

## Effect of particle size of fly ash and solid to liquid ratio on microstructure and mechanical properties of geopolymer

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**Abstract.** This paper describes the effect of particle size of fly ash and solid to liquid ratio on the microstructure and flexural strength of fly ash geopolymer for coating applications. Sodium hydroxide concentration of 12 M was used for the preparation of geopolymers. The mechanically activated fly ash was divided into two parts based on the particle size (MFA A (11.81  $\mu\text{m}$ ) & MFA B (8.59  $\mu\text{m}$ )). The decrease of particle size of fly ash and increase of S:L ratio produced dense and compact geopolymer which is due to the increase of reactivity of fly ash with the decrease of particle size and increase of water content. The decrease of particle size increased the flexural strength of geopolymer from 13.39 MPa (OFA-1) to 23.84 MPa (MFA B-III). The decrease of S:L ratio showed irregular trend with optimum flexural strengths of 13.39 MPa, 16.74 MPa, and 23.84 MPa obtained for OFA-1, MFA A-II, and MFA B-III respectively. The optimum flexural strength of 23.84 MPa was obtained. The mechanical activation is a useful technique to increase the reactivity of fly ash and produce dense and compact geopolymer with higher flexural strength.

### Introduction

Geopolymers are inorganic polymer materials introduced by J. Davidovits in 1979 [1,2]. In geopolymer preparation, aluminosilicate materials provide silica and alumina, the major building blocks of geopolymer network which can be obtained naturally (kaolin, metakaolin) and from industrial byproducts (fly ash, slag and etc.) [3]. Alkaline activation by sodium hydroxide (NaOH) and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) or mixture of the two dissolves the reactive species of silicate and alumina ions from aluminosilicate source materials via dissolution. Subsequently, polycondensation forms the aluminosilicate gel where the last stage involves rearrangement and reorganization of the network resulting in 3D geopolymer network comprising of tetrahedral  $\text{SiO}_4$  and  $\text{AlO}_4$  [1, 2].

Geopolymers are considered as green and sustainable materials due to low  $\text{CO}_2$  production during their synthesis and they can be produced from various waste or byproduct materials such as coal fly ash, slag, and others. The excellent properties of geopolymers such as high early strength [12], resistance towards aggressive environment [13,14], stable at high temperature and long-term durability [15,16] makes it a prominent material in structural (geopolymer brick, cement, concrete etc.) and nonstructural applications (coating, soil stabilizer, radioactive and heavy metals waste treatment etc.). Geopolymer as a coating material has been used for metal

plates and urea fertilizer [3, 4]. Investigation on the mechanical properties is crucial to evaluate the capability and performance of geopolymer in handling sudden impact and prolonged exposure to load. Flexural strength plays an important role in the coating application of geopolymers.

Many studies have been conducted on the increase of flexural strength of geopolymers using various techniques such as increase of NaOH concentration, reinforcement by reduced graphene oxide (rGO), wollastonite ( $\text{CaOSiO}_2$ ), additively manufactured metallic rebars (Ti6Al4V), steel fibres, steel and polymer fibre, self-assembled nanofiber networks, and graphene oxide/geopolymer nanocomposite [1, 5-13]. However, no study has focused on the improvement of flexural strength of geopolymer by particle size reduction of fly ash through mechanical activation. Therefore, this study determines the effect of particle size of fly ash and different solid to liquid (S: L) ratios.

This paper describes the effect of particle size reduction of fly ash and variation of S:L ratios on flexural strength of fly ash geopolymer and microstructure. S:L ratio in the range of 3:1-2.2:1 was used to synthesize geopolymer.

### Materials and Methods:

Materials: Class F fly ash obtained from a local coal thermal power plant located in the northern region of Malaysia was utilised for the synthesis of geopolymer. Chemical composition of fly ash is shown in Table 1. Sodium hydroxide (NaOH) and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) were purchased from Merck in pellet form with 99% purity.

