Design, Processing and Characterization of Fly Ash-Based Geopolymers for Lightweight Concrete Application

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The mix design of geopolymers plays important role in obtaining desirable compressive strength. Optimum mix design of geopolymers can be applied for application, such as lightweight concrete. In order to determine the maximum compressive strength for lightweight concrete production, fly ash geopolymers were produced with various ratios of fly ash/alkaline activator (0.5 - 3.0), Na₂SiO₃ solution/NaOH solution (0.5 - 3.0) and 12 M of NaOH solution. The geopolymer materials were mixed and cured at 70°C for 24 h and tested on 7 days. Maximum compressive strength was obtained when the ratios of fly ash/alkaline activator and Na₂SiO₃ solution/NaOH solution were 2.0 and 2.5, respectively. The characterization and morphology of geopolymers were performed by using X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). It was clearly shown that the best mix design of geopolymers produced denser matrix and less unreacted fly ash compared to other samples.

Keywords: fly ash, geopolymers, mix design, lightweight, compressive strength

The manufacturing of ordinary Portland cement (OPC) produces more than 13 billion tons of carbon dioxide (CO_{2}) every year. This CO, emission is equivalent to 7% of the total global emission of CO, to the atmosphere. CO, emission may lead to environmental problems such as global warming and greenhouse effect. To address this problem, geopolymers were produced and applied in construction field. Geopolymers are inorganic aluminosilicate polymers synthesized predominantly from silicon (Si) and aluminum (Ål) materials of geological origin or by-product materials such as fly ash [1, 2]. The production of geopolymers is now well accepted because it involves fewer emissions of CO₂ to the environment which is more environmental friendly. Past researcher [3] has verified that the manufacturing of geopolymers emits an average five times lesser CO₂ than that of OPC. Geopolymers are produced by mixing alkaline solution (usually containing mixture of sodium silicate solution (Na₂SiO₂) and sodium hydroxide (NaOH) solution) with a solid aluminosilicate source such as fly ash, clay, metakaolin or blast furnace slag forming an aluminosilicate gel phase [4]. The reaction of formation of aluminosilicate gel is known as geopolymerisation. Many researchers have agreed that the geopolymerisation process may occur in three main stages: (1) Dissolution of species from the source material; (2) Transportation of species, coagulation/ gelation; and, (3) Condensation forming a threedimensional network of silicon-aluminates [5-7]. This 3D network gives mechanical and chemical properties that are equivalent, or even superior to those of OPC concrete.

As geopolymer was widely produced nowadays, hence it has been used in many areas such as concrete [2, 8], lightweight concrete [9], cement powder [10], coating application [11], and refractory paint [12] by using various aluminosilicate sources. However, in order to produce a successful product, the mix design of geopolymer paste is important. Hardjito et al. [13] investigated on the development of fly ash-based geopolymer. Two different ratios of Na₂SiO₃/NaOH that is 0.4 and 2.5 were used to produce geopolymer samples. He found that geopolymer samples produced using ratio of 2.5 generate maximum compressive strength. In addition, the continuity of this research [2] has concluded that the production of fly ash geopolymers should use Na₂SiO₃/NaOH ratio in range of 0.4 to 2.5 and fly ash/alkaline activator ratio in range of 2.5 to 3.3 with NaOH concentration between 8M to 16M. Furthermore, it was showed that geopolymer paste with 12M of NaOH concentration produced maximum compressive strength at 2, 3 and 7 days of testing [14].

From the previous studies [1-3, 15-17], parameters affecting the synthesis of fly ash geopolymers such as concentration of NaOH solution, curing temperatures, types of curing and chemical resistance have been carried out extensively. However, the effect of fly ash/alkaline activator and Na_SiO_/NaOH ratios on properties of the fly ash-based geopolymers has not been fully investigated. Hence, the effect of fly ash/alkaline activator and Na_SiO_/ NaOH ratios on the properties of fly ash-based geopolymer was studied and presented in the current paper for lightweight concrete application.

