

Stabilization and Evaluation of Modified Nanofiber Flour Wood on the Properties of Cement-Baszd Mortar

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Abstract: The influence of nanofiberwood on the properties of the fresh condition of cement based mortars is not known in detail, despite recent advances in nanocellulose technology and it is related composite materials. Nanofiber wood from industrial waste, produced by high-pressure homogenization, was used as cement partial replacement for cement paste at a content ranging from 0% to 2% by weight of cement. The effect of the nanofiber wood content on the porosity, the compressive strength and the degree of hydration of the cement was investigated. Results have shown an improvement in the compressive strength by more than 50% with 1% of added fiber wood. The chemical modification of nanofibers wood by grafting of chains alkyls in their surfaces can reduce the quantity of water absorbed by the sample. The addition of an anionic additive (SDBS) in the water of mixing improves of more the surface of samples by minimizing the size of pores by emulsion effect, from where the absorption of water reduces. The degree of hydration of the cement has increased with the cellulose content containing nanofibrils. The analyze revealed that the presence of nanofiber wood favored the hydration of the cement by producing more calcium silicate gel and portlandite, probably the main reason for this improvement in compressive strength.

Keywords: Cement; nano-fiber; adjuvant; surfactant; emulsion; hydratation; thermal conductivity

1 Introduction

Nowadays, in the face of environmental problems and the current energy crisis, a construction whose reinforcement is constituted by plant fibers is of increasing interest because of its capacity to substitute for synthetic fibers. Indeed, fibers have many advantages: renewable resources, abundant, a good market and specific mechanical properties of interest. In developing countries development, the reinforcement of materials by plant fibers is a way to explore; these countries possess huge amounts of agricultural waste to be valorized. Since natural fibers have been used as reinforced inorganic materials such as straw and reeds for brick and mortar. Other fibers such as bamboo, wood, wool or chips, dust, seed and fruit are also used in cement and sand-based products [1]. Fibers may be natural or manmade [2]. In this context, the nanofibrils of wood fiber are composed of nanoscale-sized fibrils forming a network structure. Wood fibers, collected waste carpentry plants showed outstanding performance in composites and nanocomposites. The wood fiber nanofibers have several properties and characteristics, such as their morphology, low density, and large surface area when they are modified, good mechanical properties, including a strong Young modulus, high tensile strength and low coefficient of thermal expansion [3,4]. Based on these exceptional properties, it is important to examine the growing interest in the development of modified fiber-based (esterified) nanofiber composites in cement matrix mortar prepared by surfactant

emulsion. anionic agent (SDBS) [5-7], to stabilize the dispersion of wood fiber nanofibers as a reinforcing agent in polymer-based composite materials to improve mechanical properties (compressive strength) on the one hand and to transform the surface of a hydrophilic state has a hydrophobic state (the nanofibers of esterified wood fibers have a hay hydrophobic surface) [8,9]. For a certain percentage of critical loads which depends on the aspect ratio of the reinforcing phase, an excellent improvement of the mechanical properties of the nanocomposite of these materials was noticed. Numerous publications have discussed the interest and emphasis of these applications. Seydibeyoğlu et al. have shown that the addition of 15% by weight of nano-fibrillated cellulose to polyurethane has increased the force by almost 500% and the rigidity by 3000% [10]. Shimazaki and all have shown that the reinforcement of conventional epoxy resin with cellulose nanofibers improves the thermal conductivity from 300% to 500%, which generates a storage capacity of 140% [11]. Recently, few studies have worked on the dispersion and stability of cellulose nanofiber as reinforcing materials in a [12-15] cement matrix. Onuaguluchi et al. [13] have noticed that the addition of a small amount of the order of 1% up to 5% by weight of cellulose nanofibers improves the bending strength up to 100% and the absorption energy of the cement paste up to 150%. Other works Cao et al. [14] have shown that the addition of cellulose nanocrystals (CNC) modify the stress on the strength of the mortar based on cement paste, more specifically a strong improvement in the resistance to bending of cement, this increase is attributed to the increase in the degree of hydration of the cement pastes with the cellulose nanocrystals. Ardanuy et al. [15] have shown that NFC-reinforced cement mortar composites exhibit high flexural modulus performance compared to those reinforced with untreated cellulose fibers.

In this manuscript, the 2% dispersion of modified wood fiber nanofibers in the emulsion cement mortar in the presence of an SDBS anionic surfactant was studied. In the same way, the mechanical and microstructural properties of the cement paste nanocomposites were studied as well as the surface state of the elaborated mortar showed a better hydrophobicity in the relation of the water.

