Mechanics of Atomic Scale Interfaces in Carbon Nanotube Reinforced Composites

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Summary

Interfaces can be defined as regions of separation between two different bodies. The basic issue raised in this work is how the mechanics at nanoscale interfaces in carbon nanotube (CNT) based composites differ from that of interfaces in conventional. We model interfaces in CNT based composites as hydrocarbon chemical attachments between the matrix and CNT using molecular dynamics. Some interesting observations unique to nanoscale are presented. Effect of chemical attachments on the mechanical properties of CNTs is also investigated.

Introduction

Carbon nanotubes possess excellent combination of mechanical and thermal properties with high aspect ratio. Stiffness of CNTs measured experimentally [1] and calculated from simulations [2] is about 1000 GPa. The tensile strength of CNTs is measured to be of the order of 150 GPa [3]. This combination of mechanical properties has great possibility of obtaining super-strong and stiff composites with CNTs as reinforcements.

In order to translate these excellent mechanical properties of CNTs to that of composites, CNT- matrix interfaces have to be engineered to obtain maximum strength. Chemical cross-linking of CNTs and matrix is a possible method to improve the interface strength. Chemical attachments to CNTs can possibly change the mechanical properties of fibers [4]. We first study the mechanical properties of CNTs with chemical attachments using molecular dynamics (MD) and compare with those of defect free CNTs. We then perform MD simulations of CNT pullout from matrix with interfaces modeled as hydrocarbon chemical attachments. The interface strength obtained with different densities (number of attachments /Area) and novel features observed in CNTs are discussed. We further suggest methods to obtain interface constitutive relation in form of traction-displacement plots for cohesive zone models form atomic simulations. These traction-displacement plots can be used in a continuum setting to study the mechanical behavior of CNT based composites.

Deformation of Functionalized Carbon Nanotubes

We use molecular dynamics and statics simulations based on Tersoff-Brenner bond-order potential [5] to evaluate the tensile stiffness and stress-strain response of various zigzag and armchair CNT with and without hydrocarbon functional attachments. Stiffness can be evaluated as the second derivative of energy with respect to strain, or as the ratio of stress and strain. The later method is preferable as it involves fewer assumptions and

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further enables the calculation of local properties. Various stress and strain measures used in MD applicable to CNTs are discussed in detail elsewhere [6]. We primarily use Lutsko stress to characterize stress Strains are calculated as derivative of displacement field, heavily borrowing from the concepts of finite elements discussed in the above reference [6].

Zigzag and armchair nanotubes with varying diameter were considered for this study. All the nanotubes are about $120\overset{\circ}{A}$ in length, tensile stresses were applied by fixing and displacing both the ends of nanotubes (15 $\overset{\circ}{A}$ on either side) followed by stabilization for 1500 time steps with a step size of 0.2 fs. The temperature is maintained at 77K. Hydrocarbon chains are attached to the nanotubes at randomly selected positions in the central region of nanotube. Stresses and strains are computed in this central region where the hydrocarbon chains are attached and compared with defect free nanotubes.

Figure 1 shows the Lutsko stress vs. strain plots for (10,10) nanotube without any chemical attachments, and with 21 vinyl attachments in the central region. There is a marginal increase in local stiffness when the carbon chains are attached (For e.g. 0.84 to 0.92 TPa for (10,10) CNT). Table 1 provides the computed stiffness values for various cases of diameters, chirality, number and type of hydrocarbon attachments studied here. In all the cases, the local stiffness increases with any type of chemical attachment. This effect is more pronounced in nanotubes with smaller diameter. For e.g. there is an increase in local stiffness from 0.86 TPa to 1.05 TPa in (8,0) CNT of radius 3.13 $\overset{\circ}{A}$ while, in the case (15,0) nanotube with radius 5.87 $\overset{\circ}{A}$ stiffness increases to 0.95 TPa. (See rows 1 to 4 and 5 to 7 of the table). In order to observe the effect of number of chemical attachments, different numbers of chains (21, 31 and 50) are attached to (10,10) nanotube. Stiffness increases from 0.83 TPa to 0.93 TPa with 21 vinyl attachments; it increases to 1.02 and 1.11 TPa with 31 and 50 attachments respectively (Rows 11 and 12 of Table1). This is understandable based on concentration of chemical attachments. Evidently, the concentration of chemical attachments is higher in CNTs with lower radius; also increasing the number of hydrocarbon chains increases the concentration of chemical attachments.

There is an alteration in chemical bonding at the site of hydrocarbon attachment; the SP2 hybridization in CNT is altered to diamond like SP3 hybridization. It is observed that the radius at these locations is about 7.3 $\overset{\circ}{A}$ as compared to 6.78 $\overset{\circ}{A}$. In addition, there is a decrease in radius of curvature in regions adjoining the location of attachment (see figure 2). Because of this, there is a reasonable deviation from the ideal cylindrical structure of nanotubes resulting in sort of 'serrations' in the region of chemical attachments, which is possibly responsible for the increased stiffness.

