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# FLEXURAL PROPERTIES OF THIN FLY ASH GEOPOLYMERS AT ELEVATED TEMPERATURE

This paper reports on the flexural properties of thin fly ash geopolymers exposed to elevated temperature. The thin fly ash geopolymers (dimension = 160 mm × 40 mm × 10 mm) were synthesised using12M NaOH solution mixed with designed solids-to-liquids ratio of 1:2.5 and $Na_2SiO_3$/NaOH ratio of 1:4 and underwent heat treatment at different elevated temperature (300°C, 600°C, 900°C and 1150°C) after 28 days of curing. Flexural strength test was accessed to compare the flexural properties while X-Ray Diffraction (XRD) analysis was performed to determine the phase transformation of thin geopolymers at elevated temperature. Results showed that application of heat treatment boosted the flexural properties of thin fly ash geopolymers as the flexural strength increased from 6.5 MPa (room temperature) to 16.2 MPa (1150°C). XRD results showed that the presence of crystalline phases of albite and nepheline contributed to the increment in flexural strength.

*Keywords:* thin geopolymer; fly ash; elevated temperature; flexural strength

## 1. Introduction

Geopolymers which commonly referred as inorganic polymers are a broad class of materials synthesised by alkali activation and polycondensation of aluminosilicates in alkaline medium [1-8]. Amorphous gel with short-range ordered arranged in three-dimensional structure [9,10] was formed as the product from the reaction of aluminosilicates with the alkaline solution. This enables geopolymers to possess wide range of physical and mechanical properties and increase the versatility in utilisations which ranging from conventional binders to high temperature resistant materials [11,12].

Several researches had been studied to evaluate the thermal properties of geopolymers towards elevated temperature [13-15]. Studies found that geopolymers exhibit excellent thermal properties. When extended heating is applied, geopolymers would not ignite and incombustible. Geopolymers also possess superior thermal stability as no smokes or toxic gases were released when geopolymers were on fire. Thus far, the flexural properties of geopolymers reported in the past studies was considerably low at room temperature [16]. These impressive thermal properties of geopolymers aforementioned proved that the implementation of heat treatment on geopolymers could improve the flexural properties of geopolymers. The enhancement in flexural properties could further widen the application of geopolymers towards various fields.

The superior thermal stability of geopolymers with good thermal properties and fire resistance not only enable geopolymers to withstand high temperature, but also enhance its mechanical properties. Sakkas et al. [17] figured out that the strength and toughness of potassium based geopolymers increased with the exposure of high temperature. The alkali activation of fly ash geopolymers was enhanced and excellent strength retention was achieved after heating at higher temperatures from 100°C to 800°C. Kong et al. [18] observed a rise in strength when the fly ash geopolymers activated by sodium silicate and potassium hydroxide was heat treated at 800°C. Besides, Schmücker & MacKenzie [19] analyzed polysialate geopolymers that heated upon 1200°C using Energy Dispersive Spectrometry (EDS), and found that the geopolymer matrix compositions remained stable and unchanged.

Furthermore, the exposure of geopolymers towards elevated temperature could lead to the phase transformation and densification happen in the geopolymer structure. Ranjbar et

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al. [20] observed that phase transitions occurred in fly ash geopolymers which exposed to elevated temperature. Crystalline nepheline ($NaAlSiO_4$) was formed when the geopolymer was subjected to 800°C while quartz remained as the major phase and mullite was still found in the XRD pattern. The formation of these crystalline phases results in the increment of strength of geopolymers [21].

Thus far, past studies reviewed that fly ash geopolymer possessed low flexural strength at room temperature which constraints the utilisation of geopolymers such as tile industry, floor imprint, concrete and beams. The implementation of heat treatment has the potential in enhancing the flexural properties of geopolymers. This paper reports on the flexural properties of thin neat (without addition of fillers or aggregates) fly ash geopolymers at elevated temperature as this field of study is still less explored. XRD analysis was accessed to evaluate the relationship between the phase transformation and physical and flexural properties of thin fly ash geopolymers.

