coatings

Article

Effect of a New Multi-Walled CNT (MWCNT) Type on the Strength and Elastic Properties of Cement-Based Mortar

Sergiu-Mihai Alexa-Stratulat [1], George Stoian [2], Iulian-Adrian Ghemeş [2], Ana-Maria Toma [1], Daniel Covatariu [1] and Ionut-Ovidiu Toma [1,*]

[1] Faculty of Civil Engineering and Building Services, The "Gheorghe Asachi" Technical University of Iasi, No. 1, Prof. dr.doc. D. Mangeron Street, 700050 Iasi, Romania
[2] Magnetic Materials and Devices Department, National Institute of Research and Development for Technical Physics, No. 47, Prof. dr.doc. D. Mangeron Street, 700050 Iasi, Romania
* Correspondence: ionut.ovidiu.toma@tuiasi.ro; Tel.: +40-232-701455

Abstract: Creating new construction materials with improved strength, elasticity, and durability properties represent the focus of many research works. Significant research effort has been invested in investigating the use of carbon nanotubes (CNTs) in cementitious materials, especially multi-walled carbon nanotubes (MWCNTs) which consist of a series of concentric graphite tubes. The use of MWCNTs is closely related to the use of surfactants and ultra-sonication procedures which may alter their properties and the properties of cement-based materials. The paper presents the preliminary results of an experimental investigation on the suitability of using a new, modified, MWCNT type aimed at eliminating the need of using surfactants and ultrasonication. The modified MWCNTs have a much lower surface energy compared to "classical" ones which would result in a decreased tendency of self-aggregation. A comparison was carried out from the point of view of density, flexural and compressive strength as well as dynamic modulus of elasticity of the obtained mortars. The mortar mix incorporating the modified MWCNTs showed improved mechanical properties even for a low percentage of CNT addition (0.025% by mass of cement). The results are discussed based on the material structure determined from a series of scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses.

Keywords: modified multi-walled carbon nanotubes; mechanical properties; uniform dispersion; dynamic modulus of elasticity

check for updates

Citation: Alexa-Stratulat, S.-M.; Stoian, G.; Ghemeş, I.-A.; Toma, A.-M.; Covatariu, D.; Toma, I.-O. Effect of a New Multi-Walled CNT (MWCNT) Type on the Strength and Elastic Properties of Cement-Based Mortar. *Coatings* **2023**, *13*, 492. https://doi.org/10.3390/coatings13030492

Academic Editor: Michał Kulka

Received: 28 January 2023
Revised: 19 February 2023
Accepted: 21 February 2023
Published: 23 February 2023

1. Introduction

The need to build taller and more durable structures resulted in a growing demand for construction materials with improved elastic, mechanical, and durability properties. A lot of effort has been invested into creating new materials with improved elastic and mechanical characteristics. At the same time, the developed materials would also have to be competitive from the point of view of manufacturing cost vs. improved performance. Another goal would be the applicability of the already existing design guidelines, without the need for major revisions.

The use of nanomaterials in the construction industry was quickly embraced by researchers and practitioners alike due to the added value in terms of improved material properties and behavior [1–5]. Significant research effort has been invested in investigating the use of carbon nanotubes (CNTs) in cementitious materials [3,6–8]. It is generally agreed upon that their use leads to improvements in the physical and mechanical properties. Based on conducted research works, 0.075% was proposed as being optimal for obtaining the lowest sorptivity, the lowest porosity, and a significant improvement in the values of the mechanical strengths [9] of cementitious matrices. Percentages between 0.01%–0.07% of CNTs used together with nano-silica were reported to improve the microstructure of cement mortar in a synergistic effect which resulted in better corrosion resistance and improved durability [10]. Nano-silica contributed towards enhancing the pozzolanic activity whereas the CNT acted as fiber reinforcement between the aggregates and the paste, at the level of the interfacial transition zone (ITZ), bridging the micro-cracks and arresting their development.

There are two distinct categories of CNTs that are currently investigated in terms of their beneficial effect on cementitious materials. Single-walled carbon nanotubes (SWCNTs), are tubes of graphite, sometimes capped at their ends, having the wall made of a single layer of molecules. On the other hand, there are multi-walled carbon nanotubes (MWCNTs), which consist of two or more open concentric graphite tubes [11]. The main advantage of SWCNTs resides in their greater flexibility in terms of being twisted, flattened, or bent around sharp edges (e.g., of aggregates) compared to MWCNTs. On the other hand, taking into account the large amounts of CNTs that would be necessary for large-scale concrete elements, the unit price of SWCNTs vs. MWCNTs and the corresponding production capacity, the use of MWCNTs seems the better choice, even though their structure is not as well understood and are prone to defects compared to their SWCNT counterparts [11,12].

Although MWCNTs show very high values for moduli of elasticity and high aspect ratios coupled with excellent thermal and electrical conductivity, they tend to bundle and coalesce [13]. There are currently two widely used approaches to overcome this issue: the mechanical and the chemical approach. The former involves sonication and high shear mixing which may break the nanotubes, thus reducing their aspect ratio. It is also a time-consuming procedure and not always very efficient. The latter approach implies the use of a dispersive agent, in the form of a surfactant or plasticizer, in order to overcome the strong bonding forces on the surface of CNTs [13]. There have been many attempts to obtain the ideal combination of surfactant type and sonication duration and input energy, most often ending with reporting conflicting results [14]. While some researchers noticed a beneficial contribution of using surfactants together with sonication [15], other studies reported a lack of improvement [16]. Moreover, there is a high probability that, due to their high surface energy, MWCNTs will still bundle together after being mixed with cement and aggregates.

The downside of using surfactants resides in the fact that high concentrations of surfactants are needed to obtain stable and uniform CNT dispersions. Moreover, the use of dispersants/surfactants was previously reported to negatively impact the properties of cementitious matrices due to inhibition of cement hydration and air entrapment [17,18] resulting in lower values for the mechanical properties of cement-based materials [19]. It has been suggested that the use of antifoaming agents could be applied as a countermeasure to the undesired effect of surfactants [20,21].

The paper presents the preliminary results of an experimental investigation on the suitability of using a new, modified, MWCNT type aimed at solving the above-mentioned shortcomings of "traditional" MWCNTs when used in cement-based materials, namely the use of surfactants together with sonication procedures to ensure their uniform dispersion. The modified MWCNTs were obtained using the same procedure as "traditional" MWCNTs with the key difference consisting in the fact that they are capped at their ends. In this aspect, the new MWCNTs are very similar to SWCNTs. A comparison was carried out from the point of view of density, flexural and compressive strength as well as dynamic modulus of elasticity of the obtained mortars. The results are discussed based on the material structure determined from a series of SEM and XRD analyses. The mortar mix incorporating the new MWCNTs exhibited improved elastic and mechanical properties compared to the reference mix, even though no surfactant was used, and no sonication procedure was applied. The statistical analysis of the results leads to small values for the coefficient of variation for each investigated material property. This supports the conclusion that the new, modified, MWCNTs were uniformly distributed within the mortar mix.

