

# **Effect of calcined nanoclay on the durability of NaOH treated hemp fabric-reinforced cement nanocomposites**

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## **ABSTRACT**

Cement nanocomposites reinforced with hemp fabrics and calcined nanoclay (CNC) have been fabricated and investigated. The treated hemp fabric-reinforced cement composites and nanocomposites were subjected to 3 wetting and drying cycles and then tested at 56 and 236 days. The influences of CNC dispersion on the durability of these composites have been characterized in terms of porosity, flexural strength, stress-midspan deflection curves and microstructural observation of hemp surface. The microstructure of matrix was investigated using X-ray Diffraction. Results indicated that the CNC effectively mitigated the degradation of hemp fibre. The durability and the degradation resistance of hemp fibre were enhanced due to the addition of CNC into the cement matrix and the optimum content of CNC was 1 wt%.

**Keywords:** Nanoclay-cement composites, hemp fabric, durability, microstructure.

## 1. Introduction

Recently, natural fibres are gaining increasing popularity to develop ‘environmental-friendly construction materials’ as alternative to synthetic fibres in fibre-reinforced concrete [1, 2]. These fibres are cheaper, biodegradable and lighter than their synthetic counterparts. Some examples of natural fibres are: Sisal, Flax, Hemp, Bamboo, Coir and others [3]. However, the long term durability of natural fibres in cement composites has been the major issue in which it has limited their applications in cementitious composites. These issues could be the degradation of fibres in a high alkaline environment of cement composites and also the interfacial bonding between the natural fibre and the cement matrix is relatively weak [4, 5]. In order to improve the durability of fibre reinforced cement composites, there are two possible methods: (i) modification of fibre surfaces and (ii) modification of the cement matrix [6, 7]. Regarding the first method, some researchers have showed that pre-treatments of natural fibre surfaces via some chemical agents such as alkalization,  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  have slightly improved the fibre-matrix interface of the composites. As a result, the mechanical properties of such composites are enhanced [8, 9]. Troedec et al. [10] reported that the modification of hemp fibres with NaOH has reasonably improved the interfacial bonding between the fibres and the lime-based mineral matrix. Regarding the second approach, it should be noted that the alkalinity (high pH value) of cement matrix come from two sources. The first source is minor compounds (alkalis) of cement clinker which are  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , in which these alkalis increase alkalinity of hydrated cement paste [11, 12]. Some researchers reported that high alkali content can increase the early strength but reduce the long-term strength [13, 11]. The  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  can affect the strength through water-soluble  $\text{K}_2\text{O}$  or alkali-silica reaction (alkali reactive-aggregates) [14, 15]. In contrast [12] reported that alkalis did not affect the compressive strength of concrete. The second source is the highest

amount of calcium hydroxide that comes from hydration reaction and it is considered as the major portion of alkalinity of cement matrix and concrete. The calcium hydroxide has also been proven as an important factor leading to the degradation of natural fibers. However, in the second approach for modification of the cement matrix, calcium hydroxide in cement matrix can be reduced by using pozzolanic materials such as silica fume, fly ash, metakaolin and amorphous nanomaterials. Thus this approach could improve the interfacial bond, mechanical properties and durability of natural fibre-reinforced cement composites [16, 17]. On the other hand, one of the most effective techniques to obtain a high performance cementitious composite is by reinforcement with textile (fabrics), which are impregnated with cement matrix. Synthetic fabrics such as polyethylene (PE) and polypropylene (PP) have been used as reinforcement for cement composites [18, 19]. This system has superior filament-matrix bonding which improves the mechanical properties such as tensile and flexural strengths than continuous or short fibres [20]. In contrast, the use of natural fibre sheets and fabrics is more prevalent in polymer matrix when compared to cement-based matrix [21, 22].

