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Nanocomposites Produced with the Addition of Carbon Nanotubes Dispersed on the Surface of Cement Particles Using Different Non-Aqueous Media

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Abstract: The inclusion of carbon nanotubes (CNTs) in cementitious composites has been studied due to their electrical, thermal, and mechanical enhancing properties. Considering the hydrophobic characteristics of CNTs, these nanomaterials need to be well dispersed in the aqueous media in which they are inserted to guarantee those gains. Among the methods applied to produce such composites is the dispersion of CNTs on the surface of anhydrous cement particles using non-aqueous suspensions such as acetone, ethanol, or isopropanol. Even though those non-aqueous media have been individually studied by researchers, comparisons of the efficiency of CNTs dispersion was not found in the literature. Therefore, as a novelty, the present article aims to analyze the influence of the addition of the multi-walled CNTs dispersed in the cited three types of non-aqueous suspensions on the cement paste's electrical and mechanical properties. Pastes containing 0%, 0.5%, and 1.0% of CNTs were prepared on the surface of anhydrous cement particles using a pre-dispersion technique based on simultaneous sonication and mechanical agitation in the three cited media. Tests to determine electric-volumetric resistivity, compressive strength, and splitting tensile strength were performed. It was observed that acetone dispersion decreases the cement paste's electrical resistivity, even without the addition of CNTs. The cementitious composites with CNTs demonstrated increased mechanical strength (both compressive and tensile) using all three dispersion media. Statistical analysis (analysis of variance—ANOVA—and Tukey's Test) was performed to evaluate the significance of the results.

Keywords: dispersion; carbon nanotubes; isopropanol; acetone; ethanol; electric resistivity; mechanical properties

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1. Introduction

Carbon nanotubes (CNTs) have drawn the attention of the scientific community in recent decades due to their extraordinary mechanical, thermal, and electrical properties, such as their higher tensile strength and Young's modulus [1]. Kamedulski et al. (2021) [2] affirms that some key parameters, such as porous structure, the introduction of heteroatoms, carbonization temperature, and modification of structure on the properties of carbon hybrids, lead to an electrode material catalyzing oxygen reduction. Due to these properties, CNTs have been used for different applications. Shoukat and Khan (2021) [3] reinforced the use of CNTs for electrochemical system applications, electric double layer capacitance, chemical sensors, and medicinal applications.

Besides the applications in the field of electronics, biomedicine, and chemical sensors [2,3], graphene-based nanomaterials have been suggested for application in the fabrication of modified asphalt and cement composites [4]. Han et al. (2021) [4] proposes that the addition of proper amounts of this nanomaterial awards the asphalt certain conductivity, in addition to improving its mechanical, high temperature performance, fatigue resistance, ultraviolet self-healing, and microwave self-healing properties. On the other hand, those authors [4] also emphasize the possibility of agglomeration leading to issues resulting from their uneven dispersion, causing decreased overall strength and performance.

The use of an effective dispersion method is necessary because of the hydrophobic behavior of CNTs and the resulting possibility of agglomeration leading to cluster formation, which could compromise the composites' properties [5,6]. A good dispersion method is crucial for a homogeneous distribution of the CNTs and a good bond between the nanomaterial and the cement matrix.

The research concerning CNTs in cement-based materials suggest an improvement in the mechanical properties of cement pastes [7], a reduction of the porosity [8], an increase in the fracture energy [9], and a higher fracture toughness, making it possible to support heavier loads until the failure when CNTs are well dispersed and bonded to the cement matrix [10]. The presence of CNTs in a cement matrix is shown to be responsible for nucleation of the hydration products, contributing to the reduction in the porosity and interconnectivity of the pores in a such a way that the transference of electrons occurs through calcium silicate hydrate (C-S-H) gel, causing the increase in the electrical resistivity [11], which is important to take into consideration when electrical properties are assessed. On the other hand, the significantly better conductivity of CNTs with respect to the components of the hardened cement paste matrix may contribute to reduce the overall electrical resistivity of the composite if the addition of the CNTs is enough to allow for the percolation threshold.

Research involving the dispersion of carbon nanomaterials in non-aqueous environments of ethanol, acetone, and isopropanol, combined with sonication, have shown evidences of an effective dispersion by registering increased results regarding the mechanical strength of the composites in which they were inserted [12–18]. The positive results may be explained by the ease of dispersion of CNTs in non-polar solvents. These solvents, when added to hydrated cement pastes, act as inhibitors of the hydration process [19]. It is, therefore, important to note that the purpose of the evaluation of the dispersion of CNTs involves the removal of the solvent by evaporation before the start of the hydration process (adding water to the anhydrous cement particles).

Effective dispersions of CNTs have been observed on the surface of cement particles in a non-aqueous environment of ethanol through electron microscopy [1]. Followed by adequate removal of the solvent, the resulting material can be used to produce cement pastes, mortars, or concretes. The previous dispersion of CNTs in ethanol led to the 95% increase in the tenacity with the presence of 0.75% of CNTs, and 204% with a combined presence of 0.75% of CNTs and 1% of nano aluminum oxide in cement-based composites [1]. In the same study, the compressive strength improved by 36.16% and 58.31%, respectively, suggesting a good interaction between CNTs and the cement matrix [12].

The dispersion of CNTs on the surface of the cement particles in acetone, combined with sonication, is also considered promising [20]. An improvement of almost 100% in mechanical strength were observed in cement pastes with the inclusion of CNTs up to 0.03% [13]. This might be caused by the chemical interaction between the cement matrix and the carboxyl and hydroxyl functional groups (-COOH and -OH, respectively), since the cement pastes produced using functionalized CNTs dispersed with surfactants, without the process of the dispersion of acetone, showed weaker mechanical performance [13]. With the same dispersion method, an increase in compressive and tensile strengths was observed adding up to 0.5% of CNTs. Using 1% and 1.5% of CNTs, the reduction of the mechanical performance was observed, which might indicate that the limit of effective dispersion by this method might be around 0.05% of CNTs by weight of cement [16,17].

