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REVIEW

The effect of using multi-walled carbon nanotubes on the mechanical properties of concrete: a review

Ali Ebrahim[1] · **Selvaraj Kandasamy**[1]

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Abstract

Nanotechnology has grasped the attention of scientists in several fields during the past decade because of its huge role in developing unique characteristics and behaviors for materials, as it deals with understanding, controlling, and modification of matter at the atomic level in the range of 0.1–100 nm (10^{-9} mm). Nanotechnology could be a paradigm shift in the civil engineering field as the studies showed that inducing different types of nanoparticles in concrete contributed dramatically to improving the mechanical characteristics and durability of concrete as well as creating innovative properties such as self-sensing, self-cleaning, fire-resisting, etc. This paper will show the recent results that were concluded by researchers about the effect of adding nanoparticles in construction materials and especially the effect of multi-walled carbon nanotubes as an enhancing material.

Keywords Nanotechnology · Multi-walled carbon nanotubes (MWCNTs) · Atomic level · Nanoparticle · Mechanical properties

Introduction

Concrete is a fundamental material used in construction; it is the most commonly utilized material in building construction and infrastructures such as dams, bridges, and pavements. Its benefits include simple and low-cost production, long-term durability, and excellent structural characteristics if executed correctly. This makes it the world's second most used material (after water). No material compares to concrete in terms of high compressive, flexibility to take any shape and form, fire resistance, corrosion resistance, and low maintenance cost [1]. On the other hand, concrete has poor mechanical properties such as toughness, flexural strength, and low chemical resistance, which reduces its durability. Therefore, there has been a wide range of research in the past to acquire more favorable concrete specifications, and there has been a growing focus on the use of nanotechnology in the civil engineering field in recent decades. Nanotechnology is an application of science that uses tiny particles to modify matter at the atomic level. Nanotechnology manipulates matter at the atomic level, so the materials' characteristics are severely affected. The nanometer scale (10^{-9}m) has led to other studies focusing on the effect of nano-sized composites on material because the performance of materials is dramatically influenced by using nano-size particles. Many scientific studies and experiments have been conducted to incorporate nanotechnology into the field of cementation composites to enable the creation of novel hybrid materials, as well as increase concrete durability and provide ultra-high-performance materials [2]. Among the various nanoparticles; carbon nanotubes, titanium dioxide, silica, clay, copper, and aluminum oxide (Fig. 1) are the most commonly utilized nanoparticles in the structural engineering industry [3].

Carbon nanotubes; history and types

Among the different types of nanomaterials, nanotubes have attracted the most attention of scientists in recent years in both fields academia and industry. In 1991, Japanese physicist Sumio Iijima made a ground-breaking

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✉ Ali Ebrahim
aliibrahim09551@gmail.com

Selvaraj Kandasamy
drskandasamy@veltech.edu.in

[1] Department of Civil Engineering, Vel Tech Rangarajan Dr, Sagunthala R&D Institute of Science and Technology, Chennai, Tamil Nadu, India

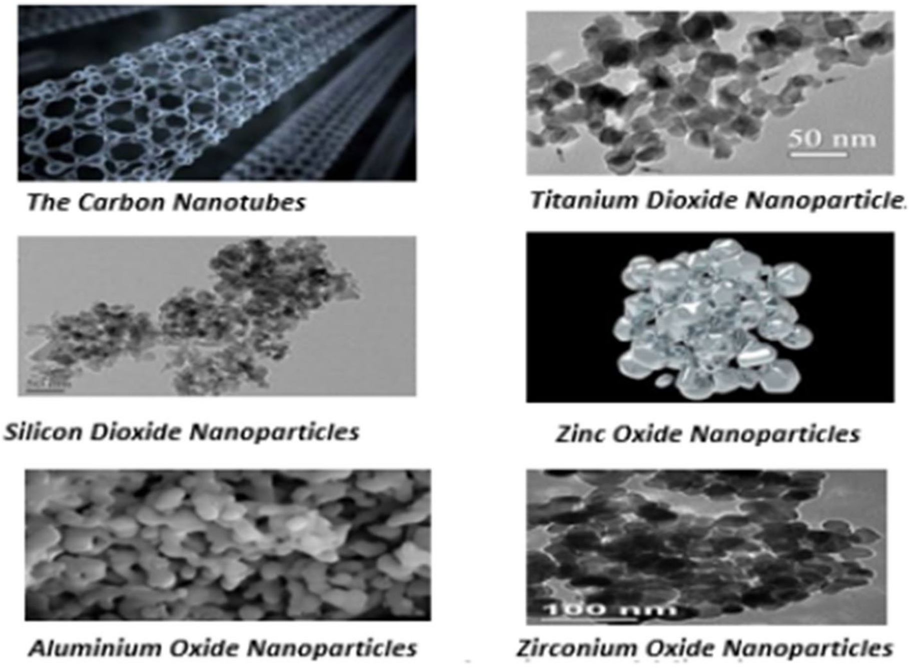
The Carbon Nanotubes
Titanium Dioxide Nanoparticle
Silicon Dioxide Nanoparticles
Zinc Oxide Nanoparticles
Aluminium Oxide Nanoparticles
Zirconium Oxide Nanoparticles

Fig. 1 SEM image of different types of nanoparticles used in civil engineering

discovery using transmission electron microscopy (TEM). He observed and characterized the unique cylindrical structure of carbon nanotubes for the first time, revealing the remarkable properties of nanoscale carbon [4]. This discovery sparked immense interest in the synthesis and usage of these materials, leading to extensive research and development. Carbon nanotubes (CNTs) are cylindrical very small structures made of rolled-up sheets of single-layer carbon atoms (graphene) [5]. For their small size, CNTs are surprisingly strong. In general, CNTs can have different structures including single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), and multi-walled carbon nanotubes (MWCNTs) as shown in Fig. 2. The comparison of SWCNTs and MWCNTs is presented in Table 1.

