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AN INVESTIGATION OF NANOTUBE-INTEGRATED BUCKYSHEETS' PROPERTIES WITH MOLECULAR DYNAMICS MODELING AND ANALYSIS

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Abstract:—To better understand the mechanical properties of structures strengthened by carbon nanotubes integration and/or embedding, the Young's moduli of carbon nanotubes and carbon nanotube embedded thin structures are evaluated using atomic-based mechanics and molecular dynamic (MD) simulation studies in this work. Buckysheets with defined ingredients with 50 mg SWNT in 500 ml surfactant-NaOH solution have been fabricated in house for the investigation with the objectives to discovering mechanical properties alteration due to carbon nanotubes integration. The results show that the Young's moduli of single walled (10, 10) carbon nanotubes are ranging from 0.75 TPa to 0.9 TPa, which yields good agreement with the relevant data in the literature. For single layer buckysheets of single-walled tubes, the simulations result in a Young's Modulus around 0.3 TPa. A Four-wall nanotube [(5, 5), (10, 10), (15, 15), (20, 20)] model is built to examine Young's modulus of multi-walled nanotubes. A slightly lower value than that of the single walled model is obtained. The Young's modulus of the fabricated buckysheets exhibits similar characteristics as that of the multi-walled nanotubes'. It is also found that the larger the separation distance between nanotubes in the buckysheet model, the smaller the value of Young's modulus of the structure. The comparisons of the results between the MD simulations and the previously done experimental testing on buckysheets' mechanical properties reveal some discrepancies for their Young's moduli. The higher Young's moduli values for buckysheets obtained in the MD simulations are due to the exclusion of particles impurity, uneven thickness, imperfect nanotubes' alignments, and so on. The study implies that when the fabrication techniques of buckysheets are continuously improved, these thin films carbon nanotube-integrated structures being created will possess higher strengths approaching those of the nanotubes.

Keywords:—Nanotubes, Buckysheets, Engineering properties, Molecular dynamics computation, Young's moduli

I. INTRODUCTION

The outstanding mechanical properties of carbon nanotubes (CNTs) attracted intense researches and motivated proposal of many applications in engineering. One of the "macroscale" forms of carbon nanotubes is the CNT thin film or "buckysheet", has been proposed in recent years and applied in many fields, such as actuating, sensing, field emission [1], and structure damping enhancements [2]. Low density, extremely high stiffness, excellent thermal stability and large aspect ratio make carbon nanotubes an ideal damping material and excellent filler candidate of composites, and we expected that the buckysheets have a good performance in structure damping as well. However, compared to the carbon nanotubes, the modulus of elasticity, or Young's modulus of buckysheets was extreme small, ranging from 1.1 GPa to 24 GPa, according to some experimental works [1], which limited the potential applications of buckysheets. In this section, we introduce molecular mechanics and dynamics simulation method to investigate the Young's modulus (Y) of single-walled CNTs and buckysheets. The simulation models and calculation methods were developed and/or explained, the simulation results were analyzed. In this paper, we apply molecular dynamics (MD) study and computer simulation techniques to help further understand the characteristic properties of carbon nanotube-fabricated, the so-called Buckysheets. Molecular Dynamics (MD) Simulation is a computer simulation technique where the time evolution of a set of interacting atoms is followed by integrating their equations of motion, which provides a powerful tool to obtain the time-dependent properties of N-body system on the nano/molecular/atomic scale [2,3].

In molecular dynamics, the classical Newton's law is used: $F_i = m_i a_i$ (1)

here, m_i is the atom mass, $a_i = {dr_i^2}/{dt^2}$ is the acceleration (r_i is the position of the atom), and F_i is the force acting upon it, due to the interactions with other atoms, which is determined by the gradient of the total potential energy of the system. Given an initial set of positions and velocities, the subsequent time evolution will be completely determined.

A classical algorithm for MD is the Verlet Algorithm [4]. The procedure begins by casting the system in terms of its Newtonian equation of motion of each individual particle of the system.

