



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.

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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 ₃ S (%)	63.8
C ₂ S (%)	13
C ₃ A (%)	0
C ₄ AF (%)	–
C ₄ AF + C ₂ F (%)	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 thermogravimetric 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

Table 2

Experimental matrix for CNC-reinforced cement pastes (CP).

Mixture number	wt. (g)			vol. (cm ³)			CNC/cement (vol.%)
	Cement	Water	CNC	Cement	Water	CNC	
CP-1 (reference)	500	175	0.000	160.3	175	0.000	0.000
CP-2	500	175	0.103	160.3	175	0.064	0.040
CP-3	500	175	0.256	160.3	175	0.160	0.100
CP-4	500	175	0.513	160.3	175	0.321	0.200
CP-5	500	175	1.282	160.3	175	0.801	0.500
CP-6	500	175	2.564	160.3	175	1.603	1.000
CP-7	500	175	3.846	160.3	175	2.404	1.500

into the TGA chamber for measurement. First the temperature in chamber was increased from ambient temperature to 140 °C (the critical temperature reported in reference [13]) by 20 °C/min. For the second step the chamber was kept at 140 °C for 25 min to remove the evaporable water in the sample. Subsequently, the sample was heated, from 140 °C to 1100 °C at a rate of 20 °C/min, in an attempt to extract all chemically bound water (CBW). TGA was performed to obtain the DOH because at later ages the heat release rate from IC is so small that the measuring error might be considerably large. The TGA measurements were also performed on the individual materials of CNC and cement for corrections.

2.4. Zeta potential

The zeta potential ζ is the potential between the liquid layer adjacent to the solid phase and the liquid layer constituting the bulk liquid phase [14] and is a measure of the magnitude of the electrostatic repulsion or attraction between particles [15,16]. In this work, the zeta potentials of the CNC and cement particles were measured to investigate the affinity between them in the fresh cement paste from the point of view of colloidal chemistry. The measurements were taken with a Zetasizer Nano ZS equipment from Malvern Instruments Ltd. [17]. The CNC and cement particles were, respectively, diluted in DI water or simulated pore solution (introduced in later section) to a concentration of about 0.2 wt.% for measurements.

2.5. Water adsorption

Due to the high surface area of CNCs, the adsorption of water may result in a lowered effective water to cement ratio (w/c) in cement mixing and hence a change in the rheological properties of the fresh CNC–cement paste. To study this possible effect, the water adsorption of the dry CNC materials was measured with a Q5000 SA absorption/desorption equipment from TA instruments [18]. The CNC film was obtained by allowing the CNC suspension to dry in an oven at 50 ± 2 °C for 24 h. After the film was weighed, the film was kept in the oven at the same temperature for another 12 h leading to a mass change of less than 0.5%. Then the CNC film was allowed to dry for 36 h in the desorption analyzer at 0% RH. After an initial equilibrium period, the initial relative humidity (RH) in the chamber was increased to 97.5% in steps of 10% increments, with a final step of 7.5%.

2.6. Rheology

The rheological behavior was measured with a Bohlin Gemini HR nano rheometer from Malvern Instruments Ltd. [19]. The testing geometry consisted of two 40-mm parallel plates with serrated surface, which helped to avoid the slippage [20], separated with a gap of 1 mm. Fig. 1 shows the nominal surface geometry of the plates and the testing set-up with the fresh cement paste sample. All the tests were started at an age of about 12 ± 1 min. As the

cement pastes are in the dormant period it is expected that the material behavior does not change significantly during the testing period due to hydration. A cover was placed around the fresh cement during the test to mitigate the edge drying/water evaporation. The five mixtures with low CNC concentration (0–0.5 vol.%) were measured with a shear stress controlled ramp from 5 to 200 Pa in 6 min with a logarithmic increase. The two systems with high CNC concentrations (1.0 and 1.5 vol.%), had a much higher yield stress than the previous five, therefore the testing ramp was set from 20 to 1000 Pa, also in 6 min with a logarithmic increase.

2.7. Optical and scanning electron microscopy

To further investigate the interaction between CNCs and cement matrix and to obtain direct evidence of the CNCs location in the cement matrix, optical and backscattered scanning electron (BSE–SEM) microscope images of hardened cement pastes were obtained and investigated. The samples were demolded at the age of 7 days and cut into 2 cm × 2 cm × 0.5 cm specimens with a water cooled diamond tipped saw blade, and subsequently soaked in acetone for 48 h to replace the pore water and cease hydration. After oven-drying at 55 °C for 24 h, the samples were epoxy-saturated at low vacuum for 4 h and the epoxy solidification was done at 70 °C for 8 h. As the BSE–SEM imaging requires a flat surface, the epoxy-impregnated samples were cut with a low-speed oil saw to expose a fresh surface and a polishing procedure was conducted on the sample surfaces using 15, 9, 3, 1, 0.25 µm diamond paste for 4 min each on top of Texmet paper. The polished samples were first imaged with an Olympus BX51 optical microscope, and then coated with gold/palladium for subsequent BSE–SEM imaging using an FEI Quanta 3D FEG equipment.

2.8. Ball-on-three-ball flexural test

The characterization of the flexural strength of the cement pastes was carried out with a multi-axial ball-on-three-ball (B3B) flexural test. In this testing set-up, the load is given by one ball pressuring downward at the center of the disc sample. Three ball supports are located beneath the sample in the corners of an equilateral triangle. Fig. 2(a) shows a photo of one sample being tested with this fixture. There are several advantages of the B3B flexural tests over other, more traditional, flexural tests performed on beam specimens [3]. For instance, the B3B flexural test requires round-disk samples, which can be easily obtained in large quantities from sectioning a cylinder. The geometry and loading conditions generate a state of biaxial tensile state in the center of the specimen, that makes it more sensitive to defects in all the in-plane directions of the disk [21,23]. For example, longitudinal cracks are not likely to be detected in three- or four-point bending tests because of their orientation with respect to the tensional direction [22].

