Effect of POFA as a replacement material on fly ash based geopolymer mortar

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Abstract. Ordinary Portland Cement (OPC) is widely used as the material for the construction. The production of OPC has caused an issue on the environment, due to the release of CO₂ in the air. The use of by-product or waste material from the industry as an alternative material in the concrete was considered to be a solution to cover this issue. Geopolymer was the advance method that was able to use by-product or waste material to replace OPC as the binder in the construction. However, this material should be rich in content of Si and Al, it was due to the reaction of waste material with the alkaline solution formed the gel of Si-O-Si and Si-O-Al that contributed to the mechanical properties especially compressive strength. Palm oil fuel ash (POFA) is a waste material from the furnace of oil palm that is also rich in the content of Si and Al so that it was considered a new material in geopolymer binder. The method to general geopolymer binder referred to the conventional method. The results showed that the analysis of XRD described the material of POFA in the crystalline with mullite, magnetite, hematite, and rutile. The analysis of FTIR identified that the material POFA has the stretching in the gel of Si-O-Al. The analysis of SEM showed that the particle of POFA has a rough surface that reduced the workability and longer setting time compared to the mixture of FA based geopolymer. Furthermore, the maximum compressive strength is 23 Mpa with the replacement of 5% POFA.

1. Introduction
Ordinary Portland Cement (OPC) is a famous material that is often used in the construction as the binder. The production of OPC was known to have increased pollution in the environment. There were more million tons of OPC production in the world that played an important role in the increase of CO₂ emission, exploitation the natural resources and consumed the energy. The use of waste material from the industry as the alternative material in the construction was believed to be able to control the emission of CO₂ from the environment [1]. Yet, the waste material can be used only in high Si and Al content. The total replacement of OPC in the construction with the waste material was known as a geopolymer system which it was green technology having lower CO₂ compared to OPC. Geopolymer is a material of inorganic polymeric that is formed by an aluminosilicate and calcium content. The binder of geopolymer was generated by the reaction of Si, Al and Ca content with the alkaline solution that formed the gel of Si-O-Si and Si-O-Al contributing on the mechanical properties, whereas the gel of N-A-S-H or C-A-S-H contributed to the setting time [2,3].

Palm oil fuel ash (POFA) is a waste material from the disposal of fuel for palm oil production. Some southeast Asian countries, especially Indonesia, Thailand, and Malaysia were famous for having the production of palm oil in abundant scale, so that appeared a new issue in the environment. Some investigation indicated that the material of POFA contained SiO₂ of 29.9%, Al₂O₃ of 1.9%, and CaO
of 26.9%, so that was categorized as the pozzolanic material [4,5]. Furthermore, the increase of POFA replacement in the FA geopolymer mortar reduced the compressive strength so that it was able to be a sustainable material in the construction [6,7].

The feasibility of POFA as a binder in the geopolymer referred to the material of fly ash and metakaolin. It was due to these materials were famous as the binder in the geopolymer system. However, the material of POFA contained the low Ca content that caused the prolonged setting time during the reaction [8]. So that, the previous investigation treated POFA base geopolymer by using the high temperature to accelerate the reaction. This study used the material of POFA as the replacement in fly ash class C base geopolymer to improve the Ca content in the material, so that it did not require the treatment to accelerate the reaction.

2. Material and experimental program

This study used the material of POFA that was from the Syaukat Sejahtera Crude Company Oil in Bireun, Indonesia whereas the material of fly ash was from power plantation in Nagan Raya, Acheh, Indonesia. Furthermore, the alkaline solution was generated by a combination of NaOH and Na$_2$SiO$_3$ solution with a certain ratio which was obtained from CV. Rudang Jaya company in Medan, Indonesia. The material was evaluated by XRD to indicate the particle structure of the material, FTIR to indicate the geopolymer binder gel and SEM to indicate the shape and surface of the particle. The mix proportion was designed based on the constituent material of geopolymer, whereas the mixing procedure followed the conventional method which referred to the standard of ASTM C305. The fresh and hardened properties of geopolymer mortar was evaluated by workability, setting time and compressive strength.

