ICOSSAR 2005, G. Augusti, G.I. Schuëller, M. Ciampoli (eds)
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Fracture resistance of single-walled carbon nanotubes through atomistic simulation

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Keywords: Atomistic simulation, carbon nanotube, fracture resistance, strain-energy, brittle, toughness

ABSTRACT: The mechanical behavior of Carbon Nanotubes (CNTs) has drawn much attention because of their ultra-high stiffness and strength. From the perspective of durability and reliability of CNT-based materials and devices, fracture of CNTs due to mechanical loading becomes an important issue. Presumably, because of their small size, few experiments are available in the literature to directly investigate the details of fracture process. According to existing studies (most of which are numerical modelings), zigzag tubes generally favor brittle mode, while armchair tubes, under high temperature and high strain, can undergo significant plastic deformation before they break. Nevertheless, brittle fracture could be one of the important failure modes, or even the dominant mode of Single-Walled Nanotube (SWNT) failure due to mechanical loading. However, based on the authors' knowledge, the fracture resistance of CNTs has not been quantified so far. In this paper, the brittleness of CNTs with preexisting defects is calculated using fracture mechanics concepts. Such mechanistic modeling is an essential ingredient to understanding the stochastic fluctuations in fracture properties. The strain energy release rate, G, is computed through a series of simulated mechanical loading of SWNTs with preexisting cracks of various lengths. Atomistic simulation is used to model the tensile loading of these SWNTs. The interatomic forces are modeled with a modified Morse potential. The loading is displacement controlled, applied through moving the outmost layer of atoms at one end of the SWNT at constant speed. This computation is applied to (35,0) SWNTs with cracks up to 29.5Å long. A significant dependence of G_c on crack length is observed: G_c increases with crack length at small length, and tends to reach a constant value as crack length is large. For example, at 300 Kelvin, G_c converges to 6 Joule/m^2 as the crack length exceeds 20 Angstrom. This value is comparable with the fracture toughness of graphite and Silicon.

1 INTRODUCTION

Carbon nanotubes are known to be one of the strongest and stiffest materials in the world and bear the promise of revolutionizing engineering at the small-scale. The fracture of CNTs due to mechanical loading is thus a very important issue. The most direct investigation of the fracture behavior of CNTs would be through laboratory experiments. However, due to the small size of CNT samples, only a few experiments in the literature have been reported to provide the fracture of CNTs in details. Tensile loading tests for MWNTs were reported in studies such as (Yu et al. 2000) and (Demczyk et al. 2002), the Young's modulus and tensile strength were measured, but further details of fracture behavior were not available. In a series of studies (Troiani et al. 2003; Marques et al. 2004), fracture of SWNT was investigated by high resolution TEM and tight binding simulation. It was reported that both brittle and ductile fracture could be possible for SWNTs. However, under what conditions the SWNT would favor brittle/ductile fracture modes was not explained by the experiment.

Based on tight-binding simulation (Troiani et al. 2003; Marques et al. 2004) and other atomistic simulation studies (Nardelli et al. 1998b), the fracture of CNTs can be either brittle or plastic, depending on the external conditions and tube symmetry. The plastic deformation is believed to result from successive formation of Stone-Wales

(SW) rotations and gradually changing of CNT configurations. However, above explanations of plastic deformation were challenged by two other studies. Dumitrica et al. (2003) argued that the energy barrier for SW defects formation at room temperature is high enough to inhibit stress-induced SW defects formation, and showed the direct bond-breaking is a more likely failure mechanism for defect-free nanotubes. In their study, by modeling the energy states of SWNTs with 1~5 bond cut were modeled with electronic structure programs, they showed that brittle fracture is the dominant failure model at low temperature. A quantum mechanical study (Troya et al. 2003) pointed out that the results in Nardelli et al. (1998b) and related works were not reliable since the potential model they used (i.e., the Bond Order model) was not capable of correctly describing breaking of the bond connecting the two pentagons in the SW pair. They (Troya et al. 2003) further found that pre-existing SW defects caused successive bond breakings instead of bond rotations as reported by Nardelli et al. (1998b),Yakobson (1998) Jiang et al.(2004) Liew et al.(2004).

