PHYSICAL DISPERSION OF NANOCARBONS IN COMPOSITES–A REVIEW

Jamal M. A. Alsharef[a]*, Mohd Raihan Taha[a,b], Tanveer Ahmed Khan[a]

[a]Department of Civil and Structural Engineering, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia
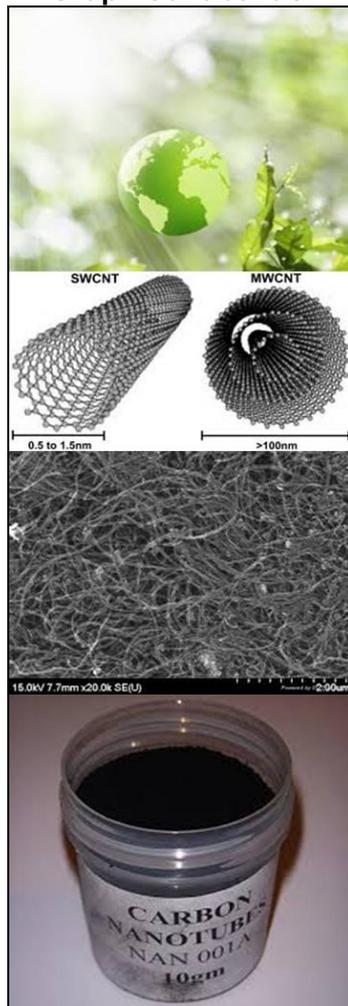[b]Institute for Environment and Development (LESTARI), Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

*Corresponding author
jamalshref@siswa.
ukm.edu.my

Graphical abstract

Abstract

Recently, nanocarbons (carbon nanofibers (CNFs) and carbon nanotubes (CNTs)) have been used efficiently in numerous research works to significantly enhance the mechanical properties of composites. With their amazing mechanical properties and exceptionally high aspect ratios, nanocarbons (NCs) are seen as one of the most beneficial nanomaterials for nano-reinforcement. The dispersion of NCs is one of the key factors that strongly influence the properties of nanocomposites. Several researches have been carried out with chemical agents to achieve a consistent dispersal of carbon nanomaterials in water, although, if the process is uncontrolled, it can shorten or damage the NCs or even dissolve them, and this can have a negative effect on the composites as well. Therefore, if NCs are to be used as reinforcement for composites, physical methods have to be employed to disperse the NCs before they can be mixed into the composites. This paper presents an overview of the different types of NCs, their different uses and the research conducted for the dispersion of NCs by chemical and physical methods. Furthermore, a summary is given of the measurement and characterization of the dispersibility of NCs.

Keywords: Nanocarbon tubes, fibres, physical dispersion, ultrasonic, microstructures

Abstrak

Baru-baru ini, karbon nano (nano fiber karbon (CNF) dan nano tiub karbon (CNT)) telah digunakan dengan berkesan dalam pelbagai kerja penyelidikan untuk meningkatkan sifat mekanikal komposit. Dengan sifat mekanikal yang luar biasa dan aspek nisbah yang sangat tinggi, nano karbon (NC) dianggap sebagai bahan nano yang paling bermanfaat untuk peneguhan nano. Penyerakan NC adalah salah satu faktor utama yang mempengaruhi ciri komposit nano. Banyak penyelidikan telah dijalankan dengan menggunakan agen-agen kimia untuk mencapai penyerakan homogen bagi bahan nano karbon di dalam air, meskipun tanpa kawalan yang sempurna, ia boleh merosakkan atau memendekkan NC tersebut, malahan melarutkannya, dan ini boleh juga memberi kesan yang negatif terhadap komposit itu. Oleh yang demikian, untuk menggunakan NC sebagai peneguhan rencam tanpa kesan kimia, kaedah fizikal perlu digunakan untuk penyerakan NC, sebelum mencampurkannya dengan komposit. Kertas ini membincangkan tentang pelbagai jenis NC, kegunaannya dan penyelidikan penyerakan NC melalui kaedah fizikal dan kimia. Pengukuran dan pencirian penyerakan NC telah juga disimpulkan.

Kata kunci: Tiub-tiub nanocarbon, serat, penyerakan fizikal, ultrasonic, mikrostruktur

1.0 INTRODUCTION

Nanocarbon (NC) particles have been used primarily in industrial sectors such as the automotive, electronics, sports, concrete, marine, and aeronautics industries. NCs are also one of the capable innovative materials in the construction industry. NC particles, particularly carbon nanofibers (CNFs), and carbon nanotubes (CNTs) have good material properties such as electrical properties, elastic modulus, high tensile strength and hardness.

Carbon nanofibers have a history that goes back more than a century, when a category of carbon nanomaterials, known as vapour-grown carbon nanofibers (VCNFs), was first explored in 1889 by Hughes and Chambers. It was discovered that carbon filaments could be grown from carbon, and their hollow graphitic structure was first revealed by Radushkevich and Lukyanovich in the early 1950s [1, 2]

VCNFs can be catalytically synthesized by hydrocarbons such as natural gas, propane, acetylene, benzene, and ethylene using the chemical vapour deposition (CVD) of carbon monoxide with a metal (Fe, Ni, Co, Au) or metal alloy (Ni-Cu, Fe-Ni) as a catalyst at a temperature of 500–1500 °C [3-8].

2.0 CARBON NANOTUBES

Carbon nanotubes, discovered by Iijima in 1991 [9] are one of the most favourable classes of original materials to have emerged from nanotechnology so far. Nanotubes, which belong to the fullerene structural family, derived their name from their long, hollow structure, with walls moulded by one-atom-thick sheets of carbon known as graphene. Allotropes of carbon that have a cylindrical nanostructure are known as carbon nanotubes (CNTs). They were discovered in Damascus steel in the 17th century, and probably assisted in justifying the renowned strength of swords made from them [10-12].

Carbon nanotube constructions, with a length-to-diameter ratio of up to 132,000,000:1, are considerably bigger than those of any other material, with a perfect structure shaped by carbon atoms in a single dimension [13]. The unusual properties possessed by the cylindrical carbon molecules make them valuable for electronics, nanotechnology, optics and various fields of material science and technology [14]. Furthermore, as CNTs show pronounced mechanical properties together with exceptionally high aspect ratios (length-to-diameter ratios), they are expected to yield composites that are considerably stronger and tougher than traditional reinforcement materials (e.g. glass fibres or carbon fibres) [15].

Research has been piloted for possible CNT usage in environmental protection applications. CNTs are being used as a selective sorbent for the removal of organic/biological contaminants, for example, carcinogenic cyanobacterial microcystins in water streams [16]. Additionally, research on the usage of carbon nanotubes as an effective source and storage of hydrogen is also significant as they have predominant adsorption features owing to their high surface area of 50-1315 m^2/g [17], [18-20]. Moreover, CNTs have been efficiently used for the adsorption of dissolved heavy metals and actinides comprised of Cd(II), Cu(II), Ni(II), Pb(II), Zn(II), and M(III) [21-23], which are significant adsorbers of phenol [24].

Carbon nanotubes (CNTs) are seen as one of the most valuable nanomaterials for nano-reinforcement, with their amazing mechanical properties and exceptionally high aspect ratios [25]. The electrical and chemical properties of CNTs make them attractive for the reinforcement of composite materials [9, 26]. Their Young's modulus and tensile strength are described as being as high as 1 TPa and 200 GPa, respectively, with a density of approximately 1.33 g/cm^3 [27], and a tensile stress in the region of 65 to 93 GPa [28]. However, CNTs have distinctive physical properties. For instance, their thermal stability can potentially be up to 2800 °C, their thermal conductivity is equally good in comparison to diamond, and their electrical conductivity is approximately 1000 times better than that of copper [29]. With their more unique properties, CNTs are also extremely malleable. Like macroscopic tubes, they have the capability to bend in circles and form knots, and to be clasped or compressed under appropriate loadings [30].

2.1 Synthetic Methods for the Preparation of Carbon Nanotubes

Various methods have been utilized for the preparation of CNTs. These comprise arc discharge [31], laser ablation [32], and chemical vapour deposition (CVD) [33], each of which has its own benefits and shortcomings. The first two methods can produce high quality CNTs, but the quantities produced are rather low. The third method (CVD) has the ability to produce larger batches of CNTs (despite having a huge number of defects), and it appears to be an encouraging method for reducing future costs, and for large scale production, which would intensify the usage of CNTs in environmental protection applications [21, 34, 35].

2.2 Structures and Types of Carbon Nanotubes

Two renowned carbon nanotube types are explained below:

2.2.1 Single-Walled Carbon Nanotube (SWCNTs)

The SWNT structure can be conceptualized as graphene, which is a one-atom-thick layer of graphite, wrapped into a seamless cylinder, as displayed in Figure 1. The majority of single-walled nanotubes (SWNTs) have a diameter that is close to 1 nanometre, with a tube length that can be millions of times longer [36, 37].
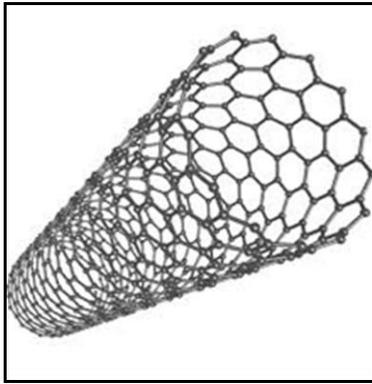
Figure 1 Single-walled carbon nanotube (SWCNT) [1]

Figure 3 Multi-walled carbon nanotubes (MWCNTs): (a) Parchment model, (b) Russian Doll model

2.2.2 *Multi-Walled Carbon Nanotubes (MWCNTs)*

Generally, multi-walled nanotubes (MWNTs) are made up of multiple rolled layers (concentric tubes) of graphene, with diameters ranging from 5 to 50 nm [38], as shown in Figure 2. The two models that are used to describe multi-walled nanotube structures are first, the Parchment model, where a single sheet of graphite is rolled around itself to resemble a parchment scroll or a rolled newspaper, as in Figure 3(a); and second, the Russian Doll model, where the graphite sheets are arranged in concentric cylinders, as in Figure 3(b).