Nowadays, nanotechnology is one of the most active research areas in the civil engineering and construction materials [23, 24]. In the construction industry, several types of nanomaterials have been incorporated into concretes such as nano-SiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub>, nano-Fe<sub>2</sub>O<sub>3</sub>, nano-ZnO<sub>2</sub>, nano-CaCO<sub>3</sub>, nano-TiO<sub>2</sub>, carbon nanotubes, nano-metakaolin and nano-ZrO<sub>2</sub> in order to improve the durability and mechanical properties of concrete and Portland cement matrix [25-30]. Supit and Shaikh [31] reported that the addition of 1% nano-CaCO<sub>3</sub> increased the compressive strength of mortar and concrete significantly. Nanoclay (NC) is a new generation of processed clay for a wide range of high-performance cement nanocomposite. Some examples of nanoclay are nano-halloysite, nano-cloisite 30B and nano-kaolin [32]. As a kind of nano-pozzolanic material,

nanoclay not only reduces the pore size and porosity of the cement matrix, but also improves the strength of cement matrix through pozzolanic reactions. Farzadnia et al. [33] reported that the incorporation of 3% halloysite nanoclay into cement mortars increased the 28-day compressive strength up to 24% compared to the control samples. Calcined nanoclay is prepared by heating nanoclay at certain temperature for certain period of time in order to transform nanoclay to amorphous state in which the calcined nanoclay can behave as a highly reactive artificial pozzolan such as silica fume, metakaolin, nano-SiO<sub>2</sub>, and nano-metakaolin [29]. An interesting study on using nanoparticles and natural fibres as reinforcements in cement nanocomposites was obtained by Aly et al. [34]. They studied the durability of flax fibre reinforced cement mortar containing 2.5 wt % nanoclay and 20 wt% ground waste glass powder at 28 days and after 50 wet/dry cycles (378 days). They reported that the flax fibre reinforced nanocomposites after accelerating ageing cycles showed small reduction (19%) in the flexural strength when compared to its initial strength at 28 days due to the small degradation of flax fibre. The authors concluded that the presence of nanoclay reduced the degradation of flax fibres in such composites. In this paper, in order to improve the durability of hemp fibre reinforced cement composites, the combination of both methods (modification of fibre surfaces and the cement matrix) are used. The effect of calcined nanoclay (CNC) on the durability properties of treated hemp fabric-reinforced cement composite is studied. The durability of the treated hemp fabric-reinforced cement composites and nanocomposites is discussed based on the porosity and flexural strength obtained at 56 days and 236 days.

## **2. Experimental procedure**

### *2.1 Materials*

The nanoclay platelets (Cloisite 30B) used in this investigation is a natural montmorillonite modified with a quaternary ammonium salt, which was supplied by Southern Clay Products, USA. Physical properties and chemical composition of the nanoclay are shown in Table 1 [21, 35]. The woven hemp fabric of 0.54 mm thickness and 0.3 mm opening size between bundles was supplied by Hemp Wholesale Australia Pty, Kalamunda, Western Australia. The chemical composition of hemp fabrics is: 58.7 wt% of cellulose residue, 16.8 wt% of pectins, 14.2 wt% of hemicelluloses, 6 wt% of lignins and 4.3 wt% of waxes and fat. Ordinary Portland cement (ASTM Type I) was used in all mixes. Amorphous calcined nanoclay (CNC) was prepared by heating the nanoclay at 900° C for 2 h, details of that can be found in previous work [26]. In order to treat the surface of the fibres, the hemp fabrics were chemically treated by 1.7 M NaOH solution (pH=14) for 48 hours, details of this treatment can also be found in the previous work of the authors [26].

## *2.2 Sample preparation*

### *2.2.1 Nanocomposites*

The ordinary Portland cement (OPC) is partially substituted by calcined nanoclay (CNC) at 1, 2 and 3 % by weight of OPC. The OPC and CNC were first dry mixed for 15 minutes in Hobart mixer. The binder is CNC-cement powder. The cement nanocomposite matrix was prepared with a water / binder ratio of 0.485.

### *2.2.2 Treated hemp fabric-reinforced nanocomposites*

Firstly, six layers of treated hemp fabrics were first soaked into the nanocomposite matrix and then laid on polished timber plate by hand. After that, the compacted fabrics were left under heavy weight (30 kg) for 1 hour to reduce air bubbles and voids inside the specimens. Secondly,

a thin layer of nanocomposite matrix was poured into the prismatic mould followed by the compacted pre-soaked hemp fabrics into the mould. Finally a thin layer of matrix was poured into the mould as upper layer and the specimens were left for 24 hours to cure at room temperature. The position through the depth of specimen containing 6 treated hemp fabrics is shown in Fig. 1. The total amount of treated hemp fabrics in each specimen was about 6.9 wt%. The mix proportions are given in Table 2.

