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Macro- and nanodimensional plant fiber reinforcements for cementitious composites

13

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s0010 13.1 Introduction

p0010 The civil construction industry is majorly dominated by cement as the binding material. Cementitious materials or composites have good compressive properties but they lack tensile strength. Steel reinforcing bars and synthetic fibers, such as glass, carbon, poly vinyl alcohol, or aramid fibers, are used to overcome the disadvantages of cementitious composites and also to achieve long postcrack behavior. The use of steel reinforcement makes cementitious materials more susceptible to environmental attacks causing corrosion. Steel or synthetic fiber reinforcement both have environmental impacts caused by its production process, which includes high energy consuming steps and leads to the release of harmful chemicals and gases to the atmosphere.

p0015 Since 1970, the civil construction sector has been focusing on the sustainability of structures. Plant fibers are the most promising solution towards sustainability due to their eco-friendly nature along with good reinforcing performance. Therefore, over the last three decades researchers and scientists have focused increasingly on plant-based plant fiber reinforcements. Plant fibers are used in cementitious composites to increase the postcracking ductility, toughness and fracture energy.[1]

p0020 Plant fibers have many advantageous properties such as good tensile and flexural modulus, low density, low coefficient of thermal expansion, and so on. One of the major problems of plant fibers is the degradation and deterioration of their properties with time. Therefore, for successful application of plant fibers in cementitious matrix, the influence of different degradation parameters should also be thoroughly studied to understand and improve the durability of plant fibers in highly alkaline cementitious composites.[1] Different chemical or physical modifications could also be performed on the surface of plant fibers to improve their durability.[1]

p0025 Plant fiber derivatives such as microcrystalline cellulose (MCC), microfibrillar cellulose (MFC), nanocrystalline cellulose (NCC), etc. and bacterial cellulose (BC) are now being considered as good options for the reinforcement of cementitious matrix. Their extraordinary mechanical, thermal, and optical properties can make them a potential substitute for steel and synthetic fibers.[2] Owing to their higher crystallinity, MCC, NCC, and BC are considered to be much more stable towards degradation than plant fibers because of their highly crystalline structures and,

Sustainable and Nonconventional Construction Materials using Inorganic Bonded Fiber Composites.
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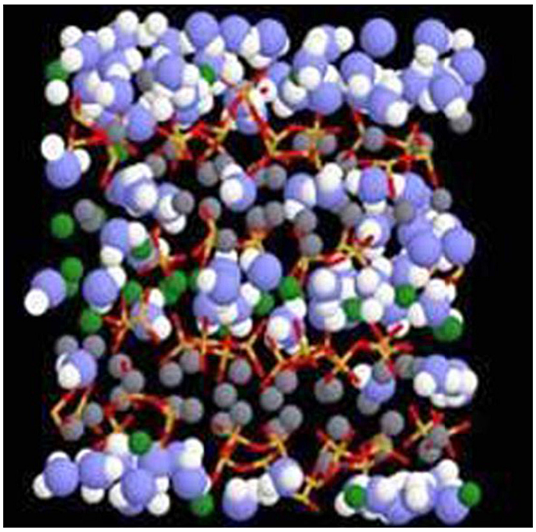
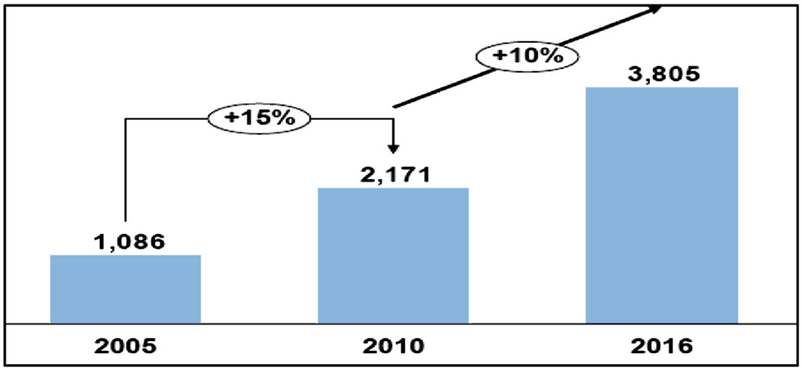
therefore, their utilization within cementitious composites can provide superior durability as compared to ordinary plant fiber-reinforced cementitious composites. The application of nanocellulose in polymer composites has been included in this chapter just to provide the readers with sufficient background information and the techniques that can be used in cement-based composites.

s0015 13.2 Properties of portland cement

p0030 Concrete generally consists of Ordinary Portland Cement (OPC), which is known as the principal hydraulic binding agent), coarse aggregates, and fillers such as sand, admixtures, and water.[3,4] The dry portion of Portland cement is composed of 63% calcium oxide, 20% silica, 6% alumina, 3% iron (III) oxide, and small amount of other materials including some impurities. These materials react with water with an exothermic reaction forming a mineral glue (known as "C-S-H" gel), calcium hydroxide, ettringite, monosulfate, unhydrated particles, and air voids. The molecular structure of C-S-H gel was not fully understood until recently. Researchers at the Massachusetts Institute of Technology (MIT, USA)[5] recently proposed a structure, and according to that, cement hydrate consists of a long tetrahedral silica chain and calcium oxide in long range distances, where water causes an intralayer distortion in otherwise regular geometry (Fig. 13.1). The distortion in the structure due to the addition of water makes the cement hydrate robust.



f0010 **Figure 13.1** The molecular model of C-S-H: the blue and white spheres are the oxygen and hydrogen atoms of water molecules, respectively; the green and gray spheres are inter- and intralayer calcium ions, respectively; the yellow and red sticks are silicon and oxygen atoms in silica tetrahedral.
Source: Pellenq et al.[5]



f0015 **Figure 13.2** Growth in plant fiber composites market.
From: Lucintel, http://www.lucintel.com/lucintelbrief/potentialofnaturalfibercomposites-final.pdf

s0020 13.3 Properties of plant fibers and nanocellulose

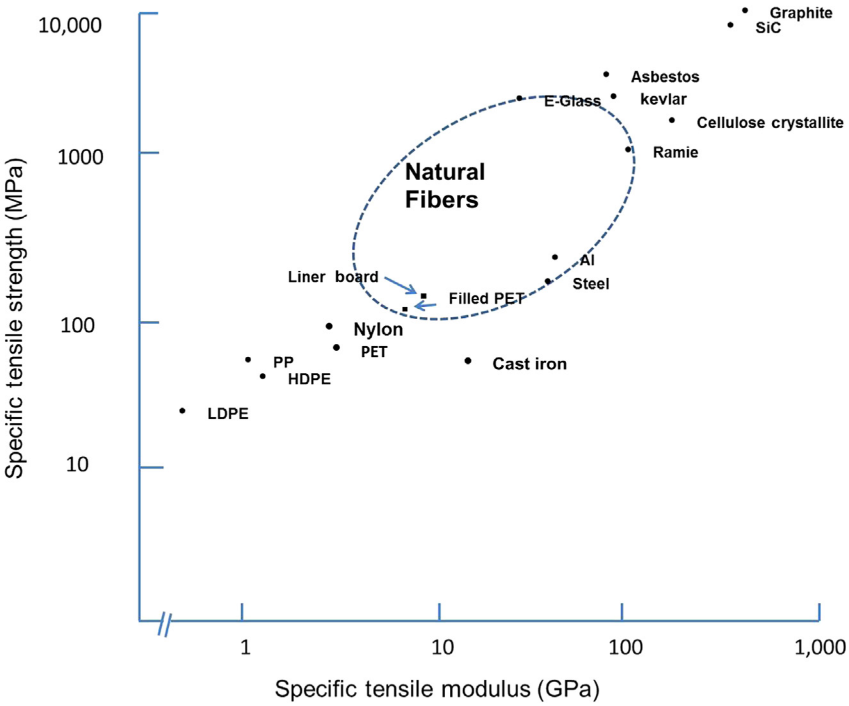
p0035 In recent times, tremendous interest has been paid to various plant fibers (such as sisal, jute, flax, hemp, coir, etc.) both by the scientific community and industrial sectors for various applications including civil construction, automobiles, sports, aerospace, and geotechnical engineering. The global plant fiber composites market reached 1.6 billion euros in 2010, with a compound annual growth rate of 15% over the last five years.[6] By 2016, plant fiber composite market is expected to reach 2.8 billion euros with a growth rate of 10% (Fig. 13.2).

s0025 *13.3.1 Properties of plant fibers*

p0040 Plant fibers are low cost, light weight, nonhazardous, eco-friendly, and renewable materials possessing high specific mechanical properties and require lower energy during their growth and applications.[7] Due to their lower carbon footprint and environmental benefits, plant fiber-based products are considered to possess a lower carbon footprint and higher sustainability.[8−13] Table 13.1 lists the physical and mechanical properties of various plant fibers and compares them with the commonly used synthetic fibers.[7,14] Among these fibers, cotton is known to be the most popular fiber for apparel sectors because of their comfort properties. Other fibers like sisal, jute, flax, coir, etc. have been mainly used for various technical applications. Flax fibers show the best mechanical properties among the various plant fibers. In comparison with the synthetic fibers, plant fibers present much lower mechanical properties, as can be seen from Table 13.1. However, owing to their much lower density as compared to synthetic fibers, they present very good specific mechanical properties (Fig. 13.3) and therefore, are of tremendous interest in applications demanding light weight.[15] Therefore, these materials have huge potential to t0010 **Table 13.1** Properties of selected plant and synthetic fibers

Type of fiber	Density (g/cm^3)	Tensile strength (MPa)	Elastic modulus (GPa)	Elongation (%)
Jute	1.3–1.45	393–773	13–26.5	7–8
Flax	1.5	345–1100	27.6	2.7–3.2
Hemp	1.48	514	24.8	1.6
Ramie	1.51	400–938	61.4–128	1.2–3.8
Sisal	1.45	468–640	9.4–22	3–7
Coir	1.15	131–175	4–6	15–40
Cotton	1.5–1.6	287–800	5.5–12.6	7–8
E-glass	2.5	2000–3500	70	2.5
S-glass	2.5	4570	86	2.8
Aramid	1.4	3000–3150	63–67	3.3–3.7
Carbon	1.7	4000	230–240	1.4–1.8

Source: Fangueiro, R.; Rana, S. (Eds.), *Natural Fibres: Advances in Science and Technology Towards Industrial Applications*. Springer, ISBN: 978-94-017-7515-1.

