

# Influence and Dispersion of Nanofiber of Wood Modified on Properties of Cement Based Mortars

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**Abstract:** Wood nanofibers from industrial waste have been used as polymeric material to reinforce the cement paste to a content of up to 2% by weight of cement. The effect of the wood nanofibre content on the porosity, the compressive strength and the degree of hydration of the cement was studied. The results showed an improvement in compressive strength of over 50% with 1% of added fiberwood. Chemical modification of nanofiber wood by grafting alkyl chains to their surface can reduce the amount of water absorbed by the sample. Addition of an anionic additive (SDBS) to the mixing water improves the surface of the samples more and more by minimizing the pore size by emulsion effect, hence the water absorption decreases. The degree of hydration of the cement increased with the cellulose content containing nanofibrils. The analysis revealed that the presence of nanofibers favored the hydration of the cement by producing more calcium silicate gel and portlandite, probably the main reason for this improvement in compressive strength.

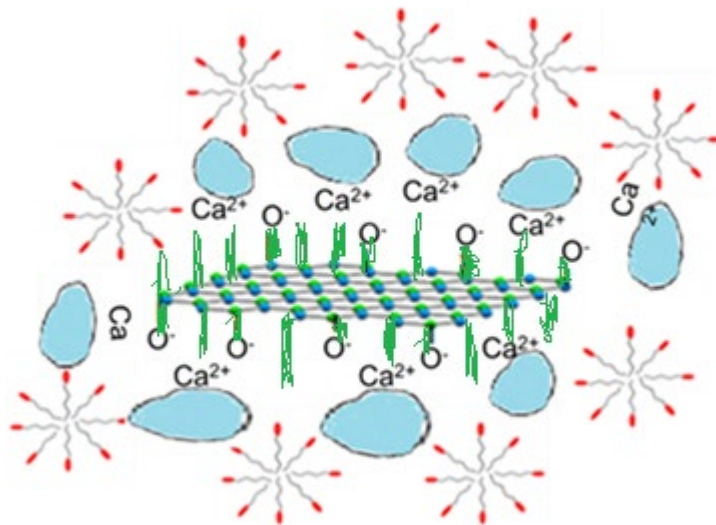
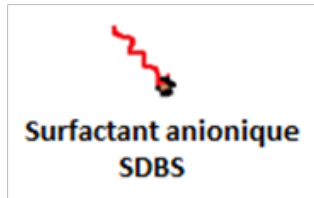
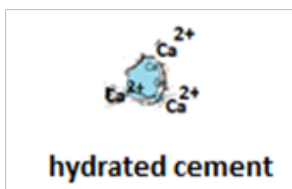
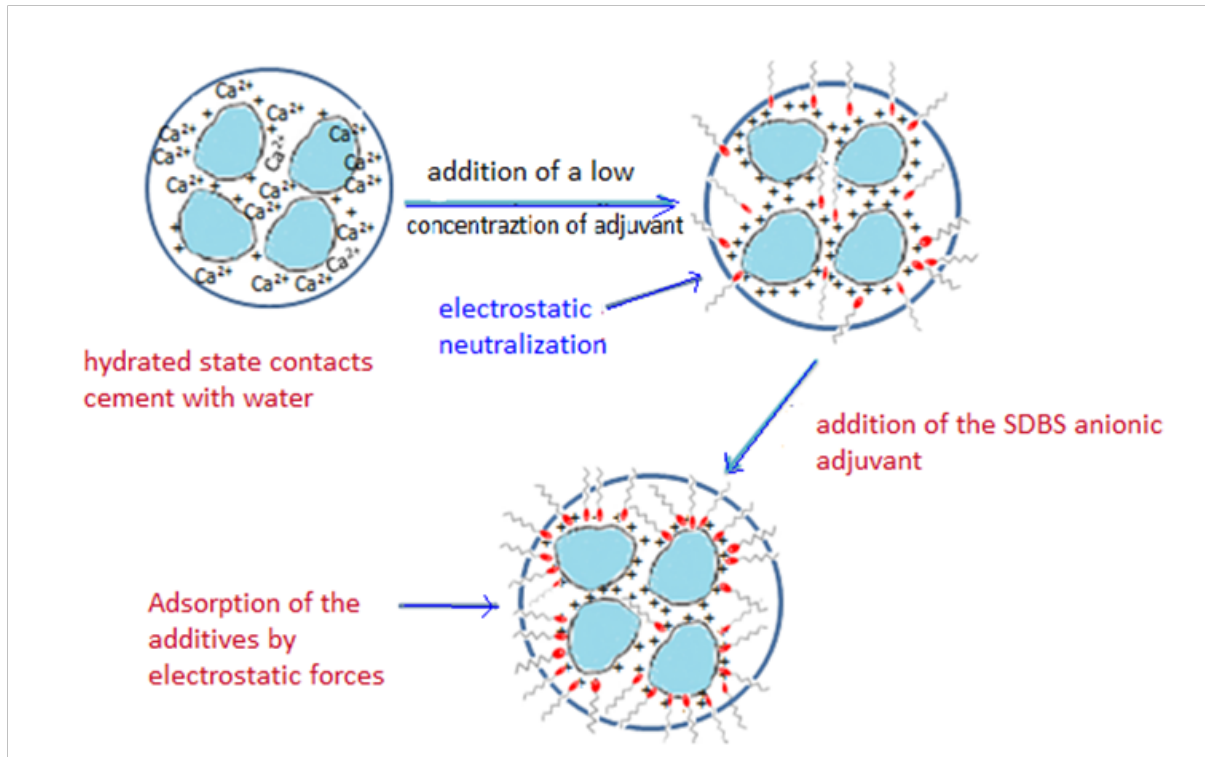
**Keywords:** Cement; nano-fiber wood modified; adjuvant, surfactant; emulsion

