DETRIMENTAL EFFECT OF HYDROGEN ON THE FRACTURE STRENGTH OF SINGLE-WALLED CARBON NANOTUBES

S.Q. Shi[1,@] and L.G. Zhou[2]

[1]Department of Mechanical Engineering, Hong Kong Polytechnic University,
Hong Kong, China
[2]Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

ABSTRACT

Molecular dynamics simulations have been performed to study the mechanical properties of single-walled carbon nanotube under tensile loading with and without hydrogen storage. Advanced bond order potentials were used in the simulations. (10,10) armchair and (17,0) zigzag carbon nanotubes have been studied. Two deformation stages of armchair carbon nanotube were found. In the first stage, the elongation of nanotube was primarily due to the altering of angles between two neighbor carbon bonds. The Young's Modulus observed in this stage is comparable with experiments. In the second stage, the lengths of carbon bonds were extended up to break point due to the increase of tensile loading. The tensile strength in this stage is higher than that observed in the first stage. Similar result was also found for the zigzag carbon nanotube. Hydrogen molecules stored inside and/or outside of nanotubes reduced the fracture strength of both types of carbon nanotubes. The competition in formation of hydrogen-carbon and carbon-carbon bonds was found to be responsible for the detrimental effect. During the deformation, some carbon-carbon bonds were broken and reconstructed. If hydrogen molecules were around, H atoms would compete with the carbon atoms, to form hydrogen-carbon bonds.

KEYWORDS

Carbon nanotubes, hydrogen, fracture, simulation

INTRODUCTION

A single-walled carbon nanotube (SWNT) can be described as a graphene sheet rolled into a cylindrical shell and is a quasi one-dimensional system [1]. Apart from the well-known electrical property [2] of SWNT, its remarkable mechanical properties and potentially high hydrogen-storage capacities are also intensively studied. Due to the nanosize of SWNT, a direct measurement of its mechanical properties is rather difficult. However, this extreme size is very suitable for performing atomistic simulations. Currently, the atomistic simulations on hydrogen in SWNTs are mainly focused on two issues: how much hydrogen can be stored and where the atoms are stored. An interesting question is, since carbon nanotubes are both promising for

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[@] mmsqshi@polyu.edu.hk

use in structure and hydrogen storage, what is the effect of hydrogen on mechanical properties of carbon nanotubes? In this article, we report our MD simulations on single-walled nanotubes under a tensile loading with hydrogen storage.

METHODOLOGY

Brenner's hydrocarbon potential, a bond order potential, is used in this simulation [3-5]. Nanotubes in this paper are $(10,10)\times100_u$ armchair type and $(17,0)\times58_u$ zigzag type, respectively. The subscript u denotes a repeat unit of SWNT along the axial direction. These units were chosen so that the two types of nanotubes have a similar diameter and tube length.

To simulate the tubes under tensile loading, we followed two steps. First, the tubes were annealed at simulation temperature for 5,000 MD steps. The time interval between two MD steps is 0.5 fs. Then, the tube was pulled in axial direction (i.e., z-direction) with a strain of 5×10^{-4}. Following each step of pulling, some additional MD steps were used to relax the structure. A periodic boundary condition has been used along the axial and horizontal directions and the simulations were performed at 300 K and 600 K, respectively.

Unlike the continuum shell model, SWNT is constructed by hexangular carbon rings so that its mechanical properties are strongly depended on its chiral directions. Bond angle and bond length are the two crucial factors that control the deformation. For armchair SWNT, the elongation of tube due to the altering of bond angles can be up to 15 % if the C-C bonds are assumed to be rigid. While for zigzag SWNT, one-third of the C-C bonds are parallel to the axis. The loading force is then directly acting on these bonds so that they are easy to break. Fig.1 shows the tensile force (F_z) along the axial direction of the armchair (10,10) and zigzag (17,0) SWNTs as a function of strain (F_z-ε curve) without hydrogen. The tensile force F_z is deduced from an early work [6] by changing the volume to tube length.

