The Effect of Carbon Nanotubes on the Flowability, Mechanical, Microstructural and Durability Properties of Cementitious Composite: An Overview

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Abstract: Excellent mechanical properties and chemical stability make carbon nanotubes (CNTs) some of the most promising nanomaterials that can be used in cementitious composites to improve their performance. However, the difficulty of CNTs' dispersion within the cementitious structure still exists and thus prevents the homogeneous distribution of CNTs. The homogeneous distribution of CNTs within a composite structure plays an essential role that can have a positive effect on the mechanical performance of CNT-cement composites. This paper introduces the methods for the production of CNTs and provides useful information about the influence of CNTs on the flowability, mechanical performance, microstructural changes and hydration of cement composites. The influences of water-cement ratio, used surfactants and various doses of CNTs on the properties of cementitious composites were also studied.

Keywords: carbon nanotube; cementitious composites; flowability; application of CNTs; compressive strength; flexural strength; microstructure

1. Introduction

Concrete is one of the most frequently used materials in the construction industry worldwide. However, the formation of cracks and nanoscale pores are significant drawbacks that reduce the mechanical performance and durability of concrete. Recently, the concept of utilizing well-dispersed nanomaterials within the concrete structure has developed to make concrete more durable and crack-free [1–3]. Excellent performance characteristics of carbon nanotubes (CNTs) make them an attractive material [4,5], able to increase the mechanical performance of cement-based composites. According to Van Der Waals' attraction theory, it is very difficult to disperse this nanomaterial uniformly within the cement-based composite due to its extremely small size. The nanoscale size materials have a strong agglomeration tendency that can effectively influence the mechanical and microstructural performance of cementitious composites [6,7]. Several investigations were carried out utilizing sonication, surfactants to disperse CNTs within composite structures [8–11]. Without a proper fabrication technique or the direct addition of raw CNTs into a fresh concrete mixture, the conventional concrete mixing process cannot ensure the homogeneous dispersion of CNTs and mechanical performance. Carbon nanotubes are categorized into single-walled and multi-walled. Due to expansive synthesis and production costs, multi-walled carbon nanotubes are commonly used. Recently, CNTs functionalized with -COOH (carboxyl) and -OH (hydroxyl) were introduced. They can affect the physical properties of cement and might result in chemical reactions [12] that influence the mechanical and microstructural performance [13] of concrete. In addition to improved

mechanical and structural performance, the properties of fresh cement-based composites, such as flowability, are also influenced by the incorporation of CNTs. Literature studies show that CNTs caused the flowability of cement paste and mortar to decrease [7,14,15]. Some authors report a slight increase in the flowability of modified concrete where a proper CNT dispersion technique and mixing process was used [10,16–18]. Some studies were carried out to investigate the effects of CNTs on the hydration of cement composites [19–24] and research results show that CNTs effectively influence the hydration of cementitious composites. CNTs most often accelerate the hydration process and add to the development of higher heat during hydration. Even though several investigations have reported the relevant properties of CNTs incorporated in cement-based composites, this paper aims to provide valuable information about CNTs incorporated in cement-based composites for further studies.

2. Overview of CNT Types

Carbon nanotubes are a quasi-one-dimensional nanomaterial, classified into single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) according to their crystallization organization. Generally, SWCNT and MWCNT have different Young's modulus, thermoelectric, electrical conductivity and optical properties [25]. In the CNT each carbon atom in the atomic scale is aligned at 120° in the XY plane and part of a hexagonal structure. Figure 1 shows the structure of single and multi-wall carbon nanotubes.
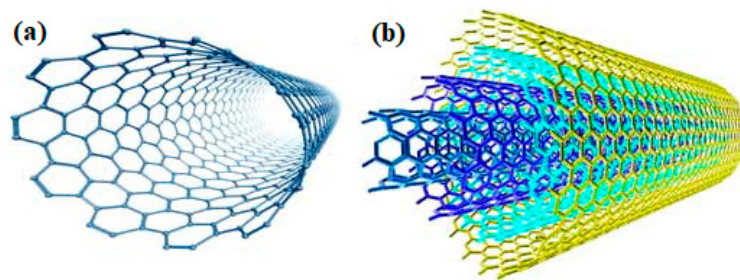

Figure 1. (**a**) Single-wall and (**b**) multi-wall carbon nanotube [26].

Chemical Vapor Deposition (CVD) technique is mostly used to synthesize CNTs in sizeable amounts, while the arc-evaporation method is well known for producing the best quality CNTs. A carbon nanotube is expected to exhibit exceptionally high stiffness and axial strength, attributed to its C-C bonding. According to computer simulation calculations by Overney G, Zhong W et al. [27], the Young's modulus of SWCNT is expected to be 1.5 TPa. The mechanically calculated Young's modulus of MWCNT was about 1–1.8 TPa [28]. Due to the excellent properties of CNTs, they have been widely used in cementitious composites by various researchers to improve the properties of concrete. Because of lower cost and higher availability, MWCNTs are preferred over SWCNTs in CNT-cement-based composites. A small amount of CNT can effectively influence the fresh and mechanical properties of cementitious composites. The basic properties of CNT are shown in Table 1.

Table 1. Characteristics of different types of CNTs [10].

Notation	CNTSS	CNTSL	CNTPL	CNTCOOH	CNTOH
Commercial Name	TNIM8	TNIM6	TNIM6	TNIMC6	TNIMH4
Form as Supplied	Suspension	Suspension	Powder	Powder	Powder
Purity (%)	>90	>90	>90	>90	>90
Outer diameter (nm)	>50	20–40	20–40	20–40	10–30
Inner diameter (nm)	5–15	5–10	5–10	5–10	5–10
Length (µm)	10–20	10–30	10–30	10–30	10–30
Aspect ratio	~300	~667	~667	~667	~1000
True density (g/cm^3)	~2.1	~2.1	~2.1	~2.1	~2.1
COOH (%)				1.36–1.5	
OH (%)					2.48

3. Dispersion of CNTs

The dispersion of carbon nanotube material in the cement matrix is more challenging than in the conventional concrete mixture. Due to the reliable van der Waals forces between carbon nanotubes, the separations of aggregated carbon nanotube bundles are necessary to protect from defects in cement composites. Besides, all nanomaterials should be dispersed discretely to achieve the maximum performance. Ultrasonication can be used to achieve a homogeneous dispersion of CNTs in the cementitious matrix, combining sonication with shear mixing methods, such as the mechanical, magnetic, and hand-stirring methods. The ultrasonication process is the most used technique [3,9,29] due to its rapid separation of nanoparticles from aggregated bundles and collapsing cavitation bubbles. Well-designed ultrasonication with sufficient ultrasonication energy can disperse the CNTs uniformly. Insufficient ultrasonication energy cannot disperse the nanomaterials uniformly, while excess sonication energy can cut into smaller fragments [8]. Chemical techniques like surfactants, solvents and functionalization techniques were also used to disperse the CNT in aqueous suspensions. Polycarboxylate-based superplasticizer is a commonly used surfactant to disperse CNTs [8]. The chemical CNT dispersion method typically introduces covalent and noncovalent bonds to enhance the wettability of the surface of the nanotubes. The functionalization technique is used to modify the surface of CNTs by forming a covalent bond by adding hydroxyl, carbonyl and carboxyl polar functionalized groups [30,31]. Studies also reported that the incorporation of silica fume to the composite can break the clusters of CNTs [32]; silica fume has a very similar size to that of CNTs and can help to break the aggregations without sonication during the mixing process [33]. The utilization of combinations of surfactants and ultrasonication to disperse the CNTs in water is found most often in the research literature. The fabrication process of CNTs in cementitious composites used by various researchers is shown in Table 2.

Table 2. The fabrication process of CNT in cementitious composites.

Matrix	The Fabrication Process		Refs.
	Ultrasonication	Surfactant and Flowing Mixing Process	
Paste	yes	Dispersed with polycarboxylate-based superplasticizer and mixed according to ASTM standard C1738	[6]
Paste	Yes, 30 min (6 times with 5 min duration)	Dispersed with TNWDIS, dispersed CNT mixed under stirring	[3]
Paste	Yes, 5 h (5 times with 1-h duration)	Dispersed with water, CNT mixed into cement simultaneously stirred by multifunctional mixer	[29]
Paste	Yes, 3 h	Dispersed with methylcellulose and Stirred with cement for 5 min	[34]
Mortar	Yes, 2 h	Dispersed with epoxy resin by magnetically stirred at 800 rpm for 2 h	[9]
Mortar	Yes, 3 min	Dispersed with (70–90 °C) distilled water for 15 min under mixing,	[35]
Mortar	Yes, 30 min	Dispersed with polycarboxylate-based superplasticizer and mixed d with cement under stirring	[23]
Mortar	Yes, 1 h	Dispersed with a defoaming agent, magnetic stirring for 10 min for proper mixing of CNT.	[14]
Mortar	No	Mixed with cementitious material in a dry state by electrical hand mixer for 6 min, after adding superplasticizer and water again mixed for 3 min.	[36]
Concrete	Yes, 45 min	Dispersed with a polyethylene-based surfactant, mixed by magnetic stirring for 1 h	[11]
Concrete	Yes, 30 min	Dispersed with water containing an anionic surfactant, Dolapix PC67, after that suspension was magnetically stirred for 4 h	[10]

Zou, Bo et al. [6] showed in their study that sonication energy significantly influences the mechanical and microstructural performance of a CNT cementitious composite. The composite sample achieves better dispersion in high ultrasonication energy (Figure 2), which significantly influences the mechanical performance of the composite. An optimum level of sonication not only provides better dispersion but can also help to obtain maximum mechanical performance by filling the pores and increasing adhesion with cementitious and hydration products. Alrekabi et al. [2] reported that sonication duration also efficiently influences the dispersion of CNTs. A significant improvement in dispersion was identified with increased sonication time. Besides, the addition of a certain chemical as a surfactant also influences the dispersion of CNTs within the composite structure.
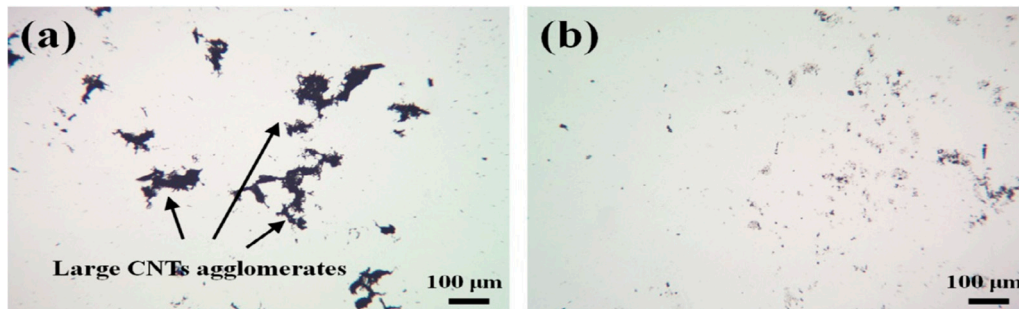

Figure 2. CNT suspensions at the UE of (**a**) 25 J/mL and (**b**) 400 J/mL at 200·magnification [6].