The flexural B3B strength is obtained by the following expression derived by Börger et al. [23,24]:

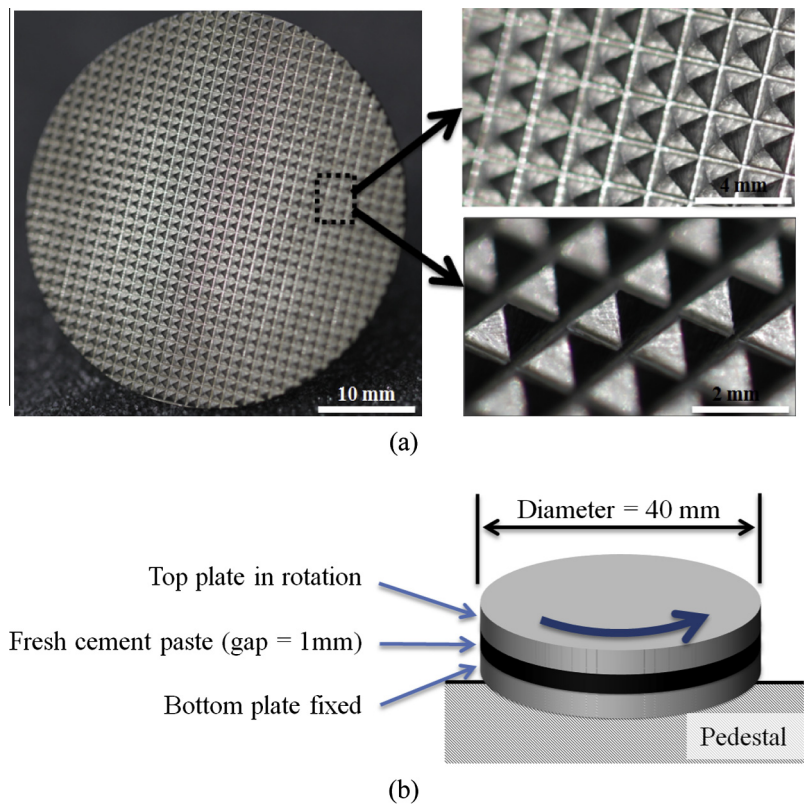


Fig. 1. (a) The pyramid-shaped surface serrations of the plates. (b) The schematics of the testing set-up.

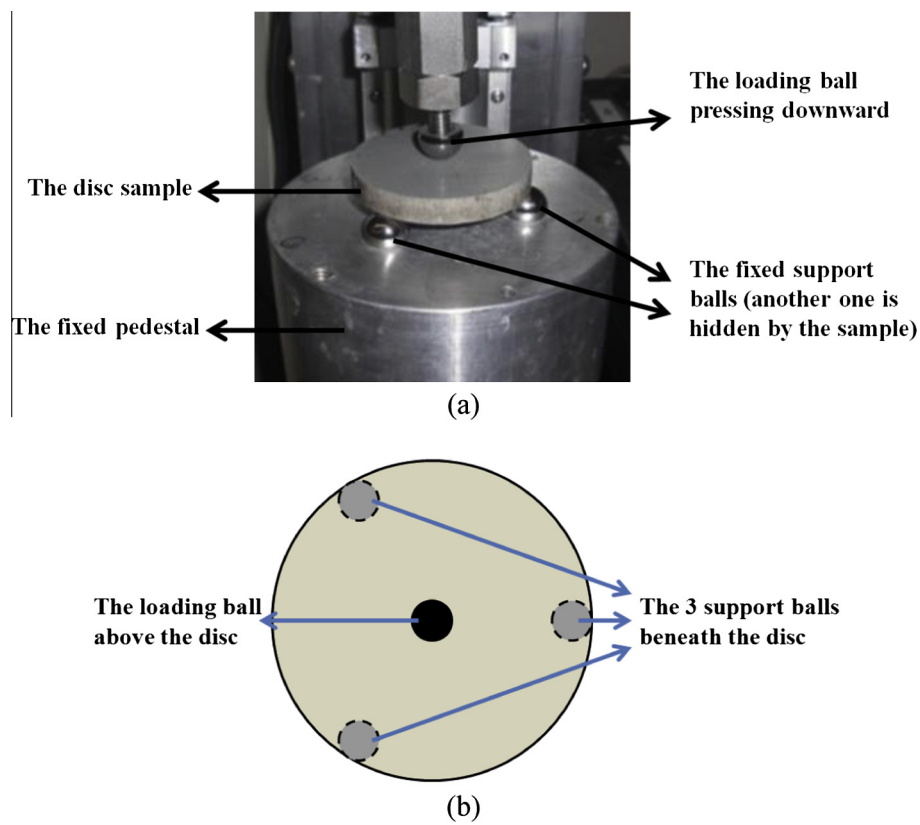


Fig. 2. (a) Image of the B3B fixture and a specimen. (b) Top view of the testing set-up. The dotted circles represent the three support balls beneath the disc sample.

$$\sigma = f(\alpha, \beta, \nu) \frac{F}{t^2}$$

where σ is the B3B flexural strength, α and β the geometry parameters, ν the Poisson's ratio, F the peak load, t the sample thickness [23,24].

3. Results and discussion

3.1. Degree of hydration

Since cement hydration is an exothermic reaction, the rate of heat flow (dQ) and cumulative heat evolution (Q) measured in the cement can be directly related to the rate of hydration and degree of hydration (DOH). The DOH was estimated by the ratio Q/Q_∞ , where Q represents the cumulative heat released before a certain age and Q_∞ is the theoretical amount of cumulative heat when the cement is fully hydrated. Q_∞ can be obtained by multiplying the theoretical value of each hydration component (C_3S , C_2S , C_3A , and C_4AF) with the proportion of each component [25]. With the measurements of isothermal calorimetry (IC) described above, Fig. 3 shows the results of the cumulative heat for the first 200 h of the seven mixtures with different CNC concentrations. It is observed that after the first 25 h, the cumulative heat increases with the CNC concentration. This trend continues until the end of the test (at an age of 200 h) where the increase of cumulative heat with CNC content prevails. It is found that the cumulative heat for the mixture with 1.5% of CNC at 200 h is 280 J/g, which is about 16% higher than that of the reference mixture (without CNC) at the same age. This means that the DOH of the cement paste is increasing with the CNC addition. It is noteworthy that during the first 25 h the cumulative heat shows an opposite trend that, with more CNCs the mixture has less heat release at a certain age. This retardation may be caused by the CNCs adhering to the cement particles and reducing the reaction surface area between cement and water. As a result, the hydration is slowed down in comparison with the surface in the plain system (this is similar to what is observed with some water reducing admixtures).