Verlet algorithm only considers the contribution of inter-particle potential to the force term. The inter-particle potential is modeled as the Lennard–Jones type will be addressed in later section. The solution procedure begins with integration of Eq. (1), where a simple difference equation for the integration was employed:

$$r_i(r+h) = -r_i(t-h) + 2r_i(t)\sum_{i \neq j} F(r_{i,j}(t))h^2 \quad (2)$$

where h is the time step. The particle trajectory can be readily mapped from Eq. (2) with available current and past positions. The rate-limiting step in this algorithm lies in the computation of the inter-particle force, which for a system of N particles requires $N(N-1)/2$ computations at each time step. For a given particle, many of the terms in its summation of forces will be

insignificant due to a large inter-particle separation with a given potential "cutoff distance". So, the algorithm could be accelerated by implementing the Verlet's neighborhood list, which selects the nearest neighbors to include in the computation of Eq. (2). The use of the Verlet's neighborhood list derives a cut-off inter-particle separation, r_M, beyond which the force terms are negligible.

The criterion for the cut-off separation is given as below:

$$r_M - r_V < n\bar{v}h \quad (3)$$

where r_v is the cut-off radius for the particle potential in units of the particle radius σ, n is chosen number of time steps, and $\bar{v}$ is a root-mean-square velocity of the particles. For a chosen n, the algorithm would proceed for n-1 time steps where only particles inside a distance r_M to the particle at the initial time step are included in the force term.

II. MECHANICAL PROPERTIES OF NANOTUBES BY MD SIMULATION

II.1 Young's Modulus

Young's Modulus (or elastic modulus) is one of the important mechanical properties of materials. In classical mechanics the Young's modulus is defined as the ratio of stress to strain before the material sample yields:

$$Y = \frac{\sigma}{\varepsilon} = \frac{F/A}{\Delta L/L_0} \quad (4)$$

where σ is the axial stress, ε is the strain, F is the axial tensile force acted on the objects, A is the cross-sectional area of the object, L_0 is the initial length and ΔL is the elongation under the force F.

In MD simulation, we add the tensile force on the CNTs in axial direction and calculate the variation of the total potential and length, then get the Young's moduli of CNTs.

II.2 Tensile strength

Reference [5] gives a method to predict the tensile strength of single-walled carbon naotubes by MD simulation. A nano-scale finite element approach, named molecular-mechanics based finite element approach was used to derive the SWCNTs' tensile strength as well as tensile stiffness. The nanotube strength was predicted at 77-1-1GPa with the fracture strain around 0.3. The nanotube strength was found to be moderately dependent of the nanotube helicity, but independent of the nanotube diameter.

II.3 Vibration properties

The MD simulation can give all the dynamic information (acceleration, velocity and position) of atomic system, then it has been used for CNTs' vibration properties study by many researchers [6-8].

III. STUDY BUCKYSHEET'S PROPERTIES BY MD SIMULATION

The first step is to investigate the elastic and vibration properties of a cantilevered or bridged single walled carbon nanotube, as shown in Figure 1.

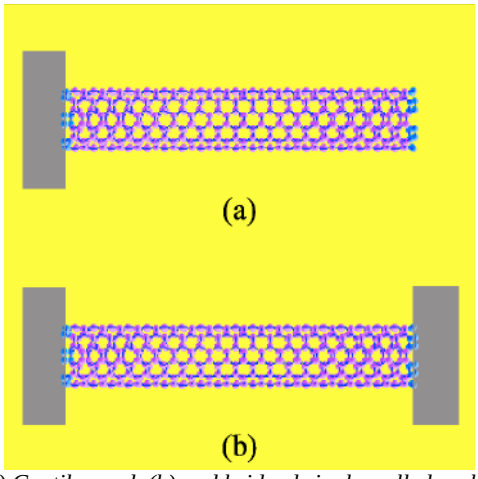

Figure 1 (a) Cantilevered (b) and bridged single walled carbon nanotube

For determining the natural frequencies and mode of a single-walled carbon nanotube, we consider its equivalent space frame-like structure under the condition of free vibration. For the problem of free vibration of an undamped structure, the equation of motion is

$$[M]\{\ddot{y}\} + [K]\{y\} = \{0\} \quad (5)$$

where [M] and [K] are, respectively, the global mass and stiffness matrices, and {y} and $\{\ddot{y}\}$ are, respectively, the nodal displacement vector and acceleration vector. The global stiffness matrix [K] of the frame structure can be assembled from the elemental stiffness matrix $[K]^e$, i.e., $[K]=\sum_{e=1}^{n}[K]^e$, where n is the number of beam elements. The assembling procedure follows the node-related technique in the finite element method.