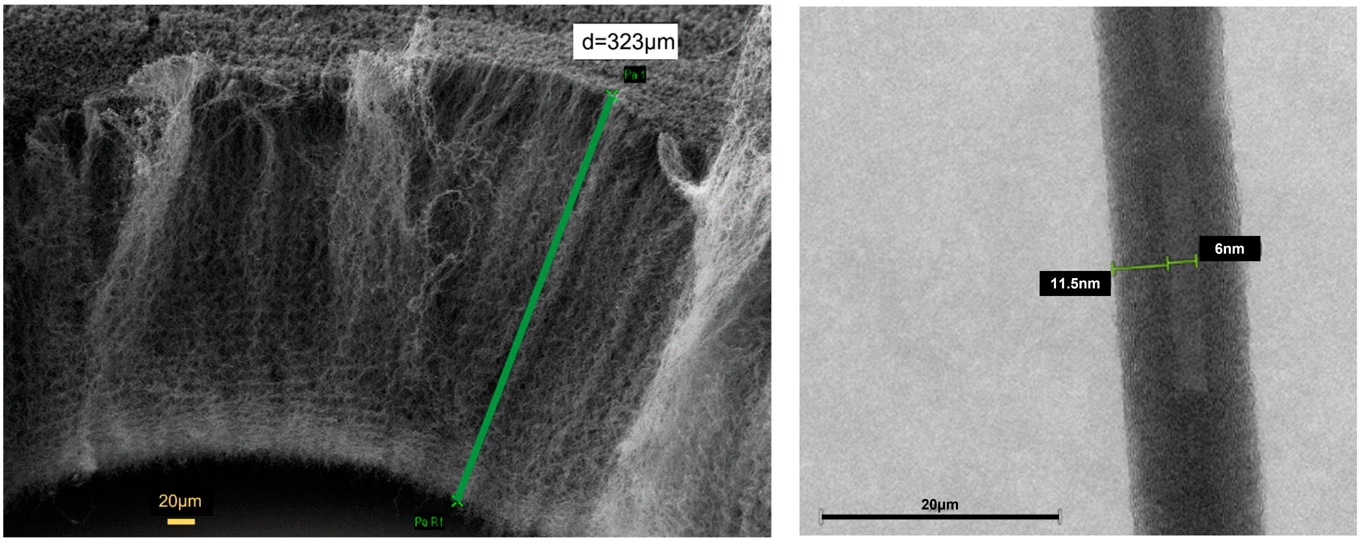
2. Materials and Methods

2.1. Materials

The chosen mortar mix, by volume, was 1:3:0.6 for cement, sand, and water, respectively. A rapid hardening CEM II B-M (S-LL) 42.5R cement complying with standard specifications [22] was used. It is classified as a composite cement consisting of 65% ÷ 79% cement clinker and 21% ÷ 35% a mixture between ground-granulated blast furnace slag (GGBS) and limestone.

The natural sand, readily available on the market, had a particle diameter range from 0 to 4 mm. Tap water was used in the mortar mix.

The new, modified, MWCNTs were produced in the laboratory of the National Institute of Research and Development for Technical Physics based on the chloride-mediated chemical vapor deposition (CVD) method [23]. The structure of the obtained MWCNTs, after 20 min of growth, is shown in Figure 1. The length of the MWCNTs was about 300 µm, as seen in Figure 1a, whereas the outer diameter was around 30 nm, according to the HR-TEM image presented in Figure 1b.



(**a**) (**b**)

Figure 1. Structure of MWCNTs: (**a**) SEM image of vertically aligned MWCNT arrays; (**b**) HR-TEM image of a single nanotube.

The new MWCNT used in this research as a possible solution to mitigate the issues related to using surfactants and sonication procedures was based on the same CVD method. These new carbon-based nanotubes (CBN) had a diameter of 30–40 nm and a length in the range of 200–400 nm, as measured from the SEM image shown in Figure 2. Anhydrous iron chloride ($FeCl_2$) was introduced in the center of a quartz tube electric furnace which was then evacuated to a pressure of about 1 mTorr using a rotary pump. The furnace was then heated up to a temperature of 900 °C with ramping rate of 40 °C/min. When the synthesis temperature was reached, acetylene (C_2H_2) was introduced into the reaction chamber at a flow rate of 0.5 L/min. The growth pressure was kept constant around the value of 10 Torr for a growth time of 60 min. Finally, the chamber was naturally cooled down to room temperature under vacuum and particles were collected using a permanent magnet.

These new, modified, MWCNTs (CBN) can be considered as precursors of "traditional" MWCNTs. They were obtained using the same procedure with the main difference consisting in the fact that they are capped at both of their ends. A Fe particle (white end in Figure 2) closes one end of the new MWCNT whereas the other end is capped by a C particle [24]. This results in a lower surface energy compared to regular MWCNTs and therefore they would be much easier to disperse and avoid self-aggregation, even in the absence of surfactants and/or sonication procedure.

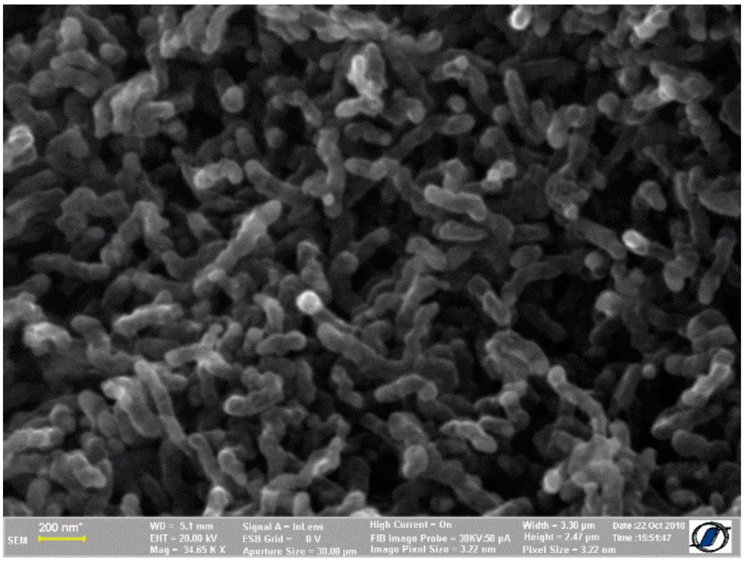


Figure 2. SEM image of new CBN.

To confirm the structure of these new CBN, a SEM-EDS mapping analysis was conducted. As it can be seen from Figure 3, a higher concentration of carbon leads to a more compact material structure. The results on SEM-EDS analysis are presented in Table 1 in terms of chemical constituents for the four investigated spectra.

