Modelling Considerations for Nanomaterials- A Review

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Abstract: *Over the course of years, the field of computer simulation has reached new heights, exposing us to a variety of resources that make our work in computation easier and faster. The advanced resources make simultaneous simulation of nano-arrays feasible. The theoretical understanding of nano materials is gaining interest all over the world due to ease of atomic scale simulations. The characterization of nano materials can be done in various forms, such as mechanical characterization, chemical, physical, electrical etc. This paper mainly concentrates on the modelling of mechanical properties of nano materials and nano composites, Softwares in use, the criteria adopted, concluding the paper with advantages and disadvantages highlighting key points of the experiments conducted so far.*

Keywords: *CNT, Characterization, Modelling, Software, Nano-materials*

1. INTRODUCTION

Ever since the discovery of carbon nano tubes by Iijima in 1991, almost every industry has seen a revolution. The introduction of use of nano materials in construction industry is fairly new, but the advantages are already there. Due to their high stiffness, strength, electrical and thermal conductivity, it is postulated that nano materials will lead to the development of new class of nano composites. Various experimental and numerical investigations have put the properties of nano materials at the forefront. It has been demonstrated that only 1pct (by weight) of CNT added in a polymeric matrix material can increase the stiffness of a resulting composite between 36 pct to 42 pct and the tensile strength by 25 pct.[1]

The major hurdle of the experimental process of determining nano material properties is the establishment of analytical model at the nano scale, which is extremely difficult, not to mention the expensiveness of conducting experiments. With the help of simulation techniques, the computation of nano composites is can be achieved in a cost effective manner just by the help of a desktop computer.

There are various methods available to study the mechanical properties of nano materials but the most commonly used approaches are:

1) Atomistic simulation at the nano scale level i.e. Molecular dynamics (MD)
2) Structural mechanics modelling which incorporated atomistic characteristics i.e. Continuum Mechanics (CM)
3) Multiscale modelling and simulation that bridges the length and time scales. [2]

MD approach though provides abundant simulation results for understanding the behaviour of nano materials, is limited to smaller scales of very small length and time of the order of several hundred carbon atoms and length upto several nanometers. Solution using MD approach requires computation of molecular orbital functions in the form of complex integrals which relatively increases the cost. In order to achieve cost effectiveness in this scenario, one has to ignore the electron motions and express the system potential as a function of position of atoms. Hence, in the initial stages, CM approach is adopted for studying the overall response before delving deeper into the atomic response.

CM approach basically involves FE modelling of nano composites. Though the credibility of it still remains debatable, but its use is justified by the fact that the method has been successful in studying single or bundled CNT's and their effects in a nano composite state. In CM, the CNT's are considered to be isotropic and homogenous. Material properties such as Young's modulus, Poisson's ratio etc have been successfully determined.

2. MODELLING CONSIDERATIONS AND RESULTS

F. KARIMZADEH ET AL[1] et al in 2007 in his paper Modelling Considerations and Material Properties Evaluation in Analysis of Carbon Nano-Tubes Composite explained the criteria for modelling of CNT nano composites in 5 steps:

1) Selection of the computational models for CNTs in nano-composites: MD approach require great computer resources and are limited to small scales of length and time, hence the more feasible option to use is the Cm approach.
2) Types of the representative volume element (RVE) for the simulation: RVE's can either be circular, square or hexagonal depending on the requirement. They provide basic representation yet detailed analysis of CNT interaction with the matrix. For better

understanding, square or circular RVE's are adopted as they are closer to the practical representation of the nano composites.

3) Modelling of the interfaces: the load transfer mainly takes place through the CNT matrix interface. At nano scale, the interface is not a smooth surface, yet, the assumption that the bonding between the interface can be perfect has yielded better results, plus the existence of such bond has been demonstrated by research.

