Cellulose Nano-composites for Performance Enhancement of Portland Cement-based Materials

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CELLULOSE NANO-COMPOSITES FOR PERFORMANCE ENHANCEMENT OF PORTLAND CEMENT-BASED MATERIALS

By

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B.Tech Jawaharlal Nehru Technological University, 2013

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Cellulose Nano Fibrils (CNF) having a high aspect ratio, elastic modulus, tensile strength and reactive surface area for functionalization was considered as a promising nanomaterial for improving chemo-mechanical properties of the cementitious matrixes. CNFs are typically less than 0.2 mm in length and 50nm in width that can be extracted from plants and trees. Overall, in this thesis the study is broadly divided in to three stages: (i) In the first stage, a hybrid silica coated CNF (Si-CNF) was developed and investigated for its effects on cement based systems in addition to Pure CNF (PCNF). (ii) In the second stage, effect of varied fine content percentages of PCNF and lignin containing CNF (LCNF) in Portland cement paste systems were evaluated. (iii) And for the final stage, long term stability of cellulose nanofibrils (CNF) in high alkaline cement pore solutions was studied. For the first two-phases of the study described here, a comprehensive investigation on the effects of CNFs (Si-CNF, PCNF and LCNF) on dispersion stability of fibrils, cement paste workability, hydration, microscopic phase formation, compressive strength and fracture properties were studied. For the final stage of study on long-term stability of CNFs, several laboratory experiments that focused on crystallinity degree of CNF,
intensity ratios of hydrogen bonds in CNF, alkali ion concentrations in artificial pore solution (APS), pH concentration of APS and morphology of CNFs were investigated.

The central hypothesis assumed for developing Si-CNF is, coating CNF with silica nanoparticles will improve the dispersion and long-term stability of the CNF, thus resulting in further enhancement of the microstructure and mechanical properties of cement-based composites. Silica coating helped in the dispersion of CNFs by increasing overall zeta potential measurements. The effect of Si-CNF on cement hydration was found to be dependent on the water to cement (w/c) ratio. Specifically, CNFs accelerated the early age cement hydration at 0.35 ratio and it retards the hydration at 0.45 w/c ratio. Such water dependent effect was attributed to the negatively charged hydroxyl and carboxyl surface sites of CNF which can bind alkali ions or cement particles. The increase of compressive strength due to the addition of Si-CNF was prominent at 0.35 w/c ratio compared to that of 0.45 w/c ratio. Addition of Si-CNF was found to increase the flexural strength and compressive strength of cement paste up to 52% and 22%, respectively.

The main objective for 2nd phase of the study is to determine the optimum fine content percentages for PCNF and LCNF in portland cement pastes, such that mechanical grinding cost can be reduced at lower fine content percentage usage. The CNFs used in this study were obtained through the process of mechanical grinding of pulps, in which the fibers are broken down to fraction of small particles called 'fines'. The fine content percentages considered in this study are 60%, 75%, 80%, 90% and 95% for both PCNF and LCNF. LCNFs being colloidally semi-stable showed improvement in workability of cement pastes at 0.35 w/c ratio compared to PCNF. Maximum improvement in the compressive strength of the cement paste cube samples was achieved at 75% fine content percentages for both LCNF and PCNF. Addition of 75% fines content percentage of PCNF and LCNF was found to increase the flexural strength of the cement pastes up to 112% and 96%, respectively.
respectively. Overall, based on the results obtained from this study, optimum fine content percentages for CNFs is considered to be around 60% to 75%.

The main hypothesis assumed for investigating the durability of CNFs in alkaline pore solution of cement (APS) was, in the presence of high alkaline medium CNFs having high amorphous phase initially will be transformed into more crystalline phase due to the process of alkaline hydrolysis. Degradation of CNF films in APS were obtained using XRD, which represents the degree of crystallinity (crystallinity index, C.I) in CNF. Increased C.I by 86% for CNF indicates higher crystallinity in CNFs due to alkaline degradation of cellulose. Increase in intensity ratios of inter to intra molecular O-H bonds of cellulose is about 0.989 and 0.982 for PCNF and LCNF films respectively. Increase in intensity ratio can be related to transformation of amorphous phase in cellulose to crystalline phase through the process of alkaline degradation.
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A confluence of phenomena has led to an increase interest in cellulosic-based nano materials as they relate to portland cement concrete. First, pressure to improve the durability and resiliency of infrastructure has pushed the research community to further refine and enhance properties of concrete, the most common infrastructure material. Second, the enormous annual production of portland cement, and its resulting CO$_2$ emissions, has spurred interest ways to reduce overall environmental impact[1]. Finally, applications of nanotechnology in cement and concrete have shown that new combinations of early-age and long-term properties are now possible[2]. Bio-based nanocomposites have the potential to play a role in each of these areas.

Bio-based materials have attracted substantial research interest in recent years because of their great potential for producing a variety of high value products with low impact on the environment[3]. As summarized by Onuaguluchi and Banthia[4], there is a fairly substantial body of work covering the use of natural fibers, including cellulose, in cement-based composites. Traditionally cellulose microfibers are used in cement-based composites as reinforcing ingredients [4, 5]. However, nanocellulose materials are observed to provide better enhancement of flexural strength of cement-based composites compared to that of microfibrils [6, 7]. Nanocellulose materials include cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), bacterial cellulose (BC) and cellulose filaments (CF) [8]. Due to their nanoscale size, fibril morphology, reactive surfaces for functionalization, and large specific surface area, these materials provide a wide range of potential applications in cement-based composites[8].
While traditionally considered as a reinforcement, at the nano-scale cellulosic materials have been shown to modify the hydration, microstructure and properties of cement paste [9]. Most interestingly, nanocellulose materials have shown to retard the early-age cement hydration [10], but increase the degree of hydration at later ages [10, 11, 12, 9]. Flores et al. [11] attributed the enhancement of later-age cement hydration to steric stabilization due to the addition of cellulose nanomaterials. Whereas, Cao et al. [9] showed that steric stabilization can not be the only mechanism attributing to the enhanced cement hydration. Rather CNC provides a channel to diffuse water from pore solutions to unreacted core of cement particles which increases the degree of hydration [9]. Authors termed this mechanism as ‘short-circuit diffusion (SCD)’ [9]. Sun et al. [12] also attributed the hydration enhancement of oil-well cement due to the addition of CNF to a similar mechanism. Fu et al. [10] also reported that such early age hydration retardation effects of CNC depend on the aluminate (C₃A) content of cement as well as the production process of CNC.

Another noticeable effect of cellulose nanomaterials on cement-based composites is observed in case of flexural strength [8, 12]. Nanocellulose fibrils have shown to increase the flexural strength of cement composite but with decreased fracture energy due to the brittle failure of the matrix [7]. To overcome this issue, Adanuy et al. [7] recommended to combine nano and micro cellulose fibrils in cement composites. The enhancement of flexural properties of cement matrix is also dependent on the aspect ratio of the added nanocellulose materials [13].

Due to the higher degree of hydration, addition of cellulose nanomaterials increases the total calcium-silica-hydrate (C-S-H) content in the cement matrix [14]. These nanomaterials also enhance the intrinsic modulus of C-S-H as observed from nanomechanical tests [15]. Another benefit of CNF is that it reduces the potential for shrinkage cracks of cement composites [72, 17]. Kolour et al. [72] attributed the shrinkage
reduction of cement-based composites to the possible internal curing effect of CNF. CNFs have shown to increase the thermal conductivity and coefficient of thermal expansion (CTE) of cement-based composites by reducing the overall porosity [18]. The porosity reduction due to the addition of CNC was reported to be as much as 40% [19]. In addition to OPC systems, Calamunt et al. [20] have shown beneficial effects of cellulose nanomaterials on the performance of calcium aluminate cement. Considering all of the above-discussed benefits, nanocellulose materials have emerged as a promising resource for the performance enhancement of cement-based composites.

1.1 Objectives

The work described in this thesis is mainly focused on evaluating the performance of cellulose nanofibrils (CNF) in Portland cement systems. The main objectives of this research are broadly divided in to three chapters as follows:

1. To develop hybrid silica-cellulose (Si-CNF) nanocomposites and investigate for its effects in cement-based systems.
   - Coating CNF with silica nanoparticles might improve the dispersion and long-term stability of nanofibrils.
   - Enhancement in microstructure and mechanical properties of cellulose cement-based composites.

2. To evaluate the effects of various fine content percentages of pure cellulose nanofibrils (PCNF) and lignin containing cellulose nanofibrils (LCNF) in cement-based systems.
   - Reduction in the production costs of pure cellulose (PCNF) by using unbleached cellulose i.e., lignin containing cellulose nanofibrils (LCNF).
   - Determination of optimum fine content percentages of CNFs.
3. To evaluate the long-term stability of cellulose nanofibrils in the highly alkaline environment of cement pastes.

- Durability of cellulose nanofibrils in artificial pore solution of hydrated cement pastes.

1.2 Organization

- The second chapter of the thesis describes first research objective i.e., using hybrid Si-CNF composites in Portland cement systems in which materials, experimental methods adopted and the corresponding results are discussed.

- The third chapter of thesis corresponds to second research objective i.e., using different fine content percentages of PCNF and LCNF in cement based systems in which materials, experimental methods and results were discussed in detail.

- The fourth chapter mainly focuses on longterm stability of cellulose nanofibrils in cement paste pore solution.

- Overall conclusions and future recommendations are described in chapter five.
CHAPTER 2
DEVELOPMENT AND UTILIZATION OF SILICA-CELLULOSE NANO-COMPOSITES IN PORTLAND CEMENT SYSTEM

2.1 Introduction

Natural fibers have been used as a reinforcement phase in cementitious composites, though having lower reinforcement effectiveness than metallic reinforcements, natural fiber are increasingly being used as they are renewable, economical, and abundant compared with other commonly used fibers [21]. Cellulose nanofibrils (CNF) derived from various cellulose sources have gained much attention as a green alternative for producing a variety of high value products with low impact on the environment [63]. Over the recent years, nanocellulose materials have emerged as a promising resource for the performance enhancement of cement-based composites.

In the work described here, a hybrid silica-CNF nanocomposite was developed and investigated for its effect on cement-based systems. The central hypothesis was that coating CNF with silica nanoparticles will improve the dispersion and long-term stability of the CNF resulting in further enhancement of the microstructure and mechanical properties of cement-based composites. This hypothesis was tested through a series of laboratory experiments that focused on nanocomposite fabrication, cement hydration analysis, and measurement of resulting strength and fracture properties.

2.2 Materials and methods

2.2.1 Raw materials

The raw materials used in this study include ordinary portland cement (OPC, type I/II), cellulose nanofibrils (CNF), tetraethyl orthosilicate (TEOS) and sodium hydroxide (NaOH). The OPC contained 20.1% SiO$_2$, 63.7% CaO, 4.7% Al$_2$O$_3$, 3.5% Fe$_2$O$_3$, 3.1% SO$_3$.
and 0.7% MgO and the Blaine fineness was 364 m²/kg. The CNF was used in a white odorless aqueous slurry form. The solid concentration of CNF slurry was about 3% (3 gm of cellulose nanofibrils dispersed in 97 gm of water). The CNF slurry was supplied by the Process Development Center (PDC) at the University of Maine. This CNF slurry was produced by mechanical treatment of bleached softwood pulp and the average fiber diameter was around 20 to 500nm [61, 62]. Tetraethyl orthosilicate (TEOS, C₈H₂₀O₄Si, 98% purity) and sodium hydroxide (NaOH) were used as the precursor and catalyst, respectively, to coat the CNF with silica nanoparticles (details in section 2.4). Both of these chemicals were procured from Sigma Aldrich.

### 2.2.2 General mixture proportions, sample preparation and curing

Table 4.1 presents the relative proportions of the ingredients used to prepare paste mixture in this study with respect to 1000g of cement. Nearly all of the experiments were performed for cement pastes with two different water-to-cement ratios (w/c): 0.35 and 0.45, except heat of hydration was monitored for cement pastes with 0.35, 0.4 and 0.45 w/c ratios. Cellulose nanomaterials were added at concentrations of 0.025%, 0.05%, 0.1%, 0.3% and 0.5% (solids) by weight of cement. Two different cellulose nanomaterials were used, namely pure CNF (addressed as ‘PCNF’) and silica coated CNF (addressed as ‘Si-CNF’). The control batch denotes paste mixture with only OPC and water. The free water demand of each mixture was determined after subtracting the amount of water present in the cellulose slurry (3% solid CNF in 97% water) from the total water required to maintain w/c ratio. Our laboratory measurements showed that this 97% of water in cellulose slurry are weakly bound moisture which can be evaporated at room temperature. As such, it was considered that the water present in cellulose slurry is available for cement hydration. The cement pastes were mixed in a conventional 8-qt rotary mixer. The following procedure was used for mixing the cement pastes: (1) the PCNF or Si-CNF slurry was first mixed with water in the rotary mixer for 180 secs at a speed of 95 rpm for homogenization; (2)
cement was then added to this suspension and mixed at the speeds of 60, 95, 115, and 135 rpm for about 60 secs each with 15 secs rest between every change in speed interval (different speeds were used to obtain the rheological parameters), (3) paste mixtures were then used to cast required samples shapes/ sizes and were subjected to sealed curing condition (details in the following section). Cement paste mixtures were evaluated for heat of hydration, rheology, compressive strength, microscopic phase formation, flexural strength and fracture properties.