3. Results and discussion

3.1. Characterization of material

3.1.1. Chemical composition

The basic investigation to evaluate the characterization of material was started by analysis of chemical composition as seen in Table 1. The oxide content of Si, Al and Ca in the particle of fly ash is 37.16%, 17.61%, and 8.72%, respectively. Furthermore, the particle of POFA has the oxide content of Si, Al, and Ca of 59.3%, 6.32%, and 6.71%, respectively. It is seen that the content of Si in the particle of POFA is significantly higher than the particle of fly ash. Yet, it is in contrast with the content of Al. It provides the Si/Al content of 2.1 in the particle of fly ash, whereas the particle of POFA is 9.38. It means that the higher Si/Al content in the particle of POFA caused worse chemical stability in the air. It was indicated by the presence of efflorescence on the surface which was due to the higher residual free K$^+$ in the particle of POFA. However, it provided a higher mechanical property with the presence of more Si-O-Si bonds and residual silica as reinforcement. Also, the content of Ca in the particle of fly ash is categorized as moderate Ca content contributing on the normal setting time that is similar to the setting time of OPC (5-6 hours), whereas the particle of POFA is categorized as low Ca content causing the prolong setting time.
Table 1: Chemical composition of fly ash and POFA

| Chemical composition | Analysis, % by weight |
|----------------------|-----------------------|
|                      | Fly ash   | POFA      |
| SiO$_2$              | 37.16     | 59.3      |
| Fe$_2$O$_3$          | 18.79     | 4.15      |
| Al$_2$O$_3$          | 17.61     | 6.32      |
| CaO                  | 8.72      | 6.71      |
| MgO                  | 6.43      | 3.49      |
| K$_2$O               | 0.79      | 8.52      |
| SO$_3$               | 1.96      | 2.72      |
| Na$_2$O              | 0.49      | 0.35      |
| P$_2$O$_5$           | 3.67      | 2.32      |
| TiO$_2$              | 0.75      | 0.25      |
| LOI                  | 3.11      | 5.87      |

3.1.2. Crystalline analysis of material

The crystalline identification of FA and POFA particle was investigated by X-ray diffraction test. The result of this study can be seen in Figure 1 that shows the spectrum in the particle of FA and POFA follows the similar peak of dispersion refers to the database of XRD. The trend of the graph indicates that the material of FA consists of quartz (SiO$_2$), mullite (3Al$_2$O$_3$·2SiO$_2$ or 2Al$_2$O$_3$·SiO$_2$) and hematite (Fe$_2$O$_3$) while the material of POFA consists of quartz (SiO$_2$), mullite (3Al$_2$O$_3$·2SiO$_2$ or 3Al$_2$O$_3$·SiO$_2$), magnetite (Fe$_3$O$_4$), hematite (Fe$_2$O$_3$), dan rutile (TiO$_2$). The figure also shows that the dispersion peak is at 20º-30º, which indicates that the material was categorized as the amorphous material.

![Figure 1](image.png)

**Figure 1.** Identification material of FA and POFA by the analysis of XRD

3.1.3. Surface image of material

The particle image of the material was analyzed by scanning electron microscope (SEM). This image in figure 2a shows that the particle of FA has the shape of spherical that is covered by the misty surface. It impacted rheology properties especially the workability of fresh mixture. The misty surface of FA absorbed the alkaline solution in the fresh mixture so that caused the reduction of workability. Also, the spherical shape of FA was indicated to be able to fill the concavity of the binder.
Furthermore, figure 2b shows that the particle shape of POFA is spherical with the surface of agglomerate and rough. The spherical shape of POFA is similar to the particle shape of FA. It indicates that the particle of POFA contributed as the filler in the geopolymer binder. However, the surface of agglomerate and rough also absorbed the alkaline solution from the fresh mixture of geopolymer so that reduced the workability. Generally, there is no difference between the particle of POFA and FA.