Multi-walled carbon nanotubes; production, properties, and applications

Multi-walled carbon nanotubes production

Carbon can exist in nature in different solid forms such as diamonds, coal, and graphite. They are all composed of carbon molecules, but those molecules are bonded together in various ways, giving them unique characteristics such as graphite's smoothness and diamond's brilliance. Over the years, numerous research efforts have been conducted in laboratories to explore various forms of carbon, including graphene (sheets consisting of a single layer of carbon atoms) and carbon nanotubes (tubes consisting of carbon atoms arranged in a lattice structure). Initially, many commercial applications primarily focused on MWCNTs, which are composed of multiple tubes nested within one another [6].

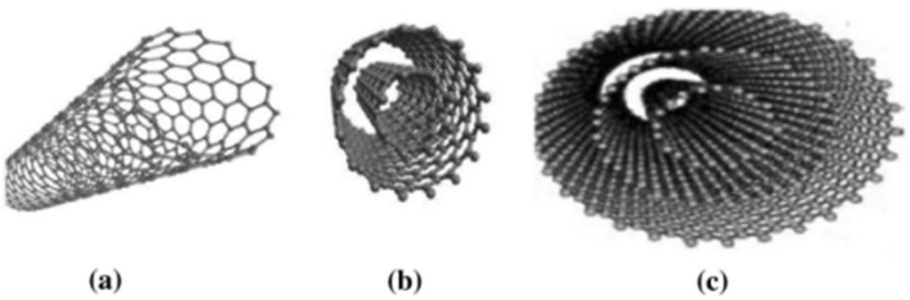

Fig. 2 Types of carbon nanotubes; **a** SWCNT, **b** DWCNT, and **c** MWCNT [15, 53]

Table 1 Comparison of MWCNTs and SWCNTs

Aspect	Multi-walled carbon nanotubes (MWCNTs)	Single-walled carbon nanotubes (SWCNTs)
Structure	Multiple concentric graphene layers	A single layer of rolled graphene
Diameter range	Few to tens of nanometers	0.4–2 nm [54]
Length range	Micrometers to millimeters	Micrometers to millimeters
Electrical properties	Variable conductivity based on layers	High electrical conductivity [58]
Mechanical properties	Enhanced mechanical strength	High flexibility [55]
Optical properties	Variable based on layers	Variable based on chirality [56]
Thermal conductivity	High	High
Surface area	Lower	Higher
Manufacturing complexity	Relatively simpler [57]	More challenging [57]
Applications	Reinforcement, thermal management, and energy storage [59]	Electronics, sensors, nanoelectronics, and composites [59]

In the early 1990s, researchers began exploring methods to produce MWCNTs [5]. The production of MWCNTs involves various methods and techniques. Here are some common approaches for MWCNT synthesis:

- Chemical Vapor Deposition (CVD): This method was first utilized for the production of MWCNTs by Morinobu et al. in 1993 [5]. CVD is a widely used method for MWCNT production. It involves the catalytic decomposition of hydrocarbon gases, such as methane or ethylene, in the presence of a metal catalyst, typically iron (Fe), cobalt (Co), or nickel (Ni). The hydrocarbon gas is introduced into a reactor at high temperatures (typically 600–1000 °C), and the catalyst nanoparticles facilitate the growth of MWCNTs [7].
- Arc Discharge: Ebbesen and Ajayan, in 1992 [5, 8], were the first to employ this technique for the synthesis of MWCNTs. In the arc discharge method, an electric arc is generated between two graphite electrodes in an inert gas atmosphere. The high temperature and electric field cause carbon vapor to condense into MWCNTs [9]. This method was one of the earliest used for CNTs production but is less commonly employed today due to scalability challenges.
- Laser Ablation: The initial application of this technique for the production of MWCNTs was attributed to Smalley and Rice in 1995 [5]. Laser ablation involves irradiating a carbon target, such as graphite, with a laser in the presence of a gas, typically a mixture of inert gases such as argon or helium. The laser energy causes the carbon atoms to evaporate and condense into MWCNTs. This method allows precise control over the size and structure of the produced nanotubes [10].
- Floating Catalyst Method: The pioneering work of Iijima in the early 1990s was a significant milestone in the field of carbon nanotube research and established the floating catalyst method as the preeminent technique for the synthesis of MWCNTs [11]. In the floating catalyst method, a catalyst precursor, typically ferrocene or metal salt, is vaporized along with a carbon source, such as a hydrocarbon gas or liquid. The vapor mixture is then passed through a reactor where MWCNTs grow in the presence of catalyst nanoparticles [12].

Physical properties of multi-walled carbon nanotubes

MWCNTs are long hollow tubes. However, in many situations, length is not the most important factor. The aspect ratio, or the length-to-diameter ratio, is more critical. The aspect ratio of MWCNTs with typical diameters between 7 and 100 nm is typically between 50 and 4000. The mechanical properties of cement-based materials can be significantly influenced by the different diameters of MWCNTs employed [13]. Carbon nanotubes have several unique features compared to other materials. To begin with, their dimensions are small enough to be used in microscopic studies [14]. Nanotubes, for example, are already being used to replace traditional tungsten tips due to their comparatively stable form. Second, its tensile strength is far greater than that of high-strength steel alloys (45 billion pascals versus 2 ~ billion pascals). Third, its current-carrying capacity is approximately 1 billion amps per square centimeter, which is much more than copper wires that burn out at around 1 million amps per square centimeter. Furthermore, compared to conventional materials, their temperature stability and heat transmission efficiency are significantly higher [15].

