

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Recent Trends of Reinforcement of Cement with Carbon Nanotubes and Fibers

Oxana V. Kharissova, Leticia M. Torres Martínez and Boris I. Kharisov

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/62292>

Abstract

Recent achievements in the area of formation of carbon nanotubes (CNTs), nanocomposites, with cement are reviewed. The peculiarities of dispersion of CNTs in cementitious matrices are discussed, paying major attention to the CNT diameter, length and length-to-diameter ratio, concentration, functionalization, annealing, combination with other nanomaterials, and water-cement ratio. Several effects upon dispersion of carbon allotropes in concrete-water media are emphasized. It is also pointed out that the health impact should also be considered in further experiments on construction materials reinforced with CNTs.

Keywords: Carbon fibers, Carbon nanotubes, Cement, Composite, Dispersion, Reinforcement

1. Introduction

Concrete, steel, and asphalt coatings are conventional materials used in large scale and produced in huge quantities worldwide. In case of concrete (a mixture weak in tension and strong in compression), more than 2 tons per person are produced annually. Quantitatively, more than 11 billion metric tons are consumed every year all over the world. The cement industry is responsible for approximately 5–8% of all anthropogenic emissions of carbon dioxide worldwide [1]. Portland cement (containing, in dry phase, 63% calcium oxide, 20% silica, 6% alumina, and 3% iron (III) oxide, and small amounts of other substances) is a product with great, but not completely explored potential, despite intensive studies in the

last century. In the last century, when the nanotechnology era began, at the end of the 1980s, novel nanomaterials started to be used as additives in numerous applications, in particular for reinforcement of construction materials, and certain attention was given to cement composites. Their complex structure, when studied at the nanolevel, will definitely lead to new generations of highly durable concretes with “smart” properties. In order to improve concrete properties, a series of nanomaterials can be applied, such as nanoengineered polymers, superplasticizers, high strength fibers, or silicon dioxide (**Figure 1**).

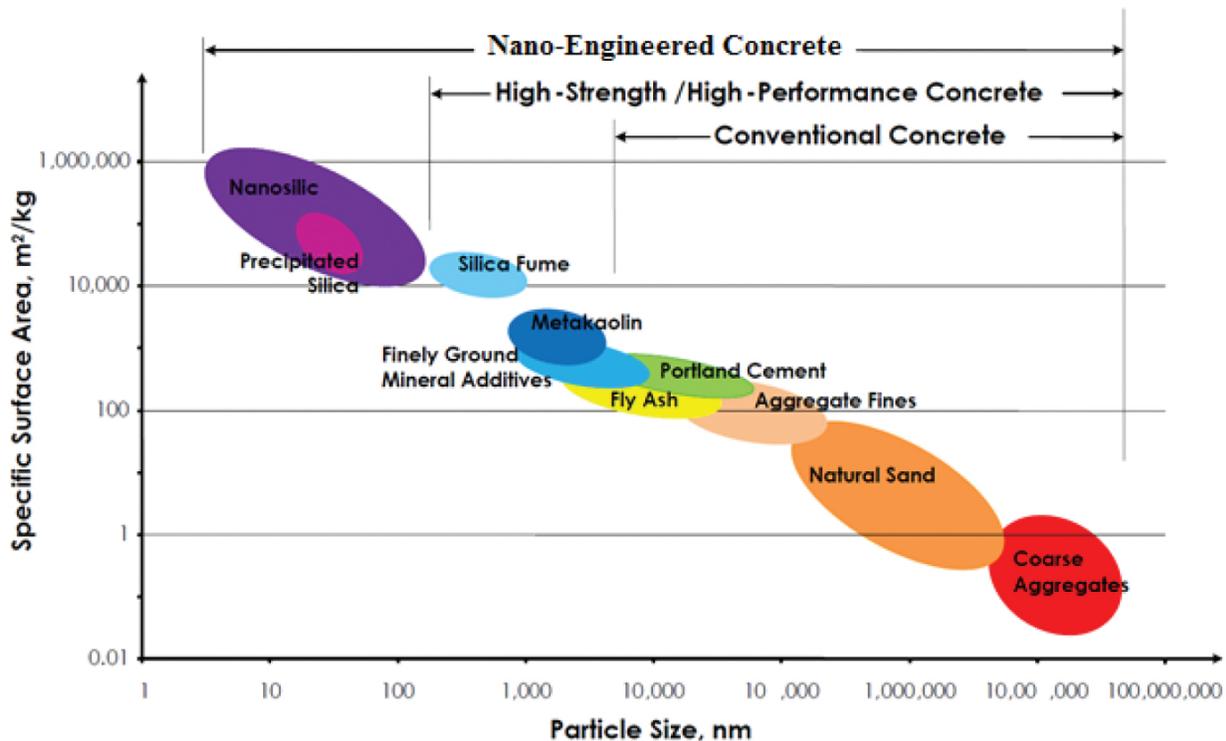


Figure 1. Particle size versus specific surface area scale in to concrete materials [2]. Reproduced with permission.

Carbon nanotubes (CNTs), well known for having extraordinary properties, are considered as major candidates for diverse applications in nanotechnology. CNTs have been incorporated into materials for cement production, with excellent results, upon low quantities of added material. Thus, reinforcing cement with low additions of multiwalled carbon nanotubes (MWCNTs), ranging from 0.05 to 0.5 wt%, can represent a remarkable enhancement in the mechanical properties of cement. It is expected that CNTs, when added to concrete, will increase compression strength beyond 200 MPa, thus allowing the construction of mile-high skyscrapers. Nowadays, CNTs and carbon nanofibers (CNF) are two of the most prospective advanced materials for application in cement-based products, for the construction industry, due to their excellent material properties. According to the reported results, CNTs can reduce the occurrence of cracks, decrease porosity, and improve mechanical properties, thus extending the cement durability. However, CNTs are insoluble in organic solvents and water, so surfactants should be normally added upon classic combination of ultrasonication and

vigorous agitation, in order to disperse CNTs. There are other well-known less common specific methods for CNT “dissolution” in liquid media [3, 4]; some of which can be adjusted to concrete fabrication.

In this chapter, we discuss recent achievements of cement reinforcement with carbon allotropes. Taking into account a recently published excellent comprehensive review [5] in this area and other related publications [6, 7], we refer the particular aspects and peculiarities of dispersion of CNTs in cement mixtures.

2. Peculiarities of CNTs and CNFs dispersion in concrete

There are at least three main ways to add CNTs uniformly to concrete: addition to cement, to water, and as admixture. In the majority of reports, ultrasonic dispersion techniques have been widely used to uniformly disperse CNTs [8]. Ultrasonication can be applied alone after adding CNTs to the concrete mass, or together with surfactants. Generally, pristine CNTs can be directly mixed with cement, but their hydrophobicity limits solubilization in aqueous media. So, frequently the CNTs are functionalized with $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture, forming -OH and -COOH functionalized CNTs, before being added to cement [9]. Alternatively, carboxylic functionalization can be done upon ultrasonication and polyacrylic acid polymer addition [10]. The use of superplasticizers (see below), magnetic stirring [11], CNT growth onto cement particles [12], and dry mixing with cement [13] are other options to disperse CNTs and CNFs in concrete, frequently accompanied by ultrasonication [14].

Generally, two main strategies are applied to provide an interfacial bonding between cementitious matrix and CNTs: (a) formation of hydration products of the cement matrix and (b) formation of covalent bonds on CNT surface using functional groups. **Figure 2** shows a scheme of interaction of the C-S-H (this means calcium-silicate-hydrate) cement product and a -COOH (carboxylic group) on the CNT surface [15]. These effects of *surface functionalization* of MWCNTs with -COOH groups on the strength and structure of Portland cement composites have been deeply studied [16]. Thus, grafting of functional groups on the surface of the nanotubes allowed acceleration of cement hydration. The authors established that the use of carboxylated nanotubes contributed to early strength development. The MWCNT-reinforced composites are characterized by high content in calcium silicate hydrates and very dense structure. The maximal compressive strength of 64 MPa (20% increase over the reference material) was observed for the composite with 0.13% of MWCNTs (by the weight of cement). The addition of carboxylated MWCNTs, in the very low amount of 0.05%, provides a 30% increase of 1-day compressive strength of developed composites.

