MECHANICAL AND PHYSICAL PROPERTIES OF FLY ASH GEOPOLYMER - MULLITE COMPOSITES

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Received: July 24, 2015; Revised: September 26, 2105; Accepted: February 16, 2016

Abstract

This work aims to investigate how compressive strength of a typical class C fly ash-based geopolymer would be changed with addition of mullite. In preparation of basic geopolymer, fly ash was collected from Mae Moh power plants, Lampang province, was alkaline activated and cured for a total period of 7 days. In making the composites, 20-60% of mullite powder was added to the basic geopolymer mixture and cured at the same condition. Porosity, density, and water absorption of the samples were determined by following ASTM C-642. The results showed that the compressive strength of the geopolymer mortar could be remarkably improved from 14 MPa to 71 MPa with mullite addition. The mechanical property variation of the composites was discussed along with their physical properties and microstructures.

Keywords: Geopolymer, class C fly ash-based geopolymer, fly ash geopolymer-mullite composites

Introduction

In May 2015, the NOAA/Earth System Research Laboratory has announced that the level of average global atmospheric CO_2 concentration reached a new high of 401 ppm (Dlugokencky and Tans, 2015). This alarmed us that we need to deal with CO_2 emission more seriously. There are several sources that can contribute to CO_2 emission in the world. Cement industry from all over the world generates about 7% of global CO_2 emission (Davidovits, 1994). Nowadays, geopolymer is a promising product that can either partially or totally replace cement (Akbari *et al.*, 2015 and Wanjari *et al.*, 2015). Using geopolymer helps not only reduce CO_2 emission by reducing cement production, but also utilize waste material such

Suranaree J. Sci. Technol. 23(1):45-52

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as fly ash (Palomo *et al.*, 1999). Fly ash is a byproduct from coal combustion process that abundant over a total of 600 metric ton per year (Joshi *et al.*, 1997). Utilization of class C fly ash for making geopolymer was widely studied but commonly achieved low compressive strength (Guo *et al.*, 2010; Zheng *et al.*, 2010; Somna *et al.*, 2011; Li *et al.*, 2013; Abdulkareem *et al.*, 2014; Bagheri and Nazari, 2014; Abdollahnejad *et al.*, 2015; Embong *et al.*, 2015). Therefore, engineering class C fly ash based geopolymer for high compressive strength applications is a great challenge. In order to realize that, it might need to be reinforced or composited.

One of the candidates suitable for compositing with a geopolymer is mullite. Since mullite is a crystalline aluminosilicate material, it should be a highly compatible reinforcement for the geopolymer matrix system. Therefore, this study was aimed to improve the mechanical properties of fly ash based geopolymer by compositing mullite as reinforcement.

Meterials and Methods

Materials

Fly ash used in this study was collected from Mae Moh power plant, Lampang province, Thailand, while an industrial grade mullite powder was purchased from a local supplier in Thailand. Figure 1 presents SEM pictures of raw materials. Fly ash particle can be seen consist of spherical vitreous particles and mullite powder has irregular shape. Figure 2 presents the X-ray diffraction analysis result of raw materials. TABLE 1 presents chemical composition of fly ash and mullite as detected



Figure 1. SEM pictures of raw materials



Figure 2. X-ray diffractogram of raw materials

by X-ray Fluorescence. The chemical composition of fly ash is classified to class C as specified in ASTM C-168. The particle distribution of fly ash and mullite powder was measured by laser diffraction analysis (Malvern Instrument Mastersizer, 2000) as presented in TABLE 2. In this study, a mixture of chemical-grade sodium hydroxide solution and commercial sodium silicate was used as the alkaline activator.

Sample Preparation

The optimum concentration of sodium hydroxide solution in preparation of alkaline activator was predetermined by mixing various sodium hydroxide solutions ranging from 8-16 mol/l with sodium silicate. Dry fly ash was mixed with alkaline activator and hand stirred for 1 minute. The mixture was then poured into cylindrical PVC molds (\emptyset 15 mm \times 30 mm). The geopolymer-mullite composite was prepared by adding mullite powder, ranging from 20-60 wt% of dry fly ash, to the optimized geopolymer mixture followed by the same curing procedure. The detail of various mixtures of fly ash-based geopolymer and its composites with mullite is given in TABLE 3. The samples were cured at 90°C for 1 day and then at 40°C for 6 days.

