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Effect of nanocellulose on mechanical properties of cementitious composites – A review

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ABSTRACT

In the quest for innovative construction materials that enhance sustainability and performance, cementitious composites incorporating nanocellulose (NC) have unveiled a new chapter. NC-reinforced composites have been successfully applied in areas such as medical, food, paper and electrochemical industries. However, their application within civil engineering remains in its infancy, despite their unparalleled reinforcing capabilities for cementitious composites. This study examines the influence of NC as both a standalone and a hybrid reinforcement in cementitious composite materials, systematically summarizing the research and key findings. Concurrently, it critically assesses the constraints and challenges identified in literatures, proposing viable avenues for future research. It is expected that this comprehensive review will provide insights for future research and promote applications of NC as a reinforcement in cementitious composites.

1. Introduction

Within the civil engineering discipline, there is a constant pursuit for innovative construction materials that enhance mechanical performance, economic efficiency and sustainability. Although concrete remains the most prevalent construction material, its inherent brittleness limits its applications. This raises concerns about material durability and structural resilience, along with the environmental concern stemming from the significant carbon emissions produced during the manufacturing process, particularly from cement, the main ingredient of concrete. A wide range of research has been carried out improving the performance of cementitious materials, especially through the incorporation of reinforcing material such as fibres [1–3], which have been found to significantly reduce brittleness while enhancing ductility and durability [4–6]. The development of fibre-reinforced cementitious composite materials has advanced through multiple stages. Initially, cementitious composites were reinforced with short fibres of macro length, derived from a diverse range of materials such as glass, carbon, synthetic and natural fibres [4,7,8]. Subsequently, this method evolved into the development of hybrid fibre reinforcements, which entailed combining various fibre types or lengths [7,9,10]. A significant advancement in fibre-reinforced cementitious composites was realized in the 1990 s with the creation of unique engineered cementitious composites (ECC) [3,11–15].

ECC is a cementitious composite material characterised by superior ductility, achieved through microfibre reinforcement, which typically constitutes 2% of volume fraction (vol%) [16]. It has demonstrated notable enhancements in tensile strain capacity (3–8%), tensile strength (4–10 MPa) and fracture toughness ($> 35\,kJ/m^2$), markedly surpassing conventional concrete and cementitious composite in tensile ductility by several hundred times [17,18]. However, due to the absence of coarse aggregates, large quantity of cement is required to achieve sufficient compressive and flexural strength [19,20]. Existing research suggests that this can be alleviated by integrating nanomaterials [21–23]. While microfibres such as polymer fibres can create covalent bonding with the cement matrix, their low specific surface area compared to nanofibres may lead to weaker interfacial strength [24], potentially resulting in the entrapment of air voids and compromising strength [25]. Thus, reinforcement at the nanoscale emerges as a viable approach to counteract the adverse impact.

According to the definition of National Nanotechnology Initiative (NNI), a material is classified as a nanomaterial if it possesses at least one dimension smaller than 100 nm. The particle size distribution of different type of concrete and the ingredients on the micro and nanoscale is portrayed in Fig. 1.

Nanofillers ensure a more uniform distribution of reinforcement within a matrix, allowing those dispersion particles to be positioned in closer proximity to each other [27,28]. This arrangement facilitates a more uniform stress distribution within the composite, thereby enhancing the overall mechanical properties by optimizing the interactions between the dispersion phase and the matrix. When nanomaterials

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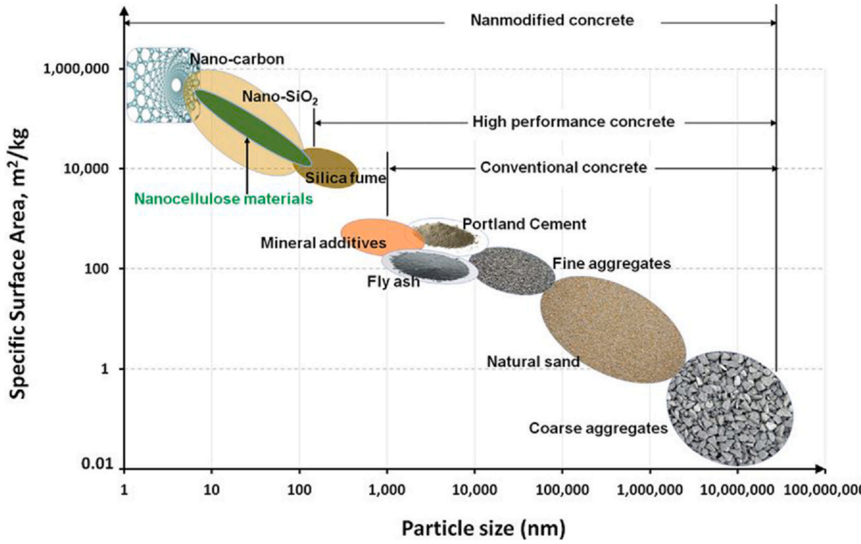

Fig. 1. Comparison of particle sizes of concrete materials [26].

are added to the cement mix, they act as a filling agent, hindering the formation of micron-sized pores or gaps and densifying the matrix. [29]. Nanomaterials such as nano silica, nano clay, carbon nanotubes and graphene oxide have been used as reinforcement in cementitious composites [30–32]. However, difficulties in dispersing and the high cost of production have limited the widespread application of these materials [27,33]. Additionally, the extensive surface area and high aspect ratio of graphene oxide and carbon nanotubes lead to Van der Waals forces which may promote the aggregation of these nanomaterials into clumps. This could adversely affect the mechanical properties of nanocomposites by impeding the uniform distribution and effective integration of the nanomaterials within the matrix. Therefore, researchers have made constant efforts in assessing the suitability of alternate nanomaterials to address these challenges and broaden the application of nanomaterials in cementitious composites.

The advent of plant-derived nanomaterials, particularly nanocellulose (NC), coupled with the growing demand for sustainable construction and building materials, has redirected the focus of nanomaterial research towards environmentally friendly alternatives. Being an abundant natural ingredient, NC has been regarded as one of the most sustainable raw materials [34], with environmental advantages such as renewability, biodegradability, minimal environmental impact and reduced health hazards during production. It also has potentially low manufacturing costs, given that NC is sourced from widely available natural resources; thus it would be more cost-effective compared to other nanomaterials [35]. Studies have demonstrated that even minimal additions of NC significantly influence the performance of matrices, underscoring its potent efficacy as a green reinforcement agent. This is attributed to their large surface area and surface effects dominating over bulk properties, thereby playing a key role in property enhancement [29,36]. Furthermore, NC possesses remarkable mechanical and physical benefits such as high modulus and strength, extensive specific and reactive surface, significant aspect ratio, hydrophilic and hygroscopic properties [23,37]. As such, with the growing need to reduce the carbon footprint of infrastructure materials, NC is undoubtedly a better alternative than the conventional nanomaterials for cementitious nanocomposites.

Despite these benefits and the wide adoption of NC in multitude of sectors such as medical, food, paper and electrochemical industries [38], its application in the construction industry has been limited so far. To advance its application in construction materials, extensive research and development are needed to fully understand the effect of incorporating NC into cementitious materials. This is crucial to provide a clear roadmap on how NC can be effectively employed to enhance specific properties and identify potential areas for improvement in cementitious materials. To date there are a number of review papers providing comprehensive overviews on the state-of-the-art research on NC [34,38]. Nevertheless, the applications of NC in cementitious composites have received less attention. While some recent reviews have captured research in the realm of NC applications in cement systems they mainly focus on its basic effects, such as strength improvement [21–24]. However, there are still areas in NC based cementitious composites that require further recognition. One such area is NC's impact on mechanical properties of hybrid fibre reinforced cementitious composites, in particular its effect on hybrid ECC. To recognise the significant role NC can play by hybridising with micro fibres, it is vital to present a comparison of the effects of NC as a single reinforcement in contrast to hybrid reinforcement. However, this has not been addressed in any existing review papers.

This paper address this gap while providing a comprehensive discussion on NC's functionalities that promote cement hydration and its excellent performance as a green reinforcing agent. It compiles and summarises the findings of existing research on the effect of NC on the mechanical properties of cementitious composites, while providing a comparison of its role as a single and a hybrid reinforcement. This review underscores the contribution of NC to the development of high-performance, environmentally friendly ECCs. By highlighting the advantages of NC, this paper aims to encourage further research and development of new NC-based cementitious materials that surpass traditional options, meet contemporary demands in concrete technology, and provide sustainable solutions in civil engineering.

2. Nanocellulose overview

2.1. Source and structure of nanocellulose

Nanocellulose (NC) is a type of nanofibres derived from cellulose which is an organic polymer composed of glucose units. It is the main substance found in plant cell walls and is the most abundant biobased polymer on earth [39,40]. The general term 'nanocellulose' refers to cellulosic extracts or processed cellulose in nanoscale dimensions [39]. Nanofibres are embedded in the cellulose cell walls and can be extracted and isolated using different treatment processes [41]. Cellulose is derived from a wide range of natural sources, including hardwood, softwood, seed fibres, bast fibres, grasses and marine sources such as tunicates, algae and fungi [39]. However, wood has been the most commercially used natural resource containing cellulose [34]. Cellulose composes approximately up to 50% of wood mass [40,42]. Its molecules are biosynthesized as nanosized fibrils, where glucan chains bundle together to form elementary fibrils, which then aggregate to