With regard to the "Global Market for Carbon Nanotubes" report, SWNTs, which were observed as being too costly for extensive applications, are now estimated to have a great impact on electronic applications by 2020. In addition, the presence of MWCNTs in composites is more beneficial compared to SWCNTs. Campillo *et al.* [39], in utilizing carbon nanotubes (MWCNTs and SWCNTs) in cement composites, showed that those cement composites that contained MWCNTs have a considerably higher compressive strength compared to their counterparts that contain SWCNTs.
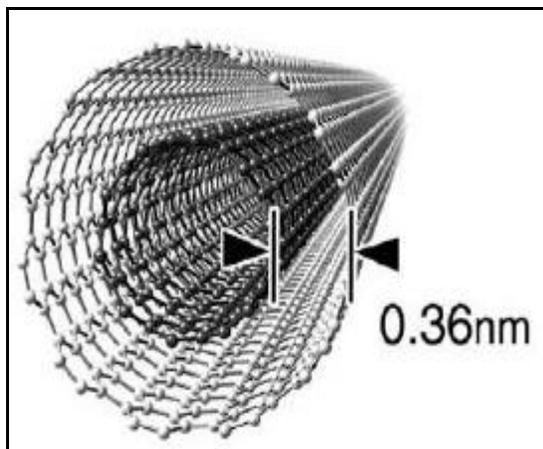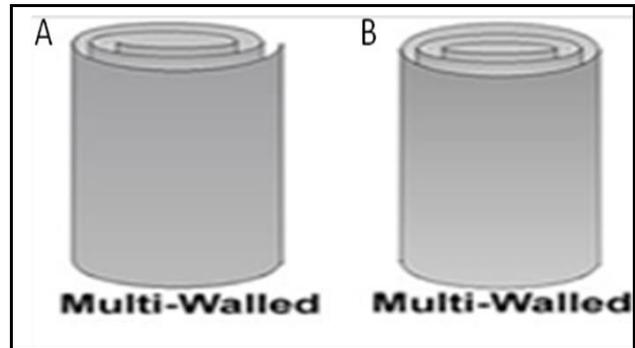
2.3 Carbon Nanotube (CNT) Applications

There seems to be an infinite variety of carbon nanotubes ranging from electronic, biological, and chemical composites to multi-functional composites [27, 40]. A carbon nanotube is theoretically described as possessing a very high strength that is 100 times more than that of steel, yet which is 6 times lighter, and with a perfect arrangement shaped by carbon atoms [41-43].

Due to their outstanding physical properties, as well as high strength and small dimensions, these structures are distinctive materials with a varied series of favourable applications in areas such as field emission, biomedical science, and structural composites [44-47].

It has been discovered that the utilization of CNTs improves the properties of polymer–CNT composites by intensifying their mechanical properties [48, 49]. It has been stated that the addition of carbon nanotubes significantly improves the mechanical behaviour of polymer-based composites. Studies have indicated that more than 500 MPa of stress is transferred via the interface between a polymer and a carbon nanotube, which is 10 times higher than that between a polymer and carbon fibres [50, 51].

Concrete is the most extensively used construction material in the world, and a distinctive cementitious material reinforcement is generally prepared on a mesoscale (millimetre scale) level and/or on a micro-scale level utilizing macrofibres and microfibres, respectively [52]. The first researchers to assimilate CNTs in cement paste were Makar and Beaudoin [25], [53], and the product displayed the positive bridging of micro-cracks, thereby preventing the formation of micro-cracks, and this was validated by [54] as well. They discovered that the morphological structure of the samples displayed the MWCNTs as bridging the cement particles, leading to an efficient and good load transfer from the cement matrix to the nanotubes in tension. Initial experimental characterization studies concentrated on the reinforcing effect of CNTs on cement composites [55-57]. Konsta-Gdoutos *et al.* [6], Konsta-Gdoutos *et al.* [58], and Abu Al-Rub *et al.* [59] investigated the improved mechanical properties of cement pastes reinforced by pristine multi-walled CNTs

Figure 2 Multi-walled carbon nanotubes (MWCNTs) [1]

of different lengths. The mechanical properties and transport properties of CNT–cement composites have been studied by various researchers, and the incorporation of CNTs will possibly efficiently improve the resilience of the cement-based composites [29, 56, 60, 61], increase the strength of the cement-based materials [62, 63], fill the pores between the Portland cement hydration products [64], produce electrical, electromagnetic, thermal and sensing properties in the cementitious materials [65], increase the ductility and flexural strength [66, 67], improve the tensile strength [68], increase the Young's modulus [58, 69], and decrease the porosity of the cement [55, 64].

3.0 CARBON NANOFIBERS (CNFs)

Carbon nanofibers are hollow-core nanofibers containing a single or double layer of graphite planes, as shown in Figure 4. Further, the dimensions and structures of CNFs are highly dependent on their manufacturing and post-treatment methods [70, 71]. In addition, the graphite planes can be angled in a certain way, or can be parallel stacks from the fibre axis and planted with one another to form diverse structures, for example, bamboo-like, parallel, and cup-stacked structures [72, 73]. In the same context, their stacked shape (as displayed in Figure 5) is advantageous as it presents unprotected, non-existent edge planes in the carbon nanotube, thereby introducing an increased surface area and better bond features [74]. Furthermore, the outer surface generally involves conically-shaped graphite planes canted in relation to the longitudinal fibre axis. The presence of the edges along the circumference of the fibre can be utilized to benefit the fibre anchor in the matrix and avoid interfacial slip. The nanofiber sidewalls are thin lines on the surface [71, 75].
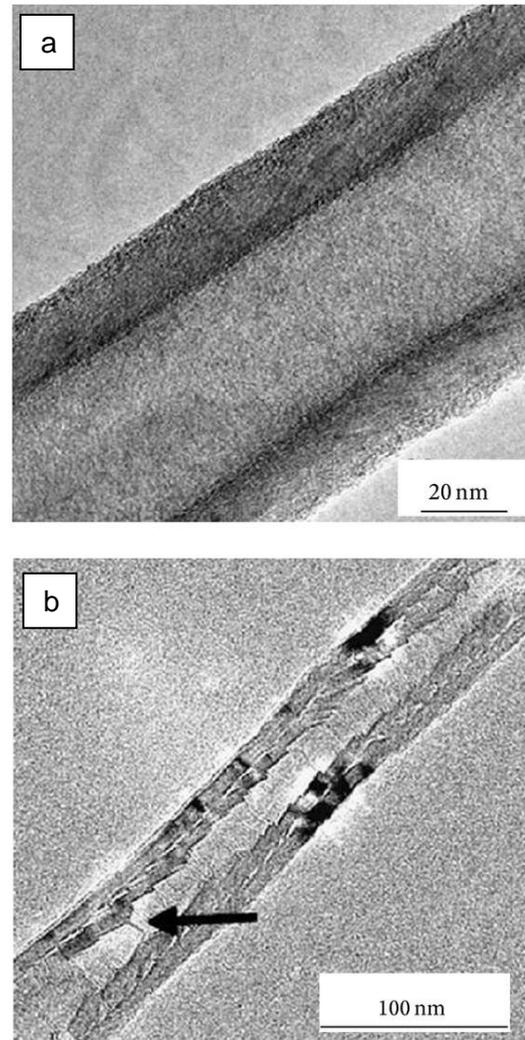

Figure 4 CNF TEM micrograph displaying (a) a single layer. and (b) a double layer [71, 72]
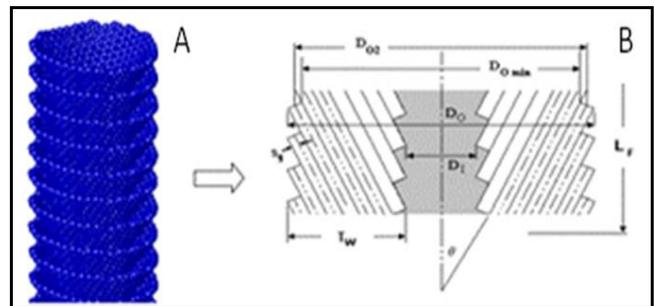

Figure 5 A) Stacked-cup CNF. B) Cross section view showing the internal structure of a CNF stacked-cup (Source: Pyrograf).

On the other hand, carbon nanofibers (diameters ranging from 3–100 nm; lengths ranging from 0.1–1000 µm) have been identified for a substantial number of years as a nuisance that often appears throughout the catalytic conversion of carbon-containing gases. CNFs possess excellent properties, including electrical properties, high stiffness, tensile strength, thermal conductivity and corrosion resistance. Nanoscale three-point bending tests revealed that the Young's modulus of the individual nanofibers varied from 25 to 200 GPa, depending on the thickness of the nanofiber wall [76]. Reports from prior studies showed higher tensile strength and Young's modulus of 12 GPa and 600 GPa, respectively [7]. Ozkan *et al*. [77], in investigating CNTs and CNFs, performed direct mechanical measurements on CNFs, and found that the tensile strength of CNFs is between 2 and 5 GPa, with an average modulus of elasticity of 300 GPa.

3.1 Carbon Nanofiber Applications

Considering these unique properties, the expectation is that CNFs are perfect for the development of advanced nanocomposites. Tennent [78] discussed the unique mechanical and electrical properties of carbon nanofibers, thereby triggering the search for applications for composite materials. The reinforcement of materials, in addition to the enhancement of electrical conductivity has been keenly considered. Lafdi and Matzek [79] investigated numerous issues impacting the capability of carbon nanofibers to improve the tensile strength of composite materials. The factors consisted of the weight fraction, strength and dispersion of the nanofibers, the aspect ratio, and the interface strength. However, the studies showed that nanofibers that are heat-treated to 1500 °C offer optimal properties to nanofiber-enhanced polypropylene composites [80].

