Fundamental Study on Processing and Characterization of Kaolin-Modified Ground Granulated Blast Furnace Slag Ceramic via Geopolymerization Process

by

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LIST OF ABBREVIATIONS

XRF	X-ray Fluorescence
XRD	X-ray Powder Diffraction
FTIR	Fourier-transform Infrared
TGA	Thermogravimetric Analysis
DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimetry.
XAS	X-ray Absorption Spectroscopy,
SL	Solid to Liquid
SiO_2	Silicon Dioxide
CaO	Calcium Oxide
Na_2O	Sodium Oxide
Al_2O_3	Aluminium Oxide

LIST OF SYMBOLS

^{o}C	Degree Celcius
Ɵ	Theta
M	Molarity
%	Percentage

Kajian Asas Terhadap Pemprosesan dan Pencirian Seramik Kaolin-Terubah Suai Sanga Relau Bagas Berbutir melalui Proses Pengeopolimeran

ABSTRAK

Kaolin secara teorinya dikenali mempunyai kereaktifan yang rendah semasa pengeopolimeran akan digunakan sebagai sumber aluminosilikat dalam kajian ini. Kajian sedia ada menggunakan kaolin yang telah dirawat melalui rawatan haba, mekanikal dan kimia sebelum pengeopolimeran. Disebabkan keprihatinan ini, ia menjadi satu cabaran untuk menghasilkan geopolimer kaolin secara terus tanpa pra-rawatan. Oleh itu, penambahan sanga relau bagas berbutir (GGBS) akan mempercepatkan proses pengeopolimeran. Objektif kajian ini adalah untuk mengkaji pengaruh komposisi kimia di dalam bahan mentah, suhu pengawetan dan suhu pensinteran terhadap kaolin-GGBS geopolimer tersinter. Nisbah pepejal terhadap cecair yang dipilih adalah 1:1, 1.5:1, dan 2:1 untuk analisis mengenai sumbangan komposisi kimia. Kesan suhu pengawetan akan dikaji berdasarkan empat perbezaan suhu iaitu suhu bilik, 40 °C, 60 °C dan 80 °C.0. Parameter terakhir yang dipilih adalah suhu pensinteran iaitu 800 °C, 900 °C,1000 °C dan 1100 °C. Nisbah pepejal terhadap cecair yang optimum diperolehi adalah 2:1 (SL 2) beserta mikrostruktur yang padat. Penambahan GGBS di dalam buburan geopolimer kaolin tidak hanya mempercepatkan proses pengerasan semasa proses pengeoplimeran, kehadiran CaO dan MgO di dalam GGBS telah mempercepatkan pembentukan fasa nefelin, gehlenit, akermanit, dan albit selepas pensinteran. Taburan unsur daripada kajian micro-XRF membuktikan bahawa konsentrasi Ca yang tinggi di kawasan setempat dan pengedaran Si adalah seragam sejajar dengan fasa akermanit di SL 2. Pengawetan pada suhu 60 °C telah menghasilkan kekuatan mampatan tertinggi selepas proses pensinteran. Hal ini disebabkan mikrostruktur padat bersama liang pori terbuka di dalam struktur kaolin-GGBS geopolimer tersinter. Ini dapat dilihat dengan jelas transformasi fasa dari yang geopolimer terawet kepada yang disinter. Transformasi fasa utama kristal iaitu kaolinit kepada fasa nefelin disebabkan tindak balas terhadap pengaktif alkali. Kaolin-GGBS geopolimer telah disediakan dengan nisbah pepejal terhadap cecair 2:1 dan suhu pengawetan 60 °C untuk parameter terakhir iaitu suhu pensiteran. Pensinteran pada 900 °C telah menghasilkan kekuatan mampatan tertinggi disebabkan pembentukan mikrostruktur padat. Pembentukan fasa akermanit telah menyumbang kepada kepadatan itu. Suhu pensinteran melebihi 900 °C menyebabkan pembentukan liang yang saling berkaitan kerana penguraian dan penguapan $CaCO_3$. Sementara itu pensinteran pada 800 °C menunjukkan proses pengeopolimeran yang tidak lengkap. Analisis haba menunjukkan kestabilan kaolin-GGBS geopolymer tersinter apabila didedahkan kepada suhu 1100 °C. Oleh itu, ia membuktikan bahawa kaolin boleh digunakan secara langsung tanpa rawatan haba dalam geopolimer. Proses pengeopolimeran telah meningkatkan kestabilan sampel yang diawet untuk disinter secara langsung selain memainkan peranan penting sebagai agen fluks kendiri untuk mengurangkan suhu dalam menghasilkan kaolin-GGBS geopolimer tersinter.