2 Experimental Methods

2.1 Sample Preparation

A mortar of cement-based composite materials (MCP) cement with a water-cement ratio (w/c) of 0.6 was applied for all the mixtures according to the Tunisian standard NT 47.05 [16] (Tab. 1). The cement pastes were mixed in a mixer specified according to NT 47.07 were prepared incorporating 0% NWF, 0.1%, 0.5%, 1%, 1.5% and 2% by weight of cement.

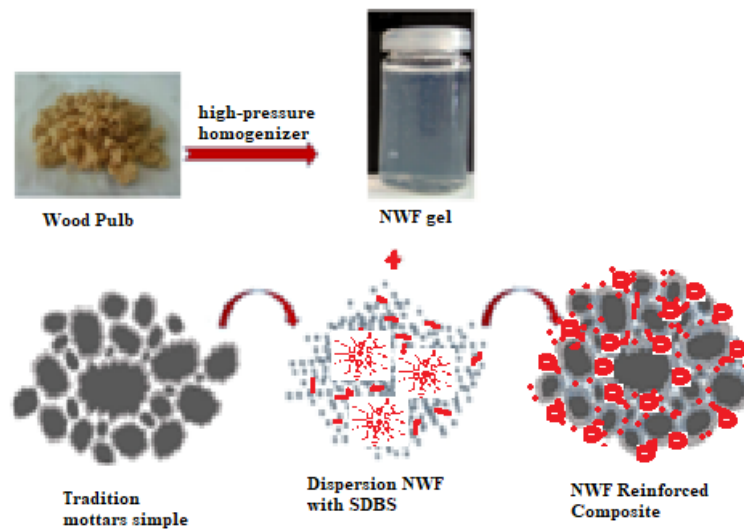
To ensure nanofiber wood (NWF) dispersion, the NWF gel was premixed with a solution of an anionic surfactant of concentration at the critical micelle concentration (CMC of SDBS) at 5 minutes using a mixer until the total dispersion of the nanofiber modified (Fig. 1). After the mixing procedure, cylindrical burrs with a cross-section of 3.5 mm and a height of 7 mm were prepared for each mixture as samples for compressive strength tests (Tab. 2).

After 24 h, the samples were de-molded and cured at 95% relative humidity and $23.0^{\circ}\text{C} \pm 2.0^{\circ}\text{C}$ before the test days.

The compressive strength tests were performed after 1, 7 and 28 days of curing according to NT 47-30 [17]. The compressive strength results are the average of the three test values.

Table 1: Chemical composition of Portland cement

Chemical composition	Anount present (%)
SiO ₂	19.4
Al ₂ O ₃	4.8
Fe ₂ O ₃	3.6
CaO	63.7
MgO	1.9
SO ₃	2.7
Na ₂ O	0.2
K ₂ O	0.8
Loss on ignition	2.4

**Figure 1:** Dispersion of NWF by SDBS: emulsion effect




2.2 Thermal Conductivity

The thermal conductivity of the control mixture and nanocomposites was measured after 28 days of curing, using a TCI. Specimens $22 \times 22 \times 15$ cm cured for days were used for this measurement.

The porosity of pastes was measurement using the methanol displacement method. High purity methanol, which can penetrate into the microstructure without damage, was used. After 28 days of curing, specimens were crushed into small particles. The crushed particles were then vacuum-dried until attaining a constant weight W_0 . After that, the dried particles were immersed in methanol for 24 h, and the weight of sample dipped in the methanol was noted W_1 . Afterward, particles were brought out of the methanol and were surface dried, and the measured weight was noted W_2 . The porosity of cement pastes was calculated as:

$$P = (W_2 - W_0)(W_2 - W_1)$$

Table 2: Shapes, sizing and need to manufacture test pieces specimens

Shapes	Pictures	Sizing	Need to measurement
Pellet		$\varnothing = 3.3 \text{ Cm}$ $h = 1.5 \text{ Cm}$	Absorbance measurement of water
Cylinder		$\varnothing = 3.5 \text{ Cm}$ $h = 7 \text{ Cm}$	Measurement of the compressive stress
Booklet		$L = 17 \text{ Cm}$ $l = 8 \text{ Cm}$ $h = 1.1 \text{ Cm}$	Measurement of contact angle and thermal conductivity

2.3 FTIR Analysis

The Fourier transform infrared (FTIR) spectroscopy was used to analyze the composition change of the treated sisal. FTIR spectrum was obtained from KBr pellets with a Perkin Elmer spectrometer used in transmission mode with a resolution of 2 cm^{-1} in the range of $400\text{-}4000 \text{ cm}^{-1}$.

2.4 CP/MAS ^{13}C Solid-State NMR

Cross polarization/magic angle spinning (CP/MAS) ^{13}C solid-state NMR experiments were performed with Bruker 300 spectrometer operating at a ^{13}C frequency of 75 MHz. the contact time for CP was 1 ms and the delay time for acquisitions was 5 s. Chemical shifts were referred to tetramethylsilane.

