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Performance-based study on the rheological and hardened properties of blended cement mortars incorporating palygorskite clays and carbon nanotubes

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HIGHLIGHTS

- CNTs increased rheological parameters in cement system and decreased them in blended system.
- Palygorskite clays increased yield stress and decreased plastic viscosity in both systems.
- Combining CNTs and palygorskite clays led to a superimposed effect on rheological parameters.
- Palygorskite clays, as a rheological modifier, can also enhance mechanical properties.

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ABSTRACT

In this performance-based study, the effect of palygorskite clays and carbon nanotubes (CNTs) on the rheological and hardened properties of a cement mortar and a blended mortar containing cement, fly ash and blast furnace slag were compared. Results showed that although the control cement mortar and control blended mortar exhibited similar rheological parameters, the additives had differing effects on each system. Palygorskite clays increased yield stress and static cohesion and decreased plastic viscosity in both systems but these effects were more marked in the cement mortar than in the blended. On the other hand, CNTs increased all measured rheological parameters in the cement mortar and decreased them in the blended. The rheological results highlighted the importance of considering the binder system when utilizing additives with exceptional surface properties like CNTs and palygorskite clays. In the hardened state, electrical resistivity, compressive strength, and tensile strength were evaluated. Results indicated that although the palygorskite clays are utilized primarily as a rheological modifier, they can also enhance mechanical properties.

1. Introduction

The heterogeneity of concrete exists at all length scales, from the macro- to nanoscale. Nanomaterials can be used to modify the structure at the nanoscale to enhance the performance of cementitious materials at the macroscale. Given their significantly high specific surface area, nanomaterials exhibit remarkable changes in surface energy, surface morphology, chemical reactivity and mechanical properties. The novel properties of nanomaterials have roused considerable interest in nanomodification of cementitious materials in both the fresh and hardened states [1].

Nano-sized highly purified palygorskite clays, which are commonly used as a rheological modifier, can significantly increase the yield stress and shape stability of fresh state cementitious materials [2–4], which has been found to effectively reduce formwork pressure [5]. Studies have found that palygorskite clays improve the flocculation strength and floc size, which can explain the increase in yield stress [6,7]. And many other early-age properties have been investigated, including flowability [8], thixotropy [9] and chemical phase change [10]. However, the data on hardened properties are scarce, especially in the presence of dispersants.

Carbon nanotubes (CNTs) exhibit significantly enhanced mechanical properties, i.e. Young's modulus on the order of TPa and tensile strength on the order of GPa, as well as unique electrical and chemical properties [1]. To leverage these properties, numerous studies have demonstrated the ability of CNTs to act as nano-reinforcement and enhance the mechanical properties of cement composites when effectively dispersed in the matrix

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[11–14]. However, very few studies exist in the literature regarding the effect of CNTs on the fresh state properties, especially in cementitious materials containing supplementary cementitious materials (SCMs).

Due to the complexity of SCMs with respect to chemical composition and physical properties, including specific gravity, particle size distribution and specific surface area, the results of SCMs on the rheology of fresh cement-based materials are inconsistent [15–23]. For example, Some studies [22,24] reported an increase in viscosity with fly ash while others show it leads to a decrease [15,18]. Given the prevalence of SCMs, there is a need to investigate the effect of these novel additives on blended systems.

This performance-based study aims to examine the effect of palygorskite clays and CNTs on the rheological and hardened properties of two different systems – a unitary cement mortar and a ternary mortar prepared with cement, fly ash and blast furnace slag. Moreover, the combined effect of palygorskite clays and CNTs was also studied to explore the potential of enhancing the various performance properties of cementitious materials through the addition of nanomaterials with different desired functions.

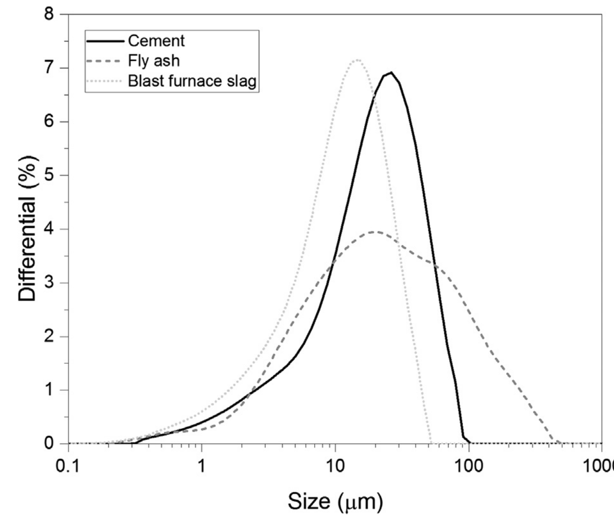

Fig. 1. Particle size distributions of the cement, fly ash and blast furnace slag.

