POTENTIAL SUPER-TOUGHNESS BEHAVIOR OF CHIRAL (10,5) CARBON NANOTUBES

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ABSTRACT

Improvements in construction materials have been evolutionary and not revolutionary. We are attempting to change this paradigm by exploiting the extreme properties of carbon nanotubes, and by designing materials at the molecular level using molecular-based predictive rheology. As an initial step, we have modeled pristine and defective (5,5) carbon nanotubes and a defective (10,5) carbon nanotube using Tight-Binding Molecular Dynamics. The (5,5) carbon nanotubes exhibited extraordinary tensile strengths and brittle failures in agreement with the findings of other researchers. Their strengths and Young's moduli were degraded by the molecular flaws. By contrast, the defective (10,5) carbon nanotube exhibited lower, but still extraordinary, tensile strength and postyield toughness behavior many times greater than toughened 4340 Steel. Such toughness behavior is an important and beneficial material characteristic for construction materials.

1. INTRODUCTION[1]

Military engineering and infrastructure engineering are heavily dependent on available materials and their rheological properties. These fields of engineering can be divided into three major areas: tactics/policy (what is to be done); processes/procedures (how it is to be done); and material and personnel resources (who/what is going to be used to do it). Material performance constrains tactics/policy and process/procedures in that these have to operate within the bounds that materials will support. Accordingly, drastic improvements in material performance will be a disruptive and positive force for infrastructure and military engineering.

Improvements in material performance for the last half-century have been evolutionary and not revolutionary, with improvements measured in terms of a few tens of percent or less. Two developments have occurred that allow dramatic improvements in materials to be realized. The first is the discovery of several new forms of carbon. Buckminsterfullerene or Carbon 60, also known as Bucky Balls, was discovered in the 1980's (Kroto et al., 1985). A related form of carbon, carbon nanotubes, was discovered in the early 1990's (Iijima, 1991). These carbon mineral forms have enticed material developers with their extraordinary and potentially useful material properties since their discovery. Carbon nanotubes are up to 150 times stronger in tension than high-strength (100 ksi) steel, have a Young's modulus 5 times that of steel, have 1/3 to 1/6 the density of steel (dependent on whether the form is multiwall carbon nanotubes or single-wall carbon nanotubes), have 5 times the thermal conductivity of copper (2000 W/(m*K)), and can be electrical conductors or insulators depending on their chirality. These molecular properties offer tremendous opportunities for improvements in material performance for a variety of uses, including military and infrastructure engineering; but before such improvements can be had, useful macromaterials have to be formed from these molecules.

It is well known that many materials exhibit enormous strength at the molecular or microscale. As these micromaterials are scaled to macrolevels, the well-accepted theory of dislocations and their effect on fracture, fatigue, and material failure comes into play and significantly degrades their strength. For example, in a classic paper, Brenner (Brenner, 1956) performed experiments on microscale samples of common materials.

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Some of his results are provided in Table 1. In his experiments, small-diameter single crystal whiskers of common materials such as copper, iron, and silver were subjected to tensile tests. These were found to exhibit ultimate tensile strengths many times the strength of the associated bulk materials. For example, the micro-whiskers of iron were found to have tensile strengths of about 1.9 million psi (13.1 GPa), whereas the maximum tensile strength for bulk iron ranges from 22.7 to 32.7 ksi, or only about 1 to 2 percent of that of the single crystal iron whiskers. Brenner found that as the length or diameter of the specimens increased for a given material, the tensile strength decreased. Fig. 1 (after Brenner) displays the tensile strength of iron whiskers of similar length as a function of 1/diameter of the whisker in which a linear relationship is inferred. The same order strength degradation has been observed for other materials, and might be expected for carbon nanotube-based materials unless intelligent material design intercedes.