Since 1990, carbon fibres have frequently been added to cement paste by investigators. The addition of carbon fibres to cement-based materials has many beneficial mechanical and electrical properties comprising ductility, increased strength and conductivity [81-86]. Currently, the reinforcement of concrete with carbon nanomaterials is a fast-growing research area. However, there exists a large difference in the structure and chemistry of a polymeric and a cementitious matrix, and, therefore, a great deal of research activities is being directed toward understanding the interaction between these nanomaterials and cementitious matrices for their successful application [87-89]. Carbon nanofibers and nanotubes have rapidly become two of the most favourable nanomaterials as a result of their distinctive mechanical properties. In turn, there have been improvements in the microstructure and mechanical properties of cementitious materials [90]. Certain studies have revealed enhancements of up to 50% and 75% in the flexural strength and Young's modulus, respectively [90-93]. Hunashyal *et al*. [94] mentioned that CNFs augmented the load carrying capability

and failure strain of cement composites by 54% and 44%, respectively, and increased the tensile strength [95], enhanced the refraction behaviour [86], and produced tougher concrete with the interruption of crack formation immediately on initiation [96].

Metaxa *et al*. [97] provided evidence from SEM nano-imaging that CNFs have the ability to control cracking by linking the nanocracks and pores in a cementitious matrix. As a consequence of these features, it has been shown that CNFs bring about significant improvements to the mechanical properties of a matrix. Additionally, it has been observed that there is a good bond between CNFs and cement hydration products, indicating that in the matrix, the nanofibers can be adequately secured to ensure that the full capacity of the fibres is used to transfer the load.

4.0 DISPERSION OF NANOCARBONS

Dispersion is one of the main factors that strongly influence the properties of nanocomposites. Nanomaterials tend to agglomerate as a result of the presence of attractive forces (Van der Waals forces) originating from their polarizable, extended π-electron systems. Nanocarbons have a comparatively high melting point of 4000 K or 3675 °C [98], thereby indicating that they are super hydrophobic and chemically inert materials [99], and due to the attraction of the Van der Waals forces, the fibres tend to agglomerate to avoid being dispersed in solvents [100-102].

It is very difficult to permeate agglomerates with composite matrices, and therefore, their presence is the source of potential defects in nanocomposites. The deagglomeration process and subsequent distribution of nanomaterials within the matrices or solvents is known as dispersion. The occurrence of dispersion can be caused by the agglomerates abruptly splitting up into small crumbs under high stress (rupture) or as a result of small crumbs continuously detaching at a moderately lower stress (erosion). The dispersion behaviour of CNFs and CNTs depends on a small number of serious factors, for example, the length, volume fraction, sonication duration, entanglement density, and attractive forces of the nanomaterials [103].

However, it should be noted that various chemical routes (such as the use of a surfactant, polymers, or functionalization) cannot directly disperse nanomaterials in water; instead, they assist in the dispersion process by wetting the nanomaterials with water, and improving the dispersion stability. Therefore, these chemical routes are always used together with physical routes (such as ultrasonication) for the immediate dispersion of nanomaterials.

Therefore, various methods have been employed recently to improve the dispersion of carbon nanomaterials in composite matrices, and these can be generally characterized as chemical and physical techniques.

4.1 Chemical Methods

Numerous chemical approaches have been examined in an attempt to achieve the homogeneous dispersion of carbon nanomaterials in water and various polymers, for example, by utilizing solvents [104], surfactants [105, 106], functionalization with acids [107], amines [108], fluorine [109], plasma [110], microwave [111] and matrix moieties [112], non-covalent functionalization [113], using block polymers [114, 115], and wrapping conjugated polymers [116].

In the same context, extensive efforts have been carried out to improve the dispersion of carbon nanomaterials in cementitious composites. Ordinarily, two categories of techniques have been utilized in the dispersion of carbon nanomaterials (CNMs). One technique involves the use of mechanical methods, such as the adoption of ultrasonic machines [29, 117, 118], ball mills or high-shear mixers [119, 120], to separate the CNMs. Meanwhile, changes to the surface of the CNMs are brought about by chemical methods through the use of covalent or non-covalent modification approaches [55, 121]. Nevertheless, mechanical methods are often utilized in combination with chemical methods [2, 65, 122].

However, it has been shown that many of the chemicals that are used have negative effects on CNMs as the fibres are digested by these chemicals, thereby rendering the fibres less effective, and the formation of bubbles in the composite caused by the surfactants will decrease the strength of the materials [123]. Furthermore, the use of a cationic surfactant will decrease the dispersion capability because of the absence of a benzene ring on the long chain and positive charges which might neutralize the negative charges in the MWCNTs in an aqueous solution [2].

In utilizing surfactants as nanomaterial dispersants, Yu and Kwon [124], discovered that nanomaterials lack connectivity within a cementitious matrix as a result of blockages by the surfactant molecules, which affect the electrical and piezo-resistive properties of the nanocomposites. Yazdanbakhsh *et al*. [125] encountered cement hydration problems when surfactants were used for the dispersion of carbon nanomaterials in polymeric matrices, where they retarded or stopped the hydration, trapped air in the cement paste or counteracted with the water-reducing admixtures, causing re-agglomeration.

The results of previous studies on the treatment of CNFs–CNTs with acid indicated that the fibres are more soluble than in their pristine form, and if not duly controlled, they can destroy or reduce the nanocomposites or even liquefy them. The adverse effects do not permit remarkable enhancements in the mechanical properties of the hardened cement paste [55, 126], Additionally, there will be a deterioration in the qualities of the CNT along with serious material loss due to the acid treatment [127]. Another functionalization method that was described was the solid-phase mechanochemical reaction, where potassium hydroxide (KOH) was applied for the treatment of multi-walled CNTs (MWNTs). In this case,

the reactants (KOH and CNTs) rigorously agglomerated and could not be mixed equitably [128].

Cwirzen *et al*. [29] and Li *et al*. [55] used functionalized carbon nanotubes to form chemical bonds between the –COOH groups in the nanotubes and the calcium silicate hydrate (CSH) in the cement matrix so as to enhance the stress transfer. Al-Rub *et al*. [129] studied the compatibility of the surfactant utilized in the dispersion of CNTs in cement, and discovered that the chemical reaction and cement hydration can be severely affected, with the possibility of the hydration being delayed or stopped, and the cement paste hardening during the process. Sobolkina *et al*. [103] utilized the selective adsorption of anionic sodium dodecyl sulphate (SDS) on CNT surfaces, and discovered that it resulted in a high concentration of surfactant in water, leading to foam formation and consequently, high cement paste porosity. Cui [130] observed the effects on CNT of two types of treatments, with and without chemicals (surface functionalization), with the potential to improve the properties of the concrete. They discovered that there was no significant difference in the improvement to the compressive strength.

The addition of clay minerals to polymers [131]], salts [132, 133], or surfactants [134, 135], have different effects on the electro-kinetic and rheological properties of the suspensions caused by interactions between the particles and the ions or molecules [136].

The interactions between ionic and non-ionic polymers with clay particles are different. The adsorption of ionic polymers on the surface of clay particles is caused by electrostatic interactions, whereas the adsorption of non-ionic polymers is caused by steric interactions. The interactions between the clay particles and the polymers can be affected by the polymer concentration, molecular weight and functional group of the polymers, the size, shape and changes to the surface of the clay particles, the suspension concentration, and the pH and temperature [137]. The placement of surfactant molecules between the clay layers by the formation of H-bonds may decrease the electrostatic interactions between the clay particles, hence reducing the zeta potential of the system [138]. Moreover, when surfactants are used in soil, they are involved in an amplified chemical absorption, thereby decreasing the double-layer thickness. The result is that the particles come closer together, making the net force attractive [139]. The particles gather randomly together in this environment to form loose groups, thereby yielding a changing structure. This soil structure will finally give rise to increased pores or voids for fluids to pass through, thus increasing the soil penetrability [140].

On the basis of the above, in order to use nanocarbons as soil reinforcement without any chemical effects, physical methods must be used for the dispersion of the nanocomposite, before it is mixed with the soil composite.

4.2 Physical Methods

Ultrasonication is frequently used to achieve a good dispersion of nanoparticles in an aqueous solution Carbon nanomaterials (CNTs and CNFs) can be effectively distributed ultrasonically in a water solution [130, 141]. Moreover, Edwards and Bremner [142], and Firoozi *et al.* [143] utilized ultrasonication to disperse soil particles without any pre-treatment or addition of a diffusing surfactant. The advantages of ultrasonic dispersion are that it does not terminate organic soil matter, and does not change the pH of the soil, its electrical conductivity, or cation exchange capability, and the resultant suspension is stable. Consequently, there is no occurrence of flocculation during the sedimentation process.

The electrical voltage in the ultrasonic process is converted to mechanical vibrations, which are then shifted to a liquid medium (water or solvent), leading to the formation and collapse of microscopic bubbles. Throughout this process (identified as cavitation), millions of shock waves are created, and a high level of energy is released [144].

Based on the abovementioned literature, the effect of CNTs on the compressive strength is most probably due to the physical enhancement, with no chemical interaction between the cement matrices. SEM micrographs of CNTs exhibited the respective interactions between the carbon nanotubes and the fly ash cement matrix, with the carbon nanotubes acting as a consequential filler in a denser microstructure which had a higher strength when compared to the referenced fly ash mix without CNTs [145]. Carbon nanotubes are well-dispersed by ultrasonication. It was reported by Jiang *et al.* [146] that there is an exterior mechanical energy in ultrasonication that helps the particles overcome the attraction by Van der Waals forces at contact.