Table 1: Chemical Composition of fly ash [14]

Oxide	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
Composition (wt%)	40.8	35.4	1.86	3.71	0.69	2.96	1.36

### Methods

Mechanical activation: Original fly ash (OFA) was subjected to pre-treatment via mechanical activation which produced mechanically activated fly ash (MFA). High energy planetary ball mill (FITSCH, Pulverisette 5 classic line) was used for mechanical activation which consists of two milling slots of stainless-steel jar (250 ml capacity) and 5 mm diameter of stainless-steel balls as the grinding chamber and media respectively. The mill was run at 1300 W full rated power of the milling motor engine capacity and operating voltage of 200-220 V. Dry mechanical milling method was implemented where 150 g of grinding media was first loaded into each of the grinding chambers followed by the fly ash and subsequently closed with the lid that comes together with a Teflon seal then tightened and clamped with the safe locks. The hood of high planetary ball mill was closed and automatically locked as the process began. Milling operation was performed in accordance with the parameters; Ball-to-powder (BPR) weight ratio, residence time of mechanical activation, and revolution speed as summarized in Table 2. Throughout the process, impact and collision occurred in the chamber causing the heat to build up. Cooling interval was allowed to take place with 3 min pause for every 15 min of continuous milling to prevent overheating. When the grinding process completed, the ground fly ash was separated from the grinding media. Fine sand grinding at slow operational speed carried out at moderate time also helped in removing any remaining samples attached to both chambers and media. Later they were cleaned with water, dried, and kept in a dry place. Finally, mechanically activated fly ash (MFA) with particle size of interest was characterized and used in the preparation of geopolymer.

*Table 2: Operational parameters of mechanical activation*

Revolution speed (rpm)	Ball to powder ratio (BPR)	Residence time (min)
300	2:1, 3:1, 4:1, 5:1, 6:1	60

### *Synthesis of geopolymer*

The 12 M alkaline solution was prepared by dissolving NaOH pellets in distilled water, the desired quantity of sodium silicate was also added into the alkaline solution. Fly ash and alkaline solution mixed in a plastic container using overhead mechanical mixer (IKA RW20 Digital) for 10 minutes. Geopolymer samples were prepared at varying S:L ratios as described in Table 3. Geopolymer slurry was put into the mould and cured at 80 °C for 24 hours in an electric oven.

*Table 3: Composition of fly ash geopolymer samples*

S: L ratio (by weight)	Code	Sample Codes		
		OFA (15.33 $\mu\text{m}$ )	MFA A (11.81 $\mu\text{m}$ )	MFA B (8.6 $\mu\text{m}$ )
3:1	I	OFA-I	MFA A-I	MFA B-I
2.8:1	II	OFA-II	MFA A-II	MFA B-II
2.6:1	III	OFA-III	MFA A-III	MFA B-III
2.4:1	IV	OFA-IV	MFA A-IV	MFA B-IV
2.2:1	V	OFA-V	MFA A-V	MFA B-V

### *Microstructural characterization*

Microstructural images of fly ash geopolymer samples were captured by scanning electron microscope (Phenom Pro X). The specimen was directly mounted onto the clamping device on the sample holder by adjusting the gap of 4 mm for the sample prior to analysis. Deposition of any conductive layer of metallic coating was not required as the sample holder was specifically designated as metallurgical charge reduction. Microscopic examination of the samples was done using an operating set up of 2.00 kV EHT acceleration voltage and magnification from 300 X to 5000 X.

### *Flexural strength of geopolymer*

Flexural strength of prepared geopolymer samples was investigated using Universal Testing Machine (UTM), model series of AI-7000S, GOTECH with 5 kN load capacity. The flexural test was performed as per specified in ASTM D790, adopting a three-point bending fixture method with a centre loading. Rectangular bar shape specimens with dimensions of 127 mm length, 12.7 mm height and 3 mm wide were produced by casting the geopolymer paste onto the acrylic mould as depicted in Fig.1. The cured and hardened geopolymer bar specimen was loaded and horizontally aligned on the 48 mm length of the support span. The test was run with the crosshead speed of 1.28 mm/min and the results were recorded and analysed with software (U60) equipped with the UTM. Replicates of 5 geopolymer specimens were tested and the average was taken as the result.

