Characterization of the uncertainties in the constitutive behavior of carbon nanotube/cement composites

Lai Yin Chan and Bassem Andrawes

Department of Civil and Environmental Engineering, Newmark Civil and Environmental Engineering Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

E-mail: andrawes@illinois.edu

Received 4 June 2009
Accepted for publication 7 September 2009
Published 12 October 2009
Online at stacks.iop.org/STAM/10/045007

Abstract
This paper addresses the uncertainties associated with using carbon nanotubes (CNTs) as reinforcement for cement. These uncertainties emerge mainly from the CNTs’ wide range of mechanical properties and their interfacial behavior with cement. This study sheds light on the basis of choosing the optimal combinations of CNTs mechanical and interfacial parameters to improve the structural strength and ductility of CNT-reinforced cementitious composites. The finite element method (FEM) is employed to study the individual and interactive effects of five parameters, including interfacial shear (bond) strength, allowable slip, CNT Young’s modulus, residual bond stress and aspect ratio. Numerical results show that the parameters, at certain ranges of values, interact substantially and greatly alter the mechanical properties of the composite. It is also found that the governing parameter is the CNT Young’s modulus, which determines whether the composite is ductility critical or strength critical. Furthermore, the level of residual bond stress substantially influences the effect of other parameters, especially in the case of composite ductility.

Keywords: carbon nanotubes, cementitious composite, bond strength, ductility

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the field of fiber reinforced concrete (FRC), various types of fibers, such as steel, glass, carbon, and some synthetic materials [1] have been used to control cracking in brittle cementitious materials. Recently, other potential type of carbon fibers known as carbon nanotubes (CNTs) has been investigated. CNTs are classified as either single-walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWNTs). An SWNT is like a planar sheet of carbon atoms, known as graphene, seamlessly wrapped into a tube with thickness equal to a single atom and diameter ranging from 0.4 to 5.6 nm [2]. MWNTs appear as multiple concentric SWNTs, with diameter of 0.3 to 100 nm [3]. The length of CNTs can be up to centimeters, which gives an aspect ratio exceeding 10^7, while the density of CNTs is generally reported as less than 1500 kg m^-3 [4, 5]. The concurrent benefits of high aspect ratio and low mass density led to the idea of using CNTs as reinforcement in concrete, which could be more effective than conventional fibers due to the enormously large interfacial contact area provided without much weight penalty.

Being a novel type of fibers used in FRC, only few studies on CNT/concrete composite have been found in the literature, and significant improvements have been reported regarding the reinforcing efficacy of CNTs. Those studies primarily focused on evaluating the enhancements to the mechanical properties of cement/concrete provided by CNTs. Campillo [6] tested CNT/concrete composite under compression and found that SWNTs and MWNTs increased the strength of plain concrete paste by 6 and 30%, respectively. Besides, Li et al [7] demonstrated that MWNTs surface-treated by H_2SO_4 and HNO_3 substantially improved the compressive strength and the flexural strength of Portland Cement concrete by 19 and 25%, respectively. Lastly, experimental work conducted by Chan and Andrawes [8] proved that, by adding CNTs of 0.25% by the total weight

1468-6996/09/045007+13S33.00 © 2009 National Institute for Materials Science Printed in the UK
of cement, the load-carrying capacity and toughness of plain cement beams were increased by an average of 47 and 25%, respectively. All these results consistently suggest that CNTs can serve as an effective reinforcement in FRC and further investigations to understand the reinforcing mechanism are valuable.

To understand the enhancements in mechanical properties introduced by CNTs, it is constructive to study how CNTs transfer stresses across a crack. Owing to their sizes and aspect ratio, it is demanding to thoroughly examine the pull-out process of CNTs from a cementitious matrix. Also, it would be unpractical and costly to study the effects of the CNT material properties and the interfacial characteristics in an experimental setting. As a result, the finite element method (FEM) was employed in this study to accomplish this task by modeling the three basic components in the composite, i.e. the embedded CNT, the surrounding cement matrix, and the interface between the two materials. The FEM model has been developed and calibrated in an earlier study by the authors [8]. In this work, more in-depth studies were conducted to investigate the individual and interaction effects of key parameters governing the composite behavior. This study would be of an interest for future experimental work to verify the effects of CNT mechanical properties and interfacial behavior on the CNTs’ reinforcing effectiveness.

More importantly, the manufacturing process of CNTs can be more precisely controlled in recent years and the cost of CNTs depends on their mechanical properties, such as aspect ratio, and purity; therefore, it is helpful to acknowledge the interaction relationship of the associated parameters and provide preliminary guidelines for selecting the optimal type of CNTs as cement reinforcement.