In addition to the CNT functionalization above, *surfactants* can be applied to decrease aggregation of CNTs, by modification of their surface, since CNTs tend to aggregate together in most solvents, due to van der Waals forces, and form nanotube clusters and bundles. CNTs need to be completely dispersed in concrete in order to explore their outstanding physical properties. Application of classic surfactants, such as sodium dodecyl sulfate (SDS) and Triton X-100, has been observed in a series of reports. The effect of surfactants on pressure-

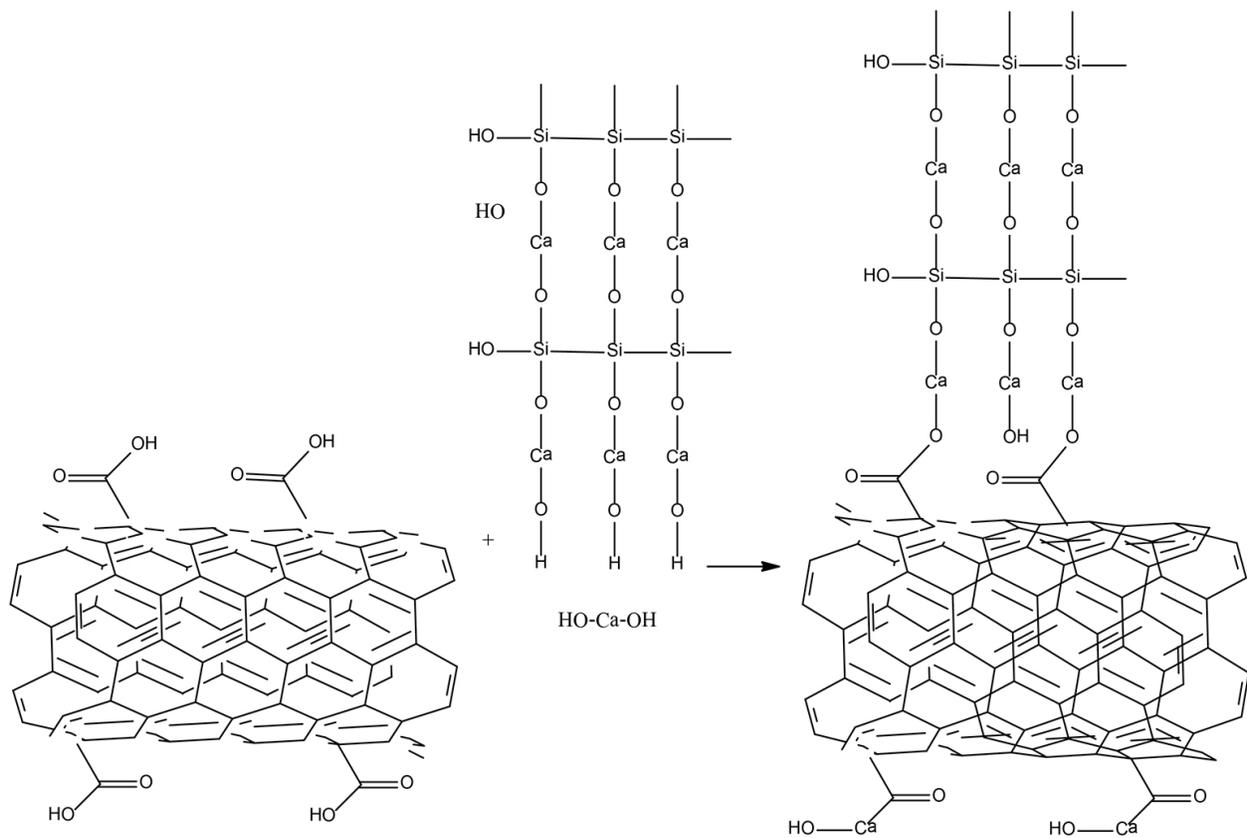


Figure 2. Reaction scheme between carboxylated nanotubes and cement hydration products ($\text{Ca}(\text{OH})_2$ and C-S-H).

sensitivity of CNT-filled cement mortar composites has been studied using sodium dodecyl sulfate and sodium dodecylbenzene sulfonate (NaDDBS) as surfactants to disperse MWNTs-COOH (OD < 8 nm, ID 2–5 nm, length 10–30 μm) in cement mortar (**Figure 3**) [17]. The authors revealed that, in comparison with SDS-based composites, the composites with NaDDBS show a more stable and sensitive response of electrical resistance to external force. In this respect, NaDDBS is a more efficient surfactant, in comparison with SDS, for dispersion of MWCNTs in cement.

Other nanotechnology classic surfactants are less common to use for CNT solubilization in concrete. Stable homogeneous suspensions of MWCNTs were prepared using gum arabic (GA) as dispersant (with an optimum GA concentration of 0.45 g/L^1) and were incorporated into Portland cement paste [18]. The authors revealed that the compressive strength, as well as the flexural strength of the Portland cement composite, can be considerably improved by adding the treated carbon nanotubes. At 0.08 wt% MWCNT concentration, the flexural strength reached an increase in 43.38%. MWCNTs act as bridges and networks across cracks and voids, which transfer the load in case of tension, and the interface bond strength between the

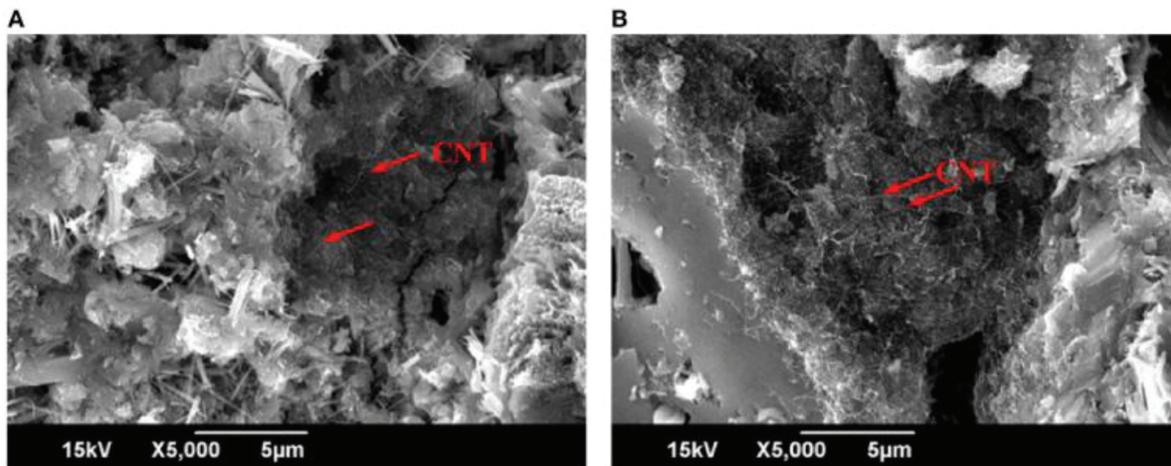


Figure 3. SEM images of CNT-filled cement mortar composites. (A) With NaDDBS and 1 wt% of MWNTs. (B) With SDS and 1 wt% of MWNTs. Reproduced with permission from [17].

nanotubes and matrix is very strong. The interfacial interactions between surface-modified nanotubes and hydrations (such as C-S-H and calcium hydroxide) of cement produce a high bonding strength, and increase the load-transfer efficiency from cement matrix to the reinforcement.

Among superplasticizers for concrete applications, we note polycarboxylate ether solution (“super plasticizer”), high-molecular-weight polyelectrolyte (i.e., poly (sodium 4-styrenesulfonate) or PSS) [19]. In a related report [20], the dispersity of MWCNTs in water and in cement paste, as well as its effect on the compressive strength of composition with MWCNTs and cement, was comparatively investigated using ultrasonic dispersion and three kinds of surface active agents: polycarboxylate superplasticizer, polyvinylpyrrolidone (PVP), and washing powder (WP). Agglomeration of MWCNTs takes place easily in cement paste and in water. The reinforce ability is poorly exhibited, even if the ultrasound is applied, in case of using, as a surface-active agent, a single polycarboxylate superplasticizer. WP and PVP are able to create MWCNT dispersions in cement paste and also in water under ultrasonic treatment; in addition, PVP enhances the compressive strength, while WP decreases it, as more air bubbles are brought inside the cement paste. In addition, several peculiarities exist on the dispersing carbon nanoparticles, in particular CNFs, in cement paste [21]. When a superplasticizer is used as surfactant, CNFs can be uniformly dispersed in water by ultrasonic processing. However, a uniform distribution of CNFs in cement paste will not be obtained by mixing water-superplasticizer-CNF dispersion with cement (used superplasticizer = high-range polycarboxylate-based water-reducing agent). To reach a better distribution in paste, either functionalized and highly dispersible CNFs should be used or the CNFs should initially be implanted or grown on cement particles. In addition, large cement particles prevent a uniform distribution, particularly when fibers are very small or are used in high doses. However, breaking cement grains into smaller particles is impractical and problematic. Fine-grain cement is very reactive and consumes a lot of water at a high rate. As a result, producing paste with typical water-

cement ratios such as 0.40 or 0.45 is very difficult or even impossible. Therefore, the authors consider it important to use fresh cement with a minimal amount of large grains and clumps for making CNF-CNT reinforced composites.

3. Improvement of concrete properties by addition of CNTs and CNFs

It is well-known nowadays that mechanical and various other properties of concrete, indicated below, are considerably improved by addition of CNTs. Thus, the inclusion of MWCNTs (outer diameter > 50nm, length 10-20 mm) in the cement mix improves both the tensile fracture characteristics and compressive strength when not mixed with a surfactant compound [22]. The improvement in the mechanical properties in specimens with the addition of CNTs was observed more clearly with increasing curing age. The fracture mechanics test results indicated that the fracture properties of microconcrete and mortar are increased through proper dispersion of very low amount of MWCNTs (CNTs/c = 0.005). The vibration damping capacities of cement-based matrices with additions of MWCNTs (external diameter 20-40 nm, length 5-15 μm) were investigated with a free vibration testing method in an elastic system [23]. Adding small amounts of MWCNTs, several positive effects on the critical damping ratio (ζ) were observed for the cement matrix. This magnitude is increased in the MWCNT-cement composites because of frictions among MWCNT matrix and multiple intertubes.

