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Utilization of fly ash blends from pulverized coal and fluidized bed combustions in geopolymeric materials

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ABSTRACT

This paper presents the utilization of fly ash obtained from fluidized bed combustion (FBC) as a source material for geopolymer. FBC-fly ash has low reactivity, and high content of CaO and $CaSO_4$, which limits its use. To solve this problem, it was blended with reactive fly ash obtained from pulverized coal combustion (PCC). This blend powder was then used as a source material for geopolymer. Sodium hydroxide, sodium silicate and temperature curing were also used for synthesis of the geopolymer. XRD, SEM, degree of reaction, FTIR were performed on geopolymer pastes. In addition, compressive strengths of geopolymer mortars were determined. Results showed that FBC-fly ash could be used in conjunction with PCC-fly ash as source material for geopolymer. PCC-fly ash helped to increase the workability and strength of the geopolymer. Relatively high strength of 30.0 MPa was obtained with 40% content of FBC-fly ash in the blend material.

1. Introduction

Fluidized bed combustion (FBC) is a promising clean coal technology for achieving air emission requirements. This FBC technology is growing particularly in the small enterprises and is competing with the traditional pulverized coal combustion (PCC) due to the reduction of SO_2 and NO_x gasses released in flue gas [1]. Combustion temperature of FBC unit takes place at 800–900 °C. In addition, a variety of fuels including low-grade ones can be efficiently burnt using the FBC process. Limestone is particularly added to the bed as an absorbent for sulfur by direct injection, resulting in economic SO_2 removal without the need of expensive flue gas desulphurization (FGD) equipment. Thermal decomposition of $CaSO_4$ in FBC does not occur due to low combustion temperature.

In general, FBC-fly ash significantly differs from PCC-fly ash in terms of particle shape, chemical composition and amorphous phase [2,3]. FBC-fly ash particles are approximately 1–300 μm with irregular shape, while PCC-fly ash particles are normally slightly finer at approximately 1–200 μm and the amorphous phase is usually higher than that of FBC-fly ash. PCC-fly ash is widely used as pozzolanic material for partial replacement of Portland cement [4–6] due to its spherical shape and high reactivity. Comparing with PCC-fly ash, FBC-fly ash has high contents of lime (CaO), gypsum ($CaSO_4$), and high crystalline phase thus its usage as pozzolanic material is limited. It has also been suggested that typical FBC-fly ash could not be used as a cement replacement in concrete due to its unacceptably high sulfur content [2].

Attempts have been made to use FBC-fly ash as source materials for making geopolymer [3,7]. This alumino-silicate compound possesses good mechanical properties viz., high compressive strength and stability at high temperature of above 1000 °C [8]. FBC-fly ash may need to be properly ground to remove large and highly irregular particles containing pores and cavities [3]. However, grinding requires extra effort and time to obtain proper fineness which is cost prohibitive for the commercial utilization of this FBC-fly ash.

This paper attempts to use FBC-fly ash as cementitious material without grinding to conserve energy. FBC-fly ash was blended with PCC-fly ash and used as source material for making geopolymer. The knowledge would be crucial for commercial utilization of FBC-fly ash. The fly ash blends were mixed with alkaline solutions and temperature cured. XRD, SEM, degree of reaction, FTIR and compressive strength tests were performed on the geopolymer specimens.

2. Materials and methods

2.1. Materials

Source materials for making geopolymer were FBC-fly ash from a small power plant in central Thailand and PCC-fly ash from Mae Moh power plant in the north. Typical chemical compositions of fly