## 2. Methodology

### 2.1. Materials

The source of aluminosilicate used in this study was fly ash from Sultan Azlan Shah Power Station, TNB Janamanjung Sdn. Bhd., Seri Manjung, Perak, Malaysia The X-Ray Fluorescence (XRF) analysis (TABLE 1) stated that the fly ash composed of 56.30% $SiO_2$, 28.00% $Al_2O_3$ and 3.89% CaO. It was classified as Class F (ASTM C618). The chemical composition of sodium silicate solution ($Na_2SiO_3$) was 30.1% $SiO_2$, 9.4% $Na_2O$ and 60.5% $H_2O$ with 3.2 modulus $SiO_2/Na_2O$, 0.4 Pa·s viscosity and 1.4 specific gravity at 20°C. The sodium hydroxide solution was prepared using caustic soda pellets with 97.0% purity.

TABLE 1

Chemical composition of fly ash by XRF

| Compound | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | $TiO_2$ | $K_2O$ | Others |
|---|---|---|---|---|---|---|---|
| Mass (%) | 56.3 | 28.0 | 6.86 | 3.89 | 2.17 | 1.49 | 1.29 |

### 2.2. Thin geopolymer formation

The liquid alkali activator was first prepared by mixing liquid $Na_2SiO_3$ with 12M NaOH solution using 4.0 $Na_2SiO_3$/NaOH ratio. Then, solid fly ash was mixed with the liquid alkali activator with solid/liquid ratio of 2.5. After achieving homogenous slurry, it was casted and compacted into the moulds (dimension of 160 × 40 × 10 mm). The thin geopolymers were then cured in oven at 60°C for 6 hours followed by curing at ambient temperature for another 24 hours. After curing, the thin geopolymers were kept at ambient temperature for 28 days before heat treatment.

### 2.3. Heat treatment

The thin geopolymers were then heat-treated at 300°C, 600°C, 900°C and 1150°C after 28 days. The upper boundary of heat treatment temperature was set at 1150°C as the thin geopolymer would melt beyond that (Fig. 1). The heating rate was set at 3°C/min with soaking time of 2 hours. A set of geopolymers was left unexposed to high temperature for comparison purpose.

Fig. 1. Thin fly ash geopolymers heated beyond 1150°C

### 2.4. Testing and Analysis

The bulk density measurement was obtained by measuring the mass and dimension of the samples according to BS EN 12390-7. The water absorption was measured by the wet mass (immersed in water for 24 hours) and dry mass (heated 100°C in oven for 24 hours) while apparent porosity was measured by the wet mass, dry mass and suspended mass (after immersed in water for 24 hours) based on ASTM C642.

The flexural strength of thin fly ash geopolymers was evaluated using Instron Machine Series 5569 Mechanical Tester in accordance with ASTM C348. The span length used was 110 mm with crosshead speed of 1 mm/min. 5 samples were tested for each temperature to obtain the average flexural strength of the thin geopolymers.

The phase of fly ash and thin fly ash geopolymers at different elevated temperature was identified using model of D2 Phaser, Bruker X-Ray Diffractometer. The samples were examined with scan range 10-80° and scan rate of 2° per minute. The XRD pattern was analyzed using X'pert High Score Plus software equipped with ICDD PDF-2 database.

## 3. Result and discussion

### 3.1. Physical observation

Fig. 2 shows the physical image of thin fly ash geopolymers heat-treated at different elevated temperatures. The thin fly ash

geopolymers experienced colour changes from grey to reddish-orange and then dark red with increasing temperature. These changes of colour were associated with the iron oxidation and carbon loss in fly ash geopolymers [22].