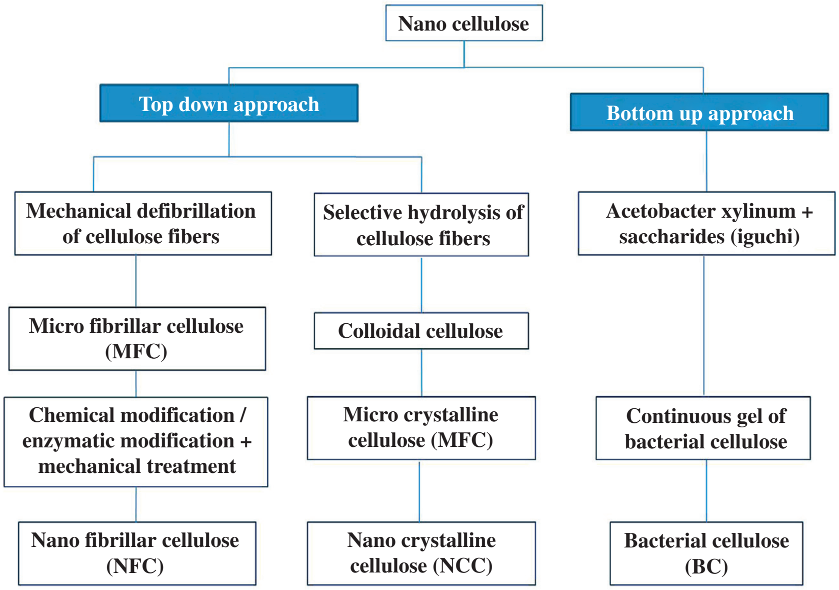


f0020 **Figure 13.3** Comparison of specific mechanical properties of natural fibers with synthetic fibers.
Source: Rana and Fangueiro.[15]

reduce the consumption of nonrenewable, nonenvironmentally friendly, and energy-consuming materials, such as concrete, metals, or synthetic fibers, in the above applications.

s0030 13.3.2 Properties of micro- and nanocellulose

p0045 Cellulose is an abundant biopolymer, and with the progress in nanotechnology the nano form of cellulose, i.e., nanocellulose has gained tremendous attention. The terminology MFC was first coined in the early 1980s when ITT Rayonier issued patents and publications based on a totally new nanocellulose composition.[16,17] In later years MFC was modified by acid hydrolysis to obtain NCC. Nanocellulose has now become a good alternative for other nanomaterials in various applications due to its remarkable mechanical properties, transparency, ability to form chiral nematic structures, and above all, owing to its lower health risk, environmental friendliness, and biodegradability.[18,19] Researchers are working with nanocellulose in diverse fields. It can act as a reinforcing agent for various matrices because of excellent mechanical properties, as well as due to the presence of free hydroxyl groups which can be modified according to the needs. Nanocellulose is also being explored in the biomedical field for drug delivery, enzyme immobilization, tissue culture, etc. Because of its transparency and barrier properties it can be utilized in packaging and as transparent flexible films.[18,19] Nanocellulose can be obtained by mainly two different approaches: a top-down approach and a bottom-up approach, as presented in Fig. 13.4.



f0025 **Figure 13.4** Different approaches for production of micro- and nanocellulose.

t0015 **Table 13.2 Comparison of properties of nanocellulose with other high strength materials**

Material	Density (g/cm^3)	CTE (10^{-6}/K) axial	Tensile strength (GPa) axial	Elastic modulus (GPa)	
				Axial	Transverse
Crystalline cellulose	1.6	0.1	7.5	120–220	11–57
Kevlar-49 Fiber	1.4	2	3.5	124–130	2.5
Clay nanoplatelets	–	–	–	170	–
Carbon nanotubes	–	–	11–63	270–950	0.8–30
Boron nanowhiskers	–	6	2–8	250–360	–

Source: Moon, R.J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. Cellulose Nanomaterials Review: Structure, Properties and Nanocomposites. *Chem. Soc. Rev.* **2011**, *40*, 3941–3994.

p0050 The top-down approach involves enzymatic or chemical/physical processes to isolate nanocellulose from wood and forest/agriculture residues. In the bottom-up approach nanocellulose is obtained from glucose by bacteria. The isolated cellulosic materials with one dimension in the nanometer range are referred to as nanocellulose. Nanocellulose can be categorized as nanowhiskers or NCC and nanofibrillar cellulose (NFC). When plant products are subjected to strong acid conditions combined with sonication, they produce nanowhiskers or NCC. Nanowhiskers are rod-like structures resulting from the hydrolysis of noncrystalline domains. The dimension of the nanowhiskers depends on the source of cellulose; their length ranges between 100–300 nm.[18–26] On the other hand, when plant products are subjected to high mechanical shearing without undergoing the hydrolysis steps, it results in NFC. The lateral dimension of NFC lies in the range of 10–30 nm. They are generally present in bundles, in which the individual fibril's lateral dimension is 5 nm.[18–26] The production method of nanocellulose is presented in Fig. 13.4 and the properties of nanocellulose have been compared with other materials in Table 13.2.

s0035 13.4 Processing of plant fiber-reinforced cementitious composites

p0055 Due to the corrosion problem of steel, there is an increasing need for alternative reinforcing materials for cementitious composites which can replace steel rebars. Following the use of various synthetic fibers, concrete has been also reinforced with various plant fibers, such as bamboo, coconut, sisal, flax, etc., for developing cost-effective and sustainable building constructions. However, prior to the use of t0020 **Table 13.3 Selected chemical surface treatment methods of plant fibers**[27]

Type of treatments	Advantages
Alkali treatment	Removal of lignin and hemicellulose, increases fiber tenacity, increase in surface roughness of fibers
Acetylation	Reduction of moisture absorption, improvement of chemical resistance and durability
Etherification	Introduction of desired chemical groups to enhance compatibility with different matrices
Peroxide treatment	Improvement of interface, decrease in moisture absorption, increase in fiber tenacity
Benzoylation	Decrease in plant fiber's hydrophilic nature
Acrylation	Significant improvement of fiber/matrix interface through covalent bonding
Silane treatment	Significant improvement of fiber/matrix interface through covalent bonding
Permanganate treatment	Decrease in plant fiber's hydrophilic nature
Graft copolymerization	Introduction of desired groups to enhance compatibility with different matrices and improvement of fiber/matrix interface

plant fibers in cementitious materials, they require various surface treatments, which have been discussed in Section 13.4.1.

s0040 13.4.1 Surface treatment of plant fibers

p0060 More commonly, plant fibers are treated with various chemicals such as alkali, water repellents, silane, peroxides, permanganates, etc. to reduce their moisture absorption and to improve their compatibility with various matrices.[27] Table 13.3 lists some commonly practiced chemical surface treatment methods of plant fibers and associated advantages.

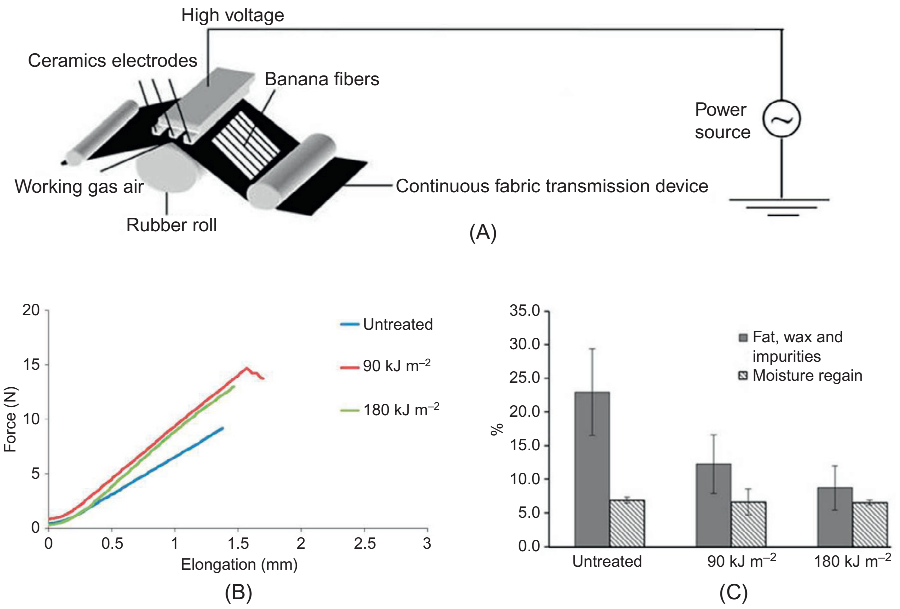
s0045 13.4.2 Plasma surface treatment and grafting process

p0065 Although quite efficient, the chemical surface treatment methods are not environmentally favorable due to production of waste chemicals and effluents. Recently, plasma surface modification has come out as a clean and dry surface modification technique of various polymeric fibers including plant fibers.[28–30] Plasma treatment can alter the surface characteristics in the nano scale without changing the bulk properties of the fibers.[28]

p0070 Industrial scale atmospheric plasma treatment machines have been developed for surface treatment of plant fibers in bulk at high processing speeds. Besides improving surface functionalities, wettability, as well as better plant fiber/matrix interfacial properties, plasma treatment could also improve the mechanical properties of plant fibers.[28,30] This opened the doorway of utilizing some newly explored plant fibers such as Quiscal in technical applications through improvement of their surface and mechanical properties by plasma treatment. Fig. 13.5 shows the atmospheric plasma treatment process and improvement of mechanical properties of Quiscal fibers through treatment with atmospheric plasma.[30]

p0075 Although plasma treatment can provide different types of functionalized surface depending on the type of gas used in the plasma reactor (air, oxygen, nitrogen, etc), this technique has limitations in terms of variety of surface modifications and stability of surface functional groups. Therefore, grafting of various polymers has also been carried out at the plasma functionalized surfaces in order to produce various stable functional groups as per the applications. This process, known as the plasma-induced grafting process, has been used recently by researchers to modify some plant fibers used in the apparel sectors, such as cotton, wool, silk, etc., to introduce flame retardancy properties.[31,32]

p0080 However, this process contains a chemical reaction step (grafting) and therefore, is associated with environmental pollution. The grafting step can be eliminated using the plasma polymerization process in which surface activation and



f0030 **Figure 13.5** Schematic of continuous atmospheric plasma treatment process for plant fibers (A), improvement in fiber tenacity (B), and removal of fiber impurities at different plasma treatment doses (C).
Source: Relves et al.[30]

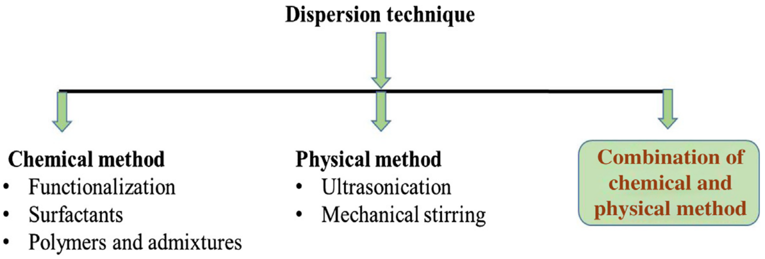
polymerization occur simultaneously. Plasma polymerization has been extensively used in anticorrosive surfaces and scratch resistance, chemical barrier, and water repellent coatings, since this is a clean and green (no solvent) process, reliable, reproducible, and suitable for wide varieties of monomers, different surfaces, and sample geometries.[33,34] Recently, plasma polymerization of hexamethyldisiloxane and tetramethyldisiloxane on to polyester and high performance fibers have been reported to impart superhydrophobicity and heat resistance properties.[33,34] Therefore, plasma polymerization process can also be utilized for plant fibers to create varieties of surface chemistries and topographies.