Nevertheless, based on these studies, a general conclusion can be drawn: zigzag tubes favor brittle mode, while armchair tubes, under high temperature and high strain, can sometimes undergo significant plastic deformation before they break. Therefore, brittle fracture could be one of the important modes, or even the dominant mode of SWNT failure under tensile loading. However, to the authors' knowledge, the question "How brittle is a CNT?" has never been answered with any precision, and fracture toughness of SWNT has never been quantified. The fracture toughness of SWNT could be a key factor when SWNTs are used as load-bearing or load-sensing devices. It is important to note that defects in the nanotubes (either resulted from manufacture process or intentionally introduced to improved the functions of CNTs) are likely to initiate fracture (cite previous studies). Defects such as vacancies, metastable atoms, pentagons, heptagons, Stone-Wales (SW or 5-7-7-5) defects, heterogeneous atoms, discontinuities of walls, distortion in the packing configuration of CNT bundles, etc. are widely observed in CNTs (Iijima et al. 1992; Zhou et al. 1994; Banhart 1999; Charlier 2002; Saether 2003). According to an STM observation of the SWNTs structure, about 10% of the samples were found to exhibit stable defect features under extended scanning (Ouyang et al. 2001). Defects can also be introduced by mechanical loading (Nardelli et al. 1998b; Nardelli et al. 1998a) and electron irradiation (Banhart 1999).

Therefore, it is important to quantify the brittleness of CNTs with preexisting defects. Elegant fracture theories have been developed during the past decades as reviewed in Lu and Bhattacharya (2005b) for fracture of materials at macro-scales. In this paper, the authors try to investigate the brittleness of SWNTs using metrics commonly used in fracture mechanics.

Based on the stress solution proposed by Inglis (1913), Griffith (1920) treated fracture as an equilibrium process in which the loss of strain energy can be equated to the surface energy generated due to the growth of cracks. Consider a solid body containing a crack with length a, and subject to a constant stress, σ, at far end. For the crack to extend, enough energy must be provided to overcome the surface energy of the material. According to Griffith theory, the critical condition of energy balance for an incremental increase in crack area is,

$$\frac{dE_T}{dA} = \frac{d\Pi}{dA} + \frac{dW_s}{dA} = 0 \tag{1}$$

where E_T is the total energy, Π is the potential energy, and W_s is the work required to create new surfaces. $\frac{dW_s}{dA} = 2\gamma_s$, γ_s is the surface energy of the material. A is the crack surface area.

Irwin (1956) developed an energy approach for fracture that is equivalent to the Griffith model. He introduced the parameter strain energy release rate G, as a measure of the energy available for crack extension,

$$G = -\frac{d\Pi}{dA} \tag{2}$$

At the onset of fracture, $G = G_C$, which is a measure of fracture toughness. It is also Irwin's contribution to connect the global concepts of strain energy release rate to an easier-to-use crack-tip parameter, stress intensity factor, K. K is usually a function of the stress applied at far end, the crack length and the geometry of the specimen. At fracture, $K = K_C$. For mode I fracture (opening crack),

$$G = K_I^2 / E' \tag{3}$$

where $E' = E$ for plane stress, $E' = E/(1-\nu^2)$ for plane strain (E stands for Young's modulus, and ν

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stands for Poisson's ratio). However, the relationship may not hold for cylindrical shells.

These elegant theories and methods introduced above are the foundations for fracture mechanics and have been widely applied in fracture analysis. However, one may note that these approaches, as well as many engineering concepts such as stress, Young's modulus, tensile strength, etc., are all based on continuum assumptions, which does not hold at the atomic scale. Carbon nanotubes, at atomic scale, are nanostructures constructed of sheets of hexagonal-shaped carbon units rolled up into cylinders, they are essentially engineering structures, not continuum materials. In some cases where details at nano-scale are concerned, continuum approaches may not always be appropriate.

