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Graphene Nanosheets (GNs) Addition on the Palm Oil Fuel Ash (POFA) Based Geopolymer with KOH Activator

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Abstract. Graphene Nanosheets (GNs) have been successfully added to the palm oil fuel ash (POFA) based geopolymer with KOH activator to improve the geopolymer compressive strength. The graphene was synthesized using turbulence assisted shear exfoliation (TASE) method and identified using Raman spectroscopy. The influence of concentrations and weight percent of graphene against the compressive strength, porosity, and morphological properties were investigated. The crystallinity phases of geopolymer and graphene were also identified using XRD. Raman spectroscopy revealed that graphene produced by TASE method had ≥ 3 layers (graphene nanosheets, GNs). Furthermore, Raman maping constructed by the intensity D band showed the graphene had different atomic arrangements at the edge (armchair and zigzag). The compressive strength and the porosity tests showed that increasing the concentration and the weight percent of graphene increased the compressive strength and reduced the porosity. The highest compressive strength and the lowest porosity (10.8 MPa and 5.92%, respectively) were exhibited by the geopolymer synthesized using 0.7 wt% graphene with concentrations of 30 mg/ml. The SEM micrographs indicated that the graphene reduced the porosity of geopolymers with a pores fulfilling mechanism due to of very small of graphene nanosheets size (~60 - ~80 nm).

1. Introduction

Mortar and concrete are the essential elements in the field of construction. The problem that has arisen so far is that the mortar or concrete made from conventional cement has some major weakness, namely, high energy consumption in production and CO_2 gas disposal which is highly detrimental to the environment. Approximately 5% of CO_2 gas is derived from the conventional cement industry (Ordinary Portland Cement, OPC) [1]. Geopolymer is the promising material to substitute the conventional cement (OPC). Geopolymer is a new type of adhesive / binding agent formed by alkaline activation of alumina-silica-containing material, with the formula of $Mn.((SiO_2)_z-AlO_2)_{n.w}H_2O$ where "z" is a number 1, 2, or 3, up to 32; "M" is a monovalent cation such as potassium or sodium; "N" is the degree of polycondensation, and w is the level of hydration which is a function of the type and amount of alkaline solution of polysilicate used [2].

Geopolymer shows the same mechanical properties as OPC but with better performance in extreme environmental conditions. For example, it has been reported that geopolymer showed excellent resistance to acid and sulfate attacks when compared to OPC [2]. In addition, geopolymer have other advantages such as resistance to alkali-silica reactions, reducing air pollution, resistance to fire, and

low cost because it may be synthesized from a variety of low-cost material or industrial by-products, such as fly ash, POFA, rice husk ash, and furnace slag [1].

Palm oil fuel ash (POFA) is a waste material generated in the power plant as a result of the combustion of palm oil industry waste for electricity generation. They are generally disposed to open fields causing traffic hazards besides potential of health hazards and environmental pollution problems [3]. Due to its abundance and high pozzolanic characteristics, POFA has potential to be used as geopolymer raw materials. However, POFA geopolymers have weaknesses which are fragile characterized by low compressive strength and fracture toughness [4]. To overcome this, the POFA-based geopolymer could be strengthened by using graphene material. Graphene is a single atomic monolayer of graphite. Graphene has received unprecedented attention over the last decade owing to its ultrahigh theoretical specific surface area and excellent mechanical properties [2]. Therefore, this study aims to modification of POFA-based geopolymer (KOH activator) with the addition of graphene produced by a turbulence-assisted shear exfoliation (TASE) method to improve the compressive strength properties.

2. Experimental

2.1 Materials
The materials used in this study were palm oil fuel ash (POFA) obtained from PT. Bangun Tenera Riau (passed no.200 mesh sieves and heated with a furnace at 500°C for 1.5 hours) with with the chemical composition was shown in Table 1, potassium hydroxide (KOH) (Merck Chemical Indonesia), sodium silicate (Na_2SiO_3) (Merck Chemical Indonesia), white cast sand (passed no.12 mesh sieves), aquadest, graphite from the pencil rod, surfactant (sodium lauryl sulfate).

