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ORIGINAL ARTICLE

Effect of ultrasonication on carboxyl-functionalized multiwalled carbon nanotubes in fresh and hardened Portland cement pastes

Efeito da ultrassonicação em nanotubos de carbono de paredes múltiplas funcionalizados com grupo carboxílico no estado fresco e endurecido de pastas de cimento Portland

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Abstract: The effects of chemical and physical methods on multiwalled carbon nanotube (MWCNT) dispersion in Portland cement pastes were investigated. Consistency, rheology, compressive strength, dynamic elastic modulus, flexural strength, water absorption, and void content tests were performed to evaluate these effects. Changes in the rheology of the cement pastes and surfactants resulted in a significant reduction in apparent viscosity and yield strength. Additionally, cement pastes containing carboxyl- functionalized MWCNTs (MWCNT-COOH) and surfactant showed higher compressive strengths at 28 d. However, the ultrasonic dispersion method did not significantly influence the properties of hardened Portland cement compared with Portland cement produced using the non-sonicated aqueous solution.

Keywords: physical and chemical dispersion, multiwalled carbon nanotube, cement paste, compressive strength.

Resumo: Foram investigados os efeitos dos métodos químicos e físicos na dispersão de nanotubos de carbono de paredes múltiplas (MWCNT) em pastas de cimento Portland. Para avaliar estes efeitos, foram realizados testes de consistência, reologia, resistência à compressão, módulo elástico dinâmico, resistência à flexão, absorção de água, e teor de vazio. As alterações na reologia das pastas de cimento e surfactantes resultaram numa redução significativa da viscosidade aparente e da resistência ao escoamento. Além disso, pastas de cimento contendo MWCNT funcionalizados com grupo carboxílicos (MWCNT-COOH) e surfactante mostraram maiores resistências à compressão a 28 d. No entanto, o método de dispersão ultrassônica não influenciou significativamente as propriedades do cimento Portland endurecido em comparação com o cimento Portland produzido utilizando a solução aquosa não sonicada.

Palavras-chave: dispersão física e química, nanotubo de carbono com múltiplas paredes, pasta de cimento, resistência à compressão.

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1 INTRODUCTION

Recently, the incorporation of nanomaterials into Portland cement matrices has been the subject of numerous investigations [1]–[4]. These studies clearly indicated that the presence of nanomaterials in cement matrices improves both mechanical performance and durability, depending on their effective dispersion within the composites [5]–[8].

Carbon nanotubes (CNTs) are among the common nanomaterials used in cementitious matrices [9]. One way to classify them is based on the number of walls or layers present in their structure; multiwalled carbon nanotubes (MWCNTs) or single-walled carbon nanotubes (SWCNTs). It is noteworthy that MWCNTs are readily available owing to the low complexity of their production compared with SWCNTs, which provides a reduction in the final cost of the product.

Several studies [4], [10], [11] emphasized that the incorporation of MWCNTs, 0.10% relative to the mass of Portland cement (w.c.), creates connections that enhance stress distribution when sufficient adequate MWCNT-matrix adhesion is achieved. This effect was reported to control or mitigate the propagation of microcracks and reduce the porosity of Portland cement-based composites.

In addition to modifying the structure of the composite in its hardened state, the incorporation of CNT has been reported to promote variation in the rheological properties of cement pastes because it can increase the yield strength and viscosity of the mixtures. A reduction in mortar dispersion was achieved by incorporating MWCNTs (0.10% w.c.) and a fixed surfactant admixture content [8]. Notably, a reduction in the scattering diameter (slump test) by 30 mm was confirmed, which verified that the nanomaterial interacts with the mixture and promotes improved dispersion based on a mechanical response. Moreover, the amount of free surfactant in the system decreased, which reduced its lubricating capacity and, consequently, decreased dispersion.

The interaction of functionalized CNTs with water was capable of reducing the amount available for lubrication of the system [3]. Consequently, greater friction between the particles is generated owing to the higher solid content in the mixture. When comparing the dynamic yield strength and apparent viscosity of mortars without and with MWCNT (0.25% w.c.), an increase of 25 to 125 Pa and 1.6 to 2.25 Pa.s was observed, respectively. This behavior was attributed to the high specific surface area of the nanomaterial and the adsorption of the dispersant admixture on its surface.

However, studies have indicated that the main challenge regarding CNT utilization is their effective dispersion in the matrix. [12]–[14]. CNTs tend to agglomerate owing to Van der Waals forces of attraction, in addition to their high specific surface area and aspect ratio (length/diameter), which further contributes to agglomeration. Moreover, it is noteworthy that its hydrophobic character further complicates its dispersion in an aqueous medium.

A combination of physical and chemical methods can be used to promote the dispersion of these nanomaterials. Among the existing physical methods, ultrasonication is the most common because it provides high dispersion by applying ultrasonic pulses to the solution and disaggregating the nanotubes [15]–[17]. Two ultrasonication procedures are possible: probe (tip) or bath, the former is the most common and effective [4]. However, the time and energy applied requires careful consideration. When these factors are too low, efficient dispersion of the nanomaterial cannot be achieved. In contrast, when they are too high, damage such as shortening and reduction of the diameter of the nanomaterial may occur, which reduces its performance [10], [18].