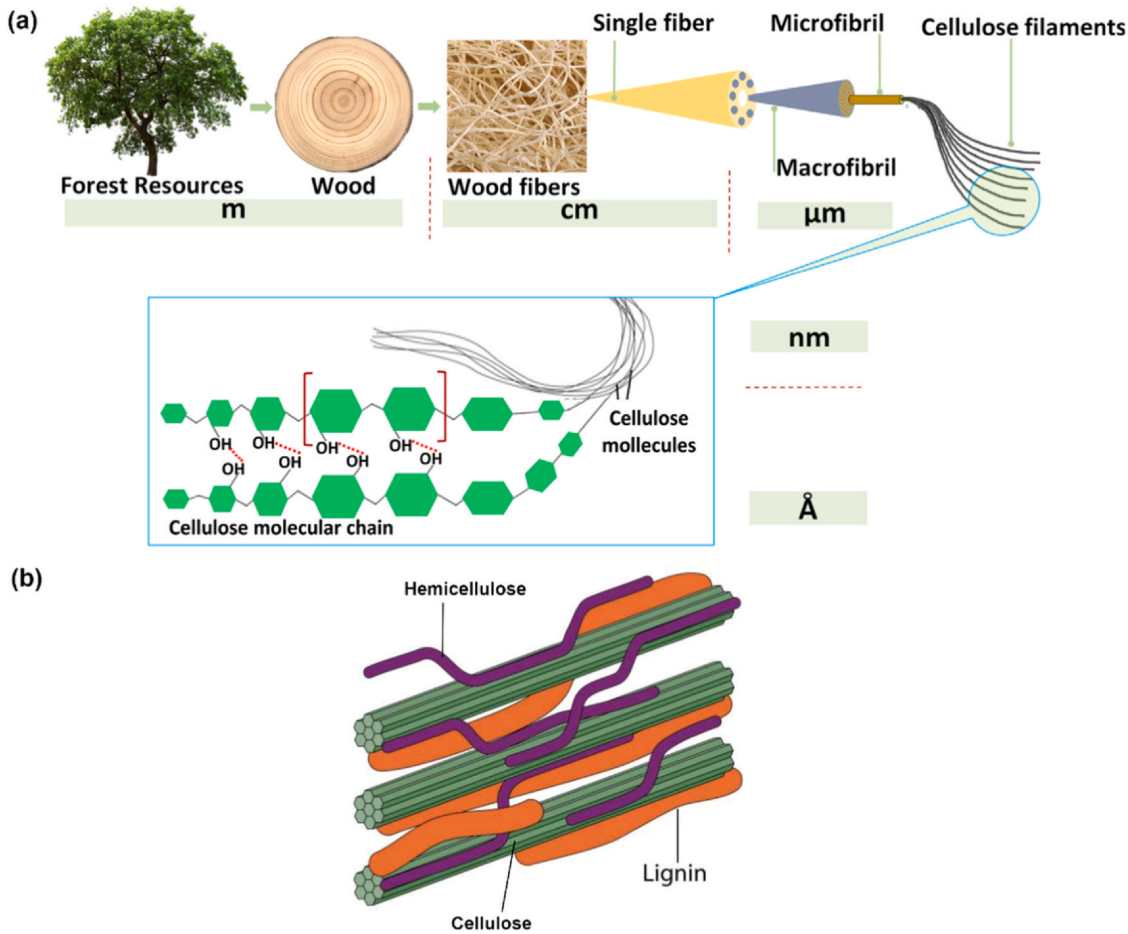

Fig. 2. Simplified model of the structural hierarchy of cellulose filaments and plant cell wall. (a) Hierarchical structure of cellulose filaments [44]; (b) Hemicellulose and lignin surrounding cellulose in a plant secondary cell wall before extraction[45].

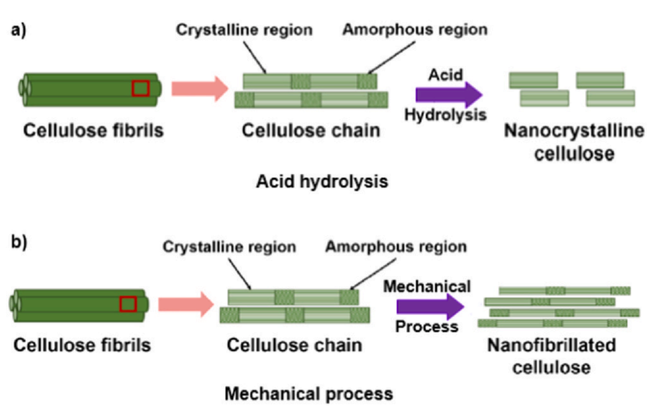

Fig. 3. Schematic of the extraction process of nano cellulose[47]. (a) Cellulose nanocrystals extraction using acid hydrolysis; (b) Cellulose nanofibrils extraction using mechanical process.

form microfibrils. These microfibrils are densely packed in crystalline domains linked by amorphous regions, ultimately forming cellulose fibres. It is the hierarchically fibrous structure within plant fibres that facilitates the extraction of elementary fibrils from cellulose at the nanoscale [43]. A simplified model of the hierarchical structure of cellulose filaments is depicted in Fig. 2(a).

2.2. Types of nanocellulose

Different isolation processes can be used to extract NC from cellulose. The most common processes are simple mechanical methods such as homogenization, ultrasonication and ball milling, acid hydrolysis or a combination of chemical and mechanical methods [41,46,47]. During the extraction and isolation processes, the less stable and weaker components or impurities, such as hemicellulose, lignin (Fig. 2b), pectin, wax and soluble sugars, are removed leaving the purified cellulose fibre [44]. Consequently, the amount of amorphous material present is reduced and nanofibres of high crystallinity are produced [34].

The different approaches used to extract nanoparticles from cellulose sources result in particles with varied crystallinities, surface chemistries and mechanical properties [38]. NC is often divided into the following types:

- *Cellulose nanocrystals (CNC):* These are also referred to as nanocrystalline cellulose and cellulose nano-whiskers. CNC are mainly produced by acid hydrolysis and heat-controlled techniques, with sulphuric acid being the most utilized acid. Acid hydrolysis removes the amorphous regions of the cellulose, resulting in the isolation of pure cellulose crystals as illustrated in Fig. 3(a) [38,47]. They comprise rod-like, highly crystalline cellulose particles whose dimensions vary by source, typically ranging 2–20 nm in diameter and 50–500 nm in length for plant-derived sources. CNC have a lower aspect ratio, lower moduli (50–100 GPa) and limited flexibility due to the absence of amorphous portions compared to cellulose nanofibrils (CNF) [40].
- *Cellulose nanofibrils (CNF):* These are alternatively called nano-fibrillated cellulose. CNF are composed of flexible, micrometre-long fibrils made up of bundled cellulose chain molecules, distinguished by their entangled configuration. Unlike CNC which have near-

perfect crystallinity [34,38], CNF have alternating crystalline and amorphous domains (Fig. 3(b)). They are approximately 1–100 nm in diameter and 500–2000 nm in length [46]. The extraction of CNF from cellulosic fibres can be achieved by mechanical treatments (e.g., homogenization, grinding and milling), chemical treatments (e.g., TEMPO oxidation) or a combination of chemical and mechanical treatments [38]. CNF mainly contains cellulose (> 95%) and a small amount of hemicellulose (< 5%) [44].

- *Cellulose filaments (CF)*: These are mechanically processed cellulose fibrils without any treatment. CF share some similarities with CNF in structural characteristics but are distinguished by their elongated length (100–2000 μm) in comparison to their diameter (30–400 nm), resulting in a notably higher aspect ratio (100–1000) [36].
- *Bacterial cellulose (BC):* BC particles are microfibrils secreted by various bacteria and have different morphologies, but they are typically ribbon like fibrils (6–10 nm wide and 30–50 nm long) [34]. Different from plant-source NC which may require pre-treatment to remove lignin and hemicelluloses before hydrolysis, BC is synthesized as pure cellulose [38].

A general microscopical images of entangled fibrils CNF, rod-like CNC, CF network and ribbon like BC are further shown in Fig. 4, with a summary of their characteristics compiled in Table 1.

2.3. Properties of nanocellulose in comparison to natural cellulose

NC possesses exceptional properties that combine the properties of cellulose as well as the unique features of nanomaterials offering several advantages over cellulose. When transforming natural cellulose fibres into nanostructured cellulose fibres, the treatment process not only enhances properties absent at the microscale but also eliminates degradable compounds. This purification step significantly mitigates the inherent limitations of natural cellulose, such as issues with long-term durability and susceptibility to mineralization, thereby elevating the performance and utility of the cellulose fibres.

Furthermore, nano fibrillation addresses the issues such as low Young's modulus, poor fibre-matrix compatibility and variable fibre properties, which lead to inconsistencies in quality and performance. Fibres have relatively low strength when used in natural form as bundles, but a higher intrinsic strength can be observed when these are used as nanofibrils. For instance, the strength of vegetable fibres improves from 600 MPa to 1500 MPa in nanofibril form [50]. As the irregular and variable cross-sections and the lumens are removed when extracting NC, consistency in the mechanical properties such as Young's modulus [51–53] and tensile strength [22] is increased. Hence, nano fibrillation allows the exploitation of high stiffness of cellulose crystals.

Additionally, NC mitigates issues such as the delayed hydration as seen in natural fibres [54–56]. This is achieved by removing chemical constituents and soluble sugars through fibre processing to enhance the compatibility and performance [35]. Moreover, the higher aspect ratio and surface area resulting from the nanoscale size of NC make it a superior reinforcing material compared to traditional cellulose [34,39]. It has been reported that the specific surface area increases significantly (from 50 to 500/gm) when cellulose fibre are nano fibrillated as shown in Fig. 5 [50]. Thus, NC allows a higher reinforcement capacity without increasing the fibre percentage in a nanocomposite [39].

3. Main functionalities of nanocellulose affecting the mechanical properties of cementitious composites

Numerous studies have been conducted focusing on the investigation of cementitious nanocomposites containing nanocellulose (NC). The main functionalities of NC as reported in the literature are compiled and discussed below.

3.1. Internal curing and degree of hydration

Due to their hydrophilic nature, cellulose fibres absorb water during mixing and act as internal water reservoirs [39,58]. This phenomenon is commonly referred to as internal curing [59]. According to Cao et al.