Setting Time and Compressive Strength

The setting time of geopolymer paste was tested according to ASTM C-191 with a manually operated standard Vicat apparatus. The compressive strength was measured after 7 days of curing. The samples were demolded from cylindrical PVC molds, and subjected to the compressive test by using Universal Testing Machine (Instron 5566) with the loading speed of 1 mm/min. Each reported value is the average of five samples.

Scanning Electron Microscopy

A scanning microscopy was used to analyze the morphology of polishing surfaces. All samples were polished with SiC grinding paper number P600 for 1 min with a rotational speed of 180 rpm and then on number P1200 for 30 sec with a rotational speed of 200 rpm. Finally, the samples were polished using 6 μ m diamond particles. All the samples were gold coated prior to SEM observation.

Density, Voids, and Apparent Density Measurement

Determination of porosity, density, and water absorption of geopolymer was performed by following ASTM C-642. The average values were obtained from five samples.

Results and Discussion

Effect of NaOH Concentration

The compressive strength of fly ashbased geopolymers activated by various sodium hydroxide-sodium silicate solutions are given in Figure 3. The compressive strength is increasing with the increase of sodium



Figure 3. The effect of sodium hydroxide concentration on compressive strength of geopolymers

hydroxide concentration. The significant improvement starts at 10 mol/l and the compressive strength does not increase significantly after 12 mol/l. In this condition, small error bar indicates that the compressive strength result was consistent. However, at 16 mol/l the compressive strength was still a high value, but the strength result was inconsistent. Therefore, the optimum sodium hydroxide concentration at 12 mol/l was chosen. This result was also in good agreement with previous work (Al Bakri *et al.*, 2012 and Arioz *et al.*, 2012). Figure 7 presents the effect of NaOH concentration on microstructures. It can be seen that at 8 mol/l of NaOH concentration was insufficient to dissolve fly ash particle sincea large amount of unreacted particles still exist after polymerization. This is because strong alkalis are required to activate the silicon and aluminum presented in the fly ash to allow the glassy structure to be partially or totally dissolved and transformed into a very compacted composite (Guo *et al.*, 2010). However, leftover fly ash particles started to be further dissolved with increasing the NaOH



Figure 4. The effect of mullite addition on compressive strength of geopolymers



Figure 5. XRD diffractograms showing the effect of mullite addition (Mu: mullite, F: faujasite, Q: quartz)

concentration. At 10 mol/l, unreacted fly ash particles were substantially reduced and were almost completely dissolved at 12 mol/l and 14 mol/l. In addition, with such optimum conditions, pre-existing crack of geopolymer could be reduced significantly. According to Griffith's principle, specimens containing larger pre-existing crack would exhibit low compressive strength. The use of 12 mol/l NaOH solution resulted in smooth surface, less existing crack, and less existence of unreacted fly ash particles. Therefore, this concentration used as alkaline activator for the preparation of fly ash based geopolymer-mullite composites.

Effect of Mullite Addition

The compressive strength of 20-60 wt% mullite added geopolymer composite is given in Figure 4. It showed that by adding just 20 wt% of mullite the compressive strength of the geopolymer was increased significantly to 44 MPa, i.e. three times stronger than the fly ash-geopolymer without addition. By adding 40 wt% of mullite, a remarkable improvement in compressive strength, 71 MPa, was achieved. However, at 60 wt% of mullite addition, the compressive strength decreased to 58 MPa. It can be concluded that 40 wt% is the optimum level of mullite addition into fly ash-based geopolymer.

microstructures, as shown in Figure 8. Ina composite with 20 wt% addition, small mullite crystals could be observed within the matrix of geopolymer, associated with an improvement in compressive strength. At 40 wt% addition, more mullite crystals with longer and larger needle-like shape were detected. Small needlelike structure and interlocking of mullite crystals were proposed to be the key factor for achieving high strength (Carty and Senapati, 1998). With its high aspect ratio, mullite crystal could effectively help resist crack propagation and successfully reinforce the matrix in composite system. As a result, the compressive strength was the highest with such microstructure. However, even though the mullite crystal was found overa broader area in the case of 60 wt% addition, but compressive strength in this condition was not as high as at 40 wt%. It could be because the ratio of solid to liquid has become too low, so the activator was insufficient to dissolve the raw materials, indicated by the presence of unreacted fly ash particles under SEM observation.