Several studies have been carried out to increase the dispersibility of CNTs without the application of surfactants, thereby leading to useful applications [147]. Inam *et al.* [148] carried out the dispersion of carbon nanotubes by sonication before mixing them into an epoxy matrix. It was found that the nanocomposite with the carbon nanotubes had a high tensile strength, elastic modulus, fracture strain, and fracture toughness. Similarly, Nochaiya and Chaipanich [64] reported that the addition of CNTs to Portland cement without a surfactant improved the compressive strength of the cement-based material by filling the pores between the hydration products. Li *et al.* [56] observed through SEM images that untreated CNT has a uniform dispersion, and a bridging effect.

Researchers investigating the effects of CNT dispersion on the engineering properties of CNT-OPC pastes by means of ultrasonication discovered that physical techniques (ultrasonication) have the ability to increase the workability, Young's modulus, flexural strength, and fracture energy of cement paste [57]. Moreover, Chen *et al.* [149], based on experience with regard to the dispersion of CNTs by ultrasonication,

predicted the optimal ultrasonic energy (UE) for yielding the best reinforcing effects in composites, thereby decreasing the costs of experimental trials. CNT suspensions prepared with different time periods and at the same power of sonication, present different levels of dispersion [150], and studies have determined that the optimum value of the ultrasound time for CNTs and CNFs is generally 5-15 minutes [91, 122, 148, 151, 152].

The bonds between particles and fibres are weakened when the fibres are shortened. Yazdanbakhsh *et al.* [153] distributed CNFs by ultrasonic processing for 15 minutes in a water–superplasticizer solution. The TEM images revealed that after sonication, the CNFs were broken and shortened. This was significant as some of the important properties of fibrous materials, for example, improved toughness, are related to the elastic and frictional bonds of the fibres in the composite. Thus, the ultrasonic timing must be controlled and optimised for the best dispersal and minimum damage. Meanwhile, sonication. particularly if it is carried out for a substantial period of time, damages and shortens CNFs and CNTs [152-154].

Vera-Agullo *et al.* [141] tried other physical methods for breaking the agglomerates and dispersing the nanofilaments (CNTs and CNFs) individually, without the use of a surfactant. High-energy mixing machines were utilized to disperse the CNTs and CNFs into the cementitious matrices, and it was observed that in the early stages both the nanofibers and nanotubes increased the compressive strength of the mortar.

5.0 MEASURING THE DISPERSIBILITY OF NANOCARBONS

The dispersibility of carbon nanomaterials was studied by analysing the zeta potential after dispersion by mechanical (sonication) and chemical methods [105, 152, 155]. A solid surface may become charged when fluid flows across it. Counteractive charged ions in the liquid medium are attracted to the surface in order to equalize the surface charge to create what is generally known as an electric double layer (EDL), as shown in Figure 6. The strength and polarity of the EDL is characterized by the parameter identified as the zeta potential [156].
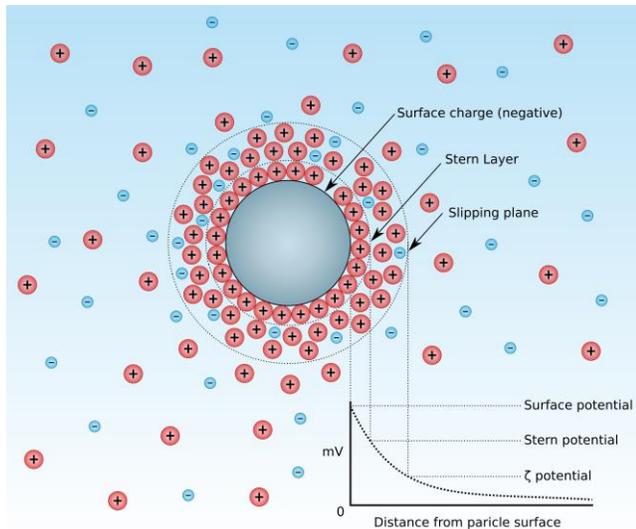
Figure 6 Electric Double Layer (EDL)

Moreover, the significance of the zeta potential is that it is an essential fragment of different applications such as flocculation, electro-osmosis, and CNT stability. Advances in the study of the electrical properties of solid-liquid interfaces led to the expansion of fresh methods, where electrophoresis, electro-osmosis and streaming were the three electro-kinetic effects that were utilized to develop the zeta potential [157].

With reference to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, as shown in Figure 7, particles are dispersible when electrostatic repulses, prompted by correspondingly charged electrical layers around the particles, overcome the attraction of the Van der Waals interactions [158]. The net interaction of the particles is attained by summarizing these two terms. If the repulsion potential surpasses the attraction potential, an energy barrier that opposes aggregation results. If the magnitude of the energy barrier surpasses the kinetic energy of the particle, the suspension is stable [105].
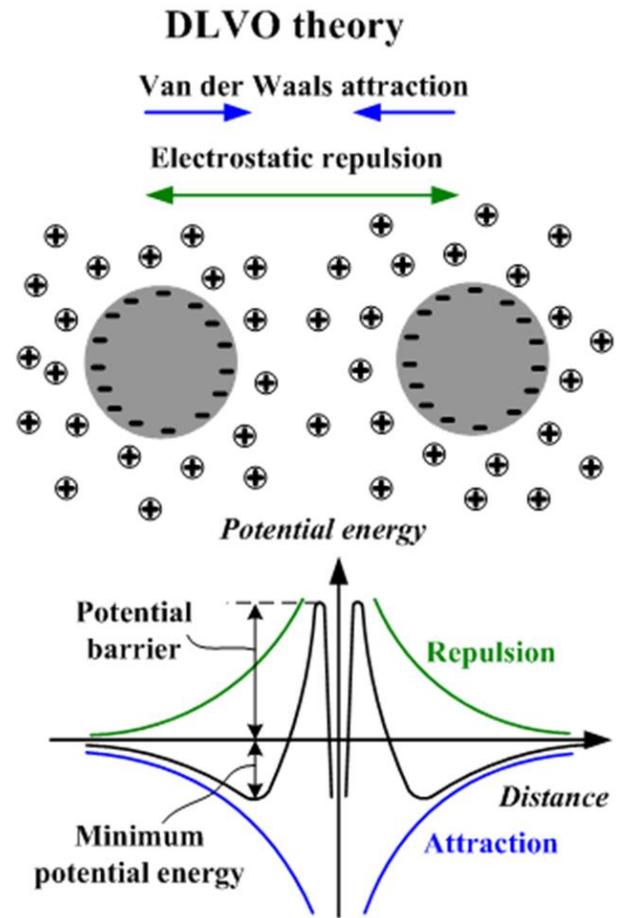

Figure 7 Illustration of the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory

Jiang *et al*. [146], and Sano *et al*. [159], reported that CNMs are negatively charged. As a rule, particles have the tendency to avoid coagulation via electrostatic repulsions above certain surface potentials, generally ± 35 mV. Consequently, knowledge of the magnitude of the net surface potential makes the possible aggregation behaviour of CNTs predictable [105]. Previous studies, such as those by áO'Brien [160], and Hanaor *et al*. [161], have indicated that colloids with low zeta potentials (negative or positive) have the tendency to coagulate or flocculate, while colloids with high zeta potentials are electrically stable, as charted in Table 1.

Table 1 Zeta potential [mV] values [2].

Zeta potential [mV]	Stability behaviour of the colloid
from 0 to ±5,	Rapid coagulation or flocculation
from ±10 to ±30	Incipient instability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

6.0 CHARACTERIZATION OF DISPERSIBILITY OF NANOCARBONS

The dispersion of nanocarbons can be characterized by two approaches. The first involves observing the nanocarbon solution with advanced instruments, for example, optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy, Raman spectroscopy, energy dispersive X-ray spectroscopy, environment scanning electron microscopy, ultraviolet visible spectroscopy, X-ray photoelectron spectroscopy, and small angle light scattering and atomic force electron microscopy [55, 63, 90, 120, 145, 162-165]. Nevertheless, the dispersal of nanocarbons in solutions cannot completely exemplify their dispersion in composites. The second approach involves the observation of the distribution of nanocarbons in composites through microanalysis methods comprised of atomic force electron microscopy, SEM, TEM, environment scanning electron microscopy, laser ablation inductively coupled plasma mass spectrometry, and so on [6, 53, 63, 145, 163-165].

7.0 CONCLUSIONS

The disadvantages of the dispersion of nanocarbons in aqueous solutions with the use of an agent (surfactant), and the advantages of not using an agent (physical methods), in terms of the characteristics of nanocarbons, are summarized as follows:

1- CNTs and CNFs have distinctive properties which produce an array of composite applications in the construction field. Although CNFs have a lower strength and modulus of elasticity compared to CNTs, they are very strong and stiff compared to other materials, for example, steel.

2- The integration of nanocarbons as fillers has important effects on the mechanical properties of mortars.

3- Nanocarbons, in the form of nanofibers, exhibit a super-hydrophobic property, and are chemically passive materials that do not absorb or react with natural non-absorbing or non-reacting composites (soil moisture) or leachates.

4- The key to the successful use of nanocarbons in concrete is proper mixing. Two types of mixing techniques are used, specifically chemical and physical mixing. Chemical mixing has the tendency to damage the nanocarbons. Consequently, this problem can be overcome by physical mixing

5- Studies on the mixing of nanocarbons in nanocomposites by physical methods are rare. Therefore, more research is required to explore methods for the mixing of nanocarbons in nanocomposites.

6- The dispersion of nanocarbons can be characterized by observing the nanocarbon solution and the distribution of nanocarbons in composites through microanalysis methods.

References

[1] K. P. De Jong and J. W. Geus. 2000. Carbon Nanofibers: Catalytic Synthesis And Applications. *Catalysis Reviews.* 42: 481-510.