2.5 Contact Angle Measurements

The measure of the angle of contact is a technique bound to the capacity of a liquid in Spread out on a surface by wet ability. The principle of this characterization thus consists to measure the angle enter the tangent of the profile of a drop of the liquid put down on the substratum, and the surface of the substratum. She allows measuring the surface energy of the liquid or of Solid. In our work, we used the method of the angle of contact to deduct Hydrophilic or hydrophobic character of the surface of the sample. In our case, we used the water, polar solvent, as the liquid of measure of contact-angle, this liquid allows deducting the hydrophobic character (short angle, low energy of surface) or hydrophilic (small angle, big energy of surface) from the surface.

3 Results and Discussion

3.1 Characterization of Modified Fibers

The modified nanofibrillated wood used in this study was obtained by heterogeneous esterification with linear octyl anhydride at a degree of substitution level 0.3. The modified nanofibrillated wood fiber were analysed by FTIR and solide state NMR.

FTIR spectra (Fig. 2) exhibited the presence of ester carboxyl absorption band at 1755 cm^{-1} , methylene peak at 2855 cm^{-1} and 1450 cm^{-1} . The other characteristic peaks of acyl moiety are hidden by the overlapping of nanofibrillated wood fiber bands.

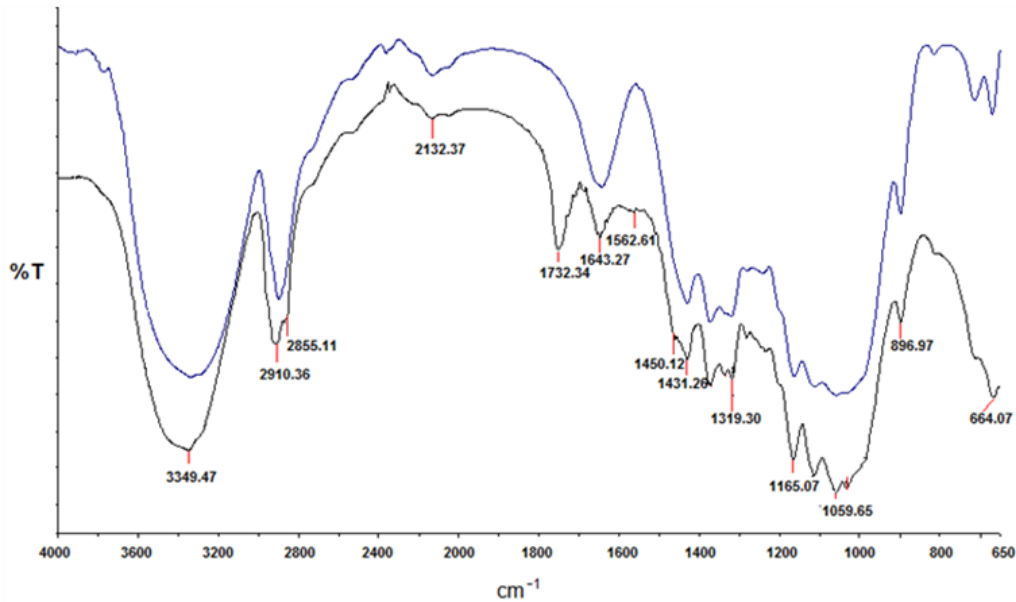


Figure 2: FTIR spectra of wood fiber (WF) and the modified one after esterification with octanoic anhydride at DS = 0.3.

The NMR spectra of fiber wood and fiber wood modified are shown in Fig. 3. In the spectrum of fiber wood, all signals, i.e., those at 104.7 ppm (C-1), 89.8 ppm (C-4 of crystalline cellulose), 74.7 ppm (C-5), 72 ppm (C-2 and C-3), and 69.5 ppm (C-6 of crystalline cellulose), are attributed to six carbon atoms of the glucose unit. However, there is no signal of C-4 and C-6 of amorphous cellulose in the spectrum, suggesting the complete disruption of the cellulose amorphous structure during the acid hydrolysis of cotton. Notably, two more intense signals appear in the spectrum of fiber wood modified in addition to those of fiber wood, due to carbon atoms of carboxylic groups C-7 at 173.8 ppm and methylene carbon in the alkyl moiety at 20-40 ppm.

