Compressive strength and microstructural analysis of fly ash/palm oil fuel ash based geopolymer mortar

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Abstract
This paper presents the effects and adaptability of palm oil fuel ash (POFA) as a replacement material in fly ash (FA) based geopolymer mortar from the aspect of microstructural and compressive strength. The geopolymers developed were synthesized with a combination of sodium hydroxide and sodium silicate as activator and POFA and FA as high silica–alumina resources. The development of compressive strength of POFA/FA based geopolymers was investigated using X-ray florescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and field emission scanning electron microscopy (FESEM). It was observed that the particle shapes and surface area of POFA and FA as well as chemical composition affects the density and compressive strength of the mortars. The increment in the percentages of POFA increased the silica/alumina (SiO 2/Al 2O 3) ratio and that resulted in reduction of the early compressive strength of the geopolymer and delayed the geopolymerization process.

1. Introduction

The contribution of carbon dioxide (CO 2) to global warming by the cement industry is well established. CO 2 emission is about 0.7–1.1 tonnes per ton of cement produced and about 50% of this can be attributed to limestone calcination, 40% for fuel combustion in the kiln, and the remaining 10% to manufacturing processes and product transportation [1]. After aluminum and steel, Portland cement is among the most intense energy constructional material used [2]. CO 2 reduction by minimizing the use of Portland cement has recently realized; the use of cementitious materials such as fly ash (FA), silica fume (SF), ground granulated blast furnace slag (GGBS) and metakaolin as partial replacements for cement were efforts taken seriously by the cement industry to decrease cement consumption. Agro-industrial by-products such as rice husk ash (RHA) and palm oil fuel ash (POFA) are available in abundance in the South-East Asia; countries like Indonesia, Thailand, Vietnam, Philippines and Malaysia produce these waste by-products and many researchers focus on utilizing the above products as cement replacement material. Waste from the palm oil industry is not limited to POFA, but includes empty fruit bunches (EFB), oil palm shells (OPS) and oil palm clinker [3–5]. OPS has been used as lightweight coarse aggregate in the development of structural grade concrete [6,7]. POFA is produced by the palm oil industry due to the burning of EFB, fibre and OPS as fuel to generate electricity and the waste, collected as ash, becomes POFA. About 3 million tons of POFA was produced in Malaysia in 2007 and 100,000 tons of POFA is produced annually in Thailand, and this production rate is likely to increase due to increased plantation of palm oil trees [3,8,9]. POFA disposal problems cause environmental pollution and recent research on the use of silica rich POFA as cementitious material paves the way for the development of sustainable material. Global annual ash production is about 500 million tons, consisting mainly, about 75–80%, of FA; environmental issues are due to disposal problems associated with FA which has led researchers to utilize it in the production of Portland cement. Further, many researchers have focused their attention on the use of FA as a source material for the development of cementless concrete, widely known as geopolymer concrete [10–12].

Fly ash is the most common source material for geopolymer because it is available in abundance throughout the world. It also contains amorphous alumina silica. Malaysia uses coal for power
geopolymer and that process consumes about 8 million tonnes of coal annually. However, in 2010, the Government of Malaysia decided to increase the percentage of coal powered electricity by about 40% from 28%, raising FA production [13]. The use of FA in the development of geopolymer concrete could lead to sustainable concrete. The introduction of geopolymer in 1978 by Joseph Davidovits generated interest in the development of sustainable material through geopolymeric reaction of alkali activated solution such as appropriate combinations of sodium hydroxide and sodium silicate with rich sources of silica and alumina. A new inorganic environmentally friendly geopolymer binder, which is free of Portland cement, has enhanced properties such as high early strength, durability against chemical attack, high surface hardness, and higher fire resistance [10,14,15].