The DOH can also be estimated by measuring the total mass of the chemically bound water (CBW) in the hardened cement pastes with thermogravimetric analysis (TGA). The TGA tests were performed for (i) pure cement and (ii) dry CNC films for correcting the weight loss from the CBW. Fig. 4 shows the weight loss after corrections between 140 and 1100 °C with the mass at 140 °C as

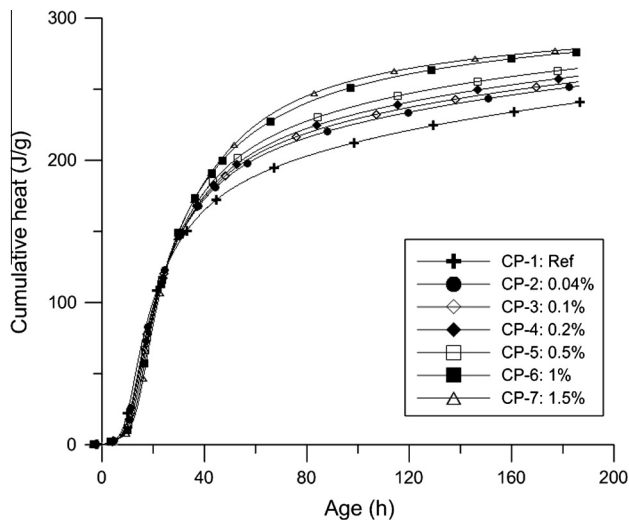


Fig. 3. Cumulative heat of CNC-reinforced cement pastes for the first 200 h.

the base (100%). These results clearly show that the weight loss of the CNC–cement paste is increased with increasing concentrations of the CNC. For example, the reference sample has a final weight of 91.8% while the 1.5 vol.% mixture is 88.4% and the weight loss difference between these two samples is 3.4%. This means that more water reacts with cement when the CNCs are present at any given age. This evidence, together with the IC results, supports the hypothesis that CNCs help to improve the DOH of the cement pastes. There are two interesting features shown by Fig. 4: (1) The decrease in mass observed between 440 °C and 520 °C correlates with the decomposition of $Ca(OH)_2$ [13]; (2) The weight loss differences between the seven mixtures after about 500 °C are much higher than before this temperature. This characteristic is nontrivial and might be directly related with the mechanism of the DOH improvement, which will be discussed in Section 3.2.

DOH is calculated with the method introduced by Pane and Hansen [13] that states that the weight loss between 140 and 1100 °C is considered as the amount of CBW, which is divided by the final weight the material to obtain the mass of CBW per unit gram of unhydrated cement. With the assumption that the CBW is 0.23 g per unit gram of cement when fully hydrated [13,26], the DOH can be easily obtained by dividing the mass of CBW per unit gram of unhydrated cement with 0.23 g. Fig. 5 summarizes all DOHs at the three different ages from TGA measurements, from which it can be observed that the DOHs for cement pastes with 1.5 vol.% of CNC are improved with respect to the reference case to 14%, 16%, 20% for 7, 14 and 28 days, respectively.

One possible explanation for the improvement in DOH with CNC additions at the same w/c, is that the CNCs are helping the cement particles react more efficiently with water. This could be due to steric stabilization, which is the same mechanism observed in some types of water reducing admixtures (WRA) (e.g., polycarboxylated based) to disperse cement particles during cement mixing resulting in finer and more uniform distributions of cement [27].

3.2. The interaction between CNCs and cement particles

To understand how CNCs interact with cement particles it is important to determine where the CNCs are located in the cement matrix. In this investigation a series of experiments were performed to achieve this goal.

3.2.1. Water adsorption

Following the method and the experimental details described in Section 2.5, the water adsorption with relative humidity (RH) was measured for dry CNC film and the results are shown in Fig. 6. The

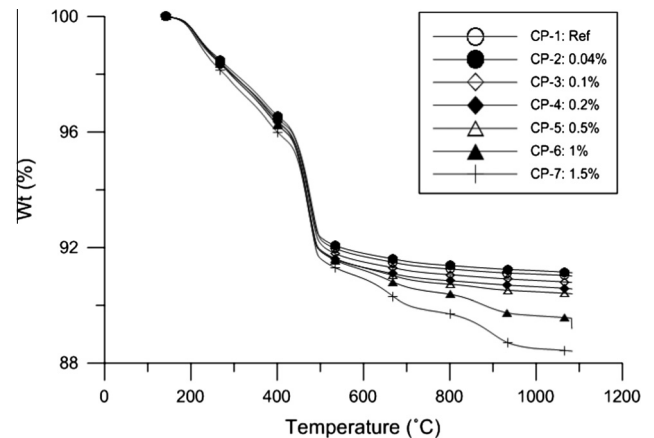


Fig. 4. 7-day TGA results from 140 to about 1100 °C with the mass at 140 °C as a base (100%). The weight loss increases with CNC volume fraction.

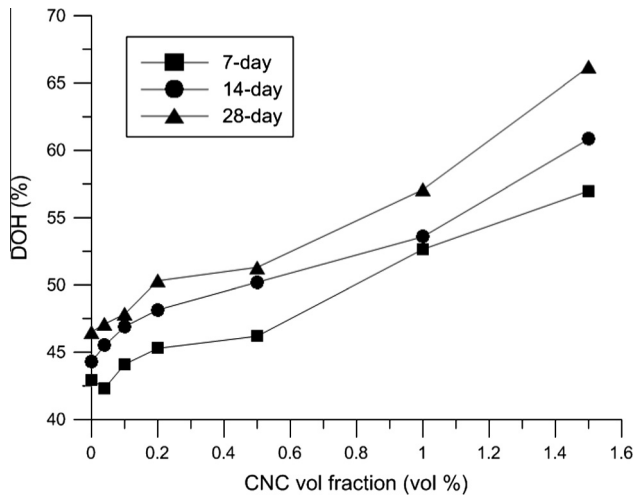


Fig. 5. The DOHs obtained from TGA at three ages.