3.2 Contact Angle Measurement

We used contact angle measurement to analyze the appearance of sample surfaces, and to see the effect of different wood fiber treatment treatments on the absorbance in water. Indeed, measures of the water contact-angles on samples were realized by means of a camera CCD which allows registering, in a speed of images/s 30, the aspect of a calibrated drop of water. Then, powerful software of image processing allows to analyze the outline of the drop and to determine with a big precision the angle of contact with the plane surface. The evolution of the angles of contact for the various samples is presented on Fig. 4. The analysis shows that the grafting of the hydrocarbon chains the surface of fibers makes tip over their characters of the surface of a hydrophilic state very marked in a hydrophobic state. By analyzing the result concerning the evolution of contact angles as a function of time, a clear difference can be seen in the variation of these angles.

Indeed, when the degree of substitution by grafting hydrocarbon chains increases, the contact angle increases that suggests that the evolution of the surface character is related to the presence of alkyl chains that will cover the surface while adopting a configuration perpendicular to the surface.

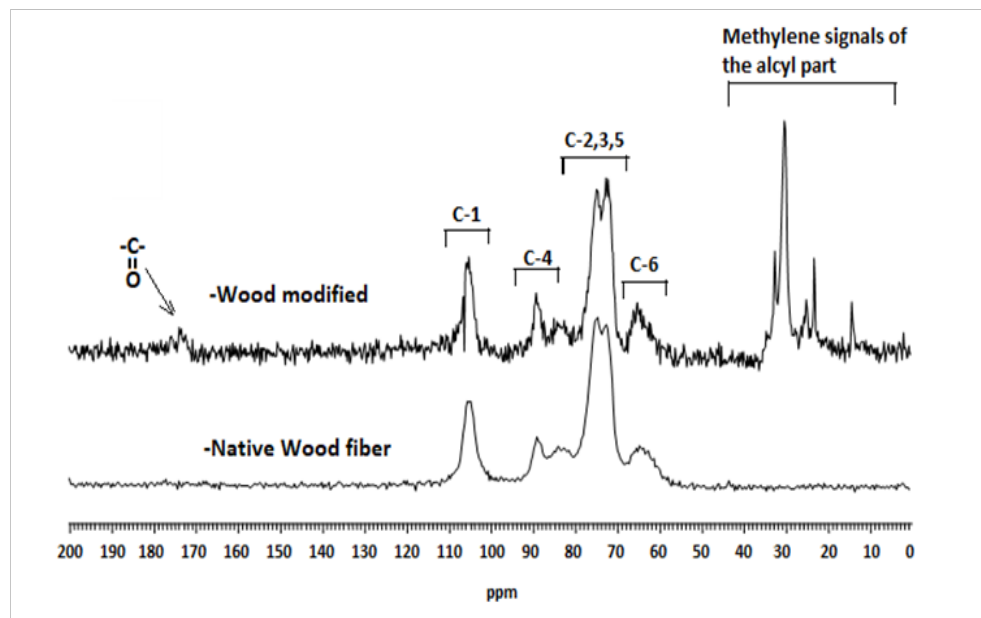


Figure 3: CP MAS ^{13}C MNR spectra of native wood fiber (WF) and the modified one after esterification with octanoic anhydride at DS = 0.3

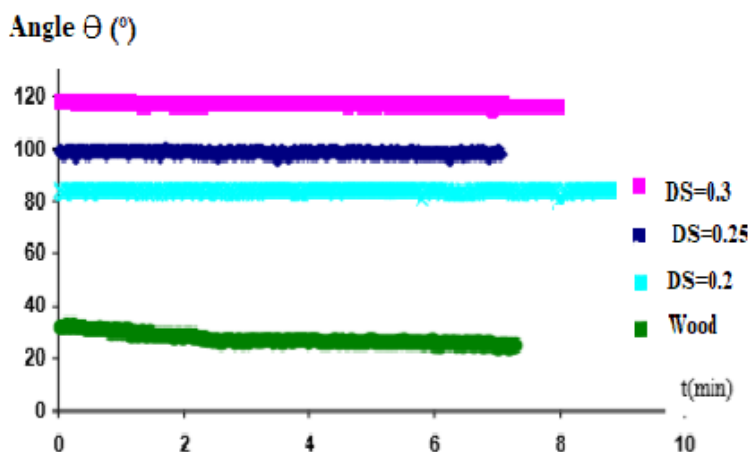


Figure 4: Evolution of the surface of the MCP material from the hydrophilic state (with wood fiber: unmodified WF) to the hydrophobic state (with modified wood fiber for (DS = 0; 0.2; 0.25; 0.3)

3.3 Electrokinetic Study of the Fibrous Suspensions Handled by An Additive in the Presence of A Cement Matrix

From a certain molar concentration called critical micelle concentration (CMC), from which it will be able to form micelles clustering on the surface of the composite, giving rise to an emulsion phenomenon (Fig. 5). According to the Zeta potential curve, we notice that the addition of the additive in the manufacturing of composites, pass by several stages. Indeed, for a low concentration of the SDBS (0,1 mmol/L), the Zeta potential is of the order of 35 mV, this value results from the ionization of calcium during the hydration of cement.

