Revista ALCONPAT

www.revistaalconpat.org

eISSN 2007-6835

Revista de la Asociación Latinoamericana de Control de Calidad, Patología y Recuperación de la Construcción

Cellulose nanofibers (CNF) as reinforcement for cementitious matrices: a systematic literature review

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DOI: https://doi.org/10.21041/ra.v12i3.594

Reception: 13/03/2022 | Acceptance: 08/07/2022 | Publication: 01/09/2022

ABSTRACT

The aim of this study is to conduct a systematic literature review of the last five years on the use of cellulose nanofibers (CNF) in cementitious composites. The main production and dispersion methods are presented with emphasis on their effect on the behavior of cement-based materials. The study considered the influence of CNF on the fresh and hardened state properties: rheology, hydration, compressive strength, flexural strength, fracture energy, among others. CNF show positive effects on mechanical properties. However, further research is still necessary to optimize the production and pretreatment processes of CNF, establishing relationships regarding the durability of composites with CNF, and identifying possible environmental impacts of their use.

Keywords: cellulose nanomaterials; cementitious composites; fresh state; hardened state; mechanical properties.

Cite as: Rocha, J. H. A., Farias, L. do N., Siqueira, T. P. L. (2022), "*Cellulose nanofibers (CNF) as reinforcement for cementitious matrices: a systematic literature review*", Revista ALCONPAT, 12 (3), pp. 311-327., DOI: https://doi.org/10.21041/ra.v12i3.594

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Contribution of each author

In this work, the author J. H. A. Rocha, contributed with the original idea in 33%, data collection in 40%, choice and development of work methodology in 40%, writing and discussion of results in 40%; the author L. do N. Farias contributed with original idea in 33%, data collection in 30%, choice and development of work methodology in 30%, writing and discussion of results in 30%, and the author T. P. L. Siqueira contributed 34% original idea, 30% data collection, 30% choice and development of the work methodology, 30% writing and discussion of results in 30%.

Discussions and subsequent corrections to the publication

Any dispute, including the replies of the authors, will be published in the third issue of 2023 provided that the information is received before the closing of the second issue of 2023.

Nanofibras de celulose (NFC) como reforço de matrizes cimentícias: revisão sistemática da literatura

RESUMO

O objetivo deste estudo é realizar uma revisão sistemática da literatura dos últimos cinco anos sobre o uso de nanofibras de celulose (NFC) em compósitos cimentícios. São apresentadas as principais formas de produção e dispersão, com destaque para o efeito sobre o comportamento dos materiais à base de cimento. O estudo considerou a influência das NFC nas propriedades no estado fresco e endurecido: reologia, hidratação, resistência à compressão, resistência à flexão, energia de fratura, entre outras. As NFC têm efeitos benéficos nas propriedades mecânicas. No entanto, maior pesquisa ainda é necessária para otimizar a produção e os processos de pré-tratamento das NFC, estabelecer relações sobre a durabilidade dos compósitos com NFC, e identificar possíveis impactos ambientais da sua utilização.

Palavras-chave: nanomateriais de celulose; compósitos cimentícios; estado fresco; estado endurecido; propriedades mecânicas.

Nanofibras de celulosa (NFC) como refuerzo para matrices cementicias: revisión sistemática de la literatura

RESUMEN

El objetivo de este estudio es realizar una revisión sistemática de la literatura de los últimos cinco años sobre el uso de nanofibras de celulosa (NFC) en compuestos a base de cemento. Se presentan las principales formas de producción y dispersión, con énfasis en el efecto sobre el comportamiento de los materiales a base de cemento. El estudio consideró la influencia de las NFC en las propiedades en estado fresco y endurecido: reología, hidratación, resistencia a la compresión, resistencia a la flexión, energía de fractura, entre otras. Las NFC tienen efectos beneficiosos sobre las propiedades mecánicas; sin embargo, aún se necesita más investigación para optimizar la producción de NFC y los procesos de pretratamiento, establecer relaciones sobre la durabilidad de los compuestos con NFC, e identificar los posibles impactos ambientales de su uso.

Palabras clave: nanomateriales de celulosa; compuestos de cemento; estado fresco; estado endurecido; propiedades mecánicas.

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1. INTRODUCTION

The search for more sustainable building materials with reduced CO2 emissions has been growing significantly over the last decades, mainly due to global warming and the fact that the construction industry is considered one of the most polluting industries in the world (UN Environment *et al*., 2018; CAO *et al*.., 2020). In this pursuit for materials with lower environmental impact there is the use of the so-called biomaterials, that is, materials that incorporate in their formulation plant derived products (Barnat-Hunek *et al*., 2019; Nishimura *et al*., 2019; Abdellaoui; Bouhfid, 2020; Barría *et al*., 2021). According to Hoyos *et al.* (2019) the sustainability of a material is defined by its capacity and regeneration rate and the possibility of being reassimilated to the environment after its use.
Moreover, the potential use of nanoscale materials, called nanomaterials, in construction materials has also been growing over the last few years. Through nanomodification it is possible to alter the nano- and microstructure of cementitious matrices in order to modify several properties of the material (Santos *et al*., 2021; Tang *et al*., 2019; Zhang *et al*., 2021). These changes impact the macro behavior of the matrices, and can increase the strength, deformability, and thermal conductivity of the materials. Therefore, cellulose nanofibers (CNFs) are presented as a promising material to be incorporated into building materials (Hisseine *et al*., 2019; Claramunt *et al*., 2019).
CNFs are a biopolymer class that can be synthesized by plants, bacteria, and algae (Hoyos *et al*., 2019; Ogura *et al*., 2020) and exhibit high strength, stiffness, and elastic modulus, being able to improve several characteristics of traditional cementitious matrices (Mejdoub *et al*., 2016; Dongre; Suryawanshi, 2021). In addition, CNFs show high biodegradability, low toxicity and minimal environmental and health risks as one of the main environmental advantages (Hisseine *et al*., 2019). Studies show that the incorporation of cellulose nanofibers can increase the viscosity of the matrices, acting in a similar way to a viscosity modifier admixture, and have the ability to retain water which, consequently, reduces the exudation of the mixtures (Hisseine *et al*., 2018a; Bakkari *et al*., 2019). Analyzing the mechanical performance of the matrices with CNF incorporation, a tendency to increase the compressive and flexural strength of the matrices is noticed when compared to the reference mixtures (Cengiz *et al*., 2017; Kolour *et al*., 2020). However, when the addition is done in very high levels, the effects can be negative due to the increased porosity of the mixtures (Sun *et al*., 2016; Correia *et al*., 2018; Alzoubi *et al*., 2020).
Therefore, the present study aims to perform a systematic literature review (SLR) to collect existing data on the use of cellulose nanofibers (CNF) in cementitious matrices and identify unexplored knowledge gaps. To this end, both a survey of the most recent works published on the subject, and an analysis of the data found were performed. So that this work can serve as a basis for future studies.

2. METHODOLOGY

To conduct this study some questions were set that were the basis for the selection and analysis of the studies found. The formulated questions were:
1. - What are the dimensions of the most commonly used fibers and the incorporation percentage currently employed in the literature?
2. - What are the most commonly used CNF treatment/dispersal methods observed in the studies?
3. - What are the most analyzed properties of CNF-reinforced composites and, consequently, what are the most performed tests?
In addition to these questions, a mapping of the studies found was performed by analyzing the countries, institutions, and authors that most published on the subject and the most used keywords.

To answer these questions, two databases were chosen to collect the articles: *ScienceDirect* and *Google Scholar*. The first database encompasses several journals indexed in Scopus and *Web of Science*. In addition, using the method known as "snowballing", we added relevant and highly cited articles from Google Scholar that were not present in the first database and that were published in journals with an impact factor (*Scopus* and *Web of Science*).
This study analyzed all research articles related to the topic published between the years 2016 and 2021 that were written in English. The search string used to collect the articles was: "*CELLULOSE NANOFIBERS*" *AND* ("*CEMENT MATRICES*" *OR* "*MORTAR*" *OR* "*CONCRETE*") resulting in a total of 163 articles for analysis.
After excluding the book chapters and literature review articles and adding the relevant articles using the "snowball method", the titles and abstracts of the articles were analyzed. Those that did not answer the proposed questions or did not incorporate fibers into cementitious matrices were excluded. Finally, all 29 papers considered relevant were analyzed in their entirety.
The *VOSViewer* program (version 1.6.17) was used for further bibliometric analysis of the selected articles.

