Compressive Strength of Coal Fly-ash Based Geopolymer with Integration of Graphene Nanosheets (GNs)

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Abstract. The compressive strength of coal fly ash-based geopolymers has been improved by integrating the graphene nanosheets (GNs) as additive. Proximate analysis and crystal structure were also investigated using atomic absorption spectroscopy (AAS) and X-ray diffractometer. The geopolymer composites were created by mixing the solid fly ash and sand (weight ratio of 1:3) with 10 M NaOH and sodium silicate (Na₂SiO₃) solutions (weight ratio of 1: 2.5), where the liquid to solid weight ratio reached an economical composition of 1: 4. Low-cost GNs with various concentrations of 5 – 20 mg/ml was then added to the mixtures. The prepared mixtures were poured into mortar molds and allowed to stand for few hours at room temperature before heat treatment (curing) in the oven at various temperatures of 40°C, 60°C, and 80°C for 24 hours. Investigation results showed that the average compressive strength of geopolymer increased about 113.8 % or more than double compared to geopolymer without the addition of GNs. The highest compressive strength (29.5 MPa) was shown by a sample with GNs of 20 mg/mL and a curing temperature of 80°C. Meanwhile, geopolymer without GNs showed the lowest compressive strength in all curing temperatures. Proximate analysis showed that fly ash used in this work was the high calcium of type-C fly ash with the CaO content of 11.18%. XRD analysis results indicated that the GNs had integrated well in the geopolymer matrix. The presence of graphene-like structure was also detected, but it was not agglomerated with GNs. Good compressive strength and inexpensive production processes make this geopolymer very prospective for further development.

1. Introduction
Geopolymer is a term for mortar/concrete material that is formed without using conventional cement but using inorganic binder formed from a reaction between a very alkaline solution and a material containing silica and alumina (Si-Al) [1-3]. Sources of materials containing silica and alumina can be from fly ash waste either from coal or from agro-industries [4]. Geopolymer is very interesting as an alternative to conventional cement, because it can be produced through a low cost and environmentally friendly process. Geopolymer is also known to have good chemical stability, high heat resistance, as well as low shrinkage [5]. With these properties, geopolymer is very suitable as a material for paving block, canal block for peatlands fire prevention (Indonesia case), etc.

To further maximize the mechanical properties, many researchers have tried to add or modify the geopolymer with various fillers or additives such as sand, polypropylene, polyvinyl chloride, basalt fibers, etc [6-9]. They found that fillers or additives could effectively improve the mechanical properties of geopolymers. This occurred due to the bridging effects of the additives on the pores and
cracks in the matrix. However, in actual implementation, a low ratio of liquid to solid is more desirable in the geopolymer molding process, where only a small amount (~20-25 wt.%) of NaOH activator and sodium silicate solutions are used. This aims to facilitate the ease of molding process and to reach the economical cost of production due to the high price of solutions. This low liquid to solid ratio normally leads to the low compressive strength of produced geopolymer. To deal with this situation, an appropriate additive is needed to maintain high compressive strength and economical process.

This paper reports the compressive strength of geopolymer mortars synthesized using a low liquid to solid ratio with an additive of graphene nanosheets (GNs). GNs used in this work were obtained from a low cost and environmentally friendly turbulence-assisted shear exfoliation (TASE) process [10]. Research results showed that the average compressive strength of geopolymer increased about 113.8% or more than double compared to the geopolymer without the addition of GNs. The integrated graphene did not undergo an agglomeration in the geopolymer matrix.

2. Experimental

2.1. Materials
Coal fly ash was obtained from a steam power plant, and its composition was analyzed using atomic absorption spectroscopy (AAS). Sodium hydroxide (NaOH) was purchased from Tianjin, China, with a purity of 99%. Sodium silicate (Na$_2$SiO$_3$) was purchased from Sinar Sakti Chemical with chemical compositions of 32.6% SiO$_2$, 14.8% Na$_2$O, and 52.6% H$_2$O (SiO$_2$/Na$_2$O ratio of 2.3). Graphite powder was purchased from Qingdao Yanhai Material Carbon Co. Ltd., China. Sand, with a bulk density of 1509 kg/m$^3$ was used as fine aggregates. Other materials used included a surfactant (sodium lauryl sulfate 18%) and distillate water from Bratako Chemical, Indonesia.

2.2. Geopolymer – GNs composites preparation
Geopolymer – GNs composites were prepared by mixing the solid fly ash and sand (weight ratio of 1:3) with 10 M NaOH and sodium silicate (Na$_2$SiO$_3$) solutions (weight ratio of 1: 2.5) where the liquid to solid weight ratio of 1: 4. GNs obtained from the TASE process [10] with various concentrations of 5 – 20 mg/ml were then added to the mixture. The prepared mixtures were poured into the mortar mold (20 x 10 x 7.5 cm$^3$) and allowed to stand for few hours at room temperature before heat treatment (curing) in the oven at various temperatures of 40°C, 60°C, and 80°C for 24 hours. All samples were then allowed to stand for 28 days before the tests were carried out.

