Effects of Cellulose Nanocrystals as Extender on Physical and Mechanical Properties of Wood Cement Composite Panels

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The effects of cellulose nanocrystal (CNC) particles were investigated relative to the physical, mechanical, and microstructural properties of wood cement composite panels. Wood and cement were mixed at three ratios of 1:3, 1:3.5, and 1:4. Calcium chloride was added at 3 and 5%. CNC was added to the mixture at five levels (0, 0.1, 0.2, 0.5, and 1%, based on dry weight of cement). The results showed that CNC content of 0.5% had the best impact on the properties. The overall trend showed that with the addition of CNC, tensile, flexural, and physical properties of the composites were considerably enhanced. Scanning electron microscopy demonstrated that the addition of CNC was associated with an improved integrity in the micro-structure of panels.

Keywords: Cellulose nanocrystal; Cellulose; Nanocomposite; Portland cement; Wood cement panels

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INTRODUCTION

Cement wood composites have been on the market for over a century (Papadopoulos 2006). Today, wood cement panels have found acceptance in a number of countries as a result of certain desirable characteristics. The development and use of wood-cement panels attest to their attraction as building materials. In addition to their resistance to fire, these materials have a special attraction for use in warm, humid climates (Jorge *et al.* 2004). The main problem faced during the production of wood-cement composites is the incompatibility between cement and wood. Some soluble chemicals of wood are found to hinder or stop the hydration of cement when they are attacked by the alkaline environment and diffuse into the cement paste, resulting in the lower mechanical strength of wood-cement composites compared with the neat cement (Zhengtian and Moslemi 1986). The coating of wood surface can isolate the wood from the cement paste and enhance the resistance to the alkali or water attack so improve the compatibility between wood and cement (Hou and Zhu 2010). The precise mechanism of inhibition effect of wood on ordinary Portland Cement (OPC) hydration is yet to be fully understood. Two possible mechanisms have been proposed. First is that the extractives composed of various organic compounds form complexes with the metal ions present in the cement solution. This decreases the concentration of Ca^{2+} ions in the cement and possibly disturbs the equilibrium of the solution, which delays the start of nucleation of $Ca(OH)_2$ and CSH gel (Miller and Moslemi 1991). Another suggested mechanism is that the organic compounds form a thin adsorption layer on the surface of cement grains and slow the hydration process (Gartner *et al*. 2002).

Due to the extremely small size of cellulose nanocrystals (CNCs), they adsorbed on the cement particles surface and transported water from the capillary pores to the unhydrated cement. The strength improvement reached a maximum value at a CNC concentration of 0.2% by volume (Cao *et al*. 2015). The dispersion of CNCs can potentially improve the mechanical properties by removing agglomerates, which act as defects or stress concentrators. This shows that the dispersion of CNCs plays a key role in improving the flexural strength of the cement paste, particularly at a high concentration of CNCs (Liu *et al*. 2019).

The dispersion of CNCs can potentially improve the mechanical properties by removing agglomerates. There have been two common methods to disperse the agglomerated nanoparticles. The first method is to use mechanical energy to separate the particles. The second method alter is to the surface energy of the particles by surfactants (Cao *et al.* 2016).

Development of novel bio-based nanocomposites is fundamental to reduce the dependence on fossil resources and provide a sustainable future. In light of this global problem, cellulose nanocrystals (CNCs) have attracted interest due to their remarkable mechanical properties (Benavides 2011; Taghiyari *et al.* 2020). Cellulose nanocrystals (CNCs) are crystalline nanoparticles made from cellulose, and they are highly relevant for the development of new bio-based materials with enhanced properties. They are a potential nanocomposite reinforcement agent given their relatively low density (1.6 g/mL), high strength (10 GPa), and high modulus (143 GPa) (Šturcova 2005). CNCs can also be processed into materials with unique optical properties that reflect a specific wavelength of light or are transparent (Shopsowitz *et al*. 2010). They are relevant for the preparation of biomedical devices, implants, and textiles given that they are biocompatible and nontoxic (Azizi Samir *et al*. 2005). CNCs have been successfully used in many applications such as additives (to adhesives, paper-based products, drilling fluids, and cement-based materials), food coatings, transparent-flexible electronics, catalysis support structures, and many biomedical applications (Zubik *et al*. 2017). Moreover, CNCs are extensively available all around the world and a potential byproduct of the future cellulosic biofuels industry (Fu *et al*. 2017).

