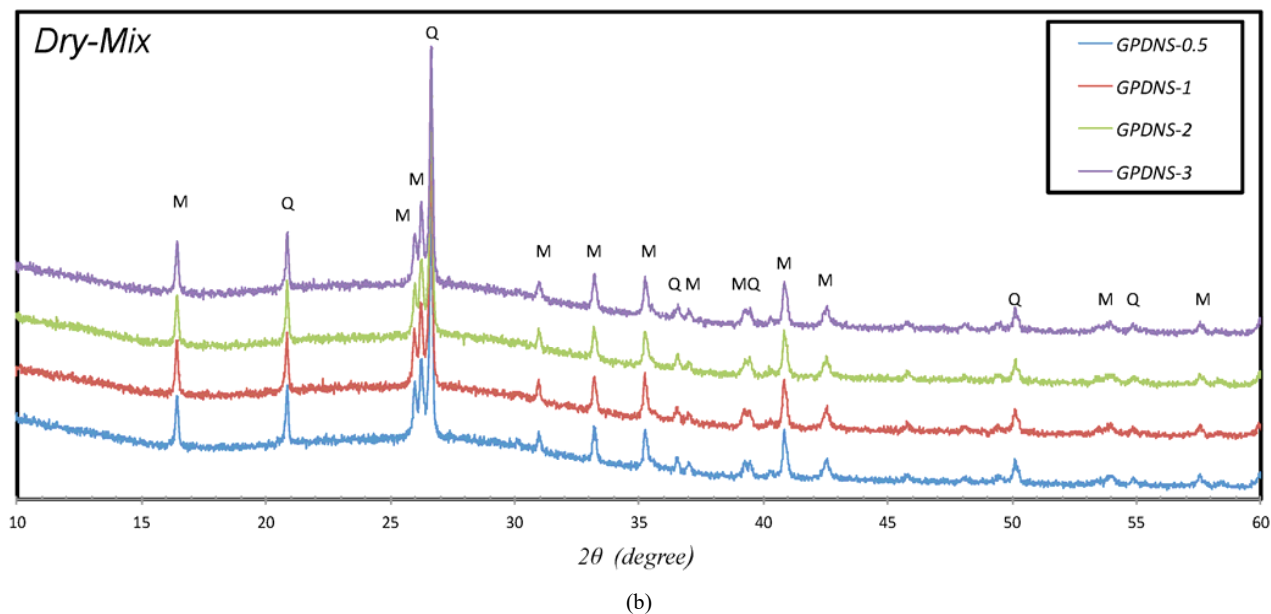
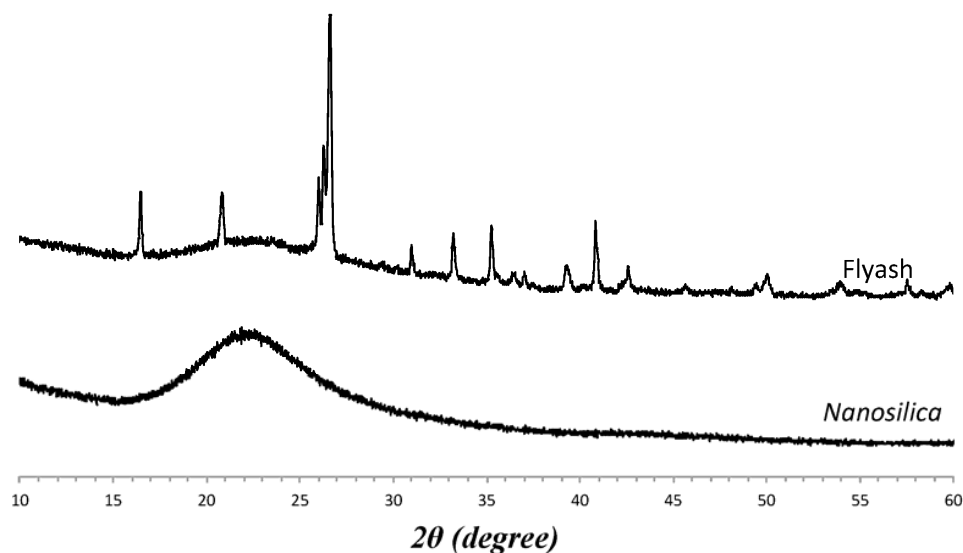
A LLOYD Material Testing Machine (50kN capacity) with a displacement rate of 1 mm/min was used to perform the mechanical tests. Rectangular bars of 60×18×15 mm³ with a