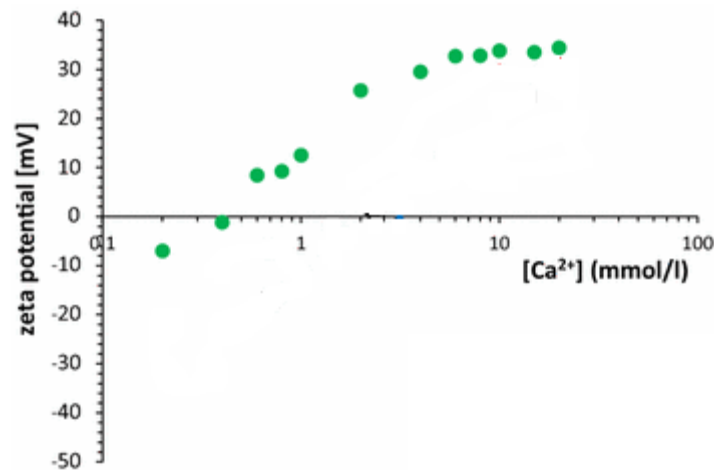


Figure 5: variation of the zeta potential as a function of the concentration of adjuvant

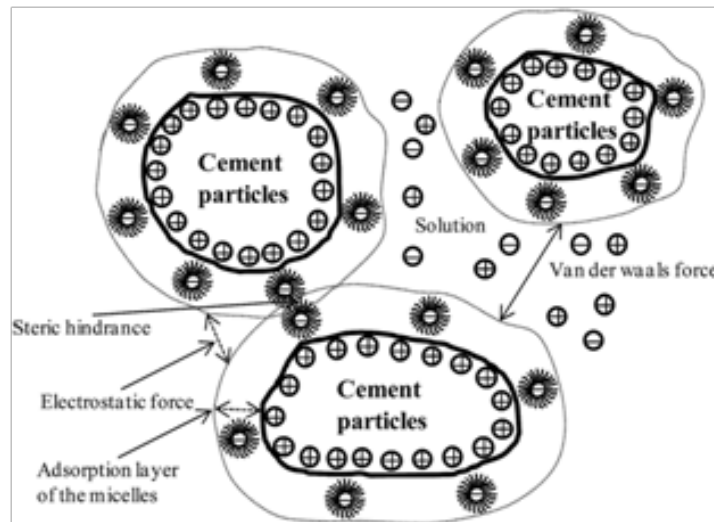


Figure 6: Adsorption of the micelles

The more the concentration by adjuvant increases, the more the Zeta potential decreases, and this relation informs us about the role of the molecules of the anionic surfactant in the neutralization of the ions Ca^{2+} . By arriving at a certain concentration (CMC) of surfactant, the total neutralization was made and we have negative values of the Zeta potential. These show that the molecules of the additive are in excess, where from the formation of micelles from the CMC (Fig. 6).

3.4 Mineralogical Analysis of the Hydration Products by X-Ray Diffraction

To investigate how the addition of NFCs is likely to affect the phase composition of cement, XRD of cement with different contents of NFW was performed. The corresponding diffraction patterns, at an early age of curing (one curing day), are shown in Fig. 7. The XRD patterns of the three samples showed the expected hydration products, including portlandite, ettringite and unreacted calcium silicate phases (C3S and C2S). However, as the calcium silicate hydrates (C-S-H gel) are poorly crystallized, the corresponding diffraction peaks cannot be clearly identified in the patterns. Therefore, the evolution of C-

S-H gel is evaluated referring to the unreacted anhydrous cement phases. The intensity of calcium silicate main peaks decreases with NFW addition, as a greater amount of anhydrous cement phases reacts in the presence of NFW (C₃S and C₂S are transformed into C-S-H). Besides, higher amounts of portlandite and ettringite are formed in NFW 0.5% and NFW 1% samples, compared to the control paste NFW 0%. It can be observed that the intensity of peak changes continues to increase as a function of NFW amount. Compared to the neat cement sample, it can be seen that the presence of NFW promotes the early hydration of cement by producing more Portlandite, Ettringite and C-S-H gel. As C-S-H is one of the major hydration products and the main binding phases in Portland cement controlling cement mechanical properties, the higher content in C-S-H phase is likely the main reason accounting for the strong enhancement in the compressive strength of the cement matrix