Setting Time

The setting time of the mixtures was measured using Vicat apparatus. The measurement was performed in accordance with ASTM C-191 with 10 min interval. Figure 6 presents the



Figure 6. The effect of mullite addition on setting time of geopolymers

X-ray diffractograms in Figure 5 showed that mullite peaks appeared in the composite samples and their intensity increases proportionally with the percentage of mullite addition. Increasing mullite also resulted in different initial and final setting time of fly ash-based and fly ash-mullite composites geopolymer. Fly ash-based geopolymer takes around 3.5 h and 4.5 h for the initial and final setting time, respectively. The initial setting time tends to

Compound	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	CaO	Mn ₂ O ₃	TiO ₂	SO ₃	LOI	Total
Fly ash	33.41	15.03	16.48	2.40	3.29	21.46	0.13	0.54	7.23	0.03	100
Mullite	60.06	35.99	0.68	1.90	-	0.37	-	0.90	-	0.1	100

Table 1. Chemical composition of raw materials wt% (LOI: Loss on Ignition)

Table 2. Particle size distribution of raw materials

Material	D10 (µm)	D50 (µm)	D90 (µm)	Average (µm)
Fly ash	1.243	14.312	69.540	26.581
Mullite	1.833	12.577	36.268	16.421

Table 3. Detail mixture preparation of geopolymers

	Solid			Liquid			Final	Solid to
No.	Fly ash	Addition of mullite		NaOH		Na ₂ SiO ₃	mixture	liquid ratio
1	40 g	-	-	8-16 mol/l	12 g	12 g	64 g	1:0.60
2	40 g	20 wt%	8 g	Selected	12 g	12 g	72 g	1:0.50
3	40 g	40 wt%	16 g	Selected	12 g	12 g	80 g	1:0.42
4	40 g	60 wt%	24 g	Selected	12 g	12 g	88 g	1:0.37

Table 4. Physical properties of geopolymers

Geopolymers	Bulk density (g/cm ³)	Apparent density (g/cm ³)	Volume of permeable voids (%)	Water absorption (%)
FA-Geopolymer	1.65	2.21	24.9	12.86
FA-M 40 wt%	1.81	2.24	19.0	9.90

decrease with increasing of mullite addition. At 20 wt% addition, the initial setting time of geopolymer was shorten to around 2.2 h and final setting time was only 3.2 h. The initial setting time of the paste with 40 wt% mullite was around 2.1 h. By adding more mullite, the initial setting time is getting shorter. Mullite addition reduces water content proportionally with the percentage added. The mullite addition has an effect on reducing initial water content which could play a significant role either in controlling compressive strength or initial setting time. However, further addition to 60 wt% the initial setting time of did not cause a significant change.

Density, Voids, and Apparent Density Measurement

Table 4 presents physical property of fly ash and fly ash-mullite composites geopolymer. Fly ash-based geopolymer has lower bulk and apparent density, and relatively high volume of permeable voids at 24.9 %. This existing voids tend to absorbs more water. In contrast, fly ash geopolymer -mullite composite has higher bulk and apparent density, low volume of permeable voids, and low water absorption. By adding 40 wt% of mullite, the permeable voids was reduce to 5% with only 3% of water absorption. It indicates that mullite addition could lead to more dense and low porosity material than fly ash-based geopolymer.

Conclusions

The concentration of alkaline activator affected compressive strength of geopolymers. At low concentration of 8-10 mol/l, the NaOH solution could not effectively dissolve fly ash particles. However, when the concentration was increased to 12 mol/l, the fly ash was successfully dissolved, resulting in an average compressive strength with great consistency of 14 MPa. The addition of mullite into fly ashbased geopolymer could increase the compressive



Figure 7. The SEM pictures of fly ash-geopolymer prepared using different concentration of NaOH solution (UF: partially or totally unreacted fly ash)

strength significantly i.e., specimen with 40 wt% of mullite addition reached an average of 71 MPa. This could be due to the presence of mullite crystal effectively reinforcing the matrix of the composite system. The addition of mullite could also reduce permeable voids and water absorption of the geopolymer.