Experimental part

Raw Materials

Fly ash used in this study was obtained from Manjung power station, Lumut, Perak, Malaysia. Through X-ray fluorescence (XRF) analysis, the chemical composition of fly ash is given in table 1. The alkaline activator used in this study was sodium silicate solution and NaOH solution. Na₂SiO₃ solution was obtained from South Pacific Chemical Industries Sdn. Bhd. (SPCI), Malaysia. The Na₂SiO₃ solution composed of SiO₂ = 30.1 %, Na₂O = 9.4 % and H₂O = 60.5 % (SiO₂/Na₂O = 3.2) with specific gravity at 20°C = 1.4 g/ cm³ and viscosity at 20°C = 0.4 Pa·s. The NaOH was in pellet form with 99% purity, made in Taiwan with brand name Formosoda-P. The NaOH solution was prepared by dissolving NaOH pellets in distilled water to obtain 12 M of NaOH concentration [14, 18]. *Mix Design*

 Table 1

 CHEMICAL COMPOSITION OF FLY ASH

Chemical Composition	Mass (%)
SiO ₂	26.40
Al_2O_3	9.25
Fe_2O_3	30.13
TiO ₂	3.07
CaO	21.60
K ₂ O	2.58
P_2O_5	0.67
SO3	1.30
MnO	0.27
L.O.I	4.73

The fly ash/alkaline activator ratio used in this study was set at 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0. After many trials, fly ash/alkaline activator ratio lower than 2.0 caused highly workable fly ash-based geopolymer paste while the geopolymer paste become sticky when fly ash/alkaline activator ratio is exceeding 2.5. Table 2 summarizes the workability of fly ash geopolymers. Thus, only three ratios were considered in this investigation, which were 1.5, 2.0 and 2.5. Six Na₂SiO₃/NaOH ratios (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0) were used. The details of the mixtures are shown in table 3.

Mixing, Molding and Curing Process

The fly ash and alkaline activator were mixed for five minutes until the homogeneous mixture was obtained. It was placed in 50mm x 50mm x 50mm molds. Minimum 3 samples were produced for each mix design in order to determine the average value of the compressive strength. The samples were cured at temperature 70°C for 24 h. Previous research has found that curing at 70°C for 24h caused a substantial increase in compressive strength [19]. Curing at longer period reduced the compressive strength. After curing, the samples were kept at room temperature until day 7 for testing. It is important to note that 90% of the final compressive strength is reached within 7 days in case of geopolymer concrete, and there is not much variation in compressive strength after 7 days [20].

Testing Methods

The compressive strength of geopolymer samples were measured according to ASTM C 109/ C 109 by using the Shimadzu Universal Testing Machine. Three samples were tested to evaluate the compressive strength by taking the average of those samples. The samples were tested on day 7.

For XRD analysis, the geopolymer samples were prepared in powder form and analyzed using XRD-6000, Shimadzu X-ray diffractometer with Cu K α radiation. From the analysis, the pattern of crystalline phase was determined.

FTIR spectra were obtained by using Perkin Elmer FTIR Spectrum RX1 Spectrometer. The samples were scanned from 750 cm⁻¹ to 4000 cm⁻¹.

The microstructure of fly ash and geopolymer samples with different mix design were observed using JSM-6460LA model Scanning Electron Microscope (JEOL).

WORKABILITY OF FLY ASH GEOPOLYMERS			
Fly Ash/Alkaline Activator Ratio	Workability		
0.5	High		
1.0	High		
1.5	Workable		
2.0	Workable		
2.5	Workable		
3.0	Low		