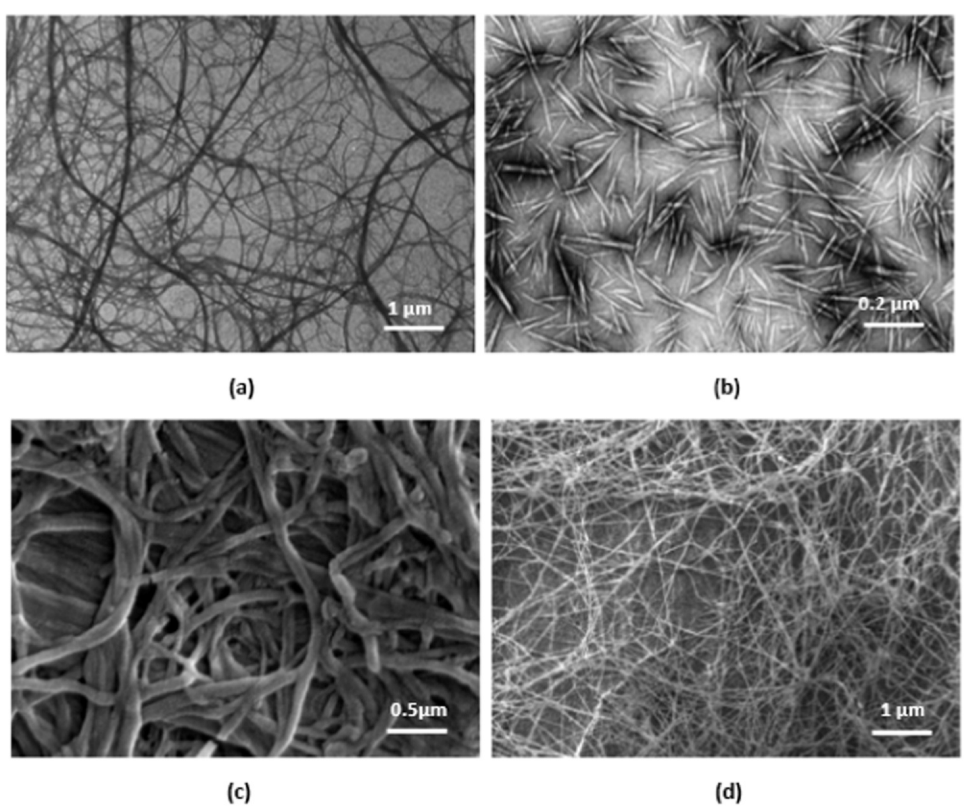

Fig. 4. Microscopical images of (a) Cellulose nanofibrils; (b) Cellulose nanocrystals; (c) Cellulose filaments; and (d) Bacterial cellulose [36,48,49].

Table 1
Characteristics of main types of NC.

	Cellulose nanofibrils	Cellulose nanocrystals	Cellulose filaments	Bacterial cellulose
Shape	long, flexible and entangled	Rod like or whisker shaped	Entangled but less intricate than CNF	Ribbon like fibrils
Diameter	1–100 nm	2–20 nm	30–400 nm	6–10 nm
Length	500–2000 nm	50–500 nm	100–2000 µm	30–50 nm
Distinctive characteristic and shape	High aspect ratio and refined from wood and plant fibre	Lower aspect ratio compared to CNF and a limited flexibility due to the absence of amorphous portions	Very high aspect ratio and more unform structure than CNF	Micro fibrils secreted by various bacteria

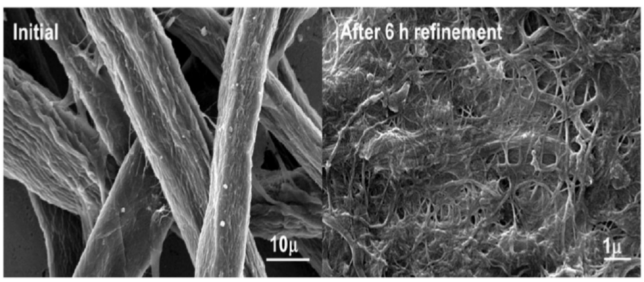

Fig. 5. Sisal pulp initial (diameter = 10–20 µm conventional) and after 6 h of refinement - mechanical treatment (diameter = 25–250 nm) [57].

[60], the additional surface area provided by NC works as nucleation sites. NC can bind to the surfaces of cement particles, serving as a conduit for transporting water into the cores of unhydrated cement. This process not only delivers additional water but also facilitates the hydration process, enhancing the overall cement matrix [61,62]. Fig. 6 provides a schematic of the formation of hydration products around a cement particle with and without cellulose nanocrystals. As depicted, the cellulose nanocrystals adhere to the shell of hydration products, aiding in achieving a higher degree of hydration (DOH). The water-retention capability of NC plays a crucial role in reducing self-desiccation throughout the hydration process, consequently diminishing autogenous shrinkage.

Kawashima et al. [63] noted reductions of 13% and 32% in autogenous shrinkage by using 1 wt% and 2 wt% of NC, respectively. Kolour et al. [64] also reported a significant 49% reduction in autogenous deformation by using 0.06 wt% of NC. Studies have further reported that DOH increased due to addition of NC in cementitious composites and escalated further as the dosage of NC increased [37]. Cao et al. [60] noted that the DOH increased by 20% (~42% improvement with respect to the control sample) for cement pastes containing 1.5 vol% of cellulose nanocrystals after 28 days using chemically bonded water as a metric. Onuaguluchi et al. [35] employed non-evaporable water content in mixtures as an indicator of DOH and observed increments of 9.2, 10.4, 11.6 and 12.7% in cement mixtures containing 0.05, 0.1, 0.2 and 0.4 wt% of NC, respectively, compared to the control mix without NC after 28 days. The enhancement in DOH was linked to the internal curing effect of NC and the process of steric stabilization. Steric stabilization occurs when large molecules attach to the surface of nanoparticles, forming a protective layer that inhibits particle aggregation by preventing them from coalescing with each other. This action allows a more uniform distribution of NC within the composite, contributing to its improved hydration properties [60]. Fig. 7 presents the enhancements of DOH due to addition of NC as reported in the existing literatures. It can be observed that the addition of even very small dose (0.05 wt%) of NC can significantly improve the DOH. This improvement could be further augmented by increasing the dosage or altering the type of NC.

3.2. Matrix densification and porosity

The high aspect ratio and enlarged surface area resulting from the NC fibrillation should serve as nucleation sites, enhancing the

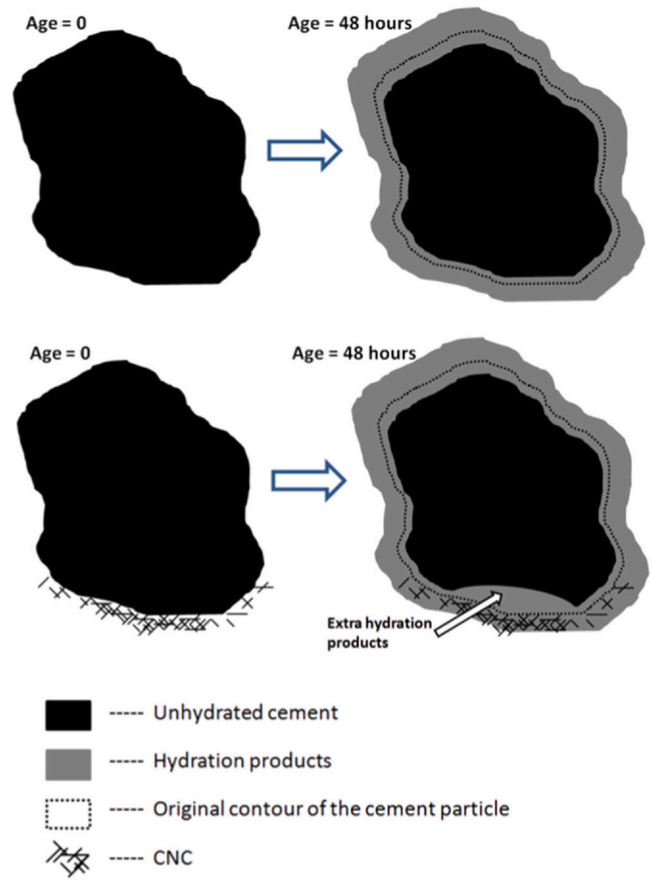

Fig. 6. A conceptual schematic of the hydration products forming around the cement grains in the presence of cellulose nanocrystals and without cellulose nanocrystals [60].

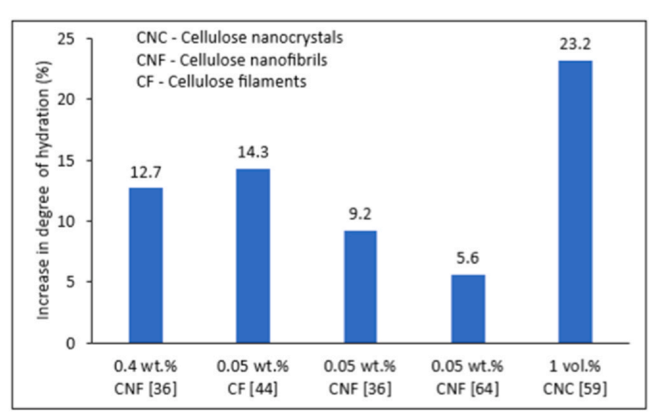

Fig. 7. Enhancements of degree of hydration in cementitious composites due to addition of nano cellulose.