3. RESULTS AND DISCUSSIONS

3.1 Mapping of the studies

The map in Figure 1 shows that the countries that have published the most on this subject are the United States with 10 articles, Canada with 7 articles, China with 4 articles, and Spain and Brazil with 3 articles each. All the other countries represented in a lighter shade of green contributed with one publication each. With these results we can see a predominance of the Northern Hemisphere countries in publishing on the theme, being present in 43% of the publications. Despite this, it can be seen that this is a subject that is being studied around the world, with the involvement of 16 different countries in the articles found.
The authors who have published the most on the theme are presented in Figure 2, where the light colors (yellow) indicate a greater number of published papers, differentiated by groups of authors. It was noted that some authors were involved in more than one publication on the topic. While 70% of the studies presented different authors. This analysis shows that there is a high interest in the incorporation of CNF in cementitious matrices since several institutions and several authors are involved in this research.
Figure 3 shows the most used words in the titles and keywords of the articles studied. According to the data collected, it is possible to notice a predominance of the words "*cellulose nanofibers*". Furthermore, it is possible to note the presence of the properties that the articles analyzed, among them, "*mechanical properties*" and "*compressive strength*". Through the results found it is clear that there is a wide variety of approaches being currently employed regarding the use of CNF, indicating the range of advantages that this material can offer when incorporated into various types of matrices.

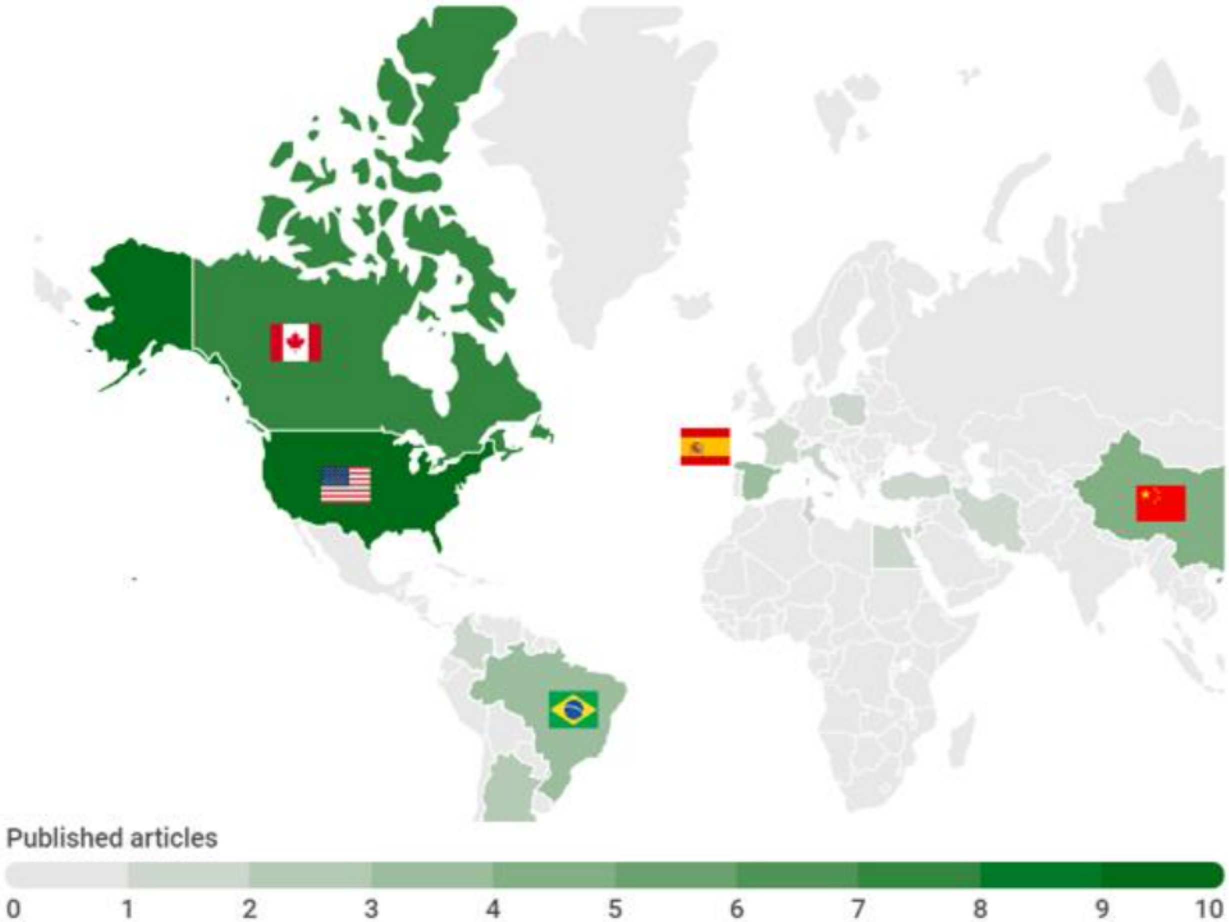


Figure 1. Countries that have most published on the subject.

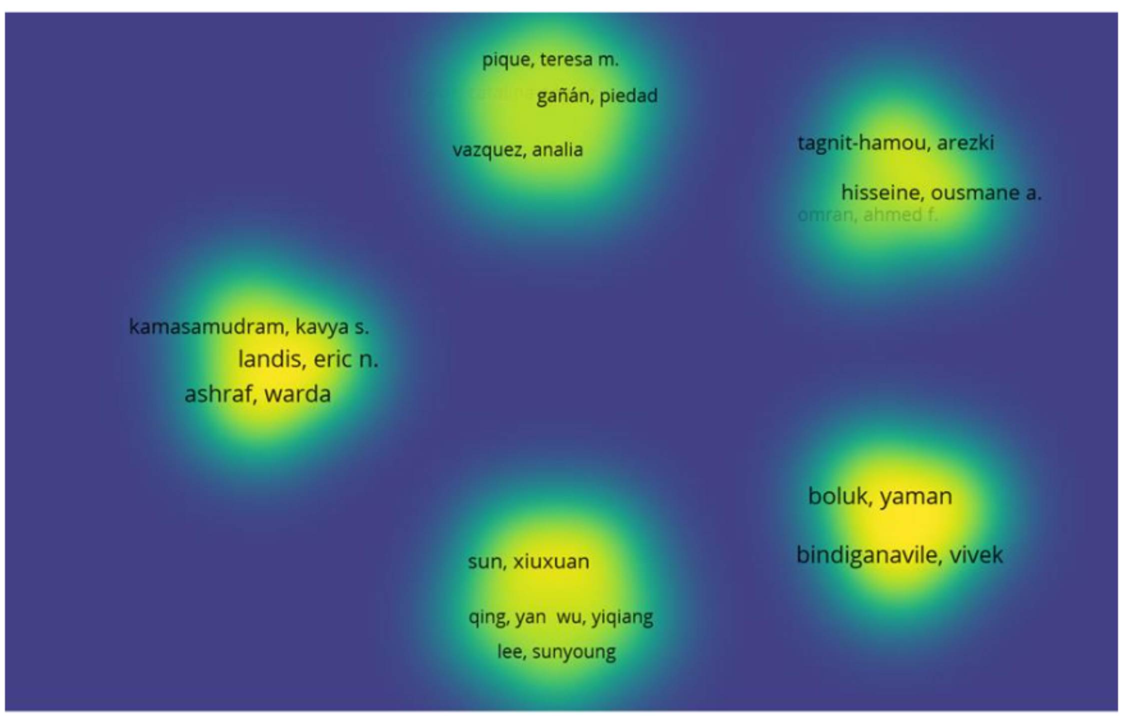


Figure 2: Density map of the authors who have most published on the subject.