## Highlights

- Synthesis of materials composites: cement reinforced with wood fiber by Emulsion treated with SDBS.
- The compressive strength increases with the addition of wood fibers which reflects an increase in mechanical properties.
- 1 %wt wood fiber and SDBS surfactant were optimum in enhancing compressive strength and porosity.
- The dispersion of the wood fibers is controlled and assumed by an anionic surfactant SDBS as an emulsion phenomenon.
- The elaborate materials has thermal properties can be used as phase change materials (PCMs).
- The wood fibers favored the hydration of the cement which generates portlandite gel and calcium silicate, which explains the strong improvement of the compressive strength.

Graphical Abstract:

Emulsion Mechanism



## Abbreviations

PC: Ordinary Portland cement NT 47-01:1983

CNC: Cellulose Nanocrystals

SDBS: Sodium dodecylbenzene sulfonate

KBr: Potassium bromide

TMS: Tetramethylsilane

CMC: Critical micellar concentration

NWF: nano-wood fiber

Wood modified: wood fiber modified by esterification with anhydride

DS: Degree of substitution

## 1 Introduction

In the face of environmental problems and the current energy crisis, construction whose reinforcement consists of vegetable fibers, are of interest growing, because of their ability to substitute for synthetic fibers. Indeed, fibers have many advantages: renewable resources, abundant, 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 [1-5]. Fibers may be natural or manmade [6,7]. Sisal fibers are presently used as reinforced materials in concrete constructions

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 nanofibers of wood fibers have several interesting properties such as their morphology, their low density and their large surface area when they are modified, and their good mechanical properties [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 composite materials in order to improve the mechanical properties (compressive strength) and to transform the surface from a hydrophilic state to a hydrophobic state (nanofibers esterified wood fibers have a hydrophobic hay surface) [8,9]. For a certain percentage of nanofibre addition, the mechanical properties of nanocomposite materials become more efficient. Numerous publications have discussed the interest and emphasis of these applications. Seydibeyoğlu and Oksman have shown that the addition of 15% by weight of nano-fibrilated cellulose to polyurethane has increased the force by almost 500% and the rigidity by 3000.% [10]. Shimazaki et al. showed that the thermal conductivity was improved by the addition of cellulose nanofibers in the matrix of the epoxy resin, which generates a storage capacity of the order of 140% [11]. Recently, few studies have focused on the dispersion and stability of cellulose nanofiber as renewable materials in the cement matrix for enhanced mechanical properties [12-15]. Onuaguluchi et al. [13] found that a small amount added in the range of 1% to 5% by weight of cellulose nanofibers improves flexural strength to 100%. Cao et al. [14] have noted that the addition of cellulose nanocrystals (CNC) modifies the stress on the strength of the cement matrix mortar, more specifically a strong improvement in the bending strength of the cement, this increase is to an improvement in the degree of hydration of the cement pastes in the presence of 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 model of composite materials based on cement (MCP) with a water/cement ratio of 0.6 was used for the preparation of all the blends of the Tunisian standard [16] (Tab. 1).