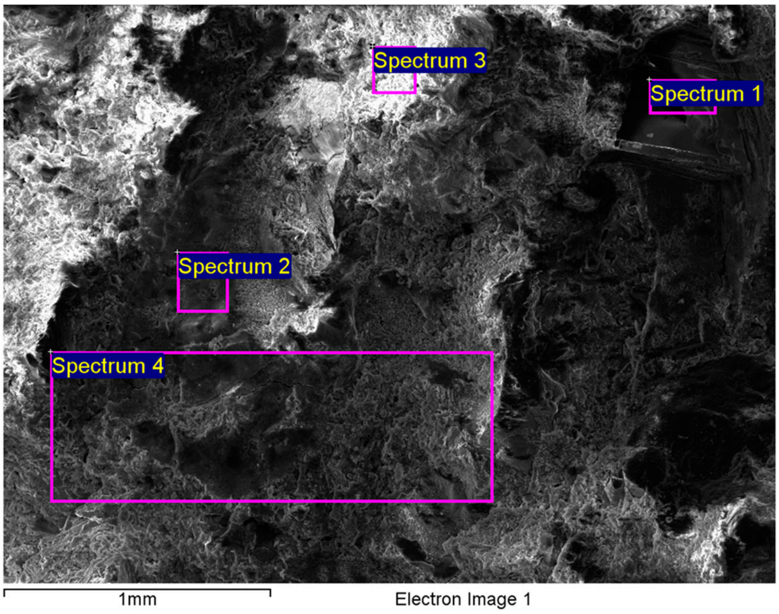


Figure 3. SEM-EDS analysis of new CBN.

Table 1. Composition of the four investigated spectra.

Spectrum	C	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe
Spectrum 1	7.98	59.33	-	-	21.88	10.57	-	-	0.24	-	-
Spectrum 2	18.13	66.85	-	0.31	0.98	3.94	0.35	0.07	9.20	-	0.16
Spectrum 3	15.37	66.95	-	0.67	1.59	4.97	0.28	0.08	9.57	0.07	0.45
Spectrum 4	-	76.73	0.29	0.54	1.66	7.23	0.45	0.12	12.61	-	0.35

The mix proportions used in this research are shown in Table 2. The quantities stated in Table 2 were enough to cast 3 prisms of 40 mm × 40 mm × 160 mm that were used to determine the mechanical and dynamic elastic properties. A total of three batches were cast for each mix proportion resulting in 9 prisms per mix. This would imply that for each of the mix proportions 9 values for the flexural tensile strength of mortar and 18 values for the compressive strength would be obtained.

Table 2. Mix proportions.

Mix Designation	Cement (g)	Sand (g)	Water/Cement	SDS (mMol)	Tributyl Phosphate/Cement (%)	CNT/Cement (%)	CBN/Cement (%)
Ref	500	2050	0.6	-	-	-	-
CNT *				1	-	0.025	-
CNT2 **				1	0.13	0.025	-
CBN				-	-	-	0.025

* mix with MWCNT and SDS (sodium dodecyl sulfate) only; ** mix with MWCNT, SDS, and anti-foaming agent (tributyl phosphate).

The MWCNTs/cement (CNT mix) and CBN/cement (CBN mix) content was chosen as 0.025%. The scientific literature reports a wide range of CNT content from 0.005% [12] to 1.5% [25]. A 0.025% content of CNTs from cement mass was considered to be satisfactory in terms of expected improvements in the values of the mechanical properties of mortars and to assess whether the new CBNs would be a viable alternative to classical MWCNTs. The choice of such a content percentage of CNT was based on the results reported in the scientific literature. Mohsen et al. [26] concluded in their study that a 0.03% content of CNT would not only be the optimum concrete mix in terms of strength gain but also in terms of cost saving. Xu et al. investigated the influence of MWCNTs on the mechanical properties and microstructure of cement pastes. A 6.25% increase in the value of the flexural strength was obtained for 0.025% MWCNTs by mass of cement [27]. In the study of Morsy et al., it was concluded that a 0.02% MWCNT by mass of cement resulted in the highest increase in the values of the mechanical properties of mortar mixed with nano-clay [28]. It was also suggested that lower percentages of MWCNT would prevent re-agglomeration during the mixing phase with cement and aggregates.

2.2. Methods

The cement and the sand were dry mixed before water (in case of Ref mix) or water with nano-tubes (in case of CNT and CBN mixes) was added. The MWCNTs in the CNT mix were dispersed by ultra-sonication for 1 h into a 1 mM sodium dodecyl sulfate (SDS) solution at room temperature. No other anti-foaming agent was used. For the CNT2 mix, however, tributyl phosphate was used as defoaming agent in order to reduce the volume of voids [20]. The content of defoaming agent was chosen at 0.13% wt. of cement, similar to the data provided in [29]. The new CBN was mixed with tap water without any ultrasonication or surfactants being used.

The resulting mortar was cast into 40 mm × 40 mm × 160 mm prismatic molds and covered by wet cloths and plastic foil to prevent the excessive drying of the mortar surface. After 24 h, the prisms were demolded and place in water for curing until the age of 28 days.

The prisms were measured and weighed after demolding and before being tested. Four measurements were taken for the length of each prism and six values for the cross-sectional dimensions. The height and the width of the cross-section were measured at both ends of the prism and at the middle. This was performed both to check for changes in the dimensions and to determine the density of the hardened mortar. The obtained data were then used to compute the dynamic modulus of elasticity for mortar mixes presented in Table 2.

The dynamic modulus of elasticity, E_d, was determined in accordance with ASTM C215:14 [30] and was based on the first resonant frequency obtained from the impact echo method. The dynamic modulus of elasticity for the prisms was computed as shown in Equation (1):

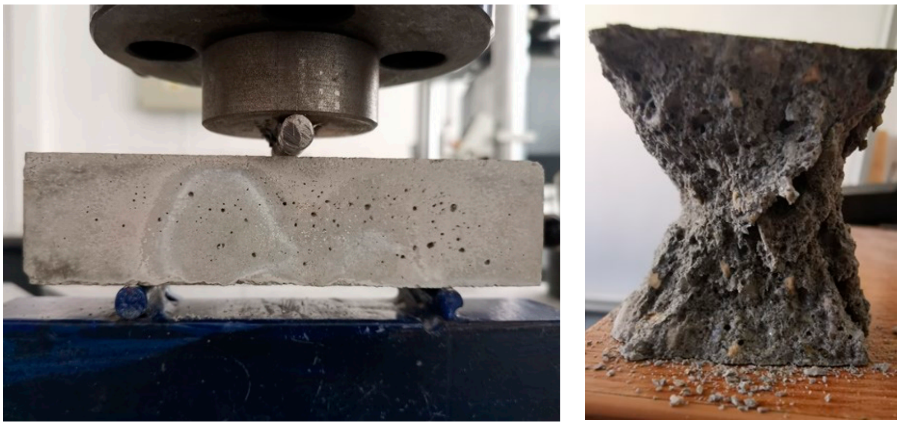
$$E_d = D \cdot m \cdot f_{ln}^2 \quad (1)$$

where m is the mass of the sample [kg], f_{ln} is the fundamental longitudinal frequency of vibration (Hz) and D is a coefficient that depends on the dimensions of the prism (Equation (2)):

$$D = 4 \cdot \frac{L}{b \cdot t} \quad (2)$$

where L is the length of the prism [m], and b and t are the cross-sectional dimensions [m].

