

Characterization and Influence of Nanofiber Flours of Wood Modified on Fresh State Properties of Cement Based Mortars

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Abstract: Nanofibrillated wood fiber was used as fillers in the partial cement matrix replacing the cement to a content of up to 2% by weight of cement. The nanofibrillated effect of wood fibers on porosity, thermal properties and compressive strength was studied. The results obtained showed an improvement in compressive strength of more than 40% with 1% by weight of wood fiber nanofibrillate. The addition of nanofibrillated wood fiber shows a good pore reduction, and the best result was obtained with emulsion of a mixture incorporating 1% by weight of wood fiber nanofibrillate in the presence of an anionic surfactant (SDBS). Thermal conductivity measurements and thermal expansion coefficient, compared to nanofibrillated wood fiber reinforced cement pastes, showed the reinforcing efficiency of cellulose fiber nanofibrillate. The degree of hydration of the cement increased with nanofibrillated wood fibers. This property has been confirmed by Fourier transform infrared spectroscopy. These analyzes revealed that the presence of nanofibrillated wood fibers generates and promotes the hydration of the cement, producing more portlandite and calcium silicate gel, which influences the compressive strength which gives a strong improvement.

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

1 Introduction

Nano-fibers, in particular the carbon nanotube (CNT) and the carbon nanofibers, have recently been used as materials to improve the mechanical properties of a cement matrix composite mortar for cementitious materials [1-2]. Nanofibers, particularly carbon nanotubes (NTCs) and carbon nanofibers, have recently been used as materials to improve the mechanical properties of a cementitious matrix composite mortar for cementitious materials [1-2]. In this context, the use of nanofibers of wood fibers which are composed of nano-sized fibrils forming a lattice structure play a large role in the improvement of mechanical properties. The wood fibers used are extracted from the wood waste of carpentry plants. The nanofibers wood (NWF) 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 (CTE) [3].

Modified mortars with polymers and concretes such as polymers nanofiber cellulose (NFC) esterified, have been widely used in the world. Since then, polymers have been added to mortars and concretes to improve certain properties, including workability, water retention, permeability, strength and dimensional stability. Polymer-modified mortars using cellulose fibers are widely used performance, low cost construction materials especially for finishing work due to their improved workability, mechanics and durability properties. The polymeric cellulose nano fiber is a colloidal dispersion of small polymer particles in water, which is typically produced by emulsion polymerization of monomers with surfactants sodium

dodecyl benzene sulfonate (SDBS) [4-7]. Surfactants are an important group of surfactants substances with many applications because of their relatively complex behaviors. The surfactants have a hydrophobic part and a hydrophilic part. All the adsorbed surfactants have their hydrocarbon chain towards the liquid phase and an increase in the hydrophobicity of the cement surface. However, SDBS has undergone a change from a hydrophilic state to a hydrophobic state due to the formation of adsorbent micelles filled by the esterified cellulose nano fiber [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 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 and al 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]. Antonio NN and Hiroyuki Y have claimed that microfibrils-reinforced phenolic resin composites cause a decrease in thermal expansion [12].

Recently, few studies have worked on the dispersion and stability of cellulose nanofiber as reinforcing materials in a [13-15] 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 [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 Raso 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 opposite the water.

2 Experimental Methods

2.1 Preparation of Modified Nano-Fiber Wood: NWF

The modification of the NWF was carried out by grafting a hydrocarbon chain through heterogeneous esterification of fiber wood surface hydroxyl groups with octanoic anhydride using a solvent exchange procedure. Woodfiber (5 g) was introduced in the flask containing 110 ml of toluene/triethylamine (80/20 v/v). The flask was firstly kept under reflux ($T = 110-120^{\circ}\text{C}$) and constant stirring until all water contained on the fibers was evacuated by azeotropic distillation, then octanoic anhydride (5 g) was added drop-wise over a period of 1 h. The reflux was continued under nitrogen atmosphere over a period of 6 h. The obtained product was cooled and then purified by soxhlet extraction with THF/ethanol (50/50 v/v) for 24 h. The degree of substitution (DS) was determined by saponification and titration according to a well-described procedure.

