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Cement-Carbon Nanotube Composites and Their Multifunctional Behavior: A Brief Overview

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The author has tried to provide a brief overview of the constituents of cement-carbon nanotube composites, their interactions and some examples of research on functional behavior of the composites. Many interactions are at the nanoscale and the functional behavior is strongly affected by such factors as the type and features of carbon nanotube, the proportion carbon nanotube in cement, the method adopted for dispersion of carbon nanotube in cement-water mixture, admixtures and others. Though MWCNT' (Multiwalled carbon nanotube) is by far the more widely used, little information is available other than the diameter and length of the MWCNT, pointing out towards the need for optimization of the MWCNT features. There is thus a huge potential for optimization of structure-property relationships in the constituents of the cement-carbon nanotube composites and interested researchers are encouraged to study the full publications cited in this paper and the references cited in each publication.

The structure and properties of carbon nanotubes are first reviewed, to indicate why this material is so unique. Next, nanoscale structure development in cement is reviewed, with the hope that further research on nanoscale interactions between carbon nanotube and cement will lead to more improvements in the functional behavior of the composite. Finally, papers dealing with chosen functional properties relevant to cement-carbon nanotube composites composite, are reviewed.

Keywords: *Cement, carbon nanotube, nanostructure, functional behavior, piezoresistivity, vibration damping*

1.0 INTRODUCTION

This paper gives a brief review of some cases of multifunctional behavior of carbon nanotube dispersed in cement matrix. While cement is long-established as a load-bearing structural material (as the principal part of concrete), recent research has indicated that by dispersing carbon nanotube in cement it is possible to develop to realize multifunctional behavior in the cement-carbon nanotube composite, similar to the case of carbon fiber-cement composite as excellently described by Chung. [1]. A detailed description of multifunctional behavior of cement reinforced with various materials is available in a book by Chung [2]. As stated in this book, multifunctions may include, as needed in the particular application, structural vibration control, structural health monitoring, damping, thermoelectricity, piezoresistivity and others, singly or in combination.It is possible to develop nanoscale sensors for better measurement and quantification of these effects as compared to external sensors. An added advantage would be if cement-based structure attains superior mechanical behavior, which is possible when carbon nanotube is added to cement.

The principal constituents considered in this paper are cement and carbon nanotube. While it is well known that nanoscience considerations explain the properties of carbon nanotubes, recent research has established that the bondingand structure development of cement are also governed by nanoscale behavior [3,4]. While multifunctional behavior of cement-carbon

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nanotube composite may be primarily attributed to the properties of the carbon nanotube, it is quite possible that good nanoscale continuity between the cement and carbon nanotube (assuming uniform dispersion of carbon nanotube) aids more effectivemultifunctional behavior of the composite.

The contents of this paper are presented in three sections. In the first section the structure and properties of carbon nanotubes are reviewed, throwing light on why this material is so unique. In the second section, nanoscale structure development in cement is reviewed, with the hope that further research on nanoscale interactions between carbon nanotube and cement will lead to more improvements in the functional behavior of the composite. In the third section, papers dealing withchosen functional properties relevant to cement-carbon nanotube composites composite, are reviewed.

2.0 STRUCTURE AND PROPERTIES OF CARBON NANOTUBES

Research on carbon nanotubes has grown exponentially after the publication of the classic papers by Iijima [5], on multiwalled carbon nanotubes and single-walled carbon nanotubes Iijima and Ichihasi [6] and Bethune, et al [7]. The impact of these activities may be likened to the socio-economic impact of the internet [8] .