The dispersion of CNTs on the surface of the cement particles in isopropanol showed some evidence of the nanotubes acting as nucleation sites of the hydration products and densification of C-S-H, a strong bond between CNTs and the cement matrix and also an influence on cracking control [21,22]. Following the same dispersion method in isopropanol, it was possible to obtain improvements of 50% in compressive and tensile strengths with the addition of 0.05%, compared to the addition of 0.1%, of CNTs [18].

Besides many promising results regarding the use of non-aqueous dispersion media, combined with the sonication of non-functionalized CNTs to produce cement composites, no comparative analysis is found in the literature between these dispersion environments. At the same time, the assessment of mechanical strength is pointed out in the literature as an indirect method to evaluate the efficiency of the dispersion of the cement particles [23,24], as well as the assessment of the electrical conductivity of the composite [25–27]. It is expected that by an efficient CNTs dispersion, the cement composites may achieve smaller electrical resistivity due to their electrical conduction properties, in addition to the increase in mechanical strength due to CNT-matrix load transfer and matrix densification by the nucleation sites of the hydration products.

Thus, this study aimed to analyze the efficiency of the dispersions using three different solvents through the behavior of the composites in terms of electrical-volumetric conductivity and the mechanical strength of cement pastes produced with CNTs. CNTs were previously dispersed on the surface of anhydrous cement particles in suspensions of isopropanol, ethanol, and acetone, with the help of sonication. After the adequate drying and production of the cement paste mixtures, specimens were tested to evaluate their electrical resistivity, compressive strength, and splitting tensile strength. With the results obtained, it was possible to correlate the effectiveness of the dispersion in each of the adopted environments. The main novelty obtained by this paper is the possibility to compare the dispersion efficiency of the three non-aqueous media used according to electrical resistivity and mechanical strength performance of the cement paste.

2. Materials and Methods

The materials used were as follows: Brazilian type CP-V Portland Cement (similar to European CEM-I, produced by Lafarge-Holcim, Pedro Leopoldo MG, Brazil), because of its low percentage of mineral additions; multi-walled carbon nanotubes (MWCNTs), with estimated tube lengths between 5 μm and 30 μm (Gaussian information, referring to the extremes of diameter and length), 99% of external diameter between 0.8 nm and 30 nm, and purity greater than 95%, produced by CTNano (Belo Horizonte, MG, Brazil); isopropanol absolute grade; pure propanone acetone; absolute ethyl alcohol (all from Emfal, Belo Horizonte, MG, Brazil).

The CNTs employed in this study are low cost; therefore, there is less control of the quality, and the sizes vary over a larger range compared to other products from the same manufacturer.

The figures below (Figures 1 and 2) indicate the scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetry (TG) analyses of the CNTs used. Through the figures it was possible to visualize images on the surface of the nanomaterial and the information on loss of mass according to the temperature variation, allowing for the characterization of dimensions and purity information provided by the supplier.

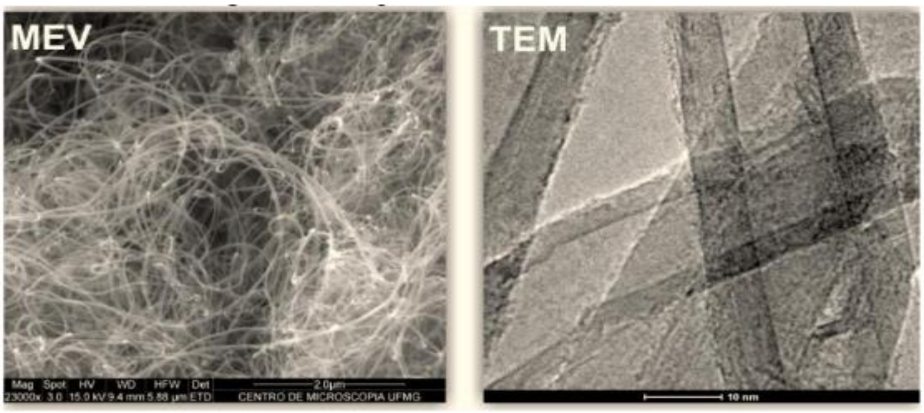

Figure 1. MEV and TEM images of CNTs used.