Collins, Frank et al. [7] showed that a polycarboxylate superplasticizer worked positively and improved the dispersion of CNTs within the ordinary Portland-cement-based composite (OPC). A composite with air entrainer and a plain composite without any admixture showed the agglomeration of CNTs within the composite structure (Figure 3).
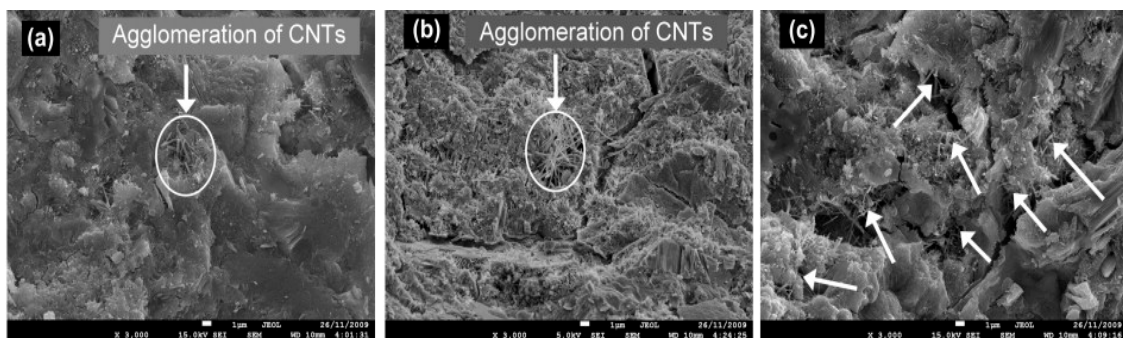

Figure 3. SEM images of CNT–OPC hardened paste samples. Effect of admixtures on the dispersion of CNTs: (**a**) No Admixture; (**b**) Air Entrainer; and (**c**) Polycarboxylate [7].

Vesmawala et al. [37] also noted the importance of polycarboxylate to disperse CNTs uniformly within a cement-based composite structure. Besides, polycarboxylate-based superplasticizers have a double-dispersion capacity to disperse cement and CNT particles [38]. The improvement of dispersion by polycarboxylate is attributed to the strong static hindrance effect which pushes the cement particles apart. Polycarboxylate superplasticizer mainly consists of a hydrophobic main chain and hydrophilic pendant groups with a comb molecular structure (Figure 4b). This can easily warp the surface of CNT via hydrophobic and other intermolecular interactions, while the hydrophilic part helps to disperse and prevent agglomeration in the aqueous solution through static stabilization. Xu, Shilang et al. [3] reported that uniformly distributed CNTs provide sites for the growth of hydration products, while agglomerated CNTs create weak zones and lead to the formation of pores. The study also showed that CNTs were well dispersed and were connected to hydration products.
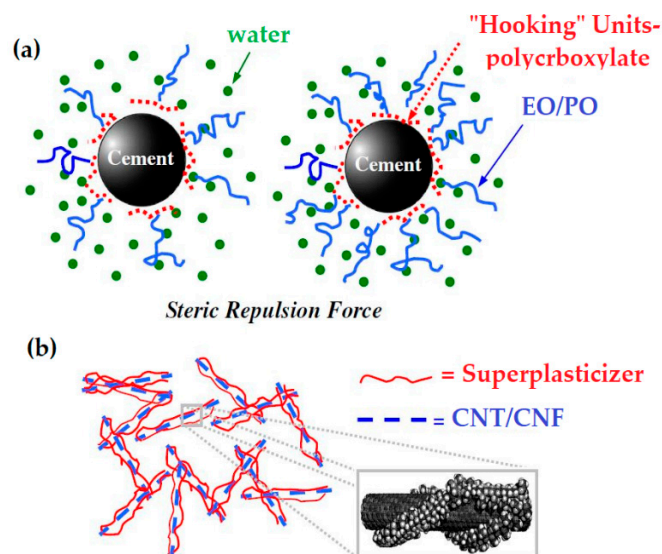
Figure 4. Double-dispersion mechanism of polycarboxylate superplasticizer to cement particles and CNTs/CNFs: (**a**) mechanism of steric repulsion of comb polymer; (**b**) dispersion mechanism of polycarboxylate superplasticizer to CNT/CNF [38].

4. The Effect of CNTs on Cementitious Composite Hydration

Carbon nanotube is a chemically inert material, but it can promote the pozzolanic reaction of cementitious materials, mainly during the early age hydration. CNT within the cement composite can act as a nucleation agent and promote the sedimentation and growth of hydration products. Preferably, calcium silicate hydrate (C-S-H) gel should be observed around the CNTs within the cement composites. Several studies were carried out to investigate the influence of CNTs on the hydration of cementitious composites.

Makar et al. [19] investigated the influence of SWCNTs on the hydration of cement paste. Cement paste combining OPC and 1% CNTs and cement paste without CNTs were sonicated for 2 h, and then an isothermal conduction calorimetry test was conducted. OPC with CNTs showed a higher heat of hydration initially and after 6 h of hydration than the sonicated paste without CNTs. The composite sample with nanotubes showed a higher level of initial surface activity than the sonicated OPC. The development of the maximum heat flow peak of the composite sample containing CNTs was accelerated. Besides, the derivative heat flow of the composite paste significantly increased. The acceleration in the development of the maximum heat flow peak and a higher derivative heat flow peak indicates the acceleration in the hydration of the composite material. Sonicated OPC with CNTs produced much more initial heat than sonicated OPC but less coverage of exposed OPC surface by tricalcium aluminate (C_3A) hydration products. The carbon nanotube is a chemically inert material, and the acceleration in hydration may be attributed to the nucleation effects. SEM results also indicate the preferential presence of C-S-H around the CNTs, which supports the concept of carbon nanotubes as a nucleation agent. The heat flow measured by the isothermal conduction calorimetry test of the composite samples is shown in Figure 5.
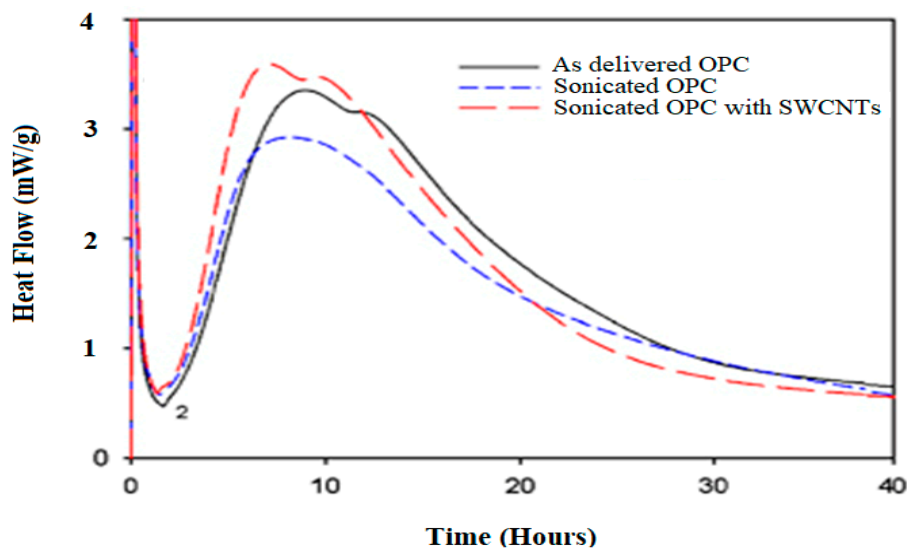
Figure 5. Heat flow is measured by isothermal conduction calorimetry [19].

Cui, Hongzhi et al. [20] investigated the influence of CNTs (0 to 1% CNT) on the heat of hydration of cement paste containing Microencapsulated Phase-Change Material. The study results reported that the incorporation of CNTs in the cement matrix did not influence the heat of hydration for the first 3 h, while at 12 h the cement matrix containing 1% CNT showed the highest hydration rate. It was also observed that the presence of CNT accelerated the cement hydration reaction and shortened the final setting time.

Wang et al. [22] investigated the exothermic rate of cement composite containing 0 to 0.8% MWCNTs. The incorporation of CNTs into the cement paste had a positive influence on the exothermic rate. The acceleration in hydration and a higher produced heat were identified in the sample containing CNTs compared to the control sample without CNTs. The addition of CNTs to cement particles provided reaction sites for the hydration reaction mechanism, which resulted in calcium ions hydrolyzed and absorbed in high concentration, speeding up the hydration reaction.

Alatawna et al. [39] showed in his study that when CNTs were incorporated into the cement paste, the heat flow curves shifted to shorten hydration times and enlarge the heat flow peak. The shorter hydration time of CNTs embedding cement paste indicates the acceleration of the hydration reaction mechanism, which can be attributed to the enhanced dispersion of cement paste by nucleation sites in the paste.

