Biomass-derived nanocellulose modified cementitious composites: A review

Biomass-derived nanocellulose modified cementitious composites: A review

Dongyu Wang[1], Sufen Dong[2, *], Ashraf Ashour[3], Xinyue Wang[1], Liangsheng Qiu[1], Baoguo Han[1, *]

[1]*School of Civil Engineering, Dalian University of Technology, Dalian, 116024 China*
[2] *School of Transportation and Logistics, Dalian University of Technology, Dalian, 116024 China*
[3] *Faculty of Engineering & Informatics, University of Bradford, Bradford, BD7 1DP, UK*
** Corresponding author: dongsufen@dlut.edu.cn, hithanbaoguo@163.com*

Abstract

Cementitious composites, the most abundant human-made materials in the world, are challenged to be more sustainable, durable and cost-effective to adapt to the development of structural engineering, economy and environment. Owing to their excellent strength, toughness and durability, nano-fillers reinforced cementitious materials have attracted broad attention in civil engineering researches and applications. However, it is worth noting that nano-fillers reinforced cementitious materials achieve their proprieties by using of different industrial nano-fillers, i.e., graphenes, carbon nanotubes, carbon nanofibers, etc. Although the properties of conventional cementitious materials are improved, the incorporation of the above nano-fillers are high cost and environmental footprint. Different from high-energy consuming carbon nanofillers, nanocellulose is one of the biomass-derived nanofillers with excellent nanometer properties, biological performances and composite effects, and it has proved to be a promising green filler to enhance the mechanical properties, durability and functional properties and lower the carbon footprint of cementitious composites. Therefore, this paper provides an overview on biomass-derived nanocellulose modified cementitious composites, mainly focusing on their fabrication, properties (early performance, mechanical performance, durability, and functional performance) and applications. It also concludes with an outline of some future opportunities and challenges in the development of biomass-derived nanocellulose modified cementitious

composites.

Key words: Nanocellulose; Cementitious composites; Fabrication; High-performance; Application

Content

1. Introduction

Cementitious composites are the most widely used construction materials for infrastructures due to their good workability, durability and high strength [1-4]. However, using cement as glue materials poses a vast array of growing threat for social sustainable development, resulting in some environmental issues, such as high carbon footprints, dust emissions and energy consumption [3, 5]. Therefore, it is the future development direction of cementitious composites to achieve both extraordinary mechanical properties and sustainable development characteristics [3, 5-15]. Previous studies have proved that the incorporation of industrial nanomaterials, such as

graphenes, carbon nanotubes (CNTs), nano carbon black (NCB), nano-TiO_2 (NT) and nano-ZrO_2, can greatly improve the strength, toughness and durability of cementitious composites, endowing infrastructures with high safety and low life cycle cost [1-2, 7-9, 16-20]. The study of Zhang et al. [1] showed that an addition of 1.41 % CNT/NCBs can increase the flexural and compressive strengths of cementitious composites by up to 7.7 MPa and 30.7 MPa, respectively. Li et al. [7] reported that the compressive strength of cementitious composites can be increased by 18.5% when NTs with the diameter of 10 nm are used as nanofillers. The enhancement of mechanical properties and durability of cementitious composites can be attributed to the small sizes, high specific surface area, high tensile strength, and high elastic modulus of nanofillers [2, 6-9, 16-18, 21]. Meanwhile, nanofillers can also bridge cracks and transfer stress at the nano-scale to further improve the toughness of cementitious composites [2, 21-22]. However, the manufacturing cost, energy consumption and carbon footprint of the above industrial nanofillers are high, thus restricting the wide application of nanofillers reinforced cementitious composites in civil engineering infrastructures [5, 21, 23-24].

Biomass-derived nanocellulose, as one of the economical, environmentally-friendly, pollution free, renewable, and sustainable nanofillers, is now attracting extensive attention of researchers [3, 5, 9, 13, 15, 25-29]. Fig. 1(a) illustrates the production process of nanocellulose from the plants [12]. According to different preparation methods, nanocellulose can be divided into three categories: cellulose nanocrystal (CNC), cellulose nanofibril (CNF) or nano fibrillated cellulose (NFC) and bacterial nanocellulose (BNC) [5, 13, 18, 21, 30]. CNC can be produced by acid hydrolysis. In this process, the strong acid can destroy the amorphous zone arranged loosely while retain the nanocrystals in cellulose, as shown in Fig. 1 (b) [3, 31-32]. CNF is obtained by the mechanical treatment of cellulose, and the inner structure of CNF contains

crystallized and amorphous state [33-34]. Because the crystallinity of BNC is prepared by bacteria between common high plant fibers and animal fibers, as shown in Fig. 1(c), its production mainly includes bacterial fermentation and purification [3, 35].

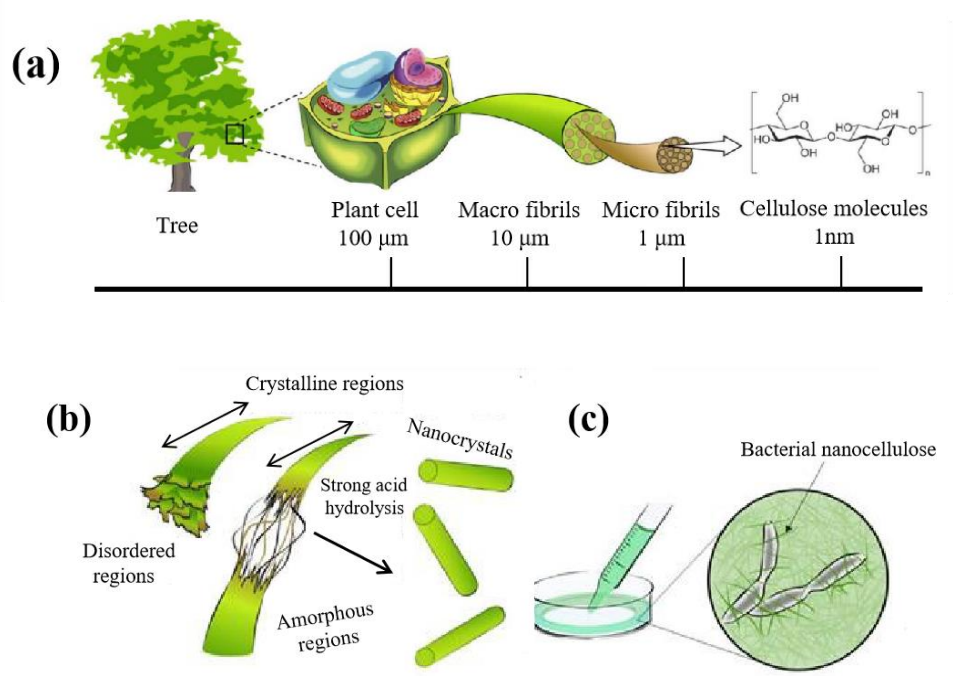

Fig. 1. Production process of nanocellulose: (a) The structure of cellulose derived in plants from the micro scale to the nanometer scale; (b) The extraction process of cellulose nanocrystal (CNF); (c) The preparation of bacterial nanocellulose (BNC) [12]

Because nanocellulose is derived from natural-based cellulose in wood, plants, and bacteria, it has unique biological performances and becomes a promising biopolymer to minimize carbon footprint, facilitate the resources cycle and promote sustainable development of ecosystem. For example, biomass-derived nanocelluloses have been successfully used in the form of adhesives, paper-based products, and drilling fluids [16, 21, 28, 35-36]. Meanwhile, the biological and nano-size effect of nanocellulose makes it an excellent filler for improving the mechanical and durability performance and lowering the carbon footprint of cementitious composites [9, 22, 28-29]. Lv et al. [37] first proposed that the addition of BNCs can increase the content of calcium-

silicate-hydrate (C-S-H) in the hydration products of cementitious composites. Flores et al. [38] also observed that more generated C-S-H can be found in cementitious composites with CNCs, but the addition of CNCs delays hydration of cementitious composites at early stage while enhances hydration at later stage. Mejdoub et al. [29] revealed the addition of 0.3 wt.% NFCs increases the degree of hydration (DOH) by 102%, 23% and 28%, compared to the control mixture at the curing ages of 1 day (d), 7 d and 28 d, respectively. Similar enhancement effect of nanocellulose on DOH of cementitious composites is observed by Onuaguluchi et al. [27]. In addition, Cao et al. [9] studied the mechanical properties of nanocellulose filled cementitious composites and revealed that the flexural strength of cementitious composites with CNCs is increased by 20%-30% compared to the control group. In the study of Sun et al. [39], the effect of CNFs on the rheological properties of oil well cement (OWC) was investigated. They showed the yield stress and plastic viscosity of cementitious composites are increased with the content increase of CNFs. When the content of CNFs increases from 0 to 0.28 wt.%, the yield stress and plastic viscosity rates of the composites can be enhanced by 108% and 149%, respectively. Barnat-Hunek et al. [40] first reported the modification effect of nanocellulose on durability of cementitious composites in detail, including the permeability resistance, frost resistance and resistance to sulfides.

According to the above survey, the incorporation of biomass-derived nanocellulose can not only modify the workability of cementitious composites but also enhance the microstructure of hydration products, consequently, improving the macroscopic mechanical properties of cementitious composites. Meanwhile, the nano-size of nanocellulose is clearly beneficial in achieving more compactness and excellent durability of biomass-derived nanocellulose modified cementitious composites.

Furthermore, the environmentally-friendly and pollution free impact of biomass-derived nanocellulose significantly reduce the environmental footprint of cementitious composites, thus endowing engineering structures with sustainability and low-carbon characteristics. To our knowledge, there is no research to systematically conclude the effect of different types of biomass-derived nanocellulose on the properties of cementitious composites from early hydration to later hardened performance. Therefore, the fabrication, early performance, mechanical properties, durability, and multi-function performance of biomass-derived nanocellulose modified cementitious composites are comprehensively analyzed in this paper. Moreover, the engineering applications and further research directions are proposed in order to lay a foundation for the development and application of composites.

2. Fabrication of biomass-derived nanocellulose modified cementitious composites

2.1 Raw materials

The main raw materials of biomass-derived nanocellulose modified cementitious composites mainly include nanocellulose, cement, fine aggregate, coarse aggregate, admixture and water. The commonly used admixtures include bentonite, metakaolin, eucalyptus pulp, fiber and superplasticizer (SP). Nanocellulose with high specific surface area was mainly used in two different forms, i.e. powder and gel, as shown in Table 1. Table 1 indicates that the particle size of powder type nanocellulose varies from 3 nm to 250 nm and the length is from 0.044 μm to 0.8 μm. The density of used powder type nanocellulose is 1.4-1.6 g/cm^3. Besides, the particle size of gel type nanocellulose is between 5 nm and 93 nm. Fig. 2 exhibits the relationship between specific surface area and particles of nanocellulose used in cementitious composites [31].