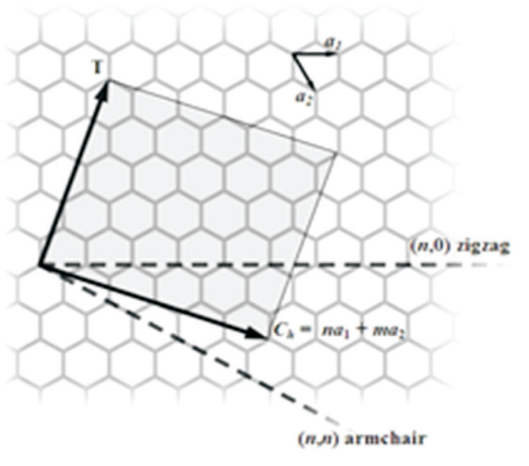

FIG. 1 GRAPHENE SHEET FROM WHICH A SINGLE-WALLED CARBON NANOTUBE IS MADE BY ROLLING AROUND THE CHIRAL VECTOR (CH) [9]

Carbon nanotube is an allotrope of carbon. In Figure. 1 is shown a schematic diagram of a graphene sheet from which a single-walled carbon nanotube is made by rolling around the chiral vector (C_h) [9]. Unlike its allotrope, diamond, each carbon atom in graphene has three nearest neighbors and it has a two-dmensional structure and strong covalent bonds between carbon atoms

Graphene has a single layer of hexagon, with a carbon atom at each corner of the hexagon. a1 is the unit vector in the horizontal direction and a_2 is the unit vector inclined at 60° to a_1. The length of each is √3 times the side of the hexagon. Ch is the chiral vector defined by na1 +ma2. The angle between a1 and Ch is defined as the chiral angle (θ). The length of the vector Ch is the circumference of the single-walled nanotube (hereafter denoted bt SWCNT) the SWCNT that relates to the length of the SWCNT.

from which the diamter of the SWCNT may be calculated. T is the axial vector of Chiral axis with m = 0 leads to as zigzag configuration, while one with n = m leads to armchair configuration. When m lies between 0 and n, the the resulting configuration is defined by the chiral angle θ., which is the angle between na1 and C_h.The diameter d of a SWNT may be calculated from:

$$d = a\sqrt{(n^2 + nm + m^2)}/\pi \qquad ....(1)$$

is the lattice constant and a value of $a=\sqrt{3}x0.142=0.246$ nm, assuming that the nearest carbon-carbon spacing is 0.142 nm. For zigzag configuration (m=0) $d=0.246n/\pi$ nm. For armchair configuration (n=m), $d=0.246(\sqrt{3}n)/\pi$ nm.

Multiwalled carbon nanotube (MWCNT) consists of several concentric graphene layers, the latter held together by weak van der Waals forces, similar to flake graphite in cast iron, but having only a few layers. While SWCNT can have a diameter of 0.4-10 nm, the diameter of MWCNT can be in the range of 10-80 nm, depending on the number of layers. The interlayer spacing of MWCNT is typically 0.34 nm [10].

Typical values of tensile strength and Young's modulus of MWCNT are 150 MPa and 1200 GPa respectively. While the typical tensile strength of SWCNT is about half of that of MWCNT, its Young's modulus is close to about 90% of that of MWCNT[11]. These values are fairly consistent regardless of the chiral vector orientation. It is interesting to note that in the spun fiber form (~106 SWCNT) strength values of 14 GPa for highest quality, 8 GPa for high quality and 2 GPa for low quality have been reported for 1 mm diameter samples. Similar Kevlar 49 sample tested by these authors showed a value of 3 GPa. [12].

The electrical behavior of carbon nanotubes on the other hand, is strongly affected by the chirality and the number of graphene layers. In pure SWCNT the band gap tends to zero when n=m,leading to metallic behavior. When (n-m) = (3 x integer), there will be a small band gap promoting weak semi-conductor behavior. When neither of these conditions are met the SWCNT exhibits moderate semi-conducting behavior [13].Deviations from these rules are observed in small diameter SWCNT due to curvature effects. The electrical behavior of MWCNT is difficult to predict in the strightforward manner as in SWCNT, as there may be different orientations in the multiple layers. It is generally believed that MWCNT is metallic unless special treatments are provided to promote semi-conducting behavior.In theory, metallic nanotubes can carry an electric current density of 4×10^9 A/cm^2, which is more than 1,000 times greater than those of metals such as copper [14].The conduction however, occurs mostly in the axial direction of the carbon nanotube and as a result, carbon nanotubes are often called one-dimensional conductors.