Effect of multi-walled carbon nanotubes on concrete, an overview

1. Many types of research have been carried out to study the effect of MWCNT on concrete:

Experimental research was conducted by Elena Cerro-Prada et al. [16] on cement mortar specimens with dimensions of 160 × 40 × 40 mm. MWCNTs with an external diameter of 6–13 nm, length of 10 μm, and in the form of powder were added to cement mortar using a sonication dispersion procedure in four different concentrations by the mass of cement: 0.00, 0.01, 0.015, and 0.02 wt%. Various parameters were assessed to evaluate the effects of MWCNTs, including consistency, density, setting time, and compressive and flexural strength of the mortar mixes at 28- and 90-day curing times, including consistency, density, setting time, and compressive and flexural strength of the mixes at 28- and 90-day curing times. Additionally, one sample was manufactured for each MWCNT proportion, for every curing period, to investigate the thermal variation of electrical resistivity of MWCNT-mortars. The measurement of electrical resistivity was conducted using the 4-point probe Wenner technique. The results demonstrated improved compressive and flexural strength by 25.4 and 20.3% at 28 and 90 days, respectively. At 28 days of curing, the compressive strength increased by 25.4%, while the flexural strength increased by 20.3% at 90 days. The presence of MWCNTs in the cement matrix resulted in a decrease in resistivity, even with very low nanomaterial additions. Notably, incorporating 0.02 wt% MWCNTs led to shorter initial and final setting times, suggesting a denser microstructure and a finer porous structure.

Anand Hunashyal et al. [2] conducted experiments to examine the effects of introducing MWCNTs and nano-SiO2 on the mechanical characteristics of hardened cement paste. Ordinary Portland cement (OPC) of 43 grade, silicon dioxide nanomaterials, and MWCNTs with a diameter of 10–30 nm, length of 1–2 nm, and purity of 95% were used in the research. The MWCNTs were sonicated in a glass beaker in an ultrasonic bath to achieve full dispersion in water. Specimens of size 20 mm × 20 mm × 80 mm were subjected to a 3-point bending test using a load frame with a capacity of 10 kN, with a constant strain rate of 0.125 mm/min. Compression tests were performed on 20 mm × 20 mm × 20 mm cubes. Different concentrations of MWCNTs and nano-silica were utilized: 0.75% MWCNTs, 0.25% nano-silica, and 0.75% MWCNTs plus 0.5% nano-silica by weight of cement. The results indicated a physical bonding between the cement matrix and MWCNTs. The incorporation of MWCNTs and nano-SiO2 significantly improved the mechanical properties of the cement composite, with the addition of these nanoparticles nearly doubling the flexural strength compared to the control beam.

Liulei Lu et al. [17] conducted a study on ultra-high-strength concrete (UHSC) to investigate the influence of MWCNTs on its mechanical characteristics and durability. The materials used in this study included MWCNTs, polyvinyl pyrrolidone (PVP) surfactant, OPC, silica fume (SF), ground granulated blast-furnace slag (GGBS), polycarboxylate-based superplasticizer (SP), natural river sand (NRS), crushed granite (CG), and tributyl phosphate (TP). The MWCNTs were dispersed using PVP as a dispersant in a surfactant-milling method. FE-SEM observation was performed on a cement paste containing MWCNTs at a concentration of 0.3% by weight of cement (bwoc) after 28 days of standard curing. For the preparation of UHSC mixtures, five different mixtures were created with varying levels of MWCNTs (0.00, 0.03, 0.05, 0.10, and 0.15% bwoc). The water-to-cementitious materials ratio was kept constant at 0.20 for all the mixtures. The aggregates were air-dried, and the sand was mixed with the cementitious materials (C, SF, and BS). Coarse aggregates were added, and dry materials were mixed for 2 min before adding water and SP. In the case of mixtures containing MWCNTs, the MWCNTs were first dispersed in water. After adding water and SP, the concrete mixtures were mixed for 4 min. Flexural strength tests were conducted on cuboid-shaped specimens with dimensions of 100 mm × 100 mm × 300 mm, while compressive strength tests used cuboid specimens with dimensions of 100 mm × 100 mm × 100 mm. The results showed that the inclusion of 0.05% MWCNTs significantly improved the compressive and flexural strength of UHSC. Furthermore, incorporating MWCNTs reduced the chloride diffusion coefficient by 24.0% in UHSC. FE-SEM analysis revealed that MWCNTs acted as load-bearing bridges and exhibited good pull-out behavior.

Grigory Yakovlev et al. [18] conducted research on modifying traditional construction materials using carbon nanotubes. They investigated the effects of adding ultra-small amounts of MWCNTs (0.02–0.0025% of the binder mass) to mineral matrices, such as cement concrete, silicate paint, anhydrite binders, and fire-retardant coatings based on liquid glass. The MWCNTs used had specific characteristics, including a diameter of 10–15 nm, length of 1–15 μm, and an average density of 50–150 kg/m^3. The researchers observed that the addition of carbon nanotubes led to the structuring of the mineral compositions, resulting in increased density and strength. The modified anhydrite binding matrix showed intensified processes of hydration and structure formation. When modifying silicate coatings with carbon nanotube dispersions, they found an absorption of electromagnetic radiation up to 70%. Furthermore, the addition of carbon nanotubes to fire-proof compositions based on liquid glass improved the structure and efficiency of intumescent protective coatings under flame exposure. It was noted that the cost of the modified products increased by 0.5–3%, depending on the chosen technology for material modification.

Research conducted by Wenhua Zhang et al. [19] aimed to evaluate the impact of MWCNTs on the mechanical and damping characteristics of ultra-high-performance concrete (UHPC). The study utilized raw materials including OPC 52.5, Grade I fly ash, slag, silica fume, and a polycarboxylic acid superplasticizer. MWCNTs were added in the form of a water dispersion with a mass fraction of 10%. Compressive strength and flexural strength test conducted on specimens sized at 160 × 40 × 40 mm, while damping test specimens were 50 × 10 × 5 mm. The researchers concluded that the addition of MWCNTs at varying concentrations (0.03, 0.05, and 0.07%) in UHPC led to increased compressive strength compared to the reference sample, resulting in improvements of 1.4, 2.7, and 2.1%, respectively. Additionally, the inclusion of MWCNTs significantly enhanced the flexural strength of UHPC, with specimens containing 0.03, 0.05, and 0.07% MWCNTs exhibiting 51, 68, and 43% higher flexural strength, respectively, compared to the reference sample. Regarding damping properties, specimens with 0.03 and 0.05% MWCNTs demonstrated significantly higher loss factors, with improvements of 89.1 and 98.3%, respectively, compared to specimens without MWCNTs. However, the specimens with 0.07% MWCNTs only showed a 15.5% improvement in the loss factor. Therefore, MWCNTs not only improved the mechanical properties but also enhanced the damping properties of UHPC. Importantly, the researchers discovered that high concentrations of MWCNTs caused mutual adsorption and agglomeration, indicating a potential limitation.