span of 40mm were cut from the fully cured samples for three-point bend tests to evaluate the mechanical properties. All samples were aligned horizontally to the applied load in all mechanical tests. Five samples of each nanocomposite were used to evaluate the flexural strength according to the standard ASTM D790. The values were recorded and analysed with the machine software (NEXYGENPlus) and average values were calculated. The compressive strength of the geopolymer composites was tested according to the standard ASTM C109. However, due to the limitation of the testing machine, 20 mm

cubes were used instead of using the recommended 50 mm cube specimens for the determination of compressive strength.

III. RESULTS AND DISCUSSION

The XRD spectra obtained for nanosilica and nanocomposites samples are given in Figs. 2 (a)-(c). The crystalline phases were indexed using Powder Diffraction Files (PDFs) from the Inorganic Crystal Structure Database (ICSD).



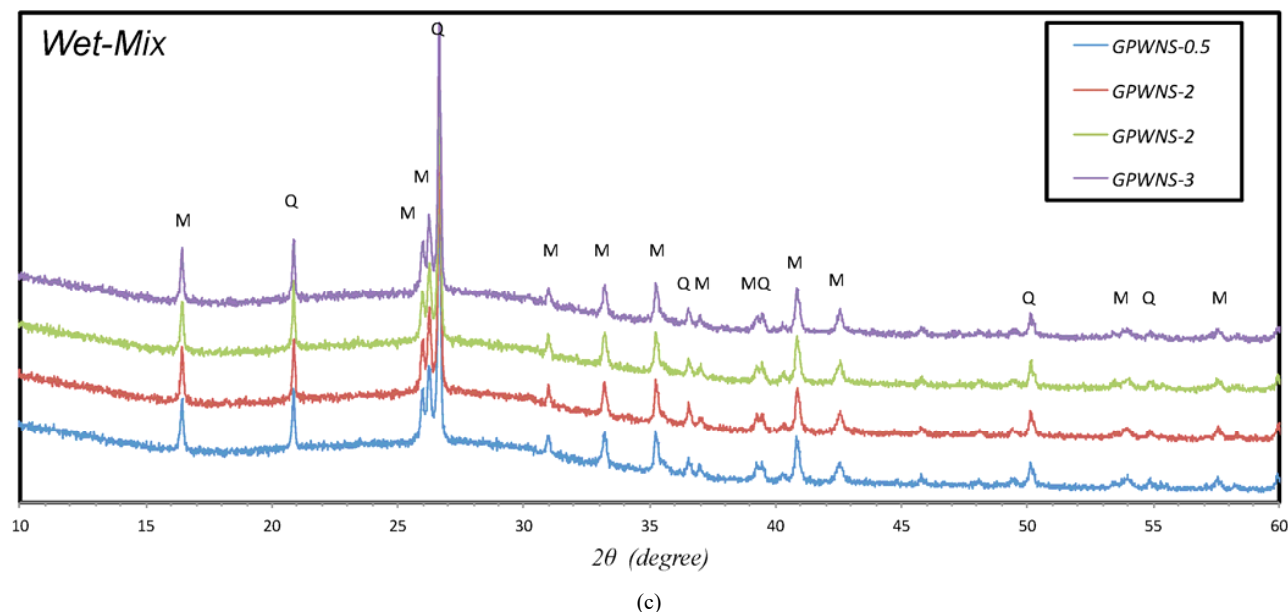


Fig. 2 (a) X-ray diffraction pattern of flyash and nanosilica, (b) X-ray diffraction patterns of Geopolymer nanocomposites prepared by dry-mix method. Letters indicate: M=Mullite, Q=Quartz, (c) X-ray diffraction patterns of Geopolymer nanocomposites prepared by wet-mix method. Letters indicate: M=Mullite, Q=Quartz

