Transversely Isotropic Elastic Properties of Vacancy Defected Boron Nitride Nanotubes Using Molecular Dynamics Simulations

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Abstract: Recent breakthroughs in the synthesis of boron nitride nanotubes (BNNTs) attracted researchers’ attention again for developing their nanocomposites. This is due to the fact that BNNT possesses wide band gap (~5.5 eV, independent of geometry), strong hardness, chemically and thermally stable, and excellent piezoelectric properties than its carbon-based counterpart. Furthermore, BNNTs have comparable mechanical and thermal properties compared to carbon nanotubes. As the first of its kind, this study reports the transversely isotropic elastic properties of pristine and vacancy defected BNNTs within the framework of MD simulations using a Tersoff force field. This is achieved by imposing axial extension, twist, in-plane biaxial tension, and in-plane shear to the pristine and defective BNNTs. Our results reveal that vacancy concentration of 2% affects profoundly the axial Young’s, shear, plane strain bulk and in-plane shear moduli of BNNTs, and decrease their respective values by 14%, 25%, 14% and 18%. The current fundamental study highlights the important role played by vacancy defected BNNTs in determining their mechanical behaviours as fillers in multifunctional nanocomposites.

Keywords-Boron nitride nanotube, molecular dynamics, transversely isotropic properties, vacancy defects.

I. INTRODUCTION

The milestone experimental finding of carbon nanotubes (CNTs) by Iijima and their exciting mechanical [1]–[3], electrical [4], and thermal [5] properties were encouraged the study of another types of nanotubes. Boron nitride nanotubes (BNNTs) were theoretically predicted in 1994 [6] and synthesized in 1995 [7]. Experimental and theoretical studies showed that BNNTs are constant band gap (5.5 eV) materials regardless of the tube chirality and morphology [8]. BNNTs thermally and chemically more stable than the CNTs. On the other hand, BNNTs display a comparable mechanical [9] properties to CNTs. Such remarkable properties make BNNTs suitable for many multifarious applications such as composite material [10], [11], hydrogen storage [12], transistors and optoelectronic [13]. With the rapid use of BNNTs in load-carrying composite structures, it becomes essential to investigate mechanical properties of BNNTs accounting inherent impurities and defects evolved in them during their production.

The synthesizing processes of BNNTs promote the presence of topological defects such as atom vacancies, anti-sites, doping [14] and Thrower-Stone-Wales (TSW) [15] defects. On the other hand, defects in BNNTs are being introduced controllably by irradiation [16] which can help the tailoring of tubes properties. Evolved defects [17] play a key role to alter unique mechanical properties of BNNTs. Therefore, it is necessary to study the influence of defects on the mechanical behavior of BNNTs. There have been numerous studies conducted to investigate the mechanical properties of BNNTs subjected to uniaxial loadings using various techniques such as tight-binding [18], molecular dynamics (MD) simulations [19], and molecular mechanics [20]. Li and Chou [21], and Santosh et al. [22] used molecular mechanics approach to study the torsional properties of BNNTs. Krishnan and Ghosh [23] studied the chirality dependent elastic properties of BNNTs under uniaxial and torsional loadings. For the first time in literature, vacancy defects were observed by Schmidt et al. [14] in BNNTs. A further study carried out by Li et al. [24] showed that vacancy defects affect the reactivity of BNNTs and play a critical role in their electronic structures. A MD study by Griebel et al. [17] on the vacancy defected BNNT indicated that its Young’s modulus decreases with increase in vacancy defects. Wang et al. [25] studied the stiffness, intrinsic strength and failure strain of TSW and single vacancy defected BNNTs. Their results revealed that vacancy defects significantly affect the mechanical properties of BNNTs compared to that of TSW defects.

In the literature, to the best of our knowledge, BNNTs are considered as isotropic for studying their mechanical properties as well as influence of defects. This indeed provided us the motivation for the current study. In this work, MD simulations were performed to investigate the influence of vacancy defects on the transversely isotropic properties as well as fracture behavior of BNNTs.

II. MODELING

One of the most widely used tools in the theoretical study of nanostructures is the method of MD simulations. The MD approach calculates the time-dependent behaviour of a molecular system and permits accurate predictions of interactions between atoms and molecules at the atomic level with the integration of the corresponding Newton’s equation of motion [17]. In the current study, all MD simulations were
performed using open source software, LAMMPS [26], and molecular interactions were modeled in terms of three-body Tersoff-type potential force field [27]. The investigation of transversely isotropic elastic properties of BNNTs was accomplished via the use of the strain energy density-elastic constant relations. An annular structure of a BNNT was assumed as the equivalent continuum structure considering its effective wall thickness \( t \) as 3.4 Å [19], its cross-sectional area (A) as \( \pi(D_{\text{o}}^2 - D_{\text{i}}^2)t/4 \) and volume (V) as \( A l \), where \( D_{\text{o}} \) and \( D_{\text{i}} \) are the outer and inner diameters, and \( l \) is the length of a BNNT. In the current work, we applied the load to a BNNT and then computed the energy as the result of interatomic interactions of atoms. A direct transformation to continuum and then computed the energy as the result of interatomic interactions of atoms is equal to the strain energy density of the continuous substance occupying the same BNNT volume. This approach has been widely used by many researchers for single walled carbon nanotubes [2], [19].