Isfahani et al. [23] observed the opposite phenomenon. The author prepared different samples with and without sonication, containing 0.1% and 0.3% CNTs. Study results reported that sonicated cement composites with CNTs decelerate the hydration of C_3A, which leads to lower heat produced with respect to not sonicated samples. The sample containing 0.3% CNTs after 30 min sonication remarkably (approx. 43.4%) decreased the cumulative heat compared to the control sample without CNTs and sonication. Besides, the reduction in the heat produced was noticed for all samples containing CNTs with respect to the control sample, and the head reduction rate grew by increasing the quantity of CNTs. The reduction in generated heat can be attributed to the agglomeration of CNTs around the cement grains, hindering C_3A hydration

Similarly, Leonavičius et al. [24] show the opposite phenomenon and argue that CNTs effectively extend the setting time of cementitious composites. In cement paste samples incorporating 0.005% and 0.5% CNTs, the initial setting time is prolonged by 25.1% and 130%, respectively, while the final setting time is extended by 29.5% and 110%, respectively. By increasing the quantity of CNTs in the cement paste, the induction period was prolonged and the maximum temperature of the exothermic reaction was reduced. In cement paste containing 0.5% CNTs the exothermic reaction strung out by 148.3%, and the generated maximum temperature due to hydration was reduced by 18.4%.

Study results suggest that the incorporation of CNTs significantly influences the hydration of cement-based composites. Most of the studies indicate that the incorporation of CNTs accelerates hydration and shortens the setting time of cement-based composites. Besides, several studies reported that the presence of CNTs also promotes the exothermic reaction and produces higher heat during the hydration process. However, the degree of dispersion and properties of CNTs can influence the hydration of CNT-based cement composites. Few studies reported the prolonged hydration of CNT-based cement composites.

5. Flowability of Cementitious Composites Incorporating CNTs

Flowability, or workability, is one of the important factors in concrete mix design. Several factors, like the fineness of cement, cement content, increased ratio of coarse and fine aggregates, water/cement ratio and the use of chemical admixtures, usually influence the flowability of conventional concrete. Mini slump, flow table and slump flow tests are the commonly used methods to determine the consistency or mobility of freshly prepared cement paste/mortar/concrete. The incorporation of CNTs into cementitious composites increases the viscosity and reduces the flowability of the composite [9]. According to Skripkiunas et al. [40], 0.25% doses of CNTs added by weight of cement increase plastic viscosity by about 29.59%. The flowability of cement composite containing CNTs is influenced by various parameters, such as water/cement ratio, additions of fine fillers, such as fly ash and silica fume, sonication, treatment of CNTs, concentration of CNTs and types of CNTs. Several researchers investigated the influences of CNTs on the fluidity of fresh cementitious composites. Their findings are presented in Table 3.

Table 3. Flowability of concrete incorporating CNT.

Matrix	W/C	Carbon Nanotube Content (wt%)	Changes of Fluidity/Flowability		Ref.
			Method	Increased/Decreased	
Mortar	0.5	0.1% MWCNT	Flow table	3.17% decrease in flow	[14]
		0.1% SWCNT		6.34% decrease in flow	
Concrete	0.4	0.08% MWCNT	T500 test	7.48% increase in flow	[16]
Paste	0.21	0.022% MWCNT	Flow table	0.6% increase in flow	[41]
Concrete	0.22	0.023% MWCNT		1.42% decrease in flow	
Paste	0.4	0.1% MWCNT	Flow table	~4.16% decrease in flow	[42]
Mortar	0.4 (w/b)	0.1% MWCNT	Flow table	8.5% decrease in flow	[15]
		0.5% MWCNT		23.4% decrease in flow	
Mortar	0.2 (w/b)	0.5% MWCNT	Flow table	18.18%decrease in flow	[43]
SCC[4]	0.45	0.3% MWCNT	Slump flow test	4.54% increase in flow	[17]
		0.5% MWCNT		1.51% increase in flow	
Paste	0.35 (w/b)	0.1% MWCNT	ASTMC 1437	6.25% decrease in flow	[44]
Paste	0.5	0.5% MWCNT	Mini slump	14.5 decrease in flow	[7]
		1% MWCNT		32.8 decrease in flow	
		2% MWCNT		48.9 decrease in flow	
Concrete	0.49	2.5%CNT-liquid admixture	slump test	22.72% increase in flow	[18]
		5% CNT-liquid admixture		63.63% increase in flow	
		10% CNT-liquid admixture		109% increase in flow	
Concrete	0.55	0.1% MWCNT	EN 12350-2	11.81% increase in flow	[10]
		0.5% MWCNT		23.62% increase in flow	
Paste	0.25 (w/b)	0.1% MWCNT	ASTM C230	6.71% decrease in flow	[45]
		0.3% MWCNT		2.23% decrease in flow	

Zou et al. [6] showed the importance of ultrasonication energy on the properties of composites containing CNTs. A mini slum test was carried at different ultrasonic energies to determine the flow of the sample containing a constant amount of superplasticizer. Figure 6 shows that the composite sample achieved a lower slump at a higher ultrasonication energy. Composite samples R1 and R2 were prepared with plain OPC with 0.55 wt% and 0.70 wt% p/c, respectively. In the case of the CNT-OPC paste, CNT-1 series and CNT-2 series were prepared with a c/c of 0.038 wt% and 0.075 wt%, respectively. The explanation is that at a higher ultrasonication energy the dispersion of CNT is more effective, and CNT bundles leave more surface area available for the superplasticizer to absorb onto it, and thus less free superplasticizer is left to control the rheology of the composite sample.
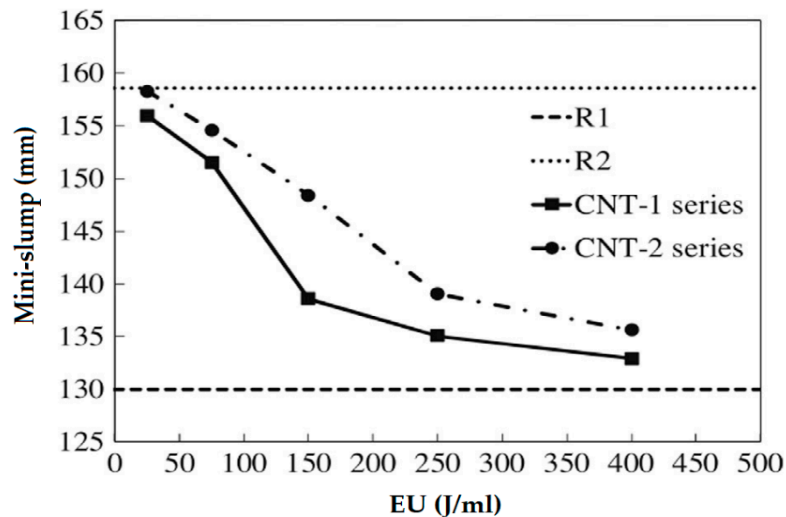

Figure 6. Mini slump spread of Portland cement pastes with superplasticizer and CNTs when different sonication energies are used [6].

Kim et al. [36] scrutinize the influence of CNT/cement mortar at different loadings of carbon nanotubes, from 0.1% to 0.5%, at different water/binder ratios. At 0.4% water-binder ratio, the composite sample achieved 240 mm flowability at 0.1% loading of CNTs, which reduced to 104 mm at 0.5% CNT concentration. Ha, Sung-Jin et al. and Collins et al. [7,15] also reported the decrease in flowability with the increasing concentration of CNTs.

Similarly, Collins et al. [7] inspected the influences of different water/cement ratios on the fresh properties of CNTs added to cement pastes. The study report suggests that by increasing the water/cement ratio the flowability of the sample can be enhanced. At 0.5% content of CNTs, the measured flowability was about 45 mm at 0.4 water/binder ratio. The flowability increased 51% and 92% at 0.5 and 0.6 water/cement ratios. Similarly, at 2% content of CNT, the measured fluidity of the cement paste was around 38 mm at 0.4 water/cement ratio. The flowability increased around 7.9% and 38% at 0.5 and 0.6 water/cement ratios, respectively. Figure 7 shows the flowability of the cement paste incorporating CNTs at different water/cement ratios. The authors concluded that by increasing the doses of CNT in the cementitious composite the fluidity decreases and it can be adjusted by increasing the water/cement ratio.
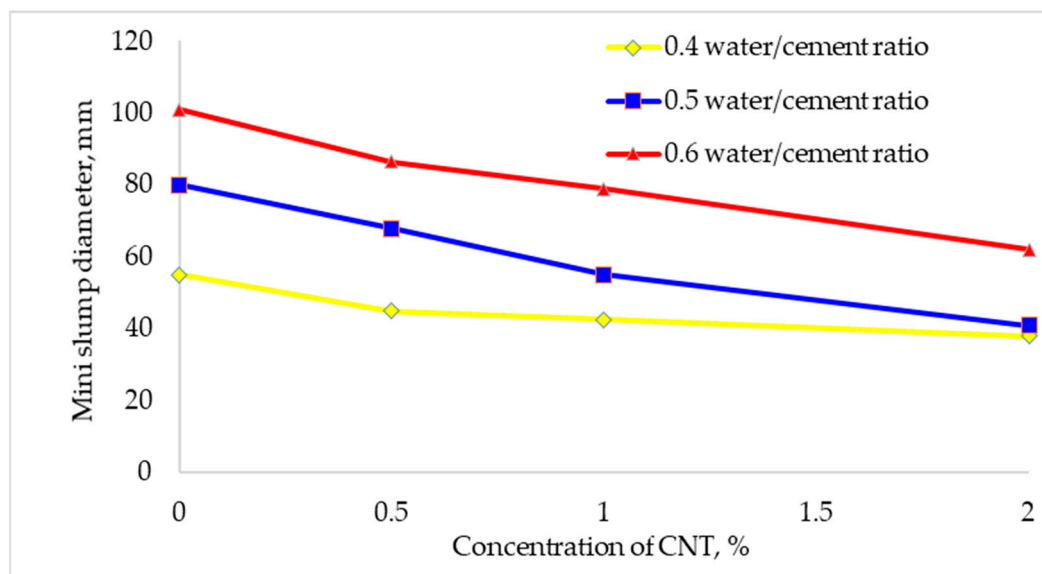
Figure 7. Flowability of cement paste under different water/cement ratios [7].

