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The influence of cellulose nanocrystal additions on the performance of cement paste

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ABSTRACT

The influence of cellulose nanocrystals (CNCs) addition on the performance of cement paste was investigated. Our mechanical tests show an increase in the flexural strength of approximately 30% with only 0.2% volume of CNCs with respect to cement. Isothermal calorimetry (IC) and thermogravimetric analysis (TGA) show that the degree of hydration (DOH) of the cement paste is increased when CNCs are used. The first mechanism that may explain the increased hydration is the steric stabilization, which is the same mechanism by which many water reducing agents (WRAs) disperse the cement particles. Rheological, heat flow rate measurements, and microscopic imaging support this mechanism. A second mechanism also appears to support the increased hydration. The second mechanism that is proposed is referred to as short circuit diffusion. Short circuit diffusion appears to increase cement hydration by increasing the transport of water from outside the hydration product shell (i.e., through the high density CSH) on a cement grain to the unhydrated cement cores. The DOH and flexural strength were measured for cement paste with WRA and CNC to evaluate this hypothesis. Our results indicate that short circuit diffusion is more dominant than steric stabilization.

1. Introduction

One of the new engineering frontiers is the design of renewable and sustainable infrastructure materials with novel combinations of properties that radically break traditional engineering paradigms. One promising family of materials are the nano-reinforced materials that can exhibit improvement in properties such as elastic modulus, tensile strength, flexural strength, fracture energy, and impact resistance [1]. On one hand, nano-reinforced materials offer remarkable opportunities to tailor mechanical, chemical, and electrical properties. On the other hand, the intense research in the use of nano-reinforcements has been criticized due to perceived environmental, cost, health and safety issues [2]. Currently, there is a growing push for "greener" products, which includes materials made from renewable and sustainable resources. In addition, there is a goal of minimizing the carbon footprint of infrastructure materials driving interest in biodegradable, non-petroleum based and low environmental impact materials. By increasing the performance of infrastructure materials, it may be possible to greatly reduce the volume of these materials that are used thereby reducing the demand on raw materials. The use of higher performance materials is one way to 'do more with less'.

Nano-fibers have recently been of interest in the studies of cementitious materials, among which, carbon nanotube (CNT) reinforced cement composites have been investigated in the last decade. Due to their high aspect ratio, CNTs are believed to be able to bridge microcracks thereby increasing strength [3]. Li et al. [4,5] showed an improvement of 25% in flexural strength and a 19% increase in compressive strength with a 0.5 wt.% loading of processed multi-walled carbon nanotubes (MWCNTs). Metaxa et al. [6] found the presence of CNTs increased flexural strength of cement paste by 25% and improve the elastic modulus by 50%. Konsta-Gdoutos et al. [3] reported that the flexural strength of cement pastes reinforced with MWCNTs showed an improvement of 30–40% with respect to the plain system. However, reinforcing brittle cement matrices has been a challenge due to reinforcing materials degradation, difficulty to add a sufficient volume without causing difficulties in mixing, enabling fiber dispersion, and the high costs of the reinforcing materials [7].

Cellulose nanocrystals (CNCs) are rod-like nanoparticles (typically, 0.05–0.5 μm in length and 3–5 nm in width) that can be extracted from plants and trees [2]. CNCs are promising nanoscale

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reinforcing materials for cements in that they have several unique characteristics, such as high aspect ratio, high elastic modulus and strength, low density, reactive surfaces that enable functionalization and are readily water-dispersible without the use of surfactant or modification [2]. It is considered here that CNCs can offer new possibilities for cementitious composites for improved mechanical performance, in which the small size of CNCs allows for reduced interfiber spacing, more interactions between cellulose and the cement system, and as a result the CNCs have a greater potential to alter micro-cracking and can therefore increase the strength of the system. Additionally, other benefits of CNCs include, but are not limited to, their renewability, sustainability, low toxicity, low cost (estimated production costs of <$10/lb) [2,8]. Moreover, CNCs are extracted from sources (e.g., plants and trees) that are themselves sustainable, biodegradable, carbon neutral, and the extraction processes have low environmental, health and safety risks [2]. In this work, CNCs are added into cementitious materials to modify the microstructure and improve the mechanical performance.