Table 2.1. Mix design of pastes based on 1000g of binder for w/c 0.35 and 0.45

<table>
<thead>
<tr>
<th>0.35 w/c ratio</th>
<th>Cement (g)</th>
<th>Free water (g)</th>
<th>CNF slurry (g)</th>
<th>Water from CNF (g)</th>
<th>Total water (g)</th>
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<tr>
<td>0</td>
<td>1000</td>
<td>350</td>
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<tr>
<td>0.025</td>
<td>1000</td>
<td>341.9</td>
<td>8.3</td>
<td>8.1</td>
<td>350</td>
</tr>
<tr>
<td>0.05</td>
<td>1000</td>
<td>333.8</td>
<td>16.7</td>
<td>16.2</td>
<td>350</td>
</tr>
<tr>
<td>0.1</td>
<td>1000</td>
<td>317.7</td>
<td>33.3</td>
<td>32.3</td>
<td>350</td>
</tr>
<tr>
<td>0.3</td>
<td>1000</td>
<td>253</td>
<td>100</td>
<td>97</td>
<td>350</td>
</tr>
<tr>
<td>0.5</td>
<td>1000</td>
<td>188.3</td>
<td>166.7</td>
<td>161.7</td>
<td>350</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>0.45 w/c ratio</th>
<th>Cement (g)</th>
<th>Free water (g)</th>
<th>CNF slurry (g)</th>
<th>Water from CNF (g)</th>
<th>Total water (g)</th>
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</thead>
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<tr>
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<td>1000</td>
<td>450</td>
<td>0</td>
<td>0</td>
<td>450</td>
</tr>
<tr>
<td>0.025</td>
<td>1000</td>
<td>441.9</td>
<td>8.3</td>
<td>8.1</td>
<td>450</td>
</tr>
<tr>
<td>0.05</td>
<td>1000</td>
<td>433.8</td>
<td>16.7</td>
<td>16.2</td>
<td>450</td>
</tr>
<tr>
<td>0.1</td>
<td>1000</td>
<td>417.7</td>
<td>33.3</td>
<td>32.3</td>
<td>450</td>
</tr>
<tr>
<td>0.3</td>
<td>1000</td>
<td>453</td>
<td>100</td>
<td>97</td>
<td>450</td>
</tr>
<tr>
<td>0.5</td>
<td>1000</td>
<td>288.3</td>
<td>166.7</td>
<td>161.7</td>
<td>450</td>
</tr>
</tbody>
</table>

### 2.2.3 Experimental methods

#### 2.2.3.1 Transmission electron microscopy (TEM)

The morphologies of the PCNF and Si-CNF were evaluated using CM10 TEM. Approximately 1 gm of cellulose (PCNF or Si-CNF) slurry was diluted with at least 10 times more deionized water and were dispersed uniformly until turbidity was visibly reduced and no macroscopic particles could be seen. A droplet (5µl) of diluted suspension was deposited onto carbon coated grid. After 1 minute the excess water from the sample was removed by dabbing with a filter paper. A drop of negative stain with 1% uranyl
acetate solution was added on to the sample to enhance the contrast. The TEM images of the samples were collected using Philips/FEI CM10 with acceleration voltage of 120V.

2.2.3.2 Zeta potential measurements

The zeta potential of the cellulose nanomaterials in various pH solutions were measured using Malvern Zetasizer 3000. The selected pH values for the solutions were 7, 9 and 11. NaOH and deionized water were used to prepare pH solutions. 1 gm of cellulose nanomaterial suspension was mixed with 80 gm of each pH solution (pH 7, 9 and 11) and allowed to homogenize for 2 minutes using magnetic stirrer before the zeta potential measurement. Dispersion stability of CNFs in artificial pore solution of hydrated cement paste was also measured. The chemical composition of the artificial pore solution (APS) (given in Table 2.2) used in this study was obtained from a previously published article [7].

<table>
<thead>
<tr>
<th>Salt</th>
<th>Weight (gm per 1L of water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$</td>
<td>0.0181</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.0553</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>4.3794</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.7777</td>
</tr>
<tr>
<td>KOH</td>
<td>36.1745</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.0864</td>
</tr>
</tbody>
</table>

2.2.3.3 Rheology

A custom-built rheometer was used to quantify the rheological properties of cement paste. This rheometer setup contains a rotary mixture connected with a data-logging ammeter which was used to monitor the current at different speeds. This rheometer setup provides data in terms of current and voltage that were converted to shear stress and shear strain measurements [23]. Torques required to move the fresh pastes at different mixing speeds were used to develop a torque-rotational speed relationship. The concept behind this method is that a higher viscosity of cement paste would require more torque to drive
the electric mixer at a selected speed. The details method of calculating torque from this rheometer setup is discussed in a previously published article [72].

2.2.3.4 Heat of hydration

Paste samples with w/c ratios of 0.35, 0.40 and 0.45 were prepared using both PCNF and Si-CNF. The mixing procedure of these paste samples were same as that of rheology measurements. After mixing (details in 3.2.2), approximately 15gm cement paste sample was placed into a glass vial which was then used for heat release measurements. The heat measurement started approximately 45 minutes after the mixing. This time delay was required for the signal stabilization. The heat of hydration of the paste samples were monitored using an isothermal calorimeter (TAM Air, TA instruments) for 100 hours at 23±1 °C. The heat data presented in this article were normalized with respect to the weight of cement.

2.2.3.5 Thermogravimetric analysis (TGA)

Paste samples with w/c ratios of 0.35 and 0.45 were prepared for thermogravimetric analysis (TGA). Acetone was used to stop the hydration of cement paste samples after 28 days of sealed curing. The cement paste samples were then dried in a vacuum oven at 50°C for 24 hours to avoid atmospheric carbonation. Finally, the dried paste samples were ground using mortar-pestle and the powder was used for TGA measurements. Commercially available instrument (TA instrument, TGA 55) was used for TGA measurements. Approximately 30-45 mg powder sample was tested for each batch. The powdered sample was loaded into the pan and kept under the isothermal condition for 5 min. The temperature of the TGA furnace chamber was then raised up to 980°C at an increment rate of 10°C per minute.
2.2.3.6 Compressive strength

A total of 24 batches of cement paste with w/c ratios of 0.35 and 0.45 and with different CNF contents were prepared for compressive strength test. Sealed curing condition was adopted by covering the fresh paste samples with a plastic sheet and kept at 23°C for 24±1h. After this period, the samples were demolded and stored in sealed plastic bags such that no external moisture can pass through the samples in a storage room at 23°C temperature until the age of testing. Compressive strengths were measured for the paste cube (50 mm sides) samples as per ASTM C109 using a loading a rate of 200 to 400 lb/sec. Compressive strengths were determined after 7, 28, 56 and 90 days of sealed curing.

2.2.3.7 Fracture properties

The three-point bending tests of notched beams were performed to determine the fracture parameters as per the International Union of Testing and Research Laboratories for Materials and Structures (RILEM)[10, 11]. This test was conducted using a closed-loop crack-mouth opening displacement control. This type of test configuration allows for stable failure of the test specimen. A linear variable displacement transducer (LVDT) was used in these tests to control the crack opening so that it grew at a constant rate. The LVDT was mounted across the notch with aluminum brackets that attached directly to the beam specimen. The test consisted of loading the specimen until a crack formed; then the specimen was unloaded and reloaded so that crack grew steadily (as controlled by LVDT). The following fracture parameters were calculated from the obtained data set: critical stress intensity factor ($K_{s1c}$), critical crack tip opening displacement ($\text{CTOD}_{c}$), critical crack length($a_{c}$), and fracture energy ($G_{F}$). Four batches of notch beam (3cm x 4cm x 18cm) samples were prepared for each w/c ratio. The concentrations of PCNF and Si-CNF by weight of cement in the mixture were 0.025%, 0.1% and 0.5% including control batch.
2.2.4 Synthesis of silica-cellulose nanocomposites (Si-CNF)

Modification of the CNF with the deposition of the SiO$_2$ nanoparticles was carried out by the sol-gel process [24]. 10 gm of CNF slurry was mixed with 35 mL of deionized water at a constant and moderate mechanical stirring of 300 rpm for about 5 minutes. After this 0.045 mL of 5M NaOH was added to maintain the pH of solution around 11. TEOS solution was then slowly added drop by drop and allowed to homogenize using mechanical stirring. All modifications were performed at a temperature of about 70°C (details in section 3.1). The amount of TEOS varied depending on target silica to cellulose ratio. The resultant modified silica-cellulose nanocomposites slurry were stored in the plastic container for characterization and performance evaluation.

2.3 Results and discussions

2.3.1 Morphology of PCNF and Si-CNF

Utilization of silica nanoparticles in cement matrix leads to the formation of additional C-S-H by both nucleation and pozzolanic reaction [41]. To capitalize on this effect, the goal of this work was to coat the cellulose nanofibrils with silica layer which would form additional C-S-H at the interface between fibrils and paste matrix. This additional C-S-H can eventually protect the fibrils from alkali attack and can enhance the bonding between fibers and cement matrix. To achieve this goal, CNF was coated with silica nanoparticles using the Stöber process (sol-gel method). The Stöber process is particularly well-known for synthesizing monodispersed silica nanoparticles [26]. The size of silica nanoparticles prepared in this approach depends on the catalyst and pH of the synthesis medium [27]. Ammonium hydroxide (NH$_4$OH) is the commonly used catalyst in this approach [26]. Nevertheless, NaOH was used in this study as it was reported to produce silica nanoparticles with high surface area and with higher conversion efficiency [27]. A total of three different silica contents were investigated, these are: 0.12%, 0.3% and 1% by weight of solid cellulose nanofibrils. These percentages of silica nanoparticles are based on
Figure 2.1. TEM images of CNF with different silica nanoparticle contents, (a) 0%, (b) 0.12%, (c) 0.3%, and (d) 1.0%

stochiometric calculations of sol-gel method. The TEM images of these samples were collected to confirm the deposition of silica nanoparticles on the cellulose fibers (Figure 2.1). As it can be observed from these TEM images, even though the diameter of individual cellulose strand is around 20 nm, these are mostly present in agglomerated or bundle forms. Such agglomeration was prominent in PCNF batch (Figure 2.1 (a)). CNF bundles/agglomerations are due to both van-der-waals force and the hydrogen bonding on the surface of the fibrils. Our initial study showed that even ultrasonication was not effective to
eliminate such agglomerations. Addition of 0.12% of silica formed a limited amount of silica nanoparticles and the agglomeration of CNF was still observable (Figure 2.1 (b)). With 0.3% silica content, higher amounts of silica nanoparticles were observed to deposit on the surface of the CNF. However, such deposition of silica nanoparticles on the cellulose fibrils were not uniform. At higher content (1%), silica nanoparticles deposited in multiple layers on some locations of the cellulose nanofiber while bare surfaces were available at other locations. At 0.3% and 1% silica content, the CNF was still found to be present in bundles, but lesser degree of agglomeration was observed (Figure 2.1 (c) and (d)). At 1% silica content, qualitatively a higher fraction of silica nanoparticle agglomeration was observed. Such agglomerations are expected to reduce the efficiency of silica nanoparticles and also reported to create weak zones in hydrated cement system because of low stiffness [28]. Accordingly, 1% silica containing batch was avoided and 0.3% silica containing Si-CNF was used for the remainder of this study. The diameters of the silica nanoparticles were found to be between 20 to 50 nm.

2.3.2 Dispersion stability of PCNF and Si-CNF

In a colloidal system zeta potential is the electrical potential in the interfacial double layer of a dispersed particle or droplet versus a point in the continuous phase away from the interface [29]. In general, high positive or negative zeta potentials (greater than 30 mV) lead to better colloidal stability. Low absolute value of zeta potential indicates the tendency of colloids to agglomerate[9]. Figure 2.2 shows the potentials of PCNF and Si-CNF at different pH concentrations. Higher potential value was achieved for Si-CNF when compared to PCNF. This indicates the deposition of the silica nanoparticles on the surface of the CNF breaks intermolecular forces between the cellulose fibers itself and created a better colloidal stability for the fibrils. Both 0.12% and 0.3% silica containing Si-CNF batches had higher potential compared to 1% batch. Thus, adding up to a certain amount of silica helps dispersing the CNF and after this level, the dispersion stability is
reduced. The potentials of the CNF were low at cement artificial pore solution which had a very high pH (around 13). However, such high pH of pore solution can be expected in fully hydrated cement system [30]. The stability of CNF with 0.3% silica nanoparticle was highest for the pH range of 8 to 9.