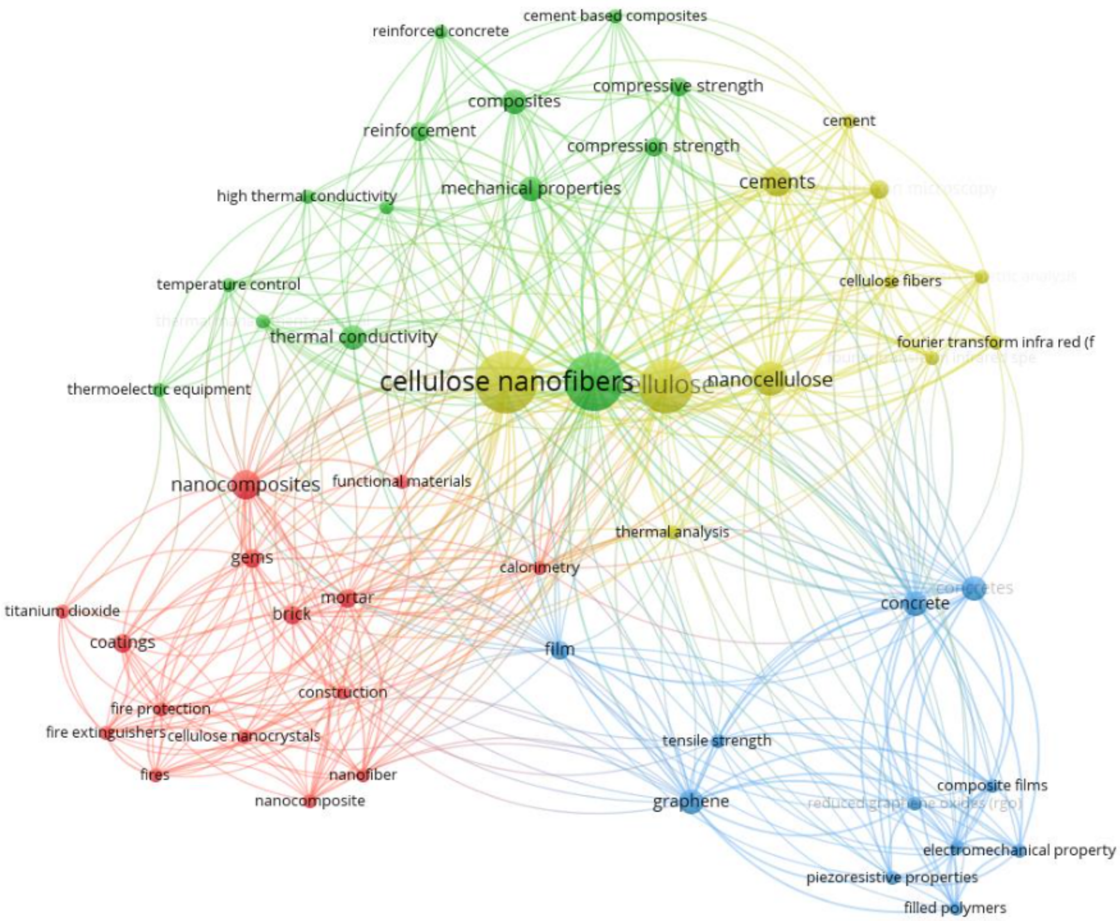


Figure 3: Main words in titles and keywords of articles.

3.2 Cellulose nanofibers (CNF)

Cellulose undergoes several chemical or physical treatments until it results in nanocellulose. Depending on the extraction method employed, nanocellulose can also be divided into a few groups, such as nanofiber cellulose (CNF) and nanocrystals of cellulose (NCC). NCC are commonly known as nanocrystalline cellulose, nanowhiskers, nanocrystals and the monocrystals, while CNF are much finer as they are extracted from the cellulose microfibers present in the biomass, they are usually cited as cellulose microfibrils, nanofibrils or nanofibrillated cellulose and basically consist of long flexible nanoparticles/nanofibrils with interchanged crystalline and amorphous domains (Abdul Khalil *et al*, 2012; Guo *et al*., 2020; Dhali *et al*., 2021).

CNFs have dimensions ranging from 5-50 nm in width and 1-5 µm in length, have 50-70% crystallinity and an extremely high surface area (Goncalves *et al*., 2021). CNFs exhibit a hydrophilic nature, so a low content, between 0.1% and 5% by weight, is generally used as reinforcement in cementitious matrices. However, even in small amounts, CNF diluted in water can create a stable and uniform gel (Zhang; Scherer, 2020).

Some studies report the use of CNF as reinforcement in cementitious composites, and this has been seen in the present literature review. Appendix 1 summarizes the general characteristics of the nanofibers used by the authors, it is observed among the studies that the CNF dimensions used ranged from 10-500 nm in diameter, 2-20 nm in width and reached up to several microns in length. However, it is important to note that in the literature the cross-sectional dimension of CNFs is designated as both diameter and width. As for the percentage of CNF used as reinforcement in the cementitious matrix, they varied between 0.02% and 3%. In addition to the so-called CNF, studies have designated other names/types of cellulosic nanofibers, such as hydrophilic cellulose nanofibrils (Zhang; Scherer, 2020), nanofibrillated cellulose (Correia *et al*., 2018) and the bacterial CNFs (Akhlaghi *et al*., 2020; Barría *et al*., 2021). Studies such as Cengiz *et al*. (2017) conducted comparisons between natural and commercial nanofibers. The natural nanofibers were derived from Cladophora sp (algae) which has a residual form in a river. In general, the CNFs studied by the authors were used in cementitious matrices of pastes (62%); pastes and concretes (17%); pastes and mortars (13.7%) - some studies simultaneously linked two types of matrices. An exception to this is the work of Panesar *et al*. (2017) who only conducted a study of alkali treatment in CNFs.

The crystallinity of the nanofibrils is reduced due to the amorphous characteristic of the lignin and hemicellulose present in cellulose, which also affects the mechanical properties provided to the cementitious composites. In this way, chemical or enzymatic treatment methods are also performed (Dhali *et al*., 2021).

The alkaline pretreatment, also known as mercerization, performed by the authors Panesar *et al*. (2017) and Fonseca *et al*. (2019), consists of exposing the nanofibers to a solution such as sodium hydroxide. Fonseca *et al*. (2019) explain that the alkaline treatment was performed in order to improve the defibrillation of the jute fibers into nanofibrils. According to Abdul Khalil *et al*. (2012), alkaline pretreatment also has the function of completely removing lignin and hemicellulose from CNFs. However, alkaline treatment is not sufficient for removing cellulosic constituents, in this case, further removal of a residual lignin can be done by the bleaching method.

The homogenization method has been performed by authors such as Hoyos *et al*. (2019), Tang *et al*. (2019), Sun *et al*. (2017), Mejdoub *et al*. (2016), and Jiao *et al*. (2016), and is a type of mechanical treatment for cellulose fibers that consists of high-pressure refining and homogenization processes. The fibers are generally subjected to repeated cyclic stress. According to Abdul Khalil *et al*. (2012), this treatment increases the utilization potential of the fibers because it modifies part of their morphology.

The TEMPO-mediated oxidation system was also mentioned and employed by Jiao *et al*. (2016). Oxidation performed in the presence of TEMPO is a method used to modify the hydrophilic characteristic of the nanocellulose surface. However, the efficiency of this type of method has been proven in NCC as they show better dispersibility due to the introduction of dense carboxylate groups on their surfaces (Hassan *et al*., 2021).

Sonication is considered one of the most widely used methods for CNF dispersion and was also found in the present review, in the studies by Sun *et al*. (2017), Claramunt *et al*. (2019), Barnat-Hunek *et al*. (2019), Nassiri *et al*. (2021) and Ez-zaki *et al*. (2021). Yet, although sonication can be effective in dispersing nanocellulose, Guo *et al*. (2020) reported challenges for this treatment, such as the difficulty of converting the adsorbed nanocellulose on cement particles into free nanocellulose that enables the formation of fiber clusters in cementitious matrices.