Cellulose nanocrystals are renewable and low-cost nanomaterials with important optical and mechanical properties. They have been incorporated into renewable polymer matrices to create environmentally friendly nanocomposites with improved mechanical properties. Cellulose is the most abundant polymer of earth (Habibi *et al*. 2010). The first report of a nanocomposite material was done in 1989; researchers from Toyota prepared a polyamide reinforced with montmorillonite clay obtaining significant improvements in tensile strength, modulus, and heat resistance.

The reinforcement effect of nano size fillers is strongly related to their large surface area, which facilitates the stress transfer from the matrix to the filler. Moreover, nanoparticles induce crystallization of the matrix, improving its thermo mechanical properties (Capadona *et al*. 2007). Currently, there is increased interest in the preparation of nanocomposites from cellulose nanoparticles.

In this study, wood fiber-cement composites were reinforced with CNCs. The morphological, mechanical, and physical properties of wood fiber-cement composites with different compositions were studied.

EXPERIMENTAL

Materials

Type II cement Portland was purchased from Abyeil Company (Qazvin, Iran). *Populus alba* strands had an average size of 10 mm × 2 mm × 0.75 mm (length × width × thickness). The strands were air-dried to approximately 4% moisture content (MC). The cellulose nanocrystal suspension was supplied by Nano Novin polymer knowledge-based company (Sari, Iran). The CNCs were extracted from pure cellulose fibers of woods and agricultural residues. Firstly, the microcrystalline cellulose part was hydrolyzed with 64 wt% H_2SO_4, after which the solution was diluted with distilled water and the suspension was centrifuged. After repeating the dilution and centrifugation, the precipitates collected were further dialyzed with distilled water from a dialysis tube (Biosharp; molecular mass cutoff = 14400, USA) until its pH was 7.0. Subsequently, the CNC suspension was ultrasonically dispersed for 30 min. Therefore, the CNC material was a suspension at a concentration of 2 wt%. and calcium chloride purchased from Merck, powder type with a molecular mass of 147 and a purity of 99% (Hohenbrunn, Germany). Calcium chloride ($CaCl_2 \cdot 2(H_2O)$) was also used to accelerate the setting of cement. These materials delay the formation of an alkaline environment around lignocellulosic particles, which delays the conversion. The sugars are converted to saccharin acid, which causes the cement to become entangled (Wei *et al*. 2000).

Table 1. Composition of the Cellulose Nanocrystal

Name	Cellulose Nanocrystal Gel
Formula	$C_5H_{10}O_5$
Material State	Gel (2%)
Color	White
Production method	Chemical Synthesis
Diameter	Ave.20-30nm
Length	200-800nm
Purity	99%<

Table 2. Specifications of Cement

Material	Percentage
Lime (CaO)	60 to 67
Silica (SiO_2)	17 to 25
Aluminum oxide (Al_2O_3)	3 to 8
Iron oxide (Fe_2O_3)	0.5 to 6
Magnesium oxide (MgO)	0.1 to 4
Sulfate (SO_3)	1 to 3

Table 3. Chemical compounds of *Populus alba* strands

Material	Percentage
Lignin	23.11
Cellulose	51.72
Extractives	3.68
Ash	1.29
Hemicellulose	19.8

Sample Preparation and Mechanical Tests

Test specimens were prepared according to DIN EN 634-2 (2007), and their physical and mechanical properties including flexural strength and modulus of elasticity (EN 310 2006) using a universal testing machine (Model STT-5T Universal Tensile Tester, Tehran, Iran). The specimens were trimmed to the dimensions of 35 mm × 25 mm × 12 mm for the mechanical tests. Three samples were evaluated for each treatment. The load and deflection were continuously recorded, and the data were used to calculate flexural modulus of elasticity (MOE) and modulus of rupture (MOR). The samples for water absorption (EN 317 1993) were prepared with the dimensions of 50 mm × 50 mm. Studies on the morphology were carried out using a scanning electron microscope (SEM). Samples with dimensions of 10 mm × 10 mm was prepared for SEM imaging for each treatment.