Table 1. Chemical composition of POFA

Parameter	SiO_2	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	MnO	P_2O_5	H_2O
Value (%)	58.09	12.21	7.49	4.04	4.94	0.33	7.64	0.32	5.54	0.08

2.2 Equipments
The equipments used in this work were analytical balance, blenders, ice containers, furnace, 500 ml beaker glass, 1000 ml measuring cylinder, 200 mesh sieves, 12 mesh sieves, aluminum foil, mold sizes (5×5×5) cm^3. Equipment or instruments for characterization included compressive strength testers, porosity, scanning electron microscopy (SEM), X-Ray Diffraction (XRD), and Raman Spectroscopy.

2.3 Research Variables
Reseach variables included fixed variables and change of variables. The fixed variables were the composition of geopolymer consisting of 72-wt% solids (POFA+sand), and 28-wt.% liquid (sodium silicate + KOH + graphene) with a concentration of 10 M KOH, weight ratio (sodium silicate/KOH) was 2.5, the ratio of fly ash and sand was 1:3 and the curing time was 24 hours at 60 °C [2]. While the change of variables were variation of the graphene addition (0.1, 0.4, and 0.7%wt) and concentrations of graphene (10, 20, and 30 mg/ml).

2.4 Research Procedure
2.4.1. Formation of Graphene. Graphene was prepared using Turbulence-assisted shear exfoliation (TASE) method [5]. In this method, graphene was synthesized from graphite pencil rod using household blender with addition of 18.9% anionic surfactant (sodium lauryl sulfate). A 10 grams of flake graphite, 1.227 ml surfactant and aquadest were added to blender until a total solution of 500 ml was reached. The blender operated at a speed of 1500 rpm within 1 hour (1 minute on/1 minute off). As long as the blender did not operate, the blender must be cooled by providing a cooling jacket. After the process was complete, a graphene solution with a concentration of 20 mg/ml will be produced [5]. The same procedure had also been applied to produce graphene with concentration of 30 mg/ml with

the addition of surfactant of 1.875 gr. While for graphene concentration of 10 mg/ml was obtained from the dilution of the produced graphene solution.

2.4.2. Formation of Mortar Geoolymers. The alkaline activator solution was prepared by mixing 10M KOH with sodium silicate solution at ratio of 2.5. The alkaline solution was then mixed with graphene (0.1; 0.4; and 0.7%wt) and sonicated for 1 hour. The resulted solution was gradually added to the POFA and sand with POFA: sand ratio of 1:3 and mixed until homogenous and workable mixture. The mixtures were poured into a mold and compacted by applying pressure to the mold. Afterward, the samples were maintained in the 60℃ oven for 24 hours. Specimens were demolded and maintained in ambient conditions until 28 days.

3.   Results and Discussion

*3.1 Graphene Identification via Raman Spectroscopy*

Figure 1 is Raman spectra of the raw graphite sample and the graphite after undergoes a turbulence-assisted Shear Exfoliation (TASE) process. The raw graphite spectrum shows the D and G bands which indicates that the raw graphite used is not a defect-free. The raw graphite used also has low and broad noticeable 2D band at around 2700 cm^{-1}. It could be related to the impurity of C-C disorder/amorphous, edge carbon or chemical modification in the graphite pencil used. It has been commonly known that during the pencil process production, the graphite and clay are combined and burned. This process may lead to the occurrence of chemical modification. The Raman spectrum of graphite after the TASE process shows the G band at wavenumber of 1583.4 cm^{-1}, the defects peak D band at 1353.46 cm^{-1} and the 2D band at 2679.55 cm^{-1}. This 2D band comes from the double resonance which is quite sensitive to vibration and electron properties of Graphene [6]. Qualitatively based on the shape and position, it can be seen that the 2D band of graphite after TASE process is relatively symmetry and located at a lower wavenumber compared to the 2D wavenumber of raw graphite spectra. It indicates a low number of graphene layers. Quantitatively based on the G band position, the number of layers (n) can be counted using formula presented by Wall [7], and it is obtained the layers are ≥ 3 layers or graphene nanosheets (GNs).
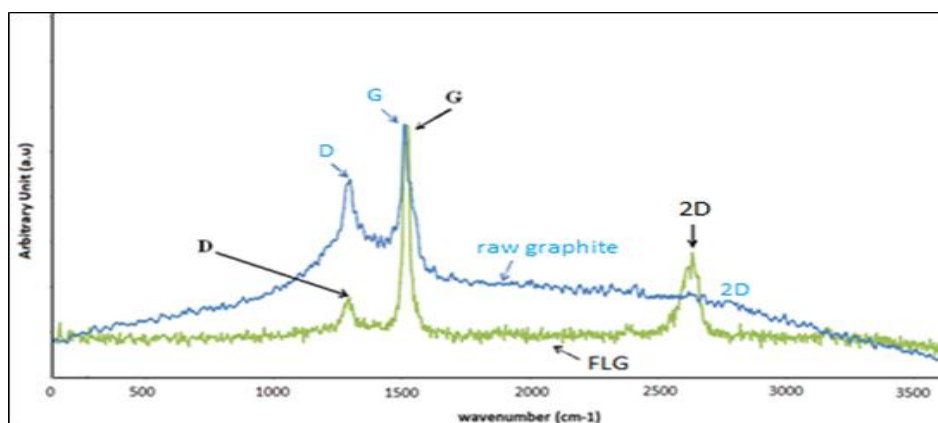
Figure 1. Raman Spectra of raw graphite and raw graphite after TASE Process