Chemical methods involve the functionalization of nanomaterials and are divided into covalent and noncovalent modifications. The former refers to the treatment of nanotubes using acids that alter the surface of the CNTs, promoting the insertion of functional groups such as -OH or -COOH. Conversely, noncovalent functionalization utilizes surfactants that interact with CNTs, promoting their dispersion and preventing re-agglomeration, while preserving the structure and properties of the nanomaterial [19]–[21]. Based on these reports, MWCNTs dispersion techniques are complex and often applied in combination to improve the performance of the final product.

Although several studies have evaluated the addition of nanomaterials to cementitious matrices, the application of different dispersion methods (combined and separately) to MWCNTs in aqueous solutions and the probable existence of a synergistic effect, based on the mechanical and rheological properties, has not been reported thus far. This study aims to investigate the combined effect of the different dispersion methods of CNTs functionalized with carboxyl groups (-COOH) on their performance in Portland cement pastes. Thus, this study includes the characterization of compressive strength, flexural strength, Young's modulus, water absorption, and pore volume, in addition to rheological analysis by scattering and rheometry. The fresh and hardened states of the pastes are evaluated to determine the effect of mainly ultrasonication, in terms of its promotion of CNT dispersion.

2 MATERIALS AND EXPERIMENTAL PROGRAM

The CNTs used in this study were purchased from Nanostructured & Amorphous Materials Inc. (Figure 1). These CNTs, with a length of 10–30 μm, internal diameter of 5–10 nm, external diameter of 20–30 nm, and 95% purity, were functionalized by the addition of carboxyl groups (-COOH) to their structure (1.9 to 2.1 wt%). The MWCNTs content used in the cement paste was 0.10% relative to the cement mass (c.w.) because it is the most commonly used nanomaterial content to achieve an improved mechanical response in literature [22]. A common Portland cement was used for the preparation of the pastes, and its physicochemical characterization is listed in Table 1. Notably, the C4AF content was determined based on the Bogue equation. Additionally, two types of surfactants (SA and SB), based on polycarboxylate, were used at a 1:1 ratio (nanotube:surfactant).

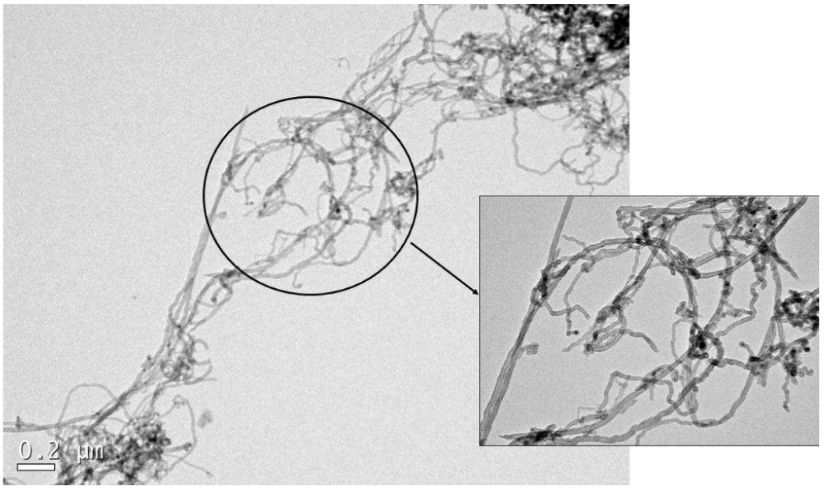

Figure 1. Transmission electron microscopy (TEM) on the CNTs

Table 1. Physical and chemical characterization of ordinary Portland cement.

Physical Analysis	
Specific gravity (kg/dm^3)	3,09
Blaine (cm^2/g)	4698
Chemical analysis	
Loss on ignition (%)	4,8
C3S (%)	55,8
C2S (%)	14,36
C3A (%)	7,1
C4AF (%)	9,59

The solid contents of the surfactants (SA and SB) were characterized according to literature [23]. Surfactants SA and SB were composed of 30.17% and 42.04% solids, respectively. Moreover, Fourier transform infrared spectroscopy (FTIR) was performed to qualitatively identify its components according to absorbance peaks (Figure 2).

FTIR confirmed the presence of polycarboxylates, which is associated with the peaks observed between 3400 and 3200 cm^{-1}, corresponding to -OH stretching vibrations, and the presence of ether groups observed at 1250–950 cm^{-1} [24]–[26]. Surfactants SA and SB exhibited characteristic peaks at 2865 and 2950 cm^{-1}, associated with the symmetrical and asymmetrical stretching vibrations of aliphatic CH, respectively. The peak observed between 1680 and 1620 cm^{-1} corresponds to the absorption of the =C=C group and the stretching vibration band observed at 1105 cm^{-1} corresponds to C-O-C. Additionally, carboxylic acids (1696 cm^{-1}) and CO stretching vibrations (1130–1070 cm^{-1}) were observed. The higher hydroxyl peak for SA may indicate that the surfactant was less concentrated than SB, confirming the solid content test results. Moreover, the peak identifying the carbonyl group was higher in SB than that in SA.

Initially, the solutions were prepared as follows (Figure 3): (1) water only (with and without ultrasonication), a mixture of water with surfactant SA or SB (with and without ultrasonication), a mixture of water with MWCNTs (with and without ultrasonication), and mixtures of water with SA or SB and MWCNTs (with and without ultrasonication). Thus, the type of surfactant, presence/absence of MWCNT, and presence/absence of the ultrasonication process were used as variables. For the sonicated solutions, a Vibra-Cell 750 Watts sonicator coupled to an ultrasonic processor (Series VCX) was used. Ultrasonication was performed for 5 min at 20 s intervals of shaking and rest, at a frequency of 20 kHz and 50% amplitude.