Hawreen et al. [10] investigated the influences of different types of CNTs on the flowability of concrete under 0.55 water/cement ratio. The CNTs used were CNTSS (Commercial name TNIM8), CNTPL(TNIM6), CNTCOOH(TNIMC6), CNTOH(TNIMH4) and CNTSL(TNIM6), and the characteristics of CNTs are presented in Table 1. The study results reported that the type of CNTs slightly influences the flowability of concrete under the same water/cement ratio. Ordinary concrete at 0.5 water/cement ratio achieved 127 mm slump, while concrete samples with a similar water content modified by adding 0.5% of CNTs achieved 157, 153 and 151 mm for CNTSS, CNTPL and CNTCOOH, respectively, demonstrating 23%, 20% and 18.89% increment in slump flow. Concrete samples containing low doses of CNT content (0.05%) achieved 125 mm, 150 mm, 127 mm and 135 mm slump flow for CNTOH, CNTSL, CNTPL and CNTCOOH, respectively. A concrete sample with CNTSS and CNTSL achieved a comparatively higher slump flow, presumably due to dispersant's effect, and higher air content of those mixes.

Aydın et al. [16] conducted experimental research to examine the influences of nano-silica (2% replacement by weight of cement) and fly ash (40% replacement by weight of cement) on the fluidity of concrete at a constant water/cement ratio (0.4) and CNT content (0.08%). Study results suggest that the incorporation of nano-silica into the concrete matrix without CNTs and fly ash reduced the fluidity by 29.25%, presumably because of the higher water demand due to the addition of nano-silica. While the flowability of the composite sample improved significantly after the addition of fly ash compared to the sample prepared with nano-silica and CNTs, it did not exceed the flow of the control sample (without fly ash, CNTs and nano-silica). It can be concluded from the study results that the incorporation of nano-silica and CNTs increases the viscosity of concrete, whereas fly ash controls the fluidity of concrete irrespective of the addition of nano-silica and CNTs. Nevertheless, fly ash did not help to significantly improve the flowability of concrete modified with CNTs and nano-silica.

Kang et al. [42] investigated the influences of acid treatment (sulfuric acid and nitric acid) on the fluidity of CNT/cement composites. Study results reported that the flowability of the AT-S (acid treatment containing a high-performance superplasticizer) and AT-NS (acid treatment without superplasticizer) decreased by almost 8.3% and 16.8% compared to plain composites. The loss of flowability by the composites can be attributed to the fact that acid treatment leads to the formation of hydroxyl and hydrophilic carboxyl groups, and the water absorption of these compounds causes the flowability to reduce. The flowability of acid-treated composite samples decreased at lower rate in composite samples containing a high-performance superplasticizer due to its positive effect on the flowability.

Study results clearly indicate that the incorporation of CNTs significantly reduces the flowability of cementitious composites. The improvement of flowability has not yet been studied by researchers in detail. The reasons for the decrease in flowability can be explained by the necessity to use sonication and surfactants in order to disperse the CNTs uniformly within the cementitious matrix. Acid treatment by carboxylic acid, combinations of nitric and sulfuric acid and functionalized CNT leads to the absorption of a high amount of water due to its hydrophilic surface. Besides, due to the high surface area, it has the potential to control the rheological properties of the composite, and the suggested sonication process for the uniform dispersion of CNTs also influences the flowability of the composites. The incorporation of a high amount of superplasticizer and fly ash also does not help to significantly improve the flowability of concrete samples incorporating carbon nanotubes [16,32]. It can be concluded that the incorporation of CNTs has a positive effect on the mechanical and microstructural properties of the composites, but it shows a negative influence on the flowability. The improvement of flowability should be further researched.

6. Mechanical Properties of Cementitious Composites Incorporating CNTs

CNTs are well known and acknowledged due to their ultra-high surface area, high aspect ratio, chemical stability and mechanical properties. The mechanical properties of CNTs incorporated in cementitious materials researched in several studies is summarized in Table 4. The highest improvement for compressive and flexural strength was 83.33% [46] and 30% [3] for cement paste; ~35% [4] and 28.04% [47] for mortar; and 38.62% and 38.63% for concrete [17], respectively. CNTs also work as crack-bridgers by filling the cracks or pores (Figure 8). They also provide a load transfer mechanism across the pores or cracks. CNTs in the cementitious composites bridge macro and nanopores with the hydration products and help to delay the crack growth within the composite structure. The addition of CNTs into the cement paste helps to reduce the nano porosity by filling the gaps and pores between the hydrates' gel. Moreover, the reinforcing effect of CNTs observed in the structure was more intensive by increasing the concentration of CNTS, and they exhibited a network-like distribution. Li et al. [34] reported that the incorporation of CNTs reduces the porosity of cementitious composites and intensifies the mechanical properties. Manzur et al. [5] reported that CNTs with a finer scale work more efficiently to fill the nanopores and increase the mechanical properties of cementitious composites. Besides, the incorporation of CNTs into cementitious composites can change the microstructure of hydration products. Singh et al. [48] identified new compounds by the X-ray Powder Diffraction analysis method, due to the chemical bonds between the hydrates and carbon nanotubes. Carbon nanotubes can also alter the multiform interfaces and multiphase boundaries which can effectively influence the mechanical properties of concrete. Moreover, the compatibility between cement hydration and CNTs was observed to be very good, and the microstructure of the hydration product improved.
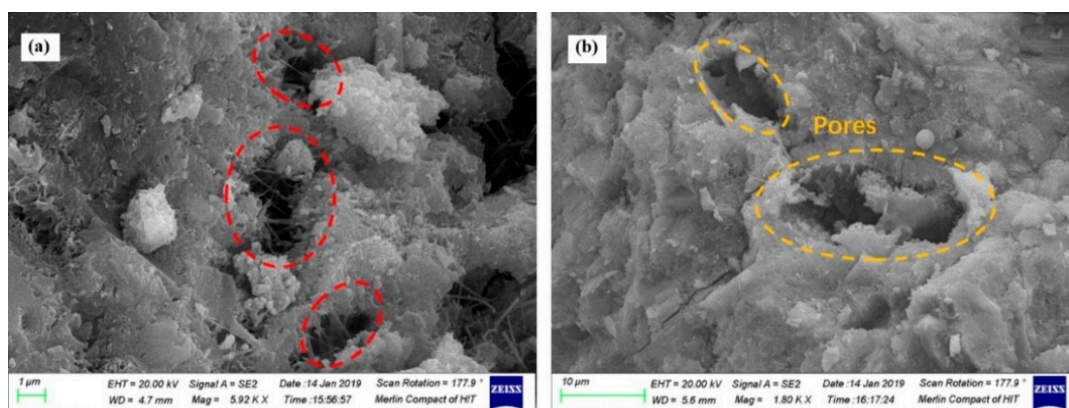

Figure 8. CNTs as crack-bridgers or fillers (**a**) cementitious composite with CNTs; (**b**) cementitious composite without CNTs [29].

Table 4. Compressive and flexural strength of cementitious composites containing CNTs.

Matrix	W/C	Carbon Nanotube Content (wt%)	Compressive Strength (Increase/Decrease)	Flexural Strength (Increase/Decrease)	Ref.
Mortar	0.5	0.1%MWCNT	~8.98% decrease	~16.09% decrease	[14]
		0.1%SWCNT	~19.1% increase	~6.71% increase	
Concrete	0.5	0.1% MWCNT	+19.76% increase	2.81% increase	[49]
Paste	0.33	0.025	6.25% increase	7.5% increase	[3]
		0.100	14.62% increase	30% increase	
Mortar	0.45	0.5% MWCNT	19% increase	25% increase	[34]
Paste	0.35	0.05% MWCNT	~8.33% increase	16.9% increase	[29]
		0.2% MWCNT	~7.4% increase	8.6% decrease	
Mortar	Uk [1]	2.0% MWCNT	14% decrease	Nt [2]	[9]
Concrete	0.4	0.1% MWCNT	7.11% increase	10.25% increase	[37]
		0.4% MWCNT	24.5% increase	20.5% increase	
Mortar	Uk	0.2% MWCNT	15.9% increase	20.7% increase	[50]
NAC (mortar)	0.51, W/S [3]	0.004% MWCNT	7.35% increase	11.23% increase	[32]
		0.04% MWCNT	8.08% increase	8.99% increase	
AAC	0.55, W/S	0.001% MWCNT	10.7% increase	19.4% increase	
		0.02% MWCNT	24.5% increase	24.10% increase	
Concrete	0.32, W/B	0.1% CNT	14.3% increase	Nt	[51]
Concrete	0.55	0.05% MWCNT	9.68% increase	Nt	[11]
Paste	0.4	0.2% MWCNT	19.2% increase	Nt	[13]
		0.4% MWCNT	4.3% increase	Nt	
Mortar	0.6 W/B	0.4% MWCNT	~8.02% increase	~10.5% increase	[52]
		1.2% MWCNT	~26.54% increase	~2.7% increase	
Concrete	0.55	0.1% MWCNT	21.05% increase	Nt	[10]
		0.5% MWCNT	7.79% increase	Nt	
Mortar	0.55 W/B	0.05% CNT	14.58% increase	0.91% increase	[47]
		0.15% CNT	10.41% increase	28.04% increase	
Paste	0.485	0.3% MWCNT	4.86% decrease	Nt	[53]
Paste	0.4	0.02% MWCNT	83.33% increase	Nt	[46]
		0.09% MWCNT	63.8% increase	Nt	
Mortar	0.3 W/B	0.25% MWCNT	~33% increase	~25% increase	[4]
		0.50% MWCNT	~35% increase	~12% increase	
SSC	0.45	0.1% MWCNT	16.58% increase	21.25% increase	[17]
		0.5% MWCNT	38.62% increase	38.63% increase	

[1]: Unknown; [2]: Not tested; [3]: water/solid ratio.