The cement paste samples were prepared by incorporating 0% NWF, 0.5%, 1%, 1.5% and 2% by weight of cement into a mixer specified according to NT 47.07. 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. 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. The samples were demolded after 24 hours and cured at 95% relative humidity before the test days. The compressive strength tests were performed after 28 days of hardening according to NT 47-30 [17].

**Table 1:** Chemical composition of Portland cement (PC) (wt%)

Material	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Loss on ignition
Cement	19.4	4.8	3.6	63.7	1.9	2.7	0.2	0.8	2.4

### 2.2 Thermal Conductivity Test

22 × 22 × 1.5 cm samples were prepared and cured for 28 days to conduct thermal conductivity measurements using a TCI. The method of displacement with methanol was used to measure the porosity. After 28 days of hardening, the samples were ground into small particles. The particles ground after 28 days were cured and then vacuum dried to a constant weight of W<sub>0</sub>. The dried particles were immersed in methanol for 24 h and the weight of the sample which contains the methanol was noted W<sub>1</sub>. Subsequently, the particles were extracted from the methanol and dried on the surface, and the measured weight was noted W<sub>2</sub>. The porosity of the samples was calculated as follows:

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

### 2.3 Fourier Transform Infrared Spectroscopy

FTIR measurements were performed using a Perkin Elmer spectrometer using the standard KBr pellet technique in transmission mode with a resolution of 2 cm<sup>-1</sup> in the 400-4000 cm<sup>-1</sup> range.

### 2.4 Solid-State NMR Spectroscopy

NMR measurements in the solid state were carried out on Bruker Avance-300 spectrometer operating at a frequency of 13 C of 75 MHz. the contact time of the CP was 1 ms and that of the acquisitions of 5 seconds. Chemical shifts were referred to tetramethylsilane.

### 2.5 Contact Angle Measurements

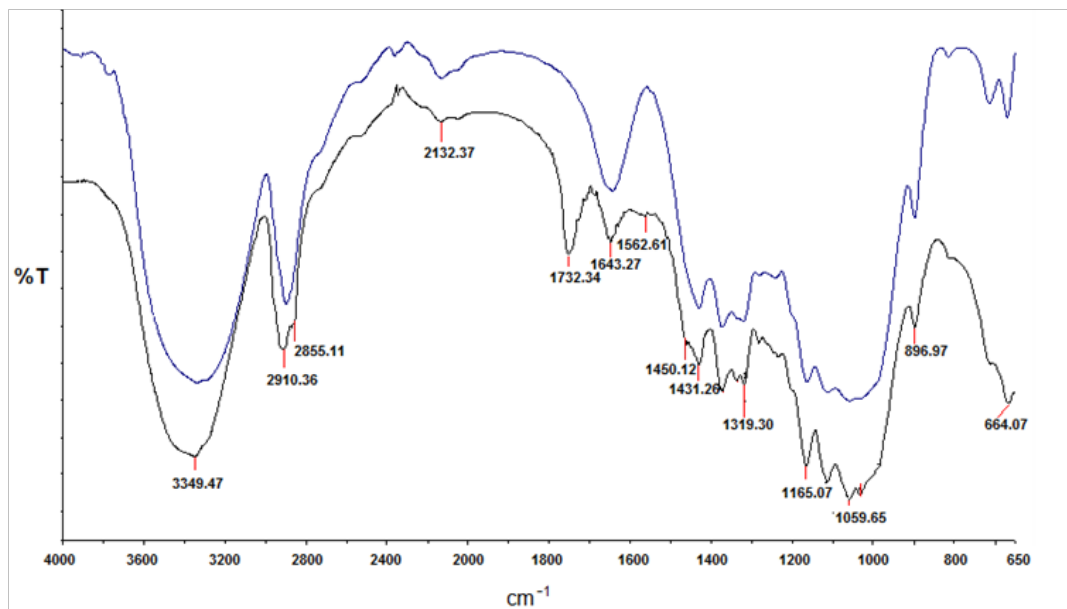
The contact angle measurement tests were performed by depositing a calibrated drop of liquid (distilled water) on the cellulose fiber pellets. The contact angle apparatus used was a Dataphysics OCA 15, equipped with a CCD camera, with a resolution of 752.582 square pixels, working at an acquisition rate of 4 frames per second. The collected data was processed using OCA Software.