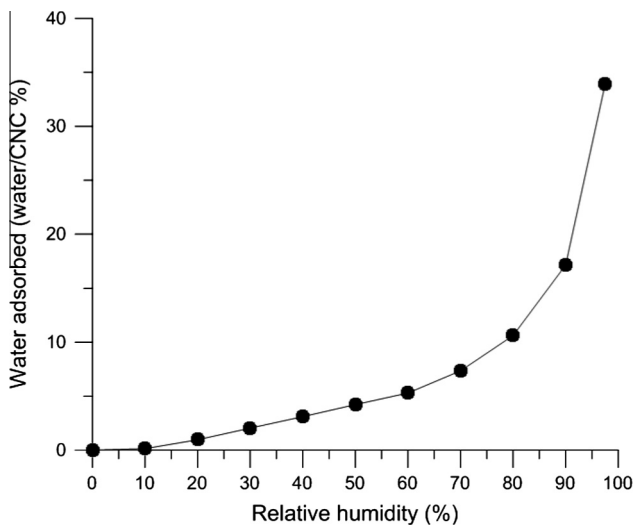


Fig. 6. Water adsorption of dry CNCs with increasing relative humidity.

mass of water adsorbed is plotted with respect to the CNC film mass. At the RH of 97.5%, which can be considered as the environment in which CNCs are immersed in water, the water adsorption is 34%. This amount is considered negligible in cement mixing. For example, for the mixture with 1.5% of CNC, the adsorbed water is only about 0.7% of the total mixing water in mass. As the water adsorption is only an insignificant amount, the effect of the affinity between CNC and water can be disregarded when discussing the rheological properties of fresh mixtures.

3.2.2. Rheological properties

The yield stress of the mixtures is obtained with the rheological experiments using the testing geometry and parameters described in Section 2.6. For this tests, eleven different mixtures were measured, four more mixtures than those described in Table 2. These extra mixtures (i.e., 0.02%, 0.03%, 0.06% and 0.07%) were added to investigate the yield stress in the low CNC concentration region. Fig. 7 summarizes the yield stress of fresh cement pastes with different CNC/cement volume fractions, among which the reference sample (0% CNC) has a yield stress of 48.5 Pa. The trend observed here is that the yield stress decreases with increasing CNC content from the plain mixture and reaches a minimum 15.9 Pa at a

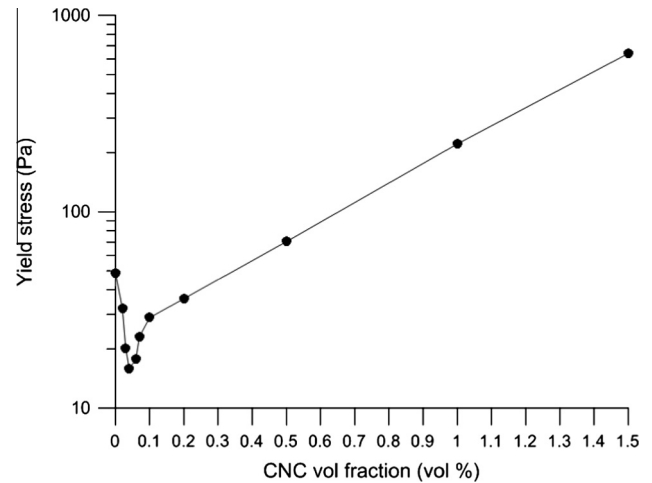


Fig. 7. Yield stress of CNC-reinforced cement pastes with different concentrations.

concentration of 0.04% and then increases with further increasing the CNC additions. At approximately 0.3% CNC, the yield stress reaches the initial yield stress for the reference case. While for CNC concentrations higher than 0.3%, the stress increases dramatically reaching values of up to 600 Pa for a concentration of 1.5%. There are two dominant mechanisms that could be responsible for the trend of the decrease and increase in the yield stress. On one hand, the decrease of yield stress at low concentration of CNC may be due to the steric stabilization, a mechanism that has also been observed with water reducing admixtures [27]. On the other hand, the increase in yield strength at high CNC concentrations is likely due to the agglomeration of CNCs in the fresh cement paste pore solution. The yield stress increases as the CNCs form a network and require larger forces to break or align them. As a result, the changes in yield stress of cement pastes with CNCs could be explained by a combined effect of steric stabilization and agglomeration. When the concentration is low (e.g., below 0.3%), steric stabilization dominates, while the agglomeration determines the yield stress after the concentration is much higher (e.g., higher than 0.3%).

3.2.3. Isothermal calorimetry

Cement hydration is a sum of chemical reactions between cement and water. If a third type of nonreactive materials adhere

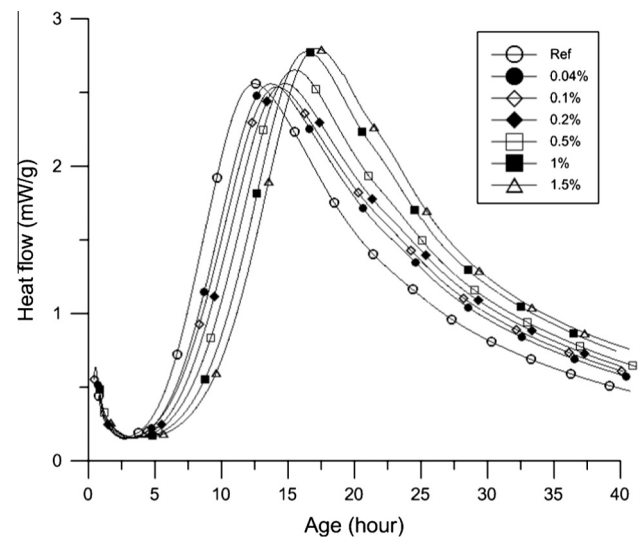


Fig. 8. Heat flow curves of the CNC-reinforced cement pastes for the first 40 h.