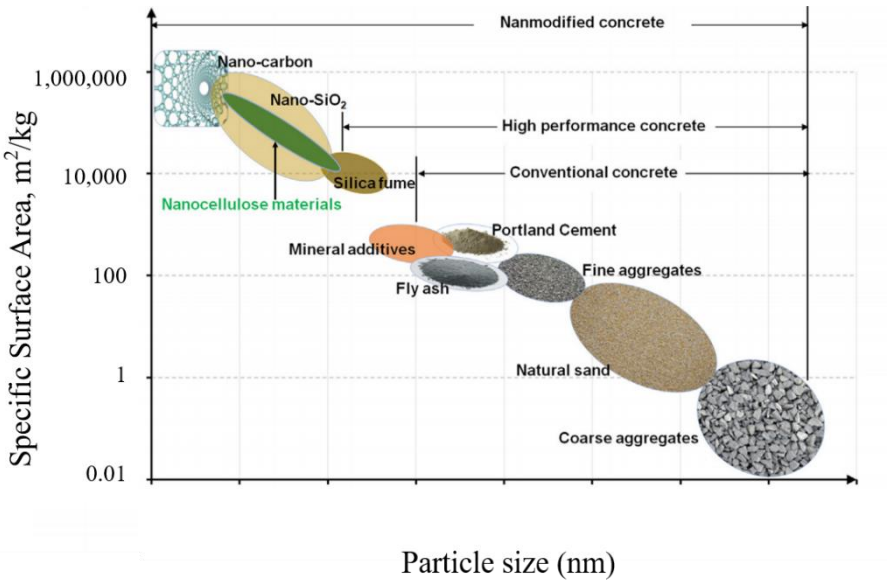

Fig. 2. Relationship between particle size and specific surface area of biomass-derived nanocellulose [31]

Table 1 Physical properties of biomass-derived nanocellulose

Nanocellulose types	Particle size (nm)	Length (μm)	Specific surface area (m^2/g)	Density(g/cm^3)	References
Powder	5-10	0.10-0.30	-	-	[41]
	22-80	-	-	-	[42]
	25-250	-	-	-	[43]
	20	0.10	-	-	[44]
	50-90	0.40-0.80	-	-	[45]
	5-20	-	-	-	[46]
	20-50	-	-	1.4	[47]
	4-20	0.50-2.00	140-160	-	[39]
	90	0.70	-	-	[38]
	83-93	0.996-1.209	-	-	[28]
	10-60	0.05-0.60	-	-	[16]
	2.3-4.5	0.044-0.108	400	-	[25]
	3-5	0.05-0.50	-	1.6	[48]
	3-5	0.20		-	[49]
Gel	22-80	-	-	-	[42]
	5-10	-	-	-	[29]
	83	-	-	-	[28]
	85-90	0.935-1.080	-	-	
	5-20	0.50-3.00	-	-	[50]
Coating	22-80	-	-	-	[42]

Note: "-" indicates no measurement in the references given.

2.2 Mix proportions

The mixing proportion of biomass-derived nanocellulose modified cementitious composites is mainly determined by types of cement, aggregate, water to cement ratio

(w/c), contents of nanocelluloses and types of admixtures. The types of cement used in previous researches for biomass-derived nanocellulose modified cementitious composites are shown in Table 2 [6, 16, 9, 28-32, 39-40]. Because nanocellulose is likely to exert enhancement effect in the dense matrix, the application matrix in previous studies mainly focused on cement paste and cement mortar [32]. The detailed mix proportions of biomass-derived nanocellulose modified cementitious composites are listed in Table 2.

Table 2 Mix proportions of biomass-derived nanocellulose modified cementitious composites

Matrix Types	Cement types	Aggregate types and size	Nanocellulose content (wt.% of cement)	Admixture types and content	Proportion of C (B), W, S and G	References
Cement paste	Type G oil well cement	-	1	Bentonite (3% w/v of water)	C: W=1:0.44	[41]
	Ordinary Portland Cement	-	1	Metakaolin (25 wt.% replacement of C); Eucalyptus pulp (8 wt.% of cement)	-	[51]
	Portland Cement type II	-	6, 7 wt.% of fiber	Calcium chloride (5 wt.% of C) SP (0.5 wt.% of C) Fiber (6, 7 wt.% of fiber)	-	[42]
	Type V Cement	-	0.04, 0.1, 0.2, 0.5, 1.0, 1.5 (vol.% of cement)	-	C: W=1:0.35	[9]
	Type H Well Cement	-	0.04, 0.12, 0.20, 0.28	-	C: W=1:0.38	[39]
	Ordinary Portland Cement	-	0.01, 0.05, 0.1, 0.2, 0.3, 0.5	-	C: W=1:0.26	[29]
	Ordinary Portland Cement	-	0.05, 0.10, 0.15, 0.25, 0.40	-	C: W=1:0.35	[45]
	Portland Cement type I/II	-	0.4, 0.8	-	C: W=1:0.4	[38]

Portland Cement type I/II	-	0.2, 0.5, 1.0 1.5	-	C: W=1:0.4	[28]
Type V Cement	-		-	C: W=1:0.36	
Portland Cement type I/II	S, G	CNF (0.1-0.3)	-	C: W=1:0.45-1:0.75	[31]
Type H Well Cement	-	CNC, CNF (0.05, 0.10, 0.15, 0.20)	-	C: W=1:0.40-1:0.60	[52]
UNE-EN14647:2006 Calcium aluminate cement (CAC) UNE-EN 197-1:2011 OPC	-	CNC or CNF (0.1-0.8)	SP	-	[32]
Class G Oil Well Cement	-	-	-	C: W=1:0.44	[16]
Argentinian Low-alkali Cement	-	CNF (0.1-0.4)	-	C: W=1:0.45	[53]
Portland Cement type I	-	CNF（1.5 wt.% of w/c）	-	C: W=1:2/1:1/1:3	[50]
Portland Cement type I	-	0.0, 0.05, 0.10, 0.20, 0.30 (vol.% of cement)	HRWRA	C: W=1:0.3	[6]

	High Early Strength Cement (Votoram)	-	CNC (0.0-1.0)	SP	C: W=1:0.35	[30]
	Portland Cement type I 42.5 R	-	CNC（0.2, 1.0）	SP	C: W=1:0.35	[42]
Cement mortar	-	S	15, 25, 50, 75	-	C: W:S=1:0.45:3	[48]
	-	Silica sand	1, 3, 5	SF Silica flour SP	C: W=1:0.2415	[54]
	Portland Cement	S	1, 3, 5	SP, SF and silica flour (1.6, 39 and 28 wt.% of C)	C: W: S=1: 0.21:0.98	[55]
	Class H Well Cement	Silica sand	0.1, 0.5, 1.0	SF, silica flour and SP (37.90, 27.68 and 1.45 wt.% of C)	C: W=1:(0.2155/0.2522/0.2995)	[44]
	UNE-EN 197-1:2000 Type I cement	S (<0.1mm)	-	Fluidizer (4 wt.% of C) Sisal pulp	-	[43]
	UNE-EN 197-1:2000 Type I cement	S	2, 4, 6, 8	SF (10 wt.% replacement of C) Fluidizer (4wt.% of C) Sisal pulp	C: W:S=1:(0.65/ 0.63/ 0.59/0.56):1.11	[46]
	Portland Cement type I 52.5	S (0-2 mm)	2.33	Slag (83.3 wt.% of C) SP (5.5 wt.% of C)	C: W:S=1:0.31:1.64	[47]
	Ordinary Portland Cement	20-30 S (850-600 μm); Graded sand (600-150 μm)	0.2, 0.4, 0.6	-	C:W=1:(0.475/0.5/0.55/0.6)	[56]

-	S	0.5, 1.0, 1.5, 3	Silane Acrylic resin	-	[57]
Portland Cement CEM I 32.5	G, Quartz	0.5, 1.0	-	C:W=1:0.45	[40]
-	Quartz	0.5, 1.0, 1.5			
Ordinary Portland Cement	ISO (with a SiO_2 content of 98% or more); Fly ash (SiO_2:45%, density:1.95g /m^3)	0.4, 0.8, 1.2	SP	C: W:S=1:0.375:0.369	[34]

Note: C (B), W, S and G represent cement (binder), water, fine aggregate and coarse aggregate, respectively. SP represents superplasticizer. OWC denotes oil well cement.

2.3 Fabrication process

During the fabrication process of biomass-derived nanocellulose modified cementitious composites, the dispersion methods of nanocellulose and curing methods of cementitious composites require special attention. The poor dispersion of nanocellulose results in entrapped pores, voids and air in cementitious composites, thus restraining their reinforcement effect on mechanical performance [20, 35, 42, 58]. Therefore, the dispersion of nanocellulose is a crucial step to fabricate biomass-derived nanocellulose modified cementitious composites and it plays a decisive role on the performance of the composites [2, 49]. The dispersion methods used in previous studies mainly include shear mixing, ultrasonic treatment, magnetic stirring, and high-pressure dispersion [25, 38, 40, 44, 51, 54].

As shown in Table 3, shear mixing can improve the dispersibility of nanocellulose, but it increases the Van der Waals force between nanocellulose [30]. Ultrasonic treatment is also a method for dispersing nanocellulose. Cao et al. [20] reported that ultrasonic treatment can homogeneously disperse CNCs on the cement surface. As a result, the agglomeration of CNCs is reduced in the fresh cement paste, and the capillary pores are decreased in the hardened cement paste. Similar results can also be found in the study of Sun et al. [39]. The detailed fabrication process of cement samples, CNF-OWC composites and CNF/graphene nano platelet (GNP)-OWC composites is shown in Fig. 3. Moreover, Lee et al. [25] found the magnetic stirring has better dispersion effect on nanocellulose than ultrasonic treatment through decreasing the average particle size of aggregation CNCs. However, magnetic stirring consumes a lot of energy and is only moderately effective. High-pressure dispersion is also used to disperse CNCs, as illustrated in Fig. 4 [25]. It is worth noting that these existing dispersion methods cannot completely guarantee the dispersion of nanocellulose, because the ions

in cementitious composites may change the charge on the surface of nanocellulose, leading to that nanocellulose easily adheres to each other and forms large aggregates [30].

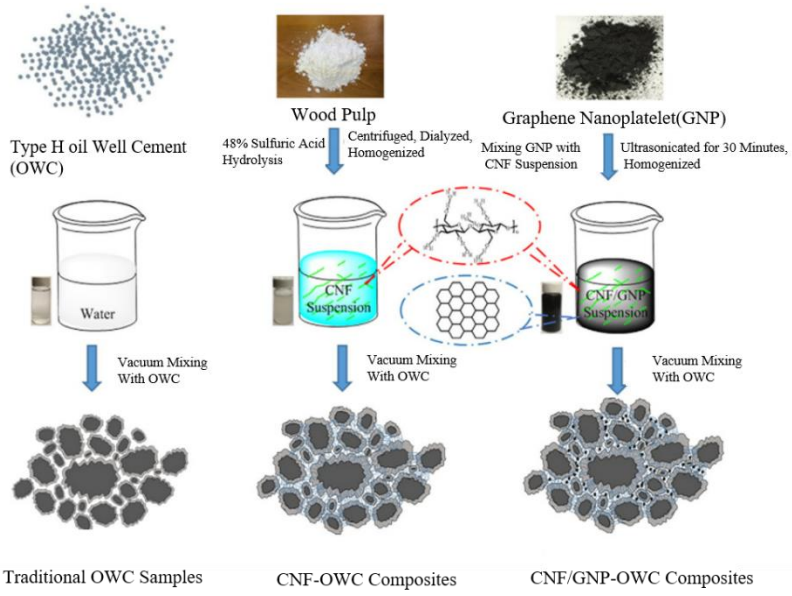

Fig. 3. Fabrication process of cement samples, CNF-OWC composites and CNF/GNP-OWC composites (Note: CNF, OWC and GNP represent cellulose nanofibril, oil well cement and graphene nano platelet, respectively) [39]

The curing methods during the fabrication process of biomass-derived nanocellulose modified cementitious composites mainly include water curing, wet curing, air curing, and CO_2 /air curing [51, 59]. Claramunt et al. [46] cured the specimens of biomass-derived nanocellulose modified cementitious composites for 28 d at 20±1℃ and 95% relative humidity (RH). After that, half of them are cured in water at room temperature and dried in an open air circulation at 60℃. As a result, the heat of the hydration and the cracks of the cementitious composites are obviously reduced. In addition, the curing way of CO_2 is used by Vignesh et al. [59] and Correia et al. [51] to form the carbonate to modify the cracks, reducing the inter-particle spacing and bridging the gap between nanocellulose and cement matrix. Generally, the early performance and the hardened properties of biomass-derived nanocellulose modified cementitious composites are

affected by the curing condition. Detailed preparation processes of biomass-derived nanocellulose modified cementitious composites are summarized in Table 3.

