Chapter 2
Materials and Methodology

2.1 Materials

Hemp fabric (HF) and nanoclay platelets (Cloisite 30B) were used as reinforcements for the cement-matrix composites in this research. The hemp fabric was supplied by Hemp Wholesale Australia, Kalamunda, Western Australia as shown in Fig. 2.1. The chemical composition and also the physical properties and structure of hemp fabric are shown in Tables 2.1 and 2.2 respectively. The nanoclay platelets (Cloisite 30B) used in this investigation are based on natural montmorillonite clay (hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$). Cloisite 30B is a natural montmorillonite modified with a quaternary ammonium salt, which was supplied by Southern Clay Products, USA. The specification and physical properties of Cloisite 30B are outlined in Table 2.3. Ordinary Portland cement (OPC) was used in all mixes. The chemical composition and physical properties of OPC are listed in Table 2.4. Calcined nanoclay (CNC) was prepared by heating the nanoclay at 800, 850 and 900 °C for 2 h in an electric furnace with a heating rate of 10 °C/min. The calcined nanoclay was then characterized by XRD and TEM in order to determine the amorphous phase of calcined nanoclay at calcination temperature. In order to treat the surface of the fibres, the hemp fabrics were immersed in 1.7 M NaOH solution (pH = 14) for 48 h at 25 °C and then neutralized with 1% vol. acetic acid. They were then washed several times with deionized water until the pH reached about at 7. Finally the fabrics were dried in an oven at 40 °C for 24 h.

I.-M. Low et al., *High Performance Natural Fiber-Nanoclay Reinforced Cement Nanocomposites*, Biobased Polymers, DOI 10.1007/978-3-319-56588-0_2

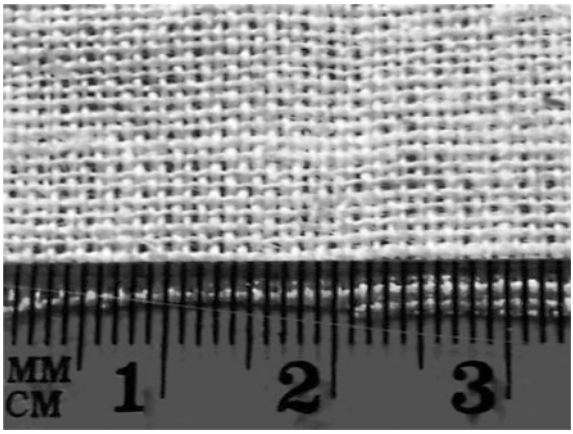

Fig. 2.1 Optical micrograph of hemp fabric [1]

Table 2.1 Chemical analysis of hemp [2]

	Cellulosic residue (wt%)	Pectin (wt%)	Hemicellulose (wt%)	Lignin (wt%)	(Wax, fat, protein) (wt%)
Hemp fibre	56.1	20.1	10.9	6	7.9

Table 2.2 Properties and structure of hemp fabric [2, 3]

Fabric thickness (mm)	0.43
Fabric geometry	Woven (plain weave)
Yarn nature	Bundle
Filament size (mm)	0.04253
Number of filaments in a bundle	24
Bundle diameter (mm)	0.21
Opening size (mm)	0.3
Fabric density (gm/cm^3)	0.6
Modulus of elasticity (GPa)	38–58
Tensile strength (MPa)	591–857

Table 2.3 Physical properties of the nanoclay platelets (Cloisite 30B) [4]

Physical properties of the (Cloisite 30B)	
Colour	Off white
Density (g/cm^3)	1.98
d-spacing (001) (nm)	1.85
Aspect ratio	200–1000
Surface area (m^2/g)	750
Mean particle size (μm)	6

Table 2.4 Physical properties and chemical composition of OPC [5]