onto the cement particles, reducing their reactive surface, the hydration process may be affected. A direct way to monitor the extent of reaction is to measure the heat flow rate with IC (which can be obtained as the derivative of the cumulative heat versus age shown in Fig. 3). Fig. 8 shows the heat flow curves for the seven CNC–cement pastes during the first 40 h, from which it can be observed that the heat flow is delayed with increasing CNC concentrations. For instance, the heat flow peak is reached at the age of about 12 h for the reference mixture (0%) while the peak is reached at around 17 h for the mixture with 1.5% CNC. The retardation of the peak heat flow could be an indication of CNCs adhering to the cement particles and, therefore, blocking the cement particles from reacting with water at early age. A similar observation is made with some WRAs where the DOH is improved at later ages, while the hydration is delayed at early ages [28].

3.2.4. Optical and scanning electron microscopy

To further investigate the locations of CNCs in the cement matrix and to obtain visual evidence, imaging was taken for hardened cement pastes with and without CNCs. The hardened cement

pastes were epoxy-impregnated and polished following the procedure described in the previous section. Both the BSE–SEM and optical images were taken for the reference and the 1.5% mixture to capture the features related with CNCs. Fig. 9 is a comparison between the BSE–SEM images of the reference and the 1.5% CNC cement pastes at the age of 7 days.

Comparing the images of the reference and the 1.5% mixtures, one interesting feature shown by the CNC cement pastes is that a ring or shell formed around many unhydrated cement particles, which are highlighted and zoomed in Figs. 9 and 10. As discussed in previous sections, the CNCs tend to adhere onto the cement particles, which ultimately lead to the steric stabilization effect. As a result, the concentration of CNCs around the cement particles is expected to be higher than that in the hydration product, which can explain the presence rings in the 1.5% mixture.

3.2.5. Zeta potential

In colloidal chemistry, the zeta potential of different particles indicates the degree of repulsion or attraction in a dispersion [16]. As the zeta potential is susceptible to variations of pH values

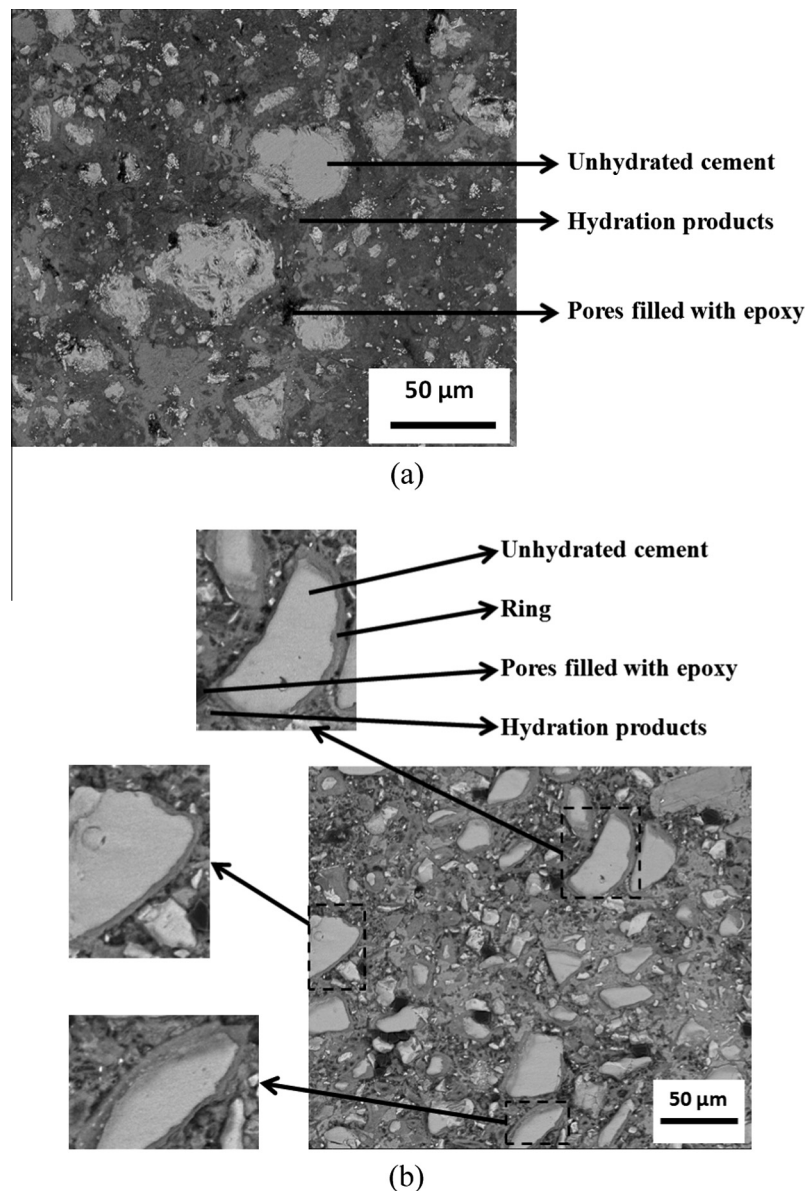


Fig. 9. BSE–SEM images of (a) reference and (b) 1.5% mixture at the age of 7 days. The 1.5% CNC mixture shows ring features surrounding the unhydrated cement cores.