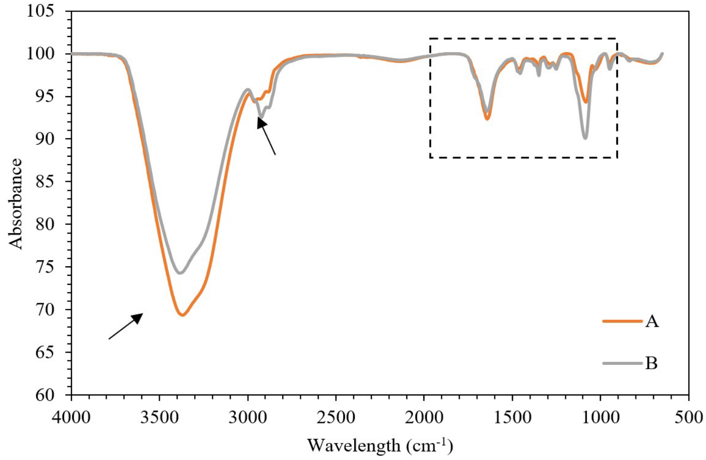

Figure 2. FTIR spectra of surfactants SA and SB.

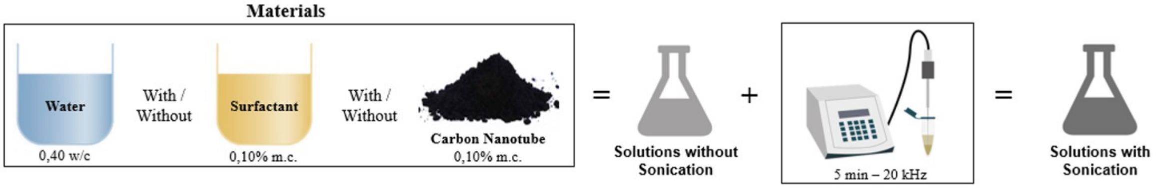

Figure 3. Preparation of solutions containing water, surfactants, and carbon nanotubes with and without the application of ultrasonication.

After obtaining the solutions for the production of the cement pastes, a high-power mixer was used at a speed of 10,000 rpm. A water/cement ratio of 0.40 was selected to obtain pastes without exudation, even in the presence of a surfactant, and ensure an adequate consistency for molding.

The mixing procedure started with the addition of Portland cement to the solution (Figure 4), which was manually mixed for 1 min, followed by 1 min of mixing using a high-power mixer. Subsequently, the mixture was allowed to rest for 1 min. Finally, the process was completed after 1 min of mixing using the high-power mixer. The amount of material used in each Portland cement paste, and the presence or absence of ultrasonication, are listed in Table 2.

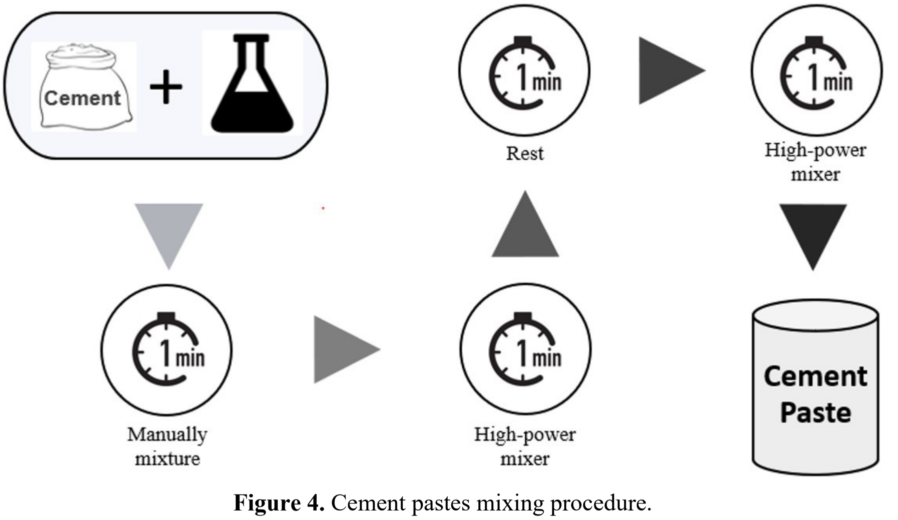

Figure 4. Cement pastes mixing procedure.

Table 2. Mixture compositions of Portland cement pastes.