For example, the concept of stress, which is defined on *material points* (based on continuum assumption), is not a clear concept at nano-scale and represents a discrete field with singularity. The stress at the cross-section of a nanotube must involve the tube's sectional area, A, which is not well defined. Several arbitrary definitions of A are used in previous studies, and result in inconsistence in the comparison among results (Hernandez et al. 1998; Sanchez-Portal et al. 1999). Actually, force, rather than stress, is the more natural measure of mechanical interaction in this case. However, to connect atomic systems with continuum-based analysis, continuum concepts are still used in this paper, with additional assumptions and restrictions.

2 METHODOLOGY

Before the details of SWNT fracture are investigated, we first give a brief description of the atomistic simulation we used to model the fracture tests. The SWNTs are modeled with a modified Morse potential (Belytschko et al. 2002), that has been applied to study CNT fracture. Temperature is controlled with Anderson thermostat (Anderson 1980). A set of zigzag SWNTs are simulated. In the simulation, the tube is first relaxed for a while, and then stretched by forcing the atoms at one end to move at constant speed. During the process, the time history of energies, temperature, force and displacement are recorded until the tube breaks. Because we are mainly interested in the brittle mode, only zigzag tubes are adopted and the room temperature (300 Kelvin). All tubes exhibit brittle behavior at fracture, i.e., the failure is catastrophic. Once the tube deformation reaches a critical level, atomic bonds break successively and lead to a complete fracture in a very short time.

From each simulation, time histories of energies, forces, displacement etc. can be obtained, as shown in Figure 1. A force-displacement curve can also be obtained. An idealized example is illustrated in Figure 2. The deformation of SWNT is not purely linear, the stiffness decreases gradually up to the break point. Based on this curve, the work done by the external force (Let us denote this work by W) can be calculated by integrating the area under this curve (shadowed area in Figure 2). As we find from benchmark simulations, the change of kinetic energy of the system is negligible compared to the change of strain energy (less than 5%, as shown in Figure 1). Because the only net energy input is the work done by the external force, the net change of potential energy Π-Π_0 (Π_0 is the potential energy of the system at equilibrium) approximately equals W.

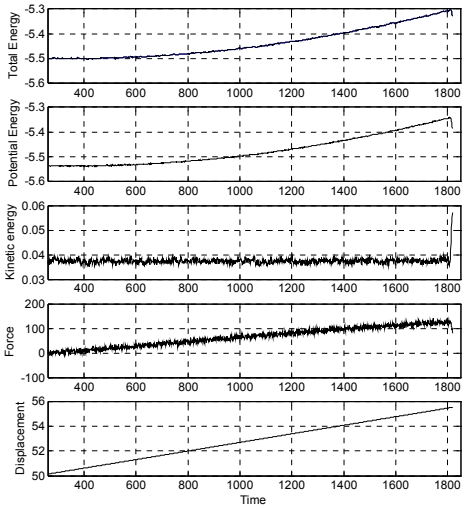

Figure 1. Time histories of total energy, potential energy, kinetic energy, force and displacement from atomistic simulation of a (35,0) SWNT to fracture

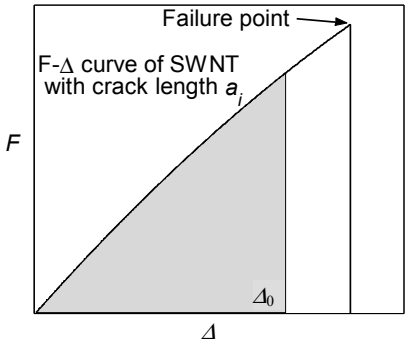

Figure 2 Force-Displacement curve of a tensile test of a SWNT with crack length a_i. The shadowed area is W, the work done by the external force

The method used in this study to calculate the strain energy release rate is based on the displacement-controlled test method commonly used for macro scale fracture specimens. In the displacement-controlled test, a cracked specimen is loaded to a fixed displacement Δ_0. As the crack grows from a to $(a + \delta a)$, the strain energy stored in the elastic body, drops from W to $W-\delta W$. As shown in **Figure 4**, the shadowed area is the change of strain energy. These changes are used to calculate the critical strain energy release rate $G_c = \delta W/\delta A$, when a reaches its critical value a_c at the onset of catastrophic failure at displacement Δ_0.

