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Modification of cement-based materials with nanoparticles

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ABSTRACT

This is a summary paper on the work being done at the Center for Advanced Cement-Based Materials at Northwestern University on the modification of cement-based materials with nanoparticles, specifically nanoclays, calcium carbonate nanoparticles, and nanosilica. The rheological properties of clay-modified cement-based materials are investigated to understand the influence of nanoclays on thixotropy. The influence of the method of dispersion of calcium carbonate nanoparticles on rate of hydration, setting, and compressive strength are evaluated. And an in-depth study on the mechanisms underlying the influence of nanosilica on the compressive strength gain of fly ash–cement systems is discussed. The motivation behind these studies is that with proper processing techniques and fundamental understanding of the mechanisms underlying the effect of the nanoparticles, they can be used to enhance the fresh-state and hardened properties of cement-based materials for various applications. Nanoclays can increase the green strength of self-consolidating concrete for reduced formwork pressure and slipform paving. Calcium carbonate nanoparticles and nanosilica can offset the negative effects of fly ash on early-age properties to facilitate the development of a more environmentally friendly, high-volume fly ash concrete.

1. Introduction

Due to the complexity of concrete, which is heterogeneous at all length scales, and the recent innovations in nanotechnology, nanomodification of cement-based materials has generated much research interest. Nanomodification is the manipulation of the structure at the nanoscale (less than 100 nm) to develop cement composites that exhibit enhanced or novel properties and functions. Carbon nanotubes (CNTs) dispersed by ultrasonication can significantly improve the flexural strength of cement composites by controlling cracks at the nanoscale [1]. Through other mechanisms, often attributed to filler and/or seeding effects, nanoparticles can accelerate rate of hydration and improve early-age mechanical properties of cementitious materials, including those with cement replacement by fly ash. Among the types of nanoparticles investigated are titanium dioxide (TiO_2) nanoparticles [2], zinc dioxide (ZnO_2) nanoparticles [3], calcium carbonate ($CaCO_3$) nanoparticles [4,5], and nanoclays [6], although the majority of studies thus far have focused on nanosilica [7–12]. However, due to the novelty of the technology, more investigation needs to be done to further understand the mechanisms underlying the effect of the nanoparticles, to improve processing, and to evaluate their influence at later-ages.

At the Center for Advanced Cement-Based Materials at Northwestern University (ACBM-NU), work is being done on modifying the fresh-state and hardened properties of cement-based systems (including those containing fly ash) with nanoclays, nano$CaCO_3$ and nanoSiO_2. This paper is a summary of the current studies. The rheological properties of nanoclay-modified cement-based materials are investigated to further understand the influence of nanoclays on fresh-state stiffening and formwork pressure. The influence of the method of dispersion of nano$CaCO_3$ powder on early-age properties is evaluated. And an in-depth study on the mechanisms underlying the influence of nanoSiO_2 on the compressive strength gain of fly ash–cement systems is discussed.

With proper processing techniques and fundamental understanding of the mechanisms underlying the effect of the nanoparticles, they can be used to enhance the fresh-state and hardened properties of cement-based materials for various applications. Nanoclays can increase the green strength of self-consolidating concrete (SCC) for reduced formwork pressure and slipform paving. Nano$CaCO_3$ and nanoSiO_2 can offset the negative effects of fly ash on early-age properties, namely slowed rate of hydration and compressive strength gain, to facilitate the development of a more environmentally friendly, high-volume fly ash concrete.

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2. Experimental methods and materials

2.1. Material properties

Tap water and ordinary Portland cement (OPC) were used in all mixes, along with a type F fly ash in select mixes. The chemical properties are given in Table 1. The fly ash particles are round with a size range of 2–20 microns, as shown in the scanning electron microscopy (SEM) image, Fig. 1a. The spherical morphology of fly ash helps increase the flowability of cementitious materials, including those with nanoparticles, which increase stiffness due to their high specific surface area.

The three types of nanoparticles used in the current studies are nanoclay, nano$CaCO_3$, and nanoSiO_2. The nanoclay was a purified magnesium aluminosilicate, or palygorskite, with a rod-like shape (1.75 μm in length, 3 nm in diameter). The nanoclay has been chemically exfoliated to preserve its uniform shape and size while removing all impurities (such as quartz and swelling clays). As received, they are highly-agglomerated. To disperse the nanoclay, they are blended with water in a household blender prior to mixing with the other dry ingredients. The nano$CaCO_3$ came in dry powder form, with a particle size range of 15–40 nm. Similarly to the nanoclay, they are agglomerated to the micron scale in the as-received state. Two types of colloidal nanoSiO_2 (CNS) with an average particle size of 20 nm (CNS-20) and 10 nm (CNS-10) were used. The transmission electron microscopy (TEM) images of CNS-10 (Fig. 1b) and CNS-20 (Fig. 1c) indicate that most of the nanoparticles are well-dispersed, although some agglomeration may occur.