2. Overview of modeling techniques

Many researchers utilize computer simulations to study the behavior of this nano-material, and works have been conducted using either molecular dynamics (MD) or continuum mechanics. Due to the high computational demand of a MD simulation, it is currently used to model a single CNT in a matrix only. To investigate the global response of CNT-based composites, such as the displacement and stress fields at the boundaries, continuum mechanics models are more widely used, such as representative volume element (RVE) [9] and boundary element method (BEM) [10].

The RVE technique was employed in this paper to investigate the interaction between CNTs and cement at the nano level and to develop a constitutive relation for CNT/cement composite from a macroscopic view. Liu and Chen [11] proved the feasibility and accuracy of evaluating material constants by applying the concept of RVE and simulating a single CNT and its surrounding matrix. Moreover, RVE modeling was employed by Chan and Andrawes [8] to evaluate the mechanical responses of CNT/cement composite, which had been validated by empirical results.

RVE modeling is based on continuum mechanics for predicting the effective properties of random heterogeneous materials by considering a given volume of microstructure; and, in this work, the effective post-crack tensile behavior of CNT/cement composite was extracted from a RVE with an embedded CNT being steadily pulled out from the cement matrix. Figure 1(a) shows how CNTs bridged the crack on a fractured surface of CNT/cement paste composite after being analyzed in a Vickers hardness test [12]. The spacing between the white bars in the images is one-tenth that of the full scale (in this case the full scale is 2 µm in the upper image, while 500 nm in the lower one). Figure 1(b) depicts one of the numerous CNTs crossing the crack and its surrounding matrix, and figure 1(c) shows how half of the CNT with the matrix (as enclosed by the dotted line in figure 1(b)) can be modeled by symmetry. The post-crack tensile resistance is provided by the interfacial shear when CNTs, instead of the cement matrix, is sustaining the tensile stress across the crack, which induces a pull-out force on the CNTs. Due to its exceptionally high tensile strength, it is more likely that the composite will fail by fiber pull-out than by fracture of CNTs. As a result, the post-crack tensile behavior of the composite was evaluated by modeling a RVE with a CNT embedded in cement matrix (see figure 2) and the interfacial properties prescribed based on the literature. The embedded CNT was 0.34 nm thick and had a diameter of 10 nm. The thickness was based on the lattice spacing of graphitic layers [13], and the diameter was fixed so that the aspect ratio could be adjusted by varying the length. The assumed diameter of 10 nm was within the limit reported in the literature [14]. The dimensions x and y in figure 2 are variables used to define the weight percentage of CNTs in the composite and the aspect ratio of the embedded CNT, respectively. Besides, the cement matrix was extended by 10% of y (i.e. represented by z in figure 2) to minimize the influence from the fixed supports at the left end of the RVE. In addition, the matrix was fixed in the longitudinal direction at all sides, except face A (see figure 2). This model is referred to in this study as RVE pull-out model.

The finite element program, ANSYS [15] was used for numerical modeling and simulation. SOLID65 in ANSYS, a three-dimensional (3D), 8-node element, was utilized to model the cement material. This element is capable of predicting smeared cracks and crushing in cement. Furthermore, SOLID65 allows rebars, fibers or both to be characterized as smeared reinforcement by defining the volume ratio, orientation and corresponding material properties. To model the embedded CNT, SOLID45, another 3D 8-node element, was employed to mesh the hollow cylinder. It is worth noting that, instead of solid tubes, CNTs are actually like cylindrical graphene sheets being made of carbon atoms bonded in hexagon configurations. The key of FEM employed in this work was based on continuum mechanics to simulate the response of an isolated CNT which was treated as a thin shell. This technique was supported by the results published by Liu and Chen [11], which proved that the modeling of CNTs using 3D elements in FEM was a simple yet valid approach to find the mechanical properties of the composite. Lastly, the interface was modeled using contact element (CONTA174)/target element (TARGE170) pairs. CONTA174 and TARGE170 are
Figure 1. Schematic illustrating the concept of using RVE model to describe the pull-out phenomenon in CNT/cement composite: (a) fracture surface [12], (b) CNT and surrounding matrix and (c) RVE model.

Figure 2. Pull-out RVE model of CNT/cement composite: (a) side view and (b) free end.
2D elements (face-to-face contact pair), which work together to allow the shear stress-bond slip relationship between two faces to be characterized adequately.

