Wall thickness dependencies of carbon nanotube reinforced nanocomposites

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Abstract. Indentation analyses are conducted to investigate the CNT’s wall thickness dependencies of the mechanical properties of nanocomposites. This study incorporates Berkovich nanoindentation analyses for chemically non-bonded CNT/matrix interface, including the size effects of nanocomposites. For non-bonded interface, the properties of nanocomposite are generally controlled by mechanical interlocking, thermal residual stress, Poisson’s contraction and van der Waal’s (vdW) interaction between CNT and matrix. Considering all these parameters, a series of finite element models for nano-indentation tests have been constructed, aiming to investigate the mechanical properties of CNT reinforced nanocomposites. The model is validated and numerical results are compared with that of existing experimental indentation test. Analysis has been run for ten different wall thicknesses of CNTs in a range of wall thickness starting from 0.034 nm to 0.334 nm. Elasto-plastic behavior of steel and CNT including strain gradient is considered in the program. The study on wall thickness dependencies of CNTs in nanocomposite shows that mechanical properties of nanocomposites largely depends on the wall thickness of CNTs. A minimum wall thickness for a particular tube diameter to achieve a pick value of hardness and modulus of elasticity of nanocomposites is determined. The minimum wall thickness of CNTs is suggested to be 0.2 for an outer diameter of 1nm in order to achieve the maximum value of composite properties. In addition, a wall thickness smaller than 0.05 nm may even reduce the hardness and modulus of elasticity of CNT reinforced composites compare to that of pure matrix.

1. Introduction
Carbon nanotubes have already been considered as one of the super reinforcement materials of high-performance nanocomposites [1-6]. Existing research suggests that the load carrying capability of composites can be enhanced significantly by the addition of carbon nanotubes or nano-ropes [4, 7]. Mechanical properties like modulus of elasticity and hardness of such nanocomposites, are some of the key features that are essential to determine before their application. Numerical indentation test is one of the approaches that is capable of determining mechanical properties of such nanocomposites using indentation model quite accurately [8-11].

Instrumentation for depth sensing indentation procedure was first successfully experimented and developed by Doerner and Nix (1986). The determination of elastic modulus of any solid materials using finite element-based indentation analysis was originally proposed by Larsson et al. (1996). Later, nano-indentation test on polymeric surface was primarily conducted by Briscoe et al. (1998). Based on the indentation technique, Fazio et al. (2001) conducted nano-indentation tests for diamond and hence results were also compared with their finite element model [9].
This study aims to investigate wall thickness dependencies CNT reinforced composites using FE based nanoindentation simulation considering strain gradient plasticity for chemically non-bonded carbon nanotube reinforced composites. This noble approach would be a breakthrough to simulate indentation test at nanoscale using advanced finite element analysis and hence predict the material properties of nanocomposites for different wall thickness of CNTs before conducting difficult experiments or practical applications.

2. Finite Element Model

In this study, an axisymmetric finite element model has been developed primarily to conduct numerical indentation test as shown in Figure 1. The figure presents a representative FE model of single-wall carbon nanotube (SWCNT) and multi-wall carbon nanotube (MWCNT) reinforced nanocomposites. The inclination angles of the faces with respect to the loading axis are 65.30 for Berkovich indenter. In the model, very fine meshes are selected using mesh sensitivity analysis so that Finite Element models can be simulated more accurately by providing minimum run time for models. Additionally, mesh biasness is also considered, as more numbers of elements are chosen near the indenter tip to make the analysis more efficient and hence desired convergence of output is achieved. Both material non-linearity in the mechanical properties of CNT and matrices and geometric non-linearity for the elements are employed in the FE model simulation. The indenter is considered to be analytically rigid; moreover, surface to surface interaction between CNT and matrix is also considered to be friction for non-bonded interface where matrix is the master surface and CNT - the slave. In the non-bonded interface, thermal stress is considered as uniform radial pressure acting on the nanotube.

3. General equations for indentation relationships

In order to obtain the mechanical properties of the nanocomposites, the results are extracted from the FE analysis that is finally processed as force displacement relationships of the indenter tip as shown in Figure 3. In the analysis process, it is assumed that the area of contact between the indenter and the specimen remains constant while the unloading stage begins. The mechanical properties such as hardness and modulus of elasticity are extracted from the force-displacement relation as per well-known procedure proposed by Doerner and Nix (1986).
Figure 3. Schematic drawing for the determination of the material properties from indentation test proposed by Doener and Nix method (Doerner and Nix 1986).

