Assessing the Impact of Petroleum Sludge Ash on the Compressive Strength of Fly Ash-Palm Oil Clinker Geopolymer Mortar

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Abstract Oil industries are one of the most critical industries with substantial production and closely related to the public interest. Two major oil industries, namely petroleum and palm oil, represent primary sources of consumer groups in Malaysia. However, these sectors inevitably generate waste and require disposal systems. Massive amounts of petroleum sludge generated from the refinery process, possess toxic contaminants requiring careful disposal. Similarly, palm oil production generates a hefty amount of by-products from its extraction process. Encapsulating these wastes in a cementitious medium is considered a more feasible solution than converting them for landfilling. Therefore, this study aims to utilize two wastes from palm oil and petroleum industries as binder materials in a geopolymer framework. To achieve this, palm oil clinker and petroleum sludge as the by-products from those respective industries, were subjected to mechanical grinding and incineration processes to improve their reactivity. Palm oil clinker powder (POCP) was included in the geopolymer mixture to replace 2.00–10.00% of fly ash as the source material. After obtaining the optimum POCP replacement, 0.20–1.00% of petroleum sludge ash (PSA) to be included in the geopolymer mortar to assess its impact on geopolymerization. Compressive strength was evaluated on 7, 28, and 90 days to determine the optimum proportion of fly ash, palm oil clinker, and petroleum sludge ash in geopolymer, particularly the proportion that carries the least negative effect onto the compressive strength performance. Based on the results, the ratio of 91.30% fly ash, 7.60% POCP and 1.10% PSA provided the most significant strength improvement among its peers. The encapsulation task of petroleum sludge

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ash in geopolymer has been well performed by the fly ash—palm oil clinker blend. It provides new opportunities to explore the alternative disposal method for these industrial by-products.

Keywords Palm oil clinker · Petroleum sludge · Geopolymer · Compressive strength

1 Introduction

1.1 Background

In recent years, geopolymer has emerged as a promising construction material due to its environmental and performance benefits [1]. Geopolymer production produces fewer greenhouse gas emissions in comparison to conventional concrete production methods. The elimination of the high-temperature calcination process used in traditional cement production also leads to a reduction in energy consumption and cost in the production of geopolymer.

Geopolymer is a three-dimensional polymeric Si-O-Al amorphous microstructure formed through the geopolymerization of aluminosilicate precursors in an alkaline activation solution. The four processes of geopolymerization are condensation, dissolution, reorganisation, and polymerization [2]. Aluminosilicate materials are dissolved in an alkali solution, resulting in the formation of aluminate and silicate monomers. These monomers are then rearranged and condensed into polymers, resulting in the final geopolymer structure. Aluminosilicate materials are commonly recycled from manufacturing waste, some of these wastes are, but not limited to, fly ash [3], ground granulated blast slag [4], rice husk ash [5] and the combination of these materials [6]. Out of all source materials for geopolymer, fly ash has exhibited exceptional strength and durability, owing to its amorphous nature and pozzolanic reactivity.

Fly ash is a byproduct generated from coal-fired power plants [7], with an annual production of approximately 270 million metric tons. It appears as light, fine, spherical, glassy particles with physical diameters ranging from 1 to 150 μm, and consists primarily of silica, alumina, calcium oxide, and iron oxide [8]. Fly ash has gained popularity as a binder for geopolymer due to its abundance and low cost. Combining fly ash with other pozzolanic materials can help improve some properties of geopolymer [9]. Pozzolanic materials, such as palm oil clinker, are ideal for this purpose.

Palm oil clinker is a powdery by-product generated from incinerating lignocellulosic biomass such as oil palm shells (OPS) and mesocarp fibres as a self-sufficient fuel source [10]. It is considered solid waste, with a colour ranging from blackish to grey depending on the amount of unburned carbon residues, and often has an irregular shape and porous structure. Due to the high cost of disposal, palm oil clinker is

frequently discarded in open areas or landfills, which contributes directly to pollution by impacting groundwater and altering the natural composition of the soil [11]. Utilizing palm oil clinker powder as a binder in geopolymer as an aluminosilicate material source would help to address its disposal issue.

Conversely, petroleum sludge ash is a hazardous waste generated by petroleum refineries and contains heavy metals, toxic organic compounds, and inorganic substances [12]. It is classified as hazardous waste due to its potential harm to the environment and human health. This ash is usually disposed of in landfills or incinerated to reduce environmental risks. However, petroleum sludge ash still poses a major environmental challenge due to high levels of heavy metals and other contaminants. Former research works have shown that heavy metals and toxic compounds present in petroleum sludge ash can be entrapped in geopolymer medium, whilst improving its compressive strength [13].

