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INFLUENCE OF CALCINED NANOCLAY ON FRACTURE TOUGHNESS OF NAOH-TREATED HEMP FABRIC REINFORCED CEMENT NANOCOMPOSITES

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The influence of calcined nanoclay (CNC) on the porosity and fracture toughness of treated hemp fabric-reinforced cement nanocomposites is presented in this paper. Characterisation of microstructure is investigated using Quantitative X-ray Diffraction Analysis (QXDA) and High Resolution Transmission Electron Microscopy (HRTEM). An optimum replacement of ordinary Portland cement with 1 wt% CNC is observed through reduced porosity and increased fracture toughness of treated hemp fabric-reinforced nanocomposite. The microstructural analysis indicates that the CNC affect not only as a filler to improve the microstructure, but also as the activator to support the pozzolanic reaction and thus improved the adhesion between the treated hemp fabric and the matrix. Cost-benefit analysis indicates the benefit of such cement eco-nanocomposites to develop new environmentally friendly nanomaterials and it can be used for various construction applications such as, ceilings and roofs.

Keywords: Nano particles, Reinforcement, Cement, Concrete, Microstructure, QXDA.

1 INTRODUCTION

Nowadays, nanotechnology is one of the most active research areas in the civil engineering and construction materials (Sancher *et al.* 2010, Hakamy *et al.* 2014). In the construction industry, several types of nanomaterials have been incorporated into concretes such as nano-SiO_2 and nano-ZrO_2 in order to improve the durability and mechanical properties of concrete and Portland cement matrix (Nazari *et al.* 2011, Jo *et al.* 2007). Recently, natural short fibres are gaining increasing popularity to develop ‘environmental-friendly construction materials’ as alternative to synthetic fibres in fibre-reinforced concrete (Sedan *et al.* 2008). In contrast, the use of natural fibre sheets and fabrics is more prevalent in polymer matrix when compared to cement-based matrix (Alamri *et al.* 2012). However, one of the major drawbacks of natural fibres is relatively weak fibres–matrix interface which can adversely affect the mechanical properties of natural fibre reinforced cement composites (Pacheco *et al.* 2011). In this paper, the use of CNC in hemp fibre-reinforced cement composite is expected to overcome the above disadvantage of hemp fibres in cementitious composites.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

The nanoclay platelets (Cloisite 30B) were supplied by Southern Clay Products, USA. The woven hemp fabric with 0.54 mm thickness and 0.3 mm opening size between bundles was supplied by Hemp Wholesale Australia Pty**.** Kalamunda, Western Australia. Ordinary Portland cement (ASTM Type I) was used in all mixes. Calcined nanoclay (CNC) was prepared by heating the nanoclay at 800, 850 and 900° C for 2 h. It is found in this study that nanoclay transferred to amorphous state (calcined nanoclay) at 900 °C. Moreover many platelets in calcined nanoclay were destroyed and some of them broken to small nanoparticles with average size 5 nm (Figure 1). 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 in the reference (Sedan *et al.* 2008).

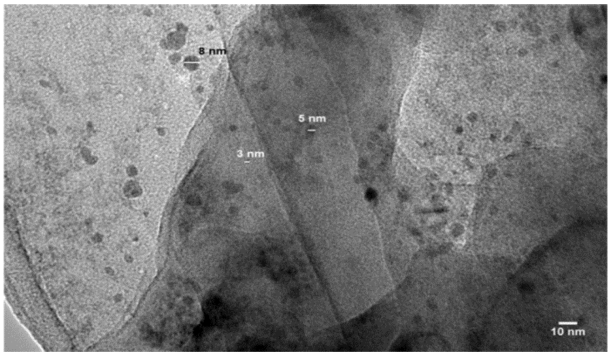

Figure 1. HRTEM images of calcined nanoclay (at 900 °C) at high magnification.

2.2 Sample Preparation and Curing

2.2.1 *Nanocomposites*

The ordinary Portland cement (OPC) is partially substituted by calcined nanoclay (CNC) of 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, the 6 layers of treated hemp fabrics were first soaked into the nanocomposite matrix and then laid on polished timber mould 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 total amount of treated hemp fabrics in each specimen was about 6.9 wt% .The mix proportions are given in Table 1. The position through the depth of sample for 6 treated hemp fabric layers is indicated in Figure 2. Five prismatic plate specimens of 300×70×10 mm in dimension were cast for each series and all specimens were demolded after 24 h of casting and kept under water for approximately 56 days.

Table 1. Mix proportions of specimens.