We now proceed to examine how the interface strength is affected if CNTs are chemically bonded to the matrix.
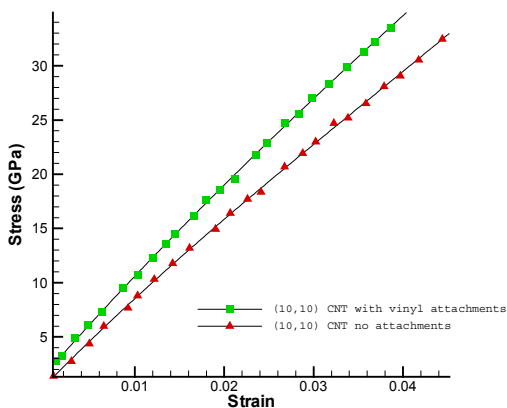
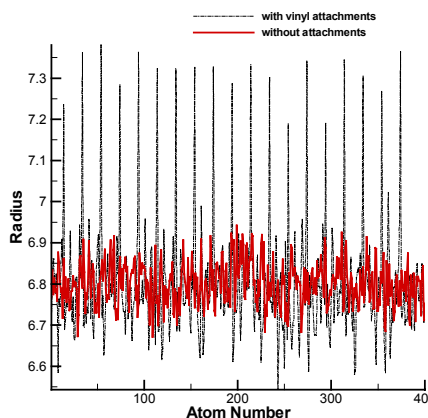Fig 1. Stress-Strain Plots of functionalized CNT

Fig 2. Radius variation in functionalized CNT

Table 1: Stiffness of various functionalized CNT

S.No	Nanotube	Radius (A)	Chemical Group	Number of Attachments	Stiffness (TPa) (w/o attachments)	Stiffness (TPa) (with attachments)
1	(8,0)	3.13	$-C_2H_3{}^*$	21	0.862	1.05
2	(10,0)	3.91	$-C_2H_3$	21	0.854	1.04
3	(12,0)	4.69	$-C_2H_3$	21	0.859	0.977
4	(15,0)	5.87	$-C_2H_3$	21	0.849	0.951
5	(8,8)	5.42	$-C_2H_3$	21	0.721	0.889
6	(10,10)	6.78	$-C_2H_3$	21	0.837	0.932
7	(12,12)	8.13	$-C_2H_3$	21	0.784	0.906
8	(10,10)	6.78	$-C_3H_5$	21	0.837	0.94
9	(10,10)	6.78	$-C_4H_7$	21	0.837	1.03
10	(10,10)	6.78	$-C_5H_9{}^*$	21	0.837	0.95
11	(10,10)	6.78	$^-C_2H_3$	31	0.837	1.02

Atomic Simulations of CNT pullout tests

Evaluation of interfacial properties in composite materials is typically done using single fiber pullout and pushout tests. In the case of CNT reinforced composites, experimental application of mechanical loads on single fibers extremely difficult because of the nanometer size of fibers. Hence, molecular dynamics simulations become a natural choice for studying the interface behavior by simulating pullout tests. We consider the situation where matrix and nanotube are chemically bounded by hydrocarbons chemical attachments.

The boundary conditions applied for the pullout test simulation are as follows (see figure 4). The corner atoms of the hydrocarbon attachments are fixed indicating that they are connected to matrix at those locations. Displacement of 0.05 A is applied to the atoms at one end of the nanotube, about 15 A^o in length in order to simulate the effect of pullout. Following each displacement, the system was equilibrated for 1500 time steps of 0.2 fs duration. The simulations were carried out until some of the hydrocarbon chains fail. Typically, simulations lasted for 500000-800000 time steps. Variations in the length and density (number per unit area) of chemical attachments were investigated for a (10,10) CNT 122A in length.   The reaction force on the fixed atoms is monitored throughout the simulation and is averaged over 100 time steps before applying next set of displacements.

 Figure 5 shows typical force vs. displacement for any hydrocarbon attachment. Though there are statistical variations for different chemical attachments, the general shape of the force displacement plot is as shown. The initial region of curve is flat (parallel to X-axis) marked as region (a). This region corresponds to stretching of the hydrocarbon attachment. The flat region shows that there is minimal load transfer in this portion of curve and is similar to the mechanical analogue of loose strings becoming taut. The length of this flat portion is directly dependant on the length of hydrocarbon chain i.e. the flat region is longer for hydrocarbon chains with four and five carbon atoms than with two carbon atoms. After this flat region, there is a gradual increase in the reaction force corresponding to region (b) of the curve. In this part the carbon chain contributes to the load transfer. Though there are statistical variations from plot to plot, the typical force experienced in this portion of the curve is about 3eV/A (4.8 x 10^{-3} μN). This value of force is very small but it must be noted that the area on which this force acts is of the order of angstroms; consequently, the resulting shear stress is very high. Region (c) of the plot as shown consists of region of fluctuations in the reaction force. This is due to an interesting behavior of bond separation and rejoining with adjacent atoms; when separation occurs there is a sudden drop in force but this is followed by rejoining of the hydrocarbon chain with adjacent atom of CNT. After a series of jagged region in the force -displacement curve there is a sudden increase in reaction force as shown in region (d) of the figure and then total failure occurs. The force at which the failure occurs is about 6eV/A (~10^{-2} μN). This is the force required to break one chemical attachment; the overall force required to break all the chemical attachments is much higher and is sum of all individual reaction forces.