This study aims to investigate the impact of petroleum sludge ash on the compressive strength of fly ash-based geopolymer mortar containing palm oil clinker powder as a partial binder replacement. The results from this study would provide valuable information on the suitability of geopolymer mortar for use in construction applications and help to mitigate the environmental risks associated with the use of petroleum sludge ash.

2 Experimental Investigation

2.1 Material

This study utilized palm oil clinker (POC) and petroleum sludge (PS) as binder replacement materials in fly ash-based geopolymer after they have undergone treatment processes to reduce toxicity, and relatively increase reactivity. POC collected from a palm oil plantation at Lepar Hilir, Pahang, Malaysia, was treated in a mechanical grinding to become palm oil clinker powder (POCP) passing 75 microns sieve. Meanwhile, PS was collected from oil refinery in Malacca, Malaysia and underwent thermal and mechanical treatment to become petroleum sludge ash (PSA). Physical appearances of POCP and PSA after treatment are illustrated in Fig. 1.

Both of these materials were then tested for their chemical composition using x-ray fluorescence (XRF) analyser, compliant with ASTM C114, along with main binder fly ash. For this test, 10 g of each powdery ash was collected and kept in seal bag prior to the testing using Bruker Machine. XRF analysis was conducted to determine the proportion of major oxides that present in these raw materials, since understanding the oxides composition could help to evaluate the rate of geopolymerisation process later.

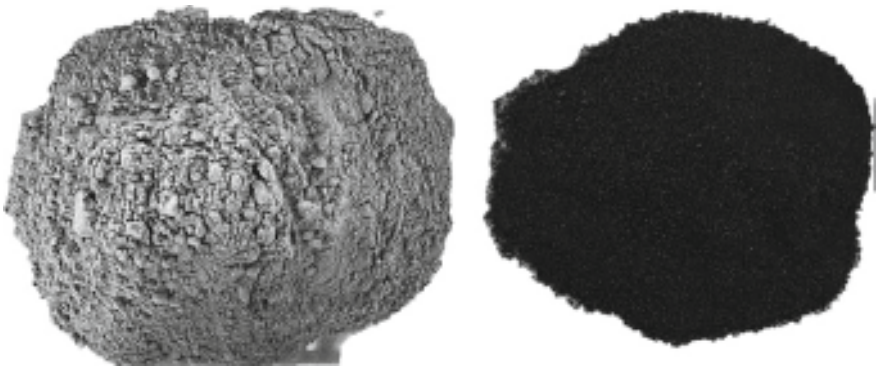

Fig. 1 Physical appearances of palm oil clinker powder (left) and petroleum sludge ash (right) after treatment process used in this study

2.2 Mix Proportion of Geopolymer Mortar with POCP

This study adopted the OPC concrete mixing procedure to ensure a homogeneous geopolymer mixture, and extend the mix proportion used in Kusbiantoro et al. (2012) work [14]. Geopolymer mortar was manually prepared by mixing dry materials, such as fly ash, POCP, PSA, and fine aggregates for 150 s. After the dry mixture has been thoroughly mixed, the alkaline activators, namely sodium silicate and sodium hydroxide, and extra water were then added into the dry mixture and continued with the wet mixing for 90 s. After the mixture has been homogeneously mixed, it was cast in 50 × 50 × 50 mm cube moulds for compressive strength test purpose.

The specimens were left to harden at room temperature for 24 h, before they were demoulded and cured in electronic oven. The temperature in the oven was set at 65 °C, and the specimens were covered in the plastic bag to prevent excessive moisture evaporation and cured in the oven for 24 h. After 24 h of curing, the specimens were stored at the room temperature until the testing day.

Geopolymer mortar was cast with different POCP levels at 2.0, 4.0, 6.0, 8.0 and 10.00% (by weight of fly ash) and compressive strength performance was observed on 7 and 28 days to determine optimum proportion. Pozzolanic reactivity of POCP is the evaluation highlight in the compressive strength development of geopolymer mortar. Table 1 shows the detail of geopolymer mortar mix proportion used in this study.