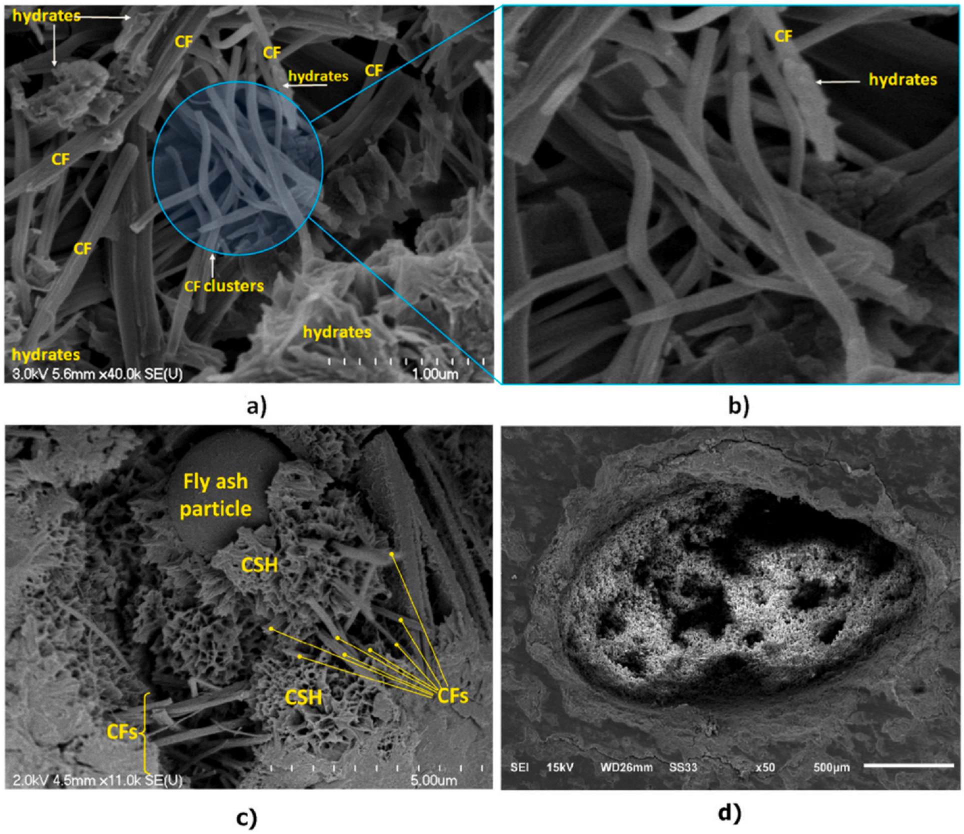

Fig. 8. SEM images of a cement paste mixture reinforced with different fractions of nanocellulose. (a) Interaction of nanocellulose in a paste mixture with 0.3 wt% dosage; (b) Spot of nanocellulose clusters in the paste mixtures with 0.3 wt% dosage [44]; (c) Interaction of nanocellulose in a paste mixture with 0.1 wt% dosage forming more hydrates [72]; (d) Fibre agglomeration in a 0.4 wt% dosage showing fibre pockets [35].

interaction between the fibres and the matrix. Consequently, the cement hydration is accelerated due to the water-retaining mechanism of NC, producing more calcium silicate hydrate (CSH) gel. As a result, the total porosity is reduced and a more densified matrix is formed in the resulting nanocomposite cement pastes in comparison with the pastes without NC [60,65].

It has been observed that it is easier and faster for the water molecules to diffuse in the nanofibril network than in the matrix [60], and this can accelerate the production of CSH gel during hydration at the fibre-matrix interface. Thus, the open pores that were originally filled with water can now be filled with hydrated products forming a more homogeneous, dense and compact microstructure [39]. The literature consistently reports that incorporating NC into cementitious compositions effectively reduces porosity. Mejdoub et al. [66] observed a reduction of 36% in the porosity by adding 0.3 wt% of cellulose nanofibrils to cement in comparison with the control sample [66]. Cao et al. [67] reported a 16% porosity reduction in comparison to plain cement pastes by using 1.5 vol% of cellulose nanocrystals. However, achieving a reduction in porosity relies on ensuring fibres are evenly dispersed with minimal clustering.

3.3. Hydration time

Studies have demonstrated that cement pastes containing NC exhibit a delay in reaching the peak of heat flow [68]. Delays of 0.8, 3.2 and 6.9 hour in the peak hydration time were reported by Onuaguluchi et al. [35] in the mixtures containing NC at 0.05, 0.1, 0.2 and 0.4 wt%, respectively. The enhanced viscosity and reduced fluidity observed in nanocomposite cement pastes were linked to a delayed peak hydration time. Several studies have also indicated that the heightened need for superplasticizers, when incorporating NC, may contribute to delaying the hydration process [69,70]. Haddad et al. [64] reported a deceleration of the hydration reaction during the early stages when high dosages of cellulose nanofibrils were employed. Cao et al. [60] observed a deceleration in the hydration process within the initial 25 hours for cellulose nanocrystals concentrations ranging 0.04–1.5 vol %. This deceleration was linked to the interaction of nanocrystals with cement particles, which reduced the available surface area for water contact, thereby slowing the hydration reaction.

3.4. Agglomeration

Studies have indicated that as the NC concentration increases, there are increments in viscosity and yield stress [60] and a decrease in workability [71]. At low concentrations, NC is mostly in the form of free particles in the water and therefore have higher mobility. As NC concentrations rise, the interaction among NC particles intensifies, leading to the formation of agglomerates or network structures. This phenomenon is attributed to the presence of surface hydroxyl (–OH) groups, which facilitate bonding between particles [44,60]. These –OH groups try to bond with adjacent –OH groups by hydrogen bonds, resulting in agglomeration or entanglement of the nanofibres [32]. When fibres agglomerate, the benefits targeted by incorporating NC as a reinforcing material are lost. This is because the high porosity in the mix caused by agglomeration acts as stress concentrators, resulting in a strength reduction. Therefore, the effective dispersion of fibres is crucial to acquire the desired properties. It has been reported that as the NC concentration increases, mixes always reach a threshold where agglomerates start to prevail regardless of the dispersion technique [35,60]. For instance, the additions of cellulose filaments beyond 0.2 wt % [44], cellulose nanocrystals [60] beyond 0.2 vol% and cellulose nanofibrils [35,65] beyond 0.1 wt% have caused decline in the flexural strength enhancement. The scanning electron microscope (SEM) images of cement pastes with NC of different dosages are portrayed in Fig. 8. The presence of CSH formation is more noticeable in paste mixtures containing 0.1 wt% of NC (Fig. 8c) compared to those with 0.3 wt% NC (Fig. 8a), whereas air pockets are observed in the mixture containing 0.4 wt% NC (Fig. 8d).

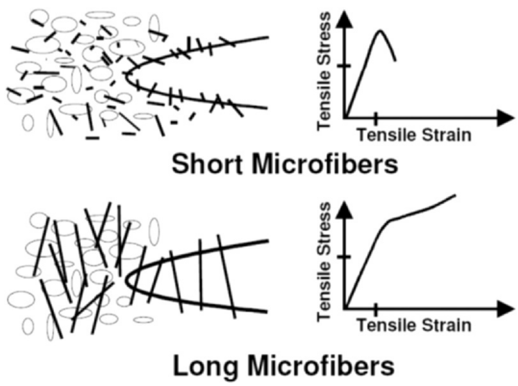

Fig. 9. A schematic illustration of the effect of fibre length on the toughness of cementitious composites [61].

3.5. Crack bridging capacity

It is known that microfibres can bridge the cracks at the micro-level and are effective in preventing cracks from further growing. Consequently, they promote toughness or energy absorption of cementitious composites. On the other hand, when the fibres are short (length ≤ 1 mm), they do not have sufficient length to bridge the cracks with large widths as shown in Fig. 9, and hence, are not able to improve the toughness of the composites [60]. The short fibres can, however, bridge the cracks with width smaller than the fibre length. Thereby, they can effectively arrest the cracks and prevent them from further growing and coalescing with each other. As a result, short fibres contribute to strength enhancement but are inconsequential to improving the toughness of the matrix [60]. Studies further indicate that both adequate fibre length and fibre count are essential for effectively transferring stress across microcracks in concrete, thereby mitigating the crack propagation [72]. Therefore, to inhibit cracks, an ample volume of fibres must be present at the crack tip. The tight arrangement of NC fibres enhances their presence at crack tips. Therefore, adding significant quantities of fibres is expected to enhance crack bridging at the micro level, assuming that the fibres are properly dispersed.

Therefore, unlike the conventional fibre cementitious composites, NC-reinforced cementitious composites suffer a sharp decrease in load carrying capacity and exhibit an abrupt matrix rupture as the small size of the NC fibres prevents them from acting as a link after cracking of the matrix [73]. Ardanuy et al. [50] reported a 36% increase in flexural strength but a 53% reduction in fracture energy when using the same quantities of cellulose nanofibrils (CNF; 3.3 wt%), as compared to microfibre-reinforced composites. Similar observations were reported by Claramunt et al. [73] where flexural strength was increased by 6% while fracture energy was decreased by 6%, at the same cellulose nanofibrils dosage.

4. Mechanical properties of nanocellulose-reinforced cementitious composites

Mechanical properties of cement matrices employing nanocellulose (NC) as a single reinforcement and as a hybrid reinforcement encompassing natural cellulose and synthetic fibres have been investigated by researchers. The main findings from these studies are discussed herein and a concise summary of the analysis is presented in Table 2. This section primarily focuses on discussing the properties of fine aggregate cementitious composites incorporating cellulose nanofibrils (CNF), cellulose nanocrystals (CNC) or cellulose filaments (CF). The majority were focused on flexural properties and energy absorption capacity. Moreover, the studies predominantly focus on CNF and CNC extracted from sisal, eucalyptus and kraft pulps. Various dosages of CNF or CNC, ranging 0.1–8 wt%, have been effectively utilized through different dispersion techniques. The fine aggregate cementitious composites reinforced with NC are compared against the counterparts without NC, as well as the counterparts with natural fibre and polyvinyl alcohol (PVA) fibre.

4.1. Effect of NC on flexural strength

Generally, the current studies have indicated an enhancement in flexural strength, varying from 6.1% to approximately 106% with the use of CNF, and from 13% to about 25.3% for CNC. The improvement is attributed to the high degree of hydration (DOH) caused by the filler hydrophilic nature, high intrinsic properties and the dense matrix that enables better stress transfer. This is reviewed in detail below.