### *2.2.3 Curing and specimens*

For each series, five prismatic plate specimens of 300×70×10 mm (length × width × depth) in dimension were cast. In first 24 h of casting, samples were cured in moist condition at 20±2 °C and 80% relative humidity and also they were sealed by plastic sheets to prevent evaporation of water from their top surfaces in prismatic mold. All specimens were demolded after 24 h of casting and kept under water for approximately 56 days. For durability test, the period of the wetting and drying cycles was determined as 30 days under water followed by 30 days of drying in air for one cycle and it was performed for 3 cycles, after that the samples tested at 236 days counting from the casting day. Five rectangular specimens of each series with dimensions 70×20×10 mm (length × width × depth) were cut from the fully cured prismatic plate for each mechanical and physical test at 56 and 236 days.

## *2.3 Material Characterisation*

### *2.3.1 The X-ray Diffraction (XRD)*

XRD patterns were obtained using CuK<sub>α</sub> ( $\lambda = 1.5406 \text{ \AA}$ ) radiation with a Bruker D8 Advance diffractometer equipped with a LynxEye detector (1-dimensional detector, Bruker-AXS,

Karlsruhe, Germany). The diffractometer was scanned from 7° to 70° (2 $\theta$ ) in step size of 0.015° and the counting time per step was 1.8 s.

### 2.3.2 Scanning electron microscopy (SEM)

Scanning electron microscopy imaging was obtained using a NEON 40ESB, ZEISS. The SEM investigation was carried out in detail on microstructures and the fractured surfaces of samples.

### 2.4 Apparent porosity test

Five specimens, measuring 70×20×10 mm, in each composition were used to measure the apparent porosity. Prior to measuring the apparent porosity, the samples were dried in an oven at 80° C for 24 hours to obtain the dried mass. The apparent porosity was calculated according to ASTM C20 [36].

### 2.5 Flexural strength test

Five specimens, measuring 70×20×10 mm, in each composition were used to measure the flexural strength. Three-point bend tests were conducted using a LLOYD Material Testing Machine to evaluate the flexural strength of the composites. The support span used was 40 mm with a displacement rate of 0.5 mm/min. The flexural strength  $\sigma_F$  was evaluated using the following equation:

$$\sigma_F = \frac{3P_m S}{2BW^2}$$

Where  $P_m$  is the maximum load at crack extension,  $S$  is the span of the sample,  $W$  is the specimen depth and  $B$  is the specimen width.

### 3. Results and discussion

#### 3.1 Porosity of nanocomposites

The porosity of cement paste and nanocomposites was shown in Table 3. Overall, it can be seen that the porosity of C, CNCC1, CNCC2 and CNCC3 decreased slightly in periods of between 56 and 236 days. Firstly, it is known that after 90 days curing, the compressive strength of control concrete or cement paste increase slightly with increasing ages as a result of reduction in porosity due to further hydration reaction. Secondly, in nanocomposites, slight reduction in porosity with increasing ages can be attributed to both hydration reaction and pozzolanic reaction as well as filling effect. For example, in CNCC1 cement nanocomposite, the porosity at 56 days is decreased by 31.2% compared to cement paste, however at 236 days it decreased slightly from 16.5 to 15.1% by about 8 % decrease. This indicated that nanocomposites containing 1, 2 and 3 wt% CNC had both filling and pozzolanic effects in the porosity of cement paste composites as well as to further hydration reaction (in between 56-236 days), in which the nanocomposite matrix becomes more a consolidated microstructure due to filling of the micro pores and densification by the enhanced pozzolanic activity and further hydration reaction [37]. This result is in agreement with the work done by Supit and Shaikh [38] reported that the addition of 2 wt% nano-silica significantly reduced the porosity of high volume fly ash (HVFA) concrete after 90 days. However, the addition of more CNC leads to increase in porosity. This could be attributed to the poor dispersion and agglomerations of the CNC which create more voids in the matrix [39].