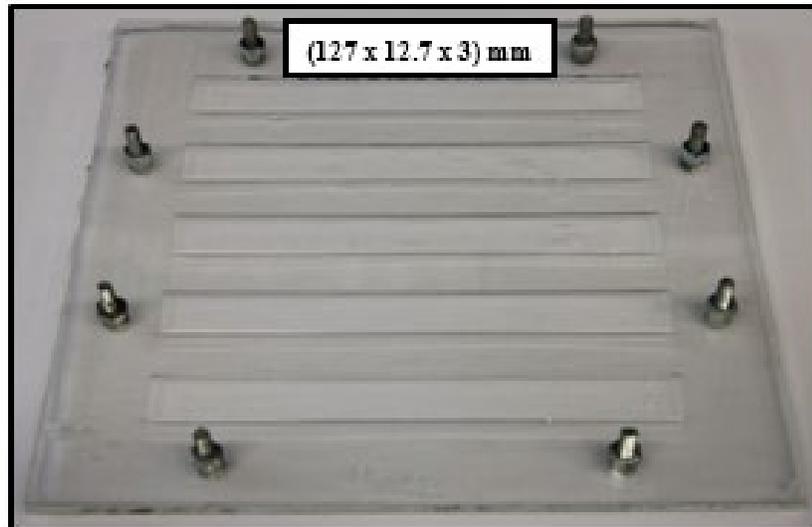


Figure 1: Acrylic mould for flexural strength sample

## Results and Discussion

### *Microstructure of mechanically activated fly ash geopolymer*

Morphological and microstructural characteristics of OFA, MFA A, and MFA B based geopolymer samples prepared at varying S: L ratios are shown in Fig. 2 (a-c). Fly ash geopolymer samples are only shown at highest S:L ratio of 3:1. Generally, dense, and compact microstructure was obtained at higher S: L due to higher degree of reaction while incomplete or moderate degree of geopolymerisation resulted in the formation of loose microstructure with the emergence of voids or cavities as well as the presence of considerable large portion of unreacted and partially reacted fly ash particles at lower S:L ratios.

Geopolymer samples show heterogeneous microstructure consisting of geopolymer gel with traces of unreacted and partially reacted fly ash particles as shown in Fig. 2 (a-c). The appearance of voids and cavities in geopolymer microstructure could be due to the air bubbles that were appeared during mixing or from the water molecules entrapped in the gel. As the specimens were cured, the water or moisture eventually evaporated leaving a hollow shaped space (voids).

Samples prepared at higher S:L ratio (MFA A-I) displayed more unreacted and partially reacted particles embedded within the geopolymer matrix. For MFA B based geopolymer, it is worth noting that, though geopolymer matrix still coexists with unreacted and partially reacted fly ash particles, the amount is considerably less than that of OFA and MFA A based geopolymers. Moreover, it is evident that high formation of geopolymer with better microstructure where more uniform geopolymeric gel is produced as shown in Fig.2(c). It can be inferred that geopolymerisation occurred at higher degree and way more efficiently with fine fly ash particles.

According to Cheng et al. high S:L ratio caused the increase of oligomer size which affected the exchange kinetics of the silicate unit during geopolymerisation [15]. This lead to increase of viscosity and subsequently reduced the workability of geopolymer mixture [16]. Low workability cause difficulties in moulding and compacting the mixture during sample preparation, consequently, results in porous and non-uniform microstructure. Addition of water would enhance the workability allowing the mixture to flow nicely in the mould and compact easily. Thereby, avoiding the presence of air bubbles that may cause the formation of voids. However, excessive liquid is undesirable as it also could result in highly porous geopolymer structure due to inefficient geopolymerisation caused by the gap created by the water molecules that hinder the formation of geopolymer network. These results are consistent with literature findings [17, 18].