Table 1 Properties of Micro-Scale Samples of Common Materials

Material	Diameter 10^{-6} m	Tensile Strength GPa
Iron	1.60	13.1
Copper	1.25	2.93
Silver	3.80	1.72

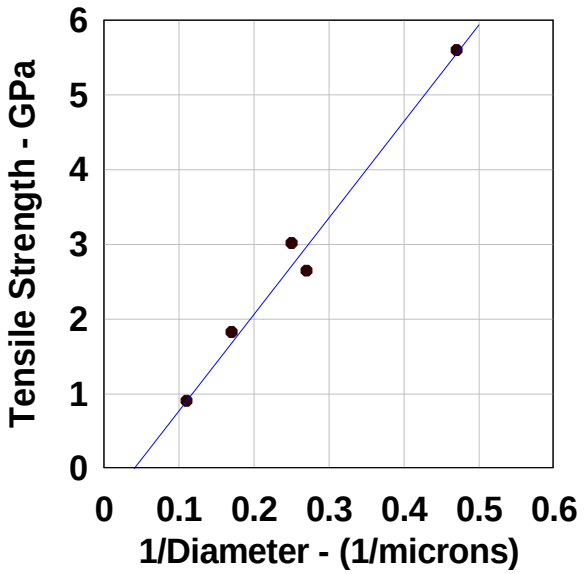


Fig. 1. Tensile strength of iron whiskers of similar length (after Brenner, 1956)

Carbon nanotubes have several attributes that should aid in producing macromaterials with significantly enhanced characteristics. As mentioned previously, carbon nanotubes have densities that are but 1/3 to 1/6 of steel and start with molecular properties that are significantly stronger than those of steel. High-strength steels tend necessarily to trade other desirable properties for a high ultimate tensile strength. These steels tend to have minimal elastic properties, low ductility, and poor fatigue and corrosion resistance. Fundamentally, the strength of a material at the molecular level derives primarily from the strength of atomic bonds. The enthalpy of dissociation for the carbon double bond is 614 kJ/mol, whereas for iron the enthalpy of dissociation is 75 kJ/mole. As a result, carbon nanotubes begin at an ultimate tensile strength approximately 10 times greater than that for iron whiskers; so even with a proportional degradation of properties, the strength and strength-to-weight properties would still be significantly improved. Furthermore, because carbon nanotubes have a very stable structure exhibiting an interlocking sp2 hybridization (in-plane threefold symmetry) made up of covalent pi bonds, thermodynamically, it is expected that vacancies and other dislocations would have a much lower probability of occurring. This suggests that a proportional degradation of properties at the macroscale may not occur for carbon nanotubes, and that more of their potential for high strength, as well as better ductility, can be exploited. This exploitation will require careful attention to the design of these materials at the molecular level, so that the molecular structures that make up the macromaterials remain strong, and so that these molecular structures themselves bond or interlock well with each other. It is probably the case that the bonds or interlocking strength between molecules will be the weakest component in the design of carbon nanotube based materials. Optimum exploitation of molecular strengths for macromaterials has not been achieved for construction materials (perhaps for any materials), and is wrought with many challenges.

Today carbon nanotubes are too expensive and are not available in large enough quantities to be practical as significant components of building materials. This situation is changing rapidly. Carbon nanotube production capability is spiraling upward, and the costs for carbon nanotubes are spiraling downward. A study in August 2002 (Baughman et al., 2002) listed the costs for low-grade carbon nanotubes as $60/gm. In March 2006, Nanocraft, Inc., listed low-grade carbon nanotubes on eBay for $1.2/gm, a 98 percent reduction in cost. When carbon nanotubes were discovered in 1991, production was in laboratories and in the micrograms. In January 2005, Frontier Carbon, a subsidiary of Mitsubishi Corporation, claimed yearly production capability of 40 metric tons, with the intention of expanding this to 1,500 metric tons (Herrera, 2005). A recent study (Blau, 2006) found 26 companies in the United States that manufacture carbon nanotubes, with the United States leading the world in the production of multiwall and single-wall carbon nanotubes.

The second occurrence that supports revolutionary improvements in material development is the emergence of molecular-based predictive rheology. Still in its infancy, molecular-based predictive rheology was made practical only within the last decade or so because of advances in high-performance computers and multi-processor software. This technology allows prediction of material properties (moduli, stress-deformation response, rupture strength, etc.) from the atomic and molecular structure of the material. It is based on *ab initio* simulations and molecular dynamics simulations of material at the molecular and atomic levels. This science can guide and test molecular designs of materials before the material is synthesized, or can be used to understand causes of material weaknesses after synthesis. Before molecular-level predictive rheology, material properties were determined after material synthesis via laboratory tests; or at best the material's rheology was predicted based on its similarity with a material whose rheology was known. Some of the underlying strength dependencies of important engineered materials such as concrete were never uncovered using traditional methods and today are the subject of new investigations.