Figure 2. The surface image of FA and POFA particle

4. Chemical bonding identification of material
Figure 3 shows the FTIR result of FA and POFA particle that identifies the chemical bonding structure. Peak band at a wavenumber of 3400 cm\(^{-1}\) is presented by the material of FA and POFA that indicates the presence of Ca\((\text{OH})_2\) in its material. However, they have the opposite peak in the wavenumber. The material of FA has the bottom peak number, whereas the material of POFA is at top. It indicates that the material of POFA has more Ca(\text{OH})\(_2\) compared to the material of FA. It was proven by the presence of efflorescence on the surface of geopolymer mortar. Peak band in the wavenumber range of 3440 cm\(^{-1}\)-1380 cm\(^{-1}\) is presented by the material of POFA that indicated the stretching and bending of water band and CaCO\(_3\) (carbonate) in its material. Peak band at the wavenumber range of 880-1140 cm\(^{-1}\) is presented by the material of FA and POFA that indicate the stretching of Si-O-Si and Al-O-Si in the crystalline of quartz and mullite. Furthermore, there was not found the presence of alkali content in the material of POFA. But, it was a presence in the material of FA. It is seen through peak band in the wavenumber of 680 cm\(^{-1}\)-800 cm\(^{-1}\). Finally, Peak band in the wavenumber below 680 cm\(^{-1}\) is presented by the material of FA. It indicates that the bending of Si-O was only presented by the material of FA. It means that the gel of Si-O was found in the material of FA that provided a high compressive strength on geopolymer mortar.
5. Workability
Rheology properties in fresh geopolymer mixture were measured by the workability and setting time. The workability of the fresh mixture was conducted by the flow table apparatus with measuring the diameter flow after a certain number of cycling. The workability was affected by the surface of the material that contacted with the water-cement in the conventional concrete or alkaline solution in the geopolymer concrete. The glassy surface of material did not absorb the water-cement or alkaline solution in a short time, whereas the rough surface of material absorbed them by a direct time that caused the loss of workability on the fresh mixture of geopolymer mortar. It can be seen in Figure 4 which the increasing replacement of POFA in the FA based geopolymer mixture caused the reduction of workability. It is attributed to the surface of POFA as mentioned in the SEM section which in the agglomerate and rough surface.

![Figure 3. the FTIR analysis of FA and POFA material.](image)

![Figure 4. Workability of POFA on FA mortar geopolymer](image)
The particle shape of POFA is spherical with the surface of agglomerate and rough. The spherical shape of POFA is similar to the particle shape of FA. It indicates that the particle of POFA contributed as the filler in the geopolymer binder. However, the surface of agglomerate and rough also absorbed the alkaline solution from the fresh mixture of geopolymer so that impacted the workability. Figure 4 shows that the increase of POFA replacement causes the reduction of workability. It was attributed with the increase of rough surface of POFA in the fresh mortar geopolymer mixture that absorbed more alkaline solution in the fresh mortar geopolymer mixture. Generally, there is no difference between the particle of POFA and FA.

6. Setting Time
Figure 5 shows the initial and final setting time of POFA replacement on the fresh mortar geopolymer. It is noted that the trend of initial and final setting time is consistent to increase. The figure shows that the increase of POFA replacement caused the reduction of FA in the binder. It means that the percentage of Ca content in the binder will be reduced so that caused the increase of setting time. The initial setting time indicated the plastic condition that described 80% reaction of geopolymer. Whereas, the final setting time indicated the static condition that described rest reaction of geopolymer.

7. Compressive strength
Figure 6 shows the compressive strength of FOFA replacement on FA based geopolymer. It is seen that the replacement of 5% POFA provides higher compressive strength compared to the other replacement. However, it was lower than the compressive strength of FA based geopolymer. It was attributed to the content of Si and Al in the material. It was known that the chemical content of Si and Al in the material of POFA was lower than the material of FA. The increase of POFA replacement on FA based geopolymer caused the reduction of Si and Al content so that caused the reduction of gel Si-O-Si and Si-O-Al in the binder. Even, the compressive strength of POFA was lower than the compressive strength of FA. Yet, it was still acceptable to be used as the material in the geopolymer binder. Furthermore, the reduction of compressive strength in the POFA replacement was also caused by retarding of reaction causing the prolong setting time. There is a correlation between the compressive strength and setting time which the presence of POFA on the FA based geopolymer mortar retarded the setting time and also reduced the compressive strength.
Figure 6. Compressive strength of POFA on the mortar geopolymer.

8. Conclusion
The study had been investigated with the following conclusion:
1. The material of POFA was rich in the content of Si and Al but poor in the Ca content compared to the material of FA.
2. The analysis of SEM showed that the particle of POFA was spherical with the surface of agglomerate and rough. While the particle of FA was spherical that is covered by the misty surface.
3. The analysis XRD showed that the material of FA consisted of quartz (SiO$_2$), mullite (3Al$_2$O$_3$·2SiO$_2$ or 2Al$_2$O$_3$·SiO$_2$) and hematite (Fe$_2$O$_3$). While, the material of POFA consisted of quartz (SiO$_2$), mullite (3Al$_2$O$_3$·2SiO$_2$ or 2Al$_2$O$_3$·SiO$_2$), magnetite (Fe$_3$O$_4$), hematite (Fe$_2$O$_3$), and rutile (TiO$_2$).
4. Peak band at wavenumber range of 880-1140 cm$^{-1}$ was presented by the material of FA and POFA that indicated the stretching of Si-O-Si and Al-O-Si in the crystalline of quartz and mullite.

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