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The Relationship between Vickers Microhardness and Compressive Strength of Functional Surface Geopolymers

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Abstract. An experimental study to investigate the relationship between Vickers microhardness and compressive strength of geopolymers made from metakaolin has been conducted. Samples were prepared by using metakaolin activated with a sodium silicate solution at a different ratio of Si to Al and Na to Al and cured at 70^{o}C for one hour. The resulting geopolymers were stored in an open air for 28 days before conducting any measurement. Bulk density and apparent porosity of the samples were measured by using Archimedes's method. Vickers microhardness measurements were performed on a polished surface of geopolymers with a load ranging from 0.3 – 1.0 kg. The topographic of indented samples were examined by using scanning electron microscopy (SEM). Compressive strength of the resulting geopolymers was measured on the cylindrical samples with a ratio of height to the diameter was 2:1. The results showed that the molar ratios of geopolymers compositions play important roles in the magnitude of bulk density, porosity, Vickers's microhardness as well as the compressive strength. The porosity reduced exponentially the magnitude of the strength of geopolymers. It was found that the relationship between Vickers microhardness and compressive strength was linear.

INTRODUCTION

Scientific and industrial applications of geopolymers have reached a state as a promising material that could substantially substitute for conventional cements, ceramics, composites, plastics and many mineral-based products [1]. Geopolymers are well known for their excellent physico-mechanics properties such as high-early compressive strength, heat and fire resistant as well as acid attack-resistance [2-4]. Therefore, they are suitable to be applied as concrete, floor panel, ceiling, partitions and sidewalls. Other promising applications of geopolymers are thermal insulation, thermal shock refractories, composites for infrastructures repair and strengthening, high-tech composites for aircraft interior and automobile, hybrid inorganic-organic composite, arts and decoration, anti-bacterial composite, anti-biofouling bricks, and self-cleaning material [5-7].

The fabrication of geopolymers involves a chemical reaction between various aluminosilicate oxides with silicates under highly alkaline conditions, yielding polymeric sialate (-Si-O-Al-O-) bonds. The atomic ratio of Si:Al in geopolymer structures plays an important role in determining the properties and subsequent application. Materials with a low ratio of Si:Al (1-3) initiate three dimensional networks that are very rigid and they are suitable for the

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manufacture of bricks, ceramics and composites while those with the composition of 20<Si:Al<35 provides polymeric character to the geopolymer. They are applicable for fire and heat resistant composites which withstand up to 1000 – 1200^{o}C [8-10].

Geopolymers for functional surface applications such as floor panels, table top, arts and decorations are required to have excellent physical and mechanical properties such as high bulk density, low apparent porosity, high Vickers hardness and high compressive strength. These properties can be tailored from Si:Al ratio of the starting materials, type of alkaline solution and water content.

Hardness is a measure of material's resistance to localized plastic deformation. Hardness testing is a method commonly used to evaluate the quality of material surface, particularly metals and ceramics.

This test is based on forcing an indenter into the surface of the material by dynamic or static loading and determining the response in terms of the size of indentation [11, 12]. Compressive strength is a critical characteristic required for many of the proposed applications for geopolymers. It has been recognized that the compressive strength of mortar or concrete is an important parameter in structural design while flexural strength is of interest for the design of highway and airfield slabs [13].

In this research, a relationship between Vickers microhardness and compressive strength of geopolymers based on metakaolin having various molar ratios of SiO_2/Al_2O_3, Na_2O/SiO_2, and H_2O/Na_2O for functional surface applications was investigated and characterized. Metakaolin was used as the starting material due to its purity as aluminosilicate mineral compared to fly ash. Besides that, the compressive strength of metakaolin-based geopolymers cured at 60-80^{o}C is relatively high [10, 20].

EXPERIMENT

Geopolymers was produced by using metakaolinite obtained by dehydroxylation of kaolinite at 750 ^{o}C. Dehydroxylation was performed using a low-temperature furnace at a heating rate about 10 ^{o}C/minutes. The temperature was maintained at 750^{o}C for about six hours to ensure a complete dehydroxylation of the kaolinite. Chemical compositions of the activation solution in terms of the molar oxide ratio used in this study were adjusted to obtain the nominal Si:Al ranged from 1 to 2 while varying Na:Al from 0.6 to 1.0.

