



*Research article*

## **Effect of nano silica addition on enhancing the performance of cement composites reinforced with nano cellulose fibers**

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**Abstract:** The utilization of cellulose nano fibers (NCell) as reinforcement to cement composites may account for enhancing particle packing and decreasing the crack growth at the nano level. Besides that, their high specific surface area can improve the bond between the cement hydration products. nano silica particles can also influence the performance of fiber reinforced cement composites through increasing the calcium-silicate-hydrate gel content, as well as enhancing the fiber to matrix interface cohesion. The aim of this investigation is to evaluate the effects of different contents of nano silica particles (0, 1, 1.5, and 2% by weight of cement) on the mechanical properties, and microstructure of cement composites reinforced with various contents of nano cellulose fibers (0, 0.35, 0.55, and 0.75% by weight of cement). The results out of studying such nano systems revealed that the addition of the NCell particles separately, helped in improving the tensile strength by about twice the value of the control mix when appropriate content of NCell was incorporated (0.35%). Moreover, the microstructural analyses demonstrated the effectiveness of nano silica particles to modify the transition zone between the nano cellulose fiber and the cementitious matrix and subsequently allowing greater reinforcement efficiency especially when external compression or tensile forces were transferred to the composite.

**Keywords:** nano silica; nano cellulose fibers; EDAX; SEM; XRD; mechanical properties

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## 1. Introduction

Ordinary Portland cement based composites generally show brittle behavior under subsection to tensile, and flexural loadings. This brittle fracture firstly occurs at the nano and micro levels. In fiber reinforced cement composites it is crucial to consider the mechanical behavior of the hydration products especially those at the nano scale like the calcium silicate hydrate (C-S-H), the binding phase in all the cementitious materials. The incorporation of nano fiber particles in the cement matrix proved to be a partial solution to the challenge of the cracking due to the mentioned brittleness of the cementitious materials, this is due to the action of the nano fibers in performing as stress transfer bridges in the nano level of cracking. Many investigational studies have been conducted about the utilization of the nano fiber particles and the carbon nanotubes [1–5], which act as bridges over the cracks creating nano reinforcement mechanisms and consequently arrest cracking in the nano level before being propagated. Thus, there are reported enhancements in flexural, tensile, and compressive strengths of these materials [6–12].

Recently, cellulose nano crystals (NCell) are receiving increasing attention as nano fiber reinforcements in different types of composites, and a wide range of applications [13–20]. This is because of its tremendous physical properties (including high aspect ratio and low density), chemical characteristics (such as its possible functionalizable surface), and high axial elastic modulus [21,22]. NCell is prepared through the chemical treatment of cellulose fibers, which generally comprise the structure of trees and plants [21,22]. Thus, the superior sustainable nature and the nano size characteristics of NCell have the potential to beneficially affect cement based materials by improving their strength and durability which consequently increase the lifetime of the structures and reduce the need for repair works and structures replacements, the condition that will lead to significant reduction of the carbon footprint of these building and construction materials. Previous studies explored the effect of nano materials such as nano silica [23–38], carbon nanotubes [4,39–41] and nano clay particles [42–46] on the behavior of cement-based materials. Regardless of the increasing research about the utilization of NCell in the assembly of nano composites in other disciplines [13–18], and despite possible benefits resulting from the use of NCell in cement based materials, related work on this topic seems to be very scarce and limited. The use of NCell in cement based composites has not been examined until the very recent publications by Cao et al. [47–49]. In their work, the authors reported enhancements in the hydration, flexural strength, and microstructure of cement mixtures [48,49].

Natural fibers have been already considered as potential alternatives to synthetic fibers taken into account the advantages such as being renewable, sustainable, and readily available materials, in addition to their low density and being nonabrasive materials, plus the fact that they can be extracted at low energy consumption and low cost [50,51]. Cement based composites reinforced with natural fibers exhibit enhanced ductility, toughness, flexural capacity, and crack resistance compared with non-fiber-reinforced cementitious composites [52,53]. The major advantage of fiber reinforcement is the post-cracking performance, where the fibers bridge the cement matrix cracks and transfer the applied loads [54]. The interfacial interaction of the fibers with the matrix is often hampered by high dimensional instability of the cellulose fiber due to their hydrophilic character. The cellulose fibers absorb Ca- rich hydration products of the cement, leading the fibers to the so-called mineralization process and causing the fibers to become stiffer. Concerning inorganic matrixes of Portland cement, the use of nano materials based on cellulose fibers and silica could serve as an enhancer of different

properties of cement composites leading to massive practical advantages [55]. Buch et al. [55] investigated the influence of processed cellulose fibers on the compressive strength and dimensional stability properties of Portland cement composites. There was a 10% enhancement in mechanical properties and a 40% increase in impact strength and this enhancement was attributed to the crack arresting and stabilization characteristics of fibers. Pinto et al. [56] produced new nano based composites consisting of both nano-cellulose fibers and nano-silica particles. The nano silica film on the fibers reduced significantly the water uptake capacity of the fibers. Therefore, the incorporation of inorganic nano sized materials on the surface of cellulose fibers may result in a promising hybrid nano material leading to the formation of an innovational level of reinforcement that gathers the major characteristics of inorganic and organic materials. The deposition of nano silica particles on the surface of cellulose fibers will allow a homogeneous coating and result in a decrease of water absorption capacity of the fibers [56,57]. This hybrid will most probably promote an enhanced interface between the cement based matrix and the fiber and will act on accelerating the cement hydration, due to the reduction of competition by water, and consequently reduces the mineralization of the fibers in an alkaline medium.

This research plan aims to provide considerable advances in the understanding of cellulose fiber-nano silica hybrid cement, through investigating their effect on the hydration of the cement which is rarely realized and has not been sufficiently explored yet. Effective interaction between matrix and fiber can be considered primordial because it may assist in increasing the productivity and performance of cement composites. This will be addressed via testing the mechanical properties (compressive strength, and tensile strength), as well as the microstructural analysis via; scanning electron microscopy, X-ray diffraction, thermo-gravimetric analysis (TGA), energy dispersive X-ray analysis (EDAX).

## 2. Experimental plan

### 2.1. Materials

Ordinary Portland cement complying with the requirements of ASTM C150 [58] standard was used with grade 42.5 N, cement properties could be found in Table 1. Natural Siliceous sand free of alkali-reactive materials from Suez quarries, in Egypt was used complying with ASTM C33 [59] standards. The properties of fine aggregate are listed in Table 2. Only potable water for mixing with the use of a sprinkling system for the dispersion of the nano materials. The SEM micrographs representing the utilized nano cellulose particles and the nano silica particles are shown in Figure 1. The nano cellulose used was locally synthesized from rice straw by the National Research Centre of Egypt, while the nano silica particles were commercially purchased from WINLAB-England. The average particle size of the nano silica was 30 nm size, while the nano cellulose average diameter was under 100 nm and the lengths were in the range of 200 to 500 nm.

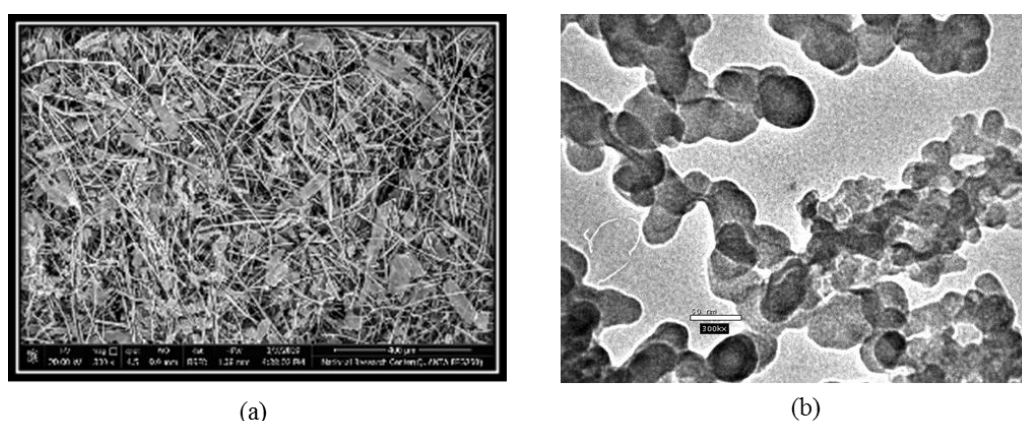
**Table 1.** Chemical composition of Portland cement.

