Influence of Solid-To-Liquid Ratio on Properties of Fly Ash Geopolymer Ceramics

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Abstract. Ceramics has come to be progressively very important in industry because of their exceptional mechanical and physical properties. The motivation to develop fly ash geopolymer ceramics was to overcome the problem associated with the conventional technical ceramics like alumina, silicon, carbide, aluminium nitride that fracture easily under mechanical or thermo-mechanical loads. The novelties of this research were providing new material to fabricate geopolymer as ceramic precursor and move towards green technology. Geopolymer substrates were activate by adding the alkaline activator gradually with different ratios of solid to liquid ranged from 0.5, 1.0, 2.0 and 3.0 into fly ash at ambient temperature. The samples were cured before undergo powder metallurgy method. The best and optimum solid to liquid ratio is determined at ratio 2.0 based on flexural strength. The broad, amorphous peak showed by phase analysis indicates that geopolymerization has occurred. The formation of almost fully crystalline phase such as albite has been detected which contributes to the flexural strength of fly ash geopolymer ceramic. Microstructure image shows smoother and complete geopolymer matrix which gives denser structure as supported by the excellent density.

1. Introduction
Ceramic usually are from clay that widely used in the manufacture of many traditional ceramics. Each ceramic product requires clays having particular and appropriate characteristics, which must not contain a swelling phase, low loss of weight and low shrinkage after drying firing process [1]. Firing characteristics such as shrinkage, water absorption, and mechanical properties are very important characteristic to produce a good ceramic. Typically producing ceramic specifically used many types of fabricating method basically performs at high temperature which is complex and high cost process. A wide vary of process routes have indeed been proposed for the production of ceramics, using raw materials of varied nature and resulting in a range of morphologies that affected the properties [2].

Conventional ceramic materials fabrication require high sintering temperature up to 1600 °C (Kriven et al., 2013). The use of geopolymer technology is an alternate way in fabricating ceramic materials as the amorphous and semi-crystalline phase of geopolymer will convert into crystalline phases during sintering [4]. With the advantage of geopolymerization reactions, high temperature
routes are no longer required to produce ceramic-like structure materials (Iwahiro et al., 2001). Besides, geopolymer also can be directly converted into final structural leucite, pollucite or nepheline ceramic part and thus the chemical compositions of final product also can be design (Peigang et al., 2010). Thus, geopolymer is parts of ceramic which are a well-known material for composites industry that become demands lately.

Inorganic polymers referred as geopolymers, are aluminosilicate materials which display superior physical and chemical properties with a diverse range of possible potential applications such as coating, high temperature ceramics, and cement for concrete and binder for fireplace resistant fiber composite [7]. Fly ash that contain a large amount of silica and alumina can be used as a source material for geopolymer [8]. Other than composition of the source material, several factors were identified as important parameters and solid to liquid ratio is one of the main factor as it rules the amount of solid and liquid concerning on homogeneous mixing, which specifically affect the dissolution, geopolymerization reaction, workability, and the strength of the final product. Therefore, this study is focusing on the effect of solid to liquid ratio on the mechanical and microstructural properties of the fly ash geopolymer ceramics.

2. Methodology

2.1. Materials

Fly ash is the main raw materials to produce the geopolymer ceramics. In general, the components of fly ash typically include SiO$_2$, Al$_2$O$_3$, CaO and Fe$_2$O$_3$, which exists in the form of amorphous and crystalline oxides or various minerals as shown in Table 1. The fly ash used in this study was obtained from Manjung power station, Lumut, Perak, Malaysia. The physical forms of fly ash used were in powder state with the mean particle size ($X_{50}$) of 46.22 μm.