s0050 *13.4.3 Dispersion of micro- and nanocellulose*

p0085 This section will help the readers to have a general idea about the nanocellulose dispersion techniques, and to know the application potential of these techniques for cementitious composites as well. These are general dispersion techniques used for mainly aqueous system, various solvents and polymer matrices. The dispersion of nanocellulose within cementitious composites has not been much studied. On the other hand, Section 13.4.4 contributes some information about nanocellulose dispersion within a cementitious matrix.

p0090 NCC (nanowhiskers) have excellent mechanical and physicochemical properties.[19] NCC can be used in various sectors due to its advantageous properties (such as high surface area, interesting mechanical and optical properties), renewability and abundance. The properties of nanomaterials can be fully explored when they are well dispersed within the matrix. Incorporation of NCC in aqueous medium, solvents, or polymeric resin is carried out using physical or chemical techniques, as shown in Fig. 13.6.[19] In some cases, both physical and chemical techniques are used to obtain better dispersion in the matrix. Typically, NCC are produced as aqueous suspensions.

p0095 The dispersion of NCC in hydrophobic resins, therefore, requires evaporation of water. Drying of NCC can be achieved through a freeze drying or spray drying process.[35–41] However, NCC tend to agglomerate during the drying process. The formation of agglomerates can be reduced by optimizing the rate, time period, and temperature of drying, and also by surface modification of NCC.[35–41]



f0035 **Figure 13.6** Classification of NCC dispersion techniques.

s0055 13.4.3.1 Chemical modification of micro and nanocellulose

p0100 Chemical modification of NCC is performed to make desirable changes on the surface to widen its application in various matrices and solvents. Surface modification of NCC increases the compatibility with hydrophobic matrices and nonpolar solvents by decreasing the surface energy. NCC contain three hydroxyl groups in each pyranose ring. The hydroxyl group present on the 6th position is the primary hydroxyl group, which is more susceptible to any type of chemical modification.[42] The chemical modification techniques can be classified as noncovalent and covalent techniques. Noncovalent modifications are mostly carried out using surfactant or polymer coating. Surfactants/polymer coatings are adsorbed on the surface of NCC without affecting the chemical morphology and therefore, securing the integrity and strength of NCC. Covalent modifications include acetylation, esterification, cationization, silylation, fluorescence labeling, polymer grafting, etc.

s0060 13.4.3.2 Noncovalent modification of micro and nanocellulose

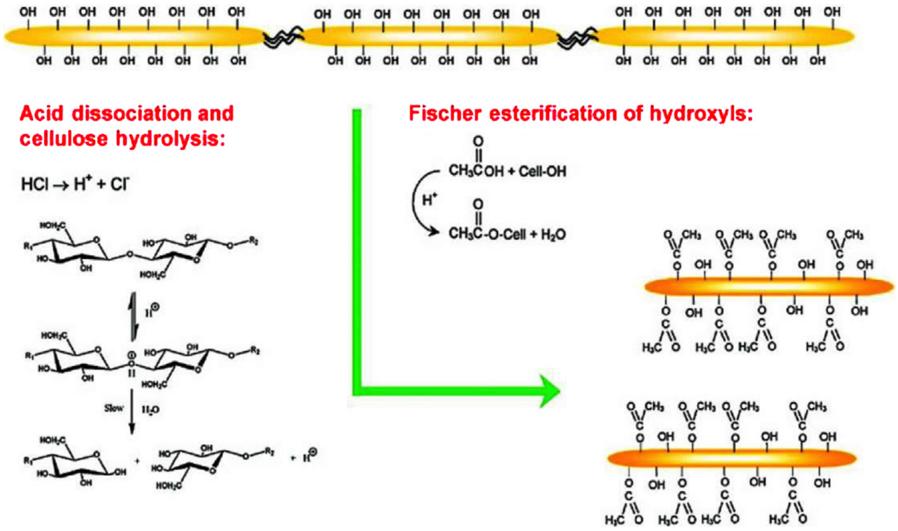
p0105 Noncovalent modification of MCC was first reported by Heux et al.[43] MCC was dispersed in aqueous suspension with the help of an anionic surfactant (acid phosphate ester of alkyl phenol ethoxylate) using MCC-surfactant ratio of 4:1. The resultant surfactant coated MCC was freeze dried in the form of pallets. The surfactant coated MCC pallets were easily dispersed in nonpolar solvents using ultrasonication energy for a small duration.[43] A similar procedure was also followed by Ljungberg et al.[44] and Fortunati et al.[45] for the dispersion of NCC.[44,45] Researchers also used cationic surfactants to form a stable dispersion in organic solvents. Kaboorani et al.[46] and Salajkova et al.[47] used quaternary ammonium surfactant, hexadecyltrimethylammonium (HDTMA) bromide, in aqueous medium to obtain surfactant coated NCC. Surfactant coated NCC suspensions were then centrifuged to eliminate excess surfactant from the NCC surface and then freeze dried to obtain dried NCC powder.[46,47] Cationic surfactant coated NCC can be easily dispersed in low polar solvents like tetrahydrofuran (THF). Another quaternary ammonium surfactant, cetyltrimethylammonium bromide (CTAB) has also been utilized due to its good adsorption onto NCC surface. According to Beaupré et al.,[48] almost 60% of surface hydroxyl groups were covered by CTAB when used at 5−7.5 wt% with respect to NCC. CTAB coated NCC has been used for drug deliveries.[48] Nanometal synthesis can also be done on the NCC surface using CTAB.[49] The density and particle size of metal nanomaterials synthesized on NCC surface were controlled by CTAB concentration, pH, and the reduction time.[48−50] The use of cationic alkyl ammonium surfactants, didecyldimethylammonium bromide (DMAB) and CTAB, have also been reported to prepare NCC Pickering emulsions.[51] The use of nonionic surfactant is also common to disperse NCC in hydrophobic polymer matrices. Kim et al.[52] used sorbitan monostearate to improve the dispersion of NCC in THF. Sorbitan monoesterate was found to improve the stability of NCC dispersion within hydrophobic polystyrene matrix.[52] Recently, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized NCC whiskers were dispersed using Pluronic surfactants (Pluronic L61 and L121) for fabrication of epoxy nanocomposites.[53] The use of

Pluronic led to better NCC dispersion and NCC/epoxy interfacial interactions, resulting in improved mechanical and thermal properties of the nanocomposites.

s0065 *13.4.3.3 Covalent functionalization of micro- and nanocellulose*

s0070 Acetylation and esterification

p0110 Acetylation and esterification of NCC have been carried out using a number of methods. In one of these techniques, acetylation was performed by treating fibrous as well as homogeneous NCC with acetic anhydride and acetic acid.[54] In case of fibrous NCC, acetylation only occurred in the cellulose chains present on the surface of NCC, which surrounded the unreacted NCC core. On the other hand, uniform acetylation was obtained in case of homogeneous NCC caused by the progress of acetylation reaction into the core, owing to dissolution of surface acetylated cellulose. In another method, an NCC suspension was mixed with an aqueous emulsion of alkyenyl succinic anhydride and the mixture was subjected to freeze drying and heating to perform acetylation of NCC.[55] Reaction with vinyl acetate in the presence of potassium carbonate catalyst has also been used to perform surface acetylation of NCC whiskers.[56] An increase in the reaction time, however, led to complete destruction of the crystalline structure of NCC whiskers. A combined method of NCC synthesis and functionalization has also been developed recently.[57] A mixture of acetic acid, hornificated cotton linters (HCL), and organic acids was used for the single-step synthesis and functionalization of NCC through the Fischer esterification process, as presented in Fig. 13.7. Gas phase esterification of NCC through evaporation in a large excess of palmitoyl chloride has also been



f0040 **Figure 13.7** Single-step synthesis and functionalization of NCC through the Fischer esterification process.
Source: Braun and Dorgan.[57]

reported.[58] Refluxing of hydrolyzed NCC in organic acid chloride is another approach for the esterification of NCC.[59] This method did not affect the crystalline core of NCC and resulted in grafting of NCC with organic fatty acids of different aliphatic chain lengths.

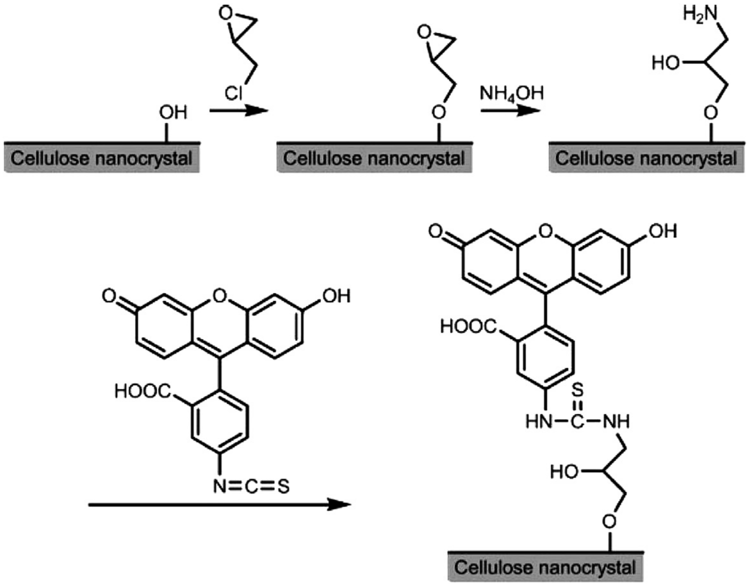
s0075 Cationization

p0115 Recently, a one-step process of cationization of NCC surface has been developed. In this process, epoxypropyltrimethylammonium chloride (EPTMAC) was grafted to the NCC surface.[60] The grafting occurred as a result of nucleophilic addition reaction of alkali-activated hydroxyl groups of NCC to the epoxy group of EPTMAC. The surface charge of NCC changed from negative to positive due to this grafting process and, as a result of positive surface charges, a stable aqueous suspension was obtained. The use of mild alkaline conditions in this process did not affect the original morphology or crystal structure of NCC.

s0080 Functionalization with fluorescein isothiocyanate

p0120 For fluorescence bioassay and bioimaging applications, which are based on tracking of localization of the fluorophores, NCC has been covalently functionalized with fluorescein-5′-isothiocyanate (FITC).[61] For this covalent functionalization, a three-step reaction route has been used, as shown in Fig. 13.8.

p0125 In the first step, NCC surface was functionalized with epoxy functional groups through reaction with epichlorohydrin. In the second step, primary amino groups were introduced by opening the epoxy rings through reaction with ammonium hydroxide.