The global mass matrix [M] can be assembled from the elemental mass matrix. By considering the atomistic feature of a carbon nanotube, the masses of electrons are neglected and the masses of carbon nuclei (m_c=1.9943×10^{-26}) are assumed to be concentrated at the centers of atoms.

Then, the natural frequencies f and mode shapes are obtained from the solution of the Eigen problem

$$([K]_s - \omega^2[M]s)\{y_p\} = \{0\} \quad (6)$$

where, $[K]_s$, $[M]_s$ are the condensed stiffness matrix and condensed mass matrix, respectively, $\{y_p\}$ is the displacement vector corresponding to the primary coordinates, i.e., the translational displacements of carbon atoms, and $\omega=2\pi f$ is the angular frequency.

The second step, more nanotubes will be framed in a square space, they are cantilevered or bridged and entangled with each other. The area of the square is still in nano/micro scale, with the nanotubes aspect ratio 100-1000.

We are trying to simulate the mechanical properties of the nanotube system shown in Figure 2 using the same method as described in the first step.

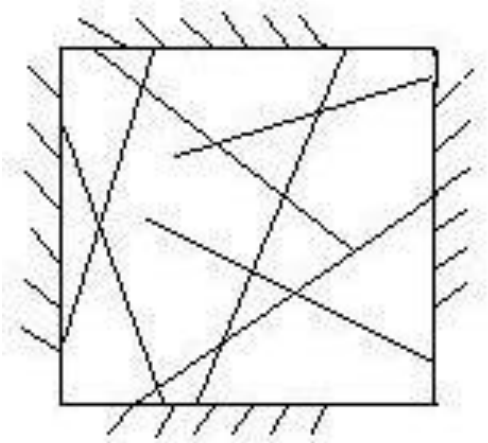

Figure 2 Framed carbon nanotubes

Finally, the framed "nanotube system" in Figure 2 is used as constitutive "elements" of the CNT-integrated thin film (or buckysheet, see the photo shot in Figure 3) and finite element method is used to model and solve the free vibration problem.

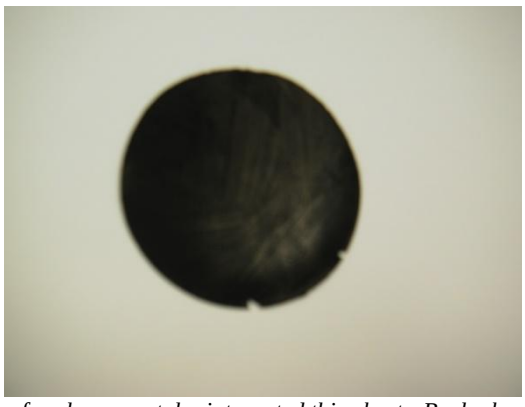

Figure 3 Photograph of carbon nanotube-integrated thin sheet - Buckysheet (Diameter = 40mm, thickness = 30-50 microns)

Multi-walled carbon nanotubes is used to fabricate buckysheets. The properties of the raw materials are listed below with chemical vapor deposition (CVD) technique for the synthesizing method. The material properties for the nanotubes utilized are having purity of 95%, diameter of 10~30nm, length 0.5~ 40μm, and specific surface area in the range of 40 – 300 m^2/g. An SEM snapshot of the thin sheet fabricated is shown in Figure 4 below.