Sample	**Hemp fabric (HF)**		**Mix proportions (wt %)**		
	Content (wt %)	**Fabric layers**	**Cement**	**CNC**	**W/binder**
C	0	0	100	0	0.485
6THFRC	6.9	6	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
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

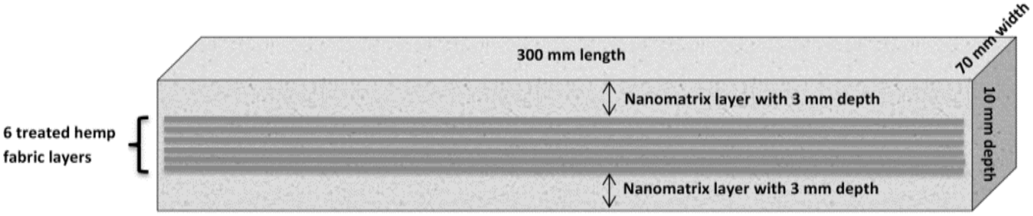

Figure 2. Schematic representation of 6 treated hemp fabric layers position through the depth of cement nanocomposite matrix.

2.3 Characterisation

HRTEM imaging was done using 3000F (JEOL company) operating at 300 kV. The Quantitative X-ray Diffraction Analysis (QXDA) with Rietveld refinement was done with Bruker *DIFFRAC*^{plus} TOPAS software associated with the International Centre for Diffraction Data PDF-4 2013 database. Scanning electron microscopy (SEM) imaging was obtained using a NEON 40ESB, ZEISS.

2.4 Apparent Porosity and Fracture Toughness Test

The apparent porosity was determined according to the ASTM Standard (C-20). Three-point bend tests were conducted using a LLOYD Material Testing Machine to evaluate the fracture toughness of the composites. The support span used was 40 mm with a displacement rate of 0.5 mm/min. The ratio of crack length to depth was about 1/3 (Hakamy *et al.* 2014).

3 RESULTS AND DISCUSSION

3.1 Quantitative X-Ray Diffraction Analysis (QXDA) of Nano-Matrix

Table 2 shows the quantitative analysis with Rietveld refinement of cement paste and nanocomposites containing 1, 2 and 3 wt% CNC. As can be seen from Table 2, CNC1 nanocomposite reduced the amount of $Ca(OH)_2$ by about 28% reduction. This indicates that an obvious consumption of $Ca(OH)_2$ crystals mainly due to the effect of pozzolanic reaction in the presence of CNC and good dispersion of CNC in the matrix leads to produce more amorphous C-S-H gel (Wei *et al.* 2012, Hakamy *et al.* 2014). On the other hand, For CNC3nanocomposites, the amount of $Ca(OH)_2$ was decreased by about 16% reduction compared to cement paste. This may be attributed to agglomerations of CNC at high contents which lead to relatively poor dispersion of CNC and hence relatively poor pozzolanic reaction.

Table 2. QXDA results for cement paste and nanocomposites containing 1, 2 and 3 wt% CNC.

Weight % (Phase abundance)				
Phase	**C**	**CNCC1**	**CNCC2**	**CNCC3**
Portlandite [$Ca(OH)_2$]	16.8	12.1	13.2	14.1
Ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$]	2.0	1.3	1.5	1.8
Tricalcium silicate [C_3S]	1.3	2.0	1.7	1.4
Dicalcium silicate [C_2S]	4.4	6.6	6.1	5.4
Gypsum [$Ca(SO_4)(H_2O)_2$]	0.7	0.4	0.6	0.4
Calcite [$CaCO_3$]	3.7	2.1	2.7	3.3
Quartz [SiO_2]	0.9	0.6	0.4	0.7
Amorphous content	70.1	74.8	73.7	72.8

3.2 Porosity

The porosity of cement paste, 6THFRC composites, nanocomposites and 6THFR-CNCC nanocomposites are shown in Table 3. It can be seen that the addition of CNC decreases the porosity of nanocomposites and 6THFR-CNCC nanocomposites when compared to control cement paste and 6THFRC composites. For 6THFR-CNCC1 nanocomposite, the porosity decreased by 12.4% decreases compared to 6THFRC composites. This indicates that CNC has filling effect in the porosity of cement paste composites with and without 6 treated hemp fabric, in which nanocomposite matrix become more consolidated microstructure (Jo *et al.* 2007).