The gradient of the Force-indentation displacement curve during unloading is given by the following relation

\[ S = \left| \frac{dF}{dh} \right| = \mu E_{ef} \sqrt{A_p} \]  \hspace{1cm} (1)

Where,

- \( S \) represents contact stiffness
- \( h_i \) is the total indentation depth
- \( A_p \) is the projected area
- \( \mu = 2\sqrt{\pi} \) for axisymmetric indenter
- \( \mu = 1.167 \) for Berkovich indenter
- \( E_{ef} \) is the effective elastic modulus
- \( E_i \) is indenter elastic modulus
- \( E_f \) is elastic modulus of the composite

The relationship between the indentation and the projected area of contacts can be expressed through the following equation

\[ A_p = k h_p^2 \]  \hspace{1cm} (2)

where,

- \( h_p \) is the effective indentation depth
- \( k = 24.5 \) for Berkovich & Vicker indentation
The hardness \( (H) \), being expressed as the ratio of maximum applied load to the projected contact area for Berkovich indenter that becomes equal to
\[
H = \frac{F_{\text{max}}}{A_p} = \frac{F_{\text{max}}}{24.5 \ h_p^2}
\] (3)

Using equation (2) and equation (3), the mechanical properties of nanocomposites such as modulus of elasticity and hardness can be obtained.

4. Finite Element Analysis
Many researchers have studied finite Element Modeling for indentation analysis. However, most of them consider perfect CNT/matrix interface and their models does not account the hollowness of the CNTs. The hollowness effect can be a very important factor when diameter to wall thickness ratio is significantly high. To the best of author’s knowledge, a combination of length scale effect and non-bonded CNT/matrix interface for nanocomposite to investigate up to a fraction of nanometer scale has never been studied. Considering all practical factors of CNTs and their potentials matrices, a series of Finite Element model has been simulated to obtain the accurate indentation output and the influences of different composite parameters. The parameters used in the finite element model are presented in Table 1.

Table 1. Value of parameters.

| Property Description                      | Value                  |
|-------------------------------------------|------------------------|
| Domain Size of the axisymmetric Model     | 10 nm × 10 nm          |
| Diameter of CNT                           | 1 nm                   |
| Indenter tip displacement                 | 0.788 nm               |
| Number of CNT in the domain               | 9                      |
| Bias Ratio for meshing                    | 10                     |
| No of element in each dimension           | 100                    |
| Modulus of Elasticity of CNT, \( E_t \)   | 1000 GPa               |
| Poisson’s Ratio of CNT, \( \nu_t \)       | 0.27                   |
| Modulus of Elasticity of Epoxy, \( E_m \) | 3000 MPa               |
| Poisson’s Ration of Epoxy, \( \nu_m \)    | 0.35                   |
| Thickness of CNT                          | 0.034 nm               |
| Radial Stress due to thermal contraction  | 60 MPa                 |
| Coefficient of Friction, \( \mu \)        | 0.25                   |
| \( \epsilon \)                           | 0.004656 ev(1ev = 1.602 × 10^{-19} j) |
| \( n_p \)                                | 3.1×10^{28} / m^3     |
| \( n_i \)                                | 3.82×10^{19} / m^3    |
| \( O_i \)                                | 0.2 nm                 |

4.1. Model Validation
Before going to discuss the study on wall thickness dependencies of CNT reinforced nanocomposites, the proposed model is validated with the experimental work conducted by Nouri et al. (2012). In the modeling process, Berkovich indenter having 65.30 indentation angle and a depth of 740 nm,
mechanical properties of aluminum and MWCNT are exactly followed as per their experimental indentation test.

Nanoindentation model for 2% (by vol.) MWCNT reinforced AL-2024 nanocomposite is created and compared with that of the experimental indentation test. The stress strain relation of AL-2024 is extracted from the previous study conducted by Bastawros et al. (2006). Figure 4 shows a comparison of the force displacement relationship between numerical and experimental indentation test for 2% MWCNT reinforced AL-2024 nanocomposite. Von mises stress distribution of the nanocomposite is presented on Figure 5. The stress distribution shows that MWCNT experiences larger stress than the adjacent matrix that justify the reinforcing potential of MWCNT. It is also observed from the stress distribution that there are breaks of stress flows once they reach the MWCNTs. The numerical result for the nanocomposite well agrees with the experimental result in both loading and unloading stage. Though the curves intersect each other in some indentation depths, they follows the same trends and similar material behavior. The minor differences between the results may arise from the considerations that the numerical model considers the uniform dispersions of CNT, the indenter as analytical rigid and perfect orientation. However, it’s nearly impossible to achieve uniform dispersion, perfect rigid indenter with infinite stiffness and theoretical orientation of a nanocomposite that is experimentally tested. The correlation obtained by numerical analysis appears indistinctly uneven in some points that actually happens due to the account of material and geometric non-linearity as well as the vdW interactions at the non-bonded interfaces.