Properties/Compositions	OPC (ASTM Type I)
Physical properties	
Specific gravity	3.17
Specific surface, Blaine (cm^2/gm)	3170
Chemical analysis	
SiO_2	21.10
Al_2O_3	5.24
Fe_2O_3	3.10
CaO	64.39
MgO	1.10
SO_3	2.52
Na_2O	0.23
K_2O	0.57
LOI	1.22

2.2 Sample Preparation

2.2.1 Cement Nanocomposite

Ordinary Portland cement (OPC) is partially substituted by nanoclay (NC) or calcined nanoclay (CNC) of 1, 2 and 3% by weight of OPC. The OPC and NC or CNC were first dry mixed for 5 min in a Hobart mixer at a low speed and then mixed for another 10 min at high speed until homogeneity was achieved. The binder is either nanoclay-cement dry powder or calcined nanoclay-cement dry powder. The cement nanocomposite paste was prepared through adding water with a water/binder ratio of 0.485. The cement nanocomposite containing 1, 2 and 3 wt% NC is termed as NCC1, NCC2 and NCC3, respectively. And also the cement nanocomposite containing 1, 2 and 3 wt% calcined NC is termed as CNCC1, CNCC2 and CNCC3, respectively. The cement paste (C) was considered as a control. The mix proportions are shown in Table 2.5.

Table 2.5 Mix proportions of specimens in Chap. 3

Sample name	Hemp fabric (HF) (wt%)	Mix proportions (wt%)		
		Cement	Nanoclay	Water/binder
NCC-0	0	100	0	0.485
NCC-1	0	99	1	0.485
NCC-2	0	98	2	0.485
NCC-3	0	97	3	0.485
NCC-0/HF	2.5	100	0	0.485
NCC-1/HF	2.5	99	1	0.485
NCC-2/HF	2.5	98	2	0.485
NCC-3/HF	2.5	97	3	0.485

2.2.2 Untreated and Treated Hemp Fabric-Reinforced Cement Nanocomposites

The cement paste (C) was prepared through adding water (W) with W/C ratio of 0.485. The fabrication of untreated hemp fabric-reinforced cement composite (UHFRC) samples was done in two stages. In the first stage, the hemp fabric (295 mm in length and 65 mm in width) was first soaked into the cementitous matrix in order to achieve better penetration of matrix into the openings of the fabric. Then layers of pre-soaked hemp fabric were laid on a polished timber plate. The compacted layers of fabric were then left under a 30 kg weight (or 4.9 kPa compressive pressure) for 1 h to reduce the air bubbles and voids which might otherwise be trapped inside the samples. This step is essential to ensure better penetration of the cement matrix into the filaments of the hemp fabric and thus improves the interfacial bonding between the fibre and the matrix. In the second stage, a thin layer of cement matrix was first poured into the prismatic mould followed by the compacted pre-soaked hemp fabrics. Finally a thin layer of matrix was poured into the mould to form the upper layer and the samples were left to cure for 24 h at room temperature. Samples of un-treated hemp fabric-reinforced cement composites were fabricated with various contents of hemp fabric: 4.5 wt% (4 layers of fabric), 5.7 wt% (5 layers of fabric), 6.9 wt% (6 layers of fabric) and 8.1 wt% (7 layers of fabric). For the fabrication of treated hemp fabric-reinforced cement composite (6THFRC) samples, only 6 layers of treated hemp fabric were used because they have been shown to exhibit the best mechanical performance. The fabrication procedure of 6THFRC was similar to that of UHFRC described above. A schematic of of 6 treated hemp fabric layers position through the depth of sample is shown in Fig. 2.2. The mix proportions are shown in Table 2.6.