2.3.3 Rheology measurements

The rheological properties of fresh cement-based materials are often described using the Bingham model [31, 32]. Based on this model, the relationship between shear stress and stain rate is linear after the minimum stress required to initiate the flow. The minimum level of stress required to initiate the flow of cement paste is termed as yield stress. By definition yield stress is the transition stress between elastic solid-like behavior and viscous liquid-like behavior [33]. The experimental setup used in this study provided the net torque (N.m) required for different rotational speed of cement paste. Figure 2.3(a) shows an example of net torques (N.m) vs. rotational speeds (r/s) for cement paste containing 0.3% by weight of nanomaterials (PCNF and Si-CNF). As observed from this figure, higher
torque was necessary to initiate a higher rotational speed. This observation was similar for all of the batches containing different amounts of CNF. The linear relationship between torque and rotational speed confirms that the rheological parameters of cement paste are following the Bingham model. As such, the lowest torque required to initiate the rotation represents an index of yield stress and slope of each line represents an index of viscosity for the cement paste mixtures. Thus, both yield stress and strain rate can be calculated from initial torque and rotational speed, respectively. Details of this approach can be found in a previously published article [72]. Nevertheless, the torque and rotational speeds are directly presented here as the goal was to present a qualitative comparison of the paste mixtures with different CNF contents. Figure 2.3(b) represents the initiation torque (relative yield stresses) for paste mixtures containing different concentrations of cellulose nanomaterials (PCNF or Si-CNF) for two different w/c ratios (0.35 and 0.45). The initiation torque (relative yield stress) of the paste mixture was increased with the addition of nanomaterials. This is because addition of nanomaterials increases the total surface area and hence, increases the water demand [34]. The tendency of CNF to agglomerate also
increased the required shear to initiate the flow. The increase of yield stress of cement paste with the addition of pure CNF has been reported before[72, 12]. However, as observed from this study, the cement pastes having PCNF has more initiation torque (i.e., higher yield stress) when compared to Si-CNF. Thus, coating the CNF with silica helped to enhance workability of cement paste mixture containing these nanofibrils. This benefit of Si-CNF was attributed to the improved colloidal stability and lesser degree of agglomeration of CNF in the presence of silica nanoparticle coating as observed from the zeta potential measurements and TEM images, respectively.

2.3.4 Effects of CNF on cement hydration

Figure 2.4 shows the rate of heat evolution of cement pastes with different CNF (PCNF and Si-CNF) contents up to first 40 hours of hydration. The effect of CNF on cement hydration was evaluated by comparing the maximum heat flow and duration of the primary exothermic peak. At low w/c ratio (0.35), the peak of heat flow of cement hydration was observed to increase due to the addition of both PCNF and Si-CNF (Figure 2.4 (a) and (b)). At this w/c ratio, the heat flow peak was also shifted to the left (i.e., the dormant period was reduced) indicating that CNFs accelerated the cement hydration. Such accelerating effect was attributed to the additional surface area provided by the CNFs. This additional surface area works as the nucleation sites for C-S-H that also increased the nucleation rate of C-S-H [35, 36, 37]. The increased rate of C-S-H nucleation enhances the cement hydration during acceleration period [65, 39]. Essentially CNF work as seeding agent on to which C-S-H can nucleate and grow. Similar acceleration of cement hydration due to the addition of nanosilica was observed before [40, 41]. The hydration acceleration effect of both PCNF and Si-CNF was similar for cement pastes with 0.35 w/c ratio. At this 0.35 w/c ratio, the increase of peak heat flow due to the addition of CNFs (PCNF or Si-CNF) was around 2mW per g of cement or 50% increase from the control batch.
Figure 2.4. Normalized heat flow curves for cement pastes containing different amounts of Si-CNF and PCNF

However, hydration acceleration effect of CNFs was decreased with increasing w/c ratio (Figure 2.4 (c) to (f)). Specifically, at w/c = 0.4, the acceleration stage of cement paste containing PCNF overlaps with that of the control batch. At 0.3 and 0.5%, Si-CNF batch showed slight increase of peak heat flow due to the acceleration effect of silica
nanoparticles, while all other batches showed similar or lower peak heat flow as that of control batch. At 0.45 w/c ratio, the cellulose nanomaterials reduced the rate of hydration as observed by the decrease in heat flow peak compared to that of the control batch.

Several recent studies also reported that addition of cellulose nanomaterials can reduce the

Figure 2.5. Normalized heat release from cement pastes containing different amounts of Si-CNF and PCNF
early age cement hydration rate [11, 10, 67]. This is because of the presence of hydroxyl and carboxyl surface groups of CNF [67]. The oxygen atom in hydroxyl and carboxyl group has unpaired electrons, that binds calcium ion and as a result, cellulose can be adsorbed on cement particles [67]. Such adherence of cellulose nanomaterials on cement particles reduces the active nucleation sites and thus, reduce the cement hydration rate [67, 10]. However, as observed in this study, the hydration reduction effect of cellulose is dependent on the w/c ratio. The possible reason of such w/c dependent effect is discussed below:

For pure cement paste, a decrease in w/c ratio increases the rate of heat release at the early stage of hydration [43, 44]. As reported by Justs et al. [43], an increase in w/c ratio of cement paste makes the pore solution diluted with respect to alkalis and hydroxyl ions which provides less acceleration of the cement hydration and hence, results in lower heat release. Based on the finding of this study, it is postulated that the unpaired electron of hydroxyl and carboxyl groups of CNF initially binds with positively charged alkali groups in cement pore solution (Na$^+$, K$^+$, etc.). Such alkali binding balances the surface charge of CNF and eliminates its tendency to adhere on cement particles. Accordingly, when the w/c ratio is low (0.35 in this study), the high concentration of alkali ions balances the surface charge of CNF and minimize the hydration retardation effect due to adherence of CNF on cement particles. Whereas, with increasing w/c ratio, the concentration of alkali ions decreases in pore solution and thus, the tendency of CNF to adhere on cement particles remains. As a result, CNF reduces the rate of cement hydration with increasing w/c ratio. Accordingly, there are at least two mechanisms by which CNFs can affect cement hydration:

- Nucleation effects provided by the surface area of cellulose nanomaterials which accelerate the cement hydration.

- Adherence of cellulose nanomaterials on cement particles which retards the cement hydration.
As observed in the current study, the extent of these effects depends on the w/c ratio (pore solution chemistry, to be specific) of the cement paste. Due to these mutually conflicting mechanisms, the acceleration or retardation of cement hydration do not show any linear trend with the amounts of PCNF or Si-CNF added to the paste. Comparing the effects of PCNF and Si-CNF (Figure 2.4), the peak heat flow of cement hydration of the paste batches containing Si-CNF were consistently higher than those of PCNF. This is because of two reasons; (i) the additional surface area provided by the silica nanoparticles also accelerated cement hydration during the first hours [41] and (ii) during the sol-gel process, some of the Na⁺ ions were bound with the cellulose fibers resulting a lesser degree of adsorption of Si-CNF on cement particles.

Irrespective of the variable effects on the heat flow during early stage cement hydration, CNFs (both PCNF and Si-CNF) were observed to increase the total heat release after 80 hours of hydration (Figure 2.5). Increase in total heat release within this duration indicates enhanced cement hydration. The hydration enhancement as observed here was attributed to ‘short circuit diffusion (SCD)’ mechanism as proposed by Cao et al. [9]. As per this mechanism, cellulose nanomaterials work as channels within the C-S-H layer to diffuse moisture from the pore solution to the core of the unreacted cement particles. Due to this enhanced diffusion mechanism, a higher level of cement hydration can be achieved [9, 12]

2.3.5 Hydrated phase assemblage using thermogravimetric analysis (TGA)

The composition of hydrated cement paste was evaluated by TGA and derivative of thermogravimetric graphs (DTG). Figure 2.6 (a) and (b) represent the TGA and DTG measurements for different concentrations of Si-CNF and PCNF, respectively, for w/c ratio of 0.35 at the end of 28 days of sealed curing. The DTG can be used to locate the temperature ranges corresponding to thermal decompositions of different hydrated phases present in cement paste [45, 46]. The observed weight losses of cement paste during TGA were attributed to phase decomposition as follow [46]: (1) the first weight loss at about
Figure 2.6. TGA-DTA curves for cement paste containing (a) Si-CNF and (b) PCNF after 28 days of sealed curing, w/c = 0.35

150°C is due to the dehydration of gel water in C-S-H, ettringite (AFt) and monosulphate (AFm), (2) the weight loss within the range of 400°C - 450°C is due to the dehydration of Ca(OH)$_2$, (3) the final weight loss within the range of 600 to 800°C is due to the de-carbonation of CaCO$_3$, and (4) the gradual weight loss between 150°C and 980°C was attributed to the loss of chemically bound water in C-S-H. It is interesting to note that both PCNF and Si-CNF containing paste batches showed a decrease in the weight loss due to the ettringite dehydration (see insets in Figure 2.6 (a) and (b)). Such decrease in ettringite formation due to the addition of cellulose nanomaterials can be important to reduce/ prevent sulfate attack in cement paste. A recently published article also reported that the CNF additions enhance the resistance of cement paste against sulfate attack [47]. According to Goncalves et al. [47], CNF chemically traps the calcium ions Ca$^{2+}$ through electrostatic links, and reduces the amount of Ca(OH)$_2$ in the pore solution. A reduction of the available Ca(OH)$_2$ will lead to a drop in the formation of gypsum, and in the eventual production of ettringite[47]. Nevertheless, additional investigations are required to confirm this mechanism of reduced ettringite formation due to the presence of CNF.
Figure 2.7. Ca(OH)$_2$ and chemically bound water contents for different nanomaterial additions (a,b) w/c-0.35 and (c, d) w/c-0.45.

The TGA data was further analyzed to quantify the amounts of Ca(OH)$_2$ and chemically bound water present in C-S-H. The amounts of Ca(OH)$_2$ were determined by integrating the DTG peak in the temperature range of 400 to 500$^\circ$C (details of this method can be found in [46]. The chemically bound water content of C-S-H was determined by
subtracting the weight loss corresponding to CaCO$_3$ and Ca(OH)$_2$ decomposition from total weight loss between the temperature range of 105°C and 980°C.

Figure 2.7 is showing the Ca(OH)$_2$ and C-S-H bound water contents in cement paste with 0.35 and 0.45 w/c ratios, and with different concentrations of PCNF and Si-CN F after 28 days of sealed curing. At low w/c ratio (0.35), the CNFs resulted in a lower bound water content of C-S-H compared to that of the control batch. Indicating that even though CNFs accelerated the early age hydration, the total extent of reaction after 28 days curing was lesser for 0.35 w/c ratio. This suggests all of the physi/chemisorbed water present in CNF was not completely available for cement hydration within 28 days. At this w/c ratio, the Si-CN F provided higher Ca(OH)$_2$ contents compared to pure CNF batch. This increased hydration extent of Si-CN F batch was attributed to the nucleation effect of nanosilica as observed in the heat of hydration measurements (Figure 2.4). At 0.45 w/c ratio, there is plenty of water for cement to achieve full hydration (minimum w/c ratio for complete hydration is 0.42 to 0.44 based on Power’s model [48, 49, 50]. Accordingly, for these batches the addition of cellulose nanomaterial does not have any prominent influence on cement hydration as all of the physi/chemisorbed water in cellulose was not necessary to achieve full hydration.

2.3.6 Effects on compressive strength

Figure 2.8 represents the effects of PCNF and Si-CN F on the compressive strength of cement paste for 0.35 and 0.45 w/c ratios. For w/c ratio of 0.35, at 7 days the mixtures with 0.1%, 0.3% and 0.5% Si-CN F showed about 4%, 2% and 6% increase in strength when compared with PCNF. The higher strength of Si-CN F batch was attributed to the nucleation effect of the silica nanoparticles during the early ages of hydration. Other than these, CNFs did not show any significant benefit on compressive strength until 90 days of sealed curing. This is because nucleation effect of cellulose helps only at the early stage. Any potential pozzolanic effect from agglomerated silica would be very slow and such
agglomerations might not even provide any positive effect either [41]. A more significant effect of Si-CNF on the compressive strengths of cement paste was observed when used at higher concentrations and after 90 days of curing. For cement paste with 0.35 w/c ratio, 0.5% Si-CNF showed about 22% increase in strength when compared with PCNF batch and about 15% increase in strength when compared with control batch. PCNF shows beneficial effect on compressive strength only at lower dosage (0.05%) as also observed in a previous study [72]. In the case of cement paste batches containing PCNF with 0.35 w/c ratio, the compressive strength after 90 days curing was increased by 24% due to the addition of 0.05% by wt. of CNF. After this level, increasing the CNF content decreased the compressive strength. However, for the similar cement batch (0.35 w/c ratio and 90 days curing), increasing the Si-CNF content showed an increasing trend in compressive strength of the paste.

A similar trend in compressive strength variation was observed for cement paste containing PCNF and Si-CNF at 0.45 w/c ratio. Cement paste batches with 0.45 w/c ratio and containing 0.05% by wt. of PCNF showed 15% increase in compressive strength after 90 days of curing. Beyond this level, addition of PCNF decreased the compressive strength of cement paste. After 90 days of curing, 0.5% concentration of Si-CNF showed about 32% increase in the compressive strength when compared with PCNF and about 14% increase with respect to control mix (0.45 w/c ratio).

In general, the increase in compressive strength due to the addition of cellulose nanomaterials (both PCNF and Si-CNF) was prominent for mixtures with 0.35 w/c ratio compared to that of 0.45 w/c ratio (Figure 2.9). It should be noted that at 0.35 w/c ratio, addition of PCNF resulted in a lower degree of cement hydration (Figure 2.7 (a)). Irrespective of this lower degree of hydration, the beneficial effects of CNF on the compressive strength at 0.35 w/c ratio compared to that of 0.45 ratio was attributed to the following mechanisms:
Figure 2.8. Compressive strength of cement pastes containing PCNF and Si-CNFR for w/c ratios 0.35 and 0.45 after (a) 7 days of curing, (b) 28 days of curing, and (c) 90 days of curing.