Carbon nanotubes can act as a nucleating agent [19,29] for calcium silicate hydrate (C-S-H) and enhance the mechanical properties of cementitious composites (Figure 9). CNTs introduced into cement-based composites create sites for the hydration process and lead to a stronger and denser microstructure. CNTs were found to coat the calcium silicate hydrate (C-S-H) and provide a larger

contact area between themselves and the hydration product. As a result, stronger bonds were created between them which significantly help to improve the mechanical properties of cementitious composites [54]. Moreover, CNTs improve the load transfer efficiency of the cementitious composites by their pulling out behavior and crack bridging effects [6,55]. Figure 10 represents the crack bridging and pulling out behavior of CNTs. It can be clearly observed that one end of a pulled out CNT stands freely, while the others remain connected with the nanopores of the composites. Literature studies indicate that the mechanical properties of CNTs incorporated in cementitious composites can be influenced by various parameters, such as water/cement or water/binder ratio, CNT properties, utilized surfactant, CNT concentration, volume of binding materials, types of fine fillers (fly ash, silica fume), acid treatment of CNTs and the proper dispersion of CNTs into the cement composites.
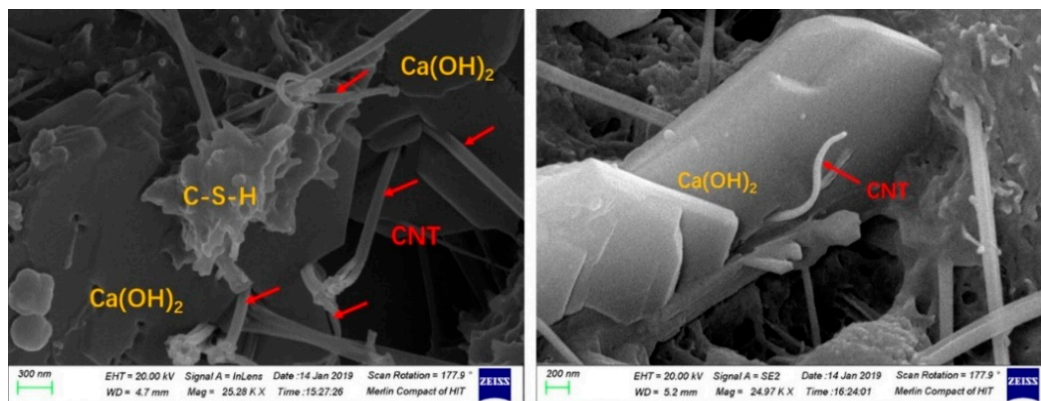
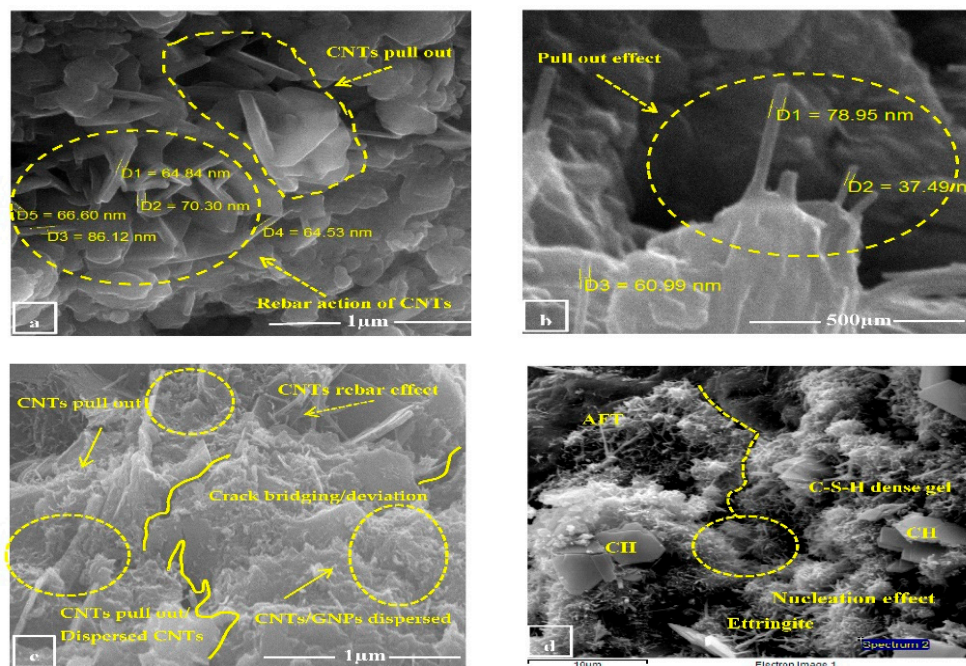**Figure 9.** Bonding between CNTs and hydration products [29].

Figure 10. (**a**,**b**) Rebar and pull out effect of CNTs, (**c**) crack deviation and pull out of CNTs, (**d**) crack discontinuity and the presence of dense calcium silicate gel with AFT [55].

The concentration of CNTs is one of the determining factors of the mechanical performance of CNTs incorporated in cementitious composites. The compressive and flexural strength of composites increased until a certain concentration was reached, and once the optimum concentration was exceeded, it started decreasing. The influence of CNTs was observed to be different for the type of cement

composites. These phenomena were observed for CNTs incorporated in cement paste, mortar and concrete, as shown in Figures 11–13. Guan et al. [29] reported that the maximum improvement in the compressive strength of CNTs incorporated in cement paste was identified at 0.1 wt% of CNTs by weight of cement, while at 0.5 wt% CNTs loading the maximum improvement were noticed for the flexural strength of cement paste. Zhan et al. [52] evaluated the performance of cementitious mortar under different loadings of CNTs and reported that the maximum flexural strength and compressive strength were achieved at 0.8 wt% and 1.2 wt% CNT loadings (Figure 12). Similarly, Vesmawala et al. [37] investigated the influences of the concentration of CNTs on the mechanical properties of concrete. The study results show that the flexural strength of concrete increased until 0.4 wt% of CNTs and then started decreasing. While the compressive strength of the concrete was increasing along with the increased concentration of CNTs, at 0.5% maximum loading of CNTs the compressive strength was measured (Figure 13) and found to be 27.35% higher compared to plain concrete. The reduction in compressive strength at a higher concentration of CNTs can be explained by the fact that agglomerations of CNTs within the hardened structure raise the local stress and thus weaken the strength.
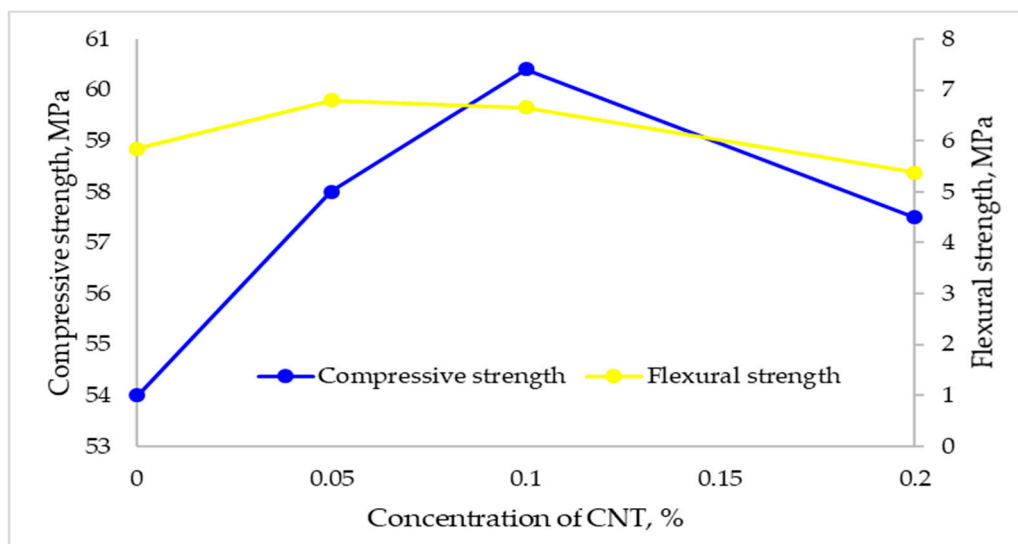

Figure 11. The relation between compressive and flexural strength of cement paste with different concentrations of CNTs [29].
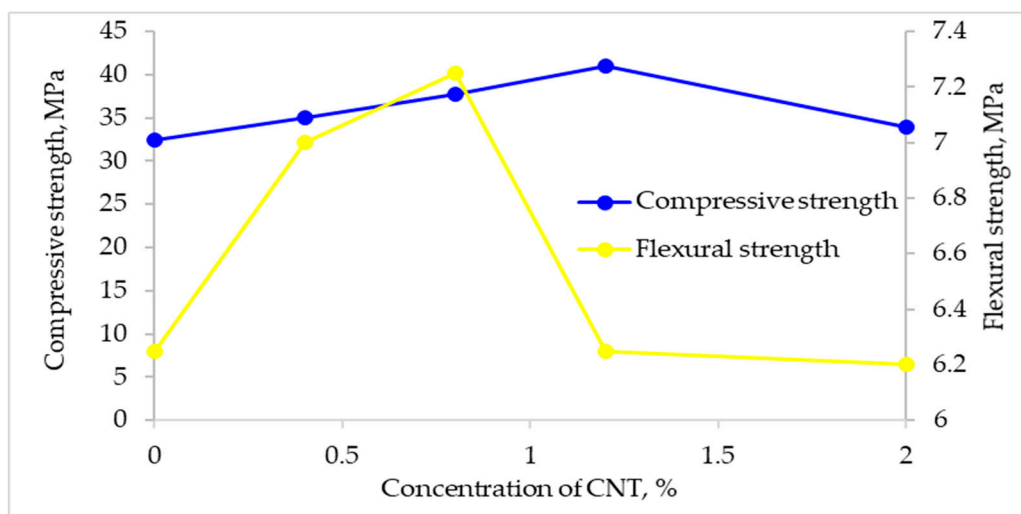

Figure 12. Relation between compressive and flexural strength of cement mortar with different concentrations of CNTs [52].
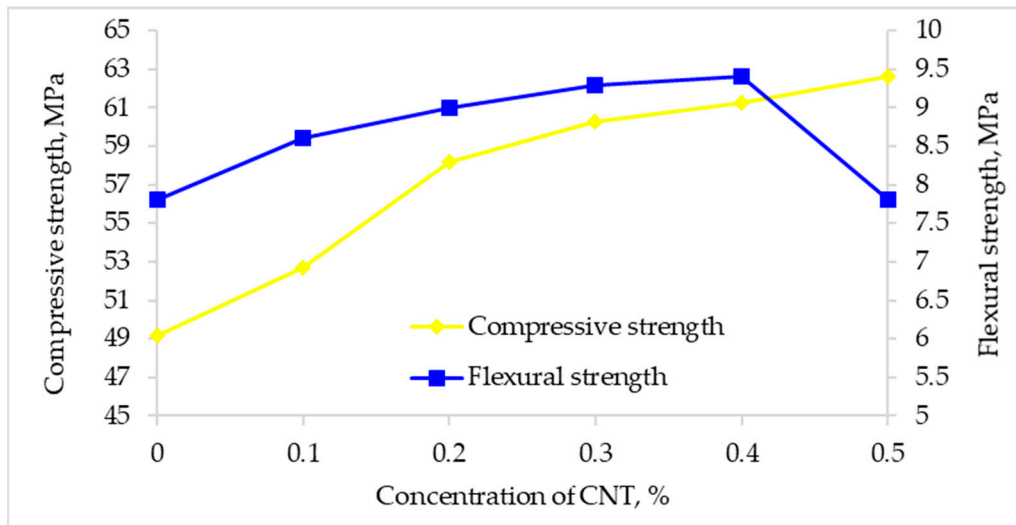
Figure 13. Relation between compressive and flexural strength of concrete with different concentrations of CNTs [37].