Furthermore, the structure of graphene edge can be identified via Raman imaging. Figure 2 shows Raman image of a TASE graphene constructed by the intensity of D band. From the image, it can be seen that there is a difference in D band intensities, indicating the TASE graphene has different atomic arrangements at the edge (armchair and zigzag) with armchair structure more dominant than zigzag. The stronger D band intensity indicates armchair structure, while the weaker D band intensity indicates a zigzag structure. This is consistent with the research reported by Concado et al [8] and Pimenta et al [9] about double resonance theory of the edge graphene. They claimed that the double

resonance process could only fulfill at an armchair edge (stronger D band), while for zigzag edge, the resonance process was forbidden (weaker or vanished D).
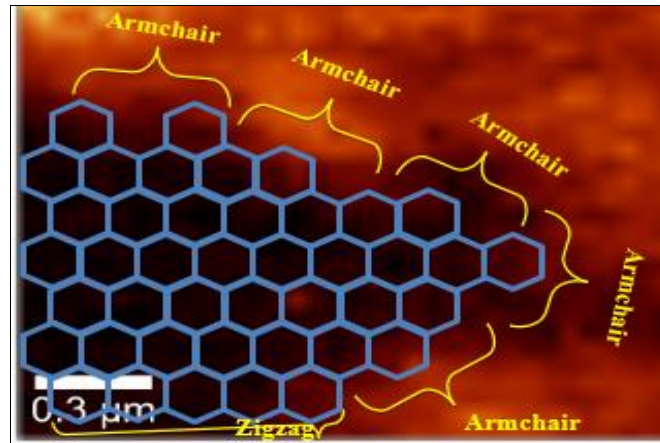
Figure 2. Raman image constructed by the intensity
D band with the expected arrangement in blue

3.2 *Compressive Strength of Geopolymer*

Figure 3 shows the compressive strength of POFA-based geopolymer at different concentrations and weight percent of graphene (ASTM C 579-01 standard). As observed, the compressive strength is improved progressively by increasing the concentration and the weight percent of graphene. The compressive strength increases from 6.2 MPa to 10.8 MPa after the addition 0.7%wt graphene with concentrations of 30 mg/ml. This indicates that the incorporation of graphene will have a significant effect on the increase in compressive strength due to the superior mechanical properties of graphene and graphene layers[10]. In addition, graphene has ultrahigh specific surface area and well distributed in geopolymer composites [11], in such away that it can increase contact and interaction between the graphene and the geopolymer matrix. These results also indicate that the presence KOH activator does not prevent the graphene role to strengthen the geopolymer.

