



## THE EFFECT OF SODIUM HYDROXIDE SURFACE TREATMENT ON THE TENSILE STRENGTH OF CELLULOSE NANOFIBRE

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### Abstract

The use of cellulose nanofibres in the reinforcement of polymers has applications in bio-based building materials. However, one problem observed when using cellulose nanofibres within composites is the difficulty of ensuring their adequate dispersion. The phenomenon of agglomeration is attributed to the high density of polarized hydroxyl groups at the surface of cellulose nanofibres. Initial observations of cellulose nanofibre agglomeration, in a cement matrix at volume fractions larger than 0.1%, are theorized to have contributed to the brittle failure mode of the casts. In order to expand the use of cellulose nanofibres in bio-based building materials, it is necessary to reduce their agglomeration and improve their dispersion within a polymer through surface modifications in effort to improve their reinforcing capability. As such, a mild alkali treatment with sodium hydroxide (NaOH), also known as mercerization, was chosen for use in this study due to its longstanding establishment as a common, low cost, and simple process. Alkali treatment was found to improve the values of tensile strength and modulus, compared to the untreated strips, by 20% and 24%, respectively. These results could be attributed to the rearrangement of fibrils along the direction of tensile deformation, as a result of the dissolution of lignin and hemicelluloses fractions. This paper reports the initial results of a larger, ongoing study into the feasibility of utilising cellulose nanofibres as reinforcements within cement composite building materials.

### Keywords:

Cellulose nanofibre; Tensile Strength; Mercerization

## 1 INTRODUCTION

The concept of using fibres as reinforcement in building materials is timeworn, such as with horsehair in mortar, or straw in mud and bricks. Since concrete displays relatively low tensile strength and ductility as a composite building material, research into steel and polymer fibres has shown how fibre reinforcement can be used to enhance ductility, tensile strength, toughness, fatigue strength, impact resistance and energy absorption [Banthia 1994] [Zhang 1998] [Balendran 2002] [Khaloo 2005]. However, with a pressing demand for building materials from renewable sources, the mechanical reinforcement of cement composites with vegetable fibres is of interest, also considering their availability at a relatively lower cost in comparison to synthetic fibres [Onuaguluchi 2014].

Nonetheless, load-induced failures in cement-based materials occur as a gradual multi-scale process in which cracks start at the nanoscale level, where traditional macro and micro-scale fibre reinforcements are not effective [Metaxa 2010a]. Thus, theory suggests that nanofibre reinforcement would delay the formation of nanocracks, necessitating higher loads to initiate cracking and, therefore, improve the tensile strength of cement composites, which recent research into carbon nanofibres has tested [Metaxa 2010b]. Yet, depending on the synthesis method, the production of carbon-based nanofibres has been shown to be highly energy intensive at the current moment [Khanna 2009] [Kim 2013], rousing a subsequent interest in cellulose nanofibres as an alternative reinforcement.

Indeed, the use of cellulose nanofibre reinforcement in polymer composites has resulted in substantial improvements to mechanical properties, as reported in

several recent papers [Wang 2007] [Seydibeyoglu 2008] [Xu 2013]. Wang and Sain reported that the tensile strength and the stiffness of a polyvinyl alcohol (PVA) composite reinforced with 5% soybean nanofibre increased by 58% and 170%, respectively, compared to pure PVA [Wang 2007]. Additionally, Seydibeyoglu and Oksman observed that the strength and the stiffness of polyurethane (PU) matrix reinforced with 16.5% by weight of wood cellulose nanofibrils increased by approximately 500% and 3000%, respectively, compared to pure PU [Seydibeyoglu 2008]. More recently, Xu et al showed that the flexural strength and the toughness of a polyethylene oxide (PEO) matrix reinforced with an additional 7% by weight of cellulose nanofibre improved by 92% and 732%, respectively [Xu 2013]. Thus, the use of nano-sized cellulose fibres in building materials, such as cement composites, has the potential to significantly enhance mechanical strength as a reinforcing agent with a very high specific surface area [Onuaguluchi 2014].