| Element | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | MgO  | SO <sub>3</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | L.O.I |
|---------|------------------|--------------------------------|--------------------------------|-------|------|-----------------|-------------------|------------------|------------------|-------|
| Cement  | 20.13            | 5.32                           | 3.61                           | 61.63 | 2.39 | 2.87            | 0.37              | 0.13             | -                | 1.96  |

\*Note: L.O.I. = Loss of ignition

**Table 2.** Properties of sand.

| Property                       | Sand | Specification according to ASTM C33                           |
|--------------------------------|------|---|
| Specific Weight                | 2.89 | -   |
| Bulk Density                   | 1.67 | -   |
| Fineness Modulus               | 2.75 | 2.3:3.1   |
| Water absorption (%)           | -    | -   |
| Crushing Value (%)             | -    | not more than 45%   |
| Clay and Fine Dust Content (%) | 1.95 | not more than 3% for fine aggregate & 1% for coarse aggregate |

**Figure 1.** SEM micrographs showing the particles of the nano cellulose (a) and the nano silica (b).

## 2.2. Mixtures

A total of sixteen cement mortar mixtures were prepared for the required investigation, as it can be seen in Table 3. The dry mixing was made first for about 3 min, and then the water including the nano particles; powder added as received to the mixing water in a closed chamber and then stirred by a stirrer (of speed 120 rpm) for 2 min, and then sprinkled via mechanical sprinkler with micro nozzles directly after being stirred over the dry components during the rotation of the mixer blades until reaching homogenous composite, the mentioned method was based on a previous techniques that have been utilized by the authors [60]. None of the super-plasticizers types were used in the investigation. The composite was then cast in the moulds and after 24 h the mixes were de-moulded and cured by water submersion until the testing dates (after 7 and 28 d).

**Table 3.** Mixtures constituents.

| Mix | Ratios |      |       | Percentages      |        |
|-----|--------|------|-------|------------------|--------|
|     | Cement | Sand | Water | NS(nano silica)% | NCell% |
| 1   | 1      | 2.5  | 0.45  | 0                | 0      |
| 2   | 1      | 2.5  | 0.45  | 1                | 0      |
| 3   | 1      | 2.5  | 0.45  | 1.5              | 0      |

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| Mix | Ratios |      |       | Percentages      |        |
|-----|--------|------|-------|------------------|--------|
|     | Cement | Sand | Water | NS(nano silica)% | NCell% |
| 4   | 1      | 2.5  | 0.45  | 2                | 0      |
| 5   | 1      | 2.5  | 0.45  | 0                | 0.35   |
| 6   | 1      | 2.5  | 0.45  | 0                | 0.55   |
| 7   | 1      | 2.5  | 0.45  | 0                | 0.75   |
| 8   | 1      | 2.5  | 0.45  | 1                | 0.35   |
| 9   | 1      | 2.5  | 0.45  | 1                | 0.55   |
| 10  | 1      | 2.5  | 0.45  | 1                | 0.75   |
| 11  | 1      | 2.5  | 0.45  | 1.5              | 0.35   |
| 12  | 1      | 2.5  | 0.45  | 1.5              | 0.55   |
| 13  | 1      | 2.5  | 0.45  | 1.5              | 0.75   |
| 14  | 1      | 2.5  | 0.45  | 2                | 0.35   |
| 15  | 1      | 2.5  | 0.45  | 2                | 0.55   |
| 16  | 1      | 2.5  | 0.45  | 2                | 0.75   |

### 2.3. Testing

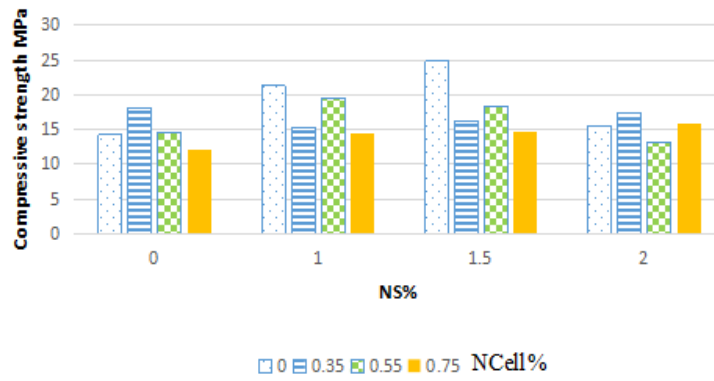
Compressive and tensile strengths were performed using universal testing machine 1000 KN at the rate of  $0.5 \text{ N/mm}^2 \cdot \text{s}$  for the compression test, and  $0.25 \text{ N/mm}^2 \cdot \text{s}$  for the tensile test, the compressive strength result of each mix was the average of three samples of the size  $50 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$  at each single testing date, while the tensile strength test met the recommendations of ASTM C496. The concept of this test is to apply a compressive force along the length of a cylindroid core of concrete with a rate that is within a specified extent until failure occurs. 3 specimens were cast for each mix for this test with dimensions (50 mm in diameter  $\times$  100 mm in height) and tested at 28 d of curing. The rate of loading is constantly and without impact with a fixed rate within the extent of 100 to 200 psi/min (0.7 to 1.4 Pa/min). Finally, recording the maximum indicated applied load by the testing machine at failure.

The total number of samples for the whole mechanical testing program was 144 samples. And the presented results were for the average of 3 samples per test.

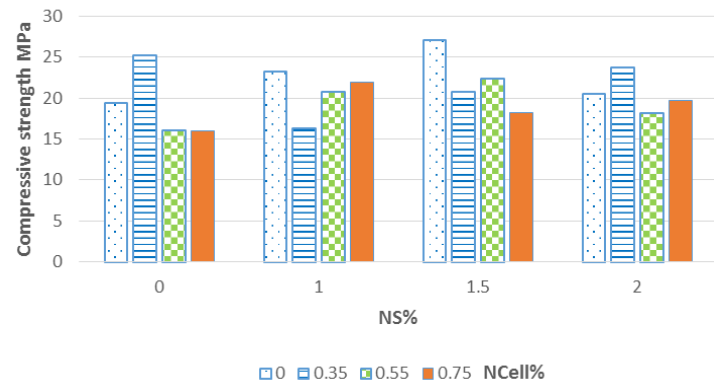
## 3. Results and discussion

### 3.1. Compressive strength

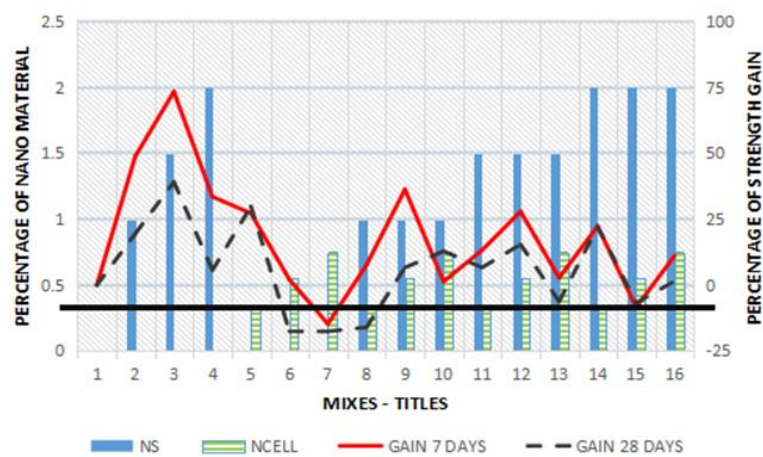
As it could be found from Figures 2–4, compressive strength at the early age (tested after 7 d of curing) of all mixes incorporating nano particles showed a significant increase as compared to the control mix (mix without nano particles) except for 2 mixes. The early strength gain ranged from 3% to 73% for the mix incorporated 1.5% nano silica, the average gain of all mixes was about 18%. The highest gain for a mix containing nano cellulose fibers was the one with 0.35% content, and the gain reached about 27% which is almost one third the gain of the nano silica (NS) highest value. The optimum mix incorporated both nano materials was the mix with 1% nano silica, and 0.55% nano cellulose fibers. The rest of the mixes with both materials showed average strength gain at the early age of about 11% only.