In this study, there was no predetermined statistical population, and sampling was done randomly. The effect of various factors was studied as follows. The amount of nanocrystalline cellulose (five levels of 0, 0.1, 0.2, 0.5, and 1%), the amount of calcium chloride (two levels of 3 and 5%), and the ratio of wood to cement (three levels of 1 to 3, 1 to 3.5 and 1 to 4) were varied, and the physical and mechanical properties of the composites were examined. Therefore, there was a total of 30 treatments. Six replicates were produced for each treatment, for a grand total of 180 samples. The physical and Characterizations were analyzed in a completely randomized design with factorial test using SPSS software (version 23, IBM, Armonk, NY, USA), and Duncan's multiple range tests at 95% confidence level was used to compare the means. Excel software was used to draw charts. Contour and surface plots were designed in Minitab software, version 16.2.2 (Minitab Inc., Philadelphia, PA, USA).

After weighing all the compounding agents for each board, calcium chloride and nanocrystalline cellulose were first dissolved in water, and the resulting solution was sprayed on the fibers and stirred to ensure uniform moisture throughout the fibers. The cement was sifted onto the fibers and thoroughly mixed manually with the fibers. The following formula was used in this study to obtain the amount of water consumed in the manufacture of each board,

$$W\ (\%) = 50\ C + (0/30 - MC)*F \qquad (1)$$

where W is the amount of water consumed, C is the weight of cement, F is the fiber weight, and MC is the moisture content.

The mat was evenly distributed to provide a uniform density, and the resulting mix was evenly poured into a mold sized 40 × 40 ×15 cm. Then it was pressed in a laboratory press (160-Burkle LA type hydraulic press). The diameter of the piston in this press is 25 cm, its useful area is 50 × 50 cm. The upper plate of the press is fixed and the lower plate is movable. Cement wood cake was pressed for 5 minutes at a pressure of 43 kg / cm^2 and then pressed for 20 hours. They were air conditioned (temperature 23 ± 2 ° C and relative humidity 60 ± 2%). The density of the panels by measuring the weight and dimensions of the samples prepared by means of a digital scale with precision, respectively. 0.01 g and caliper were measured with 0.01 mm accuracy and calculated with the following formula: Density = M/V. In this equation, M and V are the dry weight of the sample and the volume of the dried sample in environmental conditions, respectively (after 28 days).

RESULTS AND DISCUSSION

Mechanical Properties

The addition of CNC was associated with improvement in MOR and MOE (Figs. 1 and 2). An increase in cement content resulted in an increase in MOR. The highest (1928/6 MPa) and lowest (901/07 MPa) MOR were observed in panels with 1:4 and 1:3 ratios, respectively. Cellulose nanocrystals (CNCs) have become a potential nanofiber material that can improve the properties of cement paste. Previous research has shown that the addition of CNCs can prevent microcracking and improve the mechanical properties of cement paste (Cao *et al.* 2016a).

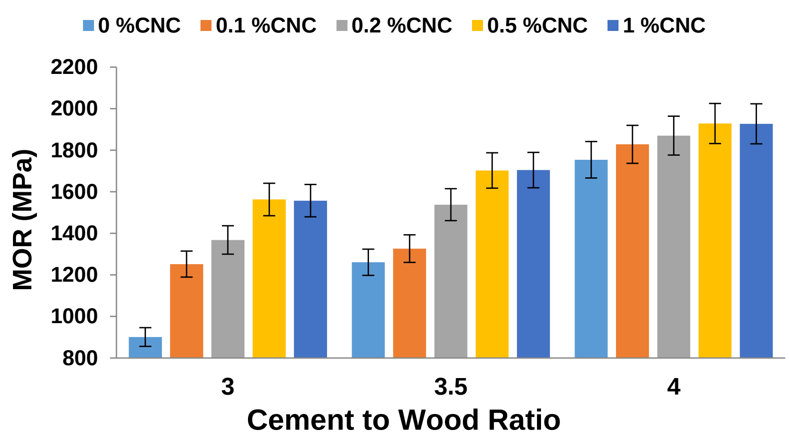


Fig. 1. Effect of varying levels of CNC and cement to wood ratio on MOR

The MOE increased as the cellulose CNC content increased from 0 to 1%. The highest bending strength (7.75 MPa) was in panels containing 1% CNC, and the lowest (5.74 MPa) was in panels with no CNC.