3.3 CNF in cementitious composites

Appendix 2 presents the detailed properties evaluated in the literature of pastes, mortars and concrete with CNF. This section presents a brief summary on the influence of CNF addition on hydration, rheology, shrinkage, mechanical properties (compressive and flexural strength), among others.

3.3.1 Hydration

Several studies indicate that the degree of cement hydration increases with the presence of CNF, as it promotes hydration to produce more calcium silicate hydrate (C-S-H) and calcium hydroxide (CH); therefore, an improvement in mechanical properties is presented (Mejdoub *et al*., 2016; Sun

et al., 2017; Hoyos *et al*., 2019; Hisseine *et al*., 2019). Although no adverse effect is reported on the degree of hydration, there is an influence on its kinetics (Hisseine *et al*., 2018a).
Jiao *et al*. (2016) point out that cement paste samples with and without CNF show no differences in hydration at early ages (10 hours), since the exposed surface of the cement particles dominates heat release and there is enough water around the particles for hydration (Lootens; Bentz, 2016). The addition of CNF prolongs induction periods and delays the peak heat flow rates. The hydroxyl and carboxyl groups of cellulose molecules are hydrophilic (Klemm *et al*., 2011), the oxygen atom found in these groups has unpaired electrons that can react with the Calcium ion (Ca^{2+}) and form a hydrophilic compound that delays the induction period of hydration and hardening. Therefore, fewer contact sites are generated between cement particles and water, decreasing the rates of C-S-H and CH formation (Sedan *et al*., 2008).
Due to this same phenomenon, Goncalves *et al*. (2019) and Kamasamudram *et al*. (2020) reported there is also a reduction in ettringite formation. Kamasamudram *et al*. (2021a) found that lignocellulose nanofibers (LCNF) and delignified cellulose nanofibers (DCNF) reduce the amounts of ettringite and CH in the hydrated cement paste. However, CNF with silica nanoparticles was shown to increase the amount of CH, around 4%, due to the enhanced cement reaction speed (filler effect); whereas, for the CNF-only samples, a reduction in CH was observed (Kamasamudram *et al*., 2020).
On the other hand, at long times, CNFs release water in the surrounding regions and contribute to the hydration of unhydrated cement particles, improving the microstructure and mechanical properties of cement pastes (Jiao *et al*., 2016). In this regard, Ez-zaki *et al*. (2021) pointed out the same trend when using alkali activated ground granulated blast furnace slag with CNF. Kolour *et al*. (2020) suggest that the degree of hydration increases with the presence of CNF after 3 days. Zhang and Scherer (2020) also mention that CNFs improve cement hydration in the long term; however, this may vary depending on the CNF source.
In contrast, Mejdoub *et al*. (2016), Kamasamudram *et al*. (2020) and Kamasamudram *et al*. (2021b) indicate that CNF accelerate early-stage cement hydration as a result of the nucleation effect and that this effect is greater for CNF with silica nanoparticles. After 80 h of hydration, CNF additions showed no significant effects on the hydration degree (Kamasamudram *et al*., 2021a). Kamasamudram *et al*. (2021b) conclude that the influence of CNF on hydration depends on the w/c ratio (the concentration of alkali ions in the pores depends on the w/c ratio), where for a w/c ratio of 0.35 there is accelerated hydration at early ages; whereas, for a w/c ratio of 0.45, hydration was not as prominent.
Although no adverse effects on hydration are reported, further studies of hydration kinetics at early ages are needed in order to define possible applications in construction, in addition to analyzing other variables such as cement type, different w/c ratios, etc.

3.3.2 Rheology
Every study that analyzed the rheology of cement paste and concrete with CNF reported improvements, such as yield strength and viscosity (Hisseine *et al*., 2018a; Bakkari *et al*., 2019; Ez-zaki *et al*., 2021). In general, CNFs act as a modifying agent on the viscosity of cement pastes, increasing their yield strength at small additions of CNFs, this is due to two main reasons: a) water retention capacity, since hydrophilicity is an intrinsic characteristic of CNFs (Hisseine *et al*, 2018a; Hisseine *et al*., 2018b; Ez-zaki *et al*., 2021), and b) the formation of CNF networks, which are prominent in longer and more flexible CNF (Hoyos *et al*., 2019; Nassiri *et al*., 2021).
Hisseine *et al*. (2018a) and Hisseine *et al*. (2019) indicate that CNF incorporation requires the use of high-range water-reducing admixtures (HRWRA), due to the viscosity modification produced by CNFs. This is associated with the hydrophilicity of CNFs, increasing water retention and also it is associated with a high surface area and high aspect ratio of CNFs, increasing the formation of

CNF chains. On this last point, Hisseine *et al*. (2018a) found that CNF chains increase the viscosity of the mixture at low shear rates; however, for high shear rates, CNF chains led to a lower viscosity, due to the streamlining of CNFs in the flow direction, exhibiting a shear thinning behavior.
The CNF addition increased the elastic limit of oil well cement (OWC) suspension, improving its rheological properties (Sun *et al*., 2016). Tang *et al*. (2019) found that the gel strength, elastic limit, and viscosity of CNF and OWC suspensions were higher when compared to cellulose nanocrystal (NCC) suspensions, this is because CNF are more likely to form the interlocking grid. In another study of CNF with OWC, it was found that the addition of graphene nanoplates (GNP) leads to higher yield stresses in the fresh state (Sun *et al*., 2019). It is observed that CNFs have an important influence on the rheological behavior of cementitious materials; however, few authors have considered this aspect, and it is an important topic for future research.

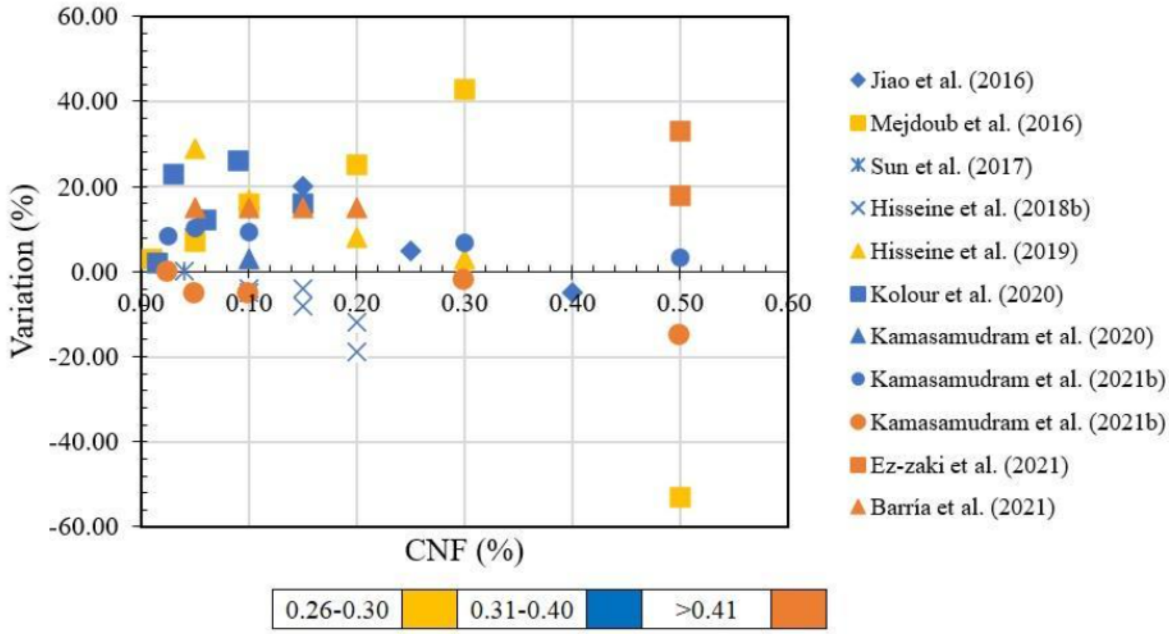
3.3.3 Shrinkage

Zhang and Scherer (2020) demonstrated the use of CNF to investigate the chemical shrinkage of high w/c ratio cementitious pastes at early ages (3 days), since there is no chemical effect on short-term hydration. The CNFs created a stable structure to support the cement particles and allowed them to hydrate without sedimentation.
Kolour *et al*. (2020) found that adding an amount of 0.06% CNF (by weight of cement) leads to a reduction in autogenous shrinkage by up to 49% in cement pastes with a w/c ratio of 0.30. For self-compacting concretes, Hisseine *et al*. (2018b) reported that the use of CNF reduced autogenous shrinkage deformations by up to 31% in 7 days.
The use of CNF with higher levels of carboxyl groups in Portland cement systems mitigates dimensional shrinkage-related changes and cracking in cement pastes (Bakkari *et al*., 2019).
Studies show that CNFs mainly reduce chemical and autogenous shrinkage. However, there are no long-term studies, such as drying shrinkage and creep, as well as relating these properties to the materials, dosage, humidity, temperature, curing, among others.