As an example of improvement of other cement properties, MWCNT (external diameter 20-40 nm, length 5-15 μm) reinforced cement composites (MWFRCs) were prepared with surfactant dispersion, ultrasonic treatment, and subsequently high-speed shear mixing processes [24]. Several following parameters can be considerably improved by adding MWCNTs: critical crack mouth opening displacement (δ_C , up to 119.4%), flexural strength (σ_{sr} , up to 54.8%) of the cured nanocomposite, and the stress-intensity factor (K_{IC} , up to 56.4%). The authors explained these values mainly by “the superior pulling-out effect of dispersed and tough MWCNT fiber upon the notched cracks”. The σ_{sr} , K_{IC} , and δ_C values can be balanced by incorporation of MWCNTs treated with acids. Additional short carbon fibers provoked a negative effect, meanwhile nanophase carbon black improved the fracture toughness.

There are controversial results for cement paste with admixed CNT of up to 500 μm in length, showing an increase or decrease in flexural or compressive strength. A small increase in fracture energy and tensile strength of a CNT-reinforced cement paste with $50 \times 50 \mu\text{m}$ was reported [25]. CNT clustering was proved to be the crucial factor for an increase in fracture energy and for an improvement in tensile strength. Data from **Table 1** demonstrate that even CNTs shorter than 10 μm can be effective in providing added strength. In addition, the general transport properties (i.e., water sorptivity, water permeability, and gas permeability) of carbon-nanotube/cement composites were investigated [26]. Carboxyl-functionalized MWCNTs (outside diameter < 8 nm, inside diameter 2-5 nm, -COOH content 3.86 wt%, length 10-30 μm) were dispersed into cement mortar to fabricate the CNT-reinforced composites, by applying ultrasonic energy, in combination with the use of surfactants (sodium dodecylbenzene sulfonate, SDS, and NaDDBS). Several coefficients of cement mortar (water

permeability coefficient, water sorptivity coefficient, and gas permeability coefficient) can be decreased by adding even small quantities of MWCNT-COOH (0.2%), thus increasing the durability of composites.

CNT length, μm	w/c	Compressive strength, MPa		Flexural strength, MPa	
		Plain	CNTs	Plain	CNTs
<10	P 0.30	38.3	61.8	2.3	2.3
<30	P 0.30	–	–	9.2	12.6
<10	M 0.40	28.9	54.3	6.0	8.23
<500	P 0.45	52.3	62.1	6.7	8.4
<100	P 0.50	–	–	5.5	7.2
<5	P –	49	56	16	8

Table 1. Strength gain when CNTs are added to cement (P = paste, M = mortar). Reproduced with permission from Ref. [25].

In cement composites, carbon fibers (CFs) can be applied alone or in combination with carbon nanotubes. The behavior of reinforced cement mortar composites round bars with MWCNTs (0.5 wt%; diameter 10-30 nm, length 1-2 μm , surface area 350 m^2/g) and CFs (2.25 wt%; length of fiber 5 mm, fiber thickness 0.3 mm), ultrasonically dispersed in the cement matrix, was elucidated [27]. Composite round bars were tested under direct tension, in order to evaluate their mechanical properties, such as ultimate load, deflection criteria, and stress-strain behavior. It was shown that the load carrying capacity of composite bars, under direct tension, is substantially higher than the plain controlled bar. Resulted plain cement bars with 2.25% carbon fiber reinforcement showed 38% increase in the ultimate load, whereas plain cement bars with 2.25% carbon fibers and 0.5% MWCNT showed 54% increase in the load carrying capacity. The presence of both carbon fibers and MWCNTs mainly contributed to the improvement of tensile load carrying capacity. Higher failure strain capacity of 44% was observed in bars with randomly distributed CF and MWCNTs as compared with plain bars.

Allotropes and hybrids of carbon can be obtained *in situ* on clinker particles as supports. Thus, the formation of a hybrid material (carbon clinker/nanofiber, **Figure 4**) was achieved by direct interaction of carbon nanofibers on clinker supporting particles (conditions: 550°C, fluidized bed reactor, gaseous C_2H_2 , and CO_2) [28]. This interaction resulted in an excellent CNFs/clinker matrix dispersion and a strong final composite. At the 0.4% CNFs concentration, the enhancement of the mechanical properties of the mortar resulted in an increase of more than 2.5-fold in the compressive strength. In a similar manner, carbon nanotubes were grown *in situ* by chemical vapor deposition on a Portland cement clinker, in order to produce a nanocomposite material using clinker as support and catalyst [29]. Iron sources such as iron ore, steel mill scale, and red mud were used as additional transition metal catalysts to increase the carbon nanotube content. Thus, the clinker contains tetracalcium aluminoferrite (C4AF phase) that can be used as a catalyst for CNT growth. In a CVD process using ethylene as carbon source,

and pure PC clinker both as a support and catalyst of CVD process, a CNT yield of 4.03%, in mass of clinker-CNT nanocomposite, was obtained.

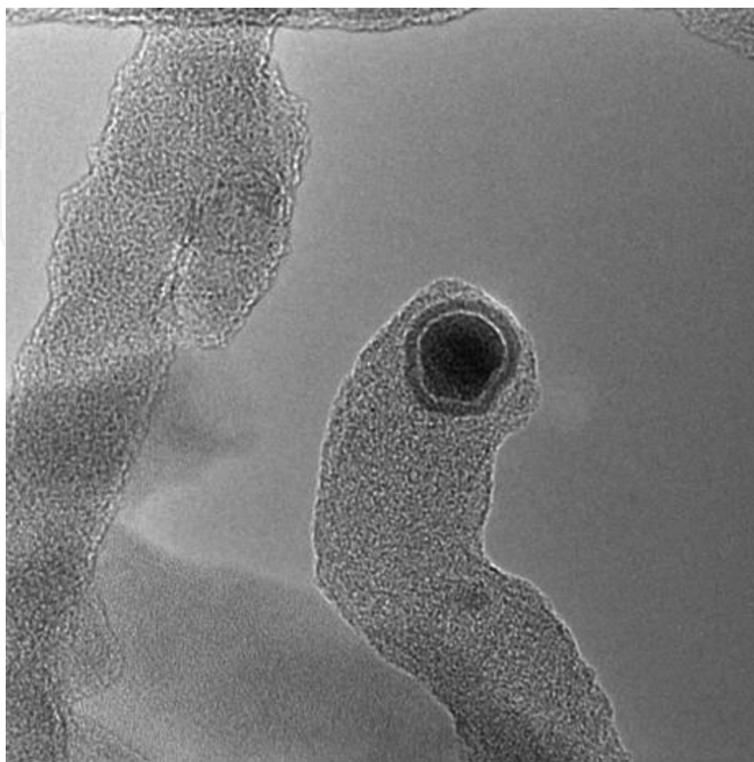


Figure 4. TEM image of the CNFs produced on the surface of clinker particles. Reproduced with permission.

4. Effects observed upon concrete reinforcement with carbon nanotubes

4.1. Effects of CNT functionalization, annealing, concentration, and water-cement ratio

–OH and –COOH functionalized CNTs have distinct physical properties and are more hydrophilic in comparison with pristine CNTs, so their effects on concrete properties can be different. The influence of functionalized MWCNT–OH and MWCNT–COOH on the impact resistance and compressive and flexural strengths of high-performance mortars (HPM) was studied [30]. The results of tests on reinforced high-performance mortar containing 0.1 wt% functionalized MWCNTs showed that the impact resistance, compressive strength, and flexural strength were 1400, 25.58, and 2% higher than those of HPM without MWCNTs. A more detailed comparison of distinct CNTs in cement matrix composites, prepared by addition of 0.5 wt% CNTs to plain cement paste, “was carried out [31]”. Three different kinds of MWCNTs (**Table 2** and **Figure 5**) were used and compared: as-grown, annealed (high temperature (2100–2600°C); annealing effects on MWCNTs are described in [32, 33]), and carboxyl functionalized MWCNTs. The authors stated that high temperature annealing treatments remove lattice defects from the walls of CNTs, hence improving their mechanical