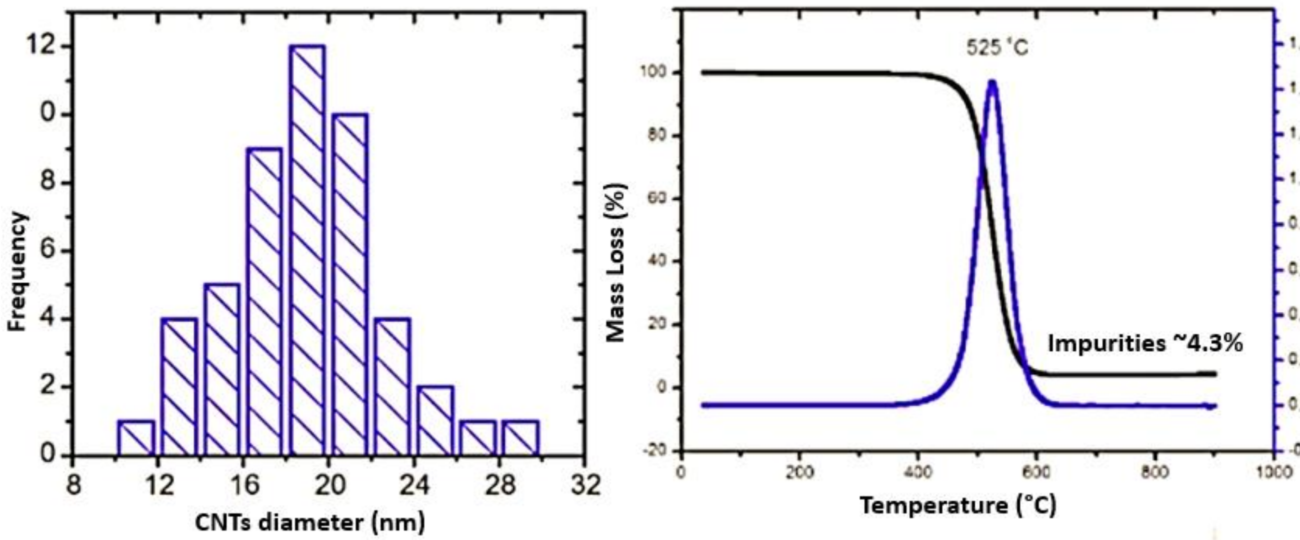

Figure 2. Characterization of dimensions and purity information of the CNTs, provided by the supplier.

The purity information was provided by the manufacturer. It is noteworthy to mentioned that the CNTs are multiwalled "as-grown", produced by chemical vapor deposition (CVD), without any further treatment (purification or functionalization).

2.1. CNT Dispersion on the Surface of Anhydrous Cement Particles in Non-Aqueous Suspensions

The dispersion process of CNTs on cement was performed in three concentrations: 0%, 0.05%, and 0.10%, with respect to cement mass, and followed the method described by Rocha and Ludvig (2017) [18]. The dispersion process is described in Figure 3. The same method was used for the dispersion of CNTs in cement in different non-aqueous environments, i.e., acetone and alcohol.

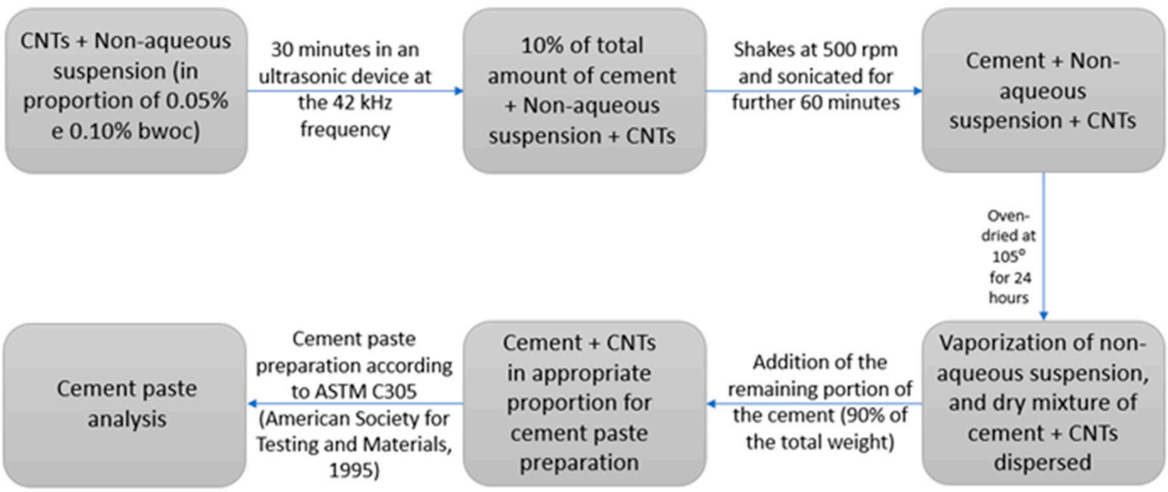

Figure 3. Flowchart of the dispersion process of the CNTs in the anhydrous cement particles in a non-aqueous suspension [25].

2.2. Preparation of Specimens

In this research, there are two reference samples: the reference samples using cement without undergoing the dispersion processes in non-aqueous environments and without CNTs (REF), and the samples with cement dispersed in non-aqueous environments (ISO-0, ACE-0 and ETA-0). The other nanostructured samples, besides the addition of cement and water, have CNTs added to the mixture in concentrations of 0.05% and 0.10% by weight of cement and dispersed, as previously described. A water–cement ratio of 0.33 was adopted.

The cement paste was prepared in a mechanical mortar blender [28]. The cement paste mixtures are described in Table 1.

Table 1. Cement paste mixtures.

Mixture	Description and CNTs Content	Non-Aqueous Media
REF	Cement paste without CNTs and without sonication process.	-
ISO-0 ACE-0 ETA-0	Cement paste without CNTs and with cement dispersed in a non-aqueous environment.	Isopropanol Acetone Ethanol
ISO-0.05 ACE-0.05 ETA-0.05	Cement paste with addition of 0.05% of CNTs and with the dispersion process in a non-aqueous environment.	Isopropanol Acetone Ethanol
ISO-0.10 ACE-0.10 ETA-0.10	Cement paste with addition of 0.10% of CNTs and with the dispersion process in a non-aqueous environment.	Isopropanol Acetone Ethanol

A total of 8 cylindrical specimens of 5 cm in diameter and 10 cm in height were cast for each mixture: 4 specimens for compressive strength tests and 4 specimens for splitting tensile strength tests to be determined at 28 days of age. The molds were filled with cement paste in two layers and compacted using a vibrating table. Curing was performed in lime-saturated water for 28 days.

2.3. Fresh Properties of Cement Paste

Immediately after the cement paste preparation, the cement pastes were analyzed according to the following: (i) consistency, based on ASTM C187 [29]; and (ii) setting time, using a Vicat needle, in accordance with ASTM C191 [30].

Consistency tests were performed in a Vicat apparatus with cement pastes confined in a ring resting on a plate. The plunger of the apparatus was brought into contact with the surface of the paste (the upper zero mark) and released for 30 s. The cement paste consistency was recorded at the mark where the rod settled.