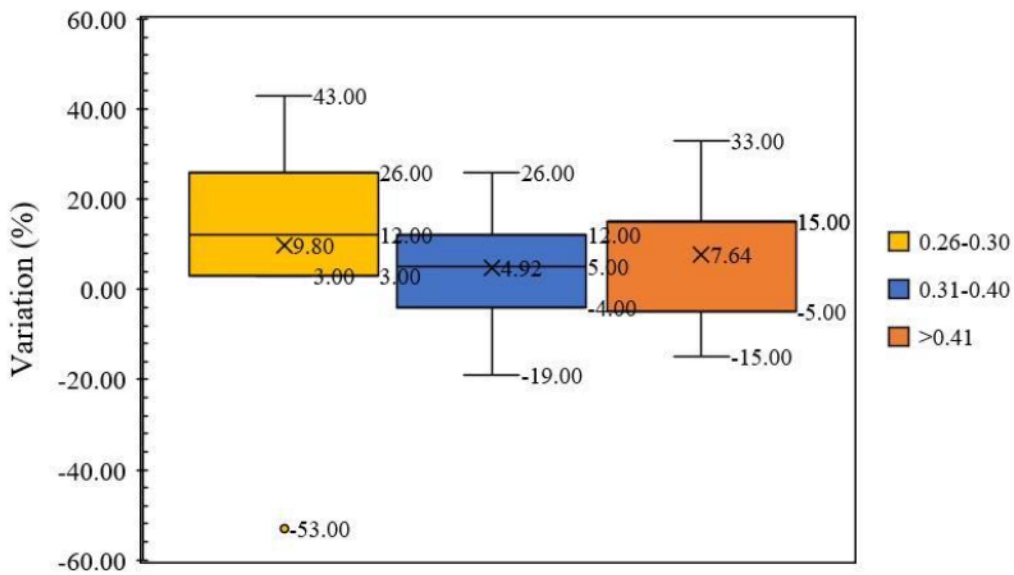
3.3.4 Mechanical properties

As mentioned earlier, the mechanical properties of cementitious pastes improve with CNF addition, due to the water retention of CNF and the increased degree of hydration (internal curing), as well as the increased adhesion of CNF and the cementitious matrix. However, high CNF contents are detrimental as they increase porosity and other factors must be taken into consideration for the development of mechanical properties (Sun *et al*., 2016; Correia *et al*., 2018; Hisseine *et al*., 2018a; Hisseine *et al*., 2019; Kolour *et al*., 2020; Alzoubi *et al*., 2020).
a) Compressive strength: Most studies report an increase in compressive strength with the addition of CNF (Hisseine *et al*., 2019; Sun *et al*., 2017). Mejdoub *et al*. (2016) found more than 50% increase in compressive strength with 0.3% CNF. In the results of Kolour *et al*. (2020) for a mixture with 0.15% CNF, there was an increase of up to 31% after 7 days, and for a mixture with 0.09% CNF, there was an increase of up to 16% after 28 days. In self-compacting concrete, Hisseine *et al*. (2018b) indicate a positive tendency in the addition of CNF, as compressive strength increased by up to 16%.
Kamasamudram *et al*. (2020) showed that by adding 0.1% CNF with silica nanoparticles the compressive strength increased by 13% (at 90 days) over the control batch and by 10% over the batch without silica nanoparticles.
The addition of DCNF showed a maximum 15% increase in compressive strength for 0.05% and 0.1% DCNF after 90 days of curing. The maximum increase in compressive strength of cement paste cured for 90 days with the addition of 0.1% LCNF was approximately 16% (Kamasamudram *et al*., 2021a).

The addition of CNF and phase change material led to an increase in the compressive strength of cement mortar, where the best result is achieved with the addition of 0.5% CNF, due to the reduction in the mortar porosity (Alzoubi *et al*., 2020).
On the other hand, some studies have reported that CNF addition does not have a considerable effect on the compressive strength of cement pastes (Kamasamudram *et al*., 2021b), partly because it can be adversely affected by air entrainment and CNF agglomeration (Hisseine *et al*., 2018b). Although Nasiri *et al*. (2019) report an increase in compressive strength (17-18%) with the addition of CNF, concentrations above 0.065% resulted in small improvements in strength at 7 days and decreased strength at 28 days when compared to the reference mixtures.
Figure 4a shows the summary of the variation rate of the compressive strength at 28 days as a function of the added content of CNF. It is important to note that only the studies that provided data were considered. When the variation results are classified by w/c ratio (Figure 4b), it is observed that the lower the w/c ratio, the higher the positive variation (9.80% for a w/c ratio from 0.26 to 0.30), presenting a single atypical data. Additionally, it is observed that for this w/c ratio there are only positive rates and a smaller data dispersion (3-43%). For other w/c ratios, the dispersion of the data is higher and the reduction in compression strength results are reported.
b) Flexural strength: For flexural strength, a generally positive effect is reported (Hisseine *et al*., 2018a; Hisseine *et al*., 2018b; Hisseine *et al*., 2019). Hisseine *et al*. (2019) described an increase of up to 25%. Kamasamudram *et al*. (2020) found that with the addition of 0.1% CNF, flexural strength increased by 70%, a rate close to that reported by Kamasamudram *et al*. (2021b), 75%. Even higher percentages were presented by Kolour *et al*. (2020), 116% and Cengiz *et al*. (2017), 169.7%.
Sun *et al*. (2016) found that flexural strength increased by 20.7% for a CNF/CPP ratio of 0.04, attributed to increased hydration and the binding effect of CNF, but they also noted that excessive addition of CNF is damaging due to nanoparticles agglomeration. In more recent work from the same authors, it was indicated that both compressive and flexural strength increased with the addition of CNF (2017).
In the study by Cengiz *et al*. (2017) it is reported that the flexural strength in mortars increased 2.7 times with the addition of algal CNF, due to the high aspect ratio of CNF, which improves the bonding interface between the CNF and cement paste. However, the use of commercial CNF has a negative effect on the bending stress due to its low aspect ratio and insolubility.
Hisseine *et al*. (2018a) indicated positive effects of CNF on the mechanical performance of cementitious pastes, due to greater homogeneity and stability. As for self-compacting concrete, the authors demonstrated that bending capacity and tensile strength at rupture increased by up to 21 and 26%, respectively. Hisseine *et al*. (2018b) also reported the same trend in self-compacting concrete, where all measured mechanical properties were improved, only in flexural 22%, as a result of nanoreinforcement and internal curing.