**Figure 2.** Compressive strength in MPa of 16 mixes at 7 d.



**Figure 3.** Compressive strength in MPa of 16 mixes at 28 d.



**Figure 4.** Compressive strength gain (percentages as compared to the control mix) pattern of 16 mixes.

While for the late age compressive strength (tested after 28 d of curing), the observations from the figures revealed that generally the same gain in strength was followed but with lower gain values. Mixes with the highest gain were; mix incorporating 1.5% nano silica, mix incorporating 0.5% nano cellulose fibers, and mix incorporated 2% nano silica with 0.35% nano cellulose with gains in strength of 39%, 30%, and 22% respectively as compared to the control mix.

The combination of nano silica (NS) and a low amount of nano cellulose fibers thought to be affecting the hydration reaction due to the existence of single dispersed nano cellulose fibers that work as extra nucleation spots for the hydrates and enhance the activity of the NS. The only reported effect for fiber shaped nano materials in enhancing the quality of the hydration products had been returned to the nucleation site effect as previously mentioned where the nano fibers act as nucleus to the hydration gel helping in enhancing the core of the finally produced C–S–H within the cement matrix. But for this effect to take place, these nano particles should be well dispersed and not in an agglomerated form [4].

While the combination of NS and a high amount of NCell thought to be of a negative effect on the hydration reaction because of the re-agglomeration process of the NCell, which hinders the activity of the NS and affects negatively the production of hydrates of the cement. The effect of the re-agglomeration process of the NCell dispersions on the activity of the NS and the hydration of the cement depends on the concentration of NCell and the hydration time. A higher amount of NCell will be more susceptible to re-agglomeration, and as hydration time progresses the amount of  $\text{Ca}(\text{OH})_2$  released in the matrix by the cement will be higher, and the re-agglomeration will be accelerated.

The reactivity of the nano silica particles with the residual calcium hydroxide from the cement hydration is accelerated, decelerated or completely inhibited based on the amounts of NCell and calcium hydroxide crystals present in the matrix. The re-agglomeration process of the NCell will decrease the surface area available for the particles to work as extra nucleation spots and consequently will hinder the reactivity of the NS and affect the hydration of cement. In addition, well-dispersed nano silica particles were observed to have filler effect and fill the voids between cement grains, resulting in better compaction of the cement mortar. The NS can also act as nucleating centers for the chemical generation of cement hydrates and thereby accelerated gain of strength could be achieved. The NS has the potential to favor the formation of both small-sized crystals of Calcium hydroxide and uniform gel clusters of C–S–H. Nano silica particles, very efficiently participate in the pozzolanic reactions, resulting in the consumption of calcium hydroxide crystals and the formation of additional C–S–H. The nano-size and superior pozzolanic activity of NS could improve, refine, and densify the interfacial transition zone (ITZ) between aggregates as it will be represented by the scanning electron microscope images.

The standard deviation for the samples tested in compression at the 28 d, were in the range of 1.2 to 1.8 MPa.

### 3.2. Tensile strength

In the present case, the effect of cellulose nano fibers appears obviously in the mortars with NCell only, in which the fibers efficiently bridge the gap between nano and micro cracks within the cement matrix and this increases the tensile strength of the cement composites significantly. For mixes with the addition of nano cellulose fibers only, the tensile strength of mortars was found to increase at all nano fiber contents. At 0.35%, the maximum tensile strength of 4.9 MPa was reached with almost twice the value for the control mortar (without any cellulose nano fibers). While by using higher content of cellulose nano fibers, the results showed that the mortar with 0.55%, NCell

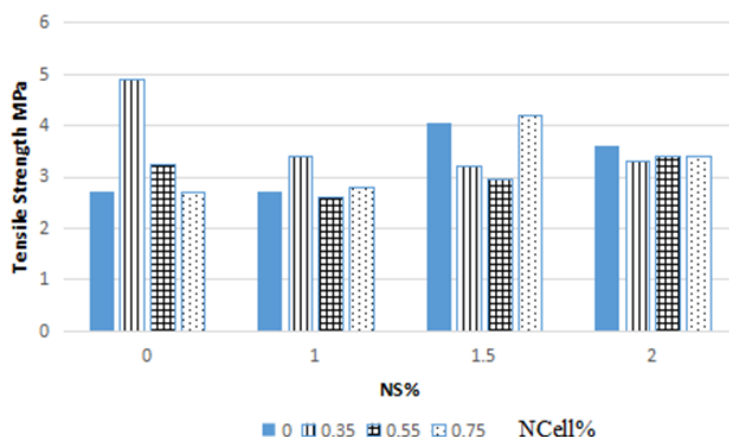
had tensile strengths lower than the one with 0.35% but still higher than the control mix by almost 20%, moreover, increasing the NCell content to 0.75% resulted in tensile strength equal to that of the control mortar. Thus, there is an optimum value range of fiber content where increased NCell enhances the tensile strength, and the crack bridging property of NCell can be fully utilized, the observed lowering in trend after the use of 0.35% NCell, could be attributed to the fact that nano materials got highly agglomerated when being used in relatively high contents due to the van der Waals forces which result in the fibers to get entangled and create weak void spots within the cement matrix, and consequently reducing the efficiency of the NCell's and reducing the strength in such case. Moreover, for mixes containing nano silica in combination with the cellulose nano fibers, it had been found that the nano silica enhanced only mixes with high nano cellulose fibers, and at high nano silica contents as well, this may be due to the collision of the nano silica spherical particles with the cellulose nano fibers resulting in reducing the entanglements and consequently enhancing the tensile strength. While at low dosages of nano silica, this collision did not take place and on contrary, the nano silica and the nano cellulose fibers gathered and bigger void spots were produced resulting in weak tensile strength values instead. It should be noted here that because of nano-dimensions of NCell, visual observation for identifying the presence and actual dispersion of the fibres in the matrix is difficult unlike in case of conventional fiber reinforced cement concrete matrix. Nano-silica (NS) The differences in the properties of hardened Portland cement matrix can be used to illustrate the effects of the nano-sized materials such as NS and NCell. However, nano materials have to be well dispersed throughout the volume of the matrix to maximize their contributions to improve the various engineering characteristics of the matrix.

Tensile strength of mortar at 28 d nano cellulose fibers content in cement matrix surface and the cement paste, resulting in an increased bond between cement matrix and fine aggregates. Crack arrest and interlocking effects between the slip planes provided by nano-particles would increase the toughness, tensile and flexural strength of Portland cement based composites such as mortar and concrete.

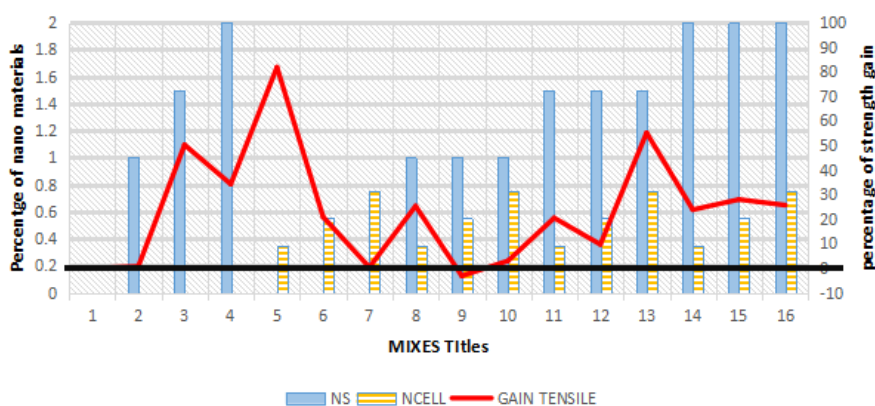
Use of nanoparticles normally accelerates the hydration process of cement because of their large surface area increasing nucleation sites for the hydration product [61,62]. This effect is effective if the nanoparticles are uniformly dispersed within the space between the cement particles in the mixture. However, it is seen from the results shown in Figures 5 and 6 that in some cases the increase in the nano cellulose fibers had an opposite effect. A possible explanation for such behavior could be related to the interaction between the cement particles and NCell. In case the interaction forces between the cement particles and NCell favor the adsorption of NCell onto cement particles, a delay in the hydration of cement particles is expected. This is because of the decrease in the available surface area of cement particles to participate in the hydration reaction. Due to the larger surface charge of NCell compared to cement particles, the likelihood of agglomeration of NCell particles is less than their adsorption onto cement particles. A similar mechanism was suggested by [48] regarding the effect of NCell on early age hydration of cement particles.