2. Materials and methods

2.1. Materials

Type I Portland Cement was used in all mixes. Type F fly ash and Grade 120 Blast furnace slag were used as SCMs to partially replace the cement. The chemical compositions are shown in Table 1. The particle size distribution of the binders is shown in Fig. 1. The total specific surface area (SSA) of cement, FA and slag were 775, 794 and 1213 m^2/kg, respectively. D10, D50 and D90 are the particle size value where 10%, 50% and 90% of the particles are finer. They are 3.72, 18.82, and 45.17 μm for cement; 3.62, 20.60, and 111.18 μm for fly ash; and 2.41, 10.75, and 25.11 μm for slag. It could be seen that slag is finer than cement in both higher SSA and lower D10, D50 and D90 values. Fly ash has similar SSA and D10 as cement; however larger D90, indicating that fly ash has some large size particles.

The effect of fly ash and blast furnace slag on 28 day compressive strength was evaluated in preliminary tests. The results of blended mortars with binders composed of 50% cement and different dosages of fly ash and/or blast furnace slag are shown in Fig. 2. The control mix with 100% cement content is represented by the horizontal dotted line. As expected, fly ash reduced strength due to delayed pozzolanic reaction and dilution, while slag enhanced strength due to increased reactivity [25]. The grade of blast furnace slags were determined by their slag activity index, SP/P × 100%, where P is compressive strength of portland-cement mortar cubes and SP is the compressive strength of mortar cubes made with the same mass of a blend that is 50% slag cement and 50% portland cement by mass [26]. The slag activity index of the slag in this study is 115 which can be classified as Grade 120 according to ASTM C989 [26]. To compare the effect of the nanomaterials on the two systems, cement versus blended, the strength of the base mix was fixed between the two. Fig. 2 shows that the mix with 25% fly ash and 25% blast furnace slag replacement exhibited 28 day strength that was comparable to that of the 100% cement mortar, thus was selected for this study.

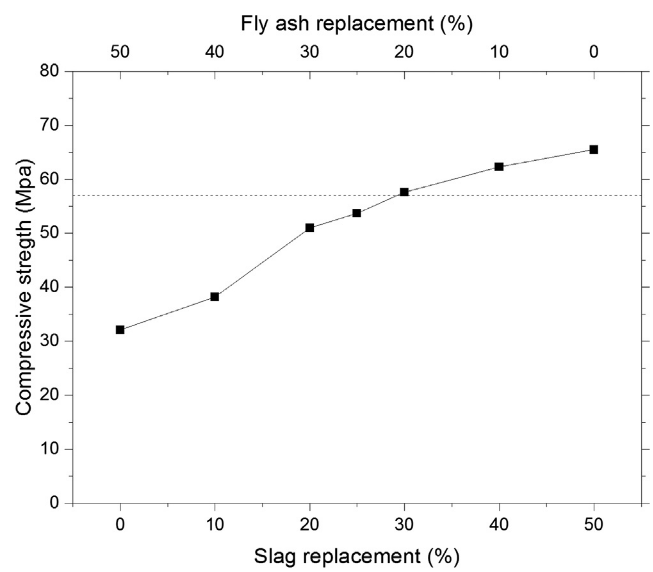

Fig. 2. 28 day compressive strength results of blended mortars with binders composed of 50% cement and different dosages of fly ash and/or slag. Dashed line represents 100% cement mortar.

Table 1
Chemical composition of Type I Portland Cement and Type F Fly Ash.

Chemical Oxide	Type I Cement (%)	Type F Fly Ash (%)
SiO_2	19.2	47.2
Al_2O_3	5.0	23.4
Fe_2O_3	3.4	16.6
CaO	62.4	4
MgO	3.9	–
SO_3	2.7	1.3
Free Lime	1.0	–
Loss on ignition	2.6	2.1
CO_2	1.9	–

A commercially available, multiwalled carbon nanotube with a carbon purity of 90% was selected in order to explore materials that would be more cost-effective and suitable for large-scale application. The average diameter is 9.5 nm and the average length is 1.5 μm. The dosage of 0.01% CNTs by mass of cement was used in this study based on the results of previous work by other researchers [12,27,28]. To disperse the CNTs (dry, as received) they were combined in mixing water with a polycarboxylate-based superplasticizer at a dispersant-to-CNT mass ratio of 5, based on the results of a separate study [11]. The mixture was ultrasonicated in a high intensity ultrasonic processor for 1 h at 40% amplitude. The power of the processor is 500 Watts. To avoid overheating and evaporation of water during ultrasonication, the metal beaker containing the mixture was partially immersed in an ice bath.