Journal of Material and Process Technologies

Available online at http://journal.aastu.edu.et/

Nano-metakaolin-enhanced fly ash and cement-based geopolymer mortar

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Article Information

Article history:
Received 18 May 2024
Received in revised form 12 August 2024
Accepted 30 August 2024

Keywords:
Nano-metakaolin
Geopolymer
Polymerization
Mechanical properties
Microstructure

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https://doi.org/10.69660/jmpt.v1i1.62

Abstract

The addition of Nanomaterials to Geopolymer mortar causes substantial modification in the kinetic of polymerization. The purpose of this research is to study, the effect of nano metakaolin in cement-based fly ash geopolymer mortar. The ratio of alkaline activators and molar concentration of NaOH was kept constant at 1.5 and 12M respectively, while the proportion of Portland cement and fly ash constitutes 30% and 70% of the total starting materials respectively. The replacement level of nano metakaolin was (0%, 5%, 10%, 15%, and 20% by weight of binders). Mortar mechanical and microstructural Properties were evaluated by conduct compressive strength, flexural strength, ultrasonic pulse velocity, scanning electron microscope (SEM) and x-ray diffraction (XRD) analysis. The result shows significant improvement in mechanical performance and denser morphology than the control mix. Therefore, geopolymer mortar containing 10% replacement of nano metakaolin has shown particularly good results and enhancement in various aspects of the material performance and properties, indicating its potential for wider implementation in the construction industry.

1. Introduction

Construction technology has undergone some considerable changes. The major thrust is to renovate the various techniques involved in construction and at the same time to use alternative construction materials. Research has been in progress to evaluate both short and long-term mechanical characteristics of cementation composites and has found importance throughout the world [1]. Thus, it can find many new different forms of additives being used, besides the conventional ones which focus on enhancing the mechanical and physio-chemical properties of conventional concrete.

Nanotechnology is the study and use of any structures with a size between 1 nanometer (nm) and 100 nanometers [2]. It enables the control and modification of material properties on the Nanoscale. Nanomaterials successfully change the quality of concrete and mortar [3]. Those materials include Nano silica, Nano titanium dioxide, Nano clay, Nano aluminium dioxide, carbon Nanotubes, Nano ferrous oxide, and Nano Metakaolin. The large specific surface area of the entire nanoparticles imparts unique properties during their interaction with an alkali-activated solution to form the geopolymer.

In the recent past, various studies have been conducted on the application of nanotechnology in geopolymer mortars. Assaedi et al. [4], and Gao et al. [5] have reviewed the effect of different nanomaterials such as nano silica, nano titanium, nano alumina, and nano clay and nano carbon tubes. Mohsin et al. [3] has reported that their usage can significantly improve the mechanical and durability properties of geopolymers. Also, incorporating Portland cement into the system leads to significant effects on the setting behavior and early strength development [6]. The compressive strength values of metakaolin and those containing up to 40% OPC are higher than traditional OPC mortar with 30%, as the hardening time progresses, the (N, C)-A-S-H type gels, so-called hybrid gels, and aluminium-modified calcium silicate hydrated C-A-S-H type gels in combination densify the cementitious matrix and are responsible for the mechanical performance of this type of material [7]. The microstructure of the geopolymer containing nanoparticles was more compact and uniform. Nanomaterials in geopolymers enhance the polymerization process [8, 9]. Kaur et al. [8], and Shilar et al. [9] studied the microstructure and strength development of fly ash-based geopolymer mortar with nano-metakaolin, and the pozzolanic action of nano metakaolin in the mortar achieved approximately 70-80% of its 28-day compressive strength after 3 days of curing at ambient temperature. Korniejenko et al. [10] also studied the Hybrid Geopolymer materials based on Fly ash, Metakaolin, and cement to see the improvement of mechanical properties and investigate the positive properties of OPC with the properties of alkali-activated materials. The hybrid cementitious system is generally classified as an alkali-activated Portland blended cements or alkali activated Portland fly ash cement [11]. It has been consistently found that the use of nano Metakaolin and the addition of cement have a significant effect on the mechanical properties of geopolymer. Despite this, Ordinary Portland cement production emits large amount of gases to convert raw material into cement products [12, 13]. Alternatives have been studied to partially or replace the consumption of Portland cement [11]. During the last few decades, research has been focused on developing alternative cementitious materials to reduce the release of greenhouse gases, which can help in the development of a sustainable environment [14]. Geopolymers are gaining popularity as an alternative to Portland cement due to their reduced carbon footprint [15]. Geopolymers are an inorganic alumino-silicate polymer that is synthesized by alkaline activation of various aluminosilicate materials such as fly ash, ground granulated blast furnace slag and metakaolin [13]. The problems lie in the limited research and knowledge available on the specific combination of nano Metakaolin, fly ash, and cement in geopolymer mortar and the usage of nanoparticles in geopolymer [16]. The lack of comprehensive studies and guidelines hinders the widespread adoption and optimization of this innovative material in construction applications.