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ashes were determined by X-ray fluorescence (XRF) as shown in Table 1. FBC-fly ash had high CaO content of 47.0% due to the addition of lime to absorb sulfur. The main compositions of FBC-fly ash were lime (CaO), quartz (SiO_2), alumina (Al_2O_3) and gypsum ($CaSO_4$). PCC-fly ash was also used to increase the reactive phase of the starting material for geopolymer mixture. The particle sizes (D_{50}) of FBC and PCC-fly ashes were 28 μm and 24 μm, respectively. The particle size distribution of the original fly ashes is given in Fig. 1. The specific gravity of FBC-fly ash was 2.34 and that of PCC-fly ash was slightly lower at 2.21. Liquid phase consisted of 10 M sodium hydroxide solution (NaOH) and sodium silicate solution (Na_2SiO_3) with 9% Na_2O and 30% SiO_2 by weight. The viscosities of 10 M NaOH and sodium silicate solutions were 0.0093 and 0.0606 Pascal second (Pa s), respectively. River sand with specific gravity of 2.65 and fineness modulus of 2.8 was used to prepare mortar for strength test in accordance with ASTM C109.

2.2. Mix compositions

FBC-fly ash and PCC-fly ash were mixed together at various proportions. The mass ratios of FBC-fly ash to PCC-fly ash were 0:100, 20:80, 40:60, 60:40, 80:20 and 100:0. Liquid was prepared by mixing 10 M NaOH with Na_2SiO_3 with the Na_2SiO_3-to-NaOH ratio of 1.5 by weight. Due to irregular shape of FBC-fly ash, increase in liquid content was needed to produce a workable mix, particularly in the mixtures with high FBC-fly ash content. The mix proportion is tabulated in Table 2. Calcium oxide and gypsum in large quantity can adversely affect the setting time and strength of geopolymers [3,9]. The total calcium oxide and gypsum contents in the geopolymer mix could be reduced by addition of PCC-fly ash.

Table 1
Chemical composition of fly ashes.

Composition (%)	PCC-fly ash	FBC-fly ash
SiO_2	39.5	21.0
Al_2O_3	21.2	8.0
Fe_2O_3	15.6	6.9
CaO	19.7	42.2
Na_2O	1.3	2.9
TiO_2	0.5	2.2
MgO	1.3	0.8
SO_3	2.7	15.0
LOI	0.8	1.0

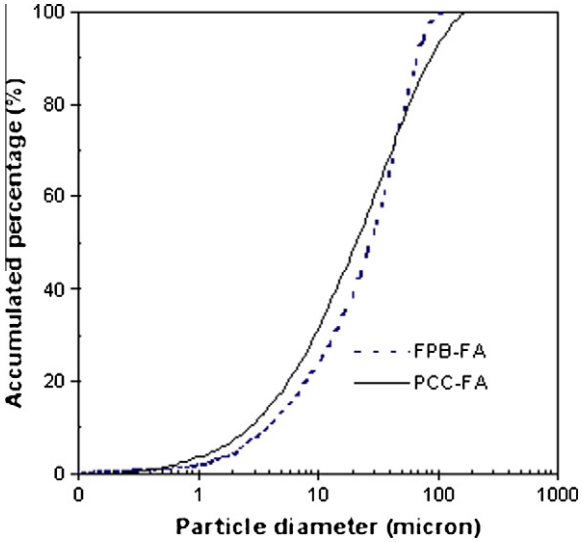

Fig. 1. Particle size distribution of the original fly ashes.

2.3. Preparation of geopolymer

The ashes were thoroughly mixed in a pan mixer. The liquid was prepared by mixing NaOH and Na_2SiO_3 together in a container, then added to the blend ash. The paste mixture was mixed for 5 min and was then cast into 25 mm diameter × 25 mm height plastic cylinder molds. Specimens were vibrated for 10 s and covered with cling film to avoid moisture evaporation during heat curing. The specimens were subsequently cured in oven at 65 °C for 48 h. After that, the specimens were cooled down and cured continuously at controlled 25 °C.

In preparation of mortar for strength test, sand was added to the paste at final mixing step with the sand-to-solid binder ratio of 2 (by weight). Mixture was then mixed for another minute. The mortar mixture was cast into 50 mm cubic molds in accordance with ASTM C109. The curing condition was the same as for the paste preparation.

2.4. Details of test

2.4.1. Determination of degree of reaction

The degree of reaction of fly ash in geopolymer was based on the identification of unreacted ash [3]. The unreacted ash was con-

Table 2
Mix proportion of geopolymer pastes.