The diffraction pattern of flyash and nanosilica are shown in Fig. 2 (a), nanosilica displays a complete amorphous (glass) phase. For geopolymer nanocomposites samples, two main phases are recognized clearly: quartz [SiO_2] (PDF 00-046-1045) and mullite [$\text{Al}_{2.32}\text{Si}_{0.68}\text{O}_{4.84}$] (PDF 04-016-1588) (Figs. 2 (b), (c)). It can be recognized that samples prepared by wet-mixing procedure have higher intensities of the quartz main peak at $2\theta = 26.5^\circ$, which reflects higher amounts of crystalline contents in the wet-mixes samples. The crystalline phases of all geopolymer samples are the crystalline phases of the fly ash (Fig. 2 (a)); therefore, they are unresponsive to geopolymeric reactions, and their role is limited in geopolymer matrices as filler materials. However, the amorphous aluminosilicate hump that formed around $2\theta = 27^\circ$ in geopolymer diffraction patterns is an indicator of geopolymerisation. The major difference between the flyash diffraction pattern and geopolymers patterns is that the amorphous hump was shifted from around 23° for flyash to around 27° for geopolymer samples [8]. The amorphous content in the fly ash is the reactive and dissolvable content in alkaline solution throughout the geopolymer formation [9]. The physical structure and mechanical performance of geopolymer matrix are affected through the amorphous phase. When the amorphous phase is high, the strength of the geopolymer is also high [10].

Physical and mechanical properties of geopolymers are reliant on their relative amounts of silicon-aluminum and silica-alumina ratios. Table III shows the theoretical calculation of Si/Al and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in all samples, and Si/Al ratios as determined experimentally using EDS analysis.

The Si/Al and $\text{SiO}_2/\text{Al}_2\text{O}_3$ increase with increase in the nanosilica contents. The theoretical ratios are equal for dry

and wet mix nanocomposites because the amounts of silica added to the system are the same in both cases. However, the mixing procedure could control the way the nanoparticles disperse in the matrix, which produces samples with different properties depending on mixing approach.

TABLE III
BINDER RATIOS FOR ALL SAMPLES. %WATER, $\text{SiO}_2/\text{Al}_2\text{O}_3$ AND $(\text{Si}/\text{Al})_{\text{TH}}$: AS CALCULATED THEORETICALLY; $(\text{Si}/\text{Al})_{\text{EDS}}$ AS DETECTED EXPERIMENTALLY FOR GEOPOLYMER SAMPLES USING QUANTITATIVE EDS TECHNIQUE