This study sets out to address this gap and examine the effect. Nano Metakaolin was prepared by calcined kaolin clay. Kaolin deposit is found in a different part of Ethiopia. Bombawuha and Belessa Kaolin is found in southern Ethiopia, Kombolcha kaolin is found in Harer. The investigations also characterize the properties of metakaolin, understand the physical and chemical characteristics, and enable the understanding of the pozzolanic action of Nano Metakaolin in geopolymer Mortar by conducting different physical and microstructural tests.

2. Materials and methods

2.1. Materials

The Nano Metakaolin that is partially replaced with binder was obtained by calcined Kaolin clay. The fly ash was from Ayka Addis Textile and Investment Group PLC and Dangote with 42.5 N grades was used as Ordinary Portland cement. Commercially available sodium silicate solution and sodium hydroxide were obtained from Chemical Trading PLC. The pellets were commercial grade and 97% pure. Locally available river sand was used as fine aggregate.

2.2. Method

The physical properties and the chemical composition of Metakaolin were tested. Kaolinite is a pure clay mineral crystal of one part alumina and two parts silica. The sample preparation method starts with drying the collected and crushed kaolin sample and then breaking it up into small pieces. The crushed sample was then calcined in a muffle furnace for 2 h. At 700 °C it turns into metakaolin. During calcination, a source of kaolinite is heated to a temperature between 650 °C and 750 °C. Finally, the samples were sieved through a 75 µm sieve.

Table 1. Chemical and physical properties of metakaolin and fly ash.

Properties	Metakaolin	Fly Ash
Chemical Compositions		
SiO_2	57.42	46.94
Al_2O_3	40.63	28.4
Fe_2O_3	0.02	4.42
CaO	0.08	1.04
MgO	<0.01	0.46
Na_2O	0.04	0.18
K_2O	<0.01	0.28
MnO	0.04	0.06
P_2O_5	0.21	0.11
TiO_2	0.42	0.75
LOI	0.49	14.91
$\Sigma SiO_2 + Al_2O_3 + Fe_2O_3$	98.07	79.76
Physical Properties		
Particle Size	40 nanometers	Below 75 µm
Color	White	Dark gray
Specific Gravity	2.63	2.4

Table 1 summarizes the chemical and physical properties metakaolin and fly ash. According to ASTM C 618 classification, both powders can be classified as natural pozzolan material. In addition, the chemical compositions of fly ash shows that the loss of ignition is 14.9 despite summation of ($SiO_2 + Al_2O_3 + Fe_2O_3$) = 79.76 which is greater than 70 % and it can be class F type Pozzolanic material. Furthermore, because CaO is less than 10 which is 1.04 it is low calcium fly ash. The chemical composition of fly ash and metakaolin has influence factors such as reactivity and mechanical properties.