The standard deviation for the samples tested in tension at the 28 d, were in the range of 0.15 to 0.25 MPa.





**Figure 5.** Tensile strength in MPa presented in the vertical axis of 16 mixes at 28 d.



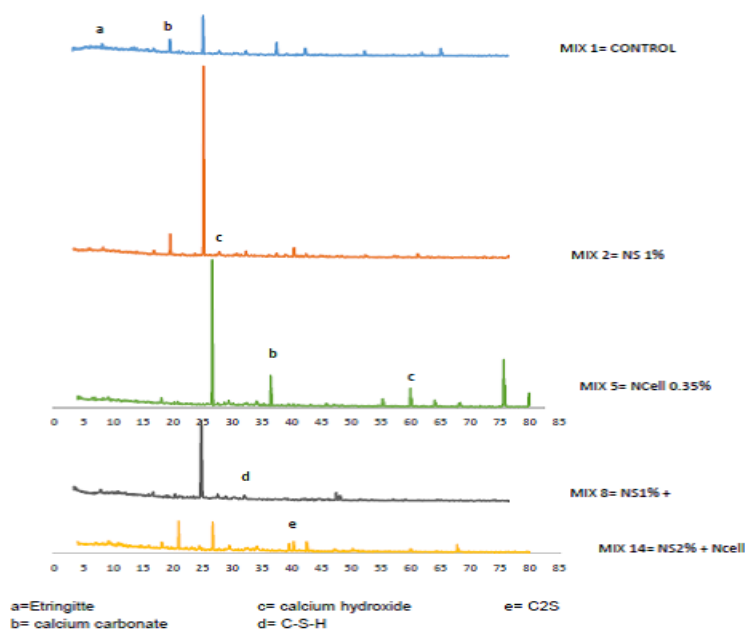
**Figure 6.** Tensile strength gain (percentages as compared with the control mix) pattern of 16 mixes.

### 3.3. Microstructural analysis

#### 3.3.1. XRD

The diffraction spectra corresponding to the control mixture and the mixtures with optimum content of nano silica particles, and optimum content of nano cellulose particles, as well as the mixes with the highest and lowest mechanical properties out of all hybrid mixes, will be presented in Figure 7. The peaks at  $2\theta$  of 18.00, 34.10, 47.12 and 50.81 are attributed to portlandite (P) [63]. The peaks in the  $2\theta$  range of 29–33 are attributed to tricalcium silicate ( $C_3S$ ) and dicalcium silicate ( $C_2S$ ) [63], which comprise the main constituents of the un-hydrated cement particle. The XRD results are useful in the qualitative investigation of the phase composition of cementitious materials. Statistically significant changes in the peak values of crystalline phases, such as  $Ca(OH)_2$  and  $CaCO_3$ , as well as the appearance of new peaks, are indicative of a change in the phase composition of existing phases or formation of new phases, respectively, in the microstructure. The comparison of the spectra of the cement mixtures does not show the presence of any new phases in the microstructure as a result of NCell addition within the

resolution of the measurement. The P peaks at 18.00, and 34.10 of the cement mixture with nano silica and NCell appear to be slightly smaller than those of the control mixture. However, it should be noted that XRD measurements are qualitative and any definitive conclusions should be made with caution. Thus, it can be concluded from the XRD spectra that no significant difference can be observed in the phase composition of the cement mixtures modified with NCell compared to the control mixture. The only exception is the peaks of the mix that contained nano silica particles, where the peaks of the calcium hydroxide, as well as the peaks of the un-hydrated cement, were lowered by the nano silica as compared to the control mix.

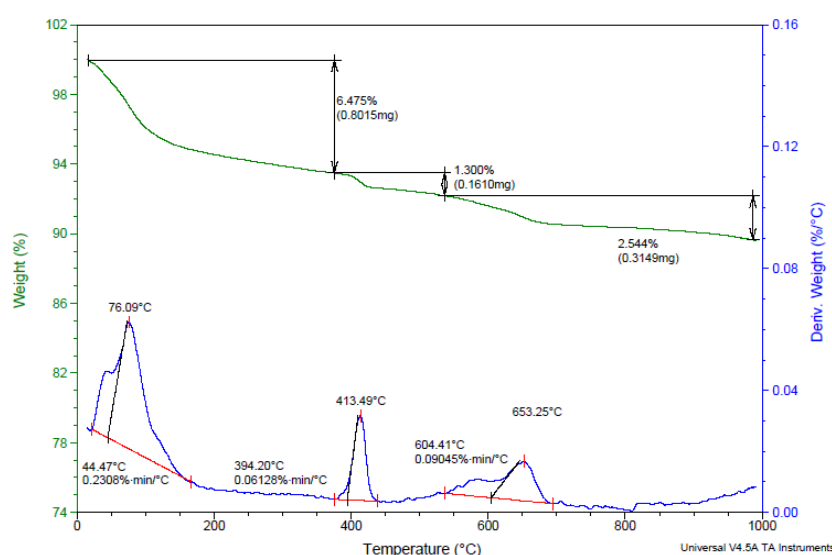


**Figure 7.** XRD of 5 mixes representing the control and highest and lowest strength values.

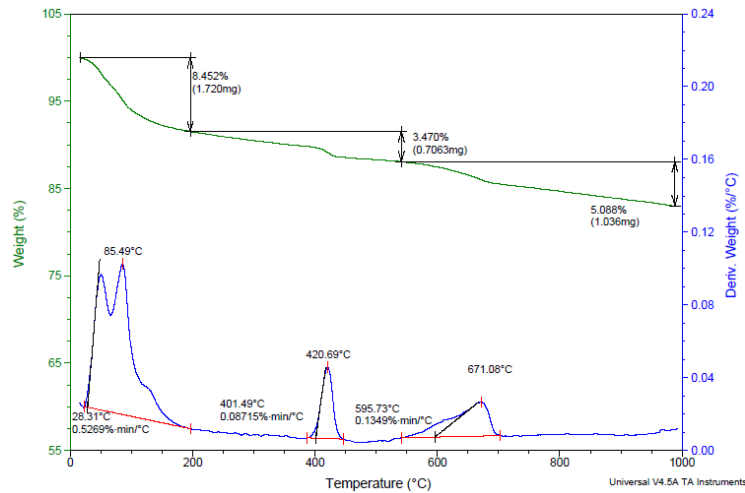
### 3.3.2. TGA

Influence of nano cellulose fibers and nano silica particles in combination on cement hydration were presented in Figures 8–10 which compares the control mix with mix 8 (the one with the lowest mechanical properties out of all hybrid mixes) and mix 14 (the one with the highest mechanical properties out of all hybrid mixes). The curves represented 3 major peaks, as indicated by first, second, and third. These peaks are due to evaporation of free water and water present on the C–S–H surface and layers as well as due to dehydration of ettringite and calcium aluminate hydrates (first peak), decomposition of calcium hydroxide crystals (second peak) and decomposition of calcium silicate hydrate (third peak), respectively. It can be observed in Figures 8 and 9 that the first peak was shifted to a higher temperature in case of nano cellulose-nano silica incorporated cement matrix of mix 8. This could be due to the formation of higher amount calcium hydroxide hydration products retaining more bound water in case of nano cellulose presence especially with low content of nano silica. Moreover, the second peak, as shown in Figures, became sharp and shifted to a higher temperature in the case of mix 8 mortar specimens. A similar change in the second peak was previously observed in cement mortar with the increase in hydration period [64]. At lower hydration period (i.e., 7 d) the second peak was broad and located at slightly lower temperature and as the