### 3 Results and Discussion

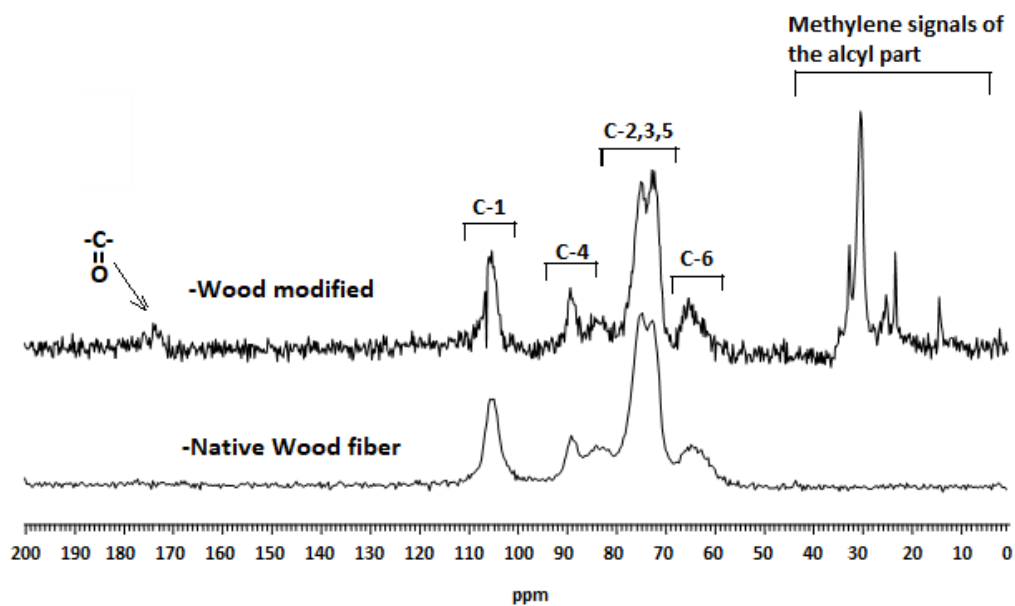
#### 3.1 Characterization of Modified Fibers

The modified wood nanofibers used in this work were obtained by heterogeneous esterification with octyl anhydride at a degree of substitution of the order of 0.3, analyzed and characterized by FTIR and solid state NMR.

Fig. 1 shows the FTIR spectra of wood fibers (WF) and the modification of the one after the esterification with octanoic anhydride at DS = 0.3. These spectra showed the presence of a carboxylic ester absorption band at  $1755\text{ cm}^{-1}$ , a methylene peak at  $2855\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$ .