Sodium-based alkaline solutions were used to react with the fly ash to produce the binder. Sodium hydroxide solution made dissolving pellets in distilled water. 12 molar solutions were made by dissolving 480 g of sodium hydroxide pellets in distilled water and adding water until the solution reaches 1 L. The two alkaline solutions, sodium silicate solution, and sodium hydroxide solution were mixed 24 h before casting to allow the liquid's exothermic heat to cool at room temperature.

Table 2. Test results of fine aggregate.

Type of Test	Result
Fineness Modules	3.09
Bulk specific gravity	2.36
Saturated surface dry	2.38
Apparent sp. gr	2.41
Water Absorption Capacity	1.31%
Silt content	1.80 %

After characterizing materials, the mortar was prepared by determining the correct proportion of the materials suggested by Reddy et al. [17]. The binder-to-sand ratio was set to 0.5; the molarity of NaOH solution and the ratio of sodium silicate to NaOH solution were 12 M and 1.5, respectively. Table 3 presents the mix proportions of the mortar’s ingredients.

Table 3. Mix designation for different percent replacement of nano metakaolin (g/cm^3).

Mix ID	Nano metakaolin	Fly ash	Cement	Fine aggregate	NaOH	Na_2SiO_3
NMK0%	0	1190	510	2550	1020	1530
NMK5%	85	1130	490	2550	1020	1530
NMK10%	170	1070	460	2550	1020	1530
NMK15%	260	1010	430	2550	1020	1530
NMK20%	340	950	410	2550	1530	1530

3. Results and discussion

3.1. Harden properties

3.1.1. Compressive strength

The compressive strength test result of nano metakaolin modified geopolymer mortars are illustrated in Fig. 1. The 7 and 28 days average compressive strength was performed and calculated based on maximum load. It is marked that Metakaolin geopolymer mortar compressive strength slightly rises with 5 and 10% nano. This is attributed due to the contribution of silica and alumina oxide of nano metakaolin in the polymerization reaction. Metakaolin replacement levels while declining with further increments. This result confirms that the addition of nano metakaolin improves compressive strength in every percent replacement compared to the control mix.

The reason for an increase in compressive strength of fly ash-based geopolymer mortar with different percentage levels of nano metakaolin may be attributed to the contribution of silica and alumina oxide of nano metakaolin in the polymerization reaction. However, there is a slight difference between the 7 and 28 days of test results this is because geopolymer mortar gets its strength in the early stage. 28 days test result increases by 1.97%. This complies with the results obtained by Kaur et al. [8]. Fly ash-based geopolymer mortar incorporated with nano metakaolin gained its 28-day compressive strength in the early stage.

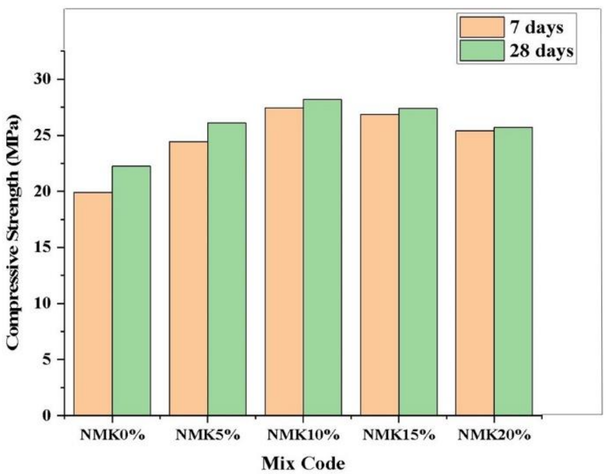


Fig. 1. Fig. 1. 7 and 28 days average compressive strength test result.

