coatings

MDPI

Article

The Effect of Multi-Walled Carbon Nanotubes on the Compressive Strength of Cement Mortars

Nelli G. Muradyan [1], Harutyun Gyulasaryan [2], Avetik A. Arzumanyan [1], Maria M. Badalyan [1], Marine A. Kalantaryan [1], Yeghiazar V. Vardanyan [1], David Laroze [3], Aram Manukyan [2] and Manuk G. Barseghyan [1,*]

1 The Educational, Scientific and Experimental Laboratory on Building Materials and Items, National University of Architecture and Construction of Armenia, 105 Teryan Street, Yerevan 0009, Armenia
2 Laboratory for Solid State Physics, Institute for Physical Research, NAS RA, Ashtarak 0204, Armenia
3 Instituto de Alta Investigación, CEDENNA, Universidad de Tarapacá, Casilla 7D, Arica 1000000, Chile
* Correspondence: manuk.barseghyan@nuaca.am or manuk.g.barseghyan@gmail.com

Abstract: In this work, multi-walled carbon nanotubes (MWCNTs) have been synthesized using a modified method of solid-phase pyrolysis. The MWCNTs are effectively dispersed using a simple and facile method such as ultrasonic energy without and with surfactant for two different sonication times (15 min and 40 min). In the present study, the effect of MWCNT concentration (0.001, 0.01, 0.05, 0.1 wt.%) on the compressive strengths of cement mortars has been investigated. Compressive tests were carried out on an automatic pressure machine (C089) with a loading rate of 0.5 kN/s at the age of 7 days and 28 days. It is shown that the optimal value of the nanotubes' concentration does not exist in the case of 15 min of sonication time, whereas the optimal value for 40 min of sonication time without and with surfactant is 0.01%. Moreover, in the absence of surfactants, the strength of the specimen over 7 days of hardening increased by 13%, and by 19.5% in the presence of surfactants. The compressive strength for a curing period of 28 days increased by 6.3% and 13.8%, respectively.

Keywords: carbon nanotubes; sonication time; surfactant; compressive strength; cement mortar

check for updates

Citation: Muradyan, N.G.; Gyulasaryan, H.; Arzumanyan, A.A.; Badalyan, M.M.; Kalantaryan, M.A.; Vardanyan, Y.V.; Laroze, D.; Manukyan, A.; Barseghyan, M.G. The Effect of Multi-Walled Carbon Nanotubes on the Compressive Strength of Cement Mortars. *Coatings* **2022**, *12*, 1933. https://doi.org/10.3390/coatings12121933

Academic Editor: Peng Liu

Received: 17 October 2022
Accepted: 9 November 2022
Published: 8 December 2022

1. Introduction

Due to the increasing demand for high-performance cement composites, the properties of cement composites, such as architectural versatility, excellent mechanical properties, and durability, have been undergoing continuous improvements [1].

To this end, in the literature, various agricultural wastes [2,3], industrial wastes [4,5], natural minerals [6], and synthetic materials [7] have been successfully incorporated. These binders exhibited enhancement in the fresh, mechanical, durability, shrinkage, and microstructural properties of construction products. One such material sparingly used in the literature is carbon nanotubes (CNTs).

CNTs can be considered as seamless cylinders formed of one or more graphene roll sheets and can be classified based on the number of graphene layers [8]. Based on the number of graphene layers, there are two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [9]. MWCNTs comprise manifold-wrapped graphene sheets arranged in concentric hollow tubes with outside diameters ranging from 2 nm to 100 nm [10]. High modulus of elasticity (≥1 TPa), outstanding tensile strength (65–93 GPa), excellent thermal conductivity (two times more than that of a diamond), high aspect ratio (100–2500), and excellent electrical conductivity are the physical and mechanical characteristics of MWCNTs [11].

