Australian Journal of Basic and Applied Sciences, 5(10): 824-828, 2011
ISSN 1991-8178

Properties And Microstructural Characteristics Of Geopolymers Using Fly Ash With Different Percentages Of Kaolin At Room Temperature Curing

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Abstract: Geopolymers are inorganic polymeric materials. Geopolymerization involves a chemical reaction between alumino-silicate oxides and alkali metal silicate solutions under highly alkaline conditions. The strength of a geopolymer depends on the nature of the source materials. Geopolymers made from calcined source materials, such as metakaolin (calcined kaolin), fly ash, and slag, for example, yield higher compressive strengths when compared to those synthesized from non-calcined materials, such as kaolin clay. This study focused on the processing of geopolymer by using fly ash in the geopolymerization process. The fly ash was replaced accordingly with 10%, 20%, 30%, 40%, and 50% of kaolin, based on weight. A solution of sodium hydroxide and sodium silicate was used as the alkali activator for the geopolymerization reaction. The samples were tested to determine their compressive strength, water absorption, and porosity. As the percentage of kaolin was increased, the strength of the geopolymer decreased. In this study, 10% kaolin replacement was the optimum replacement and produced the maximum compressive strength of geopolymer at both 7 and 28 days.

Key words: *geopolymer; microstructure; XRD; FTIR*

INTRODUCTION

In recent years, there have been significant developments around the world related to geopolymer cement, a novel family of building materials. Geopolymer cement is a type of three-dimensional, CaO-free, aluminosilicate binder that was developed by Davidovits (1988). Geopolymers are ceramic materials that are produced by alkali activation of aluminosilicate raw materials, which are transformed into reaction products by polymerization in a high-pH environment with a relatively low curing temperature. Because of their low energy requirement to manufacture, their inflammability at high temperatures, and their resistance to acid damage, these novel products are more useful and ecologically responsible than Portland cement (Davidovits 1989; Davidovits 1994; Marty 1996; Bakharev 2005; Mustafa *et al*. 2011). According to ASTM C 618, class F fly ash is a finely divided mineral residue resulting from the combustion of finely-divided coal, e.g., ground or powdered. Geopolymers prepared using either fly ash or kaolin have framework structures that originate from the condensation of tetrahedral aluminosilicate units of varying Al/Si ratios, such as (Al-O-Si-O-)M^+, (Al-O-Si-O-Si-O-)M^+, (Si-O-Al-O-Si-O-Si-O-)M^+. M^+ denotes an alkali ion, usually Na^+ or K^+, which stabilizes the balance of charge of the tetrahedral Al (Davidovits *et al*. 1990). Based on previous research, kaolin should have a low Si/Al ratio, while fly ash should result in more heterogeneous matrices (i.e., a larger percentage of unreacted fly ash particles), with higher Si/Al ratios. The main difference between kaolin and fly ash geopolymers is that the kaolin geopolymers contain pores that are predominantly in the mesopore size range, whereas the fly ash geopolymers contain pores that are predominantly in the micropore size range. In this study, we attempted to provide essential information on fly ash geopolymers, including their water absorption rate, and porosity. Additionally, we discussed the strength performance development process: our elucidation of the microstructural characteristics of geopolymer made from different ratios of kaolin and fly ash, to identify the optimal improvements in the formulation and utilization of this product.

Experimental Method:

Raw Materials:

The kaolin used in this study was obtained from Associated Kaolin Industries Sdn. Bhd (AKI). AKI mines, processes, and supplies kaolin products from its reserves in Tapah. The fly ash used in this study was obtained from Manjung power station in Lumut, Perak, Malaysia. The fly ash had low calcium content (class F fly ash) due to an SiO_2 + Al_2O_3 + Fe_2O_3 content of more than 70% and an SO_3 content of less than 5%, and it had a