[2] S. Parveen, S. Rana, and R. Fangueiro. 2013. A Review on Nanomaterial Dispersion, Microstructure, and Mechanical Properties of Carbon Nanotube and Nanofiber Reinforced Cementitious Composites. *Journal of Nanomaterials.* 2013. 1-19.

[3] W. Brandl, G. Marginean, V. Chirila, and W. Warschewski. 2004. Production And Characterisation Of Vapour Grown Carbon Fiber/Polypropylene Composites. *Carbon.* 42: 5-9.

[4] E. Hammel, X. Tang, M. Trampert, T. Schmitt, K. Mauthner, A. Eder, *et al.* 2004. Carbon Nanofibers For Composite Applications. *Carbon.* 42: 1153-1158.

[5] C. Kuzuya, W. In-Hwang, S. Hirako, Y. Hishikawa, and S. Motojima. 2002. Preparation, Morphology, And Growth Mechanism Of Carbon Nanocoils. *Chemical Vapor Deposition.* 8: 57-62.

[6] M. S. Konsta-Gdoutos, Z. S. Metaxa, and S. P. Shah. 2010. Multi-scale Mechanical And Fracture Characteristics And Early-Age Strain Capacity Of High Performance Carbon Nanotube/Cement Nanocomposites. *Cement and Concrete Composites.* 32: 110-115.

[7] V. Mordkovich. 2003. Carbon Nanofibers: A New Ultrahigh-Strength Material For Chemical Technology. *Theoretical Foundations of Chemical Engineering.* 37: 429-438.

[8] K. Mukhopadhyay, D. Porwal, D. Lal, K. Ram, and G. N. Mathur. 2004. Synthesis Of Coiled/Straight Carbon Nanofibers By Catalytic Chemical Vapor Deposition. *Carbon.* 42: 3254-3256.

[9] S. Iijima. 1991. Helical Microtubules Of Graphitic Carbon. *Nature.* 354: 56-58.

[10] M. Reibold, P. Paufler, A. A. Levin, W. Kochmann, N. Patzke, and D. C. Meyer. 2006. Materials: Carbon Nanotubes In An Ancient Damascus Sabre. *Nature.* 444: 286.

[11] A. K.-T. Lau and D. Hui. 2002. The Revolutionary Creation Of New Advanced Materials—Carbon Nanotube Composites. *Composites Part B: Engineering.* 33: 263-277.

[12] N. Grobert. 2007. Carbon Nanotubes–Becoming Clean, *Materials Today.* 10: 28-35.

[13] B. Philip. 1996. The Perfect Nano-Tubes. *Nature.* 382: 207-8.

[14] Y. S. Wang, X. S. Cheng, and L. Wang. 2009. Regularity Of VEGF Expression In Bone Marrow Mesenchymal Stem Cells Under Hypoxia. *Zhongguo Ying Yong Sheng Li Xue Za Zhi.* 25: 475-7.

[15] M. S. Morsy, S. H. Alsayed, and M. Aqel. 2011. Hybrid Effect Of Carbon Nanotube And Nano-Clay On Physico-Mechanical Properties Of Cement Mortar. *Construction and Building Materials.* 25: 145-149.

[16] H. Yan, A. Gong, H. He, J. Zhou, Y. Wei, and L. Lv. 2006. Adsorption Of Microcystins By Carbon Nanotubes, *Chemosphere.* 62: 142-148.

[17] A. Peigney, C. Laurent, E. Flahaut, R. Bacsa, and A. Rousset. 2001. Specific Surface Area Of Carbon Nanotubes And Bundles Of Carbon Nanotubes. *Carbon.* 39: 507-514.

[18] H.-M. Cheng, Q.-H. Yang, and C. Liu. 2001. Hydrogen Storage In Carbon Nanotubes. *Carbon.* 39: 1447-1454.

[19] A. Dillon and M. Heben. 2001. Hydrogen Storage Using Carbon Adsorbents: Past, Present And Future. *Applied Physics A.* 72: 133-142.

[20] Iango, Vijaya, and Avika Gupta. 2013. Carbon Nanotubes–A Successful Hydrogen Storage Medium. *World Academy of Science, Engineering and Technology.* 7(9): 678-681.

[21] C. Chen and X. Wang. 2006. Adsorption of Ni (II) from Aqueous Solution Using Oxidized Multiwall Carbon Nanotubes. *Industrial & Engineering Chemistry Research.* 45: 9144-9149.

[22] Rao, Gadupudi Purnachadra, Chungsying Lu, and Fengsheng Su. 2007. Sorption Of Divalent Metal Ions From Aqueous Solution By Carbon Nanotubes: A Review. *Separation And Purification Technology*. 58(1): 224-231.

[23] X. Wang, C. Chen, W. Hu, A. Ding, D. Xu, and X. Zhou. 2005. Sorption of 243Am (III) To Multiwall Carbon Nanotubes. *Environmental Science & Technology*. 39: 2856-2860.

[24] R. Nuraini and M. R. Taha. 2010. Adsorption Behavior Of Phenol On Residual Soil-Multiwalled Carbon Nanotubes Mixtures. *Environmental Engineering and Applications (ICEEA), 2010 International Conference on*. 157-159.

[25] J. Makar and J. Beaudoin. 2004. Carbon Nanotubes And Their Application In The Construction Industry. *SPECIAL PUBLICATION-ROYAL SOCIETY OF CHEMISTRY*. 292: 331-342.

[26] P. G. Collins and P. Avouris. 2000. Nanotubes For Electronics, *Scientific American*. 283: 62-69.

[27] J.-P. Salvetat, J.-M. Bonard, N. Thomson, A. Kulik, L. Forro, W. Benoit, *et al.* 1999. Mechanical Properties Of Carbon Nanotubes. *Applied Physics A*. 69: 255-260.

[28] T. Belytschko, S. Xiao, G. Schatz, and R. Ruoff. 2002. Atomistic Simulations Of Nanotube Fracture. *Physical Review B*. 65: 235-430.

[29] A. Cwirzen, K. Habermehl-Cwirzen, and V. Penttala. 2008. Surface Decoration Of Carbon Nanotubes And Mechanical Properties Of Cement/Carbon Nanotube Composites, *Advances in Cement Research*. 20: 65-73.

[30] Lourie, O., D. M. Cox, and H. D. 1998. Wagner. Buckling And Collapse Of Embedded Carbon Nanotubes. *Physical Review Letters*. 81(8): 1638.

[31] Y. Ando.1994. The Preparation Of Carbon Nanotubes. *Fullerenes, Nanotubes, and Carbon Nanostructures*. 2: 173-180.

[32] W. K. Maser, A. M. Benito, and M. T. Martínez. 2002. Production Of Carbon Nanotubes: The Light Approach. *Carbon*. 40: 1685-1695.

[33] Ç. Öncel and Y. Yürüm. 2006. Carbon Nanotube Synthesis Via The Catalytic CVD Method: A Review On The Effect Of Reaction Parameters. *Fullerenes, Nanotubes, and Carbon Nonstructures*. 14: 17-37.

[34] X. Li, A. Cao, Y. J. Jung, R. Vajtai, and P. M. Ajayan. 2005. Bottom-up Growth Of Carbon Nanotube Multilayers: Unprecedented Growth. *Nano Letters*. 5: 1997-2000.

[35] S. Musso, S. Porro, M. Giorcelli, A. Chiodoni, C. Ricciardi, and A. Tagliaferro. 2007. Macroscopic Growth Of Carbon Nanotube Mats And Their Mechanical Properties. *Carbon*. 45: 1133-1136.

[36] J. W. Mintmire, B. I. Dunlap, and C. T. White. 1992. Are Fullerene Tubules Metallic? *Phys Rev Lett*. 68: 631-634.

[37] R. Dekkers.1999. Apple Juice And The Chemical-Contact Softening Of Gallstones. *Lancet*. 354: 2171.

[38] S. Iijima. 2002. Carbon Nanotubes: Past, Present, And Future. *Physica B: Condensed Matter*. 323: 1-5.

[39] I. Campillo, J. Dolado, and A. Porro. 2004. High-performance Nanostructured Materials For Construction. *SPECIAL PUBLICATION-ROYAL SOCIETY OF CHEMISTRY*. 292: 215-226.

[40] C. Li and T.-W. Chou. 2003. Elastic Moduli Of Multi-Walled Carbon Nanotubes And The Effect Of Van Der Waals Forces. *Composites Science and Technology*. 63: 1517-1524.

[41] N. Khandoker, S. Hawkins, R. Ibrahim, C. Huynh, and F. Deng. 2011. Tensile Strength Of Spinnable Multiwall Carbon Nanotubes. *Procedia Engineering*. 10: 2572-2578.

[42] E. T. Thostenson, Z. Ren, and T.-W. Chou. 2001. Advances In The Science And Technology Of Carbon Nanotubes And Their Composites: A Review. *Composites science and Technology*. 61: 1899-1912.

[43] E. W. Wong, P. E. Sheehan, and C. M. Lieber. 1997. Nanobeam Mechanics: Elasticity, Strength, And Toughness Of Nanorods And Nanotubes. *Science*. 277: 1971-1975.

[44] A. M. Esawi, K. Morsi, A. Sayed, A. A. Gawad, and P. Borah. 2009. Fabrication And Properties Of Dispersed Carbon Nanotube–Aluminum Composites. *Materials Science and Engineering: A*. 508: 167-173.

[45] W. Chen, J. Tu, L. Wang, H. Gan, Z. Xu, and X. Zhang. 2003. Tribological Application Of Carbon Nanotubes In A Metal-Based Composite Coating And Composites/ *Carbon*. 41: 215-222.

[46] S. Polizu, M. Maugey, S. Poulin, P. Poulin, and L. H. Yahia. 2006. Nanoscale Surface Of Carbon Nanotube Fibers For Medical Applications: Structure And Chemistry Revealed By TOF-SIMS Analysis. *Applied Surface Science*. 252: 6750-6753.