The XRD patterns of cement paste and nanocomposites containing 1, 2 and 3 wt% CNC after 236 days are shown in Fig. 2(a-d). It can be seen from Figs. 2(b-d) that the addition of 1, 2, 3

wt% CNC reduced the intensities of major peaks of  $\text{Ca(OH)}_2$  when compared to cement paste (Fig. 2a). For example intensity of  $\text{Ca(OH)}_2$  at  $2\theta$  of  $18.01^\circ$  for CNCC1 (Fig. 2b) is decreased by 13.9% compared to cement paste (Fig. 2a). This indicated an obvious consumption of  $\text{Ca(OH)}_2$  in the pozzolanic reaction due to the presence of CNC and good dispersion of calcined nanoclay in the matrix which produce more amorphous calcium silicate hydrate gel (C-S-H). The formation of more C-S-H gel in CNCC1 nanocomposites can be also confirmed by the inspection of the increase in intensity peaks corresponding to  $2\theta$  of  $31^\circ$  (as mentioned by Hosino et al. [40]) in the close-up of Fig. 2 where peak for  $\text{C}_3\text{S}$  at  $2\theta$  of  $29.4^\circ$  is also reduced. Moreover, it can also be seen in the same close-up figure that the  $\text{Ca(OH)}_2$  peak at  $2\theta$  of  $28.7^\circ$  is also lower in CNCC1 nanocomposite than the cement paste due to pozzolanic reaction. In the same close-up figure the XRD for CNCC1 at 56 days (as reported by our previous work, Hakamy et al. [26]) is also plotted. By comparing the peaks for CNCC1 at 56 and 236 days it can also be seen that the XRD peak of CNCC1 at 236 days at  $2\theta$  of  $31^\circ$  is slightly higher than at 56 days indicating the formation of more C-S-H and consumption of CH after 236 days. The reduction of  $\text{C}_3\text{S}$  peak of CNCC1 at 236 days at  $2\theta$  of  $29.4^\circ$  compared to the same at 56 days and cement paste is another indication of pozzolanic and hydration reaction [41]. Shaikh et al. [42] reported in their XRD results that after 28 days the cement paste containing 2% nano-silica exhibited less calcium hydroxide peaks than the control cement paste.

On the other hand, as can be seen from Fig. 2d for nanocomposites containing 3 wt% CNC, the intensities of major peaks of  $\text{Ca(OH)}_2$  were slightly decreased when compared to cement paste (Fig. 2 d and a). For instance, the intensity of  $\text{Ca(OH)}_2$  at  $2\theta$  of  $18.01^\circ$  for CNCC3 (Fig. 2d) decreased by 6.9% compared to cement paste (Fig. 2a). This may be attributed to agglomerations of CNC at high contents which led to relatively poor dispersion of CNC and hence relatively

poor pozzolanic reaction. This agglomeration can be explained as follows; nanoparticles, due to their small size, have high inter-particle van der Waal's forces causing them to lose the desirable specific surface area to volume ratio [38]. Therefore, due to their higher van der Waal's forces, the 3 wt% CNC agglomerate more than other 1 wt% CNC and 2 wt% CNC. As a result of this, the efficiency of 3 wt% CNC (or nanoparticles) in consuming  $\text{Ca(OH)}_2$  could be less due to the reduction of total surface areas that contribute in pozzolanic reaction. Shaikh et al. [42] also stated that nanoparticles agglomerate more than other micro-pozzolanic materials (e.g. silica fume, metakaolin) due to their higher van der Waal's forces. In summary, it is important to note that the reduction of the porosity could be attributed to two reasons: (i) filling effect of CNC due to its good dispersion, (ii) the pozzolanic reaction by amorphous nanoparticles (i.e. CNC) that lead more C-S-H gel being produced.