**Figure 1:** FTIR spectra of wood fiber (WF) and the modified one after esterification with octanoic anhydride at DS = 0.3

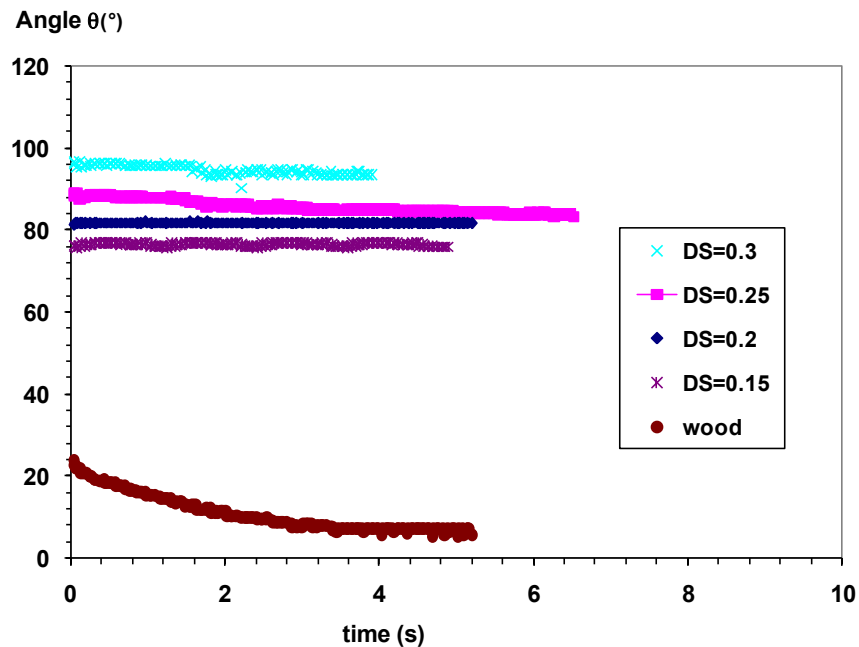


**Figure 2:** CP MAS  $^{13}\text{C}$  MNR spectra of native wood fiber (WF) and the modified one after esterification with octanoic anhydride at DS = 0.3

Fig. 2 shows the CP-MAS spectra obtained before and after the chemical modification. The starting wood nanofibers have signals of 105 ppm (C-1), 90 ppm (crystalline cellulose C-4), 75 ppm (C-5), 72 ppm (C-2 and C-3) and 69 ppm (C-6 crystalline cellulose) which are assigned to six carbon atoms of the glucose unit. The appearance of new peaks at 14, 23, 33 and 173.8 ppm attributed to the carbon atoms of the terminal  $\text{CH}_3$ ,  $\text{CH}_2$  of the internal methyl group of the octanoic anhydrid chain and to CO due to carbon atoms of the carboxyl groups C-7.

### 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. Fig. 3 shows the evolution of contact angles as a function of time of wood fibers (unmodified WF) and modified wood fibers for (DS = 0.15, 0.2, 0.25, 0.3). The analysis shows that when the degree of substitution by grafting of hydrocarbon chains increases, the contact angle increases, which suggests that the evolution of the surface character is linked to the presence of alkyl chains which will cover the surface while adopting a configuration perpendicular to the surface, which confirms that the grafting of the hydrocarbon chains on the surface of the fibers switches their characters from the surface of a hydrophilic state very marked in the hydrophobic state.