[47] T. Wei, Z. Fan, G. Luo, and F. Wei. 2008. A New Structure For Multi-Walled Carbon Nanotubes Reinforced Alumina Nanocomposite With High Strength And Toughness. *Materials Letters*. 62: 641-644.

[48] J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko. 2006. Small But Strong: A Review Of The Mechanical Properties Of Carbon Nanotube–Polymer Composites. *Carbon*. 44: 1624-1652.

[49] R. Andrews and M. Weisenberger. 2004. Carbon Nanotube Polymer Composites. *Current Opinion in Solid State and Materials Science*. 8: 31-37.

[50] D. Qian, E. C. Dickey, R. Andrews, and T. Rantell. 2000. Load Transfer And Deformation Mechanisms In Carbon Nanotube-Polystyrene Composites. *Applied Physics Letters*. 76: 2868-2870.

[51] H. Wagner, O. Lourie, Y. Feldman, and R. Tenne. 1998. Stress-induced Fragmentation Of Multiwall Carbon Nanotubes In A Polymer Matrix. *Applied Physics Letters*. 72: 188-190.

[52] P. N. Balaguru and S. P. Shah. 1992. *Fiber-reinforced cement Composites*. New York: McGraw-Hill.

[53] Makar, J. M., Margeson, J., Luh, J. 2005. Carbon Nanotube/Cement Composites–Early Results And Potential Applications. In: Banthia N, Uomoto T, Bentur A, Shah SP, Editors. *Proceedings Of 3rd International Conference On Construction Materials: Performance, Innovations And Structural Implications*. Vancouver, BC August 22–24. 1-10.

[54] Y. Hu, D. Luo, P. Li, Q. Li, and G. Sun. 2014. Fracture Toughness Enhancement Of Cement Paste With Multi-Walled Carbon Nanotubes. *Construction and Building Materials*. 70: 332-338.

[55] G. Y. Li, P. M. Wang, and X. Zhao. 2005. Mechanical Behavior And Microstructure Of Cement Composites Incorporating Surface-Treated Multi-Walled Carbon Nanotubes. *Carbon*. 43: 1239-1245.

[56] G. Y. Li, P. M. Wang, and X. Zhao. 2007. Pressure-Sensitive Properties And Microstructure Of Carbon Nanotube Reinforced Cement Composites. *Cement and Concrete Composites*. 29: 377-382.

[57] B. Zou, S. J. Chen, A. H. Korayem, F. Collins, C. M. Wang, and W. H. Duan. 2015. Effect Of Ultrasonication Energy On Engineering Properties Of Carbon Nanotube Reinforced Cement Pastes. *Carbon*. 85: 212-220.

[58] M. S. Konsta-Gdoutos, Z. S. Metaxa, and S. P. Shah. 2010. Highly Dispersed Carbon Nanotube Reinforced Cement Based Materials. *Cement and Concrete Research*. 40: 1052-1059.

[59] R. K. Abu Al-Rub, A. I. Ashour, and B. M. Tyson. 2012. On The Aspect Ratio Effect Of Multi-Walled Carbon Nanotube Reinforcements On The Mechanical Properties Of Cementitious Nanocomposites. *Construction and Building Materials*. 35: 647-655.

[60] B. Han, Z. Yang, X. Shi, and X. Yu. 2013. Transport Properties Of Carbon-Nanotube/Cement Composites. *Journal Of Materials Engineering And Performance*. 22: 184-189.

[61] A. Cwirzen, K. Habermehl-Cwirzen, A. Nasibulin, E. Kaupinen, P. Mudimela, and V. Penttala. 2009. SEM/AFM Studies Of Cementitious Binder Modified By MWCNT And Nano-Sized Fe Needles. *Materials Characterization*. 60: 735-740.

[62] T. Manzur and N. Yazdani. 2010. Strength Enhancement Of Cement Mortar With Carbon Nanotubes: Early Results And Potential. *Transportation Research Record: Journal of the Transportation Research Board*. 102-108.

[63] G. Yakovlev, J. Kerienė, A. Gailius, and I. Girnienė. 2006. Cement Based Foam Concrete Reinforced By Carbon Nanotubes. *Materials Science [Medžiagotyra]*. 12: 147-151.

[64]   T. Nochaiya and A. Chaipanich. 2011. Behavior Of Multi-Walled Carbon Nanotubes On The Porosity And Microstructure Of Cement-Based Materials. *Applied Surface Science*. 257: 1941-1945.

[65]   B. Han, X. Yu, and J. Ou. 2011. Multifunctional And Smart Carbon Nanotube Reinforced Cement-Based Materials. In *Nanotechnology In Civil Infrastructure*. ed: Springer. 1-47.

[66]   R. K. A. Al-Rub, A. I. Ashour, and B. M. Tyson. 2012. On The Aspect Ratio Effect Of Multi-Walled Carbon Nanotube Reinforcements On The Mechanical Properties Of Cementitious Nanocomposites. *Construction and Building Materials*. 35: 647-655.

[67]   Z. S. Metaxa, J.-W. T. Seo, M. S. Konsta-Gdoutos, M. C. Hersam, and S. P. Shah. 2012. Highly Concentrated Carbon Nanotube Admixture For Nano-Fiber Reinforced Cementitious Materials. *Cement and Concrete Composites*. 34: 612-617.

[68]   P. Ludvig, L. Ladeira, J. Calixto, I. Gaspar, and V. Melo. 2009. In-situ Synthesis Of Multiwall Carbon Nanotubes On Portland Cement Clinke. In *11th International Conference on Advanced Materials, Rio de Janeiro, Brazil*. 2009.

[69]   S. P. Shah, M. Konsta-Gdoutos, Z. Metaxa, and P. Mondal. 2009. Nanoscale Modification Of Cementitious Materials. In *Nanotechnology in Construction*. 3rd ed: Springer. 125-130.

[70]   H. Miyagawa, M. J. Rich, and L. T. Drzal. 2006. Thermo-Physical Properties Of Epoxy Nanocomposites Reinforced By Carbon Nanotubes And Vapor Grown Carbon Fibers. *Thermochimica acta*. 442: 67-73.

[71]   G. Tibbetts, M. Lake, K. Strong, and B. Rice. 2007. A Review Of The Fabrication And Properties Of Vapor-Grown Carbon Nanofiber/Polymer Composites. *Composites Science and Technology*. 67: 1709-1718.

[72]   M. Endo, Y. A. Kim, M. Ezaka, K. Osada, T. Yanagisawa, T. Hayashi, *et al.* 2003. Selective And Efficient Impregnation Of Metal Nanoparticles On Cup-Stacked-Type Carbon Nanofibers. *Nano Letters*. 3: 723-726.

[73]   T. Uchida, D. P. Anderson, M. L. Minus, and S. Kumar. 2006. Morphology And Modulus Of Vapor Grown Carbon Nano Fibers. *Journal of Materials Science*. 41: 5851-5856.

[74]   Y. L. Mo, and R. H. Roberts. 2013. Carbon nanofiber Concrete For Damage Detection Of Infrastructure. In: R. Maguire (Ed.). Advances in Nanofibers, InTech, Rijeka. 125-143.

[75]   J. G. Lawrence, L. M. Berhan, and A. Nadarajah. 2008. Structural transformation Of Vapor Grown Carbon Nanofibers Studied by HRTEM. *Journal of Nanoparticle Research*. 10: 1155-1167.

[76]   J. G. Lawrence, L. M. Berhan, and A. Nadarajah. 2008. Elastic Properties And Morphology Of Individual Carbon Nanofibers. *Acs Nano*. 2: 1230-1236.

[77]   T. Ozkan, M. Naraghi, and I. Chasiotis. 2010. Mechanical Properties Of Vapor Grown Carbon Nanofibers. *Carbon*. 48: 239-244.

[78]   H. G. Tennent. 1987. Carbon Fibrils, Method For Producing Same And Compositions Containing Same. ed: Google Patents.

[79]   K. Lafdi and M. Matzek. 2003. Carbon Nanofibers As A Nano-Reinforcement For Polymeric Nanocomposites. In *The 35th international SAMPE technical conference*. 2003.

[80]   J. Y. Howe, G. G. Tibbetts, C. Kwag, and M. L. Lake. 2006. Heat Treating Carbon Nanofibers For Optimal Composite Performance. *Journal of Materials Research*. 21: 2646-2652.

[81]   P.-W. Chen and D. Chung. 1993. Concrete Reinforced With Up To 0.2 Vol% Of Short Carbon Fibres. *Composites*. 24: 33-52.

[82]   X. Fu and D. D. L. Chung. 1998. Submicron-diameter-carbon-filament cement-matrix composites, *Carbon*. 36: 459-462.

[83]   H. Li, H.-g. Xiao, J. Yuan, and J. Ou. 2004. Microstructure Of Cement Mortar With Nano-Particles. *Composites Part B: Engineering*. 35: 185-189.

[84]   H. Li, M.-h. Zhang, and J.-p. Ou. 2006. Abrasion Resistance Of Concrete Containing Nano-Particles For Pavement. *Wear*. 260: 1262-1266.

[85]   V. C. Li. 2002. Large Volume, High-Performance Applications Of Fibers In Civil Engineering. *Journal of Applied Polymer Science*. 83: 660-686.

[86]   R. N. Howser, H. B. Dhonde, and Y. L. Mo. 2011. Self-Sensing Of Carbon Nanofiber Concrete Columns Subjected To Reversed Cyclic Loading. *Smart Materials and Structures*. 20: 085031.

[87]   Z. Metaxa, M. Konsta-Gdoutos, and S. Shah. 2010. Carbon Nanofiber-Reinforced Cement-Based Materials, *Transportation Research Record. Journal of the Transportation Research Board*. 2142: 114-118.

[88]   S. Chen, F. Collins, A. Macleod, Z. Pan, W. Duan, and C. Wang. 2011. Carbon Nanotube–Cement Composites: A Retrospect. *The IES Journal Part A: Civil & Structural Engineering*. 4: 254-265.