In this paper we report on our use of molecular-based predictive rheology to predict the dependency of carbon nanotubes' tensile strength on molecular defects. During the course of the investigation, we discovered that one form of carbon nanotube had significantly improved post-yield behavior over that observed in other forms, and, indeed, displays toughness behavior many times higher than very high strength, toughened conventional material such as 4340 Steel.

2. RECENT EMPIRICAL AND MOLECULAR-BASED PREDICTIVE RHEOLOGY STUDIES OF CARBON NANOTUBES

Understanding the rheological behavior of carbon nanotubes is necessary if these molecules are to be used as strength members in a carbon nanotube-based matrix material or in neat form. Fig. 2 shows a section of a (5,5) carbon nanotube. Carbon nanotubes are extremely small, with diameters of a few tens of nanometers, depending on their chirality, and lengths typically on the order of a few thousands of nanometers, although a few researchers have grown them to several centimeters in length (Los Alamos, 2004). Carbon nanotubes are produced in multiwall configurations in which the multiple carbon nanotubes are contained within each other as with Russian dolls, or they are produced as single carbon nanotubes, with the latter being the most difficult to produce. Their other property is one of chirality (see Pipes et al., 2002), which determines the diameter, electrical conductivity, and, as we will show, their uniaxial stress-strain behavior. The present study is only of single wall carbon nanotubes.

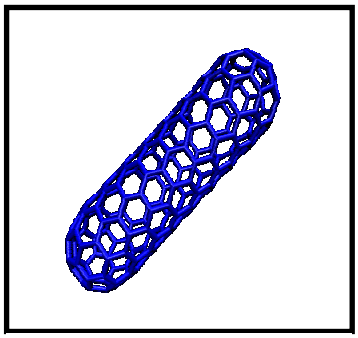


Fig. 2. Pristine (5,5) carbon nanotube with closed end caps

The extremely small size of carbon nanotubes has limited the number of available laboratory studies of their rheological properties as it is difficult to perform mechanical tests of single molecules. By contrast, because their molecular geometry is relatively simple and repetitive over a few tens to a few hundreds of atoms, more studies exist that use molecular-level and atomistic-level simulations to investigate their mechanical response. These molecular-based predictive rheological studies of even simple molecular systems require enormous computational resources and can challenge the most advanced computer systems that exist today. Some past empirical and numerical simulation studies pertinent to the current study are as follows. Yu et al. (2000) report measured tensile strengths of multiwall carbon nanotubes of between 11 and 63 GPa (1.6 to 9.1 million pounds per square inch), with brittle failure of the carbon nanotubes occurring at between 10-13 percent strain. Qian et al. (2002) and Yu (2004) review some of the difficulties in measuring phenomena at the molecular level and provide insight as to the reasons for the large data scatter. Belytschko et al. (2002), using molecular mechanics simulations, predicted the brittle mode of failures correctly, but also predicted tensile strengths of 65-93 GPa (9.1-13.5 million pounds per square inch) and speculated that the difference between the calculated and observed tensile strengths was due to the effects of molecular defects and chirality of the nanotube structures. Barber et al. (2003), using atomic force microscope pull-out tests of single multiwall nanotubes from a solid polymer matrix, show pull-out forces that are significantly higher than can be accounted for by the strength of the polymer. Bozovic et al. (2003) and Cronin et al. (2005) likewise used atomic force microscopes on single wall carbon nanotubes but inferred significant differences in the strain at failure dependent on the portion of the carbon nanotube assumed being strained. Frankland et al. (2003, 2004) used atomistic-level and molecular-level simulations to predict the rheological properties of nanotube/polymer composites, as did Griebel and Hamaekers (2004). Zhang et al. (2005) used molecular

dynamics simulations, including a modified Brenner potential (see Brenner et al., 2002), to predict the effect of one- and two-atom vacancies on the ultimate tensile strength of carbon nanotubes. Troya et al. (2003) compared the results of using empirical Brenner potential, Density Function Theory, and a semi-empirical PM3 method to predict the tensile strain behavior of carbon nanotubes. They found that the Brenner potential predicted lower stress and strain at failure than did the other two methods.