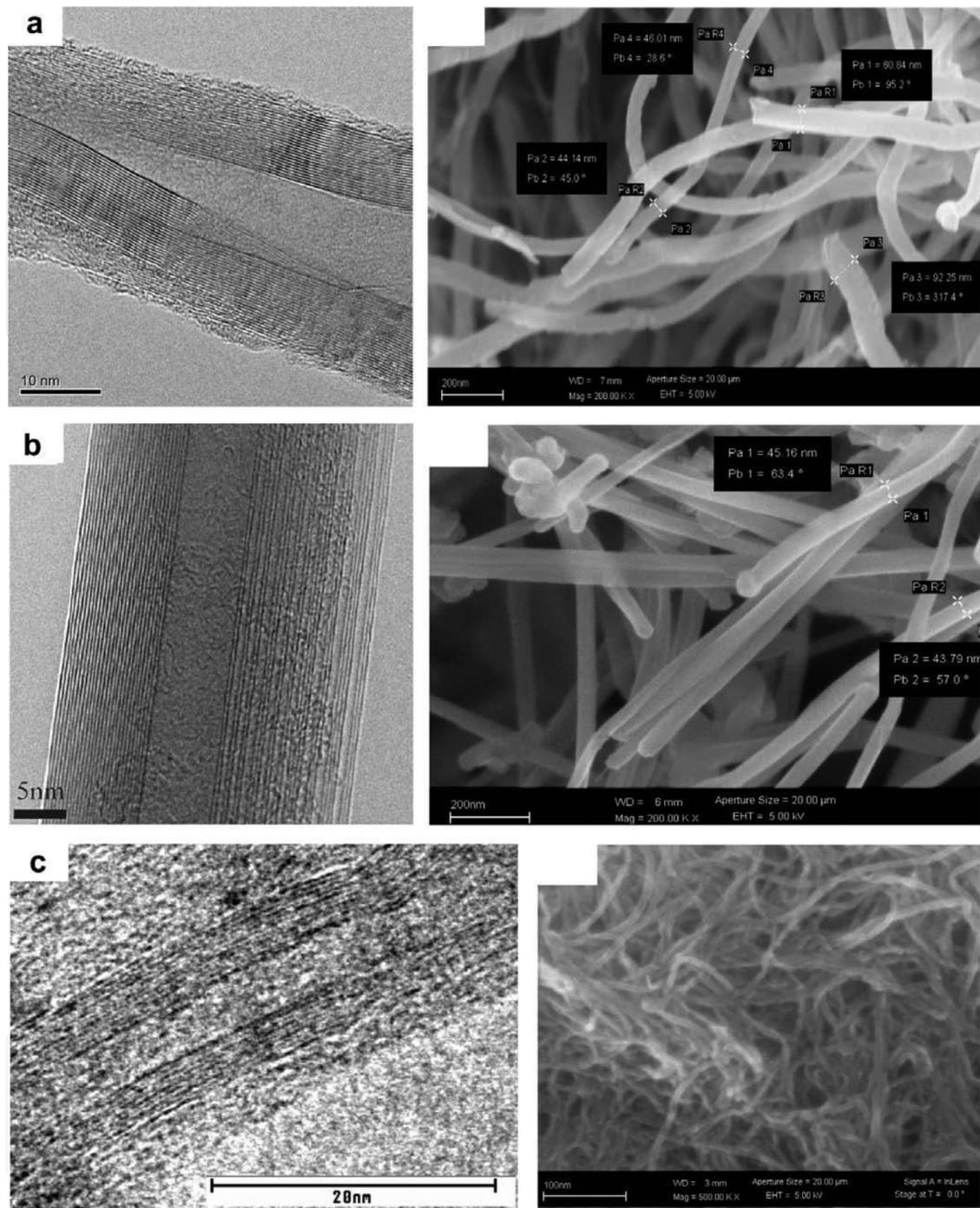


Figure 5. Electron microscopy analysis showing p-CNTs (a), a-CNTs (b), and f-CNTs (c). TEM images are reported on the left, while SEM images are on the right. Reproduced with permission.

strength. On the other hand, acid oxidative treatments increase chemical reactivity of pristine material, consequently chemical bonds between the reinforcement and the cement matrix are supposed to enhance the mechanical strength. Flexural and compressive tests showed a deterioration of the mechanical properties with functionalized MWCNTs, while a significant improvement is observed with both as-grown and annealed MWCNTs.

Property	p-CNTs	a-CNTs	f-CNTs
Deposition technique	CVD	CVD	CVD
Average diameter, nm	40–80	40–80	10–20
Average length, μm	400–1000	200–400	0.1–10
Carbon purity, wt%	>92	>99	>95
Metal oxide, impurity, wt%	<6	<1	<5
-COOH functionalization, wt%	0	0	<4

*p-CNTs: pristine MWCNTs; a-CNTs: annealed MWCNTs; f-CNTs: functionalized MWCNTs.

Table 2. Characteristics of the three different MWCNTs* dispersed in the cement. Reproduced with permission.

The piezoresistive property of the CNT/cement composite (**Figure 6**) shows an acidic treatment on CNTs (for their functionalization) and was used to explore its feasibility as an embedded stress sensor for civil structures, such as roadways, levees, and bridges [34]. It was shown that the electrical resistance of the CNT/cement composite changes with the compressive stress level, indicating the potential of using the CNT/cement composite as a stress sensor for civil structures (**Table 3**). It was also established that the dispersion-assistant surfactants could block the contacts among carbon nanotubes, thus impairing the piezoresistive response of the composite, while a higher CNT doping level could improve the sensitivity of the composite stress response. In addition, the effect of MWCNTs on strength characteristics and durability of concrete was investigated [35] by adding MWCNTs in different quantities (diameter 20–40 nm; length 1–10 μm ; 0.015, 0.03, and 0.045%) with surfactants (super plasticizers-polycarboxylate 8H, 0.25% by weight of cement). Results showed an increase in compressive and splitting-tensile strengths of the samples with increasing MWCNT concen-

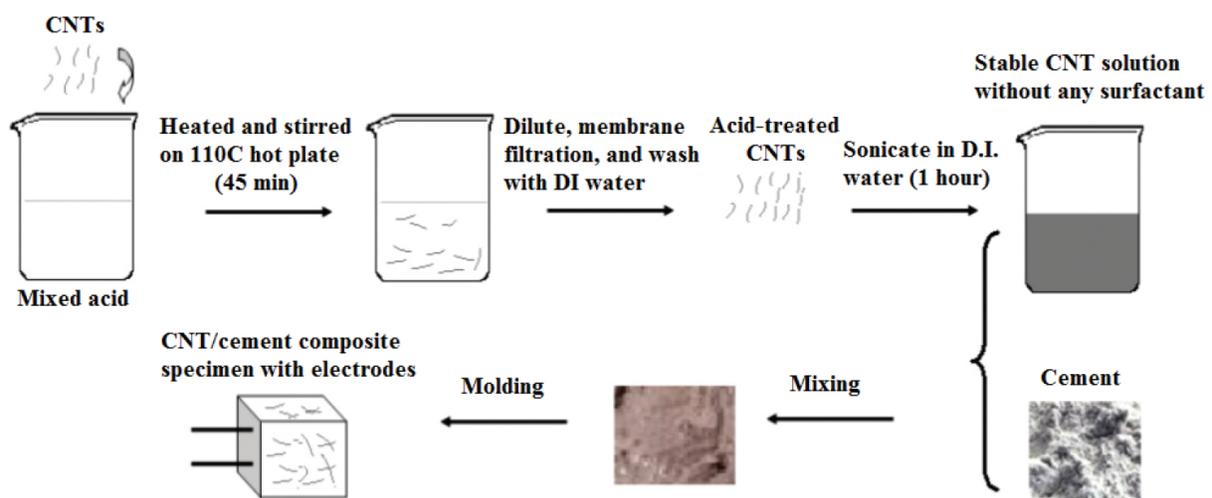


Figure 6. Illustration of the CNT/cement fabrication process based on the acid treatment of CNTs. Reproduced with permission.

tration (**Table 4**). By increasing the percentage of MWCNTs in the concrete, the water absorption is reduced to a greater extent, which helps in improving the concrete durability and water resistance.

CNT/cement composites	Resistance change (5.2 MPa load)	Resistance change (8.6 MPa load)
Cement only	0%	0%
0.06 wt% MWCNT	8.8%	10.3%
0.1 wt% MWCNT (by different methods)	5.0–9.4%	7.2–11.4%

Table 3. Comparison of electrical resistance changes of CNT/cement composites with different CNT doping levels and under different compressive loads. Reproduced with permission.

Concrete type	Comp. failure load (kN)	Compressive strength (N/mm ²)	Compressive strength % increase	Split tensile strength failure load (kN)	Split tensile strength	% increase
Conventional concrete	875	38.22	–	160	2.27	–
0.015% MWCNTs 930		41.48	2.75	210	2.97	30.84
0.030 % MWCNTs1010		45.18	16.38	235	3.30	45.37
0.045 % MWCNTs1100		49.18	26.69	265	3.775	66.30

Table 4. Compressive and split tensile strength. Reproduced with permission.

Additionally, two mechanical properties (28-day compressive strength and flexural strength) of CNTs (diameter <1 nm up to 50 nm and length from 1 μm to 1 cm) and CNFs (diameter of 70-200 nm and length of 50-200 μm) cement composites were investigated [36]. Composites with 0.1 and 0.2% of CNTs and CNFs, and water/cement ratios between 0.35 and 0.5, were prepared under sonication. Both CNT and CNF composites demonstrated significant increase in compressive strengths, when compared to plain mortar control samples (maximum 154% for CNT and 217% for CNFs samples). Water/cement ratios in the range of 0.35-0.4 were found to produce the higher strengths, together with a 0.1% dosage rate for the CNTs/CNFs. It seems that the CNTs are better dispersed in the cement matrix than the CNFs, because a correlation between the flow test results and the compressive strengths was detected for the CNT samples. One other example that CNT concentration should not exceed certain levels was described for the heavy-weight oil well cements [37]. When only 1 wt% of CNTs was added to the cement slurry, the yield point and plastic viscosity increased by 8 and 5 times, respectively, while the free water and fluid loss of cement slurry were reduced by 85 and 70%, respectively. In addition, compressive strength of cement stone increased by 73.8%. However, the increase in the additive concentration leads to reduced compressive strength and Young's

modulus, because of unsuitable dispersion of nanoparticles in the cement stone matrix; thus, an optimum level of CNTs should be used.