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ABSTRACT

Kaolin which is theoretically known having low reactivity during geopolymerization will be used as a source of aluminosilicate materials in this study. Current research had pretreated the kaolin via thermal, mechanical and chemical treatment before geopolymerization. Due to this concern, it becomes a challenge to directly produce kaolin geopolymer without pre-treatment. Hence addition of ground granulated blast furnace slag (GGBS) will accelerate the geopolymerization process. Kaolin-GGBS geopolymer ceramic can be prepared at low sintering temperature due to the reaction of chemical composition during the initial stage of geopolymerization. The objective of this work is to study the influence of the chemical composition in raw materials, curing temperature and sintering temperature on the sintered kaolin-GGBS geopolymer. The ratio of solid-to-liquid chosen were 1:1, 1.5:1, and 2:1 to analyze the contribution of chemical composition. The effect of curing temperature will be a study based on four different temperature, which is, room temperature, 40 ˚C, 60 °C and 80 °C. The last parameter chosen was the sintering temperature varied at 800 °C, 900 ˚C, 1000 °C and 1100 °C. The optimum ratio of solid to liquid obtained was 2:1 (SL 2) with densified microstructure. The addition of GGBS to the kaolin geopolymer slurry did not only hasten the hardening process during geopolymerization, the presence of CaO, and MgO in GGBS had accelerated the formation of nepheline, gehlenite, akermanite, and albite phase after sintering. Elemental distribution from micro-XRF investigation proves the high concentration of Ca in a localized area and uniformly distribution of Si aligned with the phase of akermanite in SL 2. The curing temperature at 60 °C had resulted the highest compressive strength after the sintering process. This is due to the densified microstructure with open pores in the structure of sintered kaolin-GGBS geopolymer. It can be clearly seen the phase transformation from as-cured to sintered geopolymer. Transformation of the main crystalline phase which is kaolinite to nepheline phase due to reaction with alkali activator. Kaolin-GGBS geopolymer was prepared with a ratio of solid to liquid 2:1 and 60 °C of curing temperature were prepared for the last parameter varied, which are sintering temperature. Sintering at 900 °C had resulted in the highest compressive strength due to the formation of densified microstructure. The formation of akermanite phase had contributed to the densification. The sintering temperature exceeds than 900 °C had led to the formation of interconnected pores due to the decomposition and vapourisation of $CaCO_3$. Meanwhile, sintering at 800 °C indicates an incomplete geopolymerization process. Thermal analysis shows the stability of sintered kaolin-GGBS geopolymer when being exposed to 1100 °C. Therefore, it proves that kaolin can be directly used without heat treatment in geopolymer. The geopolymerization process had facilitated the stability of as cured samples to be directly sintered besides playing a significant role as a self-fluxing agent to reduce the temperature in producing sintered kaolin-GGBS geopolymer.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

Geopolymers belong to a group of materials with increased interest due to low CO_2 emission and energy consumption (Zannerni et al., 2020). Hence, environmental preservation has become a driving force behind the search for new sustainable and environmentally friendly materials (Pacheco et al., 2019). The hardening process of geopolymers at ambient temperature results in materials with ceramic-like properties, such as resistance against acids and high temperatures. The silica-rich materials such as clay or kaolin, fly ash, and bottom ash can be used as an aluminosilicate material to react with the liquid alkali activator (Zhenming Li et al., 2019; Sukmak et al., 2013).