Mix	Cement (g)	Water(g)	Surfactant (g)		MWCNT (g)	Ultrasonication			
			SA	SB		Water	SA	SB	CNT
Ref	100	40	-	-	-	-	-	-	-
A	100	40	0.10	-	-	-	-	-	-
B	100	40	-	0.10	-	-	-	-	-
Son	100	40	-	-	-	x	-	-	-
SonA	100	40	0.10	-	-	x	x	-	-
SonB	100	40	-	0.10	-	x	-	x	-
CNT	100	40	-	-	0.10	-	-	-	-
Son_CNT	100	40	-	-	0.10	x	-	-	x
SonA_CNT	100	40	0.10	-	0.10	x	x	-	x
SonB_CNT	100	40	-	0.10	0.10	x	-	x	x
A_CNT	100	40	0.10	-	0.10	-	-	-	-
B_CNT	100	40	-	0.10	0.10	-	-	-	-

For the analysis of fresh Portland cement pastes, scattering tests (mini-spreading) and rotational rheometry using parallel plate geometry were performed to evaluate the following rheological parameters: apparent viscosity, dynamic yield strength, and static yield stress. The mini-scatter test was developed by Kantro in 1980 using a conical trunk with smaller and larger diameters of 19 and 38 mm, respectively, and a height of 57 mm supported on a glass plate. After filling and densifying the paste in the mold, it was removed, and the spread was measured in a perpendicular direction. For the rheometry test, approximately 1 mL of sample was added to the rheometer container, and the tests were performed at 23 ± 1 °C according to the following procedure: (i) 60 s pre-shear at 100 s^{-1}; (ii) 60 s rest; (iii) shear from 0.1 to 10 s^{-1} in four steps of 20 s each distributed logarithmically; (iv) shear from 25 to 100 s^{-1} in six steps of 20 s each distributed linearly; (v) reduction of the shear rate to 0.1 s^{-1} in the same steps as (iv) and (iii), to evaluate the yield and dynamic yield stress. The following procedure was used to determine the static yield stress: (i) 60 s pre-shear at 100 s^{-1}; (ii) rest for 30 s; (iii) shear from 0.05 to 10 s^{-1} for 60 s. The rheometry and scattering results were measured 10 min after the production of the mixtures to standardize the time of the analyses. The Herschel–Bulkley model was used to determine the dynamic flow stress of the mixtures because it fits the non-Newtonian fluid behavior of Portland cement pastes better. The linear fit of the Herschel–Bulkley model proposed by de Larrard et al. [23] in Equation 1 was used to determine the equivalent viscosity [27].

$$\tau = \tau_0 + K\gamma n \tag{1}$$

where τ is the shear stress (Pa), τ_0 is the yield stress (Pa), K is the consistency factor, $\dot{\gamma}$ is the shear rate (s^{-1}), and n is the pseudoplastic index. In this analysis, the apparent viscosity was calculated at the maximum shear rate (100 s^{-1}).

To determine the compressive strength at 28 d, five cylindrical specimens (20x40 mm) were molded for each mixture. Subsequently, the specimens were demolded after 24 h and submerged in water containing lime prior to testing. A universal testing machine (model Instron 5569) was used at a load speed of 0.50 MPa.s^{-1} with a 30 mm hinge positioned on top of the specimen.

For the dynamic modulus of elasticity and bending at three points, three prismatic specimens (20x20x100 mm) were molded. The three-point bending test was performed using the same equipment as for the compressive strength test, at the same velocity load. The dynamic modulus of elasticity test was performed on equipment from Sonelastic® Systems at ATCP Engenharia using the impulse excitation technique based on the ASTM-E 1876 standard [28].

The test results for the hardened state of the cement pastes were analyzed using the two-way analysis of variance (ANOVA) statistical analysis, and the conclusions were based on the F parameter with a reliability of 95%. OriginPro 2019 software was used for analysis.

3 RESULTS AND DISCUSSIONS

3.1 Fresh state of portland cement pastes

Figure 5 shows the spreading of the produced cement pastes. A decrease in pulp flow was observed with the incorporation of MWCNTs and ultrasonication, which may be attributed to the high specific surface area of the nanomaterials and the quality of their dispersion.

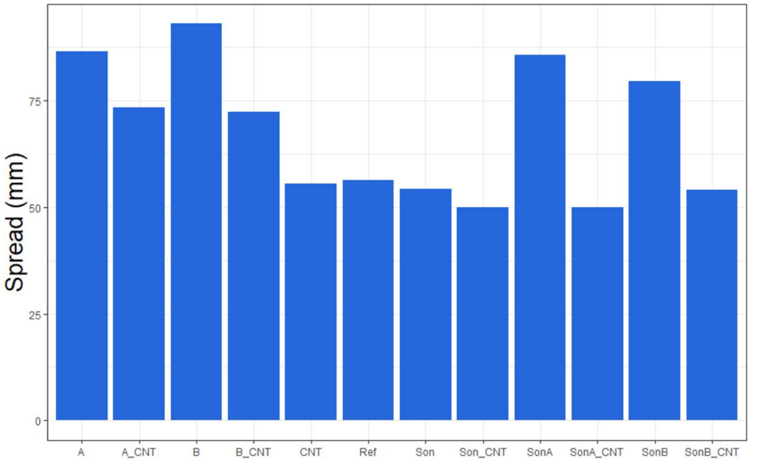

Figure 5. Spread of cement Portland pastes.

As shown in Figure 6, for the present study, both the modified Bingham model and the Herschel-Bulkley model can be used to calculate the rheological parameters of the paste curves. However, the model that best suited the behavior of the pastes was the Herschel-Bulkley model. This better fit can be visualized through the r^2 factor presented in Figure 6.