4.2. Length-to-diameter (l/d) aspect ratio effect

In addition to the effects of CNT length described above (**Table 1**), the intriguing effects of different concentrations of long (diameter <8 nm, length $10\text{--}30\ \mu\text{m}$) MWCNTs-high length/diameter aspect ratios of $1250\text{--}3750$ -and short MWCNTs (diameter 9.5 nm, length $1.5\ \mu\text{m}$)-aspect ratio of about 157 -in cement paste were studied for 7, 14, and 28 days [38]. Both short and long MWCNTs were produced by the catalytic chemical vapor deposition (CCVD) process. **Figure 7** shows the relationships between the length-to-diameter aspect ratio and the surface-area-to-volume (SA/V) ratio for different lengths of SWCNTs, MWCNTs, carbon nanofibers, and carbon microfibers (CMFs). The authors noticed that only CNTs can provide a very high surface-area-to-volume (SA/V) ratio, which is one of the most important and desired elements in fiber-reinforced composite systems, in order to obtain the best and the most efficient materials. SWCNTs are the only materials that have a SA/V ratio that exceeds $2.0\ \text{nm}^{-1}$, especially when considering the ultra-long ones that have aspect ratios that can reach several millions. A higher SA/V ratio means a larger contact area between the fibers and the surrounding matrix, hence higher interaction with the matrix and more efficient reinforcing.

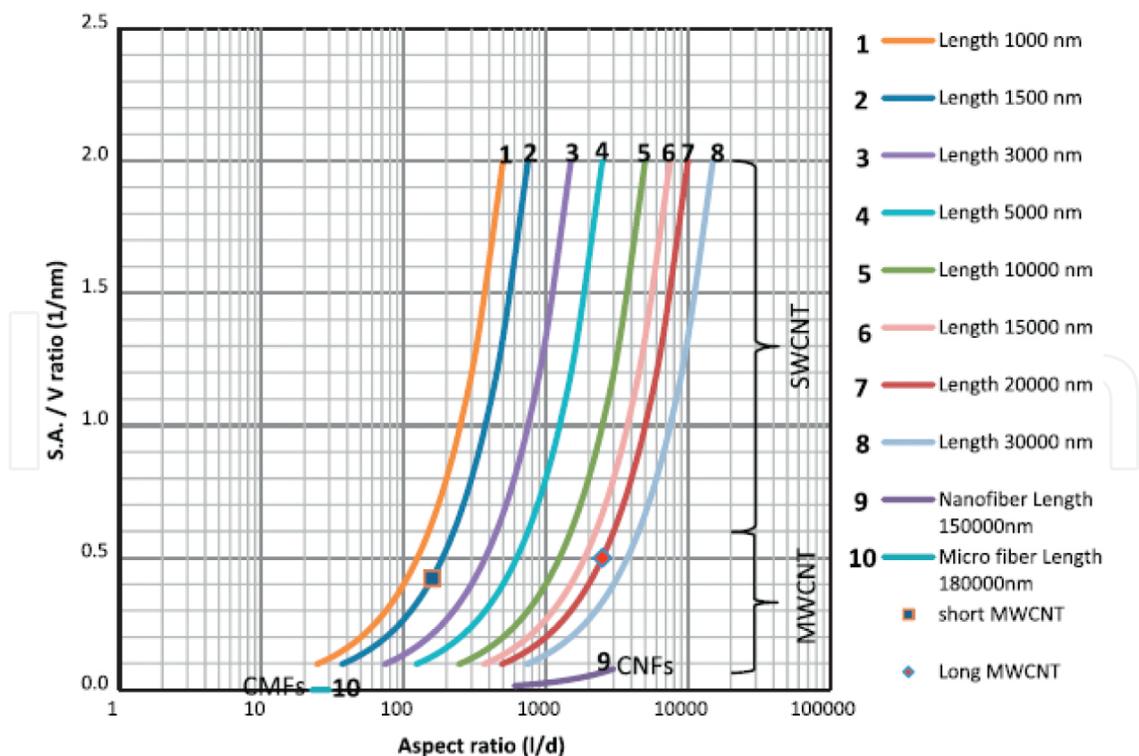


Figure 7. Length-to-diameter (l/d) aspect ratio effect on the surface-area-to-volume (SA/V) ratio for different lengths of SWCNTs, MWCNTs, CNFs, and CMFs. Reproduced with permission.

It was established that nanocomposites with low concentration of long MWCNTs yield comparable mechanical performance to the nanocomposites with higher concentration of short MWCNTs. **Figure 8** shows that the Young's modulus increases as the long CNTs' concentration decreases, whereas the Young's modulus increases as the short CNTs' concentration increases. Also, the authors noticed that low concentrations of long CNTs can lead to a much higher increase in the Young's modulus, as compared to higher concentrations of short CNTs. In addition, an example of the microcrack bridging by the MWCNTs, within the cement paste, is shown in **Figure 9**, clearly indicating that many CNTs are bridging the microcrack. Both

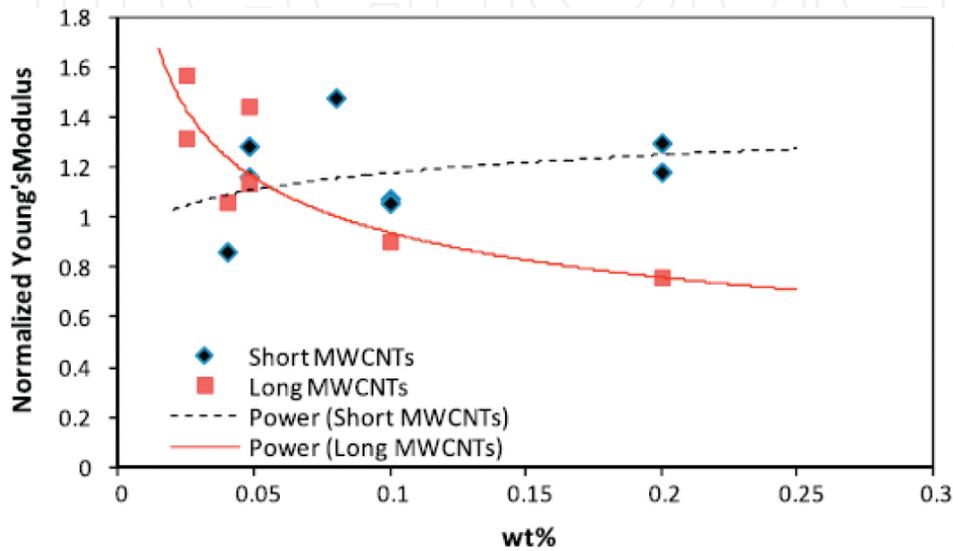


Figure 8. Variation of the normalized Young's modulus with the CNT concentration for two different aspect ratios; long and short. Reproduced with permission.

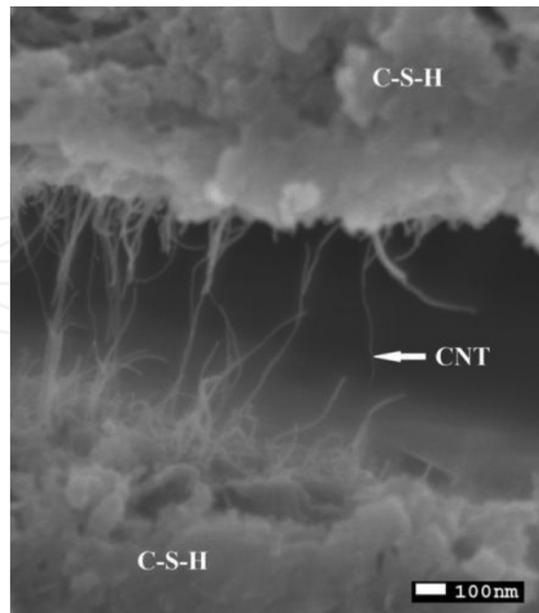


Figure 9. SEM image showing the microcrack bridging and breakage of the MWCNTs within the cement paste composite ((C-S-H) means calcium-silicate-hydrate). Reproduced with permission.

pull-out and breakage of CNTs can also be observed from images. In fact, the CNT breakage implies a good bonding between the CNT surfaces and the surrounding cement paste. However, it was noted by authors that the presence of CNTs affects the chemical reaction of the hydrated cement.

4.3. Effect of combination of CNTs with silica nanoparticles

Nanosilica (NS) is applied as an additive to improve the cement properties, giving a 15–20% increase of compressive strength [39]. Its combination with CNTs could lead to better results. Thus, the behavior of hardened cement paste reinforced with MWCNTs (0.75% by weight of cement; diameter 10–30 nm, length 1–2 μm) and NS (0.5%; particle size 10–20 nm) was investigated (**Figure 10**) after both MWCNTs and NS being dispersed using an ultrasonic energy method [40]. MWCNTs were used to reinforce the cement paste at the nanoscale, while NS was used to increase strength by forming an additional CSH gel. It was shown that the addition of MWCNTs and NS almost doubled the flexural strength in comparison with PC (the control beam).

