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Characterisation and Performance of Nigerian Kaolin and Metakaolin in Geopolymer Synthesis

Maria Kaka Etete Enoh[1*], Ekanem Benedict Agbonko[2] & Milliscent Orok Ededet[3]

[1]Department of Mechanical Engineering, University of Cross River State, Calabar, Nigeria

*Corresponding Author's Email: mariabisong@unicross.edu.ng

[2]Department of Mechanical Engineering, University of Calabar, Calabar, Nigeria

ekanemben@unical.edu.ng

[3]Department of Wood Products Engineering, University of Cross River State, Calabar, Nigeria

milliscentmail@unicross.edu.ng

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Abstract

This study is aimed at characterising and understanding the mechanical and microstructural behaviour of natural and calcined kaolin clay for geopolymer applications. The clay samples obtained from Kaduna State, Northern area of Nigeria, were calcined within the temperature range of 700 and 900°C and are represented by MK7, MK8 and MK9. The raw kaolin and metakaolin were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM). To produce geopolymer binders, the precursors were reacted with a 1:1 combination of sodium hydroxide and sodium silicate solution and a precursor to activator ratio of 1.2 was suitable for preparation. The compressive strength of the samples was determined at three testing age of 7, 14 and 28 days. From the results obtained, the kaolin-based geopolymer generally had a long setting time and testing was impossible at the 7-day testing age. The compressive strength of other samples however, increased with increase in the calcination temperature. The values obtained at the maximum testing age of 28 days for all samples fall between 5.1 -14.9 MPa. The scanning electron microscope morphology of the produced binder, show the presence of air trapped in the paste which may have reduced the strength value. Vibrating samples before setting can improve the performance of the geopolymer binders by removing most of the trapped air. Geopolymers produced from this study based on strength obtained, can be used in less critical areas of the construction industry.

Keywords: *Geopolymers, Metakaolin, Calcination Temperature, Mechanical Tests, Scanning Electron Microscopy*

1.0 INTRODUCTION

Clay is an abundant rock base mineral on the earth crust that is made up of various element with varying composition. In Nigeria, there are vast deposits of different types of clay which are untapped with large estimated reserves (Ojo, Igbokwe, Egbuachor & Nwozor, 2017). The different types of clay include kaolinite bentonite, montmorillonite, illite and a number of others. For geopolymer applications however, the kaolinite is the most utilized because they have exhibited superior performance compared with other clay types (Tchakouté & Rüscher, 2017). In addition, the kaolinite has a a high silica and alumina content which makes it suitable for use as a geopolymer precursor. Kaolinite which is widely known as kaolin has a chemical structure $Al_2Si_2O_5(OH)_4$ and possesses a 1:1 sheet structure of SiO4 or $[Si_2O_5]^{2-}$ tetrahedral sheet and $[Al_2OH_4]$ octahedral sheet with a silicon and aluminum ratio of 1 (Khaled, Mohsen, Soltan & Kohaol, 2023). The octahedral and tetrahedral sheets are linked by oxygen atoms and held together by weak Van Der Waals forces and hydrogen bonds which gives rise to a layered structure. For geopolymer research, the kaolin is often dehydroxylated through thermal treatment method known as calcination. This process increases the reactivity of the clay when there are mixed with the activators which results to and improved strength of the binders (Albidah, Alghamnam, Abbas, Almusallam & Al-Salloum, 2021).

Geopolymers are produced by simply mixing aluminosilicate source (s) or precursors with alkaline activator(s) (Davidovits, 2002; Provis, 2009). There are a number of precursors available in literature for synthesising geopolymers but the prominent ones are fly ash, slag and kaolin (Nodehi & Taghvaee, 2022). Fly ash and slag have however, been more widely investigated for geopolymer applications because their raw materials can already be classified as wastes which makes it a more environmentally friendly option (Krishna, Mishra, Zribi, Adeniyi, Saha, Baklouti, Uddin, Shaikh & Gokce, 2021). In areas like Nigeria, where steel industries and coal fired plants are almost inexistent, it is not feasible to use these industrial by-products because there are not readily available unlike the kaolin. In the synthesis of geopolymers, a number of factors such as; calcination temperature, curing time, source of precursors, ratio of activators, concentration of activators and mixing methods affects the performance of the binders (Morsy, Alasayed & Al-Salloum, 2014; Phoo-Ngernkham, Maegawa, Mishima, Hatanaka & Chindaprasirt, 2015). On the other hand, activators commonly utilized for geopolymer synthesis are hydroxides and silicates of Na or K alkali metal. Carbonates, sulphates and aluminates of alkali metals are also suitable activators for producing the geopolymer binder.