Sears and Batra (2004) report that the values of Young's modulus reported by 10 different groups varied from 0.94 to 1.24 TPa (136 million to 180 million pounds per square inch). The value of Young's modulus is dependent on the cross-sectional area used for the carbon nanotube (see the discussion in Srivastava et al., 2003). Pipes et al. (2002) suggested standard definitions for single-walled carbon nanotubes structures, such as chirality, and standard definitions for rheological parameters to associate with fullerene molecules. Kaplan-Ashiri et al. (2004) and Lu and Bhattacharya (2005) also provide a survey of carbon nanotube Young's modulus results. Gates and Hinkley (2003) and Meyyappan and Srivastava (2002) provide overview articles on carbon nanotube rheological studies.

In a recent summary article on molecular dynamics and atomistic simulations, Galli and Gygi (2005) state that "full prediction of physical and chemical phenomena based on basic laws of Nature, using computer simulations, is a revolution still in the making, and it involves some formidable theoretical and computational challenges." Their view of molecular-level prediction of rheological properties is akin to that of the authors: much of the field has yet to be developed and validated, and to date only simple structures and very small material volumes have been simulated.

3. ANALYSIS METHODS AND MOLECULAR GEOMETRIES

We considered five carbon nanotube geometries. The first four were (5,5) nanotubes, three of which had defects, and one of which was defect free (pristine, Fig. 2). The three (5,5) carbon nanotubes with defects (Fig. 3) consisted of a carbon nanotube with a Stone-Wales (5-7-7-5) defect, a carbon nanotube with two single carbon atom vacancies on sites opposite one another, and a carbon nanotube with a pair of clustered atom vacancies adjacent to each another on a single side. The fifth simulation was of a (10,5) carbon nanotube with a single vacancy defect.

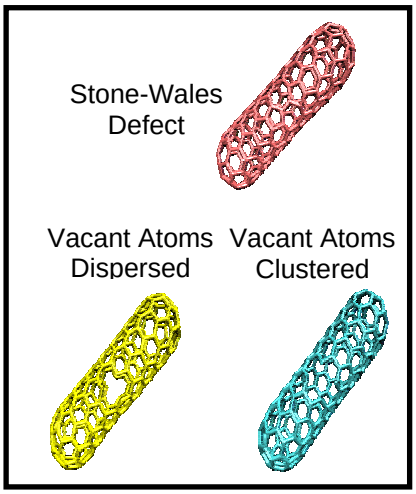


Fig. 3. Molecular defects modeled in the (5,5) carbon nanotube simulations

For all five scenarios the Department of Defense Parallel Tight-Binding Molecular Dynamics code was used to calculate the changes in the potential energy of the molecular systems as a function of the straining of the systems. The carbon parameters for these simulations were fitted to Linearized Augmented Plane Wave and Local Density Approximation results for various solid carbon energy and band structure. These parameters were favorably validated on C_{60} (Papaconstantopoulos et al., 1998).

The (5,5) simulations included both capped nanotubes of 200 atoms and virtual infinite nanotubes simulated with periodic boundary conditions and 120 atoms (12 repeats in the axial direction), less any defects. The results from both types of simulations were in agreement, indicating that the finite length of the capped carbon nanotubes did not appreciably influence the results and that the two methods used to derive the uniaxial constitutive relations, discussed below, were consistent. The (10,5) simulation was performed using two repeats of periodic boundary conditions in the axial direction and consisted of a total of 280 carbon atoms. JCrystal Nanotube Modeler was used to construct the initial molecular configurations.

We employed a series of Tight-Binding Molecular Dynamics simulations to calculate the uniaxial stress-strain behavior for each of the geometries. For each, the molecule was strained, and then equilibrated, and then strained again, until failure occurred. The magnitude of the strain increment was varied to ensure that quasi-static conditions were being simulated. The strain increments varied from .05 to 2 percent and were small enough to capture individual bond failure. Equilibrium at each stage was achieved by allowing the molecule to reach its minimum potential energy (with the temperature T =

0 degrees Kelvin). The strain was simulated in the periodic simulations by an affine extension of all atoms. The strain was simulated in the capped molecular simulations by a finite displacement of the 30 atoms that composed the base of each cap. While this caused some small necking due to Poisson straining, the carbon molecules were long enough that the effect was minor.

