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The morphology and temperature dependent tensile properties of diamond nanothreads

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ABSTRACT

The ultrathin one-dimensional sp^3 diamond nanothreads (NTHs), as successfully synthesised recently, have greatly augmented the interests from the carbon community. In principle, there can exist different stable NTH structures. In this work, we studied the mechanical behaviours of three representative NTHs using molecular dynamics simulations. It is found that the mechanical properties of NTH can vary significantly due to morphology differences, which are believed to originate from the different stress distributions determined by its structure. Further studies have shown that the temperature has a significant impact on the mechanical properties of the NTH. Specifically, the failure strength/strain decreases with increasing temperature, and the effective Young's modulus appears independent of temperature. The remarkable reduction of the failure strength/strain is believed to be resulted from the increased bond re-arrangement process and free lateral vibration at high temperatures. In addition, the NTH is found to have a relatively high bending rigidity, and behaves more like flexible elastic rod. This study highlights the importance of structure-property relation and provides a fundamental understanding of the tensile behaviours of different NTHs, which should shed light on the design and also application of the NTH-based nanostructures as strain sensors and mechanical connectors.

1. Introduction

Past decades have witnessed huge interests from both scientific and engineering communities on the carbon-based nanostructures, such as fullerenes (0D), carbon nanotube (CNT, 1D) [1], diamond nanowire (DNW, 1D) [2], and graphene (2D) [3]. Their intriguing chemical and physical properties have enabled them as versatile and excellent integral parts for the next generation of devices [4,5] or multifunctional materials [6] (from 1D nano-fibers/yarns [7,8] to 2D nanomesh [9], and 3D porous structures [10]). Particularly, driven by their high elastic modulus [11], strength-to-weight ratio, chemical inertness, high thermal conductivity, and relatively easy functionalization, the sp^3 bonded DNWs have received an increasing research focus [12–14]. Studies have shown that DNWS have appealing applications as energy absorbing material under UV laser irradiation [15], high efficiency single-photon emitters (with stable and room-temperature operation) [16], and DNA sensing [17,18].

The attractive usages of DNW have motived researchers to seek effective ways to fabricate/synthesis DNWs with different sizes [19]. Very recently, a new 1D sp^3 diamond nanostructure has been reported, termed as diamond nanothread (NTH) [20], which is synthesised through the slow decompression of crystalline benzene in large volume high-pressure cells. Essentially, the diamond NTH is a close-packed sp^3-bonded tubular carbon structure, which can be regarded as hydrogenated (3,0) CNTs connected with Stone-Wales (SW) transformation defects [21]. The SW transformation defects interrupt the tubular structure of the diamond NTH. Generally, the diamond NTH is similar to the ultra-thin DNW as formed inside the CNT from diamantine dicarboxylic acid [22].

In fact, different 1D thread-like sp^3 C–H polymers have been proposed previously from different perspectives, e.g., tube (3,0) [21], polymer I [23], and polytwistance [24,25]. Encouraged by this experimental success, several systematic theoretical studies have been carried out to predict other possible atomic structures of NTHs, By enumerating the hexavalent bonding geometries of the benzene molecules, Xu et al. [26] have identified 50 topologically

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distinct NTHs, 15 of which are within 80 meV/carbon atom of the most stable member. Excellent mechanical property has been observed in one of the possible diamond NTHs[19]. However, considering such diversity in the NTH family, it is of great interest to know how the mechanical properties of the NTH will differ from each other. Furthermore, the effect of temperature and dynamical information about the bond-rearrangement process under strain still remain elusive. In this work, we explore the mechanical properties of NTHs through large-scale molecular dynamics simulations. We find that the mechanical properties of NTH can vary vastly from each other, and the temperature has a significant influence on their mechanical performance.

2. Methods

Various NTHs were constructed by varying the bonding patterns between benzenes, which leads to the formation of pentagon, hexagon, heptagon and octagon carbon rings. The 15 most stable NTH members can be classified into three groups including achiral (six models), stiff-chiral (four models) and soft-chiral (five models) [26]. In this work, we selected one representative NTH from each group, denoted as NTH-I (achiral), NTH-II (stiff-chiral) and NTH-III (soft-chiral), respectively. The atomic configurations of these three NTHs are illustrated in Fig. 1. It is seen that these NTHs have totally different morphologies, i.e., NTH-I shows a zigzag structure, NTH-II appears more like a tube, while NTH-III has a helical morphology. The mechanical properties of different diamond NTHs were acquired through a series of tensile tests performed using large-scale molecular dynamics (MD) simulations.