[89]   I. Szleifer and R. Yerushalmi-Rozen. 2005. Polymers And Carbon Nanotubes—Dimensionality, Interactions And Nanotechnology. *Polymer*. 46: 7803-7818.

[90]   B. M. Tyson, R. K. Abu Al-Rub, A. Yazdanbakhsh, and Z. Grasley. 2011. Carbon Nanotubes And Carbon Nanofibers For Enhancing The Mechanical Properties Of Nanocomposite Cementitious Materials. *Journal of Materials in Civil Engineering*. 23: 1028-1035.

[91]   Z. S. Metaxa, M. S. Konsta-Gdoutos, and S. P. Shah. 2013. Carbon Nanofiber Cementitious Composites: Effect Of Debulking Procedure On Dispersion And Reinforcing Efficiency. *Cement and Concrete Composites*. 36: 25-32.

[92]   S. Shah, M. Konsta-Gdoutos, and Z. Metaxa. 2010. Exploration Of Fracture Characteristics, Nanoscale Properties And Nanostructure Of Cementitious Matrices With Carbon Nanotubes And Carbon Nanofibers. In *Proceedings Of The 7th International Conference On Fracture Mechanics Of Concrete And Concrete Structures*. 2010.

[93]   A. Peyvandi, L. A. Sbia, P. Soroushian, and K. Sobolev. 2013. Effect Of The Cementitious Paste Density On The Performance Efficiency Of Carbon Nanofiber In Concrete Nanocomposite. *Construction and Building Materials*. 48: 265-269.

[94]   A. M. Hunashyal, S. J. Lohitha, S. S. Quadri, and N. R. Banapurmath. 2011. Experimental Investigation Of The Effect Of Carbon Nanotubes And Carbon Fibres On The Behaviour Of Plain Cement Composite Beams. *The IES Journal Part A: Civil & Structural Engineering*. 4: 29-36.

[95]   C. Gay and F. Sanchez. 2010. Performance Of Carbon Nanofiber-Cement Composites With A High-Range Water Reducer. *Transportation Research Record: Journal of the Transportation Research Board*. 109-113.

[96]   A. Keyvani. 2007. Huge Opportunities For Industry Of Nanofibrous Concrete Technology. *International Journal of Nanoscience and Nanotechnology*. 3: 3-12.

[97]   Z. Metaxa, M. Konsta-Gdoutos, and S. Shah. 2010. Mechanical Properties And Nanostructure Of Cement-Based Materials Reinforced With Carbon Nanofibers And Polyvinyl Alcohol (PVA) Microfibers. *ACI Special Publication*. 270.

[98]   A. Jorio, G. Dresselhaus, and M. S. Dresselhaus. 2007. *Carbon Nanotubes: Advanced Topics In The Synthesis, Structure, Properties And Applications*. 111: Springer Science & Business Media.

[99]   Z. Wang, L. Ci, L. Chen, S. Nayak, P. M. Ajayan, and N. Koratkar. 2007. Polarity-Dependent Electrochemically Controlled Transport Of Water Through Carbon Nanotube Membranes. *Nano Letters*. 7: 697-702.

[100]   I. Kang, Y. Y. Heung, J. H. Kim, J. W. Lee, R. Gollapudi, S. Subramaniam, *et al.* 2006. Introduction To Carbon Nanotube And Nanofiber Smart Materials. *Composites Part B: Engineering*. 37: 382-394.

[101]   R. H. Baughman. 1999. Carbon Nanotube Actuators. *Science*. 284: 1340-1344.

[102]   J. Hilding, E. A. Grulke, Z. George Zhang, and F. Lockwood. 2003. Dispersion of Carbon Nanotubes in Liquids. *Journal of Dispersion Science and Technology*. 24: 1-41.

[103] A. Sobolkina, V. Mechtcherine, V. Khavrus, D. Maier, M. Mende, M. Ritschel, *et al.* 2012. Dispersion Of Carbon Nanotubes And Its Influence On The Mechanical Properties Of The Cement Matrix. *Cement and Concrete Composites.* 34: 1104-1113.

[104] K. D. Ausman, R. Piner, O. Lourie, R. S. Ruoff, and M. Korobov. 2000. Organic Solvent Dispersions Of Single-Walled Carbon Nanotubes: Toward Solutions Of Pristine Nanotubes. *The Journal of Physical Chemistry B.* 104: 8911-8915.

[105] L. Vaisman, G. Marom, and H. D. Wagner. 2006. Dispersions of Surface-Modified Carbon Nanotubes in Water-Soluble and Water-Insoluble Polymers. *Advanced Functional Materials.* 16: 357-363.

[106] J. Pang, G. Xu, S. Yuan, Y. Tan, and F. He. 2009. Dispersing Carbon Nanotubes In Aqueous Solutions By A Silicon Surfactant: Experimental And Molecular Dynamics Simulation Study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 350: 101-108.

[107] H. Peng, L. B. Alemany, J. L. Margrave, and V. N. Khabashesku. 2003. Sidewall Carboxylic Acid Functionalization Of Single-Walled Carbon Nanotubes. *Journal of the American Chemical Society.* 125: 15174-15182.

[108] Y. Wang, Z. Iqbal, and S. V. Malhotra. 2005. Functionalization Of Carbon Nanotubes With Amines And Enzymes. *Chemical Physics Letters.* 402: 96-101.

[109] Y. V. Lavskaya, L. Bulusheva, A. Okotrub, N. Yudanov, D. Vyalikh, and A. Fonseca. 2009. Comparative Study Of Fluorinated Single-And Few-Wall Carbon Nanotubes By X-Ray Photoelectron And X-Ray Absorption Spectroscopy. *Carbon.* 47: 1629-1636.

[110] A. Felten, C. Bittencourt, J.-J. Pireaux, G. Van Lier, and J.-C. Charlier. 2005. Radio-Frequency Plasma Functionalization Of Carbon Nanotubes Surface O2, NH3, and CF4 Treatments. *Journal of Applied Physics.* 98: 074308.

[111] Y. Wang, Z. Iqbal, and S. Mitra. 2006. Rapidly Functionalized, Water-Dispersed Carbon Nanotubes At High Concentration. *Journal of the American Chemical Society.* 128: 95-99.

[112] J. M. González-Domínguez, Y. Martínez-Rubí, A. M. Díez-Pascual, A. Ansón-Casaos, M. Gómez-Fatou, B. Simard, *et al.* 2012. Reactive Fillers Based On Swcnts Functionalized With Matrix-Based Moieties For The Production Of Epoxy Composites With Superior And Tunable Properties. *Nanotechnology.* 23: 285702.

[113] J. U. Lee, J. Huh, K. H. Kim, C. Park, and W. H. Jo. 2007. Aqueous Suspension Of Carbon Nanotubes Via Non-Covalent Functionalization With Oligothiophene-Terminated Poly (ethylene glycol). *Carbon.* 45: 1051-1057.

[114] E. Nativ-Roth, R. Shvartzman-Cohen, C. Bounioux, M. Florent, D. Zhang, I. Szleifer, *et al.* 2007. Physical Adsorption Of Block Copolymers To SWNT And MWNT: A Nonwrapping Mechanism. *Macromolecules.* 40: 3676-3685.

[115] X. Xin, G. Xu, T. Zhao, Y. Zhu, X. Shi, H. Gong, *et al.* 2008. Dispersing Carbon Nanotubes In Aqueous Solutions By A Starlike Block Copolymer. *The Journal of Physical Chemistry C.* 112: 16377-16384.

[116] R. Haggenmueller, S. S. Rahatekar, J. A. Fagan, J. Chun, M. L. Becker, R. R. Naik, *et al.* 2008. Comparison Of The Quality Of Aqueous Dispersions Of Single Wall Carbon Nanotubes Using Surfactants And Biomolecules. *Langmuir.* 24: 5070-5078.

[117] F. Sanchez, L. Zhang, and C. Ince. 2009. Multi-Scale Performance And Durability Of Carbon Nanofiber/Cement Composites. In *Nanotechnology in Construction 3.* ed: Springer. 345-350.

[118] S. Shah, M. Konsta-Gdoutos, and Z. Metaxa. 2011. Advanced Cement Based Nanocomposites. *Recent Advances in Mechanics.* ed: Springer. 313-327.

[119] A. P. Singh, M. Mishra, A. Chandra, and S. Dhawan. 2011. Graphene Oxide/ferrofluid/cement Composites For Electromagnetic Interference Shielding Application. *Nanotechnology.* 22: 465701.

[120] A. P. Singh, B. K. Gupta, M. Mishra, A. Chandra, R. Mathur, and S. Dhawan. 2013. Multiwalled Carbon Nanotube/Cement Composites With Exceptional Electromagnetic Interference Shielding Properties. *Carbon.* 56: 86-96.

[121] Y. Saez de Ibarra, J. Gaitero, E. Erkizia, and I. Campillo. 2006. Atomic Force Microscopy And Nanoindentation Of Cement Pastes With Nanotube Dispersions. *Physica Status Solidi (A).* 203: 1076-1081.

[122] D. T. R. Figueiredo, A. A. S. Correia, D. Hunkeler, and M. G. B. V. Rasteiro. 2015. Surfactants For Dispersion Of Carbon Nanotubes Applied In Soil Stabilization. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 480: 405-412.

[123] Y. Mo and R. H. Roberts. 2013. Carbon Nanofiber Concrete for Damage Detection of Infrastructure. ed: InTech.

[124] X. Yu and E. Kwon. 2009. A Carbon Nanotube/Cement Composite With Piezoresistive Properties. *Smart Materials and Structures.* 18: 055010.

[125] A. Yazdanbakhsh, Z. Grasley, B. Tyson, and R. A. Al-Rub. 2009. Carbon Nano Filaments In Cementitious Materials: Some Issues On Dispersion And Interfacial Bond. *ACI Special Publication.* 267.

