The Influence of Reduced Graphene Oxide Nanoparticles (rGO NPs) on The Microstructure of Metakaolin Geopolymer

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Abstract. Reduced graphene oxide nanoparticles (rGO NPs) is one of the advanced green nano-materials with valuable properties that offer promising novel applications particularly when it is combine with other materials. The main objective of this study was to investigate the influence of rGO addition on the microstructure character of metakaolin based geopolymer. Graphene oxide nanoparticles (GO NPs) was synthesized from graphite by using modified Hummer’s method and rGO NPs was produced from GO through thermal calcination at 160°C for 4 hours in an autoclave. Geopolymer paste was produced through alkali activation method of metakaolin and cured at temperature 70°C for 2 hours. rGO NPs was dispersed into geopolymer paste with various concentrations, 0, 3, 6 and 9% relative to the mass of metakaolin. The crystal structure and morphology of rGO NPs and geopolymer-rGO NPs composites were investigated by means of x-ray diffraction (XRD), Fourier Transform Infrared (FTIR), scanning electron microscopy (SEM) and The results indicated that rGO NPs as two-dimensional material were successfully produced and characterized. The addition of rGO NPs was found to form strong bond with geopolymer species and hence improve the microstructure character of geopolymer.

1. Introduction

It is well-known that geopolymer have received huge research activities and publications recently. As a relatively new structural material, geopolymer exhibit excellent properties such as low temperature synthesis, high-early strength, fire and heat resistance, excellent binder, and affordable [1-3]. Besides that, this material is also recognized as environmentally friendly material since its production almost free from CO2 emission [4,5]. Geopolymer is inorganic aluminosilicate polymer fabricated from aluminosilicate minerals such as metakaolin, fly ash, and slags under strong alkaline environment [6-8].

Metakaolin is a meta-phase of kaolin formed through dehydroxylation process at temperature between 500°C – 750°C for several hours. Nowadays, metakaolin based geopolymer has reached a new stage in the development of portable electronic devices such as super-capacitor based energy storage. This is possible due to the excellent properties of geopolymer such as high mechanical strength, anti-corrosion, and high porosity [6,9,10]. The presence of pores and oscillation properties in the structure of metakaolin based geopolymer creating excellent ionic transmission space [11,12]. This
condition makes geopolymer as a suitable matrix for other material to form super-capacitor. Initially, graphene oxide (GO) was used as aggregate in geopolymer since GO exhibit high surface area, high strength and flexibility [13,14], but for super-capacitor application, the addition of GO do not improve the electrical conductivity [11]. The use of reduced graphene oxide (rGO) is expected to replace GO in the matrix of geopolymer for super-capacitor application.

In the last few years, reduced graphene oxide (rGO) has attracted a lot of attention from researchers since its functional properties such as high chemical reactivity, mechanical strength, optics and electrical tenability, thermal resistance, and high specific area [15]. Therefore, rGO NPs is a promising material to be applied in various aspects such as energy storage, chemical or strain sensor, medical application as photo thermal therapy. The procedure of rGO NPs synthesis can be conducted through chemical reduction method [16,17] or hydrothermal [18, 19]. In this study, rGO NPs was produced through chemical reduction method and the resulting rGO NPs was used as aggregate to form geopolymer composite and subsequently investigate its influence in the microstructure properties of the composite.

2. Experimental

The rGO NPs powders were produced with a chemical reaction by using a modified Hummer Method of Graphite. It produced from GO through thermal calcination at 1600°C for 4 hours in an autoclave. 1 gram graphite produce approximately 2 grams of GO and after reducing process produces 1 grams of rGO. This is because GO contained a high quantity of water, therefore its mass increases relative to the mass of graphite. However, after the reduction process, the mass was low compared to GO due to the loss of oxygen during the reduction process. For physical appearance, graphite was grey in color whereas the GO was brownish, and graphene had a very dark color [20].

The geopolymer samples with addition of rGO NPs aggregate were prepared from Metakaolin as raw material and activated with high alkaline solution. Geopolymer paste were initially synthesized in 5 different compositions, keeping the mass of metakaolin constant with varying the mass of rGO NPs namely 0%, 1%, 3%, 6%, and 9%. The mixture of geopolymer samples was put in the molds and cured at 70 °C for 2 hours.

The crystal structure and phase of the samples were measured by using X-ray diffraction (XRD) with Cu Kα radiation in the range of 2θ 10°-70°. The XRD patterns were analyzed by using powder diffraction analysis (PDXL2) software. The surface morphology of the samples was investigated by Scanning Electron Microscopy (SEM) and The bond of geopolymer and rGO NPs was studied by using Fourier Transform Infrared Spectroscopy (FTIR) spectrum.