- Cement paste with 0.35 w/c ratio is expected to experience higher degree of self-desiccation compared to that of 0.45 w/c ratio due to the water consumed by cement hydration [51, 49]. Such self-desiccation results in shrinkage cracks in cement paste in a sealed curing condition which eventually decreases the compressive strength.
Figure 2.9. Compressive strength (MPa) evolution of cement paste with time; (a) at 0.35 w/c ratio and (b) at 0.45 w/c ratio

strength. Presence of CNF was reported to reduce the shrinkage of cement paste due to the internal curing effect [72] and also due to the potential reinforcing effect. Thus, CNF has the potential to reduce shrinkage crack in cement paste with low w/c ratio. Because of such lower extent of shrinkage cracks, cement paste containing cellulose nanomaterials (both PCNF and Si-CNF) showed higher strength compared to control batch. Such shrinkage cracks are not expected to form in cement paste with w/c ratio of as high as 0.45 due to the presence of more water than required for cement hydration.

- The available amount of pore solution is expected to be higher in cement paste with 0.45 w/c ratio compared to that of 0.35. The alkaline pore solution of hydrated cement paste is known to degrade the cellulose [52] and such degradation is expected to be faster in cement paste with 0.45 w/c ratio due to the higher amount of pore solution. This alkaline degradation of cellulose nanofibrils creates excess porosity in cement paste which eventually results in a decrease of compressive strength due to
the addition of CNFs. This mechanism was further confirmed by the observation that the strength was reduced after 90 days for cement paste containing PCNF (Figure 2.9). Nevertheless, 0.5% by wt. of Si-CNF addition in cement paste resulted in higher compressive strength compared to PCNF batch after 90 days of curing (see Figure 2.9) and hence, confirming that nanosilica coating helps to delay or eliminate the degradation of cellulose fibrils in alkaline pore solution of cement paste.

2.3.7 Effects on fracture properties

![Load vs CMOD plot with loading and unloading cycles](image)

Figure 2.10. Load vs CMOD plot with loading and unloading cycles

Flexural strength and fracture toughness of the PCNF and Si-CNF was measured using the three-point bending tests described in section 3.2.3.7. Example load-CMOD plots are shown in Fig. 2.10. The plots show the characteristics of the test with the loading, unloading, and reloading cycles, as well as the strain-softening behavior of the different mixes.
Flexural strength was calculated here as the stress at peak load. Size-independent fracture parameters $K_{Ic}$ and $CTOD_c$ were calculated from the initial specimen compliance and the compliance after initial cracking\cite{53}\cite{54}. From $K_{Ic}$ and $CTOD_c$, the effective equivalent crack length, $a_c$ was calculated. While in general, $a_c$ is not an appropriate
fracture parameter because of its size dependence, all specimens tested had the same dimensions, so $a_c$ was a simple way to judge fracture toughness. As part of this analysis, the elastic modulus of the material is also determined. Finally, a measure of the full work of fracture was also determined by taking the area under the envelope of the load-CMOD (i.e. no unloading/reloading portion).

Fig. ??(a) shows the flexural strength of the different materials for different CNF dosages. Both pure CNF and Si-CNF increased the flexural strength, however, pure CNF provided a greater enhancement than that of Si-CNF. Specifically, a 0.5% addition of pure CNF increased the tensile strength by 75%, whereas for Si-CNF, the increase was 55%. With respect to fracture toughness, the picture is different. As shown in Fig. 2.11(c), the pure CNF specimens show an increase in crack initiation toughness ($a_c$), but the Si-CNF show a decrease. This is also true for fracture energy, $G_F$, as seen in 2.11(d).

Perhaps the most interesting result is the effect of the CNF on elastic modulus. Fig. 2.11(b) shows that while Si-CNF had little to no effect on elastic modulus, additions of pure CNF produced a three to four-fold increase. Such a result cannot be explained by traditional rule of mixtures-type analysis, rather suggesting a modification of microstructure, as has been observed with additions of carbon nano fibers.[55]

### 2.4 Conclusions

This study provided a comprehensive investigation on the effects of pure CNF and Si-CNF on the hydration, hydrated phase formation, compressive strength and fracture parameters of cement paste samples. Followings are the concluding remarks from this study:

1. Sol-gel method was successfully used to deposit silica nanoparticles on the surface of cellulose nanofibrils. The diameter of silica nanoparticles was around 20 to 50 nm.

2. Addition of nanosilica improves the stability of the cellulose nanofibers in the colloidal system and thus, helps to avoid agglomeration of the fibers.
3. Cellulose nanomaterials reduced the ettringite formation in the cement paste samples when used at higher concentration (i.e., above 0.1%).

4. Addition of cellulose nanomaterial did not show any significant positive effect on the compressive strength of paste samples after 28 days of sealed curing. After 90 days of curing, 0.05% PCNF addition in cement paste resulted in 24% and 15% increase in the compressive strengths of cement paste with 0.35 and 0.45 w/c ratios, respectively. Beyond this level, addition of PCNF decreased the compressive strength of cement paste matrix. The compressive strength of cement paste increases with the addition of Si-CNF. The maximum strength enhancement was achieved for 0.5% Si-CNF addition. At this level, the compressive strength was increased by 22% and 14% for the cement pastes with 0.35 and 0.45 w/c ratios, respectively, after 90 days of curing.

5. The flexural strength of cement paste increases with an increase of the cellulose content. The flexural strength of cement paste increased by 75% and 52% due to the addition of 0.5% of PCNF and Si-CNF, respectively.

6. 0.025% and 0.5% of PCNF addition increases the elastic modulus by around 200% and 250%. The addition of 0.5% Si-CNF has a very little effect on elastic modulus with an increase of about 15%. The lesser benefit of Si-CNF indicates that apparent the high-alkali sol-gel process have weakened the CNF fibers.
CHAPTER 3
EFFECT OF VARIED FINE CONTENT PERCENTAGES OF CELLULOSE
NANOMATERIALS ON PERFORMANCE ENHANCEMENT OF
PORTLAND CEMENT SYSTEMS

3.1 Introduction

Similar to cellulose, lignin as a component in the cell wall of plants is used to strengthen their structure and it is the most abundant three-dimensional aromatic polymer on Earth [55]. In paper industry, the main component of wood that needs to be removed to turn it into paper is lignin and also the compound that makes wood pulp brown, so it is removed from all wood pulp except that used to make brown paper and some cardboards. Since, till date the use of lignin as a raw material has been limited since found as an isolated product of the pulp and paper industry, has been largely discarded[56]. Lignin-containing CNF, commonly known as lignocellulose nanofibrils (LCNF) isolated directly from unbleached wood without pretreatments is a promising material[60] and is starting to gain much attention in construction sector where cement-based materials are widely used. Spence et al, had estimated the total energy cost during the isolation of cellulose nanofibrils (CNF) from bleached hardwood using 9 passes microgrinding to be $95/ton, providing a final cost of the material to be about $445/ton [57]. The saving of pulp bleaching step, easy processing and lower energy consumption make LCNF a low-cost material compared to pure CNF (PCNF) with the potential to be used on industrial scale.

The reduction in particle size of wood-based materials well below cell level has attracted increasing interest. Such micro and nanomaterials (cellulose nanofibrils, CNF) have a very high specific surface area. This further disintegration of wood cell wall can be carried out using extensive mechanical treatment with or without chemical pre-treatments [58]. The CNF is usually made from chemically- pulped fibers, in which the lignin has been
removed from the middle lamellae, during the production of pure cellulose nanofibrils (PCNF). In the production of lignin containing cellulose nanofibrils (LCNF), pulped fibers without any chemical preatment were used [58]. Mechanical pulping methods are not capable of disintegrating intact fibers from cell wall, fibers are generally broken down at some levels and the resulting furnish includes a fraction of small particles known as "fines". The term 'fines' refers to particles that can pass through a 200-mesh screen, which has an aperture width of 76 µm (Tappi Testing Method T 261 pm-80) [59]. Similar to cellulose nanofibrils (CNF) obtained from bleached pulp, LCNF are branched and random filaments with diameters varying between 10 to 50 nm and length of several micrometers. Its structure and dimension confer it has a high aspect ratio and large surface area. In addition to their high strength and modulus, LCNF fibrils are biocompatible and can be functionalized [60].

The aim of this study was to evaluate the effect of different fine content percentage additions of pure cellulose nanofibrils (PCNF) and lignin containing cellulose nanofibrils (LCNF) in cement-based materials. The variation in fine contents were obtained during the process of mechanical grinding of cellulose nanomaterials. The fine content percentages considered in this study were 60%, 75%, 80%, 90% and 95% for both PCNF and LCNF. The main objective of the study was to determine the optimum fine content percentages of PCNF and LCNF in portland cement pastes, such that production cost can be reduced with lower fine content percentage usage. The effect of these nanomaterials in cement paste were studied for workability, cement hydration, microstructure phase formations and mechanical performance in terms of compressive strength and fracture toughness. Different dosages of PCNF and LCNF were studied for the same water-cement ratio to evaluate the above mentioned properties.
3.2 Materials and methods

3.2.1 Raw materials

The raw materials used in this study include ordinary portland cement (OPC, type I/II), lignin containing cellulose nanofibrils (LCNF), pure cellulose nanofibrils (PCNF). The OPC Type I/II contained 20.1% SiO$_2$, 63.7% CaO, 4.7% Al$_2$O$_3$, 3.5% Fe$_2$O$_3$, 3.1% SO$_3$, and 0.7% MgO and the Blaine fineness was 364 m$^2$/kg. The production of LCNF and PCNF undergoes similar process except LCNF does not undergo bleaching procedure as of PCNF. Both PCNF and LCNF used were in a odorless aqueous slurry form. The solid concentration of CNF slurry was about 3% (3 gm of cellulose nanofibrils dispersed in 97 gm of water). Both CNF materials were supplied by the Process Development Center (PDC) at the University of Maine. This CNF slurry was produced by mechanical treatment of bleached softwood pulp and the average fiber diameter was around 20 to 500nm [61, 62].

3.2.2 General mixture proportions, sample preparation and curing

Table 3.1 presents the relative proportions of the ingredients used to prepare paste mixture in this study with respect to 1000g of cement. Nearly all of the experiments were performed for cement pastes with a constant water-to-cement ratio (w/c) of 0.35. Two different cellulose nanomaterials were used, namely pure CNF (addressed as ‘PCNF’) and lignin containing CNF (addressed as ‘LCNF’). Cellulose nanomaterials with fine contents ranging from 60%, 75%, 80%, 90% and 95% fines were added at concentrations of 0.05% and 0.1% (solids) by weight of cement. The control batch denotes paste mixture with only OPC and water. The free water demand of each mixture was determined after subtracting the amount of water present in the cellulose slurry (3% solid CNF in 97% water) from the total water required to maintain w/c ratio. Our laboratory measurements showed that this 97% of water in cellulose slurry are weakly bound moisture which can be evaporated at room temperature. As such, it was considered that the water present in cellulose slurry is available for cement hydration. Based on the previous work on cellulose nanomaterials, it
Table 3.1. Mix design of pastes based on 1000g of binder for w/c 0.35 and 0.45

<table>
<thead>
<tr>
<th>0.35 w/c ratio</th>
<th>Cement (g)</th>
<th>Free water (g)</th>
<th>CNF slurry (g)</th>
<th>Water from CNF (g)</th>
<th>Total water (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1000</td>
<td>350</td>
<td>0</td>
<td>0</td>
<td>350</td>
</tr>
<tr>
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<td>1000</td>
<td>333.8</td>
<td>16.7</td>
<td>16.2</td>
<td>350</td>
</tr>
<tr>
<td>0.1</td>
<td>1000</td>
<td>317.7</td>
<td>33.3</td>
<td>32.3</td>
<td>350</td>
</tr>
</tbody>
</table>

has been noticed that mixing of cement paste using ASTM C305 was not satisfactory as the paste was not thoroughly mixed due to the agglomeration of nanofibrils. The shear imparted to the cement paste is significantly higher for high-shear mixing procedure, thus providing uniform mix. The following procedure was used for mixing the cement pastes using high-shear mixer: (1) the PCNF or LCNF slurry was first mixed with water in the rotary mixer for 60 secs at a speed of 3330 rpm for homogenization; (2) cement was then added to this suspension and mixed at a speed of 4960 rpm for about 60 secs with 15 secs rest and then for 180 secs for same speed of 4960 rpm; (3) paste mixtures were then used to cast required samples shapes/ sizes and were subjected to sealed curing condition (details in the following section). Cement paste mixtures were evaluated for heat of hydration, Workability, compressive strength, microscopic phase formation, flexural strength and fracture properties.

3.2.3 Experimental methods

3.2.3.1 Transmission electron microscopy (TEM)

The morphologies of the PCNF and LCNF were evaluated using CM10 TEM. Approximately 1 gm of cellulose (PCNF or LCNF) slurry was diluted with at least 10 times more deionized water and were dispersed uniformly until turbidity was visibly reduced and no macroscopic particles could be seen. A droplet (5μl) of diluted suspension was deposited onto carbon coated grid. After 1 minute the excess water from the sample was removed by dabbing with a filter paper. A drop of negative stain with 1% uranyl
acetate solution was added on to the sample to enhance the contrast. The TEM images of the samples were collected using Philips/FEI CM10 with accelerating voltage of 120V.