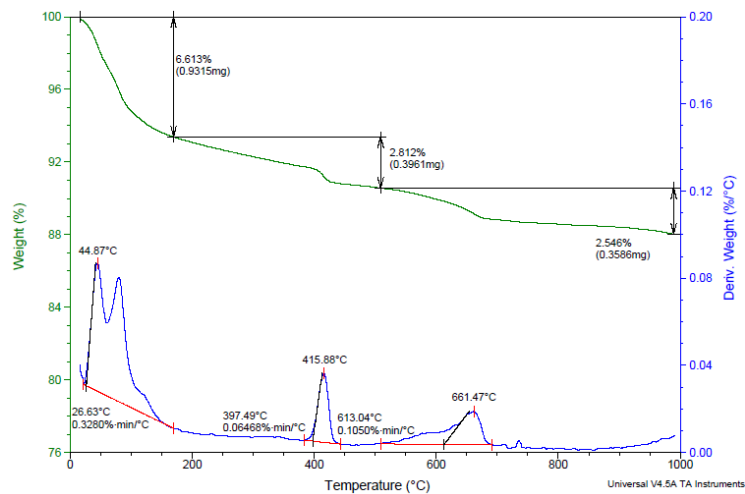
hydration period increased to 28 d, it became shaper and shifted to higher temperature [64]. In addition, this was attributed to the formation of more perfect and larger crystals of  $\text{Ca}(\text{OH})_2$  with the increasing hydration period. Besides, this also could confirm the previously mentioned explanation of the interaction between the cement particles and NCell. In case the interaction forces between the cement particles and NCell favor the adsorption of NCell onto cement particles, a delay in the hydration of cement particles occurs. Another interesting point to note here is the significantly lower height of the third peak. This indicates the lower amount of calcium silicate hydrate products in mix 8. While by seeing Figure 10 for mix 14 with higher content of nano silica and higher content of nano cellulose, peak one occurred at very low temperature than both mixes indicating the lower presence of unbounded water due to the high reactivity of nano silica particles resulting in increasing the calcium hydroxide consumption and increasing the calcium silicate hydrate content within the cement matrix. This analogy is confirmed by the value of weight loss equivalent to the second peak, the weight loss for mix 14 is significantly lower than mixes, 8 and 1 due to the lower content of calcium hydroxide to be de-hydroxylated at that temperature. Moreover, the presence of NCell particles when being well dispersed accounts for better hydration of the cement particles. In the current investigational study, the change in the second peak (shape and temperature) could be due to better hydration in the presence of NCell. As reported earlier, nano cellulose could improve the degree of hydration through: (1) better dispersion of cement particles owing to steric stabilization and (2) due to formation of a water diffusion path towards the core of hydrating particles by the surface nano cellulose layer (a mechanism which is called short circuit diffusion) [48]. Owing to similar chemical structure, nano cellulose particles used in the current research could facilitate these mechanisms also and consequently improving the formation of hydration products. Finally, for the third peak, the loss in weight determined for the control mix at the third peak was lower than the optimum mix 14 which confirms the presence of much more C-S-H within the sonicated matrix than the as-received cement matrix, the matter that is in good agreement with the compressive strength results as well.



**Figure 8.** TGA of the control mix.



**Figure 9.** TGA of mix 8 representing the lowest strength value.



**Figure 10.** TGA of mix 14 representing the highest strength value.

Since the TGA results were expressed as the mass remaining in the crucible with the increasing temperature. The concept suggested by Mounanga et al. [65] was used for this purpose. The water of crystallization of CH is released in the temperature range of 400–500 °C. The loss of water in this range of temperature can be directly used to estimate the mass of CH that was lost due to heating. The CH content in the hydrating cementitious paste is expressed as:

$$\text{MCH} = [(74.09/18.01)/(M400 - M500)/MC] \quad (1)$$

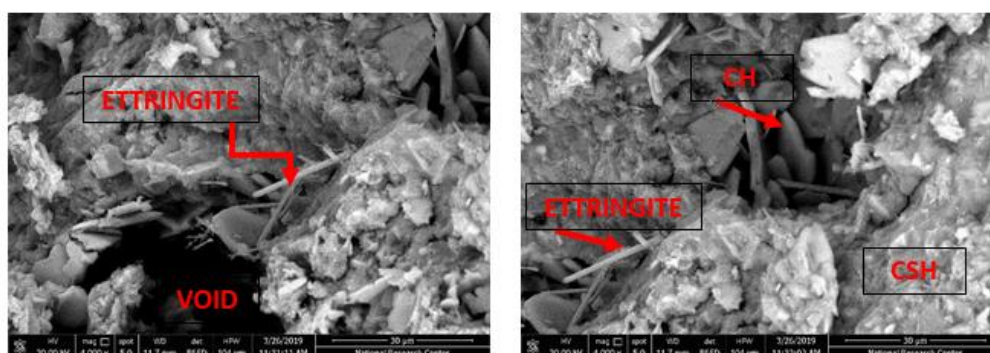
where MCH is the mass fraction of CH in the cementitious paste; M400 is the mass of the paste specimen at 400 °C; M500 is the mass of the paste specimen at 500 °C; MC is the initial mass of the specimen, and the values; 74.08, and 18.01 are the molecular weights in gm/mol of the CH, and water respectively. The calculated values for the CH content were 4.440, 2.938, and 2.059 for the control, lowest strength mix (mix 8), and the highest strength mix (mix 14) respectively. These values indicate the decrease in CH content with the nano silica-nano cellulose hybrid presence rather than the control mix.

### 3.3.3. SEM

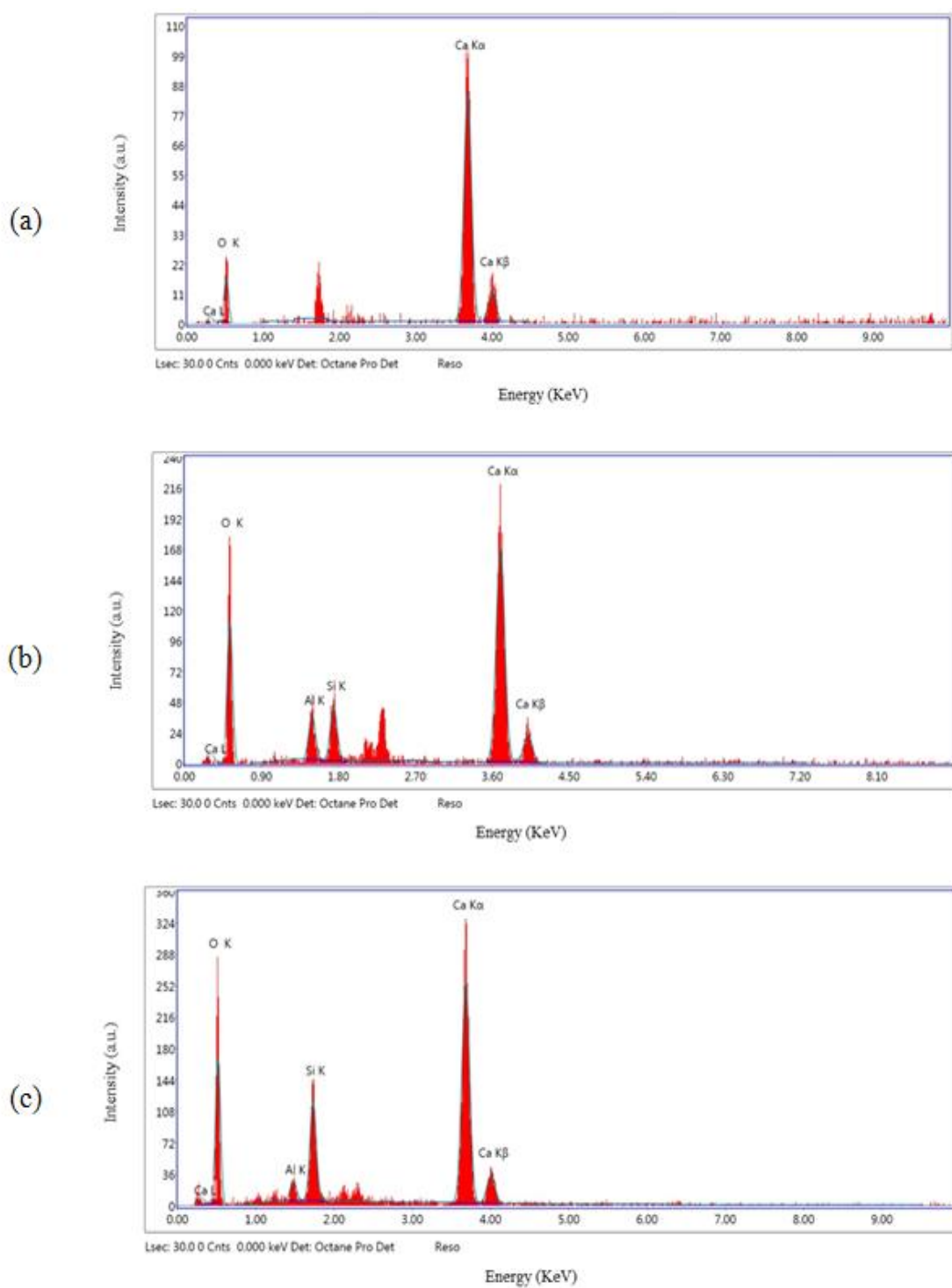
Fracture surface of plain mortar and mixes 8, and 14 with the lowest, and highest strengths out of the studied hybrid mixes respectively, the cement composite of the control mix represented with the SEM micrographs in Figure 11, and the EDAX peaks in Figure 12, showed the presence of the normal cement hydration products; the calcium hydroxide crystals, the ettringite needles, and finally the calcium silicate hydrate particles spreading and intersecting. The matrix could be easily described as weak, not highly compacted, and with relatively large void size, the condition that affected the mechanical properties of the composite. EDAX of CH, CSH, and Ettringite needles are represented in Figure 12 to ensure the spots represented by the arrows on the SEM micrographs. The presence of agglomerated nano silica and nano cellulose particles in the fracture surface of mix 8 (the mix with the lowest mechanical properties) can be identified and indicated by the arrows in Figure 13.