The setting time test was also performed in a Vicat apparatus. The initial time of setting was determined by the elapsed time required for the Vicat needle to achieve a penetration of 25 mm. The final time of setting is the total time elapsed until the plunger does not leave a complete circular impression on the paste surface.

2.4. Evaluation of Electrical-Volumetric Conductivity

The evaluation of the electrical-volumetric conductivity was performed following the method proposed by Neto (2019) [31] and the procedures established by NBR 9204 (2012) [32], according to the following description.

To perform the test, five cylindrical specimens were used at 28 days of age. The specimens were saturated with water and placed between two copper boards with wet pieces of steel wool on the contact surface. A potential difference of 8V was applied between the two electrodes by using a continuous voltage source (ICEL-PS). The values of the total electric voltage of the circuit and the continuous electric current passing through the specimen were registered by a multimeter Minipa Et 2042c, with a scale of 200 mA. The electrical-volumetric resistivity of the cement paste was determined using the following equation:

$$\rho = \frac{R \times S}{L} = \frac{V \times S}{L \times I}, \tag{1}$$

where:

ρ = electrical resistivity ($\Omega \times$ m);
R = electrical resistance (Ω);
I = current (A);

V = potential difference (V);
L = length of the specimen (m);
S = cross sectional area (m^2).

Figure 4 represents an illustrative image of the test performed.

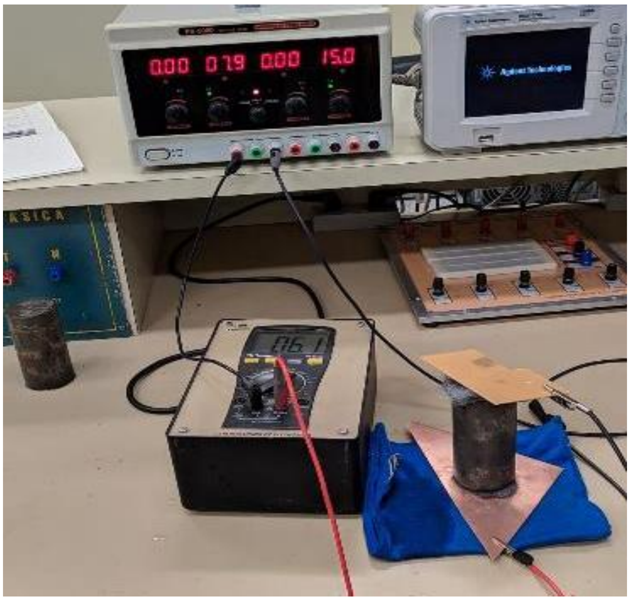

Figure 4. Experimental setup of the electric-volumetric resistivity test.

2.5. Axial Compression

After curing for 28 days, the specimens' surface was flattened to obtain a uniform distribution of the applied stress. The samples were tested in an EMIC universal testing machine with a load cell of 300 kN and a load increment of 0.20 MPa/s.

2.6. Tensile Analysis by Diametrical Compression of Cement Pastes

The specimens were submitted to a splitting tensile strength test at 28 days of age, with the support of a specially fabricated apparatus for this purpose, as shown in Figure 5. The apparatus is used to avoid any misalignment of the load application surface.

Figure 5. Splitting tensile strength test setup.

The specimens were tested in an EMIC universal testing machine with a load cell of 20 kN and a load increment of 1 mm/min. The splitting tensile strength was calculated following the equation given by NBR 7222 [33]:

$$\sigma_T = \frac{2F_{max}}{\pi l d}, \tag{2}$$

where

σ_T = splitting tensile strength (MPa);
F_{max} = maximum load (N);
l = length of the specimen (mm);
d = diameter (mm).

2.7. Helium Pycnometry

The density of fragments of the hydrated cement pastes specimens at 28 days of age were analyzed by helium pycnometry in a multipycnometer device from Quantchrome Instruments. The fragments (approximately 12 g) were obtained from the specimens used for mechanical tests after the tests were performed. At least 10 measurements were performed, and the mean value of the last five measurements was considered as the result for that sample.

2.8. Statistical Analysis of Results

The results of the tests were submitted to statistical analysis by variance testing (ANOVA) at a confidence interval of 95%. The analysis was based on the following null hypothesis: the variances of the mean electric conductivity are not significant or the variances of the values of the mechanical properties are not significant. For statistical analyses where the null hypothesis is rejected, and the variation of the results is significant ($p < 0.05$), a Tukey's test was performed to assess the variance between the samples and to identify exactly where the significant variance is found. The analysis results are presented among the results of each test. All the specimens were randomly selected within the same composition for testing to ensure sample randomness.

3. Results and Discussion

In this section, for comparison, two distinct sets of analysis were performed with each of the three tests; first, a comparison between the behavior of the cement pastes' REF, ISO-0, ACE-0, and ETA-0, that is, an analysis of the cement pastes without the addition of CNTs. The objective of this study was to identify any interaction between anhydrous cement particles and each of the three types of solvents. Afterwards, the behavior of the samples prepared using the same non-aqueous environment with the addition of CNTs in different concentrations was investigated.

3.1. Consistency and Setting Time

The consistency and setting time results are presented in Table 2.

Table 2. Consistency and setting time results. (bold: parameters' names that are specified in the following columns).

			Isopropanol			Ethanol			Acetone	
	REF	**ISO-0**	**ISO-0.05**	**ISO-0.10**	**ETA-0**	**ETA-0.05**	**ETA-0.10**	**ACE-0**	**ACE-0.05**	**ACE-0.10**
Start of Setting (Hours: Minutes)	01:40	01:42	01:56	01:54	01:52	01:56	01:58	01:27	02:27	02:03
End of Setting (Hours: Minutes)	02:20	02:22	02:52	02:41	02:30	02:41	02:38	01:57	03:17	02:38
Setting Time (Hours: Minutes)	00:40	00:40	00:56	00:47	00:38	00:45	00:40	00:30	00:50	00:35
Consistency (mm)	17	17	15	14	16	16	14	17	17	15

As noticed, the consistency of the specimens without CNTs was almost the same: 17 mm for REF, ISO-0, and ACE-0, and 16 mm for ETA-0. These results suggest that the sonification process of cement particles in non-aqueous suspension did not affect the consistency, as the particles were not disintegrated into smaller particles.