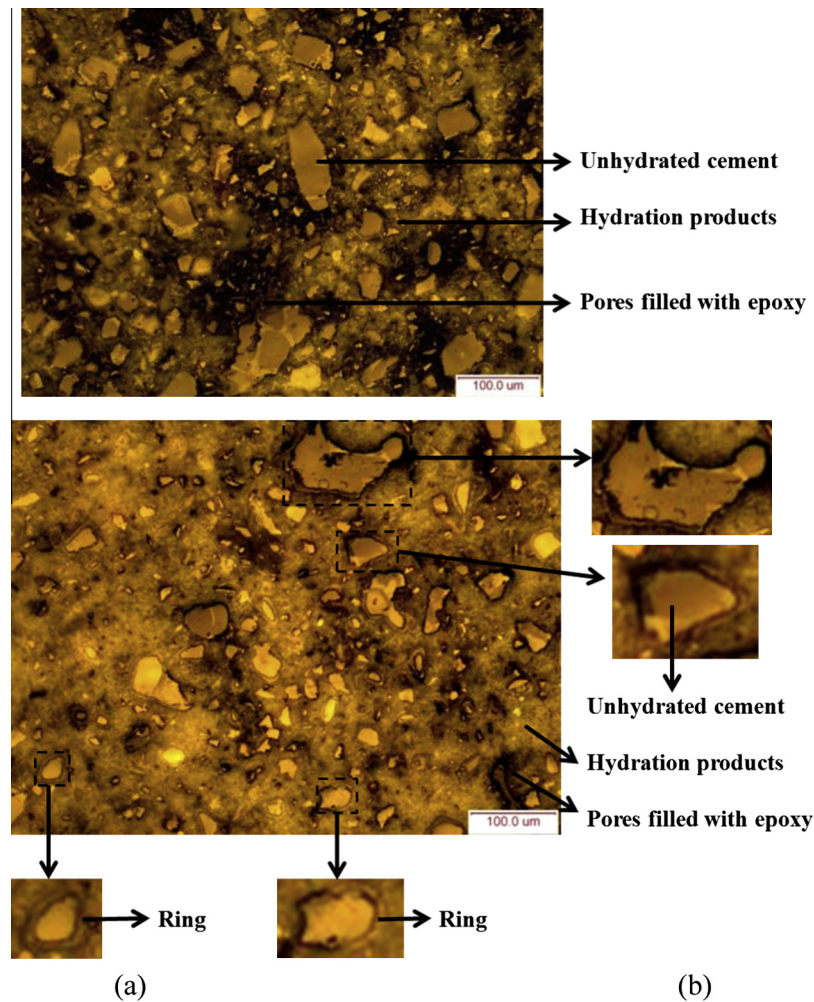


Fig. 10. Optical images of (a) reference and (b) 1.5% mixture at the age of 7 days. The 1.5% CNC mixture shows ring features surrounding unhydrated cement cores.

Table 3
The zeta potentials of CNC and cement particles.

Environment (pH)	Cement	CNC
DI water (7)	−10.4 mV	−64.0 mV
Pore solution (12.71)	−9.1 mV	−51.0 mV

[29], the investigation was carried out in a controlled pH environment. Two different values of pH are considered in this investigation: a neutral environment with a pH of 7, and the fresh cement with a pH of 12.71. As such, a simulated pore solution was prepared with the same composition given by Rajabipour et al. [30] at the age of 1 h, diluted with deionized water to achieve a pH of 12.71 for the zeta potential measurements. The zeta potentials for the CNC and cement particles at the two different pH environments – neutral and as-measured fresh cement pH (12.71) are listed in Table 3.

As these results show, the pH does not significantly change the zeta potential and the absolute value of the zeta potential for cement is much lower than that of CNC, which means that compared with CNC, cement particles have a much stronger tendency to agglomerate. The affinities between the particles have following order:

$$f(\text{cement} - \text{cement}) > f(\text{cement} - \text{CNC}) > f(\text{CNC} - \text{CNC})$$

In other words, CNCs tend to adhere onto cement particles rather than to agglomerate themselves, which is consistent with

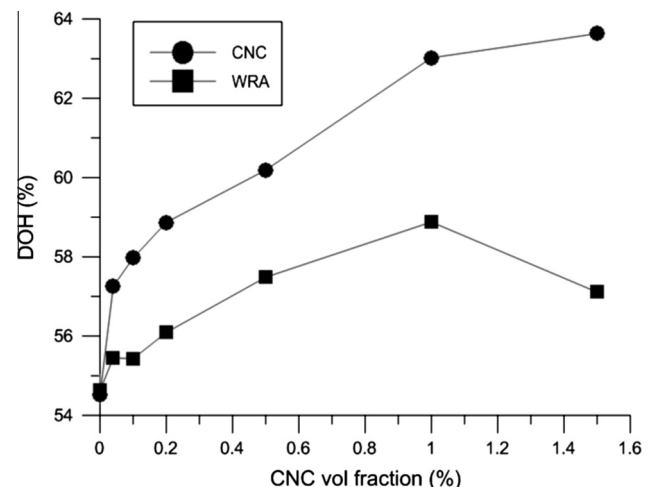


Fig. 11. 7-day DOHs from IC of the cement pastes with the same volume fraction of CNC and WRA. CNC mixtures exhibit higher DOHs than the WRA mixtures in all range.

the mechanism of steric stabilization that an affinity between CNC and cement particles is required. However, this mechanism also indicates that the CNCs should be relatively well dispersed and able to separate the cement particles from each other. While the zeta potential results show that the affinity between cement

particles is stronger than that between cement and CNC, the steric stabilization might not be the dominating mechanism in this system. To verify this, a polycarboxylate-based WRA (ADVA 140) was chosen for its dispersion mechanism of steric stabilization to make a parallel comparison with the CNC–cement pastes. The first parameter compared is the DOH – the cement pastes with the same amount (volume fraction) of CNC and WRA were tested with IC, and the results are plotted in Fig. 11.

The results show that the improvement of DOH achieved by the presence of WRA is lower than that caused by CNC. For instance, 1 vol.% content of WRA exhibits an increase in DOH of only 4% with respect to the reference case, while the increase in DOH for 1 vol.% of CNC is about 8%. It should also be mentioned that the DOH decreases when the WRA is increased from 1% to 1.5%. This is likely due to the excess WRA causing a significant segregation of cement in water. Considering that the main function of WRA is steric stabilization, this indicates that steric stabilization is likely not the only mechanism responsible for the improvement of DOH.