The uniaxial stress-strain relation was derived from the capped carbon nanotube simulations by integrating the tensile forces on the end atoms and calculating strain as the change in the length of the affected areas divided by the original length of these areas. The cross-sectional area of the molecule was taken in agreement with common convention (see Pipes et al., 2002) as the area of an annulus with thickness of a graphene sheet (0.34 nm) and diameter of the associated carbon nanotube.

For the periodic simulations, the uniaxial stress constitutive relations were derived from

$$\sigma = \frac{1}{V}\frac{dU}{d\varepsilon} = \frac{1}{A}\frac{dU}{d(L\varepsilon)} = \frac{F}{A}$$

where V, L, and A are the volume, length, and area of the nanotube, respectively, $V=LA$, ε and σ are the components of strain and stress along the axis of the nanotube, and U is the potential energy of the system at each strain increment as determined by the tight-binding molecular dynamics simulations. In this equation, $d(L\varepsilon)$ is the change in nanotube length, and $F = dU/d(L\varepsilon)$ is the tensile force exerted at the nanotube ends.

As the simulations considered only uniaxial stress, secant Young's modulus was calculated from the numerical results as

$$E_s \equiv \frac{\sigma}{\varepsilon}$$

The simulated regions were long compared with the areas with defects. Thus the simulations provide reasonable estimates of the uniaxial constitutive properties of carbon nanotube molecules with a given defect density. The defect density for the three (5,5) nanotube simulations corresponded to 2 of 140 non-cap atoms, or 1.4 percent. For the (10,5) nanotube simulation the defect density was lower and was 1 of 140 atoms, or about 0.7 percent. While we simulated vacancy defects that were singular as well as adjacent, note that a micron-length (5,5) carbon nanotube molecule would have on the order of 10^4 atoms and, given a 1 percent vacancy defect rate, would have a significant chance of two or more vacancies occurring at some site adjacent to each other. As we will see, clustered vacancies represent the weakest of the (5,5) carbon nanotubes considered. It could also be argued that given the strong attraction of carbon-carbon bonds, the likelihood of a true vacancy occurring in a carbon nanotube is less than 1 percent, even for crude material synthesis techniques. With no additional data, both conjectures appear reasonable and produce contradictory results with regard to the expected realized material strengths of reasonably long carbon nanotubes.

4. PREDICTED RHEOLOGY

Fig. 4 provides the uniaxial stress-strain relationships derived from the tight-binding molecular dynamics simulations for the four (5,5) carbon nanotubes considered. The stress at rupture for the pristine case was about 107 GPa (15.5 million pounds per square inch), with a corresponding rupture strain of 17 percent. The weakest (5,5) geometry of the four was the carbon nanotube with the clustered vacancy pair. The predicted rupture stress and strain for this case was 74 GPa (10.7 million pounds per square inch) and 10.5 percent strain. The other cases considered are bounded by these values.

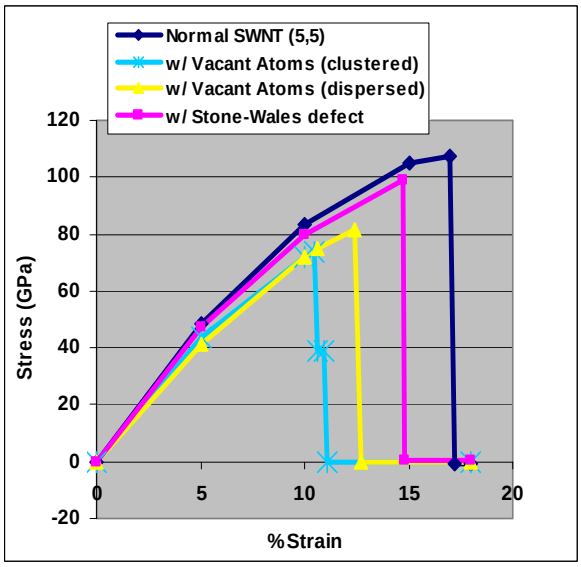
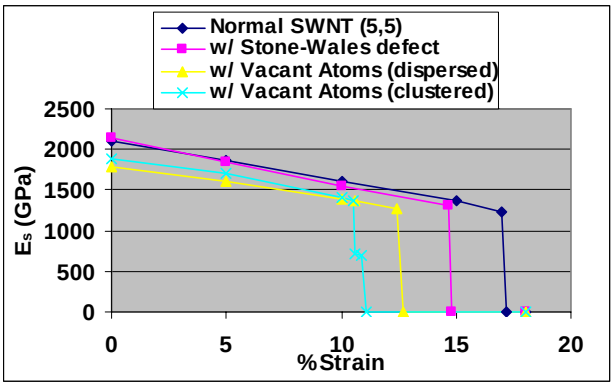