The presence of CNTs, however, reduced the consistency of the cement pastes from 17 mm to 14 mm at the maximum, suggesting that the addition of CNTs to a cement matrix requires a higher amount of water to acquire the same consistency, even though it did not significantly influence the workability of the cement composite. The reduction in the consistency due to the presence of CNTs may be explained by the formation of a network of the well-dispersed filaments that somewhat restrain the cement particles from moving, as was observed in other studies [5,34,35].

Setting times suffered some influence due to the use of different dispersing media. Isopropanol did not influence the time of setting. On the other hand, ethanol caused a delay of setting (both starting and ending times) while maintaining the same total setting time. At the same time, acetone had an opposite effect: the start and end of setting were as anticipated, but total setting time apparently did not suffer with expressive impact. One can assume that the treatment of cement particles in the three different solvents had different effects with respect to the initial solubility, as ethanol made initial dissolution and precipitation of the hydration products easier; acetone, on the contrary, made this process more difficult, whereas isopropanol had an insignificant effect. The details of the observed phenomenon remain to be further investigated, but this exceeds the objectives of the present study.

Regardless of the suspension media, CNTs also had a delaying effect on the start and end of setting, as well as the total setting time. This result means that the cement paste reinforced with CNTs presents more workability for a slightly longer period, mainly in the presence of 0.05% of CNTs, in which was recorded the largest time difference between the initial and final setting time. The longer workability recorded may be indicative of the influence of CNTs in cement hydration kinetics. The observed delays might be an effect of the previously mentioned three-dimensional network formed by the nanotubes: they may immobilize some part of the cement particles, which will consequently suffer some delay in dissolving their constituents and subsequently, in the precipitation of the hydration products. Similar effects have already been observed in other studies [5,34,36].

3.2. Evaluation of Electrical-Volumetric Conductivity

The results of the mean electrical resistivity obtained by the electrical-volumetric conductivity tests are presented in Table 3 and Figure 6.

Table 3. Results of the electrical-volumetric conductivity tests.

	Mean Resistivity ρ (Ω·m)	Standard Deviation	Coefficient of Variation (%)	Variation of Resistivity (REF)	Variation of Resistivity (Same Environment)
REF	23.261	0.172	0.74%	-	-
ISO-0	22.921	0.167	0.73%	−1.46%	-
ISO-0.05	24.165	0.526	2.18%	+3.89%	+5.43%
ISO-0.10	24.561	0.859	3.50%	+5.59%	+7.16%
ETA-0	23.015	0.504	2.19%	−1.06%	-
ETA-0.05	23.177	0.282	1.22%	−0.36%	+0.71%
ETA-0.10	23.349	0.290	1.24%	+0.38%	+1.45%
ACE-0	19.630	0.297	1.51%	−15.61%	-
ACE-0.05	19.762	0.527	2.66%	−15.04%	+0.68%
ACE-0.10	19.392	0.425	2.19%	−16.63%	−1.21%

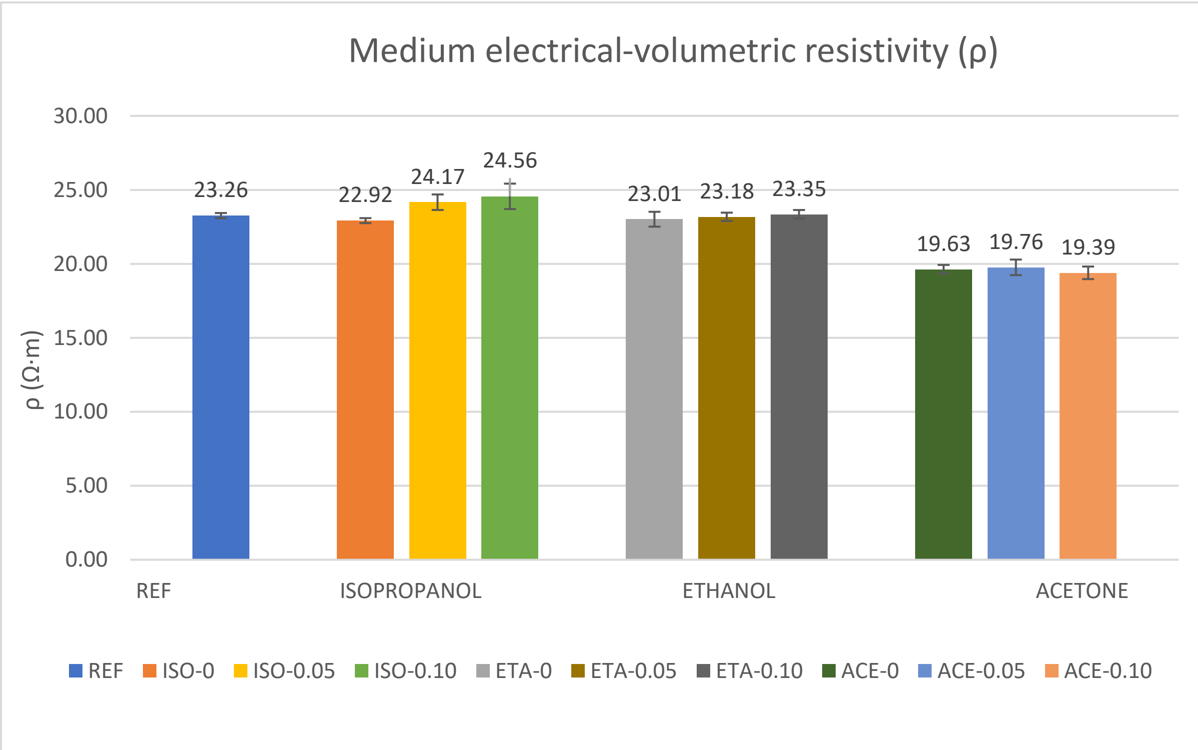

Figure 6. Results of the electrical-volumetric resistivity.