For researches that have employed metakaolin as activators, the calcination temperature for different sources or researchers have varied from 600 to 850^{o}C (Khaled, Mohsen, Soltan & Kohaol, 2023; Longhi, Rodriguez, Walkley, Zhang & Paula, 2019; Tchakouté & Rüscher, 2017). Elimbi, Tchakoute & Njopwouo (2011) suggested the best optimum calcination temperature for producing the geopolymer binder as 700^{o}C. Others have suggested using them at a temperature of 600^{o}C (Khaled et al., 2023).

In all these various temperatures investigated, varying properties of the geopolymers were obtained. It is therefore important to carry out analysis on new sources to get a more specific characterisation of that source. In order to determine the most suitable calcination temperature for the investigated source of kaolin on the mechanical properties of the binder, three different calcination temperatures based on suitable ranges suggested by other researchers was used. The geopolymers were synthesised from the calcined clays and the compressive strength and morphological property was investigated.

2.0 METHODOLOGY

Materials

The white kaolin used for this study originated from Kaduna state which is located in the Northern part of Nigeria. The extracted clay was crushed in a mortar to achieve smaller sizes because the clay was extracted in lump form of lumps. The raw kaolin was calcined in a muffle furnace set at 25ºC /min at three different temperatures of 700ºC, 800ºC and 900ºC.

The conventional sodium hydroxide (SH) and sodium silicate (SS) were used for this study. These two activators were prepared in a ratio of 1:1 while the aluminosilicate precursor to alkaline activator (AP/AA) ratio used was 1.2. The SH solution was prepared by dissolving the 98% purity pellets in distilled water to achieve the required concentration. SS was composed of 30% SiO_2, 12% Na_2O and 58% H_2O.

Characterisation of Kaolin and Metakaolin

After preparation of the raw samples of kaolin to remove surface impurity and obtained more consistent sizes, the samples were calcined at three different temperatures; 700ºC, 800ºC and 900ºC. Chemical composition of these raw and calcined kaolin was determined using x-ray fluorescence (XRF) while X-ray diffraction was carried out on the samples to determine their mineralogical compositions with the Empyrean diffractometer system.

Sample Preparation

The geopolymer binders are prepared by mixing a measured quantity of the liquid solution (alkali activators) and the solid precursors (metakaolin). 10M concentrated sodium hydroxide solution was prepared and used for the synthesis by dissolving 400g of SH pellets in 1000ml of distilled water at least 24 hours before the synthesis. The SS solution was procured in liquid form and thus required no further preparation. The two activators were mixed in a ratio of 1:1, poured into the solid precursor with a precursor to activator ratio of 1.2 followed by mixing for 10 minutes. Samples were poured into a mould, and allowed to set at room temperature. Table 1 represents the mix proportions of the samples. For the mix notation, the first letter (s) signifies the source of the precursor (K for kaolin and MK for metakaolin), the number signifies the calcination temperature (i.e., 7 for 700ºC) and the letters HS represents hydroxides and silicates respectively. Five samples were prepared for each mix ID test and the average of the results were recorded and used for analysis.

Table 1: Mix Proportions of Samples

S/N	Mix ID	Precursor	Precursor (g)	SH (g)	SH Molarity	Sodium Silicate (g)	SS/SH ratio	AP/AA
1	KHS	Kaolin	140	50	10	50	1	1.2
2	MK7HS	Metakaolin	140	50	10	50	1	1.2
3	MK8HS	Metakaolin	140	50	10	50	1	1.2
4	MK9HS	Metakaolin	140	50	10	50	1	1.2

Testing Analysis and Methods

Sieve Analysis

The method of sieve analysis was used to determine the particle size distribution of the raw and calcined clay according to the ASTM C136 standard.