3.2.3.2 Zeta potential measurements

The zeta potential of the cellulose nanomaterials in various pH solutions were measured using Malvern Zetasizer 3000. The selected pH values for the solutions were 7 and 13. NaOH and deionized water were used to prepare pH solutions. 1 gm of cellulose nanomaterial suspension was mixed with 80 gm of each pH solution (pH 7 and 13) and allowed to homogenize for 2 minutes using magnetic stirrer before the zeta potential measurement.

3.2.3.3 Workability

The workability of the cement paste with different cellulose nanomaterials were measured using the flowtable test as per ASTM C1437-15 standard. ASTM C305-14 standard mixing procedure for cement pastes was adopted throughout the study for all nanomaterials.

3.2.3.4 Heat of hydration

Paste samples with constant w/c ratio of 0.35 were prepared using both PCNF and LCNF for different percentage fines. The mixing procedure of these paste samples were same as that of workability measurements. After mixing (details in 3.2.2), approximately 15gm cement paste sample was placed into a glass vial which was then used for heat release measurements. The heat measurement started approximately 45 minutes after the mixing. This time delay was required for the signal stabilization. The heat of hydration of the paste samples were monitored using an isothermal calorimeter (TAM Air, TA instruments) for 100 hours at 23±1 °C. The heat data presented in this article were normalized with respect to the weight of cement.
3.2.3.5 Thermogravimetric analysis (TGA)

Paste samples with a constant w/c ratios of 0.35 was prepared for thermogravimetric analysis (TGA). Acetone was used to stop the hydration of cement paste samples after 28 days and 90 days of sealed curing. The cement paste samples were then dried in a vacuum oven at 50°C for 24 hours to avoid atmospheric carbonation. Finally, the dried paste samples were ground using mortar-pestle and the powder was used for TGA measurements. Commercially available instrument (TA instrument, TGA 55) was used for TGA measurements. Approximately 30-45 mg powder sample was tested for each batch. The powdered sample was loaded into the pan and kept under the isothermal condition for 5 min. The temperature of the TGA furnace chamber was then raised up to 980°C at an increment rate of 10°C per minute.

3.2.3.6 Compressive strength

A total of 21 batches of cement paste with a constant w/c ratio of 0.35 with varied fine contents of CNF for two different concentrations were prepared for compressive strength test. Sealed curing condition was adopted by covering the fresh paste samples with a plastic sheet and kept at 23°C for 24±1h. After this period, the samples were demolded and stored in sealed plastic bags such that no external moisture can pass through the samples in a storage room at 23°C temperature until the age of testing. Compressive strengths were measured for the paste cube (50 mm sides) samples as per ASTM C109 using a loading a rate of 200 to 400 lb/sec. Compressive strengths were determined after 7, 28, 56 and 90 days of sealed curing.

3.2.3.7 Fracture properties

The three-point bending tests of notched beams were performed to determine the fracture parameters as per the International Union of Testing and Research Laboratories for Materials and Structures (RILEM)[10, 11]. This test was conducted using a closed-loop crack-mouth opening displacement control. This type of test configuration allows for stable
failure of the test specimen. A linear variable displacement transducer (LVDT) was used in these tests to control the crack opening so that it grew at a constant rate. The LVDT was mounted across the notch with aluminum brackets that attached directly to the beam specimen. The test consisted of loading the specimen until a crack formed; then the specimen was unloaded and reloaded so that crack grew steadily (as controlled by LVDT). The following fracture parameters were calculated from the obtained data set: critical stress intensity factor \( K_{\text{c}} \), critical crack tip opening displacement \( \text{CTOD}_{\text{c}} \), critical crack length \( a_{\text{c}} \), and fracture energy \( G_F \). Four batches of notch beam (3cm x 4cm x 18cm) samples were prepared for 0.35 w/c ratio. The concentrations of PCNF and LCNF by weight of cement in the mixture were 0.05% and 0.1% including control batch.

3.2.3.8 Scanning electron microscope imaging (SEM)

Surface morphology of cement pastes containing cellulose nanofibrils (PCNF and LCNF) was achieved through AMRay 1820 scanning electron microscope (SEM) which has a resolution of 5 nm, a magnification range of 20-150,000X and an accelerating voltage range of 100V to 30kV.

3.3 Results and discussions

3.3.1 Morphology of LCNF and PCNF

Figure 3.1 shows morphologies of PCNF and LCNF obtained through TEM images. Pure cellulose nanofibrils have diameters up to 20 nm and lengths up to several hundred microns as shown in figure 3.1 (a). Agglomerations of pure CNF are due to high magnitude of van-der-waals forces and intermolecular hydrogen bonding between the fibrils in itself due to high hydrophilic nature. In contrast to PCNF, Lignin containing cellulose nanofibrils are hydrophobic in nature [63].
3.3.2 Dispersion stability of nanofibrils

The surface chemistry of cellulose nanofibrils is critical in determining how the nanomaterials will interact with their environment, controlling their dispersion in colloidal systems, rheology, self-assembly, agglomeration and CNF-CNFi interfacial bond strength.
Zeta potential measurements for both PCNF and LCNF with different fine content percentages ranging from 60%, 75%, 80%, 90% and 95% fines were performed for two pH conditions (pH-7 and pH-13) for 0.05% and 0.1% CNF concentrations. From figure 3.2 (a) it can be seen that with the increase in pH of solution the zeta potential value decreases, this can be related to higher intermolecular forces between the cellulose fibrils causing agglomeration of fibers. Whereas, LCNF particles has an anionic surface charge making them colloidally semi-stable in water (pH-7) [59] as shown in figure 3.2 (b). Increase in the alkalinity (pH-13) of solution showed very little effect on zeta potential values for LCNF due to their hydrophobic property when compared to hydrophilic PCNF.

3.3.3 Workability

Workability of the fresh cement pastes with 0.05% and 0.1% concentrations of both PCNF and LCNF for varied fine contents ranging from 60%, 75%, 80%. 90% and 95% were measured using flowtable test as per ASTM standard C1437-15 as shown in figure 3.3 ((a) & (b)). For PCNF containing cement pastes, the workability was reduced with the increase in addition concentrations of PCNF. At 0.05% PCNF addition the workability was increased by 11%, 11%, 9%, 8% and 5% for 60%, 75%, 80%. 90% and 95% fines respectively when compared to control batch. With increased concentration of PCNF to 0.1% the workability of cement pastes was reduced by about 10% for almost all fine contents. This is explained through the pronounced hydrophilic nature and high surface area of pure cellulose nanofibrils (PCNF), for which the adsorption of water can lead to the reduction in effective water to cement ratio (w/c) of cement mixing, by changing the workability of fresh PCNF-containing cement pastes[10]. Thus, increased addition concentrations of PCNF results in increased water adsorption capacity of cellulose nanofibrils. Increase in fibril content increases the friction between cellulose chains thus reducing the effective w/c ratio of the cement pastes by reducing workability of the mix.
Workability of cement pastes with 0.05% and 0.1% LCNF with varied fine contents was shown in figure 3.3 ((a) & (b)). LCNF due to their semi-stable property [59] improved the workability of cement pastes for both concentrations. At 0.05% addition of LCNF, the workability of fresh cement pastes were increased by 17%, 15%, 14%, 10% and 12% for 60%, 75%, 80%, 90% and 95% fines respectively when compared with the control batch. At 0.1% addition of LCNF, maximum improvement in the workability was achieved for 60%, 75% fines by 10%, 14% respectively compared to the control batch. Increased fine content percentages from 80% to 95% showed very little improvement in flow index. Overall, improved workability of fresh cement pastes containing LCNF can be related to the much more hydrophobic nature of lignin when compared to PCNF [64], which might not affect the effective w/c ratio of the cement pastes.

3.3.4 Effect of CNF’s on cement hydration

The effect of different fine content additions of pure cellulose and lignin cellulose nanofibrils in cement paste with 0.35 w/c ratio were studied for the rate of heat evolution
Figure 3.4. Normalized heat flow curves of cement pastes with w/c=0.35 for (a) LCNF with 0.05% , (b) PCNF with 0.05% , (c) LCNF with 0.1% and (d) PCNF with 0.1% concentrations for first 40 hours of cement hydration. Concentrations of PCNF and LCNF for 60%, 75%, 80%, 90% and 95% fines contents were 0.05% and 0.1% by weight of cement. The effect of CNF on cement hydration was evaluated by comparing the maximum heat flow and duration of the primary exothermic peak. Figure 3.4 shows the heat flow rate for 0.05%, 0.1% PCNF and LCNF additions. At this w/c ratio, the heat flow peak was shifted to the
left (i.e., reduction in the dormant period) indicating the acceleration of cement hydration due to CNF addition. The acceleration rate was attributed to the additional surface area provided by CNFs which can enhance the hydration mechanism. The additional surface area provided acts as a nucleation site for the C-S-H formation during the cement hydration acceleration period[65, 39].

Figures 3.4 ((a) and (b)) shows the peak heat flow rate of cement pastes with 0.05% addition concentration of PCNF and LCNF with different fine content percentages. The peak of heat flow was observed to increase for PCNF containing cement pastes with almost all fine content percentages when compared to the control batch. Highest heat release was obtained for 90% fines with 0.5 mW per gram of cement followed by 80%, 75% fines when compared to the control batch. For LCNF containing cement pastes with 90%, 80% and 75% fines, increased heat flow peaks were observed with almost 2.2 mW per gram of cement or 140% increase from the control batch. However, according to Bishop et.al [66] it was observed that lignosulfonates retard the cement hydration by forming a semipermeable layer on the cement grains. Nevertheless, effect of LCNF on cement retardation was not prominent. The heat flow release for LCNF modified cement paste with 60% fines was observed to be lower than the control batch.

Heat flow release rate for 0.1% addition concentrations of PCNF and LCNF are shown in figures 3.4 ((c) and (d)). For 0.1% PCNF 3.4 (c) containing cement pastes, very little increase of heat flow rate was observed only for 60% and 95% fines when compared to control batch. Pure cellulose due to its high number of hydroxyl groups in which oxygen atom having unpaired electrons binds the Ca$^+$ ions resulting CNF adsorption on the cement particles[67] causing reduction in the active nucleation sites for cement hydration. However, for LCNF 3.4 (d) modified cement pastes the heat flow rate for almost all fine contents showed very little improvement with control batch, since addition of lignin delays the cement hydration [68, 69, 70, 66].
Irrespective of the varied fine content percentages and addition concentration, both PCNF and LCNF a little to no increase in the total heat release for 80 hours of cement hydration as shown in figure 3.5. The initial 20 hours of cement hydration (i.e., acceleration period) showed increase in the heat release for almost all fine contents for PCNF and LCNF, which can be related to the additional surface area provided by the
cellulose nanomaterials. With the increase in hydration reaction time reduction in total heat release can be related to no additional surface area available to increase the hydration reaction rate.

3.3.5 Hydrated phase assemblage using thermogravimetric analysis (TGA)

The composition of hydrated cement paste was evaluated by TGA and derivative of thermogravimetric graphs (DTG). Figure 3.6 (a) and (b) represent the TGA and DTG measurements for different fine content percentages of PCNF and LCNF for 0.05% addition concentration, respectively, for w/c ratio of 0.35 at the end of 28 days of sealed curing. The DTG can be used to locate the temperature ranges corresponding to thermal decompositions of different hydrated phases present in cement paste [45, 46]. The observed weight losses of cement paste during TGA were attributed to phase decomposition as follow [46]: (1) the first weight loss at about 150°C is due to the dehydration of gel water in C-S-H, ettringite (AFt) and monosulphate (AFm), (2) the weight loss within the range of 400°C - 450°C is due to the dehydration of Ca(OH)₂, (3) the final weight loss within the
Figure 3.7. AFt phase (Ettringite) Phase reduction for 0.05% (a) and 0.1% (b) PCNF and LCNF materials at 28 days of sealed curing.

Range of 600 to 800°C is due to the de-carbonation of CaCO$_3$, and (4) the gradual weight loss between 150°C and 980°C was attributed to the loss of chemically bound water in C-S-H.

The first stable hydration product forming is ettringite (AFt phase) which forms as long as there are enough sulphate ions in solution. When all gypsum is consumed and the sulphate ions reach a critical low value ettringite becomes unstable product[71]. It is interesting to note that both PCNF and LCNF containing paste batches showed a decrease in the weight loss due to the ettringite dehydration (figure 3.7) for (a) 0.05% and (b) 0.1% concentrations. Such decrease in ettringite formation due to the addition of cellulose nanomaterials can be important to reduce/ prevent sulfate attack in cement paste. A recently published article also reported that the CNF additions enhance the resistance of cement paste against sulfate attack [47]. According to Goncalves et al. [47], CNF chemically traps the calcium ions Ca$^{2+}$ through electrostatic links, and reduces the amount of Ca(OH)$_2$ in the pore solution. A reduction of the available Ca(OH)$_2$ will lead to a drop...
Figure 3.8. Ca(OH)$_2$ and chemically bound water in C-S-H for PCNF and LCNF for 0.05% and 0.1% concentrations at 28 days of sealed curing in the formation of gypsum, and in the eventual production of ettringite[47]. For 0.05% addition, PCNF and LCNF showed around 35% reduction in the ettringite formation for all fine content percentages. At 0.1% addition, reduction in ettringite followed an increasing trend with the increase in fine content percentage for both PCNF and LCNF.
The highest ettringite reduction was about 87% and 70% when compared to the control batch for LCNF and PCNF respectively.

