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Facile production of nano-scale metakaolin: An investigation into its effect on compressive strength, pore structure and microstructural characteristics of mortar

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HIGHLIGHTS

- Facile production of nano metakaolin (NMK) via exfoliation of metakaolin is proposed.
- Specific surface area, mineralogical composition and nano-morphology were investigated.
- The exfoliation treatment is very effective in enhancing the surface area of kaolinite.
- Compressive strength and pore structure of mortars incorporating NMK were evaluated.
- NMK considerably enhanced the compressive strength and reduced mean pore size.

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ABSTRACT

The use of nano materials as partial replacement for cement has been considered all over the world, particularly in the production of high strength and high performance cement based structures. This study aims at facile production of nano-scale metakaolin (NMK) and investigating its influence on the mechanical, pore structure, phase composition and microstructure characteristics of hardened mortar. NMK with superior surface area was effortlessly prepared via exfoliation of thermally activated ordinary kaolin (MK) with the aid of organic ammonium chloride. SEM micrographs confirm the formation of nanoplates of few nanometers in thickness; furthermore, specific surface area was evaluated by the BET analysis. The exfoliated NMK showed greatly enhanced surface area. Two groups of MK-blended mortars were prepared in which cement was partially replaced with 0, 1, 2, 3, 4, and 5 wt% of MK and Exfoliated NMK. Exfoliated NMK was found to be highly effective in enhancing the compressive strength of mortar and an optimum replacement within 3% can be concluded. There were enhancements by about 24% compared with the unexfoliated MK blended mortar and 54% compared with the plain ordinary mortar. The BET analysis confirmed that; NMK provides significant refinement in pore structure of blended mortar. The phase composition analysis by TGA and SEM indicate that NMK acts not only as a filler to improve the packing inside the cementitious matrix, but also as an activator to promote hydration and pozzolanic reactions.

1. Introduction

The research in nanomaterials has revealed a lot of possibilities in varied industries and scientific endeavors. As concrete is one of the most used materials in the construction industry, it is advantageous to improve its performance. The mechanical performance of cementitious structures depends on phenomena that occur at the micro and the nano-scale. Carbon nanotubes (CNTs) are found to enhance the tensile strength of cementitious materials by bridging cracks at the nanoscale [1]. Nanomaterials have been widely used in the development of cement paste and mortar with improved mechanical, physical, structural and durability characteristics. Nano materials with various morphologies have been widely investigated for enhancing cement and concrete composites including spherical materials (e.g., nano-SiO_2, nano-TiO_2, nano-Al_2O_3, nano-$CaCO_3$, nano-Fe_2O_3, nano-Fe_3O_4, etc.) or as nanotubes or fibers (e.g., carbon nanotubes and carbon nanofibers, respectively) or as nano sheets (e.g., nano-clay) or as nano platelets

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(e.g., nano graphene oxide) [2]. The role of the nano particles (NPs) can be explained through the mechanisms summarized as follows: NPs not only act as fillers to improve the microstructure, but also as an activator to promote hydration and pozzolanic reactions [3]. It also act as a nucleation seeds for the calcium silicate hydrate (CSH) which lead to accelerating hydration rate and improving early-age mechanical properties of cementitious materials [4]. Nano silica (NS) was found to accelerate the consumption of C_3S and the creation of portlandite (small CH) crystals and homogeneous clusters of CSH phase [5], and NPs modify the microstructure of the interfacial transition zone between aggregates and cement paste [6]. Recent studies reported that nano-scale materials containing an amorphous silica (SiO_2) such as colloidal nano-silica (CS), nano metakaolin (NMK) and nanostructured slag which characterized with high surface areas, are unstable and tends to react faster when used as an additive in the cementitious matrix [6–8].

Many researchers have affirmed that replacing cement with very small amounts of NS has revealed good impact on the mechanical performance of cement-based composites by accelerating the pozzolanic reaction; in addition, NS improves workability and enhances durability [9–12]. Recently, a growing concern in the use of high-reactivity metakaolin (MK) as a supplementary cementitious material in the concrete industry has been observed. MK is an ultrafine pozzolana, produced by calcining of kaolinite clay at a temperature ranging from 600 to 900 °C to release the chemically bound water and destroy the crystalline structure to form an active amorphous material [13]. Metakaolin (MK) is characterized with particle size less than 2 µm. Recent studies have shown that the incorporation of MK significantly improved the mechanical and durability characteristics of concrete. The best performance of cement mortar can be achieved at MK replacement levels between 10% and 20% [13] When MK reacts with calcium hydroxide released during cement hydration, the main phases produced are CSH, C_2ASH_8 and C_4AH_{13} which contribute to strength [14]. The inclusion of nano metakaolin (NMK) into cement paste and mortar significantly enhances the compressive and flexural strength and resulted in quite dense, compact and uniform microstructure [15,16]. A previous study reported an enhancement of compressive strength by about 24% which was achieved for the mortars incorporating of 3% nano-clay [17]. the effect of doping of nano-metakaolin (NMK) into ordinary Portland cement (OPC) on the hydration and microstructural characteristics of hardened OPC–NMK pastes was recently investigated, The OPC was partially substituted by NMK at 4, 6, 10 and 15% (by weight). The incorporation of NMK into cement has improved the compressive strength of the hardened pastes during all ages of hydration, an enhancement by about 28% was attained for the paste containing 10 wt% NMK at 28 days of hydration [18].