To separately assess the influence of the dispersion media on the properties of the cement pastes, without the influence of CNTs, the results of the samples prepared without the addition of CNTs (REF, ACE-0, ETA-0, and ISO-0) were statistically analyzed. A small variation in the electrical resistivity was observed in mixtures ETA-0 and ISO-0 (variations lower than 1%), which contrasts with the variation of 15.61% observed in the ACE-0 mixture. By means of a Tukey's test, it is noted that only the cement paste dispersed in acetone ACE-0 showed any significant variance when compared to the REF sample. This result suggests that the dispersion of the cement particle in acetone affects the electrical resistivity of cement pastes, possibly due to the chemical interaction between the cement matrix and the functional groups present in this solvent [13], which apparently did not occur with other solvents. For isopropanol and ethanol, the variance caused by these dispersing media did not significantly affect the electrical resistivity.

It is worth mentioning that the methods commonly used in civil engineering are quite empirical. Usually, a coefficient of variation below 15% is considered acceptable.

Moving on to the second analysis, when assessing the electrical resistivity in each of the environments of dispersion, a small variation was noted between the mixtures prepared with acetone and ethanol. According to the statistical analysis, the variances were not considered significant for either environment.

For the cement pastes prepared in an isopropanol environment, the electrical resistivity presented a higher variation when compared to acetone and ethanol, increasing by 5.43% and 7.16% for 0.05% and 0.10% of CNTs, respectively. The null hypothesis is rejected for the variance between the nanostructured cement pastes and ISO-0, and there is not a statistically significant difference in the electrical resistivity when adding 0.05% or 0.10% of CNTs. On the other hand, the results for ISO-0.05 and ISO-0.10 suggest the incidence of unconnected pores in the cement paste matrix, leading to electrical conductivity through the C-S-H gel, resulting in an increase in electrical resistance (Hansson and Hansson, 1983) [37]. This may be evidence of the CNTs acting as nucleation sites of the hydration products and the densification of C-S-H [21].

The statistical assessment of the variance of all the samples supports the individual results. The null hypothesis is rejected, and therefore, the results of the nanostructured samples with dispersion in isopropanol and acetone significantly differ. Besides the influence of CNTs on the electrical conductivity not being observed, the dispersion in an environment with acetone can increase the electrical conductivity. This effect is further discussed below.

Initially, due to the conductive properties of CNTs, it was expected that the presence of well dispersed CNT filaments could interfere and increase the electrical conductivity, reducing the electrical resistivity. However, due to the low proportions used (up to 0.10%, well below the percolation threshold), the results support the research pointing out that the incorporation of CNTs up to 2% does not contribute to the increase in conductivity [13,38].

The reduction of electrical resistivity noted in samples with cement dispersed in acetone (with and without CNTs) might be due to some chemical interaction between the cement matrix and the functional groups of acetone (-COOH and -OH), which contribute to the reaction of ion exchange, as pointed out by Nasibulina et al. (2012) [13], and this issue is an opportunity for future research involving this specific theme.

The increase in electrical resistivity of the cement composites with the addition of dispersed CNTs and isopropanol might indicate an efficient dispersion of CNTs by this dispersion method, allowing the nanomaterial to act as a nucleator of the formation of hydration products. Although the presence of CNTs up to 0.10% is not enough to increase the electrical conductivity of cement pastes [13], the electrical resistivity of the cement composites depends on the degree of hydration, which increases as the amount of hydration products increases [39]. The porosity reduction in the matrix of the cement paste reinforced with CNTs recorded by helium pycnometry allows the conductivity to occur through the C-S-H gel, contributing to increasing the electrical resistance and, consequently, the electrical resistivity [37]. This could explain the increase in electrical resistivity of the mixtures ISO-0.05 and ISO-0.10.

3.3. Compressive Strength

The results of the compressive strength test are presented in Table 4 and Figure 7.

Table 4. Compressive strength test results.

	Mean Compressive Strength (MPa)	Standard Deviation (MPa)	Coefficient of Variation (%)	Variation of Compressive Strength (REF)	Variation of Compressive Strength (Same Dispersion Environment)
REF	57.94	3.632	6%	-	-
ISO-0	55.07	3.190	6%	−4.95%	-
ISO-0.05	79.86	7.478	9%	37.82%	45.00%
ISO-0.10	62.30	1.843	3%	7.52%	13.12%
ETA-0	58.70	2.337	4%	1.30%	-
ETA-0.05	75.09	3.241	4%	29.59%	27.92%
ETA-0.10	62.96	16.128	26%	8.65%	7.25%
ACE-0	58.45	4.530	8%	0.88%	-
ACE-0.05	72.71	8.964	12%	25.49%	24.40%
ACE-0.10	68.16	3.651	5%	17.63%	16.61%

Comparing the mixtures REF, ACE-0, ETA-0, and ISO-0 with the reference, a small variation in the compressive strength results was observed, which is shown in the girth column of Table 5. The null hypothesis that the means of the mixtures are different could not be rejected, which means there is no significant variation in the means caused by the dispersion media.