2.3 Mix Proportion of Geopolymer Mortar with POCP and PSA

After an optimum mix proportion is known, the addition of 0.20, 0.40, 0.60, 0.80 and 1.00% of treated PSA (by weight of POCP) into the geopolymer specimens

Table 1 Detail of fly ash-based geopolymer mortar mix proportion with POCP replacement

POCP (%)	FA (kg/m^3)	POCP (kg/m^3)	NaOH (kg/m^3)	Na_2SiO_3 (kg/m^3)	Fine agg (kg/m^3)	Extra water (kg/m^3)
0.0	700.0	0.0	82.0	206.0	1290.0	25.8
2.0	686.0	14.0	82.0	206.0	1290.0	25.8
4.0	672.0	28.0	82.0	206.0	1290.0	25.8
6.0	658.0	42.0	82.0	206.0	1290.0	25.8
8.0	644.0	56.0	82.0	206.0	1290.0	25.8
10.0	630.0	70.0	82.0	206.0	1290.0	25.8

Table 2 Detail of fly ash-based geopolymer mortar mix proportion with POCP and PSA replacement

POCP (%)	PSA (%)	FA (kg/m^3)	POCP (kg/m^3)	PSA (kg/m^3)	NaOH (kg/m^3)	Na_2SiO_3 (kg/m^3)	Fine agg (kg/m^3)	Extra water (kg/m^3)
0.0	0.0	700.0	0.0	0.0	82.0	206.0	1290.0	25.8
8.0	0.0	644.0	56.0	0.0	82.0	206.0	1290.0	25.8
7.8	0.2	588.0	54.6	1.4	82.0	206.0	1290.0	25.8
7.6	0.4	588.0	53.2	2.8	82.0	206.0	1290.0	25.8
7.4	0.6	588.0	51.8	4.2	82.0	206.0	1290.0	25.8
7.2	0.8	588.0	50.4	5.6	82.0	206.0	1290.0	25.8
7.0	1.0	588.0	49.0	7.0	82.0	206.0	1290.0	25.8

were introduced to understand the effectiveness of geopolymer in encapsulating the PSA from the compressive strength perspective 8.00% of POCP replacement was selected as the control specimen in this the subsequent mix proportion. The mixing method was relatively similar as mentioned previously and these geopolymer mortar specimens were tested for their compressive strength on 7, 28, and 90 days. Table 2 tabulates the detail of geopolymer mortar mix proportion in this second stage.

3 Experimental Results

3.1 Chemical Composition

The chemical composition of fly ash, petroleum sludge ash, and palm oil clinker powder was studied to understand their behaviour in geopolymer framework after undergoing mechanical treatment (palm oil clinker powder) or incineration (petroleum sludge). The chemical oxide composition is crucial in determining the properties of these binders, which are derived from combustible organic and inorganic

Table 3 Chemical composition of binder materials fly ash, palm oil clinker powder and petroleum sludge ash

Oxides	FA	POCP	PSA
Al_2O_3	29.10	3.87	0.37
Na_2O	–	0.08	1.37
MgO	–	2.11	0.12
SiO_2	51.70	68.30	1.17
P_2O_5	1.70	1.84	0.09
SO_3	1.50	0.16	64.30
Cl	–	0.02	0.33
K_2O	1.60	9.26	0.29
CaO	8.84	4.08	0.80
TiO_2	0.70	0.31	0.28
Cr_2O_3	–	0.04	0.06
MnO	–	0.11	0.24
Fe_2O_3	4.76	9.63	29.10
NiO	–	0.02	0.02
CuO	–	0.02	0.04
Others			

matter. Table 3 tabulates the chemical oxides compositions of fly ash, palm oil clinker powder and petroleum sludge ash. Based on the results, major oxides compositions for all binder materials are relatively similar but with different percentage.

FA is made up of five major oxides, with percentages of 51.70, 29.10, 8.84, 4.76, and 1.70% of SiO_2, Al_2O_3, CaO, Fe_2O_3, and P_2O_5, respectively. These oxide compositions are similar, with slightly different proportion percentages, with the findings from previous research work [15]. The fly ash used in this study is classified as Class F fly ash because the sum of $SiO_2 + Al_2O_3 + Fe_2O_3 = 85.86\%$, which is >70.00%. During geopolymerisation, Class F has a high amorpous aluminosilicate content, which reacts reactively with alkaline solution to produce 3D aluminosilicate networks. This explains the widespread use of FA as the principal binder in geopolymer.

Contrarily, the primary constituents of POCP are SiO_2, K_2O, Fe_2O_3, CaO, and Al_2O_3, with the proportion of 68.30, 9.63, 9.26, 4.08, and 3.87%, respectively. Similar to FA, the sum of SiO_2, Al_2O_3, and Fe_2O_3 in POCP used in this study was more than 70.0%, thus meets with the standard pozzolanic reactivity [16]. Different studies recorded different oxide constituents, but all have mentioned the presence of SiO_2 as a primary oxide [10, 17]. Silica is a critical component in the geopolymerization, since it is part of the backbone in the developed aluminosilicate frameworks. It shares the same function with the formation of calcium silicate framework in the pozzolanic reaction.