4.1.1. NC-reinforced cementitious composites

The addition of NC to cement pastes (without any other fibre reinforcement) has shown improvements ranging 17–106% in flexural strength. Hisseine et al. [72] explored the impact of CF at concentrations as low as 0.1, 0.15 and 0.2 wt% in cement pastes, studying flexural strength under both moist (22°C, 100% relative humidity (RH)) and sealed curing (22°C, 50% RH) conditions. While the flexural strength was found to increase under both conditions, the results revealed higher enhancements under the sealed curing conditions (19, 34 and 38%, respectively) than the moist curing conditions (10, 25 and 28%). The study asserted that excessive water saturation under moist conditions is responsible for this phenomenon. Hydrophilic and hygroscopic CF serves as an internal curing agent as the cementitious matrix hardens at later stages (after 24 hours) and when curing in moist conditions, water saturation can result in fibre softening and weaker fibre-matrix bonds.

While the research indicated improvements in flexural strength with rising concentrations of CF, a follow-up study employing the same type of NC identified a threshold at 0.2 wt% CF [44]. This study reported 16.1, 18.8 and 20.7% increments with 0.05, 0.1 and 0.2 wt% CF dosage, respectively. Beyond this concentration, more NC resulted in a decline in enhancement due to fibre agglomeration [44]. However, it is worth noting that the former study utilized a viscosity-modifying agent in the mixes, which could have contributed to better dispersion and less agglomeration.

For CNF reinforced composites, Onauguluchi et al. [35] and Haque et al. [65] both observed a threshold at 0.1 wt% of NC, whereas Souza et al. [75] reported a threshold at 0.075 wt% CNF where flexural strength reached the maximum. Onauguluchi et al. [35] observed enhancements of 56.3, 106.3 and 31.3% and a decrease of 6.3% in flexural strength when using CNF at 0.05, 0.1, 0.2 and 0.4 wt%, respectively. Similarly, Haque et al. [65] observed flexural strength improvements by 41%, 55% and 51% when using CNF in 0.05, 0.1 and 0.3 wt%. Souza et al. [75] also observed 31–43% of improvements in flexural strength when using CNF of 0.05 wt% and 0.075 wt%, respectively, when compared to the cement pastes with no CNF. Any further addition of NC beyond 0.1 wt% and 0.075 wt% in these studies showed a decline in strength due to fibre agglomeration. Similar behaviour was reported by Cao et al. [60] in cement pastes using CNC wherein a threshold was observed at 0.2 vol% of CNC. Flexural strength exhibited an increase from 5.6% to 17.5% as the dosage increased from 0.04 to 0.2 vol%. However, beyond this point, the improvement started to decline, reaching the lowset improvement of 1.9% at 1.5 vol%.

4.1.2. NC and natural cellulose microfibre reinforcement with hybrid fibre reinforcement

Incorporating nanofibres into cement mortars and pastes, along with traditional cellulose pulps at the microscale as a hybrid fibre reinforcement, has been shown to enhance flexural strength by approximately 6–37% compared to reference mixes without NC. Claramunt et al. [57] demonstrated that increasing the nanofibre content in cement mortars by 2 wt%, through substituting conventional cellulose fibres (sisal fibres of 1.14 mm in length and 15.9 μm in width), resulted

Table 2
Summary of literature–mechanical properties of cement or mortar nanocomposites incorporating NC.

Author	Type	NC Source	NC Preparation	Curing	NC dosages	Mix	Results after 28 days
Claramunt et al. [57]	CNF	Sisal	Prepared by authors Used high-intensity refining process in a valley beaker	Sealed in plastic bags 23 ± 1^0 C	Hybrid & single 8% NC 2% NC + 6% sisal 4% NC + 4% Sisal 6% NC + 2% sisal 8% Sisal fibre (by wt%)	Cement 1 Water 0.69–0.56 Sand 1.11 Silica fume: 0.11 Super Plasticiser (SP) - max 4 wt% of cement (Sika Viscocrete fluidizer)	Flexural Modulus Increased with addition of NC. Threshold at 6% Maximum of 114% increase with 2% sisal + 6% NC compared to mix with 8% sisal + 0% NC Flexural strength Increased with addition of NC. No threshold. Max of 37% increase in mix with 8% NC compared to mix with 8% sisal + 0% NC. Fracture energy: Decreased with addition of NC 90% decrease compared to mix with 8% sisal + 0% NC.
Ardanuy et al. [50]	CNF	Sisal	Prepared by authors Used High intensity refining process in a valley beaker	In a curing box 20 ± 1^0 C 95% RH	Single 3.3% NC 3.1% sisal (by wt%)	Cement 1 Water 0.67 Sand 1 SP- max 4 wt% of cement (Sika Viscocrete fluidizer)	Flexural Modulus 70% increase in mix with 3.3% NC compared to mix with sisal microfibre Flexural strength 36% increase in mix with 3.3% NC compared to mix with sisal microfibre Fracture energy: 53% decrease in mix with 3.3% NC compared to mix with sisal microfibre
Claramunt et al. [73]	CNF	Sisal	Prepared by authors Used High intensity refining process in a valley beaker	In a curing box 20 ± 1^0 C 95% RH	Single 3.3% nano 3.1% sisal (by wt%)	Cement 1 Water 0.63 Sand 1.43 Silica fume 0.43 SP- max 4 wt% of cement (Sika Viscocrete fluidizer)	Flexural Modulus 61% increase in mix with 3.3% NC compared to mix with sisal microfibre Flexural strength 6% increase in mix with 3.3% NC compared to mix with sisal microfibre Fracture energy 6% decrease in mix with 3.3% NC compared to mix with sisal microfibre
Onauguluchi et al. [35]	CNF	Bleached Softwood pulp	Provided by Domtar Canada in gel form. Partially prepared by authors by mechanical defibrillation using a super fine disc grinder for 10–15 times. Then distil water was added to the ground pulp.	95% RH 23.0 ± 2.0^0 C	Single 0.05% 0.1% 0.2% 0.4% (by wt%)	Cement 1 Water 0.5 SP 0.016	Flexural strength Increased with addition of NC up to 0.2% NC. Threshold at 0.1% NC Maximum of 106% increase in mix with 0.1% NC compared to mix with 0% NC. Flexural energy Increased with addition of NC up to 0.2% NC. Threshold at 0.1% NC Maximum of 182% increase in mix with 0.1% NC compared to mix with 0% NC.

(*continued on next page*)

Table 2 (*continued*)

Author	Type	NC Source	NC Preparation	Curing	NC dosages	Mix	Results after 28 days
Hisseine et al. [72]	CF	Wood pulp	Provided by a commercial company in semi dispersed form. Partially prepared by authors As received CF was diluted in water by applying high shear mixing for 60 s using a 700-watt blunt-blade blender.	Wrapped with adhesive plastic sheets and kept in a controlled medium (50% RH and 22^0 C) for 7 days, followed by unwrapping and storing in the same environment	Single 0.1% 0.15% 0.2% (by wt%)	Cement 1 Water: 0.5 FA: 0.33	Compressive strength No improvement in any mix Flexural strength Increased with addition of NC Maximum of 38% increase in mix with 0.2% NC compared to mix with 0% NC.
Cao et al. [60]	CNC	Eucalyptus	Provided by a commercial company as a suspension (5.38 vol% CNC in water) Used as received		Single 0.04% 0.1% 0.2% 0.5% 1.0% 1.5% (by vol%)	Cement 1 Water 0.35	Flexural strength Increased with addition of NC Threshold at 0.2% NC Maximum of 17.5% increase in mix with 0.2% NC compared to mix with 0% NC.
Hisseine et al. [44]	CF	Kraft wood pulp Length 100–2000 µm Diameter 30–400 nm	Provided a commercial company in fully dispersed form Used as received Readily dispersed CF suspensions.	In a fog room at 100% RH and 22 ± 1^0 C.	Single 0.05% 0.1% 0.2% 0.3% (by wt%)	Cement 1 Water 0.3 SP 0.075–0.222	Compression Increased with addition of NC Threshold at 0.05% NC Maximum of 26% increase in mix with 0.05% NC compared to mix with 0% NC. Elastic modulus Increased with addition of NC Maximum of 18% increase in mix with 0.05% NC compared to mix with 0% NC. Flexural strength Increased with addition of NC Threshold at 0.2% NC Maximum of 21% increase in mix with 0.2% NC compared to mix with 0% NC. Fracture energy Increased with addition of NC Maximum of 73% increase in mix with 0.3% NC compared to mix with 0% NC.
Haque et al. [65]	CNF	bleached sulfate hardwood pulp Length several µm Diameter 20–60 nm	Provided by a commercial company slurry form	Sealed in plastic bags at 23^0 C	Single 0.05% 0.1% 0.3% (by wt%)	Cement 1 Water 0.35	Compression Increased with addition of NC Threshold at 0.1% NC Maximum of 48% increase compared to mix with 0% NC. Flexural strength Increased with addition of NC Threshold at 0.1% NC Maximum of 54% increase compared to mix with 0% NC.
Masoudzadeh et al. [74]	CNC	Pulp kraft paper PVA Diameter 20 µm Length 6 mm Aspect ratio 300 CNC Diameter	Prepared by authors by using acid hydrolysis along with mechanical stirring and sonification		Single NC 0.5% 1% 1.5% Hybrid 1.5% PVA + 0.5% CNC	Cement 1 Water 0.57 Sand 0.8 Fly ash 1.2 SP 0.012–0.2%	Single fibre RF with NC Flexural strength Increased only in the mix at 1% NC (10.4 MPa) 25% increase compared to mix with 0% NC. Flexural toughness Increased with addition of NC

(*continued on next page*)

Table 2 (*continued*)

Author	Type	NC Source	NC Preparation	Curing	NC dosages	Mix	Results after 28 days
		20–60 nm Length 100–200 nm Aspect ratio 10–2			1% PVA + 1% CNC 1% PVA + 0.5% CNC (by vol%)		Threshold at 1% NC (56 mJ) 52.6% increase compared to mix with 0% NC. Hybrid with PVA and NC Flexural strength Decreased by 2% in 1.5% PVA + 0.5% NC (8.96 MPa) and by 21% in 1% PVA + 1% NC (7.35) compared to 2% PVA (9.13) Flexural toughness Decreased by 37% in 1.5% PVA + 0.5% NC (733 mJ) and by 51% in 1% PVA + 1% NC (570 mJ) compared to 2% PVA (1165 mJ)

Note: NC- Nanocellulose, CNC-Cellulose nanocrystals, CNF- Cellulose nanofibrils, PVA-Polyvinyl alcohol, RH-Relative humidity, SP-Super plasticiser

in a consistent rise in flexural strength from 11.6 MPa to 15.9 MPa. Additionally, Ardanuy et al. [50] reported a 6% enhancement in flexural strength, while Claramunt et al. [73] reported a 36% enhancement, both when employing 3.3% nanofibres, compared to the mixes with 3.1% conventional cellulose fibres (sisal fibres of 1.14 mm long and 15.9 µm wide). It is noteworthy that the previous study utilised silica fume (replacing 30 wt% of cement), which could have led to improved hydration of the cementitious matrix and may have been responsible for the subdued increase at a later stage.