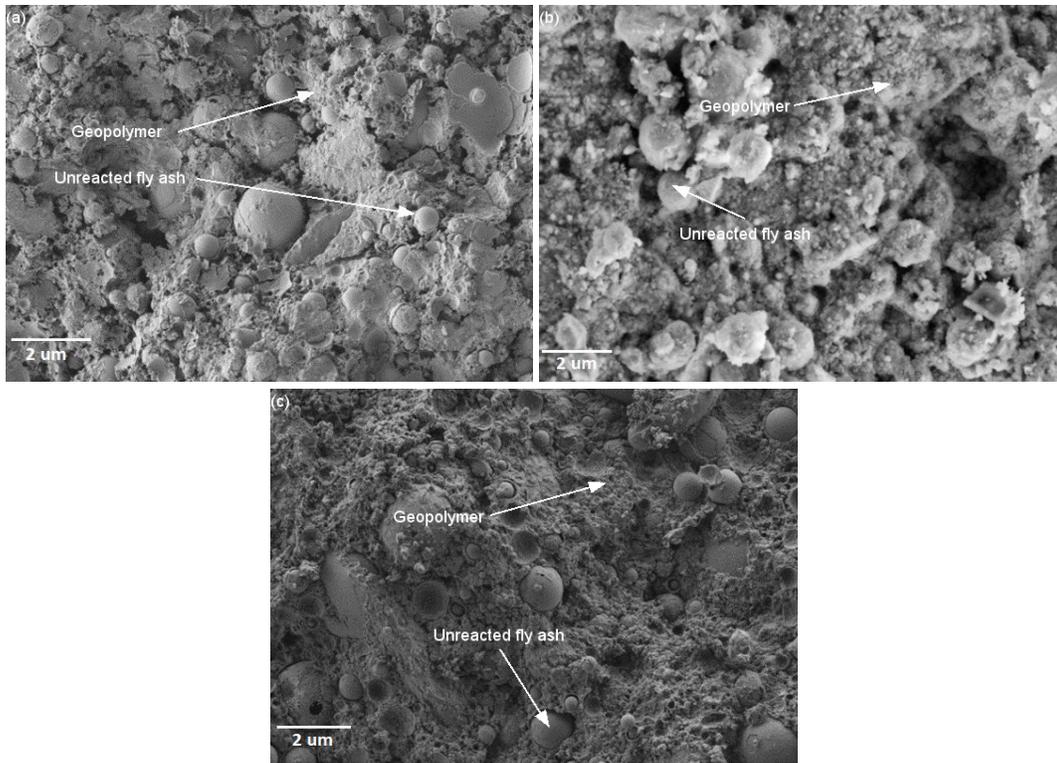


Figure 2: Microstructure of fly ash geopolymer (a) OFA-I, (b) MFA A-I, (c) MFA B-I.

#### *Mechanical properties of mechanically activated fly ash geopolymer*

Flexural strength of geopolymer samples is shown in Fig.3. The low S: L ratio negatively affected the quality of geopolymer as shown in OFA based geopolymer where flexural strength dropped from 13.39 MPa to 4.65 MPa. The low S: L ratio indicates high water content. Water does not take part in the chemical reactions involved during geopolymerization, thus excessive amount of water results in the dilution of NaOH activator and consequently lowers the concentration. It has been noticed that strong alkalis are required to completely or partially dissolve aluminosilicate source materials [19]. Dilution of alkali solution by addition of water hinders the interaction of fly ash particles with  $\text{Na}^+$  and  $\text{OH}^-$  and hampers the dissolution process of Si and Al active species. Furthermore, water also serves as the medium in transporting the dissolved active species (Si and Al) to form geopolymer network with other active species. However, high amount of water molecules reduces the particle-to-particle reaction and the active species are unable to form the geopolymer network [20]. Delayed dissolution process and inefficient formation of geopolymer network, affect the quality of geopolymer. It was evidently confirmed by microstructural analysis where porous geopolymer was obtained at low S: L ratio. The presence of pores and voids produces a less compact geopolymer and eventually results in lower flexural strength.