	10 mg/ml	20 mg/ml	30 mg/ml
■ 0 %wt	6.2	6.2	6.2
■ 1 %wt	7	8.6	9.2
■ 0.4 %wt	7.2	9.2	10
■ 0.7 %wt	7.6	9.8	10.8
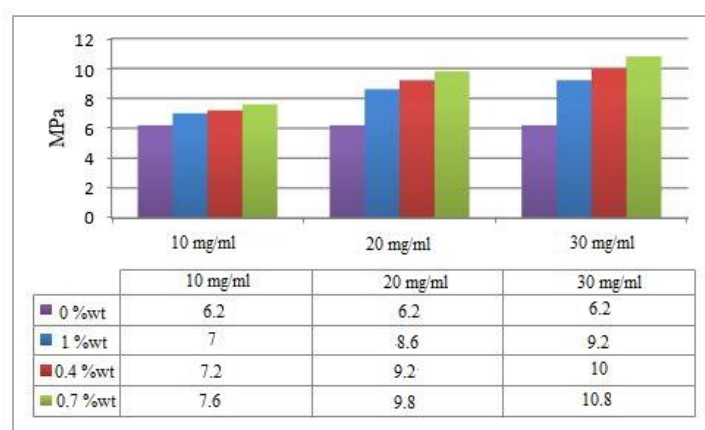
Figure 3. Compressive strength of POFA-based geopolymer
mortar at different concentration and weight percent of graphene

Figure 4 shows the estimated graphene interaction in the geopolymer matrix with the presence of KOH activator. It can be assumed that when the graphene is added to an alkaline activator solution (KOH + Sodium silicate ($Na_2O.2SiO_2$ + H_2O)), there is no reaction between them due to of inert

properties of graphene. However, when a geopolymerization reaction occurs, the graphene will be bonded secondarily to the O atom in the geopolymer matrix (Si-O-Al or Si-O-Si), as shown in Figure 4. The interaction between graphene and geopolymer matrix has an important impact on the mechanical properties of geopolymer composites, especially on the compressive strength. This is because graphene in the geopolymer matrix can initiate and optimize various toughness mechanisms such as stress dispersion, crack deflection, crack bridging, and crack branching in such a way that the strength and toughness of geopolymer mortar improve [10].
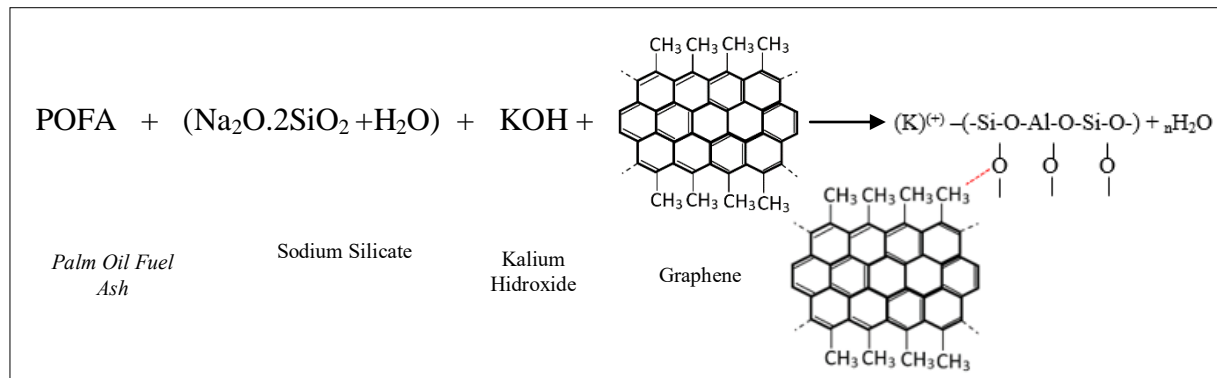
Figure 4. Scheme of estimated graphene interaction in geopolymer matrix

3.3 Porosity of Geopolymer

The influences of concentration and weight percent of graphene on the geopolymer porosity are displayed in Figure 5. As observed, the porosity decreases with increasing of concentration and weight percent of graphene. The lowest porosity (5.92%) is showed by the geopolymer with addition of 0.7%wt graphene at concentration of 30 mg/ml. Likewise the highest porosity (16.09%) is exhibited by geopolymer with the lowest content and concentration of graphene. This attributes to the unique two-dimensional morphology and nano size of graphene which can easily fill the pores in the geopolymer matrix.