These studies have consistently indicated that the enhancement in strength can be ascribed to a denser matrix, which arises from increased interactions between the nanofibres and the matrix. The high aspect ratio, primarily due to the high fibrillation of nano scale fibres, is responsible for this increased interaction. On the other hand, the interfacial properties of composites with natural fibres are weaker compared to those with nanofibres due to the relatively low specific surface area of the microfibres. Consequently, substituting these microfibres with nanofibres has led to enhanced strength.

4.1.3. NC and synthetic microfibre reinforcement with hybrid fibre reinforcement

Research into the impact of NC on the mechanical properties of cementitious composites reinforced with micro-synthetic fibres is notably scarce. Masoudzadeh et al. [74] studied the effect of CNC on the flexural properties of a PVA fibre reinforced engineered cementitious composites (ECC) by employing CNC and PVA (20 µm diameter and 6 mm length). They investigated the effects of CNC when utilised as a single reinforcement in plain cement systems as well as in combination with PVA as a hybrid NC-PVA reinforcement. The study reported a reduction of 2% in flexural strength when 2 vol% PVA was replaced by 25% of CNC (1.5 vol% PVA & + 0.5 vol% CNC) and 20% reduction when 2 vol% PVA was replaced by 50% of CNC (1 vol% PVA + 1 vol% CNC). However, when 0.5 vol% CNC was added to 1 vol% PVA, the flexural strength increased by approximately 20% compared with the instance where 1 vol% CNC was combined with 1 vol% PVA.

The study suggested that when hybridising CNC with PVA fibres at higher content, the required water was adsorbed from the matrix and the cement hydration was disordered. Consequently, the PVA cement bonding was disrupted mitigating the strength. On the other hand, a 13% higher flexural strength was achieved with only 0.1 vol% CNC in comparison the mix with only 2 vol% PVA microfibres. These findings indicate that the interfacial properties of CNC reinforced composites surpass those in the micro PVA case, attributable to the extensive fibrillation of nanofibres leading to a denser matrix. This results in enhanced strength when utilising CNC over PVA fibres. However, the performance of CNC is hindered in the presence of PVA fibre due to the interference of water absorbed by the hydrophilic PVA fibre when high quantities are used [74].

All the aforementioned studies have conclusively linked the increase in flexural strength to the enhanced DOH resulting from nanofibres. This is attributed to the hydrophilic nature of nanofibre, their superior intrinsic properties and the strong interface bond between the nanofibres and the cement paste, which facilitates improved stress transfer. The decrease in strength at higher concentrations (0.2 wt% for cellulose filaments, 0.1 wt% for cellulose nanofibrils and 0.2 vol% for cellulose nanocrystals) in these studies was attributed to the inhomogeneous dispersion leading to fibre agglomeration. Fig. 10 further shows the improvements of flexural strength by NC as reported in literature in comparison with certain microfibre reinforced composites and the composites with no fibre reinforcement. It can be seen that the improvement can range anywhere from 6.1–37.1%. The wide range observed may have been influenced, in part, by the choice of binder and the type of fibre used. For instance, the relatively low increase exhibited in the study by Claramunt et al. [73] might stem from complete hydration achieved through the inclusion of silica fume in the mixture.

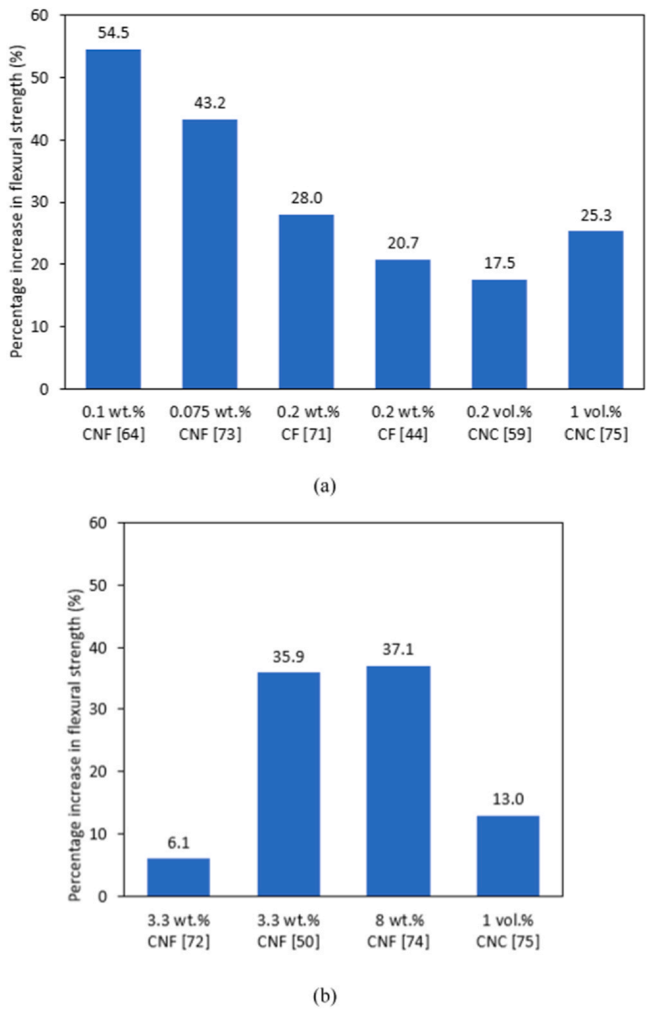

Fig. 10. Effect of nano cellulose on flexural strength. (a) Percentage increase in flexural strength with respect to plain cement composites with no fibre reinforcement; (b) Percentage increase in flexural strength with respect to cement composites with microfibre reinforcement.

4.2. Effect of NC on energy absorption capacity/toughness

The majority of studies concentrating on the mechanical properties of cement mixes reinforced with NC have noted minimal or no enhancements in energy absorption capacity (toughness) when compared to composites reinforced with microfibre. However, enhancements are observed relative to plain cement composites without any fibre.

4.2.1. NC-reinforced cementitious composites

Nanofibre-reinforced cementitious composites have demonstrated 52–182% improvement in flexural energy as compared to composites with no fibre reinforcement. Onauguluchi et al. [35] showed 69.8, 181.8 and 47.2% improvement by employing CNF of 0.05, 0.1 and 0.2 wt% respectively compared to the mix with no CNF. The maximum increment was observed with the 0.1 wt% concentration of CNF, indicating a threshold. The addition of CNF beyond 0.1% resulted in mitigation in the improvement and a reduction at concentration over 0.4% was noticed due to fibre agglomeration and inhomogeneous dispersion. On the other hand, Hisseine et al. [44] observed continuous enhancement in fracture energy with increasing CF fractions in cement mortar. They reported 25, 43, 69 and 74% improvement compared to the reference mix without NC by using CF concentration of 0.05, 0.10, 0.20 and 0.30 wt%, respectively. The study documented improvement in fracture energy with increasing dosage, without any threshold.

In general, the presence of fibres at the crack tip was considered responsible for the improved fracture behaviour [44]. The cracking and deformations of cementitious composites initiate at the nanoscale, and the nanofibres can intercept the cracks and delay the matrix fracture. Cao et al. [60] observed that short fibres bridge cracks at the micro-level, which are narrower than the fibre length. Thus, they effectively arrest the propagation of these micro-level cracks and prevent them from expanding and coalescing with each other. However, to suppress cracks, an adequate volume of fibres must be present at the crack tip, since the fibre content should be ample to transfer the stress across the cracks before they evolve into microcracks [72]. Thus, the higher the fibre count at the crack tip, the higher the number of cracks intercepted. The compact arrangement of NC fibres enhances their occurrence at crack tips, thereby, incorporating substantial quantities of fibres should promote crack bridging at the micro-level and enhance toughness, provided that an even dispersion is accomplished. Moreover, it was proposed that the high aspect ratio, high tensile strength and stiffness of NC fibre can augment the resistance to cracking by sustaining the peak load across an extended range of micro deflections before failure, thus improving toughness.

4.2.2. NC and natural cellulose microfibre reinforcement with hybrid fibre reinforcement

Reductions in fracture energy of about 7–90% have been reported in literature when incorporating NC in cementitious composites reinforced with conventional cellulose pulps at macro scale. Claramunt et al. [57] observed a decrease in fracture energy with the addition of nanofibres as a replacement to conventional sisal fibres with 1.14 mm in length and 15.96 µm in width. As the dosage of CNF increased to 2, 4, 6 and 8 wt%, substituting the natural cellulose fibres, those observed reductions in fracture energy were 51, 74, 84 and 90% respectively, in comparison with the reference mix containing 0% CNF and 8 wt% microfibre. Similarly, Claramunt et al. [73] reported a 6.4% reduction and Ardanuy et al. [50] reported a 36% reduction in fracture energy when using 3.3 wt% CNF as compared to using 3.1 wt% natural cellulose fibre.