The kaolinite used in this study was paint/filler Grade Kaolin Clay. The particle size distribution of the material is: 0.05 % > 53 μm screen residue, 8.0 % > 10 μm, 24 % < 2 μm and 68 % < 2 μm. The pH (20% suspension) is 7.0 and specific gravity is 2.6. The mineralogical analysis showed that the material contained 99 % kaolinite and a trace of quartz (Table 1).

Sodium silicate solutions were used as activator and its soda content was increased by the addition of sodium hydroxide (NaOH) pellets. Tap water was used throughout the processing of the materials. Sodium silicate solution and sodium hydroxide were supplied by Sigma Chemical Ltd. The chemical composition of the sodium silicate is presented in table 1.

Throughout this study, the oxide molar ratio of H_2O to Na_2O was kept at a value of 10. At this value, the water content of the sodium silicate mixture was adequate to facilitate geopolymerisation without deterioration of the mechanical properties of the geopolymer. The sodium silicate solution, sodium. hydroxide pellets and water were mixed and hand-stirred until dissolution occurred. Geopolymer resins were obtained by the addition of metakaolinite powder to this solution followed by hand mixing or using a shake mixer to ensure homogeneity.

Figure 1 shows the representative of geopolymers produced in this study having diameter of 2.50 cm and height of 5.00 cm.

The bulk density (D_b) and apparent porosity (P_a) of geopolymers were determined using the Archimedès principle according ASTM Standard (C-20) with deionised water as the immersion medium. Bulk density and apparent porosity measurements samples were sectioned with a diamond saw to obtain a specimen 0.50 cm high and 2.50 cm in diameter. Each measurement was performed on three samples, and the measurement uncertainty was taken as the standard deviation.

Hardness testing was conducted using a ZWICK microhardness tester with a Vickers diamond pyramid indenter. Selected samples for the indentation test were polished using a Struers Pedamat polisher finishing with 1 μm grade diamond. The size of the samples was about 1.00 cm in height and 2.50 cm in diameter. Based on the standard test method for microhardness of materials (ASTM E384), the test loads used in this study were between 300 – 1000 g. The indentation diagonal lengths were measured directly using a micrometer attached to the sample stage or using an optical microscope and the topography of indented sampel were examined using SEM.

TABLE 1. Chemical composition of the starting materials.

Component wt (%)	Kaolinite	Sodium silicate
Al_2O_3	37.8	-
SiO_2	46.4	30.1
K_2O	0.21	-
Na_2O	0.01	9.4
CaO	0.08	-
MgO	0.15	-
Fe_2O_3	0.8	-
TiO_2	0.8	-
LOI (1000^{o}C)	13.8	-
H_2O	-	60.5

FIGURE 1. Metakaolin based geopolymers produced in this study.

Vickers hardness number, H_v is a number related to the applied force (P) and the surface area of the permanent impression made by a square-based pyramidal diamond indenter having included face angles of 136^o. The Vickers hardness (H_v) in MPa is calculated using the following formula:

$$H_v = \frac{P}{A_s} = 2P\,\frac{\sin\left(\alpha/2\right)}{d^2} = 1.8544\,\frac{P}{d^2} \qquad (1)$$

where:
P = load (N)
A_s = surface area of indentation (mm^2).
d = mean diagonal of indentation (mm) and
α = face angle of indenter (136^o).

The compressive tests were conducted after ageing the specimen at 28 days. These tests were performed using a Wykeham Farrance 50 ton compression test machine with a loading rate of 0.33 mm/minutes. The test specimens were cylindrical in shape, 5.00 cm in length and 2.50 cm in diameter and hence the length to diameter ratio of 2:1 fulfils the standard requirement for compression test ASTM C773. Each measurement was conducted on three samples.

