Thermal Exposure of Fly Ash-Metakaolin Blend Geopolymer with Addition of Monoaluminum Phosphate (MAP)

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Abstract. Recent research reveals that formulation of blended geopolymers based on the association of two aluminosilicate precursors had a better performance than one precursor geopolymers. This study presents a facile method to enhance the compressive strength of fly ash-metakaolin blend geopolymer by incorporating monoaluminum phosphate (MAP) during the geopolymerization reaction. The effect of the thermal exposure on the microstructure and compressive strength of the geopolymer are investigated. Results show that the MAP is transformed to granule structures, bonded and surrounded by geopolymer gel. The unique microstructure increases the compressive strength of the room temperature curing geopolymer from 54.7 MPa to 64.21 MPa (14.8%) with an optimum addition of 1.0 wt% MAP. This enhancement in compressive strength was ensured by the formation of an amorphous structure of aluminosilicophosphate (SiO₂.Al₂O₃.P₂O₅.nH₂O) phase. At higher temperatures, the formation of stable crystalline phase of berlinite and nepheline contribute to strength retention of the geopolymer. Hereby, it can be concluded that the addition of 1.0wt% MAP in the geopolymer reinforced the structure.

1. Introduction
Geopolymers have been proposed as alternative building materials to Ordinary Portland Cement (OPC). A wide variety of aluminosilicate materials could be possible sources for geopolymer synthesis depending on their mineralogical composition, particle size and others [1-5]. The main common raw materials used to develop geopolymer precursor can be natural origins (metakaolin [6]) or wastes (e.g. industrial ashes [7-9] or slag [10, 11]). Previous studies [12-17] have shown that geopolymers are superior in mechanical strength, chemical resistance, low shrinkage and long-term durability than OPC. These characteristics favour their use in many applications: toxic waste immobilization, sealing, building and high temperature-resistant materials [18-20]. In a study by Nazari et al.[18], the testing found that as the temperature increased to 400°C, the fly ash geopolymer experienced an increase in compressive strength. Nevertheless, according to Saavedra and Gutirrez [21], fly ash-based geopolymer’s strength decreased consistently when subjected to the same type of testing.

There has been a lack of research on the compressive strength capabilities of geopolymer under high temperatures when adding admixtures or fillers such as slag, nano-silica, phosphate and nano-ZnO [18, 22]. Rashad et al.[14] studied the high-temperature performance of metakaolin geopolymer with addition of nano-silica. High strength retention is associated with activation and conversion of the more compact microstructure. They found that incorporation of 0.5% of nano-silica exhibited superior compressive strength after exposure to 1000°C in comparison with their counterpart without firing. Wu
et al. [23], found that the compressive strength of geopolymer concrete is reliant upon parameters such as the types and content of reinforcement fillers. Compared with other fillers, phosphates have many advantages, such as it is superior in terms of the thermal stability, mechanical properties and dielectric performance [23]. Different high-temperature phases are built, depending on the chemical composition of the geopolymer itself [24-26]. The phase transformation at high temperatures may also be influenced by the type of filler materials used.

Recent studies [6, 24] have shown that using phosphate improves the thermal stability is contributed by the phase transition of aluminium hydrogen phosphate to berlinite. Berlinite (AlPO$_4$) was observed when the geopolymers was subjected to elevated temperature above 600°C [19]. They addressed that berlineite effectively effect the mechanical and microstructural properties of the geopolymers. Contrarily, Tchakoute et al. [27] as well as Louati et al. [12] and Douiri et al. [28] claimed that crystalline phase of berlineite are formed at room temperature during geopolymerisation reaction. This statement was further supported by Wagh et al. [29] who stated that this crystalline compound is formed rapidly during the geopolymerization owing to the dealumination of precursor in acidic medium. According to Liu et al. [30], the thermal stability of geopolymer has been inspired by the research idea of replacing partially [SiO$_2$] by [PO$_4$] to form a Si-Al-P binder system. In the literature, it has rarely researched the effect of elevated temperatures on the strength of phosphate geopolymer.

