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Predicting mechanical properties of carbon nanosprings based on molecular mechanics simulation

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ABSTRACT

A carbon nanospring (CNS) is formed by coiling a single-walled carbon nanotube around a cylindrical surface with a uniform pitch length and a uniform spring rise angle. Using the displacement-controlled tension method, the mechanical properties of small-radius and large-radius CNSs are investigated based on a molecular mechanics (MM) simulation. The tension behaviour of a small-radius CNS with more turns is similar to that of a mechanical spring. The spring stiffness of a three-turn CNS is calculated to be 0.36 N/m with a maximum of 38% elongation for its elastic deformation. Although a large-radius CNS with more turns cannot be uniformly stretched along its axial direction, it has excellent flexibility without structural damage even when the CNS is stretched to a carbon nanotube (CNT). It is found that the spring stiffness of a large-radius CNS with one turn and two turns are both nonlinear. For a one-turn CNS, the stiffness first decreases and then increases with the tension displacement and less influenced by the chiral type.

1. Introduction

Carbon nanotubes are perhaps one of the greatest scientific discoveries which possess superior material properties [1–3]. Carbon nanotubes can be used for reinforcements in composite structures [4–7]. Coiled carbon nanotubes (CCNTs) have attracted much attention because of their special helical tubular structure, superelasticity and large surface area [8–12]. To date, among the many CCNT morphologies that have been observed, the two main categories are amorphous and regular CCNTs, where the former is composed of nano-graphite grains through linked disordered carbon atoms [13–15] and the latter is formed from and coiled by carbon nanotubes [16–19].

Because the regular CCNTs can uniformly and dispersedly absorb metal atoms and have better aero-tolerance to corrosion than the amorphous shapes, they have great potential for applications in new energy applications [13,20], such as acting as the carriers of electrode materials in fuel cells or supercapacitors. Therefore, researchers have shown greater interest in the regular CCNTs than in the amorphous ones. Liu et al. [21] fabricated single N-doped helical carbon nanotubes (N-HCNTs) and reported both high generation of photocarriers and high bimolecular recombination rate. Moreover, CCNTs formed from different carbon nanotubes (CNTs) demonstrate special electronic properties. Akagi et al. [22] employed tight-binding models to study the general features of the electronic states of helically coiled cages of graphite layers. These authors reported that the topological structure of the cages, as determined by the distributions of five- and seven-membered rings, governed the electronic behaviour nears the Fermi level. In studies of the structural properties of CCNTs, Ihara and Itoh [23] used a molecular dynamics simulation to determine the helical structures (C_{360}, $C_{540,}$ C_{1080}) consist of sevenfold, sixfold and fivefold carbon-atom rings and provide the thermal stability.

Like CNTs, the regular CCNTs, which have been investigated using both experimental and theoretical methods, also exhibit extraordinary mechanical properties [24–29]. Volodin et al. [24] studied the elastic properties of helical nanotubes by employing a circular beam approximation to model the elastic response of a single winding of a coiled nanotube, and the results showed that coiled multi-walled CNTs maintained a very high Young's modulus, comparable to that of the hexagonal graphene sheets. By loading an amorphous carbon nanocoil under tension inside a scanning electron microscope (SEM), Chen et al. [25] measured the spring constant of the nanocoil to have a value of 0.12 N/m in the

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low-strain regime (approximately 12%). Wang et al. [26] employed the classical molecular dynamics (MD) simulations to investigate the specific properties of a CCNT under compression, tension, recompression, retension, and pullout from a polyethylene (PE) matrix. The results showed that the spring constant was 10.1 N/m and the yielding strain was 30% for a two-turn nanocoil with a rising angle of 13.2°. Using the density functional theory, Liu et al. [27] computed the Young's moduli and spring constants of small-radius CCNTs, showing that CCNTs exhibit superelastic properties upon elongation and compression. Fonseca and Galvao [29] studied the elastic properties of amorphous nanosprings based on a Kirchhoff rod model and derived expressions that can be used to obtain the Young's modulus and Poisson's ratio of a nanospring material composite.

Despite these promising reports, little work has been performed on CCNTs without topological defects, called carbon nanosprings (CNSs) in this study. However, the presence of defects may reduce the excellent performance of CCNTs, e.g., their efficiency as carriers of applied micro-reactors or bio-sensors, because the activity of a pentagonal carbon-atom ring is much higher than that of a hexagonal one. Moreover, a CNS can also be viewed as part of a multi-filament spun yarn, and its tension behaviour and spinnability [30] should be worth to examine. Therefore, it is highly significant and valuable to investigate the mechanical properties of CNSs.