As a conclusion the nano particles when being well dispersed in the cementitious matrix directly allowed greater reinforcement efficiency and performance when external compression or tensile forces were transferred to the composite. The case is represented by mix 14, contrary to the case of mix 8.

The matrix of mix 8 is weak, with a large number of small voids, moreover, the CH crystals were also identifiable. The condition explains the reasons behind the weak mechanical performance of that mix cement composite. Finally, the micrographs of mix 14 (the mix with the highest hybrid mechanical performance) represented in Figure 14, showed that the cellulose structures were seen protruding from the fracture surface while still embedded within the cementitious matrix, where the CSH particles are spreading throughout the matrix indicating the ideal interaction of the nano silica particles in producing extra CSH resulting in highly compacted, dense matrix. Good interface between nano cellulose particles and cementitious matrix prevented complete pull-out of the NCell from the cement matrix. The images confirmed the ability of the nano cellulose fibers high surface area to form bonds and enhance the packing with the hydration particles in the matrix. The elemental analysis data, as obtained from EDAX analysis, of protruded end of the observed structures represented in Figure 15b confirmed that these structures were nano cellulose particles, while Figure 15a represented and confirmed the very small agglomerated nano silica particles as well. The weight% of C increased strongly in the case of nano cellulose particles due to the presence of pyranose ring in cellulose. However, a substantial amount of Ca and Si in the EDAX data of NCell were also noticed and these could be from the surrounding cement matrix since the electrons could also penetrate beyond the analyzed particles.

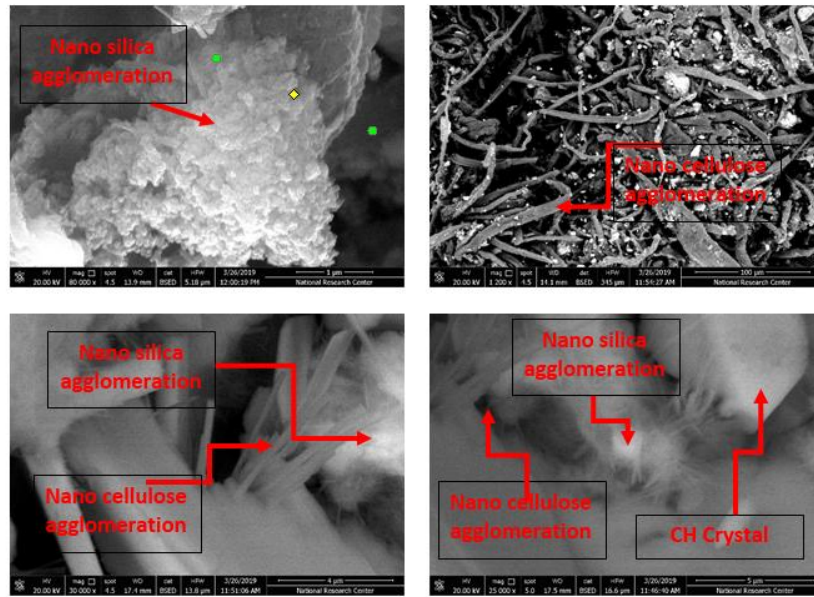


**Figure 11.** SEM of control mix.

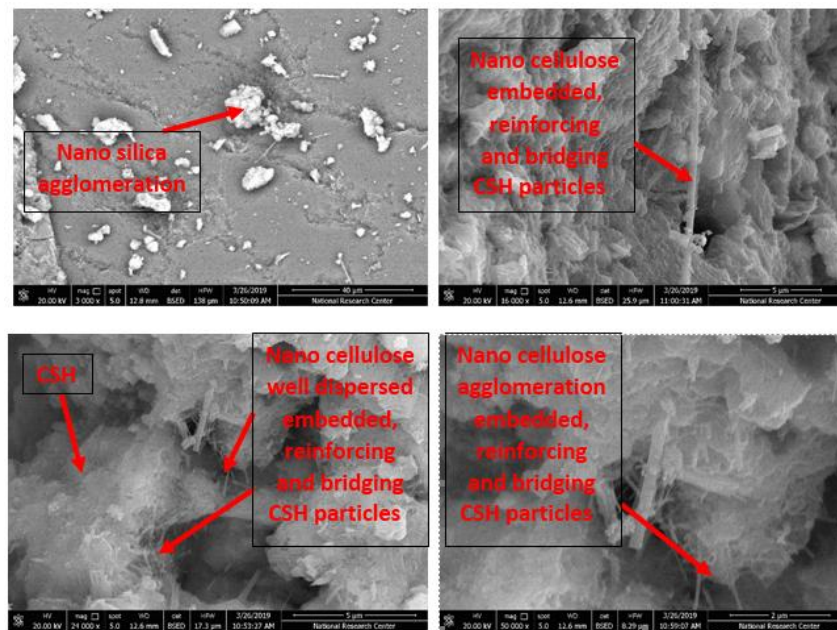


**Figure 12.** EDAX of control mix. (a) CH, (b) Ettringite, and (c) CSH. Where the X-axis is representing the energy (KeV), and the Y-axis representing the intensity (a.u.).