Collins et al. [7] evaluated the influences of the water-cement ratio on the mechanical properties of cement paste containing different CNT concentrations. Study results reported that by increasing the water-cement ratio the strength properties decreased. The composite sample at 0.5 wt% loading of CNTs achieved a compressive strength of around 25 MPa at 0.4 water/cement ratio. The compressive strength decreased to around 21.25 MPa and 12.5 MPa at 0.5 and 0.6 water/cement ratios, respectively. This was compared to a 0.4 water/cement ratio of almost 14% and a 50% reduction in strength for 0.5 and 0.6 water/cement ratio composites at the same CNT doses. Similarly, the decrease in strength at a higher water/binder ratio was observed by Kim et al. [36]. At 0.1% CNT loading and 0.6 water/binder ratio an almost 32.5% decrease in compressive strength was noticed for cement mortar over the composite prepared at 0.4 water/binder ratio. Choi et al. [56] reported a decrease in compressive strength at a higher water/cement ratio (Figure 14). The decrease in strength at a higher water-cement ratio can be explained by the fact that after the evaporation of water concrete becomes a more porous structure, which leads to a decrease in strength. Besides, a higher water-cement ratio delays the hydration process and produces lower heat during the hydration process, which leads to lower strength properties.
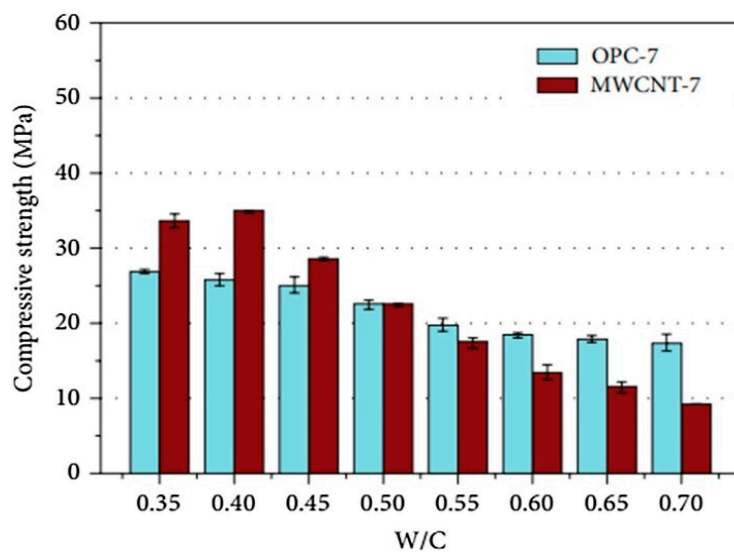

Figure 14. Compressive strength on a 7-day curing process for various water-cement (W/C) ratios containing 1 wt% multi-wall carbon nanotubes (MWCNTs) [56].

Vesmawala et al. [37] present the importance of a polycarboxylate superplasticizer as a dispersant of CNTs in the cementitious composite. Based on the study results, the author argues that a polycarboxylate superplasticizer not only increases the mechanical properties but also improves the microstructure by distributing the CNTs homogeneously within the hardened cement composite. At 5% loading of CNTs with polycarboxylate, compressive and flexural strengths improve almost 28.75% and 28.09%, respectively, compared to the sample prepared without superplasticizer. The increase in strength properties was explained by the rise in the concentration of C-S-H and the crack bridging effect provided by CNTs. Collins et al. [7] investigated the influences of chemical dispersants on the mechanical properties of cementitious composites. Three different types of chemical admixtures, such as air-entraining, polycarboxylate and lignosulfonate plasticizer, were used to prepare different types of CNT-cement-based composites. The study results indicate that composites of plain CNT concrete without chemical admixtures have a significant increase in compressive strength, while a slight decrease in compressive strength was noticed with chemical admixtures (except for polycarboxylate; a slight increase in strength was noticed). Interestingly, CNT composite samples with air-entraining admixture and lignosulfonate-based admixture show a reduction in compressive strength and consistency attributable to the agglomeration of CNTs within the structure. While a slight increase in compressive strength was identified for polycarboxylate, no agglomerations were visible in the composite sample incorporating CNTs. Study results suggest that the polycarboxylate-based superplasticizer is the most effective, when compared to other types of chemical surfactants, in terms of dispersing CNTs and enhancing mechanical performance.

Du et al. [8] summarized the findings of the literature studies and concluded that ultrasonication not only helps to separate the aggregated CNTs but also improve the mechanical properties of CNT-cement-based composites. Similarly, Alrekabi et al. [2] and Zou et al. [6] stated the importance of ultrasonic energy for improving the mechanical properties of CNTs incorporated in cement-based composites. An optimum level of ultrasonication can disperse the CNTs monogamously and provide maximum mechanical performance, while improper sonication leads to the agglomeration of CNT within the composite structure and decrease the positive effects of CNTs. It was suggested that up to 31.54% flexural strength could be enhanced by incorporating ultrasonic energy, which decreases the porosity and increases the crack-bridging capacity of the cement-based composite at the nanoscale [6]. Besides, Alrekabi et al. [2] stated that the duration and sonication intensity also significantly influence the mechanical properties of CNT-cement-based composites. A composite sample with a dispersed superplasticizer at moderate sonication intensity showed the maximum mechanical performance at 10 min of sonication of the samples containing 0.025 wt% and 0.05 wt% CNTs. Meanwhile, it took longer to reach the maximum level of dispersion and mechanical performance for the low CNT (0.01%) composite sample. Similarly, composite samples at high sonication intensity achieved the maximum level of mechanical performance at a very low time (at 3 min for 0.025 wt% and 0.05 wt% CNTs), while the 0.01 wt% composite achieved the maximum level of mechanical performance at 5-min sonication. Excess sonication energy can cut CNTs into smaller fragments and influence the mechanical performance. However, the degree of dispersion and mechanical performance also depends on the used surfactant and its compatibility with cementitious materials. ElKashef et al. [57] reported that CNTs dispersed with Sodium Dodecyl Sulfate (SDS) and Triton X-100 (X-100) (non-ionic surfactant) showed the maximum level of mechanical performance at 30 min of sonication (Figure 15), and thereafter it started decreasing. So, it can be concluded that sonication duration and sonication energy are both influencing factors. A well-designed sonication can provide a maximum level of positive effects of CNTs. Moreover, moderate sonication energy was observed to disperse and provide the maximum mechanical performance.
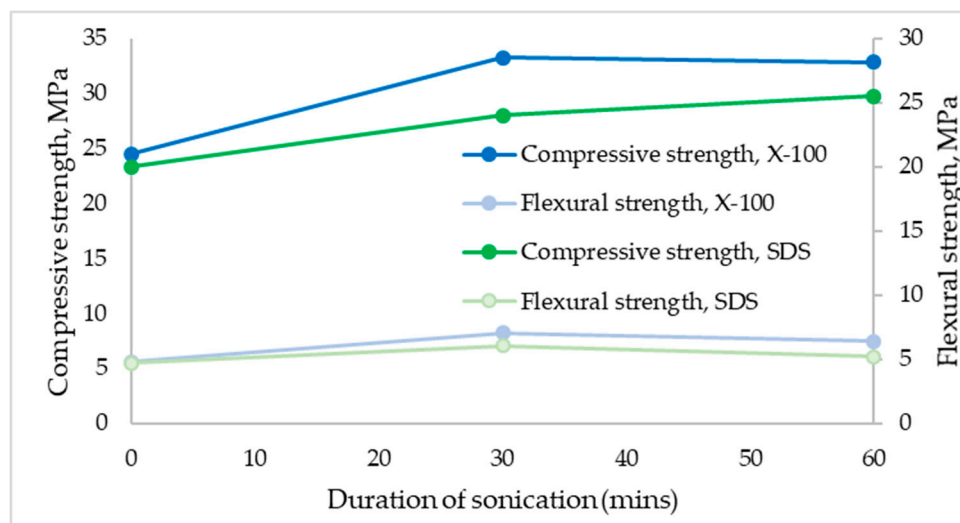
Figure 15. Performance of CNT cement composite at different durations of sonication [57].