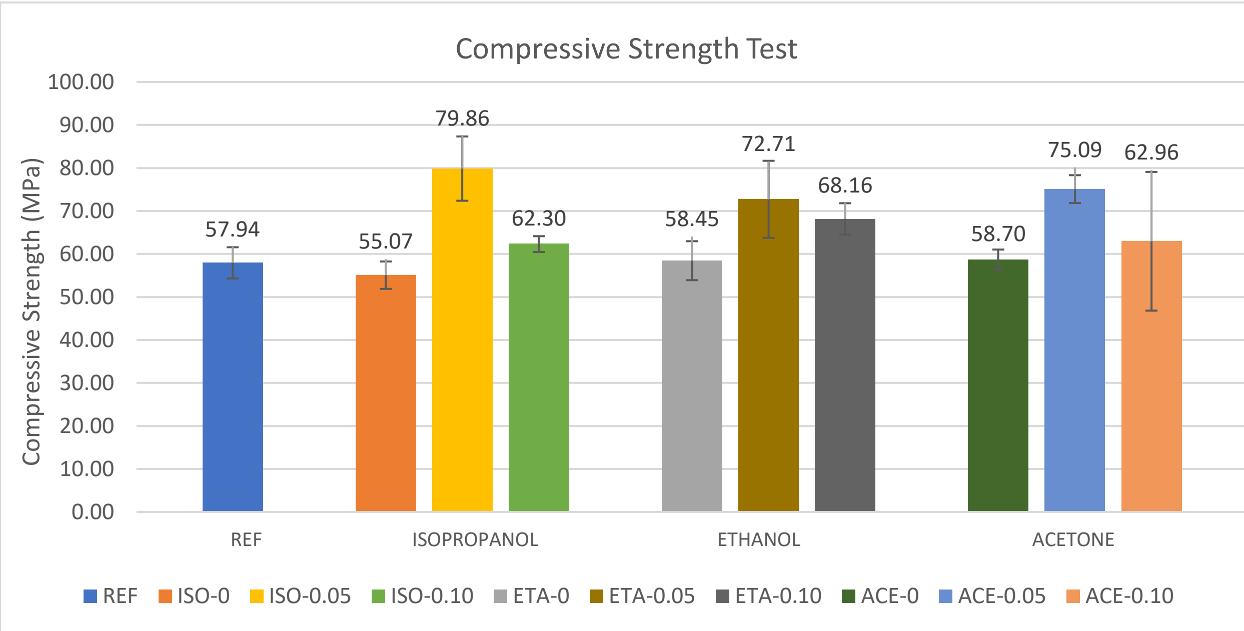

Figure 7. Results of the compressive strength tests.

Table 5. Splitting tensile strength test results.

	Mean Splitting Tensile Strength (MPa)	Standard Deviation (MPa)	Coefficient of Variation (%)	Variation of Compressive Strength (REF)	Variation of Compressive Strength (Same Dispersion Environment)
REF	2.32	0.130	6%	-	-
ISO-0	2.32	0.212	9%	−0.39%	-
ISO-0.05	3.32	0.157	5%	42.79%	43.35%
ISO-0.10	2.70	0.037	1%	15.93%	16.39%
ETA-0	2.24	0.254	11%	−3.49%	-
ETA-0.05	2.25	0.163	7%	−3.42%	0.07%
ETA-0.10	2.27	0.239	11%	−2.22%	1.32%
ACE-0	2.50	0.228	9%	7.62%	-
ACE-0.05	2.89	0.562	19%	24.48%	15.67%
ACE-0.10	2.55	0.417	16%	9.55%	1.80%

Analyzing each of the dispersion environments individually, it is possible to observe a pattern of increasing splitting tensile strength with the presence of CNTs. More expressive values are observed with the addition of 0.05% of CNTs, regardless of dispersion environment. This result is indicative of a better dispersion of CNTs in this addition, avoiding agglomeration formation in a cement paste. Once CNTs are well dispersed and adhered to the matrix, they may act as bridges [8] in the pores' capacity by transferring the load applied and increase the resistance [40].

For the addition of 0.10% of CNTs, an increased strength is observed, but it is less expressive, which suggests the addition of 0.05% as ideal for all the studied dispersion environments. Beyond this addition, agglomerates could compromise the hydration process and could also act as stress concentration sites, reducing the compressive strength of the cement paste [5].

However, in the statistical analysis of each of the non-aqueous environments, it is possible to note that the null hypothesis was rejected for isopropanol. Thus, only this environment possessed samples with significant differences. In the other environments, due to the higher standard deviation, the increases observed in the mean values are not significant, accepting the null hypothesis.

3.4. Analysis of the Splitting Tensile Strength

The results of the splitting tensile strength test are presented in Table 5 and Figure 8.

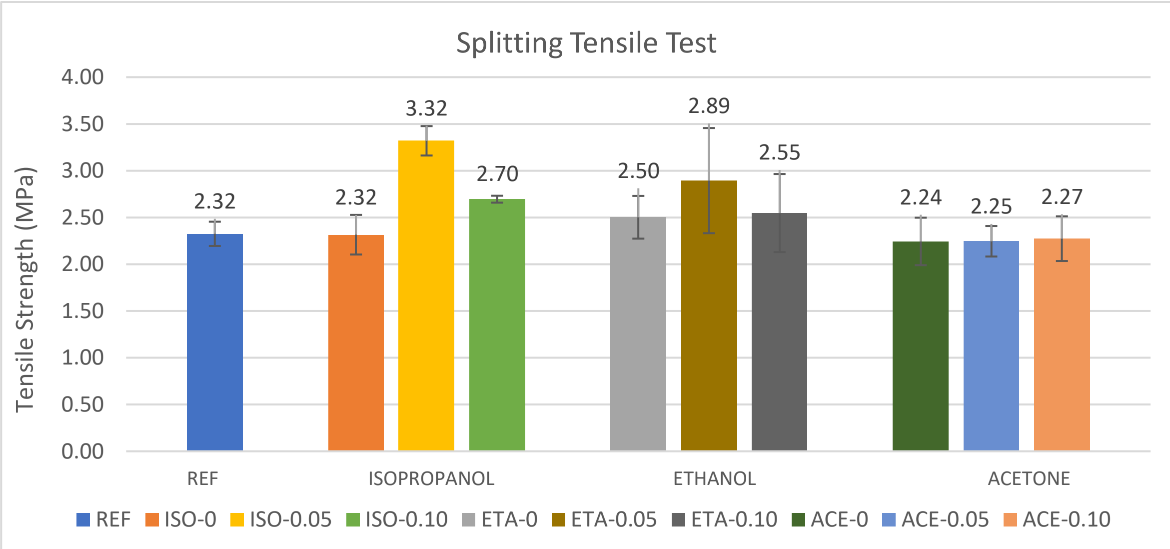

Figure 8. Results of splitting tensile strength tests.