4) Effects of the caps at the ends of CNTs: caps don't play much of a role in the overall mechanical response of an isolated CNT, however, free ended CNTs will be modelled as a cylinder with high stiffness and small thickness leading to high stress concentration at the interface causing a bi-material singularity.

5) Scaling or units for nano-scale simulations: using standard units for nano materials causes numerical difficulties due to the actual dimensions being in nano scale hence the use of units such as nano-meter(nm) for dimensions and nano-Newton (nN) for forces is feasible.

To determine the effective material constants of CNT as proposed by F Karimzadeh et al, both cylindrical and square RVE's with long and short CNT subjected to axis-symmetric and lateral loading were modelled and analysed using ANSYS software. The stress distribution under axial stretch is as shown below.

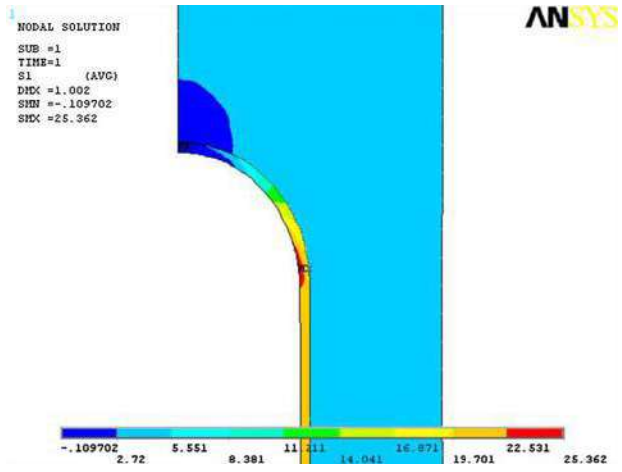

Fig1: Stress distribution in cylindrical RVE under axial stretch (long CNT) (Source: DOI: 10.1007/s11663-007-9065-y, The Minerals, Metals & Materials Society and ASM International 2007)

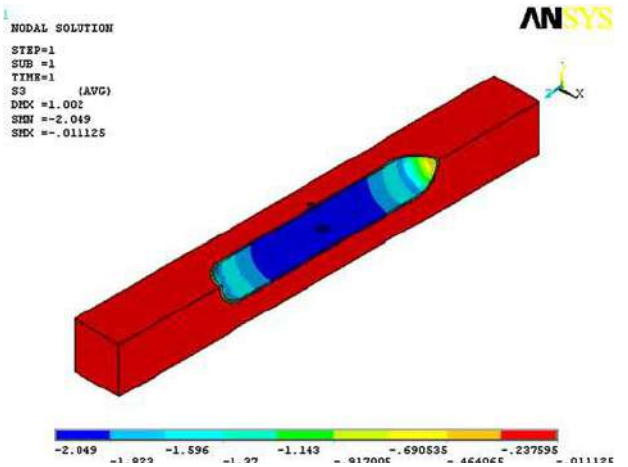

Fig2: stress distribution for square RVE under axial stretch (long CNT) (Source: DOI: 10.1007/s11663-007-9065-y, The Minerals, Metals & Materials Society and ASM International 2007)

The analysis yielded the following results:

- There was significant increase in the stiffness of CNT composite in cylindrical RVE with 10 times increase in case of axially loaded long CNT and 2.75 times in case of transversely loaded long CNT.
- In case of short CNT, there was moderate increase in stiffness at the same volume fraction of CNT but remained less than the stiffness of the matrix as shown in table below.
- For square RVE's loaded similar to cylindrical RVE's, the increase in stiffness in axial direction was three 10 times that of the matrix.
- For short CNT's the increase in stiffness was moderate in both axial and lateral directions.

The results are tabulated as below:

Table 1: *For axial loading*

Computated effective material constants	Cylindrical RVE		Square RVE	
	Short CNT	Long CNT	Short CNT	Long CNT
Stress	0.0916	0.5346	0.0737	0.4105
Young's modulus	9.165	53.462	7.377	41.056
Poisson's ratio	0.274	0.30	0.36	0.30

It can be noticed that in both the types of RVE, use of short CNT may not be as effective as long CNT. Similar results are found for lateral loading but haven't been mentioned in the paper for the sake of brevity.