|	0.1%wt	0.4%wt	0.7%wt
■ 10 mg/ml	16.09	14,27	12,96
■ 20 mg/ml	11,42	10,03	9,25
■ 30 mg/ml	7,54	6,28	5,92
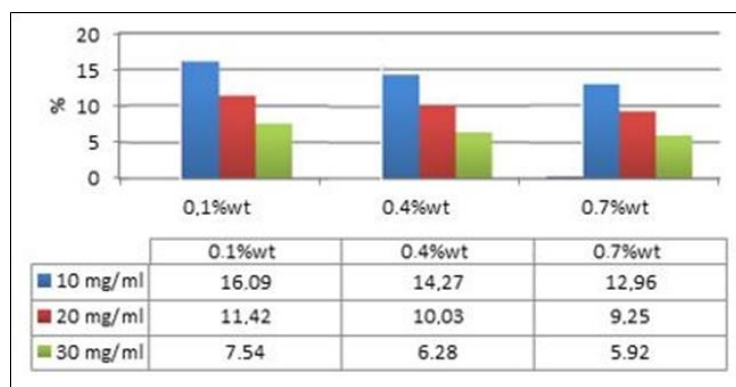
Figure 5. Porosity of POFA-based geopolymer mortar at different concentration and weight percent of graphene

3.4 Surface Morphology of Geopolymer

Figure 6 shows the surface morphologies of POFA-based geopolymer with addition of graphene at different concentration and weight percent. Surface morphologies of geopolymer without the addition of graphene is also shown for comparison (Figure 6(a)). It is seen that the geopolymer without the

addition of graphene has a high pore structure. The geopolymer pore structure decreases with increasing concentration and weight percent of graphene (Figure 6 (b), (c), (d) and (e)). These indicate that the concentration and weight percent of graphene have a significant effect on the decrease in porosity, where graphene can cover the pores of the geopolymer matrix thus as to produce geopolymers with denser structures as indicated in previous Porosity Section.