The area under the force-displacement curve denotes the energy required for detaching of the hydrocarbon group from CNT. Calculations based on molecular statics indicate that the energy required for separation is of the order of 3 eV, however the area under the force displacement curve is much higher and is of the order of 20±4 eV for various attachments. This shows that the dynamic process of nanotube pullout requires much higher energy than that predicted based on statics. The main reason for increase in the energy is due to the bonding and rebonding process associated with nanotube pullout. Energy of 3 eV is associated with each time the bond is broken, as this process is

repeated number of times for each chemical attachment the total energy consumed in the separation process is much higher.
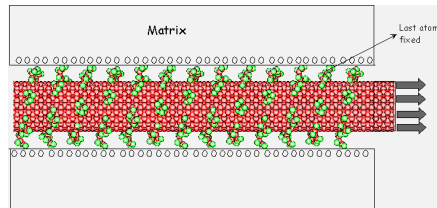

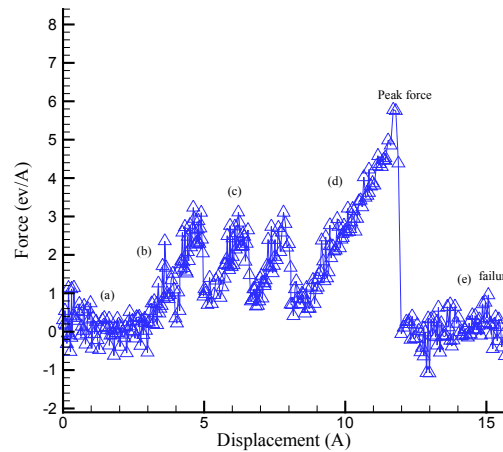Fig 3.Schematic of pullout test

Fig 4. Reaction force Vs displacement plot

The debonding-rebonding behavior observed in pullout test is unique to nanoscale and is generally not observed in conventional composites at macroscopic scale. This phenomenon is not entirely new, for example, similar observations have been made during atomic simulations of stick slip friction and that of metal cutting processes. Zhang and Tanaka [7] have performed simulations of friction on copper surfaces; they observe variation of frictional force in oscillatory manner similar to that of reaction force observed in our simulations. However, significance of this phenomenon is increased here since it affects the load transfer considerably.

The individual force-displacement plots are homogenized based on the force experienced across the length of CNT and then used to generate traction displacement plots for cohesive zone model. The interface strength given by the peak traction is found to be very sensitive to the density of chemical attachments. The interface strength varies from 5 GPa for high density to 50 MPa for low density of functional attachments. To provide a perspective the interface strength of conventional composites is of the order of 50 MPa. These traction displacement plots for CZM can be used in finite element setting to determine the composite properties.

It can be concluded based on the simulations reported here that (a) functionalization of CNTs does not change stiffness of CNTs appreciably. (b) Chemical attachment between matrix and nanotube can enhances the interface strength considerably.
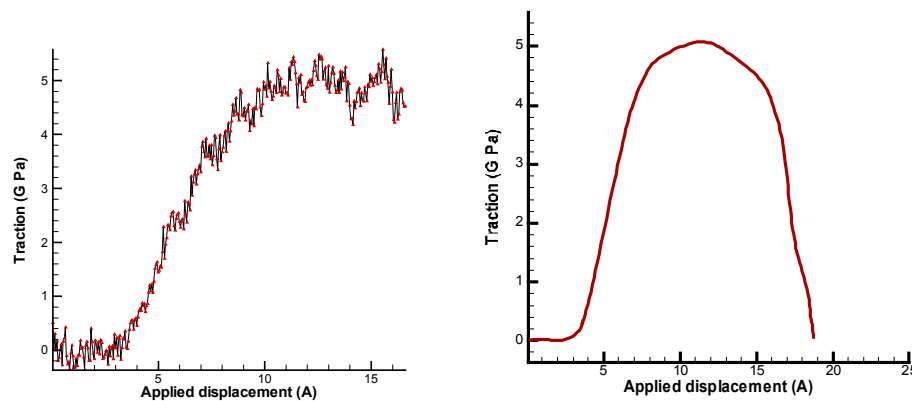
Fig 6. Construction of traction displacement plot for CZM from MD simulations

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