In our previous work [31], by exploring the molecular mechanics (MM) simulations, we studied the stability of CNSs and demonstrated that all large-radius CNSs are stable, while the stability of a small-radius CNS is primarily determined by its rise angle. In this work, we focus our study on various parameters of CNSs, such as the spring diameter, chiral type, rise angle and number of turns, to investigate their effects on the mechanical characteristics of CNSs using the MM simulations. The spring stiffness is determined through the calculation of the stored potential energy for a CNS subjected to a uniform displacement-controlled tension on one end.

2. Molecular modeling and simulation of CNSs

2.1. Modeling details

The critical spring diameter for distinguishing large-radius and small-radius CNSs (5, 5) is 8.5 nm [31]. In this study, only stable CNSs are discussed. A stable small-radius CNS has a flat shape and a small rise angle, and the allowable range of rise angle for stable CNS differs depending on its radius. Here, small-radius CNSs (5, 5) with a spring diameter of 4.6 nm and various numbers of turns are considered. For large-radius CNSs (5, 5), four nanosprings with spring diameters of 12.4, 16.3, 20.2 and 24.2 nm are analysed. These springs have different spring rise angles and different numbers of turns. In addition, to elucidate the effect of the chiral type on the mechanical properties of CNSs, CNS (6, 3) and CNS (9, 0) samples that have a tube diameter similar to that of the CNS (5, 5) are also studied.

After preparing the molecular structure of a CNS, its two ends are constrained before performing the potential-energy minimisation. Because the CNS is constructed from a bent and twisted CNT, it will seek a minimum energy until it expands into a CNT during the optimisation process if its two ends have not been constrained. We then use the optimised structure as the initial structure and the potential energy at a tension displacement of $x = 0$ as the initial potential before the CNS is placed under tension. We give a one-turn CNS (5, 5) with a diameter of 12.4 nm and a rise angle α of 17.1° as an example, as presented in Fig. 1, where the spring diameter D is measured from the spring's centre line, and the pitch P is calculated using the formula

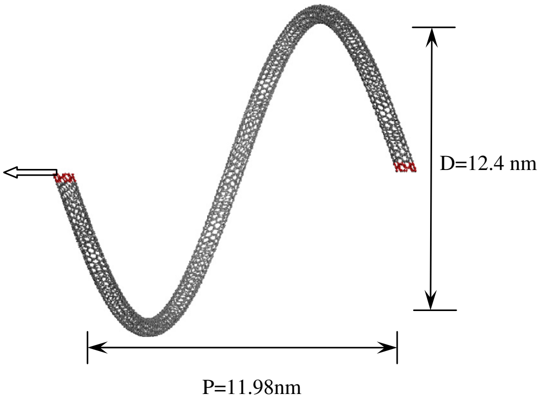

Fig. 1. Initial structure of a CNS (5, 5) under axial tension, where $D = 12.4$ nm and $P = 11.98$ nm.

$$P = \pi D \tan \alpha.$$

Thus, the value of P here is 11.98 nm. The fixed carbon atoms are coloured in red, and the arrow indicates the axial direction of tension. In the tension process, the red part at right end remains locked in place (no translation and no rotation), and the red part at the stretching (left) end is maintained at a constant angle (no rotation) but is required to translate laterally for accomplishing the extension of the CNS.

Applying a very small tension displacement to the CNS incrementally and minimising the potential energy, the resulting change in potential energy, which equivalent to the stored deformation energy in the CNS, can be monitored at each tension–displacement step. To protect the carbon–carbon (C–C) bond from damage (C–C bond length greater than 1.8 Å) after each tension–displacement step, especially in the tension position, small tension steps of less than 0.05 nm are used for the various CNSs. The spring stiffness of each tension case is then calculated using the energy method ($k = \frac{\partial^2 V}{\partial x^2}$), where V is the potential energy.

2.2. Dreiding force field

In this work, a Dreiding force field [32] is used to describe the potential-energy surface. Dreiding force fields are useful for predicting the structure and dynamics of organic, biological and main-group inorganic molecules. The general force constants and geometric parameters for the Dreiding force field are based on simple hybridisation rules rather than individual force constants and geometric parameters, which depend on the particular combination of atoms involved in the bond, angle or torsion terms. Thus, all bond distances are derived from the atomic radii, and there are only six different values for torsional barriers and only one force constant for bonds, angles and inversions.

The Dreiding force field is a purely diagonal force field with harmonic valence terms and a cosine-Fourier expansion torsion term. The umbrella functional form is used for inversions, which are defined according to the Wilson out-of-plane definition, and the van der Waals interactions are described by the Lennard–Jones potential. Electrostatic interactions are described by atomic monopoles and a screened (distance-dependent) Coulombic term, and hydrogen bonding is described by an explicit Lennard–Jones 12–10 potential:

$$E = D_0 \left[5\left(\frac{R_0}{R}\right)^{12} - 6\left(\frac{R_0}{R}\right)^{10} \right],$$

where D_0 is an ab initio parameter in units of kcal/mol, and R_0 is the initial distance between atoms.