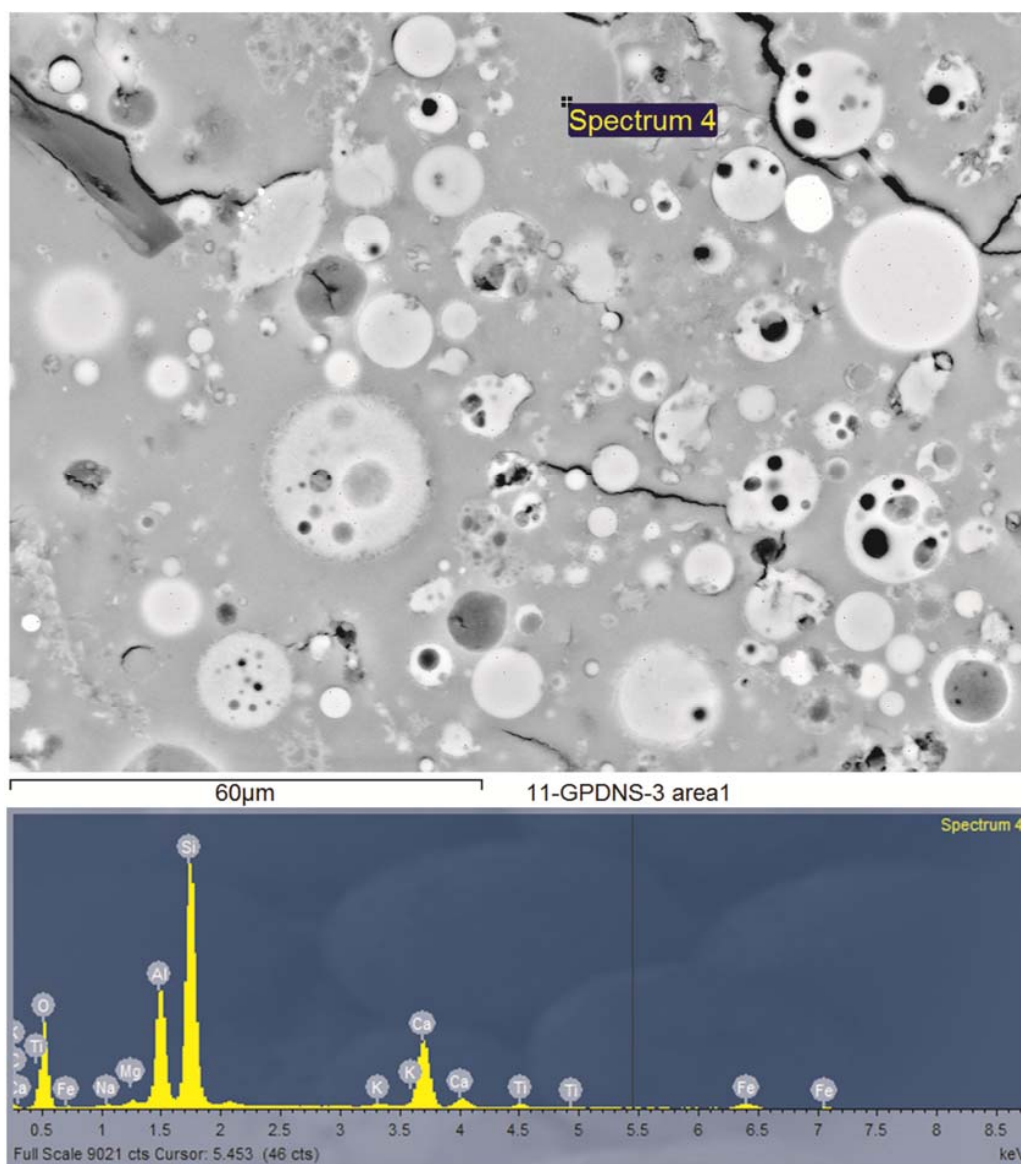
| Sample | $\text{SiO}_2/\text{Al}_2\text{O}_3$ | $(\text{Si}/\text{Al})_{\text{TH}}$ | $(\text{Si}/\text{Al})_{\text{EDS}}$ |
|-----------|--------------------------------------|-------------------------------------|--------------------------------------|
| GP | 5.39 | 2.69 | 2.29 (0.2) |
| GPDNS-0.5 | 5.73 | 2.86 | 2.66 (0.3) |
| GPDNS-1.0 | 6.07 | 3.04 | 3.02 (0.2) |
| GPDNS-2.0 | 6.75 | 3.38 | 3.41 (0.2) |
| GPDNS-3.0 | 7.44 | 3.72 | 3.57 (0.3) |
| GPWNS-0.5 | 5.73 | 2.86 | 2.75 (0.2) |
| GPWNS-1.0 | 6.07 | 3.04 | 3.63 (0.2) |
| GPWNS-2.0 | 6.75 | 3.38 | 3.91 (0.2) |
| GPWNS-3.0 | 7.44 | 3.72 | 4.10 (0.4) |

EDS analysis is used to determine the experimental ratios of Si/Al. Five spots at different location from the geopolymer gel are detected and averaged. The results are presented in Table III as $(\text{Si}/\text{Al})_{\text{EDS}}$. It can be seen that the Si/Al ratios increased with increase in nanosilica in all samples due to the addition of silica to the system. The ratio started from 2.3 at pure geopolymer and rose up to 3.57 in the dry-mix samples and 4.10 in the samples prepared by wet-mixing procedure. All wet-mix samples gave higher ratios of Si/Al when compared to their counterpart's dry-mix samples. This is because that all the silica particles dissolved in the case of wet-mixing approach, increasing the silicon contents of geopolymer pastes, while in the dry-mixing approach a part of the

