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Composites of palm oil fuel ash (POFA) based geopolymer and graphene oxide: structural and compressive strength

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Abstract. This research studies the influence of graphene oxide (GO) addition and NaOH molarity to the mechanical, morphological and physical-chemical properties of Palm Oil Fuel Ash (POFA) based geopolymer. Geopolymer was made by using alkali activator solution (NaOH + Na₂SiO₃) with NaOH molarity variations of 6 M, 10 M and 14 M, while graphene oxide variations 0%, 0.2% wt, 0.4% wt, and 0.6% wt. The mechanical tests showed that the addition of graphene oxide, even though in small portion, increased the compressive strength of geopolymer significantly, likewise with the increase of NaOH concentrations. The highest compressive strength was 13.2 MPa exhibited by the geopolymer GO composites synthesized using 14 M NaOH and 0.6% wt of GO addition. X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy revealed that the NaOH reduced the GO via in situ reduction became reduced graphene oxide (rGO) sheets which filled the void sand creating a denser geopolymer structure. GO is the promising filler for compressive strength improvement of POFA based geopolymer.

1. Introduction

Palm oil fuel ash (POFA) is one of solid wastes generated from palm oil mill industry. In Indonesia, the number of POFA increases year by year inline with the increase of palm oil plantations. The conversion of POFA become useful and high grade products relatively has not been performed yet. It is only dumped around the palm oil mill area. The small part of POFA is only used as alternative fertilizer. The increasing amount of POFA can be source of contaminations of soil, air, water and surrounding ecosystems, therefore it needs more attention in order to not adversely affect the environment [1]. One high value product which can be created from POFA is geopolymer concrete. Geopolymer is a new class of inorganic binder formed via chemical reactions between the highly alkaline solutions with silica and alumina-containing (Si-Al) base materials. Geopolymers are very attractive as an alternative to the conventional cement (Ordinary Portland Cement, OPC). Production of geopolymer is relatively low cost and with energy-efficient processes, geopolymers also have good chemical stability (acid resistance), high heat resistance and low shrinkage speed [2]. Research in geopolymer is also driven by the need to reduce OPC consumption, as the OPC production process is a major contributor to greenhouse gases in the form of releasing carbon dioxide (CO2) into the atmosphere.

Research on the utilization of POFA as a geopolymer raw material has been carried out [3, 4]. It can be generally concluded that the POFA-based geopolymers have relatively low compressive strength compared to the coal fly ash based geopolymers. This limits its application as geopolymer. The efforts to improve the POFA based geopolymers should be
the main attention. Ranjbar, et al. [5] reported that graphene in the form of graphene nanoplatelet (GNP) could be used as an additive to improve the microstructure and mechanical properties of coal fly ash based geopolymers. The distribution of GNP was relatively homogenous in the geopolymer matrix. They showed that the compressive strength and flexural strength of geopolymers were increasing by 1.44 and 2.16 times, respectively, by adding 1% GNP. The addition of even small amounts of GNP filler would increase the geopolymer toughness. Furthermore, the wettability of the geopolymer decreased with increasing of GNP content. Saafi, et.al. [6] reported that the slight addition of graphene oxide (GO) in coal fly ash based geopolymer (0.35 wt.%) could increase the bending strength by 134%, the Young’s modulus by 37%, and the toughness improvement by 56%. They also reported that GO could be converted to reduced-GO (r-GO) which played an important role in geopolymer strengthening and pore / void closure in geopolymers [7].

The aim of this research is to study the effects of the graphene oxide addition including the variation of NaOH concentrations on the compressive strength of POFA based geopolymer. Morphology, FTIR and XRD analyses were also carried out. The research results show that the addition of graphene oxide, even though in small portion, can increase the geopolymer compressive strength significantly and the NaOH can reduce the GO become rGO sheets via insitu reduction.

2. Experimental
2.1. Materials
Palm Oil Fly Ash (POFA) was from one of palm oil mill in Riau Province, Indonesia. Sodium hydroxide NaOH (Merck Chemical Indonesia), sodium silicate $\text{Na}_2\text{SiO}_3$ (Merck Chemical Indonesia), aquades (H$_2$O), the addition of graphene oxide (Merck Goographene) and aquadest (PT Bratako Chemika) were used as received.

2.2. Geopolymer Manufacture
Geopolymer mortar preparation was begin by preparing an alkali activator solution. Mixing process of mortar was carried out manually by mixing the POFA and sand then was continued by addition of alkali activator. Sodium silicate was first dissolved into NaOH (12 M, 14 M and 16 M). After that the graphene oxide solution was added with variation of 0%, 0.2 wt.%, 0.4 wt.% and 0.6 wt.%. The POFA, sand, NaOH, sodium silicate and graphene oxide then were mixed evenly. The mixed materials were moulded with size 50 x 50 x 50 mm$^3$ continued with solidification. The wet mortar was then dried at 80°C for 24 hours before drying naturally for 7 days.