The use of CNTs in Portland cement matrices applied in civil engineering has a significant potential to enhance the mechanical properties of composites [12–14]. MWCNTs are used more frequently than SWCNTs because of their lower manufacturing costs and improved reinforcement. According to Lai and Basem [15], adding 0.25 percent MWCNTs to cement mass increased the flexural and tensile strengths of cement-based mortars by 25%. Using small amounts of MWCNTs at 0.08%, the authors reported enhanced flexural strength of 25% [16]. According to Jeevanagoudar et.al [17], MWCNT-reinforced mortars exhibit improved engineering properties compared to ordinary mortars. In particular, it has been discovered that 0.4 percent is the optimum concentration of MWCNT concentration in order to get the highest compressive strength.

CNTs' optimal dispersion is one of the important factors for the preparation of enhanced cement-based composite materials. There are two main methods for dispersing nanotubes: mechanical and chemical [18,19]. In this work, the dispersion of nanotubes by mechanical, in particular ultrasonication, method has been carried out. It is worth noting that the ultrasonication efficiency for MWCNT dispersion depends on many factors, including duration, sonicator type, energy, temperature, and the properties of MWCNTs [20–23]. Due to their high surface energy, MWCNTs have a tendency towards agglomeration, which may lead to the creation of week zones in the final product. By using surfactants, the efficiency of sonication increases; as a result, a more uniform dispersion of MWCNTs in cementitious matrices can be seen [24].

The effect of the concentration of MWCNTs synthesized by different methods, the duration of sonication, and the use of surfactants on the mechanical properties of cement-based materials, particularly cement mortar, still requires further investigation.

In the present work, the effects of concentration of MWCNTs, duration of sonication, and the use of surfactants on the compressive strength of cement-based mortar were investigated.

2. Experiment

2.1. Materials

Ordinary Portland cement 52.5 (GOST 31108-2020, which is available in Araratcement Factory, Yerevan, Armenia) has been used as a binder in the mortars within the framework of this study. The short MWCNTs have been synthesized (Figure 1) using a modified method of solid-phase pyrolysis of cobalt phthalocyanine. The pyrolysis was carried out in a closed quartz ampoule at a temperature of 900 °C and a duration of 30 min using pyrolysis analogs of Ni and Fe phthalocyanines [25,26]. The physical properties and the chemical composition of the used cement [27] (GOST EN 196-1-2002, 196-2-2002, 196-3-2002) are shown in Table 1, while the physical properties of the used sand are shown in Table 2.