RESULTS AND DISCUSSION

A detailed examination of nanotube structures in Fig. 2 reveals that the elongation of the (10,10) nanotube is initially due to the altering of bond angles (Stage 1). Under further pulling, the contribution from the elongation of the C-C bonds becomes significant and plays the main role (Stage 2). When the strain is up to a critical level, some groups of the C-C bonds are broken. Then, the tube starts necking and the force F_z decreases dramatically (Stage 3).

Compared with the (10,10) SWNT, the (17,0) zigzag SWNT has significantly smaller maximum strain and maximum tensile force. Here, we define the maximum strain (MS) and the maximum tensile force F_z (MTF) at the turning point on F_z-strain curve that has the highest value of F_z. Due to the nature of the hexagonal carbon ring, pulling the zigzag tube along its axial direction would cause some second nearest neighbor C-C atoms to become closer and to form new C-C bonds. In the local regions of these newly formed bonds, some old carbon-carbon bonds have to break due to the saturation of covalent bonds. This would lead to the necking and breakage of the zigzag SWNT.

A range of 4~10wt% of hydrogen stored in SWNT were reported [7]. In the following simulations, the armchair (10,10) and zigzag (17,0) SWNTs were used again for comparison. In our simulation, these SWNTs were pre-stored with 4.17 or 8.34 wt% of hydrogen gas (H_2), both are in the reported range. The absorption of hydrogen in carbon nanotubes has been theoretically studied [8, 9]. In the current simulation, however, the details of the absorption procedure are not of primary concern. We place H_2 molecules into tubes directly. The initial positions and the orientations of H_2 molecules in the tubes are chosen randomly. To avoid the overlap of atom positions, atomistic relaxation was performed. When this is done, 5000 MD steps were used to anneal the structures of carbon and hydrogen atoms at simulation temperatures and the tensile loading were then carried out. The results show that the maximum tensile force and the maximum strain both decreased due to the storage of H_2, see Figures 3(a) and (c).

The effect of stored molecular hydrogen on mechanical properties of SWNT was found to strongly depend on temperature. It can be seen from Figures 3(a) and (c) that the reductions of MS and MTF caused by hydrogen storage at 600K are much larger than that at 300K. As proposed in the following text, the competition between the carbon-carbon bonds and the carbon-hydrogen bonds are believed to be the main reason that causes the reductions in MS and MTF. The effect of H_2 on the zigzag (17,0) SWNT seems not as significant as on the armchair (10,10) one (Figures 3(b) and (d)).

The interstitial channels between adjacent nanotubes in a rope of SWNTs may also be the possible sites to accommodate H_2, although there are still some debates at present on this issue. Motivated by this possibility, we also studied the case in which H_2 is stored in outside surface of the tubes. The simulation procedure is as follows. A (10,10)×100_u SWNT was placed in the center of a box of 3nm×3nm in length and width. The height of the box was set equal to the length of the SWNT. H_2 molecules were stored in the box, while the space inside the tube was kept empty. In order to compare to those tubes with H_2 stored inside, the molar fractions of H_2 were chosen to satisfy that the pressure of the hydrogen gas outside the tubes is equal to that of those tubes with H_2 stored inside (4.17 and 8.34 wt%). Periodic boundary conditions were used in the X, Y and Z directions of the box. The simulation temperature was 300K. Compared to the hydrogen-free SWNT, the reductions in the maximum force are 37.7eV/Å and 82.7eV/Å for 4.17 and 8.34 wt% hydrogen storage, respectively, see Figure 3(c). The increase in reduction of MTF might be due to the increase in effective contact area between H_2 and the nanotube surface, because the outer surface area of the nanotube is larger than the inner surface area.