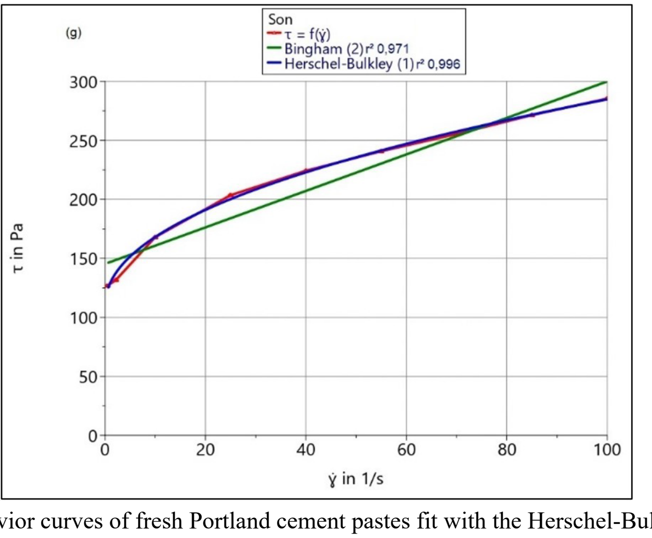

Figure 6. Rheological behavior curves of fresh Portland cement pastes fit with the Herschel-Bulkley and Bingham model.

Figures 7, 8, and 9 show the results of the static and dynamic yield stress and apparent viscosity of the cement pastes, respectively, with and without ultrasonication. It was observed that the combination of ultrasound/MWCNT generated higher static yield stresses compared to the other mixtures. This phenomenon can be due to the ultrasound process, which is responsible for the deagglomeration of MWCNTs. The deagglomeration increases specific surface area and, by doing so, improves the flow [29].

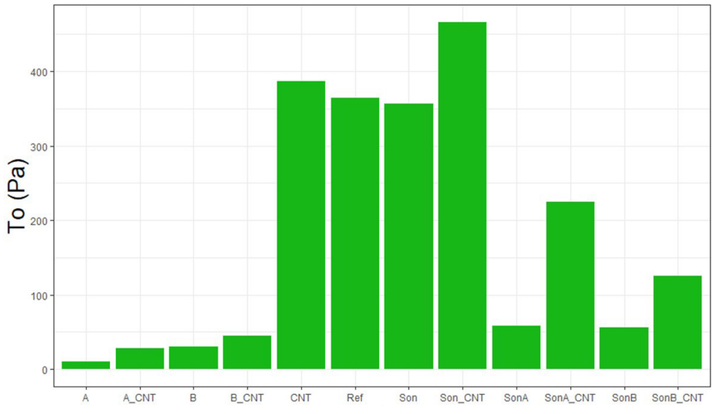

Figure 7. Static yield stress of the fresh Portland cement pastes.

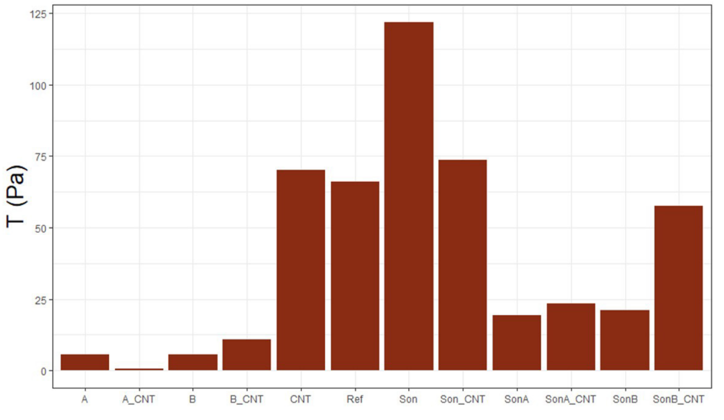

Figure 8. Yield stress of the fresh Portland cement pastes.

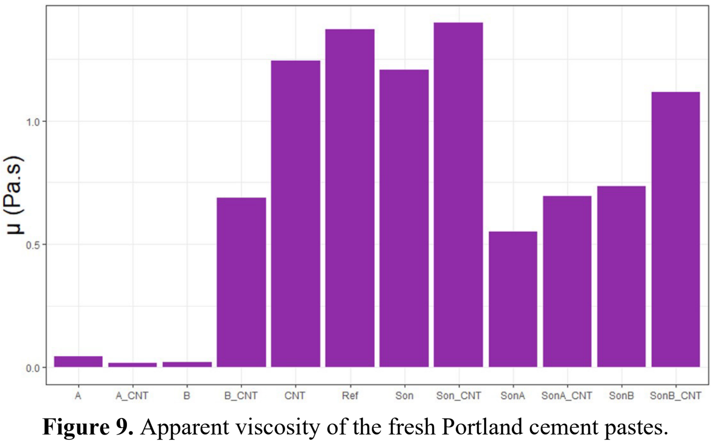

Figure 9. Apparent viscosity of the fresh Portland cement pastes.

Surfactants are used to disperse Portland cement particles, releasing water molecules that can be trapped between the cementitious material by doing so, reducing the yield stress of the system. However, when MWCNTs were added to the mixtures, an overlap of dispersion effects was observed. Therefore, the surfactant acted both in the dispersion of Portland cement particles and in the deagglomeration of the nanotubes [13].

A decrease in the static and dynamic yield strength of the A_CNT and B_CNT pastes was observed compared to the CNT mixture. This behavior may be attributed to the improved dispersion of the nanomaterial, which increases the specific surface area. Thus, the adsorption of the surfactant onto the surface of MWNCTs is enhanced, which reduces their interactions with the cement [30]. Moreover, [30], [31] the hydrophobic part of the surfactant molecules adhered to the nanotubes, leaving the hydrophilic part available to bind to water molecules. Therefore, the combined utilization of the surfactant and nanomaterial contributed to reducing the amount of water required to lubricate the system.