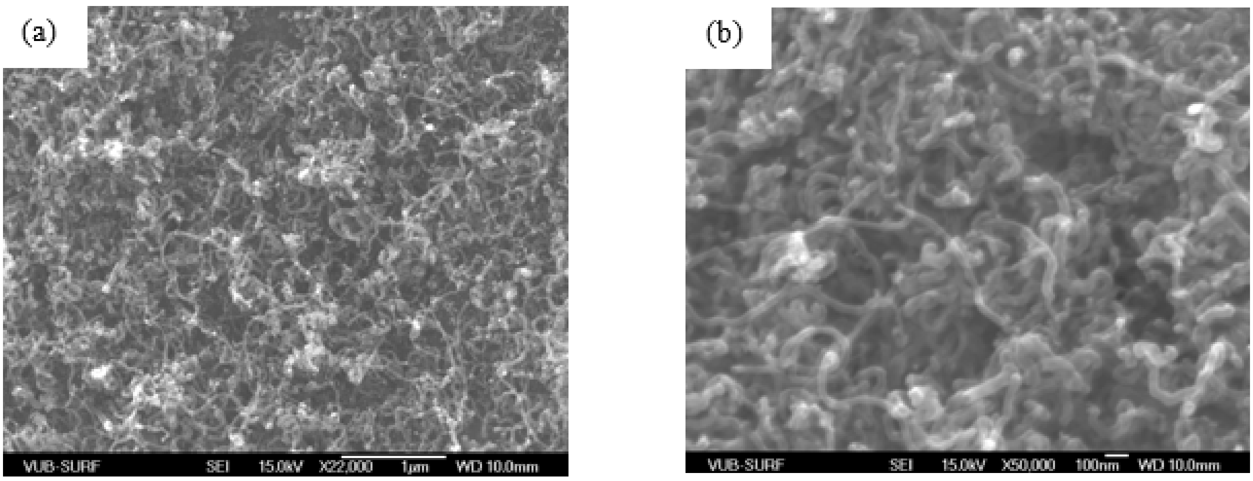

Figure 1. Scanning electron microscope (SEM) images (**a**) × 22,000 (**b**) × 50,000 of MWCNTs.

Table 1. Physical properties and chemical composition of cement.

<table>
<tr><th colspan="3">Characteristics</th><th colspan="3">Days</th><th colspan="3">Results Obtained</th></tr>
<tr><td colspan="3">Standard consistency (%)</td><td colspan="3">-</td><td colspan="3">31</td></tr>
<tr><td colspan="3">Specific gravity (g/sm^3)</td><td colspan="3">-</td><td colspan="3">3.1</td></tr>
<tr><td colspan="3">Blain’s fineness (m^2/kg)</td><td colspan="3">-</td><td colspan="3">354.8</td></tr>
<tr><td colspan="3" rowspan="3">Compressive strength (MPa) (EN 196-1)</td><td colspan="3">3 days</td><td colspan="3">23</td></tr>
<tr><td colspan="3">7 days</td><td colspan="3">38</td></tr>
<tr><td colspan="3">28 days</td><td colspan="3">52</td></tr>
<tr><td colspan="3" rowspan="2">Setting time (min)</td><td colspan="3">Initial</td><td colspan="3">60</td></tr>
<tr><td colspan="3">Final</td><td colspan="3">330</td></tr>
<tr><td colspan="9">Chemical composition of cement (wt.%)</td></tr>
<tr><td>Al_2O_3</td><td>SiO_2</td><td>Fe_2O_3</td><td>CaO</td><td>MgO</td><td>SO_3</td><td>Loss of Ignition</td><td>Insol. Resid.</td><td>Free CaO</td></tr>
<tr><td>3.21</td><td>23.2</td><td>1.25</td><td>57.5</td><td>5.1</td><td>2.9</td><td>3.7</td><td>2.1</td><td>1.13</td></tr>
</table>

Table 2. Physical properties of sand and MWCNTs.

Sand	**Fineness Modulus 2.43**	**Specific Gravity 2.17**	**Zone II**	**Bulk Density in Compact State (kg/m^3) 1829**	**Bulk Density in Loose State (kg/m^3) 1609**
MWCNTS	Outer diameter 40–50 nm	Length < 1 μm	Purity > 90%		

2.2. Dispersion of MWCNTs

Many researchers have reported MWCNT dispersion using various techniques. In this work, MWCNTs, in the required amount, were mixed with water and stirred continuously to ensure proper mixing. Two different sonication times were considered (15 min and 40 min). The sonication process is conducted at room temperature using the ultrasonic device UP400S. In the present investigation, DISPERBYK 199 was also used in order to increase the efficiency of the MWCNT dispersion process in the water. A similar procedure was followed for solutions containing different wt.% of MWCNT content (0.001, 0.01, 0.05, 0.1).

2.3. Mixing and Sample Preparation

The w/c ratio used in the present work was 0.47, and the cement to sand proportion used was 1:4. First, cement and sand were mixed (E095 Mortar mixer, Matest, Treviolo, Italy) for 2.0 min, then the MWCNTS/water mixture was added and mixed for 5 min. The size of the molds were 40 mm × 40 mm × 160 mm. The mortar was compacted through a vibration machine (C278 Vibrating table, Matest, Treviolo, Italy) for 30 s. Similarly, a series of mortars and the one without different MWCNT contents (0.001%, 0.01%, 0.05%, and 0.1% by weight of cement) were cast. The specimens were also prepared by adding in the MWCNTS/water surfactant DISPERBYK-199 (produced by company BYK, Wesel, Germany). The weights of the surfactants were 4.4, 44, 220, and 440 mg, respectively. After 24 h, the specimens were de-molded, and the mortar sample was immersed in water at 20 ± 0.2 °C temperature (Figure 2).