The TGA data was further analyzed to quantify the amounts of Ca(OH)$_2$ and chemically bound water present in C-S-H. The amounts of Ca(OH)$_2$ were determined by integrating the DTG peak in the temperature range of 400 to 500$^\circ$C (details of this method can be found in [46]). The chemically bound water content of C-S-H was determined by subtracting the weight loss corresponding to CaCO$_3$ and Ca(OH)$_2$ decomposition from total weight loss between the temperature range of 105$^\circ$C and 980$^\circ$C.

Figure 3.8 represents the Ca(OH)$_2$ and C-S-H bound water contents in cement paste with 0.35 ratio, for 0.05% and 0.1% concentrations of PCNF and LCNF after 28 days of sealed curing. For 0.05% and 0.1% (3.8 (b) and (c)) addition concentrations, both PCNF and LCNF showed low bound water content of C-S-H when compared to the control batch. Indicating that even though CNFs accelerated the early age hydration, the total extent of reaction after 28 days curing was lesser for 0.35 w/c ratio. Accordingly, lower amount of calcium hydroxide content is observed for 0.05% and 0.1% (3.8 (a) and (d)) concentrations than the control batch as well.

### 3.3.6 Compressive strength

Figure 3.9 represents the effects of different fine contents of PCNF on the compressive strength of cement paste with 0.35 ratio. 0.05% and 0.1% addition concentrations of PCNF by weight of cement were considered. For 0.05% concentration of PCNF, at 7 days the mixtures with 60%, 75%, 80%, 90% and 95% fines showed 2%, 7%, 12%, 13% and 4% increase in the compressive strength when compared to control batch. With the increased sealed curing age to 28,56 days PCNF with 0.05% concentration did not show any significant improvement in the compressive strength up until 90 days. At 90 day sealed curing, 60%, 75% and 80% fine contents showed improved compressive strength up to 8%, 15% and 15% respectively.
Figure 3.9. Compressive strength of cement paste cubes with w/c 0.35 for PCNF with 0.05% and 0.1% concentration

With increased CNF concentration to 0.1%, at 7 days only 95% fines showed 6% increase in the compressive strength compared to control batch. At 28 and 56 days sealed curing age, 0.1% showed very little effect similar to that of 0.05% PCNF concentration. 60% and 75% fines improved the compressive strength by 7% and 8% respectively at 90 days. PCNF shows beneficial effect on compressive strength only at lower dosage (0.05%) as
Figure 3.10. Compressive strength of cement paste cubes with w/c 0.35 for LCNF with 0.05% and 0.1% concentration also observed in a previous study [72]. Results have shown that PCNF with 60% and 75% improved the compressive strength of the pastes irrespective of the addition concentrations. PCNFs with lower fine content percentage reduces the mechanical grinding of the cellulose nanofibrils, by enhancing the cost-effectiveness of nanomaterial usage.
Figure 3.10 represents the effects of different fine contents of LCNF on the compressive strength of cement paste with 0.35 ratio. At 7 day sealed curing, 75% fines of 0.1% addition concentration showed 13% improvement in the compressive strength compared to control batch. For 0.05% addition concentration, little to no improvement in the compressive strength was achieved up until 90 days. At 90 day, mixtures with 60%, 75%, 80%, 90% and 95% fines showed 6%, 11%, 6%, 8% and 9% improvement in the compressive strength. Increased LCNF concentration to 0.1% improved compressive strength of 75% fines by about 16% at 90 days when compared to control batch. For both concentrations, LCNF with 75% fines improved the compressive strength of cement paste cubes.

3.3.7 Fracture properties

Flexural strength and fracture toughness of the PCNF and Si-CNF was measured using the three-point bending tests described in section 3.2.3.7. Flexural strength was calculated here as the stress at peak load. Size-independent fracture parameters $K_{Ic}^S$ and $CTOD_c$ were calculated from the initial specimen compliance and the compliance after initial cracking[53][54]. From $K_{Ic}^S$ and $CTOD_c$, the effective equivalent crack length, $a_c$ was calculated. While in general, $a_c$ is not an appropriate fracture parameter because of its size dependence, all specimens tested had the same dimensions, so $a_c$ was a simple way to judge fracture toughness. As part of this analysis, the elastic modulus of the material is also determined. Finally, a measure of the full work of fracture was also determined by taking the area under the envelope of the load-CMOD (i.e. no unloading/reloading portion).

3.3.7.1 Effect of CNF on flexural strength of cement paste

Figure 3.11 shows the flexural strength of PCNF and LCNF cement paste beam samples at 0.35 w/c ratio for 28 and 56 day sealed curing at different fine content percentages. For 0.05% (3.11 (a) and (b)) PCNF addition, at 28 day sealed curing 90% fines showed 150% increase in flexural strength compared to control batch. However, at 56 day curing age 95% fines showed 52% increase in flexural strength compared to the control batch.
Figure 3.11. Flexural strength of cement paste beam molds with 0.05% and 0.1% CNF for 28 days (a & c) and 56 days (b & d) batch. On the contrary, with the increase in PCNF concentration to 0.1% (3.11 (c) and (d)) at 28 day sealed curing, 60% fines showed 55% increase and at 56 days with 75% fines improvement in flexural strength was about 112% compared to control batch.

As shown in figure 3.11 ((a) and (b)) 0.05% LCNF modified cement pastes showed enhanced improvement in flexural strength than PCNF. At 28 and 56 days, 60% fines of
LCNF showed highest increase in the flexural strength of about 130% and 106% respectively when compared to control batch. For 0.1% LCNF concentration (3.11 (c) and (d)) at 28 days sealed curing 80% fines showed 130% increase in flexural strength, further increased curing age to 56 days the flexural strength of 60% fines showed about 96% increase compared to control batch.

In general, increase in the flexural strength due to the addition of cellulose nanomaterials (PCNF and LCNF) was prominent at 0.05% and 0.1% additions. The main objective of the study is to determine the optimum fine content percentage of fibrils for which highest strength was achieved, since the production cost can be reduced at lower fine contents. The summary of the results for flexural strength is as follows:

1. The flexural strength of PCNF at 56 day curing with 0.05% addition has shown improvement for all fine contents, but maximum strength improvement of about 55% was achieved at 95% fine content compared to control batch.

2. With increased PCNF addition to 0.1%, though 95% fines showed increased flexural strength, 80% fines achieved 87% maximum improvement compared to control at 56 days.

3. In contrast to PCNF, LCNF followed same pattern in enhancing the flexural properties at 0.05% and 0.1% additions, i.e., 60% fine content addition enhanced the flexural strength by 106% and 96% for 0.05% and 0.1% respectively at 56 days.

Adding the nanofibrils to cement matrix makes it a homogenous and isotropic material (nanofibrils randomly distributed through out volume of cement paste at relatively small spacings and thus provide equal resistance to stresses in all directions) and converts its brittle characteristics to a ductile one [73].
Figure 3.12. Modulus of elasticity from 3-point bending test for PCNF and LCNF

3.3.7.2 Effect of CNF on elastic modulus of cement paste

Figure 3.12 represents the elastic modulus of cement pastes reinforced with 0.05%, 0.1% PCNF and LCNF with varied fine content percentages by weight of cement, at 28 and 56 days. For 0.05% (3.12 (a)&(b)) PCNF modified cement paste, 95% fines improved the elastic modulus by about 45% at 28 days and for 56 day curing 90% fines improved the elastic modulus to 169% compared with control batch. At higher concentrations of PCNF
i.e, 0.1% (3.12 (c)&(d)) at 28 days, almost all fine contents maintained similar elastic modulus. However, at 56 day curing age increase in percentage fines decreased the elastic modulus, although 60% fines showed better improvement up to 97% compared with control batch. Based on the recent published article on carbon nanotubes and carbon nanofibers, well dispersed nanofibrils can strongly reinforce the cement paste matrix at the nanoscale by increasing the amount of high stiffness C–S–H[55].

Effect of LCNF modified cement pastes on elastic modulus for 0.05% and 0.1% concentrations by weight of cement were shown in figure 3.12. At 28 days, 0.05% (3.12 (a)&(b)) LCNF addition showed 87% and 62% improvement in elastic modulus for 75% and 80% fines respectively. Further at 56 day curing age, LCNF with 60%, 75% and 80% fines improved the elastic modulus by 140%, 114% and 147% respectively. For 0.1%(3.12 (c)&(d)) LCNF addition the maximum increase in the elastic modulus was achieved for 95% fines with 91% at 28 days and 200% at 56 days sealed curing condition. All the results were compared to the 28 and 56 days results of control batch.

Enhanced elastic modulus with addition of CNF can be attributed to the high surface area and widespread surface hydroxyl (OH\(^{-}\)) groups [74] in cellulose nanomaterials leading to surface reactivity and interactions with hydrates containing hydrogen in their structure, namely C–S–H and CH [75]. The important take away points are listed as follows:

1. Enhanced elastic modulus of the cement paste is achieved for both PCNF and LCNF additions at lower fines contents at 56 days i.e, 60% and 75% fine content range.

2. Lower production cost through lesser mechanical grinding makes these nanomaterials more sustainable in cement-based systems.

3.3.7.3 Effect of CNF on fracture energy of cement paste

The fracture energy was considered as a measure of crack initiation and growth of the crack through specimen. Figure 3.13 represents the relative fracture energy of the notched beam specimens with 0.05%, 0.1% concentrations of PCNF and LCNF with varied fine
Relative fracture energy for both PCNF and LCNF with 0.05% concentration at 28 days did not have any significant improvement. However at 56 days, PCNF with 95% fines showed 35% increase in the fracture energy compared with control batch. In contrast to 0.05% addition, 0.1% concentration of PCNF and LCNF at 28 days enhanced the fracture energy in a decreasing trend with increase in the fine content.
percentages compared to the control batch. At higher concentration additions of PCNF and LCNF 75% fines showed a very little improvement in fracture energy. This brittle failure can be attributed to the low crack bridging capacity of the nanofibrils, since the composite toughness is mainly governed by the fiber-matrix bonding. An excessively strong bonding between the fibrils and cement matrix leads to an embrittlement of the composite [76].

3.3.7.4 Effect of CNF of fracture toughness of cement paste

The fracture toughness of the cement paste beams with PCNF and LCNF can be explained through the critical effective crack length. The critical effective crack length is the initial crack length plus the fracture process zone, which can be related to the crack propagation. Since, critical effective crack length is a size dependent property, constant dimensions for beam specimens were maintained to avoid complexities. Figure 3.14 represents the critical effective crack length for cement paste notched beam specimens with 0.05%, 0.1% PCNF and LCNF addition. For the cement pastes containing CNFs, the crack bridging property of the nanofibrils were not significant or relatively low crack bridging was appeared. This can be correlated at 28 day values of effective crack length for both PCNF and LCNF. With the increase in age up to 56 days, at lower concentrations of PCNF showed improved crack bridging property. Overall improvement in the effective crack length was achieved only at 0.05% addition concentration of PCNF at 56 days. LCNF showed little to no effect in terms of increasing the effective crack length for both curing ages.

3.3.7.5 Scanning electron microscope images

Figure 3.15 shows the scanning electron microscope micrographs of PCNF and LCNF containing cement pastes with 75% fine content addition. SEM micrographs for PCNF modified cement pastes are shown in figure 3.15 (a) and (b), in which the failure of crack bridging property of cellulose nanofibrils was observed. Since due to the high fiber-matrix interaction between the nanofibrils and cement matrix during the crack propagation
Figure 3.14. Critical effective crack length measurements for PCNF and LCNF rupture of the fibrils can be seen. This failure of the crack bridging can lead to the lower toughness for PCNF modified cement matrix. Similar mechanism was observed in terms of LCNF containing cement pastes as well, shown in the figure 3.15 (c) and (d). In the figure 3.15 (c) failure of the lignin cellulose nanofibrils can be observed.
This study provided a comprehensive investigation on the effects of pure CNF and Lignin CNF on the workability, hydration, hydrated phase formation, compressive strength and fracture parameters of cement paste samples. Followings are the concluding remarks from this study:

1. Workability of LCNF containing cement pastes showed maximum improvement at 60% and 75% fine content percentages for 0.05% and 0.1% additions. At 0.05% and 0.1% addition the improvement was about 17%, 15% and 10%, 14% for 60%, 75% fines respectively when compared to control batch.
2. Cellulose nanomaterials especially LCNF reduced the ettringite formation in the cement paste samples when used at higher concentration (i.e., around 1.75%).

3. Addition of cellulose nanomaterials did not show any significant positive effect on the compressive strength of paste samples after 28 days of sealed curing. After 90 days of curing, maximum improvement in compressive strength for PCNF containing cement pastes was achieved at 75% fines by about 15% and 8% for 0.05% and 0.1% PCNF additions respectively. Compressive strength of cement pastes with LCNF showed maximum improvement at 75% fines by about 11% and 16% for 0.05% and 0.1% LCNF additions respectively.