For the splitting tensile strength, isopropanol and ethanol retained the behavior noted in the compressive strength test, where the more noticeable increases in strength were more expressive with the addition of 0.05% of CNT, with values 43.35% and 15.6% of the samples in non-aqueous environments of isopropanol and ethanol, in relation to the ISO-0 and ETA-0 samples. A more expressive variation between the samples with a non-aqueous dispersion environment of ethanol is noted. This was confirmed by rejecting the null hypothesis in the ANOVA test.

The better improvement in strength recorded, mainly in presence of 0.05% of CNTs, is evidence of the interaction of the hydration products with the CNTs which ensures load transfer when subjected to stress [40]. Thus, by this dispersion methodology, CNTs filaments seem to be well adhered to the cement matrix, contributing to the higher compressive and tensile strength recorded [1].

The results for the dispersion environment of acetone, unlike the others, did not show any increase in tensile strength. The observed difference of the means is not statistically significant in relation to ACE-0, accepting the null hypothesis of the ANOVA test.

3.5. Helium Pycnometry

The densities recorded by helium pycnometry are presented in Table 6.

Table 6. Density results as determined by helium pycnometry.

	Isopropanol			Ethanol			Acetone		
REF	ISO-0	ISO-0.05	ISO-0.10	ETA-0	ETA-0.05	ETA-0.10	ACE-0	ACE-0.05	ACE-0.10
2.379	2.372	2.384	2.393	2.377	2.388	2.391	2.375	2.385	2.384

The results presented in Table 6 indicate that the three different dispersion media alone did not affect the density of the hydrated pastes (differences up to 0.3%). When examining the effect of the CNT addition to the hydrated cement pastes, it can be clearly seen that the pastes reinforced with CNTs have slightly higher densities. However, this increase is not expressive (up to 0.9% with respect to the paste with the same dispersion media, but without CNTs); this result, in addition to the electrical conductivity and mechanical strength results, may be evidence that the CNTs act as nucleation sites for cement hydration product formation, contributing to a denser matrix and porosity reduction. Similar results were observed by Xu, Liu, and Li (2015) [40].

4. Conclusions

The dispersion of CNTs in non-aqueous environments of acetone, ethanol, and isopropanol was investigated in this research. The analysis of the results of electrical-volumetric conductivity, compressive strength, and splitting tensile strength tests led to the following conclusions:

- Acetone, isopropanol, and ethanol have proven efficient in the dispersion of CNTs in amounts up to 0.10% by weight of cement, considering the enhancement in the mechanical properties of reinforced cement pastes. This result strengthens the hypothesis that the CNTs are well bonded to the hydration products and behave as bridges in the pores [8], allowing a mechanism of CNT-matrix load transfer [40], contributing to the increase in the mechanical properties and durability due to the control of cracking propagation;
- CNTs slightly affect the workability and delay the setting time under fresh conditions. Besides that, hydrated cement paste reinforced with CNTs is denser. These findings suggest an influence of the CNTs addition in cement hydration kinetics, implying porosity reduction that leads to improvements in mechanical properties;
- Both compressive and splitting tensile tests recorded higher strengths in the presence of 0.05% of CNTs, suggesting an optimal range for the incorporation of CNTs in all three media analyzed. As an exception, acetone media did not record mechanical improvements in the presence of CNTs in the splitting tensile test, whereas isopropanol media recorded the most expressive gains in both the compressive and splitting tensile tests;
- The results of electrical resistivity are less expressive when compared to the mechanical properties tests. Cement pastes with dispersion environments of isopropanol and ethanol showed increased electrical resistivity. The inverse correlation proposed by Ma et al. (2018) [11], in which the higher mechanical properties are associated with a lower electrical resistivity, and vice versa, was not observed in this study, possibly due to the fact that the concentrations of CNTs (less than 2%) did not contribute to the increase in electrical conductivity [35];
- A significant reduction in electrical resistivity was observed for the cement paste mixtures dispersed in a non-aqueous environment of acetone. This suggests that acetone might be responsible for the reduced electrical resistivity due to the interaction between the functional groups and the cement matrix. However, for a better understanding of the influence of the dispersion of the cement particles in a non-aqueous environment of acetone in the electrical resistivity of the cement composite, further and more specific studies are suggested;
- It is suggested that the presence of CNTs might have acted as nucleator of hydration for the nanostructured cement pastes dispersed in isopropanol, since the higher hydration of the cement paste, the higher the electrical resistivity [39]. This behavior can also be related to the porosity reduction recorded by helium pycnometry, causing the conductivity through C-S-H gel and contributing to the increase in electrical resistivity [37].

In addition to the above conclusions, some research opportunities can also be listed:

- The evaluation of the chemical interaction between the cement matrix and the acetone functional groups (-COOH and -OH), investigating the possibility of the ion exchange reaction [13] and electrical conductivity for cement compositions reinforced with CNTs;

- Further microstructural investigation involving pore distribution in cement paste with the addition of CNTs, in order to assess the influence of CNTs on pore refinement to support helium pycnometry results;
- The evaluation of CNTs performance as nucleators of cement hydration products by cement paste composition analysis.

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