### *3.2 Porosity of treated hemp fabric-reinforced nanocomposites*

The effect of wetting and drying cycles on the porosity of 6THFRC composites and 6THFR-CNCC nanocomposites was also shown in Table 3. Generally the porosity increased significantly after 3 wetting and drying cycles (at 236 days). The porosity of 6THFRC composites increased from 32.1 to 36.3 % by about 13 % increase. This was due to increase in voids in between fibres and matrix, whereas in 6THFR-CNCC1 nanocomposite, the porosity is increased by 8.5 % at 56 days. This indicates that CNC relatively reduced the voids between the hemp fibre and the cement matrix containing CNC after 3 wet/dry cycles and thus fibre-matrix interfacial bonding was slightly maintained. Roma et al. [43] reported that in the period from 28 to 155 days, a tendency of increase in the permeable void volume was observed for the sisal fibres reinforced cement composite containing silica fume. It could be a consequence of the fast degradation of

sisal fibres in the alkaline environment of Portland cement or even due to the detachment of the cellulose fibre during wet–dry cycles attributed to its shrinkage into the cement matrix.

### *3.3 Flexural strength of nanocomposites*

The effect of 3 wet/dry cycles on the flexural strength of cement paste and nanocomposites (CNC) is shown in Fig. 3. Overall, the incorporation of CNC into the cement composite led to significant enhancement in the flexural strength at all ages. At 56 days, the flexural strength of cement nanocomposite containing 1, 2 and 3 wt% CNC was increased by 42.9%, 34.8% and 30.6%, respectively compared to cement paste. This improvement clearly indicates the effectiveness of CNC in consuming calcium hydroxide (CH), supporting pozzolanic reaction and filling the micro pores in the matrix [44, 45]. Thus the microstructure of cement nanocomposite is denser than the cement matrix, especially in the case of using 1 wt% CNC, which is evident from its higher flexural strength. However, after 3 wet/dry cycles at 236 days, the flexural strength of nanocomposites increased slightly compared to their values at 56 days. For example, the flexural strength of CNCC1 nanocomposite increased from 7.75 to 8.27 MPa by about 7% increase. Rong et al. [46] studied the effects of 3% nano-SiO<sub>2</sub> particles on the durability of concrete containing 35% fly ash at 28 and 90 days, they reported about 11% improvement in flexural strength at 90 days compared to 28 days. Mohamed [47] also reported that flexural strength of concrete containing 1% nano-SiO<sub>2</sub> improved from 12.08 to 13.27 by 10 % after 90 days compared to its strength at 28 days.

SEM images of the microstructure at 236 days of cement paste and the cement nanocomposite containing 1 wt% CNC (CNCC1) are shown in Fig. 4 a-b. For cement paste matrix, Fig. 4a demonstrates more Ca(OH)<sub>2</sub> crystals and Ettringite as well as more pores which revealed a weak microstructure. On the other hand, Fig. 4b displays the SEM micrograph of CNCC1

nanocomposite matrix, which is different from that of cement matrix, the microstructure is denser and more compact with fewer pores and more C-S-H gel.

### *3.4 Flexural strength of treated hemp fabric-reinforced nanocomposites*

The effect of wetting and drying cycles on the flexural strength of 6THFRC composites and treated hemp fabric reinforced-nanocomposites (6THFR-CNCC) are shown in Fig. 5. Generally all composite showed reduction in the flexural strength after 3 wetting and drying cycles (at 236 days). This was attributed to some partial degradation of hemp fibre in cement matrix that led to slightly deteriorate fibre-matrix bonding and also the mineralization of the fibres in which fibre became more brittle. The incorporation of CNC into the 6THFRC composite led to significant enhancement in the flexural strength of all treated Hemp fabric reinforced nanocomposites. At 56 days, the flexural strength of 6THFR-CNCC1 increased from 14.52 to 20.16 MPa, about 38.8% increase compared to 6THFRC composite. However, after 3 wet/dry cycles (at 236 days) the flexural strength of 6THFRC composite dropped to 26.2 % of the initial strength at 56 days, whereas the flexural strength of 6THFR-CNCC1 nanocomposites reduced by about 17.4 % compared to its value at 56 days. Moreover, the flexural strength of 6THFR-CNCC2 and 6THFR-CNCC3 nanocomposites reduced by about 18.3 % and 19.7% compared to their values at 56 days. Based on this result, it can be concluded that the reduction in the flexural strength for 6THFR-CNCC3 nanocomposites was less than the reduction of 6THFRC composite after 3 wet/dry cycles (at 236 days). This improvement is explained as follows: the degradation of natural fibres in Portland cement matrix is due to the high alkaline environment (especially calcium hydroxide solution) which dissolves the lignin and hemicellulose parts, thus weakening the fibre structure [1, 2, 17]. In order to improve the durability of natural fibre in cement paste, the matrix could be modified in which calcium-hydroxide (CH) must be mostly consumed or