The thermal behavior of all nanotubes in terms of thermal conduction is very good along the tube, exhibiting a property known as ballistic conduction. Also they are good insulators lateral to the tube axis. Measurements show that a SWCNT has a room-temperature thermal conductivity along its axis of about 3500 $W \bullet m^{-1} \bullet K^{-1}$ [[15]; compare this to copper, a metal well known for its goodthermal conductivity, which transmits 385 $W \bullet m^{-1} \bullet K^{-1}$. A SWNT has a room-temperature thermal conductivity across its axis (in the radial direction) of about 1.52 $W \bullet m^{-1} \bullet K^{-1}$[16] which is about as thermally conductive as soil. The temperature stability of carbon nanotubes is estimated to be up to 2800°C in vacuum and about 750°C in air [17].

3.0 NANO SCALE STRUCTURE DEVELOPMENT IN CEMENT AND DISPERSION OF CARBON NANOTUBE PRIOR TO HYDRATION

Cement-based materials such as concrete have long been used for the civil infrastructure, such as highways, bridges and buildings. However, the deterioration of the civil infrastructure all over the U.S. has led to the realization that cement-based materials must be improved in terms of their properties and durability [18]. Among the different factors to be considered for improvement, better understanding of nanoscale structure development of hydration products of cement has become important [19]. This is particularly relevant to be considered in the present paper as it deals with cement-carbon nanotube composite.

Cement is a silicate material, which microscopically involves interconnected tetrahedra with a silicon atom at the body center of each tetrahedron and an oxygen atom at each of the four corners of the tetrahedron. In Portland cement (OPC) the principal constituents are $3CaO\text{-}SiO_2$ and $2CaO\text{-}SiO_2$. When mixed with water cement sets and hardens. An example of this hydration reaction is $2CaO\text{-}SiO_2 + xH_2O = 2CaO\text{-}SiO_2 - xH_2O$, where x depends on the amount of water available [20]. In cement chemistry, CaO, SiO_2 and H_2O are represented by C, S and H respectively. Also, 3CaO-SiO2 is shown as C_3S and 2CaO-SiO2 as C_2S. The hydrated product is represented as C-S-H because of indefinite stoichiometry. This is the principal binding agent in the cement paste and is responsible for strength and shrinkage. Resolving the structure at the nanoscale is an essential part of understanding and predicting its behavior [21].

An extensive review of cement nanoscience and nanotechnology has been published by Raki, et al [21]. It is pointed out in this paper that analysis at the nanoscale may provide further insight into the nature of the hydrated cement phases and their interactions with dispersed materials such as carbon nanotube. Makar and Chan [22] have shown that SWCNT acts as nucleating agent for C-S-H, which preferentially form on the surface of nanotube bundles instead of adjacent unhydrated cement grains. The C-S-H thus nucleated tightly bonds with SWCNT providing reinforcing effect. It is likely that similar effect is observed with MWCNT and C-S-H. This perhaps explains the lack of electrical connectivity in MWCNT dispersed in cement, as observed by Wansom, et al [23].

Shah and his associates [4] at Northwestern University have developed techniques for nanoscale characterization of cementitious materialsusing AFM (Atomic Force Microscopy) they have observed that the C-S-H showed spherical particles of sizes in the range of 40 nm to 200-700 nm. By careful polishing, many areas were found to have predominance of 40 nm spherical particles, establishing the typical nanosize of the samples studied. Sakulich and Li [24] and Lindgreen, et al [25] have also shown that C-S-H is not a homogeneous material and occurs in the form of nanoscale grains mixed nanoscale porosity.

It is thus clear that the interaction between cement and carbon nanotube is an important factor in affecting the properties of the composite. SWCNT and MWCNT are used not in thick fiber form as in fibrous composites, but as short, thin bundles. Thus for proper interaction with cement, the dispersion of CNT in the composite needs careful consideration. In what follows literature on this aspect will be briefly reviewed..