First, the BNNT structures were prepared. Then, simulations were performed with an energy minimization using a conjugate gradient method to obtain the optimized atomic structures of BNNTs. Each simulation was performed in the constant temperature and volume canonical (NVT) ensemble using a time step of 0.5 fs with a total time of 50 ps to equilibrate the BNNT structures. Velocity Verlet algorithm was used to integrate Newton’s classical equations of motion. Vacancy defected BNNTs were created by removing the same number of boron (B) and nitrogen (N) atoms from the middle segment of (10, 10) pristine BNNTs as shown in Fig. 1. The vacancy concentration (\( \rho \)) is calculated using the below relation:

\[
\rho = \frac{\text{number of removed atoms}}{\text{total number of atoms}} \times 100\% \tag{1}
\]

To evaluate the five independent elastic moduli, four loading conditions i.e., uniaxial tension for axial Young’s modulus and major Poisson’s ratio, the torsional moment for axial-shear modulus, in-plane biaxial tension for plane strain bulk modulus, and in-plane shear for in-plane shear modulus were applied to the BNNTs. Schematics of these loading conditions are shown in Fig. 2. Defined strain increments of 0.05% were applied to the BNNTs followed by the potential energy minimization process. We deformed a BNNT in small strain increments to equilibrate its deformed state over an interval of 30 ps to reduce the effect of interatomic fluctuations. The temperature of the system was maintained at 300 K using Nose-Hoover thermostat. The loading steps were repeated until the BNNT’s structure fractured to seize its true failure response. Under applied deformations, potential energy of BNNT was calculated throughout the simulations. The change in the potential energy is equivalent to stored strain energy in the BNNTs and then we used these data to obtain the stress-strain curves to determine five independent elastic moduli.

**Axial Young’s modulus (\( E_1 \))**: The value of \( E_1 \) was calculated from the initial slope of the stress-strain curve and deformation energy density-elastic constants relations. The axial stress was determined by assuming a uniform tensile stress distribution over the cross-sectional area of the BNNT; as follows:

\[
\sigma_{\text{axial}} = \frac{1}{V} \frac{dE}{d\varepsilon} \tag{2}
\]

where \( \sigma_{\text{axial}} \) is the longitudinal stress, \( \varepsilon \) is the axial strain, \( V \) is the volume of a BNNT, and \( E \) is the stored strain energy in a BNNT. Accordingly, the strain energy density of a BNNT can be expressed as

\[
U = \frac{1}{2} E_1 \varepsilon^2 \tag{3}
\]

in which \( U \) is the strain energy per unit volume and is given by,

\[
U = \frac{\Delta E}{A l} \tag{4}
\]

where \( \Delta E \) is the increment of the potential energy, \( A \) is the cross-sectional area of a BNNT, \( \varepsilon = \Delta l/l \) is the axial strain of a BNNT, and \( \Delta l \) is the increment of a BNNT length. Using the following definition, the major Poisson’s ratio (\( \nu_{12} \)) of a BNNT can be obtained,

\[
\nu_{12} = -\frac{\varepsilon_{22}}{\varepsilon_{11}} \tag{5}
\]

where \( \varepsilon_{22} \) and \( \varepsilon_{11} \) are the respective circumferential and axial strains.

**Longitudinal shear modulus (\( G_{12} \))**: A BNNT was subjected to a twisting moment with a constant rotation of 0.81°/ps. The strain energy density of a BNNT can be expressed as

\[
U = \frac{G_{12} \phi^2 J}{2l} \tag{6}
\]

in which \( \phi \) is the angle of twist of a BNNT and \( J \) is the polar moment of inertia; viz, ...
Using all other independent elastic constants [2], the ratio are dependent elastic constants and can be calculated with existing results [19] and the comparison was found to be in good agreement.

\[ J = \frac{\pi}{32} [D_o^4 - D_r^4] \]  

(7)

**Plane-strain bulk modulus (K23):** A BNNT was subjected to two-dimensional plane-strain condition. The plane strain bulk modulus (K23) of a BNNT can be obtained using the following definition [1], [2],

\[ U = 2K_{23}\varepsilon_{22} \]  

(8)

In-plane shear modulus (G23): A BNNT was subjected to in-plane pure shear at small strains in such way that its circular cross-section perimeter deforms into an elliptical shape. The in-plane shear modulus can be determined using the following relation [1], [2]:

\[ U = 2G_{23}\varepsilon_{22} \]  

(10)

Transverse Young’s modulus (E2) and minor Poisson’s (ν23) ratio are dependent elastic constants and can be calculated using all other independent elastic constants [2].