Geopolymer synthesis requires an aluminosilicate source, alkali metal hydroxide and/or alkali silicate material plus water to increase workability and to mediate the reaction. The accepted sequence of geopolymerization shows it can partitioned into approximately two periods: I dissolution–hydrolysis, II hydrolysis–polycondensation. However, these two steps probably occur simultaneously once the aluminosilicate material is mixed with the activator solution. The first step in the reaction is the release of aluminate and silicate monomers by alkali attack on the solid aluminosilicate sources; this step is required for the conversion of solid particles to geopolymer gel. Hydrolysis reaction occurs on the shell of the solid particles, exposing the smaller particles which are trapped inside the larger ones. This is followed by the formation of dissolved species that cross-link to form oligomers, which in turn produce sodium silicoaluminate [16]. The second stage is reaction of the remaining particles and gel generation coincide with setting and hardening which is attributed to polycondensation and the formation of a three dimensional aluminosilicate network [17]. In this stage, the silicon/aluminium (Si/Al) ratio of the main reaction product is increased [16]; the hardened alkali-activated aluminosilicate gels contain Si–O–Si and Si–O–Al bonds in a highly cross-linked amorphous network [17]. Geopolymer structures can be defined in three types: poly (sialate) (–Si–O–Al–O–), poly (sialate–siloxo) (Si–O–Al–O–Si–O) and poly (sialate–disiloxo) (Si–O–Al–O–Si–O–Si–O) based on the values of 2.4 and 6 of silica/alumina (SiO2/Al2O3) molar ratios, respectively [18]. Geopolymer setting (hardening) is believed to be the result of hydrolysed aluminate and silicate specie polycondensation. The composition of a typical geopolymer is generally expressed as nM2O·Al2O3·xSiO2·yH2O, where M is an alkali metal [19].

The availability of silica rich POFA and silica–alumina rich FA paves way for the use of these materials as geopolymer binders. Some research work has been done on the use of POFA and FA in conventional concrete to replace Portland cement [20–22]. There is very few literature available on the utilization of low alumina pozzolanic materials such as RHA and POFA in geopolymer concrete or as a replacement in FA geopolymer concrete [23,24]. Recently, another by-product of oil palm industry, OPS, has been used as lightweight coarse aggregate in the development of FA based geopolymer concrete [25–27].

Research on the development of sustainable geopolymer binders using local waste such as POFA, FA, RHA, and GGBS, is on the rise. However, there is no literature available on the compressive strength of POFA/FA using micro-structural analyses. In this investigation, different contents of POFA were introduced into the FA based geopolymer mortar. The variable, POFA content, varied from 0% to 100% and its effect on the FA based geopolymer mortar was studied using X-ray diffraction (XRD), Fourier transform infrared (FTIR) and field emission scanning electron microscopy (FESEM). In addition, the bulk density of the mortar using Archimedes method was also investigated and reported.

2. Specimen preparation and testing methods

2.1. Materials characterization

Raw POFA was obtained from the local palm oil industry and oven dried for 24 h; the POFA was then sieved in 300 µm sieve and the material which passed through the sieve was ground using Los Angeles abrasion machine for 30,000 cycles.

Low calcium FA (class F) used in this research was supplied by Lafarge Malayan Cement Bhd, Malaysia. The particle size distribution test was performed by Mastersizers Malvern Instruments and the result is shown in Fig. 1. The physical properties of both FA and POFA are given in Table 1. The oxide composition of the materials as determined by XRF using PANalytical Axios mAX instrument is provided in Table 2. The Si to Al molar ratios for FA and POFA were recorded as 4.07 and 34.03, respectively. FA and POFA morphology was studied by means of FESEM (CARL ZEISS-AURIGA 60) and the images of both source materials used in the preparation of geopolymer mortar are shown in Fig. 2. Mining sand with a maximum particle size of 1.19 mm was used as fine aggregate.

Sodium hydroxide (NaOH) and sodium silicate (Na2SiO3) solution are widely recommended alkali activators. NaOH in a pellet form with a specific gravity and purity of 2.13 g/cm³ and 99%, respectively was used. The Na2SiO3 in liquid form with a density of about 1.5 g/ml at 20 °C, a modulus ratio of 2.5 (SiO2/Na2O, SiO2 = 30% and Na2O = 12%) and specific gravity of 1.5 was used along with NaOH as alkali activator.

2.2. Specimen preparation and tests

The molarity of the NaOH and the ratio of Na2SiO3 to NaOH were 16 and 2.5, respectively. The alkali activator solution was prepared by dissolving NaOH pellets in water and then adding the Na2SiO3 solution. The activator to binder ratio was kept at 0.5 for all the mixes. The mixture proportions of eight mixes are given in Table 3. The variable studied in this investigation is the replacement of POFA by FA in increments ranging from 0% to 100%. Dry FA, POFA and mining sand were mixed in a cake mixer for about 2 min at a low rates of speed to blend the source materials and the sand uniformly. The alkali activator solution was then gradually added into the mix for about 7 min [11]. Additional water was added to the mix simultaneously with the alkali activator to increase the workability as well as homogeneity of the mortar. The mortar specimens were cast in 50 mm cube steel moulds in three layers of equal height and compacted. The samples were vibrated to remove entrained air and bubbles. Immediately after vibration, all samples were covered and kept in the oven for hot curing for 24 h at a temperature of 65 °C; the specimens were then taken out of the oven and kept in ambient condition with an average
temperature and humidity of 28 °C and 70%, respectively until testing day.