Furthermore, to determine numerical data from the pore characterization, image analysis is carried out on the scanning electron microscopy (SEM) images using ImageJ application following the protocol illustrated by Buckman et al [12] (Figure 7). The average size of pore, area fraction of pore, and solidarity are shown in Table 2. From the Table, it can be seen that the average size and the area fraction of pore decrease with increasing concentration and weight percent of graphene. On the other hand, solidity increases with increasing concentration and weight percent of graphene. This result is consistent with the previous discussion.
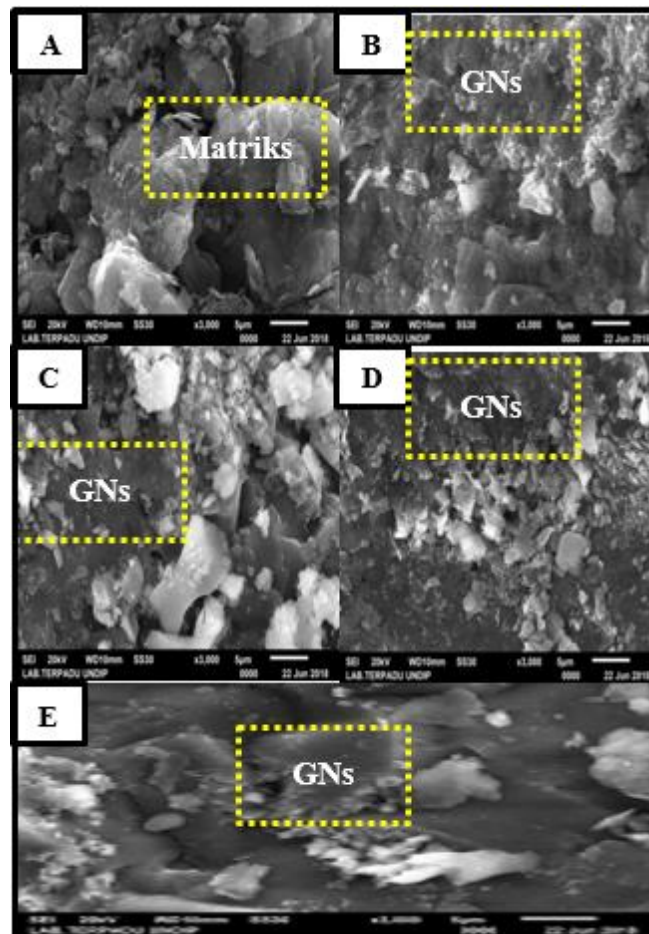
Figure 6. SEM images of (a) 0%wt GNs,
(b) 0.1%wtGNs 10 mg/ml, (c) 0.1%wt GNs
30 mg/ml,(d) 0.7%wt GNs 10 mg/ml,
(e) 0.7% GNs 30 mg/ml
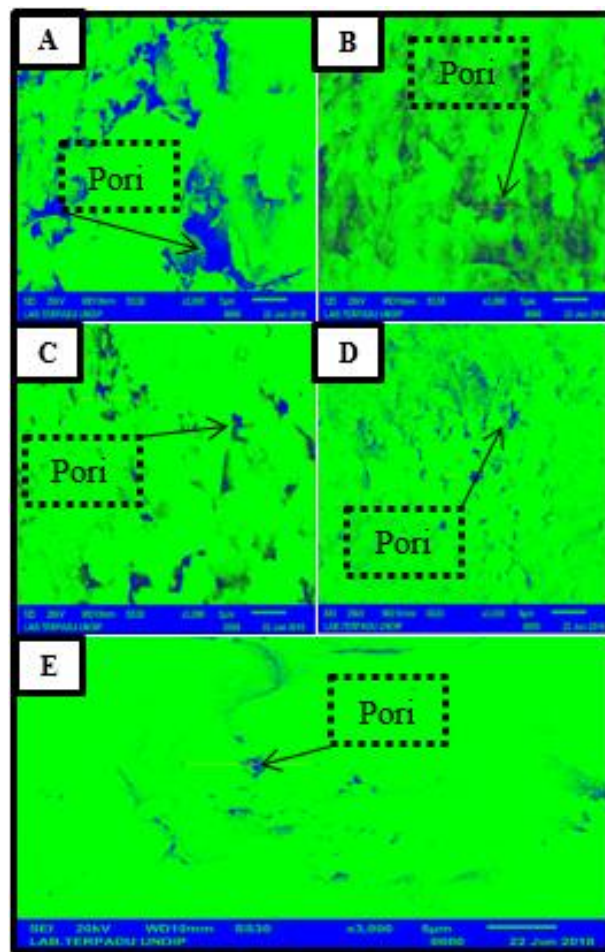
Figure 7. SEM analysis using ImageJ of (a) 0%wt GNs,
(b) 0.1%wt GNs 10 mg/ml, (c) 0.1%wt GNs 30 mg/ml,
(d) 0.7%wt GNs 10 mg/ml, (e) 0.7% GNs 0 mg/ml

Table 2. The Results of Image Analysis Using ImageJ Application

| Sampel	Average Size (μm)	Area Fraction (%)	Solidarity (%)
0% wt GNs (Control Sample)	3012	11	70.2
0,1% wt GNs 10 mg/ml	2950	8	70.5
0,1% wt GNs 30 mg/ml	2759	3	73.4
0,7% wt GNs 10 mg/ml	2624	2	73.8
0,7% wt GNs 30 mg/ml	2294	1	74.7

3.5 XRD Analysis

Figure 8 presents the XRD patterns of the geopolymer samples. The patterns show that the POFA-based geopolymer matrix consisted mainly of crystalline phase of quartz (Q), albite (A), and trace levels of dolomite (D), which are the crystalline phases in the geopolymer matrix. An additional peak appears at a diffraction angel of 25.84° indicating the crystalline plane of graphene [13]. This indicates

that the incorporation of graphene will not induce the formation of other crystalline phases on the geopolymer matrix. It is due to the graphene is inert, in such a way that the addition of graphene into the geopolymer matrix does not affect the geopolymerization reaction of palm oil fuel ash (POFA) and alkaline activator solution.