2.3. Characterizations
The Compressive Strength test was performed on a seven days test specimen. A compressive strength test using a compression test (material testing equipment) was performed for all mix variations. The loading was done until the specimen was destroyed. The maximum load incurred during inspection was recorded. The porosity test of mortar composites was carried out according to ASTM C642. The morphology of graphene oxide geopolymer composite was tested using a scanning electron microscope (SEM). Fourier infrared spectroscopic analysis (FTIR) was performed to identify functional groups and compounds contained in the composites. The crystallinity of sample was characterized using X-ray diffractometer (XRD).
3. Result and Discussion

3.1. Compressive Strength of Geopolymer

Fig. 1 shows the influences of GO and NaOH concentration on the compressive strength of POFA based geopolymer. It can be seen that, for similar in molarity, the compressive strength of geopolymer composite increases as the increase of GO content. With only addition of small portion of GO content, the compressive strengths become nearly double compared geopolymer without GO addition. When compared to the molarity, the compressive strength of geopolymer increases with an escalation of NaOH concentration from 6 M to 14 M. The highest compressive strength is 13.2 MPa reached at molarity of NaOH 14 M with 0.6% graphene oxide addition. The 14 M NaOH solution is more concentrated when compared to the 6 and 10 M NaOH solutions. The higher the molarity of the NaOH solution is used the lower amount of water present in the mixture. This causes components in the geopolymer concrete with higher molarity of NaOH quickly crushed. The NaOH solution is required in the geopolymerization reaction, for dissolving Si and Al in the fly ash particles in the gel phase. Hydroxide ions activate Si and Al oxides to form Si-O-Al monomers in geopolymer [8].

![Fig. 1. Effects of GO addition and NaOH concentration on the compressive strength of geopolymer](image)

Besides that the presence of graphene oxide in the geopolymer mortar which undergoes an in-situ reaction with NaOH, so that the increase of NaOH concentration will produce a stronger base, which it will make the deoxygenated graphene oxide sheets ie the reduction amount of carbonyl and hydroxyl groups on the graphene oxide sheet [6]. This will form a reduced-graphene oxide (rGO) sheet. This phenomenon is in accordance with what Saafi reported in his work [5], where rGO is more likely to approach graphene character with high mechanical strength and flexibility which in turn it can improve mechanical properties and can reduce the porosity on the geopolymer matrix [5]. Reduced porosity can mean that the geopolymer density is increasing. The reduction of porosity can be seen in Table 1.

From table 1, it can be seen that the increase of GO content and NaOH concentration reduce the voids and it will make the geopolymer is more solid. Reduce of porosity will make the geopolymer becomes denser and not easy to crack. The high elasticity modulus of rGO can reduce the stress concentration in the matrix and move the tension uniformly to other parts of the matrix. This mechanism will increase composite compression capacity by involving more areas in receiving pressure and overcome local failure (first crack). The increased compression of this composite can be attributed to the high elastic modulus so that the rGO sheets contained within the geopolymer composite lead to stiffness and high ability of toughness [6].
Table 1. Compressive strength, porosity and density of geopolymer

| Geopolymer Variation | Compressive Strength (MPa) | Voids (%) | Density (gr/cm³) |
|----------------------|----------------------------|-----------|-----------------|
| 6 M NON GO           | 5.1                        | 16.3      | 1.78            |
| 6 M 0.2 % GO         | 9.7                        | 15.3      | 1.88            |
| 6 M 0.4 % GO         | 11.9                       | 12.9      | 1.90            |
| 6 M 0.6 % GO         | 12                         | 10.1      | 1.98            |
| 10 M NON GO          | 5.7                        | 15.9      | 1.78            |
| 10 M 0.2% GO         | 10.7                       | 14.6      | 1.79            |
| 10 M 0.4% GO         | 12.1                       | 12.8      | 1.87            |
| 10 M 0.6% GO         | 12.7                       | 9.3       | 1.88            |
| 14 M NON GO          | 6.7                        | 14.6      | 1.80            |
| 14 M 0.2% GO         | 11.5                       | 11.8      | 1.88            |
| 14 M 0.4% GO         | 12.7                       | 11.4      | 1.89            |
| 14 M 0.6% GO         | 13.2                       | 9.1       | 1.90            |

3.2. FT-IR Analysis of Geopolymer-Graphene Oxide Composites
The analysis with FTIR is useful to look at the functional groups present in geopolymers such as Si-O and Al-O and also to compare them with the C-H, C-O, -OH and C-C functional groups present in the resulting geopolymer-graphene oxide composites. FTIR test results of geopolymer composites are shown in Fig. 2. From Fig. 2(a), it can be observed that there is an absorption peak at the wave number (3000-3700) cm⁻¹ which is the hydroxyl group (-OH) and wave number (1500-1700) cm⁻¹ which is the carbonyl group (C=O) owned commercial graphene oxide [5].