3.3 Fracture Toughness

Fracture toughness of cement paste, 6THFRC composites, nanocomposites and 6THFR-CNCC nanocomposites are shown in Table 3. It can be seen that the fracture toughness of 6THFR-CNCC1 nanocomposite increased by 38.1% compared to 6THFRC composite. This is attributed to the fact that the CNC modified the matrix through pozzolanic reaction and reduced the $Ca(OH)_2$ content. Thus, good interfacial bond between the nanomatrix and the treated hemp fibres was achieved (Alamri *et al.* 2012, Hakamy *et al.* 2014). However, facture toughness of 6THFR-CNCC nanocomposites gradually decreases, when CNC content increases after the optimum content of 1 wt%. This is attributed to the poor dispersion of high content of CNC into the matrix, which leads to increase in porosity and weaken the interfacial bond between the fibres and the matrix. Figure 3 (a-b) shows the SEM micrographs of the fracture surface and fibre-matrix interface of 6THFR-CNCC1 and 6THFR-CNCC3 nanocomposite. A variety of mechanisms such as fibre-matrix interface, fibre pull-out and rupture fibre are observed. The examination of fracture surface of 6THFR-CNCC1 nanocomposite show very good fibre-matrix interfacial bonding in terms of ruptured fibres (Figure 3a). However, in 6THFR-CNCC3 nanocomposite (Figure 3b), debonding of fibre was observed which indicated relatively poor adhesion between the fibre and the matrix.

Table 3. Porosity and Fracture toughness values for cement paste, 6THFRC composites, nanocomposites and (6THFR-CNCC) nanocomposites.

Sample	**Porosity (%)**	**Fracture toughness (MPa.m$^{1/2}$)**
C	23.93	0.35
6THFRC	32.05	1.60
CNCC1	16.45	0.49
CNCC2	17.60	0.47
CNCC3	18.89	0.44
6THFR-CNCC1	28.07	2.21
6THFR-CNCC2	29.37	2.14
6THFR-CNCC3	30.22	2.04

4 COST-BENEFIT ANALYSIS AND APPLICATIONS

Natural fibres and fabrics are increasingly being utilized due to low cost, renewability. In contrast, the nanoparticles are expensive and this could limit their applications (Sancher *et al.* 2010). However, nanomaterials are used in very small amount in the concrete or other cementitious composites. For example, in this study 1% CNC in treated hemp fabric reinforced cement composites led significant improvement in fracture toughness. From economic point of view, the addition of 1% CNC will not add any significant cost but improved the mechanical properties by about 38%. Some applications of such nanocomposites are concrete tiles, roofing sheets, sandwich panels and ceilings.

5 CONCLUSIONS

The paper presents the influence of calcined nanoclay (CNC) on microstructures and fracture toughness of treated hemp fabric-reinforced cement nanocomposite. The optimum content of CNC was found to be 1 wt%. The 6THFR-CNCC1 nanocomposites increased the fracture toughness (38.1%) compared to the 6THFRC composites. The QXDA analysis also showed that the addition of 1 wt% CNC in cement paste reduced the amount of $Ca(OH)_2$ and increased the amount of C-S-H gel. However, the addition of more CNC (beyond optimum content- 1 wt %) into the treated hemp fabric-reinforced composites adversely affected the porosity and fracture toughness.

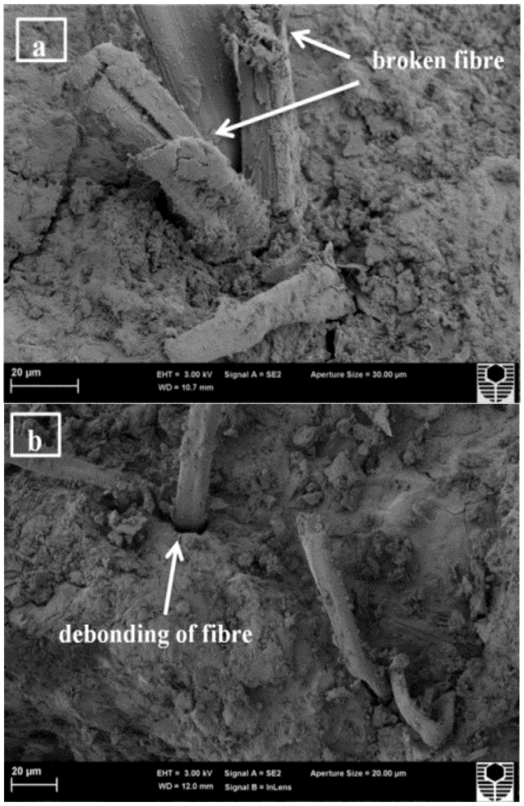

Figure 3. SEM images of the fracture surfaces for: (a) 6THFR-CNCC1, (b) 6THFR-CNCC3 nanocomposites.

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