The alkaline activators used in this research were sodium silicate (Na$_2$SiO$_3$) solution and sodium hydroxide (NaOH). NaOH in pellets form used was caustic soda micropearls with 99 % purity, Formosoda-P brand were made in Taiwan while Na$_2$SiO$_3$ with properties of Grade A53 with SiO$_2$ = 29.43 %, Na$_2$O = 14.26 % and water = 56.31 % were used.

| Table 1. Chemical composition of Class F fly ash |
|-----------------------------------------------|
| **Compound**       | **Mass (wt. %)** |
| SiO$_2$            | 55.90            |
| Al$_2$O$_3$        | 27.80            |
| Fe$_2$O$_3$        | 7.09             |
| CaO               | 3.95             |
| TiO$_2$            | 2.25             |
| K$_2$O            | 1.55             |
| SrO               | 0.37             |
| SO$_3$            | 0.33             |
| RuO$_2$           | 0.24             |
| ZrO$_2$           | 0.13             |
| V$_2$O$_5$        | 0.10             |
| MnO              | 0.06             |
| LOI             | 0.23             |

2.2. Sample Preparation

The alkali activator solution is prepared by mixing the 12M of NaOH solution with sodium silicate at alkali activator ratio of 2.5 which is fixed in this research until a clear solution is obtained to make sure the solution is well dissolved. The chosen ratio was based on previous work, as it certified for optimum properties. The geopolymer paste was prepared by mixing the fly ash with the alkali
activator at various solid to liquid ratio of 1.0, 2.0 and 3.0. The paste then were stirred well for a few minutes and poured into moulds. The samples were put into oven at 80 °C for 24 hour for the curing process.

To produce fine powder for powder metallurgy method, the fly ash geopolymer were crushed and sieved by using siever of 150μ. The fly ash geopolymer in powder form were then compacted using uniaxial compaction, hand press using 12 mm diameter mould under pressure of 4.5 ton for 2 minute. After being shaped into a pellet, the green bodies were sintered at a fixed temperature of 1000 °C with soaking time of 180 minutes and heating and cooling rate of 5 °C/minutes.

2.3. Testing

2.3.1. Flexural Strength
Flexural strength of fly ash geopolymer ceramic samples were measured using mechanical testing with Automatic Max (Instron, 5569 USA) according to the standard of ASTM C1161-02c. A minimum of five samples for each group were subjected to flexural strength testing were conducted on specimens (7 mm x 5 mm x 52 mm) using a three-point-bending fixture, with a span length of 30mm at a crosshead speed of 0.5 mm/minute.

2.3.2. Density
The theoretical density of fly ash ceramic and fly ash geopolymer ceramic was measured using densitometer model MD 300S that available in UniCITI Alam, UniMAP. A cylinder shaped sample with a diameter of 12 mm and a length of 5 mm were used in this experiment.

2.3.3. Morphology Analysis
JSM-6460LA model Scanning electron microscope (JEOL) was performed to reveal the microstructure of fly ash geopolymer ceramic at various solid to liquid ratio. The specimens were prepared and coated by using Auto Fine Coater; model JEOL JFC 1600 prior to examination.

2.3.4. Phase Analysis
The sample was characterized by using XRD 6000, SHIMADZU diffractometer. Samples were prepared by pressing the powder samples into aluminium holders. Operating conditions were 40 kV and 30 mA and performed using Cu-Kα radiation. The X’Pert High Score Plus software is used for peak identification and automated search match was used to analyse the results of diffraction patterns.

