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Effects of nanotube waviness on the modulus of nanotube-reinforced polymers

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Recent experimental results demonstrate that substantial improvements in the mechanical behavior of polymers can be obtained using very small amounts of carbon nanotubes as a reinforcing phase. Here, a method is developed to incorporate the typically observed curvature of the embedded nanotubes into traditional micromechanical methods for determination of the effective modulus of the nanotube-reinforced polymer. Using a combined finite element and micromechanical approach, it was determined that the nanotube curvature significantly reduces the effective reinforcement when compared to straight nanotubes. This model suggests that nanotube waviness may be an additional mechanism limiting the modulus enhancement of nanotube-reinforced polymers. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1487900]

Within the last ten years carbon nanotubes (NTs) have raised considerable interest in the scientific community due to their size and wide range of outstanding material properties. For example, carbon NTs have been predicted to have Young's moduli on the order of 1 TPa, tensile strengths 20 times that of high strength steel alloys, current capacities 1000 times that of copper, and thermal conductivities double that of pure diamond.[1] Experimental efforts on individual nanotubes have often validated these theoretical predictions.[2–5] These properties are a result of the near-perfect microstructure of the nanotubes, which at the atomic scale can be thought of as a hexagonal sheet of carbon atoms that is rolled into a seamless, quasi-one-dimensional cylindrical shape.[6]

One potential application that has been the subject of numerous investigations is the use of NTs as a small volume fraction filler phase in nanotube-reinforced polymers (NRPs). Of particular interest is the use of NRPs for structural applications, where recent experimental results demonstrate that substantial improvements in the mechanical behavior of the polymer can be attained through the addition of very small amounts of carbon nanotubes.[7–11] While promising, these initial results have yet to achieve the magnitude of property enhancement believed possible. Several fabrication and modeling issues have been identified and need to be addressed to optimize the properties of such materials, including dispersion of the NTs within the polymer, NT-polymer bonding and interaction, and nanotube orientation and alignment. The different forms (single-walled, multi-walled, and bundles) and various methods used to fabricate the NTs will also greatly influence the effectiveness of nanotubes as structural reinforcement.

A critical issue that has yet to be examined is the impact of the shape of the embedded nanotube on the effective mechanical properties of the nanotube-reinforced polymer. As shown in Fig. 1, embedded nanotubes seldom appear as straight inclusions but are rather often characterized by a certain degree of waviness along their axial dimension. We propose that this waviness significantly reduces the structural reinforcement that the NTs provide the host polymer material, in comparison to the theoretical reinforcement provided by straight inclusions.

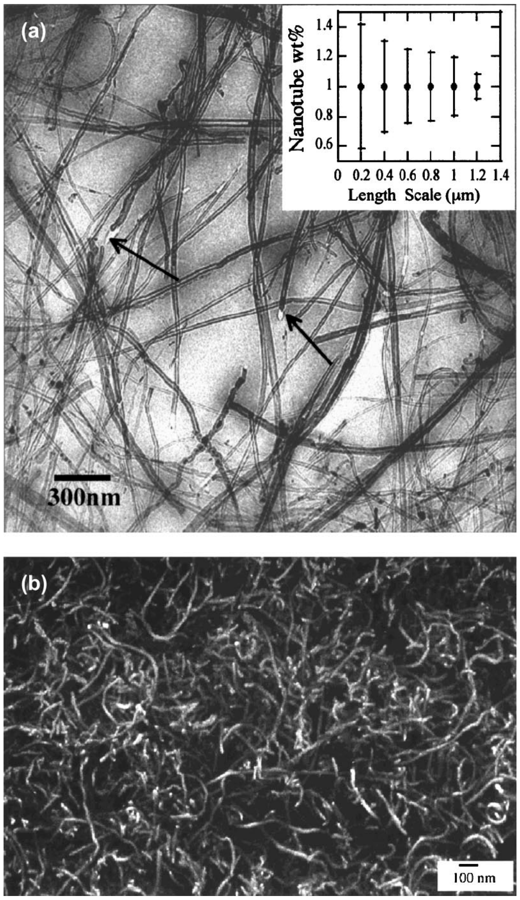

FIG. 1. Images of nanotube-reinforced polymers showing that the embedded nanotubes exhibit significant curvature within the polymer. (a) Transmission electron microscopy image of MWNTs (1 wt %) in polystyrene (Ref. 8). The arrows and inset in the figure are from the original source and show defects in the as-prepared sample and the homogeneity of the MWNT distribution over different length scales. (b) Scanning electron microscopy image of MWNTs (50 wt %) in poly(vinyl alcohol) (Ref. 10).