Table 2

Table 3

Fly ash/alkaling activator	No SiO /NoOH	Els: Ach		NaOII
Ratio	Ratio	riy Asii (g)	Na2SiO3 (g)	
1.5	0.5	506.25	112 50	225.00
1.5	1.0	506.25	168 75	168 75
1.5	1.5	506.25	202.50	135.00
1.5	2.0	506.25	225.00	112 50
1.5	2.5	506.25	241.07	96.43
1.5	3.0	506.25	253.13	84.38
2.0	0.5	562.50	93.75	187.50
2.0	1.0	562.50	140.63	140.63
2.0	1.5	562.50	168.75	112.50
2.0	2.0	562.50	187.50	93.75
2.0	2.5	562.50	200.89	80.36
2.0	3.0	562.50	210.94	70.31
2.5	0.5	602.68	80.36	160.71
2.5	1.0	602.68	120.54	120.54
2.5	1.5	602.68	144.64	96.43
2.5	2.0	602.68	160.71	80.36
2.5	2.5	602.68	172.19	68.88
2.5	3.0	602.68	180.80	60.27

Compressive Strength versus Ratio of Sodium Silicate / NaOH



Fig. 1. Compressive strength for various mix design (FA/AA = fly ash/alkaline activator ratio)

Results and discussions

Compressive Strength

Figure 1 shows the compressive strength for fly ash geopolymers at various fly ash/alkaline activator ratios and Na,SiO,/NaOH ratios. Among the three ratios of fly ash/alkaline activator (1.5, 2.0 and 2.5), maximum compressive strength (73.86 MPa) was achieved at fly ash/alkaline activator ratio of 2.0 and Na,SiO,/NaOH ratio of 2.5.

With increasing fly ash/alkaline activator ratio until 2.0, compressive strength of fly ash geopolymers increased. However, when increasing the ratio up to 2.5, the compressive strength decreased. This might be due to excess of fly ash. There are not enough liquid (alkaline activator) to mix with fly ash homogeneously. The value of compressive strength tended to decrease with Na₂SiO₃/NaOH ratio more than 2.5 for all ratios of fly ash/ alkaline activator.

For all ratios of fly ash/alkaline activator, compressive strength decreased at Na₂SiO₂/NaOH ratio of 3.0. This might be due to excess of OH² concentration [21]. In addition, the excess sodium content may also form sodium carbonate due to atmospheric carbonation and may disrupt the polymerization process [22]. Earlier study by Šathia et al. [20] showed that increasing fly ash and alkaline activator increased the compressive strength. The increasing content of alkaline activator influenced the geopolymerization process because of the Na₂O content in the solution. However, the authors from earlier study did not mention the limitation of increasing of fly ash and alkaline activator content. During the recent study, it was found that ratio of fly ash/alkaline activator more than 2.5 reduced the compressive strength of geopolymers. On the contrary, Chindaprasirt et al. [23] found that the optimum ratio of Na₂SiO₂/NaOH was ranged between 0.67 and 1.00, which produced maximum compressive strength. Different ratios were obtained due to the different fly ash used in the

study as fly ash from different countries consisted different percentage of chemical composition.

From this study, the ratio of fly ash/alkaline activator and ratio of Na₂SiO₃/NaOH influenced the compressive strength of the geopolymer paste. The above reason was valid as the previous research [14] found that the ratio of alkaline activator/fly ash had greater influence on the compressive strength of geopolymer. However, some researcher [18] showed contradictory result where the ratio of fly ash/ alkaline activator was not a relevant parameter on the compressive strength of geopolymer.

X-Ray Diffraction (XRD)

The XRD patterns in figure 2 show the original fly ash and fly ash geopolymers with different fly ash/alkaline activator ratios (1.5, 2.0 and 2.5). When the fly ash was activated with alkaline activator solution, the main reaction product formed was 'alkaline aluminosilicate gel' with low order crystalline structure [18, 24] which has no pattern but appears with low and scattered bands [25]. When comparing the XRD pattern of the original fly ash with hardened geopolymer, it can be seen that the crystalline phases originally existed in the fly ash (quartz, mullite, etc.) were not apparently altered by the activation reactions. Fly ash has an X-ray amorphous phase indicated by the broad hump registered between $2\theta = 20$ and 30° [26]. There are researchers [27] who believed that mullite and guartz were slightly altered when react with strong alkaline medium. The fly ash broad hump had been slightly shifted to the right $(2\theta = 25-30^\circ)$ in geopolymers, indicating the dissolution of fly ash amorphous phase and the formation of a new amorphous phase in these materials [25, 26, 28].