Besides, cracks are observed on the surface of thin fly ash geopolymers exposed at 900°C (Fig. 2d). The cracks formation was caused by escape of water vapour from the fly ash geopolymer [23]. Dehydration process of $2(SiO_3^{2-}.2M^+) - OH \rightarrow (SiO_3^{2-}.2M^+)_2.O + H_2O$ released gaseous $H_2O$ which results in an unconstrained expansion of volume and causes the formation of cracks [24]. Furthermore, the increase in elevated temperature may cause possible changes in phase that result in an increased volume [25]. Thus, the crack developed into larger surface area when temperature increases. However, there is no crack observed on the surface of sample heat-treated at 1150°C (Fig. 2e). The cracks are said to be healed as the temperature increases 1150°C. Rickard et al. [26] reported that the further increment of elevated temperature could heal the crack induced during the dehydration phase.

### 3.2. Bulk density, apparent porosity and water absorption

Fig. 3 illustrates the bulk density, apparent porosity, and water absorption of thin fly ash geopolymers at elevated temperatures. Generally, exposure of elevated temperature causes in the bulk density of thin geopolymer. The unexposed fly ash geopolymers kept at room temperature experienced insignificant change in bulk density. Nevertheless, the bulk density loss of fly ash geopolymer increases as the exposure temperature increases. This is due to the liberation of water from the structure of geopolymer which thus weakens the geopolymer structure. As the results, it caused the thermal shrinkage of geopolymer samples at elevated temperature [27].

From Fig. 3, both the apparent porosity and water absorption results share the similar trends as the porosity of is correlated with the water absorption [28]. The porosity and water absorption decrease when temperature rises until 600°C. This is because further geopolymerisation reaction occurs during the extended heat