At the interface of the RVE model, the cement and the CNT were overlaid by contact elements and target elements, respectively. ANSYS automatically meshes CONTA174 and TARGE170 so that their nodes would merge with those of SOLID65 and SOLID45, respectively. It is worth noting that the four types of elements mentioned above had nodes at exactly the same locations on the interface; however, the nodes on the matrix inner face (i.e. those corresponding to SOLID65 and CONTA174) were independent from those on the CNT outer surface (i.e. those corresponding to SOLID45 and TARGE170). Figure 3 shows the four types of elements employed in a quarter of the RVE model, in which symmetry about the horizontal and vertical axes was employed. Figures 3(a) and (c) illustrate the embedded CNT and cement matrix, respectively, and both are composed of 3D elements. Figure 3(b) depicts the target and contact elements at the interface, which are 2D elements laying over the CNT surface and cement inner face, respectively. For a model with CNT concentration of 0.5% by the total weight of cement paste and CNT aspect ratio of 125, the matrix dimension $x$ (see figure 2(b)) was 92 nm, while the CNT radius was 5 nm. The mesh was created using 3638 nodes, 2115 SOLID65 elements and 300 elements of each of SOLID45, CONTA174 and TARGE170. The mesh size was refined until the force-displacement results reached convergence, which was mainly determined by the size of the contact element/target element pairs.

Distinctive material properties were assigned to the four types of elements, i.e. SOLID65 SOLID45 and CONTA174/TARGE170 pairs. First, the 5-parameter William-Warnke model [16] was prescribed as the material properties of SOLID65 to describe the failure criterion of cement—crushing in compression and cracking in tension. ANSYS continually revises the material properties at integration points of the SOLID65 element, where the tensile strength is exceeded, using a smeared band of cracks. The parameters used to define the failure envelope are the compressive strength of cement, the modulus of rupture and the shear transfer coefficients for open and closed cracks. Since the crushing of cement under pure compression is not likely to occur, the crushing capability was turned off for better convergence in analysis. Also, with regard to studying the interaction between CNTs and cement paste at the nanoscale, the mechanical behavior of the cement paste were extracted from the behavior of calcium silicate hydrate (commonly known as C-S-H)—the most important product from the hydration of belite and alite in cement paste. As discussed by Bernard et al [17] and illustrated in figure 4, concrete is a composite material with aggregates embedded in a homogeneous mortar matrix, while mortar has sand particles embedded in a homogenous cement paste matrix.

![Figure 3. Element types used in RVE model: (a) SOLID45, (b) CONTA174/TARGE170 pairs and (c) SOLID65.](image-url)
Cement paste is composed of homogeneous C-S-H with unhydrated or partially hydrated clinker inclusions. CNTs primarily interact with C-S-H which has characteristic length scale of $10^{-8}$ to $10^{-6}$ m—the smallest material length scale that is comparable to the size of CNTs and is accessible by nanoindentation (a well-established technique to extract nanoscale local mechanical properties) \([17]\). The Young’s modulus of the surrounding matrix used in this study, 31 MPa, was based on the results from nanoindentation presented by Mondal \textit{et al} \([18]\). Zhu \textit{et al} \([19]\) also conducted nanoindentation tests to investigate Young’s modulus of cement paste, and the results were consistent with those of Mondal \textit{et al} \([18]\). This offered a relatively accurate method to acquire the post-crack tensile behavior at the nanoscale. On the other hand, a linearly elastic material was assigned for SOLID45 elements to simulate the behavior of CNTs assuming that the CNTs will not fracture before pull-out occurs. This assumption was later verified by acquiring the CNT stresses from ANSYS. Lastly, as a critical component in the model, the interfacial material properties was defined as a step-wise function through CONTA174/TARGE170 pairs, as shown in figure 5, to conservatively simulate the bond slip behavior proposed by some researchers for steel fiber reinforced cement (SFRC) and CNT reinforced polymer \([20, 21]\) (see figure 6).

3. Interfacial characteristics

Since FRC mainly relies on the friction between the cement matrix and CNTs to sustain the stresses through the pull-out process, it is crucial to accurately define the bond stress–slip relationship. In the literature, different methods were used to describe the interfacial friction between fiber reinforcement (either CNTs or other types of fibers) and its associated host matrix, and two models were generally proposed: the stick–slip mechanism \([22, 23]\) and the bond degradation scheme \([20, 21]\).