Generally, the uniform distribution of nano clay platelets is one of the main issues that have to be addressed while preparing nanocomposites; furthermore, the enhanced performance properties could only be achieved at nanoscale dispersion; therefore, To achieve nanoscale dispersion, delamination and, thereby exfoliation of clay platelets is a must. Although, NMK was utilized in many previous studies for nanomodification of cement and concrete structures; however, the authors did not take into account the exfoliation of NMK stacked particles, usually use only sonication to achieve good distribution through mixing/casting cement and mortar samples [15,16,18]. Limited studies have investigated the effect of exfoliated nano clay on cement based materials [19].

The preparation of exfoliated and well dispersed nano clay particles by facilely methods may highlight the significance and originality of this research. The proposed nano material (NMK) is characterized by various advantages: (i) economic – this material is very cheap (cost effective), (ii) availability – this material is locally available, and (iii) unique physical properties (e.g., large surface area and platelet-like morphology which makes it favourable to use in cementitious matrix reinforcement.

The aim of study has been extended also to investigate the influence of the prepared NMK on the mechanical, pore structural, phase composition and microstructural characteristics of hardened mortar.

2. Experimental

2.1. Materials

The cement used in this study was ordinary Portland cement, OPC (CEM I: 42.5 N). the fine aggregate was natural siliceous sand passing through a 2.36-mm sieve and with a specific gravity of 2.60. Natural kaolin clay was used in this investigation. The oxide composition of kaolin and ordinary Portland cement are summarized in Table 1.

2.2. Kaolin activation and exfoliation

In order to get active amorphous metakaolin, The kaolin has to be thermally treated at high temperature, for this purpose the DTA analysis was performed for the kaolin to specify the decomposition/calcination temperature as illustrated in Fig. 1.

As it is clear, the kaolin possessed an endothermic peak at 510 °C assigned to its dehydroxylation (i.e. the conversion of kaolin, $2SiO_2.Al_2O_3{\cdot}2H_2O$, into metakaolin. The Kaolin was thermally treated at 600 °C for 2 h to attain complete dehydroxylation and to get active glassy metakaolin (MK). The ingredients were homogenized on a roller in a porcelain ball mill with four balls for 1 h to assure complete homogeneity. As reported in previous studies, the clay minerals have strong tendency to form stacks owing to vander walls' forces. furthermore, the enhanced performance of nano modified composites could only be obtained if good dispersion is attained. To achieve nanoscale dispersion, delamination and, thereby exfoliation of these mineral platelets is prerequisite.

Dispersant solution was prepared by dissolving organic ammonium chloride powder (NH_4Cl) at a ratio of (7mg NH_4Cl: 1gm NMK) in proper a mount of distilled water (about 250 ml). The metakaolin (25 g) was added to the dispersant solution and stirred to insure homogenity. The solution is covered and left for 24 h to insure that the clay plates had been exfoliated. after that it was subjected to sudden heating at 250 °C for 2 h to release the free water, then grinded to fine powder.

The particles causing exfoliation of the clay must be such that they are very thin in cross section, but present a large surface area in their flat dimensions, with the objective of maximizing barrier properties. As the organic ammonium chloride satisfy these criteria, they can produce exfoliation of clay platelets. These molecules expand the galleries of the clay by getting between two molecules owing to their small sizes and thus causing expansion. Exfoliation

Table 1
Chemical Composition of Starting Raw Materials (Mass %).

Oxide composition, Wt%	OPC	Kaolin
SiO_2	21.54	51.40
Al_2O_3	4.02	26.20
Fe_2O_3	2.93	8.81
CaO	61.82	0.55
MgO	1.59	0.01
SO_3	3.48	0.11
L.O.I.	3.64	8.83
Na_2O	0.42	0.19
K_2O	0.25	1.9
Total	99.69	99.7