3.1.2. *Flexural strength test*

Fig. 2 illustrates the flexural strength the geopolymer mortar of different mix types cured for 7 and 28 days. The addition of nano metakaolin increased the degree of polymerization in matrix attributed to many unsaturated bonds and hydroxyl bonding in different states of nanomaterial surface [18], it was also noted that the improved strength start to decreased when the nano metakaolin content exceeded 10% similar to this researcher reported that the decrease in strength can be due to the concentration of nanoparticles which cause the aggregation of particles causing them to mass together and form layers. As a result, the nanoparticles are not evenly dispersed throughout the polymer matrix [19].

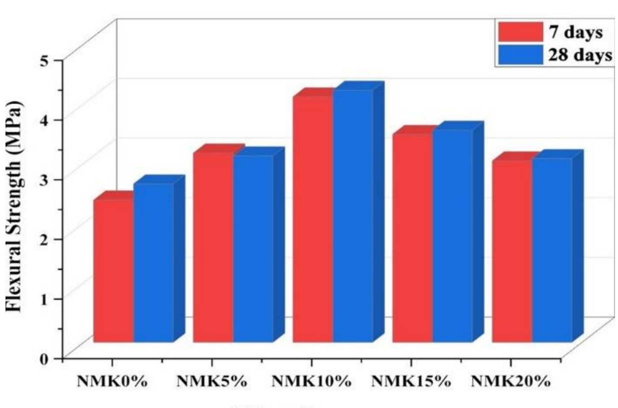


Fig. 2. 7 and 28 days Average Flexural strength test result.

3.1.3. *Ultrasonic pulse velocity*

The value indicated that the ultrasonic pulse velocity (UPV) of both mortars correlated with the compressive strength (Figure 3). Although the UPV values of mortars tended to decrease with the increase in nano metakaolin content. A previous study reported by Uysal et al. [20] showed a similar result in the relation value between UPV and compressive strength. The formation of gels consequently refines the pores of hardened mortar, which is essential for forming a compact morphology that will eventually improve the UPV, compressive strength and durability of mortars. The linear relation between compressive strength and UPV expresses that the greater the UPV values, the higher the compressive strength record. Nuaklong et al. [21] established the correlation between compressive strength and UPV based on broad data of fly ash-based geopolymer concrete, and a linear relationship was observed. Similarly, Chandak and Pawade [22] showed the variation in compressive strength values has a linear relationship with the UPV. Based on those research findings the connection between ultrasonic pulse velocity on different replacement percentages of mineral metakaolin and compressive strength has a direct relationship.

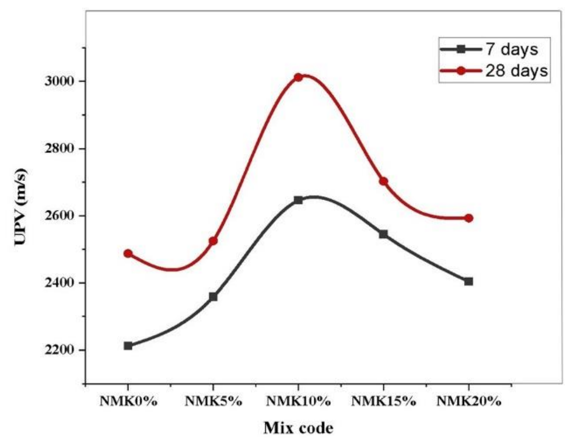
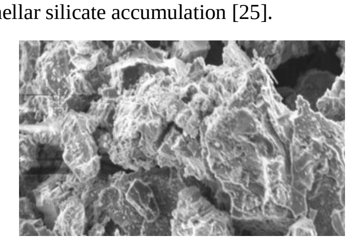


Fig. 3. 7- and 28-days Ultrasonic pulls velocity test result.