Compression Test

The universal testing machine was used to evaluate the mechanical performance of the geopolymer binders at testing ages of 7, 14 and 28 days by compressive testing measurement as specified by the ASTM C109. Compressive tests were done on five cubic samples of side 50mm for each formulation.

Scanning Electron Microscope

The Zeiss EV050 scanning electron microscope was used to study the morphology of the clay samples as well as that of the geopolymer binders with optimum performance.

3.0 FINDINGS

Particle Size Analysis

The results from the sieve analysis carried out is presented in Figure 1. The mean particle sizes of the kaolin, MK7, MK8 and MK9 are 355µm, 312µm, 268µm and 212µm respectively. A consistent decrease in mean particle size with increase in calcination temperature was observed. A finer particle size has a larger surface area and increases the area of exposure of the precursor source to the activating solution. It also allows for better mixing during the mixing operation and this generally has a positive effect on the geopolymerisation reaction (Hadi, Al-Azzawi & Yu et al., 2018).

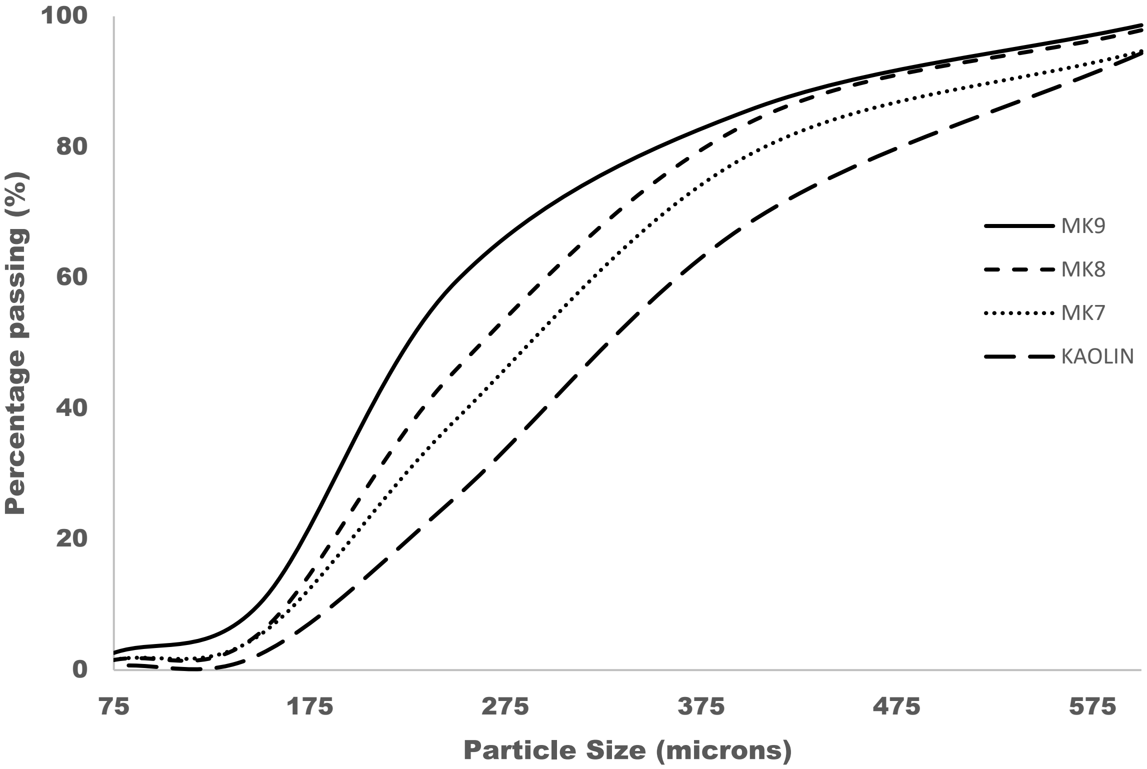


Figure 1: Particle Size Distribution of Kaolin, MK7, MK8 and MK9

X-ray Analysis of Kaolin and Metakaolin

Table 2 shows the XRF results of the chemical analysis of kaolin and metakaolin samples; MK7, MK8 and MK9. The sum of the silica and alumina was approximately 85% of the total content.