2.2.3 Thermal Treatment of Nanoclay

Calcined nanoclay (CNC) was prepared by heating the nanoclay at 800, 850 and 900 °C for 2 h in an electric furnace with a heating rate of 10 °C/min. The calcined

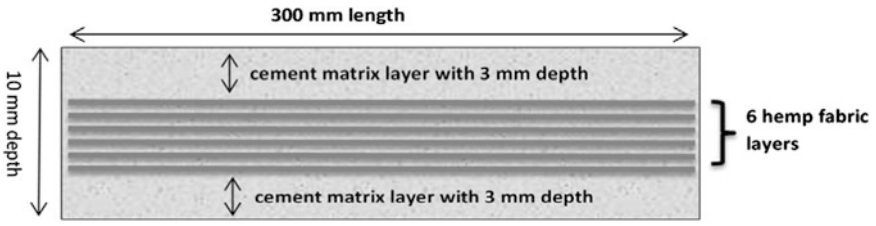

Fig. 2.2 Schematic representation of 6 treated hemp fabric layers position through the depth of sample [1]

Table 2.6 Mixing proportions of specimens in Chap. 5

Sample	Hemp fabric (HF)		Mix proportions (wt%)		
	Content (wt%)	Fabric layers	Cement	CNC	Water/binder
C	0	0	100	0	0.485
4UHFRC	4.5	4	100	0	0.485
5UHFRC	5.7	5	100	0	0.485
6UHFRC	6.9	6	100	0	0.485
7UHFRC	8.1	7	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

nanoclay was then characterized by XRD, EDS and TEM in order to determine the amorphous phase of calcined nanoclay.

2.2.4 Curing and Specimens

For each series, five prismatic plate specimens of dimensions 300 mm × 70 mm × 10 mm were cast. All specimens were demolded after 24 h of casting and kept under water for about 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 mm × 20 mm × 10 mm 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 X-Ray Diffraction

The samples were measured on a D8 Advance Diffractometer (Bruker-AXS) using copper radiation and a LynxEye position sensitive detector. The diffractometer were scanned from 7° to 70° (2θ) in steps of 0.015° using a scanning rate of 0.5°/min. XRD patterns were obtained by using Cu Ka lines (λ = 1.5406 Å). A knife edge collimator was fitted to reduce air scatter.

The Quantitative X-ray Diffraction Analysis (QXDA) with Rietveld refinement was done with Bruker *DIFFRAC*^{plus} EVA software associated with the International Centre for Diffraction Data PDF-4 2013 database. Corundum [Al_2O_3] was chosen to serve as an internal standard. It was selected because it does not overlap with important cement peaks up to 2θ of 60° as well as it does not react with water and has no influence on the hydration reaction [6–11]. By using an internal standard the concentration of the crystalline phase can be determined on an absolute basis enabling the amorphous fraction to also be determined. The samples for QXDA were prepared by mixing a dry weight of 3.0 g of cement paste or nano-composite with 0.33 g of Corundum [Al_2O_3] as the internal standard. This powder was then added to a McCrone micronising canister with 7 ml of laboratory grade ethanol and sintered alumina milling media and milled for 5.0 min. The suspension was then poured into a polypropylene dish and dried at 105 °C for 24 h. The dried powder was then brushed into a polypropylene vial, and sealed until analysis [12].

2.3.2 High Resolution Transmission Electron Microscopy

High Resolution Transmission electron microscopy imaging was done using 3000F (JEOL company) operating at 300 kV equipped with a 4 × 4 k CCD camera (Gatan). HREM is an imaging technique that creates images with atomic resolution. 3000F has excellent HREM performance including 0.195 nm point resolution and 0.104 nm lattice resolution. HRTEM was carried out at University of Western Australia. Nanoclay (Cloisite 30B) powder was dispersed in ethanol inside small glass container by using ultrasonic device for 15 min. After that few drops of suspension were mounted onto copper grid and then kept to dry.

2.3.3 Synchrotron Radiation Diffraction

Synchrotron radiation diffraction (SRD) measurement was carried out on the powder diffraction beamline at the Australian Synchrotron. The diffraction patterns of each sample were collected using a wavelength of 0.825 Å in the two-theta range of 8–52°.

2.3.4 Scanning Electron Microscopy

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. Specimens were coated with a thin layer of platinum before observation by SEM to avoid charging.