Fig. 2. The Spectrum of FTIR: (a) Commercial Graphene Oxide, (b) Geopolymer (10 M Non-GO) and Composites
There is also a peak at wavelengths of (650-900) cm\(^{-1}\) and (2000-2500) cm\(^{-1}\) that is a C-C and C=C [5]. Fig. 2(b) is the FT-IR spectrum of geopolymers at various molarities and at the addition of 0.6% GO and the geopolymer without GO. Geopolymer without GO as seen in Fig. 2(b) has a less sharp spectrum, so in this case it is suspended that the presence of GO can reduce the spectra. In Fig. 2(b) it is seen that when graphene oxide is integrated with various variations of NaOH molarity, there are reductions marked by the reduction of C=O and -OH groups, at wavelength (3000-3700) cm\(^{-1}\) and (1500-1700) cm\(^{-1}\) having stretching which are quite significant along the increasing concentration of NaOH given. This is due to the mixing of GO and NaOH resulting in deoxygenate in graphene oxide sheets forming rGO sheets, where the content of the hydroxyl and carbonyl groups in the graphene oxide is reduced [8]. The formation of rGO in geopolymer composites results in increase of compressive strength, because rGO is more like graphene with a strength of 1 TPa or 200 times harder than steel [3].

3.3. XRD Analysis of Geopolymer-Graphene Oxide Composites

Fig. 3 shows the XRD spectra of rGO integrated in geopolymer sample detected around 2θ of 23.79\(^{\circ}\). This is consistent with Stobinski, et.al. [6] which reported that the rGO had a diffraction peak at around 23.76\(^{\circ}\). It has also been observed that there is no mark of graphene oxide peak detected around 2θ of 10-12\(^{\circ}\) indicating that all GO has been converted to rGO. Fig. 3 shows that the geopolymer with higher NaOH concentration have the higher peaks intensity. The escalation of intensity proves that the higher the NaOH concentration, the more rGO are formed. The formation of more rGO in sample with 14 M NaOH concentration resulted in the highest compressive strength of geopolymer. This evidence verifies and reaffirms that the reduction of GO is formed due to the mixture of GO and NaOH resulting in deoxygenate in the graphene oxide sheets forming rGO sheets as indicated in previous section. Furthermore from the FWHM (Full Width at Half Maximum) data of the rGO peaks can be calculated the crystal sizes of the formed rGO using the Scherer equation:

\[
D = \frac{\lambda}{B \cos \theta}
\]

Fig. 3. Chart of Reduced Graphene Oxide on Variation Concentration of NaOH

where the size of the crystal is denoted by the symbol (D), the FWHM value as the expansion line at half of the maximum entity is denoted by the symbol (B), \(\lambda\) is the wavelength used in XRD (1,5406 Å) and the diffraction angle (2θ) is denoted by symbol (θ). The values of FWHM and the crystal size can be seen in table 2.
Table 2. Calculation of Crystal Size Based on FWHM by Using Scherer Equation

| Geopolymer Types | 2 Theta | Wave (Å) | FWHM (B) | Diameter of Crystal (nm) |
|------------------|---------|----------|----------|-------------------------|
| 6 M 0,6% GO      | 23.7981 | 1.54060  | 0.1725   | 38.172                  |
| 10 M 0,6% GO     | 23.7981 | 1.54060  | 0.104    | 63.315                  |
| 14 M 0,6% GO     | 23.7981 | 1.54060  | 0.078    | 84.419                  |

Table 2 shows that the greater of NaOH concentration the greater of rGO crystal size will be. Larger of rGO diameters make larger cross sections as well, that causes the geopolymer to be more resistant toward the pressure due to the rGO role as a filler having a larger cross section. The larger cross section of rGO has the better capability of retaining load pressure in all directions of other geopolymer matrix eventually decrease the possibility of cracking [8].

4. Conclusion
The addition of graphene oxide (GO) and the increase of NaOH concentration increased the compressive strength in POFA based geopolymer. Especially for GO addition, the increase of compressive strength was very significant with the increase was nearly double compared geopolymer without GO. The highest compressive strength was 13.2 MPa exhibited by geopolymer – GO composites synthesized using 6 M NaOH and 0.6 % GO. The higher the NaOH concentration caused a more intensive deoxygenate process on the sheet of graphene oxide to form rGO sheet. The more amount of GO addition, the resulting geopolymer composite was also denser as the escalation in NaOH concentration.

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