Table 2: XRF Analysis of Kaolin and Metakaolin

Oxides	Kaolin (wt%)	MK7	MK8	MK9
SiO_2	51.180	47.48	47.21	46.37
Al_2O_3	32.350	45.24	44.03	44.29
TiO_2	0.880	0.01	0.01	0.01
Fe_2O_3	0.340	0.30	0.36	0.32
Cl	0.800	0.02	0.09	0.03
CaO	0.018	0.04	0.07	0.05
MgO	0.001	2.14	2.57	3.42
Na_2O	0.013	0.19	0.24	0.22
K_2O	1.870	0.38	0.49	0.44
MnO	0.017	0.04	0.05	0.05
PbO	0.010	0.01	0.01	0.01
Ga_2O_3	0.014	0.02	0.02	0.02
ZnO	0.008	0.01	0.01	0.01
LOI	12.060	2.00	2.4	2.31

LO1 = Loss of ignition

X-Ray Diffraction of Kaolin and Metakaolin

Significant peaks of kaolinite mineral were noticeable for the raw kaolin signifying that it possesses a crystalline structure as shown in Figure 2 between the 2θ = 10^o and 30^o. These peaks diminished with increasing temperature to get a more amorphous material as represented in the combined graphs of Figure 3. The minerals present in the mix were majorly kaolinite and trace quantities of muscovite and rutile. After thermal activation, the significant minerals present from the XRD apart from kaolinite were rutile and phengite for 700^{o}C and 800^{o}C while phengite and biotite were noticeable at 900^{o}C as depicted in (Table 3).