In present study, the utilization of blended precursors in the formulation of geopolymers has been reported to have a better performance than one precursor geopolymers [31-32]. The use of geopolymer MK-FA mixtures in civil engineering increased, due to the availability of fly ash and inherent silica and alumina in metakaolin [33]. This article aims to figure out the thermal stability of fly ash-metakaolin blend geopolymer with monoaluminum phosphate (MAP) addition. The geopolymer were fabricated by adding MAP into fly ash-metakaolin blend during geopolymerization. The effects of the MAP content on the compressive strength, microstructural and phase transformation were studied in detail.

2. Methodology

The monoaluminium phosphate (MAP) powder, an industrial grade, was obtained from Sigma Aldrich, Selangor, Malaysia. It usually includes a mixture of different aluminum acid phosphates that have varying P/Al ratio (i.e., Al(H2PO4)3, AlPO4 and Al2(HPO4)3). Class F Fly ash and metakaolin (50-50) was used as blend aluminosilicate source. The fly ash was collected from Tapah Power Plant, Perak whereas the metakaolin is from Associated Kaolin Industries Sdn. Bhd., Malaysia. The chemical composition of fly ash and metakaolin as determined by X-Ray Fluorescence (XRF) analysis are given in table 1. The sum of SiO$_2$, Al2O3 and Fe2O3 contents of FA and MK are 84.3% and 96.33%, respectively. The FA is accompanied by low CaO content of 3.89%. According to ASTM C618 [34], the FA is classified as low-calcium FA (Class F) with CaO content <10%. The sodium hydroxide (NaOH) pellet used were the pellet type of Formosoda-P purchased from Formosa Plastic Corporation, Taiwan. The liquid sodium silicate was purchased from the South Pacific Chemical Industries Sdn. Bhd., Malaysia with chemical composition of 30.1 SiO$_2$, 9.4% Na2O and 60.5% H2O.

| Chemical composition (wt.%) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | TiO$_2$ | K$_2$O | ZrO$_2$ | MnO$_2$ | Others |
|-----------------------------|--------|-------------|-------------|-----|--------|--------|--------|--------|--------|
| Fly ash (FA)                | 56.3   | 28.0        | 8.66        | 3.89| 2.17   | 1.49   | 0.14   | 0.02   | 1.13   |
| Metakaolin (MK)             | 55.7   | 38.6        | 2.03        | -   | 0.78   | 2.43   | 0.04   | 0.04   | 0.28   |

2.1. Preparation of samples

The NaOH 10M solution was prepared and allowed to cool down to room temperature (RT- 30°C). A combination of fly ash and metakaolin (50-50) weight ratio were used throughout the process. The alkali activator was prepared by mixing liquid Na$_2$SiO$_3$ and NaOH solution. Then, the blend fly ash-metakaolin were combined with the alkali activator until a homogeneous paste was obtained. The geopolymer was compacted in 50-mm moulds and cured at RT until the day of testing.
of MAP were prepared with the weight ratios of 0, 1% and 3% (denoted as G-0wt.%, G-1.0wt.% and G-3.0wt.%, respectively). The dosage of MAP in G-0wt.% was the reference geopolymer and MAP was increased in the following series while, maintaining the solid-to-liquid (S/L) ratio of 1.2.

3. Results and Discussions

3.1. Compressive strength

R Compressive strength of the geopolymers at RT and after 200°C, 600°C and 1000°C exposures were illustrated in figure 1. The compressive strength of the reference geopolymer, G-0wt.%, at the age of 28th day is 54.7MPa. It could be apparently observed that the compressive strengths of geopolymer incorporated with 1.0wt.% MAP displayed the highest compressive strength of 64.2MPa. Therefore, the first significance of the reported data is that the compressive strength of geopolymer G-1.0wt.% is more than G-0wt.%, by 14.8% when tested at RT. The gradual participation of phosphate-containing phase during geopolymerization render that G-1.0wt.% slightly outperformed G-0wt.%. Therefore, it was concluded that the presence of Al and P in G-1.0wt.% permitted the formation of geopolymer at RT [28]. Further addition reaching a plateau at about 33.8MPa, for MAP content higher that 3 wt.% (G-3.0wt.%). This low compressive strength of G-3.0wt.% is attributed to the incomplete bonding of MAP in soluble particles into the geopolymeric structure formed.

