Mechanics of carbon nanotubes and their polymer composites

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Carbon Nanotube: Structures

Atomic structure:
Quasi one dimensional; C-C bond length 1.43 Å;
Radius ~ Nanometer; Length ~ μm (current upper range); Index (n,m)
Application of Carbon Nanotubes

*Nano fibers*: Strong mechanical properties

*Nano devices*: Wide variety of electronic properties and mechanical-electronic couplings

*Nano sensors*: Physical and Chemical adsorption of gas molecules, ions
Simulation Methods

(1) Molecular Dynamics: Newton’s Equation

Force Field for Carbon nanotubes:

*Tersoff Brenner potential*, fitted to carbon and hydrocarbon systems, 3-body type, bond broken and formation

(2) Tight Binding method

(3) Ab initio method (Density Functional theory)
Elastic Properties of Carbon Nanotubes

Small strain: uniform deformations, elastic behavior
continuum theory applicable

Large strain: local deformations, defects, dislocations
Tension, Compression, bending, and (Torsion):
Yield Strain of CNT

Tension


Compression

*Simulation*:
T=0K, Tersoff-Brenner potential: Super-elastic up to 20%
T=0K, Tight Binding: diamond like defects, collapsed at 12%

*Experiment*:
Collapsing of CNT within polymer matrix under compression stress 150GPA (TEM study)
11.5% tensile strained
CNT (10,0), T=1600K

9% tensile strained
CNT (5,5), T=2400K

Yielding: Strain-rate and Temperature Dependence

Tensile strain applied to a 60Å long (10,0) CNT

- Yielding: strongly dependent on strain rate and Temperature
- Linear dependent on temperature of the slope of yield strain vs. strain rate: Activated Process
Yield Strain under Tension

\[
\varepsilon_Y = \frac{E_v}{VK} + \frac{k_B T}{VK} \ln\left(\frac{N \dot{\varepsilon}}{n_{\text{site}} \dot{\varepsilon}_0}\right)
\]

\(\dot{\varepsilon}\) : Strain rate;  \(\dot{\varepsilon}_0\) : Constant related with vibrational frequency

\(K\) : Force constant;  \(V\) : Activation volume;  \(E_v\) : Activation energy

\(N\) : Number of process involving in yielding;  \(n_{\text{site}}\) : Site available

Length effect:

\[\Delta \varepsilon_Y = -\frac{k_B T}{VK} \ln\left(n_{\text{site}}/n_{\text{site}}^0\right)\]

Temperature effect:

\[
\left(\frac{\dot{\varepsilon}_1 N}{n_{\text{site}} \dot{\varepsilon}_0}\right)_{T_1} = \left(\frac{\dot{\varepsilon}_2 N}{n_{\text{site}} \dot{\varepsilon}_0}\right)_{T_2}
\]
Yielding at Realistic Conditions

- Parameters obtained from fitting of MD simulations' data
  \[ \overline{E}_r = 3.6\text{eV}; \quad V = 2.88 \text{Å} \]
  \[ \frac{\dot{\varepsilon}_0}{N} = 8 \times 10^{-3} \text{ps}^{-1} \]

- Experimental feasible conditions
  length \(\sim 1\mu\text{m}\); strain rate \(\sim 1\%\text{/hour}\); \(T \sim 300\text{K}\)

\[ \implies \text{Yield strain: } 9 \pm 1\% \]

Maximum tensile strains from experiments:
5-6\% for SWCNT ropes; 12\% for MWCNTs

Yielding of MWCNT

(1) For $\dot{\varepsilon} = 1\%$/hour, and $T=300K$

$\varepsilon_Y$ (MWCNT)>(SWCNT): 3-4%;

(2) Activation volume on MWCNT is smaller (60%-70% of that on SWCNT);

(3) Crossover point of strain rate exponentially dependent on $T$, important for high temperature situations.
Load transfer on MWCNT

Load transfer on MWCNT

![Graph showing load transfer on MWCNT](image)

- Total
- Outer shell (20,0)
- Inner shell (10,0)
- Intershell VDW

Change of potential energy (eV)

Tensile strain on outer shell (20,0) (%)

Change of strain energy of inner shell (10,0)

T = 2400K

Rate1: 0.25%/80ps
Rate2: 0.25%/40ps
Rate3: 0.25%/20ps
Rate4: 0.25%/10ps
CNT: Nano Fibers

**CNT to reinforce composites**

- High Strength & High flexibility & Toughness & light-weight (Young’s Modulus > 1TPa)

- High aspect ratio L/D, can reach 1000

  Critical length: $\frac{L_c}{D} \sim \frac{\sigma_{\text{max}}}{2\tau}$
  - $L_c$: length of CNT; $D$: diameter of the CNT;
  - $\sigma_{\text{max}}$: tensile strength of CNT;
  - $\tau$: interfacial shear stress

- Large surface area, good for bonding, adhesion
Polymer-CNT Composite

- Structural and thermal properties
- Load transfer and mechanical properties

SEM images of epoxy-CNT composite

SEM images of CNT fibers ribbon (processing in polyvinylacohol solution) & knotted CNT fibers