The presence of graphene in the geopolymer matrix can be seen in Figure 9. It can be seen that the intensity of the graphene peak increases with increasing concentration and weight percent of graphene. Furthermore the crystal size of graphene in the geopolymer matrix can be counted using Scherrer equation. The crystal sizes of graphene in the geopolymer synthesized using 0.7 and 0.1%wt of graphene at concentration of 30 mg/ml are 82.84 and 82.58 nm, respectively. While the crystal sizes of graphene in the geopolymer synthesized using 0.7 and 0.1 %wt of graphene at concentration of 10 mg/ml are 83.03 and 66.27 nm, respectively. It seem the crystal size of graphene in geopolymer is relatively constant (~60 - ~80 nm) and it is not influenced by the concentrations and the amount of graphene used in the geopolymer synthesis. Based on these graphene sizes, it is very possible for the pores fulfilling mechanisms to take place.
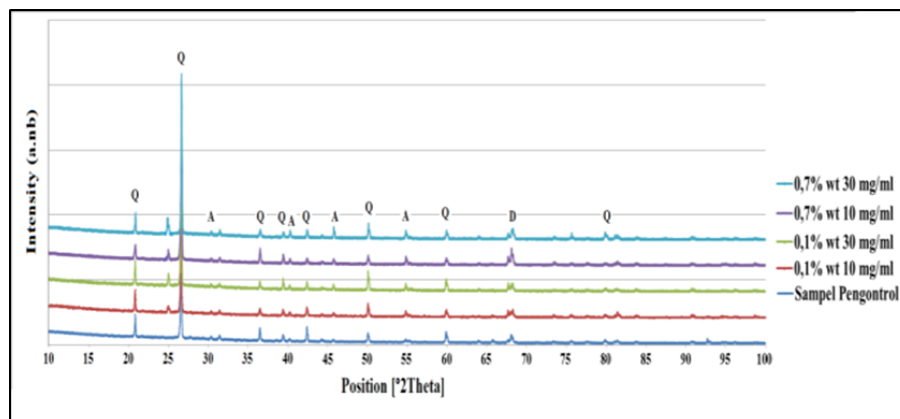
Figure 8. XRD Patterns of geopolymer samples
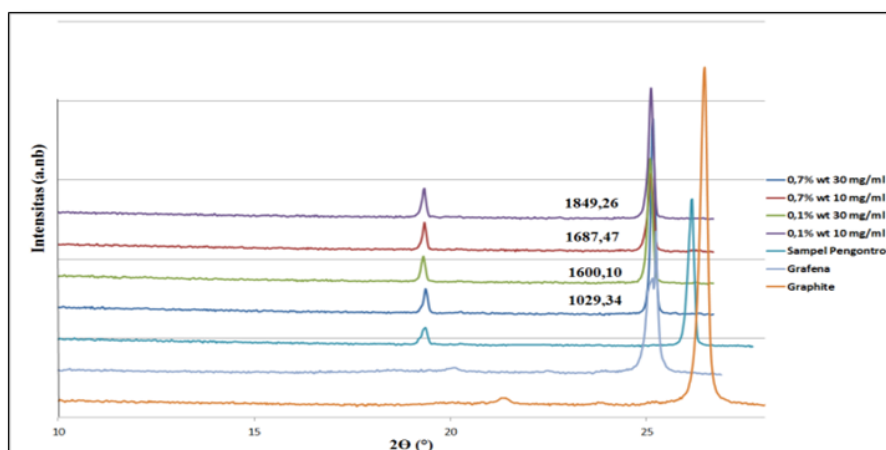
Figure 9. The peak intensity of graphene in the geopolymers

4. Conclussions

Palm Oil Fuel Ash (POFA) based geopolymer with Graphene Nanosheets (GNs) addition has been made by using KOH as activator. Increasing of concentration and the weight percent of graphene increased the compressive strength and reduced the porosity of the POFA based geopolymer mortar.

Graphene in the geopolymer matrix did not affect the geopolymerization reaction of the Palm Oil Fuel Ash (POFA) and alkaline activator solution and the presence KOH activator did not prevent the graphene role to strengthen the geopolymer. The scanning electron microscope (SEM) micrographs indicated that the graphene reduced the porosity of geopolymers with a pores fulfilling mechanism due to of very small graphene crystal size of graphene (~60 - ~80 nm).

Acknowledgement

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