RESULTS AND DISCUSSIONS

Vickers hardness tests were performed with applied load ranged between 0.3 – 1.0 kg, which provided a reasonable indent for hardness determination. A series of preliminary measurements was made to investigate the influence of the applied load (kg) on hardness. Figure 2 shows a plot of the applied load versus the hardness of geopolymer prepared with nominal composition Si:Al = 1.5, Na:Al = 0.6 and Si:Al = 1.75, Na:Al = 0.8. The curves show that the hardness of the material slightly decreases as the load increases indicating that the material is not

homogenous (if hardness is a basic material parameter, different loads should yield a constant hardness for the same material, i.e. the ratio P/d^2 in equation 1 should be constant). Microstructural examination reveals that the material consists of a large number of grains (unreacted metakaolinite) surrounded by the geopolymer matrix as well as a large number of pores. The presence of these grains as well as the pores affects the size of the indentation, which in turn influences the hardness value.

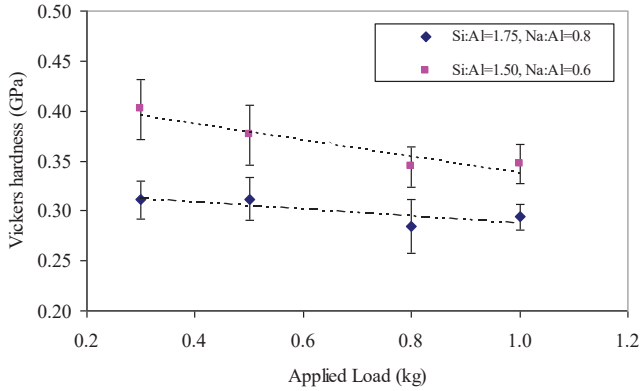

FIGURE 2. The dependence of hardness on the applied load with linear lines of best fit. Error bars represent 2SD.

Figure 3 shows the relationship between the applied load and the resulting indentation size (d) for geopolymer samples shown in figure 2. The results indicate that the indentation size is related to the applied load as showing by the best-fit lines.

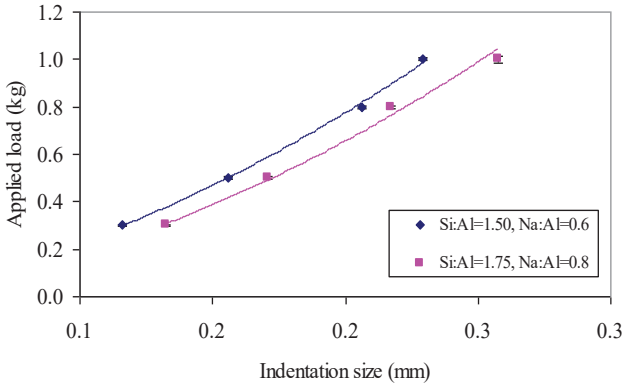

FIGURE 3. Indentation size (d) as a function of applied load for geopolymer samples shown in Figure 2. The lines indicate the best-fit satisfying equation 4.

The widely used model to describe the relationship between the applied load and the indentation size is the Meyer law [14]:

$$P = \beta d^n \tag{2}$$

where P is the applied load, d is the length of the diagonal indentation, β and *n* are constants which can be derived from curve fitting of the experimental data.

Sangwal [15] pointed out that the Meyer index (*n*) can be used to express the indentation size effect (ISE): (i) $n < 2$, the hardness is dependent on load and (ii) $n = 2$, the hardness is independent of load. The application of equation 4 to the geopolymer samples is shown in figure 3. The best-fit value of the β and *n* parameters for each sample is shown in table 2.

Based on this result (n<2), the determination of Vickers hardness for geopolymers as a function of Si:Al and Na:Al atomic ratios was performed using a 1 kg load applied for about 20 s. With this load, the indent diagonals can be determined with high accuracy under the optical microscope.

TABLE 2. Variation of β and *n* parameters derived from equation 4 for geopolymer samples shown in Figure 4.

Sample ID	β (N/mm)	n	Correlation
Si:Al=1.50, Na:Al =0.6	12.970	1.7507	0.9991
Si:Al=1.75, Na:Al=0.8	12.687	1.8404	0.9939

Figure 4 and 5 are SEM micrographs showing typical indentations for a 1 kg load. Figure 4 shows the indentation of geopolymer with Si:Al = 1.04 and Na:Al = 0.6 which has the lowest hardness and figure 5 shows the indent of geopolymer Si:Al = 1.5 and Na:Al = 0.6 which has the highest hardness.