Based on other reports, the optimum geopolymer oven curing temperature is between 60 and 65 °C in order to gain high early strength of fly ash geopolymers with acceptable physical and mechanical properties [28–31]. The selection of 65 °C is justified as the 50 mm cube with high surface to volume ratio is more susceptible to curing heat and to moisture loss compared to that of larger specimens. This could result in the reduction in strength for curing at high temperature [28]. It has been reported previously that the temperature at which geopolymer samples are cured greatly affects its final compressive strength [31,32].

A compressive strength test was done using ELE Auto Compressive Testing Machine at the rate of 0.9 kN/s in accordance with ASTM: C109. The compressive strength of the specimens was tested after 3, 7, 14, 21, 28 and 56 days. The bulk density of the mortar specimens was measured using the Archimedes method at 28 days. Similarly, microstructure analysis using XRD, FESEM and FTIR (Perkin–Elmer System 2000 series spectrophotometer (U.S.A.)) were conducted on the 28-day specimen.

3. Result and discussion

3.1. Pozzolanic particles

The XRF results as presented in Table 2 show that the major pozzolanic components of SiO₂ + Al₂O₃ + ferric oxide (Fe₂O₃) for POFA and FA are 74.24% and 87.14%, respectively, hence satisfying the requirements of ASTM: C618−12a. Fig. 2 shows the micrograph of the pristine POFA and FA; it can be seen that the FA consists of a series of spherical vitreous particles of different sizes. While usually hollow, some of these spheres might be almost intact or appear within other small size spheres in their interior [16,33]. The FESEM morphology of the POFA powder suggests that the sample consists of both agglomerated and angular particles. As shown in Table 1, the specific gravity of POFA is about 87% that of FA. The Brunauer–Emmett–Teller (BET) surface area of the POFA and FA are 12.92 and 2.96 m²/g, respectively. The higher BET of POFA would lead to the requirement for additional water to achieve the same degree of workability as that of FA based geopolymer mortar.

3.2. XRD analysis

Fig. 3 shows the XRD patterns of different compositions of FA and POFA based geopolymer mortars which were oven cured at
65°C for 24 h and kept in ambient condition until tested on day 28. The patterns show that FA based geopolymer mortar consists of main crystalline phases of quartz, mullite and goethite which originated from FA as well as trace levels of albite which has been confirmed and discussed by FTIR later on. However, the geopolymerization of POFA with alkali activators produced quartz, albite and sodalite. The amorphous to partial crystalline phases are attributed to the reaction of the POFA, FA and alkali activators. The increase in the percentages of POFA in the FA based geopolymer mortar and the resulting geopolymerization show the presence of N–A–S–H phase, albite (NaAlSi₃O₈). This might be the result of Al spice deficiency in POFA which causes the replacement of mullite phase as seen in the FA based geopolymer mortar into albite phase. Comparison of the XRD patterns of the thermal and the ambient cured specimens of POFA and FA based geopolymer mortars at the 28 day mark are shown in Figs. 4 and 5, respectively. It is seen from these figures that the thermal and ambient cured specimen peaks show similar peak trend. Further, the chemical composition of the specimens cured at 65°C and ambient condition in different curing environments had no effect on the geopolymerization.