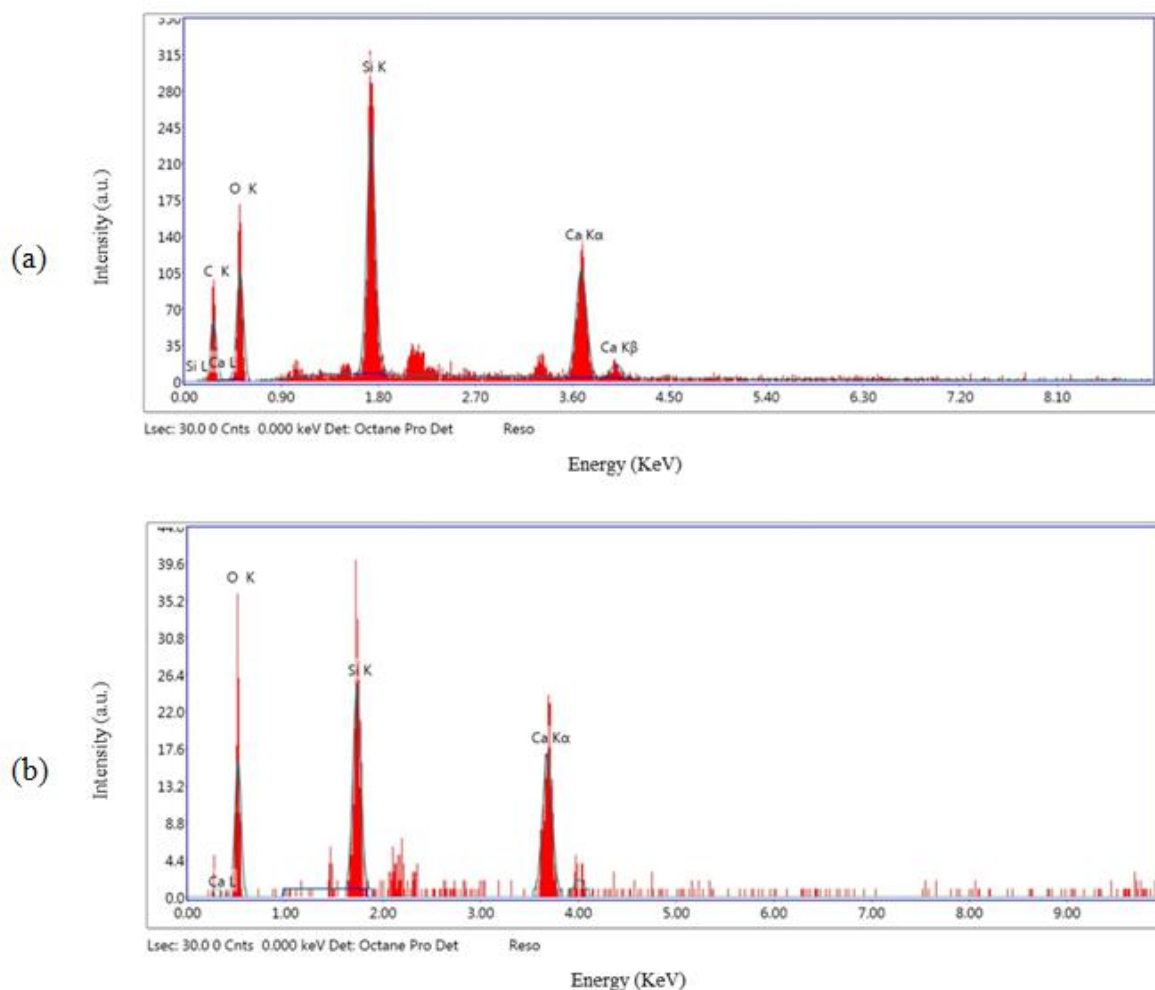




**Figure 13.** SEM of mix 8 of the lowest strength.



**Figure 14.** SEM of mix 14 of highest strength.



**Figure 15.** EDAX of nano silica and nano cellulose in mixes 8, and 14. (a) nano silica, (b) nano cellulose particles. Where the X-axis is representing the energy (KeV), and the Y-axis representing the intensity (a.u.).

#### 4. Conclusions

Based on the results presented and discussed in the preceding sections, the following conclusions can be drawn:

1. The addition of the NCell particles separately, helped in improving the tensile strength by about twice as compared to the control mix when appropriate content of NCell is incorporated (0.35%). The gain in tensile strength reached about 78%.

2. The addition of nano silica particles separately to the cement composite increases the mechanical properties of the cement matrix significantly, to reach 39%, and 49% gain in the compressive strength, and the tensile strength respectively when compared to the control mix.

3. Generally, the findings out of the research plan demonstrate the potential utilization of nano silica particles to modify the transition zone between the nano cellulose fiber and the cementitious matrix when using a high content of the nano cellulose on opposite to the utilization of lower amounts of the nano cellulose.

4. The optimum combination between the nano silica and the nano cellulose particles that



enhanced equally all of the studied mechanical properties with a gain of about 22%, was mix 14 incorporating 2% nano silica and 0.35% nano cellulose fibers.

5. The highest gain in the tensile strength out of all hybrid mixes was for mix 13. Incorporate 1.5% nano silica and 0.75% nano cellulose fiber with a gain of 54%.

6. The highest gain in the compressive strength out of all hybrid mixes was for mix 14. Incorporate 2% nano silica and 0.35% nano cellulose fiber with a gain of 22%.

7. Finally, the nano particles when being well dispersed in the cementitious matrix directly allowed greater reinforcement efficiency and performance when external compression or tensile forces were transferred to the composite.

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## References

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## References

1. Hamzaoui R, Guessasma S, Mecheri B, et al. (2014) Microstructure and mechanical performance of modified mortar using hemp fibres and carbon nanotubes. *Mater Des* 56: 60–68.
2. Hoyos CG, Cristia E, Vázquez A (2013) Effect of cellulose microcrystalline particles on properties of cement based composites. *Mater Des* 51: 810–818.
3. Kordkheili HY, Hizirolu S, Farsi M (2012) Some of the physical and mechanical properties of cement composites manufactured from carbon nanotubes and bagasse fiber. *Mater Des* 33: 395–398.
4. Ahmed SA, El-Feky MS, Hefne EE (2018) Naphthalene-sulfonate-based super-plasticizer and ultra-sonication effects on the dispersion of CNT in cement composites subjected to cyclic loading. *IJMTER* 5: 269–279.
5. El-Feky MS, El-Khodary SA, Morsy M (2019) Optimization of hybrid cement composite with carbon nanotubes and nano silica using response surface design. *Egypt J Chem* 62: 57–67.
6. Makar J, Margeson J, Luh J (2005) Carbon nanotube/cement composite-early results and potential applications. *Proceedings of Institute for Research in Construction*, Ottawa, Canada.
7. Li GY, Wang PM, Zhao X (2005) Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. *Carbon* 43: 1239–1245.
8. Yakovlev G, Keriené J, Gailius A, et al. (2006) Cement based foam concrete reinforced by carbon nanotubes. *Mater Sci* 12: 147–151.
9. Li GY, Wang PM, Zhao X (2007) Pressure-sensitive properties and microstructure of carbon nanotube reinforced cement composites. *Cem Concr Compos* 29: 377–382.
10. Konsta-Gdoutos MS, Metaxa ZS, Shah SP (2010) Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites. *Cem Concr Compos* 32: 110–115.

11. Hanus MJ, Harris AT (2013) Nanotechnology innovations for the construction industry. *Prog Mater Sci* 58: 1056–1102.
12. Galao O, Baeza FJ, Zornoza E, et al. (2014) Strain and damage sensing properties on multifunctional cement composites with CNF admixture. *Cem Concr Compos* 46: 90–98.
13. Azizi Samir MAS, Alloin F, Dufresne A (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromol* 6: 612–626.
14. John MJ, Thomas S (2008) Biofibres and biocomposites. *Carbohydr Polym* 71: 343–364.
15. Eichhorn SJ, Baillie CA, Zafeiropoulos N, et al. (2001) Current international research into cellulosic fibres and composites. *J Mater Sci* 36: 2107–2131.
16. Dufresne A (2008) Polysaccharide nanocrystal reinforced nanocomposites. *Can J Chem* 86: 484–494.
17. Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. *Prog Polym Sci* 24: 221–274.
18. Eichhorn SJ, Dufresne A, Aranguren M, et al. (2010) Current international research into cellulose nanofibres and nanocomposites. *J Mater Sci* 45: 1–33.
19. Li MC, Mei C, Xu X, et al. (2016) Cationic surface modification of cellulose nanocrystals: toward tailoring dispersion and interface in carboxymethyl cellulose films. *Polymer* 107: 200–210.
20. Huang S, Zhou L, Li MC, et al. (2016) Preparation and properties of electrospun poly (vinyl pyrrolidone)/cellulose nanocrystal/silver nanoparticle composite fibers. *Mater* 9: 523.
21. Habibi Y, Lucia LA, Rojas OJ (2010) Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chem Rev* 110: 3479–3500.
22. Moon RJ, Martini A, Nairn J, et al. (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem Soc Rev* 40: 3941–3994.
23. Senff L, Labrincha JA, Ferreira VM, et al. (2009) Effect of nano-silica on rheology and fresh properties of cement pastes and mortars. *Constr Build Mater* 23: 2487–2491.
24. Gao K, Lin KL, Wang DY, et al. (2013) Effect of nano-SiO<sub>2</sub> on the alkali-activated characteristics of metakaolin-based geopolymers. *Constr Build Mater* 48: 441–447.
25. Hou PK, Kawashima S, Wang KJ, et al. (2013) Effects of colloidal nanosilica on rheological and mechanical properties of fly ash-cement mortar. *Cem Concr Compos* 35: 12–22.
26. Singh LP, Goel A, Bhattacharyya SK, et al. (2015) Hydration studies of cementitious material using silica nanoparticles. *J Adv Concr Technol* 13: 345–354.
27. Singh LP, Goel A, Bhattacharyya SK, et al. (2015) Effect of morphology and dispersibility of silica nanoparticles on the mechanical behaviour of cement mortar. *Int J Concr Struct Mater* 9: 207–217.
28. Kawashima S, Hou P, Corr DJ, et al. (2013) Modification of cement-based materials with nanoparticles. *Cem Concr Compos* 36: 8–15.
29. Alshehy AM, Ahmed SA, El-Feky MS, et al. (2018) Utilizing nano- to micro-scale particles based additives to enhance cement-dune sand composites. *Int J Mod Eng Res* 5: 104–114.
30. Hani N, Nawawy O, Ragab KS, et al. (2018) The effect of different water/binder ratio and nano-silica dosage on the fresh and hardened properties of self-compacting concrete. *Constr Build Mater* 165: 504–513.