Mudasir and Naqash [20] conducted research on the influence of water–cement ratio on concrete modified with MWCNTs. The experimental setup involved using OPC, crushed aggregates, coarse sand, and 97% pure CNTs with a diameter of 5–15 nm. The CNTs were dispersed in 30% of the mixing water and sonicated for 20 min to achieve deagglomeration. The optimal CNT to water weight ratio was 1:35. To investigate the effect of the water-to-cement (W/C) ratio on the workability of carbon nanotube-incorporated concrete (CNTC), five different concrete samples were produced, varying the W/C ratios from 0.40 to 0.55. The ratio of cement to sand to aggregates remained constant at 1:1.76:2.66, and 1% of the weight of the cement was added as CNTs to the CNTC. A reference concrete without CNTs was also prepared for comparison. The results showed that increasing the W/C ratio led to an increase in slump, indicating improved workability, but a decrease in compressive strength. The optimum W/C ratio for CNTC samples was found to be 0.48, striking a balance between strength and slump. The researchers observed a 39% reduction in workability in CNTC samples, which was attributed to water entrapment within CNT agglomerates. They also noted that the presence of capillary porosity, which increases as the W/C ratio exceeds 0.40, negatively impacts the strength of the compositions. However, the addition of CNTs in CNTC samples helped counterbalance this effect through the bridging action of carbon nanotubes.

Arash Sedaghatdoost and Kiachehr Behfarnia [21] conducted research to explore the mechanical properties of MWCNTs in high-temperature Portland cement mortar. The study revealed that the optimal dosage of MWCNTs may be 0.1 percent of the cement weight. The materials used in the study included OPC, standard sand, and MWCNTs with an outside diameter of 8–15 nm, inside diameter of 3–5 nm, length of 50 µm, and purity of 95%. Compressive strength tests were performed on three specimens with dimensions of 50 × 50 × 50 mm after 28 days of wet curing. Additional specimens were kept under laboratory conditions for 90 days to reach maximum strength before testing for tensile and flexural strength. The influence of temperature was evaluated by conducting tests at various temperatures ranging from 20 to 800°C. The study found that the residual compressive strength of all specimens up to 400°C was higher compared to those at 20°C, and specimens containing MWCNTs exhibited increased residual compressive strength. However, the compressive strength decreased from 400 to 800°C, although the samples containing MWCNTs still showed higher strength compared to the control samples.

In a study conducted by Waqas Latif Baloch et al. [22], the researchers investigated the effect of high temperatures on the residual mechanical properties of normal-strength concrete (NSC) and lightweight concrete (LWC) containing MWCNTs. The study utilized OPC as the primary binder, with a composition consisting of 65.81% CaO, 18.83% SiO2, and 6.94% Al2O3. Fine aggregate was sourced from natural sand in a saturated surface dry (SSD) condition. Two types of concrete were prepared: LWC using expanded shale and NSC using crushed limestone. To enhance the dispersion of nanotubes in the cementitious matrix, Acacia gum (AG) powder, with a d50 average particle size of 207 mm and major elemental compounds of 49.20% CaO, 21.3% Fe2O3, and 16.21% SiO2, was utilized as a surfactant. MWCNTs, comprising 0.08% by weight, were incorporated into all modified mixes. The researchers prepared a total of 120 cylinder specimens and conducted compressive strength tests at 7, 14, and 28 days. The study focused on evaluating mechanical properties such as compressive strength, tensile strength, and modulus of elasticity, as well as material properties, including mass loss under residual conditions, for both NSC and LWC. The results revealed that all concrete types experienced a reduction in strength as the temperature increased from 23 to 800 °C. This decline in compressive strength was attributed to various chemical and physical changes occurring within the concrete matrix. Notably, significant strength loss occurred as water evaporated above 100 °C, leading to increased pore pressure and internal micro-cracking. Severe and irreversible changes were observed above 500 °C.

Ali Naqi et al. [23] conducted research on cube specimens measuring 50 × 50 × 50 mm to investigate the effect of MWCNTs on the compressive strength of concrete. The study utilized MWCNTs with a purity greater than 90% and varying concentrations (0, 0.01, 0.02, 0.03, 0.05, 0.10, 0.20, and 0.30 wt%) of binder. To disperse the MWCNTs, they were dry mixed with cement and very fine particles of silica fume in a Hobart mixer, which helped break down the agglomerates to smaller sizes (Fig. 3). The results indicated that samples with 0.01% MWCNTs exhibited the highest compressive strength, showing improvements of 4.4, 9.7, and 12.4% compared to reference specimens at 1, 3, and 7 days, respectively. However, higher dosages of MWCNTs (> 0.03 wt%) had adverse effects, such as the formation of a smaller internal pore structure and difficulties in filling the fine pores due to entanglement and clumping of MWCNTs.

In their investigation, Mahdi Feizbahr et al. [15] studied the effect of MWCNTs on mortar specimens by treating them with varying concentrations (0.045, 0.15, and 0.2% of the weight of cement). The dispersion of MWCNTs was achieved using an ultrasonic bath for 30 min. The compressive strength of the control samples was found to be the lowest at 7 days of age. However, at 28 and 90 days, the concrete samples with 0.15 and 0.2% of nanotube content demonstrated the best performance. Considering economic efficiency, the sample with 0.15% nanotube content showed the best overall performance. Notably, the 90-day samples exhibited a significant increase in strength compared to the 28-day samples, indicating ongoing reactions in the concrete that continued to enhance its strength over time. These findings clearly demonstrate the significant long-term impact of carbon nanotubes.