The flexural strength of mortar mixes was determined at the age of 28 days by means of 3-point bending test conducted at a loading rate of 50 N/s in accordance with [31], as shown in Figure 4a. The resulting half prisms were examined for signs of visible cracks and then subjected to uniaxial compression test, Figure 4b, with a loading rate of 2400 N/s [31].



(a) (b)

Figure 4. Testing of mortar prisms: (**a**) flexural test; (**b**) uniaxial compression (failed half-prism).

The structure of a single modified MWCNT (CBN) was assessed by means of an ultra-high resolution transmission electron microscope, UHR-TEM LIBRA 200MC. The obtained results are shown in Figure 1b.

The SEM (Carl Zeiss NEON 40EsB, Iasi, Romania) analysis was conducted on a Carl Zeiss NEON 40EsB cross-beam system with thermal Schottky field emission emitter and accelerated Ga ions column. The SEM is connected to an EDS (energy dispersive x-ray spectroscope, Carl Zeiss NEON 40EsB, Iasi, Romania) unit which allows a characteristic X-ray spectrum to be displayed.

The XRD (BRUKER AXS D8-Advance X-ray Diffractometer, Iasi, Romania) measurements were conducted by means of a Powder X-ray diffractometer equipped, BRUKER AXS D8-Advance X-ray Diffractometer, with a Cu X-ray source with a wavelength $\lambda = 1.5406$ Å. The powder diffraction covered the $10° < 2\theta < 90°$ range with 0.02° steps.

3. Results

3.1. Density

Figure 5 shows the change in the values of density 1 day from casting to the day of testing. The values of the density represent the mean value of nine determinations. Minor variations, less than 0.6%, were observed between the two sets of values. This would suggest a geometrical stability of the specimens and the fact that the available mixing water was replaced by cement hydration products. Similar trends were reported in the scientific literature for cement mortar incorporating superabsorbent polymers [32]. The influence of the SDS surfactant on the values of density is significant with a 20% decrease compared to the reference mix. This may be due to the increased porosity of the hardened mortar, as reported in the scientific literature [33]. As previously mentioned, no anti-foaming agent was used in the CNT mix. For the CNT2 mix, where the anti-foaming agent was used, the density was similar to the reference mix and CBN mix. The value was 5.43% and 6.26% smaller compared to the reference mix and CBN mix, respectively. The influence of the surfactant on the density of mortar could not be entirely reduced by the use of tributyl phosphate.

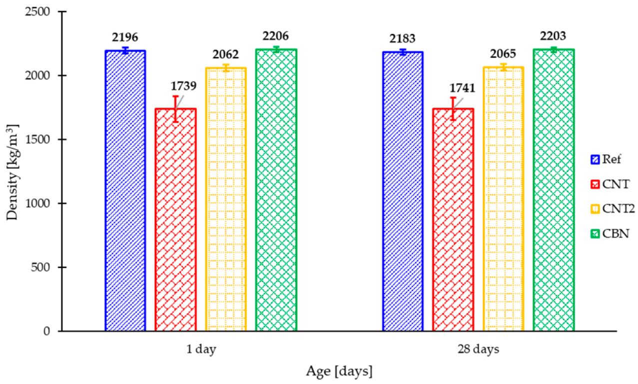


Figure 5. Density of mortar mixes.

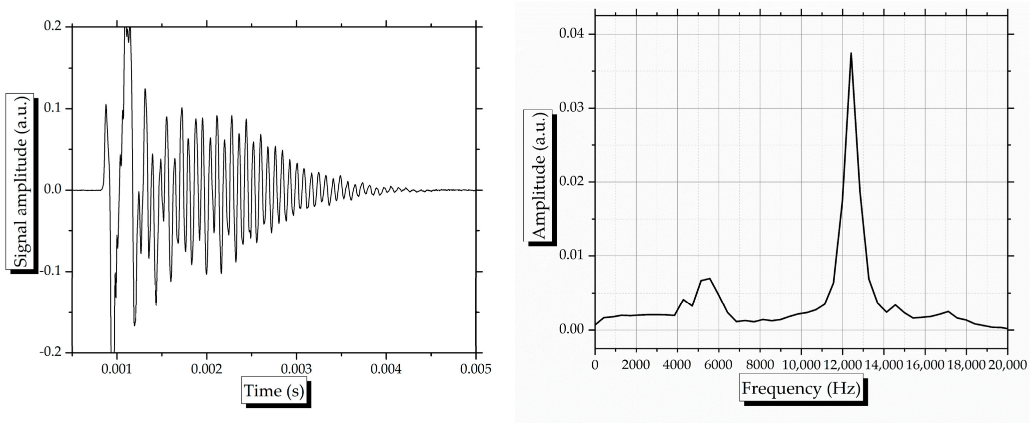
The error bars presented in Figure 5, representing the standard deviation from the mean value, show that there was a larger scattering of the values of density for the CNT mix compared to the other three mixes. This would suggest either a non-uniform distribution of the MWCNTs in the mortar mix or a non-uniform pore distribution. Using an anti-foaming agent reduced the scattering and led to an increase in the value of density for the CNT2 mix. In general, the scattering of the results decreased with the increase in the curing age of the mortar.

Considering the error bars for both CNT2 and CBN mixes, it can be concluded that: (a) in the case of the CNT2 mix, the use of surfactant and sonication procedure ensured a uniform distribution of the MWCNTs in the mortar mix. Additionally, the use of an anti-foamer led to an improvement in the material structure by reducing the number of pores in the mix. (b) The use of the new, modified, MWCNTs in the CBN mix, without surfactant and sonication procedure, proved to be effective in obtaining a uniform structure of the mortar mix.

3.2. Dynamic Modulus of Elasticity

The determination of the dynamic modulus of elasticity was based on the first resonant frequency of the prismatic specimen which was determined by means of the impact echo method. It was determined on all nine prisms for each of the four mixes shown in Table 2. For each prism, at least four determinations were conducted to check for the consistency of the recorded data. The values of the dynamic modulus of elasticity may offer insightful information in terms of the quality of the investigated material, be it mortar, concrete or any other material. Low values of the dynamic modulus of elasticity may indicate internal damages of the material or a large number of voids/pores. Considering the shape of Equation (1), this would also be reflected in the values for the density of the material.

The free vibration response of all specimens (nine for each of the mix proportions presented in Table 2) was recorded, as shown in Figure 6a for the Ref mix, using the experimental set-up presented and considerations described in [34]. The fast Fourier transform (FFT) was applied to the recorded signal in order to obtain the response spectrum of the specimens, as shown in Figure 6b. The latter was used to assess the fundamental longitudinal frequency of vibration for each specimen. For each prism, at least four measurements were considered from which the fundamental frequency of vibration was calculated as the average value.



(**a**) (**b**)

Figure 6. Free damped vibration response of Ref mix: (**a**) recorded signal; (**b**) response spectrum.

The obtained dynamic moduli of elasticity are presented in Figure 7. It can be observed that the influence of the SDS surfactant is very important, and it results in a sharp decrease in the value of E_d, by as much as 55%, compared to the reference mix. The obtained result is consistent with the already observed trend in terms of density, as shown in Figure 5, as well as the values for the fundamental frequency of vibration.