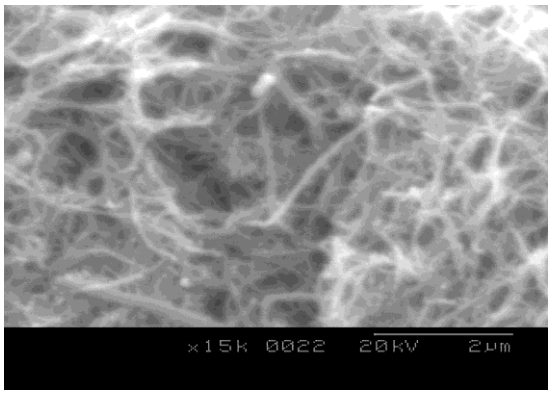

Figure 4 SEM image of a carbon nanotubes-fabricated buckysheet

The SEM image of buckysheets shown above reveals that the nanotube network has composed of continuous NT ropes, which is apparently the result of tube self-assembly by van der Waals force during buckysheet's filtration process.

IV. SIMULATION METHODOLOGY

In the single-walled carbon nanotube model, a (10, 10) CNT was used which spanned the length of the simulation unit cell as shown in Figure 5.

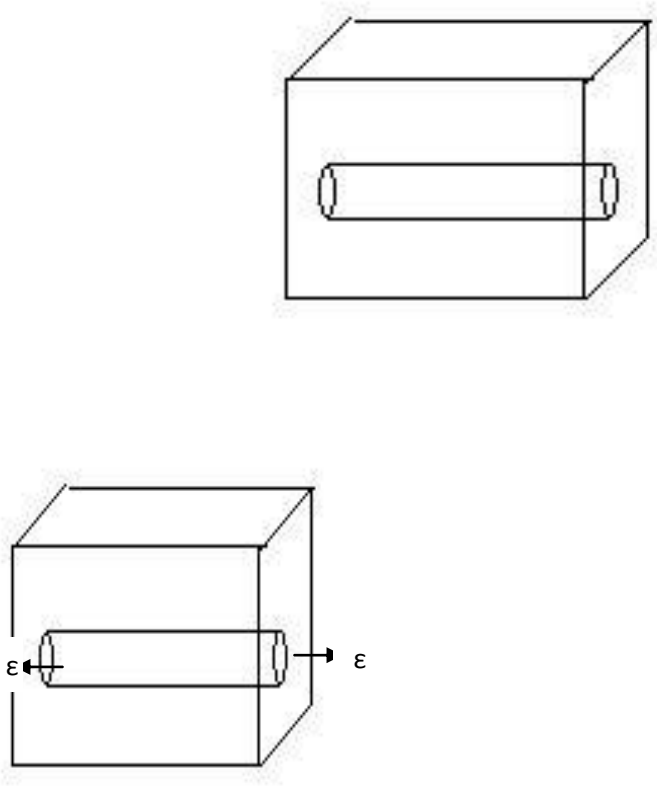

Figure 5 The single walled CNT simulation model and application of strains

The atomic models of single and multilayer buckysheets are created using crossed geometries of single-walled carbon nanotubes. A portion of the single layer buckysheet is shown in Figure 6. Infinitely large one is considered in the calculations. After vacuum filtration process, the obtained CNT thin films or buckysheets consist nanotubes that are not organized and oriented in many directions actually. Here we use an idealized atomic model which contains tube-tube interactions that are found in buckysheets also.

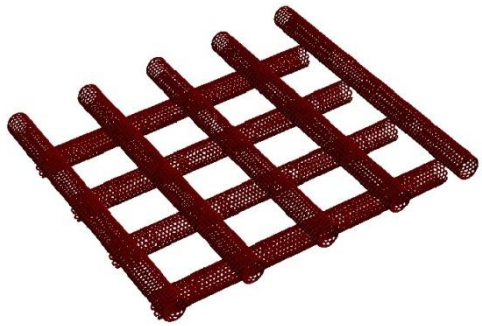

Figure 6 Atomic model of a single (crossed) layer of buckysheets

For the buckysheet atomic simulation model, two (10, 10) single-walled CNTs formed a "separated cross" in a unit cell. The separation distance between the two crossed nanotubes was initially determined by minimizing the strain energy of the model. Under the periodic boundary conditions, the unit cell was replicated in all three dimensions.
We also carried out atomic simulation of the multilayer buckysheets, where several single layer buckysheets were modeled in one unit cell and the periodic boundary conditions were applied. The separation distance among the layers was optimized in the same way as mentioned above.