4. At 56 days of sealed curing, the flexural strength of PCNF modified cement pastes at 0.05% addition with 95% fines showed 52% increase whereas, at 0.1% PCNF addition at 75% fines improvement was about 112% when compared to the control batch. Flexural strength for LCNF containing cement pastes at 56 days for 60% fines showed improvement by 106% and 96% for 0.05% and 0.1% LCNF additions respectively compared to the control batch.

5. Addition of 0.05% and 0.1% PCNF improved the elastic modulus of the cement pastes by 169% for 90% fines and by 97% for 60% fines at 56 day sealed curing when compared with control batch. At 56 days, elastic modulus for lignin containing cement pastes at 0.05% showed 140%, 114% and 147% increase for 60%, 75% and 80% fines. Increased LCNF concentration to 0.1% improved the elastic modulus of the cement pastes for 95% fines by 200% at 56 days of sealed curing when compared to the control batch.

Overall, two important conclusions can be drawn from this study,

- Addition of LCNF to cement paste enhanced the properties in terms of workability, compressive strength and fracture toughness, thus can be used instead of PCNF.
• The optimum fine content percentages that can be used for better performance in cement-based systems is around 60% to 75% fines for both PCNF and LCNF.
CHAPTER 4
LONG-TERM STABILITY OF CELLULOSE NANOMATERIALS IN HIGH ALKALINE CEMENT PASTE ENVIRONMENTS

4.1 Introduction

Usage of cellulose natural fibers as reinforcing agents in cement-based materials is limited by the relatively low resistance in alkaline environments. The nature of most hydraulic cements are alkaline. During cement production process, raw materials such as alkali metal compounds are converted by high clinkering temperatures into alkali oxides ($\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$) and sulphates, which are incorporated in the cement clinker. When cement reacts with water, these highly soluble alkalis are released into the mixing water, raising the pH significantly. As the cement hardens, the mixing water is used up and the alkalis are thus concentrated in the remaining free water, contained within the capillary porosity of the cement paste, known as pore solution (pH-13.8)\cite{78}. The concentration of alkalis in the liquid phase or pore solution of a hydrating cement paste varies continuously. According to Brouwers et al, the important parameters to determine the reactivity of cement additives was given by concentration of ions and related pH of the solution \cite{79}. In another study conducted by Diamond \cite{80} the effects of fly ashes on alkali content of pore solutions of cement-fly ash pastes were monitored, for which the pore solutions were expressed from plain Portland cement. The concentrations of potassium ($\text{K}^+$), sodium ($\text{Na}^+$), calcium ($\text{Ca}^{+2}$) and hydroxyl ions ($\text{OH}^-$) ions in the extracted solutions were determined by means of flame emission, atomic absorption spectroscopy, and acid titration as shown in figure 4.1.

Figure 4.1 shows that the concentration of $\text{K}^+$, $\text{Na}^+$ ions are approximately 0.4M, 0.2M respectively and the $\text{Ca}^{+2}$ ion has the lowest concentration of 0.004M. In addition, an increasing pH was found at early ages because of the increasing concentration of hydroxyl
ions. The latter mechanism occurs due to the need of achieving electro-chemical balance between cations and anions, and it is pushed by the concentration of alkali ions in pore solution reached after 4 days of hydration. The concentration of alkalis in pore solution becomes important because of the influence of alkali metal ions on reaction mechanism of cellulose due to presence of hydroxyl ions in the chemical structure of cellulose. Thus having such a harsh alkaline environment in cement matrix, cellulose might lose its strength when used as a reinforcement. The low durability caused by degradation of natural fiber in cement’s alkaline-mineral environment, which depletes the reinforcing effect of fiber, is often regarded as a challenge.
The work described here mainly focuses on the durability of pure cellulose nanofibrils (PCNF) and lignin containing nano fibrils (LCNF) films exposed to artificial pore solution of the 28 days hydrated cement matrix for various curing ages. Two different curing temperatures i.e, regular curing at 23°C and temperature curing at 70°C were adopted for 7, 28, 56 and 120 days. Degradation degree of cellulose nanofibrils (PCNF and LCNF) were determined by analyzing the crystallinity index using XRD, characterization of hydrogen bonding in cellulose using FTIR, alkaline ion diffusions in the artificial pore solution (APS) using ICP-OES, change in pH of the APS and surface morphology of the fibrils (SEM).

4.2 Materials and methods

In this study, two types of cellulose nanomaterials (pure cellulose nanofibrils and lignin containing cellulose nanofibrils) were used. The cellulose nanofibrils (PCNF) (3.0 wt% aqueous gel) and lignin containing cellulose nanofibrils (LCNF) (3.0 wt% aqueous gel) were obtained from The Process Development Center (PDC), University of Maine. The CNFs used in this study were produced applying mechanical forces, using double disk refiner system.

4.2.1 Sample preparation

Starting Materials: CNF/ water suspensions were obtained at 3.0% solids by weight. The solid contents of the suspensions were determined using a thermal analysis (TGA55 Thermogravimetric analyzer) before preparing the samples. The samples (CNF films in this study) were prepared for 95% fine content percentage for both PCNF and LCNF. The CNF films were soaked in the artificial pore solution (APS) of 28 days cement paste matrix for different curing ages ranging from 7, 28 56 and 120 days to study the long-term degradation mechanism. The water to solid ratio of 80 was adopted for both CNFs and two different curing conditions were adopted. For the regular curing condition, the temperature
was maintained at 23⁰C and for the temperature curing about 70⁰C was maintained. Degradation mechanisms of the PCNF and LCNF in artificial pore solution of the cement matrix were evaluated using X-Ray diffraction (XRD) for crystallinity of cellulose, Fourier Transform Infrared Spectroscopy (FTIR) for hydrogen bond analysis in cellulose, Inductively coupled plasma optical emission spectrometry (ICP-OES) for determining the various cation and anion concentrations in the pore solution and variation of pH in the solutions at different curing ages.

4.2.2 Experimental methods

4.2.2.1 Artificial pore solutions of the cement (APS)

Table 4.1 shows the chemical composition of artificial pore solution of the ordinary Portland cement at 28 days of hydration. The chemical composition of the APS was obtained from the work done by panchmatia et al[81]. APSs were produced in the laboratory by combining various chemicals containing the same species as those present in the pore solution extracted from the actual pastes. As per panchmatia et al, it was assumed that APSs used in the study adequately represented pore solutions of the plain cement paste matrices under investigation.

Table 4.1. Components used to prepare the artificial pore solution

<table>
<thead>
<tr>
<th>Salt</th>
<th>Weight (gm per 1L of water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)₂</td>
<td>0.0181</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.0553</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>4.3794</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.7777</td>
</tr>
<tr>
<td>KOH</td>
<td>36.1745</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.0864</td>
</tr>
</tbody>
</table>
4.2.2.2 pH of the artificial pore solutions

The pH of artificial pore solutions soaked with CNF (PCNF and LCNF) films were measured for 7, 28, 56 and 120 days for both curing conditions. The pH of APS were measured immediately after the removal of CNF films at corresponding curing ages.

4.2.2.3 Ion diffusions in cement pore solution

A Spectro model Genesis radial view ICP-OES instrument was used to measure the ion concentrations (millimolar/Litre or (mmol/l)) of the artificial pore solution after every curing age i.e 7, 28, 56 and 120 days. The concentrations of cations such as Ca$^{+2}$, Na$^{+}$, K$^{+}$, Al$^{+3}$ and for S$^{-}$ anion were measured, to study any chemical reactions between cellulose and APS.

4.2.2.4 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the CNF films were performed using the Nicolet iS 5 spectrometer with monolithic diamond crystal. The characterization of hydrogen bonds in cellulose was studied using FTIR spectroscopy. The CNF films are removed from APS and air dried such that no extra moisture is present on the films before testing. FTIR measurements were done for both regular and temperature curing conditions for 7, 28, 56 and 120 days.

4.2.2.5 X-Ray diffraction (XRD)

The X-Ray diffraction (XRD) analysis was carried out on the CNF films with an X-Ray diffractometer in $\theta$-2$\theta$ configuration using CuK$\alpha$ source at -45 kV and 40mA. The CNF films were scanned with a time step size of 0.3 in the angular range of 5-60°. The crystallinity index (C.I) using the peak height method[82] were calculated from the X-ray diffraction spectra.

The crystallinity index (C.I), which expresses the relative degree of crystallinity[83], was evaluated by using the following equation[84, 82]:

$$CI = \frac{I_{002} - I_{am}}{I_{002}}$$  (4.1)
Where $I_{002}$ is the maximum intensity of diffraction of the (002) lattice peak at $2\theta = 22.7^\circ$, which represents both crystalline and amorphous materials. And $I_{am}$ is the intensity of the diffraction contributing to the amorphous fraction, which is taken at a $2\theta$ angle between $18^\circ$ and $19^\circ$ where the intensity is minimum.

4.2.2.6 Scanning electron microscope imaging (SEM)

Surface morphology of cellulose nanofibril films (PCNF and LCNF) was achieved through AMRay 1820 scanning electron microscope (SEM) which has a resolution of 5 nm, a magnification range of 20-150,000X and an accelerating voltage range of 100V to 30kV.

4.2.3 Results and discussions
4.2.3.1 pH of artificial pore solution

The values of pH, calculated on a concentration basis from the measured hydroxide ion concentrations for both PCNF and LCNF containing APSs for regular and temperature
curing conditions were shown in figure 4.3. The artificial pore solution of cement initially (0 days) was observed to have a high pH value of 13.8. The pH of pore solutions was investigated to understand the alkaline hydrolysis of amorphous components of cellulose nanofibrils. The pH of APS containing PCNF and LCNF films 4.3(a) and (b) showed decrease in pH with the increase in age at 120 days for both regular and temperature curing. The reduction in pH (was around 0.3) at 120 days for APS with PCNF films was about 13.5 and 13.57 for regular and temperature curing respectively. Similarly, for LCNF containing APS the pH observed was about 13.46 and 13.44 for regular and temperature curing respectively. The hypothesis behind reduction in pH of APS can be explained through two different mechanisms. (i) Higher amount of hydroxyl groups in cellulose might react with alkali ions in APS by reducing the pH at later ages. (ii) According to Berglund et al [85] cellulose alkaline hydrolysis process involves breaking of polymeric cellulose chains into individual glucose monomeric units and eventual formation of isosaccharinic acids, which might be responsible for the reduction in alkalinity (pH-13.5) of the APS.

Figure 4.3. pH measurements for (a) PCNF and (b) LCNF with regular and temperature curing condition
4.2.3.2 Ion concentrations in pore solution with CNF

Figure 4.4. PCNF cured APS ion concentrations for (a) Ca$^{+2}$, (b) Al$^{+3}$, (c) S$^{-}$, (d) K$^{+}$ and (e) Na$^{+}$

The measured concentrations of the Ca$^{+2}$, Na$^{+}$, K$^{+}$, Al$^{+3}$ and S$^{-}$ ions in artificial pore solution of cement for PCNF and LCNF were showed in figures 4.4 and 4.5 respectively. For PCNF containing APSs, reduction in K$^{+}$, Na$^{+}$, Ca$^{+2}$, ion concentrations in (mmol/l) was about 7%, 10.4% and 0.75% respectively at 120 days of regular curing condition when compared to 0 day concentrations as observed in figures 4.4 (d), (e) and (a). The variation in ion concentrations can be related to the alkalinity of pore solution in Portland cement pastes which is mainly given by sodium and potassium hydroxide, where as the Ca$^{+2}$ ion concentration is very low (0.004M) according to Diamond[80]. As the concentration of Ca$^{+2}$ ions was very low compared to Na$^{+}$ and K$^{+}$ ions initially, the change in ion
Figure 4.5. LCNF cured APS ion concentrations for (a) Ca$^{2+}$, (b) Al$^{3+}$, (c) S$^{-}$, (d) K$^{+}$ and (e) Na$^{+}$

concentration of Ca$^{2+}$ ions at 120 days was comparatively very low. However, reduction in concentration of Ca$^{2+}$ ions can be related to the hypothesis of reduced ettringite formation in the hydrated cement systems containing CNF i.e., according to Goncalves et.al. CNF chemically traps the Ca$^{2+}$ ions through electrostatic links, and reduces the amount of Ca(OH)$_2$ in the pore solution [47]. A reduction of the available Ca(OH)$_2$ will lead to a drop in the formation of gypsum, and in the eventual production of ettringite (calcium aluminum sulfate)[47]. Little variation in the concentrations of Al$^{3+}$ ions was obtained even at 120 days of curing, but concentration of S$^{-}$ ions was reduced by 8% compared with 0 day concentration as shown in figure 4.4 (b) and (c).
The alkali ion concentrations of LCNF containing APSs showed similar decreasing trend with increase in the curing age (120 days) for K\(^+\), Na\(^+\) ions as shown in 4.5 (d), and (e). As observed from figure 4.5 (a) when compared with 7 day Ca\(^{+2}\) ion concentration, reduction was about 8% for LCNF containing APS, which can be related to the ettringite reduction in the LCNF containing cement pastes (refer figure 3.7 in chapter 3). The effect of temperature curing on the ion diffusion process showed a different pattern for both PCNF and LCNF compared to regular curing condition. According to Wang et.al. various different factors might influence degradation mechanism of cellulose [86], thus further research need to be performed to evaluate the exact mechanism for temperature curing conditions.

