Characterization of Fly Ash and Metakaolin Blend Geopolymers under Ambient Temperature Condition

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Abstract. This paper presents a characterization of fly ash and metakaolin blend geopolymers of the optimize mix proportion of 10 M NaOH concentration mixed with the solid-to-liquid ratio of 1.2 and sodium silicate and sodium hydroxide ratio of 2.6. The combination of amorphous and crystalline phase in the fly ash (FA) and metakaolin (MK) blend geopolymers showed a positive effect on the resultant geopolymers. The formation of new crystalline phases which is sillimanite as presented by XRD analysis. Fly ash and metakaolin blend geopolymers showed the presence of geopolymer bonding at around 1390 cm⁻¹ and 960 cm⁻¹. This paper discloses effect of blending fly ash and metakaolin in the synthesis promotes the continual hydration of the geopolymers.

1. Introduction

For In 1978s, Joseph Davidovits named “geopolymer” as a new family of cementitious materials that are formed in direct synthesis of alkaline alumina–silicate materials at low temperature. On the basis, geopolymer can be regarded as a class of aluminosilicate materials polymerized by the geochemical action to form a three-dimensional structure “N-A-S-H” type gel. Besides, it is a network consisting of alternating SiO₄ and AlO₄ tetrahedra linked by shared O atoms [1].

The source materials play a major role in the geopolymerization reaction, controlling the chemical composition and microstructure of the final geopolymeric products [2]. Calcined source material such as fly ash and metakaolin display a higher reactivity during geopolymerization than non-calcined material. There is emerging trend of blending two or more source materials for the production of geopolymers for high performance applications.

Fly ash were found to be the most practical source material due to the plentiful worldwide raw material supply, derived from coal power plant [3]. As for metakaolin, it offers better strength and accelerated hydration reaction [4]. Metakaolin can attain high compressive strength at an early age due to the high pozzolanic reactivity and finer particles filling effect [5]. The main reaction product of fly ash and metakaolin is a N-A-S-H type gel (Na₂O-Al₂O₃-SiO₂-H₂O) within a three-dimensional network [6]. The incorporation of blend fly ash and metakaolin is highly beneficial due to the difference in chemical composition overlook the handicaps of both starting material.

Thus, in this study, a study is carried out to investigate the characterization of fly ash and metakaolin blend geopolymers under ambient temperature curing.

2. Experimental
2.1. Material

Fly ash used in the present investigation is obtained from Tapah Power Plant, Perak, Malaysia. Whereas the metakaolin used was the calcined kaolin purchased from Associated Kaolin Industries Sdn. Bhd., Malaysia. Table 1 summarizes the chemical composition of the fly ash and metakaolin powder. The sodium hydroxide (NaOH) pellets used are the pellet type of Formosoda-P obtained from Formosa Plastic Corporation, Taiwan. Whereas the sodium silicate used in this study were supplied by South Pacific Chemical Industries Sdn. Bhd. (SPCI), Malaysia with chemical composition of 30.1% SiO₂, 9.4% Na₂O and 60.5% H₂O with a weight ratio SiO₂/Na₂O = 3.2, specific gravity at 20°C = 0.0014 g/cm³ and viscosity at 20°C = 0.4 Pa·s.

Table 1. The composition of raw materials based on XRF analysis

| Compound     | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | K₂O | TiO₃ | Na₂O | ZrO₂ |
|--------------|------|-------|-------|-----|-----|------|------|------|
| Fly ash, wt (%) | 56.3 | 28.0  | 6.86  | 3.89| 1.49| 2.17 | 1.49 | 0.139|
| Metakaolin, wt (%) | 55.7 | 38.6  | 2.03  | -  | 2.43| 0.78 | 2.43 | 0.035|

2.2. Preparation of fly ash and metakaolin blend geopolymers

The NaOH concentration of 10 M solution was prepared and allowed to cool down to room temperature. Then as-received sodium silicate solution was added to the NaOH solution, followed by mixing it thoroughly. Dry fly ash and metakaolin was blend together and was added to this solution resulting the formation of geopolymer precursor in the form of slurry. The slurry was then transferred into 50 mm cubes, vibrated for 5 min and allowed to set at ambient temperature (30°C) for 24 h before being removed from the molds and kept at room temperature before it being tested for 28 days of ageing. The formulation of the fly and metakaolin blend geopolymer was the subject of an earlier study, which highlighted an optimal proportion regarding the compressive strength performances [7, 8].

2.3. Characterization

The chemical composition of both materials (fly ash and metakaolin) was determined by X-Ray Fluorescence (XRF) spectrometry with a PANalytic, MiniPAL 4 spectrometer with PW4030 sample changer. Scanning electron microscopy (SEM) was conducted using a JSM- 6460LA model Scanning Electron Microscope (JEOL). The composition of the raw fly ash, metakaolin and the completely cured geopolymers was characterized by X-ray diffraction (XRD) using a XRD- 6000, Shimadzu x-ray diffractometer equipped with Cu X-ray tube operated at 40 kV. All XRD scans used Kα radiation, with a step size of 0.02° at a scan rate of 2° per minute. Shifting of functional groups from fly ash and metakaolin toward fly ash and metakaolin blend geopolymers were identified using spectrum RXI spectrometer. The specimen was powdered samples scanned from 4000–650 cm⁻¹ at the resolution of 4 cm⁻¹.