Regarding the apparent viscosity, Figure 9, the cement pastes prepared with surfactants exhibited lower results than the other pastes. This behavior occurred because the surfactant causes the water trapped in the Portland cement particles to be released, which contributes to the lubrication of the cement mixture owing to improved dispersion [32]. Moreover, ionic and nonionic surfactants can produce air bubbles in the cement mixture, which reduces its viscosity and thereby improves its flowability [33].

These results confirmed that cement pastes prepared with MWCNTs resulted in higher equivalent viscosities. The nanotubes interact with the nonpolar surfactant particles, reducing its availability to interact with Portland cement particles, causing the viscosity of the cement system to increase [34]. Moreover, incorporating the nanomaterial into the cement matrix promoted an increase in the solid/liquid ratio of the system and improved the specific surface area of these solids. As reported in literature [35], when removing lubricating water from the cement system, the distance between fine particles decreases, causing a greater number of collisions between them, which increases the viscosity of the mixture [36].

Therefore, the morphology of the particles directly influences the viscosity of the cement mixture [37]; the greater the sphericity of the particle, the lower the viscosity of the system. It can be concluded that the increase in the system´s rheological properties occurs due to the inclusion of the nanomaterial with tubular morphology.

Furthermore, it is noteworthy that the yield strengths (Figures 7 and 8) were reduced for all cement mixtures containing surfactants, and cement pastes prepared with MWCNTs exhibited increased static yield strength. This is owing to its high specific surface area; the smaller the agglomeration, the greater the specific surface area available for interaction with the surfactant molecules.

The interaction of the two types of surfactants with the matrix and nanomaterial is different, although they have the same chemical basis. This effect is caused by the differences in the physical and chemical properties of the raw materials used in the production of each additive. Notably, additives that adsorb more effectively on Portland cement particles tend to improve the dispersion of the cement system. According to literature [34], [38], [39], surfactants can be adsorbed by MWCNTs, which causes a loss of their dispersion effect on Portland cement particles and induces higher yield stress in the cement mixture. Moreover, these studies noted that depending on the nature of the surfactant, the hydrophobic part will be adsorbed onto the surface of MWCNTs, and the hydrophilic part will interact with water molecules or Portland cement particles.

Finally, the rheological behavior of pastes containing nanotubes, additives and sonication together, obtained worse performances. This fact may be associated with an increase in nanomaterial dispersion due to sonication or even an increase in CNT agglomerates in the composite. Therefore, to validate a possible dispersion or agglomeration, it is necessary to verify other aspects, such as their mechanical properties.

3.2 Hardened state of Portland cement pastes

The mechanical properties at 28 d are shown in Figures 10, 11, 12, and 13. In general, the majority of the cement pastes presented higher mechanical behavior of the reference.

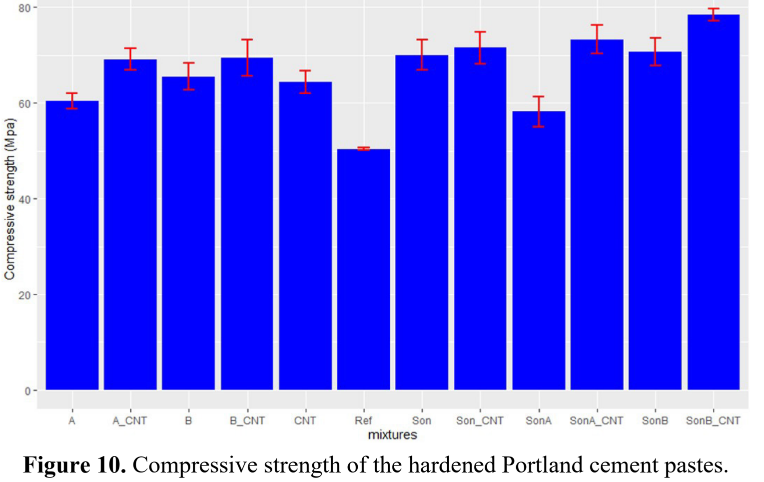

Figure 10. Compressive strength of the hardened Portland cement pastes.

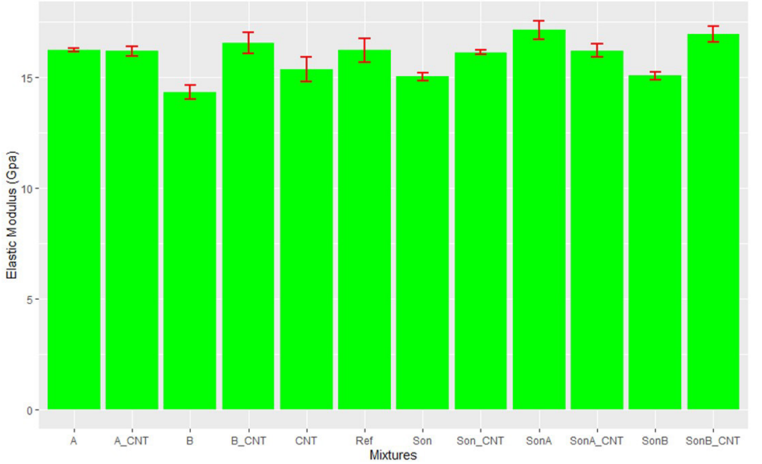

Figure 11. Elastic modulus of the hardened Portland cement pastes.