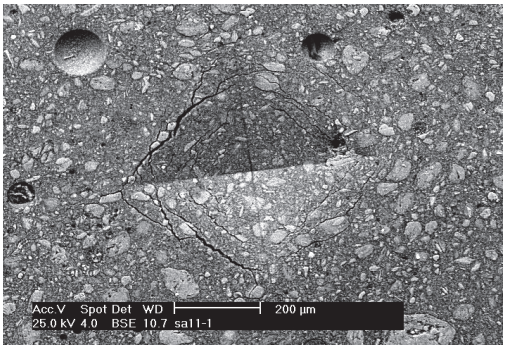

FIGURE 4. SEM micrograph of Vickers indentation of Si:Al = 1.04, Na:Al = 0.6 (load = 1 kg).

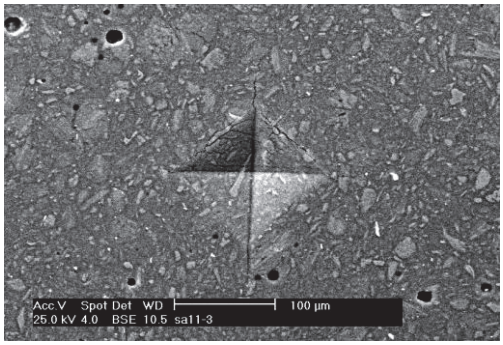

FIGURE 5. SEM micrograph of Vickers indentation of Si:Al = 1.5, Na:Al = 0.6 (load = 1 kg).

The value of Vickers hardness as a function of Si:Al is presented in figure 6. The hardness of all specimens increases in an almost linear fashion as the Si:Al increases except for the sample with Si:Al = 1.50, Na:Al = 0.6.

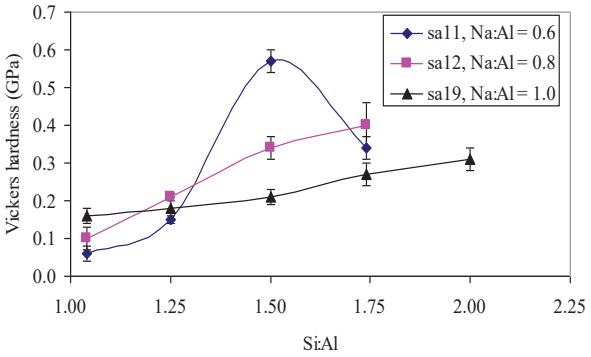

FIGURE 6. Vickers hardness as a function of Si:Al for three different values of Na:Al. Error bars repressed 2SD.

Figure 7 is a plot of compressive strength as a function of Si:Al for three different series of samples. Sample with Si:Al ratio of 1.5 (Na:Al = 0.6) was found to produce the highest compressive strength (86 ± 16 MPa). It is notable that for samples with a Na:Al = 1.0, the maximum strength occurred at Si:Al = 1.75 and Si:Al = 2.0. The trend in the measured compressive strength observed in this study is in good agreement with the results reported by Hos, McCormick & Byrne [16].

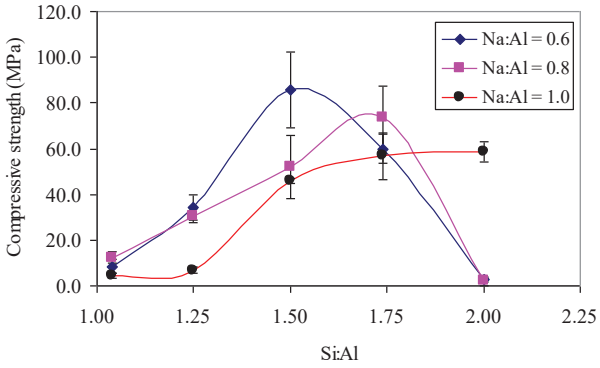

FIGURE 7. Compressive strength of geopolymers prepared with different initial ratios of Si:Al and Na:Al. Error bars represent 2SD.