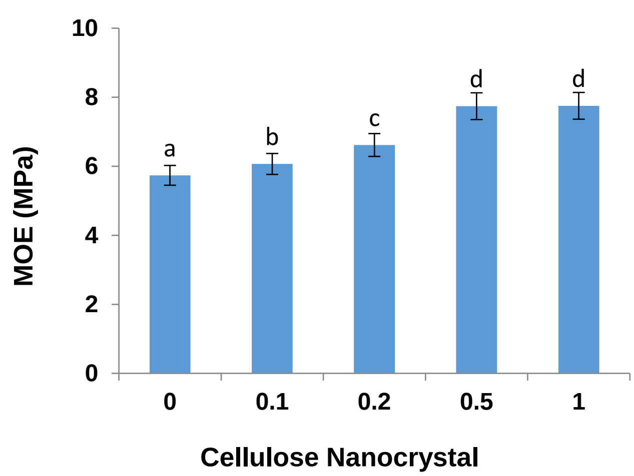


Fig. 2. Effect of CNC Independent impact on MOE (each column represents the mean value of the three wood contents in the present study)

In Fig. 2, the lowest flexural strength values were obtained using 0% nano-crystalline cellulose and 3% calcium chloride equal to 5.55 MPa, and the highest value when using 1% nano-crystalline cellulose and 5% calcium chloride equal to 7.9 MPa. As an additive to cementations materials, CNCs improve mechanical properties. Previous research showed that CNCs, even at low dosages (0.2% by volume of cement), significantly increased the flexural strength (approximately 20 to 30%) of cement pastes (Cao *et al*. 2016a). Due to the significantly smaller size of CNCs compared to conventional cellulose materials, the strength enhancing mechanism for CNC-cement composites is likely different from the fiber bridging mechanism (ACI 2009).

Figure 3 shows that the lowest composite flexural strength values for the use of 0% nano and wood to cement 1:3 ratio was 4.63 MPa and the highest value when using 0.5% nano and wood to cement 1:4 ratio was 8.98 MPa. As an additive to cement materials, CNCs improve flexural strength (Cao *et al*. 2015), increase the degree of hydration, and enhance the microstructure of cementations materials (Flores *et al*. 2017). It was observed that a small amount of hemicelluloses (0.1%) could decrease significantly the curing strength of cement and had great influence on hydration properties of cement paste (Govin *et al.* 2005). Therefore, as the amount of wood decreases compared to cement, one can see an increase in resistance.