![Figure 4](image-url)

**Figure 4.** Schematic drawing for the determination of the material properties from indentation test proposed by Doener and Nix method (Doerner and Nix 1986).
Table 2. Comparison between current study and previous experiment.

| Parameter | Hardness (GPa) | Modulus of elasticity (GPa) |
|-----------|---------------|-----------------------------|
| 2% MWCNT reinforced Aluminum nanocomposite (Experiment (Nouri, Ziaei-Rad et al. 2012)) | 2.263 | 83.3 |
| 2% MWCNT reinforced Aluminum nanocomposite (present work) | 2.20 | 82.6 |

5. Results and Discussions

Berkovich indentation analysis is performed on CNT reinforced conventional steel nanocomposites where the influence of different thicknesses are investigated. Analysis has been run for ten different wall thicknesses of CNTs keeping the same outer diameter. Elasto-plastic behavior of steel and CNT including strain gradient is considered in the program. Investigations are conducted in a wide range of wall thicknesses starting from 0.034 nm to 0.334 nm. The stress distribution of nanoindentation simulations for typical thin and thick walled CNTs are presented in figure 6a and 6b, respectively. The Berkovich simulation result shows that the higher stress is developed near the indenter tip. In addition, maximum von mises stress is observed in the CNTs compare to the adjacent matrix region. The stress distribution evidently shows that thin wall CNTs near the indenter are collapsed due to buckling inside the matrix. In contrast, thick wall CNT (having a diameter over 0.2 nm) seems to float inside the matrix without showing any buckling as indentation progresses. It is interesting to note that, though the indenter tip moves downward inside the matrix, the shape of the thick-walled tube remains unchanged. It is also observed from the stress distribution suggests that the stress flow is higher in lateral direction than that in vertical path.

Wall thickness dependency of mechanical properties of CNT reinforced nanocomposites is presented in terms of force-displacement relationship as shown in Figure 7. It can be clearly understood from the figure that force requirement increases as the indenter tip progresses through the nanocomposites.
However, the required force sharply increases for thicker nanotubes reinforced composites particularly after an indentation depth of 0.30 nm. On the other hand, the force increment of thinner walled (0.034 nm) CNT-Steel composite is not linear with the indentation depth. The difference of force requirement for same indentation depth between thin and thick walled nanocomposite is very much significant. The maximum required force of thick-walled CNT-steel composite for an indentation depth 0.788 nm is nearly 2.5 times than that of the thinnest CNT-Steel nanocomposites.

It is interesting to highlight that there is a turn at the force-displacement profile for an indentation depth in the range of 0.4 to 0.6 nm up to a wall thickness of 0.1 nm. This may happen due to the fact that buckling occurs for thin wall carbon nanotubes as presented on Figure 6a. This phenomenon can be explained by the fact that smaller wall thickness results local bucking of the CNTs, loses its stability and hence the resistance from the tube is insignificant in this region. However, the force requirement increases sharply after an indentation depth of more than 0.6 nm. This happens because though, the CNT loses its lateral stability after initial buckling, it regains stability after further buckling as they are confined by matrix materials and show high ductile behavior inside the matrix. It is to be noted that if wall thickness is more than 0.2 nm, all CNTs having similar outer diameter give almost same indentation profile. This can be explained by the fact that lateral buckling of CNT for that particular diameter can be resisted by a wall thickness of 0.2 (diameter to thickness ratio 5.0) or higher and this wall thickness may be considered as the optimum thickness to achieve maximum influence of CNT in nanocomposites for a fixed outer diameter of 1 nm.

![Figure 6](image.png)

**Figure 6.** Stress distribution of Berkovich indentation simulation of (a) thin-walled and (b) thick-walled nanotube reinforced composites.

Figure 8 shows the variation of modulus of Elasticity of nanocomposites (Enc) with the wall thickness of CNTs. The values of modulus of elasticity of nanocomposite are extracted from the force displacement relationships of wall thickness dependency study. The result shows that with the increase of wall thickness of CNT, modulus of elasticity of the composite also increases though the increment does not change linearly. Initially, the variation of Enc with respect to wall thickness is much steeper than that of the wall thickness greater than 0.2 nm. It is very worthwhile to mention that the modulus elasticity of CNT-steel nanocomposite for a wall thickness of less than 0.05nm (SWCNT) is observed to be nearly 180 GPa which is less than that of pure steel (Es = 200 GPa). Therefore, SWCNTs are found to be ineffective as a reinforcement of pure steel matrix.
Figure 7. Force displacement relationship for different wall thicknesses of CNTs in nanocomposites.

Figure 8. Influence of CNT’s wall thickness on modulus of elasticity of nanocomposites.
Figure 9. Influence of CNT’s wall thickness on hardness of nanocomposites.