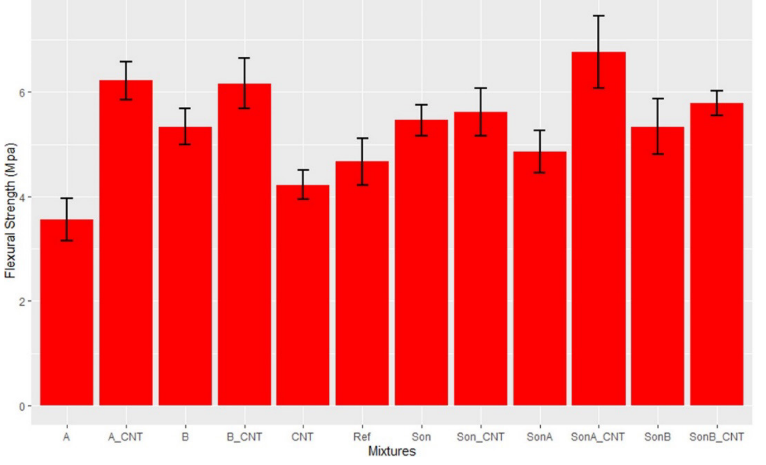

Figure 12. Flexural strength of the hardened Portland cement pastes.

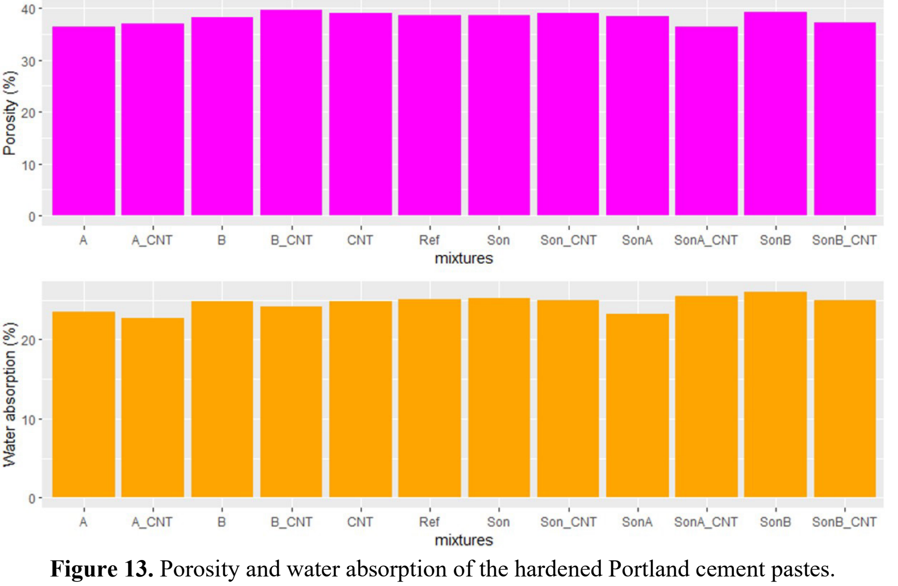

Figure 13. Porosity and water absorption of the hardened Portland cement pastes.

The reference mixture (Ref) presents a lower compressive strength compared with those containing the nanomaterial and surfactant, with or without ultrasonication. According to a report on the mechanical behavior of cementitious composites [28], [40], [41], the use of MWCNTs in pastes improved the compressive strength by up to 19%. These reports indicated that the main reason for this improvement was the performance of MWCNTs as bridging molecules connecting the matrix, which enhanced stress distribution. Furthermore, the nanomaterial acts as a nucleation site for the formation of a C-S-H gel coat on its surface [29]. Furthermore, the addition of nanotubes to cement-based materials promotes a decrease in mesopores, thereby densifying the matrix and improving its mechanical properties and durability [41].

Two-way ANOVA statistical analysis (Table 3) was used to evaluate the influence of the (i) mixture composition and (ii) ultrasonication process on the mechanical behavior of cement pastes. It was concluded that mixture composition significantly affects the compressive strength of Portland cement pastes at 28 d. However, ultrasonication did not significantly influence the compressive strength of the mixtures.

Table 3. Analysis of variance of the compressive strength results of hardened Portland cement pastes.

ANOVA					
Source	**SQ**	**GDL**	**MQ**	**F**	**F 0,05**
Dispersion method	152,59	5	30,51	0,94	5.05
Mixture	316,94	1	316,94	9,83	6,61
Residual	161,19	5	32,23	-	-
Total	630.72	11	-	-	

SQ: sum the squares of each parameter. **GDL**: Degree of spare. **MQ**: Mean Square. **F:** Factor of each calculated parameter. **F 0,05:** Factor of each tabulated parameter with 95% of reliability

To investigate the influence of the ultrasonication process on the compressive strength of the hardened cement pastes, the mixtures with different compositions were compared, considering the presence or absence of the ultrasonication process (Table 4).

Table 4. Statistical analysis of the compressive strength results of hardened Portland cement pastes, comparing the influence of ultrasonication.