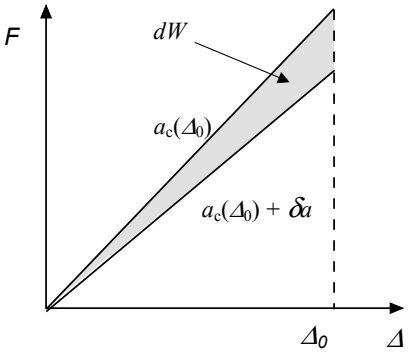

Figure 3 Displacement-controlled fracture test

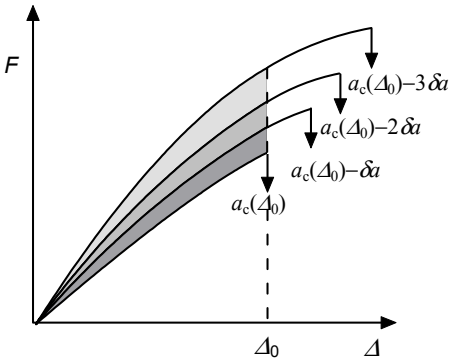

Figure 4 Method used in this study for determining strain energy release rate

However, in our study, because the fracture is catastrophic, it is difficult to obtain a stable crack growth at fixed displacement. Thus, instead of running one simulation for crack growth from $a_c(\Delta_0)$ to $a_c(\Delta_0)+\delta a$, where $a_c(\Delta_0)$ is the critical crack length corresponding to fixed displacement Δ_0, we run several separate simulations of tensile loading of SWNTs to fracture, with crack lengths, $a_c(\Delta_0)-n\delta a$, … , $a_c(\Delta_0)-3\delta a$, $a_c(\Delta_0)-2\delta a$, $a_c(\Delta_0)-\delta a$ and $a_c(\Delta_0)$, respectively. The strain energies W_n, …, W_3, W_2, W_1 and W_0, at the fixed displacement Δ_0, can be determined from the force-displacement curves, as shown in **Figure 4**. Thus a W~a curve can be drawn for this displacement Δ_0 as shown in **Figure 5**. This curve is in turn used to calculate the slope $\delta W/\delta A$ at critical crack length $a_c(\Delta_0)$. This critical strain energy release rate can thus be computed for different crack lengths.

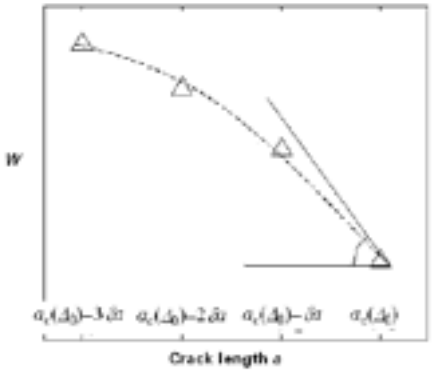

Figure 5 External work-Crack length (W-a) curve for SWNTs

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3 RESULTS

We apply this methodology to a (35,0) zigzag SWNT configuration with an aspect ratio of 4, at room temperature (300K). Simulations of tensile loading are applied to an intact nanotube, a nanotube with initially 1 bond cut, 2 bonds cut, … , up to 11 bonds cut, representing initial crack with various lengths. The maximum initial crack length is 29.52 Angstrom. The crack length for the intact nanotube is set to be 2.46 Å, which is the distance between two longitudinal bonds. The (35,0) tube with crack length 2.46, 4.92 and 7.38 Å are illustrated in Figure 6.