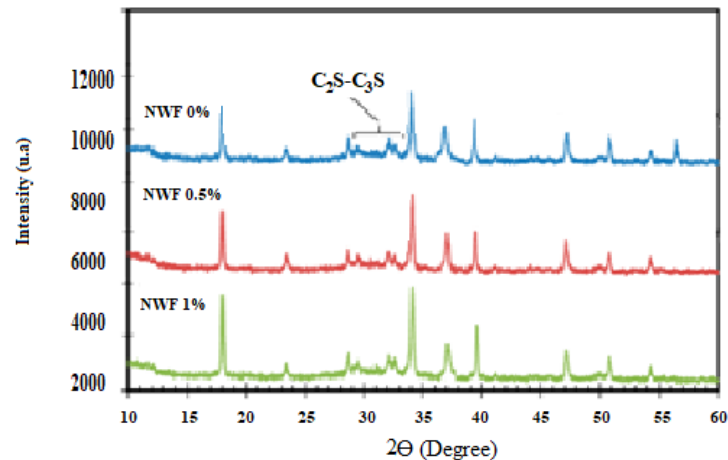


Figure 7: XRD pattern of the NFW 0%, NFW 0.5% and NFW 1% mixtures at one curing day

3.5 Thermal Conductivity

Fig. 8 shows the measured thermal conductivities of the paste mixtures as a function of NFW content. As expected, the NFW addition clearly shows a systematic trend of increasing the thermal conductivity. The maximum of thermal conductivity was achieved by adding 1wt% NFW. These results demonstrate that the use of NFW as reinforcement enhances the thermal conductivity of the cement nanocomposites.

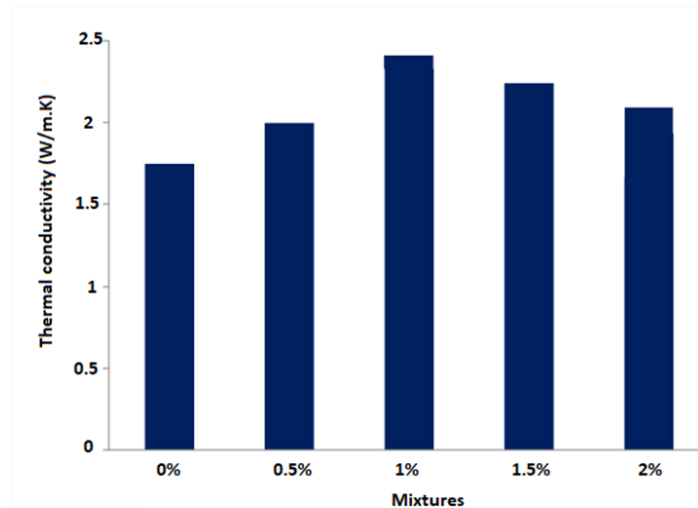


Figure 8: Thermal conductivity of the control specimen and the reinforced cement pastes (after 28 days of curing)

In fact, a small amount of NFW, as low as 1wt% NFW, was sufficient to increase the thermal conductivity. The behavior of the thermal conductivity can be related to the contribution of NFW addition to the densification of cement-matrix, since its expected effect is to decrease the porosity and to increase the bulk density. In fact, as shown in Fig. 9(b), the bulk densities of NFW cement nanocomposites evolve linearly with the NFW content, from 1.77 g/cm³ of the control cement paste, towards 1.815 g/cm³ of NFW 1% mixture. The lower porosity was achieved with the mixture containing 1wt% NFW (Fig. 9(a)).