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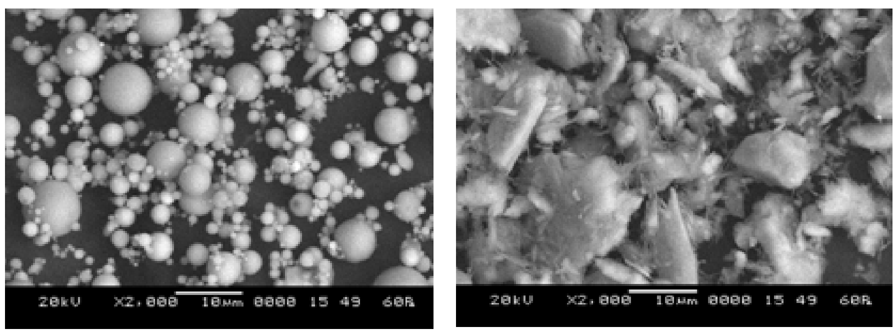
generally glassy appearance with some crystalline inclusions of mullite, hematite, and quartz. Passed through a 45-µm sieve, the fineness of the kaolin and fly ash was 100% and 91%, respectively.

The alkaline activator used in this research consisted of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH). We used 98% pure NaOH in pellet form and a liquid Na_2SiO_3 solution consisting of 12% Na_2O, 30% SiO_2, and 58% H_2O by mass. Na_2SiO_3 was used as the alkaline activator because of its low cost and wide availability. The NaOH solution was prepared to a concentration of 12 M by dissolving NaOH pellets in distilled water. In previous research, it was found that a 12 M concentration of NaOH produced the best results (Palomo *et al*. 1999; Kamarudin *et al*. 2011; Mustafa *et al*. 2011).

Compositions of the Mixtures

The fly ash was replaced accordingly with 10%, 20%, 30%, 40%, and 50% kaolin, based on weight. The investigations were conducted at room temperature. The Na_2SiO_3/NaOH ratio of 2.5 was fixed because it had been established as the optimal ratio in a previous study by Hardjito *et al.* (2008). The geopolymer pastes with different percentages of kaolin had a solid-to-liquid ratio of 2.0, which provided optimum workability. When the solid-to-liquid ratio exceeded 2.0, the workability of the pastes decreased, causing difficulties in casting and mixing.

Kaolin has a higher liquid demand than fly ash because it is composed of finer particles. As a result, greater solid-to-liquid ratios are achievable in fly ash mixtures compared to kaolin mixtures. In this study, combinations of kaolin with fly ash were made and the workability of the paste decreased as the percentage of kaolin in the mixture increased. As seen in Fig. 1, the particles of fly ash are spherically-shaped. This shape served to increase the mixture's workability compared to kaolin, which has a plate-like structure. The microstructure appearances of the original kaolin and fly ash were in agreement with those reported by Davidovits (2008). Therefore, the extra water required to increase the workability of the mixture amounted, at most, to only 10% of the total weight.



(a) (b)

Fig. 1: Microstructure of materials analyzed using scanning electron microscopy (SEM). (a) fly ash; (b) kaolin.

Specimen Preparation and Test Procedure

The geopolymeric precursors, i.e., kaolin, fly ash, and the alkaline activator solution, were mixed manually for 10 min and cast into cubic molds. The samples were vibrated to release any residual air bubbles. The dimensions of the cubic geopolymer samples were 50 mm × 50 mm × 50 mm. Six samples were prepared for each percentage of kaolin for testing at days 7 and 28, and each sample batch was prepared in duplicate. For mineralogical and microstructural analyses, the following techniques and instruments were used: X-ray diffraction (XRD, Shimadzu) and Fourier transform infrared spectroscopy (FTIR).