For comparison purposes, a similar initial length was chosen for each sample (with periodic boundary conditions in the length direction), i.e., 23.9 nm for NTH-I, 23.5 nm for NTH-II, and 22.4 nm for NTH-III. To initiate the simulation, the widely used adaptive intermolecular reactive empirical bond order (AIREBO) potential was employed to describe the C—C and C—H atomic interactions [27,28]. This potential has been shown to represent well the binding energy and elastic properties of carbon materials. The C—C cut-off distance was chosen as 2.0 Å. The structures were firstly optimized by the conjugate gradient minimization method and then equilibrated using Nosé-Hoover thermostat [29,30] for 2 ns (under isothermal-isobaric ensemble). To limit the influence from thermal fluctuations, a low temperature of 1 K was adopted initially. The tensile deformation was achieved by applying a low constant strain rate (namely, 10^{-7} fs^{-1}) to the fully relaxed structure, and the structure is relaxed for 5 ps after every 0.1% strain increment in the sample. The simulation was continued until the failure of the NTH. A small time step of 0.5 fs was used for all above calculations with all MD simulations being performed using the software package *LAMMPS* [31].

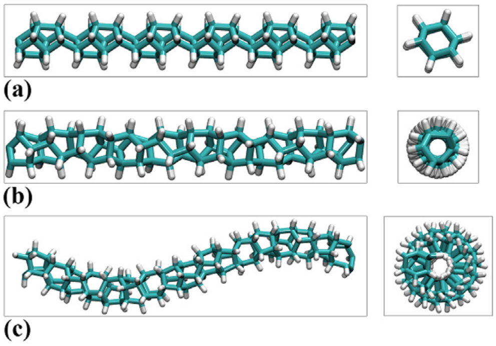

Fig. 1. Atomic configurations of the representative NTHs: (a) achiral NTH-I; (b) stiff-chiral NTH-II; (c) soft-chiral NTH-III. Left shows the view perpendicular to the axis and right shows the cross-sectional view. (A colour version of this figure can be viewed online.)

During the tensile simulation, the commonly used virial stress was calculated, which is defined as [32].

$$\prod^{\alpha\beta} = \frac{1}{\Omega}\left\{ -\sum_i m_i v_i^{\alpha} v_i^{\beta} + \frac{1}{2}\sum_i \sum_{j\neq i} F_{ij}^{\alpha} r_{ij}^{\beta} \right\} \tag{1}$$

Here, Ω is the volume of the system; m_i and v_i are the mass and velocity of atom i; F_{ij} and r_{ij} are the force and distance between atoms i and j; and the indices α and β represent the Cartesian components. Considering the large morphology difference among the studied samples, we adopted the linear atom density (λ, in the unit of atoms/Å) to calculate the volume of the structure following Xu et al. [26], which is about 2.41, 2.45 and 2.91 atoms/Å for the three NTHs, respectively. Such approach has been previously utilized to characterize the (3,0) and (2,2) sp^3 carbon tubes [21], and is further systematized for the elastic moduli calculation of nanoscale materials [33]. With the linear atom density, the cross-sectional area of the structure can be approximated by λV_0. Here V_0 is a reference atomic volume for carbon atom in bulk diamond, which is about 5.536 Å^3/atom [21]. To note that adopting different approaches to calculate the cross-sectional area of the NTH would yield to different absolute values of stress, while it will not influence the scaling behaviours as we focused in this paper. According to Eq. (1), the engineering stress is calculated after the relaxation process after each 0.1% strain increment. Correspondingly, we derived the engineering strain based on the applied constant strain rate.

3. Results and discussions

3.1. Structural influence

Initially, we assess the tensile behaviours of these NTHs. As compared in Fig. 2, the NTHs possess different stress-strain curves, whereas, all NTHs exhibit brittle behaviour, i.e., the stress experiences a sudden drop after continuously increasing to a threshold value. According to the atomic configurations, the NTH starts to fail after passing the threshold value. Thus, this threshold stress is regarded as the failure strength and the corresponding strain is designated as the failure strain. From Fig. 2, NTH-I and NTH-III have similar failure strain, i.e., ~16% and ~18%, respectively. In comparison, a much larger failure strain is observed from NTH-II, which is about 22%. Similarly, NTH-II shows the highest failure strength (around 141 GPa), followed by NTH-I (~86 GPa). As expected, the soft-chiral type NT-III exhibits the lowest failure strength of about 79 GPa. The effective Young's modulus, which is a placeholder for the tensile stiffness, is also extracted from the stress-strain curve using linear regression. Based on the assumption of linear elasticity, the initial linear regime with the strain up to 3% has been selected for the fitting, as is widely applied to evaluate the mechanical properties of nanomaterials in previous studies [19,34–36]. Consistent with the failure strength/strain, NTH-II shows the highest Young's modulus (about 1.09 TPa), followed by NTH-I (about 0.66 TPa) and NTH-III (~0.29 TPa). Of interest, we compare the estimated Young's modulus with other one-dimensional carbon allotropies, i.e., CNT and the monoatomic carbyne. According to Liu et al. [37], the monoatomic carbyne chain, has a Young's modulus around 1.3 TPa, which is close to the NTH-II, but much higher than NTH-I and NTH-III. Similarly, the single-wall CNT is reported to possess a Young's modulus around 1 TPa [38], close to our estimate for NTH-II.