Secondly, the exposure of G-0wt.% to the elevated temperatures results in a progressive strength loss of samples from 54.7MPa for RT tested samples to 9.1MPa for samples treated in 1000°C. Contrarily, the G-1.0wt.% becomes 1.5% stronger when exposed to 200°C and then starts weakening in strength after 600°C and 1000°C (table 2). The reason for such behaviour is the participation of unreacted fly ash and metakaolin in the geopolymerisation under elevated temperature exposure. According to Lahoti et al.[12], the evaporation of free water from the pores and capillary strain starts at temperature of 500°C. This implied that the removal of free water and crack formation adversely affect the strength.

Figure 1. Compressive strength of the fly ash-metakaolin blend geopolymers at various temperatures exposures (a) and the optical image of the geopolymer with 1.0wt% MAP after 1000°C exposure (b).

The constant strength loss of the reference geopolymer (G-0wt.%) under thermal exposures indicates that the addition 1wt.% of MAP enhanced the strength of geopolymer. It assigned to the filling effect of MAP particles which could fill the micro-crack and micro-pores in the geopolymer. Despite the lower reduction in strength as the temperature reach 1000°C, it is important to note that the geopolymers are stable and remain intact (figure 1). The strength change trend of geopolymer containing G-3.0wt.% are very analogous to that of G-1.0wt.% sample counterpart. In fact, the G-1.0wt.% geopolymer still retained the highest compressive strength of 11.8 MPa after 1000°C exposure. The high strength retention including suitable content of MAP could attributed to the filler effect of these particles amongst
the skeleton of the matrix. Vickers et al.[35] reported that the inclusion of filler led to general improvement in fire properties.

Table 2. Strength losses of three series of geopolymers.

| Temperature (ºC) | Strength loss (%) |
|-----------------|------------------|
|                 | G-0wt.% | G-1.0wt.% | G-3.0wt.% |
| 29              | -       | -         | -         |
| 200             | 23.4*   | Strength increase (1.5) | Strength increase (44.6) |
| 600             | 31.3    | 64.4      | 38.9      |
| 1000            | 68.8    | 49.1      | 46.6      |

3.2. Phase analysis

Figure 2 illustrates the X-ray diffraction patterns for raw materials of fly ash, metakaolin and MAP. The fly ash and metakaolin indicates the presence of the broad hump structure between 15-30º (2θ) with centered around 27º (2θ). The intensity of this broad hump structure is higher in the X-ray pattern of fly ash compared to the one of the metakaolin. According to Mo et al.[33], MK was more reactive than FA attributed to that the MK contained a higher quantity of aluminosilicate glass phase than FA. This statement was further confirmed by Lv et al.[36]. They testified that the hydration product of paste containing FA formed fewer contents of Al and Si owing to the lower reactivity in the reaction product matrix[37]. Several intense peaks of MAP can be assigned to the polymorphic aluminophosphate, such as aluminum hydrogen phosphate (Al(HPO₄)). Figure 2 presents the XRD patterns of the fly ash-metakaolin blend geopolymers (G-0wt.% and G-1.0wt.%) at RT and when it has been subjected to thermal exposures (200ºC, 600ºC and 1000ºC). XRD results clearly showed a reflection peak located at 25-35º (2θ) which related to the amorphous structure of the geopolymer[38-41]. Geopolymer samples of G-0wt.% and G-1.0wt.% synthesis at RT shows very similar peaks. The same phases, namely quartz, kaolinite, mullite and sillimanite, can be found in these samples.