2.3. Geopolymer composites characterizations
The compressive strength of geopolymers was tested using a compressive testing machine following ASTM C579-01. Two samples were tested for each parameter (Duplo). Crystallinity phase analyses were conducted using the XRD-6000 Shimadzu X-ray diffractometer. The XRD analysis was performed using Cu Kα radiation scanned from 20 of 10° to 90° at a scan rate of 2°/mins and scan steps of 0.02°. The XRD pattern was analyzed using X’pert HighScore Plus software equipped with the ICDD database.

3. Results and Discussion

3.1. Proximate Analysis of Fly Ash
Table 1 shows the analysis results of coal fly ash used in this work. It can be seen that the total composition of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ is 77.82%, while the CaO content is 11.18%. According to the American Concrete Institute (ACI) Committee 232 (2002), the fly ash type used in this work is the high calcium of type-C fly ash. Phoo-Ngerkham, et al. [11] and Singh [1] mentioned that the high calcium of type-C fly ash is good raw material for geopolymer based structure application.
Table 1. Coal fly ash compositions

| Composition | Result | Unit | Test Method |
|-------------|--------|------|-------------|
| SiO$_2$     | 51.57  | %    | SNI 15-2049-2004 |
| Al$_2$O$_3$ | 12.87  | %    | SNI 15-2049-2004 |
| Fe$_3$O$_4$ | 13.38  | %    | SNI 15-2049-2004 |
| CaO         | 11.18  | %    | SNI 15-2049-2004 |
| MgO         | 1.75   | %    | SNI 15-2049-2004 |
| SO$_3$      | 1.39   | %    | SNI 15-2049-2004 |
| Na$_2$O     | 0.20   | %    | SNI 15-2049-2004 |
| K$_2$O      | 0.15   | %    | SNI 15-2049-2004 |
| MnO         | 0.56   | %    | ASTM C1301-95 (2001) |
| P$_2$O$_5$  | 0.21   | %    | SNI 2803-2010 |
| Cu          | 7.0722 | ppm  | ASTM C1301-95 (2001) |
| Zn          | 33.6795| ppm  | ASTM C1301-95 (2001) |
| H$_2$O      | 1.78   | %    | SNI 15-2049-2004 |
| Loss on ignition | 4.96 | %    | SNI 15-2049-2004 |
| bulk density| 617.3  | kg/m$^3$ |             |

3.2. Compressive Strength
Table 2 and Figure 1 show the compressive strength of geopolymer mortar at various graphene nanosheets (GNs) addition and curing temperatures. Generally, it can be seen that for all geopolymer mortar, the compressive strength increases relatively linear as the increase of curing temperature and GNs content. The average compressive strength increase is around 113.8% or more than double compared to the geopolymer compressive strength without the addition of GNs. The highest compressive strength (29.545 MPa) is shown by the sample with GNs addition of 20 mg/mL and curing temperature of 80°C. Meanwhile, geopolymer mortars without GNs addition show the lowest compressive strength in all curing temperature. The compressive strength increase by the curing process has been revealed in many references [1, 7, 12], which is due to the geopolymerization reaction acceleration by temperature. While the increase of compressive strength by GNs addition proves that it has spread and worked well in the geopolymers matrix.

Table 2. Compressive strength of geopolymer (28 days age)

| GNs addition (mg/ml) | Room 40 | Curing temperatures (°C) | 60 | 80 |
|----------------------|---------|--------------------------|----|----|
| 0                    | 6.247   | 8.720                    | 11.453 | 13.926 |
| 5                    | 8.590   | 13.015                   | 14.447 | 16.139 |
| 10                   | 12.751  | 14.056                   | 15.748 | 18.351 |
| 15                   | 14.837  | 15.748                   | 18.742 | 22.126 |
| 20                   | 15.228  | 17.961                   | 22.126 | 29.544 |
GNs interactions in the geopolymer matrix are expected to occur via an enveloping mechanism where the GNs layers cover the particles in the matrix. There will be secondary bonds between the hydrogen atoms in the CH$_3$ of GNs edge and the oxygen atoms from the geopolymer matrix, either from Si-O-Al or Si-O-Si [13]. When the geopolymer matrix receives a compressive load, GNs sheets will reduce the pressure accumulation by transferring and distributing the crack propagation to be the crack branching, crack deflection and crack dispersion [12] (Figure 2). These distributions will certainly increase the toughness of the geopolymer when receiving compressive loads.