2.2 Determination of the Degree of Substitution (DS)

The DS represents the average number of the esterified hydroxyl groups per anhydroglucose structure unit, and was determined using two methods. The first one was based on the saponification of the ester bonds and back titration of the released acid. Thus, 40 ml of 0.25 N sodium hydroxide solution

in 95% ethanol were added to 0.5 g of dry modified fibres previously introduced in an Erlenmeyer flask. After standing for 12 h at room temperature, 10 ml of 0.5 N HCl solution was added to the reaction medium which was kept for 2 h before starting the back titration of the excess HCl. For this purpose, a 0.1 N NaOH solution using phenolphthalein indicator was used. The percent of carboxylic acid and the DS were calculated as follows: %CA = $((V_0 - V_s)/mS) * 100$

$$DS = (\%CA/MCA) * ((100 - \%CA)/162)$$

where: %CA is the percent of carboxylic acid, V_0 the volume of 0.1 N NaOH (in ml), used to titrate the blank essay, V_s the volume of 0.1 N NaOH (in ml) to titrate the saponified samples, m_s the sample weight (in g) and MCA the molecular weight of the grafts.

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 1ms and the delay time for acquisitions was 5 s. Chemical shifts were referred to tetramethylsilane (TMS).

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. 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 liquid of measure of angle of contact, this liquid allows to deduct the hydrophobic character or hydrophilic from the surface.

2.6 Degree of Hydration

The degree of hydration of the cement was calculated based on the weight loss between 140°C and 1100°C , which corresponds to the amount of non-evaporable water in the cement paste. The cement paste samples are first treated with acetone to stop hydration before being dried to a constant mass at 140°C . Then, the samples are heated up to 1100°C . a period of 3 hours. Finally, the samples are put in a decicator until they are at room temperature. The amount of water in the non-evaporable sample was calculated as a mass loss between 140°C and 1100°C .

2.7 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 min 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. After 24 h, the samples were demolded 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 day, 7 days and 28 days of curing according to NT 47-30 [17]. The compressive strength results are the average of the three test values.

3 Results and Discussion

3.1 Characterization of Modified Fibers

The Nanofibrillated wood fiber modified in this study were obtained by heterogeneous esterification with linear octyl anhydride at a degree of substitution level 0.25. The modified nanofibrillated wood fiber were analysed by FTIR and solide state NMR. FTIR spectra Figure 1 exhibited the presence of ester carboxyl absorption band at 1755 cm^{-1} , methylene peak at 2855 cm^{-1} and 1450 cm^{-1} .

Table 1: Chemical composition and physical characteristics of Portland cement (wt %)