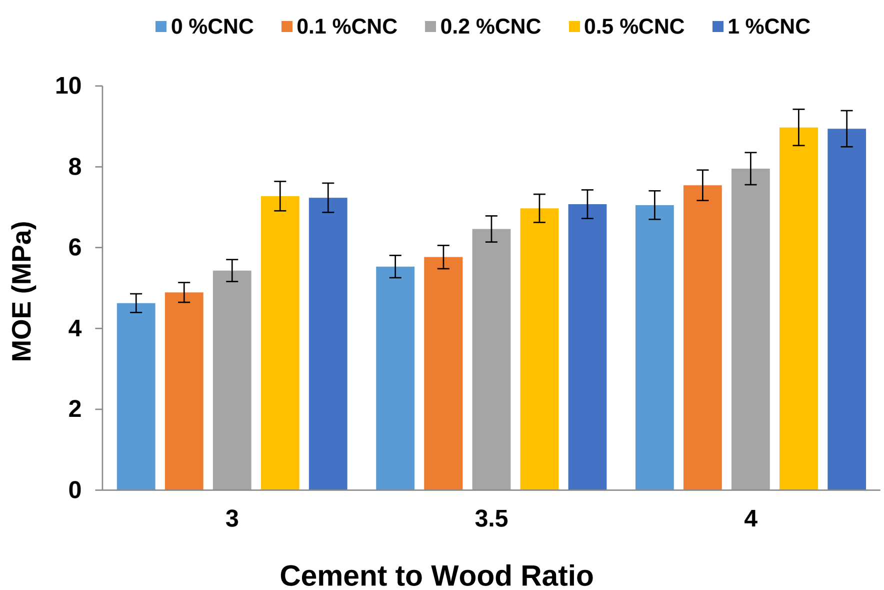


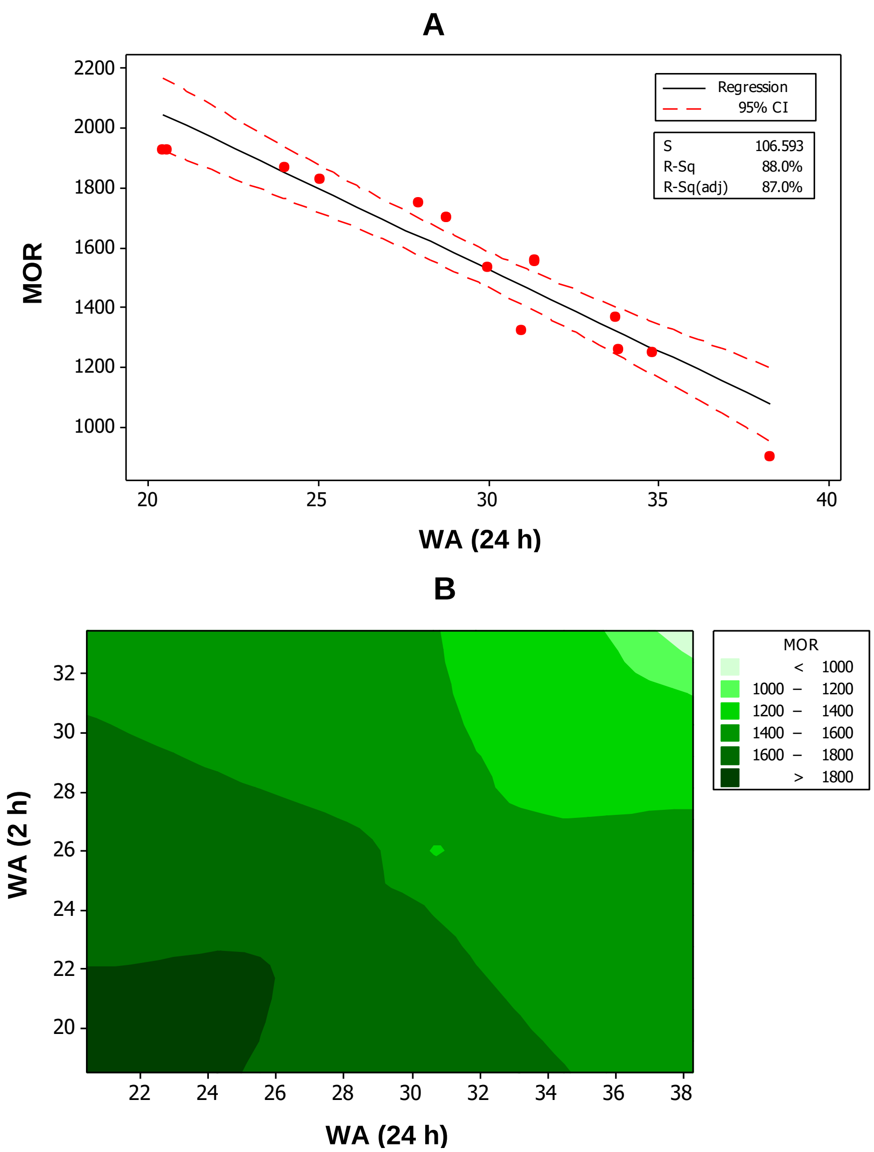
Fig. 3. Effect of varying level of CNC and cement to wood ratio on MOE

Physical Tests

Water absorption

As shown in Fig. 5, by increasing the amount of nano-crystalline cellulose from 0 to 0.5 wt%, water absorption decreased for 2 h initially and then increased with 1% nano-water uptake. The lowest amount of water uptake for 2 h was 0.5 wt% for nano-crystalline cellulose equal to 23.0% and the highest for 0 wt% for nano-crystalline cellulose equal to 29.0%. By increasing the amount of nanocrystalline cellulose from 0 to 1 wt%, water absorption decreased after 24 h. The lowest amount of water uptake for 24 h was related to the use of 1% by weight of nano-crystalline cellulose equal to 26.8%, and the highest amount was using 0% by weight of nano-crystalline cellulose equal to 33.4%.