Packing density is a key parameter for the high bond strength between steel fibers and the UHPC matrix. Kay Wille and Kenneth J. Loh [24] studied the effect of adding a small amount of MWCNTs (0.022% by weight of cement) to UHPC to enhance the behavior of the bond between the steel fibers and the matrix. MWCNTs used in this study are characterized by an average diameter of 8 nm and length–diameter aspect ratios as large as 104. Two approaches were used to disperse MWCNTs and use them in the mix. A non-covalent approach based on steric stabilization was adopted. This involved mixing MWCNTs with diluted polyelectrolyte or diluted SPL (superplasticizer) solutions. The MWCNT–polyelectrolyte solutions underwent ultrasonication and probe sonication to achieve nanotube dispersion. The resulting suspension process successfully separated individual MWCNTs in aqueous solutions without compromising their properties. To fabricate UHPP

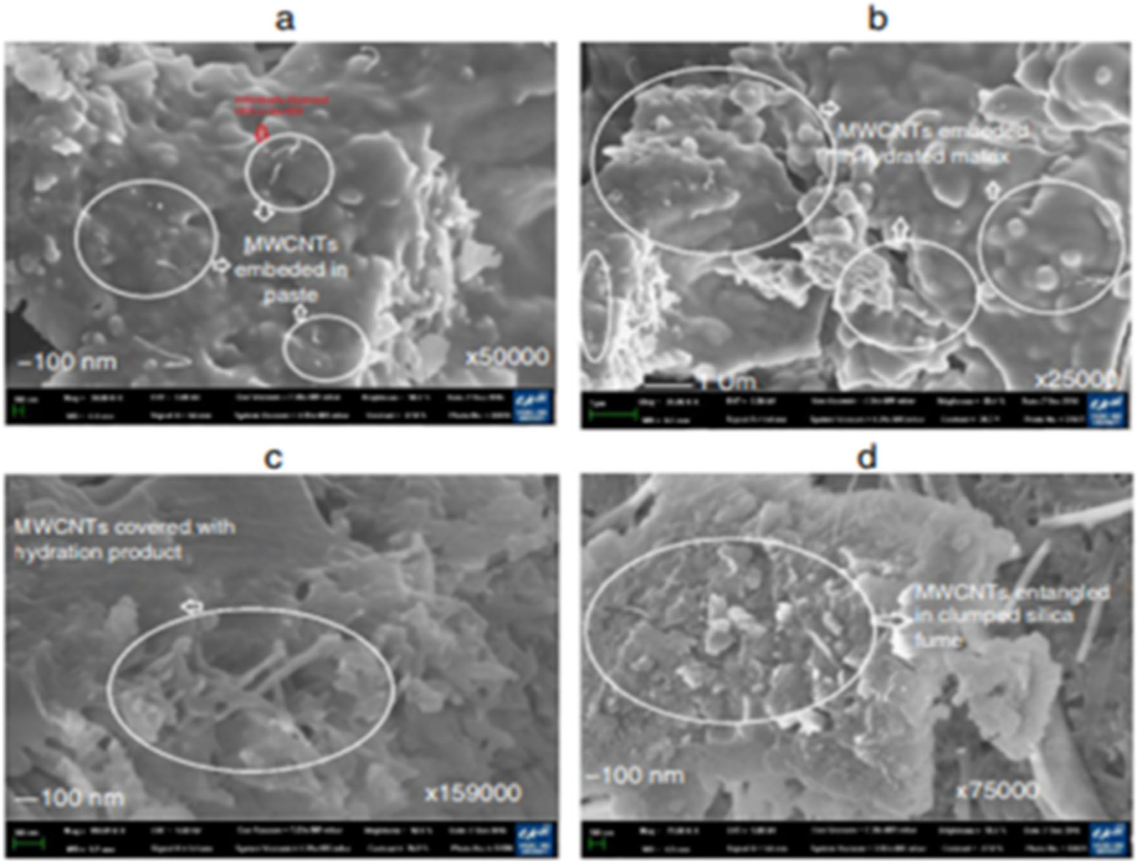

Fig. 3 SEM image of individually dispersed MWCNT fibers embedded in hydration product (**a**, **b**). MWCNTs covered with hydration product (**c**). MWCNTs entangled in clumped silica fume (**d**) [23]

and UHPC specimens, dispersed MWCNTs solutions were used. High molecular weight polyelectrolyte (poly(sodium 4-styrene sulfonate) or PSS) was employed for MWCNTs dispersion. On the other way, MWCNTs were directly dispersed in a suitable SPL based on poly(carboxylate ether). Compressive tests were performed with ultra-high-performance paste (UHPP) and UHPC as reference samples to compare their performance against UHP-MWNTRP and UHP-MWNTRC fabricated from MWCNTs-based solutions. These results revealed that heat treatment can enhance the influence of MWCNTs during heat-accelerated hydration of UHPC specimens. Besides the low concentration of MWCNTs, other factors that lead to similar performances in pristine and MWCNT-SPL enhanced UHPC specimens might be that bonding behavior is insufficient to use its material properties, and the length of MWCNTs is too short to bridge microcracks for enhancing the mechanical properties of the bulk cementitious composite. The bond behavior of steel fibers pulled out of UHPP and UHPC significantly increased with the addition of low concentrations of MWCNTs (1-mg/mL MWNT solutions or 0.022% relative to cement weight) within the concrete mix.