31. Youssef P, El-Feky MS, Serag MI (2017) The Influence of Nano silica surface area on its reactivity in cement composites. *Int J Sci Eng Res* 8: 2016–2024.
32. Sharobim KG, Hassan M, Hanna NF, et al. (2017) Optimizing sonication time and solid to liquid ratio of nano-silica in high strength concrete. *Int J Sci Eng Res* 8: 687–693.
33. Sharobim KG, Hassan M, Hanna NF, et al. (2017) Optimizing sonication time and solid to liquid ratio of nano-silica in high strength mortars. *Int J Curr Trends Eng Res* 3: 6–16.
34. Serag MI, Yasien AM, El-Feky MS, et al. (2017) Effect of nano silica on concrete bond strength modes of failure. *Int J GEOMATE* 12: 2892–2899.
35. Serag M, Elkady H, Elfeky M (2014) The effect of indirect sonication on the reactivity of nano silica concrete. *IJSER*: 334–345.
36. El-Feky MS, Serag MI, Yasien AM, et al. (2016) Bond strength of nano silica concrete subjected to corrosive environments. *ARN J Eng Appl Sci* 11: 13909–13924.
37. Du H, Dai Pang S (2019) High performance cement composites with colloidal nano-silica. *Constr Build Mater* 224: 317–325.
38. Du H (2019) Properties of ultra-lightweight cement composites with nano-silica. *Constr Build Mater* 199: 696–704.
39. Li GY, Wang PM, Zhao X (2005) Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. *Carbon* 43: 1239–1245.
40. Konsta-Gdoutos MS, Metaxa ZS, Shah SP (2010) Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites. *Cem Concr Compos* 32: 110–115.
41. Saez de Ibarra Y, Gaitero JJ, Erkizia E, et al. (2006) Atomic force microscopy and nanoindentation of cement pastes with nanotube dispersions. *Phys Status Solidi* 203: 1076–1081.
42. Strawhecker KE, Manias E (2000) Structure and properties of poly (vinyl alcohol)/Na<sup>+</sup> montmorillonite nanocomposites. *Chem Mater* 12: 2943–2949.
43. Podsiadlo P, Kaushik AK, Arruda EM, et al. (2007) Ultrastrong and stiff layered polymer nanocomposites. *Science* 318: 80–83.
44. Prasanth R, Shubha N, Hng HH, et al. (2013) Effect of nano-clay on ionic conductivity and electrochemical properties of poly (vinylidene fluoride) based nanocomposite porous polymer membranes and their application as polymer electrolyte in lithium ion batteries. *Eur Polym J* 49: 307–318.
45. Hakamy A, Shaikh FUA, Low IM (2015) Effect of calcined nanoclay on microstructural and mechanical properties of chemically treated hemp fabric-reinforced cement nanocomposites. *Constr Build Mater* 95: 882–891.
46. Hamed N, El-Feky MS, Kohail M, et al. (2019) Effect of nano-clay de-agglomeration on mechanical properties of concrete. *Constr Build Mater* 205: 245–256.
47. Cao Y, Tian N, Bahr D, et al. (2016) The influence of cellulose nanocrystals on the microstructure of cement paste. *Cem Concr Compos* 74: 164–173.
48. Cao Y, Zavatterri P, Youngblood J, et al. (2015) The influence of cellulose nanocrystal additions on the performance of cement paste. *Cem Concr Compos* 56: 73–83.
49. Cao Y, Zavatterri P, Youngblood J, et al. (2016) The relationship between cellulose nanocrystal dispersion and strength. *Constr Build Mater* 119: 71–79.

50. de Andrade Silva F, Chawla N, de Toledo Filho RD (2008) Tensile behavior of high performance natural (sisal) fibers. *Compos Sci Technol* 68: 3438–3443.
51. Santos SF, Tonoli GHD, Mejia JEB, et al. (2015) Non-conventional cement-based composites reinforced with vegetable fibers: a review of strategies to improve durability. *Mater Constr* 65: 1–41.
52. Gram HE(1983) Durability of natural fibres in concrete, Fo 1.83 (Res. Report No: 1 of 1983), Swedish Cement and Concrete Research Institute, Stockholm.
53. Balea A, Blanco A, Negro C (2019) Nanocelluloses: natural-based materials for fiber-reinforced cement composites. A critical review. *Polymers* 11: 518.
54. Ardanuy M, Claramunt J, Toledo Filho RD (2015) Cellulosic fiber reinforced cement-based composites: a review of recent research. *Constr Build Mater* 79: 115–128.
55. Buch N, Rehman OM, Hiller JE (1999) Impact of processed cellulose fibers on Portland cement concrete properties. *Transp Res Re* 1668: 72–80.
56. Pinto RJB, Marques PAAP, Barros-Timmons AM, et al. (2008) Novel SiO<sub>2</sub>/cellulose nanocomposites obtained by in situ synthesis and via polyelectrolytes assembly. *Compos Sci Technol* 68: 1088–1093.
57. Raabe J, de Souza Fonseca A, Bufalino L, et al. (2014) Evaluation of reaction factors for deposition of silica (SiO<sub>2</sub>) nanoparticles on cellulose fibers. *Carbohydr Polym* 114: 424–431.
58. ASTM C150/C150M-19a (2019) Standard Specification for Portland Cement. ASTM International, West Conshohocken, PA.
59. ASTM C33, Standard Specification for Concrete Aggregate.
60. Serag MI, Ibrahim S, El-Feky MS (2019) Investigating the effect of mixing water dispersion on concrete strength and microstructure. *J Build Rehabil* 4: 23.
61. Jayapalan AR, Lee BY, Fredrich SM, et al. (2010) Influence of additions of anatase TiO<sub>2</sub> nanoparticles on early-age properties of cement-based materials. *Transp Res Rec* 2141: 41–46.
62. Sanchez F, Sobolev K (2010) Nanotechnology in concrete—a review. *Constr Build Mater* 24: 2060–2071.
63. Powder Diffraction Standards; Joint Committee on Powder Diffraction Standards (JCPDS)—International Center for Diffraction Data: Philadelphia, PA, USA, 2000.
64. Gabrovšek R, Vuk T, Kaučič V (2006) Evaluation of the hydration of Portland cement containing various carbonates by means of thermal analysis. *Acta Chim Slov* 53: 159–165.
65. Mounanga P, Khelidj A, Loukili A, et al. (2004) Predicting Ca(OH)<sub>2</sub> content and chemical shrinkage of hydrating cement pastes using analytical approach. *Cem Concr Res* 34: 255–265.



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