There may be a couple of reasons that had caused the reduction of strength of nanotubes by hydrogen storage. One of reasons might be the high pressure of H_2 acting on the wall of the tubes. Take the (10,10) armchair tube with 4.17 wt% stored hydrogen as an example. The atomic ratio of H/C is 1:2. If we assume that all hydrogen atoms stored inside the tube are in the gas phase, the pressure of gas would be 95.2 MPa at 300K. Such high pressure of hydrogen gas acting on the wall of tubes would change the loading mode of the tube. In addition, under the high-strain tensile loading, some bonds in the carbon rings were broken and this created local defect regions on the wall. The pressure of hydrogen gas would drive molecular hydrogen passing through these defect regions and cause the regions to extend into holes. Another important reason comes from the competition in formations of the hydrogen-carbon and the carbon-carbon bonds. Fig.4 shows the total number of the C-H bonds during the tensile deformation. In this figure one can find that the number of the C-H bonds is significantly increased when the tube necking starts. Since some C-C bonds were elongated and broken during the deformation, hydrogen atoms were likely to “catch” some of the free carbon bonds to generate the C-H bonds (see Fig.5), so that the fracture of SWNT was then accelerated.

CONCLUSIONS

MD simulations based on a new bond order potential have been performed to study the mechanical properties of SWNT under tensile loading with and without hydrogen storage. The results show that:
(1) The tensile deformation of SWNTs up to the point of necking experiences two stages, controlled by altering of the C-C bond angle and the C-C bond length, respectively;
(2) Hydrogen storage in SWNT reduces the maximum tensile strength of the tube as well as the maximum tensile strain; and
(3) The competition between the formations of the H-C and the C-C bonds may be responsible for the reduction in the mechanical strength of the SWNT with H_2 storage.

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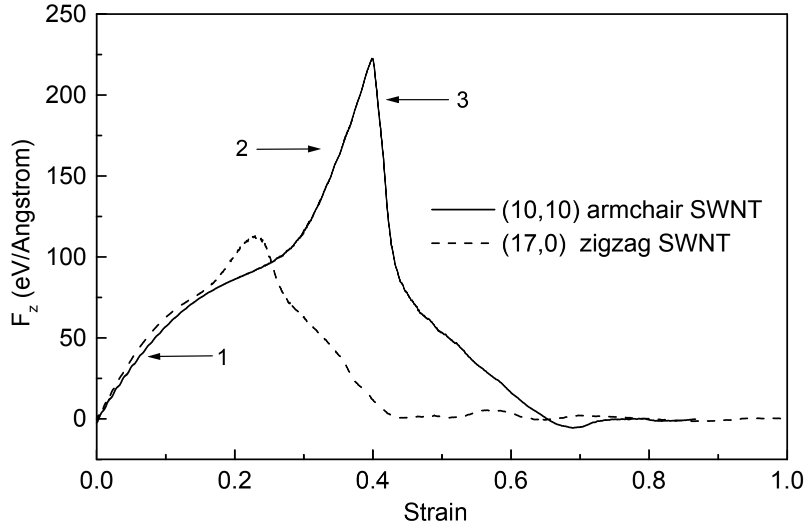

Figure 1. Tensile force along axes of the armchair (10,10) and zigzag (17,0) SWNT as a function of strain. The numbers 1, 2 and 3 denote the three deformation stages of armchair SWNT under tensile loading.

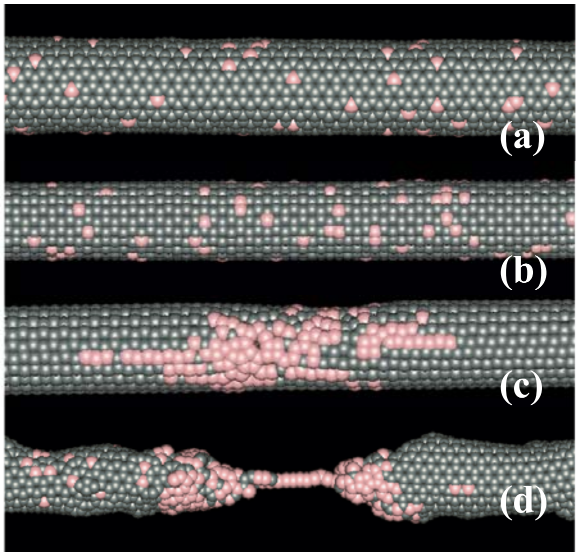

Figure 2. Typical snapshots of the armchair (10,10) SWNT without hydrogen during tensile deformation. Brighter color denotes higher kinetic energy of the carbon atoms.