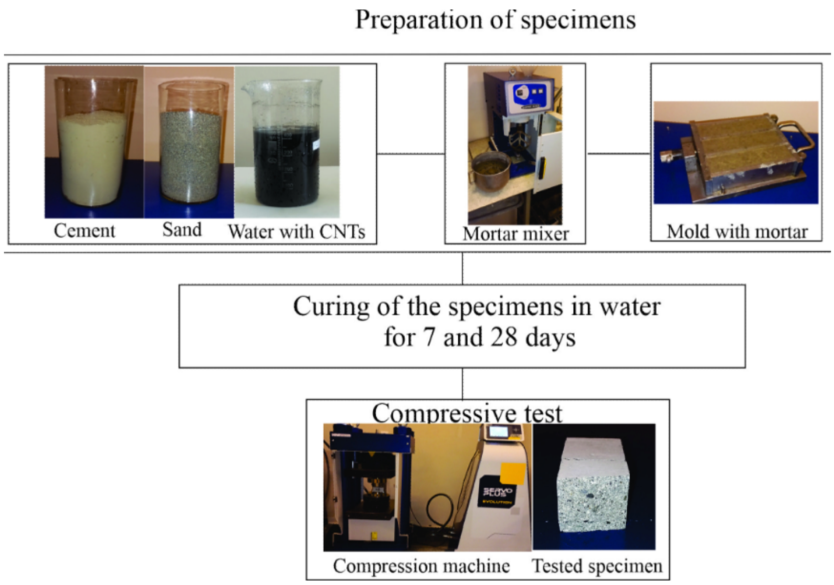

Figure 2. Diagram of the experimental procedure.

2.4. *Compressive Strength Testing*

Three cubes of each specimen were incidentally selected from each batch to test their average compressive strength according to the Concrete Compression Machine (Matest, Treviolo, Italy) 2000 kN automatic, Servo-Plus Progress (following the standard EN 196-1, and specimen sizes were 40 mm × 40 mm). Compressive tests were carried out on an automatic pressure machine (C089) (Matest, Treviolo, Italy) with a loading rate of 0.5 kN/s at the age of 7 days and 28 days.

3. Results and Discussions

First of all, the results obtained with 15 min sonication time and without surfactant are presented. Figure 3a,b show the compressive strength of the mortar with different wt.% of MWCNTs for 7 and 28 days, respectively. The results indicate that, for both cases of curing days of the cement mortar, the optimal value of MWCNT concentration does not exist. Furthermore, the compressive strength of the cement mortar in the presence of MWCNTs is lower than the compressive strength of the reference specimen. This can be explained due to the low-efficiency dispersion of the MWCNTs in the water, which will reduce the hydration degree. The results indicate that the compressive strength increases with increased curing period, which can be attributed to increased hydration with time.

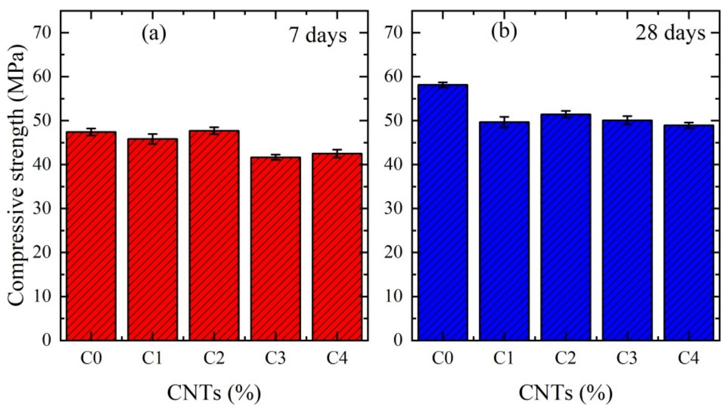

Figure 3. Compressive strength of cement mortars with different wt.% of MWCNTs. The results are for 15 min of sonication time without surfactant. (**a**) for 7 days, (**b**) for 28 days.