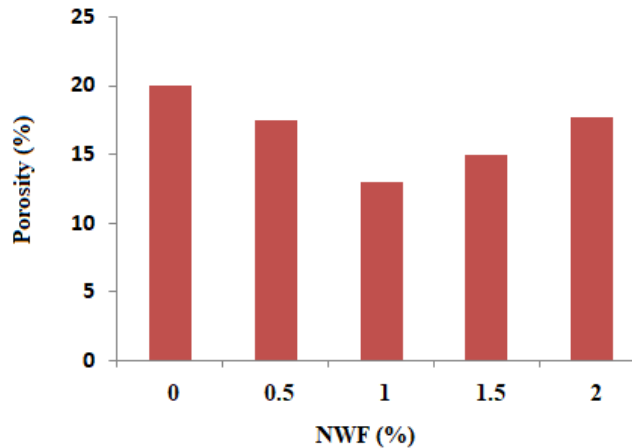


Figure 9(a): Porosity of studied mixtures as function of NFC content

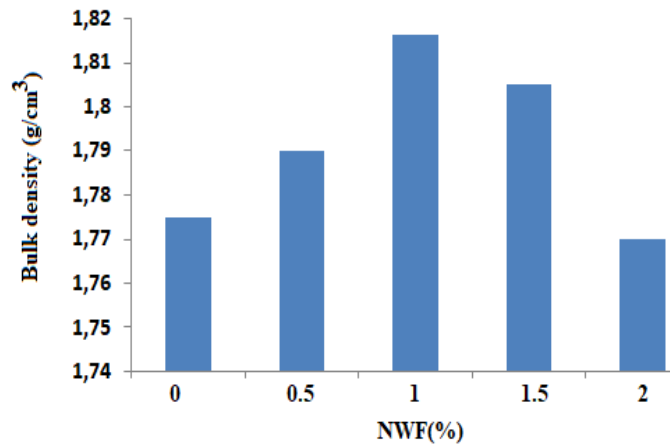


Figure 9(b): Bulk density of studied mixtures as function of NFC content

The changes in bulk density and porosity as NFW is added can be directly attributed to the increase in the degree of cement hydration. In fact, the NFW behave not only as a filler to improve the microstructure but also as an activator to promote hydration reaction. They also act as nucleating sites to form more accumulation and precipitation of hydrated products in the open pores originally filled with water, leading to the formation of more homogeneous, dense and compact microstructure than the mixture without NFW addition.

However, it was found that in this case (NFW 1% mixture), the porosity was reduced by 35%, which can justify the thermal conductivity change. The increase of conductivity was attributed to the crystalline nature of the cellulose nanofibers that provided excellent phonon pathways through the nanocomposite. It is also known that not only the porosity but also the pore's characteristics, such as the size, shape, distribution, orientation, structure and the emissivity of the pores surfaces, have some effects on thermal

conductivity. Beyond 1 wt% NFW addition level (NFW 2% mixture), NFW affected negatively the porosity and density enhancement of the nanocomposites, as result of fiber agglomeration.

In Fig. 10, the latter parameters are correlated with the measured values of the thermal conductivity to examine the relation that each makes with the thermal conductivity of the studied nanocomposites.

The results agree with the general trend that the thermal conductivity of a material increases as density increases and porosity decreases. Consequently, the higher is the porosity, the higher is moisture and air entrapped within the material and the lower is the thermal conductivity.

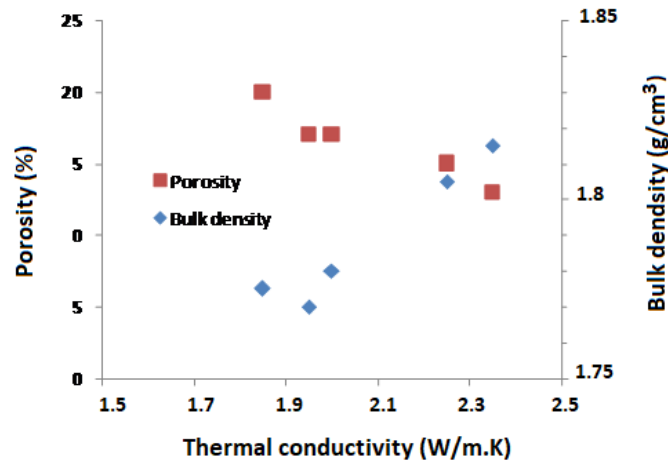


Figure 10: Thermal conductivity versus bulk density and porosity for different studied mixtures

3.6 Mechanical Characterization

The analysis of Fig. 11 examines the decrease in compressive stress with the increase in the percentage of fibers in the cement. With the addition of 2% of fibers, there is a decrease in stress up to 14.4 MPa.

By exceeding the addition of 1% of the fibers, no effect is observed on the compressive strength (stress) and in this case the incorporation of the fibers in the matrix increases the vacuum and reduces the compactness during the addition.

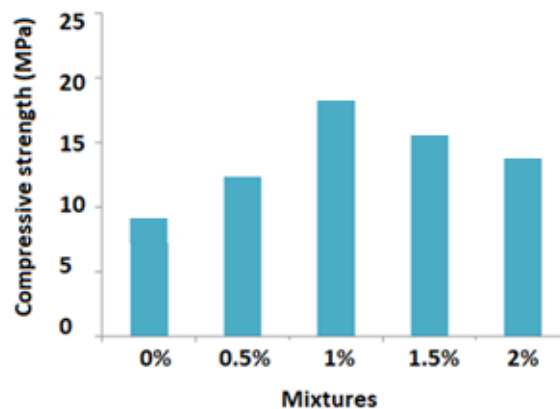


Figure 11: Constraint-strain curves of composites: effect of reinforcement rate, constraint-percentage of fibers

The elasticity properties of the composite are greater than that of a cement matrix alone, the presence of nanofibers of wood in a cement matrix confirms the increase in stiffness, which is explained by the increase in Young's modulus at 1% of fiber additions this is accompanied by an increase in the maximum stress, and the material is also more resistant.