2.2. Testing procedures

Shear rheological tests were performed in a temperature-controlled rheometer with a coaxial cylinder geometry set at room temperature. The rate of hydration of pastes were measured in a semi-adiabatic calorimeter, where a sample was placed in an insulated drum and its temperature change was recorded for 24 h. ASTM C191 was followed to measure initial and final setting time of pastes with a manual Vicat needle apparatus [13]. ASTM C230 was followed to measure the slump flow of mortars using a flow table [14].

ASTM C109 was followed to measure the compressive strength of pastes or mortars with a 1000 kip (4448 kN) MTS hydraulic testing machine [15] – the loading rate of the test was 0.008 mm/s. For each mix at each age, three samples were tested and the average value was taken to be the representative strength.

Thermogravimetric analysis (TGA, TGA/sDTA 851) was carried out to measure the calcium hydroxide (CH) content of samples. Samples of about 20 mg were heated at atmospheric pressure at a rate of 15 °C/min. The weight loss between 440 °C and 510 °C was considered to be the decomposition of CH. Before measuring, samples were oven – dried at 105 °C for 4 h.

Table 1
Chemical properties of cement and fly ash.

Materials	Type I cement	Type F fly ash
SiO_2	20.2	46
Al_2O_3	4.7	17.8
Fe_2O_3	3.3	18.2
SO_3	3.3	2.59
CaO	62.9	8.4
MgO	2.7	0.95
Na_2O	–	0.59
K_2O	–	2.16
LOI	1.1	1.49
Total	98.2	98.2

Hitachi S-4800 FE-SEM equipped with energy dispersive spectroscope (EDS) was used to analyze the morphology and elemental compositions of the cement paste. A small fractured sample was

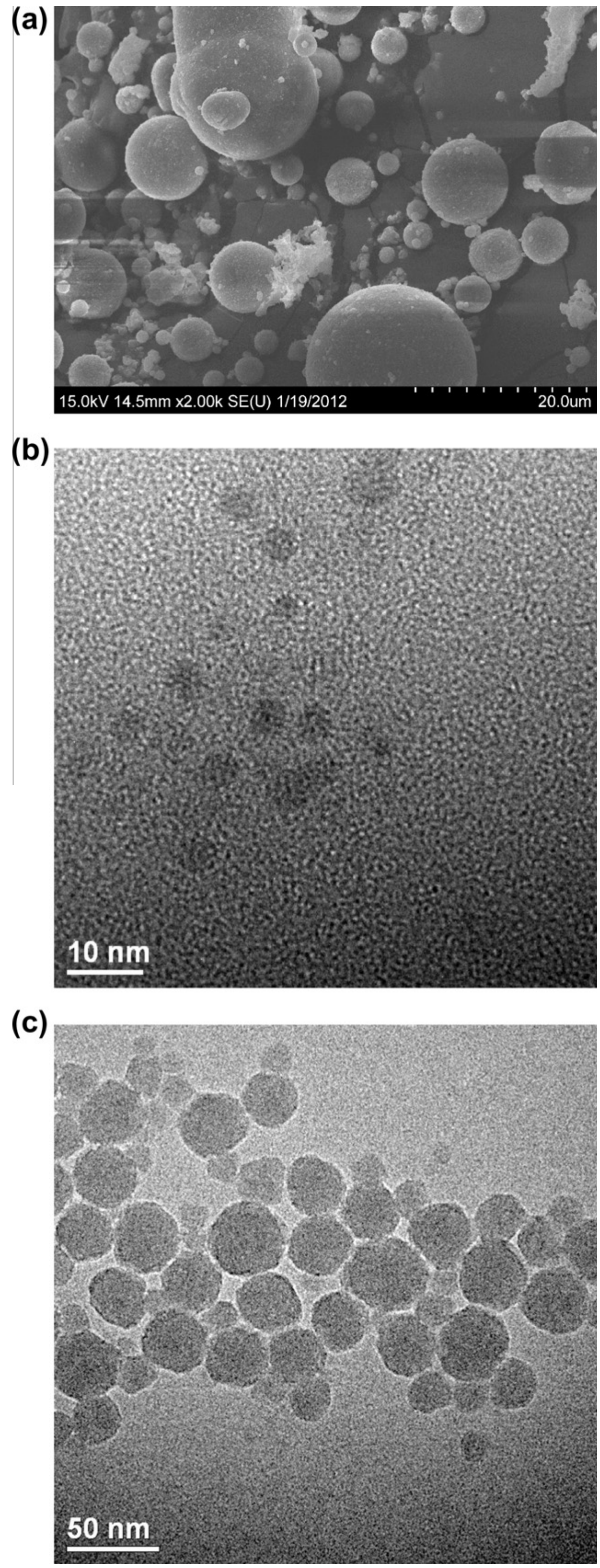

Fig. 1. Morphology of (a) fly ash (SEM), (b) CNS-10 nm (TEM) and (c) CNS-20 nm (TEM).