The majority of previous fiber-reinforced cement composites work, regardless of the dimension of the fibers, attributes the improvement in the mechanical performance to the mechanism of fiber bridging [7]. Most claims are based on the fact that fibers can help delay the crack propagation or even lead to crack arrest. However, the length of CNCs is significantly smaller than most of fibers used to date, and therefore, their ability to reinforce the material needs to be carefully examined. This work systematically studies the effect of CNCs on cement pastes and its implications on the mechanical properties at the macroscopic level. To investigate the CNC–cement pastes, two fundamental questions to be answered are: (1) where are the CNCs located in the cement matrix? (2) How do CNCs interact with the cement particles in both the fresh state and the hardened state after setting? To answer the two questions, a series of experiments were designed and performed to study how the CNCs affect the hydration process, rheological and mechanical properties of the cement pastes, and what mechanisms are responsible for the variation in the mechanical performance. An integrated approach that combines material preparation, experiments, and microscopy to better understand the physical mechanisms that underpin CNCs use in cementitious materials is presented in the following sections.

2. Materials and experimental testing procedures

The CNC–cement paste composites evaluated in this paper were prepared by mixing CNC suspensions, water and cement powder to obtain mixtures with different concentrations of CNC. After preparing the CNC–cement paste mixture, three main aspects of the resulting material were investigated: (1) the curing process, (2) the mechanical properties and (3) the microstructure. While isothermal calorimetry (IC) and thermogravimetric analysis (TGA) were used to determine the DOH of cement pastes; zeta potential, water adsorption and rheological measurements were used to investigate the interaction and affinity of CNCs with cement particles. Additionally, ball-on-three-ball (B3B) flexural testing was performed to measure the flexural strength of the cement pastes at four different ages.

2.1. Cement pastes preparation

A Type V cement was used in this investigation due to its compositional purity (i.e., low aluminates and ferrite phases), the Bogue compositions and Blaine fineness of which are shown in Table 1.

Table 1
Bogue compositions of Type V cement.

C_3S (%)	63.8
C_2S (%)	13
C_3A (%)	0
C_4AF (%)	–
$C_4AF + C_2F$ (%)	12.6
Blaine fineness (m^2/kg)	316

The CNC materials used in this work were manufactured and provided by the USDA Forest Service-Forest Products Laboratory, Madison, WI (FPL) [9]. The as-received CNC materials were in a form of dispersed suspension (5.38 wt.% CNCs in water). The CNCs were extracted via sulfuric acid hydrolysis of Eucalyptus dry-lap cellulose fibers, resulting in a 0.81 wt.% CNC surface-grafted sulfate content.

The cement pastes were mixed with a vacuum mixer (Twister Evolution 18221000 from Renfert USA Inc. [10]). This particular mixer is programmable for consistency and provides a low vacuum environment during cement mixing which can help reduce the entrained air that may develop in mixtures. The following procedure was used for the preparation of the cement pastes: (1) the cement, CNC suspension and water were measured in the mixer bowl; (2) the mixer was set to mix at a speed of 400 rpm for 90 s; (3) a spatula was used scrape the wall and bottom of the bowl (this typically lasted 15 s); (4) Another 90 s of mixing was done at 400 rpm. After the mixing was complete, the fresh cement pastes were cast in plastic cylinders (5.1 cm in diameter and 10.2 cm in height) and sealed at 23 ± 1 °C for curing. At the age of 24 ± 1 h, the cylinder samples were demolded and cut with a water saw into disc specimens with thickness of about 0.7 cm. To avoid end effects, two end pieces were discarded (0.7 cm was removed from the bottom and about 2 cm from the top). Any excess of moisture on the surface was removed with a towel and the specimens were sealed in plastic bags at 23 ± 1 °C until the age of testing. Table 2 shows a summary of the cement pastes that were tested along with CNC concentrations. The CNC concentrations were calculated based on their volume fraction with respect to cement. To avoid confusion, both the quantities in mass and volume are listed here. Cement pastes were prepared at a water to cement ratio (w/c) of 0.35 with seven different CNC concentrations. For consistency, the discussion will be based on the volume fraction in this paper.

2.2. Isothermal calorimetry

To obtain the degree of hydration (DOH) of the cement pastes, the heat flow rate and cumulative heat release were measured with a TAM Air isothermal calorimeter [11]. Immediately after mixing, 25–35 g of the paste sample was transferred to a glass ampoule (22 mm in diameter and 55 mm in height), which was then sealed and placed into the chamber (maintained at 23 ± 0.1 °C) for measurement. Before the data collection started, the isothermal condition was held for 45 min to reach equilibration and the subsequent steady heat measurement was performed for approximately 200 h.

2.3. Thermogravimetric analysis

The thermogravimetic analysis (TGA) was performed using a TA Instruments SDT 2960 Simultaneous DTA–TGA instrument [12] as a complimentary method to obtain the DOH of CNC–cement pastes at three different ages: 7, 14 and 28 days. At the ages of testing, the paste samples were demolded from the sealed plastic containers and ground into powders with mortar and pestle while evaporation was minimized, approximately 65 mg of powder was transferred