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

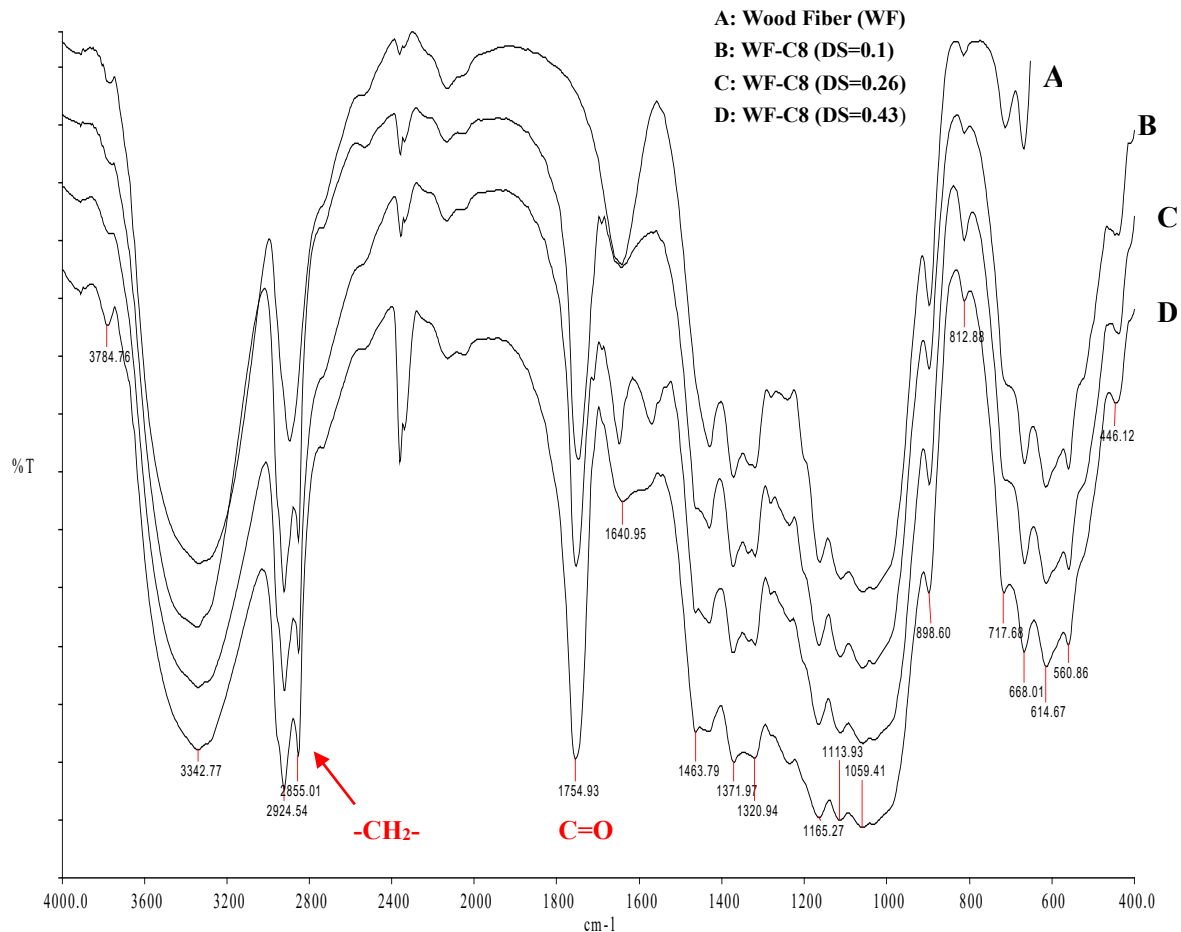


Figure 1: FTIR spectra of wood fiber (WF) and the modified one after esterification with octanoic anhydride at (A: DS = 0, B: DS = 0.1; C: DS = 0.26, D: DS = 0.43)

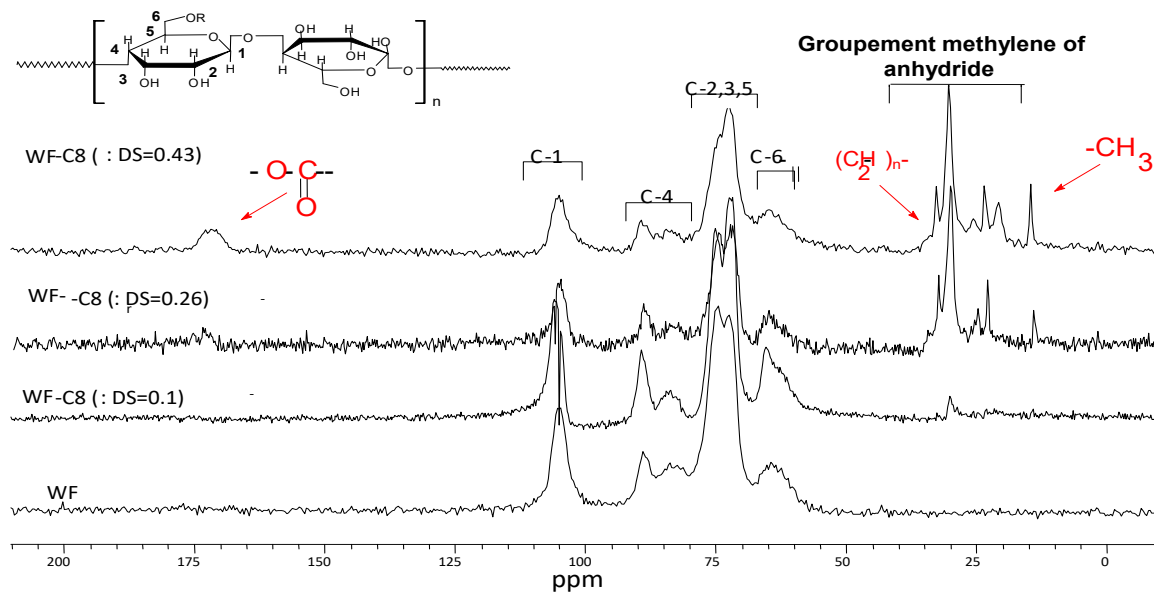


Figure 2: CP MAS ¹³C MNR spectra of wood fiber (WF) and the modified one after esterification with octanoic anhydride at (A: DS = 0, B: DS = 0.1; C: DS = 0.26, D: DS = 0.43)