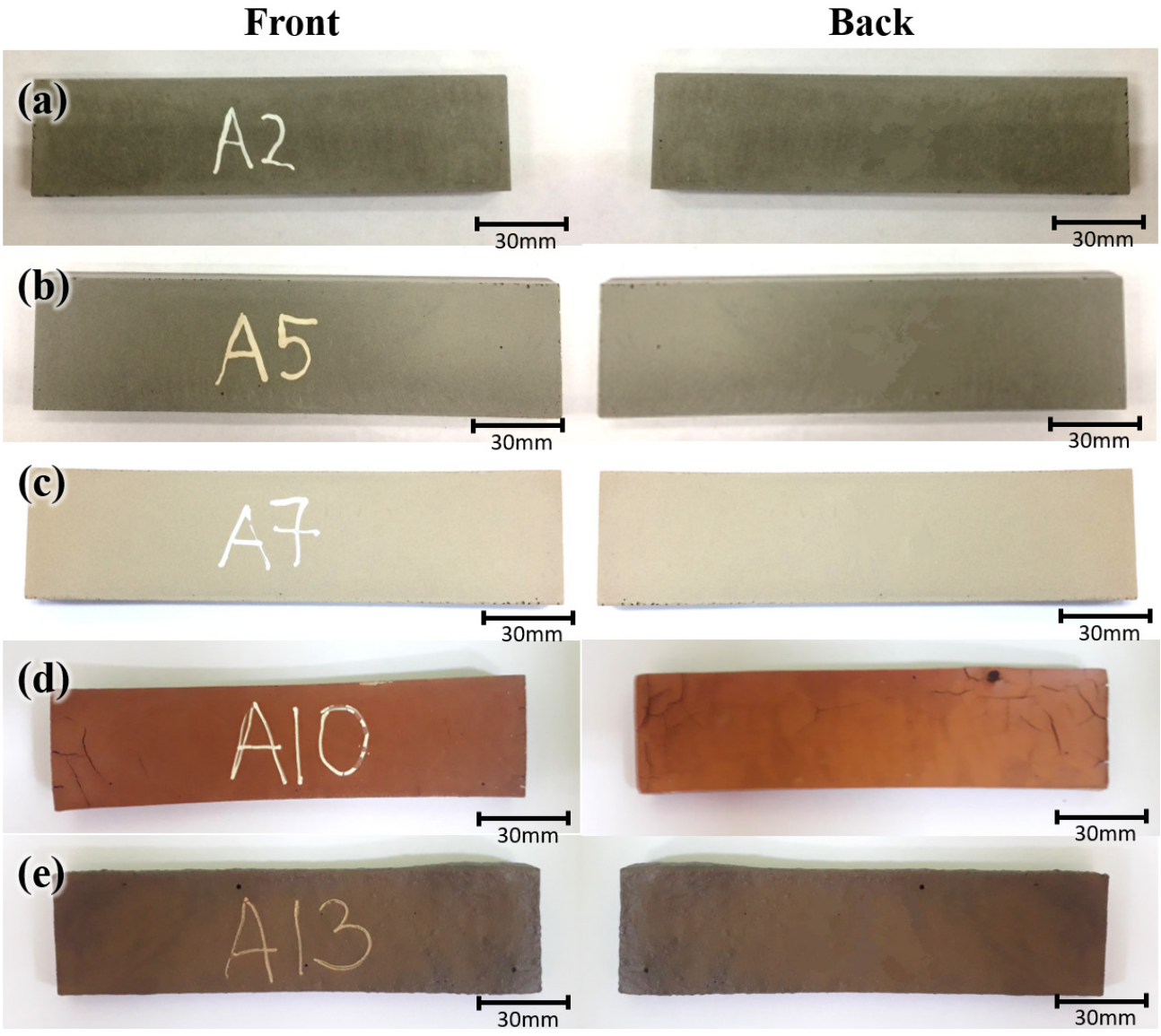


Fig. 2. Physical images of (a) untreated and heat-treated fly ash geopolymers at (b) 300°C, (c) 600°C, (d) 900°C and (e) 1150°C

curing [29]. Heat facilitated the progress of geopolymerisation towards formation of more geopolymer matrix with less pores.

However, the porosity and water absorption of fly ash experiences a dramatic increment as the elevated temperature reaches 900°C. Consequently, the fly ash geopolymers exposed at 900°C shows the greatest bulk density loss. The high temperature deteriorates the homogeneous aluminosilicate gel matrix and led to the formation of porous structure due to the escape of water molecules which is supported by Abdulkareem [30] and Mandal [31]. This also complied with the surface cracking observed in Fig. 2. In whilst, the porosity and water absorption of fly ash geopolymer reduced at 1150°C as the solidifying melt occurs in the geopolymer matrix and produces a more compact structure [32].

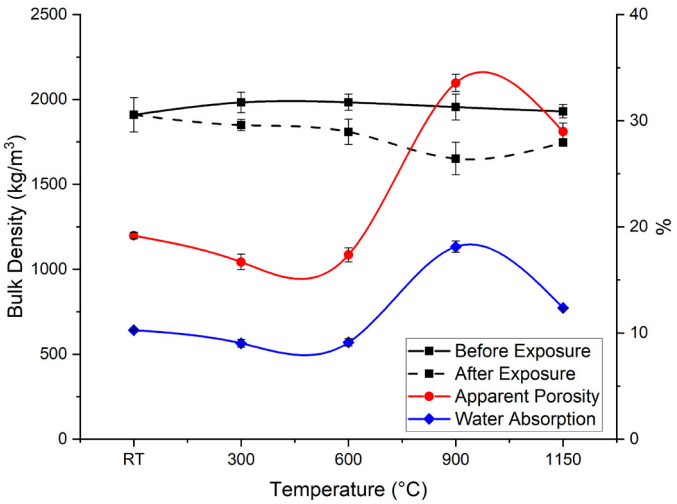


Fig. 3. Bulk density, apparent porosity, and water absorption of thin fly ash geopolymers at elevated temperatures

### 3.3. Flexural strength

Fig. 4 shows the flexural strength of heat-treated thin fly ash geopolymers at elevated temperatures. The application of heat treatment on fly ash geopolymers caused changes in the flexural strength of fly ash geopolymers. Generally, the flexural strength increases with the increase of elevated temperature. This increment in strength is attributed to the exothermic reactions [33], in which is the occurrence of further geopolymerisation that helps converting the unreacted precursor materials into reaction products.