The increase of geopolymer compressive strength is not only influenced by the GNs addition and curing process. Several factors can also affect the strength of geopolymer mortar; one of them is the type of fly ash used. The high content of calcium (Ca) in fly ash in this work can contribute to aluminosilicate dissolution [2]. But if it is too high, then the adhesive properties of fly ash in geopolymer mortar will decrease. It is because the adhesive properties arise from the high aluminosilicates mineral content, and not from high calcium content [1].

Based on ASTM C 270-07 (2007), the compressive strength of geopolymer-GNs composites mortar resulted in this work has met minimum criteria for the use of canal block application. For canal block application, the minimum compressive strength is 12.4 MPa, while the average compressive strength of the produced geopolymer composites is 16.838 MPa.

**Figure 1.** Compressive strength of Geopolymer mortar (28 days age)

**Figure 2.** Schematic illustration of crack distribution (adapted from [12])
3.3. XRD Analysis

Figure 3 (A) shows the XRD spectra of geopolymer composites synthesized using various GNs contents and curing temperatures. It can be seen that the produced geopolymer composites are polycrystalline, as seen in peaks area from 21° to 85°. These peaks indicate the presence of Quartz (21.36°, 27.7°, 36.6°, 40.46°, 50.28°, 60.22°), Mullite (~39.62°), Albite (~46.26°; ~55.00°), and Dolomite (~68,40°). Quartz (Q) is quite dominant, and it is the main mineral form of silica (SiO$_2$) crystal phase. The presence of Quartz (Q) and Albite (A) crystals in the composites indicates the formation of Si-O-Al bonds in the matrix. The peaks of Mullite (M) and Dolomite (D) are due to CaO and MgO compounds in raw fly ash. The dominant peaks at 2θ of ~26.51° are from GNs, as reported by many researchers [14-16]. Geopolymer synthesized at room curing temperature and without GNs addition shows no peak at ~26.51°, which confirms the absence of GNs in this sample. However, a geopolymer synthesized at a curing temperature of 80°C and without GNs addition has a peak at ~26.5°. The presence of this peak should not occur. When the spectra around 20 of 26.5° is viewed more closely (Figure 3 (B)), the peak form is relatively broad peak and less sharp. It could be from graphene-like structure in coal fly ash and not from the GNs. From this point, it can be revealed that the peak at around ~26.51° is actually the peak from the combination of GNs and graphene-like structures. However, the presence of this graphene-like structure fluctuates as seen in the XRD spectra of geopolymer synthesized without graphene addition and at room curing temperature where there is no peak at around ~26.51°.
Figure 3. (A) XRD spectra of geopolymer samples at various graphene content and curing temperatures; (B) XRD spectra with magnification in 2θ range of 20° − 30°.

The particle size of GNs and graphene-like structures in the composite can be approached using the Scherrer formula as reported elsewhere [17]. Particle size calculation results are shown in Table 3.

Table 3. Graphene and graphene-like particle size in geopolymers composites

| Graphene & graphene-like particles size | 2θ  | FWHM  | Diameter (nm) |
|----------------------------------------|-----|-------|---------------|
| 10 mg/ml, T room                       | 26.52 | 0.1386 | 58.92         |
| 20 mg/ml, T room                       | 26.50 | 0.1413 | 57.78         |
| 10 mg/ml, T=80°C                       | 26.54 | 0.1361 | 60.00         |
| 20 mg/ml, T=80°C                       | 26.51 | 0.1372 | 59.52         |

From Table 3, it can be concluded that the curing temperature does not significantly affect the diameter size of the GNs and graphene-like particles, which also indicates that there is no clumping between them even though the number of GNs added increases.

4. Conclusion
The compressive strength of high calcium type-C coal fly ash-based geopolymers has been improved by the addition of graphene nanosheets (GNs) additive via a low-cost process. XRD analysis results indicated that the GNs had been integrated well in the geopolymer matrix besides Quartz, Mullite, Albite, and Dolomite. The presence of graphene-like structure was also detected, but it was not agglomerated with the GNs. Compressive strength tests showed that the average compressive strength increases 113.8% or more than double compared to the geopolymer without the addition of GNs. The highest compressive strength (29.5 MPa) was shown by sample with GNs addition of 20 mg/mL and curing temperature of 80°C. Meanwhile, geopolymer mortars without GNs addition showed the lowest
compressive strength in all curing temperature. The average compressive strength of the produced geopolymer composites is 16.838 MPa, and it has met the minimum criteria for the use for canal block application (12.4 MPa). The interaction of GNs in the geopolymer matrix occurred via an enveloping mechanism where the GNs layer covered the particles through the secondary bonds between hydrogen atoms of CH₃ in the GNs edge and oxygen atoms from the geopolymer matrix, either from Si-O-Al or Si-O –Si. When geopolymers got compressive loads, GNs had the role in holding and distributing the loads and cracks to all parts below it, in such a way that there was no load accumulation occurred and led to an increase of material toughness.

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