Several investigations were carried out to research the influences of different types of CNTs (with different diameter lengths and -OH and -COOH contents) on the properties of cement-based composites. Ruan et al. [4] investigated the influences of different types of CNTs on the mechanical properties of cement-based composites at different CNT loadings. Study results indicate that cement composites containing functionalized CNT-OHs and CNT-COOHs achieve the maximum flexural strength in underwater curing conditions for 28 days. The results are presented in Figure 16. In comparison, cement composites containing non-functionalized CNTs with different diameters and lengths achieve comparatively low compressive and flexural strength. Similarly, Carriço et al. [11] showed that a concrete sample under different types of CNTs achieves different mechanical properties. All composites with a different type of CNTs achieve a higher mechanical strength than that of plain composites without CNTs, while the increasing rate varied for different types of CNTs. The increase in mechanical properties with functionalized CNTs over pure CNTs can be explained by the bonding between CNTs and cementitious materials and their hydration products. The composites were more strongly bonded by functionalized groups (-OH and -COOH). A functionalized material has chemical bonds with C-S-H and OH groups that create the stress transfer mechanism. Interestingly, Musso et al. [58] showed that a composite sample with CNTs functionalized by -COOH achieved a meager compression strength and modulus of rapture compared to other types of CNTs without functionalization by -COOH and plain composites without CNTs. The reason for the decrease is attributed to CNTs functionalized with carboxyl, which absorbs a high amount of water due to its hydrophilic surface and hamper the hydration process, thus leading to the decrease in strength. Besides, the mechanical properties of CNT-based cement composites can also be influenced by the lattice defects of the CNTs formed during the production process. Defected CNTs can provide sites for the formation of -OH and -COOH functionalized groups, while defect-free CNTs can hinder the bonding between the hydration product C-S-H [59]. Similarly, Azeem et al. [13] achieved a higher compressive strength at a 0.2% loading of carboxyl(-COOH) functionalized CNTs; however, when the concertation was increased to 0.4%, the mechanical strength dropped even below the strength of the control sample. A microstructure analysis showed that at a 0.2% loading of CNTs the weakly bonded H atoms strip off easily and leave a strongly negative-charged CNT surface, which provides a long-range order to the growth of hydration crystals. The increased concentration of –COOH, however, reduced the size of the crystals and caused the compressive strength to decrease.
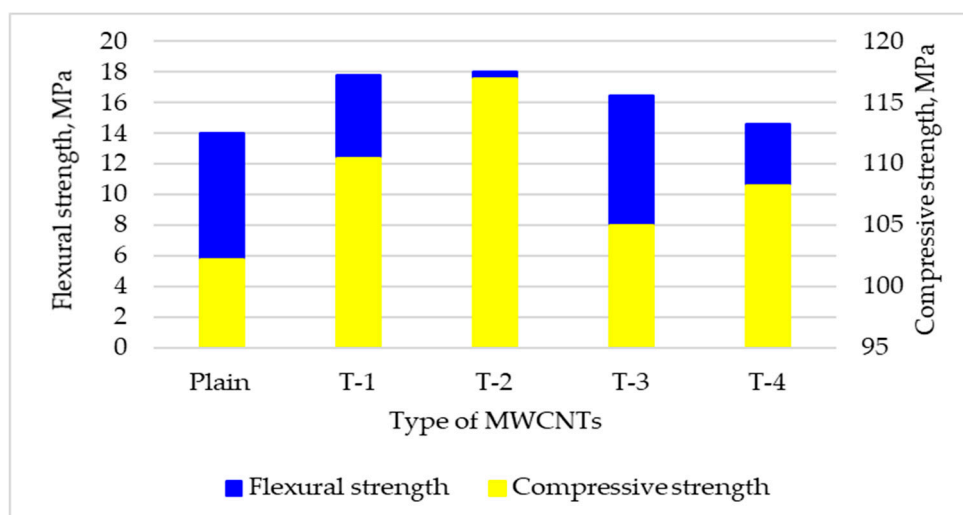
Figure 16. Compressive and flexural strength of cement-based composite containing 0.25% CNTs by weigh of cement at 28 days water curing hydration. (T-1, CNT: 0.5–2 μm length, <8 OD/nm, –3.86% COOH; T-2, CNT: 0.5–2 μm length, <8 OD/nm, 5.58%-OH; T-3, CNT: 3–10 μm length, 100–200 OD/nm; T-4, CNT: 10–30 μm length, 20–30 OD/nm [4].

Li et al. [34] treated the surface of the CNT with carboxylic acid and achieved the improvement of the composite sample's compressive and flexural strengths by up to 19% and 25%, respectively. The enhancement in mechanical performance can be attributed to the improvement in the microstructure of the composite between cement and treated CNTs. The modification of the CNT surface by carboxylic acid in the solution of nitric acid and sulfuric acid induces the chemical reactions between carboxylic acid and C-S-H or $Ca(OH)_2$ (Figure 17). This leads to the formation of strong covalent forces on the interface between the cementitious composite and the reinforcements, and thus increases the load-transfer efficiency. Similar phenomena were observed by Kang et al. [42]: the mechanical performance of composite samples with and without a polycarboxylate superplasticizer significantly improved after the modification of the CNT surface by sulfuric acid and nitric acid. The improvement of the mechanical performance attributed to the formation of the schematic structure is illustrated in Figure 17.
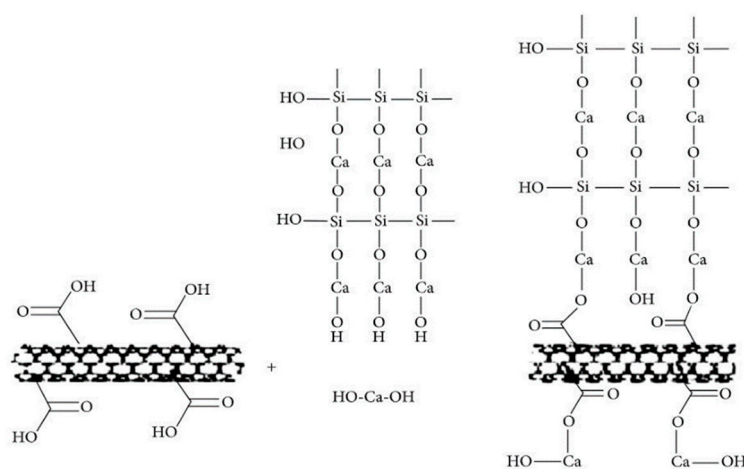

Figure 17. Reaction scheme between the carboxylated nanotube and hydrated production of $Ca(OH)_2$ and C–S–H of cement [34].

The geometry of CNTs is also considered to be an influential factor in terms of dispersion and mechanical performance. Mohsen et al. [60] reported that a cementitious composite containing CNTs with the lowest diameter and a high aspect ratio achieved higher mechanical strength when compared to CNTs with a medium or larger diameter (Figure 18). Besides, a cementitious composite containing longer CNTs achieved a slightly higher flexural strength. Similar phenomena were noticed by Manzur et al. [5]. The composite sample containing CNTs with the smallest outer diameter achieved the highest compressive strength. This can be explained by the fact that smaller CNTs were dispersed in a much finer scale and filled the nanopores of the cement composite more efficiently [5,61]. Liew et al. [54] reported that a lower amount of long CNTs provides a more effective reinforcement, and to achieve the same level of reinforcement a bigger amount of short CNTs was required (Figure 19). Study results clearly indicate that long CNTs were found to be more effective for the enhancement of flexural strength.
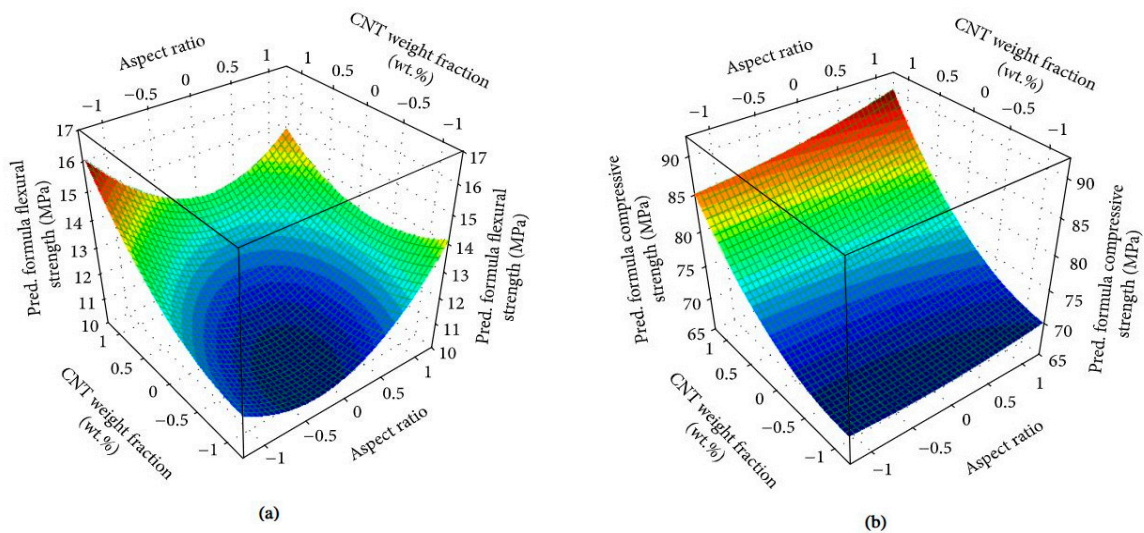

Figure 18. Response Surface Methodologies (RSM) model of strength factor against the weight fraction and aspect ratio of CNTs. (**a**) flexural strength, (**b**) compressive strength [60].
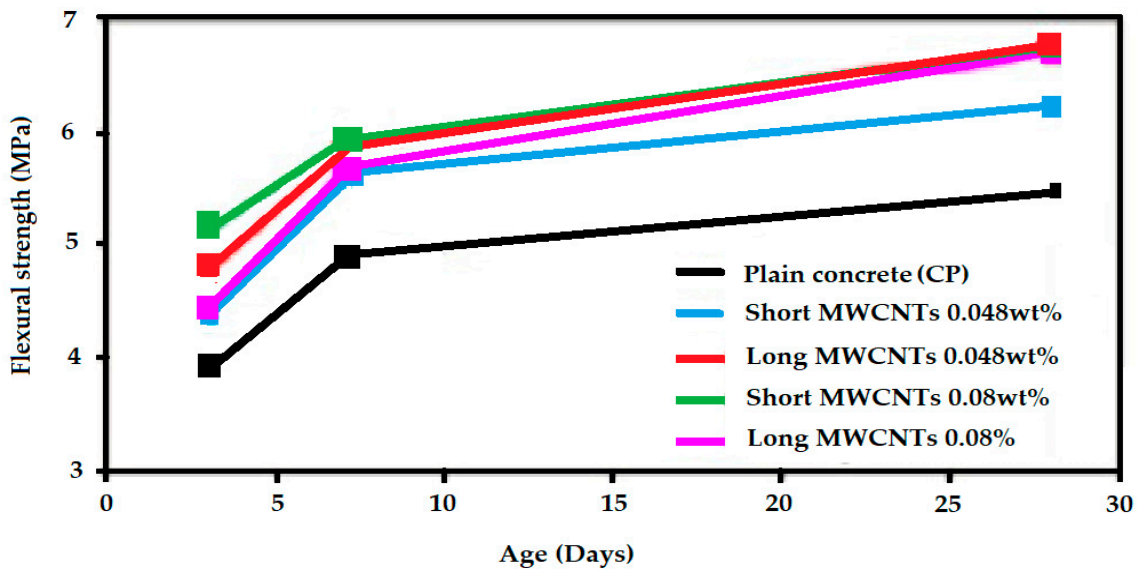

Figure 19. Effects of short and long CNTs and concentration on flexural strength [54].