Currently, research into the application of cellulose nanofibres to cement composite building materials is novel. Preliminary research from this group has reported that optimum mechanical properties were observed in cement pastes reinforced with cellulose nanofibres at a fraction of 0.1%, which increased the flexural strength and the energy absorption by approximately 106% and 184%, respectively, compared to reference cement pastes [Onuaguluchi 2014]. However, at higher nanofibre concentrations a diminishing of mechanical properties was observed of the cement pastes, including a brittle failure mode, which were attributed to the difficulty of ensuring the adequate dispersion of cellulose nanofibres within the composite matrix [Onuaguluchi 2014].

This observed phenomenon of aggregation is alternatively called agglomeration or entanglement and is attributed to the high density of polarized hydroxyl groups at the surface of cellulose nanofibres that form additional weak hydrogen bonds between adjacent parts of the nanoparticles [Islam 2013]. However, the abundance of hydroxyl groups at the surface of cellulose nanofibres also makes it possible to attempt chemical modifications in order to introduce stable surface charges or tune surface energy characteristics, so as to obtain better dispersion and improve compatibility with nonpolar composite matrices [Islam 2013]. Yet, the main challenge with chemically modifying cellulose nanofibres is to ensure that the process only changes the surface structure of the nanofibres, while avoiding any polymorphic conversions that might deteriorate their reinforcing capability [Islam 2013].

As such, a mild alkali treatment with sodium hydroxide (NaOH), also known as mercerization, was chosen for use in this study due to its longstanding establishment as a common, low cost, and simple process developed in 1844 by John Mercer for use in many textile industries.

This paper reports the initial results of a larger, ongoing study into the feasibility of utilising cellulose nanofibres as reinforcements within cement composite building materials.

## 2 EXPERIMENTAL

### 2.1 Alkali Treatment

One sample batch of mechanical pulp, procured from Domtar Canada, was treated prior to mechanical defibrillation with a 4% solution of NaOH at 60°C for one hour. A second sample batch was left untreated as a control group. After the treatment, the pulp was then washed thoroughly with distilled water until all the sodium hydroxide was eliminated and the pulp was alkali free, as determined by checking the pH periodically using pH paper. The pulp was then stored at 4°C.

### 2.2 Mechanical Defibrillation

Nanocellulose fibre gel suspensions were prepared by mechanical defibrillation of both the control and alkali treated batches of mechanical pulp. To ensure complete defibrillation, the batches of mechanical pulp were fed through a super fine disc grinder for 10-17 numbers of times. Thereafter, distilled water was added to the ground pulp to form a viscose translucent nanofibre gel suspension.

### 2.3 Cellulose Nanofibre Film Production

A volume of 200mL of nanofibre gel suspension was vacuum-filtered, producing a thin 70 µm film, 9.5cm in diameter. Each nanofibre film was then separated by filter papers and pressed under 50 psi for 15 minutes until dry. The films were then cut into multiple dumbbell shaped strips with a die according to ASTM D 638 (type V). After cutting, the nanofibre strips were dried at 60°C for 24 hours, after which they were stored in a desiccator to preserve the strips from atmospheric moisture prior to mechanical testing.

### 2.4 Mechanical Testing

The tensile tests were performed with an Instron Model 3367 testing machine linked to a computer in tensile mode with a load cell of 1 kN in accordance with standard method ASTM D 638 [ASTM International 2010]. Tensile tests were performed at a crosshead speed of 2.5 mm/min. All the reported values are the average of at least 5 successful tests.

## 3 RESULTS AND DISCUSSION

Table 1 presents the mean value and standard deviation of tensile strength and Young's Modulus of the alkali treated and untreated cellulose nanofibre strips. The coefficient of variation (COV) for the control specimens was marginally lower than that of the alkali treated specimens for both tensile strength and Young's modulus, however all COVs were low, less than 5%. It can be noted that the alkali treated strips showed improved values of tensile strength and modulus at an increase of 20% and 24%, respectively, compared to the untreated strips.

Table 1: Tensile properties of cellulose nanofibre strips

Sample	Tensile Strength (MPa)	Young's Modulus (GPa)
Control	149.20 ± 4.15	8.94 ± 0.30
Alkali Treated	179.40 ± 7.20	11.09 ± 0.50

Figure 1 presents a traction test curve, which also illustrates the alkali treated cellulose nanofibre strips as having a mean maximum applied load higher than that of the untreated cellulose nanofibre strips.