Conversely, for MFA A and MFA B based geopolymer, decrease of S: L ratio improved the flexural strength up to a certain point before it dropped. Similar trend was also exhibited in microstructural results. The MFA A-I and MFA A-II displayed an increase in flexural strength from 15.39 MPa to 16.74 MPa, respectively. As the specimen prepared from highly reactive fine particle of MFA A, the hardening process occurred rapidly especially when using high S: L ratio. Shorter setting time had caused the geopolymer slurry to lose its workability. Lower tendency in achieving homogenous mixture as well as difficult moulding process resulted in imperfect structure of MFA A-I, consequently lower flexural strength.

Water added to the system managed to improve the workability which allowed better formation of geopolymer structure and further enhanced the mechanical strength of geopolymer as shown by MFA A-II. Nonetheless, geopolymer prepared from lower S: L ratio of 2.6:1 to 2.2:1 showed gradual decrease in flexural strength from 10.14 MPa to 5.76 MPa, respectively owing to a highly porous geopolymer microstructure. Since MFA B possessed smaller particle size, lower S:L ratio is much desirable in producing geopolymer with better quality. This can be observed by the increasing flexural strength from 18.94 MPa (MFA B-I) and 20.32 MPa (MFA B-II) to 23.84 MPa (MFA B-III). When fine fly ash was mixed with the activator solution at high S:L ratio, thick geopolymer slurry was formed instantaneously due to its high reactivity. High viscosity of geopolymer slurry is less workable and led to the formation of low quality geopolymer specimen which causes the low strength of MFA B-I. More liquid was required for MFA B based geopolymer to prolong the setting time to extend the dissolution process of Si and Al species. Therefore, higher reaction degree may occur with intense formation of geopolymer network which resulted in improved geopolymer formation and subsequently enhanced the strength development as shown by MFA B-II and FA B-III. Nevertheless, the decrease of flexural strength was shown for sample MFA B-IV and MFA B-V with 19.47 MPa and 10.42 MPa, respectively when prepared at too low S: L ratio.

The influence of fly ash particle size was clearly visible where major strength was attained when geopolymer produced from the finest fly ash in this research which is MFA B. The highest strength achieved in OFA based geopolymer batch was OFA-I with 13.39 MPa, which was prepared at the highest S: L ratio of 3:1. Meanwhile, further increase in flexural strength was observed by geopolymer prepared from MFA A as shown by MFA A-II with 16.74 MPa, the highest in the batch. It is worth to note that, though produced from slightly lower S:L ratio (2.8:1), the strength of MFA A-II is better than OFA-I which was synthesised from 3:1 ratio. Finally, the ultimate flexural strength in MFA B batch was demonstrated by MFA B-III with 23.84 MPa which was prepared at much lower S: L ratio (2.6:1). Larger fly ash particle was deemed to be inert with low surface area. When subjected to mechanical activation, smaller fly ash particle size distribution was obtained. This allows higher reaction degree of geopolymerisation and more network formation [21]. It enables the production of geopolymer with denser microstructure and higher mechanical strength. These findings agree with those reported in literature [22, 23].

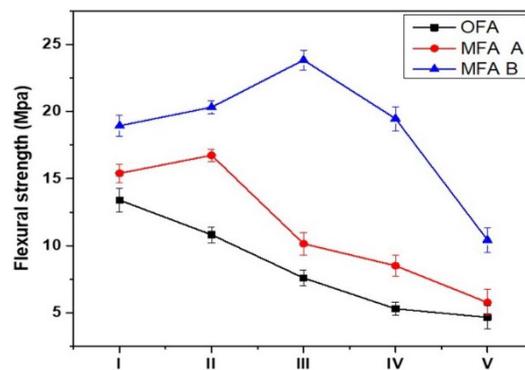


Figure 3: Flexural strength of OFA, MFA A and MFA B based geopolymer

## Conclusions

The mechanical activation of fly ash decreased the particle size and resulted in the formation of dense and compact geopolymer with higher flexural strength. The increase of S:L ratio (2.2:1-3:1) resulted in the increase of geopolymer formation with dense and compact geopolymer microstructure. The highest flexural strength of 23.84 MPa was obtained from MFA B-III. The future work can be conducted on the use of different nanomaterials to see their effect on microstructure and mechanical strength of geopolymer.

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