2.3.5 Thermogravimetric Analysis

The thermal stability of samples was studied by thermogravimetry analysis (TGA). A Mettler Toledo TGA 1 star system analyser was used for all these measurements. Samples with 25 mg were placed in an alumina crucible and tests were carried out in Argon atmosphere with a heating rate of 10 °C/min from 25 to 1000 °C.

2.4 Physical Properties

Measurements of bulk density and porosity were conducted to determine the quality of of nanocomposites and HF-reinforced nanocomposites accordance with the ASTM Standard (C-20) [13]. The thickness, width, length and weight are measured in order to determine the bulk density. The calculation for density was carried out by using the following equation:

$$\rho = \frac{m_d}{V} \tag{2.1}$$

where, ρ = density in (g/cm^3), m_d= mass of the dried sample (g) and V = volume of the test specimen (cm^3).

The value of apparent porosity P_S was determined using the Archimedes principle in accordance with the ASTM Standard (C-20) and clean water was used as the immersion water. The apparent porosity P_S was calculated using the following equation [13]:

$$P_S = \frac{m_s - m_d}{m_s - m_i} \times 100 \tag{2.2}$$

where m_i = mass of the sample saturated with and suspended in water, m_s = mass of the sample saturated in air.

For the water absorption test, the produced specimens were dried at a temperature of 80 °C until their mass became constant and then the mass was weighed (W_0). The specimens were then immersed in clean water at a temperature of 20 °C for 48 h. After the desired immersion period, the specimens were taken out and wiped quickly with wet cloth, and then the mass was weighed (W_1) immediately. The rate of water absorption (W_A) was calculated by using the formula:

$$W_A = \frac{W_1 - W_0}{W_0} \times 100 \tag{2.3}$$

2.5 Mechanical Properties

2.5.1 Compressive Strength

Compressive strength of specimens was tested according to ASTM: C109 using a loading rate of 0.33 MPa/s. The cube samples of size 50 × 50 × 50 mm are cast. Five cubic specimens of each composition were used to measure the compressive strength.

2.5.2 Flexural Strength and Fracture Toughness

Three-point bend tests were conducted using a LLOYD Material Testing Machine to evaluate the flexural strength and fracture toughness of the specimens. The support span used was 40 mm with a displacement rate of 0.5 mm/min. The flexural strength σ_F was evaluated using the following equation:

$$\sigma_F = \frac{3P_m S}{2BW^2} \tag{2.4}$$

where P_m is the maximum load, S is the span of the sample, W is the specimen depth and B is the specimen width.

In order to determine the fracture toughness, a sharp razor blade was used to initiate a sharp crack in the samples. The ratio of crack length to depth ($\frac{a}{W}$) was about 1/3. The fracture toughness was calculated using the following equation [14, 15]:

$$K_{IC} = \frac{P_m S}{BW^{3/2}} f\left(\frac{a}{W}\right) \tag{2.5a}$$

where a is the crack length (mm) and $f(\frac{a}{W})$ is the polynomial geometrical correction factor given by:

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W) \times (2.15 - 3.93a/W + 2.7a^2/W^2)]}{2(1 + 2a/W)(1 - a/W)^{3/2}} \tag{2.5b}$$

Five specimens, measuring 70 × 20 × 10 mm, of each composition were used to measure the flexural strength and the fracture toughness.

2.5.3 Impact Strength

The impact strength of the specimen was determined using a Zwick Charpy impact tester with 15 J pendulum hammer and 40 mm support span. Un-notched samples were used to compute the impact strength using the following formula:

$$\sigma_I = \frac{E}{A} \tag{2.6}$$

where E is the impact energy to break a sample with a ligament of area A. Five specimens, measuring $70 \times 20 \times 10$ mm, of each composition were used to measure the impact strength.

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High Performance Natural Fiber-Nanoclay Reinforced Cement Nanocomposites

Low, I.-M.; Hakamy, A.; Shaikh, F.

2017, VII, 94 p. 45 illus., Softcover
ISBN: 978-3-319-56587-3