It is well known that, during curing, the hydration product forms a shell around the unhydrated cement particle (i.e., the high density CSH), slowing down the diffusion of water to its interior. This phenomenon limits the hydration rate and, as a result, the cores of the cement particles hydrate slowly. When CNCs are present in the cement paste, one likely scenario is that when CNCs initially adhere to the cement particles and remain in the hydration product shell (i.e., the high density CSH), they could form a path to transport water from the pore water to the inner unhydrated cement core. This may facilitate a larger portion of cement reacting with water compared with the cement pastes without CNCs. The mechanism of water molecules diffusing along the CNC networks in the hydration products shell is here referred as short-circuit diffusion (SCD). Fig. 12 shows a conceptual illustration of how SCD may help the cement particle with CNCs adhered to a portion of its surface to achieve a higher DOH. Fig. 12(a) shows how the hydration process evolves, both inward and outward from the initial interface between cement and water (drawn with the dashed

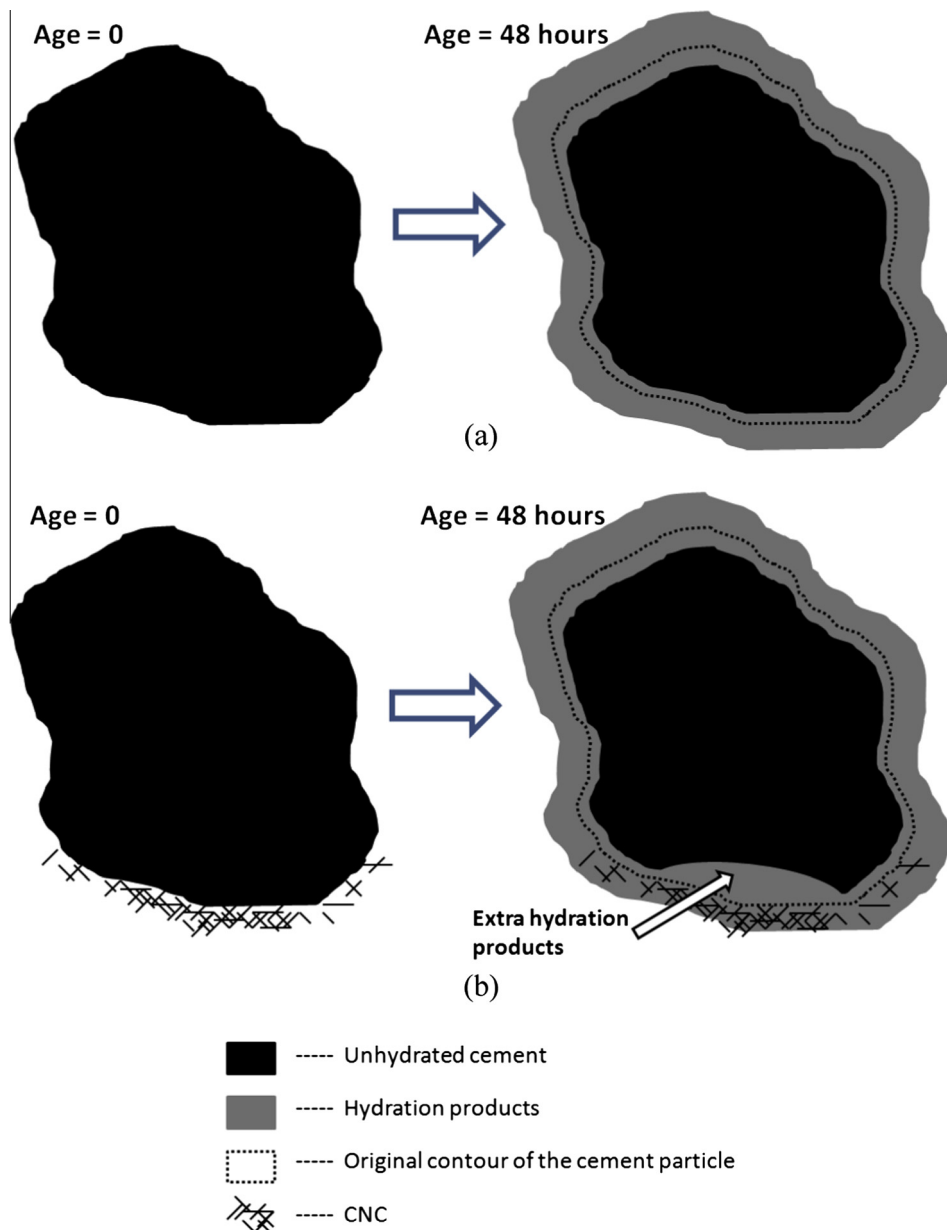


Fig. 12. A schematics illustration of the proposed hydration products forming around the cement grain from the age of 0–48 h in the (a) plain cement and (b) cement with CNCs on a portion of the cement particle showing SCD.

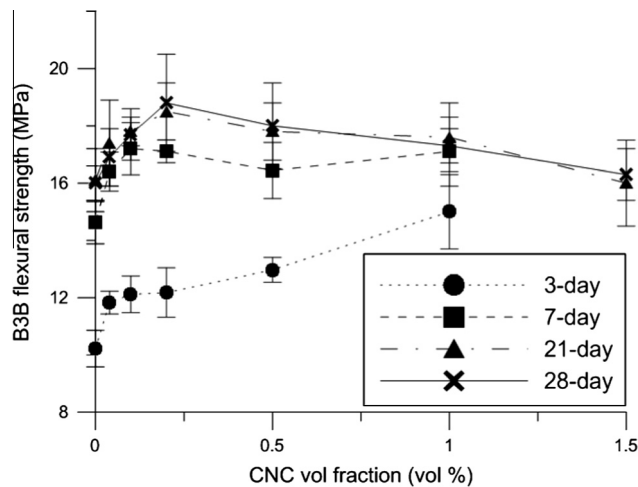


Fig. 13. The B3B flexural strengths of CNC-reinforced cement pastes at 4 different ages.