The majority of CNC particles (>95%) are small enough that they are adsorbed on the surface of the cement particles providing: (1) a steric stabilization effect similar to polycarboxylate type water reducers and (2) the creation of paths for water molecules to more easily diffuse through the hydrated shell and reach the inner anhydrates core, also known as the short circuit diffusion (SCD) effect (Cao *et al*. 2016b).



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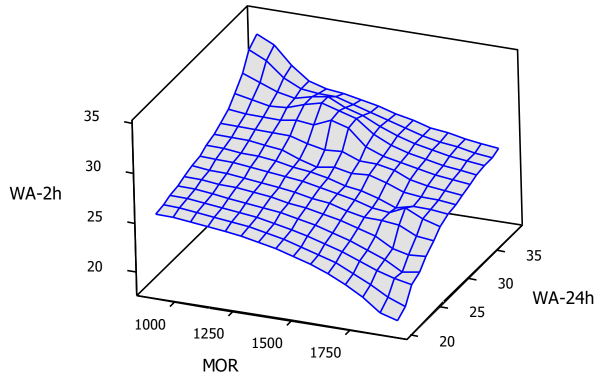

Fig. 4. Minitab graph (A) between MOR (modulus of rupture) and WA (water absorption after 24 hours immersion in water), and contour (B) and surface (C) plots

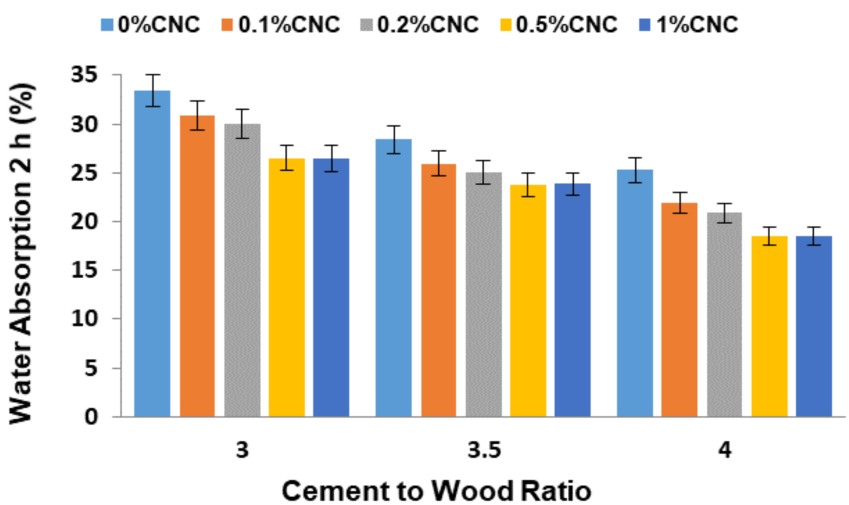

Fig. 5. Effect of varying level of CNC and cement to wood ratio on the water absorption (WA) after 2 h

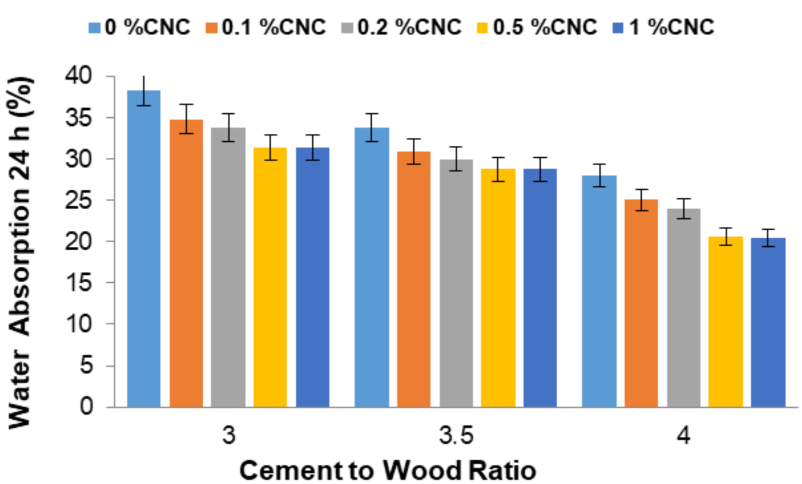

Fig. 6. Effect of varying level of CNC and cement to wood ratio on the water absorption (WA) after 24 h