In this study, the bond degradation model was chosen to define the interfacial behavior since it is more representative of the bond failure type which is most likely expected in CNT/cement composites, especially when taking into account the fact that CNTs have very smooth surfaces. The scheme (as formerly illustrated in figure 5) presents a bond stress decay structure after debonding. Both Naaman \textit{et al} \([20]\), who used pull-out experiments to develop the bond stress-slip relation for SFRC, and Wei \([21]\), who performed MD simulations to study a composite system of polyethylene with one embedded CNT under direct tension, reported that the bond stress tends to decay after the shear strength is reached. They attributed the degradation of bond stress to the decrease in the interfacial adhesion, which was contributed by van der Waals’ force. Wei’s studies also showed that interfacial shear stress drops in a staircase manner with respect to the tensile strain due to the simultaneous bond-breaking at multiple sites. Although, to the best of the authors’ knowledge, no studies were conducted on the interfacial behavior between CNTs and cement, the studies by Naaman \textit{et al} and Wei justified the applicability of the bond degradation scheme in cement reinforced by smooth fibers and CNT-reinforced polymers, respectively.

In the RVE model, the interaction between the CNT and the cement matrix was defined by the properties assigned to the contact element/target element pairs based on the relationship shown in figure 5. The initial stiffness of the interfacial material was determined by ANSYS depending on the relative stiffness of the CNT and cement matrix, and the tangential stiffness was automatically updated after each
Table 1. Master set and ranges of values used in the parametric study for MWNTs.

| Parameters          | Prime value | Range          |
|---------------------|-------------|----------------|
| Shear strength      | 10 MPa      | 5–20 MPa [8, 20]|
| Allowable slip      | 0.25 nm     | 0.25–1.00 nm   |
| Young’s modulus of the CNT | 1 TPa | 500 GPa–2 TPa [6, 7, 24–28] |
| Residual stress     | 0%          | 0–10%          |
| CNT aspect ratio    | 250         | 125–500 [12]  |

iteration with regard to the amount of slip. At the onset of debonding, the rate of bond degradation was defined by a step function, which imitated an exponential decay. It is worth noting that the step function was employed due to the limitation of contact element/target element pairs in ANSYS to simulate the continuously descending branch in figure 6. As a result, once the shear strength was reached, the interfacial bond stress would be constantly monitored and reduced relative to the amount of slip. The shear stress at the peak step was governed by the shear stress specified for the contact element/target element pairs, while the variation of shear stress with the amount of slip was achieved by redefining the shear stress according to the value of slip. The last step signified the amount of slip at which only the residual stress remained at the interface of the CNT and its surrounding matrix. The allowable slip between the contact element and the target element defined the relative displacement from which the CNT started to slide with respect to the matrix. The dotted line in figure 5 demonstrates the decaying trend approximated by the step function.

4. Parametric study

The resultant constitutive relation of CNT/cement composite from the RVE pull-out model highly depended on the interfacial behavior and material properties of CNTs, and investigating the influence of these factors is the primary goal of this work. It can be observed from figure 5 that, in the bond degradation scheme, the shear strength, allowable slip and residual stress determine the bond stress–slip relationship. Moreover, the rate of pull-out may rely on the aspect ratio and Young’s modulus of CNTs. The individual and interaction effects of these five variables were investigated in a parametric study. A challenging issue is that there is a wide range of values for every parameter due to two major reasons. Firstly, the fabrication process of CNTs influences their mechanical properties and surface conditions. Secondly, owing to the limited amount of experimental studies conducted, the interfacial behavior between CNTs and cement is of very limited knowledge. Therefore, the individual effect of each parameter and its interaction with the others were investigated. Table 1 shows the master set and the ranges of values used in this parametric study for MWNTs.

4.1. Characterization of parameters

The master set and the ranges of values were chosen to reflect the practical properties of the five parameters, and the particulars being taken into consideration are as follows.

The first parameter was the interfacial shear strength, which governs the shear transfer capacity; however, very few studies were found in the literature on the shear strength of CNT/cement composite. A wide range of shear strength values were reported for CNT/polymer composites [29–31]. So, the range of shear strength chosen for the parametric study was based on the experimental work on SFRC performed by Naaman et al [20] and the numerical studies on CNT/cement composite conducted by Chan and Andrawes [8]. Naaman et al [20] evaluated the interfacial shear strength between SFRC and cement-based matrices from experimental pull-out curves, and values measured were in the range of 1.4 to 9.6 MPa. This was a relatively in-depth pull-out study on FRC, which provided constructive information on shear strength between fibers and cement. Also, Chan and Andrawes [8] reported an effective shear strength value of 6.5 MPa between CNTs and cement by calibrating the numerical models using empirical results from three-point bending tests. As a result, the shear strength in this work was assumed to vary from 5 to 20 MPa.