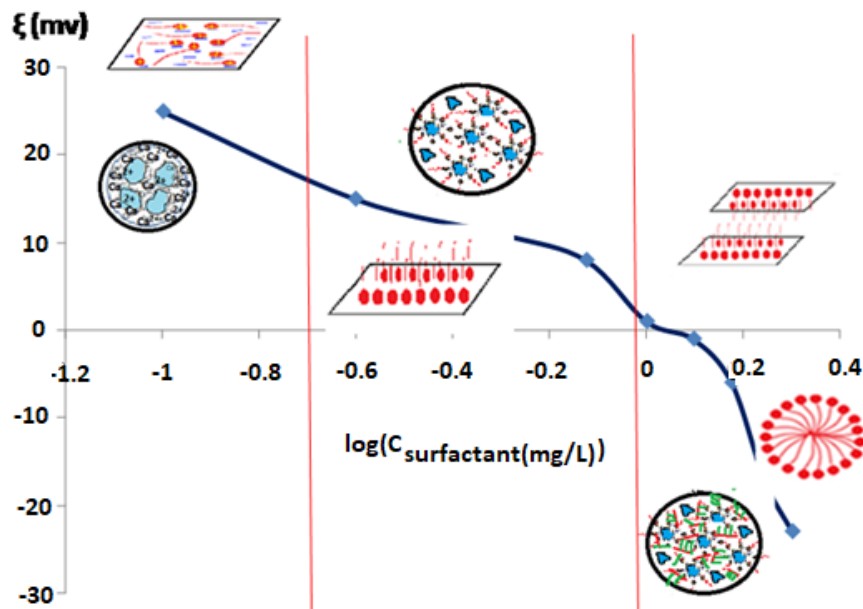


**Figure 3:** Evolution of the surface of the MCP material from the hydrophilic state (with wood fiber: unmodified WF) to the hydrophobic state (with modified wood fiber for (DS = 0.15; 0.2; 0.25; 0.3))

### 3.3 Electrokinetic Study of the Fibrous Suspensions Handled by an Additive in the Presence of a Cement Matrix

Fig. 4 shows the evolution of the zeta potential as a function of the concentration of the SDBS surfactant. For a certain concentration of SDBS, the zeta potential curve shows that the addition of SDBS in the manufacture of the mortar goes through several stages. Indeed, for a low concentration of 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 the cement. 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. On the other hand, the higher the concentration of SDBS, the lower the Zeta potential, and this relationship informs us about the role of the anionic surfactant molecules in the neutralization of  $\text{Ca}^{2+}$  ions. By reaching a certain concentration (CMC) of surfactant, the total neutralization has been carried out and the zeta potential takes negative values. These show that the SDBS molecules are in excess, hence the formation of micelles from the CMC.