Figure 4a,b show the compressive strength of the mortar with different wt.% of MWCNTs for 7 and 28 days, respectively. C0, C1, C2, C3, and C4 correspond to the 0%, 0.001%, 0.01%, 0.05%, and 0.1% of MWCNTs, respectively. The results indicate that the compressive strength of each specimen increases as the curing period increases. This is associated with increased hydration over time. The addition of nanotubes with an appropriate concentration of MWCNTs leads to an increase in compressive strength. The compressive strength reaches the maximum value, then starts to decrease. In other words, the optimal value of the nanotube concentration at which the compressive strength for both cases of curing days reaches its maximum value was obtained. The indicated optimal value of nanotubes is 0.01 wt.%. This is due to the chosen composition of the mortar, as well as the physical and mechanical properties (structure and size) of nanotubes. It is known that in order to make the effect of nanotubes on the physical and mechanical properties of cement-based mortars or concretes effective, it is first necessary to ensure a homogeneous distribution of nanoparticles throughout the volume. For each case, with the increase of nanotube concentration, under the same conditions, the degree of homogeneous distribution decreases, as a result of which the compressive strength decreases. Elsewhere [17], the authors studied rather large values of nanotube concentration, and at 0.4 wt.% of MWCNTs the maximum compressive strength was found only for 28 days of curing (in this work for 7 curing days the optimal values of MWCNTs were not obtained). It can be seen from the figures that the strength of specimens with 7 curing days increased by 13%, and in the case of 28 curing days it increased by 6.3%.

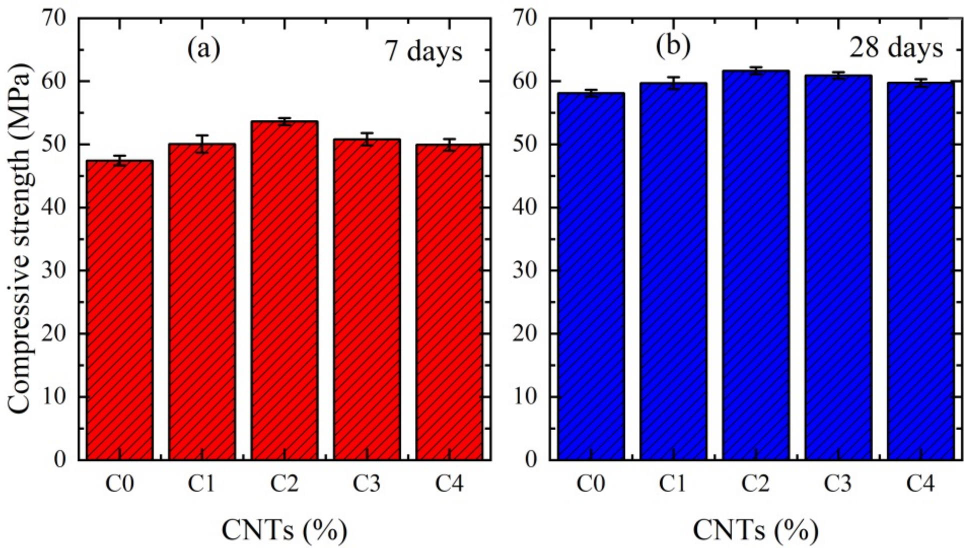

Figure 4. Compressive strength of cement mortars with different wt.% of MWCNTs. The results are for 40 min of ultrasonication time without surfactant. (**a**) for 7 days (**b**) for 28 days.