Table 3: Young's modulus values of the different samples

SAMPLE	E (GPA)	COMPRESSIVE STRENGTH (MPA)
CEMENT + 0% WFT	57	8.8
CEMENT + 0.5% WFT	60	12
CEMENT + 1% WFT	101	17.9
CEMENT + 1.5% WFT	200	15.6
CEMENT + 2% WFT	375	14.4

We note in Tab. 3 that the materials had better maximum stress approximately 17.9 MPa for 1% of the fibers treated with SDBS. The presence of nanofibers wood improves the rupture strength of composites cement, this expression was confirmed well by the obtained results.

4 Conclusion

In this work, the nanofiber wood modified potential, as nanoreinforcement for a cementitious matrix, was investigated. Due to its hydrophobic potential, high reactivity and high-specific surface area, the nanofiber wood modified addition has shown an improvement in the mechanical and microstructural properties of the new the nanofiber wood modified -Portland cement (MCP) nanocomposite.

The experimental results have shown that the incorporation of the nanofiber wood modified has greatly enhanced the compressive strength. The highest strength property was observed by adding 1 wt% of the nanofiber wood modified. On the other hand, these samples showed the effectiveness of the grafting of the hydrocarbon chains on the surface of the fibers, in the reduction of the absorbed rate in water compared with only cement. This feature has been further improved by adding to the composite in the fresh state an amount of an anionic additive (SDBS).

References

- Geng, Y. L., Pei, M. W., Zhao, X. H. (2005). Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. *Carbon*, 43(6), 1239-1245.
- Konsta-Gdoutos, M. S., Metaxa, Z. S., Shah, S. P. (2010). Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites. *Cement and Concrete Composites*, 32(2), 110-115.
- Boufi, S., Kaddami, H., Dufresne, A. (2014). Mechanical performance and transparency of nanocellulose reinforced polymer nanocomposites. *Macromolecular Materials and Engineering*, 299, 560-568
- Aloulou, F., Boufi, S., Labidi, J. (2006). Modified cellulose fibres for adsorption of organic compound in aqueous solution. *Separation and Purification Technology*, 52, 332-342.
- Alila, S., Aloulou, F., Beneventi, D., Boufi, S. (2007). Self-aggregation of cationic surfactants onto oxidized cellulose fibres and coadsorption of organic compounds. *Langmuir*, 23, 3723-3731.
- Aloulou, F., Boufi, S., Chakchouk, M. (2004). Adsorption of ocatdecyltrimethylammonium chloride and adsolubilization onto cellulosic fibres, *Colloid Polymer Science*, 282(7), 699-707.
- Aloulou, F., Boufi, S., Belgacem, N., Gandini, A. (2004). Adsorption of cationic surfactants and subsequent adsolubilization of organic compounds onto cellulosic fibres, *Colloid Polymer Science*, 283, 344-350.

8. Aloulou, F., Boufi, S., Beneventi, D. (2004). Adsorption of organic compound onto polyelectrolyte immobilized-surfactant aggregates onto cellulosic fibres, *Journal Colloidal and Interface Science*, 280(2), 350-358.
9. Alila, S., Boufi, S., Belgacem, N., Beneventi, D. (2005). Adsorption of cationic surfactant onto cellulose fibres I; surface charge effects, *Langmuir*, 21, 8106-8113.
10. Seydibeyoğlu, M. Ö., Oksman, K. (2008). Novel nanocomposites based on polyurethane and micro fibrillated cellulose. *Composites Science and Technology*, 68, 908-914.
11. Shimazaki, Y., Miyazaki, Y., Takezawa, Y., Nogi, M., Abe, K. et al. (2007). Excellent thermal conductivity of transparent cellulose nanofiber/epoxy resin nanocomposites. *Biomacromolecules*, 8, 2976-2978.
12. Antonio, N. N., Hiroyuki, Y. (2008). The effect of fiber content on the mechanical and thermal expansion properties of biocomposites based on microfibrillated cellulose. *Cellulose*, 15, 555-559.
13. Onuaguluchi, O., Panesar, D. K., Sain, M. (2014). Properties of nanofibre reinforced cement composites. *Construction and Building Materials*, 63, 119-124.
14. Cao, Y., Zavaterra, P., Youngblood, J., Moon, R., Weiss, J. (2015). The influence of cellulose nanocrystal additions on the performance of cement paste. *Cement Concrete Composite*, 56, 73-83.
15. Ardanuy, M., Claramunt, J., Arévalo, R., Parés, F., Aracri, E. et al. (2012). Nanofibrillated cellulose (NFC) as a potential reinforcement for high performance cement mortar. *Composites*, 7, 3883-3894.
16. NT 47.05:1983. Liants Hydroliques-Technique des essais: Pate Normale.
17. NT 47.30:1991. Méthodes d'essais des ciments-Détermination des résistances mécaniques.