Makar [26] has provided a concise review of methods of carbon nanotube dispersion in cement. He points out that as cement systems are water based and, as unfunctionalized carbon nanotube is hydrophobic, the dispersion of the latter is difficult. If the surface of the carbon nanotube is favorably altered during any purification process, such nanotubes may be readily dispersed in water [27-31]. However, in all other cases, different approaches have been used. In one approach, [31-33] MWCNT was functionalized by sonication in acid for 2-3 hours in order to attach carbolic acid groups to the surface of the nanotubes. The functionalization leads dual benefits of aiding dispersion in water and promotion of chemical bonding of MWCNT. The functionalized MWCNT was either mixed in water containing a polycarboxylate water reducing admixture or, sonicated in water with the same class of admixtures In another approach [34] sulfonated naphthalene formaldehyde was successfully used as dispersing agent for unmodified SWCNT, that produced stable dispersion for over 2 years. Also, polycarboxylate admixture worked successfully with unmodified MWCNT [23] , as well as sulfonated naphthalene formaldehyde [35] and gum arabic [30,31].The work of Makar and his associates [35,36], has indicated that the quality of dispersion is dependent on the methods used to purify the nanotubes or on chirality of the nanotubes from different sources. The SEM pictures provided by Makar [37] clearly illustrate this point. There is relatively little work done to evaluate the quality of dispersion. The tools used so far are the scanning electron microscope (SEM) and AC-impedance spectroscopy [23]. In dispersion studies, most researchers have used nanotube concentrations from 0.05 to 2 percent by mass of cement;the water to cement ratios range from 0.34 to 0.8.

Sobolkina, et al [38] (carried out a detailed investigation on the dispersion of carbon nanotubes and its influence on the mechanical properties of cement-CNT composites. The stimulus for the investigation was provided by the fact that the mechanical performance of these composites varies over a wide range and the likely explanation is in the choice of the type and quantity of CNT's and in the methods of dispersing the nanotubes. First, they noted that CNT's tend towards agglomeration, which impedestheir uniform distribution throughout a matrix [39-41]. Under this condition, it is difficult to form a fine, continuous network in the matrix that can support load transfer or mitigate the development of cracks. It is also possible that agglomerates could also cause low strength in the transverse direction if CNT. Kostagoudos, et al [39] achieved best results for strength when dispersion of CNT in water was done by sonication in a mixture of surfactant and CNT in the ratio of 4:1. According to these authors, the unresolved questions,How to test the compatibility of the particular CNT's and surfactants, how the duration and intensity of sonication affect the dispersion of CNT's, and, how to avoid rupture during sonication. Also, as per these authors, little is known about the relation between variables in dispersion techniques and the quality of C-S-H. These authors used two types of CNT's in their study. The first type was a mixture of SWCNT and DWCNT mixed together and then added to MWCNT (Mixed CNT) The proportion of SWCNT+DWCNT to MWCNT was about 1:1. This group had a diameter of about 1-15 nm and length of about 20 µm. The second type was nitrogen-doped MWCNT's. (N-CNT). The length in this batch was about 100-300 µm and diameter was about 15-40 nm. Two types of surfactants were used: anionic dodecylsulfate (SDS) and non-ionic polyoxyethlene laurylether (Brij 35). Compressions test and tensile test were made with the aid of piezoactuators. Prior to this, SEM and NANOSEM instruments were used to study the hydrated cement at various stages. The authors present informative schematic diagrams based on these studies. The main conclusions of these authors is that the best dispersions could be produced with a CNT-surfactant ratio of 1:1 to 1:1.5 and a sonication time of 120 minutes. Deagglomeration was found to be intensive with nitrogen-doped MWCNT using Brij 35.The drawback of this approach was the tendency of the MWCNT's to break when the sonication time was high. In contrast no such failure was observed in the case of mixed CNT (Type 1). Also in this case the dispersibility using either surfactant was about the same. Collins, et al [42] have examined the effect of admixturesincluding an air entrainer, styrene butadiene rubber, polycarboxylates, calcium naphthalene sulfonate and lignosulfonate formulations. CNT dispersion within hardened pastes was qualitatively assessed by SEM analysis. Following ultrasonication, polycarboxylate and lignosulfonate admixtures provided good dispersion of CNT, with little sedimentation. On the other hand, styrene butadiene rubber and calcium naphthalene sulfonate admixtures facilitated rapid agglomeration of CNT's making them unsuitable for further use.While most investigators have used ultrasonication to aid in dispersion of CNT, Metaxa, et al [43] used ultracentrifugation following dispersion of MWCNT and obtained highly concentrated suspensions after decanting and ultrasonication of the remaining suspension. It was observed by the authors that ultracentrifuging method preserves the solubility of the concentrated MWCNT suspensions without affecting the reinforcing properties of the admixture. As discussed in the paper, the concentrated admixture can be transported in large quantities and as such, ultracentrifugation concentration method described in the paper can be utilized for large-scale production of MWCNT admixtures in cementitious materials. A nonlinear density-gradient ultracentrifugation method for advanced sorting of SWNT developed by Ghosh et al, [44] may have the potential for consideration in cement-CNT composites