The molecular mechanics/dynamics simulations calculations were performed using Cerius2/Accelrys software [9]. The application of strain was performed by uniformly expanding the dimensions of the MD cell in the direction of the deformation, then re-scaling the new coordinates of the atoms to fit within the new dimensions [10]. After the initial deformation, the MD simulation was continued and the atoms were allowed to equilibrate within the new MD cell dimensions. In the following increments of deformation, this process was repeated. In each increment, the strain energy was minimized and recorded, then the Young's modulus could be calculated from the second derivative of the strain energy density with respect to various strains [11-13]:

$$\sigma_{ij} = \frac{1}{V}\left(\frac{\partial E}{\partial \varepsilon_{ij}}\right)_S \qquad (7)$$

where V is the volume of the solid, E is the total internal energy, ε_{ij} is the strain tensor, and the subscript S denotes constant entropy.

V. MOLECULAR DYNAMIC SIMULATION RESULTS AND REMARKS

For the single-walled CNT (10,10), the simulation results show that the Young's modulus ranges from 0.75 TPa to 0.9 TPa, which is lower than the value 0.972 TPa obtained by [10], and higher than the results (0.5~ 0.6 TPa) from [12,13].
In the simulation of the single layer buckypaper, the separation distance between the crossed CNTs in the radius direction of the model is 3.1 nm. The Young's Modulus of 0.3 TPa for the buckypaper was obtained. When increase the separation distance from 2nm to 7nm between nanotubes in the buckypaper model, the value of Young's modulus reduced from 0.349 TPa to 0.267 TPa, as shown in Figure 7.

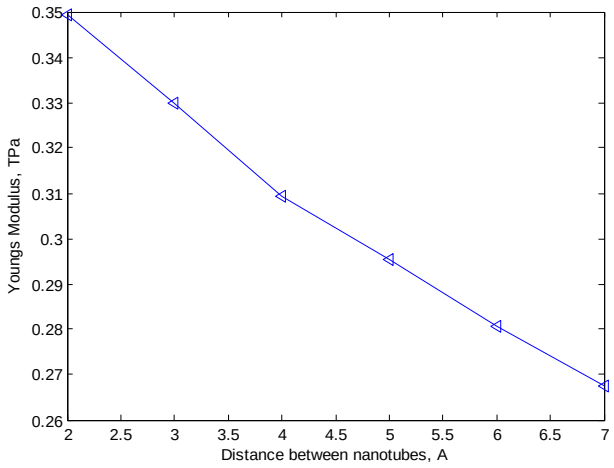

Fig. 7 Young's modulus decreases when increase the separation distance in single layer buckysheets

As to the multilayer buckysheet, the simulation results are depicted in Figure 8. The Young's modulus decreases from 0.326TPa to 0.189 TPa while the layer number of the buckysheet varies from 1 to 5, which is due to the gap between

the buckysheets reduced the stiffness. It can be found that there is a limitation of around 0.18 Tpa in Figure 8, which maygive the bottom line of the buckysheets' Young's modulus value.

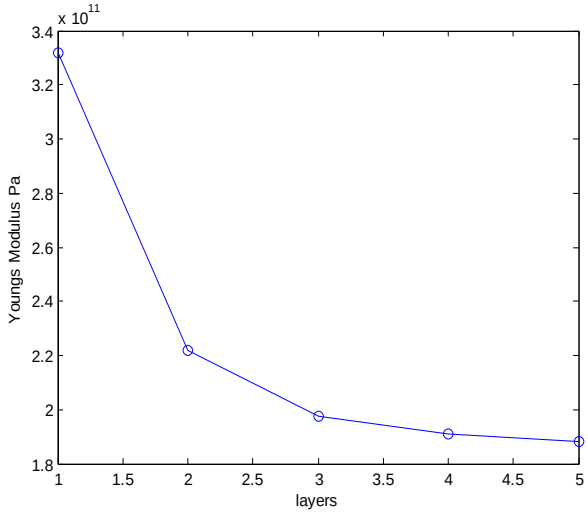

Fig. 8 Variation of Young's modulus with the layer number (X axis: layers; Y axis: Young's modulus, Tpa)