Figure 9 presents the wall thickness dependency of hardness of CNT reinforced nanocomposites. It is also observed from the figure that hardness sharply increases with the increase up to a wall thickness of 0.2 nm and it remains nearly constant after that value. This hardness behavior of nanocomposite can be described as, large distortion of CNT occurs for smaller wall thickness of CNTs. In addition, bond strength between collapsed CNT and adjacent matrix become weaker because cohesive stress due to vdW interactions becomes insignificant as the interface goes far away from the equilibrium distance. Therefore, in order to achieve a desired hardness for nanocomposite, this study may provide a preliminary guideline to design the optimum wall thickness for particular matrix so that CNTs can effectively contribute to the composite properties.

6. Conclusion
A number of finite element models have been developed to investigate indentation analysis for uniformly dispersed CNTs in different matrices in which non-bonded CNT/matrix interface and large strain elasto-plastic behavior of constituents are considered. The proposed finite element model for nanoindentation analysis is validated with the experimental indentation test on 2% (by vol.) MWCNT reinforced aluminum nanocomposites conducted by Nouri et al. (2012). The comparison shows that the proposed model demonstrates a very good agreement with their experimental result. The differences of modulus of elasticity and hardness between experimental indentation test and this advanced finite element simulation are below 1% and 3%, respectively.

The study on wall thickness dependencies of CNTs in nanocomposite shows that mechanical properties of nanocomposites largely depends on the wall thickness of CNTs. A minimum wall thickness for a particular tube diameter to achieve a pick value of hardness and modulus of elasticity of nanocomposites is determined. The minimum wall thickness of CNTs is suggested to be 0.2nm for an outer diameter of 1nm in order to achieve the maximum value composite properties. In addition, a wall thickness smaller than 0.05 nm may even reduce the hardness and modulus of elasticity of CNT reinforced composites compare to that of pure matrix. This happens due to the fact that large distortion occurs for smaller thickness. In addition, this distortion of CNTs changes the relative radial displacement at the CNT/matrix interface causing a smaller stress transfer through the interface and hence results smaller values of hardness and modulus of elasticity of nanocomposites. Therefore, this study may
contribute in designing different type of carbon nanotube reinforced nanocomposites and their appropriate application as reinforcement of different nanostructures.

7. References
[1] Ajayan P M, Schadler L S, Giannaris C and Rubio A 2000 Single-Walled Carbon Nanotube–Polymer Composites: Strength and Weakness J. Adv. Mater. 12 750-53
[2] Ashrafi B and Hubert P 2006 Modeling the elastic properties of carbon nanotube array/polymer composites Compos. Sci. Technol. 66 387-96
[3] Bakshi S R, Lahiri D and Agarwal A 2010 Carbon nanotube reinforced metal matrix composites - a review Int. Mater. Rev. 55 41-64
[4] Chen X 2004 Square representative volume elements for evaluating the effective material properties of carbon nanotube-based composites Comput. Mater. Sci. 29 1-11
[5] Chen X H, Chen C, Xiao H N, Liu H B, Zhou L, Li S L and Zhang G 2006 Dry friction and wear characteristics of nickel/carbon nanotube electroless composite deposits Tribol. Int. 39 22-28
[6] Manoharan M P, Sharma A, Desai A V, Haque M A, Bakis C E and Wang K W 2009 The interfacial strength of carbon nanofiber epoxy composite using single fiber pullout experiments Nanotechnology 20 295701
[7] Ahmed K S and A K Keng 2013 Interface characteristics of nanorope reinforced polymer composites Comput. Mech. 52 571-85
[8] Melick H G H V, Bressers O F J T, Toonder J M J D, Govaert L E and Meijer H E H 2000 A micro-indentation method for probing the craze-initiation stress in glassy polymers J. Polym. 44 2481-91
[9] Fazio L D, Syngellakisa S, Wood R J K, Fugiuele F M and Sciumé G 2001 Nanoindentation of CVD diamond: comparison of an FE model with analytical and experimental data Diam. and Relat. Mater. 10 765-769
[10] Kusano Y and Hutchings Y K 2003 Analysis of nano-indentation measurements on carbon nitride films Surf. Coat. 169 739-742
[11] Larsson P, Giannakopoulos A E, SÖderlund E, Rowcliffe D J and Vestergaard R 1996 Analysis of Berkovich indentation Int.J. Solids Struct. 33 221-248
[12] Doerner M F and Nix W D 1986 A method for interpreting the data from depth-sensing indentation instruments J. Mater Res. 1 601-609
[13] Briscoe B J, Fiori L and Pelillo E 1998 Nano-indentation of polymeric surfaces Journal of Physics D: Appl. Phys 31 2395
[14] Nouri N, Ziaei-Rad S, Adibi S and Karimzadeh F 2012 Fabrication and mechanical property prediction of carbon nanotube reinforced Aluminum nanocomposites Mater. Design 34 1-14
[15] Bastawros A F 2006 Analysis of deformation-induced crack tip toughening in ductile single crystals by nano-indentation Int.J. Solids Struct. 43(24) 7358-70