Mix no.	Sample ID	Source materials (g)		Liquid (g)	Solid fraction
		PCC-fly ash	FBC-fly ash		
1	PCC–FA	100	0	67	0.60
2	80/20 blend	80	20	67	0.60
3	60/40 blend	60	40	67	0.60
4	40/60 blend	40	60	82	0.55
5	20/80 blend	20	80	100	0.50
6	FBC–FA	0	100	100	0.50

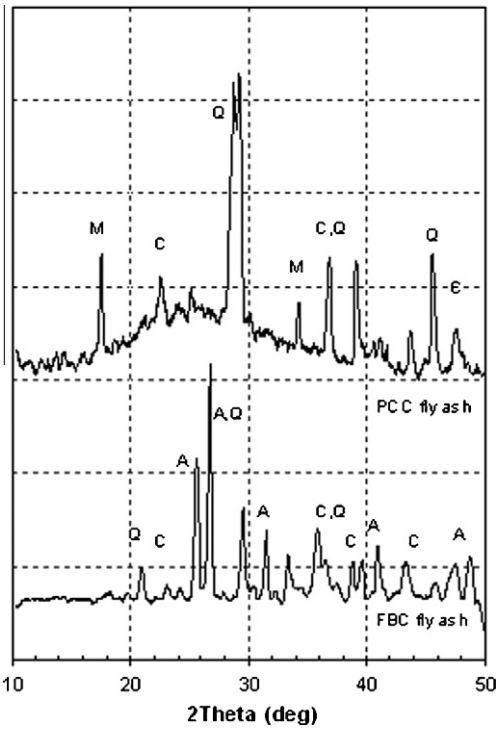

Fig. 2. XRD patterns of FBC and PCC-fly ashes: A = calcium sulfate, C = calcium oxide; M = mullite, Q = quartz.

sidered as microaggregate in system. The method involved the dissolution of powdery samples with 2 M HCl and 3% Na_2CO_3 [10]. Hardened geopolymer pastes were ground to obtain particles passed a 150-μm sieve. Three grams of powdered samples were dissolved in 30 ml of 2 M HCl in beaker and then placed in 60 °C water bath and stirred for 20 min to accelerate the dissolution. The solid phase was then filtered and washed with warm water three times to completely remove HCl. Acetone was applied in the last filtration to remove water before drying at 70 °C for 2 h. Residue was further dissolved with 30 ml of 3% Na_2CO_3 solution in beaker and placed in 80 °C water bath for another 20 min with occasionally stirring. Again, residue was filtered and repeatedly washed with water and acetone before drying. The weight of unreacted fly ash was then determined. Degree of reaction on ignited basis was calculated using Eq. (1) [11]:

$$\text{Degree of reaction} = \frac{m_{\text{sample}} - [m_{\text{residue}} \times (1 + \text{LOI})]}{m_{\text{sample}}} \times 100 \qquad (1)$$

where m_{sample} is the weight of powdery sample (g), m_{residue} the weight of dried residue (g) and LOI is the loss on ignition fraction of ground geopolymer paste. LOI of ground geopolymer paste was tested in accordance with ASTM C114. The dissolution of the blended raw material of each mix was also determined, and assigned as "blank". All results were individually subtracted with blank to obtain the corrected degree of reaction [3].

2.4.2. Additional tests

Microstructure study and FTIR spectrometry were performed on the geopolymer pastes. FTIR absorption spectra of ground samples were recorded in the wavenumber range of 4000–400 cm^{-1}. The compressive strengths at age of 7 days were tested on geopolymer mortars in accordance with ASTM C109. The reported compressive strengths were the averages of three samples.

3. Results and discussion

3.1. Characterization of fly ashes

X-ray diffraction (XRD) patterns of fly ashes are shown in Fig. 2. Due to low combustion temperature of coal in FBC, less glassy phase of FBC-fly ash was obtained as compared to the PCC-fly ash. Numerous peaks of crystalline quartz, calcium sulfate ($CaSO_4$) and calcium oxide (CaO) of FBC-fly ash were easily identified. For PCC-fly ash, a broad hump at around 16–38° indicated the presence of a large amount of amorphous phase. The peaks of quartz, mullite and calcium oxide were also present.