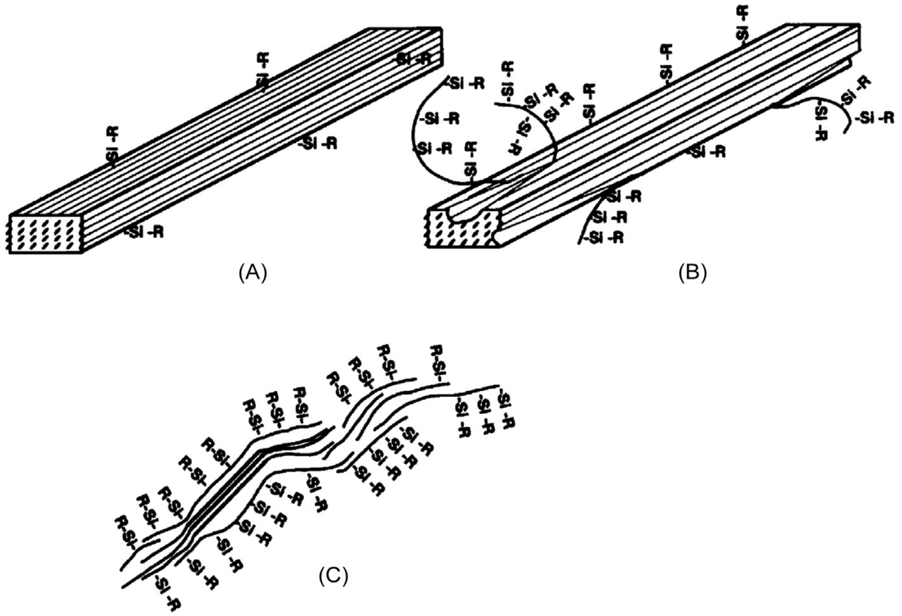


f0045 **Figure 13.8** Scheme for functionalization of NCC with FITC.
Source: Doug and Roman.[61]

In the final step, covalent bonding of FITC with NCC was achieved through reaction of primary amino groups of NCC with isothiocyanate groups present in FITC. The functionalization of NCC with FITC was confirmed through UV-Vis spectroscopy from the absorption peaks of FITC in the wavelength range of 450−500 nm.

s0085 Functionalization with silanes

p0130 Partial silylation of NCC whiskers has been carried out using a series of alkyldimethylchlorosilanes containing alkyl groups ranging from isopropyl to n-butyl, n-octyl and n-dodrecyl.[62] When the degree of substitution (DS) was between 0.6 and 1, the silylated NCC whiskers were dispersed easily in medium polarity solvents like acetone and THF. No change in morphology or crystal structure was observed when DS was maintained below 0.6. However, when DS was increased above 1, the structural integrity was disrupted. According to the model developed by the researchers, silylated NCC at low DS maintained its structural integrity and was hydrophilic (as shown in Fig. 13.9). When the DS was moderate, the surface of NCC was hydrophobic and it could be dispersed in THF (Fig. 13.9). And lastly, when the DS was high, the surface chains were solubilized and silylation progressed into the NCC core, resulting in disruption of the crystal structure of NCC



f0050 **Figure 13.9** Model explaining the silane functionalization of NCC at: (A) low DS showing onset of surface functionalization; (B) moderate DS showing surface functionalization; and (C) high DS showing disruption of NCC core.
Source: Goussé et al.[62]

(Fig. 13.9). In addition to the above process, trimethyl silylation of NCC surface, derived from BC, has also been reported.[25]

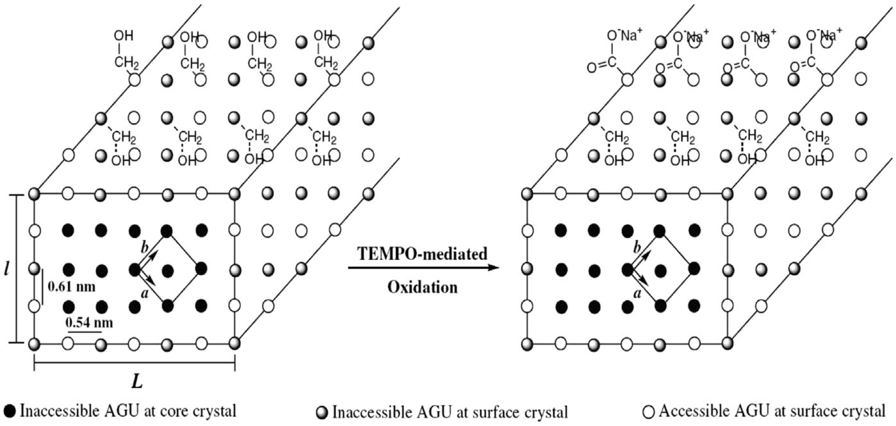
s0090 TEMPO-mediated oxidation and functionalization

p0135 TEMPO-mediated oxidation has been used to functionalize NCC with carboxylic groups.[63–65] This functionalization is carried out using TEMPO reagent in a NaBr and NaOCl environment by specifically oxidizing the primary hydroxymethyl groups.[66] Only 50% of the surface hydroxymethyl groups are oxidized in TEMPO-mediated oxidation, keeping the secondary hydroxyl groups intact. TEMPO-mediated oxidation is shown schematically in Fig. 13.10. This functionalization resulted in better aqueous dispersion of NCC due to electrostatic repulsion between the carboxylic groups and the resulting suspension showed a liquid-crystal-like behavior.

p0140 The degree of oxidation of NCC in TEMPO-mediated oxidation process could be controlled by varying the molar ratio of NaOCl over the anhydroglucose unit of hydrolyzed cellulose. Higher NaOCl molar ratio resulted in higher oxidation degree and carboxyl content; however, excessive oxidation led to the degradation of amorphous region of NCC affecting the structural integrity.[67] Once NCC is functionalized with carboxyl groups, it can be further grafted with various polymers to obtain different functionalities. Preparation of a "brush polymer" through grafting of poly (ethylene glycol) on to carboxyl functionalized NCC (obtained from TEMPO oxidation) has been reported.[68] In a recent study, NCC, after TEMPO-oxidation and amine grafting with tuned charge density, was used to control the morphology and stability of silver nanoparticles in aqueous suspensions.[69]

s0095 Functionalization through polymer grafting

p0145 Functionalization of NCC surface through polymer grafting has been frequently reported. In one approach, polymer chains were grafted to the NCC surface (known



f0055 **Figure 13.10** Schematic of TEMPO-mediated oxidation of NCC.
Source: Habibi et al.[66]

as “grafting to” approach), whereas in the second approach, polymer chains were grown on the NCC surface (known as “grafting-from” approach) through a graft polymerization process. In the first approach, polycaprolactone (PCL) of different molecular weights was grafted to NCC through the isocyanate-mediated coupling reaction.[21] At higher grafting density, crystallization of PCL on NCC surface was observed. Grafting of polyurethane onto NCC surface using the same approach has also been reported.[70] Carboxylated NCC, obtained through TEMPO oxidation, could be grafted with polymers through the peptide coupling reaction. Through this approach, grafting of PEG-NH_2 on to TEMPO-oxidized NCC surface was carried out through EDC/NHS [1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide/N-hydroxysuccinimide] carbodiimide chemistry at room temperature.[68] The same approach has also been utilized for grafting of DNA to the NCC surface.[71] Grafting of maleated polypropylene onto NCC surface has also been reported.[44] NCC with thermos reversible aggregation behavior, which can be used for designing stimuli-responsive bio-based materials, was prepared through grafting of thermo-responsive polymers onto NCC surface via a peptidic coupling reaction.[72]

p0150 In the graft polymerization approach (i.e., “grafting-from”), polymer chains have been grown on the NCC surface through the atom transfer radical polymerization (ATRP) process. In this process, first the hydroxyl groups of NCC surface were esterified with 2-bromoisobuturyl bromide (BIBB). In the second step, the selected monomers were polymerized. The grafting process on NCC surface could be controlled very precisely using this surface initiated ATRP technique.[73] The monomers which have been graft polymerized on NCC surface include styrene and N, N-dimethylaminoethyl methacrylate.[74–76] Azobenzene polymers were also grafted to NCC surface to produce a novel amphotropic hairy rod-like system exhibiting thermotropic and lyotropic liquid crystalline properties.[77] Another approach which has been tried for graft polymerization on NCC surface was through ring-opening polymerization. PCL was grafted to NCC through this approach using stannous octoate ($Sn(Oct)_2$) as the grafting and polymerizing agent.[21] The use of microwave irradiation was also used to improve the grafting efficiency onto the NCC surface.[78,79] Attempts were also made to use a novel in situ solvent exchange method for grafting of long-chain isocyanate groups onto NCC whiskers.[80]

s0100 13.4.4 Dispersion of micro- and nanocellulose within cementitious matrix

p0155 Due to the lack of research studies in the field of nanocellulose-reinforced cementitious composites, very little information is available on the dispersion of nanocellulose within cementitious matrix. The hydrophilic nature and water retention capability of NCC and MCC influence the yield stress of cement paste and hydration kinetics of cementitious composites. A suspension of MCC in water was prepared by Hoyos et al.[81] to study the amount of water absorbed by MCC. The aqueous suspension of MCC was prepared by mixing 0.5 g of MCC in 3 mL of water. The suspension was kept for three days at 25°C and centrifuged at 3000 rpm for 25 min to segregate the two phases. The saturated MCC samples were then quantified for the absorbed water. It was observed that MCC absorbed 230% of water with respect to its mass and 100% with respect to its volume. A similar procedure of MCC saturation was also adopted to prepare MCC-reinforced cementitious composites. Saturated MCC suspensions were prepared by adding MCC in an adequate amount of water and storing the suspension for two days. Then, the saturated MCC suspension was mixed with cement in a Hobart planetary mixer and additional water was added during the mixing process.[81] Cao et al.[82] used dispersed NCC (5.38 wt.%. cellulose nano crystals (CNCs) in water) obtained from the sulfuric acid hydrolysis of cellulose fibers. 0.81% surface of NCC was grafted by sulfate groups, which ensured homogenous dispersion of NCC in aqueous suspension. NCC-reinforced cement composites were prepared by mixing diluted NCC suspensions (0.1−3.8 wt.% w.r.t. cement) and water with cement with the help of a vacuum mixer. The vacuum mixer was set at the speed of 400 rpm for 180 s, and there was a pause after 90 s for scrapping the mixture from the bowl. The vacuum mixer was used to minimize the air entrapment during the mixing process and it also maintained the consistency of cement pastes.[82]

s0105 13.5 Properties of plant fiber-reinforced cementitious composites

s0110 13.5.1 Influence of plant fibers on the properties of cementitious composites

s0115 13.5.1.1 Influence of plant fibers on flow behavior of cement

p0160 It has been observed that the incorporation of plant fibers within cement mixtures reduces its workability, depending on the fiber volume fraction and aspect ratio.[83,84] The decrease in cement flow behavior caused by addition of plant fibers is attributed to their hydrophilic nature and absorption of water from the cement mixture. Therefore, in order to obtain a cement mixture with sufficient workability, either researchers needed to treat the surface to reduce their hydrophilicity or they presaturated or increased the water/cement ratio used, taking into account the water absorption of the plant fibers.[85]