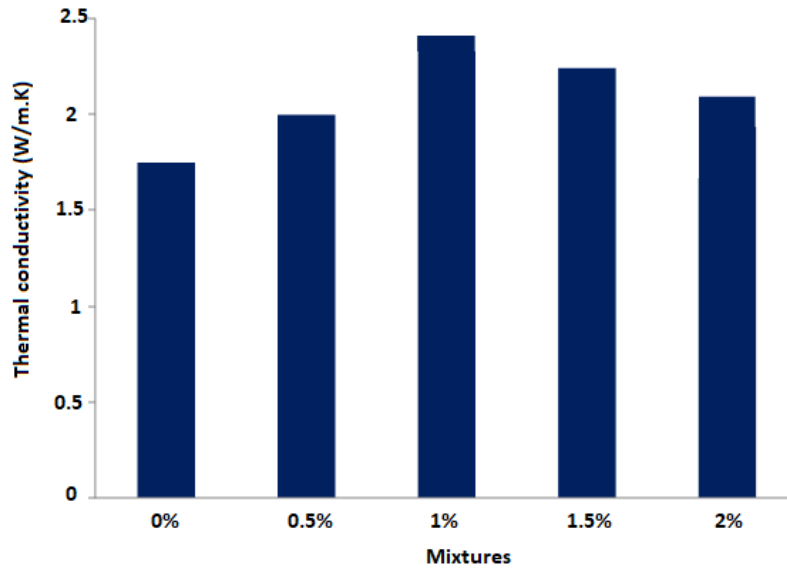


**Figure 4:** Variation of the zeta potential as a function of the concentration of adjuvant SDBS

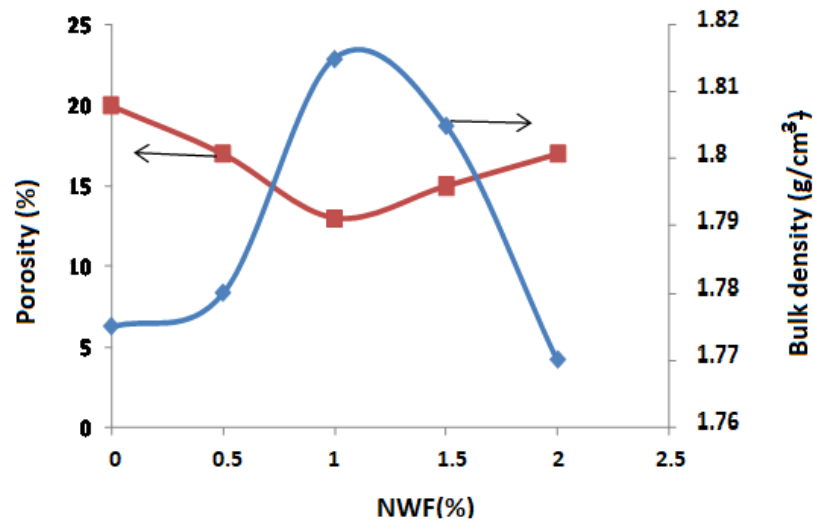
### 3.4 Thermal Conductivity

Fig. 5 illustrates the evolution of the measured thermal conductivities of the mortars as a function of the NFW content. The NFW addition clearly shows a systematic tendency to increase the thermal conductivity. The maximum thermal conductivity was achieved by adding 1% by weight of NFW. These results demonstrate that the use of NFW as a reinforcement improves the thermal conductivity of cement nanocomposites.

In addition, a small amount of NFW, of the order of 1% by weight of NFW, was sufficient to increase the thermal conductivity. This increase in thermal conductivity may be related to the contribution of NFW to the densification of the cement matrix, the reduction in porosity and the increase in bulk density. Fig. 6 shows that the apparent densities of NFW cement nanocomposites evolve linearly with the NFW content, from  $1.77 \text{ g/cm}^3$  of the control mortar to  $1.815 \text{ g/cm}^3$  for a 1% NFW mixture. The lowest porosity was obtained with the mixture containing 1% by weight of NFW.



**Figure 5:** Thermal conductivity of the control specimen and the reinforced cement pastes (after 28 days of curing)



**Figure 6:** Porosity and bulk density of studied mixtures as function of NFC content

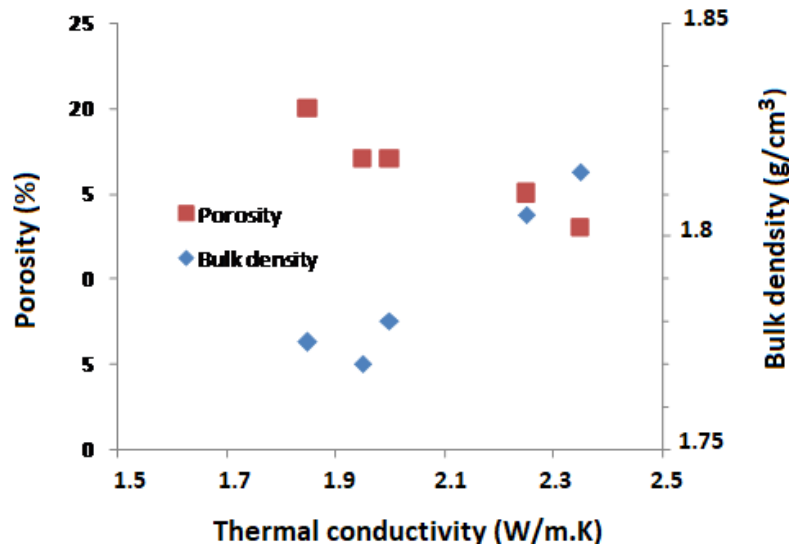
The variations in density and porosity are remarkable when adding NFW, this can be explained by the increase in the degree of hydration of the cement. In fact, NFW behaves not only as a filler to improve the microstructure, but also as an activator to promote the hydration reaction. They also act as nucleation sites to form more accumulation and precipitation of hydrated products in open pores initially filled with water, leading to the formation of a more homogeneous, dense and compact microstructure. On the other hand it is remarkable that in this case (1% NFW mixture), the porosity was reduced by almost 40%, which proves that the change in thermal conductivity.