Fig. 4. Predicted uniaxial stress-strain behavior for the (5,5) carbon nanotubes

The initial Young's secant moduli calculated from the (5,5) nanotube simulations ranged from 0.92 TPa (134 million pounds per square inch) to 1.1 TPa (160 million pounds per square inch) or roughly five times that of steel (Fig. 5). It is not clear that these differences are outside the accuracy of the analysis methods. In all four cases strain softening of the carbon nanotube was observed, with the secant moduli decreasing with strain. In all four cases the (5,5) carbon nanotubes ultimately suffered brittle failure, with the tubes being torn into approximately two equal sections with exposed end surfaces approximately perpendicular to the nanotube axis (Fig. 6). This brittle behavior may be less severe at higher temperatures.



Fig, 5. Predicted Young's secant moduli for the (5,5) carbon nanotubes

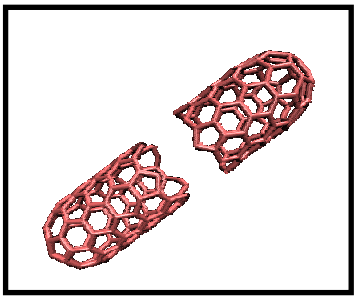


Fig. 6. Failed (5,5) carbon nanotube with the Stone-Wales defect

These results are in coarse agreement with those reported by other researchers using numerical simulations (for example, Belytschko et al., 2002; Sears and Batra, 2004; and Sammalkorpi et al., 2004). The few experimental results that are available generally do not have detailed definition of the carbon nanotube's chirality or a description of molecular defects contained by the tubes; thus a gap currently exists between the numerical simulations and experimental evidence that can refute or validate the numerical results. This is understandable given the extraordinary difficulties of observation and testing at the nanometer level and the tens of thousands of atoms that make up a single carbon nanotube.

Fig. 7 provides the derived uniaxial stress-strain relation derived for the (10,5) carbon nanotube. The abrupt changes in the stress levels are attributed to the numerical differentiation process used in deriving the stress and are not considered real. The peak stress carried by the (10,5) carbon nanotube is about 27 GPa (3.9 million pounds per square inch) and is substantially less than seen in the four (5,5) carbon nanotubes previously described. The postyield response of the (10,5) carbon nanotube is also substantially different. The (10,5) carbon nanotube does not suffer brittle failure after peak, but instead continues to carry significant loads of about 2.0 to 2.5 GPa (290 to 360 kips per square inch) while continuing to strain to about 95 percent strain. What is happening during this portion of the response is that the carbon nanotube is tearing and unraveling at a small angle relative to the axis of the tube, while it is carrying substantial load. Fig. 8 displays several time-sequences in the process from the simulation. This very favorable postyield "super toughened" is very desirable for many applications as explained below.

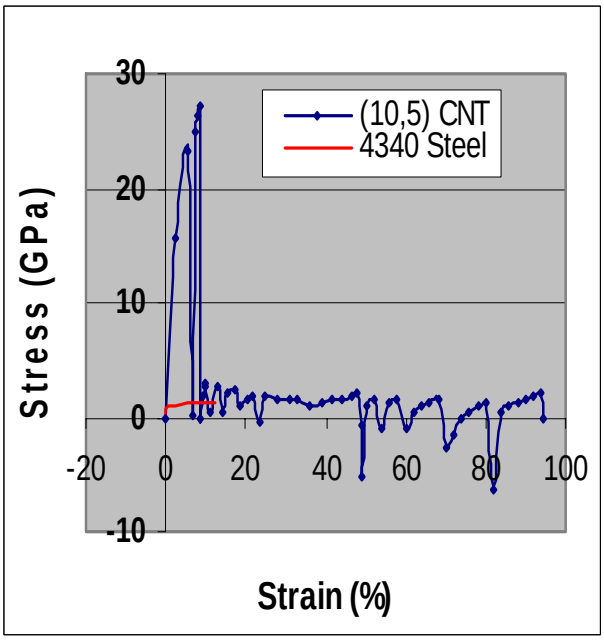


Fig. 7. Predicted uniaxial stress-strain behavior for (10,5) carbon nanotube showing extreme toughness behavior