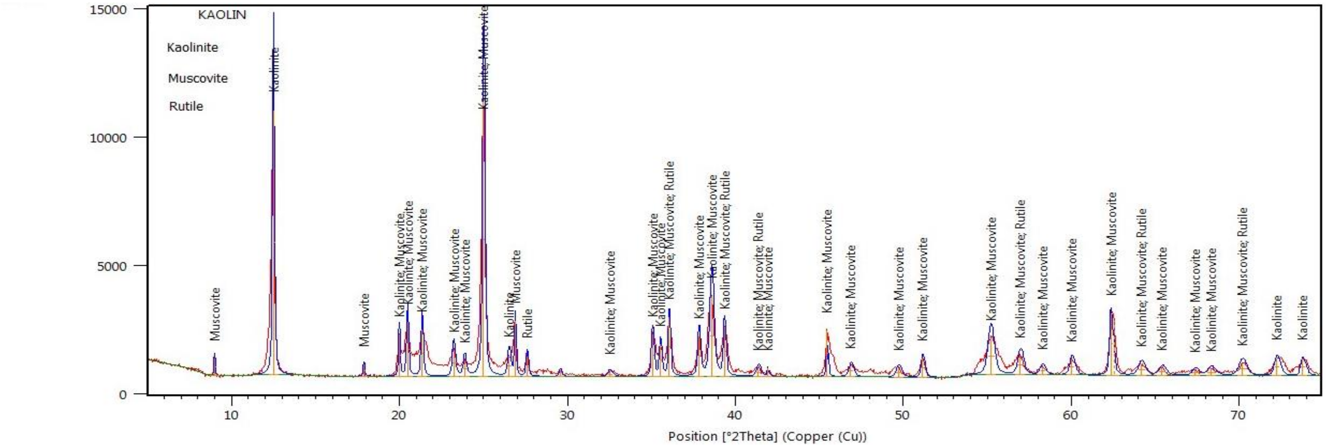


Figure 2: XRD Pattern of Raw Kaolin

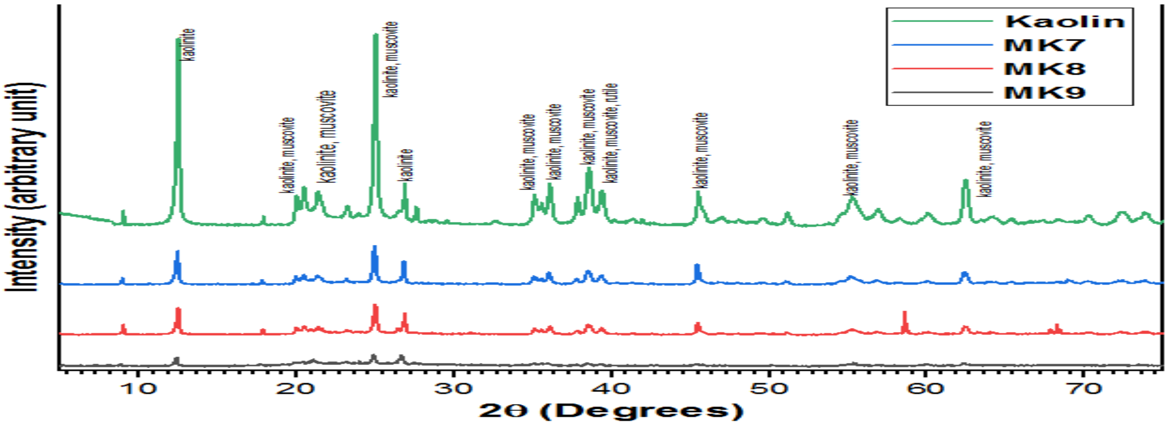