Microstructures of both fly ashes are shown in Fig. 3. PCC-fly ash particles were spherical due to the sintering of ash at high combustion temperature. On the other hand, particles of FBC-fly ash were very irregular in shape since the combustion temperature was only around 900 °C and the coal particles did not completely melt and thus the irregular shape remained.

3.2. XRD pattern of geopolymer paste

Fig. 4 shows the X-ray diffraction (XRD) pattern of geopolymer pastes at the age of 7 days. Geopolymer pastes with high amount of PCC-fly ash of 60%, 80% and 100% showed high amount of amorphous gel as indicated by the broad hump and a small amount of peaks of crystalline products. The broad hump of these pastes peaked at 30°, while it was 26° for the PCC-fly ash as shown in Fig. 2. This indicates the highly disorder of the silicate glass phase in geopolymer [3]. Peaks of CaO could also be noticed as the PCC-fly ash contained a high percentage of CaO. Calcium silicate from reaction between calcium and silicate compounds similar to hydration of Portland cement was also detected. Increase in FBC-fly ash in the mixture resulted in increase of peaks of crystalline phases. Quartz, CaO, $CaSO_4$ and calcium silicate were easily seen in samples with high FBC contents of 60%, 80% and 100%. As a result, the amount of amorphous gel, therefore, reduced with the increase in the FBC contents.

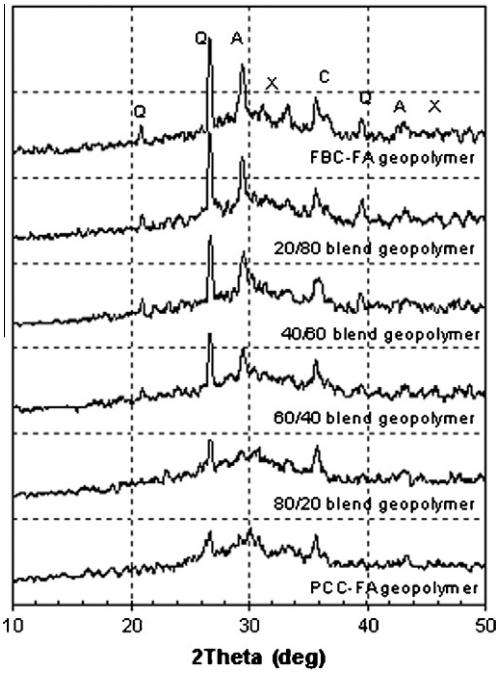

Fig. 4. XRD patterns of geopolymer pastes at the age of 7 days: A = calcium sulfate, C = calcium oxide; Q = quartz, X = calcium silicate.

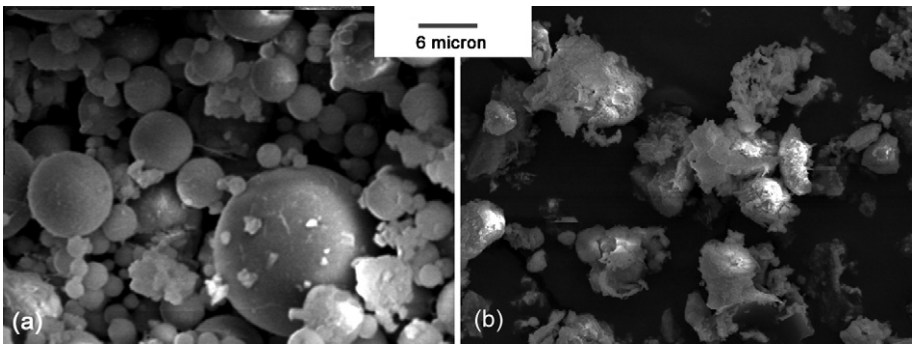

Fig. 3. SEM images of fly ash particles: (a) PCC-fly ash, (b) FBC-fly ash.