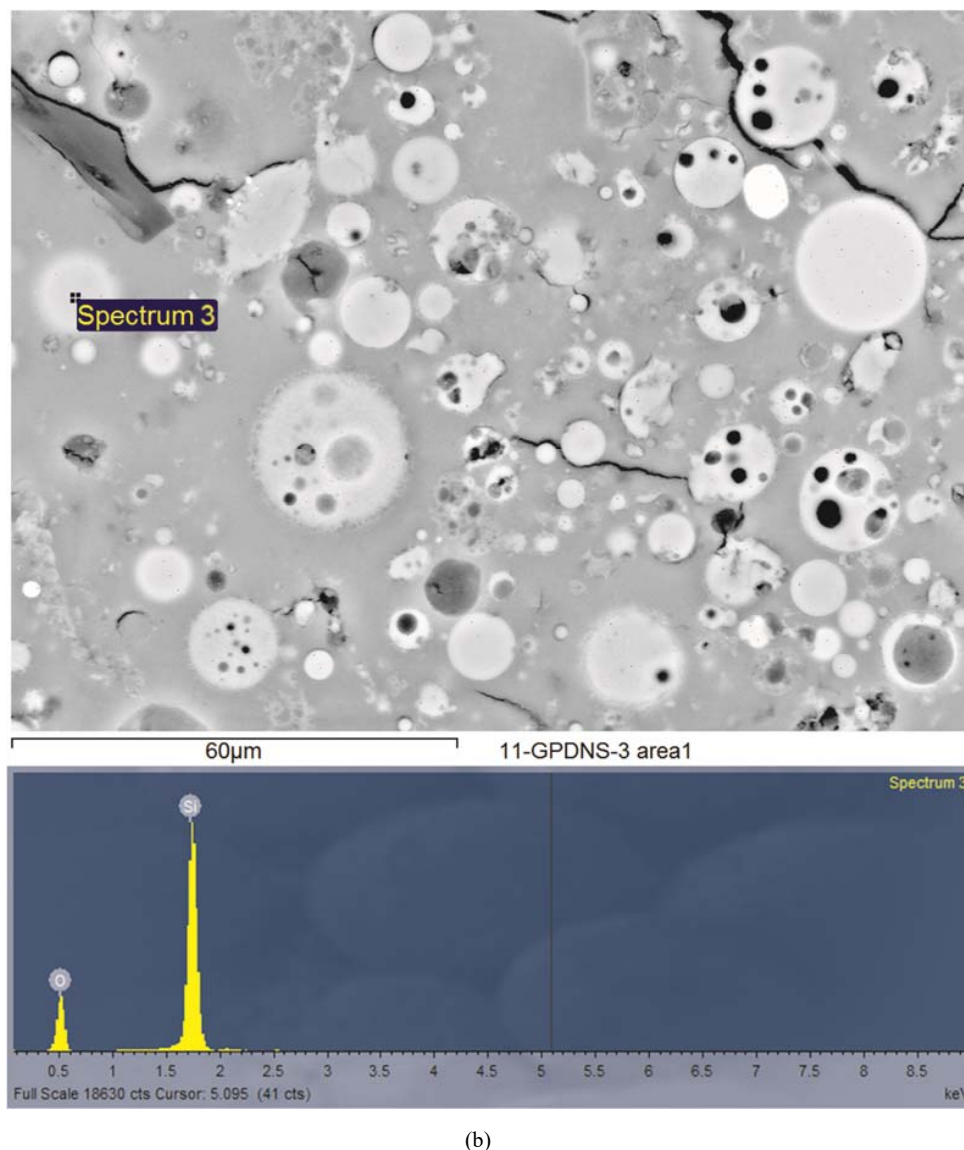
nanosilica content did not dissolve and played a filler role in the geopolymer matrices. Figs. 3 (a), (b) show the SEM images with EDS spectra of two spots chosen in the matrix of geopolymer paste containing 3.0 wt% nanosilica in dry-mixing. The point chosen in Fig. 3 (a) is located in geopolymer gel, and displays the spectra of flyash and geopolymer products (Table II). However, the point detected in Fig. 3 (b) is agglomerated nanosilica particles embedded in the matrix, which can be clearly seen in the spectra of the particles. This makes significant differences between dry-mixing samples and the counterparts wet-mixing samples in term of physical and mechanical properties.