Modelling considerations for multiwalled carbon nano tubes (MWCNT) was proposed by Moones Rahmandoust et al.[3] MWCNT consist of CNT's rotated

around a circle. This representation was drawn up in CAD. The geometry is was then transferred to a fem program, here MSC MARC.

Young's modulus, Poisson's ratio and shear modulus are the constants that determine how a material behaves under different loading. For an isotropic elastic beam element that obeys Hooke's law, the quantities can be easily determined. In molecular mechanics, the potential energy of a system or particles can be derived using high level quantum mechanical calculations, and by means of the material constants, the corresponding constants for carbon-carbon covalent chemical bond can be established.

The boundary conditions are assumed to be fixed at one end while the other end is free, this represents the state of CNT in a matrix, where one end is perfectly bonded while the other end stretches sur to loading, resulting in the increase in length. Based on the above assumptions, FE models of different types of CNT were generated.

Moones[3] suggested two new approaches to counteract the computation time and expenses. One is to use a ring model considering a reasonable length for the structure. This involves using a single ring of SWCNT rather than the entire length. The structure's boundary conditions can be modified in a way that the ring represents the entire behaviour of the structure. The difference between the two results is not predominant and can be opted. Second is the DWCNT model where a non-covalent interaction between the two adjacent tubewalls is assumed. This interaction is defined by Lennard-jones potential which is an inverse function of the distance between two walls, which provides a pertinent stiffness matrix. The same model can be adopted for MWCNT since a very small force diagram is required for computations.

Mathew G pike et al[4] used extended finite element method (XFEM) for modelling the mechanical behaviour of 3D short fibre composites considering the phenomenon of interface debonding. The modelling strategy adopted was specifically designed for failure analysis of composites with high aspect ratio which includes the following features:

- The fiber is modelled as a 2D inclusion in a 3D RVE where resolved faces are used for debonding initiation.
- 3D enrichment function used accounts for the traction-separation behaviour and strain discontinuity at the interface.
- Multiple zero measure inclusions are adopted to account for the closely spaced fibers thus avoiding excessive localised meshing.
- The current scenario is suitable for decohesion in tangential as well as normal direction. Multiscale analysis is possible from the suggested computational approach.

The enrichment function of the fiber is the distance function to the fiber body of a randomly placed short fiber in 3D where the value of the said function ranges from zero to highest possible number. This ensures the approximation includes the strain discontinuity. The debonding enrichment function on the other hand introduces a strong discontinuity in the displacement field. A heavyside function is used to model the shape of the debonding in both normal and tangential directions. The debonding is considered only along the plane of the fiber. The debonding along the sides is ignored. XFEM is used to discretize the governing equations. The complexity of the method proposed is dependent on the number of fibres as well as the enrichment degrees of freedom proportional to the fiber density. The FE simulation considering a single fiber is as shown below.

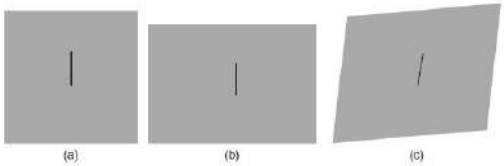

Fig3: 3D FE simulation (a) initial RVE before tensile loading; (b) amplified deformed RVE after tensile loading; (c) amplified deformed RVE after shear loading. (Source: DOI: 10.1061/(ASCE)EM.1943-7889.0001149)

The following figures were obtained from the XFEM of the fibres with respect to debonding. There exists a partial separation between fiber 1 and fiber 2 along its length, this displacement jump is illustrated in figure as a representation of the progressive debonding. The figure is amplified (1 × 105 times) to show the magnitude and shape of displacement jumps.