The other characteristic peaks of acyl moiety are hidden by the overlapping of Nanofibrillated wood fiber bands. The NMR spectra of fiber wood and fiber wood modified are shown in Fig. 2. In the spectrum of fiber wood (Fig. 2), 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 (Fig. 2) 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 on the absorbance in water. Indeed, measures of the angles of contact of drop of water 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 the Fig. 3. The analysis shows that the grafting of the hydrocarbon chains the surface of fibers makes tip over their characters of 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.

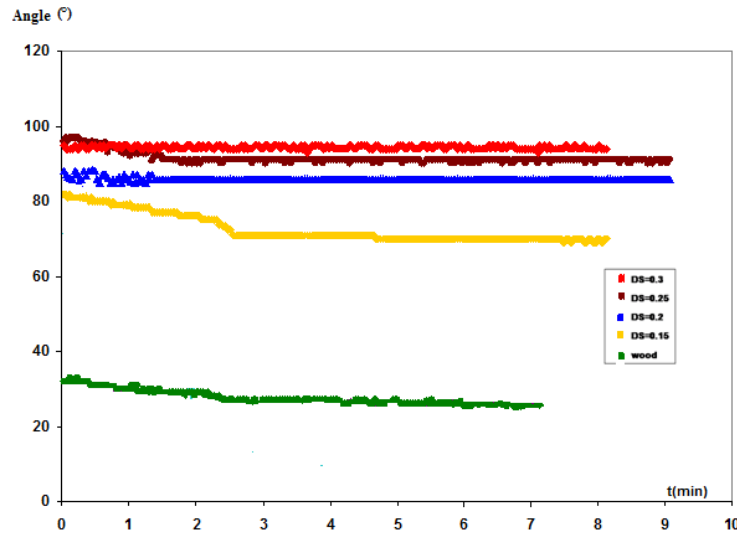


Figure 3: Evolution of the surface of the MCP material from the hydrophilic state (with wood fiber: Unmodified WF) to the hydrophobic state (with modified wood fiber for (DS = 0; 0.15; 0.2; 0.25; 0.3))

3.3 Electrokinetic Study of the Fibrous Suspensions Handle 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. 4). According to the curve of the potential Zeta, 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 potential Zeta is of the order of 35 mV, this value results from the ionization of calcium during the hydration of cement. The more the concentration by adjuvant increases, the more the potential Zeta 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 potential Zeta. These show that the molecules of the additive are in excess, where from the formation of micelles from the CMC (Fig. 5).

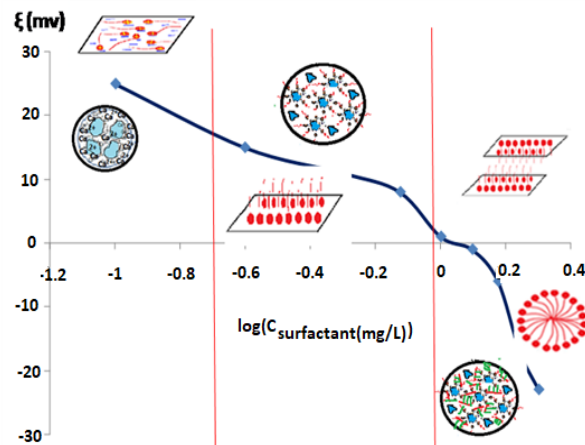


Figure 4: Variation of the zeta potential as a function of the concentration of adjuvant SDBS