MD Simulations of Polymer-CNT

Simulation method

Classical MD: Tersoff-Brenner potentials for CNT, DLPOLY for polymer, and VDW interactions

System in simulation

Polyethylene & (10,0) CNT: (80 chains of PE relaxed by Monte Carlo methods, Np=10; 20Å long CNT 8% volume ratio)

Preparations

Composites prepared at 300k; cooled down to 10K with rate 1K/1ps
composites change from liquid state through rubber state to glassy state
**Force Field**

*Intramolecular potentials*

Valence angle potential: \[ \Phi(\theta) = 0.5k_0 (\cos \theta - \cos \theta_0)^2, \]

Torsion potential: \[ \Phi(\alpha)/J\cdot \text{mol}^{-1} = C_0 + C_1 \cos \alpha + C_2 \cos^2 \alpha + C_3 \cos^3 \alpha, \]

Harmonic potential: \[ 0.5 k_b (l-l_0)^2 \]
Density Dependence on Temperature

Small system: L/D ~ 2, Np = 10

Results
- Glass transition temperature $T_g$ increased from 150K to 175K
- Thermal expansion coefficients: $(K^{-1})$

<table>
<thead>
<tr>
<th></th>
<th>PE</th>
<th>PE-CNT</th>
<th>$\uparrow$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T &lt; T_g$</td>
<td>$3.8 \times 10^{-4}$</td>
<td>$4.5 \times 10^{-4}$</td>
<td>18%</td>
</tr>
<tr>
<td>$T &gt; T_g$</td>
<td>$8.6 \times 10^{-4}$</td>
<td>$12.0 \times 10^{-4}$</td>
<td>40%</td>
</tr>
</tbody>
</table>

(Experimental value: $1.0 \times 10^{-4} K^{-1}$; $T < T_g$)
**Diffusion Coefficients**

Small system: L/D~2, Np=10

Diffusion coefficients of polymer with CNTs embedded

Diffusion coefficient increased, especially along CNT axis direction, indicating enhancement of thermal conductivity

- Experiments on ABS/CNT & RTV/CNT show larger increase (Rick Berrera’s group at RICE)
  - (Ajayan’s group at R.P.I. is investigating these subjects in detail)

* C. Wei, D. Srivastava, and K. Cho (Nano Letters, in press)
Modulus of Polymer-CNT Composites

(Halpin-Tsai's formula)

\[
\frac{E_c}{E_m} = \frac{1 + \xi \eta V_f}{1 - \eta V_f}
\]

\[
\eta = \frac{(M_f / M_m - 1)}{(M_f / M_m + \xi)}
\]

\(E_c, E_m, E_f\) : Modulus of composite, matrix and fiber

\(V_f\) : Volume ratio of fiber

\(\xi\) : Dependent on geometry, packing of fiber; aspect ratio of fiber

\[\frac{E_{cnt}}{E_m} \sim 1000\]

![Graph showing the relationship between modulus and volume ratio of CNT fiber]

- Continuous fiber
- Fiber aligned, L/D ~ 1000
- Randomly oriented fiber, L/D ~ 1000
- Fiber aligned, L/D ~ 10
Stress-Strain Curve & Load Transfer

Mechanical behavior of Composite:
Elastic region and Yielding

- Enhancement of Young’s modulus: 30%
- Load transfer: within 0.7%
- Poisson Ratio effect:
  - CNT ~ 0.1-0.2, Polyethylene ~ 0.44
- Compression pressure perpendicular to tube axis contribute to improvement
Loading Sequence

Work hardening of composite with stretching

TEM images of alignment of CNTs in a polymer matrix by stretching

- Residue strain

**Young’s Modulus**

- Young’s modulus of CNT composites 30% higher than polymer matrix
- Stretching treatments enhance Y by 50%

\[(L/D \sim 2, N_p = 10)\]

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**Graphs:**

1. **Composite** vs. **Polymer Bulk**
   - Tensile Stress vs. Tensile strain (%)
   - Composite: \[ Y = 1907 \text{MPa} \]
   - Polymer Bulk: \[ Y = 1492 \text{MPa} \]

2. **Strain** vs. **Tensile Stress**
   - Stress rate: 1 bar/1 ps
   - Temperature: 50K
   - Composite after stretching: \[ Y = 2308 \text{MPa} \]

**References:**
1. Polymer bulk; \[ Y = 1492 \text{MPa} \]
2. Polymer bulk after stretching; \[ Y = 1585 \text{MPa} \]
3. Composite; \[ Y = 1907 \text{MPa} \]
4. Composite after stretching; \[ Y = 2308 \text{MPa} \]
Conclusions

- Yielding of carbon nanotubes strongly dependent on strain rate and temperature: transition state theory

- Polymer-CNT composite has larger thermo-expansion above Tg
  - Phonon modes and Brownian motion leading to larger exclude volume of embedded CNT
  - Diffusion of polymer matrix increased above Tg

- Young’s modulus of composite enhanced by 30% through VDW interaction.
  - Load transfer happening within 0.7%; stiffness of CNT bond increases modulus of composite
  - Loading sequence can improve the enhancement of modulus of composite