The composition of petroleum sludge ash (PSA) was found to be distinct from fly ash and palm oil clinker powder. PSA consists mainly of SO_3, Fe_2O_3, Na_2O and SiO_2,

with other chemical oxides making up less than 1.00%. Hazardous heavy metals like As_2O_3, Cr_2O_3, CuO, NiO, and MnO were present in PSA. The chemical composition of PSA can vary based on factors such as sample treatment, time, storage conditions, etc. [18]. According to Pakpahan et al. (2016), the main oxides in PSA were SiO_2, CaO, Al_2O_3, Na_2O, and Fe_2O_3, at the proportion percentages of 47.28, 13.30, 12.20, 7.53, and 6.48, respectively [19]. Another study by Kankia et al. in 2021 showed the main oxides in PSA to be Fe_2O_3, SiO_2, SO_3, Al_2O_3, and CaO, with the proportion percentages of 45.90, 14.90, 11.50, 10.00, and 9.26, respectively [13]. Table 3 shows the chemical composition of binder materials used in this study.

3.2 Compressive Strength of Geopolymer Mortar with POCP

Figure 2 shows the compressive strength of geopolymer mortar with varying amounts of POCP as a replacement binder. Control specimen is referred as a specimen containing 100% fly ash without any replacement material. After 7 days of curing, the control sample had the lowest strength with 28.64 MPa, while the sample with 8.00% POCP recorded the highest strength with 44.54 MPa. The trend shows that the strength increases as the amount of POCP increases, peaking at 8.00%, but decreasing at 10.00%. The second and third highest strengths were recorded at 6.00 and 4.00% respectively. The same trend can be seen after 28 days of curing, with 8.00% still having the highest strength (45.35 MPa). No significant drop in strength was observed for any of the samples.

The strength of geopolymer mortar depends on the geopolymerization and other related chemical reaction process. Alumina and silica compounds from the source materials dissolved in an alkaline medium lead to polycondensation and formation of N-A-S-H and C-A-S-H gels [20]. The presence of POCP as a pozzolanic material, might promotes the production of secondary poly(siloxonate) and poly(sialate), contributing to the strength development of geopolymer mortar.

The compressive strength of geopolymer mortar increases with the percentage of POCP replacement, but the highest compressive strength was achieved with 8.00% of POCP replacement. Higher replacement at 10.00% of POCP resulted in a decrease in compressive strength, which may be due to the reduction in the amount of primary aluminosilicate frameworks developed from fly ash polymerisation. This finding is supported in the previous studies by Ismail et al. (2020), where they achieved a similar pattern and emphasized on a certain percentage of POCP replacement [10]. The results showed that a replacement of 8.00% POCP was the most effective, yielding the highest strength among all the samples. This proportion was therefore chosen as the standard for further testing and examination.

Figure 3 illustrates the compressive strength of geopolymer mortar with 0.20, 0.40, 0.60, 0.80 and 1.00% of PSA. The percentages were determined by subtracting the best proportion (8.00%) from previous data. The samples were tested after 7, 28 and 90 days of curing. The control sample serves as the benchmark of strength

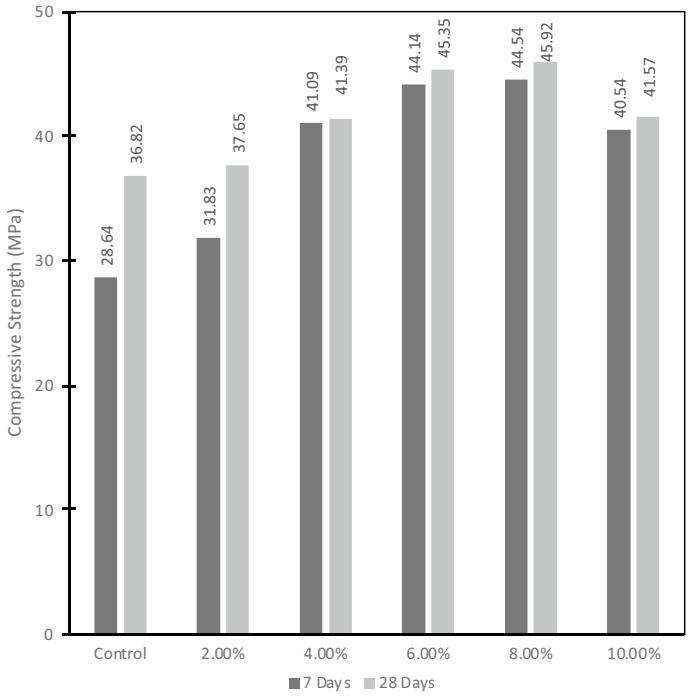

Fig. 2 Compressive strength result of fly ash-based geopolymer with various POCP replacement

designed for the mix proportion, while 8.00% indicates as the reference for strength development when using pozzolanic materials and other binders.