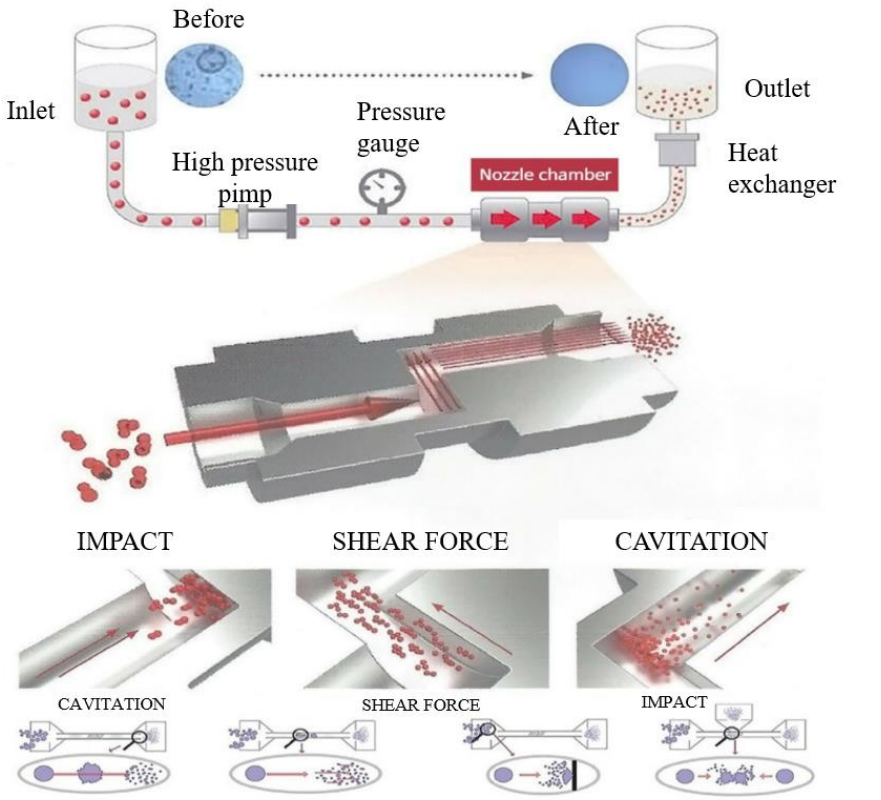

Fig. 4. Mechanisms of high-pressure dispersion [25]

Table 3 Fabrication process of biomass-derived nanocellulose modified cementitious composites

Dispersion method of nanocellulose	Feeding Order	Mixing method / Time	Molding	Curing		References
			Size (mm)	Condition/ Temperature and Relative humidity	Time	
Shear mixing	-	-	-/ (tensile strength)	Water	7d	[60]
	C+ S+ SF+ silica flour SP+ W+ cellulose	Stir/5min Stir/-	Cylinders 8×16 (splitting tensile test); 220×30×50 (notched-beam three-point bending test)	Laboratory/room temperature+ water bath/90°C+ dry oven/90°C	-	
	-	Mix/>12min				
	SF+ silica flour + C+ S (in sequence)	Stir/low speed, 5min	cylinder 8×12.7 (split cylinder test)		7d, 14d, 28d	[54]
	SP+ W+ nanocellulose (in sequence)	Stir (by hand)/-	-/30×1.6×25 (notched-beam three-point bending test)	7d Wet room/±4d water /195°F+2d air/195°F	14d	
	-	Mix/20min	2×2×2 inches (compressive test)		28d	
	CNC+ deionized water	Stir/30min+ sonicate/1h				
	C+W	Mix (low speed)/30s	50×50×50	Saturated solution of calcium hydroxide/-	3d, 14d, 28d, 91d	[38]
	-	Stop/15s+stir/medium speed, 60s				
	SF+ silica flour +C+ S (in sequence) W+ SP+ nanocellulose	Stir/low speed, 5min Stir/-	22.5×37.25×170 (notched-beam three-point bending test;	7d Wet room/±4d water /195°F+2d air/195°F	14d	[44]

-	Mix/20min	shrinkage test) 2×2×2 inches (compressive test)			
W+ (bentonite)+ CNC	Stir/high speed	-	-	-	[41]
W+C	Stir/high speed	-	-	-	
W+ fluidizer+ nano fibrillated pulp	Mix/-	Press (at 4.5MPa)/ 40×40×160 (three-point bending test)	Air/20±1°C,95%RH	28d	[46]
C+ S	Mix/-		Water/room temperature+ oven/60°C	96h+72h (×20)	
-	-	160×40×40 (drying and autogenous shrinkage tests)	Room/ 21±1°C, 50±5% RH	Within 28d	[47]
W+ NC + pulp	Stir/5min+ Rest/15s + Stir/400rpm, 90s	Cylinder 200×200×50 (three-point flexural test)	Plastic bag/25+cylinder saturated with CO_2/45°C, 20MPa+chamber/45°C,90 RH	2d+1h+5d	[51]
C+ metakaolin	Mix				
C+ CNS suspension+ W	Stir/400rpm, 90s+ Rest/15s + Stir/400rpm, 90s	Cylinder 51×102(Ball-on-three-ball flexural test)	Plastic cylinder/23±1°C	7d, 14d, 28d	[9]
-	-	50×50×50	Water/-	-	[56]

C+ CNF suspension	Mix (vacuum)/-	50 × 50 × 250	-/Room temperature	10d, 20d, 30d	[39]
NFC gel+ W	Stir/5min+ sonicate/10min	40×40×40 (compressive test) 100×100×200 (thermal conductivity test)	23±2°C, 95%RH	1d, 7d, 28d	[29]
C	Mix			28d	
Distilled water+ CNF suspension	Stir/15min+soni cate/15min	40×40×160 (flexural and compressive tests)	Chamber/20±1 °C, 95%RH	3d, 7d, 28d	[45]
C	Stir/ 500rpm, 120s+ stop /15s+stir/600rp m, 120s				
BNC (powder/gel) + C+ fiber	Mix				
W+ SP+ $CaCl_2$	Mix				
-	Stir/1min+stop/ 1min+stir/1min +stop/1min+ stir/1min	10×250×40 (flexural test)	Air/20±1°C,95%RH+ Air/20±1°C,65%RH	28d+1 month	[42]
BNC+ deionized water+ fiber	Coat	10×250×40 (flexural test); 25×25×12 (water absorption test)			
C	Mix				
W+ SP+ $CaCl_2$	Mix				

-	Stir/1min+stop/ 1min+stir/1min +stop/1min+ stir/1min				
Nanocellulose+ eucalyptus pulp+ W C+ metakaolin	Stir/5min Disperse/-	200×200×5 (four-point bending test)	Saturated air condition/25°C+thermal bath saturated with CO_2 at 20MPa pressure/45°C +chamber/45°C, 90%RH	-	[59]
CNF+W+C	Stir/45-60min Mix/90s (twice, 400rpm)	Cylinder 50×100mm (for ball-on-three-ball)	23±1°C	3d, 7d, 28d	[28]
CNF+W+C	Mix/180s (95 r/min), Mix/120s (60 r/min), Rest/15s, Stir/60s (120 r/min), Rest/15s, Stir/60s(115r/min), Rest/15s, Stir 60s(135r/min)	1×1×11.25, 25.4×25.4×285.75 (for free-shrinkage test); 76.2×152.4cylinder molds (for compressive strength)	-	3d, 5d, 7d, 11d, 14d, 21d, 28d, 90d; 24h+28d	[31]
C+W C+W+CNC	Mix/5min	-	Higher relative humidity (≥97%)	1d 7d 28d 56d	[16]
C+W+CNC/CNF	Stir/2min Mix/2min	100×100×100 (bulk density, water	Water 20±2°C	Air 24h; Water 28d	[40]

			absorption and compress strength); 50×50×250 (Tensile strength)			
	CNC+ sulfuric acid + Deionized water	Stir/120min Centrifuged for 5 cycles at 4000 rpm	-	Air at 50°C	-	[31]
	Dry CNF+ Distilled water	Stir/25min	80×80×350 (for assessing autogenous shrinkage) 100×100×400 (four-point bending test)	Air 25±1°C RH of 20%,50%,70%,90%	72h +194d 28d 91d	[6]
	CNF+ C+ Deionized water	hand stirring/1min + Swirl mixer for 3 minutes	--	Water bath maintenance 29°C	-	[50]
Ultrasonication+ surface modification	NCC+ silane+ W Acrylic resin	Sonicate/1min Mix-	(tensile test)	-/Room temperature, 55% RH	7d	[57]
	Vacuum water + CNF + OWC CNF/GNP+OWC	Mix	50×50×50 50×50×250	Curing in air	3d 7d 14d 28d	[39]

W+CNC	Mix/2 min	40×40×160	25°C 73.5%RH	28d	[40]
CNC+ SP	Sonicate/5min	10×10×70	20.0±0.5°C （RH）>95%	28d	[32]
Distilled water + CNC +suspension	-	50×50×50 40×40×160	Temperature 70-140°C	3d 7d, 28d	[34]
C+W+CNC+SP	Mix/3 min	40×40×160	-	28d	[30]

Note: BRHA denotes black rice husk ash; GGBFS represents ground granulated blast furnace slag; RHA, SF and FA represent rice husk ash, silica fume and fly ash, respectively; RH represent relative humidity.

3. Performances of biomass-derived nanocellulose modified cementitious composites

3.1 Early performance

3.1.1 Workability

The addition of biomass-derived nanocellulose with high specific surface area impacts the Van der Waals force, electrostatic repulsion, space steric hindrance and hydrogen bonding force between raw material particles [9, 19, 29, 43, 45], and then influences the workability of cementitious composites [34, 39, 43, 56, 61-62]. Kolour et al. [63] reported that the workability of CNF modified cementitious composites decreases as the content of CNFs increases, and the workability is poorest when the content of CNFs is 0.05 wt.%. However, in the study of Mazlan et al. [56], there is no significant change of workability of cementitious composites due to the incorporation of CNCs. Ardanuy et al. [43] found a slight decrease of slump with the addition of NFCs less than 0.1 wt.%. However, Hisseine et al. [64] observed that incorporating 0.1 wt.% of CNFs reduces the slump flow from 785 mm to 538 mm and the slump flow of composites is only 320 mm as 0.15 wt.% of CNFs is added. Banthia et al. [62] compared the retention value of slump loss on the reference concrete, polypropylene (PP) fibers filled cement paste and NFCs filled cement paste. They concluded that the addition of NFCs has the best modification effect on improving the consistency and the degree of collapse. The retention value of slump loss of cement paste with NFCs remains at 100 mm, while the retention value of slump loss of the other two composites decreases to 0 mm.