Densities of control paste and the geopolymer nanocomposites are shown in Fig. 4. Generally, all nanocomposites had denser structures comparing to control sample. The incorporation of nanosilica in geopolymer paste could notably improve the matrix in two ways; first by adding more silica to the system, which produce more geopolymer gel, and second by producing a denser matrix through the pore filling effect.

In the wet-mixing samples, the geopolymer densities rose up to 7.6% in GPWNS-2.0 comparing to the control sample. In a similar study, 1-2% addition of nanosilica to a high calcium flyash geopolymer was found to increase the geopolymer products creating denser pastes [4].



(a)



(b)

Fig. 3 (a) SEM image with EDS spectra shows flyash and geopolymer chemical composition, (b) SEM image with EDS spectra shows agglomerated nanosilica particles

Nanosilica particles, however, acted also as pore-filler in the dry-mixing samples, the optimum loading was found as 1.0 wt% of nanosilica, which improved the density by 15.3% when compared to the neat geopolymer. Nevertheless, the additional amounts of the silica particles reduced the density of the nanocomposite samples because of the agglomeration effect. Agglomeration and poor dispersion are common phenomena in nanoparticles. The high ratio of surface area to the volumes of the nanoparticles increases the adhesion forces between the particles resulting in agglomerated nanoparticles.

The physical structure of geopolymer pastes has significant influences on the mechanical behavior of geopolymer samples. The flexural tests are used to describe the mechanical properties of the composites as they provide a simple measure of determining the bending response. This provides useful

information on the mechanical performance of the composites. The effect of nanosilica addition on the flexural strength of geopolymer nano-composites is presented in Fig. 5. Experimental results show that the flexural strength of samples loaded with nanosilica has improved by 27% with 1.0 wt.% nanosilica in the case of dry-mixing, and by 20% with 2.0 wt.% nanosilica in wet-mixing samples.

The compressive strength of geopolymer and geopolymer nanocomposites is shown in Fig. 5 and indicates similar trends to the flexural strength. Compressive strength depends on the physical structure of the samples: denser specimens exhibited higher compressive strength values. The compressive strength of the neat matrix is improved from 37.2 to 47.3 MPa and 44.9 MPa after the addition of 1.0 and 2.0 wt% nanosilica in dry and wet mixing samples, respectively. However, the trends are

reversed after additional amounts of nanosilica in both cases. In a comparable study, it has been reported that the loading of 1.0–2.0 wt% nano-alumina and nanosilica particles into geopolymer matrices enhanced the geopolymeric reaction and

increased the geopolymer gel, which increased the density and consequently improved the compressive strength of the material.