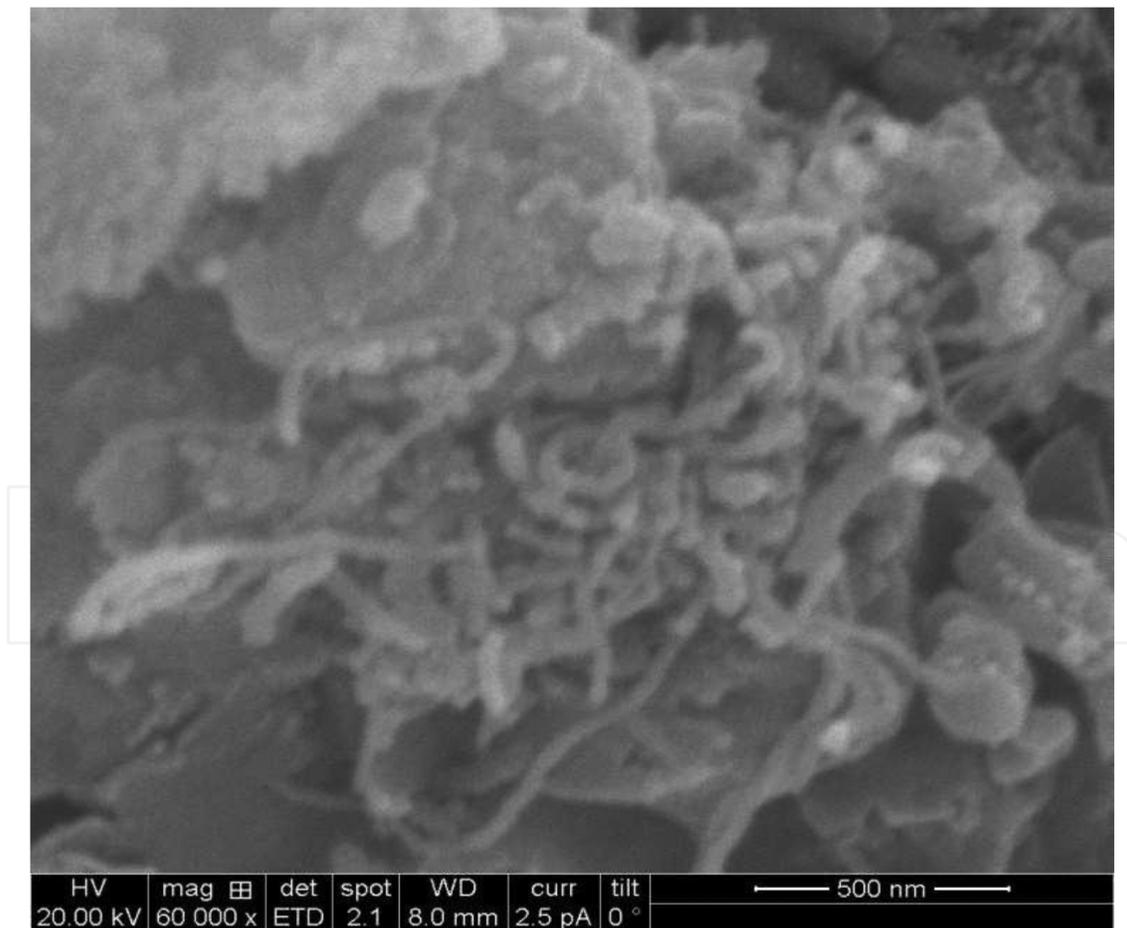


Figure 10. SEM image showing hardened cement paste modified with nanosilica and MWCNTs. Reproduced with permission.

5. Other specific studies of CNT/cement composites

5.1. Computational studies

Nanoscale and macroscale models were used to investigate the interfacial bond behavior of an individual CNT embedded in a cement matrix and the flexural response of a CNT/cement composite beam, respectively; also finite element (FE) models were applied to study the improvement in tensile strength and ductility of CNT-reinforced cement [41]. Industrial grade MWCNTs with a purity of 90 wt%, and a concentration of 0.25% by the total weight of cement paste, were ultrasonically dispersed in multiple steps before being added to cement (**Figure 11**). The FE models were successful in capturing the degradation in the CNT/cement bond strength and its effect on the flexural strength, ductility, and toughness of the composite. A comparison between the experimental and numerical behavior of the composite beams suggests an effective average shear strength value of 6.5 MPa at the interface of CNTs and cement matrix. Authors noted that, with a shear strength of up to 20.0 MPa, flexural strength, ductility, and toughness all increased with the interfacial bonding between CNTs and cement. This implies the significance of surface treatment of CNTs, which is commonly used to strengthen the bonding between CNTs and their surrounding matrix. As predicted by the FE analysis, increasing the shear strength from 6.5 to 20.0 MPa would increase the composite's flexural strength, ductility, and toughness by 141, 259, and 1976%, respectively. These results were significant, considering that the enhancement was provided by fibers alone, and highlight the great potential of surface-treated CNTs in reinforcing cement.

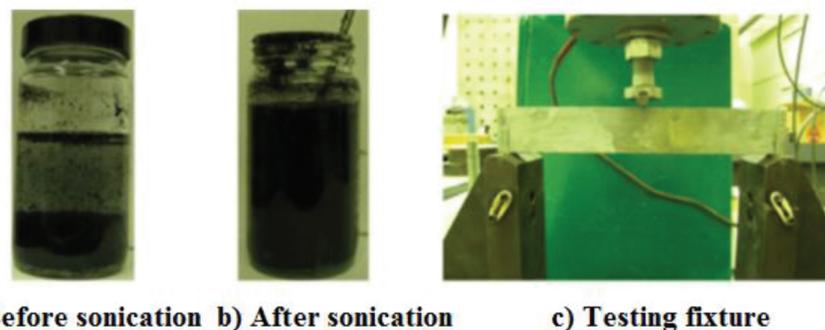


Figure 11. Experimental preparation for three-point bending tests of composite beams. Reproduced with permission.

5.2. TEM approach

A colloidal technique for transmission electron microscopy (TEM) of graphitic nanoreinforced cementitious composites was developed [42]. SWCNTs and MWCNTs (90 and 95% by mass with bulk densities of 0.14 and 0.27 g/cm³ at 20°C, respectively; the inner diameters of the tubes were specified as 0.8–1.6 and 2–5 nm with average tube lengths of 5–30 and 10–30 μm for SWNTs and MWNTs, respectively) were functionalized using an acid etching technique to obtain stable aqueous suspensions to incorporate in the mix design of a cement paste. The functionalized nanoreinforcement and binding characteristics were observed at the nano-

scale using high-resolution TEM imaging. Functionalized CNTs were found to be well distributed and preferentially associated with the cementitious matrix.

5.3. Study of electrical conductivity

A model for the electrical conductivity of heterogeneous systems based on cement and CNTs was developed [43]. The electrical properties of heterogeneous variances were shown to be dependent of such key parameters, such as the degree of aggregation of conductive particles and the electrical conductivity of a single unit. When the threshold concentration of electrical conductivity of CNT and graphite dispersions equals to 0.15, the electrical conductivity of CNT's systems were found to be 5–6 times higher than graphite. The authors emphasized that the CNTs have anomalous properties in comparison with graphite electrical dependencies due to the size and shape of the particles. It was also suggested that the small size effect of CNTs on the primary aggregation and the elongated shape of the particles affects the concentration at which a significant increase in electrical conductivity takes place.

5.4. Ultrasound tests

Tests with three different ratios (0.2, 0.4, and 0.6%, relatively high in comparison with those in reports described above) of carbon nanotubes (OD 5–60 nm, a length estimated from 5 to 30 μm) in concrete were carried out with the ultrasound technique. The measurement of the propagation delay of the signal through the specimens of cementitious materials with and without CNTs to reach the dynamic modulus of elasticity was carried out [44]. It was found that the mixture of 0.4% of CNTs was the mortar that showed the best performance, in comparison to the reference sample, reaching an increase of about 25% in the dynamic modulus of elasticity and a higher rate of structural compaction. The composites with addition of 0.2 and 0.6% of CNT did not show significant results for the same characteristics.

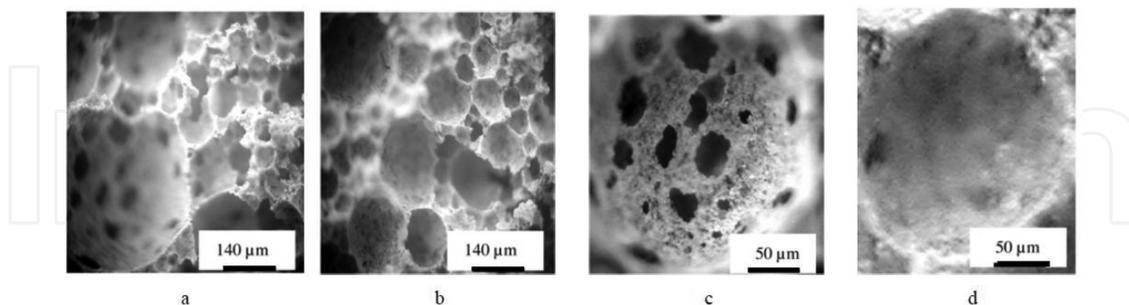


Figure 12. Cement foam concrete structure: (a) without nanotubes, (b) with 0.05% nanotubes (pore walls), (c) without nanotubes (perforated), and (d) stabilized with addition of 0.05% of nanotubes. Reproduced with permission.