Moreover, as shown in figure 2, quartz is the main crystalline phase in all geopolymer added with MAP, indicating abundant SiO₂ remain unreacted fully. With the exposure temperature increasing from RT to 200ºC, no new crystalline phase could be observed in XRD pattern. This indicates that the thermal stability of geopolymer added with MAP was determined by the properties of geopolymer itself rather than the new reactions during temperature exposure. It could be a side support that the filling effect of MAP and enrichment of gel phases contribute to the excellent thermal stability. When the temperature was elevated at 600ºC, berlinite (AlPO₄) were generated[27]. When G-1.0wt.% was exposed to 1000ºC, the enrichment and intensity of XRD peaks assigned to berlinite were further enhanced. It is worth noting that berlinite appears to be more ductile than quartz[42]. On the basis, quartz and berlinite have
identical crystal structures, but the Si atoms of quartz are replaced in berlinite by Al and P with sequence Al-P-Al.

Formation of nepheline and cristobalite could be seen in geopolymers (G-0wt.%) at high temperature exposure (1000°C). Commonly, these crystalline phases were formed at 800°C in heat-treated fly ash-based geopolymers [22]. Based on Lemougna et al. [24], nepheline phase is formed in sodium-based aluminosilicate. At 1000°C, mullite started to crystallize, probably from unreacted metakaolin leading to crystallization of residual SiO2 to cristobalite [42]. The crystallization of berlinite contribute to high residual compressive strength at elevated temperatures [27]. The concurrence in the phase evolution between the samples studied by Liu et al. [30] and in this work demonstrate that the number of crystalline phases reached maximum at 1000°C. This can occur because higher temperatures increase the internal pressure in the samples favoring the formation of these crystals. Therefore, it reinforced the structure of the samples after thermal exposure.

3.3. Microstructure analysis

The microstructures of G-0wt.% and G-1.0wt.% geopolymer before and after exposed to thermal exposures (200°C, 600°C and 1000°C) is presents in figure 3. Their amorphous textures displayed in G-1.0wt.% seemed to be more compact than G-0wt.%. The addition of 1.0wt.% MAP, obvious granules are found appeared in the smooth cross-section of the geopolymer. After the samples exposed to 200°C, its leads to rearrangement of the geopolymer matrix resulted from the removal of free and loosely bound water. This rendered the formation of geopolymer phases, considering as the fly ash and metakaolin had not fully reacted at RT. More compact with fewer voids and more intervening geopolymer matrix can be seen in G-1.0wt.% [22]. Conversely, large cracks can be seen in G-0wt.%. The possible reasons that could attributed for the crack can be due to the mechanical loading during the compressive strength test and uneven internal stress from the water evaporation during heating.

At the temperature of 600°C, the samples were mainly characterized by decomposition and crystallization events. It clearly showed that the thermal exposure at 600°C caused a significant reduction in unreacted materials for G-1.0wt.%. Besides, sintering effect was shown by the formation of connecting matrix. On the other hand, for G-0wt.% sample exposed to 1000°C, the appearance of intervening matrix was not seen but greater deterioration by heat. It was observed with pores microstructure indicates the formation of a melt fraction. The observation on the microstructure of fly ash-metakaolin blend geopolymer was supported by Sotiriadis et al. [14]. In succession, the composite
metakaolin geopolymer experienced an increase in strength. It was connected with sintering, the formation of melt and crystallization of new phases.

It is interesting to note that the maintenance of this structure after thermal exposure, coincided with their compressive strength results. Not only would the incorporation of MAP bring about the filling effect but it also promoted more formation of gel phase. This could be the rooted reason for the optimization of microstructure and enhancement of mechanical properties. Higher amounts of additional sources of Al serves as filler, but it can also act as increasing the strength [36].

4. Conclusions
Compressive strength of the fly ash-metakaolin blend geopolymer with addition of MAP served an enhancement due to the combined optimization of filling effect and enrichment of gel phases. The strength enhancement of G-1.0wt.% compared with G-0wt.% is 14.8%. The incorporation of 1.0wt.% MAP improved the thermal stability at 200°C. At the temperature of 600°C and 1000°C, the G-1.0wt.% sample had a further reduction in compressive strength. However, still retain the highest strength due to the crystallization of berlinite and nepheline phases. Besides, it resulted in an increase in porosity, which was mainly the result of decomposition of the granules. As a result, expansion occurred, which contributed to the decrease of compressive strength.

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