3. Results and Discussions

3.1. Microstructural Analysis

Fig. 1 depict characteristic morphology of the fly ash and metakaolin particles, respectively. The original fly ash consists of a series of spherical particles of different sizes and relatively smooth. Moreover, with the rounder shape particles, it ensuring more promising workability with a low water demand [9]. The microstructure of metakaolin also reveals the irregular and sheet shape can be seen having the particle sizes in the range 0.5–9 μm. It is crucial because the metakaolin particle size is reported to influence the mechanical properties of geopolymers [10]. The fly ash and metakaolin blend geopolymers in the micrograph below (Fig. 1) reflecting a gradual dissolution of geopolymers by the alkaline solution. The cracks and pores in these gel matrices may be introduced by the water evaporation and high amount of
water that eliminate from the geopolymeric networks. Even so, other research study claimed that the formation of pores and crack were due to the fly ash components [11]. The proportion of 1:1 amount of fly ash and metakaolin components, on one hand, induces the formation of pores and crack. Yet, on the other hand, the effect of blend fly ash and metakaolin provoking a larger interconnecting and homogeneous geopolymers matrix as the alkaline activation proceed.

Figure 1. SEM micrograph of raw fly ash and metakaolin powder (a) and the fly ash- metakaolin blend geopolymer product.

3.2. Phase Analysis

Fig. 2 shows the XRD patterns of the raw fly ash, metakaolin and fly ash and metakaolin blend geopolymers. The XRD pattern of fly ash shows some sharp peaks indicating quartz (Q), mullite (T) and hematite (H). On the other hand, XRD pattern of metakaolin display some peaks attributable to quartz (Q), muscovite (M) and kaolinite (K). After the reaction with the alkaline activator solution, the diffuse hump of fly ash and metakaolin shifted slightly towards higher degree at 2\(^\theta\) ranging from 20° to 40°. This hump indicates that there is amorphous geopolymer matrix formed. This was the typical characteristic of aluminosilicates matrix and the shift indicated the formation of geopolymer matrix after the geopolymerization reaction [12].

Furthermore, a few sharp peaks are also observed in the fly ash and metakaolin blend geopolymers, such as sillimanite, quartz and mullite. Quartz and mullite were originally present in the starting materials, consequently it indicates that these phases are apparently not attacked during the alkaline activation process. This reflected that not all mineral phases are participating in the geopolymerization reaction towards the formation of geopolymer matrix. Thus, this system consisted of combination of amorphous geopolymer gels and crystalline phases.

3.3. Functional Analysis

FTIR spectra of raw fly ash, metakaolin and fly ash and metakaolin blend geopolymers are given in Fig. 2. The band positioned at around 3860 cm\(^{-1}\) is attributed to OH- stretching vibration. This band was associated with the residual OH- stretching of kaolin which indirectly associated by the partial transformation of kaolin into metakaolin [13]. Band located at 1521.21 cm\(^{-1}\) in the FTIR spectrum indicate the H-O-H bending vibration of water molecule bonds. The wavenumber corresponding about 1031 to 1035 cm\(^{-1}\) represents the Si-O/Al-O stretching vibration. The spectrum band approximately at 781 to 789 cm\(^{-1}\) are attributed to Si-O-Si symmetric stretching vibrations (quartz phase) [14]. This slight difference could be related to the low quartz content and high amorphous silica in the metakaolin.

The transformation that occurred during geopolymerization was indicated by the different absorption frequencies of the source materials and of the resultant geopolymers. The region of interest in all geopolymer product lies in the range between 800 and 1300 cm\(^{-1}\). The broad absorption band between 3000- 3500 cm\(^{-1}\) and around 1640 cm\(^{-1}\) presented in all spectra are attributed to the bond vibration of water absorbed at surface or entrapped in cavities [15]. After geopolymerization, the Si- O- Si and Si-O- Al band shifts from 1031- 1035 cm\(^{-1}\) in fly ash and metakaolin to 968- 976 cm\(^{-1}\), indicating the formation of geopolymer gel. These results can be explained by the formation of a new phase rich in sillimanite.
Figure 2: XRD patterns of raw fly ash, raw metakaolin (MK) and fly ash (FA) and metakaolin blend geopolymer samples (a) FTIR spectra of raw fly ash, metakaolin powder and fly ash- metakaolin blend geopolymers.

4. Conclusions
Based on the fly ash and metakaolin blend geopolymers produced, the following conclusion can be drawn:

1. The effect of fly ash and metakaolin blend geopolymers leads to larger formation of homogeneous geopolymer matrix.
2. Through phase analysis, it was observed that fly ash and metakaolin blend geopolymers show an appearance of new crystalline phase which is sillimanite.
3. The polycondensation of fly ash and metakaolin blend geopolymers network indicate by the formation of more geopolymer bonding as determined by functional group analysis.
4. Ambient temperature condition provides a continual ion mobility giving fly ash and metakaolin particles to react between each other to form a homogenous matrix.

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