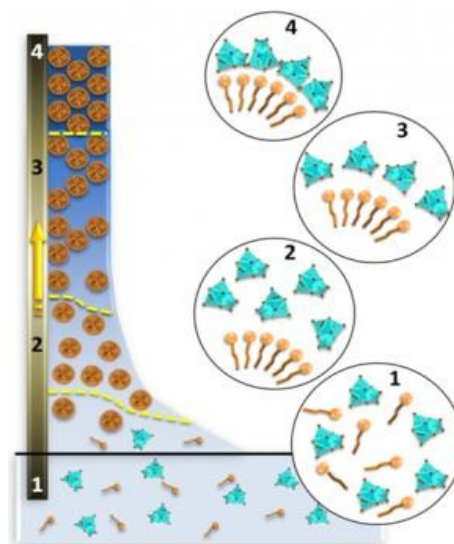
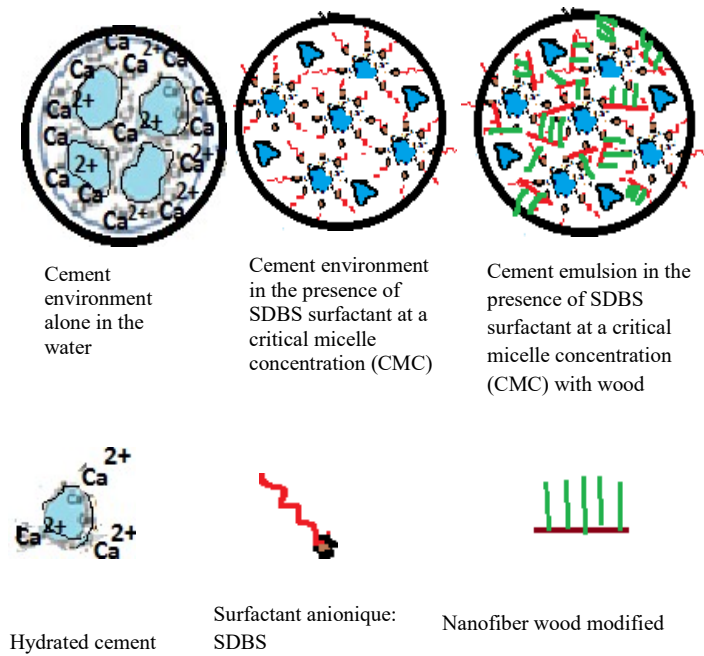


Figure 5: State of the environment of cement grains: Emulsion (1; 2; 3: Wood fiber modified/cement/SDBS); 4: Formation of micelles around wood fibers/cement

3.4 Degree of Hydration

The degree of hydration of the cement was calculated by dividing the amount of the final weight loss of the material per gram unit of unhydrated cement which is 0.23 g per gram unit of cement when fully hydrated. This value is typical of Portland cement type. Thus, the degree of cement hydration can be easily achieved by dividing the amount of chemically bonded water in the hardened cement pastes per unit gram of unhydrated cement with 0.23 g.

The Fig. 6 present the degree of hydration of the cement at different age of hardening, depending on the NWF content. the degree of cement hydration increases as the NWF content of the cement paste increases during all curing times.

The highest degree of hydration of the cement is obtained with the mixture containing 1% by weight

of NWF. At this level addition, the degree of hydration of the cement is increased by 102%, 23% and 28%, relative to the control mixture, after 1, 7 and 28 days of hydration, respectively. It can be seen that the addition of NWF to the cement paste has accelerated early hydration. During a hardening day, the percentage increase in the degree of hydration of the cement is about 1.5%, 18.5%, 30.5%, 65.5%, 85.5% and 95% for mixtures NWF0, NWF0.1, NWF0.5, NWF1, NWF1.5 and NWF2, respectively.

In conclusion, the addition of NWF improves the degree of hydration of the cement, which shows that NWF can have the same steric stabilization effect as that of water-reducing admixtures, which provide a uniform distribution of the cement particles during the process. hydration.

NWF act as water-reducing adjuvants to promote the formation of hydrated products and, therefore, to improve the early degree of hydration of the cement.