3. Results and Discussions

Figure 1 shows the XRD result of graphite. The diffractogram reveal that graphite used in this study has high purity, the highest peak intensity is centered around 26.7° corresponding to (002) plane of the graphite structure [21]. Figure 2 shows the XRD characterization of GO and rGO produced by using Hummer modification method. It can be seen that GO is characterized by the present of high peak intensity around 10.7° 20 and weak intensity at 42.9° 20 indicating the successfully oxidation process of graphite. The reduction of oxygen from GO network produced rGO and it is characterized by the shift of the highest peak intensity 10.7° of GO into a broad peak around 25° 20. The XRD characteristics of the GO and rGO NPs produced in this study is in accordance with the previous results reported by [19,20]. This results confirm that high quality of GO and rGO NPs have been successfully synthesized from graphite by using modified Hummer’s method.
Figure 1. Diffractogram of graphite.

Figure 2. XRD result of graphene oxide (GO) and reduced graphene oxide (rGO NPs).

Figure 3 showed the XRD patterns of geopolymer-rGO NPs composites with the addition of 0%, 1%, 3%, 6% and 9% of rGO NPs. All samples show that the diffractograms the amorphous nature metakaolin based geopolymer decorated with unreacted SiO$_2$ of metakaolin and graphite during geopolymerisation process indicated that SiO$_2$ is obtained from metakaolin, and graphite is obtained from rGO NPs. The differences in phase compositions were found to influence of mechanical strength, morphology, and electrical properties of samples [22,23].
The addition of rGO NPs as high as 9% relative to the mass of metakaolin starting material did not change the overall amorphous structure of geopolymer. The presence of SiC species in the form of mossanite occurred due to the reaction of SiO$_2$ of metakaolin or sodium silicate with atom C of rGO. Figure 4 showed the FTIR spectrum of geopolymer-rGO NPs composites with the addition of 0%, 1%, 3%, 6% and 9% of rGO NPs measured at the wavenumber between 4000 – 400 cm$^{-1}$. The spectrum clearly reveals the strong band of stretching vibration of Si-O-Si species at the wavenumbers 446 cm$^{-1}$ and 1020 cm$^{-1}$, stretching vibration of Si-O-Al at 876 cm$^{-1}$. Both vibrations are the main feature of geopolymer network formation. The bending vibration of H$_2$O is found at wave number 1639 cm$^{-1}$, and stretching vibration of H$_2$O strong bands are found at 3454 cm$^{-1}$ and 2360 cm$^{-1}$. Geopolymer-rGO NPs exhibited strong vibration centred around 1500 cm$^{-1}$ which is assigned as unreacted C-H vibration [24]. The vibration of C-O which is normally found as a weak vibration at the wavenumber of 1039 cm$^{-1}$ for rGO [16] did not visible in FTIR spectrum figure 4 caused by the overlapping with strong broad band of Si-O vibration around 1020 cm$^{-1}$.

The microstructure of the rGO NPs powder was analyzed using Tescan Vega3 Scanning Electron Microscopy (SEM) with energy acceleration of 15 kV as shown in figure 5. SEM image of rGO reveals the characteristic of graphene morphology as a single layer material. This sort of rGO morphology is similar with the results of [25] confirming the nature of graphene by using SEM and TEM examinations. It is known that the morphological changes of graphene are influenced by the type of solvent in the chemical process of rGO synthesis. The change of rGO morphology affects to the number of layers of graphene in accordance with the previous research [25].

**Figure 3.** XRD result of geopolymer-rGO NPs.
Figure 4. FTIR result of geopolymer-rGO NPs. A= 0% rGO NPs, B= 1% rGO NPs, C= 3% rGO NPs, D= 6% rGO NPs and E= 9% rGO NPs.

Figure 5. SEM image of rGO NPs powder.

The results of SEM examinations of geo-rGO NPs specimens contained 1%, 3%, 6%, and 9% of rGO relative to the mass of metakaolin are shown in Figure 6. The SEM images showed that the addition of 1 and 3% of rGO NPs were dispersed homogenously on the surface of geopolymer creating good quality of composite surface. The homogenous distribution of rGO NPs will play important roles in the application of this material as anti-corrosion and anti-bacterial [26] and self-cleaning composite [27] The addition of 6% and 9% of rGO showed that rGO NPs acting like aggregate to geopolymer matrix and hence improving the mechanical strength of resulting composites. The higher addition of rGO NPs was found influenced not only the morphology of geopolymer surface but also mechanical
properties of geopolymer-rGO NPs as reported by [13,28]. Geopolymer-rGO NPs composites produced in study were prepared and characterized for possible supercapacitor application and their electrochemical properties will be measured accordingly.

4. Conclusions
Geopolymer-rGO NPs composites at various rGO NPs concentrations have been successfully produced and characterized based on their microstructural properties. The dispersion of rGO NPs in the bulk of geopolymer paste did not change the typical XRD patterns and FTIR spectrum of metakaolin based geopolymer. The mass of rGO NPs addition relative to the mass of metakaolin was found to influence the appearance and the quality of geopolymer-rGO NPs composites. The addition of higher concentrations of rGO NPs were found to wrap and anchor themselves to the geopolymer
paste creating good bond between the two and it is expecting to improve the mechanical and electrochemical properties of geopolymers-rGO NPs composites.

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