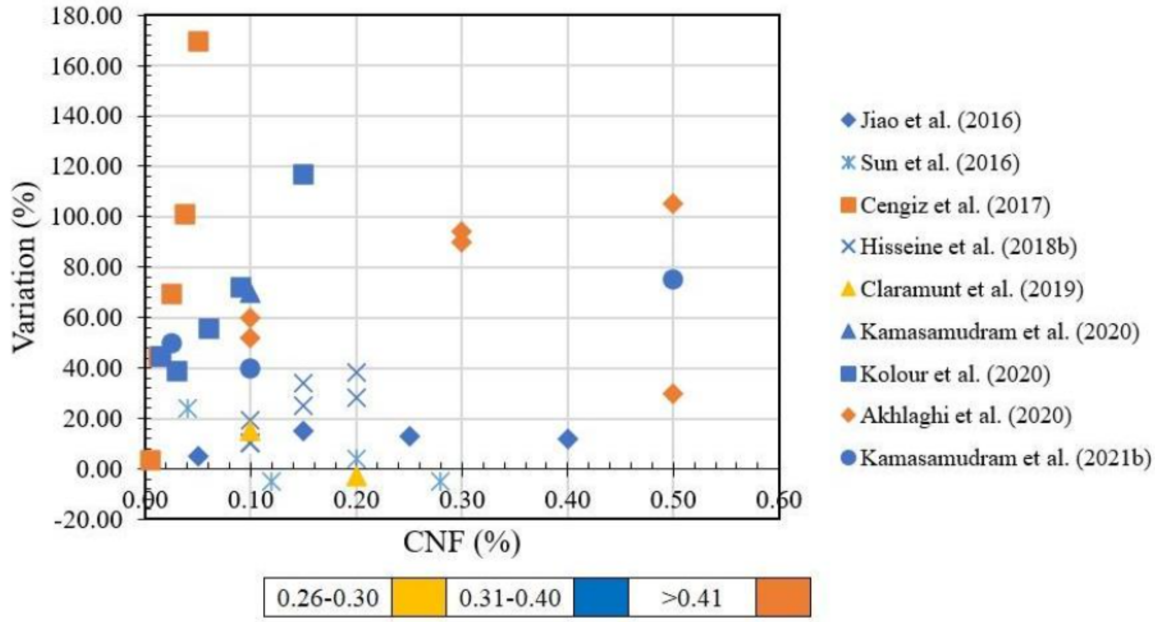
(a)



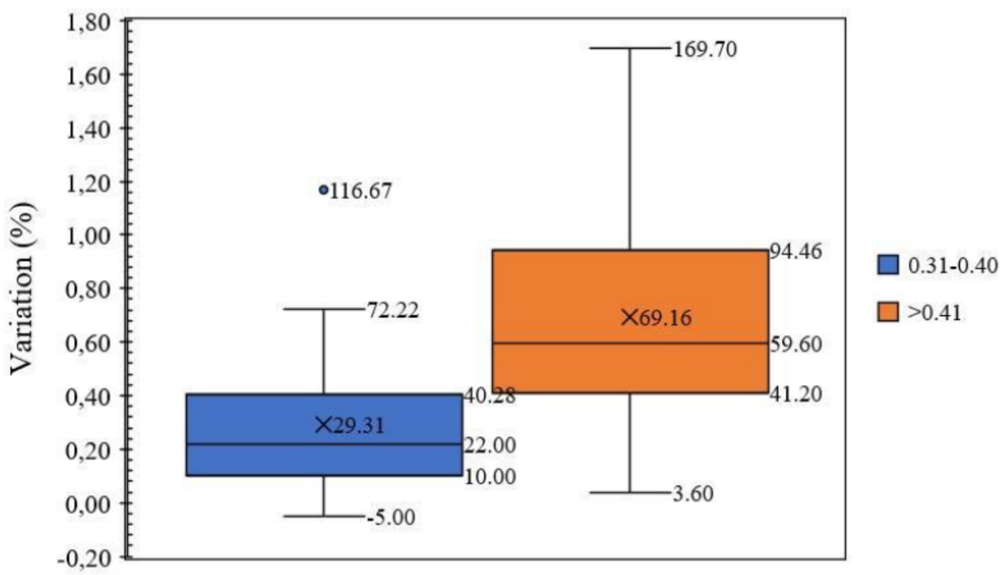
(b)

Figure 4. a) Variation of compressive strength at 28 days, and b) data dispersion considering the w/c ratio.

The flexural strength of cement pastes can increase from 20% up to 111% with CNF addition, this last value for 0.1% of CNF, both for DCNF and LCNF (Kamasamudram *et al*., 2021a).
Figure 5a shows a detailed breakdown of the results reported in the literature for flexural strength at 28 days, showing that most are positive and with higher percentages compared to compressive strength. Figure 5b presents that the results reported for a w/c ratio from 0.31 to 0.40, are less scattered, with an average of 29.3% and a single atypical data (116.67%). For a w/c greater than 0.41 there is an average of 69.16%, but a greater data dispersion. The dispersion for an w/c ratio of 0.26 to 0.30 is not presented because there is only one study within this range (Claramunt *et al*., 2019).



(a)



(b)

Figure 5. a) Flexural strength variation at 28 days, and b) data dispersion considering the w/c ratio.

Finally, Figure 6 summarizes all the results reported in the literature for both compressive strength (green) and flexural strength (red) of concretes and mortars, showing the positive effects of CNF addition, mainly for flexural strength.

c) Fracture mechanics: Hisseine *et al*. (2019) indicate that the maximum flexural capacity occurs at a low CNF content (0.05-0.10%), but the energy absorption capacity increases at higher CNF contents, up to 74%. Similarly, Hisseine *et al*. (2018b) point out that CNF improves energy absorption (96%) which is reflected in an increase in maximum displacement, up to 43%, a behavior that is required for both impact- and blast-resistant structures. Significant increases in fracture energy, up 60% in the study by Kolour *et al*. (2020), suggest that CNFs are an effective hardening mechanism, acting as bridges that increase the energy required for crack propagation.

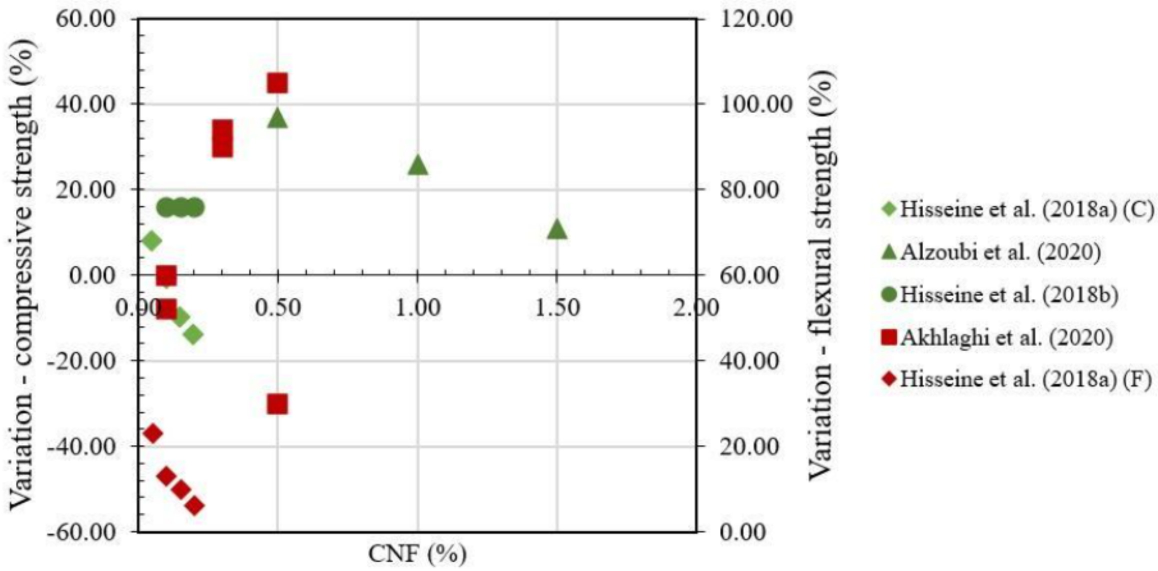


Figure 6. Compressive and flexural strength of concrete and mortar.

Hisseine *et al*. (2018b) also report the same trend in self-compacting concrete, where all measured mechanical properties were improved. Improvements of up to 16% in compression, 34% in splitting stress, 22% in bending, and 96% in energy absorption were obtained. These improvements were attributed to two effects imparted by CNF: nano-strength and internal curing.