5.5. Study of special foam-like cement

CNTs (80–90% of carbon, with a diameter of up to 100 nm and a length of up to 20 μm), agglomerated to fiber-shaped agglomerates with a diameter of up to 30 μm and a length of

up to 10 mm, were synthesized using the method of stimulation of dehydropolycondensation and carbonization of aromatic hydrocarbons in chemical active environment (melts of aluminum, copper, nickel and iron salts), and used as a high strength dispersed reinforcement for the synthesis of nonautoclave concrete foam produced on the base of Portland cement (**Figure 12**) [45]. It was established that the use of CNTs (0.05% by mass), in the production of these concretes, allows to decrease its heat conductivity to 12–20% and increase its compressive strength to 70%.

6. Health impact

Considerable experimental data related to CNT toxicity at the molecular, cellular, and whole animal levels have been published [46]. The literature indicates considerable variability and uncertainty regarding the health impacts, reactivity, ecological effects, and environmental destination and transport of CNTs. In this respect, their addition to form high-performance cements should be also evaluated from the point of view of toxicity of resulted concrete, i.e., how the addition of CNTs may affect the environmental profile of cement. A recent report [47] evaluated hypothetical high-performance cements based on CNT reinforcement with a life cycle assessment (LCA) in order to compare the environmental impact of these new developments to traditional cements. It was established that the inclusion of CNTs increases considerably the environmental impact of cement production (**Table 5**). In addition, progress in research on these kinds of systems is largely hampered by the intrinsically hydrophobic nature of CNTs and their chemical incompatibility with cement hydrates. The authors proposed alternatives to CNTs as reinforcement for cements such as inorganic nanotubes or plastic nanofibers.

Impact category	Unit	1 kg CEM I 52.5 N	1 kg reinforced cement
Abiotic depletion of resources	kg Sb eq	2.184E-07	8.642E-06
Abiotic depletion of fossil fuels	MJ	1.485	56.719
Global warming, GWP	kg CO ₂ eq	0.749	4.528
Ozone layer depletion, ODP	kg CRC-11 eq		6.396E-07
Human toxicity	kg 1,4-DB eq	0.067	1.353
Fresh water aquatic ecotoxicity	kg 1,4-DB eq	0.036	3.384
Marine aquatic ecotoxicity	kg 1,4-DB eq	100.751	5985.378
Terrestrial ecotoxicity	kg 1,4-DB eq	0.00082736	0.18839807
Photochemical oxidation	kg C ₂ H ₄ eq	5.5717E-05	0.00125085
Acidification	kg SO ₂ eq	0.00100558	0.03213931
Eutrophication	kg PO ₄ ³⁻ eq	0.00022225	0.00745367

Table 5. Comparative impacts of standard and reinforced cements. Reproduced with permission.

7. Conclusions

The addition of CNTs and CNFs into cement forming nanocomposites leads to a considerable improvement of mechanical characteristics of concrete, since CNTs can act as effective bridges to minimize and limit the propagation of microcracks through the matrix. However, in order to reach the best effects, CNTs need to be well dispersed within the matrix to provide good bonding between them and the surrounding hydrated cement matrix, this being the main factor controlling concrete microstructure of cement composites. Addition of even 0.05% CNTs results in lower density, increased compressive strength, lower thermal conductivity, lower average pore diameter, and more homogeneous pore wall structure. The central idea of each cement-CNT experiment is to determine the best way to disperse CNTs. This can be reached by ultrasonication, use of surfactants (generally sodium dodecylbenzenesulfonate (SDBS), sodium deoxycholate (NaDC), Triton X-100 (TX10), GA, and cetyl trimethyl ammonium bromide (CTAB), whose dispersion ability varies considerably depending on molecular structure), use of cement admixtures (polycarboxylate, alkylbenzene, sulfonic acid, among many others), and covalent functionalization (commonly acid treatment to form -COOH and -OH functionalized CNTs). Combination of various chemical methods, such as the combination of surface functionalization with polymers, and other techniques, like an innovative method of fabricating cementitious nanocomposites through growth of CNTs onto the cement particles, also leads to good results. It has been finally established that the homogeneous CNT dispersion can be reached in the best form by dispersing them first in water, followed by mixing of the aqueous dispersion with mortar paste.

A series of effects have been discovered upon dispersion of carbon allotropes in concrete, showing the importance of diameter, length, and length-to-diameter ratio of CNTs, their concentration, functionalization, annealing, combination of CNTs with other nanomaterials, and water-cement ratio. We note that studies on CNT/cement nanocomposites are currently a relatively hot topic in nanotechnology [48–51] leading to best combinations of well-known materials having improved properties.

Author details

Oxana V. Kharissova, Leticia M. Torres Martínez and Boris I. Kharisov*

*Address all correspondence to: bkhariss@hotmail.com

1 Department of Physico-Mathematical Sciences, Autonomous University of Nuevo León, Monterrey, Mexico

2 Department of Civil Engineering, Autonomous University of Nuevo León, Monterrey, Mexico

3 Department of Chemical Sciences, Autonomous University of Nuevo León, Monterrey, Mexico

References

- [1] Ferro, G.; Tulliani, J.-M.; Musso, S. Carbon nanotubes cement composites. *Frattura ed Integrità Strutturale*, 2011, 18, 34–44.
- [2] Sobolev K. Development of nano-SiO₂ based admixtures for high-performance cement-based materials. Progress report, CONACYT, Mexico, 2006.
- [3] Kharisov, B.I.; Kharissova, O.V.; Leija Gitierrez, H.; Ortiz Méndez, U. Recent advances on the soluble carbon nanotubes. *Industrial & Engineering Chemistry Research*, 2009, 48(2), 572–590.
- [4] Kharissova, O.V.; Kharisov, B.I.; de Casas Ortiz, E.G. Dispersion of carbon nanotubes in water and non-aqueous solvents. *RSC Advances*, 2013, 3, 24812–24852.
- [5] Parveen, S.; Rana, S.; Fanguero, R. A review on nanomaterial dispersion, microstructure, and mechanical properties of carbon nanotube and nanofiber reinforced cementitious composites. *Journal of Nanomaterials*, 2013, Article ID 710175, 19 pp.
- [6] Olar, R. Nanomaterials and nanotechnologies for civil engineering. *Buletinul Institutului Politehnic din Iași*, 2011, LIV(LVIII), 109–117.
- [7] Raki, L.; Beaudoin, J.; Alizadeh, R.; Makar, J.; Sato, T. Cement and concrete nanoscience and nanotechnology. *Materials*, 2010, 3, 918–942.
- [8] Abinayaa, U.; Chetha, D.; Chathuska, S.; Praneeth, N.; Vimantha, R.; Wijesundara, K.K. Improving the properties of concrete using carbon nanotubes. *SAITM Research Symposium on Engineering Advancements*, 2014, (SAITM - RSEA 2014), 201–204.
- [9] Li, G.Y.; Wang, P.M.; Zhao, X. Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. *Carbon*, 2005, 43(6), 1239–1245.
- [10] Cwirzen, A.; Habermehl-Cwirzen, K.; Penttala, V. Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites. *Advances in Cement Research*, 2008, 20(2), 65–73.
- [11] Luo, J.; Duan, Z.; Li, H. The influence of surfactants on the processing of multi-walled carbon nanotubes in reinforced cement matrix composites. *Physica Status Solidi A*, 2009, 206(12), 2783–2790.
- [12] Nasibulin, A.G.; Shandakov, S.D.; Nasibulina, L.I., et al. A novel cement-based hybrid material. *New Journal of Physics*, 2009, 11, Article ID 023013.
- [13] Morsy, M. S.; Alsayed, S.H.; Aqel, M. Hybrid effect of carbon nanotube and nano-clay on physico-mechanical properties of cement mortar. *Construction and Building Materials*, 2011, 25(1), 145–149.