These investigations confirmed that the natural fibres favour toughness due to their longer length as compared to nanofibres. The longer length of the fibres is more effective in bridging crack faces, whereas the short length of nanofibres is not able to act as a link after cracking of the matrix and bridge the macro-level cracks. Further, the interfacial properties of the composites with natural fibre are weaker as compared to the composite with nanofibres due to the relatively low specific surface area of microfibres, which results in debonding and fibre pullout when a failure occurs. On the contrary, the excessively dense matrix stemming from high surface area and high aspect ratio of nanofibres is not favourable for toughness.

4.2.3. NC and synthetic microfibre reinforcement with hybrid fibre reinforcement

The effect of hybridising CNC with PVA fibre (20 µm in diameter and 6 mm in length) on flexural toughness was investigated by Masoudzadeh et al. [74]. They reported that replacing PVA fibres with CNC caused decrements in flexural toughness and hardening. A reduction of 37% in toughness was observed when the 2 vol% PVA single fibre reinforcement was replaced with a hybrid fibre reinforcement of 1.5 vol% PVA and 0.5 vol% CNC and a reduction of and 51% was observed when the 2 vol% PVA single fibre reinforcement was replaced by 1 vol% PVA + 1 vol% CNC hybrid fibre reinforcement. Additionally, when comparing the single fibre reinforcements, a 95% reduction in flexural toughness was observed in the 1 vol% CNC reinforced mix compared to the 2 vol% PVA reinforced mix. The behaviour was attributed to the lower aspect ratio of CNC than PVA fibre and the longer length of PVA fibre compared to CNC which favours crack bridging [74]

Fig. 11 further shows the improvements of flexural energy achieved through the addition of NC, as compared to composites with no fibre

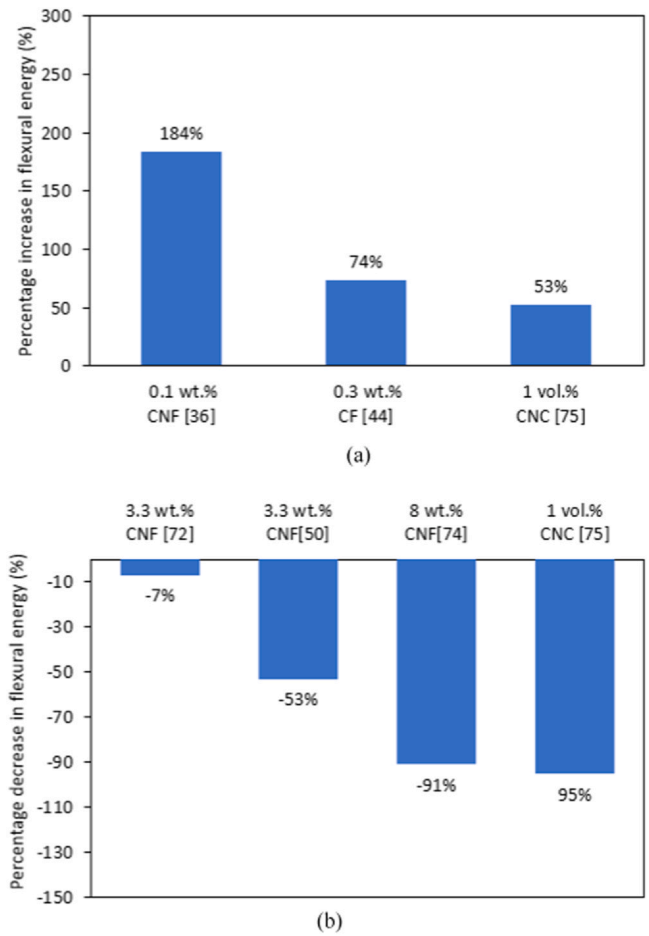

Fig. 11. Effect of nano cellulose on flexural toughness. (a) Percentage increase in flexural energy with respect to composites with no fibre reinforcement; (b) Percentage decrease in flexural energy with respect to composites reinforced with micro fibre.

reinforcement, and the reductions of flexural energy when microfibres were replaced by NC. It can be observed that the impact of NC may vary widely depending on the matrix and the dispersion techniques used.

4.3. Effect of NC on other mechanical properties

Researchers have also investigated the effect of addition of NC on other mechanical properties such as compressive strength, Young's modulus and flexural modulus. For example, Hisseine et al. [44] reported 27%, 17%, 8% and 4% improvement in compressive strength when using CF at dosages of 0.05, 0.1, 0.2, 0.3 wt% respectively. The improvements were attributed to the high DOH stemming from the hydrophilic and hygroscopic nature of NC, while the reduction in the improvements was attributed to the filament entanglement and inadequate dispersion. Hisseine et al. [72] also studied the compressive strength of NC-reinforced cement motors by employing 0.1, 0.15, 0.2 wt % dosage of CF of the same type as the previous study. In contrast, they observed a reduction in compressive strength in all mixes. These studies suggested that the dispersion technique is critical and can lead to distinct results even for the similar scale of addition. Upon implementing a process condition of high shear mixing for 60 seconds, a noticeable decline in compressive strength was observed. However, improvements in compressive strength were observed when a readily dispersed CNF suspension (15 min of high shear mixing using water at 60 ºC) was used, substantiating the effect of dispersion technique for properties. Haque et al. [65] also suggested that the compressive strength improves with

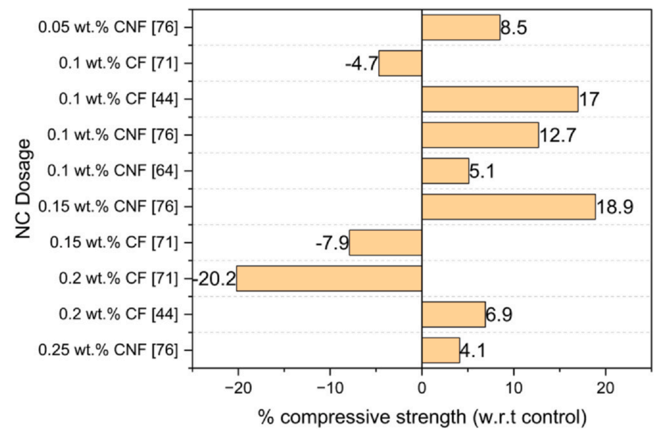

Fig. 12. Effect of nano cellulose on compressive strength of cementitious composites.

the CNF concentrations, provided a homogeneous dispersion can be achieved. When CNF concentration was increased from 0.05 wt% to 0.3 wt%, they observed increasing improvement in compressive strength from 2% to 10% respectively, compared to the control mix. This observation is supported by Fig. 12, which illustrates the extensive variation in compressive strength resulting from the addition of NC. Generally, this improvement is attributed to the NC internal curing effect, leading to a higher DOH and a denser microstructure. However, the compressive strength can also be adversely impacted, depending on the dispersion technique employed.

Similarly, NC was found to improve elastic modulus and flexural modulus. By incorporating CF at 0.05–0.30 wt%, Hisseine et al. [44] reported increment of elastic modulus ranging 2–18% as compared to the benchmark without reinforcement. The greatest enhancement was observed at 0.05 wt%, attributed to optimal dispersibility. It was suggested that the changes in the cement microstructure are due to the high surface reactivity of CF. These improvements are linked to interactions with calcium silicate hydrate (C-S-H) and calcium hydroxide (C-H), facilitated by the surface hydroxyl groups and large surface area of CF. Similarly, Claramunt et al. [57] observed approximately 56% of enhancement in flexural modulus when employing 8 wt% cellulose nanofibrils (CNF) in comparison to 8 wt% traditional cellulose fibres (sisal fibres of 1.14 mm in length and 15.96 µm in width). Further the study suggested that hybridising the reinforcement with nanofibres by replacing 2 wt% of the conventional fibres with 2 wt% of nanofibres (while maintaining the total fibre content at 8 wt%) enhanced the flexural modulus by 28%. When the nano fibre quantity in the hybrid reinforcement was increased from 4 wt% to 6 wt%, while simultaneously decreasing the conventional cellulose fibre content from 4 wt% to 2 wt% (keeping the total fibre content at 8 wt%), flexural modulus increased from 92% to 114%. Additionally, Claramunt et al. [73] observed a 60.7% enhancement while Ardanuy et al. [50] observed a 70.8% enhancement in flexural modulus in the composite reinforced with 3.3 wt% CNF, compared to the composite reinforced with 3.1 wt% conventional cellulose fibres. An extensive summary of the analysis presented above on the investigations of mechanical properties of NC based cement composites reported in literature is further compiled in Table 2, including the details of fibre type, fibre content and mix content.

5. Comparison of nanocellulose with other nanomaterials

A wide range of studies have demonstrated significant improvements in tensile strength, compressive strength and flexural strength when incorporating various synthetic nanomaterials into cementitious composites [28,31,76]. These nanomaterials have been broadly

Table 3
An overview of mechanical properties of other commonly used nanomaterials and NC.

	wt%	Percentage increments after 28 days	Mechanical property	Reference	Challenges
NC	0.05%	26%	Compressive strength	[44]	Excessive particles in the mix lead to agglomeration
Tensile Strength ≈ 7.5 GPa	0.2%	21%	Flexural strength	[44]	
Young's Modulus ≈120–145 GPa	0.1%	106%	Flexural strength	[35]	
Fibrillar/rod-like					
NS	10%	10%	Compressive strength	[105]	Excessive particles in the mix lead to agglomeration
Particles	1.5%	15%	Compressive strength	[87]	
	3%	24%	Compressive strength	[103]	
	5%	35%	Compressive strength	[83]	
CNT	0.02%	11%	Compressive strength	[27]	Difficulties in dispersing and high cost of production
Tensile Strength ≈ 11–73 GPa	0.1%	19%	Compressive strength	[27]	Van der Waals forces cause nanomaterial clumping, impairing mechanical properties
Young's Modulus ≈ 270–970 GPa	0.08%	25%	Flexural strength	[27]	
Tubes	0.1%	65%	Flexural strength	[27]	
GO	0.08%	16.4%	Compressive strength	[32]	
Tensile Strength ≈ 21 GPa	0.08%	27.1%	Flexural strength	[32]	
Young's Modulus ≈ 410 GPa	0.2%	16.4%	Compressive strength	[102]	
2D sheets	0.2%	41.3%	Flexural strength	[102]	

Note: NC-Nanocellulose, NS- Nanosilica, CNT-Carbon nanotubes, GO-Graphene oxide

classified as nanoparticles, nanofibres and nanosheets. Typical examples include nanosilica (NS), nanoclay, carbon nanotubes (CNT) and graphene oxide (GO), respectively [29,77,78].