4.0 SOME EXAMPLES OF FUNCTIONAL BEHAVIOR APPLICATIONS IN CEMENT-CARBON NANOTUBE COMPOSITES

As implied by Chung [45], if the reinforcing material possesses functional properties in addition to the ability to improve structural mechanical behavior, it would be highly advantageous. It is established that cement-carbon nanotube composites have excellent structural mechanical behavior and this will not be elaborated further in this paper. The non-structural properties include [45] vibration damping ability, strain sensing ability, electromagnetic/magnetic shielding ability, electrical conductivity, efficient thermo-electric behavior. If the reinforcing material possesses one or more of these characteristics, the need for external aids to obtain results that can be directly obtained using the reinforcement, would be eliminated. In what follows, some studies that involve these "functional" properties will be briefly reviewed.

4.1 Piezoresistivity

Piezoresistivity is a phenomenon in which the electrical resistivity of a material changes with strain, which is related to stress. Thus piezoresistivity allows a material to serve as strain/stress sensor [46]. Yu and Kwon [47] were among the early investigators to study piezoresistive behavior of cement-MWCNT composites.They prepared 2 batches of cement-MWCNT, with the first batch using MWCNT functionalized with a mixture of H_2SO_4 and HNO_3. In the second batch, instead of functionalizing, a surfactant (SDS) was used. In both cases 0.1% MWCNT by weight was employed. The functionalized batch showed stronger piezoelectric response and higher signal-to-noise ratio than the surfactant addition batch, probably due to blocking of electrical contact among the nanotubes by the surfactant. They have also pointed out that CNT may be better as a stress sensor under heavy loads as compared to carbon nanofiber, as the latter tend to break at strains exceeding about 20%. Andrawes and Chan [48] studied the piezoresistivity of cement-MWCNT composites with 0.2% and 0.3% of MWCNT by weight. Higher degree of reversibility and consistency was found in 0.3% MWCNT batch. In this batch, the changes in electrical resistance were about 6.78% and 7.31% in tension, with amplitudes of 170 kPa and 255 kPa respectively. In compression, the change in electrical resistance was 3.38% with amplitudes of 1379 kPa. These illustrative studies and others indicate that MWCNT may be used as a reliable strain sensor which can be used for structural health monitoring in structures made of cement concrete.

4.2 Piezoelectricity

Piezoelectricity is the electrical charge that accumulates in certain solid materials in response to applied mechanical stress. Gong, et al [49] have studied the piezoelectric properties of cement-PZT-MWCNT composite. Their results indicate that with increasing MWCNT content the electrical conductivity increased thereby causing more effective poling. Also, piezoelectric strain factors (d_{33}) andpiezoelectric voltage factors (g_{33}) increased with increased MWCNT content up to 0.3%, suggesting that this proportion of MWCNT could be used in sensing applications.

4.3 Optical Properties

Weisman [50] has discussed the characterization of SWNT using optical spectroscopy. Each structural species of semiconducting SWNT displays not only a set of distinct and intense absorption transitions ranging from near-infrared to ultraviolet wavelengths. The use of SWNT in cement-CNT composites is not yet a viable proposition, but should this change in future and also if semiconducting devices are developed for structural health monitoring, optical spectroscopy may prove to be a valuable tool.