s0120 13.5.1.2 Influence of plant fibers on setting time of cement

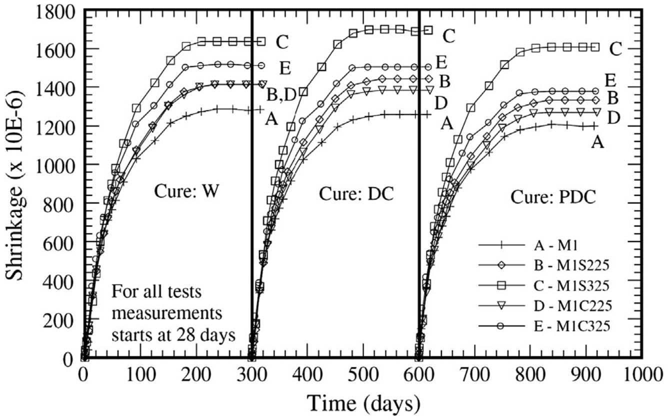
p0165 Plant fibers have shown a negative effect on the hydration behavior of Portland cement.[86−90] The reasons ascribed for this effect are (1) production of soluble sugars resulting from hydrolysis of lignin and partial solubilization of hemicellulose. Calcium compounds produced within the cementitious matrix due to dissolution of sugars retards the hydration process; (2) pectins present in plant fibers act as the inhibitor for the growth of calcium silicate hydrate (CSH); (3) carbohydrates and hemicelluloses present in wood and plant fibers decrease the rate of hydration of cement. The negative effect of plant fibers on cement hydration can be reduced through the addition of pozzolan, treatment of plant fibers to remove lignin, increased curing temperature, addition of chemical accelerators and supplementary materials, etc.[85]

s0125 *13.5.1.3 Influence of plant fibers on plastic shrinkage*

p0170 The addition of plant fibers was found to be beneficial to reduce plastic shrinkage and associated crack development in cement mortar.[91−95] The evaporation of water from the exposed surface of fresh mortar mixes results in volume contraction, which is known as the plastic shrinkage. Plant fibers could reduce considerably the maximum width and area of cracks, formed due to plastic shrinkage, owing to abridgement of cracks by fibers, reduced rate of settlement of particles, and decreased bleeding induced by fibers.[95]

s0130 *13.5.1.4 Influence of plant fibers on drying shrinkage*

p0175 Drying shrinkage is a very important property of cementitious composites influencing their durability. Drying shrinkage results from the loss of capillary water from the hardened cement mixture, leading to contraction and crack formation within concrete. According to the previous studies, the addition of plant fibers, such as sisal, to cement mortar increases its drying shrinkage.[93,96] This could be attributed to the high moisture absorption of plant fibers and also the increased porosity of mortar because of the addition of plant fibers. However, drying shrinkage of mortar strongly depends on the type and quantity of plant fiber, their surface characteristics and moisture absorption behavior. For example, Fig. 13.11 shows the influence of sisal and coconut fibers on the drying shrinkage of cement.



f0060 **Figure 13.11** Drying shrinkage of cement containing sisal and coconut fibers (*W*, water cure; *DC*, damp cloth-cured; *PDC*, pressure + damp cloth-cured; *M1*, mortar mix; *M1S225*, mortar mix with 2% sisal; *M1S325*, mortar mix with 3% sisal; *M1C225*, mortar mix with 2% coconut fiber; *M1C325*, mortar mix with 3% coconut fiber).
Source: Toledo Filhto et al.[93]

p0180 It can be observed that the addition of 2% and 3% of sisal fiber to the mortar mix led to an increase in drying shrinkage by 10% and 27%, respectively, in the case of water cured samples. Also, the drying shrinkage of composites containing 3% of sisal fibers was 8.2% higher than those reinforced with coconut fibers.[93]

s0135 13.5.1.5 Influence of plant fibers on mechanical properties

p0185 Reinforcement of cementitious matrix with plant fibers can significantly influence its mechanical properties.[97–106] Among the various properties, the impact resistance of cement mortar could be significantly improved through reinforcement of plant fibers, particularly coir fibers due to their higher elongation at break and higher toughness as compared to other plant fibers.[85] Impact resistance of cement mortar was improved by 18 times as compared to the unreinforced mortar specimens using coir fibers.[85] Table 13.4 lists the flexural strength and toughness of mortar reinforced with different plant fibers. It can be observed that the flexural toughness of mortar increased with the fiber volume fraction of plant fibers, while the optimum fiber volume fraction to achieve high flexural strength was 0.08–0.1. Among the plant fibers, due to its high aspect ratio and consequently high specific surface area, abaca fibers led to a strong improvement of cement flexural properties.[85]

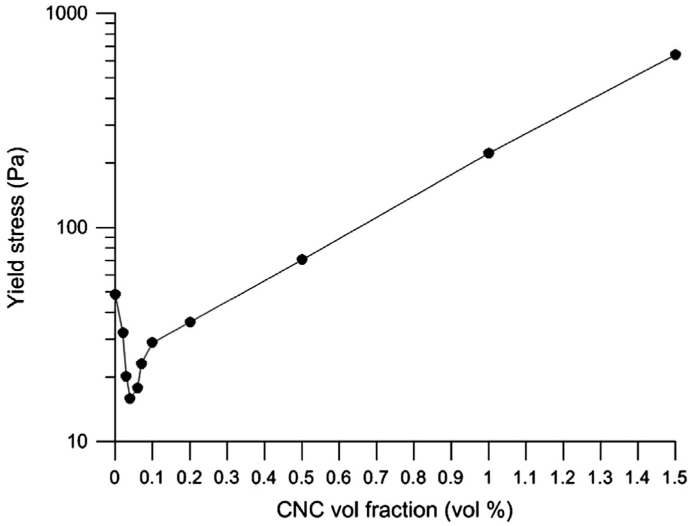
s0140 13.5.2 Effect of micro- and nanocellulose on the properties of cementitious matrix

s0145 13.5.2.1 Influence on flow behavior of cement paste

p0190 The mini slump test is performed for the analysis of flow behavior of cement to check the workability, according to Standard ASTM: C-143. In the freshly prepared cement paste, small particles interact via colloidal forces, such as Van-der Waals, electrostatic repulsion, steric hindrance, and hydrogen bonding, and some bigger particles interact via direct contact like friction or collisions. The yield stress (τ_0) is the stress necessary to break those interactions and separate the particles.[81] MCC (3 wt.% w.r.t. cement)-reinforced cement paste showed an increase of τ_0 by 2.6 times over plain cement paste. This may result in an increase of energy costs in construction. However, for certain construction applications, a higher τ_0 is necessary; for example, in rigid pavements where the fresh paste should retain its shape. Therefore, for these applications MCC reinforcement will be ideal.[81] Cao et al.[82] studied using a nanorheometer the influence of NCC [or CNC] vol.% on yield stress, as shown in Fig. 13.12. According to them, at lower NCC concentration (0.02–0.04 vol.% w.r.t cement), the yield stress decreased as compared to plain cement paste with the increase in NCC concentration. But on further increase in the NCC concentration, the yield stress again started to increase and at 0.3 vol.% of NCC (w.r.t. cement) the yield stress reached the value similar to that of plain cement. With a further increase of NCC (1.5 vol.% w.r.t. cement) the yield stress increased significantly as compared to plain cement paste. This contradictory behavior between 0.02–0.04 vol.% of NCC could be explained based on various t0025 **Table 13.4.** **Mechanical properties of cementitious composites reinforced with plant fiber**

Type matrix	Fiber type	Fiber content (%w/w)	Fiber aspect ratio	Flexural strength (MPa)	Flexural toughness $(kJ \cdot m^{-2})$
Paste	–	0	–	11.8 ± 3.7	0.04 ± 0.01
	Refined softwood sisal kraft pulp	4	53	19.2 ± 1.9	0.64 ± 0.09
		8		23.5 ± 0.8	1.32 ± 0.11
		12		25.0 ± 2.1	1.93 ± 0.42
	Unrefined waste sisal kraft pulp	4	122	16.5 ± 0.6	0.39 ± 0.06
		8		21.5 ± 1.6	0.92 ± 0.13
		12		20.3 ± 1.4	1.41 ± 0.20
	Unrefined banana kraft pulp	4	127	15.5 ± 1.3	0.21 ± 0.03
		8		19.5 ± 1.4	0.53 ± 0.08
		12		20.1 ± 2.5	1.01 ± 0.15
	Unrefined eucalaptus kraft pulp	4	61	15.6 ± 0.8	0.29 ± 0.04
		8		21.4 ± 0.9	0.82 ± 0.11
		12		22.2 ± 1.3	1.50 ± 0.18
	Sisal strand	4	89	14.4 ± 1.0	0.58 ± 0.17
	refined bamboo kraft pulp	2		10.9 ± 1.5	0.07 ± 0.01
		4		12.1 ± 1.3	0.15 ± 0.02
		6		16.2 ± 1.0	0.23 ± 0.02
		8		17.4 ± 0.9	0.32 ± 0.03
		10		18.6 ± 1.2	0.45 ± 0.07
		12		19.2 ± 1.5	0.54 ± 0.05
		14		21.8 ± 1.7	0.70 ± 0.06
	Refined abaca kraft pulp	2	400	17.5 ± 2.0	0.47 ± 0.10
		4		21.8 ± 2.1	0.93 ± 0.254
		6		26.3 ± 1.6	1.76 ± 0.48
		8		27.3 ± 3.2	2.08 ± 0.33
		10		24.7 ± 3.9	2.19 ± 0.78
Mortar	Unrefined sisal kraft pulp	0.5			0.25 ± 0.02
		1		9.2 ± 0.7	0.45 ± 0.03
		1.5		9.9 ± 0.8	0.62 ± 0.07
		2		11.3 ± 0.8	0.84 ± 0.08
		4		12.7 ± 1.2	1.64 ± 0.17
		6		15.9 ± 1.2	2.05 ± 0.29
		8		16.7 ± 1.0	2.49 ± 0.47
		10		15.0 ± 1.7	2.47 ± 0.46
		12		10.3 ± 1.6	3.07 ± 0.58

Source: Onuaguluchi, O.; Banthia, N. Plant-based Natural Fiber Reinforced Cement Composites: A Review, *J. Cem. Concr. Compos*. **2016**, *68*, 96−108.