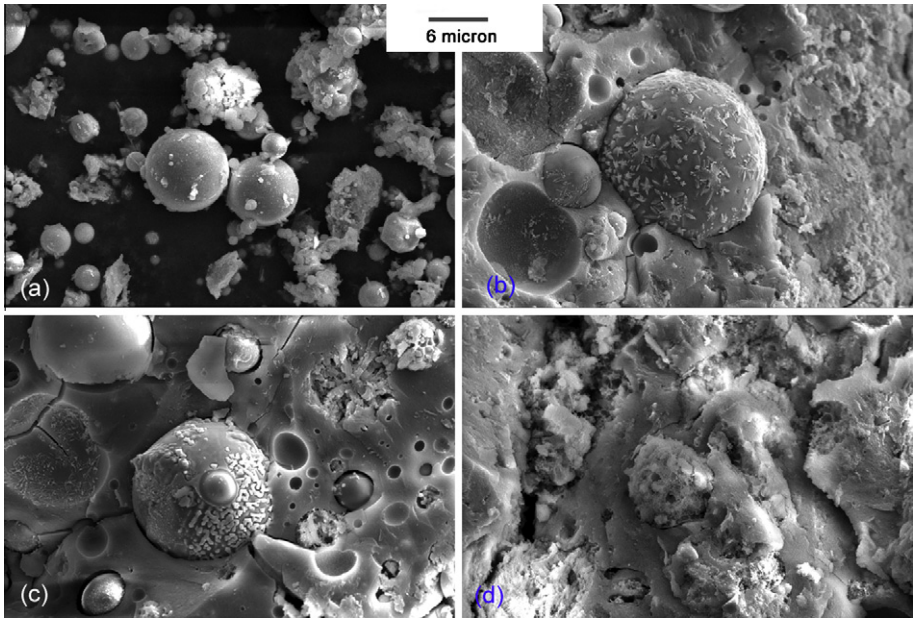

Fig. 5. Morphology of materials at the age of 7 days; (a) 60/40 blend fly ash; (b) 60/40 blend geopolymer; (c) PCC–FA geopolymer; (d) FBC–FA geopolymer paste.

3.3. Morphology of geopolymer pastes

SEM images of 60/40 blend fly ash and its geopolymer paste are shown in Fig. 5. PCC-fly ash was used to improve the workability of the mixes and to increase the reactivity. The spherical shape PCC-fly ash exerted the ball bearing effect and increased the workability of the mixture of the blend with irregular shape FBC-fly ash (Fig. 5a). Fig. 4c shows the morphology of PCC-fly ash geopolymer paste. Unreacted and partially reacted grains of fly ash and a continuous mass of alumino-silicate were the common feature. Large fly ash particles still did not completely dissolve [12]. For the 60/40 blend geopolymer paste, the morphology as shown in Fig. 5b looked similar to that of the PCC geopolymer paste indicating a relatively well developed geopolymer paste. For the FBC-fly ash geopolymer paste as shown in Fig. 5d, the paste also showed a continuous mass of alumino-silicate with unreacted and partially reacted grains of irregular FBC ash particles. However, the unreacted and partially reacted grains of FBC-fly ash were porous and could affect the denseness and exert negative effect on the strength of geopolymer. Similar finding was reported on the bottom ash geopolymer paste [9].

3.4. Degree of reaction

Fig. 6 presents the degree of reactions of geopolymer pastes. It should be noted that the solid fraction of pastes were not the same. The difference in amount of liquid to solid ratio would affect the degree of reaction. For the geopolymer with solid fraction of 0.6, the degree of reaction decreased with increase in the FBC content. The PCC-fly ash paste gave high degree of reaction of 18.6% while the 80/20 blend and 60/40 blend geopolymers gave lower degrees of reaction of 16.8% and 15.6%, respectively. The high degree of reaction was a result of the high amorphous phase of PCC-fly ash. Increase in the liquid fraction to 0.45 (solid fraction of 0.55) resulted in a slight increase in the degree of reaction of the 40/60 blend geopolymer paste. Higher amount of liquid encouraged the leaching out of the silica, alumina and other elements. Increase in the liquid portion to 0.5 (solid fraction of 0.5) resulted in an additional increase in the degree of reaction of the 20/80 blend geopolymer paste to 18.5%. At the same liquid fraction, the degree of reaction of FBC-fly ash paste was lower to 17.0% due to low amount of amorphous phase of FBC-fly ash.