4.4 Thermal properties

Zhang and Li [51] have made an experimental investigation on ice/snow melting of CNFP & MWCNT- cement composites. The role of CNFP is to act as the heating source, while cement-MWCNT acts as the thermal conductor overlay, being placed above the CFRP layer. Solar heating was the heat source. As per the authors this device has very good potential for deicing and snow melting applications.

4.5 Electrical properties

Wansom, et al [23] combined AC-impedance spectroscopy (AC-IS) with time domain reflectometry (TDR)to investigate the impedance response of cement-MWCNT composite. These authors used 0.75 vol.% and 1 vol. % MWCNT in OPC.A polycarboxylate superplasticizer (0.5% by weight of cement) was added to the water prior to hydration. In Nyquist plots (-imaginary impedance vs. +real impedance)three impedance arcs/features were observed. As per the authors, from careful analysis ofAC-IS results, it is possible to differentiate between percolation contributions from discontinuous nanotube contributions, with the potential for characterizing dispersion issues such as clumping/segregation) in cement-CNT composites.

Saafi [52] embedded wireless cement-SWNT sensors (the electrical conductivity of SWNT was in the range of 102 to 10-4 S cm-1) into concrete beams and subjected the beams to monotonic and cyclic loading to evaluate the effect of structural damage on their response. The experimental results indicate that the wireless response of the embedded cement-SWNT sensors changes due to the formation of cracks during loading. In addition the nanotube sensors were able to detect the initiation of damage at an early stage of loading. The development of such sensors will have a huge impact on large-scale structural health monitoring of concrete structures.

4.6 Vibration Damping

Duan and Luo [53] studied the vibration damping behavior and strength reinforcement MWCNT cement-composite, with cetyltrimethyl ammonium bromide (C16TAB) being used to disperse the MWCNT in de-ionized water. The amount of MWCNT used was 0 wt.% (reference sample), 0.1 wt.%, 0.2 wt.%, 0.5 wt.%, 1 wt.% and 5 wt.%. The external diameter of MWCNT was 20-40 nm, length was 5-15 µm, and the purity being over 90% .Vibration damping test was conducted on strip-like cement -MWCNT paste under flexible conditions, with a span of 270 mm, on specimens of 280 x 25 x 25 mm dimensions. The exciting signal was a light-weight and fast hammer impulse, with the hammer head being perpendicular to the specimen span and the floor. A horizontal bar and two rubber bands were used to construct the elastic system. Three specimens of each MWCNT composition were tested. The damping ratio, ζ, was determined using

$$\zeta = [1/2\pi k] \ln [A_n / A_{n+k}] \quad ....(2)$$

where, Anis the displacement amplitude of nth peak, which can be calculated from acceleration and frequency, and A_{n+k} is the amplitude of the peak k cycles after the nth peak. These authors have adopted n=1 and k=10 to illustrate typical acceleration attenuation time histories and local magnifications of two compositions, one with 0 wt.% MWCNT (reference sample) and the other with 1 wt.% MWCNT. The results indicate that the damping ratio of the cement-MWCNT composite can be enhanced by 20.55% with respect to the reference sample (0 wt.% MWCNT) by adding 1 wt.% MWCNT. However, while the flexural strength increases with increase in MWCNT, compressive strength is reduced.

5.0 CONCLUDING REMARKS

The author has tried to provide a brief overview of the constituents of cement-carbon nanotube composites, their interactions and some examples of research on functional behavior of the composites. Many interactions are at the nanoscale and the functional behavior is strongly affected by such factors as the type and features of carbon nanotube, the proportion carbon nanotube in cement, the method adopted for dispersion of carbon nanotube in cement-water mixture, admixtures and others. Though MWCNT's are by far the more widely used, little information is available other than the diameter and length of the MWCNT, pointing out towards the need for optimization of the MWCNT features. A recent review paper [54] also points out towards the lack of information on complete characterization of CNT-cement based composites. There is thus a huge potential for optimization of structure-property relationships in the constituents of the cement-carbon nanotube composites and interested researchers are encouraged to study the full publications cited in this paper and the references cited in each publication.

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