Figure 5a,b show the compressive strength of the mortar with different wt.% of MWCNTs for 7 and 28 days, respectively, when the surfactant in the MWCNT/water was added.

For both cases of curing days, the optimal values of the MWCNT concentration have been obtained at 0.01 wt.%. The improvement in the efficiency of the dispersion process of MWCNTs in the water brought an increase in the maximum value of the compressive strength. In particular, the strength of a sample with 7 curing days increased by 19.5%, and by 13.8% in the case of 28 curing days.

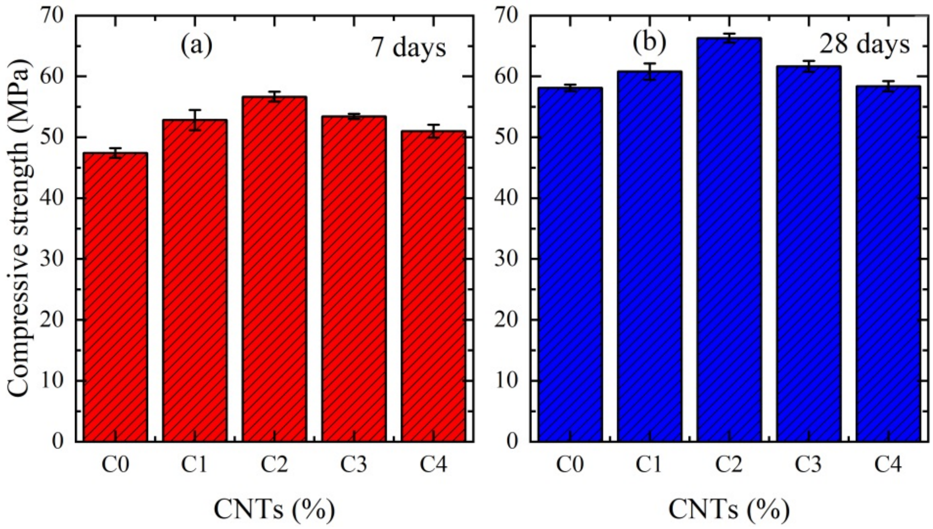

Figure 5. Compressive strength of cement mortars with different wt.% of MWCNTs. The results are for 40 min of ultrasonication time with surfactant. (**a**) for 7 days (**b**) for 28 days.

4. Conclusions

In the present research, the mechanical properties, such as compressive strength, of cement mortar with different concentrations of MWCNTs have been investigated. The sonication technique with and without surfactant, in particular DISPERBYK-199, was employed. For 15 min sonication time, the optimal values of MWCNT concentration to obtain maximum compressive strength do not exist, while in the case of 40 min of sonication it was found to be 0.01%, which is much less than the optimal value obtained in known works. In particular, in the absence of surfactants, the strength of the specimen over 7 days of hardening increased by 13%, and by 19.5% in the presence of surfactants. The compressive strength for a curing period of 28 days increased by 6.3% and 13.8%, respectively. Thus, the optimal mass of surfactants was found, and it was shown that when added to MWCNTs/water, the maximum value of compressive strength can increase by up to 7.5%.

Author Contributions: Conceptualization, M.M.B.; Data curation, N.G.M., H.G. and A.A.A.; Formal analysis, M.M.B., D.L., A.M. and M.G.B.; Funding acquisition, Y.V.V.; Investigation, N.G.M., H.G., A.A.A., M.M.B., M.A.K., A.M. and M.G.B.; Methodology, A.M.; Project administration, M.G.B.; Resources, M.A.K.; Supervision, Y.V.V.; Writing—original draft, A.A.A. and A.M.; Writing—review & editing, D.L. and M.G.B. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to acknowledge the financial support by the Science Committee of the Republic of Armenia (Project no. 21AG-1C008). D.L. acknowledges partial financial support from the Centers of excellence with BASAL/ANID financing, Grant AFB180001, CEDENNA.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