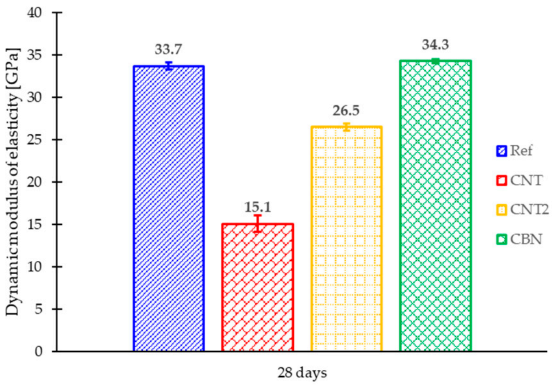


Figure 7. Dynamic modulus of elasticity.

Using an anti-foaming agent led to an increase in the value of the dynamic modulus of elasticity, compared to the mix where only SDS was used, but the obtained value was still lower than that of the reference sample. The decrease, in this case, was 21.36%, still significant considering the benefits one expects from using CNTs. However, taking into account the small percentage of CNTs, the trend observed for the density, and considering the shape of Equation (1), the obtained values of the modulus of elasticity exhibit the same pattern.

On the other hand, a small addition of the new CBN, 0.025% of the cement mass, resulted in a 1.78% increase in the value of the dynamic modulus of elasticity. This is not a very impressive increase but considering the production process of CBN coupled with the fact that there was no need for using surfactant and ultra-sonication procedure, the obtained results are encouraging.

The fact that the value of the modulus of elasticity increased for the CBN mix with respect to the Ref mix suggests that the new MWCNTs were uniformly dispersed in the mortar volume and contributed to achieving a better bond between the sand and the cement paste, as earlier studies suggested [35].

3.3. Flexural Strength

The obtained results from three-point bending tests on nine prisms for each mix proportion are shown in Figure 8. The use of surfactant without an anti-foaming agent results in a significant decrease, 53.83%, in the value of the flexural strength for the CNT mix compared to the Ref one. On the other hand, the use of new CBN results in an 18.76% increase in flexural strength compared to the reference mix. Similar trends, although by a much smaller percentage, were reported in the scientific literature for the same MWCNT dosage in the case of cement pastes [27]. The contribution of both MWCNTs and the new CBN in bridging the micro-cracks in the matrix is quite important, especially in the case of a CNT mix where the pore volume is expected to be large.

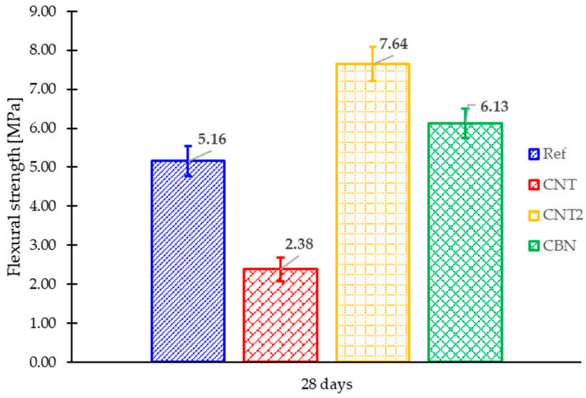


Figure 8. Flexural strength of mortars.

The use of an anti-foaming agent reduced the porosity of the samples which was reflected in the values obtained for the density. Since CNTs are longer than CBNs, they are more effective in bridging the micro-cracks and preventing their further development [11,36,37]. This would explain the higher value obtained for the flexural tensile strength of the CNT2 mix compared to the values of reference and CBN mixes.

3.4. Compressive Strength

The values of the compressive strength were assessed from 18 determinations for each considered mix presented in Table 2. The resulting parts of prisms after the flexural tests were examined for visible cracks and then subjected to uniaxial compression tests. Figure 9 summarizes the obtained results. The trend was similar to what was already observed in the case of dynamic modulus of elasticity and flexural strength.

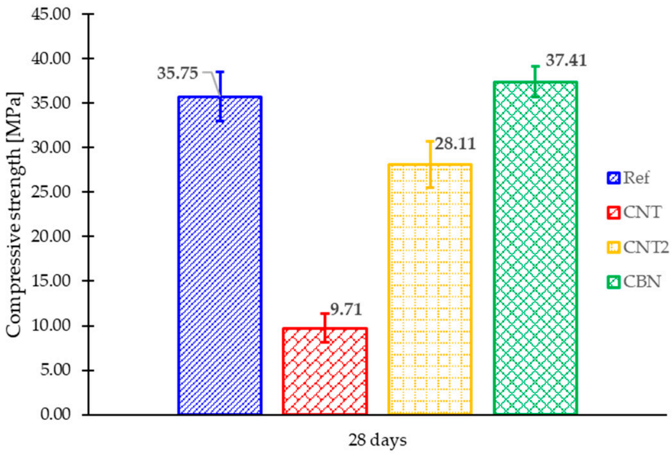
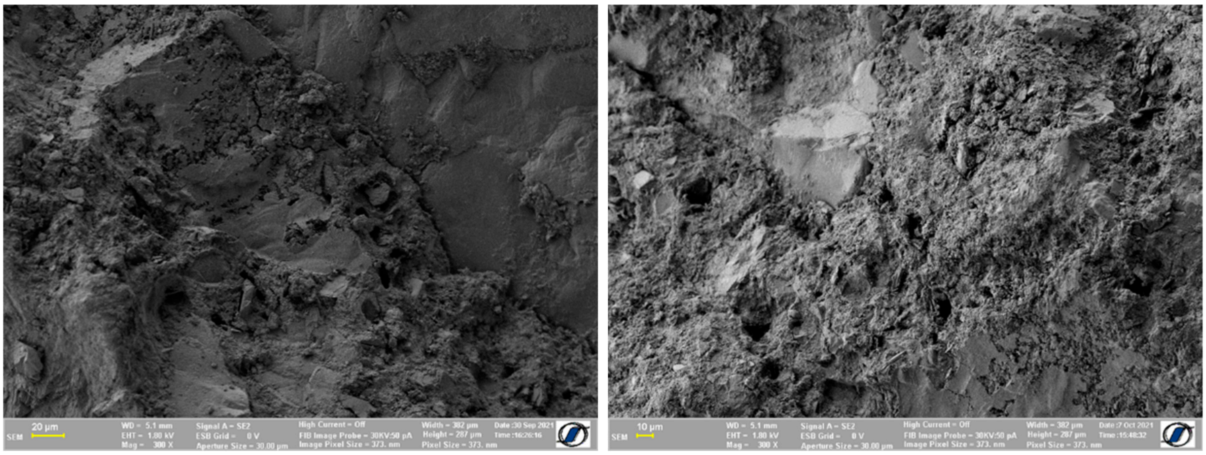


Figure 9. Compressive strength of mortars.