In this study, the magnitudes of the compressive strength were similar to those reported by Rowles & O'Connor [17]. It is believed that the samples with low compressive strength are due to the formation of zeolite or sodalite in the geopolymer network. In the formation of these geopolymers, there is insufficient OH^- to completely dissolve Si^{4+} and Al^{3+} as well as insufficient Na^+ to allow a complete geopolymerisation of the network. As a result, the resulting geopolymers cannot form large enough polymer networks that have high structural integrity.

However, it is important to also examine the dependence of strength on the porosity of each composition. Figure 8 shows the relationship between the porosity and the compressive strength of the samples is provided in figure 7. As expected, the strength of the material decreases as the porosity increases.

The best curve-fit of the data presented in figure 8 was obtained by a power function shown in Table 3. The dependence of strength on pores is not a unique property of geopolymers or Portland cement but also found in other materials in which water leaves behind pores [18, 19].

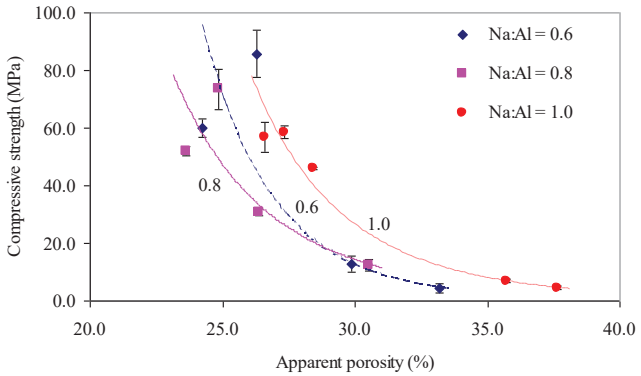

FIGURE 8. Compressive strength as a function of apparent porosity for different Si:Al ratios.

TABLE 3. Variation of the power function for curve-fit shown in Figure 8.

Sample ID	Power function	Correlation
Na:Al = 0.6	$y = 9.97^{14x^{-9.40}}$	0.8852
Na:Al = 0.8	$y = 6.30^{10x^{-6.53}}$	0.8646
Na:Al = 1.0	$y = 6.83^{12x^{-7.72}}$	0.9914

The strength of geopolymers is also dependent on the hardness. Figure 9 shows the graph of Vickers hardness as a function of the compressive strength. The curve showed a linear relationship between hardness and compressive strength. Generally, hardness is proportional to strength [12]:

$$H_v = C.\ \sigma \tag{3}$$

where H_v = Vickers hardness (GPa), σ = Strength (MPa), and C = constant.

Figure 9 clearly indicates that the compressive strength depends on the hardness of geopolymer paste. A similar result was reported by Feldman and Cheng-Yi [12] who investigated the influence of silica fume in Portland cement paste on the compressive strength and microhardness.

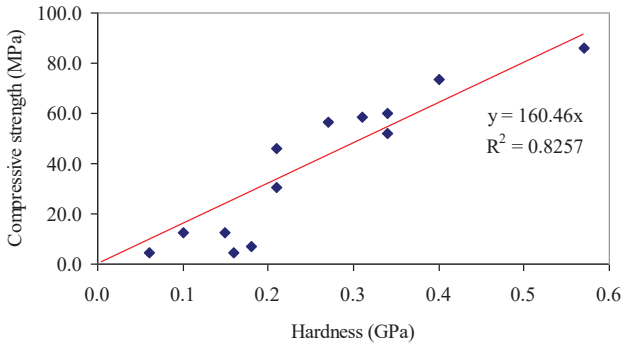

FIGURE 9. Vickers hardness versus compressive strength of geopolymers for all atomic ratios of Si:Al and Na:Al

CONCLUSIONS

The magnitude of bulk density, apparent porosity, Vickers microhardnes, and compressive strength of geopolymers produced through alkali activation of metakaolin are largely determined by the initial molar ratios of Si:Al and Na:Al. The percentage of apparent porosity is exponentially reduced the value of the compressive strength of geopolymers. The magnitude of Vickers microhadness of geopolymers has a linear relationship with their compressive strength and this should be consider in the production of functional surface geopolymers.

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