References

1. Xiao, J.; Han, N.; Li, Y.; Zhang, Z.H.; Shah, S.P. Review of recent developments in cement composites reinforced with fibers and nanomaterials. *Front. Struct. Civ. Eng.* **2021**, *15*, 1–19. [CrossRef]
2. Nasir, M.; Al-Kutti, W. Performance of Date Palm Ash as a Cementitious Material by Evaluating Strength, Durability, and Characterization. *Buildings* **2019**, *9*, 6. [CrossRef]
3. Nasir, M.; Al-Kutti, W.; Kayed, T.S.; Adesina, A.; Chernykh, T. Synthesis and SWOT analysis of date palm frond ash–Portland cement composites. *Environ. Sci. Pollut. Res.* **2021**, *28*, 45240–45252. [CrossRef]

4. Khan, M.U.; Nasir, M.; Baghabra Al-Amoudi, O.S.; Maslehuddin, M. Influence of in-situ casting temperature and curing regime on the properties of blended cement concretes under hot climatic conditions. *Constr. Build. Mater.* **2021**, *272*, 12186.
5. Nasir, M.; Johari, M.A.; Maslehuddin, M.; Yusuf, M. Sodium sulfate resistance of alkali/slag activated silicomanganese fume-based composites. *Struct. Concr.* **2020**, *79*, 1.
6. Ibrahim, M.; Salami, B.A.; Algaifi, H.A.; Rahman, M.K.; Nasir, M.; Ewebajo, A.O. Assessment of acid resistance of natural pozzolan-based alkali-activated concrete: Experimental and optimization modelling. *Constr. Build. Mater.* **2021**, *304*, 124657. [CrossRef]
7. Nasir, M.; Aziz, M.A.; Zubair, M.; Ashraf, N.; Hussein, T.N.; Allubli, M.K.; Manzar, M.S.; Al-Kutti, W.; Al-Harthi, M.A. Engineered cellulose nanocrystals-based cement mortar from office paper waste: Flow, strength, microstructure, and thermal properties. *J. Build. Eng.* **2022**, *51*, 104345.
8. Dresselhaus, M.S.; Dresselhaus, G.; Eklund, P.C.; Rao, A.M. Carbon nanotubes. In *The Physics of Fullerene-Based and Fullerene-Related Materials*; Andreoni, W., Ed.; Springer: Dordrecht, The Netherlands, 2000; Volume 23, pp. 331–374.
9. Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. Chemistry of carbon nanotubes. *Chem. Rev.* **2006**, *106*, 1105–1136. [CrossRef] [PubMed]
10. US Research Nanomaterials, Inc. Layers of Multi Walled Carbon Nanotubes, MWNTs, MWCNTs, Short MWNTs, Short MWCNTs. Available online: https://www.us-nano.com/layers (accessed on 30 April 2020).
11. Makar, J.M.; Beaudoin, J.J. *Carbon Nanotubes and Their Application in the Construction Industry*; Royal Society of Chemistry: Cambridge, UK, 2004; pp. 331–341.
12. Silvestro, L.; Gleize, P.J.P. Effect of carbon nanotubes on compressive, flexural and tensile strengths of Portland cement-based materials: A systematic literature review. *Constr. Build. Mater.* **2020**, *264*, 120237. [CrossRef]
13. Han, B.; Yu, X.; Kwon, E.; Ou, J. Effects of CNT concentration level and water/cement ratio on the piezoresistivity of CNT/cement composites. *J. Compos. Mater.* **2012**, *46*, 19–25. [CrossRef]
14. Shi, T.; Li, Z.; Guo, J.; Gong, H.; Gu, C. Research progress on CNTs/CNFs-modified cement-based composites—A review. *Constr. Build. Mater.* **2019**, *202*, 290–307. [CrossRef]