reduced. In this study, the CNC effectively prevented the hemp fabric degradation by reducing the CH in the matrix through pozzolanic reaction. Thus, the degradation of hemp fibres in nanocomposite was mostly prevented and the treated hemp fabric-nanocomposite matrix interfacial bonding was mostly improved especially in the case of 1 wt% CNC. Other two reasons of this improvement were the effectiveness of CNC in filling the micro pores in the matrix which led to denser microstructure of nanocomposite matrix than the cement matrix and also the pre-treatment of hemp fibre by NaOH solution. Filho et al. [48] investigated the durability of sisal fibre-reinforced mortar with 50% metakaolin (PC-MK) and without metakaolin (PC) at 28 days and after 25 wet/dry cycles. They observed that the flexural strength of PC and PC-MK composites decreased by 63 % and 23 %, respectively compared to their control composites at 28 days. They reported that 50% metakaolin replacement significantly prevented the sisal fibres from the degradation in cement matrix. However, the addition of CNC more than 1 wt% caused a marked decrease in flexural strength. This could be attributed to the relatively poor dispersion and agglomerations of the CNC in the cement matrix at higher CNC contents, which created weak zones and then increased the porosity.

Figs. 6 (a-b) show the effect of wetting and drying cycles on the stress-midspan deflection behaviour of 6THFRC composites and 6THFR-CNCC1 nanocomposites. The ductile behaviour can be observed in both treated composites with and without CNC, with higher flexural strength (about 40% increases) and better post-peak ductility in the composite containing CNC. It was observed that ductile behavior and bending stress are slightly reduced due to accelerated aging. This reduction was attributed to the lignin and hemicellulose deterioration of hemp fibre in matrix by  $\text{Ca}^{2+}$  ions attack and embrittlement (brittleness) of hemp fibres due to fibre cell wall mineralization in cement matrix [2, 17]. Moreover, alternating wet and dry conditioning

increased the porosity and interface fatigue that led to decrease the bond strength between the fibres and the matrix, and thus the load-transfer. However, the 6THFR-CNCC1 nanocomposite (Fig.6b) presented better ductile behavior and bending stress than 6THFRC composites (Fig.6a) after 236 days. This enhancement could be due to high fibre-matrix interfacial bonding, which increases the maximum load-transfer capacity.

### *3.5 Microstructural analysis*

Figs.7 (a-d) show the fibre-matrix interfacial bonding of 6THFRC composite and 6THFR-CNCC1 nanocomposite at 56 days and after 3 wet/dry cycles (at 236 days). At 56 days, the microstructural characteristic of the fracture surface of 6THFRC composite (Fig. 7a) showed relatively good fibre-matrix interfaces with small gaps between the fabric layers and the cement matrix. However, after 3 wet/dry cycles (at 236 days) the interface zone between the fabrics and the matrix is increased (Fig.7b), which indicated obvious deterioration of fibre-matrix interfacial bonding. Regarding the 6THFR-CNCC1 nanocomposite at 56 days, the SEM image showed better fibre-nanomatrix interfacial bonding (Fig. 7c) when compared to the 6THFRC composite (Fig.7a). However, after 3 wet/dry cycles (at 236 days) the interface zone between the fabrics and the matrix containing CNC slightly increased (Fig.7d), which indicated very small signs of degradation of fibre-matrix interface in nano-matrix. This confirmed that the CNC considerably reduced the deterioration of fibre-matrix interfacial bonding. The same phenomena was observed by Wei and Meyer [49], according to their SEM images where they reported that the use of metakaolin in cement composite reduced the deterioration of interface zone between natural fibre and matrix after accelerating ageing (30 wet/drying cycles).