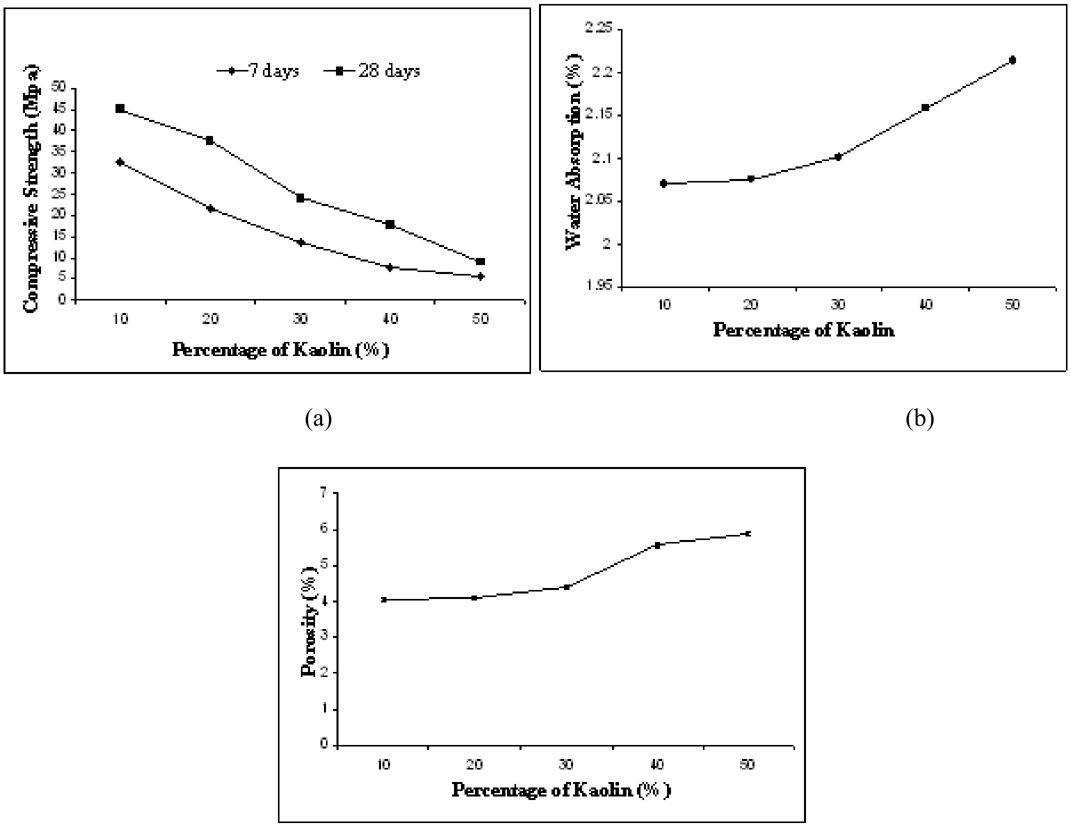
RESULTS AND DISCUSSION

Compressive Strength

Testing of the compressive strength of the geopolymer cubes was based on BS 1881-116:1983. A loading rate of 5 mm per min was used for this testing. After casting, the samples were tested for compressive strength at days 7 and 28, as shown in Fig. 2(a). These results show that the samples that contain a greater percentage of kaolin have a lower compressive strength at 7 and 28 days. It is also apparent that the compressive strength at 28 days is greater than the compressive strength at 7 days. The compressive strength of the geopolymer cube increases proportionally with time between 7 and 28 days.

Water Absorption and Porosity

Figs. 2(b) and 2(c) show that the water absorption and porosity of the samples increases as the percentage of kaolin increases. The highest value of water absorption is approximately 2.2 % when the kaolin content is 50%. The same pattern is seen for the porosity, which also reaches its maximum value of approximately 5.9% when the kaolin content is 50%. It is evident that the samples with a higher compressive strength will have lower values of water absorption and porosity. This is due to the pores at the surface affecting the bonding of the paste and the compressive strength of the samples.