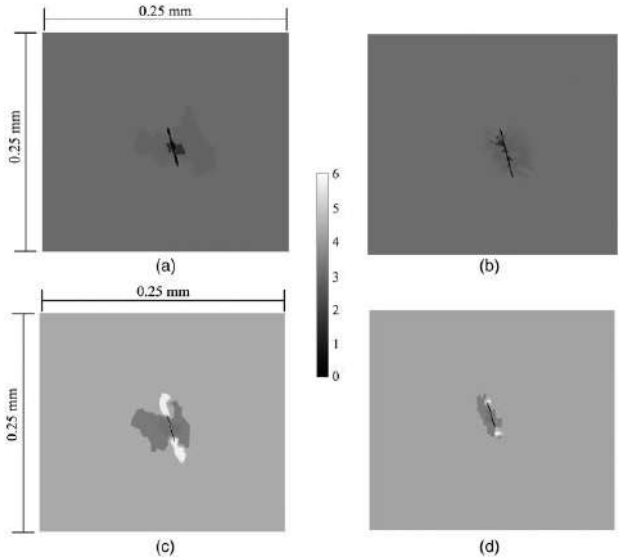

Fig4: Cross-sectional plot of the normal stress in the x-direction (a) reference simulation at peak traction; (b) proposed model of peak traction; (c) reference simulation of maximum debonding; (d) proposed

model of maximum debonding (Source: DOI: 10.1061/(ASCE)EM.1943-7889.0001149)

This debonding is attributed to the effect of fiber orientation and fiber aspect ratio. It has been found that the maximum surface separation occurs when the face of the fiber is parallel to the direction of loading. If the fiber is rotated even slightly, then there is reduction in the magnitude of separation at same loading. This displacement continuously reduces when the fiber rotation makes the face perpendicular to the loading. A fiber aspect ratio of 5 sees the maximum displacement jump. It is found to be inversely proportional to the aspect ratio. This versatility in separation is due to the fiber position and face orientation.

A O Monteiro et al[5] modelled the mechanical response of a CNT subjected to uniaxial compressive loading filled and partially filled with ZnS using FEM approach. It was the first of its kind that adopted continuum approach to model discrete filled CNTs. The model provides an alternative solution to the more complex modelling theories such as density functional theory or molecular dynamics. CNT's were subjected to TEM characterisation in order to determine the structure. The structure was then divided into two different elements, the shell form of carbon to represent the coating carbon layers and solid elements to represent crystalline continuous form of ZnS core that formed the inner filling. The images obtained from TEM is as shown below.

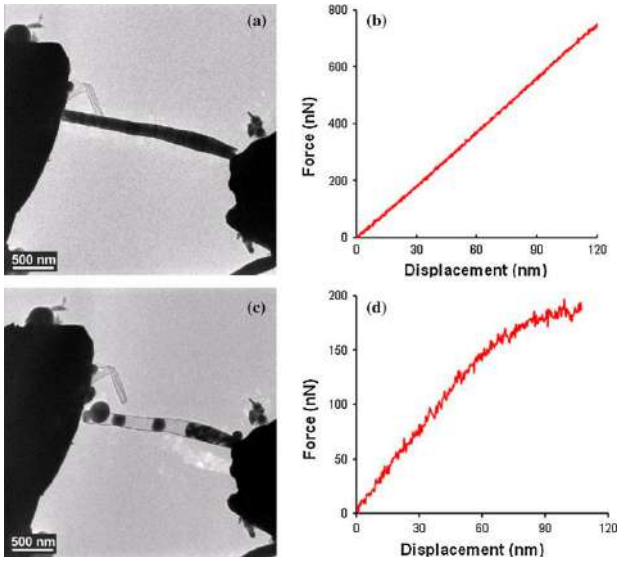

Fig5: TEM snapshot of filled CNT specimen before the application of the electrical current. b compressive F–d plot corresponding to a. c The same structure in a after the application of an electrical current pulse. d F–d plot of c using identical conditions to those in b (Source: J Mater Sci (2014) 49:648–653 DOI 10.1007/s10853-013-7745-3)