The fly ash geopolymers experienced a dramatic rise in flexural strength at 1150°C with the highest flexural strength of 16.2 MPa. This sharp increment in strength is due to the densification of the geopolymer structure caused by the solidifying melt in the microstructure and formation of more refractory phase in the fly ash geopolymers [31,32]. A more compact structure was formed from the solidifying melt process in the geopolymer matrix contributes to the high strength performance [34].

On the other hand, there was slight drop in flexural strength for 900°C-heat-treated fly ash geopolymer with the value of 6.6 MPa. The flexural strength result is in parallel with the reduction in bulk density of geopolymers and increment in porosity (Fig. 3). The loss of water due to dehydration led to pore formation in the geopolymer structure consequently decreases the flexural strength. Besides, the drop in flexural strength is also associated with the visible cracks formation of observed in Fig. 2 which initiated the damages in thin fly ash geopolymers [35].

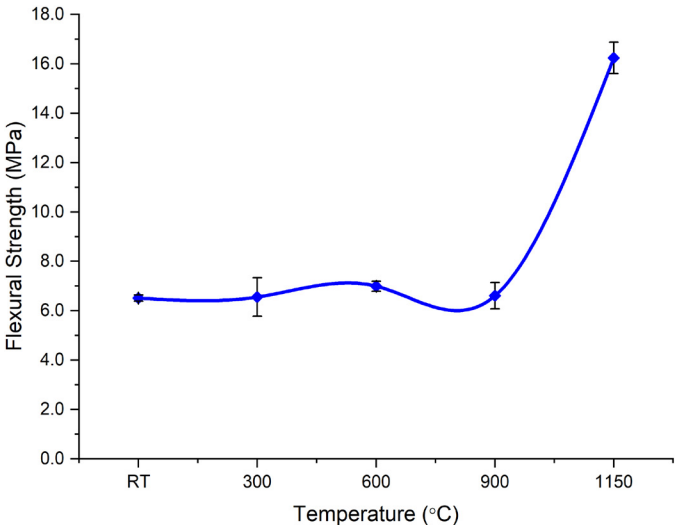


Fig. 4. Flexural strength of thin fly ash geopolymers at different elevated temperature

### 3.4. Phase analysis

Fig. 5 shows XRD patterns of fly ash and thin fly ash geopolymers after exposed to different elevated temperatures. The major peaks found in fly ash and untreated fly ash geopolymers are quartz ($SiO_2$), mullite ($3Al_2O_3{\cdot}2SiO_2$) and hematite ($Fe_2O_3$). The vitreous phase of the original ash, which is represented by the broad hump (at 15-30°) was shifted slightly to 20-40° (2θ) values after alkali activation. This shifting of phase is associated to the formation of an alkaline aluminosilicate hydrate (N-A-S-H) gel, the primary reaction product of geopolymerisation reaction in the diffraction patterns of geopolymeric materials [36]. The crystalline phases (quartz, mullite) detected in the original ash remained apparently unaltered with geopolymerisation [37].

In general, the propensity towards the formation of stable crystalline phases increases with the increasing elevated temperature [38]. From Fig. 5, the intensity of quartz and mullite started to decrease and transformed into new crystalline phases as the temperature increased. Crystalline phases of albite ($NaAlSi_3O_8$) and nepheline ($NaAlSiO_4$) could be observed in fly ash geopolymers at temperature above 900°C.