The length of the carbon nanotubes was is same as that of the unit cell of the simulation model of buckysheet. Different length of single walled nantubes at 2.35, 4.8,7.25 and 9.7 nm were used to build the one-layer buckysheet model and then the atomic simulation was accomplished to investigate its affection on the Young's modulus of buckysheets. We find that the shorter the nanotubes' length, the lower the buckysheets' Young's modulus, which is ranging from 0.355 TPa to 0.174 TPa corresponding to the above given lengths, as shown in Figure 9.

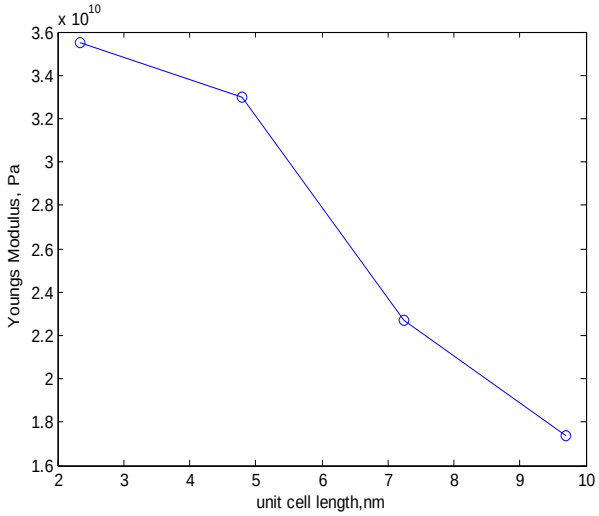

Fig. 9 Variation of Young's modulus with the unit cell length (X axis: Unit cell length, nanometer; Y axis: Young's modulus, TPa)

The obtained Young's moduli values for buckysheets were much bigger than the pervious experimental results; the most important reason for that was the simulation model disregarded lots of flaws such as impurity particles, uneven thickness and not well aligned which can significantly reduce the Young's modulus of buckysheets; at other side, these value may represent the upper limit of Young's modulus and implied that our existing fabricating method of buckysheets need to be improved.

VI. CONCLUSIONS

The physical properties of carbon nanotube sheets, i.e., buckysheets were studied through finite element analysis, experimental work and atomic scale simulation, in order to find viable applications of them in structural materials, electro-mechanical systems and multifunctional systems. Buckysheets were fabricated in house using vacuum filtration techniques. SEM images showed that buckysheets created were composed of continuous nanotube ropes network, which was the result of nanotube's self-assembly by van der Waals force and capillary forces during filtration of the carbon nanotubes' suspension phenomena. The atomic scale and molecular dynamics simulations were employed to study the mechanical properties of the carbon nanotubes and buckysheets. The atomic models of carbon nanotubes and single and multilayer buckysheets were created to investigate the molecular mechanics/dynamics of nunotubes and buckysheets so as to

understand their mechanical properties. The results pointed out that for single layer buckysheets, the Young's Modulus was approximately 0.3 TPa. When increasing the separation distance between nanotubes in the buckysheets model, the value of Young's modulus clearly reduced. It's found that the obtained Young's moduli values for buckysheets were much bigger than the experimental results we obtained previously. The most likely reason for that was that the simulation model disregarded lots of flaws due to impurity particles, uneven thickness and not well aligned tubes which could significantly reduce the Young's moduli of buckysheets. However, these higher Young's moduli may represent potential optimum strengths of buckysheets which motivates us to improve fabricating methods in such a way that we can take full advantages of carbon nanotubes' outstanding mechanical properties to benefit their integrated material strengths.

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