The content of 1% CNF with 8% cellulosic pulp contributes to the formation of stress transfer bridges in nano- and micro-cracks, improving the mechanical performance of the composites before and after accelerated aging tests: modulus of rupture (MOR), fracture toughness (KIC) and fracture energy (FE), results attributed to the adhesion between CNF and the cement matrix (Correia *et al*., 2018).

Composites reinforced with 2% cellulose micro/nanofibers showed higher limit of proportionality (LOP), MOR, and toughness than control composites after 28 days of curing (Fonseca *et al*., 2019). Ez-zaki *et al*. (2021) indicate that CNFs have the ability to swell, creating internal water deposits and can behave as stress concentrators, leading to the initiation of microcracks.

The addition of low CNF and NCC contents (between 0.1 and 0.2% by weight), in calcium aluminate cement (CAC) systems, led to an overall increase in MOR values in unaged samples, in contrast to Portland cement systems (Claramunt *et al*., 2019).

In the literature, it is observed that mechanical properties have been extensively investigated, which makes it possible to identify trends and better understand the effect of CNFs on the mechanical behavior of cementitious materials. However, most studies have only reported compressive and flexural strength results for pastes. The mechanical behavior in other specific and long-term applications still needs to be further investigated.

3.3.5 Other properties

This topic presents other properties that have been investigated in some published works, highlighting that the durability of cementitious materials with CNF is the least researched aspect, but with growing interest in recent years.

a) Sulfate ion penetration: CNF reduce the penetration of sulfate ions into a cementitious system. It was observed that the addition of CNF (0.3-0.4%) to GU Type Portland Cement provided the same or greater resistance to sulfate attack than a specially formulated HS Type Portland Cement (Goncalves *et al*., 2019).

b) Chloride ion penetration: The use of CNF prevents the penetration of chloride ions. This is attributed to the amount of carboxyl groups, which leads to the restriction of chloride entrance, besides improving workability (Goncalves *et al*., 2020).
c) Modulus of elasticity: Kamasamudram *et al*. (2021b) observed that 0.025% and 0.5% CNF increased the modulus of elasticity of cement paste by about 200% and 250%. Hisseine *et al*. (2019) reported an increase of 18% and Fonseca *et al*. (2019) indicate that in general, composites with CNF show better mechanical performance and that the dynamic modulus of elasticity increases with time even when exposed to weathering. CNFs with calcium aluminate cement (CAC) show an increase in modulus of elasticity compared to mixtures with Portland cement (Claramunt *et al*., 2019).
d) Porosity: Mejdoub *et al*. (2016) indicated that the porosity in cement pastes was reduced with the addition of CNF, the best result being with 0.3% of CNF. On the other hand, Goncalves *et al*. (2019) point out that CNF refines the pore size, showing an increase in the total volume of micro and nanopores; however, there was a reduction in porosity for sizes larger than 10 mm.
e) Coefficient of thermal expansion and thermal conductivity: The use of CNF increased both the coefficient of thermal expansion and thermal conductivity of cementitious pastes, mainly due to the potential of CNF to reduce porosity and improve the microstructure of the cementitious matrix (Mejdoub *et al*., 2016). Alzoubi *et al*. (2020) also reported an increase in the thermal conductivity of PCM/CNF composites.
f) Exudation: CNF act as a water retention agent and water reservoir to prevent segregation and exudation (Ez-zaki *et al*., 2021). Goncalves *et al*. (2021) showed that the addition of CNF significantly reduces the volume of the exudation water. CNF makes it difficult for cement grains to settle and obstructs the upward migration of free water. However, in the presence of superplasticizers, CNF are less effective in reducing exudation. The authors consider that the effect of CNF on exudation reduces both the plastic shrinkage and the autogenous shrinkage during the initial stages of hydration.
Finally, the lack of studies evaluating the environmental impacts of cementitious composites with CNF was noted; and, in this sense, Life Cycle Analysis (LCA) studies could be carried out in a complementary way.

4. CONCLUSIONS

Although the use of cellulose nanofibers (CNF) in the construction industry is a recent field, not yet widely explored, studies of CNF as reinforcement in cementitious matrices show that its use can improve their performance.
Recent studies on CNF application in cementitious matrices have focused on cement pastes, accounting for 62% of the research analyzed (for pastes exclusively).
Small percentages of CNF are added to cement-based composites, reinforcement contents usually range between 0.02% and 3%. However, there are challenges in using this material as to its dispersion in the cement matrix, thus pre-treatments on the nanofibers are of great importance because they increase their potential use. The most commonly used treatments/dispersions are sonication, homogenization, TEMPO-mediated oxidation, and alkaline pretreatment of the fibers.
As for the CNF dimensions used most in the research, the most commonly used CNFs were reported to range from 10-500 nm and 2-20 nm as diameter and width, respectively.
The addition of CNF usually increases the degree of hydration of cement, improving rheological properties, such as viscosity and elastic limit, as well as favoring the water retention capacity of the mixture with indications for reducing segregation and exudation, and improving the shrinkage performance of cementitious composites.

Most studies indicate a tendency to improve mechanical properties such as compressive strength, flexural strength, fracture mechanics, and modulus of elasticity. With an emphasis on the flexural strength property, with even more positive improvements when compared to the compressive strength.
It is important to emphasize that the good dispersion of the fibers, homogeneity of the matrix and the content of CNF used have a great influence on these results; however, a greater incorporation tends to be associated with the formation of fiber agglomerates, causing reductions or being detrimental to the results.

5. REFERENCES

Abdellaoui, H., Bouhfid, R. (2020), *Review of nanocellulose and nanohydrogel matrices for the development of sustainable future materials*. In Sustainable Nanocellulose and Nanohydrogels from Natural Sources, 155-176. https://doi.org/10.1016/B978-0-12-816789-2.00007-9
Abdul Khalil, H. P. S., *et al*. (2012), *Green composites from sustainable cellulose nanofibrils*: A review. Carbohydrate Polymers. 87(2):963–979. https://doi.org/10.1016/j.carbpol.2011.08.078
Akhlaghi, M. A., *et al*. (2020), *Application of bacterial nanocellulose fibers as reinforcement in cement composites*. Construction and Building Materials. 241:118061. https://doi.org/10.1016/j.conbuildmat.2020.118061
Alzoubi, H. H., *et al*. (2020), *Performance of cementitious composites with nano PCMs and cellulose nanofibers*. Construction and Building Materials. 236:117483. https://doi.org/10.1016/j.conbuildmat.2019.117483
Bakkari, M., *et al*. (2019), *Preparation of cellulose nanofibers by TEMPO-oxidation of bleached chemi-thermomechanical pulp for cement applications*. Carbohydrate Polymers. 203:238–245. https://doi.org/10.1016/j.carbpol.2018.09.036
Barnat-Hunek, D., *et al*. (2019), *Effect of cellulose nanofibrils and nanocrystals on physical properties of concrete*. Construction and Building Materials. 223:1–11. https://doi.org/10.1016/j.conbuildmat.2019.06.145
Barría, J. C., *et al*. (2021), *Effect of bacterial nanocellulose on the fresh and hardened states of oil well cement*. Journal of Petroleum Science and Engineering. 199. https://doi.org/10.1016/j.petrol.2020.108259
Cao, Z., *et al*. (2020), *The sponge effect and carbon emission mitigation potentials of the global cement cycle*. Nature communications. 11(1): 1-9. https://doi.org/10.1038/s41467-020-17583-w
Cengiz, A., *et al* (2017), *Flexural stress enhancement of concrete by incorporation of algal cellulose nanofibers*. Construction and Building Materials. 149:289–295. https://doi.org/10.1016/j.conbuildmat.2017.05.104
Claramunt, J., *et al*. (2019), *Effect of nanocelluloses on the microstructure and mechanical performance of CAC cementitious matrices*. Cement and Concrete Research. 119:64–76, 2019. Disponível em: https://doi.org/10.1016/j.cemconres.2019.02.006
Correia, V. C., *et al*., (2018), *Nanofibrillated cellulose and cellulosic pulp for reinforcement of the extruded cement based materials*. Construction and Building Materials. 160:376–384. https://doi.org/10.1016/j.conbuildmat.2017.11.066
Dhali, K., *et al*. (2021), A review of nanocellulose as a new material towards environmental sustainability. Science of the Total Environment. 775:145871. https://doi.org/10.1016/j.scitotenv.2021.145871
Dongre, M., Suryawanshi, V. B. (2021), *Analysis of cellulose based nanocomposites & potential applications*. Materials Today: Proceedings. 45:3476–3482. https://doi.org/10.1016/j.matpr.2020.12.943