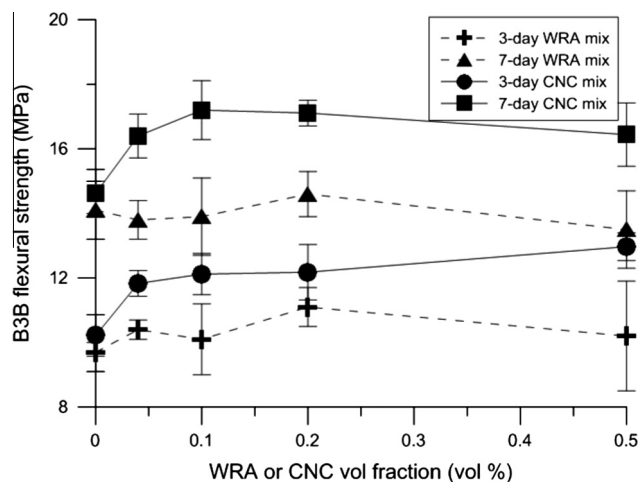


Fig. 14. The B3B flexural strengths of cement pastes with the WRA and CNC at two different ages.

line) for a cement particle without CNC. Fig. 12(b) shows the same process with CNCs. For illustration and comparison purposes CNCs are placed only over a selected region of the cement surface. SCD is shown with an arrow indicating the extra hydration products growing inwards to the center of the cement particle. It is therefore expected that the inward growth in places without CNCs will have a slower rate than those in the CNC-rich regions. It is also likely that SCD may only be triggered by a critical concentration of CNCs in the hydration product shell.

3.3. Flexural strength

The flexural strengths of the cement pastes with increasing CNC concentrations were measured for 4 different ages 3, 7, 21 and 28 days with the ball-on-three-ball tests (B3B) and the results are shown in Fig. 13. At the age of 3 days, the strength increases with increasing concentration of CNCs, while for older ages, the strength reaches a peak at around 0.2% of CNC and then decreases. This may be caused by agglomeration of CNCs at higher concentrations that act as stress concentrators (i.e., defects) in the cement. The agglomeration observed from the rheological measurements is consistent with that proposed here.

As the steric stabilization is also likely to improve the mechanical performance of cementitious materials, it is reasonable to com-

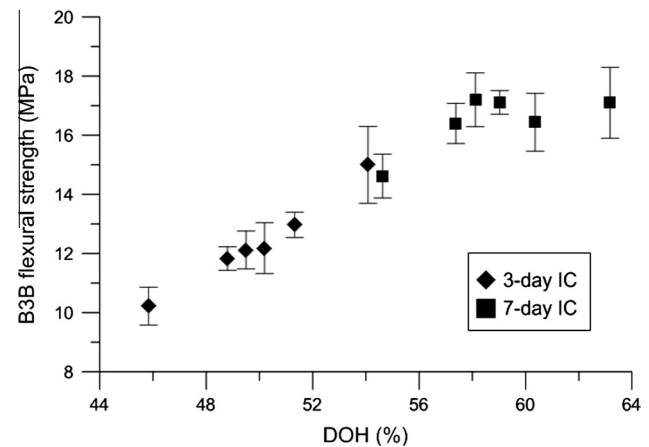


Fig. 15. The relationship between B3B flexural strengths and the DOHs. The strength is increasing with DOH.

pare the flexural strengths of the cement pastes with CNC and WRA. The B3B flexural strengths for the cement pastes with WRA were measured at the ages of 3 and 7 days and plotted against the values obtained for CNCs in Fig. 14. It should be mentioned that the comparison can only be done until 0.5 vol.% of CNC/WRA. This is due to the strong segregation in the cement and water for higher concentrations of WRA.

From Fig. 14, it is observed that there is a slight increase with increasing WRA concentration from 0% to 0.2 vol.%. The DOH results show that the CNC are more effective in improving the strength than WRA. This is consistent the increase in DOH shown in Fig. 11.

It is hypothesized that the main mechanism for strengthening can be directly attributed to the increase in DOH for high concentrations of CNCs. This can be analyzed by plotting the B3B flexural strengths against DOHs obtained from isothermal calorimetry. Fig. 15 shows the relationship between the B3B flexural strengths at the ages of 3 and 7 days with the DOH data from isothermal calorimetry (denoted as IC). The data in this plot is obtained from specimens with different CNC content (as obtained directly from Fig. 13). As it can be observed, the B3B flexural strength increases nearly linearly as a function of DOH. This increase in strength is initially linear with respect to DOH until a value of DOH 58%. The last two points do not seem to follow this linear trend. However, those points correspond to concentration of 1% and 1.5% of CNC for 7 days. As discussed before, and observed in Fig. 13, specimens with such a high concentration of CNCs begin to show signs of early failure, mainly caused by CNC agglomeration.

4. Conclusions

This paper examined how the addition of cellulose nanocrystals (CNCs) modified the performance of cement paste. It was observed that the flexural strengths of cement pastes with modest concentrations of CNC were about 20% to 30% higher than the cement paste without CNCs. It was hypothesized that this increase can be attributed to the increase in DOH of the cement pastes when CNCs are used. Based on experimental observations, two mechanisms are proposed to explain the increase on DOH: (1) Steric stabilization is responsible for dispersing the cement particles. This mechanism is also exhibited by water reducing admixtures to improve workability. This dispersion effect is verified by rheological measurements for CNC–cement pastes, in which a decreased yield stress is observed with a low concentration of CNCs. (2) The CNC systems appear to exhibit a benefit due to a mechanism that will be referred to as short-circuit diffusion: Short circuit diffusion

describes how the CNCs appear to provide a channel for water transporting through the hydration products ring (i.e., high density CSH) to the unhydrated cement particle and thereby improving hydration. The B3B flexural strengths increases with CNC concentration reaching a peak at 0.2 vol.% of CNC. At higher concentrations of CNC the strength decreases. This can be explained by the agglomeration of CNCs that acts as a stress concentrations in the cement paste. This peak of 0.2% is also consistent with the rheological results that show that for higher CNC loadings the yield stress increases significantly due to the agglomeration.

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