3.1.2 Rheology

Due to the nano size and high specific surface area, the inclusion of nanocellulose has a nonnegligible effect on the rheology of cementitious composites. Compared to

OWC slurry without nanocellulose, the yield stress and viscosity of cementitious composites with nanocellulose is increased [52]. Dousti et al. [41] investigated the rheology of OWC composites by the flow table test, and found the yield stress of the composites increases due to the addition of the CNCs. Sun et al. [39] found that the yield stress and plastic viscosity of cementitious composites is gradually increased from 19.19 Pa to 39.3 Pa and from 0.109 Pa·s to 0.271Pa·s, respectively, when the content of CNFs is increased from 0 to 0.28 wt.%. Fu et al. [28] also revealed the similar results, and pointed out that the reinforcement mechanisms can be attributed to the stress concentration caused by agglomeration in CNF modified cementitious composites. However, Cao et al. [9] reported that the yield stress of cement slurry is decreased firstly and then increased with the increases of CNC content. The yield stress of cementitious composites reaches the minimum value of 15.9 Pa when the content of CNCs is 0.04 wt.%. However, when the content of CNCs is higher than 0.3 wt.%, the yield stress of cementitious composites can be increased dramatically. In the study of Lee et al. [34], they reported that the number of water molecules in the CNF modified cementitious composites is decreased due to the high hygroscopicity of CNFs, then the rheology of the composites decreases sharply. Generally, the increase of yield stress of biomass-derived nanocellulose modified cementitious composites results from the compound effect of steric stabilization and agglomeration [9, 28], thus reducing the setting velocity and collapse degree of solid particles of nanocellulose filled cementitious composites [65]. Meanwhile, the yield stress of composites can also be decreased at a low incorporation of nanocellulose, owing to the steric stabilization or modification of water molecules [9, 34]. This indicates that slurry with different yield stress can be obtained by adjusting the amount of nanocellulose.

3.1.3 Setting time

Adding nanocellulose can adjust the setting time of cementitious composites to satisfy the requirement of construction. Jiao et al. [45] found the initial setting time of CNF modified cementitious composites is increased by 4.7%, 11.8%, 30.6%, 47.1%, 60.0% due to the addition of 0.05 wt.%, 0.1 wt.%, 0.15 wt.%, 0.25 wt.%, 0.40 wt.% CNFs, respectively. Moreover, the final setting time of the composites is increased by 4.1%, 7.8%, 24.7%, 31.5%, 41.6% when the content of CNFs is 0.05 wt.%, 0.1 wt.%, 0.15 wt.%, 0.25 wt.%, 0.40 wt.%, respectively. Zhao et al. [23] also observed the setting time of biomass-derived nanocellulose modified cementitious composites is increased, and this phenomenon can be attributed to that nanocellulose can reduce liquid-solid ratio and prevent the calcium phosphate cement (CPC) particles from reacting with water. However, Mejdoub et al. [29] found the addition of NFCs remarkably shortens the setting time of cementitious composites, which is closely related to the mix proportion and raw materials of composites.

3.1.4 Hydration characteristics

Many researches have proved that the DOH, heat of hydration and hydration products of cementitious composites are influenced by the incorporation of nanocellulose. Cao et al. [9] investigated the effect of nanocellulose on cement paste hydration by means of isothermal calorimetry (IC) and thermogravimetric analysis (TGA). They found that the DOH of the cement paste is increased when CNCs are incorporated, resulting from the hydrophilicity and wettability of nanocellulose. According to the study of Ardanuy et al. [43], the DOH of cementitious composites is increased from 52% to 57% due to the addition of 1.6 wt.% NFCs. Sun et al. [39] found that when the content of CNCs increases from 0 to 2.66 wt.%, the final weight loss of hydrated OWC samples decreases from 90.4% to 86.2%, but the value of DOH increases from 41.6% to 60.1%,

as illustrated in Fig. 5.

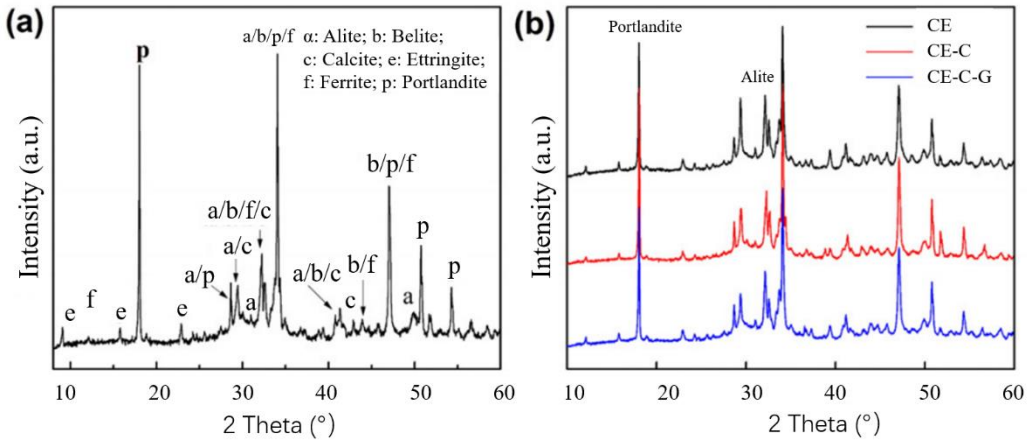

Fig. 5. X-ray diffraction (XRD) analysis of degree of hydration (DOH) of CNF/GNP modified OWC composites: (a) Indexed XRD pattern; (b) XRD patterns (Note: CNF, OWC and GNP represent cellulose nanofibril, oil well cement and graphene nano platelet, respectively) [39]

Jiao et al. [45] proposed the incorporated CNFs improves the DOH of cement pastes regardless of aging time. However, Onuaguluchi et al. [27] found the DOH is gradually delayed with the increasing content of nanocellulose. Furthermore, Flores et al. [38] proposed the incorporation of CNCs delays hydration at an early age, but accelerates hydration at late ages. A similar conclusion is also obtained by Cao et al. [9]. On the contrary, Mejdoub et al. [29] revealed the addition of 0.3 wt.% NFCs increases the DOH of cementitious composites by 102%, 23% and 28% at the curing ages of 1d, 7d and 28 d, respectively.

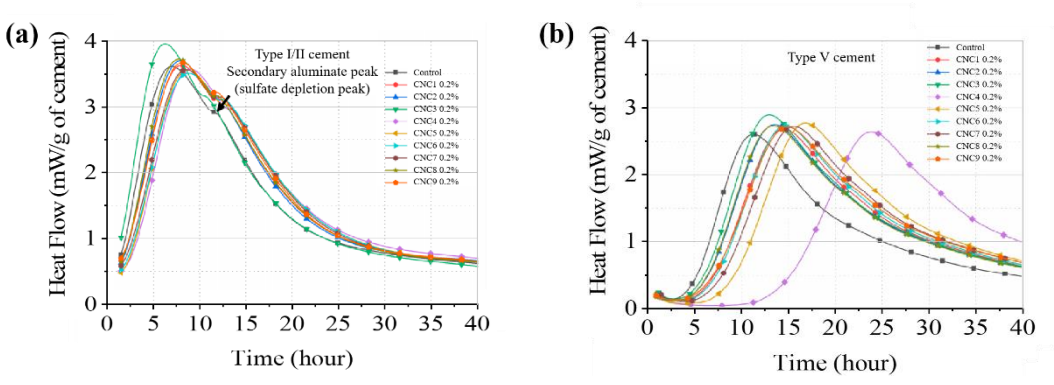

Fig. 6. Heat flow of cementitious composites with different contents of CNCs: (a) Type I/II cement; (b) Type V cement (Note: CNCs 1-9 represent CNCs with different characteristics as described in the reference [28])

It is observed that the heat flow also has a great influence on the hydration reaction of CNC modified cementitious composites. As shown in Fig. 6 (a) and (b) [28], the heat flow of CNC modified Type V cementitious composites reaches the maximum at 12 hours (h), and heat flow of CNC modified Type I/II cementitious composites reaches the maximum at 7-8 h, indicating a delay of early hydration reaction. Meanwhile, the delay effect on Type V cement is more significant than that on Type I/II cement due to the different aluminate phase content [28]. Ghahari et al. [48] also obtained similar results and pointed out that the hydration delay effect can be contributed to surface absorbed CNCs on cement particles to reduce the contact between cement and water.

According to the results of X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR), Flores et al. [38] found there is no difference in hydration product types between composites with and without CNCs, but there is a chemical bond between CNCs and hydration products. Such results have been also observed in the study of Jiao et al. [45]. They revealed that the hydrogen bond can be formed between hydroxyl groups, carboxyl groups of CNFs and hydration products of cement, thus leading to the microstructure modification and mechanical enhancement of cementitious composites (as shown in Fig. 7). Sun et al. [39] reported the increase of calcium silicate hydrate (C-S-H), calcium hydroxide (CH) and ettringite crystals in hydration products of OWC due to the addition of CNFs/GNPs. Mejdoub et al. [29] also found that the content of CH and C-S-H in cement pastes increases due to the addition of CNFs. The results of Mohammadkazemi et al. [42] indicated that hydration products including CH and C-S-H can be obtained on the surface of BNC, enhancing

the interfacial bonding between nanocellulose and cement matrix. Balea et al. [19] found that nanocellulose adsorbed on the surface of cement and CH crystals can combine with calcium ions to reduce the crystallization degree of CH. Ghahari et al. [48] found that the concentration of calcium of cementitious composites are 28%, 26%, 22% for CNC-1 wt.%, CNC-0.2 wt.% and reference sample, respectively, meanwhile, the content of silicon of cementitious composites are 7%, 7%, 5% for the three samples, respectively (as shown in Fig. 8), indicating an increase of hydration product content.

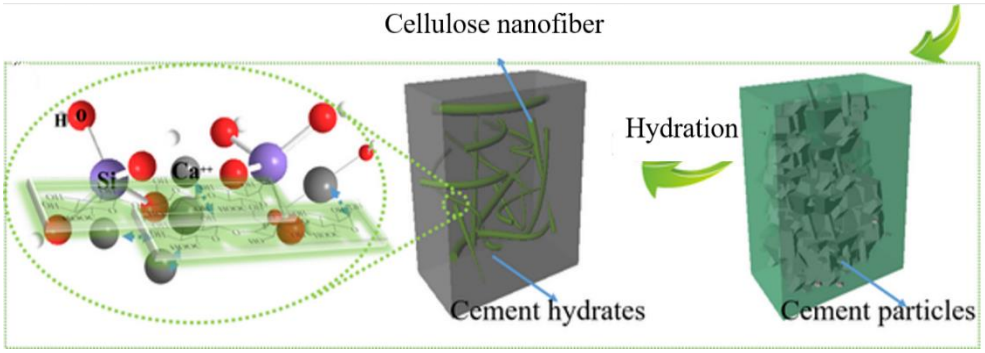

Fig. 7. A network of cellulose nanofiber (CNF) and the formation of nanocellulose modified cementitious composites [45]