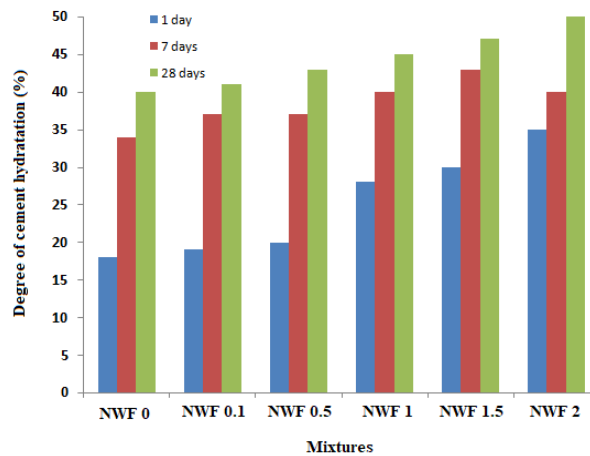


Figure 6: The degree of cement hydration at different age of hardening, depending on the NWF content

3.5 Mechanical Characterization

A. Compressive strength

The analysis of the Fig. 7 examines the decrease in compressive stress with the increase in the percentage of fibers in cement. With the addition of 2% of the fibers, there is a decrease in stress up to 8.8 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.

The influence of the incorporation of the NWF leads to a constant increase in the compression force up to a content of 1% by weight (Fig. 7). For example, the compressive strength goes from 8.8 MPa for the pure reference cement to about 18.8 MPa, which corresponds to an improvement of about 200%. However, at 2% by weight of NWF, the concentration falls considerably below that of the pure cement. Three possible reasons have been put forward for the considerable improvement of the mechanical properties with the addition of NWF in the cement. First, because of their hydrophilic nature, hydration of the cement is accelerated and larger volumes of hydration products are formed. Secondly, the high surface area of NWF enhances the nanofiber-matrix interface, which improves the transfer of stress between the matrix and the nanofibrils. Thirdly, the high ratio of surface to NWF volume has favored the nucleation of the cement phases, namely CSH, providing excellent chemical reactivity to promote hydration of the cement. Finally, the application of the addition of SDBS, as a dispersing agent, also contributed to the improvement of the resistance: This improves the dispersion of NWF in the cement matrix. The carboxylic groups on the NWF surface react with the hydrated calcium silicate and result in a strong coating force between the nanofiber and the matrix. This reaction can provide a higher stress when the

crack goes directly to the zone of the reinforced NWF zone and prevents the propagation of cracks. Furthermore, when the nanofibers react chemically with hydration products, they can behave as nucleation and form interfacial mechanical bonds. More than 1 wt of NWF, a possible reason for the decrease in resistance to be due to aggregation of NWF, leading to inhomogeneous dispersion of the nanowires in the cement matrix. This agglomeration is attributed to locating high NWF content and forming networks. These agglomerated NWF create fragile areas in the form of pores. After the curing process, these particles act as stress concentrators in the cement matrix and promote premature cracking. The cement reinforcement hypothesis can be mainly attributed to the NWF potential to improve the degree of hydration of the cement.

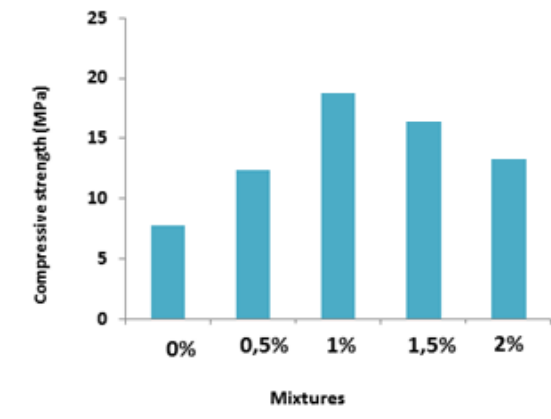


Figure 7: Constraint-strain curves of composites: Effect of reinforcement rate, Constraint-Percentage of fibers

B. Young's modulus "E"

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. We note in Tab. 2 that the materials had a better maximum stress on the order of 18.8 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.

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

Sample	E (GPa)	Compressive strength (MPa)
Cement + 0% WFT	57	9.81
Cement + 2% WFT	476	18.42
Cement + 1,5% WFT	69	18.62
Cement + 1% WFT	101	22.96
Cement + 0,5% WFT	58	12.33

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).

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