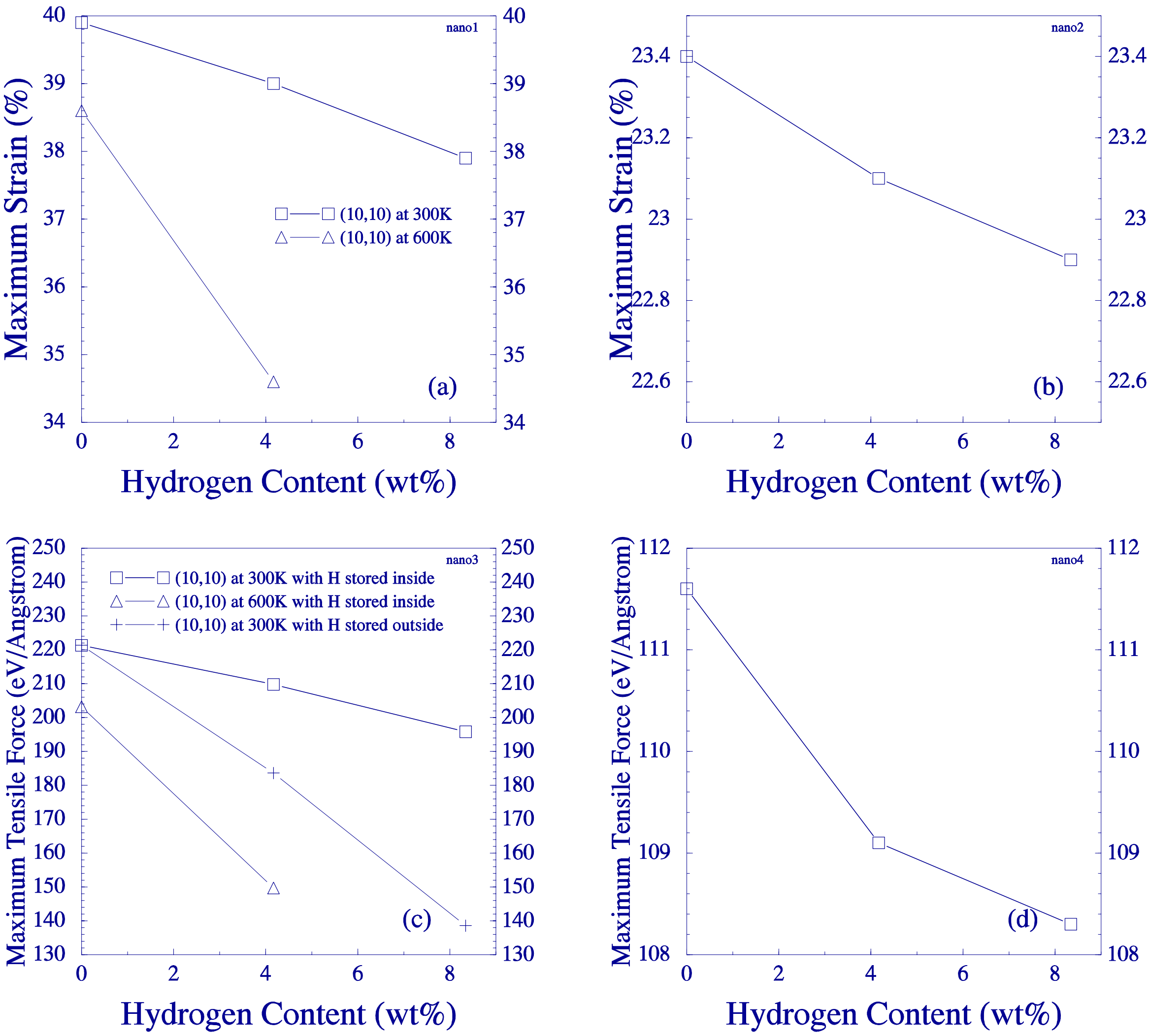

Figure 3. (a) maximum strains of (10,10) nanotubes; (b) maximum strains of (17,0) nanotubes at 300 K; (c) maximum tensile forces of (10,10) nanotubes; and (d) maximum tensile forces of (17,0) nanotubes at 300 K.