Figure 3: Combined XRD Graphs of Kaolin and Metakaolin

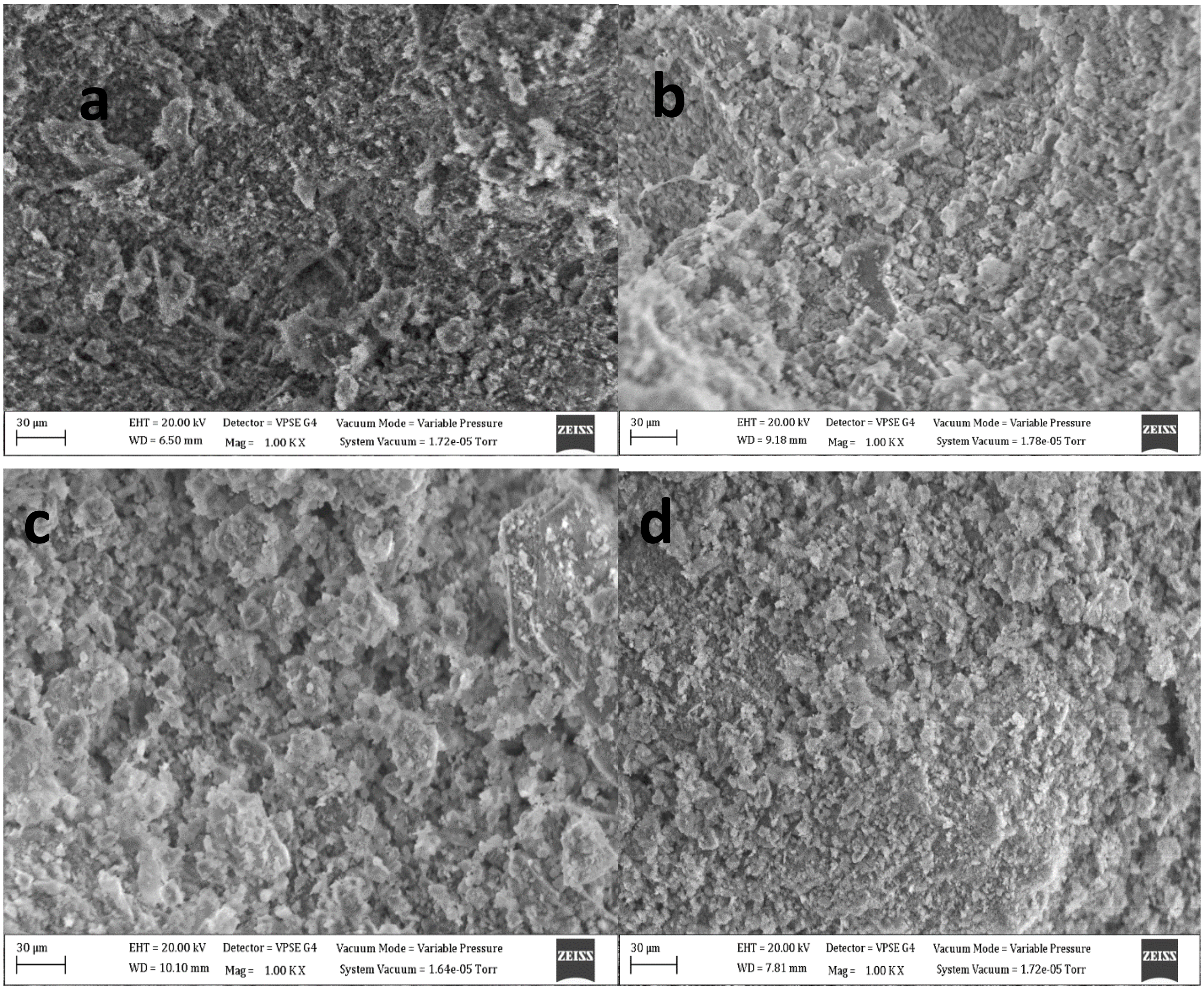
Table 3: Mineralogical Composition of Kaolin and Metakaolin