The second parameter was the allowable slip, which determines how much the CNT can displace from the surrounding matrix before the CNT is totally detached/debonded from the matrix and only residual stress is present at the interface. A comparatively conservative approach was to assume complete detachment at a slip of 0.25 nm based on the width of a hexagonal ring at the surface of a CNT [29]. A more detailed study was conducted by considering allowable slip at two, three and four times of 0.25 nm (i.e. 0.5, 0.75 and 1.00 nm).

The third parameter being investigated was the Young’s modulus of CNTs, since the stiffness affects how readily the embedded CNT can be pulled out from the surrounding matrix. A wide range of values were reported in the literature for the Young’s modulus of MWNTs [6, 7, 24–28]. Therefore, the effect of Young’s modulus ranging from 500 GPa to 2 TPa was evaluated in the parametric study, and specific values used were 500 GPa, 1, 1.5 and 2 TPa.

The fourth parameter was the residual stress expressed as a percentage of the shear strength, which was expected to affect the mechanical properties of the composite in a similar manner as the shear strength, except that it was related to the resistance after bond degradation. Ignoring the residual stress would give conservative results due to the uncertainties of estimating the friction developed on the smooth CNT surfaces, and hence residual stress equal to 0% of the shear strength was employed as the prime value. The highest residual stress considered was 10% of the shear strength, since a higher value was not realistic considering the smooth surfaces of CNTs.

The last parameter was the CNT aspect ratio (i.e. the ratio of the length of CNT to its diameter), since it was expected that the aspect ratio had a crucial effect on the pull-out resistance. In fact, the high aspect ratio of CNTs is one of the advantages of using them as cement reinforcement over other types of fibers. In this work, to balance the computational cost and accuracy, the range of aspect ratio from 125 to 500 was employed to study the effect of variation.
Figure 7. Individual effect of the five parameters on constitutive relationship of the composite: (a) interfacial shear strength, (b) allowable slip, (c) CNT Young’s modulus, (d) residual stress, (e) CNT aspect ratio and (f) initial portion for aspect ratio.

4.2. Effects of individual parameters

The individual effects of the five parameters on the CNT/cement composite behavior is compared and contrasted in this section. Figure 7 shows the average stress–strain relationship of the composite by varying the five parameters one at a time while keeping the values of the remaining four parameters as those shown in the second column of table 1. The average strain was evaluated by dividing the CNT displacement at the displaced end by the total length of the RVE (including the extended portion), and the average stress was computed by averaging the total reaction force over the cross-section area pictured in figure 2(b). To compare the performance of the composite, its strength and ultimate strain were obtained from the stress–strain plot (see figure 7) as the stress at the plateau and the strain at the end of the plateau,
The composite ultimate strain is a crucial factor which determines how ductile the composite material is, while the composite strength governs the load carrying capacities of any structural components made of the composite. Therefore, from the structural perspective of view, these two parameters were of interest.

Figures 7(a) and (b) show that the interfacial shear strength and CNT allowable slip have very similar effect on the mechanical properties of the composite, and the enhancements in both strength and ultimate strain are essentially proportional to the increase in the corresponding parameter. Compared with shear strength of 5 MPa, the case with 10, 15 and 20 MPa had the composite strength improved by 31, 73 and 89%, respectively, while the enhancements in the respective ultimate strain were 32, 69 and 90%. Regarding the allowable slip, the case of 0.25 nm was used as a point of reference, and it was found that the composite strength was increased by 27, 48 and 68% for allowable slip values of 0.5, 0.75 and 1.00 nm, respectively. The figure compares the effects of doubling the shear strength and those of allowable slip on the pull-out resistance, the shear stress–slip results from a contact element/target element pair with different shear strength and allowable slip values are shown in figure 8. The figure compares the effects of doubling the shear strength and those of doubling the allowable slip on the bond stress–slip relationship. Figure 8(a) shows that increasing the shear strength from 5 to 10 MPa enhanced the frictional force by doubling the ordinates, while figure 8(b) demonstrates that increasing the allowable slip from 0.25 to 0.5 nm enhanced the frictional force by increasing the abscissas by twice. Both figures practically implied a twofold increase in the area under the curves. To explicitly illustrate the influences introduced by the shear stress–slip behaviors illustrated in figure 8, figure 9 is used to compare the distributions of average shear stress transferred across the CNT/cement interface along the longitudinal axis of a CNT with length of 2500 nm at the sixtieth load step (LS60). The curves in both figures 9(a) and (b) are overlapped in a magnified view at the top left corner of the corresponding figure. It can be concluded that either higher shear strength or a bigger allowable slip renders a larger area underneath the shear stress distribution curve and hence an increase in the composite strength. Furthermore, it is worth noting that the pull-out effect propagates much slower when either parameter is doubled (i.e. either 10 MPa or 0.5 nm is used), which increases the ultimate strain of the composite.