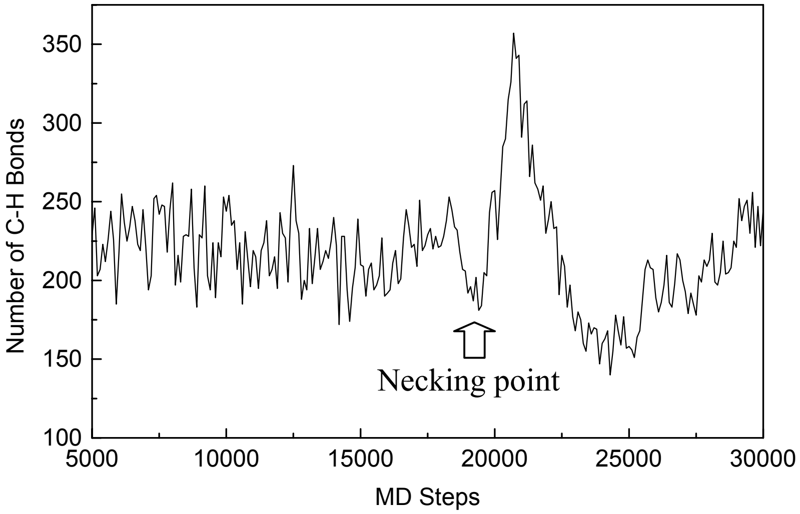

Figure 4. The variation in the number of the C-H bonds in the (10,10) armchair SWNT stored with 4.17wt% hydrogen during tensile deformation.

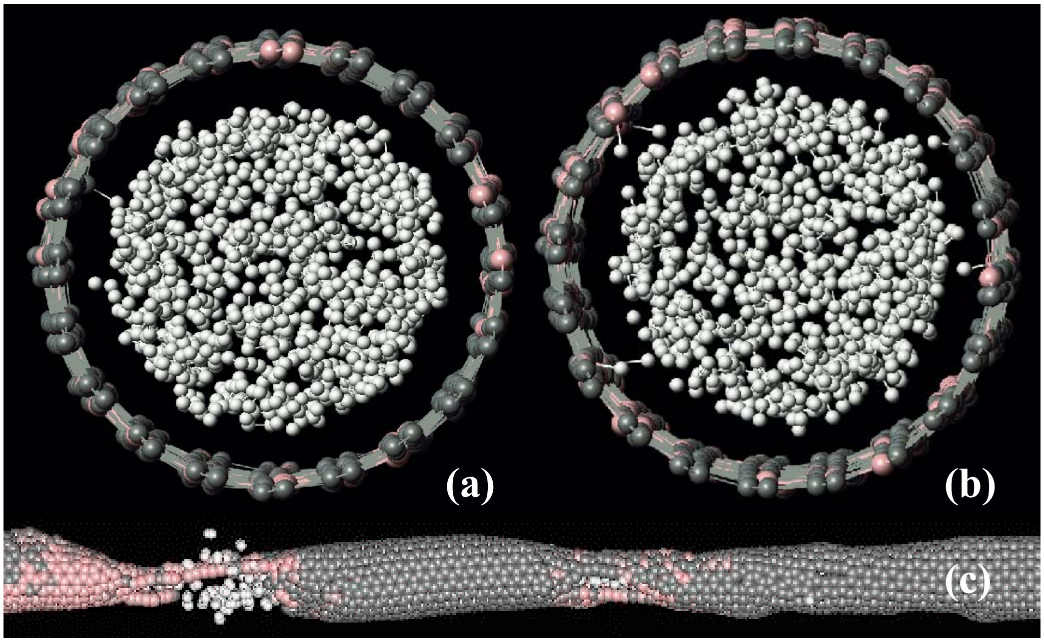

Figure 5. Snapshots of the (10,10) SWNT with 4.17wt% hydrogen storage: (a) a cross section at 4.7ps; (b) the same cross section at 7.6ps; and (c) a view at the point of fracture. Small white balls are hydrogen molecules or atoms.