3.3. Density

Fig. 6 shows the 28-day density of the specimens measured using Archimedes’ method. The specimen density with POFA replacement of 0%, 25%, 50%, 75% and 100% were measured and reported. Specimen density varies between 1671 and 1772 kg/m³, and specimen ET8 with 100% POFA produced the lowest density. The reduction in density of about 13.4% of ET8 compared to ET1 which had no POFA content might be attributed to specific gravity, particle shape & size and water demand. In the case of POFA, particles cannot easily roll over one another due its agglomerated and crushed shape, increasing inter-particle friction. Thus, this illuminates the need for more evaporable water in mixes with high POFA content in order to obtain a workable mix. However, this additional water leads to more pores, which reduces density. As seen in Table 3, the additional water required by mix ET8 to achieve a workable mix was higher than other mixes. Similar findings on the requirement for more water to achieve workable mixes with POFA as replacement material for OPC have been reported [34,35]. In contrast, the spherical shaped FA particles reduce the friction between the binder and fine aggregate resulting in an increase in workability of fresh mortar [36]. The spherical shape also minimizes the particle’s surface to volume ratio, resulting in low fluid demand. The most common reason for poor workability is that the addition of a finer powder increases demand for water as the surface area has increased [37]. A higher packing density was obtained with spherical particles compared to crushed particles in a wet state, resulting in lower water retention in the spherical case and a subsequently lower water demand for specific workability’s [38]. The specific gravity of POFA is about 94% that of FA and hence the use of a higher dosage of POFA decreases specimen density. In addition, the relatively smaller size of spherical FA particles fills the voids and makes for denser packing. In the cases of specimens containing POFA and FA, increase in POFA content shows an approximately linear decrease in the specimen density.

3.4. Field emission scanning electron microscopic analysis

FESEM micrographs of specimens ET1, ET5, ET7 and ET8 cured at a temperature of 65°C for 24 h and kept in ambient condition for 28 days are shown in Fig. 7a–h. Two different magnifications of FESEM micrographs are shown for each specimen. Fig. 7a shows the micrograph of a specimen with 100% fly ash mortar (ET1). The micrograph indicates that there is a strong bond between the unreacted or partially reacted fly ash and polymerized binder with no cracks detected along the interface. Some small fly ash particles which have reacted with the alkali activator solution are observed to co-exist with part of the remaining unreacted spheres and even with some other particles partially covered with reaction products; the Si content in the binder particles are substantially higher than that of the geopolymer gel [16] and these unreacted/partially reacted particles will react slower. The micrographs of mortar specimens ET5 and ET7, which consist of 25% and 75% POFA, respectively, show bonding similarities. Mortar specimens ET1 and ET5 which consist predominantly of FA show the presence of
a congested bulk of nanofibers produced on the surface of unreacted fly ash particles as seen in Fig. 7a, b and d. Previous study showed that hydrolysis reactions occur on the surface of the solid particles [17]. Fly ash is known to contain a significant proportion of particles with hollow spheres. When these hollow spherical particles are partially dissolved they create porosity in the matrix containing highly dispersed small sized pores. These unreacted particles were found in hollow cavities as seen in Fig. 7a–d [33]. Increasing percentages of POFA change the microstructure of POFA/FA based geopolymer mortar. The FESEM results of sample ET7 shows unreacted fly ash particles appeared in the porous form (Fig. 7f). The microstructure of mortar ET8 which contains only POFA (Fig. 7g and h) illustrate the porous structure of POFA particles as well as increased dispersion of unreacted or partially reacted particles. The unreacted POFA particles have ability to trap air because of its inherent crumbled shape as can be clearly observed in Fig. 3b. The density results also confirm the effect of porous POFA as it produced lower density compared to the compact image of FA based specimen ET1.

3.5. Fourier transform infrared spectra analysis

Fig. 8 shows the Fourier transform infrared spectra with the major bands at approximately 2300, 2110, 1450, 990, 845, 670 cm⁻¹ and 445 for geopolymer specimen with 100% POFA (ET8) and 1450, 990, 670 and 445 cm⁻¹ for the fly ash based one (ET1). The distinct intensity band at 445 cm⁻¹ is associated with the Si–O–Si bending vibration and another intense band at 990 cm⁻¹ is associated with the Si–O–Si and Si–O–Al asymmetric stretching vibration for all of the materials [39,40]. It is notable that with increases in the POFA/FA ratio, the band at the bond around 990 cm⁻¹ decreased. The intensity variation of this band is indicative of the variation of a mean chain length of aluminosilicate polymers. A weak band at about 845 cm⁻¹ was observed for POFA/FA based geopolymer mortar; its growth has been observed as the POFA content is increased (ET5, ET7 & ET8) and for the mortar without POFA, the FTIR graph shows no evidence of this weak band. This band is assigned to the bending vibration of the Si–OH [41]. According to previous literature, the presence of Si–OH will decrease the degree of matrix condensation and is responsible for low mechanical properties. The band at about 760–770 cm⁻¹ is characterized as the crystalline phase of quartz in all the samples. Consequently, other spectra bands at about 1450 cm⁻¹ appear in all the geopolymer specimens. This band is assigned to carbonate asymmetric stretching, which suggests the presence of sodium carbonate due to the atmospheric carbonation of alkaline activation media. In NaOH rich geopolymer, common atmospheric carbonation is revealed for O–C–O stretching vibration [40]. The small band at around 670 cm⁻¹ represents the functional group of AlO₂ [42]. The bands at 560 cm⁻¹ indicate the presence of Al in octahedral coordination [13,43]. The band 2100 cm⁻¹ is attributed to physically absorbed CO and H bonded CO. The band at approximately 2300 cm⁻¹ is assigned to C≡N [44]. The intensity bands 2100 and 2300 cm⁻¹ are increased by increments in the POFA/FA ratio and these bands are observable in zeolite structures.