(a) (b)

(c)

Fig. 2: Effect of different percentages of kaolin on: a) compressive strength, b) water absorption and c) porosity

Microstructural Analysis
X-ray Diffraction (XRD):

Figs. 3(a) and (b) show the XRD patterns of the raw materials, i.e., fly ash and kaolin, and also the patterns of the products resulting from the alkaline activation of different percentages of these materials. Both starting materials, i.e., fly ash and kaolin, exhibit a peak at 2θ where 2θ = 20º - 30 º, which is characteristic of structurally-disordered compounds, and a set of peaks corresponding to minor crystalline phases, i.e., quartz and kaolinite ($Al_2Si_2O_5(OH)_4$) in the case of kaolin and quartz and faujasite ($Na_{14}Al_{12}Si_{13}O_{51}\bullet 6H_2O$) and mullite in the case of fly ash (Fernandez-Jimenez *et al*. 2008). After the geopolymerization process occurs with incremental increases in kaolin percentage, the quartz peak shifts a little to the left and simultaneously decreases in amplitude. This shift is related to the formation of an amorphous reaction compound, sodium aluminosilicate, which is very important in the development of the binding properties of the material. The simultaneous increase in the kaolinite peaks was probably due to the accretion of alumina and silica content contributed by kaolin.

Fourier Transform Infrared Spectroscopy (FTIR):

Fig. 4 shows that the main FTIR adsorption bands of the geopolymers containing increasing percentages of kaolin were bands 1-5. The peak at band 1 and the relatively weak peak at band 2 are due to asymmetrical stretching vibrations of Al-O/Si-O bonds, indicating the presence of Si and Al in the geopolymer. As a result of increasing the kaolin percentage, the Al-O/Si-O bonds at band 1 shift toward higher frequencies, indicating the formation of alkaline aluminosilicate gel (Barbosa and MacKenzie 2003; Fernandez-Jimenez and Palomo 2005), while, for Si-O-Si/Si-O-Al, a bending band occurs at band 3. These bands are commonly seen in ring silicates and provide an indication of the degree of amorphization of the material, as their intensities do not depend on the degree of crystallization (Swanepoel and Strydom 2002). The relationship between Al-O, Si-O, Si-O-Si, or Si-O-

Al asymmetrical-stretch, peak positions and the extent of the geopolymerization process is complex, but it is useful in studying and understanding the mechanism of geopolymerization. The weak band seen between bands 4 and 5 characterizes the spectrum of stretching and deformation vibrations of OH and H-O-H groups from the weakly-bound water molecules, which are adsorbed on the surface or trapped in the large cavities between the rings of the geopolymeric products (Palomo *et al*. 1999; Guo *et al*. 2010).