7. Durability Properties of Cementitious Composites Incorporating CNTs

The potential of concrete to resist the degradation caused by the surrounding environment can be understood by studying its durability properties. To date, only a few works on the durability characteristics of concrete containing CNTs have been published. Wei-Wen et al. [62] reported that the incorporation of MWCNTs in cement mortar could improve the shrinkage and water-loss characteristics. Four different concentrations of MWCNTs added at 0 wt%, 0.1 wt%, 0.3 wt% and 0.5 wt% of cement were used in this study. The composite sample with 0.3% of MWCNTs showed a lower rate of drying shrinkage than the control specimens. The reduction was about 31.9% in the drying shrinkage compared to control specimens. The water-loss characteristics of 0.3% specimens were also lower compared to the control specimens. The addition of 0.3% MWCNTs led to a reduction of water evaporation by 13.3%. It is an indication of less open pores in the samples. This is due to the interlocking and bridging effects of MWCNTs during the hydration phases, leading to lower water-loss and shrinkage. Hawreen et al. [63] conducted a study on the shrinkage behavior of cement mortars incorporating carbon nanotubes. The results revealed that the inclusion of 0.05–0.1% of CNTs could help in reducing early shrinkage by up to 62%. The author mentioned that the restriction effect on free shrinkage is due to the rigidity of the cement matrix and, above all, to the aggregate skeleton. K.M. Liew et al. [54] discussed the effect of CNTs on the autogenous shrinkage of cement paste. The presence of MWCNTs in cement paste deterred the progression of shrinkage and resulted in lower autogenous shrinkage at higher CNT concentrations due to the filler effect of CNTs on fine pores. The autogenous shrinkage of both cement pastes and mortars incorporating CNTs was conducted by G.M. Kim et al. [64]. The results indicated that the amount of autogenous shrinkage of cement mortars containing CNTs decreased as the amount of the fine aggregate increased. That is indicative of the fact that the fine aggregate incorporated into the cementitious materials curtails the deformation incurred by the autogenous shrinkage of cement paste. Li et al. [34] examined the porosity of cement mortar containing MWCNTs which was modified by H_2SO_4 and HNO_3 solutions. The mixes containing 0.5% CNTs produced a result 64% lower than that of the control mixes. The porosity of the composites decreased owing to the inclusion of carbon nanotubes, and the pore sizes became finer. F. Blandine et al. [65] demonstrated the effect of CNTs on the reduction of the autogenous shrinkage of cement paste attributed to the combined effect of nano-reinforcing properties, hydration alterations and the microstructure of the hydrated matrix. A study on shrinkage and sodium sulfate attack on repair mortars containing MWCNTs was conducted [66]. In contrast to many studies, both test results showed a negative impact on the incorporation of MWNCTs. MWCNTs incorporating repair mortars have greater shrinkage caused by the development of cavities inside the specimens resulting from the release of water, which stimulates internal stress resulting in shrinkage. The author concluded that the use of MWCNTs allows for the prevalence of further reactions and the accumulation of more extensive products, such as gypsum and ettringite. A long-term study of this effect is required. The list of durability properties of CNTs incorporated in cementitious composites is listed in Table 5.

A. Carriço et al. [11] studied the addition of 0.05–0.1% CNTs to concrete by weight of cement and concluded that there was a 25% improvement in the durability properties compared to the ordinary concrete. The specific durability properties, such as water absorption, accelerated carbonation and penetration resistance to chloride, were described with two types of CNTs incorporating concrete specimens of 0.35, 0.45 and 0.55 w/c. The results showed that CNTs are likely to be more efficient in low w/c concrete specimens. The enhanced durability properties are attained by the pore filling and nucleation effect of CNTs. Hawreen et al. [10] examined the impact of various types of carbon nanotubes on both the long-term creep and shrinkage of concrete. The shrinkage and creep test results of CNT-reinforced concrete showed the reduction by up to 15% and 18%, respectively, in comparison with reference concrete. According to the test results, CNTs of different aspect ratios were similarly affected by the total creep, but CNTs with a lower aspect ratio appeared to have a more significant effect on the overall shrinkage reduction.

Table 5. Durability characteristics of the cementitious composite containing CNT.

Matrix	Material	Durability Performance	Impact +/-	References
Mortar	MWCNT	Lower rate of drying shrinkage Reduction in water-loss	+ +	[62]
Concrete	CNT	Lower water absorption rate Reduced accelerated carbonation Resistance to chloride ion penetration	+ + +	[11]
Mortar	MWCNT	Decreased porosity rate	+	[34]
Concrete/Paste	MWCNT	Decreased pore volume	+	[67]
Paste	MWCNT	Lower autogenous shrinkage	+	[54]
Ultra HSC	CNT	Reduced chloride diffusion coefficient	+	[68]
Concrete	Modified CNT	Resistance to freezing cycles	+	[69]
Mortar	CNT	Increased chloride ion penetration	-	[70]
Mortar	CNT	Improved abrasion resistance Smaller crack sizes	+ +	[71]
Paste	MWCNT	Reduced shrinkage	+	[63]
Paste	CNT	Decreased autogenous shrinkage	+	[64]
Mortar	MWCNT	Lowered shrinkage rate Resistance to sulfate attack	+ +	[66]
Paste	CNT	Lower rate of autogenous shrinkage	+	[65]
Concrete	CNT	Reduced long term creep and shrinkage	+	[10]
Mortar	CNT	Resistance to chloride ion penetration	+	[72]
Concrete	CNT	The lower chloride penetration depth	+	[73]

The influence of CNTs on the properties of cementitious substances was studied by Siddique et al. [67]. It was noticed that the porosity of concrete/pastes and their pore volume decreased with the incorporation of CNTs, resulting in a denser microstructure as well as a lower shrinkage value compared to the control mixes. The authors reported that the addition of 0.03 wt%–0.10 wt% of CNTs to ultra-high-strength concrete culminated in a decrease of the chloride diffusion coefficient of about 8.8–24.0% [68]. The refined porosity structure enhances anti-permeability and refined pores prevent the water from freezing, because water molecules are less likely to freeze in pores that have less volume and thus increase the resistance to freezing cycles [69]. The addition of CNTs without chemical treatment resulted in a dense concrete pore structure and a faster internal drainage rate than the absorption of water leading to poor freeze-thaw durability for CNT concrete [73]. A lower shrinkage has a major impact on the freeze-thaw resistance of MWCNT concretes, as the growth of micro-cracks is decreased due to volumetric changes [62].

P. Alafogianni et al. [72] concentrated on the addition of carbon nanotubes to cement mortars and the impact of this nano-reinforcement on chloride permeability in mortars. The authors concluded that nano-reinforcement had a negligible influence on the chloride ion permeability of cement mortars. The sodium-polyacrylate-treated CNT concrete was found to have the lowest [Cl⁻] penetration at a depth of 0.25 inches due to its compactness and was found to be the best chemical treatment option [73]. Dalla et al. [70] conducted the study on cement mortars containing from 0 wt% to 1 wt% of CNTs to investigate the influence of chloride ion penetration. In contrast to the results reported by other authors, it was observed that throughout the duration of the RCPT test, the passing current was lower for control specimens and increased with the increase of CNT concentration. The increasing trend in chloride ion penetration was identified due to the higher concentrations of conductive filler resulting in increased conductivity.

8. Conclusions

1. Carbon nanotubes have a remarkable chemical stability and mechanical performance and can be used, due to their structural characteristics, in concrete, to improve its performance. To get a better mechanical and microstructural performance, a proper dispersion of CNTs should be ensured. Different physical and mechanical dispersion techniques are used with certain advantages and disadvantages. Study results suggest that sonication and a polycarboxylate-based superplasticizer are the most common methods, and that both the sonication energy and duration time influence the degree of CNT dispersion.

2. Flowability is one of the most critical factors of fresh concrete influenced by the addition of CNTs. The influences of CNTs summarized in this paper reveal that the flowability of cement-based composites incorporating CNTs decrease with increased CNT concentration.

3. A CNT is a chemically inert material that does not participate in the hydration process but accelerates the hydration process by nucleation effects. Several studies show both that CNTs accelerate the hydration process and that cement composites incorporating CNTs also achieve the maximum level of generated heat during the hydration process.

4. CNTs embedding cement-based composites demonstrate an excellent mechanical performance due to CNTs' nucleation effects, crack bridging effects and better adhesion to hydration products. The studies also suggest that CNTs provide sites for the formation of C-S-H in higher quantity, leading to a higher mechanical strength of cement-based composites. The mechanical performance of cement-based composites can be influenced by several parameters, such as the degree of CNT dispersion, the techniques used for CNT dispersion, water/cement ratio, type and properties of CNTs, the surfactants used and the geometry of CNTs.

5. Long CNTs improve the microstructure of cement-based composites by crack bridging and interacting with the surrounding hydrates but reduce the degree of dispersion of CNTs within the composite structure.

6. Compared to plain cement paste, the flexural strength of CNTs incorporated in cement pastes was observed to increase with the inclusion of CNTs. In the case of CNTs with a higher aspect ratio, the flexural strength of cement-based composites was observed to increase with higher concentrations of CNTs.

7. The microstructure of CNTs incorporated in cementitious composites shows that the compatibility between cementitious materials and CNTs is excellent. The improvement of the microstructure was noticed by the addition of carbon nanotubes. Denser structure and a pore, void and crack filling ability were observed by the addition of CNTs. Besides, a better bonding between CNTs and hydration products was also noticed. The agglomerated CNTs were also observed by SEM, which can be attributed to improper CNT dispersion techniques.

8. CNT incorporating cementitious composites with a low water-cement ratio have better durability performance. In the same way, the chemically treated CNTs have a high resistance to chloride ion permeation. Moreover, CNTs have a greater effect on the long time-dependent creep and shrinkage.

9. The enhanced durability properties are attained by the pore filling and nucleation effect of CNTs, which, in turn, reduce the number of micropores and nanopores. Thus, the incorporation of CNTs not only improves the shrinkage and water loss characteristics of cementitious materials but also improves their freeze-thaw resistance.

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