Ratio Mixtures	Results
Ref: Son	Significantly different
A: SonA	No significantly different
B: SonB	Significantly different
CNT: Son_CNT	Significantly different
A_CNT: SonA_CNT	No significantly different
B_CNT: SonB_CNT	No significantly different

The analysis revealed a significant difference between the average compressive strengths of the mixtures using MWCNTs without the dispersing surfactant. Based on this result, it was concluded that MWCNTs require one of the dispersion methods, chemical (surfactant) or physical (ultrasonication), in addition to functionalization with carboxyl groups.

Based on the analysis results, it was demonstrated that there is a significant difference in the compressive strength between the Ref and sonicated (Son) mixtures. This behavior is thought to be owing to the release of hydrogen ions during ultrasonication. When these ions are released, the hydration reactions are accelerated, forming a greater amount of C-S-H, and consequently, enhancing the mechanical properties of the cement paste [39].

Figure 12 shows the flexural strength of the hardened cement pastes. The highest average values were observed for those prepared using mixtures containing the surfactant and MWCNTs, with or without ultrasonication. These results are in agreement with the results obtained from compressive strength tests. The improvement in the flexural strength of cementitious matrices with the incorporation of MWCNTs may be owing to the nanomaterial functioning as a reinforcing fiber, forming connections between cracks, and providing greater flexibility [40], [41].

SonA_CNT and SonB_CNT pastes had improved average flexural strengths of 45% and 24% higher compared with Ref, respectively. Moreover, the average flexural strength of A_CNT and B_CNT pastes increased by 33% and 32% compared with Ref, respectively. After statistical analysis was performed with 95% reliability (using the same software), the hardened cement pastes prepared with the nanomaterial and surfactant, with or without ultrasonication, exhibited greater flexural strength compared with Ref. Furthermore, the flexural strength of the hardened cement pastes prepared with MWCNTs and SA or SB did not differ significantly, with or without ultrasonication.

This result correlates with the results observed by the water absorption and pore volume tests (Figure 13), which were reduced for the pastes mentioned above (SonA_CNT, SonB_CNT, A_CNT, and B_CNT). The reduction in these properties explains the improvement in the mechanical properties of pastes prepared with MWCNTs and SA or SB because the smaller the pore volume in a cementitious matrix, the better its microstructure and, consequently, its mechanical behavior. Furthermore, CNTs are thought to occupy the existing internal pores, causing a filling effect by refining the pores. Thus, a denser C-S-H gel is formed with reduced porosity [38].

The process of ultrasonication of the water in the Son paste resulted in an improvement in the average flexural and compressive strength at 28 d. For this paste, lower pore volume and water absorption were observed compared with those of Ref. However, when performing statistical analysis with 95% confidence, no significant difference was observed between these cement pastes. Thus, it is proposed that there is no significant difference in the porosity and water absorption between the Son and Ref cement pastes. In other words, the improvement in the compressive strength of the Son paste relative to Ref is not attributable to the reduced pore volume.

The elastic modulus of the cement pastes prepared with the MWCNTs and surfactants increased compared with Ref (Figure 11). However, when the statistical test was performed, the elastic modulus results of the cement pastes containing the MWCNTs and SA or SB, with or without ultrasonication, did not significantly differ from each other or Ref.

Based on the experimental data and statistical analysis, it is proposed that the ultrasonication process does not significantly affect the cement mixtures that contain a surfactant (SA or SB) and MWCNTs in the solution. This conclusion indicates that for cement mixtures containing CNTs functionalized with -COOH groups and surfactants, it is not essential to perform ultrasonication to promote greater dispersion, thus enhancing NTC´s applicability in the construction sector.

4 CONCLUSIONS

Based on the experimental studies conducted, the following conclusions were reached:

- The use of surfactants decreased the yield strength and apparent viscosity of the cement mixtures. However, an increase in these properties was observed when MWCNTs were added to the cement mixtures.
- Rheological tests showed that the use of at least one of the dispersion methods (ultrasonication or surfactant addition) improved the dispersion of the nanomaterial in the matrix. This phenomenon has been reported by several researchers; a greater deagglomeration of the nanomaterial increased the specific surface area of the system and caused an increase in the rheological properties.
- The interaction of the two types of surfactants with the nanotubes and cement was different, indicating that surfactants with the same chemical nature may have different effects on the rheological properties of cementitious matrices.
- The cement pastes prepared with MWCNTs and surfactant A or B showed higher compressive and flexural strengths and a reduced permeable pore volume at 28 d.
- Compared with the Ref cement paste, the average compressive strength of the prepared cement pastes improved by up to 50% (SonB_CNT), the average flexural strength increased by up to 44% (SonA_CNT), and the average of elasticity modulus increased by up to 5% (SonB_CNT).
- Generally, cement pastes prepared with MWCNTs using at least one of the dispersion methods or both exhibited an increase in the mechanical properties compared with the Ref cement paste.
- These results correlated with the rheological behavior, confirming that cement pastes prepared using solutions with the application of least one of the dispersion methods had improved nanotube dispersion in the matrix, which improved their mechanical properties.
- Statistically, there was no significant difference between the means of the compressive strength, flexural strength, and modulus of elasticity between the cement mixtures prepared with and without the ultrasonication process in the presence of MWCNTs with SA or SB. Based on the mechanical tests, ultrasonication does not promote greater nanomaterial dispersion, which typically contributes to the expansion of its practical application in cementitious composites, facilitating its use in the civil construction industry.
- Notably, further investigations are required to confirm these hypotheses, which are mainly associated with the quality of nanomaterial dispersion within the cement mixture.

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