Acknowledgements

The authors are grateful acknowledge to Mae Fah Luang University and National Metal and Materials Technology Centre for financial support.

References

- Abdollahnejad, Z., Pacheco-Torgal, F., Félix, T., Tahri, W., and Aguiar, J.B. (2015). Mix design, properties and cost analysis of fly ash-based geopolymer foam. Constr. Build. Mater., 80:18-30.
- Abdulkareem, O.A., Al Bakri, A.M.M., Kamarudin, H., Nizar, I.K., and Saif, A.A. (2014). Effects of elevated temperatures on the thermal behavior and mechanical performance of fly ash geopolymer paste, mortar and lightweight concrete. Constr. Build. Mater., 50:377-387.
- Akbari, H., Mensah-biney, R., and Simms, J. (2015). Production of Geopolymer Binder from Coal Fly Ash to Make Cement-less Concrete. WOCA, 1–8.
- Al Bakri, A.M.M., Hussin, K., Binhussain, M., Nizar, I.K., Razak, R.A., and Zarina, Y. (2012). Microstructure Study on Optimization of High Strength Fly Ash



Figure 8. SEM pictures showing the microstructure of (a) fly ash based-geopolymer and (b)-(d) geopolymer-mullite composites (UF: unreacted fly ash)

Based Geopolymer. Adv. Mat. Res., 476-478:2173-2180.

- Arioz, E., Arioz, O., and Kockara, O.M. (2012). Leaching of F-type fly ash based geopolymers. Proc. Eng., 42:1114–1120.
- Bagheri, A., and Nazari, A. (2014). Compressive strength of high strength class C fly ash-based geopolymers with reactive granulated blast furnace slag aggregates designed by Taguchi method. Mat. Des., 54:483–490.
- Carty, W.M., and Senapati, U. (1998). Porcelain-raw materials, processing, phase evolution, and mechanical behavior. J. Am. Ceram. Soc., 81(1):3-20.
- Davidovits, J. (1994). Global warming impact on the cement and aggregates industries. World Res. Rev., 6(2):263-278.
- Dlugokencky E., and Tans, P. (2015) NOAA/ESRL, Trends in Atmospheric Carbon Dioxide, Available frpm: http://www.esrl.noaa.gov/gmd/ccgg/trends/
- Embong, R., Kusbiantoro, A., Shafiq, N., and Nuruddin, M.F. (2015). Strength and microstructural properties of fly ash based geopolymer concrete containing high-calcium and water-absorptive aggregate. J. Clean. Prod., 112(1): 816-822.

- Guo, X., Shi, H., and Dick, W.A. (2010). Compressive strength and microstructural characteristics of class C fly ash geopolymer. Cement Concrete Compos., 32(2):142-147.
- Li, X., Ma, X., Zhang, S., and Zheng, E. (2013). Mechanical properties and microstructure of class C fly ash-based geopolymer paste and mortar. Materials, 6(4):1485–1495.
- Palomo, a., Grutzeck, M. W., and Blanco, M. T. (1999). Alkali-activated fly ashes: A cement for the future. Cement Concrete Res., 29(8):1323–1329.
- Somna, K., Jaturapitakkul, C., Kajitvichyanukul, P., and Chindaprasirt, P. (2011). NaOH-activated ground fly ash geopolymer cured at ambient temperature. Fuel, 90(6):2118–2124.
- Wanjari, S., and Sebastian, J. (2015). Partial Replacement of Cement in the Geopolymer Quarry Rock Dust Concrete under Different Curing Conditions, p. 12-18.
- Zheng, L., Wang, W., and Shi, Y. (2010). The effects of alkaline dosage and Si/Al ratio on the immobilization of heavy metals in municipal solid waste incineration fly ash-based geopolymer. Chemosphere, 79(6):665–671.