- [14] Nochaiya, T.; Chaipanich, A. Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement-based materials. *Applied Surface Science*, 2011, 257(6), 1941–1945.
- [15] Fraga, J.L.; del Campo, J.M.; García, J.A. Carbon nanotube - cement composites in the cement composites in the construction industry: 1952–2014. A state of the art review. In 2nd International Conference on Emerging Trends in Engineering and Technology (ICETET'2014), May 30–31, 2014, London, UK.
- [16] Petrunin, S.; Vaganov, V.; Sobolev, K. The effect of functionalized carbon nanotubes on the performance of cement composites. NANOCON, October 16–18, 2013, Brno, Czech Republic, EU.
- [17] Han, B.; Yu, X. Effect of surfactants on pressure-sensitivity of CNT filled cement mortar composites. *Frontiers in Materials*, 2014, 1, art. 27, 1–5.
- [18] Wang, B.; Han, Y.; Pan, B.; Zhang, T. Mechanical and morphological properties of highly dispersed carbon nanotubes reinforced cement based materials. *Journal of Wuhan University of Technology - Materials Science Editorial*, 2013, 82–87.
- [19] Kołtuńczy, E.; Nowicka, G. Effect of poly(sodium-4-styrenesulphonate) additives on properties of cement suspensions. In *Proceedings of International Scientific Conference "Surfactants and Dispersed Systems in Theory and Practice"*, Ed., K.A. Wilk, Palma Press, Wrocław, 2007.
- [20] Li, C.; Zhu, H.; Wu, M.; Yan, M. Effect of dispersity of multi-walled carbon nanotubes on compression strength of cement. In *Fourth International Conference on Digital Manufacturing & Automation*, 2013.
- [21] Yazdanbakhsh, A.; Grasley, Z.; Tyson, B.; Abu Al-Rub, R.K. Distribution of carbon nanofibers and nanotubes in cementitious composites. *Journal of the Transportation Research Board*, No. 2142, Transportation Research Board of the National Academies, Washington, DC, 2010, 89–95.
- [22] Şener, S.; Çağlar, Y.; Belgin, Ç.M.; Şener, K.C. Modified Arcan tests for concrete with multi-walled carbon nanotubes. *Advanced Materials Letters*, 2014, 5(8), 429–434.
- [23] Duan, Z.; Luo, J. Effect of multi-walled carbon nanotubes on the vibration-reduction behavior of cement. In *Proceedings of SPIE, International Conference on Smart Materials and Nanotechnology in Engineering*, Ed., S. Du, J. Leng, A.K. Asundi, 2007, 6423, 64230R.
- [24] Luo, J.L.; Duan, Z.; Xian, G.; Li, Q.; Zhao, T. Fabrication and fracture toughness properties of carbon nanotube-reinforced cement composite. *The European Physical Journal Applied Physics*, 2011, 53, 30402.
- [25] Šmilauer, V.; Hlaváček, P.; Padevet, P. Micromechanical analysis of cement paste with carbon nanotubes. *Acta Polytechnica*, 2012, 52(6), 22–28.

- [26] Han, B.; Yang, Z.; Shi, X.; Yu, X. Transport properties of carbon-nanotube/cement composites. *Journal of Materials Engineering and Performance*, 2013, 22(1), 184–189.
- [27] Hunashyal, A.M.; Tippa, S.V.; Quadri, S.S.; Banapurmath, N.R. Experimental investigation on effect of carbon nanotubes and carbon fibres on the behavior of plain cement mortar composite round bars under direct tension. *International Scholarly Research Network, ISRN Nanotechnology*, 2011, Article ID 856849, 6 pp.
- [28] Nasibulina, L.I.; Anoshkin, I.V.; Semencha, A.V.; Tolochko, O.V.; Malm, J.E.M.; Karppinen, M.J.; Nasibulin, A.G.; Kauppinen, E.I. Carbon nanofiber/clinker hybrid material as a highly efficient modifier of mortar mechanical properties. *Materials Physics and Mechanics*, 2012, 13, 77–84.
- [29] Ludvig, P.; Ladeira, L.O.; Calixto, J.M.; Gaspar, I.C.P.; Melo, V.S. In-situ synthesis of multiwall carbon nanotubes on Portland cement clinker. In *11th International Conference on Advanced Materials*, Rio de Janeiro, Brazil, September 20–25, 2009.
- [30] Sahranavard, H.-K.; Abbasi, S.; Saeed, S.; Hasan, H.-K. Effect of multi-walled carbon nanotubes on mechanical properties of high-performance mortar. *Magazine of Concrete Research*, 2014, 66(18), 948–954.
- [31] Musso, S.; Tulliani, J.-M.; Ferro, G.; Tagliaferro, A. Influence of carbon nanotubes structure on the mechanical behavior of cement composites. *Composites Science and Technology*, 2009, 69, 1985–1990.
- [32] Ray, S.C.; Pao, C.-W.; Tsai, H.-M.; Chen, H.-C.; Chen, Y.-S.; Wu, S.-L.; Ling, D.-C.; Lin, I.-N.; Pong, W.-F.; Gupta, S.; Giorcelli, M.; Bianco, S.; Musso, S.; Tagliaferro, A. High-temperature annealing effects on multiwalled carbon nanotubes: electronic structure, field emission and magnetic behaviors. *Journal of Nanoscience and Nanotechnology*, 2009, 9, 1–7.
- [33] Kim, Y.A.; Hayashi, T.; Endo, M.; Kaburagi, Y.; Tsukada, T.; Shan, J., et al. Synthesis and structural characterization of thin multi-walled carbon nanotubes with a partially faceted cross section by a floating reactant method. *Carbon*, 2005, 43, 2243–2250.
- [34] Yu, X.; Kwon, E. A carbon nanotube/cement composite with piezoresistive properties. *Smart Materials and Structures*, 2009, 18, 055010, 5.
- [35] Madhavi, T.C.; Pavithra, P.; Baban Singh, S.; Vamsi Raj, S.B.; Paul, S. Effect of multi-walled carbon nanotubes on mechanical properties of concrete. *International Journal of Scientific Research*, 2013, 2(6), 166–168.
- [36] Yazdani, N.; Mohanam, V. Carbon nano-tube and nano-fiber in cement mortar: effect of dosage rate and water-cement ratio. *International Journal of Material Science (IJMSCI)*, 2014, 4(2). www.ij-ms.org.
- [37] Ghajari, A.; Gholinezhad, J.; Soltanian, H.; Alireza Mortazavi, S. An improvement to physical properties of heavyweight Oil well cements using carbon nanotubes. *Journal of Petroleum Science and Technology*, 2014, 4(2), 10–19.

- [38] Abu Al-Rub, R.K.; Ashour, A.I.; Tyson, B.M. On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of cementitious nanocomposites. *Construction and Building Materials*, 2012, 35, 647–655.
- [39] Sobolev, K.; Flores, I.; Hermosillo, R.; Torres-Martínez, L.M. Nanomaterials and nanotechnology for high-performance cement composites. In Proceedings of ACI Session on “*Nanotechnology of Concrete: Recent Developments and Future Perspectives*”, November 7, 2006, Denver, USA, 91–118.
- [40] Hunashyal, A.; Banapurmath, N.; Jain, A.; Quadri, S.; Shettar, A. Experimental investigation on the effect of multiwalled carbon nanotubes and nano-SiO₂ addition on mechanical properties of hardened cement paste. *Advances in Materials*, 2014, 3(5), 45–51.
- [41] Chan, L.Y.; Andrawes, B. Finite element analysis of carbon nanotube/cement composite with degraded bond strength. *Computational Materials Science*, 2010, 47, 994–1004.
- [42] Aich, N.; Zohhadi, N.; Khan, I.A.; Matta, F.; Ziehl, P.; Saleh, N.B. Applied TEM approach for micro/nanostructural characterization of carbon nanotube reinforced cementitious composites. *Journal of Research Updates in Polymer Science*, 2012, 1, 14–23.
- [43] Lopanov, A.N.; Shukhov, V.G.; Fanina, E.A.; Kalchev, D.N. Electrical conductivity and aggregation of carbon nanotubes in a heterogeneous system based on cement. *Middle-East Journal of Scientific Research*, 2013, 17(8), 1194–1199.
- [44] Fernandes de Morais, J.; Naked Haddad, A. Analysis by ultrasound of the behavior of carbon nanotubes on cementitious composites. *Journal of Nanotechnology and Advanced Materials*, 2014, 2(2), 89–98.
- [45] Yakovlev, G.; Keriene, J.; Gailius, A.; Girniene, I. Cement based foam concrete reinforced by carbon nanotubes. *Journal of Materials Science (Medžiagotyra)*, 2006, 12(2), 147–151.
- [46] Liu, Y.; Zhao, Y.; Sun, B.; Chen, C. Understanding the toxicity of carbon nanotubes. *Accounts of Chemical Research*, 2013, 46(3), 702–713.
- [47] Matanza, A.; Vargas, G.; Leon, I.; Pousse, M.; Salmon, N.; Marieta, C. Life cycle analysis of standard and high-performance cements based on carbon nanotubes composites for construction applications. In *World SB-4*, Barcelona, October 28–30, 2014.
- [48] Manzur, T.; Yazdani, N. Strength enhancement of cement mortar with carbon nanotubes. Early results and potential. *Journal of the Transportation Research Board*, No. 2142, Transportation Research Board of the National Academies, Washington, DC, 2010, 102–108.
- [49] Ghasemzadeh, H.; Akbari Jalalabad, E. Computing the compressive strength of carbon nanotube/cement composite. *International Journal of Civil Engineering*, 2011, 9(3), 223–229.

- [50] Sakulich, A.R.; Li, V.C. Nanoscale characterization of engineered cementitious composites (ECC). *Cement and Concrete Research*, 2011, 41(2), 169–175.
- [51] Ubertini, F.; Luigi Materazzi, A.; D'Alessandro, A.; Laflamme, S. Natural frequencies identification of a reinforced concrete beam using carbon nanotube cement-based sensors. *Engineering Structures*, 2014, 60, 265–275.

IntechOpen

IntechOpen