According to the results, control has the highest compressive strength among all samples on 7 days of curing. On 28 days, 7.20% achieved similar compressive strength with control, yet higher than the other POCP-PSA based samples. The 90 days curing showed how 7.60, 7.20, and 7.00% had surpassed the compressive strength of control with 49.60 MPa, 48.10 MPa and 56.06 MPa, respectively. However, despite the lower strength performance, control and 8.00% samples seemed had experienced a stable maturity after 24 h of oven curing, where no significant strength development was recorded from 7 to 90 days of curing. The highest compressive strength development was consistently recorded by 7.00% replacement throughout all curing days. This mixture achieved the increments of 7.58 and 37.16% on 28 and 90 days of curing, respectively.

Interestingly, the possible higher strength performance in control and 8.00% samples appeared to be caused by the higher packing density among the fine particle [21]. The lack of PSA in both control and the 8.00% specimen helped to ensure the distribution of finer fly ash and POCP particles to reach the optimum packing density. The interruption by PSA during the geopolymerization process had caused the strength disruption in every POCP-PSA based specimens. Nevertheless, after 28

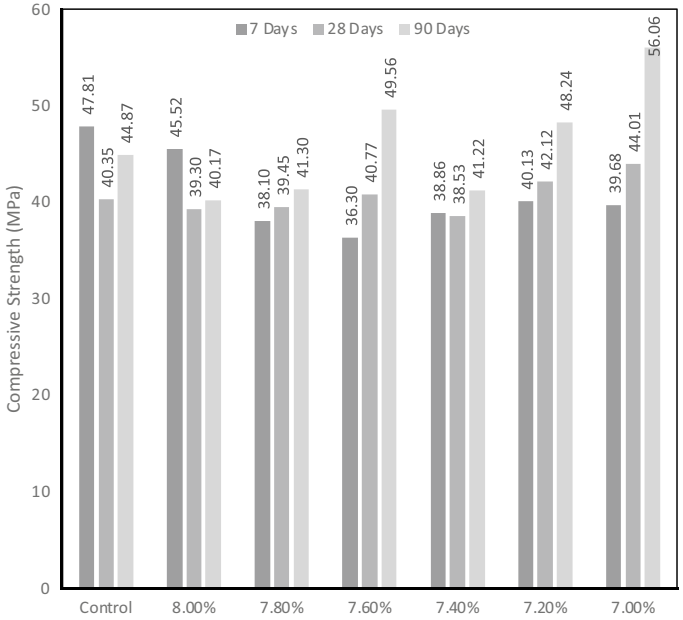

Fig. 3 Compressive strength result of fly ash-based geopolymer with optimum replacement of POCP and various PSA replacement

days of curing the compound in PSA seemed to accelerate the geopolymerization, either by liberating more alumina and silica from the unreacted fly ash to produce late poly(sialate) or poly(siloxonate), or by strengthening the weak links in the aluminosilicate frameworks. Further study is required to justify this hypothesis, by focusing on the reaction product and the chemical bonding in these specimens.

4 Conclusion

Based on the results, geopolymer mixture has presented a positive outcome in encapsulating the impurities from palm oil clinker and petroleum sludge ash in its framework without significant disruption to the compressive strength performance. The inclusion of 91.30% fly ash, 7.60% POCP and 1.10% PSA as the source material combination has displayed the highest compressive strength development after 90 days of maturity. This is obtained from the mix proportion of 7.60% which is equivalent to 588.0 kg/m^3 of fly ash, 53.2 kg/m^3 of POCP and 2.8 kg/m^3 of PSA. This late strength development seemed to be affected by the formation of secondary aluminosilicate frameworks, e.g., poly(sialate) or poly(siloxonate) that supported the microstructure of geopolymer. Nevertheless, additional experiments that would look into the presence of certain mineral structure would be beneficial to promote this

encapsulation process further, as an alternative way to dispose hazardous waste or industrial by-products.

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