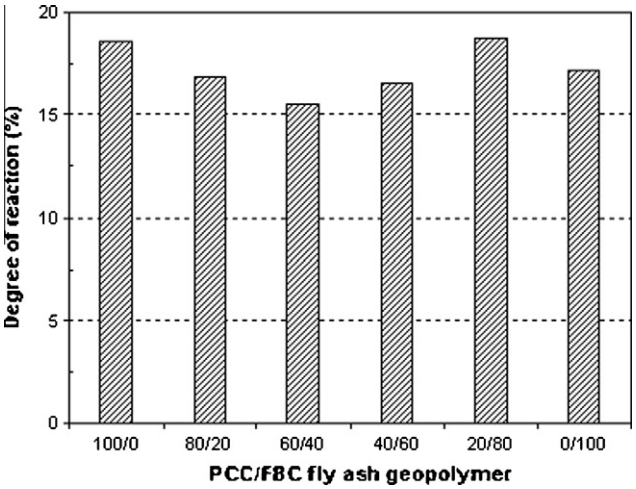

Fig. 6. Degrees of reaction of blend fly ash geopolymers at the age of 7 days.

3.5. FTIR spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was performed on the geopolymer paste. Characteristic bands were identified in geopolymer as shown in Fig. 7 consisting of Si–O bending mode near 460 cm^{-1}, Si–O stretching vibration at the wave number range of 1200–950 cm^{-1}, O–H stretching and O–H bending at approximately 3450 cm^{-1} and 1650–1600 cm^{-1}, CO_3^{2-} band at ~1460 cm^{-1} [12–14].

The IR spectra of geopolymer as shown in Fig. 7a–d were slightly different from the original fly ash. The occurrence of CO_3^{2-} band was detected in all geopolymer as a result of the carbonation between alkaline solution and CO_2 gas in environment resulted in sodium carbonate. In addition, position of Si–O stretching band was altered from the broad peak at ~1000–1200 cm^{-1} in original PCC-fly ash (Fig. 6e) to strong peak at

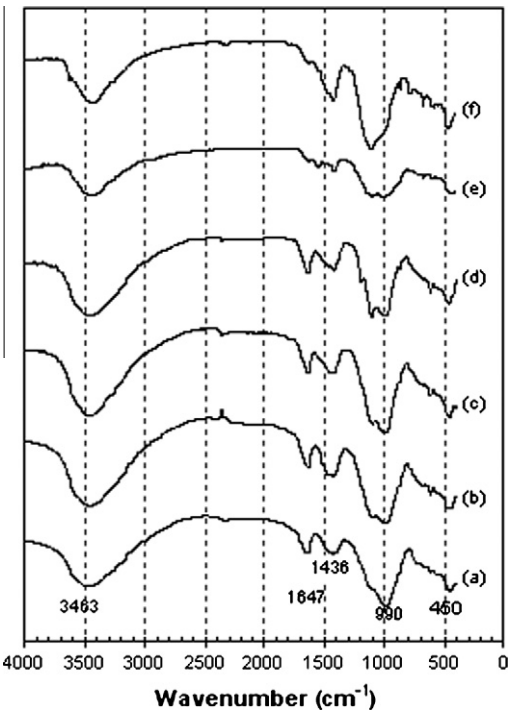

Fig. 7. IR spectrum of fly ashes and geopolymer pastes at the age of 7 days: (a) PCC-fly ash geopolymer, (b) 60/40 blend geopolymer, (c) 40/60 blend geopolymer, (d) FBC-fly ash geopolymer, (e) PCC-fly ash, (f) FBC-fly ash.