The compressive strength seems to be the most affected material property by the use of SDS surfactant and in the absence of anti-foaming agents. Increased porosity was also reported in the scientific literature when MWCNTs were used, even in the presence of foam reducing admixtures [33,38]. As with previously reported results, the values of the compressive strength for the CNT2 mix was lower than that of both the reference and the CBN mixes. The use of new CBN results in a 4.64% increase in the compressive strength compared to the reference mix.

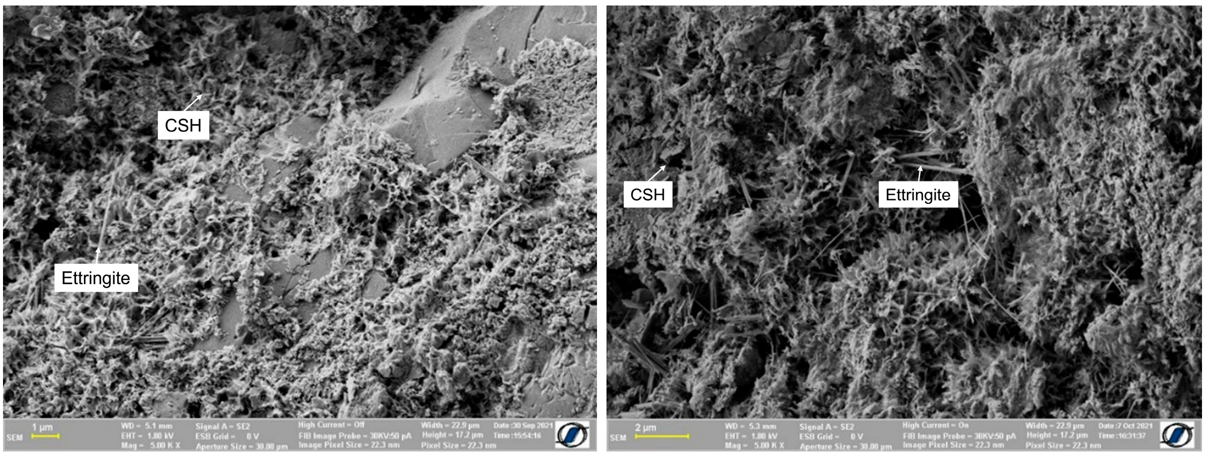
4. Discussions

Figure 10 presents the magnified view of the CBN mix as compared to the Ref mix. As it can be seen, the CBN mortar shows a more compact structure whereas in the Ref mix a more pronounced pore concentration was observed. Upon a higher magnification factor, 5000×, Figure 11, the CSH gels in both mixes became more evident. The Ref mix exhibited a less organized and more porous arrangement of the ettringite needles in the structure.



(a) (b)

Figure 10. Structure of mortars at 300× magnification factor: (**a**) CBN mix; (**b**) Ref mix.



(a) (b)

Figure 11. Structure of mortars at 5000× magnification factor: (**a**) CBN mix; (**b**) Ref mix.

This offers a possible explanation of the improved mechanical properties of the CBN mix even for a very low percentage of nanotubes of only 0.025%. Similar observations were found in the scientific literature but for longer MWCNTs used together with surfactants and anti-foaming agents [25]. The CBNs that were used in the present study helped attain the same level of performance of the mortar mix but without the need of using surfactant and ultra-sonication procedures. Their geometry and structure had an impact on the macro-scale properties of mortar [39].

The use of MWCNTs with SDS surfactant resulted both in the increase in porosity as well as promoting the hydration reaction. Figure 12 shows CH (calcium hydroxide) hexagonal crystals as well as ettringite needles formed in a porous structure. Such a porous structure has an impact on the values of both elastic and mechanical properties of the CNT mix for which both SDS surfactant was used as well as ultra-sonication procedure in order to ensure a uniform distribution within the aqueous solution of the MWCNTs.

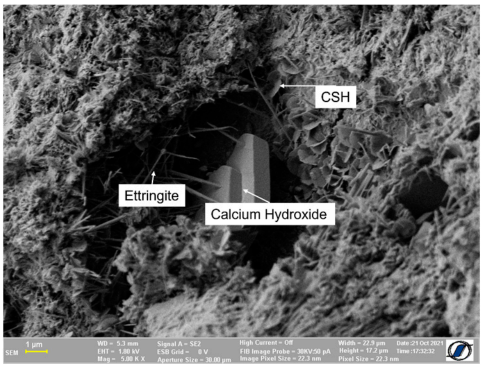


Figure 12. SEM image of the CNT mortar structure.

The XRD patterns of the three mixes are shown in Figure 13. Comparing the patterns leads to the conclusion that the introduction of nano-tubes promoted the development of additional crystallographic phases, with a different orientation of SiO_2 in the case of CNT mix compared to the Ref mix (at 2 theta = ~22 degrees) as well as in the case of CBN mix (at 2 theta = ~26 degrees).

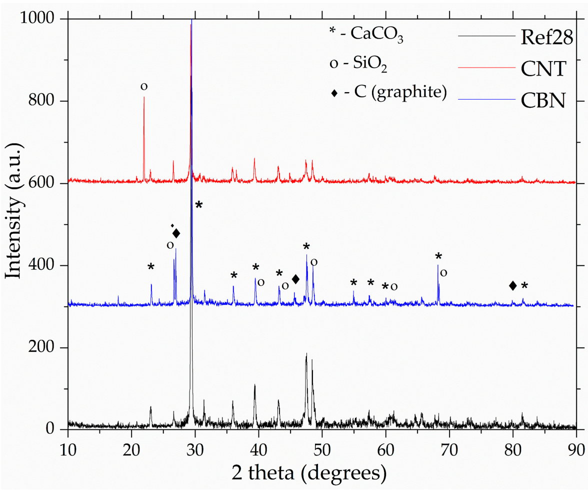


Figure 13. XRD patterns of mortars.

Table 3 presents the summary of the collected data during the preliminary stages of the research. It can be observed that the largest scattering of the results was obtained for the CNT mix with SDS surfactant and without an anti-foaming agent. Taking into account the material structure presented in Figure 12, the large number of pores induced by the SDS solution severely impacted the strength characteristics of the mortar.

On the other hand, the Ref, CNT2, and CBN mixes show a much lower scattering of the results, with respect to the median value owing to a more compact structure and to the use of the anti-foaming agent in the case of the CNT2 mix. The new type of MWCNTs provide a better material structure, are able to bridge the nano-cracks more efficiently [10,11,36,37] and thus resulting in overall better elastic and mechanical properties compared to the reference mix. The use of CNTs with an anti-foaming agent resulted in higher values of flexural tensile strength owing to longer CNTs that were able to bridge the cracks more effectively compared to CBNs.

Table 3. Statistical characterization of the experimental data (mean value ± standard deviation).