SEM micrographs of raw NaOH treated hemp fibre and the hemp fibres extracted from 6THFRC composite and 6THFR-CNCC1 nanocomposite after 3 wet/dry cycles (at 236 days) are

shown in Figs.8 (a-d). It can be seen that the fibre surface of raw NaOH treated hemp fibre was more uniform (Fig.8a), whereas in 6THFRC composite (Figs.8 b-c), the micrographs revealed some degradation on the fibre surface during accelerating ageing. Sedan et al. [9] reported that the CH content ( $\text{Ca}^{2+}$  ions) of cement matrix contributed to the degradation of hemp fibre rapidly. Regarding 6THFR-CNCC1 nanocomposite (Fig.8 d), there was slight change in the fibre surface after 236 days, which indicated that CNC slightly prevented the degradation of hemp fibre surface.

#### **4. Cost and Applications**

Natural fibres/fabrics are increasingly being utilized due to low density, low cost, renewability, recyclability and availability [1, 2]. On the other hand, nanoparticles are expensive which could limit their applications [23, 25]. Singh [50] stated that the nanomaterials have many unique characteristics which will definitely result in high strength and durable concrete, but the cost of nanomaterial is still very expensive due to novelty technology. Perhaps the nanomaterial cost will come down over time as manufacturing technologies upgrade their production efficiency [24]. However, nanomaterials are used in very small amounts in the concrete or other cementitious composites. Shaikh and Supit [51] stated that although the use of nano- $\text{CaCO}_3$  was first considered as filler to partially replace cement, some studies have shown advantages of using 1% nano- $\text{CaCO}_3$  nanoparticles in terms of compressive strength and economic benefits as compared to cement and other supplementary cementitious materials.

Among all types of nanomaterials that can be used in construction and building materials, nanoclay is considered as one of inexpensive nanomaterials. In this study the use of (very small amounts) only 1% calcined nanoclay in CNCC1 and 6THFR-CNCC1 nanocomposite led to significant improvement in mechanical properties and durability. From economic point of view,

the addition of 1% calcined nanoclay in cement paste or treated hemp fabric reinforced cement composite will not add any significant cost but improved the durability significantly after 236 days (3 wet/dry cycles).

Regarding the issue of durability/cost ratio, this study has found that (see Fig 5), after 236 days (3 wet/dry cycles), the 6THFR-CNCC1 nanocomposite showed higher flexural strength (by 55% increase) than control 6THFR composite. This means that the addition of 1% calcined nanoclay will not add significant cost but can increase the life (durability) of treated hemp fabric reinforced cement composites by 1.55 times over their counterparts without calcined nanoclay. The benefit of developing the long-term durability of natural fibre in such fibre-nanocomposite will overcome the few cost. The developed treated hemp fabric reinforced nanocomposites can also be widely employed as an alternative to synthetic fibres in some applications including concrete tiles, roofing sheets, sandwich panels, on-ground floors, ceilings and structural laminate.

## **5. Conclusions**

Cement composites and nanocomposites reinforced with hemp fabrics and calcined nano-clay (CNC) have been fabricated and characterized. The effect of CNC on the durability of treated hemp fabric reinforced cement nanocomposites and the degradation of hemp fibres are reported. The optimum content of CNC was 1 wt%. After 236 days (3 wet/dry cycles), the flexural strength of 6THFRC composites decreased by 26.2 % whereas flexural strength of 6THFR-CNCC1 nanocomposites decreased by 17.4%. SEM micrographs indicated that hemp fibre in 6THFRC composites undergo more degradation than in 6THFR-CNCC1 nanocomposites. Based on all results, the addition of CNC has great potential to improve the durability of treated hemp fabric reinforced cement nanocomposites during wet/dry cycles, particularly at 1% CNC. Indeed,

particles agglomeration increased as CNC content increased which adversely affected the mechanical properties of the composites. It is recommended that more research is required to overcome the CNC agglomerations.

## **Acknowledgments**

The authors are grateful to Ms E. Miller for her assistance with SEM imaging.