The formation of crystalline phases in fly ash geopolymers is believed to influence the mechanical properties of fly ash geopolymers. The presence of crystalline phases at high temperature contributes to the formation of ordered and densified structure [39-41]. The crystalline phases were mostly found in thin fly ash geopolymers heated at 1150°C which indicates

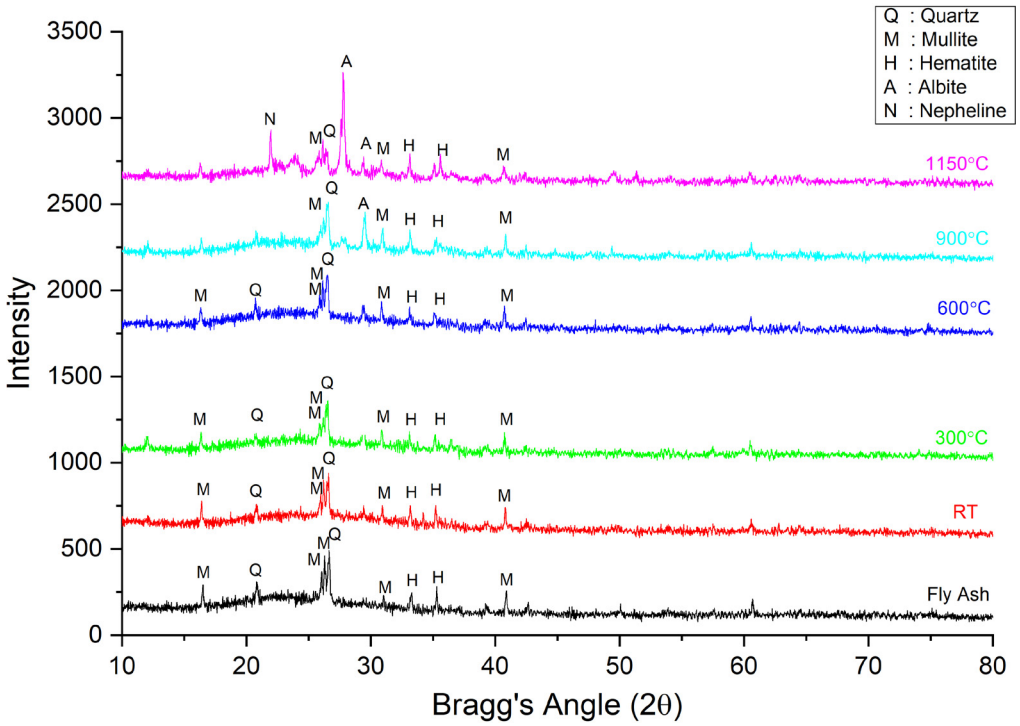


Fig. 5. XRD diffractogram of fly ash and thin fly ash geopolymers at different elevated temperature

a more compact and densified structure is present. This compact structure boosted the flexural strength of thin geopolymers which was well translated in the flexural results obtained in Fig.4. Stronger bonding strength is achieved via phase transformation at high temperature due to the crystallisation of amorphous geopolymeric gel. However, there is still a slight drop in flexural strength for sample heat-treated at 900°C even though the phase transformation began at 900°C. This reduction in strength was associated with the crack formation in the geopolymers as shown in Fig. 2.

Furthermore, the crystalline phases could act as filler in the geopolymer structure [42]. The reinforcement of filler helps increased the flexural strength of thin geopolymers. Rickard et al. [43] reported that the formation of nepheline at high temperature could increase the strength of geopolymers. The application of heat treatment causes the phase transformation that densified the geopolymer binder structure and hence enhanced the inter-particle connectivity.

## 4. Conclusion

In this study, the flexural properties of thin fly ash geopolymers at elevated temperature was evaluated. The implementation of heat treatment helps enhanced the flexural strength of thin geopolymers. The flexural strength of thin fly ash geopolymers increased with the increasing temperature and experienced a dramatic rise to 16.2 MPa at 1150°C. XRD results showed that the presence of crystalline phases of albite and nepheline contributed to the increment in flexural strength. Besides, a slight drop in flexural strength was observed on thin fly ash geopolymers exposed to 900°C. This drop in strength was associated to the reduction in bulk density due to pore formation and crack formation on the surface of thin geopolymers which initiated the damage of thin geopolymers.

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