Mix	Density	Dynamic Modulus of Elasticity	Compressive Strength	Flexural Strength
	[kg/m^3]	[GPa]	[MPa]	[MPa]
Ref	**2183** ± 20.76 COV = 0.95	**33.7** ± 0.35 COV = 1.04	**35.75** ± 2.74 COV = 7.66	**5.16** ± 0.39 COV = 7.51
CNT	**1741** ± 85.62 COV = 4.92	**15.1** ± 1.03 COV = 6.82	**9.71** ± 1.64 COV = 16.84	**2.38** ± 0.31 COV = 12.95
CNT2	**2065** ± 24.17 COV = 1.17	**26.5** ± 0.44 COV = 1.67	**28.11** ± 2.62 COV = 9.34	**7.64** ± 0.44 COV = 5.70
CBN	**2203** ± 17.55 COV = 0.8	**34.3** ± 0.65 COV = 1.89	**37.41** ± 1.69 COV = 4.51	**6.13** ± 0.38 COV = 6.23

Taking into account that, in the case of the CBN mix, there was no SDS added to the mix and that the ultra-sonication procedure was not applied, the obtained results warrant further investigations on the effect of the new type of MWCNTs on the properties of cement-based materials. Lower values for standard deviations as well as coefficient of variation suggest that a uniform distribution of the carbon-based nano-tubes was achieved without the help of classical, by now, methods.

5. Conclusions

Based on the obtained results from the laboratory investigations, the following conclusions can be drawn:

1. A new type of MWCNT was developed which has a similar structure to the SWCNTs in the sense that it is capped at both ends. The aspect ratio is smaller compared to "traditional" MWCNTs which results in a better bridging effect of the nano-cracks and a denser material structure compared to the reference mix. However, "traditional" MWCNTs are better in that aspect due to their increased lengths.
2. The new type of MWCNT achieved a uniform dispersion within the mortar mix, proven by consistently lower values of standard deviations and coefficients of variation for each of the investigated parameters. The data are even more encouraging and suggest that further research should be conducted in this direction taking into account that they are produced using the same technology applied for MWCNTs but the use of surfactants and, consequently, of anti-foaming agents is no longer necessary. Moreover, the ultra-sonication procedure required to ensure the distribution of nano-tubes within the aqueous solution, which should be carefully applied in case of long MWCNTs, is also not necessary.
3. The data are however limited to a rather small number of specimens and should be completed by large-scale laboratory investigations where significantly larger datasets should be collected before more generally valid conclusions could be drawn.
4. The improvement of mechanical properties of mortar using the new type of MWCNT is small, 18.76% in the case of flexural strength and only 4.64% in the case of compressive strength. However, these improvements were achieved with a very small percentage of CNTs in the mix, 0.025% by mass of cement. Additional percentages should be considered, and observations should be made as to whether or not the highlighted trends at this stage of the research are confirmed. Last but not least, durability studies should be conducted in order to assess the behavior of the mortar mixes to different types of chemical attacks and weathering conditions.

Author Contributions: Conceptualization, I.-O.T., S.-M.A.-S. and I.-A.G.; methodology, I.-O.T., S.-M.A.-S., G.S. and I.-A.G.; validation, I.-O.T., D.C. and A.-M.T.; formal analysis, S.-M.A.-S., G.S. and I.-A.G.; investigation, S.-M.A.-S., G.S., I.-A.G., A.-M.T., D.C. and I.-O.T.; resources, G.S. and I.-A.G.; data curation, I.-O.T.; writing—original draft preparation, S.-M.A.-S., G.S., I.-A.G. and A.-M.T.; writing—review and editing, D.C. and I.-O.T.; supervision, S.-M.A.-S. and I.-O.T.; project administration, S.-M.A.-S. and I.-O.T.; funding acquisition, I.-O.T. All authors have read and agreed to the published version of the manuscript.

Funding: The APC was funded by The "Gheorghe Asachi" Technical University of Iasi.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this research are available, upon request, from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Irshidat, M.R.; Al-Saleh, M.H. Thermal performance and fire resistance of nanoclay modified cementitious materials. *Constr. Build. Mater.* **2018**, *159*, 213–219. [CrossRef]
2. Moro, C.; Francioso, V.; Velay-Lizancos, M. Nano-TiO_2 effects on high temperature resistance of recycled mortars. *J. Clean. Prod.* **2020**, *263*, 121581. [CrossRef]
3. Nuaklong, P.; Boonchoo, N.; Jongvivatsakul, P.; Charinpanitkul, T.; Sukontasukkul, P. Hybrid effect of carbon nanotubes and polypropylene fibers on mechanical properties and fire resistance of cement mortar. *Constr. Build. Mater.* **2021**, *275*, 122189. [CrossRef]
4. Zhan, P.; He, Z.; Ma, Z.; Liang, C.; Zhang, X.; Abreham, A.A.; Shi, J. Utilization of nano-metakaolin in concrete: A review. *J. Build. Eng.* **2020**, *30*, 101259. [CrossRef]
5. Zhang, M.; Zhu, X.; Liu, B.; Shi, J.; Gencel, O.; Ozbakkaloglu, T. Mechanical property and durability of engineered cementitious composites (ECC) with nano-material and superabsorbent polymers. *Powder Technol.* **2022**, *409*, 117839. [CrossRef]
6. Song, H.; Li, X. An Overview on the Rheology, Mechanical Properties, Durability, 3D Printing, and Microstructural Performance of Nanomaterials in Cementitious Composites. *Materials* **2021**, *14*, 2950. [CrossRef]
7. Gdoutos, E.E.; Konsta-Gdoutos, M.S.; Danoglidis, P.A. Portland cement mortar nanocomposites at low carbon nanotube and carbon nanofiber content: A fracture mechanics experimental study. *Cem. Concr. Compos.* **2016**, *70*, 110–118. [CrossRef]
8. Song, C.; Hong, G.; Choi, S. Effect of dispersibility of carbon nanotubes by silica fume on material properties of cement mortars: Hydration, pore structure, mechanical properties, self-desiccation, and autogenous shrinkage. *Constr. Build. Mater.* **2020**, *265*, 120318. [CrossRef]
9. da Silva Andrade Neto, J.; Santos, T.A.; de Andrade Pinto, S.; Dias, C.M.R.; Ribeiro, D.V. Effect of the combined use of carbon nanotubes (CNT) and metakaolin on the properties of cementitious matrices. *Constr. Build. Mater.* **2021**, *271*, 121903. [CrossRef]
10. Lee, H.S.; Balasubramanian, B.; Gopalakrishna, G.V.T.; Kwon, S.-J.; Karthick, S.P.; Saraswathy, V. Durability performance of CNT and nanosilica admixed cement mortar. *Constr. Build. Mater.* **2018**, *159*, 463–472. [CrossRef]
11. Siddique, R.; Mehta, A. Effect of carbon nanotubes on properties of cement mortars. *Constr. Build. Mater.* **2014**, *50*, 116–129. [CrossRef]
12. Jarolim, T.; Labaj, M.; Hela, R.; Michnova, K. Carbon nanotubes in cementitious composites: Dispersion, implementation, and influence on mechanical characteristics. *Adv. Mater. Sci. Eng.* **2016**, *2016*, 7508904. [CrossRef]
13. Madni, I.; Hwang, C.-Y.; Park, S.-D.; Choa, Y.-H.; Kim, H.-T. Mixed surfactant system for stable suspension of multiwalled carbon nanotubes. *Colloids Surf. A Physicochem. Eng. Asp.* **2010**, *358*, 101–107. [CrossRef]
14. Torabian Isfahani, F.; Li, W.; Redaelli, E. Dispersion of multi-walled carbon nanotubes and its effects on the properties of cement composites. *Cem. Concr. Compos.* **2016**, *74*, 154–163. [CrossRef]
15. Chaipanich, A.; Nochaiya, T.; Wongkeo, W.; Torkittikul, P. Compressive strength and microstructure of carbon nanotubes–fly ash cement composites. *Mater. Sci. Eng. A* **2010**, *527*, 1063–1067. [CrossRef]
16. Coppola, L.; Cadoni, E.; Forni, D.; Buoso, A. Mechanical characterization of cement composites reinforced with fiberglass, carbon nanotubes or glass reinforced plastic (GRP) at high strain rates. *Appl. Mech. Mater.* **2011**, *82*, 190–195. [CrossRef]
17. Sobolkina, A.; Mechtcherine, V.; Khavrus, V.; Maier, D.; Mende, M.; Ritschel, M.; Leonhardt, A. Dispersion of carbon nanotubes and its influence on the mechanical properties of the cement matrix. *Cem. Concr. Compos.* **2012**, *34*, 1104–1113. [CrossRef]
18. Alafogianni, P.; Dassios, K.; Tsakiroglou, C.D.; Matikas, T.E.; Barkoula, N.M. Effect of CNT addition and dispersive agents on the transport properties and microstructure of cement mortars. *Constr. Build. Mater.* **2019**, *197*, 251–261. [CrossRef]
19. Tragazikis, I.K.; Dassios, K.G.; Exarchos, D.A.; Dalla, P.T.; Matikas, T.E. Acoustic emission investigation of the mechanical performance of carbon nanotube-modified cement-based mortars. *Constr. Build. Mater.* **2016**, *122*, 518–524. [CrossRef]