Thermal conductivity increases with the crystalline nature of cellulose nanofibers, which generates excellent phononic pathways through the nanocomposite. In addition porosity, pore characteristics, such as size, shape, distribution, orientation, structure and emissivity of pore surfaces, have a positive effect on thermal conductivity. Indeed, beyond 1% by weight of NFW addition to 2% NFW, a negative impact on



the increase of the porosity and the density of the nanocomposites resulting from the agglomeration of the fibers is noted.

Fig. 7, proves that the last parameters are correlated with the measured values of the thermal conductivity and confirme the relations establish with the thermal conductivity of the nanocomposites studied.

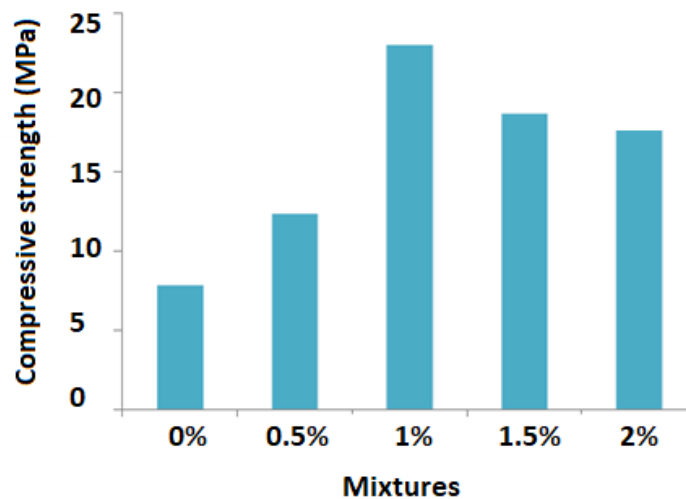


**Figure 7:** Thermal conductivity versus bulk density and porosity for different studied mixtures

Thermal conductivity increases as density increases and porosity decreases as results are found. Indeed the higher the porosity, the more moisture is trapped in the material, the lower the thermal conductivity.

### 3.5 Mechanical Characterization

Fig. 8 shows the evolution of the compression stress with the increase of the percentage of fibers added in the cement. In the case of adding 2% of fibers, note a decrease in stress up to 17.8 MPa. With 1% added fiber, no effect is observed on the compressive strength and in this case, the incorporation of fibers in the matrix increases the vacuum and reduces the compactness during the addition.



**Figure 8:** Constraint-strain curves of composites: Effect of reinforcement rate, Constraint- Percentage of fibers

The presence of wood nanofibers in a cement matrix confirms the increase in rigidity, which is explained by the increase of the Young's modulus at 1% of added fibers which proves an increase in the maximum stress, and the material also becomes more resistant. In Tab. 2, we note that the materials had a better maximum stress of about 23.5 MPa for 1% of fibers treated with SDBS. The presence of wood nanofibers improves the breaking strength of the composite cement, this expression was well confirmed by the results obtained.

**Table 2:** Young's modulus values of the different samples

SAMPLE	E (GPA)	COMPRESSIVE STRENGTH (MPA)
CEMENT + 0% WFT	57	8
CEMENT + 0.5% WFT	60	12.5
CEMENT + 1% WFT	101	23.5
CEMENT + 1.5% WFT	70	18.5
CEMENT + 2% WFT	475	17.8

#### 4 Conclusion

Based on the results obtained on the Influence and Dispersion of Nanofiber of Wood Modified on Properties of Cement Based Mortars, the following conclusions can be drawn:

The addition of the wood nanofibre has improved the mechanical and microstructural properties of the new nanocomposite containing modified wood nanofiber and Portland cement because of its hydrophobic potential, high reactivity and large surface area.

The experimental results showed that the incorporation of the modified nanofiber wood had considerably improved the compressive strength. The highest strength property was observed by adding 1% by weight of the modified nanofiber wood. On the other hand, these samples showed the efficiency of the grafting of the hydrocarbon chains on the surface of the fibers, in the reduction of the rate of absorption in the water compared to the only cement. This functionality has been further improved by adding to the composite in the fresh state an amount of an anionic additive (SDBS).

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