3. Results and Discussion

3.1. Flexural Strength
The flexural strength of fly ash geopolymer ceramics was assessed at three different solid to liquid ratio in order to determine the highest strength as shown in Figure 1. At 1.0 of solid to liquid ratio, the flexural strength was 19.64 MPa, whereas, the solid liquid ratio 2.0 achieved the highest strength which is 25.99 MPa, attributed to the increasing of fly ash content and activator solution content [9]. The strength of fly ash geopolymer ceramic is also depending on the workable mixture ratio. Less workable mixture causes difficulty in flexural testing where failure in providing good flexural properties and severely reduce the flexural strength of the samples. The flexural strength then dropped at the solid to liquid ratio of 3.0 which gives the lowest flexural strength of 18.92 MPa. The result clearly showed the best and workable solid to liquid ratio is at 2.0 where at this ratio, the most optimum ratio provided the highest flexural strength compared to other ratio which were less workable.
3.2. Density
Figure 2 shows the density of the fly ash geopolymer ceramics as a function of solid to liquid ratio. It can be seen that the density of ceramic increased with the increasing of solid to liquid ratio from 1.0 to 2.0 ranging from 1.716 g/cm³ to 1.957 g/cm³. The results were contributed by the matrix of fly ash increased in the solid to liquid ratio 2.0. The increased amounts of fly ash matrix reduce the void in the structure of fly ash and denser the particle. However, the density of the geopolymer ceramic start to decrease at solid to liquid ratio of 3.0. The recorded density of fly ash geopolymer ceramics of solid liquid ratio 3.0 was 1.873 g/cm³. The density was slightly decreased due to the workable rate of the fly ash is not optimum and the exceeded amount of fly ash matrix in the structure make it less workable in the mixing process and leads to the decrease in the density [10].

3.3. Morphology Analysis
Figure 3 shows the microstructure evolution of the fly ash geopolymer and fly ash geopolymer ceramic at various solid to liquid ratio. The image of fly ash geopolymer sample surface showed heterogeneous elements and contained more unreacted particles. As the samples were sintered, at solid liquid to liquid ratios 1.0, large sintered area was formed due to the fly ash particle begin to fuse together where it demonstrates incomplete geopolymerization. For the solid to liquid ratio 2.0, the
matrix of fly ash were started to fuse together and the appearance of pores started to presence. The samples appeared to have a smoother geopolymeric matrix and also denser as the concentration increased indicate that geopolymerization has occurred well and the effect of sintering [6]. However, at solid to liquid ratio 3.0 the pores started to increase and leave many pores in the structure. The solids to liquid ratio affect the amount of pores in the pastes which directly influences the strength of geopolymer ceramics.

Figure 3. Microstructural images of a) fly ash geopolymer and fly ash geopolymer ceramics with solid to liquid ratio of b) 1.0, c) 2.0, and c) 3.0.

3.4. Phase Analysis
Figure 4 shows the phase analysis of fly ash geopolymer and fly ash geopolymer ceramic at various solid to liquid ratio. The difference in solid to liquid ratio and the effect of sintering produces a series of reactions and transformations that lead to the formation of new phases and the disappearance of humps in the diffractogram spectra. It can be observed that the peaks of quartz which contain SiO$_2$, disappeared as the samples were sintered. The broad reflection pattern of fly ash begins to show a sharp peak indicates the transformation of amorphous to crystalline phase upon sintering [11]. As the sample of solid to liquid ratio of 1.0 was sintered, the presence of nepheline phase can be found at the peak. However the peaks change into albite at solid to liquid ratio 2.0. Finally, analbite were obtained at the peak of solid to liquid ratio 3.0. The sample of fly ash geopolymer ceramic of solid to liquid ratio 2.0 shows the highest intensity compared to solid to liquid ratio of 1.0 and 3.0.
Figure 4. Phase analysis (a) fly ash geopolymer and fly ash geopolymer ceramics at solid to liquid ratio of (b) 1.0, (c) 2.0 and (d) 3.0 (N= Nepheline, AL= Albite, ANA= Analbite,Q= Quartz, M= Mullite.).

4. Conclusions
The aim of this paper is to study the effect of addition of Ultra High Molecular Weight Polyethylene (UHMWPE) on kaolin geopolymer ceramics. Results concluded that the addition of UHMWPE affected the strength of the kaolin geopolymer ceramics. The flexural strength of kaolin geopolymer ceramics with addition of UHMWPE increased compared to the kaolin geopolymer ceramics without addition of UHMWPE. Kaolin geopolymer ceramics with addition of 4 wt. % UHMWPE give the highest strength which is 92.1 Mpa. However, the strength started to decrease due to the excessive content of UHMWPE lead to the increasing of pores size appeared in microstructure of kaolin geopolymer ceramics.

Acknowledgements
The authors of the present work wish to dedicate their great thanks to Centre of Excellence Geopolymer System Research @UniMAP.

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