Figure 7(c) demonstrates that the effect of CNT Young’s modulus was very different from the effects of shear strength and allowable slip. By increasing the Young’s modulus from 500 GPa to 1, 1.5 and 2 TPa, the composite strength was increased by 40, 75 and 100%, respectively; however, the respective ultimate strain was reduced by 24, 37 and 49%. These quantitative results imply that a stiffer CNT enhances the composite strength but makes the material less ductile. Since an increase in CNT stiffness would require a larger resistance force and hence a bigger interfacial area to sustain the same amount of CNT tip displacement, a higher composite strength was resulted. In addition, the pull-out effects will propagate more rapidly, so a lower ultimate strain was resulted and the composite became more brittle.

Figure 8. Shear stress–slip relationship from post-processing: (a) interfacial shear strength and (b) allowable slip.

Figure 9. Distributions of average shear stress transferred across the CNT/cement interface: (a) interfacial shear strength and (b) allowable slip.
Figure 10. Interactive effects between parameters on the composite ultimate strain: (a) shear strength and CNT Young’s modulus, (b) allowable slip and CNT Young’s modulus, (c) shear strength and allowable slip, (d) shear strength and residual stress, (e) CNT Young’s modulus and residual stress, (f) allowable slip and residual stress and (g) aspect ratio and residual stress.

Figure 7(d) illustrates that, by including the residual stress, a very different composite behavior was resulted. First, it is obvious that strain hardening was resulted due to the presence of residual stress, as illustrated by the positive slope after the first peak instead of a plateau as in the figures 7(a)–(c) and (e). The key effect of this parameter was that, after
debonding occurred at the fixed end (corresponding to the second peak of the curves), there was still resistance provided by the residual stress as illustrated by the residual branches. Although the contribution from one CNT was insignificant, the accumulation of residual stresses from numerous CNTs in a composite mixture would substantially increase the load carrying capacity of a structural component; and this suggested the importance of understanding the factor of residual stress. When the residual stress was increased from 0% to 5, 7.5 and 10%, the composite strength (computed as the peak stress) were improved by 42, 62 and 85%, respectively, while the enhancements of ultimate strain (considered as the strain corresponding to the peak stress) were 42, 56 and 81%, respectively.

Figure 7(e) shows that the CNT aspect ratio had the least influence among the five parameters investigated. Neither the composite strength nor the ultimate strain was affected by the embedded length; only the initial stiffness of the composite was increased due to a longer embedded length as shown in figure 7(f). The difference in the initial behavior can be attributed to the fact that, before debonding occurred at the displaced end, a larger force was required to mobilize a longer RVE (i.e. a larger volume) and hence the cases with longer lengths were stiffer. However, after the CNT was detached from the matrix at the displaced end, the resistance to pull-out would only depend on the interfacial characteristics which were exactly the same for all three cases. Since the strengthening effect from residual stress was neglected in the master set considered (see the second column in table 1), the aspect ratio did not influence the ultimate composite behavior. However, it is expected that the effect of aspect ratio would be different if the residual stress was taken into account, and this proposition will be validated in the next section which discusses the interaction between different parameters.

5. Interaction between various parameters

After studying the individual effect of interfacial shear strength, allowable slip, Young’s modulus of CNTs, residual stress and aspect ratio, on the CNT/cement composite strength and ultimate strain, it is constructive to examine the interaction effects between these parameters, which will help in determining the desired range of a parameter to improve the structural behavior of the composite if the other parameters are known. In this section, the five parameters will be discussed in pairs, and it should be noted that the interaction relationship derived would only be valid within the ranges studied (see table 1). As shown in the previous section, the effect of CNT aspect ratio on the composite mechanical properties was minimal for the given set of prime values (i.e. the second column in table 1). The results from preliminary analyses showed that inertness to CNT aspect ratio (as in figure 7(e)) pervaded regardless of the level of interfacial shear strength/allowable slip/Young’s modulus of CNTs, but the aspect ratio’s interactive effects were non-negligible when residual stress was present. Therefore, CNT aspect ratio’s interaction with interfacial shear strength/allowable slip/Young’s modulus of CNTs was not considered in this study. The interactive effects among the five parameters on the composite ultimate strain and strength will be discussed in the two sub-sections below.