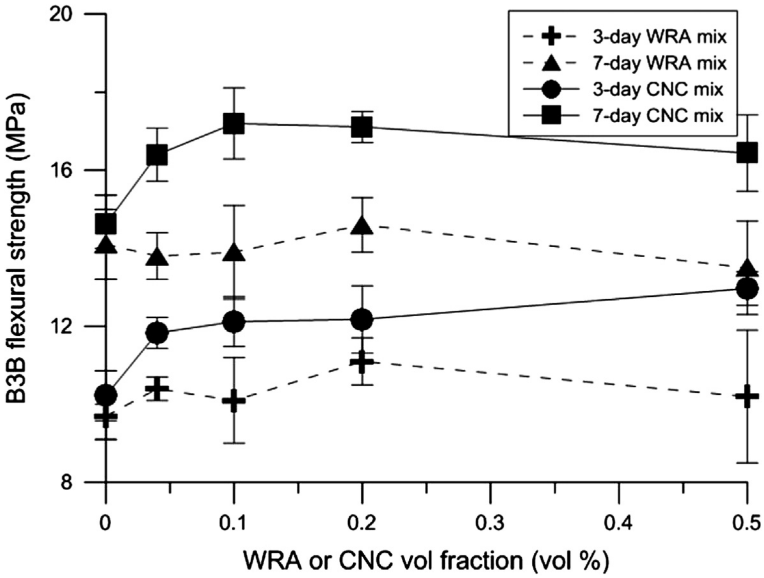


f0065 **Figure 13.12** Influence of NCC content (% by volume) on the yield stress of mortar paste. *Source*: Cao et al.[82]

interactive forces present between NCC particles during mixing with cement. At lower concentration, NCC particles behaved like cement admixtures (e.g., polycarboxylate) and promoted the degree of cement hydration by dispersing cement particles through steric stabilization mechanism. This resulted in lower yield stress as compared to plain cement paste. But, with the increase in NCC concentration, NCC particles started to agglomerate and the force required to break these agglomerates was very high, resulting in high yield stresses.[82]

s0150 *13.4.5.2.2 fluence on hydration and mechanical properties of cementitious composites*

p0195 It was observed that incorporation of 3 wt.% of MCC decreased the mechanical properties, such as flexural and compressive strength, of cementitious composite in a normal curing period of 28 days.[81] During accelerated curing conditions, which resulted in a higher degree of cement hydration, the above mechanical properties of MCC-reinforced cement just reached the values of plain cement mortar. As MCC could retain water due to its hydrophilic nature, at higher temperature (during accelerated curing) it released water leading to a greater formation of hydration products.[81] According to Cao et al.[82] NCC behaved as a water reducing agent at lower concentration (0.2 vol.%) and helped to disperse cement particles. The degree of hydration increased with the addition of an adequate amount of NCC. It was observed that NCC% could only be increased up to 0.5% as further increases resulted in the segregation of particles. The increase in flexural strength was 20%



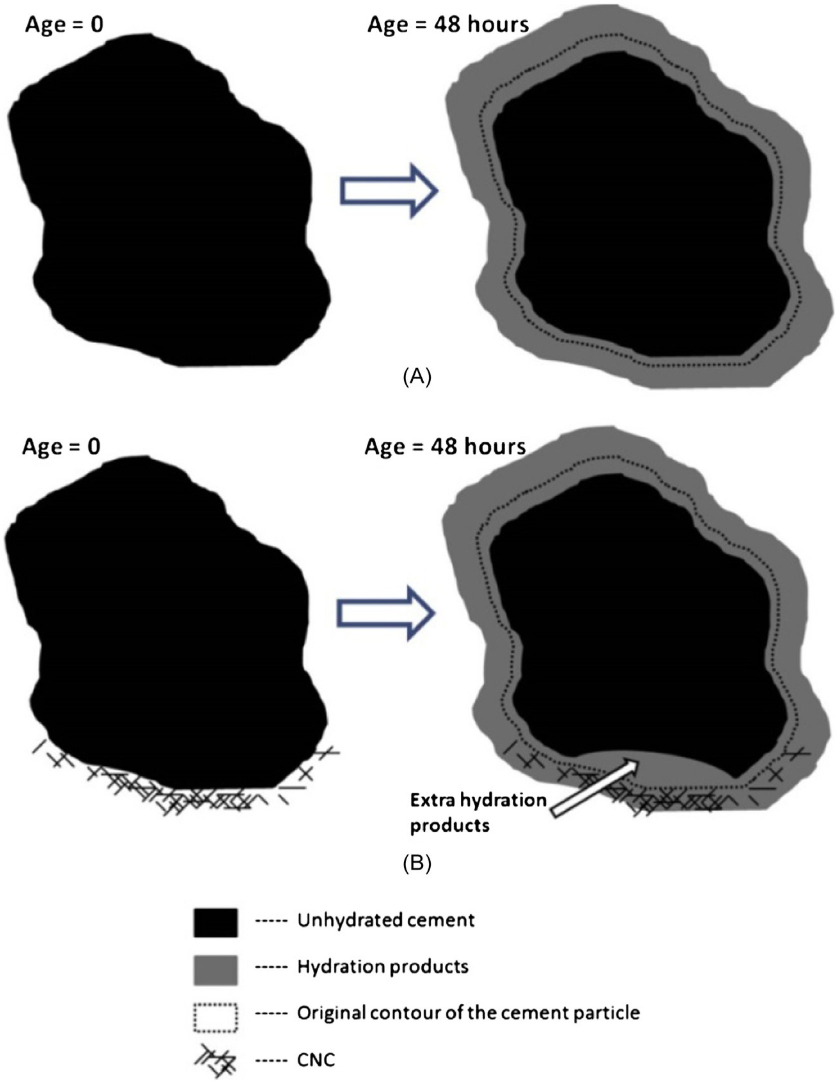
f0070 **Figure 13.13** Improvement of mortar's flexural strength due to CNC addition (*WRA*, Water reducing agent; *CNC*, Cellulose nanocrystals; *B3B*, Ball on three ball flexural testing method).
Source: Cao et al.[82]

and 30% in 3 and 7 days, respectively, with the addition of 0.2% of NCC (Fig. 13.13).

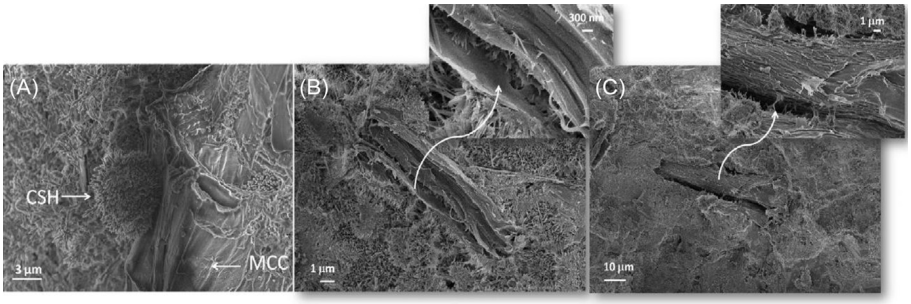
p0200 The improvement of flexural strength due to NCC addition was attributed to the improved hydration of cement owing to the steric stabilization of cement particles and short circuit moisture diffusion.[82] The short circuit diffusion was the penetration of water from the hydrated part of CSH (more dense part) to the unhydrated part with the help of NCC particles leading to better hydration,[82] as shown in Fig. 13.14.

s0155 *13.5.2.3 Effect on microstructure of cementitious composites*

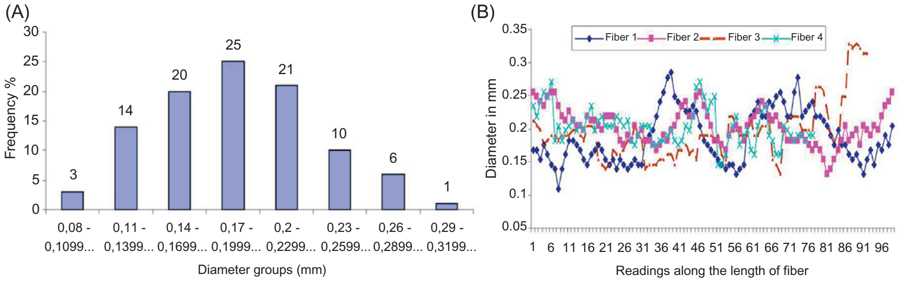
p0205 According to C. G. Hoyos et al.[81], MCC cement composites possess strong interface between MCC and hydration products of cement. The available hydroxyl groups of MCC can form hydrogen bonding with the hydration products of cement. MCC remains saturated with water and therefore, the CSH phase (cement hydration product) growing near MCC can utilize the water bound with MCC. Moreover, the size distribution of MCC is similar to CSH crystals making MCC a suitable reinforcement for cementitious matrix. The microstructure of MCC-reinforced cement is presented in Fig.13.15.



f0075 **Figure 13.14** Schematic diagrams explaining the short circuit diffusion mechanism: (A) plain cement mortar and (B) mortar reinforced with CNC.
Source: Cao et al.[82]



f0080 **Figure 13.15** FE-SEM image of cement-based materials with 3 wt.% of MCC at different magnifications.
Source: Hoyos et al.[81]



f0085 **Figure 13.16** Variability of diameter of banana fibers: (A) frequency diameter distribution and (B) diameter variation along the fiber length.
Source: Mukhopadhyay et al.[107]

s0160 13.6 Challenges with plant fiber-reinforced cementitious composites

s0165 13.6.1 Variability in plant fiber properties

p0210 One of the inherent drawbacks of plant fibers is the variability of properties.[85,107–109] The variability of their physical and mechanical properties mainly originates from the variation in their chemical structure and composition, such as cellulose content, degree of polymerization, orientation of molecular chains, crystallinity, etc.[85,107–109] These parameters are highly dependent on the growth conditions of the plant and also on the fiber extraction methods. Therefore, fibers extracted from different parts of the plants or grown in different locations and weather conditions present huge variability in their length, cross-sectional area, and mechanical properties.[85,107–109] An example of variability of plant fiber diameter is presented in Fig. 13.16. The distribution of diameter of 100 fibers, presented in Fig. 13.16(A), shows high variability among the different fibers. Even, within the same fiber, the diameter varies significantly along the length of fiber, as shown in Fig. 13.16(B). Besides chemical structure and composition, the mechanical properties of plant fibers were found to be highly dependent on the testing parameters, such as strain rate. A higher speed of testing and higher strain rate resulted in brittle failure mechanism and lower tenacity as compared to a lower strain rate which led to ductile failure of fibers, resulting in higher tenacity.[107]

p0215 High variability of plant fiber properties is a problem when developing products based on plant fibers. The prediction of properties and product designing become difficult. For structural applications, a higher safety margin is required when plant fibers are used as the reinforcement of cementitious composite-based structures.

s0170 13.6.2 Hydrophilicity of plant fibers

p0220 Plant fibers are hydrophilic owing to the presence of functional groups such as hydroxyl in their structure.[110] Therefore, plant fibers absorb a considerable amount of moisture from the surrounding environment. The moisture absorption capacity of plant fibers depends mainly on their chemical composition and crystallinity. Table 13.5 lists the moisture absorption of some selected plant fibers.[110]

p0225 The high moisture absorption of plant fibers leads to a number of problems when used for the reinforcement of cementitious materials such as[85,110]: (1) plant fibers swell due to absorption of moisture and shrink when moisture is removed due to dry atmosphere and elevated temperatures. Then, when plant fibers are used to reinforce cementitious matrix, their frequent swelling−shrinking phenomena leads to formation of cracks. This leads to reduced mechanical performance and durability of cementitious composites. (2) High absorption of alkaline solution present within the cement mixture leads to degradation of plant fibers with time. These result in the deterioration of properties of plant fibers as well as plant fiber-reinforced cementitious composites. (3) If plant fibers are not saturated, during mixing with cementitious materials they absorb considerable amount of water and reduce the water required for cement hydration. This leads to a reduced degree of cement hydration and, consequently, poor mechanical performance of cementitious

t0030 **Table 13.5** **Moisture absorption of plant fibers**

Fibers	Moisture absorption (%)
Sisal	110
Coconut	93.8
Bamboo	145
Hemp	85−105
Caesar wood	182
Banana	407
Piassava palm	34−108
Date palm	60−84