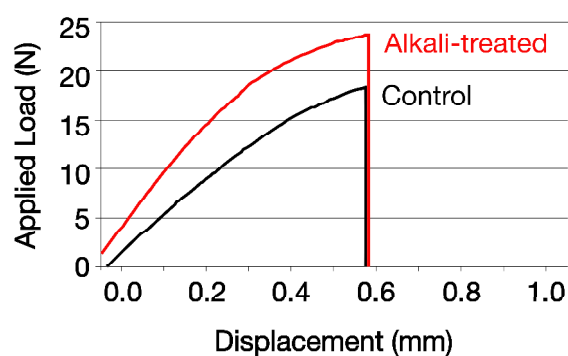


Figure 1: Measured traction test curve showing the applied load vs. displacement. The mean maximum applied load of the alkali-treated strips was 23.68 N compared to the mean maximum applied load of the control strips at 18.35 N. The mean maximum displacement for both sets of strips was 0,576 mm.

Since we cannot directly measure the tensile strength of individual nanofibres, we measured the tensile strength of nanofibre strips cut from films as a comparative approximation. Yet, it should be noted that single nanocellulose fibres, of which the films are comprised, would have a much higher strength than the films themselves, with cellulose nanocrystals estimated to have an elastic modulus of approximately 150 GPa and a tensile strength of nearly 10 GPa [Lu 2010]. Therefore, the improvements observed with the alkali treated strips were expected for a variety of reasons. During alkali treatment, it is likely that the NaOH reacted with hydroxyl groups on the surface of the cellulose nanofibres, disrupting their hydrogen bonds and increasing surface roughness [Sreekumar 2009]. With this breakdown in cellular structure, a certain amount of lignin and hemicellulose were probably removed from the cellulose nanofibres, causing them to split into smaller filaments; a phenomenon termed fibrillation [Sreekumar 2009]. As a consequence of the dissolution of these lignin and hemicellulose fractions, the intrafibrillar regions would have become less dense and rigid, allowing for the rearrangement of the fibrils along the direction of tensile deformation and strengthening their tensile characteristics [Gassan 1999] [Sreekumar 2009]. Furthermore, this fibrillation process would have increased the effective surface area available for contact with the matrix and possible modification through reaction sites [Cao 2006] [Gassan 1999].

Certainly, similar mercerization processes have also been reported to increase the crystallinity index of sisal fibres through the removal of lignin and hemicellulose fractions, leading to a better packing of cellulose chains [Sreekumar 2009]. Additionally, several authors have reported similar observations of fibrillation and a breakdown in cellular structure with sisal fibres [Vazquez 1999] [Cyra 2001], flax [Sharma 1995], jute [Ray 2001], and coir [Sreenivasan 1996].

Furthermore, several authors have reported on the successful enhancement of mechanical properties when incorporating alkali treated natural fibres in composite applications, due to better interfacial adhesion [Valadez-Gonzalez 1999] [Mwaikambo 2002] [Alvarez 2003] [Edeerozey 2007].

In future investigations, it would therefore be expected that the inclusion of alkali treated cellulose nanofibres would improve the mechanical performance of cement-

based composites, compared with those incorporating untreated fibres.

## 4 CONCLUSIONS

The chemical surface treatment of cellulose nanofibres with sodium hydroxide was investigated in this work. Alkali treatment was found to improve slightly the tensile properties of the treated nanofibre strips, which could be attributed to the rearrangement of fibrils along the direction of tensile deformation, as a result of the dissolution of lignin and hemicellulose fractions.

While the surface hydroxyl groups of cellulose nanofibres have allowed for the possibility of the chemical modifications in this study and future expansions of it, a deterioration of the reinforcing capabilities of these nanofibres is a concern of utilising these treatments, certainly at higher concentrations of chemicals. As such, alternative physical treatments using low temperature plasma or electrical corona discharge are of future interest to investigate as they may potentially modify the surface structures of cellulose nanofibres without altering their bulk morphology and reinforcing capabilities.

An immediate continuation of this study, however, is the investigation of the mechanical properties of cement composites upon incorporation of these alkali-treated cellulose nanofibres, in addition to a quantification of nanofibre dispersion within a cement paste model.

In addition to the aforementioned physical treatments, further studies on alternative chemical treatments and concentrations in relation to mechanical strength development, cement microstructure, and durability will be needed to encourage increased utilization of cellulose nanofibres in cement-based materials.

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