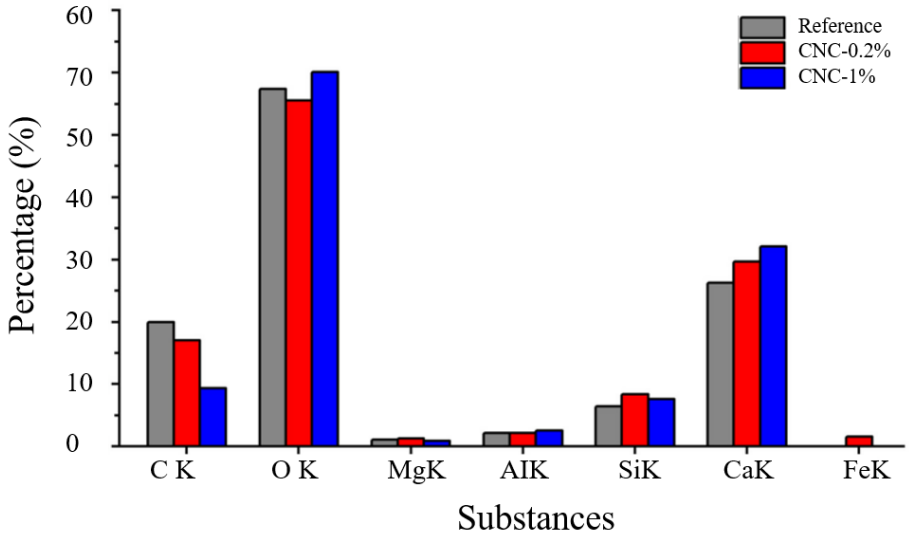

Fig. 8. X-ray spectroscopy (EDX) of cementitious composites with CNCs [48]

Different views have been proposed to explain the effect of nanocellulose on hydration of cementitious composites, as explained below. Jiao et al. [45] believed that nanocellulose has the steric stabilization effect to make the cement particles evenly

distribute during the hydration process. Meanwhile, nanocellulose can act as a nucleus to improve the early hydration degree of cement and promote the formation of hydration products. In the study of Balea et al. [19], the incorporation of BNCs decreases the calcium/silicon ratio and promote hydration reaction of cementitious composites. Dousti et al. [16] observed that the addition of CNCs can enhance the storage modulus of cementitious composites, and makes the sol-form transform to gel-form, thus enhancing the hydration of cementitious composites. Flores et al. [38] pointed out that the adsorption of CNCs on the cement particles reduces the available surface area for the hydration reaction to decrease the hydration degree of cement at the early ages. However, the decrease in hydration degree can also be attributed to the high viscosity of nanocellulose which can delay cement dissolution and reduce ion diffusion [27]. As shown in Fig. 9, CNCs can dissolve in water and attach to cement particles to become hydration core due to the short circuit diffusion (SCD), leading to the promotion of hydration and the increase of hydration product amount [9, 28, 34]. It can be proved that the hydration process of cementitious composites with nanocellulose is affected by the combined action of steric stabilization and SCD. In the early hydration process, SCD plays a decisive role. The CNCs distribute on the outermost layer of hardened hydration products, so the additional water can be transported to the cement particle core to produce additional hydration production [9, 28]. Then, if CNCs combine with SP in cement, SP will facilitate the dispersion of cement particles by space stabilization, promoting hydration process of cementitious composites. However, CNCs can easily be adsorbed on cement particles due to potential difference. High content of CNCs prevents the contact between cement particle and water, resulting in the delay of hydration [20, 28, 48]. Moreover, at later stages of hydration, the SCD effect disappears and the steric stabilization effect of SP plays the major role. The diagram of combined

effect is shown in Fig. 10 [30].

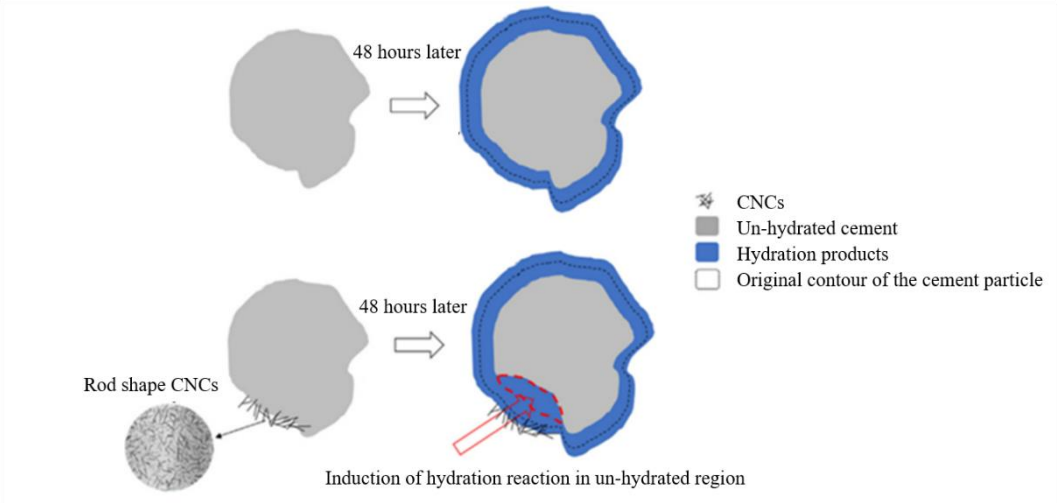

Fig. 9. The hydration products generated around cement with cellulose nanocrystals (CNCs) from 0 h to 48h: (a) Plain cement; (b) Induction of hydration in un-hydrated region through CNCs attached to cement particles in cementitious composites [34]

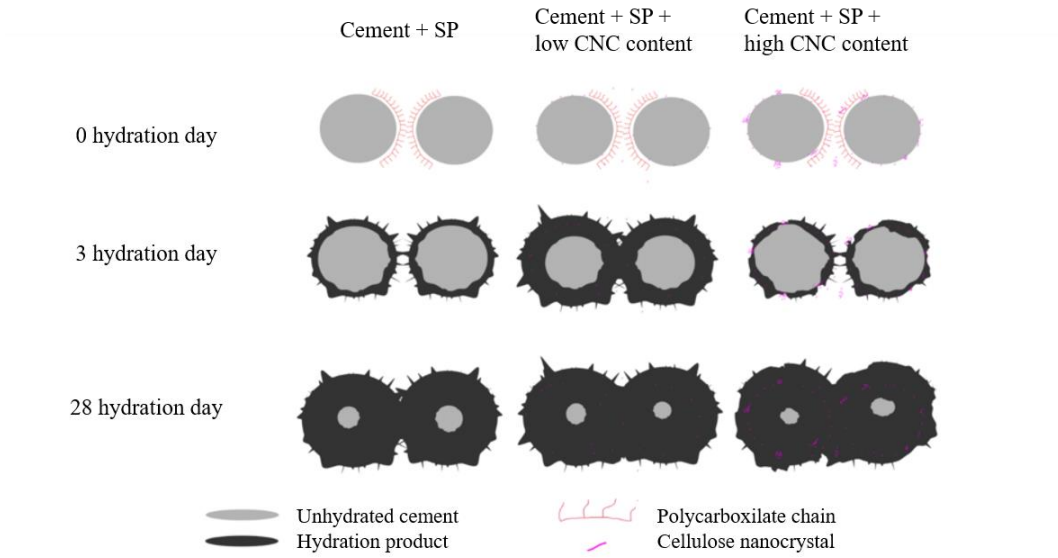

Fig. 10. Combined effect of steric stabilization of superplasticizer (SP) and short circuit diffusion (SCD) of cellulose nanocrystal (CNCs) on the cement hydration [30]

3.1.5 Shrinkage

The shrinkage of cementitious composites, caused by the loss of adsorbed water under continuous stress and migration of water in the capillaries of hydrated cement paste, can be reduced effectively by the addition of nanocelluloses [4, 26]. As demonstrated in Fig.11, Hisseine et al. [6] concluded that the autogenous shrinkage of UHPC is reduced by 45% at the curing ages of 1 d when NFCs are added. Banthia et al.

[62] reported that 0.15 wt.% CNFs can reduce the autogenous shrinkage of cementitious composites by 36%, resulting from the hydrophilic characteristics of nanocellulose. The reduction of autogenous shrinkage can be attributed to internal curing and matrix bridging of the biomass-derived nanocellulose modified cementitious composites as explained by Hisseine et al. [6]. Meanwhile, benefitting from the hydrophilicity and hygroscopicity of nanocellulose, water can be released and continue to participate in hydration of cement to improve the compactness and reduce the matrix pores of cementitious composites.

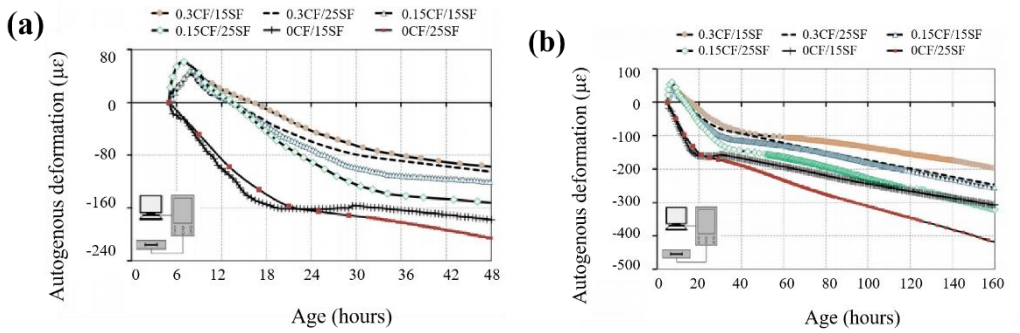

Fig. 11. Autogenous shinkage of different ultra-high performance concrete (UHPC): (a) Very early age (0-12h); (b) Early age (12h-7days) (Note: CF represents nanocellulose filaments or cellulose nanofibril, and SF represents silica fume, respectively) [6]

Lee et al. [66] conducted the drying shrinkage test and showed that the drying shrinkage strain of cementitious composites is decreased by 55% when the content of CNCs is 0.8 wt.%. Kolour et al. [63] showed that the drying shrinkage of cementitious composites can be decreased only when the content of CNFs is 0.05 wt.%, 0.1 wt.%, 0.2 wt.% and 0.5 wt.%. But the drying shrinkage is increased when the w/c of CNF filled cementitious composites is higher than 0.45 [31].

In addition, the chemical shrinkage of cementitious composites is also affected by the addition of nanocellulose. Flores et al. [38] observed that the incorporation of CNCs reduces the chemical shrinkage of cementitious composites. As the surface charge of

CNCs (-33.4 mV) is higher than that of cement particles (-10 mV), CNCs can absorb on the surface of cement particles to reduce the available surface area of cement particles for hydration reaction. Stephenson [44] found that the chemical shrinkage of cementitious composites with NCFs is less than that of composites without NCFs, because NCFs are served as miniscule water reservoirs. Related studies about the shrinkage of cementitious composites with nanocellulose are relatively limited, and further investigations on this topic are required.

3.1.6 Pore structures

The investigation of Jiao et al. [45] showed that the mean pore size and critical pore diameter of cementitious composites decrease with the increasing content of CNFs, but the porosity first decreases and then increases. Barnat-Hunek et al. [40] found that the addition of nanocellulose can decrease the porosity of cement mortars up to 19.8% compared to the reference mortar, resulting from the polymer sealing effect to the mortar structure. Dousti et al. [16] showed the porosity of pores with a radius less than 100 nm in oil well cement paste with CNCs can be reduced by more than 30% (as shown in Fig. 12 (a) and (b)), meanwhile, the specific surface area of pores is also decreased by more than 50%. In the reference of [38], the porosity of cementitious composites is also significantly reduced due to the incorporation of 0.8 wt.% CNCs. In general, the addition of nanocellulose has great potential to reduce the porosity and densify the microstructure of cementitious composites.