3.6. Compressive strength

Fig. 9 shows the compressive strength of the hardened geopolymer specimens. As can be seen the FA based geopolymer mortar gains about 70% and 98% of its 28-day compressive strength at the 3 and 7 days, respectively. After 7 days, there is no tangible strength gain in the ET1 mix. The high initial strength might be attributed to low SiO₂/Al₂O₃ in this geopolymeric system. The existence of relatively lower Si component in ET1 to ET5 mixes with SiO₂/Al₂O₃ = 4.07–5.38, make it possible that more Al(OH)₄⁻ species were available for condensation in these materials at early stages. Further, the Al component tends to dissolve easier than the silicon components, and this enables a higher rate of condensation between silicate and aluminate species than the condensation between just silicate species [45], resulting in high initial compressive strength. However, initial SiO₂/Al₂O₃ ratio will not be constant throughout the geopolymerization process. The SiO₂/Al₂O₃ increases during different stages of geopolymerization [16]. Changes in the Si/Al ratio in the original particles, the reactive ones, and the reacted product during the reaction process affects the trend of compressive strength development [46]. Fig. 9 shows that geopolymerization was almost complete after 7 days and the strength gain beyond this period was found insignificant. The strength development of the POFA based mortars can be seen from the ET6–ET8 curves. In contrast to the FA based mortars,
the POFA based mortar achieved only about 40% and 62% of the 112-day strength after 3 and 28 days, respectively. After 3 days, the strength gain was found to ascend linearly and it continued until day 112. The slow strength development in the POFA based geopolymer mortar can be analysed from the SiO$_2$/Al$_2$O$_3$ aspect. Mixes ET6-8 correspond to the family of geopolymers characterized by high Si/Al ratio. The increment in the SiO$_2$/Al$_2$O$_3$ ratio results in the reaction of Al content in the earlier stages. Therefore, the gradual increment of the Si content in further stages provides more silicate for condensation and reaction between the silicate species and this causes the dominance of oligomeric silicates. The domination of Si content reduces the rate of condensation resulting in gradual hardening of the geopolymers. As a result the increase in the POFA/FA ratio of the geopolymer mortars delays the ultimate compressive strength.

Compression tests showed increasing amounts of SiO$_2$/Al$_2$O$_3$ ratio enhance elastic behaviour deformation rather than the brittle crushing noted for the specimens of FA based specimens. This effect was more explicit in the case of ET8 which has the highest SiO$_2$/Al$_2$O$_3$ ratio of 34.03. Similar phenomenon was reported by

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**Fig. 7.** High and low magnification FESEM images of the (a and b) ET1, (c and d) ET5, (e and f) ET7 and (g and h) ET8.
The increase in the POFA/FA percentage ratios result in increases in the SiO$_2$/Al$_2$O$_3$ ratios. High SiO$_2$/Al$_2$O$_3$ cause the reaction of aluminate species in the early stages and there is a scarcity of Al species for further reactions at later stages. Hence it can be concluded that geopolimerization is dominated by the reaction and condensation of silicate species leading to gradual strength gains at later stages. In addition, continuous development of the compressive strength of POFA based geopolymer mortar between 28 and 112 days is about 38%, which contrasts with the FA based mortars which gained 97% of their ultimate compressive strength by day 7. The increase of POFA content which resulted in high SiO$_2$/Al$_2$O$_3$ up to about 34 and the elastic behaviour of compression failure was observed to be elastic in the POFA based cube specimens compared to brittle failure of FA based geopolymer specimens.

However, due to high silica content of POFA, it is worth investigating the properties of POFA based geopolymer as a high temperature resistant material. Hence, an independent study has been conducted to address POFA based geopolymer properties at elevated temperatures.

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