**4.2.3.3 FTIR analysis of CNF**

Cellulose, which used as a reinforcing material have extensive hydrogen bonding between cellulose chains. According to two phase model theory [87], two regions namely amorphous and crystalline regions exist in cellulose chain. The hydrogen bonds in cellulose mainly distribute in crystal and amorphous domains. According to Fan et.al. [87] cellulose has four polymorphic crystalline structures from cellulose I to cellulose IV 4.7 (a). The cellulose I (used in this study was PCNF) is considered to be highly amorphous, where as cellulose II is considered to be highly crystalline in nature which was obtained through the process of alkaline hydrolysis of cellulose I. The main hypothesis assumed for this study was due to presence of high alkaline conditions (pH of APS -13.83) the change in intensity peaks of intermolecular and intramolecular hydrogen bonds (O-H) of cellulose as shown in figure 4.7 (b) can result in the transformation of cellulose I to cellulose II polymorph (i.e, degradation of amorphous cellulose to crystalline cellulose)[88]. From the figure 4.7 (b) it is evident that, inter molecular OH-bond is formed between two different cellulose chains (amorphous phase) whereas intra OH-bonding is formed within the cellulose chain (crystalline phase).
Figure 4.6. FTIR measurements for PCNF (a) regular and (b) temperature curing

Figure 4.7. (a) Cellulose polymorphs and (b) inter and intra molecular hydrogen bonds in cellulose

Typical FTIR spectra for cellulose nanofibrils was shown in figure 4.6, in which amorphous region of cellulose occurs at a wavelength of 894 cm$^{-1}$, crystalline region of
Figure 4.8. FTIR measurements for PCNF (a) regular and (b) temperature curing cellulose forms at 1420 cm\(^{-1}\) and a broad range for hydrogen (O-H) bond (inter and intra molecular O-H bond) at wavenumbers ranging from 2994 to 3352 cm\(^{-1}\) was identified. The PCNF and LCNF films were used to measure the FTIR spectra for regular and temperature curing conditions for 7, 28, 56 and 120 days.

Figures 4.8 and 4.9 shows the FTIR spectra for PCNF and LCNF films for regular and temperature curing conditions. Curing ages ranging from 7, 28, 56 and 120 days was considered to understand FTIR spectra which was limited to the hydrogen bond (O-H) stretching i.e, from wavenumbers 2994 to 3352 cm\(^{-1}\). With the inclusion of alkaline solutions in the cellulose, formation of new inter- and intra molecular hydrogen bonds can be studied.
Figure 4.9. FTIR measurements for LCNF (a) regular and (b) temperature curing using the wavenumber shifts in the FTIR spectra. For both PCNF and LCNF films treated with APS, the hydrogen bond broadening was observed i.e, shift in the peak towards left was observed with increase in curing age upto 120 days for both regular and temperature curing conditions as shown in Figures 4.8 ((a) and (b)) and 4.9 ((a) and (b)). This can be related to the intensity ratio of O-H bonds at wavenumbers 3269cm$^{-1}$ and 3336cm$^{-1}$ which corresponds to inter- and intra molecular O-H bonds as shown in figure 4.10. For PCNF film with regular curing, the intensity ratios were increased from 0.961, 0.975, 0.977 and 0.989 for 7, 28, 56 and 120 days, similarly for LCNF increase in intensity ratios were 0.971, 0.979, 0.97 and 0.982 for 7, 28, 56 and 120 days respectively. These increase in intensity
ratios, can be related to change in the molecular structure of cellulose I (more crystalline), resulting in the process of degradation. Further studies can be performed to exactly monitor the wavenumber shifts of cellulose I to cellulose II.

### 4.2.3.4 X-Ray diffraction analysis

Kondo et al. describes a traditional two-phase cellulose model, in which cellulose chains contains crystalline (ordered) and amorphous (less ordered) regions [89]. A parameter termed the crystallinity index (CI) has been used to describe the relative amount of crystalline material in cellulose can be calculated using segal empiricial method [83] (refer section 4.2.2.5). Quantifying crystalline properties is considered to be a logical approach to investigate the effects of alkaline hydrolysis on cellulose nanomaterial properties. Figure 4.11 shows the typical XRD patterns for pure cellulose nanofibrils for varied curing ages with maximum age of 120 days. It can be seen that cellulose has a crystalline nature with an intensive peak at \( 2\theta \approx 22.5^\circ \) corresponding to (002) lattice plane and a broad peak (amorphous) between 13° and 18° corresponding to (1 10) and (110) lattice planes. The main hypothesis considered for evaluating the crystallinity index of cellulose was during the
Figure 4.11. Typical XRD pattern for cellulose at different regular curing ages

alkaline hydrolysis process the amorphous region of cellulose undergoes serious attack by forming more crystalline structure i.e., transformation of cellulose I (highly amorphous) to cellulose II (highly crystalline) polymorphs.

Figure 4.12 (a) and (b) shows the crystallinity index (C.I) for PCNF and LCNF films for different curing ages ranging from 0, 7, 28, 56 and 120 days. Two different curing methods were adopted i.e., regular (23°C) and temperature (70°C) conditions. It can be seen from the figure 4.12 that the crystallinity index for raw pure cellulose films was around 0.59 and it increases at different rates with the aging duration for PCNF. For PCNFs cured with artificial pore solution, the C.I for both curing conditions showed an increasing pattern with aging. The increase in C.I index for PCNF was about 46%, 56%, 66% and 86% for regular curing conditions at 7, 28, 56 and 120 days respectively when compared to C.I at 0 days. However for the temperature cured PCNF films, the magnitude of C.I index was low compared to regular curing as shown in figure 4.12 (a).
Figure 4.12. Crystalline index (C.I) values for (a) PCNF and (b) LCNF

Figure 4.12 (b) shows the C.I values for LCNFs with regular and temperature curing with increase in age. As it can be seen that, the initial C.I for raw lignin cellulose film was around 0.789 which is about 33% higher than PCNF. The magnitude of increase for LCNF cured at 23°C was about 14%, 12%, 22% and 26% for 7, 28, 56 and 120 days respectively when compared to 0 days C.I value, almost similar increased C.I values was achieved for temperature cured LCNF films( 4.12 (b)). This means that, the amorphous region of cellulose encountered serious attack in presence of artificial pore solution.

4.2.3.5 Surface morphology of PCNF and LCNF films

Figure 4.13 (a) and (b) shows the surface morphology of PCNF and LCNF films at 28 days of the artificial pore solution temperature curing. As it can be observed that, various hydration products were deposited on the surface of cellulose nanofibrils. These hydrated products are chemically bonded with cellulose, through which presence of chemical interactions between the cellulose fibrils and the ions in APS can be justified.
4.3 Conclusions

In this study a comprehensive investigation of degradation mechanisms of pure cellulose nanofibrils (PCNF) and lignin containing cellulose nanofibrils (LCNF) in a high alkaline artificial pore solution (APS) of 28 day cement paste matrix was achieved through XRD, FTIR, diffusivity of ions and variation of pH concentrations in APS. Concluding remarks of this study is as follows:

1. The alkalinity of original APS was reduced from 13.8 to 13.5 for PCNF and to 13.4 for LCNF at 120 days APS curing. The reduction in pH can be related to the decrease in Na\(^{+2}\) and K\(^{+}\) ion concentrations, since hydroxyl groups in cellulose might react with alkali ions by reducing the pH.

2. It is observed that, in the presence of APS both PCNF and LCNF showed decrease in the Ca\(^{+2}\) ion concentration by 0.75% and 8% at 120 days when compared to the 7 day Ca\(^{+2}\) ion concentrations respectively. This proves the hypothesis of CNF trapping Ca\(^{+2}\) ions and reducing the formation of ettringite in hydrated cement system (refer chapters 2 and 3 for ettringite reduction)
3. Crystallinity index for APS cured PCNF showed about 46%, 56%, 66% and 86% for regular (23°C) curing conditions at 7, 28, 56 and 120 days respectively. Similarly, C.I for regular cured LCNF was about 14%, 12%, 22% and 26% for 7, 28, 56 and 120 days respectively when compared to 0 days. Increased C.I of CNFs satisfies our hypothesis of alkaline degradation of cellulose.

4. Increase in intensity ratios of inter to intra molecular O-H bonds of cellulose at 120 days (23°C) is about 0.989 and 0.982 for PCNF and LCNF films respectively. Increase in intensity ratio proves the hypothesis this study i.e, transformation of amorphous phase in cellulose to crystalline phase through the process of alkaline degradation.
CHAPTER 5
CONCLUSIONS

Based on the experimental findings obtained from Silica-cellulose nanocomposite study and previously published articles [8, 20, 23, 77, 11, 10, 67], we have categorized the role of CNF in cement-based materials and the corresponding effects in the following section (Figure 5.1). It should be noted that these mechanisms/effects are not mutually exclusive and expected to be dependent on the pore solution chemistry of the cementitious matrix.

Figure 5.1. Effects of cellulose nanomaterials (PCNF, Si-CNF and LCNF) in cement-based materials
1. **Nucleation effect:** The surface area of CNF (with and without silica nanoparticles) provides additional nucleation sites for C-S-H. Such an effect is expected to accelerate the cement hydration at the early stage (within first 40 hours, as observed in 2.3.4, 3.3.4 chapters of this study). The acceleration of cement hydration due to the nucleation effect of CNF was observed in case of cement paste with 0.35 w/c ratio (Figures 2.4, 3.4). This nucleation effect of CNF was not prominent at high w/c ratio (0.45) (2.3.4) due to the CNF binding on cement particles as discussed below.

2. **CNF binding on cement particles:** Previous studies [90, 11, 67] have shown that the negatively charged hydroxyl (OH\(^{-}\)) and carboxyl (COOH\(^{-}\)) surface groups of cellulose can bind to calcium ions (Ca\(^{2+}\)). Because of this process, CNF fibers can be bound on cement particles and first hydrates constraining their growth [90, 67]. Such a process decreases the availability of nucleation sites for cement hydrates and thus, retards the cement hydration. Based on this study, such reduction in cement hydration was observed for cement paste with 0.45 cement hydration (chapter 2.3.4) and for cement paste with 0.35 cement hydration (chapter 3.3.4). At higher w/c ratio, there is higher probability of CNF binding on cement particles due to the low-concentration of alkali ions present in pore solution. This cement hydration reduction effect was not observable at 0.35 w/c ratio as in this case the concentration of alkali ions in pore solution is expected to be higher which help in balancing the surface change of CNF.

3. **Short-circuit diffusion (SCD) effect:** This effect was orginally proposed by Cao et al. [9]. Addition of CNF creates a channel between unreacted core of cement particle and pore solution through the C-S-H shell. Such an effect increases the degree of hydration due to the additon of cellulose nanomaterials. Sun et al.[12] also reported a similar mechanism to explain the enhanced cement hydration due to the addition of CNF. In this study, the benefit of such effect was observed for the total
heat of hydration after 80 hours of cement hydration (chapter 2.3.4). This effect was negligible after 28 days of curing in this study due to the lower CNF content used compared to those used by Cao et. al. [9].

4. **Water holding effect:** As reported by Kolour et al. [72], CNF fibrils can hold water and release it at the later age of cement paste creating an ‘internal curing’ effect. Because of this water holding capacity, the cement paste containing PCNF or Si-CNF showed enhanced compressive strength compared to the control batch at 0.35 w/c ratio. However, we also postulate that all of the water held in PCNF was not available for cement hydration within 28 days resulting in a lower degree of hydration at 0.35 w/c ratio. However, such water holding effect of CNF did not have any effects on cement paste at 0.45 w/c ratio as for these mixtures, there is already plenty of water to avoid self-desiccation and to achieve adequate hydration.

5. **Crack bridging effect:** Due to the high aspect ratio of CNF, it can bridge nano/microscale cracks. Such crack bridging effect had little effect on increased toughness of cement paste due to the addition of PCNF, Si-CNF or LCNF (Figure 2.11, 3.14). Coating the CNF with silica nanoparticles reduced the benefit of nanoreinforcement due to the disentanglement of the fibers.

6. **Alkaline degradation of cellulose:**

   - Cellulose is expected to degrade due to the high alkalinity of pore solution present in cement paste [91]. Such degradation can decrease in the compressive strength and reduced benefit of nanoreinforcement. Reduction in compressive strength due to the addition of CNF degradation was prominent only at high w/c ratio (0.45 2.3.4), due to the presence of higher amounts pore solution after 90 days of curing. This strength reduction after long-term curing (i.e., 90 days) was lower in case of Si-CNF batch indicating that silica coating was beneficial to minimize the alkaline degradation.
• Longterm stability of CNFs in artificial pore solution of cement paste showed that the degradation of amorphous phase in cellulose to crystalline phase, thus reducing the efficiency of nanofibrils as reinforcement material.

5.1 Future Recommendations

While this study provided a broader understanding on the role of cellulose nanomaterials in cementitious systems, there are a few issues which warrant further in-depth investigations. Specifically, we recommend the corresponding potential areas for future study:

1. Improving the durability performances of CNF containing cement-based systems.

2. Effect of lignin cellulose nanofibrils (LCNF) in cement pastes with varied w/c ratios.

3. To understand the effects of LCNF for internal curing and shrinkage behavior.


5. Nano-mechanical performance of the CNFs using nanoindentation techniques can be studied.
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cellulose nanocrystals (LCNC) and nanofibrils (LCNF) using an easily recyclable 


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