Barıs Şimşek [25] conducted a study to investigate the impact of various properties of MWCNTs on the properties of cement paste and to understand the underlying reasons behind these effects. The materials used in the research included pozzolanic-type cement, a second-generation high-performance polycarboxylate-based plasticizer additive, and seven types of MWCNTs as presented in Table 2. To ensure a homogeneous dispersion of carbon nanotubes in the cement paste, the method of sonication in a bath was chosen. Lower-temperature sonication was used to enhance the effect and prevent temperature increases and foaming, resulting in a more uniform dispersion. The cooled MWCNTs dispersions were then added to the pozzolanic-type cement along with the superplasticizer. A constant water-to-cement ratio of 0.43 and a superplasticizer-to-cement ratio of 0.5 were used based on preliminary trials. The mixture was cast into molds of different dimensions for measuring thermal, electrical, mechanical, and durability properties, as well as for analyzing hydration. After demolding, the specimens were cured in lime-saturated water until testing. The study revealed that the success of MWCNTs in filling gel nano-micro pores or micro-meso cracks depended on their properties such as functional group content, surface area, length, and outer diameter. MWCNTs with fewer functional groups, smaller surface areas, shorter lengths, and larger outer diameters were found to be effective in filling gel nano-micro pores. On the other hand, MWCNTs with higher functional group content, larger surface area, longer length, and smaller outer diameter were more successful in filling micro-meso cracks. The presence of carboxylated-functionalized MWCNTs increased the amount of voids and cavities in cement paste due to the formation of formic acid through hydrogen bonding mechanisms. In contrast, hydroxyl groups contributed to accelerating the hydration rate and filling the voids. Carboxylated-functionalized MWCNTs with higher surface area, more functional groups, and larger lengths were preferred for applications where large deformations such as cracks and gaps were a concern. The study also highlighted the significance of calcium hydroxide (CH) in determining the product variability of carbon nanotube-reinforced cement pastes. CH played a more important role than other properties when considering the impact of nanomaterials in mortar. By using hydroxyl-functionalized MWCNTs with a 30-nm outer wall diameter and replacing 0.1% by weight of cement using the PCA technique, significant improvements were achieved. These improvements included a 15.9% enhancement in thermal conductivity, 61.0% reduction in electrical resistivity, 9.8% increase in ultrasonic pulse velocity, 77.2%

Table 2 Properties of MWCNTs used in the study [25]

Features	MWCNT	MWCOOH18	MWCOOH28	MWCOOH48	MWOH18	MWOH28	MWOH48
Purity	>96	>96	>96	>96	>96	>96	>96
–COOH content (wt%)	N/A	1.30	0.70	0.50	N/A	N/A	N/A
–OH content (wt%)	N/A	N/A	N/A	N/A	1.70	1.0	0.75
Color	Black	Black	Black	Black	Black	Black	Black
Outer diameter (nm)	48–78	18–28	28–48	48–78	18–28	28–48	48–78
Inner diameter (nm)	5–15	5–15	5–15	5–15	5–15	5–15	5–15
Length (μm)	10–25	10–35	10–25	10–25	10–30	10–25	10–25
Tapped density (g/cm^3)	0.15	0.30	0.30	0.20	0.30	0.30	0.20
True density (g/cm^3)	2.2	2.4	2.4	2.4	2.4	2.4	2.4
Specific surface area (m^2/g)	50	120	65	50	120	65	50
Ash content (wt. %)	9	1.5	1.5	1.5	1.5	1.5	1.5
Electrical conductivity (S/cm)	90	90	90	90	90	90	90
Production method	CVD	CVD	CVD	CVD	CVD	CVD	CVD

improvement in splitting tensile strength, 50.1% decrease in CH content, 15.2% reduction in water absorption, and 6.2% decrease in porosity.

Prakasit Sokrai and Natt Makul [26] proved in their experimental investigation that insufficient CNTs dispersion causes numerous defect sites to occur in the nanocomposite, limiting the effectiveness of CNTs in the matrix. On the other hand, Musab Aied Qissab and Shaymaa Tareq Abbas [27] showed in their results that over-dispersed CNTs solution reduces the workability of CNTs concrete and results in poor strength.

In a study conducted by Yashavant Jeevanagoudar et al. [28], the researchers investigated the enhancement of mechanical properties in cement mortars reinforced with MWCNTs. The experiments focused on specimens with dimensions of 70.7 mm × 70.7 mm × 70.7 mm. The materials used included OPC-43 grade cement, M-sand with a specific gravity of 2.77 and a fitness modulus of 2.531, and MWCNTs with an outer diameter of 5–20 nm, length 10 µm, and purity greater than 90%. The dispersion of MWCNTs in water was achieved using sonication, without the use of surfactants or superplasticizers. Different concentrations of MWCNTs (0.2, 0.4, 0.6, and 0.8% by weight of cement) were added to the specimens. The researchers conducted water absorption, piezo-resistive sensitivity, compressive strength, and slump flow tests. The results showed that the compressive strength of the mortars increased with higher concentrations of MWCNTs, reaching a maximum at the optimal concentration of 0.4% by weight of cement. Regarding water absorption, the tests indicated that the lowest water absorption occurred at the concentration of 0.4% MWCNTs by weight. However, the workability of the mortars, as determined by the slump flow test, decreased with higher concentrations of MWCNTs. Additionally, the piezo-resistive experiments revealed that the resistivity of the mortars decreased as the compressive load increased. Among the different concentrations tested, the mortar containing 0.4% MWCNTs demonstrated better performance for both static and cyclic loads.

The same amount of MWCNTs can have varied effects on particular mechanical characteristics of concrete mix, for example, a lower percentage of MWCNTs could be enough for showing enhancements in tensile and flexural strength, whereas a higher fraction is demanded to increase the compressive strength [29].

One of the most commonly cited problems of utilizing MWCNT as a cementitious material reinforcement is that uniform dispersion is difficult to achieve because of the strong van der Waals interaction between CNTs particles. According to Su-Tae Kang et al. [30], there are three approaches available to increase dispersion. To aid dispersion, a solvent and a CNTs-containing solution can be treated using ultrasonic waves. Second, to increase affinity, a surfactant is added between the carbon nanotubes and the matrix. In the previous research on cement composites enhanced with CNTs, these two approaches were used. The third approach, which includes chemical modification of carbon nanotubes, adds functional groups on their surfaces, allowing for better dispersion and bonding between carbon nanotubes and the matrix. Using acid-treated CNTs increased CNTs dispersion in CNTs/cement composites, enhanced pore structure, and produced denser hydration products around CNTs.