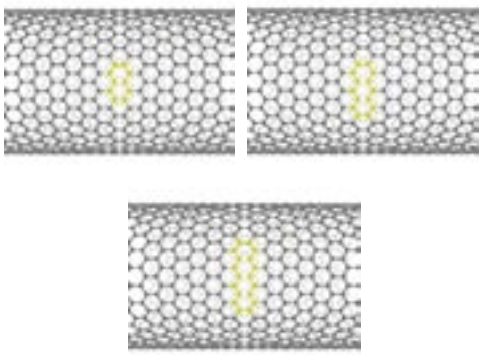

Figure 6 Zigzag SWNTs with 1,2 and 3 bonds cut

Figure 7 shows the *W-a* data for the fracture study of the (35, 0) SWNT at temperature 300K at seven different displacements Δ_5 through Δ_{11} (Δ_{Nc} is the displacement at which the critical crack length is 2.46 Å times Nc). The critical strain energy release rates are found as $G_c = d\Pi/dA$ at these critical crack lengths are shown in **Figure 8**.

A significant dependence of G_c on crack length is observed. G_c increases with crack length initially, and tends to reach a constant value, about 6.0 Joule/m^2 as crack length is large. This constant value seems not to be related with a specific tube diameter. The fracture resistance of the SWNT is found to be higher than graphite and of the same order as Al_2O_3 and Silicon.

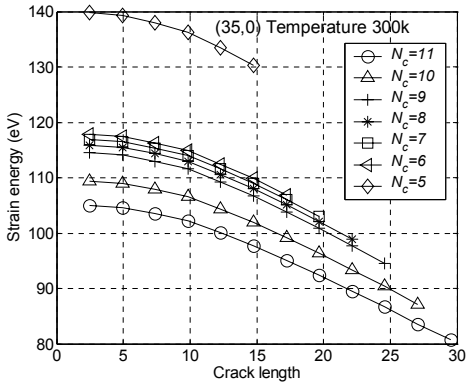

Figure 7 External work-crack length (*W-a*) curve for (35, 0) SWNT at 300 K

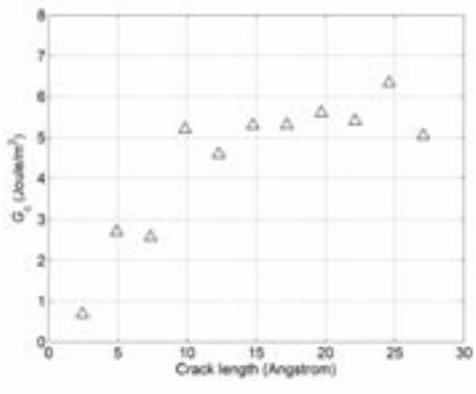

Figure 8 Critical strain energy release rate for (35,0) SWNT at 300 Kelvin

4 CONCLUSIONS AND DISCUSSIONS

The fracture resistance of zigzag carbon nanotubes are investigated quantitatively in this study, by applying fracture mechanic concepts to nanostructure and modeling the deformation with atomistic simulation.

The SWNTs' fracture resistance in the form of critical strain energy release rate G_c is determined for (35,0) SWNTs with cracks up to 29.5Å long. The fracture resistance is comparable with the fracture toughness of graphite and Silicon. A significant dependence of G_c on crack length is

observed: G_c increases with crack length at small length, and tends to reach a constant value as crack length increases. Dependence of G_c on temperature is also being investigated. This work will be extended to armchair and chiral SWNTs and MWNTs in future.

Like all materials of engineering interest, carbon nanotubes also possess inherent stochastic fluctuations in their mechanical properties. The randomness in strength, stiffness and ductility of SWNTs due randomly occurring Stone-Wales defects has recently been investigated by the authors (Lu and Bhattacharya 2005a). A companion paper at this ICOSSAR looks at the asymptotic distribution of strength of these SWNTs as their length increases (Bhattacharya and Lu 2005). In probing the randomness in fracture resistance of CNTs, a fundamentally based mechanistic modeling is essential, and it is believed that this paper will contribute to such understanding. Work is in progress in that regard.

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