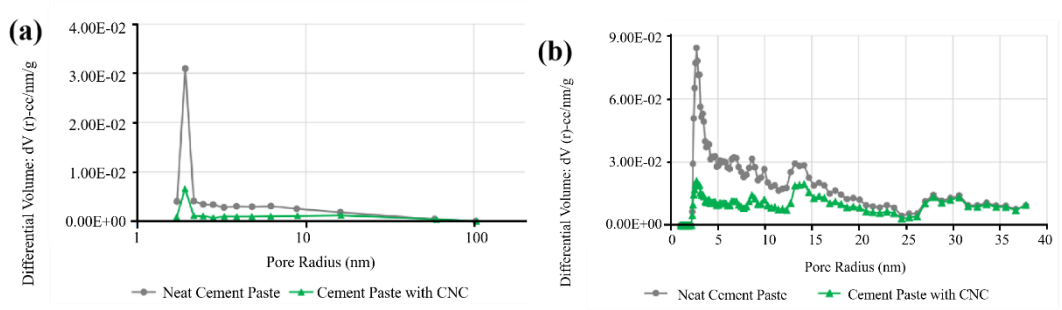

Fig. 12. The effect of cellulose nanocrystals (CNCs) on the pore size distribution of hardened oil well cement paste, obtained by different methods: (a) Barrett-Joyner-Halenda (BJH) method; (b) The density functional theory (DFT) method [16]

3.2 Mechanical performance

3.2.1 Compressive strength

Many investigations indicated that nanocellulose can be used to improve the compressive strength of cementitious composites to some degree, and the enhancement effect is mainly controlled by the types and contents of nanocellulose and the curing ages [23, 27, 45, 63, 67]. The effect of nanocellulose on compressive strength of cementitious composites is concluded in Table 4.

The compressive strengths of cementitious composites are increased by 10% and 17% due to the incorporation of 0.2 wt.% and 1.0 wt.% CNCs, respectively. It can be attributed to that the addition of CNCs with the hydrophilicity and high specific surface area improves the interface between CNCs and cement paste, thus enhancing the stress transfer between cement paste [63]. Compared with the control group, the compressive strength of cementitious composites can reach its maximum and be enhanced by 22% when the addition of BNCs is 0.3 wt.% [35]. Barnat-Hunek et al. [68] obtained that the maximum increase in compressive strength of cementitious composites is 27.6% when the content of CNCs is 1.5 wt.%. However, the compressive strength of cementitious composites is decreased when the content of nanocellulose is more than the optimum value. Hisseine et al. [6] found that an addition of 0.15 wt.% CNFs increases compressive strength of cementitious composites up to 10%, however, when the content of CNCs is more than 0.30 wt.%, the compressive strength of cementitious composites is reduced. Xie [17] observed that the compressive strength of cement paste is increased by 16%, reaching its maximum when the content of CNCs is 0.25wt.%. The decrease of compressive strength of cementitious composites with high content of CNFs is due

to the increase of internal defects caused by the agglomeration of CNFs [63]. Dousti et al. [16] showed that the compressive strength of OWC with CNCs at the curing ages of 1 d is 2.5 times higher than that of OWC without CNCs. Hisseine et al. [6] observed that the compressive strength of biomass-derived nanocellulose modified cementitious composites increases with the increasing of curing ages, and the compressive strength of cementitious composites with 0.05 wt.% of CNFs can be enhanced from 22% to 26% as the curing ages increases from 1 d to 28 d. Stephenson [44] found that at the curing ages of 28 d, the compressive strength of cementitious composites with 1.0 wt.% NCFs is increased by 14%. Mazlan et al. [56] found the compressive strength of cementitious composites reaches a maximum value when the content of CNCs is 0.2 wt.%. Meanwhile, the compressive strength of cement mortar with 0.2 wt.% CNCs is increased by 48.2%, 30.3% and 42.9% at the curing ages of 7 d, 14 d and 28 d, respectively. Similar research is performed by Mejdoub et al. [29], and they displayed that the addition of 0.3 wt.% NFCs increases the compressive strength of cementitious composites by 114.3%, 65.2% and 54.7% at the curing ages of 1 d, 7 d and 28 d, respectively.

Table 4 Effect of nanocellulose on the compressive strength of cementitious composites

Matrix types	Enhancements										Nanocellulose content (wt.%)	References
	1d		3d		7d		14d		28d			
	Abs.（MPa）	Rel.(%)	Abs.（MPa）	Rel.(%)	Abs.（MPa）	Rel.(%)	Abs.（MPa）	Rel.(%)	Abs.（MPa）	Rel.(%)		
Cement paste	2	14.3	-	-	5	21.7	-	-	1	4.6	0.01	[29]
	6	42.9	-	-	6	26.1	-	-	2	9.1	0.05	
	8	57.1	-	-	7	30.4	-	-	5	22.8	0.1	
	10	71.4	-	-	12	52.2	-	-	7	32.2	0.2	
	16	114.3	-	-	15	65.2	-	-	12	54.7	0.3	
	-9	-64.3	-	-	-15	-65.2	-	-	-18	-82.1	0.5	
	-	-	-2	-3.6	1	1.5	-	-	5	5.9	0.05	[45]
	-	-	-3	-5.5	0	0	-	-	8	9.4	0.10	
	-	-	-4	-7.3	1	1.5	-	-	13	15.3	0.15	
	-	-	-1	-1.8	3	4.5	-	-	2	2.4	0.25	

	-	-	-3	-5.5	3	4.5	-	-	-5	-5.9	0.40	
		22				25				26	0.05	[5]
		10				15				17	0.10	
Cement mortar	-	-	-	-	13	48.2	10	30.3	15	42.9	0.2	
	-	-	-	-	3	11.1	4	12.1	4	11.4	0.4	[56]
	-	-	-	-	9	33.3	6	18.2	13	37.1	0.6	
Concrete	-	-	-	-	-	-	-	-	2.4	1.4	0.1	
	-	-	-	-	-	-	-	-	23.4	14.0	0.5	[44]
	-	-	-	-	-	-	-	-	23.4	14.0	1.0	

Note: Abs. represents absolute increments, and Rel. represents relative increments.

3.2.2 Flexural/tensile strength

The flexural/tensile strength of biomass-derived nanocellulose modified cementitious composites is influenced by many factors, such as type, content and form of nanocellulose. An addition of 0.04 wt.% CNFs increases the flexural strength of OWC composites by 23.9% [39]. In the study of Hisseine et al. [6], they revealed that the flexural strength of cementitious composites can be enhanced when the content of CNFs is between 0.15 wt.% and 0.30 wt.%. The research of Onuaguluchi et al. [27] also showed that the flexural strength of cementitious composites is increased by 106% when the content of nanocelluloses is 0.1 wt.%. However, the flexural strength of cementitious composites is reduced when the content of nanocelluloses is higher than 0.1 wt.%. Barnat-Hunek et al. [68] observed that cementitious composites with 1.5 wt.% CNCs have the maximum flexural strength, 34.5% higher than that of cementitious composites without nanocelluloses. Meanwhile, the optimal content of CNFs ranges from 0.05 wt.% to 0.10 wt.% for the flexural strength of the composites, as shown in Fig. 13 [31]. In addition, Claramunt et al. [46] concluded the flexural strength of cementitious composites is enhanced because of the interaction between nanocellulose and matrix. The effect of nanocellulose on the flexural strength of cementitious composites is summarized Table 5.

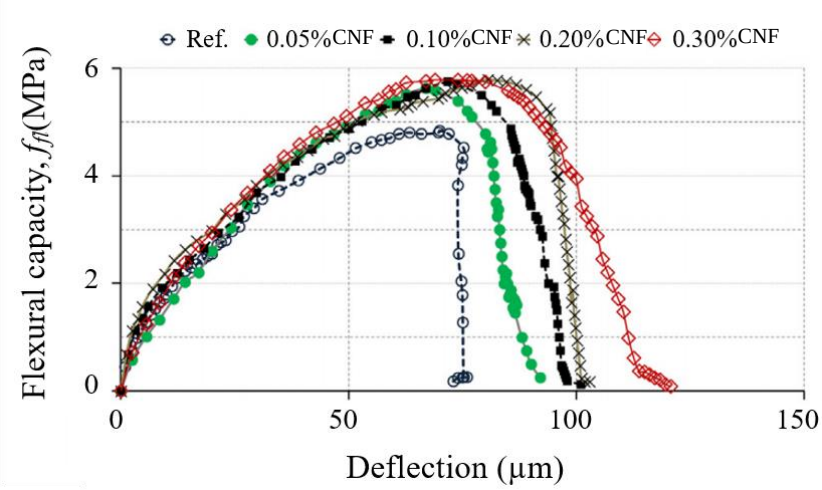

Fig. 13. Flexural strength of cementitious composites with CNFs [31]

According to the study of Barnat-Hunek et al. [40], the bending-tensile strength of cementitious composites is increased by 12%, 34.5%, 2.6%, 23.4%, respectively, due to the addition of 0.5 wt.% CNCs, 1.0 wt.% CNCs, 0.5 wt.% CNFs, and 1.0 wt.% CNFs. It can be seen that the enhancement effect on the bending-tensile strength of cementitious composites caused by the addition of CNCs is better than that caused by the incorporation of CNFs. Meanwhile, the addition of nanocellulose has a significant impact on the direct-tensile and split-tensile strength of cementitious composites. Peter et al. [55] found the addition of 0.5 wt.% nanocelluloses increases the split-tensile strength of cementitious composites by up to 18% and 21% at w/c of 0.42 and 0.5, respectively. However, the split-tensile strength of cementitious composites shows a downward trend as the content of NFCs is larger than 0.5 wt.%. The direct-tensile strength of cementitious composites is increased by 64% due to the incorporation of 0.05 wt.% NFCs [5].

Table 5 Effect of nanocellulose on the flexural strength of cementitious composites

Matrix types	Enhancements										Nanocellulose content (wt.%)	References
	3 d		7d		14d		28d		90d			
	Abs.	Rel.	Abs.	Rel.	Abs.	Rel.	Abs.	Rel.	Abs.	Rel.		

	（MPa）	(%)	（MPa）	(%)	（MPa）	(%)	（MPa）	(%)	（MPa）	(%)		
Cement paste	-	-	0	0	-	-	0.7	3.9	1	4.7	0.05	[45]
	-	-	-1	-14.3	-	-	1.1	6.1	2	9.3	0.10	
	-	-	-1.1	-15.7	-	-	1.3	7.2	3	14.0	0.15	
	-	-	1	14.3	-	-	1.7	9.4	2.5	11.6	0.25	
	-	-	-1.1	-15.7	-	-	2	11.1	2	9.3	0.40	
	-	-	-	-	-	-	0.78	16	-	-	0.05	[31]
	-	-	-	-	-	-	0.91	19	-	-	0.10	
	-	-	-	-	-	-	1.00	21	-	-	0.20	
	-	-	-	-	-	-	0.97	20	-	-	0.30	

Note: Abs. represents absolute increments, and Rel. represents relative increments.

Some researchers pointed out that the form of nanocelluloses obviously affects the flexural strength of cementitious composites. Akhlaghi et al. [35] showed BNC powder has a better enhancement effect on the flexural strength of cementitious composites than BNC gel. An addition of 0.5 wt.% BNC powder increases the flexural strength of cementitious composites by 104%, meanwhile, the flexural strength of the cementitious composites is increased by 88% when the content of BNC gel is 0.3 wt.%. Fu et al. [28] conducted the Ball-On-Three-Ball Test (B3B) to investigate flexural strength of CNCs modified cementitious composites. The flexural strength of Type V cementitious composites with 0.5 wt.% CNCs increases with the curing ages increasing. Meanwhile, the flexural strength of Type I/II cementitious composites reaches its peak value when the content of CNCs is 2.0 wt.%. This phenomenon results from the varied aluminate content of different type of cement.