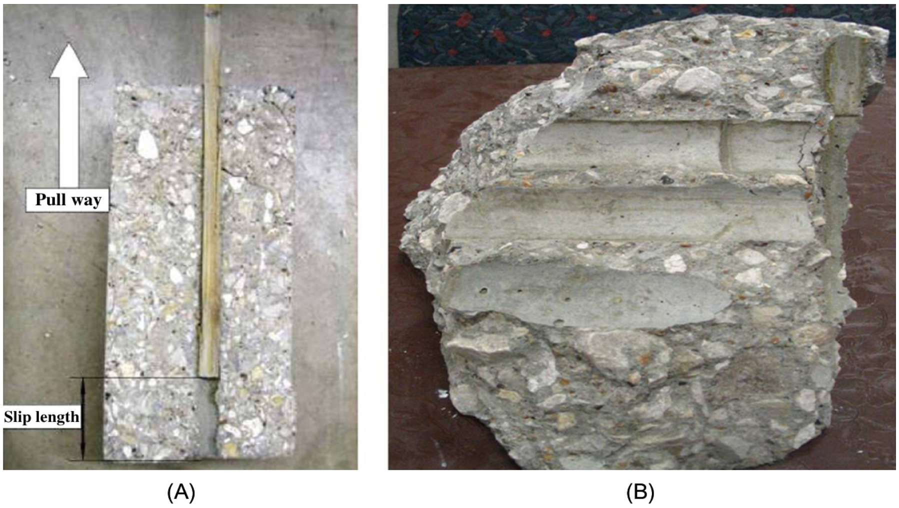
Source: Pacheco-Torgal and Jalali.[110]

composites. (4) Moisture absorption of plant fibers leads to breakage of hydrogen bonds between the fiber and cementitious matrix and, therefore, weakens the fiber/matrix interface and, consequently, it deteriorates mechanical strength. Therefore, a number of fiber surface treatment methods have been tried to reduce the moisture absorption of plant fibers for applying them in cementitious composites.

s0175 13.6.3 Fiber/matrix interface

p0230 Poor interface between the plant fibers and different matrices present one of the major problems with plant fiber composites. Poor interface results in inferior load transfer between fiber and matrix, resulting in lower mechanical performance. Before discussing interface between plant fiber/cement composites, a brief discussion has been provided about the plant fiber/polymer composite's interface, just to provide a general idea about the interface in plant fiber composites. Due to the hydrophilic nature of the fibers, the interface formed between plant fibers and hydrophobic polymer matrices is very weak.[27] On the other hand, the interface of plant fibers with hydrophilic matrices can be better as a result of interfacial hydrogen bonds. However, as discussed earlier, due to high moisture absorption of plant fibers, a breakage of interfacial hydrogen bonds occurs in the interfacial region, weakening the fiber/matrix bonding.

p0235 The interface between different types of reinforcement and brittle cementitious matrices in different scales is also very weak, which results in pullout when subjected to loading. Fig. 13.17 shows the complete pullout of a bamboo culm from



f0090 **Figure 13.17** Pullout test to measure bonding strength between bamboo culm and cementitious matrix (A) and imprint of bamboo fibers on cementitious matrix after pullout test (B)
Source: Khare.[111]

the cement composites, representing a very weak interface. The bonding strength of this type of bamboo rebars, obtained from pullout testing, is listed in Table 13.6 and compared with steel rebars. It can be observed that the bonding strength of bamboo rebars is even lower than the smooth steel rebars and much lower than the rough steel rebars used for construction applications. Therefore, it is highly essential to improve fiber/matrix bonding in case of plant fiber composites and various approaches have been tried for this purpose, as discussed in Section 13.6.4.

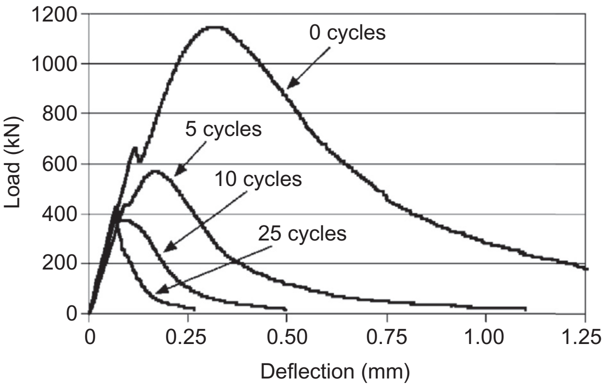
s0180 *13.6.4 Durability of plant fibers and reinforced structures*

p0240 Plant fibers are prone to degradation because of their high moisture absorption. Therefore, the long-term stability of plant fibers and plant fiber-reinforced cementitious composites is questionable. Additionally, the cement matrix presents an alkaline environment, which accelerates the degradation of plant fibers due to the dissolution of lignin and hemicellulose in alkaline solution from porous water. Fig. 13.18 shows the typical load-deflection curves in 3 point

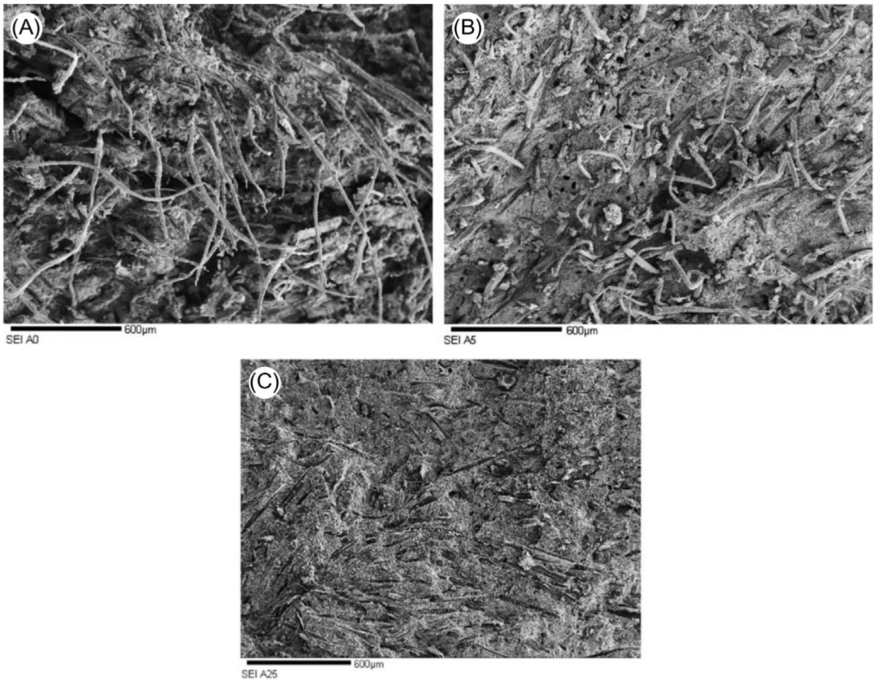
t0035 **Table 13.6 Bonding strength of bamboo and steel rebars with cementitious matrix**

Rebar type	Bonding strength (MPa)
Bamboo	0.81
Bamboo with epoxy	0.32
Smooth steel	1.33
Rough steel	6.87

Source: Pacheco-Torgal and Jalali.[110]



f0095 **Figure 13.18** Load-deflection curves of kraft fiber-reinforced cement composites subjected to different wet/dry cycles.
Source: Mohr et al.[112]



f0100 **Figure 13.19** Fracture surface of kraft pulp fiber cement composites showing progression of fiber degradation: (A) without wet/dry cycles; (B) after 5 cycles; and (C) after 25 wet/dry cycles.
Source: Mohr et al.[112]

bending mode of kraft pulp (KP) fiber (obtained from Slash pine softwood)-reinforced cement composites, subjected to wet/dry cycles.[112] The degradation of fibers due to wet/dry cycles led to 43.5%−52.0% loss of first crack strength, 50.8%−72.4% loss of peak strength, and 97.5%−98.8% loss of postcracking toughness of cementitious composites. The Scanning electron microscope (SEM) micrographs (Fig. 13.19) of fracture surface shows significant fiber pullout in the case of samples without wet/dry cycles, whereas significant fiber rupture occurred after 25 wet/dry cycles resulting from the brittleness of fibers after the degradation cycles.

p0245 Different studies which revealed the inferior durability of plant fiber-reinforced concrete are presented in Table 13.7 and various approaches to improve the durability of plant fiber-reinforced concrete are listed in Table 13.8.

p0250 One example of improved durability of pretreated plant fiber-cement composites is shown in Fig. 13.20. It can be observed that kraft softwood pulp (i.e., pulp obtained through kraft pulping of pine) and cotton linter-reinforced cementitious composites could provide better resistance to accelerated aging conditions after the hornification treatment.[130]

t0040 **Table 13.7** **Deterioration of properties of plant fiber and plant fiber-reinforced cementitious composites owing to degradation**

Type of fibers	Degrading conditions	Deterioration of properties
Coir, sisal, jute, and hibiscus fibers	Water, saturated lime, and sodium hydroxide (NaOH) solutions	Lignin, hemicellulose, and cellulose content decreased significantly.[113] Cement mortar containing the degraded fibers showed reduced mechanical strengths
Sisal and coconut fibers	Alkaline solution	Treated fibers completely lost their flexibility. Mortar containing treated fibers showed significant decrease in toughness[114]
Kraft pulp fiber-reinforced cement paste specimens	25 wet/dry cycles	Significant loss of mechanical properties[112]
Sisal and eucalyptus fiber-reinforced roofing titles	Weathering conditions	Drastic reduction in toughness of cement composites[115]