Davidovits created the term geopolymer in 1978 to define a class of materials of mineral nature with a chemical composition similar to zeolite, but with a mixed microstructure (from amorphous to semi-crystalline) (Hassaan et al., 2015). The silica (SiO_2) and alumina (Al_2O_3) species present in the raw materials react in a highly alkaline medium, organizing themselves in a continuous three-dimensional structure (Zhang et al., 2020). Geopolymers have found application in virtually all fields of industry, which provides, among its properties, high mechanical strength, high chemical inertness and excellent fire resistance. There are considered as a replacement for conventional cement-based components as well as for ceramic parts that can be used up to medium-high temperature typically below 1200 ^oC (Cilla et al., 2016; Wang et al., 2020).

There are certain factors that influence the properties of geopolymers such as composition, type and the relative amount of alkaline activator, the specific surface composition of source materials and condition during the initial period of the geopolymerization process (Belmokhtar et al., 2018a). The parameters during geopolymerization give a significant impact on the mechanical properties of geopolymer, such as solid to the liquid ratio where these crucial parameters influence the workability of geopolymer slurry (Cheng et al., 2015). The liquid content consists of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH). Sodium silicate acts as alkali activator, binder, plasticizer or dispersants. In contrast, sodium hydroxide helps the dissolution of aluminosilicates sources (Zhang et al., 2016). Other vital parameters are curing regime, that must be taken into consideration when designing a kaolin-based geopolymer product for a specific application (Heah et al., 2013; Saha & Rajasekaran, 2017).

Kaolin is one of the most commonly used raw materials in the preparation of alkali-based geopolymers; however, kaolin must undergo thermal pre-treatment to improve its geopolymerization reactivity. Through the calcination, the dehydroxylation of kaolinite occurs, accompanied by the increase in disorder of the layer structure. The kaolinite was shown to transform into dehydrated kaolinite with amorphous phases when calcined between 500 °C and 900 °C, and its reactivity was significantly improved (Zhang et al., 2020). Calcination of kaolinite forms more reactive kaolin which known as metakaolin containing highly reactive amorphous phase which readily takes part in geopolymer synthesis process (Sarkar et al., 2015). However, the needs of a thermal activation to increase the reactivity of kaolin and allow the transformation into metakaolin will affect the raises for overall elaboration cost of these materials (Aboulayt et al., 2017).

Generally, kaolin geopolymer powder was compressed using a powder metallurgy method, and the green body was sintered to produce ceramic products. This method proves that cracking was not observed after sintering as being discussed by Zhang (2016) and Liew (2017). This implied that the formation of kaolin geopolymer ceramics using kaolin geopolymer powder prevents cracking, which usually occurs in as-cured geopolymers. The as-cured geopolymers were heated and dried before sintering to avoid excessive shrinkage cracking (Zhang et al., 2016).

Ground granulated blast furnace slag (GGBS) has been used for decades as partial replacement material in concrete and has well-established standards describing is use (Hassaan et al., 2015). In general, the addition of GGBS can significantly shorten the setting time of clay-based geopolymer, improve the flowability of paste or mortar and increase the compressive strength of hardened product (Saha & Rajasekaran, 2017). However, suppose the sintering temperature is higher or/, and the melting temperature of the used residue is lower. In that case, the additives material also can start to melt, which drastically changes the sintering behaviour, phase composition and structure of final ceramic. Karamanova et al., (2011) explained that if the differences in melting temperature for the mixture materials is too high, then the appropriate sintering profile is required to obtain suitable properties of end ceramic. Therefore, by having optimum condition from solid to liquid ratio and curing conditions, it is possible to produce kaolin–GGBS geopolymer. Next, kaolin–GGBS geopolymer will be sinter at various sintering profile to evaluate the properties of kaolin-GGBS geopolymer ceramic.

Sintering of geopolymer led to the formation of sintered ceramic bodies with improved properties (Zawrah et al., 2020). Ceramics are typically produced by sintering

the clays and other natural raw materials to form a rigid product. Ceramic products that use naturally occurring rocks and minerals as a starting material must undergo special processing to control purity, particle size, particle size distribution, and heterogeneity. These attributes a significant role in the final properties of the finished ceramic. Chemically prepared powders also are used as starting materials for some ceramic products (Chen et al, 2004). The formation of ceramic particles into the desired shape was accomplished by the addition of water or additives such as binders, followed by a shape forming process. Some of the most common forming methods for ceramics include extrusion, slip casting, pressing, tape casting and injection moulding. Then, these "green" ceramics undergo a heat-treatment (called firing or sintering) to produce a rigid, finished product (Xie et al, 2010). Conventional approaches of sintering glass-ceramics usually include two steps; vitrifying raw materials at high temperatures (1300 °C to 1500 °C), followed by nucleation and crystal growth (Rincón, Desideri, & Bernardo, 2018).