[126] T. Kowald and R. Trettin. 2004. Influence Of Surface-Modified Carbon Nanotubes On Ultrahigh Performance Concrete. *Proceedings of International Symposium on Ultra High Performance Concrete.* 195-203.

[127] L. Chen, H. Xie, Y. Li, and W. Yu. 2008. Surface Chemical Modification of Multiwalled Carbon Nanotubes by a Wet-Mechanochemical Reaction. *Journal of Nanomaterials* 2008. 1-5.

[128] H. Pan, L. Liu, Z.-X. Guo, L. Dai, F. Zhang, D. Zhu, *et al.* 2003. Carbon Nanotubols From Mechanochemical Reaction. *Nano Letters.* 3: 29-32.

[129] Abu Al-Rub, Rashid K., Bryan M. Tyson, Ardavan Yazdanbakhsh, and Zachary Grasley. 2011. Mechanical Properties Of Nanocomposite Cement Incorporating Surface-Treated And Untreated Carbon Nanotubes And Carbon Nanofibers. *Journal of Nanomechanics and Micromechanics.* 2(1): 1-6.

[130] L. Cui. 2013. Incorporation of Multiwalled Carbon Nanotubes to Ordinary Portland Cement (OPC): Effects on Mechanical Properties. *Advanced Materials Research.* 641-642: 436-439.

[131] H. J. Kong, S. G. Bike, and V. C. Li. 2006. Effects Of A Strong Polyelectrolyte On The Rheological Properties Of Concentrated Cementitious Suspensions. *Cement and Concrete Research.* 36: 851-857.

[132] M. Alkan, Ö. Demirbaş, and M. Doğan. 2005. Electrokinetic Properties Of Kaolinite In Mono-And Multivalent Electrolyte Solutions. *Microporous and Mesoporous Materials.* 83: 51-59.

[133] D. Niriella and R. Carnahan. 2006. Comparison Study Of Zeta Potential Values Of Bentonite In Salt Solutions. *Journal Of Dispersion Science And Technology.* 27: 123-131.

[134] M. Janek and G. Lagaly. 2003. Interaction Of A Cationic Surfactant With Bentonite: A Colloid Chemistry Study. *Colloid and Polymer Science.* 281: 293-301.

[135] M. Clifton, T. Nguyen, and R. Frost. 2007. Effect Of Ionic Surfactants On Bauxite Residues Suspensions Viscosity. *Journal Of Colloid And Interface Science.* 307: 572-577.

[136] O. Sadek, W. Mekhemer, F. Assaad, and B. Mostafa. 2006. Adsorption of Poly (4-sodium styrene sulfonate) on Kaolinite clays. *Journal Of Applied Polymer Science.* 100: 1712-1719.

[137] A. Alemdar, N. Öztekin, F. Erim, Ö. Ece, and N. Güngör. 2005. Effects Of Polyethyleneimine Adsorption On Rheology Of Bentonite Suspensions. *Bulletin of Materials Science.* 28: 287-291.

[138] S. Tunç and O. Duman. 2008. The Effect Of Different Molecular Weight Of Poly(Ethylene Glycol) On The Electrokinetic And Rheological Properties Of Na-Bentonite Suspensions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 317: 93-99.

[139] I. S. Oweis and R. P. Khera. 1990. *Geotechnology Of Waste Management.* Butterworths.

[140] M. R. Taha, E. Ismail, Z. Chik, Y. de Miguel, A. Porro, and P. Bartos. 2005. Some Nano Aspects And Concepts In

Geotechnology. *2nd Int. Symp. on Nanotechnology in Construction, Bilbao, Spain* 2005. 373-381.

[141] J. Vera-Agullo, V. Chozas-Ligero, D. Portillo-Rico, M. García-Casas, A. Gutiérrez-Martínez, J. Mieres-Royo*, et al.* 2009. Mortar And Concrete Reinforced With Nanomaterials. *Nanotechnology in Construction 3*. ed: Springer 2009. 383-388.

[142] A. Edwards and J. Bremner. 1967. DISPERSION OF SOIL PARTICLES BY SONIC VIBRATION1. *Journal of Soil Science*. 18: 47-63.

[143] A. A. Firoozi, M. R. Taha, A. A. Firoozi, and T. A. Khan. 2015. Effect Of Ultrasonic Treatment On Clay Microfabric Evaluation By Atomic Force Microscopy. *Measurement*. 66: 244-252.

[144] K. Gopalakrishnan, B. Birgisson, P. Taylor, and N. O. Attoh-Okine. 2011. *Nanotechnology In Civil Infrastructure*. Springer 2011.

[145] A. Chaipanich, T. Nochaiya, W. Wongkeo, and P. Torkittikul 2010. Compressive Strength And Microstructure Of Carbon Nanotubes–Fly Ash Cement Composites. *Materials Science and Engineering: A*. 527: 1063-1067.

[146] L. Jiang, L. Gao, and J. Sun. 2003. Production Of Aqueous Colloidal Dispersions Of Carbon Nanotubes. *Journal of Colloid and Interface Science*. 260: 89-94.

[147] T. Yasumitsu, G. Liu, J.-M. Leveque, S. Aonuma, L. Duclaux, T. Kimura*, et al.* 2013. A Rosette Cooling Cell: More Effective Container For Solubilization Of Single-Walled Carbon Nanotubes Under Probe-Type Ultrasonic Irradiation. *Ultrasonics sonochemistry*. 20: 37-39.

[148] F. Inam, T. Vo, J. P. Jones, and X. Lee. 2013. Effect Of Carbon Nanotube Lengths On The Mechanical Properties Of Epoxy Resin: An Experimental Study. *Journal of Composite Materials*. 47: 2321-2330.

[149] S. J. Chen, B. Zou, F. Collins, X. L. Zhao, M. Majumber, and W. H. Duan. 2014. Predicting The Influence Of Ultrasonication Energy On The Reinforcing Efficiency Of Carbon Nanotubes. *Carbon*. 77: 1-10.

[150] E. F. de la Cruz, Y. Zheng, E. Torres, W. Li, W. Song, and K. Burugapalli. 2012. Zeta Potential Of Modified Multi-Walled Carbon Nanotubes In Presence Of Poly (vinyl alcohol) Hydrogel. *International Journal of Electrochemical Science*. 7: 3577-3590.

[151] A. A. S. Correia, P. D. F. Casaleiro, and M. G. B. V. Rasteiro. 2015. Applying Multiwall Carbon Nanotubes for Soil Stabilization. *Procedia Engineering*. 102: 1766-1775.

[152] L. Dumée, K. Sears, J. Schütz, N. Finn, M. Duke, and S. Gray. 2013. Influence of the Sonication Temperature on the Debundling Kinetics of Carbon Nanotubes in Propan-2-ol. *Nanomaterials*. 3: 70-85.

[153] A. Yazdanbakhsh, Z. Grasley, B. Tyson, and R. Abu Al-Rub. 2010. Distribution Of Carbon Nanofibers And Nanotubes In Cementitious Composites. *Transportation Research Record: Journal of the Transportation Research Board*. 89-95.

[154] C. P. Huynh and S. C. Hawkins. 2010. Understanding The Synthesis Of Directly Spinnable Carbon Nanotube Forests. *Carbon*. 48: 1105-1115.

[155] B. White, S. Banerjee, S. O'Brien, N. J. Turro, and I. P. Herman. 2007. Zeta-Potential Measurements Of Surfactant-Wrapped Individual Single-Walled Carbon Nanotubes. *The Journal of Physical Chemistry C*. 111: 13684-13690.

[156] D. S. Wright, B. S. Flavel, and J. S. Quinton. 2006. Streaming Zeta Potential Measurements Of Surface-Bound Organosilane Molecular Species. *2006 International Conference on Nanoscience and Nanotechnology* 2006.

[157] A. Ellis, S. Wallace, and W. Arnold. 2007. Surface Modification And Zeta Potentials Of Carbon Nanotube Polystyrene Nanocomposites. *Materials forum* 2007. 110.

[158] M. J. Rosen and J. T. Kunjappu. 2012. *Surfactants And Interfacial Phenomena*. John Wiley & Sons.

[159] M. Sano, A. Kamino, J. Okamura, and S. Shinkai. 2001. Ring Closure Of Carbon Nanotubes. *Science*. 293: 1299-1301.

[160] R. W. áO'Brien. 1990. Electroacoustic Studies Of Moderately Concentrated Colloidal Suspensions. *Faraday Discussions of the Chemical Society*. 90: 301-312.

[161] D. Hanaor, M. Michelazzi, C. Leonelli, and C. C. Sorrell. 2012. The Effects Of Carboxylic Acids On The Aqueous Dispersion And Electrophoretic Deposition of ZrO 2. *Journal of the European Ceramic Society*. 32: 235-244.

[162] J. Yu, N. Grossiord, C. E. Koning, and J. Loos. 2007. Controlling The Dispersion Of Multi-Wall Carbon Nanotubes In Aqueous Surfactant Solution. *Carbon*. 45: 618-623.

[163] O. Mendoza, G. Sierra, and J. I. Tobón. 2013. Influence Of Super Plasticizer And Ca (OH) 2 On The Stability Of Functionalized Multi-Walled Carbon Nanotubes Dispersions For Cement Composites Applications. *Construction and Building Materials*. 47: 771-778.

[164] S. Musso, J.-M. Tulliani, G. Ferro, and A. Tagliaferro. 2009. Influence Of Carbon Nanotubes Structure On The Mechanical Behavior Of Cement Composites. *Composites Science and Technology*. 69: 1985-1990.

[165] J. Zhao, D. Shi, and J. Lian. 2009. Small Angle Light Scattering Study Of Improved Dispersion Of Carbon Nanofibers In Water By Plasma Treatment. *Carbon*. 47: 2329-2336.