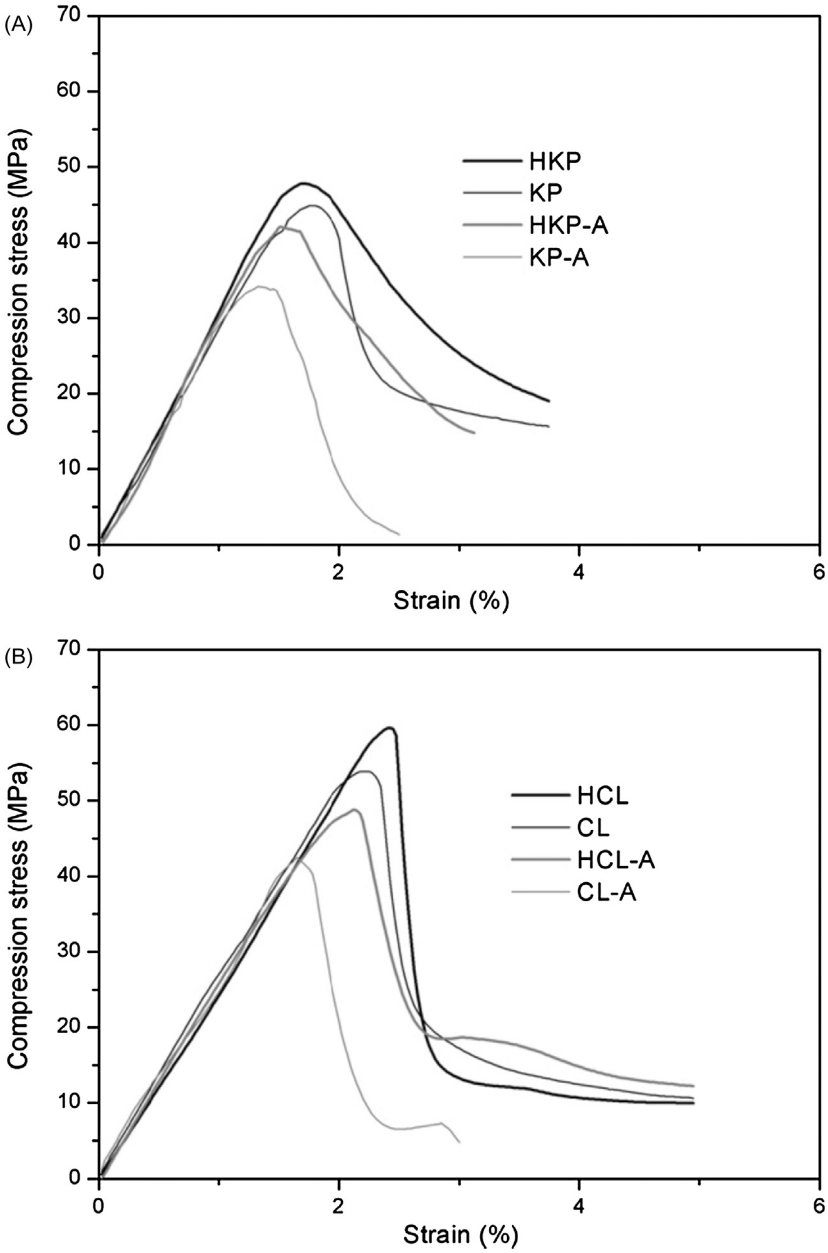
t0045 **Table 13.8** **Different approaches to reduce deterioration of performance of plant fiber-reinforced cementitious composites owing to degradation**

Approach	Strategies	Improvement of properties
Use of supplementary cementitious materials to substitute cement and reduce alkalinity	Undensified silica fume	Reduced degradation of plant fiber cement-based composites[116]
	Binary and ternary blends of slag, metakaolin, and silica fume	Reducing degradation of pulp fiber cementitious composites subjected to wet/dry cycles[117]
	Calcium hydroxide free cement matrix	Reduced loss of toughness and long-term embrittlement of sisal fiber-reinforced cement[118]
	Metakaolin and calcined waste crushed clay brick	4 times increase in ultimate bending strength and 42 times increase in toughness of sisal fiber-reinforced cement composites[119]
	Low alkaline ground granulated blast furnace slag cement	Reinforcing coir fibers appeared undamaged after 12 years[120]

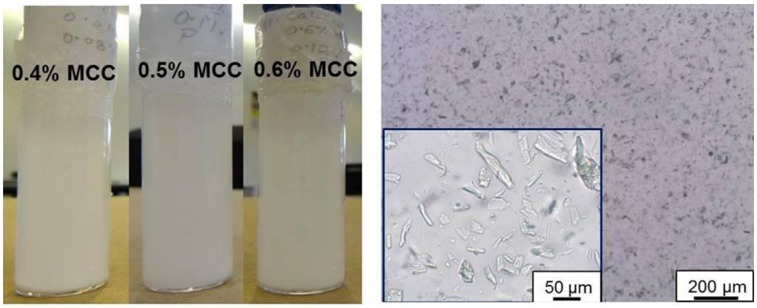
(*Continued*)

Table 13.8 **(Continued)**

Approach	Strategies	Improvement of properties
Pretreatment of plant fibers	Acetylation and silane treatment	Reduced moisture absorption of fibers leading to significant improvement in fiber/cement bond behavior[121]
	Alkali treatment	Improvement of fiber strength, fiber/cement bonding and toughness of plant fiber-reinforced cement composites[122]
	Bleaching	Removal of residual lignin and extractives resulting in deterioration of tensile strength of fibers, increased fiber softness resulting in better fiber/cement bond behavior, reduced fiber pull-out length and ductility of composites, increased peak mechanical strength of composites, reduced durability of composites resulting from increased mineralization of bleached fibers[123–126]
	Beating	Increases the fiber fineness, softness and fiber/cement interaction, modulus of rupture, limit of proportionality, and modulus of elasticity of cement composites[127,128]
	Hornification, i.e., alternate drying and rewetting of fibers to irreversibly reduce water retention	Improves fiber/matrix interface, dimensional stability of plant fibers, and durability of plant fiber cement composites[129–131]
	Pyrolysis at 200°C	Dehydrates chemical components of plant fibers, improves surface roughness and enhances fiber/cement interfacial bonding[132]
Specialized composite processing	Accelerated carbonation curing	Reduces alkalinity of cement mixtures, reduced pore volume due to precipitation of carbonate products, improves early strength gain, increases mechanical strength, increases durability by improving resistance to sulfate attack, water absorption, and chloride ion penetration, provides environmental benefits[133–137]



f0105 **Figure 13.20** Compressive strength of cementitious composites reinforced with (A) untreated kraft pulp (KP) and hornificated kraft pulp (HKP) and (B) untreated cotton linters (CL) and hornificated cotton linters (HCL); thin lines represent the aged (A) composites. *Source*: Claramunt et al.[131]



(A) (B)

f0110 **Figure 13.21** Stable microcrystalline cellulose suspensions prepared using Pluronic F 127: (A) aqueous suspensions; and (B) optical micrograph of 0.5% MCC suspension.
Source: Parveen et al.[139]

s0185 *13.6.5 Dispersion of micro- and nanocellulose*

p0255 Dispersion of nanomaterials is one of the primary problems in successful development of nanocomposites.[138] Nanomaterials form agglomerates owing to strong attractive forces acting between them and it is a challenging task to disperse them homogeneously in an aqueous medium or in different matrices. Therefore, the first and foremost step towards developing nano/microcellulose-reinforced cementitious composites is to prepare highly homogeneous and stable aqueous suspensions, which can be subsequently added to the cement mixture. Direct mixing of micro/nanocellulose powder with cement mixture may not ensure homogeneous dispersion, as is also observed in case of carbon nanotubes.[2] For practical applications in the civil construction industry, the micro/nanocellulose suspensions AWE should have high storage stability so that they can be stored for a long time period before mixing with cementitious materials. As discussed in Section 13.4.3, micro/nanocellulose can be dispersed in aqueous medium by various mechanical and chemical methods. Their dispersion stability can be improved through chemical functionalization or using surfactants. For example, Fig. 13.21 shows the stable suspensions of MCC prepared using Pluronic F 127 surfactant (BASF)[139].

s0190 13.7 Applications

p0260 Plant fibers have huge potential for applications in the construction industry. Several research studies conducted to date have proved that plant fibers could be low cost and light weight reinforcing materials for cementitious composites. The future of micro/nanocellulose-based cementitious composites is also promising for structural applications. Apart from the reinforcement of cementitious composites, plant fibers can have other applications in the building industry such as (1) plant fibers can be used as thermal insulation materials in building construction to conserve energy.[140] Plant fiber composites (from cotton and sunflower stalks) insulation materials exhibited suitable mechanical and thermal performances, which satisfactorily met the requirements of the Turkish TS 805 EN 601 insulation material application standard.[141] The use of nanocellulose-based aerogel materials to improve thermal and sound insulation in buildings can be highly effective. (2) Micro/nanocellulose can be used in building construction to significantly reduce the permeability of cement-based materials and, consequently, to improve their durability.[142] (3) Wet sprayed plant fibers can also be used as a surface curing agent for repairing concrete infrastructures.[143]

s0195 13.8 Conclusions and future trend

p0265 Plant fibers show high potential as reinforcing materials of cementitious composites. Addition of plant fibers showed significant enhancement in the impact resistance, toughness, and strength of cementitious composites. Additionally, they are advantageous to reduce the plastic shrinkage and associated crack formation of cementitious matrices. The use of nano- and micro-dimensional plant fibers such as nano- and microcellulose showed still higher improvements in the performance of cementitious composites. The problems associated with the plant fibers mainly come from their high moisture absorption. This led to their negative effect on cement hydration, drying shrinkage, interface with cement, and durability of cementitious composites. Therefore, it is highly essential to modify the surface of plant fibers to reduce their hydrophilicity. Among the various surface treatment methods, physical techniques such as plasma and corona treatments are much more favorable over the chemical techniques in terms of environmental pollution and sustainability. At present, machines for continuous plasma treatment of fibers and textiles on the industrial scale are available and can be utilized for developing plant fiber-based cementitious composites. Although micro- and nanocelluloses show huge potential as a reinforcement of cement, their dispersion still presents a big concern. Stable and well dispersed aqueous micro/nanocellulose suspensions could be obtained through their chemical functionalization, which introduces an additional step in the process. Therefore, more research and developments are required for successful application of micro- and nanocelluloses within cementitious composites.

p0270 Despite tremendous research work on plant fiber-reinforced cementitious composites, up until now their practical applications are very few. One of the main problems in applying plant fibers within cementitious composites is the lack of design standards on fiber-reinforced concrete. Therefore, considerable effort should be directed towards developing suitable design codes and guidelines to increase the application of plant fibers in the civil construction industry.

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Abstract

Nowadays, the use of plant fibers in the civil construction industry is growing rapidly due to their low cost, light weight and good specific mechanical properties, lower health hazard, and environmental benefits. Nanodimensional fibers derived from plants such as nanocellulose are also getting considerable attention due to their excellent mechanical properties. This chapter discusses these different types of plant fibers and their derivatives which have huge application potential in the civil construction sector. The influence of plant fibers on microstructure as well as on physical−mechanical properties of cementitious composites are discussed in detail. The challenges regarding plant fiber processing and dispersion, the fiber/matrix interface, and the durability of plant fiber-cement composites are also addressed. The application of nanocellulose in polymer composites has been included in this chapter just to provide the readers sufficient background information and techniques to inspire engineered cement-based composites. Finally, the chapter concludes with the current application of plant fibers in civil construction and the future trends.

Keywords: Plant fibers; nanocellulose; cementitious composites; mechanical performance