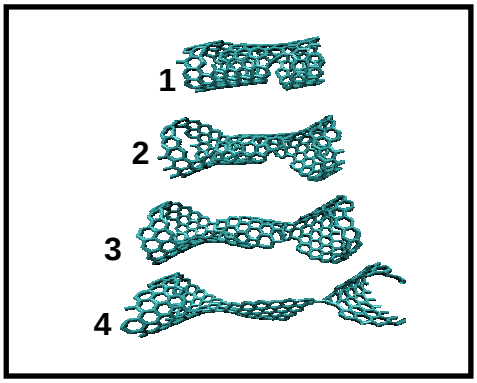


Fig. 8. Failure sequence of (10,5) carbon nanotube with single vacancy defect

Also shown in Fig. 7 is a plot of the uniaxial stress-strain curve for 4340 Steel hardened to 1.3 GPa (190 ksi)

tensile strength. Most high-strength steels suffer brittle failure. The 4340 Steel alloy heat-treated to this degree is one of few high-strength steels that have both very high tensile strength and good toughness behavior. For both the carbon nanotube and the 4340 Steel, the area under the stress-strain curves represents the amount of energy that can be absorbed by the materials during deformation. The (10,5) carbon nanotube provides an order of magnitude greater energy absorption than the 4340 Steel for the same cross-sectional area.

Brittle materials in bulk, even if very strong, often suffer abrupt failures even when loaded by an average stress that does not exceed their peak stress capabilities. This is because during dynamic loading, or because of the geometry of the structure under load, or because of material inhomgenuities, stress and strain concentrations can occur at local volumes of the material (e.g., stress concentration factors). The material within these volumes can thus be subjected to stresses beyond the material's capacity and fail. The load is then transferred to the next neighboring location, and the failure process begins again until an entire cross-section or region is failed.

Materials that have good postyield behavior, by contrast, undergo significant strain under localized loading as described above, and transfer the portion of the stress beyond their yield point to neighboring areas. These materials are thus more forgiving of dynamic loads or unfavorable geometries.

Based on these simulation results, the chiral (10,5) carbon nanotube is predicted to display this favorable toughness behavior to a greater extent than any existing building materials known to the authors.

CONCLUSIONS

We performed a series of molecular-level predictive rheological simulations using the DoD Tight-Binding Molecular Dynamics code to calculate nanotube potential energy as a function of the molecular deformation. From these results we inferred uniaxial stress-strain constitutive behavior of the systems. The systems considered were (5,5) carbon nanotubes in pristine form (no defects) and with three types of molecular defects (scattered and clustered vacancies and Stone-Wales defect). The molecular defects lowered the peak stress and the strain at failure from that exhibited by the pristine carbon nanotube. In all four cases the carbon molecules suffered strain softening leading to ultimate abrupt (brittle) failure. The peak stress and strain carried by the (5,5) carbon nanotubes ranged from 74 to 107 GPa (10.7 to 15.5 million pounds per square inch) and 10.5 to 17 percent. The calculated initial secant Young's modulus ranged from 0.92 TPa to 1.1 TPa (134 to 160 million pounds per square inch) or about five times that of steel. These numerical results are in general agreement with those reported by others.

Using the same numerical and analyses techniques, we then modeled a (10,5) carbon nanotube that had a single vacancy defect. This simulation predicted a much different uniaxial stress-strain response for the (10,5) carbon nanotube from that of other carbon nanotubes modeled. In this case, very favorable postyield toughened behavior was predicted, with significant postyield load (2 to 2.5 GPa or 290 to 360 kips per square inch) being carried by the nanotube while undergoing strain to 95 percent. The mechanism causing this super toughness response is the failure pattern of the nanotube, which consists of carbon-carbon bond breaking along a shallow angle relative to the axis of the nanotube, thus involving many bonds breaking before ultimate rupture of the tube.

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