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3 shows the IR spectra of fly ash and fly ash geopolymers. The main FTIR bands of fly ash and geopolymers are summarized and tabulated in table 4. Fly





ash showed broad band at 1004 cm⁻¹ ascribed to asymmetric stretching vibrations T-O-Si (T=Si or Al). However, the band T–O-Si at 1004 cm⁻¹ of the original fly ash became slightly sharper and shifted towards lower frequencies in fly ash geopolymers with different ratio of fly ash/alkaline activator: 971 cm⁻¹ (FA/AA = 1.5), 978 cm⁻¹ (FA/AA=2.0) and 977 cm⁻¹ (FA/AA=2.5). All these displacements indicated the reaction between vitreous component of the fly ash and the alkali activator and that new products of reaction were formed (the main one: the alkaline aluminosilicate gel) [25]. Comparing the shifting of the T–O-Si band in different geopolymer samples, it was observed that matrix (FA/AA=2.0) showed the most intense displacement. This suggested that the reaction product with FA/AA ratio of 2.0 has higher Si content than that for the reaction products with FA/AA ratio of 1.5 and 2.5 [23, 27].

The broad bands appeared in all IR spectra were 3500cm⁻¹ and 1600cm⁻¹, which corresponded to the stretching (-OH) and bending (H-O-H) vibrations of bound water molecules absorbed on surface or entrapped in the large cavities of polymeric framework, respectively [25, 26, 30]. The higher values of these bands indicated higher degree of water molecule absorption in their mass.

Meanwhile, the bands between 1410cm⁻¹ and 1 430 cm⁻¹ for all IR spectra are contributed to stretching vibrations of O-C-O bond. This indicated the existence of sodium bicarbonate suggesting the occurrence of atmospheric carbonation of the high alkaline NaOH solution, which diffused on the geopolymeric materials surface [25, 30-32].

Scanning Electron Microscopy (SEM)

The microstructures of fly ash and fly ash geopolymers for different mix designs were observed with SEM. Figure 4a showed the microstructure of the original fly ash. As seen in the figure, fly ash consisted of spherical particles of different sizes where some of these particles may contain other particles of a smaller sizes in their interior [33]. The surface texture of fly ash appeared to be smooth and dense to highly porous [34]. Regularly on the surface of the fly ash, the existence of some quartz particles or some vitreous unshaped fragments could be seen [35].

Figures 4b to 4d show the morphology of fly ash geopolymers with the best mix design for each type of ratio fly ash/alkaline activator (1.5, 2.0 and 2.5). After curing for 24 h at temperature 70°C, fly ash geopolymers showed heterogeneous phases where partially reacted and unreacted fly ash existed on the dense gel-like matrix



Fig. 4. Microstructure of (a) original fly ash and fly ash geopolymers with (b) FA/AA = 1.5, (c) FA/AA = 2.0 and (d) FA/AA = 2.5 at constant $Na_sSiO_s/NaOH$ ratio of 2.5.

geopolymers. The considerable amount of unreacted or not totally consumed spheres of fly ash indicated a moderate degree of reaction in the system. Among the three figures, the sample with fly ash/alkaline activator ratio of 2.0 (fig. 4c) showed denser matrix and lesser unreacted fly ash which contributed to maximum compressive strength (73.86 MPa). The micro-cracks existed on the sample with fly ash/alkaline activator ratio of 2.5 (fig. 4d) reduced the compressive strength of the sample.

Conclusions

Based on the results of this study, the following conclusions were drawn.

The combination of fly ash/alkaline activator ratio of 2 and sodium silicate/NaOH ratio of 2.5 contributed to optimum compressive strength of fly ash geopolymers. However, different fly ashes from other countries may not be applicable to this mix design.

The characterization of geopolymers showed that the amount of silica (Si) in source material (fly ash) influenced the compressive strength as described in FTIR analysis and SEM.

The best mix design obtained in this study will be used in the production of lightweight geopolymer concrete.

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