Therefore, biomass-derived nanocellulose modified cementitious composites possess more excellent flexural/tensile strength compared to normal cementitious composites, which can be attributed to the following two aspects. On one hand, water can be released from the unique tubular structure of nanocellulose to promote the continuation of anaphase hydration of cement in addition to filling effect and inhibiting

effect on the generation of micro cracks [35]. On other hand, the high specific surface area and hydrophilicity properties of nanocellulose can reduce the distance between particles and then increase the bonding interface between aggregates and cement matrix, improving the mechanical performances of cementitious composites [42].

3.2.3 Fracture properties

The fibrous structure of nanocellulose makes it effectively bridge cracks and hinder crack propagation of cementitious composites, leading to the enhancement of fracture properties of composites [19, 31, 46]. The effect of nanocellulose on the fracture properties of cementitious composites is summarized in Table 6.

Table 6 Effect of nanocellulose on the fracture toughness of cementitious composites
Note: Abs. represents absolute increments, and Rel. represents relative increments.

Matrix types	Critical crack length (m)		Critical stress intensity factor ($KPa \cdot m^{1/2}$)		Critical crack tip opening displacement (mm)		Fracture energy (J/m)		Nanocellulose content (wt.%)	References
	Increase									
	Abs. (MPa)	Rel. (%)	Abs. (MPa)	Rel. (%)	Abs. (MPa)	Rel. (%)	Abs. (MPa)	Rel. (%)		
Cement paste	-	-	-	-	-	-	0.06/ 0.07/ 0.04	60/ 70/ 40	6 (powder/coating/ gel)	[42]
Cement mortar	0. 1	5.3	0	0	0	0	-1	-1.7	1	[55]
	0	0	-300	-13.6	0	0	5	8.6	3	
	-	-	-	-	-	-	-0.8 (kJ/m)	-52.8	2	[46]
	-	-	-	-	-	-	-1.1 (kJ/m)	-72.6	4	
	-	-	-	-	-	-	-1.3 (kJ/m)	-85.8	6	
	-	-	-	-	-	-	-1.4 (kJ/m)	-92.4	8	
Concrete	-1.5	-9.4	-23.1	-15.4	0.002	18.2	-0.9 (N/m)	-1.5	0.1	[44]
	-5.7	-35.6	-53.9	-35.8	-0.001	-9.1	10.5 (N/m)	16.9	0.5	
	-6	-37.5	-56	-37.2	-0.002	-18.2	-1.9 (N/m)	-.31	1.0	
	-	-	-	-	-	-	0.1	7	3	[19]

As shown in Table 6, the addition of three types of BNCs (powder, gel, coating) all can increase the fracture energy of cementitious composites, of which, the fracture energy is improved by 70% due to the addition of BNCs coating [42]. In the research of Lapidot et al. [57], adding 0.05 wt.% CNCs increases the fracture energy of cementitious composites by 31%. Claramunt et al. [46] reported that the addition of 0.2 wt.% CNCs provides the highest fracture strength for cementitious composites than other content of CNCs. Moreover, Stephenson [44] found that the crack propagation toughness of cementitious composites with 0.5 wt.% nanocellulose is 17% higher than that of cementitious composites without nanocellulose, while there is no difference on the fracture toughness of composites with 0.1 wt.% and 1.0 wt.% nanocelluloses. In addition, Hisseine et al. [6] showed that the fracture energy absorption rate of cementitious composites increases with the increasing content of nanocellulose. The micro-cracks of the composites are decreased significantly by adding CNFs [53]. Zhao et al. [23] compared the stress-strain curves of CPC filled different contents of CNCs, and concluded that cementitious composites present ductile fracture when the addition of CNCs is 2 wt.% and 4 wt.%. In the study of Claramunt et al. [46], the fracture energy of cement mortar shows descending trend when the content of nanocellulose increases from 2 wt.% to 8 wt.%.

The effect of nanocellulose on the modulus of elasticity (MOE) of cementitious composites is given at Table 7. Balea et al. [19] pointed out that an addition of 3 wt.% BNCs can increase the modulus of rupture (MOR) and MOE of cementitious composites by more than 50% and 40%, respectively, resulting from the reinforcement of interaction between aggregate and matrix. As illustrated in Table 7, Claramunt et al. [46] and Mohammadkazemi et al. [42] revealed that the incorporation of 6 wt.%

nanocellulose increases the MOE of cementitious composites by 113%. Mohammadkazemi et al. [42] revealed that the MOE of cementitious composites is enhanced from 5.77 GPa to 9.71 GPa due to the incorporation of 0.3 wt.% BNCs. Dousti et al. [16] indicated that the MOE of cementitious composites is enhanced by 13%, resulting from that CNCs work as seeds in OWC to improve the interface between matrix and aggregates, as shown in Fig. 14.

Table 7 Effects of nanocellulose on the MOE of cementitious composites

Matrix types	Increase of elastic modulus		Nanocellulose content (wt.%)	References
	Abs. (GPa)	Rel. (%)		
Cement paste	0.52	11.0	6 (powder/ coating/ gel)	[42]
	1.80	38.2		
	1.55	32.9		
	3.30	18.0	0.05	[6]
	2.60	14.0	0.10	
	2.40	6.0	0.20	
	0.30	2.0	0.30	
Cement mortar	1.0	27.8	2	[46]
	3.3	91.7	4	
	4.1	113.9	6	
	2.0	55.6	8	

Note: Abs. represents absolute increments, and Rel. represents relative increments.

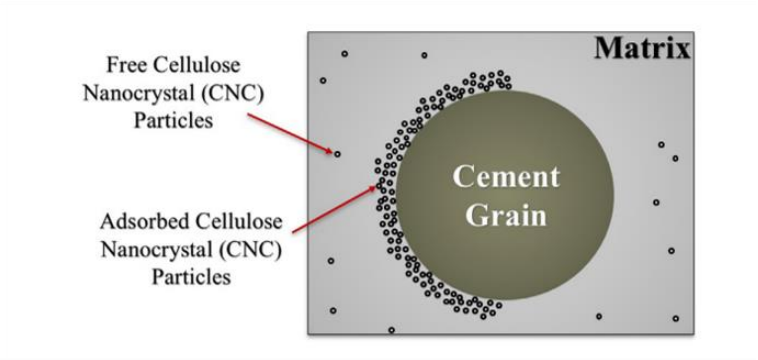

Fig. 14. Seed effect of cellulose nanocrystals (CNCs) in cement paste [16]

3.3 Durability

The enrichment of nanocellulose on the surface of aggregate enhances the interface transition zone in cementitious composites by reducing porosity and improving structure density of C-S-H gels, consequently, modifying the durability of cementitious composites [5]. The durability of biomass-derived nanocellulose modified cementitious

composites is mainly evaluated by freeze-thaw cycles, dry-wet cycles, carbonation depth, and the resistance to chloride/sulfate ion penetration. Barnat-Hunek et al. [68] tested 50 freezing and thawing cycles of cementitious composites with 1.5 wt.% nanocelluloses, and found that the frost resistance of cementitious composites is improved by 98%. Meanwhile, the surface wettability of the cementitious composites is decreased and the frost resistance is increased with the increasing of nanocelluloses. This can be contributed to the addition of CNCs decreases the pore size of cementitious composites, resulting in strong resistance to expansion pressure during freezing-thawing cycles [17, 34].

Claramunt et al. [46] conducted dry and wet cycling durability test on nanocelluloses/micron-grade sisal fibers reinforced cementitious composites, and confirmed that the incorporation of nanocelluloses increases the residual strength of cementitious composites after dry and wet cycles. However, Xie [17] found that the durability of cementitious composites after dry and wet cycles is decreased when the content of nanocellulose is more than 0.5 wt.%.

Fortunati et al. [69] proposed that the addition of CNCs can enhance the water vapor permeability of cementitious composites, reduce the diffusion of oxygen and decrease the permeability of water and harmful ions. In the study of Goncalves et al. [70], the increasing content of CNFs effectively reduces the sulfate permeability of cementitious composites. Meanwhile, the expansion of cementitious composites can be reduced due to the addition of nanocelluloses. An addition of 1.5 wt.% nanocelluloses decreases the mass loss of cementitious composites by 35 times in sulfate erosion environments [17, 34, 70]. The carbonation test results showed that the carbonation depth of CNCs modified cementitious composites is reduced more than 50% compare to that of cementitious composites without CNCs [17, 34]. In addition, Lee et al. [34] indicated

that CNCs modified cementitious composites have excellent chlorine ion penetration resistance property, which also comes from the decrease of porosity and improvement of matrix compactness.

3.4 Functional performances

Owing to the high specific surface area, easy wettability and excellent thermal property, the addition of nanocellulose is expected to endow cementitious composites with functional and smart performance. Mejdoub et al. [29] measured the thermal expansion property of cementitious composites with CNFs and found that the coefficient of thermal expansion (CTE) of cementitious composites increases with the NFCs content increasing. When the NFCs content is 0.1 wt.% and 0.3 wt.%, the CTE is increased by 0.8% and 7%, respectively. It should be pointed out that CNFs can refill pores and release absorbed water during the expansion process of composites to realize self-curing, achieving the purpose of sustained increase of strength or recovery of performance after damage. The self-curing effect of nanocellulose in cementitious composites are shown in Fig. 15, which can be divided into two stages. First, nanocellulose can absorb water to lower local water-cement ratio of composites. Second, with the progress of cement hydration and the change of osmotic pressure inside the composite, the water stored in nanocellulose is released to promote the continuous hydration of cement [71-73].