### III. RESULTS AND DISCUSSION

To verify the validity of current MD simulations, the three elastic constants: Young’s modulus, major Poisson’s ratio and shear modulus of pristine (10, 10) BNNTs were compared with existing results [19] and the comparison was found to be in good agreement.

Table 1: Five independent engineering constants of (10, 10) BNNTs

<table>
<thead>
<tr>
<th>ρ</th>
<th>Engineering constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E1 (TPa)</td>
</tr>
<tr>
<td>0 %</td>
<td>1.064</td>
</tr>
<tr>
<td>Ref. [19]</td>
<td>1.065</td>
</tr>
<tr>
<td>1 %</td>
<td>0.926</td>
</tr>
<tr>
<td>2 %</td>
<td>0.896</td>
</tr>
</tbody>
</table>

Subsequently, we performed MD simulations on pristine and vacancy defected (10, 10) armchair BNNTs until they fractured under the uniaxial loading. The variation of potential energy (PE) of BNNTs subjected to uniaxial tension is shown in Fig. 3.

![Fig. 3: Variation of PE of pristine and vacancy defected armchair (10, 10) BNNTs](image)

Fig. 4 shows stress-strain curves of armchair (10, 10) BNNTs with maximum stress being 93 GPa at strain 0.48-0.50. The sets of energy-strain and stress-strain curves obtained in the current study are found to be in good agreement with those obtained for pristine BNNTs in the existing MD study [28]. It may be observed from Fig. 4 that the defected BNNTs were fractured at lower strain levels than pristine BNNTs. Table 1 demonstrates the influence of vacancies on the axial Young’s moduli of BNNTs. As expected, larger vacancy concentration (2%) significantly affects the mechanical behaviour of BNNTs. Although it is not shown here, the trends of major Poisson’s ratios are found to be same as those shown in Fig. 4.

![Fig. 4: Stress-strain curves for pristine and vacancy defected armchair (10, 10) BNNTs.](image)

We performed MD simulations on pristine and vacancy defected armchair BNNTs until they fractured under the torsional loading, in-plane bi-axial tension, and in-plane shear. For the sake of brevity, we showed energy-strain curve for a BNNT considering only axial loading. Using strain energy density-elastic constant relations, we obtained values of G12, K23 and G23 as summarized in Table 1. Fig. 5 shows MD snapshots of BNNTs during continuous applied twist and illustrates the variation of the potential energy with the rotational angle for pristine and vacancy defected BNNTs. It shows that the BNNT first twist with a flattening effect start at angle of 150° (Fig. 5a). At this point, a BNNT begins to show localized collapse. At critical angle of 398° (Fig. 5b), failure of the bonds start begins along the spiral direction around the nanotube and bonds entirely break at an angle of 541° as illustrated in Fig. 5c. The observed twisting deformation patterns are in good agreement with the patterns found in existing study [29].

![Fig. 5: Snapshot of twisting of pristine armchair (10, 10) BNNT.](image)

The effect of vacancies on G12 found to be more pronounced (see Table 1). The values of G12 reduce by 12% and 25% for 1% and 2% vacancy concentrations, respectively. Fig. 6 illustrates the failure of a BNNT subjected to in-plane bi-axial tension. The failure under in-plane loading starts at a strain value of 0.3 (Fig. 6a) with bond-I shown in inset view of Fig.
At a critical strain of 0.38 (Fig. 6b), failure of B-N bonds occurs and a BNNT completely fractures. A similar trend was observed for the BNNT under in-plane shear loading but not shown here.

Fig. 6: Failure of BNNTs under in-plane bi-axial tension

IV. CONCLUSION

In this work, we performed MD simulations to determine the transversely isotropic elastic properties of pristine and vacancy defected BNNTs. Our results reveal that the existence of vacancy defects in BNNTs reduces their mechanical properties and strength. The vacancy concentration of 2% affects profoundly all the elastic moduli of BNNTs. The current work shows that vacancy defects play important role in BNNTs which can be engineered and used to alter the properties of their nanocomposite structures for functional applications.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support provided by the Science Engineering Research Board (SERB), Department of Science and Technology, Government of India. S.I.K. acknowledges the generous support of the SERB Early Career Research Award Grant (ECR/2017/001863).

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