15. Lai, Y.C.; Bassem, A. Finite element analysis of carbon nanotube/cement composite with degraded bond strength. *Comput. Mater. Sci.* **2010**, *47*, 994–1004.
16. Konsta-Gdoutos, M.S.; Metaxa, Z.S.; Shah, S.P. Highly dispersed carbon nanotube reinforced cement based materials. *Cem. Concr. Res.* **2010**, *40*, 1052–1059.
17. Jeevanagoudar, Y.V.; Krishna, R.H.; Gowda, R.; Preetham, R.; Prabhakara, R. Improved mechanical properties and piezoresistive sensitivity evaluation of MWCNTs reinforced cement mortars. *Constr. Build. Mater.* **2017**, *144*, 188–194. [CrossRef]
18. Assi, L.; Alsalman, A.; Bianco, D.; Ziehl, H.; El-Khatib, J.; Bayat, M.; Hussein, F.H. Multiwall Carbon Nanotubes (MWCNTs) Dispersion & Mechanical Effects in OPC Mortar & Paste: A review. *J. Build. Eng.* **2021**, *43*, 102512.
19. Hilding, J.; Grulke, E.A.; Zhang, Z.G.; Lockwood, F.J. Dispersion of Carbon Nanotubes in Liquids. *Dispers. Sci. Technol.* **2003**, *24*, 1–41.
20. Elkashef, M.; Wang, K.; Abou-Zeid, M.N. Acid-treated carbon nanotubes and their effects on mortar strength. *Front. Struct. Civ. Eng.* **2016**, *10*, 180–188. [CrossRef]
21. Alrekabi, S.; Cundy, A.; Lampropoulos, A.; Savina, I. Experimental investigation on the effect of ultrasonication on dispersion and mechanical performance of multi-wall carbon nanotube-cement mortar composites. *Int. J. Civil Environ. Struct. Constr. Archit. Eng.* **2016**, *111*, 268–274.
22. Metaxa, Z.S.; Boutsioukou, S.; Amenta, M.; Favvas, E.P.; Kourkoulis, S.K.; Alexopoulos, N.D. Dispersion of Multi-Walled Carbon Nanotubes into White Cement Mortars: The Effect of Concentration and Surfactants. *Nanomaterials* **2022**, *12*, 1031. [CrossRef]
23. 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]
24. Rashidi, Y.; Roudi, M.R.R.; Korayem, A.H.; Shamsaei, E. Investigation of ultrasonication energy effect on workability, mechanical properties and pore structure of halloysite nanotube reinforced cement mortars. *Constr. Build. Mater.* **2021**, *304*, 124610. [CrossRef]
25. Avakyan, L.; Manukyan, A.; Bogdan, A.; Gyulasaryan, H.; Coutinho, J.; Paramonova, E.; Sukharina, G.; Srabionyan, V.; Sharoyan, E.; Bugaev, L. Synthesis and structural characterization of iron-cementite nanoparticles encapsulated in carbon matrix. *J. Nanoparticle Res.* **2020**, *22*, 30. [CrossRef]
26. Manukyan, A.; Gyulasaryan, H.; Ginoyan, A.; Kaniukov, E.; Petrov, A.; Yakimchuk, D.; Shashov, S.; Nurijanyan, M.; Mirzakhanyan, A. Structural, morphological and magnetic properties of nickel-carbon nanocomposites prepared by solid-phase pyrolysis of Ni phthalocyanine. In *Fundamental and Applied Nano-Electromagnetics*; Maffucci, A., Maksimenko, S.A., Eds.; NATO Science for Peace and Security Series B: Physics and Biophysics; Springer: Dordrecht, The Netherlands, 2016; pp. 273–290.
27. Arzumanyan, A.A.; Tadevosyan, V.G.; Muradyan, N.G.; Navasardyan, H.V. Study of "Saralsk" Deposit for Practical Applications in Construction. *J. Arch. Eng. Res.* **2021**, *1*, 3–6. [CrossRef]