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## Figure Captions

1. Schematic representation of cross section of 6 treated hemp fabric layers position through the depth of sample.
2. XRD patterns of: (a) cement paste, nanocomposites containing various calcined nanoclay: (b) 1 wt% (CNCC1), (c) 2 wt% (CNCC2), and (d) 3 wt% (CNCC3). Numbers indicate to phases of: 1 = Portlandite [ $\text{Ca}(\text{OH})_2$ ], 2 = Tricalcium silicate [ $\text{C}_3\text{S}$ ], 3 = Dicalcium silicate [ $\text{C}_2\text{S}$ ], 4 = Gypsum, 5 = Quartz.
3. Flexural strength as a function of calcined nanoclay content for cement paste and nanocomposites at 56 and 236 days.
4. SEM micrographs at 236 days of: (a) cement paste, (b) nanocomposites containing 1wt% CNC. Numbers indicate to: 1= [ $\text{Ca}(\text{OH})_2$ ] crystals, 2= Ettringite, 3=pores, 4=C-S-H gel.
5. Flexural strength as a function of calcined nanoclay content for 6THFRC composite and 6THFR-CNCC nanocomposites at 56 and 236 days.
6. Stress versus mid-span deflection curves for 6THFRC composite and 6THFR-CNCC1 nanocomposites at 56 and after 3 wet/dry cycles (236 days).
7. SEM images of: 6THFRC composite (a) at 56 days, (b) after 3 wet/dry cycles (236 days) and 6THFR-CNCC1 nanocomposites (c) at 56 days, (d) after 3 wet/dry cycles (236 days).
8. SEM images of: (a) raw NaOH treated hemp fibre and the hemp fibres extracted from: (b, c) 6THFRC composite, (d) 6THFR-CNCC1 nanocomposite after 3 wet/dry cycles (236 days).

## List of Tables

**Table 1**

Physical properties and chemical composition  
of the nanoclay [21, 34]

Properties/ Compositions	
<i>Physical properties</i>	
Colour	Off white
Density (g/cm <sup>3</sup> )	1.98
d-spacing (001) (nm)	1.85
Aspect ratio	200-1000
Surface area (m <sup>2</sup> /g)	750
Mean particle size (µm)	6
<i>Chemical composition</i>	
SiO <sub>2</sub>	62.10
Al <sub>2</sub> O <sub>3</sub>	21.10
Fe <sub>2</sub> O <sub>3</sub>	4.57
CaO	0.06
MgO	2.24
Na <sub>2</sub> O	0.38
K <sub>2</sub> O	0.06
TiO <sub>2</sub>	0.13
MnO	0.01
BaO	0.01
Cr <sub>2</sub> O <sub>3</sub>	0.01
P <sub>2</sub> O <sub>5</sub>	0.05
LOI (loss on ignition)	7.40

**Table 2**

Mix proportions of specimens

Sample	Hemp fabric (HF)		Mix proportions (wt%)		
	Content (wt%)	Fabric layers	Cement	CNC	Water/binder
C	0	0	100	0	0.485
CNCC1	0	0	99	1	0.485
CNCC2	0	0	98	2	0.485
CNCC3	0	0	97	3	0.485
6THFRC	6.9	6	100	0	0.485
6THFR-CNCC1	6.9	6	99	1	0.485
6THFR-CNCC2	6.9	6	98	2	0.485
6THFR-CNCC3	6.9	6	97	3	0.485

**Table 3**

Porosity (%) values for cement paste (C), (CNCC) nanocomposites, 6THFRC composites and (6THFR-CNCC) nanocomposites at 56 and 236 days

Sample	Porosity (%) at 56 days	Porosity (%) at 236 days
C	23.9 ± 0.5	22.3 ± 0.7
CNCC1	16.5 ± 0.6	15.1 ± 0.3
CNCC2	17.6 ± 0.5	16.2 ± 0.5
CNCC3	18.9 ± 0.6	17.3 ± 0.7
6THFRC	32.1 ± 0.8	36.3 ± 0.7
6THFR-CNCC1	28.1 ± 0.5	30.5 ± 0.9
6THFR-CNCC2	29.4 ± 0.8	31.8 ± 0.9
6THFR-CNCC3	30.2 ± 0.7	33.1 ± 1.0