Among the most important aspects of fresh concrete that is affected by the introduction of CNTs is flowability [31]. The flowability of cement-based composites incorporating CNTs decreases with increased CNTs concentration. According to Suman Kumar Adhikary et al. [32], CNTs are a chemically inert material that accelerates the hydration process by nucleation effects rather than taking part in it. Various studies reveal that CNTs speed up the hydration process and that cement composites containing CNTs create the most heat during the hydration process. The flexural strength of cement-based composites was proven to increase with increased CNTs concentrations in the case of CNTs with a larger aspect ratio. In terms of durability, CNTs that incorporate cementitious composites with a low water–cement ratio perform better. CNTs have a stronger influence on long-term creep and shrinkage than carbon nanotubes. CNTs not only enhance cementitious materials' shrinkage and water loss properties, but they also increase their freeze–thaw resistance.

The connecting surfaces between gaps, aggregates, and cement particles determine the durability of concrete [32]. As a result, nanoparticles with characteristics such as strength and durability are of special interest in concrete manufacture [33].

Hawreen and Bogas [34] conducted a comprehensive research study on the effects of CNTs on the shrinkage, creep, and mechanical properties of concrete. Five types of MWCNTs with different aspect ratios were utilized; CNTSL and CNTSS were in suspension form and dispersed in water using a polyethylene glycol aromatic imidazole surfactant, while CNTPL, CNTCOOH, and CNTOH were in powder form and underwent acid treatment to introduce functional groups (–COOH and –OH) on their sidewalls. The concrete production included Portland cement type I 42.5 R, crushed limestone aggregates, and natural siliceous sands, along with a polycarboxylate-based superplasticizer (SP) for low water-to-cement ratio concrete. Different procedures were implemented for dispersing the CNTs depending on their type. The testing process involved creating concretes with varying water-to-cement ratios (w/c) and cement contents across different compressive strength grades. The concentration of CNTs ranged from 0.05 to 0.5% by the weight of the cement. Various tests were conducted, including slump, fresh density, and air content measurements. Multiple specimens were produced for compressive strength, modulus of elasticity, shrinkage, and creep tests. The modulus of elasticity was measured through loading and unloading cycles, while axial deformations were measured using displacement transducers. Shrinkage was monitored using a demountable mechanical strain gauge, and total creep was determined by measuring the longitudinal deformation under sustained stress after 28 days. SEM analysis was performed to examine the dispersion and interaction of CNTs with the cement matrix. The findings revealed that high concentrations of CNTs (up to 0.5% wt) resulted in slightly increased air content and slump. Concrete reinforced with CNTs with a smaller aspect ratio of 0.1% demonstrated superior mechanical performance. CNTs proved effective in reducing both early and long-term shrinkage of concrete by up to 54 and 15%, respectively. Furthermore, the introduction of various CNTs yielded consistent long-term shrinking behavior. CNTs also exhibited a reduction of 17–18% in long-term creep compared to conventional concrete (RC), with minimal influence from the type of CNTs on the shape of creep curves.

Carriço et al. [35] tested three types of industrial MWCNTs: pristine nanotubes (CNTPL), lower aspect ratio pristine nanotubes (CNTSS) in aqueous suspension, and carboxyl-functionalized nanotubes (CNTCOOH) in powder form. In general, CNTs were found to be more effective in low w/c concrete. This tendency can be referred to as the use of a superplasticizer to improve cement and CNTs dispersion, as well as the increasing quantity of CNTs in pastes with greater cement concentrations. Carbonation-induced corrosion lifetimes were estimated to be up to 40% longer in CNTs reinforced concrete than in reference concrete. According to the findings, in conventional CNT-reinforced concrete, carbonation should not be a major degradation mechanism.

The capacity of nanoparticles to spread efficiently without aggregation is one of the most important aspects influencing their efficiency in improving cement composite characteristics. Noha Hassan et al. [36] conducted experiments on cube specimens containing water, cement, and CNTs to study the effect of CNTs on compressive strength. They used various protocols, and their findings revealed that increasing the sonication exposure time has no significant effect on improving the properties of materials. It has been shown that when compared to the control sample, there is a nonlinear relationship between increasing the CNTs percent and increasing sample compressive strength, so adding more CNTs does not always ensure better strength. Pre-wetting the CNTs with a small amount of water aids in the replacement of the solid–air contact with a solid–liquid interface for optimal distribution. They also investigated the effect of other factors in CNTs dispersion in water, such as CNTs concentration and whisking. As seen in the interaction plot, it was concluded that maximum strength is achieved when the percentage of CNTs was around 0.85% wt. Whisking positively affects the concrete's mechanical characteristics, signifying greater CNTs particle dispersion. Pre-wetting with whisking and no sonication, along with that CNT% and a long curing period, results in the best compressive strength performance.

Jintao Liu et al. [37] conducted a comprehensive investigation on the impact of MWCNTs and graphene sheets on the fracture toughness of cement paste. OPC 42.5 was used in conjunction with MWCNTs and two-dimensional planar structure graphene sheets. The researchers ensured the homogeneous and stable dispersion of MWCNTs and graphene by employing effective surfactants and ultrasonic treatment. For flexural strength testing, prism-shaped specimens measuring $40 \times 40 \times 160$ mm^3 were cast. Additionally, cubic specimens measuring $40 \times 40 \times 40$ mm^3 were cast for compressive strength tests. Both flexural and compressive strength tests were performed on the cement composites after 7 and 28 days. The incorporation of MWCNTs and graphene sheets resulted in a significant increase in fracture toughness of the cement paste, with maximum improvements of 54.1 and 42.6%, respectively. Similarly, when the same amount of graphene was utilized, the fracture energy and fracture toughness of the cement paste increased by 37.0 and 11.0%, respectively. However, when the content of MWCNTs or graphene was increased to 0.1 wt%, the enhancement in fracture toughness was only marginal. The mechanical test results revealed that the addition of MWCNTs and graphene sheets promoted the early-age strength of the cement paste, with specimens containing MWCNTs exhibiting superior fracture properties at lower concentrations. The analysis of porosity and pore size distribution indicated that the incorporation of nano additives led to a reduction in the total porosity of the cement paste, resulting in a denser microstructure. Moreover, the morphological structure analysis of the specimens demonstrated that MWCNTs could decrease the orientation index of CH crystals, act as bridges, and inhibit the growth of microcracks.