UN Environment, *et al*., (2018), *Eco-efficient cements: Potential economically viable solutions for a low-CO2 cement-based materials industry*. Cement and Concrete Research. 114:2-26. https://doi.org/10.1016/j.cemconres.2018.03.015
Ez-zaki, H., *et al*. (2021), *Correction to: Influence of cellulose nanofibrils on the rheology, microstructure and strength of alkali activated ground granulated blast-furnace slag: a comparison with ordinary Portland cement*. Materials and Structures/Materiaux et Constructions. 54(2). https://doi.org/10.1617/s11527-021-01665-2
Fonseca, C. S., *et al*. (2019), *Jute fibers and micro/nanofibrils as reinforcement in extruded fiber-cement composites*. Construction and Building Materials. 211:517–527. https://doi.org/10.1016/j.conbuildmat.2019.03.236
Goncalves, J., *et al*. (2019), *Cellulose nanofibres (CNF) for sulphate resistance in cement based systems*. Cement and Concrete Composites. 99:100–111. https://doi.org/10.1016/j.cemconcomp.2019.03.005
Goncalves, J., *et al*. (2021), *Turbidity-based measurement of bleeding in fresh cement paste as affected by cellulose nanofibres*. Cement and Concrete Composites. 123:104197. https://doi.org/10.1016/j.cemconcomp.2021.104197
Goncalves, J., *et al*. (2020), *Cellulose nanofibres mitigate chloride ion ingress in cement-based systems*. Cement and Concrete Composites. 114. https://doi.org/10.1016/j.cemconcomp.2020.103780
Guo, A., *et al*. (2020), *A Review on the Application of Nanocellulose in Cementitious Materials*. Nanomaterials. 10(12):2476. https://doi.org/10.3390/nano10122476
Hassan, S. H., *et al*. (2021), *TEMPO-oxidized nanocellulose films derived from coconut residues: Physicochemical, mechanical and electrical properties*. International Journal of Biological Macromolecules. 180:392–402. https://doi.org/10.1016/j.ijbiomac.2021.03.066
Hisseine, O. A., *et al*. (2018a) *Feasibility of using cellulose filaments as a viscosity modifying agent in self-consolidating concrete*. Cement and Concrete Composites, 94:327–340. https://doi.org/10.1016/j.cemconcomp.2018.09.009
Hisseine, O. A., *et al*. (2018b), *Influence of cellulose filaments on cement paste and concrete*. Journal of materials in civil engineering. 30(6):04018109. https://doi.org/10.1061/(ASCE)MT.1943-5533.0002287
Hisseine, O. A., *et al*. (2019), *Nanocellulose for improved concrete performance: A macro-to-micro investigation for disclosing the effects of cellulose filaments on strength of cement systems*. Construction and Building Materials. 206:84–96. https://doi.org/10.1016/j.conbuildmat.2019.02.042
Hoyos, C. G., *et al*. (2019), *Cellulose nanofibrils extracted from fique fibers as bio-based cement additive*. Journal of Cleaner Production. 235:1540–1548. https://doi.org/10.1016/j.jclepro.2019.06.292
Jiao, L., *et al*. (2016), *Natural Cellulose Nanofibers As Sustainable Enhancers in Construction Cement*. PLoS ONE. 11(12):e0168422. https://doi.org/10.1371/journal.pone.0168422
Kamasamudram, K. S., *et al*. (2021), *Cellulose Nanocomposites for Performance Enhancement of Ordinary Portland Cement-Based Materials*. Transportation Research Record. https://doi.org/10.1177/0361198120958421
Kamasamudram, K. S., *et al*. (2021a), *Effects of ligno– and delignified– cellulose nanofibrils on the performance of cement-based materials*. Journal of Materials Research and Technology. 13: 321–335. https://doi.org/10.1016/j.jmrt.2021.04.090
Kamasamudram, K. S., *et al*. (2021b), *Cellulose nanofibrils with and without nanosilica for the performance enhancement of Portland cement systems*. Construction and Building Materials. 285:121547. https://doi.org/10.1016/j.conbuildmat.2020.121547

Klemm, D., *et al*. (2011), *Nanocelluloses: a new family of nature-based materials*. Angewandte Chemie International Edition. 50(24):5438-5466. https://doi.org/10.1002/anie.201001273
Kolour, H., *et al*. (2020), *Hydration and early age properties of cement pastes modified with cellulose nanofibrils*. Transportation Research Record. 0361198120945993. https://doi.org/10.1177/0361198120945993
Lootens, D., Bentz, D. P. (2016), *On the relation of setting and early-age strength development to porosity and hydration in cement-based materials*. Cement and Concrete Composites. 68:9-14. https://doi.org/10.1016/j.cemconcomp.2016.02.010
Mejdoub, R., *et al*. (2016), *Nanofibrillated cellulose as nanoreinforcement in Portland cement: Thermal, mechanical and microstructural properties*. Journal of Composite Materials. 51(17):2491-2503. https://doi.org/10.1177/0021998316672090
Nassiri, S., *et al*. (2021), *Comparison of unique effects of two contrasting types of cellulose nanomaterials on setting time, rheology, and compressive strength of cement paste*. Cement and Concrete Composites. 123:104201. https://doi.org/10.1016/j.cemconcomp.2021.104201
Nishimura, T., *et al*. (2019), *Effects of powdery cellulose nanofiber addition on the properties of glass ionomer cement*. Materials. 12(19):3077. https://doi.org/10.3390/ma12193077
Ogura, I., *et al*. (2020), *Measurements of cellulose nanofiber emissions and potential exposures at a production facility*. NanoImpact. 20:100273. https://doi.org/10.1016/j.impact.2020.100273
Panesar, D., *et al*. (2017), *The effect of sodium hydroxide surface treatment on the tensile strength and elastic modulus of cellulose nanofiber*. Sustainable and Nonconventional Construction Materials using Inorganic Bonded Fiber Composites. 17–26. https://doi.org/10.1016/B978-0-08-102001-2.00002-4
Santos, R. F., *et al*. (2021), Nanofibrillated cellulose and its applications in cement-based composites: A review. Construction and Building Materials. 288:123122. https://doi.org/10.1016/j.conbuildmat.2021.123122
Sedan, D., *et al*. (2008), *Mechanical properties of hemp fibre reinforced cement: Influence of the fibre/matrix interaction*. Journal of the European Ceramic Society. 28(1):183-192. https://doi.org/10.1016/j.jeurceramsoc.2007.05.019
Sun, X., *et al*. (2017), *Rheology, curing temperature and mechanical performance of oil well cement: Combined effect of cellulose nanofibers and graphene nano-platelets*. Materials & Design. 114:92-101. https://doi.org/10.1016/j.matdes.2016.10.050
Sun, X., *et al*. (2016), *Cellulose nanofibers as a modifier for rheology, curing and mechanical performance of oil well cement*. Scientific reports. 6(1):1-9. https://doi.org/10.1038/srep31654
Tang, Z., *et al*. (2019), *Influence of cellulose nanoparticles on rheological behavior of oil well cement-water slurries*. Materials. 12(2):291. https://doi.org/10.3390/ma12020291
Zhang, S., *et al*. (2021), *High-flexural-strength of geopolymer composites with self-assembled nanofiber networks*. Ceramics International. 47(22):31389–31398. https://doi.org/10.1016/j.ceramint.2021.08.014
Zhang, Z., Scherer, G. W. (2020), *Measuring chemical shrinkage of ordinary Portland cement pastes with high water-to-cement ratios by adding cellulose nanofibrils*. Cement and Concrete Composites. 111:103625. https://doi.org/10.1016/j.cemconcomp.2020.103625