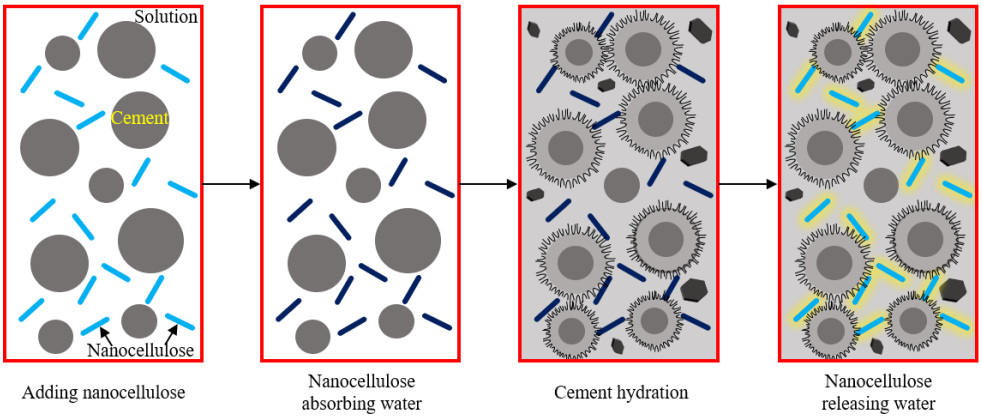

Fig. 15. Self-curing effect of nanocellulose in cementitious composites

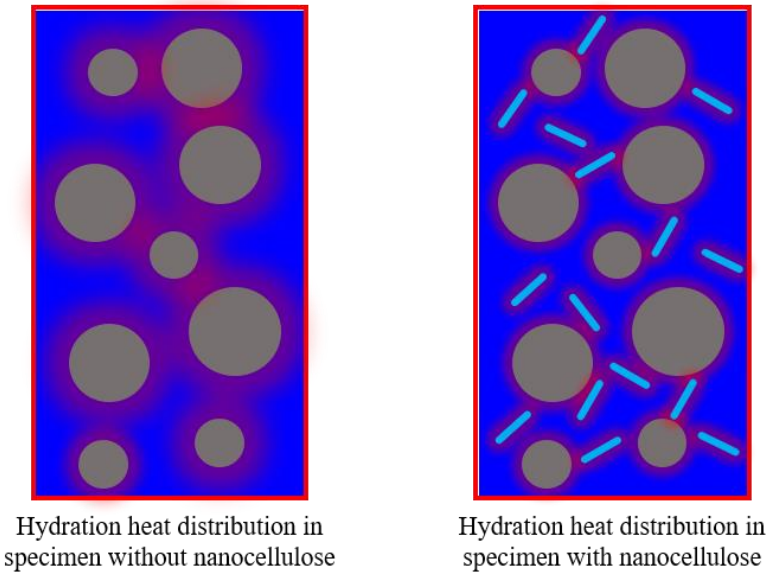

Fig. 16. Hydration heat distribution effect of nanocellulose in cementitious composites

Meanwhile, the thermal conductivity of NFCs modified cementitious composites is also investigated by Mejdoub et al. [29]. They observed that a small content of NFCs, as low as 0.3 wt.%, is sufficient to increase the thermal conductivity of cementitious composites by up to 20%. It is proved that nanocelluloses with good thermal conductivity provide channel for transferring hydration heat (as shown in Fig. 16), thus improving the uniformity of heat distribution and reducing initial cracks in cementitious composites caused by thermal stress, making it possible to use nanocelluloses modified

cementitious composites in mass structure.

Flores et al. [38] found the electrical resistivity of cementitious composites with CNCs (with content from 0.4 wt.% to 0.8 wt.%) is slightly lower than that of control sample at curing ages of 3 d. However, the resistivity of cementitious composites is gradually enhanced with the curing age increasing (after 14 days). The anionic charge density on the surface of nanocellulose can be pretreated by different chemical oxidation to promote the charge density and thermal/electric conductivity of biomass-derived nanocellulose modified cementitious composites [19].

4 Applications of biomass-derived nanocellulose modified cementitious composites

Owing to the environmentally-friendly characteristics and excellent mechanical performances, cementitious composites with biomass-derived nanocellulose have great application prospects in the field of civil engineering [5, 25, 35, 59, 74]. The addition of CNCs is conducive to adjusting rheology and reducing fluid loss of fresh OWC slurry [16, 33, 39, 75]. Sun et al. [76] found the strength of cementitious composites is improved due to the bridging effect of CNFs /GNPs between cement matrix, the reinforcement is described in Fig. 17. Sun et al. [33] used CNFs as OWC rheological modification fillers, and demonstrated that the shear stress of cementitious composites increases with the shearing rate and loading level increasing of CNFs. Ramasamy et al. [36] showed the addition of nanocellulose can endow cementitious composites with better yield stress and structural rigidity to resist disadvantageous forces outside. The pulled-out energy and fiber roughness of BNCs are improved by covering process in order to modify the contact area, anchorage property and frictional bond property between cementitious composites and nanocellulose [35]. Similarly, the mechanical properties of interfacial transition zone of cementitious composites is improved by the

addition of CNFs, due to that CNFs decrease the porosity of interfacial transition zone and enhance the polymerization of C-S-H gels. Dousti et al. [16] reported CNCs are used to improve the viscosity and stability of OWC with bentonite. Bakkari et al. [75] revealed that the incorporation of nanocellulose is beneficial to reduce the settling velocity and the flow hanging of cementitious composites in the application of plastering brick and mortar. Meanwhile, the crack area and shrinkage width of cementitious composites can be reduced by adding CNFs.

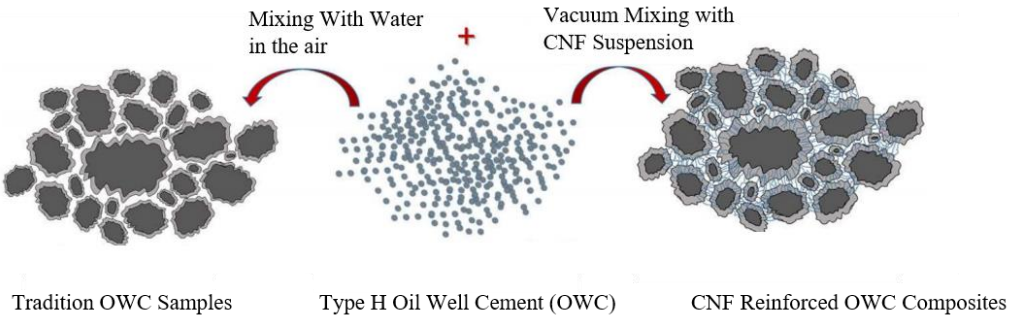

Fig. 17. Nanocellulose modified oil well cement reinforcement [76]

Furthermore, biomass-derived nanocellulose modified cementitious composites can be used as a waterproof membrane due to the hydrophobic of nanocellulose [19]. Based on the biodegradable matrix, biomass-derived nanocellulose modified cementitious composites is expected to address the issue of wastewater treatment, because the cations of nanocellulose can be reacted with sulphate ions, and the carboxyl groups (COO-) of nanocellulose can be also reacted with the cations (K+, Na+, Ca2+) in waste water, removing the redundant ions and refining the wastewater (as shown in Fig. 18) [19, 21]. Balea et al. [19] revealed that nanocellulose is a potential flocculant to form a three-dimensional network in cementitious composites, as well as to obtain flocculation efficiency and performance by grafting with flocculant or chemically modification. Hoyos et al. [53] pointed out that CNF is a viscosity improver in fresh cement and a

micro-crack prevention agent in high-temperature cement. Hisseine et al. [65] revealed that using CNFs instead of fly ash improves the ductility of strain-hardening cementitious composite by enhancing the interface transition zone performance. Furthermore, nanocelluloses is a potential internal curing agent for cementitious composites to promote cement hydration [77].

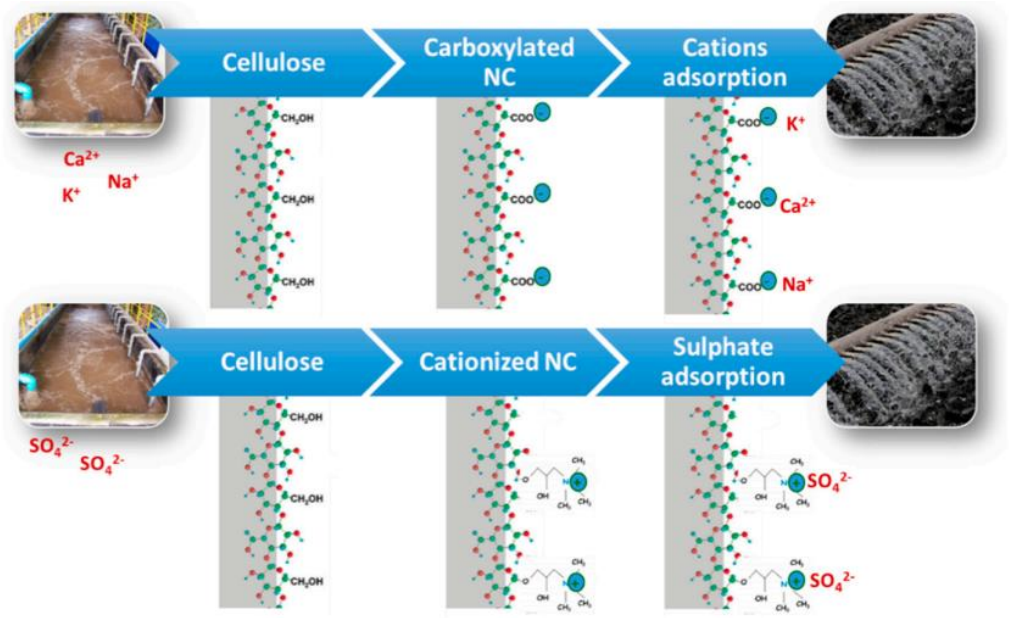

Fig. 18. A representation of cation and sulphate adsorption using nanocellulose [19]

5 Conclusions and Prospects

Despite their high brittleness and substantial environmental footprint, cementitious composites remain the dominant and most commonly-used structural materials for infrastructures in the foreseeable future. Therefore, reducing the carbon footprint, improving the sustainability, and modifying the toughness of cementitious composites are becoming a global imperative. Owing to the nano-size, environmentally-friendly, excellent mechanical properties, and good thermal conductivity, biomass-derived nanocellulose is a promising filler to fabricate cementitious composites with enhanced strength and toughness as well as durability, desired functional performance, and low life cycle cost, thus cutting down cementitious composites' environmental downsides,

developing sustainable infrastructures, and addressing the ecological issues caused by the extensive use of cementitious composites. Therefore, biomass-derived nanocellulose modified cementitious composites have drawn remarkable attention from engineers and researchers. The incorporation of biomass-derived nanocellulose can significantly modify the workability/rheology, and setting time of cementitious composites to meet engineering requirement. Meanwhile, thanks to the nano-size, large specific surface area and wettability, adding biomass-derived nanocellulose is conducive to the hydration of cementitious composites, thus reducing the shrinkage, lowering the porosity, and improving the compactness and strengths. Furthermore, the interface optimization effect of biomass-derived nanocellulose improves the toughness and durability of cementitious composites. Hence, the composites have been successfully used in oil and gas industry to modify the drilling technology and improve the efficiency of surface and wastewater treatment of civil engineering infrastructures. As a new type of cementitious composite, the research and application of biomass-derived nanocellulose modified cementitious composites will potentially provide new opportunities to develop sustainable, durable and smart infrastructures in the future.

It is worth noting that the production of biomass-derived nanocelluloses from renewable materials is still in the early stage, and most researches on biomass-derived nanocellulose modified cementitious composites are only in the laboratory investigation stages and have not been implemented in the construction industry. Meanwhile, further experiments are required to be carried out on biomass-derived nanocellulose modified cementitious composites with coarse aggregates. Furthermore, detailed research studies on the following limitations should be explored in the future, such as the dispersion influence of biomass-derived nanocellulose on cementitious composites, ways to optimize the dispersion of high viscosity cement slurry with

nanocellulose, durability, multifunctionality and the reinforced mechanisms of biomass-derived nanocellulose modified cementitious composites.

Regardless of current challenges, the utilization of biomass-derived nanocellulose is expected to provide a new direction for the development of cementitious composites and structures due to its nano-core effect, excellent internal performances and ecological characteristics. For example, the internal self-curing of cementitious composites can be realized based on the good water retention of nanocellulose, thus offering a possibility for dealing with the strength decreasing problem of cementitious composites. Biomass-derived nanocellulose can also be expected to fill in cracks and continuously hydrate to obtain self-healing cementitious composites. Biomass-derived nanocellulose is potential to improve the compactness and toughness of hydration products by developing ion adsorption and ion exchange effect, thus improving the structure of cementitious composites at the nanoscale and providing a bottom-up method for improving the service life of structures.

Compliance with Ethical Standards

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Conflict of Interest: The authors declare that they have no conflict of interest.

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