Using the stills in the above figure, the geometric modelling was done with CAD software. The analysis was performed using ABAQUS versions 6.9 and 6.11 to better represent the turbostatic texture of the carbon shell, the platelets (clamps) were kept as rigid bodies. The loads applied were corresponding to the displacements measured in TEM experiments. The behaviours of the material was considered as nonlinear elastic. A simplified bilinear tension extension diagram with yield strain of 0.05 was used.

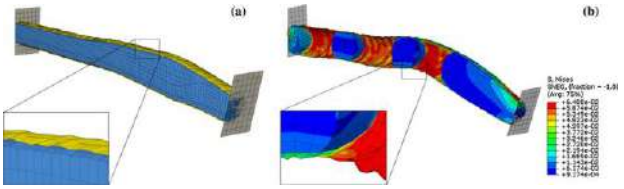

Fig.6 Modelled longitudinal cross-sectional view of the filled CNT in its initial state. b Still of the buckling FEA simulation for the partially-filled CNT. (Source: J Mater Sci (2014) 49:648–653 DOI 10.1007/s10853-013-7745-3)

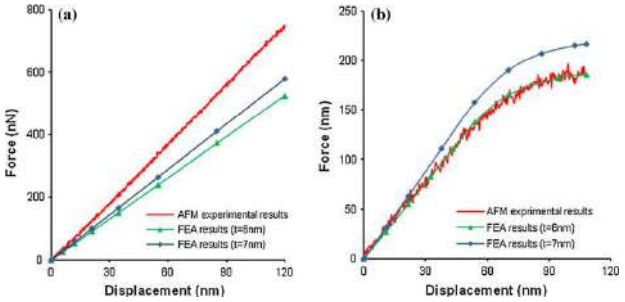

Fig7: F–d plots for experimental and modelled Zn0.92Ga0.08S@CNT subjected to a uniaxial compressive load for both filled (a) and partially filled (b) cases. (Source: J Mater Sci (2014) 49:648–653 DOI 10.1007/s10853-013-7745-3)

FEA simulation of the buckling is at a displacement of 67nm. The void interface shows selective folding in the void region, the color relating to Misses stress field output. It was observed from the TEM images that since the output was in 2D, the opposite ends do not always lie on the same plane. These minor variation will not be visible in the bucking process but they do influence the analysis. To account for this, an off plane rotation was introduced. This introduced difference provided the most coincident experimental modelled results. The optimisation process was complete once the result became consistent for both partially and fully filled conditions as expressed in fig graphs.

A more simpler technique of nano composite modelling is via nano indentation as described by E Schlangen et al.[6] the experiment consisted of preparing small cubes, loaded to failure with a Berkovich indenter to determine the global mechanical properties. This method can be adopted without forgoing the heterogeneity of the cement nano composite. The results obtained can be used as input data for simulations to determine the performance of a metal on a larger scale. The results obtained from the simulations are fracture patterns and indentation

curves which can then be verified by experimental methods on larger scale specimens.

The experiment consisted of obtaining small cubes of 100 micro meter by the use of diamond dicing saw. These samples were then soaked in an ultra-sonic bath to remove any residue from the surface. They were subjected to Agilent G200 nano indenter testing with Berkovich tip. A displacement controlled test was performed by using CSM, which made it possible to obtain crack patterns at different depths. The crushing of samples as observed in ESEM is shown below.