According to Fig. 6, the water absorption of composites increased with an increase in soaking time. The increasing amount of CNC in composites decreased the water absorption percentage of the composites. This was in agreement in the increase in mechanical strength as CNC increased. Minitab plot showed high and significant R-squared value (88%) between MOR and water absorption (after 24 hours) (Fig. 4, A). Moreover, contour and surface plots demonstrated that MOR and water absorption were closely co-related to each other (Fig. 4,B,C).

As shown in Fig. 7, the density increased with increasing the amount of cellulose nanocrystals from 0 to 1% by weight. The lowest density was related to the use of 0% nanocrystal cellulose, and the density with 3% calcium chloride was equal to 1.08 g/cm^3. The highest value of density (1.24 g/cm^3) was related to the use of 1% nanocrystal cellulose and 5% calcium chloride. Among the chemical additives, chlorides such as $CaC1_2$ and $FeC1_3$ markedly accelerate the hydration process when they add to cement paste. Some studies reported that the additives such as chlorides could be used effectively as accelerators to restrain the inhibitory influence of wood species (Wei *et al*. 2000).

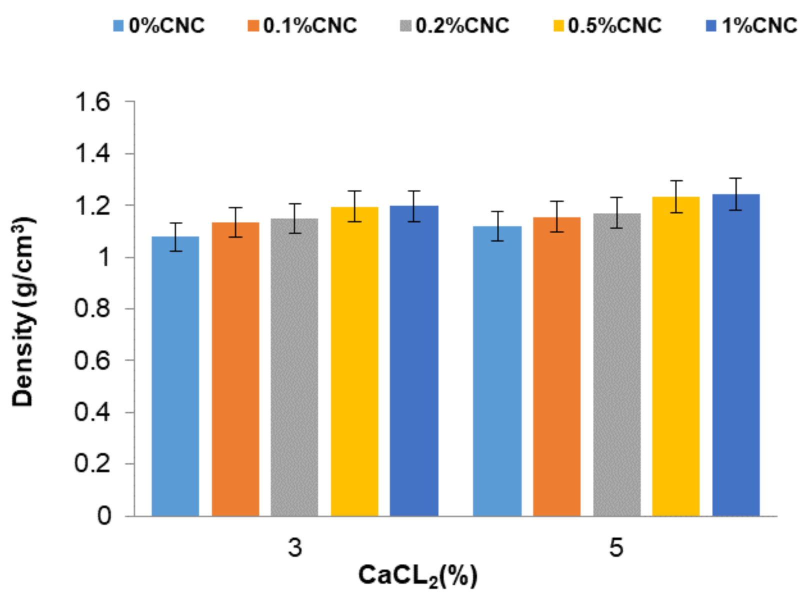

Fig. 7. Effect of Interaction of calcium chloride and CNC amount on density

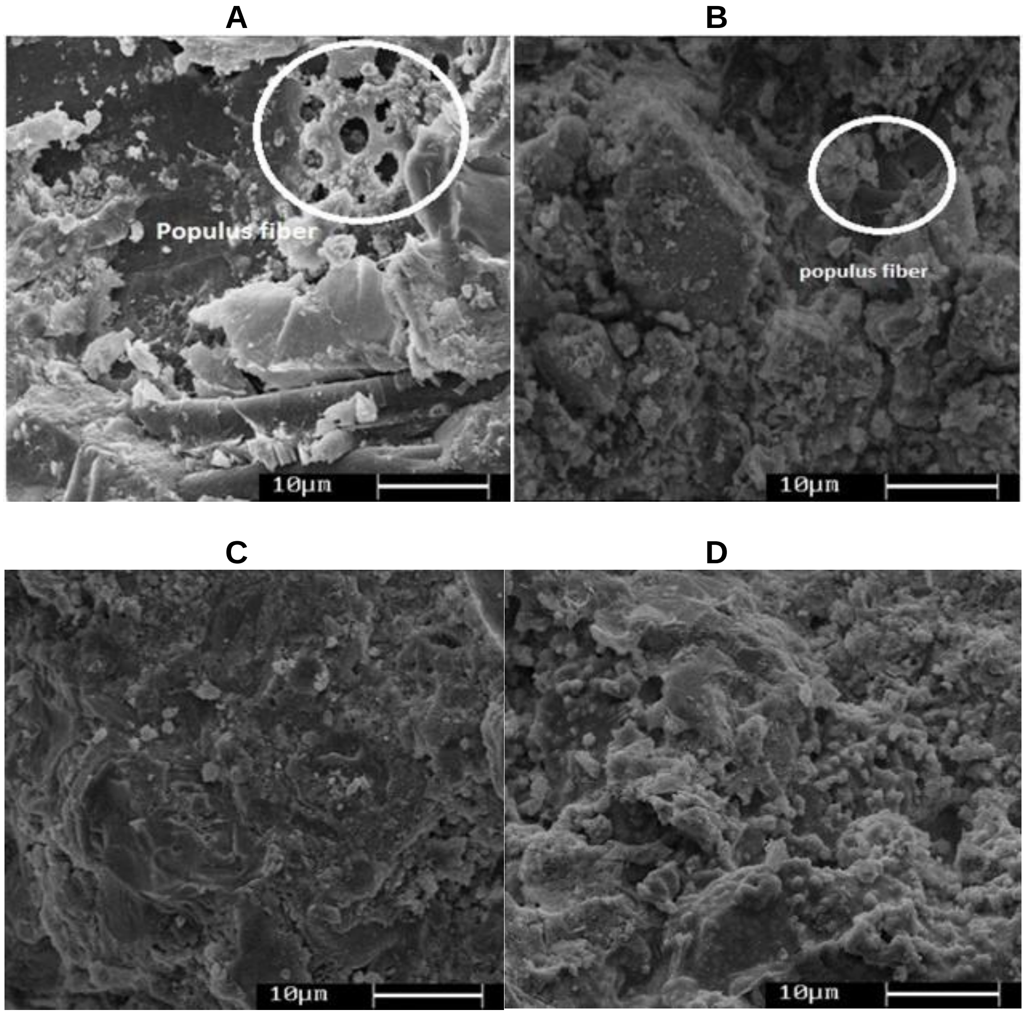

Fig. 8. SEM of (a) weak structure of composites without cellulose nanocrystals, (b) fiber-cement cellulose composites with 0.1% cellulose nanocrystals, (c) composites with 0.2% cellulose nanocrystals, and (d) composites with 1% cellulose nanocrystals,(the circle represents *Populus* fibers)