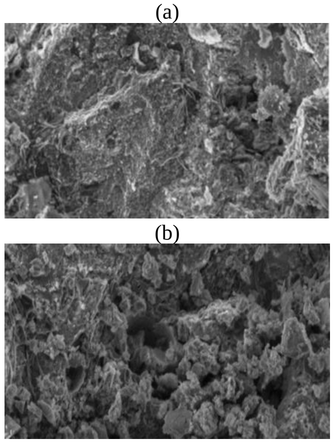
3.2. Microstructure

3.2.1. *SEM analysis*

SEM analysis was conducted for mortars with a control mix, 10%, and 20% nano metakaolin contents. Typical images from the SEM with (50µm and x600) resolution with and without nanoparticles were taken to compare the result shown in Figure 4(a) shows the matrix of control geopolymer mortar and it is porous. Furthermore, with the increased amount of nano metakaolin content Figure 4(b) it is less porous and dense because nanoparticles have a filling effect [23]. Figure 4(c) shows mortar containing 20% nano metakaolin which might have unhydrated fly ash and metakaolin particles [24]. The original unhydrated fly ash particle which is prepared to mix was spherical and unhydrated metakaolin particles were irregularly blocky with lamellar silicate accumulation [25].



(a)



(b)

(c)

Fig. 4. SEM image of selected mortar mixtures (a) NMK0%, (b) MK10%, (c) NMK20%.

3.2.2. *XRD Analysis*

The X-ray diffraction pattern for the control mix, 10 and 20 replacement levels of nano metakaolin was given in Figure 5. Major peaks were identified as quartz this result is in agreement with the XRD data reported by Hwang et al. [26]. The decomposition of the C-A-S-H phase which is responsible for durability can produce new crystalline gypsum phases, as shown by the lower corresponding peak of diffraction, which is similar to other literature observations [27]. At approximately 20-30o, 2θ all compositions showed a peak of quartz and small peaks of Al2O3. A similar report by Phoo-Ngernkham et al. [28] showed that the existence of geopolymer phases is associated at peaks of 28-35o, 2θ, and the phases of CSH and C-A-S-H are associated primarily at the peak of 38°, 2θ.

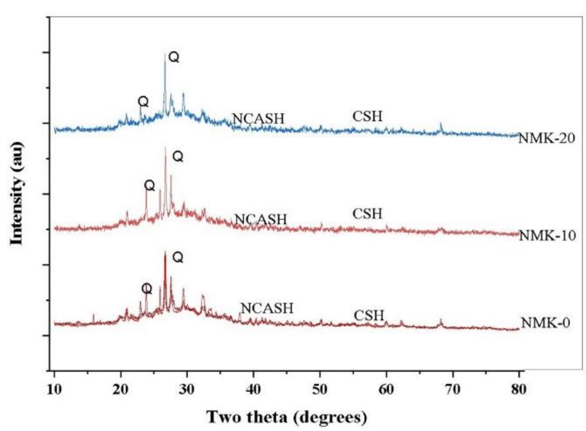


Fig. 5. X-ray diffraction patterns of NMK with 0%, 10%, and 20% mortar mixtures ,

4. Conclusions

From the analysis of the results obtained the following conclusions are made;

- The chemical composition test indicates that metakaolin from Belessa kaolin and fly ash from Ayka Addis textile factory was assigned as pozzolanic material as Prescribed by ASTM C 618 which depends on the percentage composition of SiO_2, Al_2O_3, and Fe_2O_3.
- The pozzolanic activity of nano metakaolin contributes to the formation of additional calcium silicate hydrate gel. It being a highly reactive Pozzolans enhances the workability, setting time, and rheological behavior of geopolymer.
- The compressive and flexural strength of mortar increases with an increase in nano metakaolin content from 5 to 10%, however, it decreases with further increments.
- Furthermore, nano metakaolin contributes to the densification and refinement of the microstructure, resulting in reduced porosity and increased compactness which decrease water absorption and improve microstructural properties of mortar.

Acknowledgements

We would like to express our sincere gratitude to Addis Ababa Since and Technology University for giving me this chance and also for granting me access to the construction material laboratory.

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