20. Abedi, M.; Fangueiro, R.; Correia, A.G. An effective method for hybrid CNT/GNP dispersion and its effects on the mechanical, microstructural, thermal, and electrical properties of multifunctional cementitious composites. *J. Nanomater.* **2020**, *2020*, 6749150. [CrossRef]
21. Parveen, S.; Rana, S.; Fangueiro, R.; Paiva, M.C. Characterizing dispersion and long term stability of concentrated carbon nanotube aqueous suspensions for fabricating ductile cementitious composites. *Powder Technol.* **2017**, *307*, 1–9. [CrossRef]
22. *SR EN 197-1*; Cement. Part I: Composition, Specifications and Conformity Criteria for Normal Use Cements. ASRO (Romanian Standards Association): București, Romania, 2011.
23. Inoue, Y.; Kakihata, K.; Hirono, Y.; Horie, T.; Ishida, A.; Mimura, H. One-step grown aligned bulk carbon nanotubes by chloride mediated chemical vapor deposition. *Appl. Phys. Lett.* **2008**, *92*, 213113. [CrossRef]
24. Alexa-Stratulat, S.-M.; Covatariu, D.; Toma, A.-M.; Rotaru, A.; Covatariu, G.; Toma, I.-O. Influence of a novel carbon-based nano-material on the thermal conductivity of mortar. *Sustainability* **2022**, *14*, 8189. [CrossRef]
25. Shao, H.; Chen, B.; Li, B.; Tang, S.; Li, Z. Influence of dispersants on the properties of CNTs reinforced cement-based materials. *Constr. Build. Mater.* **2017**, *131*, 186–194. [CrossRef]
26. Mohsen, M.O.; Alansari, M.; Taha, R.; Senouci, A.; Abutaqa, A. Impact of CNTs' treatment, length and weight fraction on ordinary concrete mechanical properties. *Constr. Build. Mater.* **2020**, *264*, 120698. [CrossRef]
27. Xu, S.; Liu, J.; Li, Q. Mechanical properties and microstructure of multi-walled carbon nanotube-reinforced cement paste. *Constr. Build. Mater.* **2015**, *76*, 16–23. [CrossRef]
28. Morsy, M.S.; Alsayed, S.H.; Aqel, M. Hybrid effect of carbon nanotube and nano-clay on physico-mechanical properties of cement mortar. *Constr. Build. Mater.* **2011**, *25*, 145–149. [CrossRef]
29. Wang, B.; Han, Y.; Liu, S. Effect of highly dispersed carbon nanotubes on the flexural toughness of cement-based composites. *Constr. Build. Mater.* **2013**, *46*, 8–12. [CrossRef]
30. *ASTM C215-14*; Standard Test Method for Fundamental Transverse, Longitudinal, and Torsional Resonant Frequencies of Concrete Specimens. ASTM International: West Conshohocken, PA, USA, 2014.
31. *SR EN 196-1*; Methods of Testing Cement—Part 1: Determination of Strength. ASRO (Romanian Standards Association): București, Romania, 2016.
32. Jamnam, S.; Sua-iam, G.; Maho, B.; Pianfuengfoo, S.; Sappakittipakorn, M.; Zhang, H.; Limkatanyu, S.; Sukontasukkul, P. Use of cement mortar incorporating superabsorbent polymer as a passive fire-protective layer. *Polymers* **2022**, *14*, 5266. [CrossRef]
33. Hu, S.; Xu, Y.; Wang, J.; Zhang, P.; Guo, J. Modification effects of carbon nanotube dispersion on the mechanical properties, pore structure, and microstructure of cement mortar. *Materials* **2020**, *13*, 1101. [CrossRef]
34. Alexa-Stratulat, S.M.; Covatariu, D.; Toma, I.O.; Covatariu, G. Computation and experimental considerations on dynamic testing of cement mortar. *IOP Conf. Ser. Mater. Sci. Eng.* **2021**, *1141*, 012019. [CrossRef]
35. Hawreen, A.; Bogas, J.A.; Dias, A.P.S. On the mechanical and shrinkage behavior of cement mortars reinforced with carbon nanotubes. *Constr. Build. Mater.* **2018**, *168*, 459–470. [CrossRef]
36. Guo, J.; Yan, Y.; Wang, J.; Xu, Y. Strength analysis of cement mortar with carbon nanotube dispersion based on fractal dimension of pore structure. *Fractal Fract.* **2022**, *6*, 609. [CrossRef]
37. Chen, J.; Akono, A.-T. Influence of multi-walled carbon nanotubes on the hydration products of ordinary Portland cement paste. *Cem. Concr. Res.* **2020**, *137*, 106197. [CrossRef]
38. Li, Q.; Liu, J.; Xu, S. Progress in research on carbon nanotubes reinforced cementitious composites. *Adv. Mater. Sci. Eng.* **2015**, *2015*, 307435. [CrossRef]
39. Mohsen, M.O.; Taha, R.; Abu Taqa, A.; Al-Nuaimi, N.; Al-Rub, R.A.; Bani-Hani, K.A. Effect of nanotube geometry on the strength and dispersion of CNT-cement composites. *J. Nanomater.* **2017**, *2017*, 6927416. [CrossRef]