Morphology of Composite

The morphology of the wood fiber-cement composite was examined using SEM electron microscopy. In Figs. 8a, 8b, 8c, and 8d, one can see different amounts of cellulose nanocrystals percentages in the panels. Also, by increasing the percentage of CNC from zero to 1 percent, the formation of the C-S-H gel increased and in the opposite direction, the micro cavities decreased. There was a uniform distribution of fiber in cement matrix (Fig. 8c). CNCs from wood or plant materials typically have spindle-like particle morphology with a width of 20 to 30 nm and a length of 200 to 800 nm (Moon *et al*. 2011).

The microstructure of cement pastes was enhanced when CNCs were introduced into the samples. Refinement of the pore structure took place in the cement matrix. The high bonding quality between the CNC and cement matrix with all filler, created a good interfacial region. The addition of CNCs has an excellent effect in promoting the hydration of cement and preventing cement pastes from cracking under extreme conditions (Liu *et al*. 2019).

CONCLUSIONS

1. Addition of cellulose nanocrystals (CNC) to wood-cement panels was associated with improvement in all mechanical properties.
2. Dimensional stability was improved in CNC-treated panels.
3. Scanning electron microscopy (SEM) imaging showed better distribution of building materials in panels; eventually the performance of CNC-treated panels was improved.
4. CNC facilitated dispersion of cementations materials in water, subsequently the bonding between the building materials in the composite panels were enhanced, and eventually the properties were improved.

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