5.1. Effects on composite ultimate strain

Figures 10(a)–(g) show the interactions between any two of the five parameters. The values of the composite’s ultimate strain due to the interaction of the shear strength/CNT Young’s modulus pair and the allowable slip/CNT Young’s modulus pair are depicted in figures 10(a) and (b), respectively. The figures show that the CNT Young’s modulus reacted similarly in an inverse interactive manner with both parameters. In
Figure 12. Interactive effects between parameters on the composite strength: (a) shear strength and CNT Young’s modulus, (b) allowable slip and CNT Young’s modulus, (c) shear strength and allowable slip, (d) shear strength and residual stress, (e) CNT Young’s modulus and residual stress, (f) allowable slip and residual stress and (g) aspect ratio and residual stress.
other words, the ultimate strain was affected the most when either the shear strength or the allowable slip was at its upper limit while the CNT modulus was at its lower limit. The almost-parallel lines corresponding to the CNT Young’s moduli of 1.5 and 2 TPa indicated that, at high levels of CNT stiffness, weak interactions exist between the CNT modulus and the interfacial shear strength or allowable slip. Furthermore, the effect of interaction between the shear strength and allowable slip is also depicted in figure 10(c). Compared with figures 10(a) and (b), the curves in figure 10(c) are more parallel to one another, which imply minimal interaction existed between shear strength and allowable slip.

Also, figures 10(d)–(g) show the values of the composite’s ultimate strain due to residual stress’ interactions with interfacial shear strength, CNT Young’s modulus, allowable slip and aspect ratio, respectively. In all four plots, nonlinearity was introduced because of the progressive cracking of the cement matrix in the pull-out process, as illustrated in figure 11. In the case with no residual stresses, there was no friction at the cracked interface and therefore the interfacial condition would not affect the stress transfer. The nonparallel curves also indicate strong interaction between residual stress and the other four parameters. Taking a closer look at each plot, it is clear that the residual stress strengthens the effect of each of the shear strength, allowable slip and aspect ratio parameters on the ultimate strain values as illustrated in figures 10(d), (f) and (g). The residual stress also weakens the effect of the CNT Young’s modulus on the ultimate strain (see figure 10(e)). It is interesting to note that this interaction effect diminishes when the shear strength and aspect ratio are at their lower limits and the allowable slip and Young’s modulus are at their upper limits. This observation is evident by the coincidence points in the four plots.

5.2. Effects on composite strength

Figures 12(a)–(g) show the interaction effects of any two of the five parameters on the composite strength. The behaviors depicted in figures 12(a)–(c), which present the values of the composite strength due to the interaction of the shear strength/CNT Young’s modulus pair, the allowable slip/CNT Young’s modulus pair and the shear strength/allowable slip pair show that the interaction between any two of the three parameters are quite similar. In each figure, the lines are fairly parallel, and the difference in slope is less than a factor of two. This illustrates that there was not much interaction effects, in terms of the composite strength, among the three parameters.

Moreover, figures 12(d)–(g), which present the composite strength values resulting from the residual stress’ interactions with interfacial shear strength, CNT Young’s modulus, allowable slip and aspect ratio, respectively, illustrate that the residual stress strengthens the effect of each of other fours parameters on the composite strength. This observation similar to that was observed in the ultimate strain case except in the case of CNT Young’s modulus (see figure 10(e)). Hence, it could be concluded that the CNT modulus is a key parameter which have opposite effects on the composite strength and ultimate strain. In figures 12(e) and (g), it is also observed that the interaction behavior is linear regardless of the residual stress value. This behavior contradicts with that was observed in the ultimate strain case (see figures 10(e) and (g)), where the residual stress had an exponential-like impact on the ultimate strain, especially in the case of 10% residual stress.

6. Conclusions

RVE pull-out model of a CNT embedded in a cement matrix was developed and utilized in a parametric study to investigate the individual and interactive effects of several mechanical and interfacial parameters related to CNT/cement composites. These parameters include interfacial shear strength, allowable slip, CNT Young’s modulus, residual stress and aspect ratio. The individual characteristics provided a basis to understand the interactive features among the parameters, while the interaction study was the key to evaluate the effects of each parameter on the overall structural performance of the composite. Two major structural properties were of interest and they were the composite ductility and strength. In general, considerable amount of interaction was observed among parameters for both mechanical properties investigated, but more prominent interactive effects existed within certain ranges of the parameters. Besides, nonlinear behavior was demonstrated by the interactive effects only when residual bond stress was present.