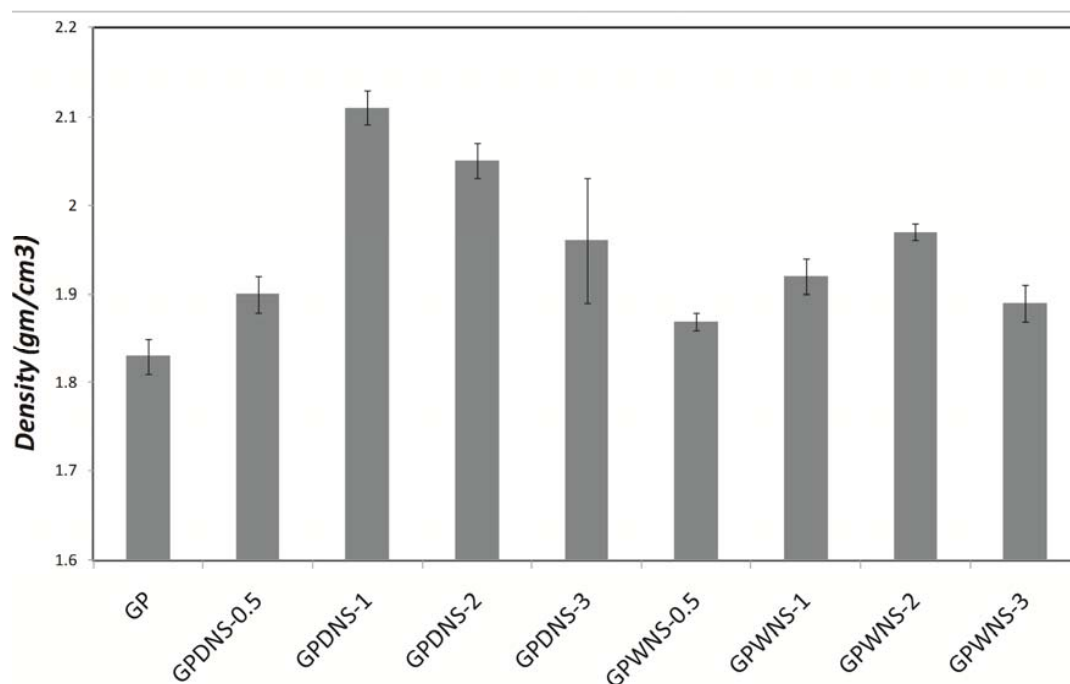


Fig. 4 Density of pure geopolymer and geopolymer nanocomposites

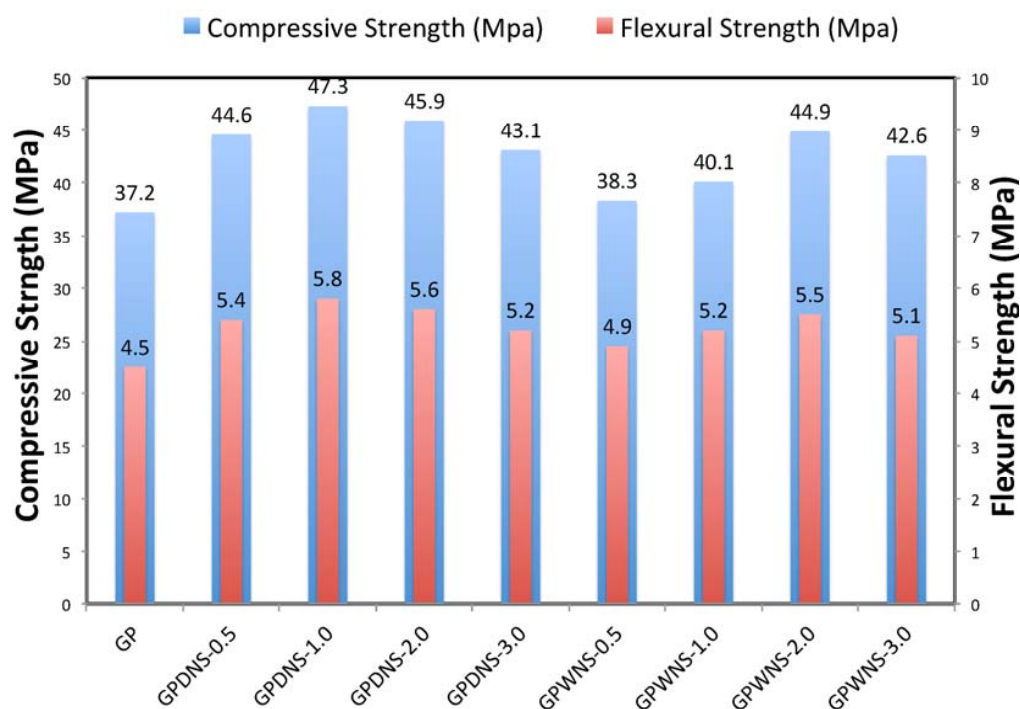


Fig. 5 Flexural and compressive strengths for all samples

IV. CONCLUSION

Pure geopolymer and geopolymer/nanosilica composites have been synthesized and characterized in terms of physical and mechanical properties in two different mix methods. It has been revealed that the dry-mixing procedure enhanced the nanocomposites giving matrices with higher densities and mechanical performance when compared to the wet-mixing method. It has been found that the loading of 1.0 wt% nanosilica to the geopolymer composites in dry-mixing method enhanced their flexural strength by 27% and compressive strength by 28%. However, adding more nanosilica showed no further improvement in these properties due to agglomeration and poor dispersion of higher amount of nanosilica, which resulted in lower density values.

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