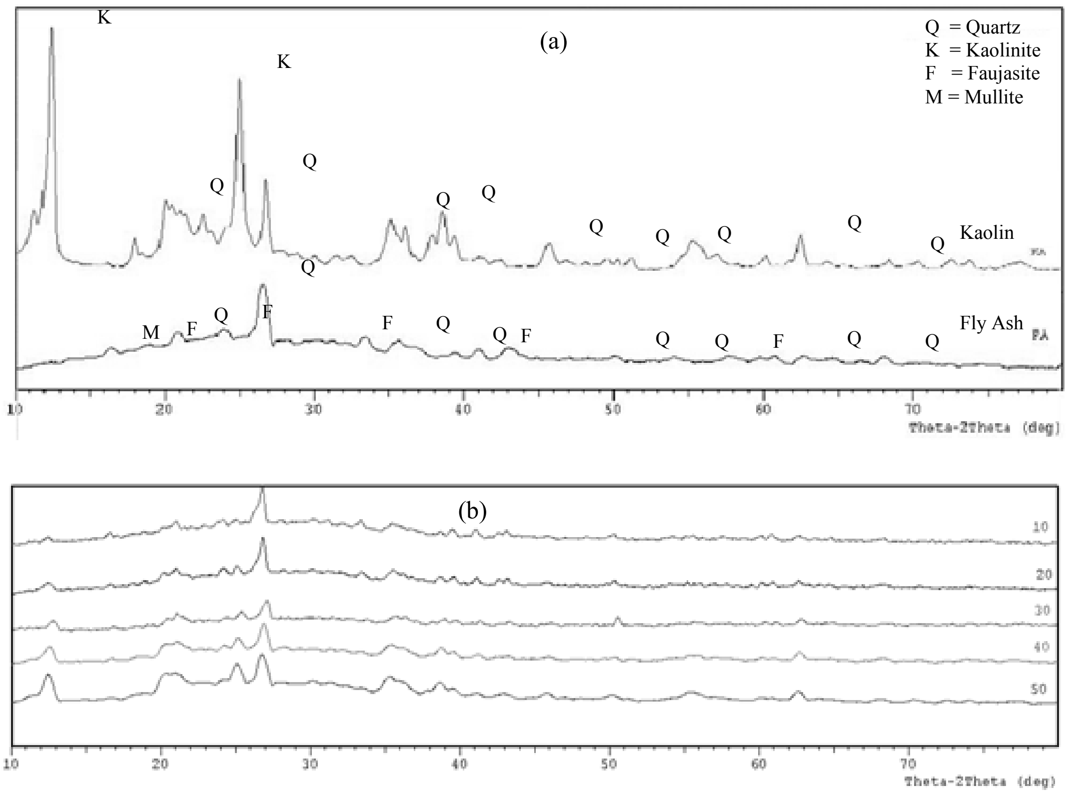


Fig. 3: X-ray diffraction patterns of: (a) raw materials and (b) geopolymer with different percentages of kaolin

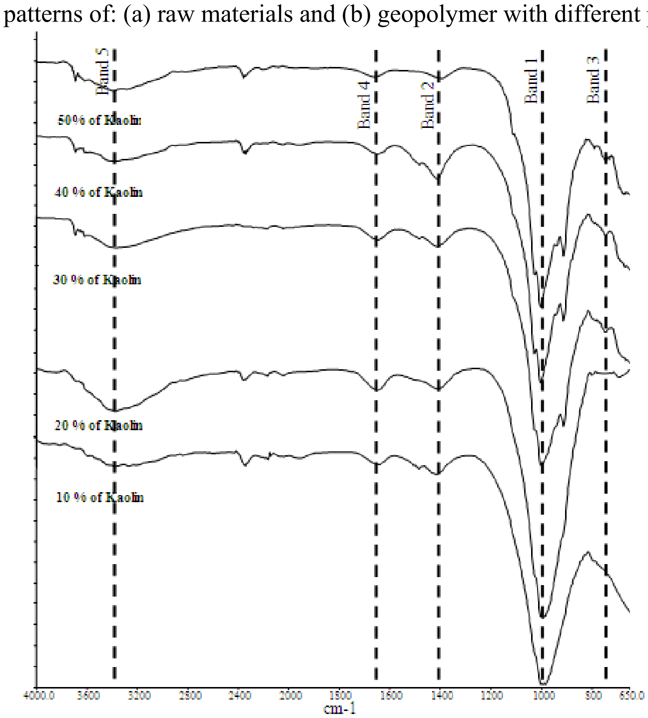


Fig. 4: FTIR spectra of geopolymer with different percentages of kaolin.

Conclusions:

Of the geopolymers tested, the one that contained 10% kaolin displayed the highest compressive strength, while the geopolymer that contained 50% kaolin displayed the lowest compressive strength. The geopolymer samples that contained smaller percentages of kaolin had lower water absorption and porosity values. This study showed that when starting with raw materials, such as quartz, kaolinite, and faujasite, geopolymerization leads to the formation of similar, but not identical, types of minerals. The FTIR peaks indicated the existence of Al-O/Si-O and Si-O-Si/Si-O-Al bonds that formed during the geopolymerization process. The utilization of these materials can save energy and resources and is an environmentally friendly option.

ACKNOWLEDGMENTS

King Abdul Aziz City Science and Technology (KACST) funded this study. Also, we extend our appreciation to the Green Concrete@UniMAP and to all of the people who contributed to the successful completion of this study.

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