The results of the study showed that in general, developing CNT/cement composite for structural applications of high ductility requires using CNTs with relatively low modulus (i.e. less than 500 GPa) and good interfacial bond with the cement. Using CNTs with roughened surface through functionalization for example will increase the value of residual bond stress, which was proven to be a key parameter in enhancing the composite ductility more than the initial interfacial bond. On the other hand, for structural applications where the composite strength rather than ductility is of main interest, using high modulus CNTs (i.e. greater than 1500 GPa) is crucial, while using CNTs with high aspect ratio is not as important. The study also revealed that developing CNT/cement composite which is characterized by both extra high strength and ductility is a challenging task. This is primarily due to the opposite effects of the CNTs Young’s modulus on both composite strength and ductility. For example, the study showed that increasing the CNTs modulus from 500 GPa to 2 TPa increases the composite strength by 100%, while decreases its strength by 49%.

References

[1] Bentur A and Mindess S 1990 Fibre Reinforced Cementitious Composites (London: Elsevier)
[2] Lebedkin S, Schweiss P, Renker B, Malik S, Henrich F, Neumaier M, Stoemer C and Kappe M 2002 Carbon 40 417
[3] Qin L, Zhao X, Hirahara K, Miyamoto Y, Ando Y and Iijima S 2000 Nature 408 50
[4] Wang G, Zhao Y and Yang G 2004 Mater. Des. 25 453

L Y Chan and B Andrawes
[5] Mateiu R, Davis Z, Madsen D, Molhave K, Boggild P, Rassmusen A, Brorson M, Jacobsen C and Boisen A 2004 Microelectron. Eng. 73 4 670
[6] Campillo I, Dolado J S and Porro A 2003 Proc. 1st Int. Symp. Nanotechnology in Construction (Paisley: Scotland) p 215
[7] Li G Y, Wang P M and Zhao X H 2005 Carbon 43 1239
[8] Chan L C and Andrawes B 2009 Proc. 2009 Structures Congress p 2686
[9] Liu Y and Otani Y 2005 Comput. Mater. Sci. 34 173
[10] Liu Y J and Chen X L 2003 Electron. J. Bound. Elem. 1 316
[11] Liu Y and Chen X 2002 Mech. Mater. 35 69
[12] Makar J and Beaudoin J 2003 Proc. 1st Int. Symp. Nanotechnology in Construction (Paisley: Scotland) p 331
[13] Lijima S and Ichihashi T 1993 Nature 363 603
[14] Baughman R H, Zakhidov A A and de Heer W A 2002 Science 297 787
[15] ANSYS, Inc. 2009 ANSYS Website http://www.ansys.com/services/ss-documentation.asp (retrieved 1 June 2009)
[16] Willam K J and Warnke E P 1975 Proc. Int. Assoc. Bridge Struct. Eng. 19 1
[17] Bernard O, Ulm F J and Lemarchand E 2003 Cem. Concr. Res. 33 1293
[18] Mondal P, Shah S and Marks L 2006 Cem. Concr. Res. 37 1440
[19] Zhu W, Hughes J, Bicanic N and Pearce N 2007 Mater. Charact. 58 1189
[20] Naaman E, Namur G, Alwan J and Najm H 1991 J. Struct. Eng. 117 2791
[21] Wei C 2006 Appl. Phys. Lett. 88 093018
[22] Lim T, Paramasivam P and Lee S 1987 ACI Mater. J. 84 286
[23] Desai A and Haque M 2005 Thin-Walled Struct. 43 1787
[24] Treacy M, Ebbesen T and Gibson J 1996 Nature 381 678
[25] Wong E, Sheehan P and Lieber C 1997 Science 277 1971
[26] Lourie O and Wagner H 1998 J. Mater. Res. 13 2418
[27] Salvetat J, Bhattacharyya S and Byron R 2006 J. Nanosci. Nanotechnol. 6 1857
[28] Yu M and Ruoff R 2002 Soc. Mech. Eng. 55 495
[29] Frankland S and Harik V 2002 Surf. Sci. 525 L103
[30] Wagner H, Lourie O, Feldman Y and Tenne R 1997 Appl. Phys. Lett. 72 188
[31] Cooper C, Cohen S, Barber A and Wagner H 2002 Appl. Phys. Lett. 81 3873