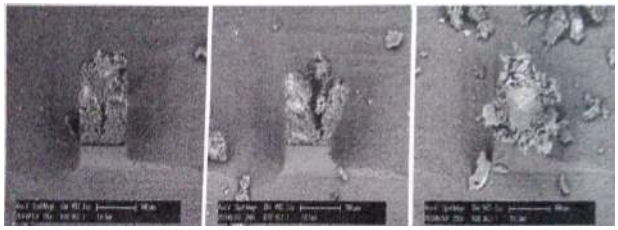

Fig 8: Nano indentation loading of small cubes in three stages as observed in ESEM (Source: concreep10, ASCE)

Modelling of the indented cubes was done using a 3D lattice network. The simulations were constructed using HYMOSTRUC3D. The 3D model was divided into a number of cubic cells and in each cell, a random location for a lattice node was selected. The material heterogeneity was accounted for by ascribing different material properties for elements representing different phases. The result of the simulation is as shown below.

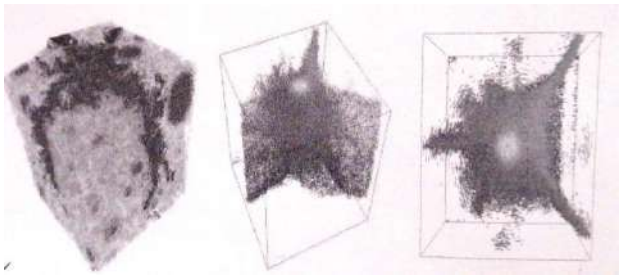

Fig 9: 3D simulation of nano indentation (a) deformed and cracked (b) crack pattern of 3 main localised cracks (c) top view of the same. (Source: concreep10, ASCE)

One can observe a deformed and cracked specimen in fig a. the damage is clearly visible and the final crack pattern shows 3 main cracks under angles of 120 degree.

3. CONCLUSIONS

Based on the above results following conclusions could be drawn from each of the studies conducted-

1. The models designed by F Karimzadeh et al[1] show that the modulus of elasticity can be increased upto 10 times in case of long CNT. There is no such change in short CNT. Also, square RVE's provide more accurate results than cylindrical RVE's as the latter tends to overestimate the effect of young's modulus.
2. It is possible to reduce the number of finite elements to get an appropriate set of results by using the techniques explained by Moones et al[3] The boundary conditions being the key factor. Also, the effect of van der waal's forces can be ignored as there is no considerable effect of the results obtained.
3. The XFEM model proposed by Mathew G Pike et al[4] while suitable to the stipulated conditions poses several challenges in more realistic and complicated expressions.
4. The high aspect ratio of fibers is the main hurdle as to model the realistic fiber fractions of 0.5 and 1% using high aspect ratio fibres results in inclusion of significant number of fibres in the RVE i.e various fibres placed in close proximity to each other, which may affect the overall approximation of the composite.
5. The interface properties were considered uniform along the length of the fiber, but it may differ at different locations depending on the bond strength.
6. In practicality, most fibres adopted have circular c/s and since debonding is determined by loading and not c/s, the method proposed can be generalised for circular c/s fibers.
7. A.O Monterio et al[5] stipulated a need for an iterative process for modelling using an FEA approach to find variables best suited for experimental observations, because of the non-availability of real time tomograms within the electron microscope.
8. The other important aspect to be considered for FEM modelling is an accurate definition of the structure's geometry. For such, CAD 3D is an essential tool. Then comes the optimisation of FEA model to account for local imperfections in the texture.
9. Due to the differential in tips heights from 2D TEM images to 3D FEA models, the young's moduli extracted remain lower than expected due to the conformance of the model to the experimental force readings. However, the agreement remains that applying continuum mechanics is a far better option than other expensive computational tools.
10. E.Schlangen et al[6] showed that a combination of experimental nano indentation technique and modelling technique using 3D discrete lattice model can be applied to study the failure mechanism of nano composite at micro scale.
11. Fitting of local sale properties is acceptable when an experiment on specimen size is available. Using the method presented in the paper, such framework for the modelling can be created. It can also be used for upscaling the modelling and validation at every scale.

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