The study of sintering behaviour of clay raw materials might be difficult because these clays have a complex mineralogical composition, which causes a series of phase transformations occurring during sintering. Those processes relate to major and minor clay minerals such as phyllosilicates, quartz, with alumina octahedral sheets (Ramasamy et al, 2015). Silicate ceramics that contain clays are complex ceramic systems due to the numerous relationships among the behaviours of mineral materials during ceramic processing and transformations during heating (Boussois et al., 2014). The propagation of cracks in silicate ceramics can be positively influenced by microstructural characteristics and the addition of reinforcement. A significant challenge is the promotion of controlled phase transformations, where the interconnected phase in a highly organized network is favourable to mechanical properties (Boussois et al., 2014).

1.2 Problem Statement

Kaolin is a kind of pozzolan that reacts with alkali solution but required a higher temperature than metakaolin to be a hardened geopolymer. This is due to the low reactivity of kaolin that needs sufficient time for the geopolymerization process to complete (Tiffo et al., 2020). The use of kaolin as a raw material was reported in few studies but more can be found on the use of metakaolin to produce geopolymer materials (Naghsh & Shams, 2017). Metakaolin was obtained from the pre-treatment of kaolin such as calcination at a temperature range of 700 ˚C to 850 ˚C or mechanical activation by milling process (Wan, Rao, Song, et al., 2017). Raw kaolin was considered for the synthesis of geopolymer without a preliminary thermal activation, to limit the overall energy demand for calcination in the way of sustainable development. Meanwhile, GGBS seems to be the candidate that can accelerate the hardening of the kaolin geopolymer. The hygroscopic properties of CaO from GGBS will help to attracts water from its surroundings and will improve the dihydoxylation reaction. The contribution of the oxides from raw materials (SiO_2, Al_2O_3, CaO, MgO) in reducing the sintering temperature of geopolymer would be an exciting discussion in geopolymer field

It is common for the hardening process of geopolymer made from raw kaolin thus will suffer from the cracking issue due to the excessive water that still remains in the geopolymer. The excessive water normally coming from the unreacted H_2O during dissolution stage in geopolymerization does not completely remove. The curing condition during geopolymerization will influence the dihydroxylation reaction thus preventing the initiation of crack. Therefore, the curing temperature will be study in order to analyse the optimum temperature for kaolin-GGBS geopolymer to be hardened.

Apart from the geopolymerization component, sintering played a vital role to produce geopolymer ceramic. However, direct sintering of geopolymer material at high temperatures will result in excessive shrinkage and cracking of the geopolymer (Zhang et al., 2016). The current method for producing sintered geopolymer is by using the powder metallurgical method where the hardened geopolymer paste needs to be in powder form. However, the paste needs to undergo a milling process which required another step of energy consumption (Zhang et al, 2016). Conventional approaches of sintering glass-ceramics usually required high temperatures ranged from 1300 ºC to 1500 ºC (Rincón, Desideri, & Bernardo, 2018). K-feldspar, Ca-feldspar rock, Na-feldspar rock and bone ash has been added fluxing agent in the mixture with kaolin used and achieved to lower the sintering temperature about 1200 ºC (Sokolář et al., 2017).

Hence, the technique to sinter geopolymeric materials at lower sintering temperature remain a challenge. Therefore, the simplified method will be studied by directly using the moulded sample after curing to the sintering process. Furthermore, it was also suggested by Zhang et al., (2016) to study the effect of phase transformation towards sintered geopolymer properties. The novelty of this research is to directly use raw kaolin in geopolymer and sinter the as-cured geopolymer.

1.3 Objectives of Study

I. To correlate the contribution of the chemical composition of source materials towards sintered kaolin-GGBS geopolymer by verifying different solid to liquid ratio.