Source	Kaolinite ($Al_2Si_2O_9$)	Muscovite ($K_{2.4}Na_{1.48}Al_{11}$)	Rutile (Ti_2O_4)	Phengite ($K_{1.9}Na_{0.1}Al_{9.1}$)	Biotite ($K_6Mg_{18}Si_{18}$)
KHS	78	12.1	9.3	NP	NP
MK7HS	84.0	NP	NP	16.0	NP
MK8HS	72.9	NP	NP	27.1	NP
MK9HS	63.9	NP	NP	NP	36.1

NP = Not present

Micrographs of Raw and Calcined Kaolin

The SEM micrographs of the raw kaolin, calcined kaolin and the MK9HS sample are presented in Figure 4. The morphology of the samples shows that the kaolin and metakaolin have plate-like irregular structures. The MK9HS binder morphology revealed the presence of air trapped in the sample which may contribute negatively to the strength of the binders.



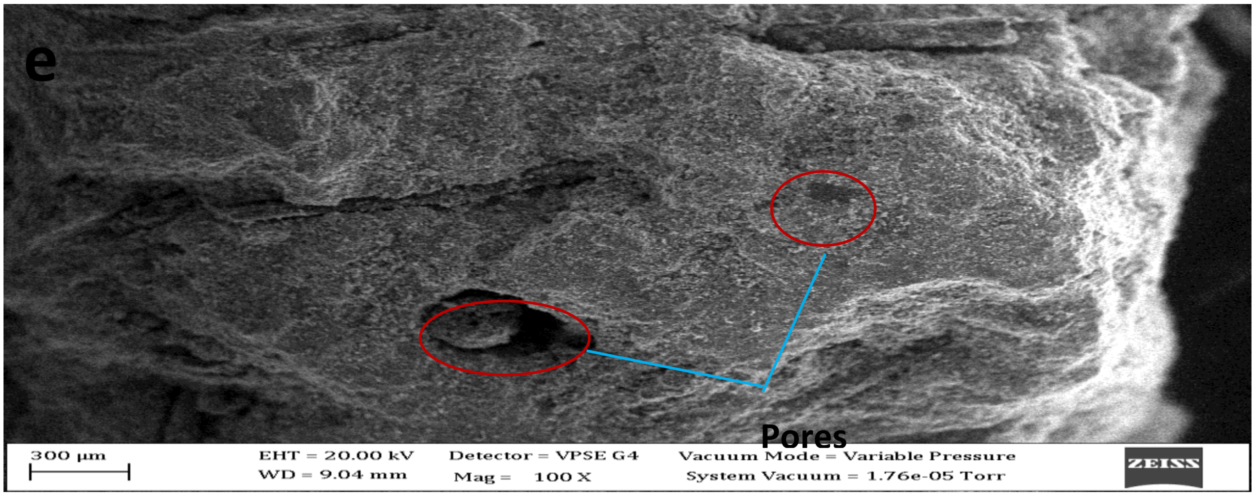


Figure 4: SEM Image of (a)Kaolin (b) MK7 (c)MK8 (d)MK9 and (e) MK9HS

Compressive Strength Test

The compressive tests for the investigated samples are represented in Figure 5. The results depicts a correlation with increasing the calcination temperature of the precursors. The compressive strength of the KHS sample could not be taken at 7 days because the sample had a longer setting time compared to those prepared from the MK and could not be demoulded on the first testing age (7 days). This slow setting time may be as a result of using kaolin which is unreactive than the metakaolin. The kaolin also had larger particle sizes which reduces the surface area and thus the reaction speed. Other samples were conveniently demoulded after 24 hours and allowed to achieve their respective testing age. A maximum compressive strength of 14.9 MPa was gotten at the 28-day curing time for MK9HS though there was no significant difference between the compressive strength obtained at 800°C (14.6 MPa).

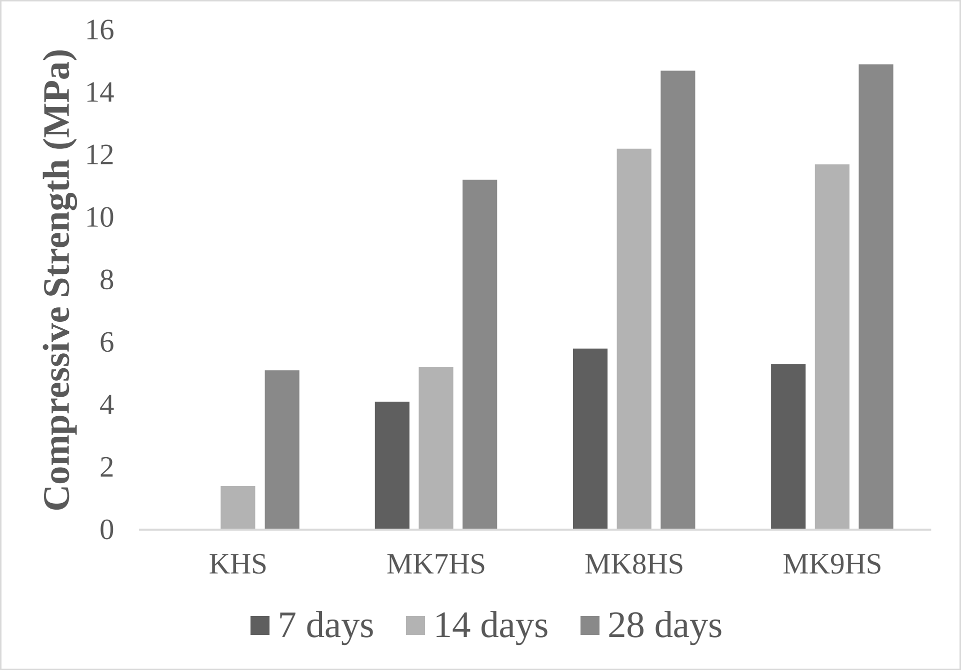


Figure 5: Compressive Strength of Geopolymer Binders

5.0 CONCLUSION

In this study, the properties of kaolin and metakaolin were investigated. There were further used to prepare geopolymer binders in which the compressive strength and microstructure of the binders were investigated. The following gives an overview of the overall study;

i. Increasing the calcination temperature increased the amorphousity of the clay sample with the MK9 having an almost totally amorphous structure.

ii. The particle size of the samples increased with increasing calcination temperature.

iii. The use of raw kaolin for geopolymer synthesis had a long setting time and as such compressive strength could not be performed at the 7 day testing age.

iv. The compressive strength of the samples increased with the calcination temperature and the maximum compressive strength was 14.9 MPa though there was no significant difference between the strength obtained with MK8.

v. The surface morphology of the samples shows that the metakaolin and kaolin has plate like structure. Also, pores were discovered on the geopolymer binder which is due to the presence of air trapped in the binder.

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