Advantages/disadvantages of using multi-walled carbon nanotubes

Advantages

1. Enhanced Mechanical Properties: MWCNTs can significantly improve the mechanical properties of concrete, including tensile strength, flexural strength, and toughness. This reinforcement can make the concrete more durable and resistant to cracking and deformation [30, 32, 38, 39].

2. Improved Electrical Conductivity: MWCNTs possess excellent electrical conductivity. Incorporating them into concrete can enhance the material's electrical properties, making it suitable for applications that require conductivity, such as smart structures and electromagnetic shielding [40].
3. Increased Durability: MWCNTs can enhance the durability of concrete by reducing the ingress of moisture and harmful chemicals, such as chloride ions, into the material. This can help mitigate the corrosion of reinforcing steel and increase the lifespan of concrete structures [32, 33, 41].
4. The Reduced Carbon Footprint: The use of MWCNTs in concrete has the potential to reduce the carbon footprint of construction materials. By enhancing the mechanical properties of concrete, structures can be designed with a lower concrete volume, leading to reduced material consumption and associated greenhouse gas emissions [42, 43].

Disadvantages

1. Cost: MWCNTs are expensive compared to traditional concrete additives. The high cost of production and purification processes involved in obtaining pure MWCNTs can make them economically prohibitive for large-scale applications [44].
2. Dispersion Challenges: Achieving a uniform dispersion of MWCNTs in concrete is crucial for their effective reinforcement. However, MWCNTs tend to agglomerate, making it challenging to achieve a homogeneous distribution within the concrete matrix. Proper dispersion techniques and additives may be required to overcome this challenge [26, 27].
3. Potential Health and Environmental Risks: There are ongoing debates and concerns regarding the health and environmental impacts of MWCNTs. Some studies suggest that long-term exposure to airborne MWCNTs may have adverse effects on human health. Additionally, the potential release of MWCNTs into the environment during the service life or demolition of concrete structures raises concerns about their impact on ecosystems [45].
4. The Lack of Standardization: Due to the evolving nature of nanomaterial research, there is currently a lack of standardized testing methods and guidelines for incorporating MWCNTs into concrete. This makes it challenging to ensure consistent quality control and reliable performance assessment of MWCNT-reinforced concrete [46].

Multi-walled carbon nanotubes in comparison with traditional/innovative materials

1. Traditional reinforcing materials (e.g., steel rebar)

Strength: Steel rebar is known for its high tensile strength, providing excellent reinforcement to concrete structures. MWCNTs exhibit comparable or even higher tensile strength, offering a viable alternative with superior mechanical properties [47].

Weight: MWCNTs are significantly lighter than steel rebar, allowing for the design of lighter structures that are easier to transport and assemble.

Corrosion Resistance: Unlike steel rebar, MWCNTs do not rust or corrode, leading to improved durability and longer service life of concrete structures.

Electrical Conductivity and Healing Cracks: MWCNTs have excellent electrical conductivity, allowing real-time monitoring of structural health, as they can sense changes in strain, temperature, and moisture. Moreover, MWCNTs can autonomously fill and heal cracks in concrete through chemical or physical processes, leading to self-healing properties and improved longevity of the material [48], whereas steel rebar is electrically conductive only when in direct contact with each other.

2. Fiber reinforcements (e.g., glass fiber and carbon fiber)

Flexibility: MWCNTs can be dispersed in the concrete matrix at the nanoscale, providing more flexibility in shaping and reinforcing complex geometries. Fiber reinforcements, on the other hand, are typically used as macroscopic elements and have limitations in intricate applications [38].

Aspect Ratio: MWCNTs have a high aspect ratio, which enables them to efficiently transfer stress and reinforce the concrete matrix [49]. This aspect ratio advantage is not typically found in traditional fiber reinforcements.

Dispersion Challenges: Achieving the uniform dispersion of MWCNTs in concrete can be challenging due to their tendency to agglomerate. Fiber reinforcements, such as glass or carbon fibers, are typically easier to disperse uniformly in the matrix [49].

Cost: MWCNTs are generally more expensive than traditional fiber reinforcements, making them less economically feasible for certain applications.

3. Innovative materials (e.g., graphene oxide and nanocrystals).

Dimensionality: MWCNTs are one-dimensional structures, whereas materials such as graphene oxide and nanocrystals possess different dimensionalities (e.g., two-dimensional or zero-dimensional). This dimensional difference influences their properties and potential applications [50].

Surface Area: MWCNTs have a larger surface area compared to some innovative materials, providing more opportunities for interactions with the surrounding matrix and enhanced mechanical properties [51].

Manufacturing Complexity: The production and integration of innovative materials such as graphene oxide and nanocrystals into concrete can be more complex and challenging compared to MWCNTs [52].

Conclusion

The purpose of the review was to explore the effect of adding MWCNTs in increasing the mechanical properties of concrete. It has been observed that adding MWCNTs will improve the compressive and flexural strength of concrete. Several studies showed that the optimum dosage of MWCNTs was 0.1% wt. Results concluded that the rate of increasing the tensile stress is greater than compressive strength. One of the most difficulties faced the researchers while doing their experiments on MWCNTs is the dispersion of MWCNTs into the water. Most of them used the sonication process to disperse MWCNTs in water, several researchers added surfactants with the using of ultrasonication to enhance the dispersion, while poor dispersion reduces the efficiency of MWCNTs in the binder.

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Declarations

Conflict of interest The authors declare that they have no competing interests.

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