The addition of nanoparticles such as TiO_2, Al_2O_3, ZrO_2, Fe_2O_3 and SiO_2 improved the mechanical properties of concrete and cement mortar [79–87]. However, existing research have predominantly favoured the addition of NS due to its pozzolanic effect, high surface area to volume ratio, filler effects and nucleation sites [30,88–91]. Research on cementitious composites with NS dosages from 1.5% to 10% has demonstrated enhancements in compressive strength from 10% to 35% and in flexural strength from 12% to 30%, compared to the reference mix (without NS) [92–96]. However, a study examining the impact of NS on the performance of cement pastes with cellulose nanofibrils (CNF) revealed that the enhancements in compressive and flexural strengths in pastes combining NS and CNF (22% and 55%, respectively) were less than those in pastes with only CNF (24% and 75%, respectively). Conversely, after 90 days of curing, pastes containing both NS and CNF demonstrated greater improvements in compressive strength compared to those with CNF alone. The findings suggested that the coating of NS disentangled the fibres, reducing the crack bridging effect, and mitigating the benefits of reinforcement. However, the additions of NS contributed to delaying the degradation of CNF in the alkaline pore solution of cement paste [97].

CNT is another widespread nanofibre that has attracted the attention of researchers. The high aspect ratio (approximately 1000) and surface area (up to 1315 m^2/g) of CNT have proven to be contributing factors to improved mechanical properties in cement mixes [27,31,76,98–101]. Enhancement in compressive strength up to 11% with 0.02 wt% of multiwalled carbon nano tubes (MWCNT) and up to 19% with 0.1 wt% single walled carbon nano tubes (SWCNT) have been documented in the literature [27]. Further flexural strength improvements ranging from of 25–269% were observed by employing 0.075–0.26 wt% of multiwalled carbon nano tubes (MWCNT) [27].

Similar to CNT, 2D nanosheets such as GO have shown to be promising nanomaterials that enhance the properties of cement-based composites owing to their exceptional intrinsic qualities. Flexural strength improvements of 27.1% and 41.3% with 0.08% and 0.2 wt% of GO, respectively, and compressive strength improvements of up to 16.4% with 0.08 wt% of GO were noted in comparison with their reference composites without GO [32,102].

However, challenges in dispersing and high production cost have limited the widespread application of both CNT and GO [27,33,98]. Due to the large surface area and high aspect ratio of GO and CNT, the presence of Van der Waals forces leads to the agglomeration of these nanomaterials, thereby impeding enhancements in mechanical properties. Hence, only low fractions (< 1 wt%) of CNT and GO have been successfully applied in studies. Agglomeration remains an issue with nanoparticles. When an excessive number of nanoparticles are present in the mix, weak zones in the form of voids are created due to the poorly dispersed mixture, hindering the mechanical performance.

On the other hand, NC has additional properties (other than the pozzolanic effect and high surface area to volume ratio), such as internal curing effect that favours strength and fibre bridging that favours toughness. Hence, better performance can be achieved with NC by using low concentrations as compared to spherical nanoparticles, CNT or GO. For instance, a 3 wt% concentration was required to enhance compressive strength by 24% when using NS [103], whereas a mere 0.05 wt% concentration of NC achieved a 26% improvement in compressive strength [44]. Similarly with 0.1 wt% CNT and 0.08 wt% GO respectively, only 19% [104] and 16% [32] of improvements in compressive strength was achieved. In all these studies, any additional increase beyond these concentrations led to a reduction in the observed enhancements. The enhancements in mechanical properties (compressive strength and flexural strength) relative to the concentrations of NS, CNT and GO compared with NC are detailed in Table 3.

6. Summary

This paper presents an extensive review of nanocellulose (NC) and its impact on the mechanical properties of cementitious composites. The literature indicates significant enhancements in these properties following the incorporation of NC into cementitious materials. Drawing on this review, the ensuing key conclusions can be summarised.

1. Being a type of nanofibres derived from cellulose, NC displays a higher reinforcing effect than microfibres, but it favours flexural strength than toughness in fine aggregate cementitious composites in comparison to microfibres. Improvements in strength up to 106.3% and energy absorption capacity up to 182% have been achieved by using 0.1 wt% of NC when compared to the cementitious composite without NC. However, a reduction in energy absorption/toughness up to 95% has been observed in NC-reinforced composites when compared with microfibre-reinforced composites. The proposed explanation for the increase in strength and decrease in toughness seems to originate from the following.

- *Cause of strength increase*: Due to its hydrophilicity and hygroscopic nature, NC improves the hydration level of the composite. Enhanced hydration reduces porosity and increases strength. Additionally, the significant aspect ratio and large specific surface area increase the availability of the cellulose hydroxyl groups for hydrogen bonding with the cementitious matrix. This facilitates strong adhesion, leading to improved fibre-matrix interaction and a denser matrix, which in turn promotes more effective stress distribution and contributes to greater strength. Furthermore, the inherent high tensile strength of NC, up to 7.5 GPa, prevents fibre rupture, and its Young's modulus ranging 65–110 GPa reduces deformation, thereby significantly reinforcing the overall composite strength.
- *Cause of toughness decrease*: Toughness is largely determined by the bonding between the fibres and the matrix; maximised interface properties can inhibit high energy absorption mechanisms such as debonding and fibre pullout, leading to fibre rupture. Consequently, when interface properties are optimised and bonding is strengthened, a brittle fracture is more likely, resulting in reduced fracture energy (toughness). The fineness and nano scale of NC prevent them from bridging or arresting the cracks at the micro level. As a result, NC based nanocomposites often experience a significant reduction in load-carrying capacity, which leads to sudden matrix rupture. In contrast, micro scale fibres (length $\gtrsim$ 1 mm) can bridge cracks at the micro-level, where crack widths are smaller than the fibre length. This effectively delays crack propagation and prevents them from further growing. Thus, nano fibres enhance strength, though they do little to improve material toughness while micro fibres improve toughness by effectively bridging cracks.

2. It was reported that NC can readily agglomerate due to the high density of –OH groups and extensive surface area. When these nanoscale fibres clump together, the intended advantages of incorporating NC as a reinforcing material are compromised. This is attributed to the increased porosity in the mix caused by agglomeration, acting as a stress concentrator and diminishing its strength. As the NC concentration exceeds a certain threshold, agglomerates dominate regardless of the dispersion technique employed. According to the findings, fractions of 0.1–0.2 wt% of NC have proven effective in enhancing both strength and toughness when used as a single reinforcement, while 3–8 wt% fractions were necessary for improvements in strength in hybrid reinforcement with natural cellulose.
3. It is clear that NC favours strength, whilst microfibres play a more pivotal role in enhancing toughness. Therefore, combining both types of fibres in a hybrid reinforcement could offer a superior solution for optimising both strength and toughness. However, careful selection of fibre types and concentrations is crucial to prevent an antagonistic effect. For instance, when combining two hydrophilic fibres at high concentrations (such as cellulose nanocrystals and polyvinyl alcohol), cement hydration can become disrupted, potentially reducing strength.

7. Future research perspectives

While nanocellulose (NC) holds considerable potential for enhancing the mechanical properties of cement mortars, research into NC-reinforced cementitious composites remains relatively limited compared to studies on other nanomaterials. Additionally, numerous aspects of NC application in cementitious systems are yet to be investigated, demanding further exploration in future studies.

- When using NC, there are many variables that affect the mechanical properties of the resulting nanocomposites. For instance, besides the dosage of NC, the type of fibre (cellulose filament, cellulose nanocrystals (CNC), cellulose nanofibrils (CNF) and bacterial cellulose), source of fibre, NC dispersion techniques, mixing processes of the mortar, curing processes and the components of the matrix will all significantly influence the outcomes. To discern the impact of each variable individually, it is essential to compare results by only modifying the variable under investigation while keeping other variables constant. Yet, existing studies have amalgamated these variables, omitting a focused examination of the effect of each variable. Therefore, further research is imperative to substantiate and elucidate the distinct influence of these parameters. Moreover, no studies have yet explored the effects of various types and sources of NC on engineered cementitious composites (ECC).

- To understand the synergetic effect of nanocellulose and microsynthetic fibres that are commonly used in ECC such as polyvinyl alcohol and polyethylene, detailed investigations into the performance of different combinations of these fibres and thorough comparisons are essential.
- A significant limitation of NC is its tendency to agglomerate when used in substantial amounts in a matrix. Nevertheless, it is anticipated that integrating higher dosages of NC, if agglomeration can be avoided, would lead to exceptional improvements in mechanical properties. Therefore, the development of more efficient and cost-effective dispersion methods will be a crucial area of focus for future research.
- Research into efficient production methods for NC remains underexplored in the literature. Cost and availability pose significant barriers to its broader application. Despite the abundance of raw materials, extraction and production techniques are not yet widely implemented beyond laboratory settings. Currently, only a few suppliers can provide NC on the market, limiting its accessibility. For NC to be viable for high-volume applications, its production must be scaled up to industrial levels to ensure ample availability.

It is anticipated that ongoing research will enhance the functionalities of NC/cement nanocomposites beyond those of current cement composites, thereby garnering recognition and interest from the civil engineering community. As a result, these composites are expected to fulfill the requirements of contemporary concrete technologies. Thus, the effective use of NC-reinforced cement composites in civil engineering applications as a sustainable material solution becomes a viable prospect

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.adna.2024.05.003.

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