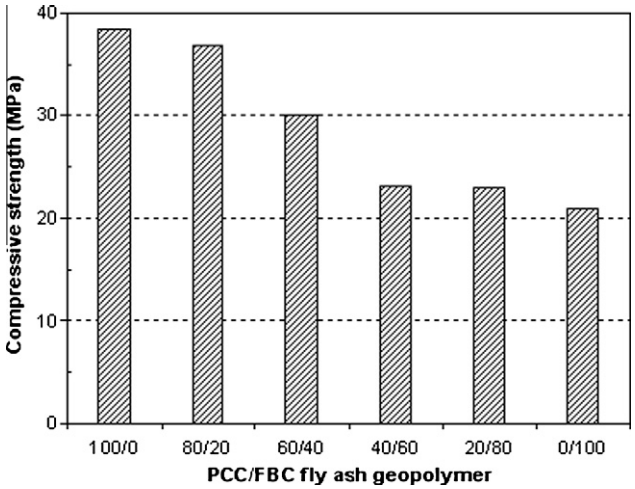

Fig. 8. Compressive strength of geopolymer mortars at the age of 7 days.

$\sim$990 cm^{-1} in geopolymer (Fig. 6a) implying the chemical change in the matrix. Small peak at $\sim$660 cm^{-1} was observed in FBC-fly ash and geopolymer corresponded to the band identification of S–O originated from sulfate compound in the matrix. It should also be noted that Al–O bands could not be detected as the bands were weak and overlapped with the position of Si–O vibration. The Si–O stretching vibration was more prominent than other mode; it was therefore logically used to indicate the degree of geopolymerization [9].

3.6. Compressive strength of geopolymer mortar

Fig. 8 presents the compressive strength of geopolymer mortars. The compressive strength decreased with increase in the FBC-fly ash content in the mixture as the reactivity of FBC-fly ash was low compared to that of PCC-fly ash. Amorphous phase in PCC-fly ash was responsible for the high leaching out of Si and Al ions to system and resulted in continuous alumino-silicate matrix with embedded fly ash particles. The compressive strength of PCC-fly ash geopolymer was high at 38.3 MPa. The strengths of 80/20 blend and 60/40 blend pastes were also high at 36.8 and 30.0 MPa. This was consistence with the results of the XRD which indicated that the PCC-fly ash, 80/20 blend and 60/40 blend pastes showed the noticeable lower peaks of crystalline products than those containing high amount of FBC-fly ash. The SEM results also confirmed that the morphology of the PCC-fly ash and 60/40 blend paste was similar. Increase in the amount of FBC-fly ash beyond this adversely affected strength of pastes. The strength of 40/60 blend, 20/80 blend and FBC-fly ash geopolymer pastes was low at 23.1, 23.0 and 21.0 MPa, respectively. The low strength with increase in FBC-fly ash content was due to its low amorphous phase and the porous partially reacted fly ash particles.

The PCC-fly ash-to-ground FBC-fly ash ratio of 60:40 was recommended for use as the proportion for source material for geopolymer considering the quantity of the ashes and reasonable strength level. This geopolymer, therefore, could be used as construction material with early strength gain and could replace the use of cement. Additionally, it is the alternative way to effectively recycle the FBC-fly ash.

4. Conclusions

The FBC-fly ash particles are highly irregular and contain relatively high amount of crystalline phase compared to the PCC-fly ash. With its spherical shape and high reactivity, the incorporation of PCC-fly ash, therefore, enhanced the workability and reactivity of the FBC-fly ash and PCC-fly ash blend geopolymer. The geopolymer with high percentage of PCC-fly ash contained a large amount of amorphous gel and gave relatively high strength. Increase in FBC-fly ash in mixture resulted in geopolymer with a larger amount of crystalline phase as detected by XRD. Although the matrix appeared dense, the porous structures of the partially reacted FBC-fly ash particles remained and adversely affected the strength of geopolymer. In addition, the test on degree of reaction also confirmed that the degree of reaction of PCC-fly ash in geopolymer paste was higher than that of FBC-fly ash. PCC-fly ash could be blended with up to 40% of FBC-fly ash and used as source material to make geopolymer with relatively high strengths of 30.0–38.0 MPa.

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