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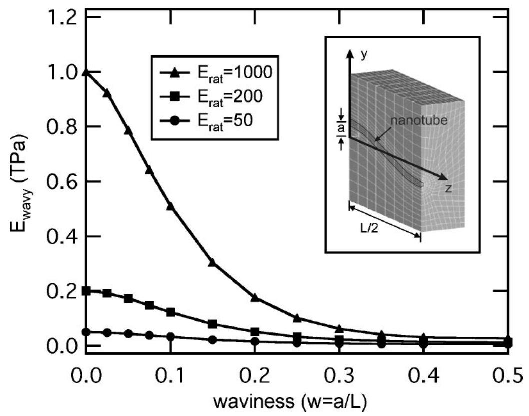

FIG. 2. Finite element modeling of an infinitely long wavy nanotube embedded in a matrix, showing the impact of the waviness ratio $w=a/L$ and the ratio of the phase moduli $E_{\mathrm{rat}}=E_{\mathrm{NT}}/E_{\mathrm{matrix}}$ on the effective reinforcing modulus of a wavy nanotube E_{wavy} for $L/d=250$. For all simulations, $E_{\mathrm{matrix}}=1$ GPa. (*inset*) A representative unit cell used in the analysis. The x axis is perpendicular to the $y-z$ plane, and the extent of the matrix is such that the dilute solution approximation is obtained.

In this letter we develop a simple model to assess the impact of nanotube waviness on the effective modulus of an NRP. Because this phenomenon does not appear in traditional microscale composites, it is necessary to incorporate a model of inclusion waviness into existing composite models.[12] To do this we first calculate the effective reinforcing modulus of a single wavy nanotube embedded in the matrix material, and then utilize a multiphase composite model to predict the modulus of the NRP. Although at the moment it is impossible to experimentally distinguish between the effect of nanotube waviness and other variables (such as NT-polymer interaction, dispersion, orientation, etc.), our theoretical results (later) suggest that NT waviness significantly influences the effective NRP properties and highlights the complexity of modeling these materials.

We used ANSYS™ to create a three-dimensional finite element model of a single, infinitely long wavy nanotube of diameter d perfectly bonded within a matrix material. Nanotube waviness was modeled by prescribing a sinusoidal NT shape[13] of the form $y=a\cos(2\pi z/L)$, where L is the wavelength of the cosine function and z is the fiber axial direction. For axial loading the problem is symmetric about the $x=0$ and $z=nL/2$ (where n is an integer) planes; thus a quarter-symmetric unit cell is used for the finite element work (see Fig. 2 inset). Symmetry conditions are prescribed on the $x=0$ and $z=0$ planes, and sufficient matrix material was modeled to provide a dilute solution approximation.[14] For the simulation an infinitesimally small displacement, Δ, is prescribed to all nodes on the plane $z=L/2$, and the effective modulus of the cell is defined as

$$E_{\mathrm{cell}}^{FEA}=\frac{F_{\mathrm{tot}}L}{2A\Delta}, \tag{1}$$

where F_{tot} is the sum of all nodal resultant forces on the $z=L/2$ plane and A is the cross-sectional area of the finite element cell. Defining E_{wavy} as the effective reinforcing modulus of the wavy NT as it exists in the polymer,[15] a parallel model independent of Eq. (1) can also be proposed

$$E_{\mathrm{cell}}^{\mathrm{Parallel}}=c_{\mathrm{NT}}E_{\mathrm{wavy}}+(1-c_{\mathrm{NT}})E_{\mathrm{matrix}}, \tag{2}$$

where c_{NT} is the volume fraction of the nanotube within the unit cell and E_{matrix} is the matrix modulus. Equating the parallel model to the result obtained by FEA modeling, E_{wavy} can be determined,

$$E_{\mathrm{wavy}}=\frac{E_{\mathrm{cell}}^{FEA}-(1-c_{\mathrm{NT}})E_{\mathrm{matrix}}}{c_{\mathrm{NT}}}. \tag{3}$$

For a straight NT $(a=0)$, we have verified numerically that $E_{\mathrm{wavy}}=E_{\mathrm{NT}}$.

Assuming that the NT and matrix materials are isotropic with equal Poisson ratios,[16] we analyzed how the waviness ratio $(w=a/L)$ and the ratio of the phase moduli $(E_{\mathrm{rat}}=E_{\mathrm{NT}}/E_{\mathrm{matrix}})$ influences the effective reinforcing modulus E_{wavy} of a curved nanotube (see Fig. 2). An aspect ratio L/d of 250 was assumed for the current work and has been shown elsewhere to have minimal influence on the resulting E_{wavy} for sufficiently large aspect ratios.[12] Finite element simulations for a wide range of these parameters applicable to nanotube-reinforced polymers were conducted and key results are summarized in Fig. 2. As expected, E_{wavy} is strongly dependent on the NT waviness and quickly decreases with increasing nanotube curvature. This effect is more pronounced as the ratio of the phase moduli is increased.

Because NRP micrographs typically show embedded nanotubes with significant curvature (see Fig. 1), modeling the NTs as straight inclusions is a simplification that will significantly overestimate the reinforcement that the NTs provide the polymer. Since the effective reinforcing modulus of the NT is strongly dependent on its geometry (see Fig. 2), and it is likely that the embedded NTs will exhibit different degrees of waviness, we suggest that an appropriate model for a NRP can be constructed from a multiphase composite approach.

Here we model the composite as consisting of N nanotube phases, each differing only in their effective reinforcing moduli E_{wavy} due to differing magnitudes of waviness as outlined earlier. In practice, such a solution could be developed by imaging a representative portion of the NRP and developing an appropriate waviness distribution function characterizing the nanotube waviness [see Fig. 3(a)]. This information, along with the spatial orientation of the NTs, can be used within an appropriate micromechanical method to estimate the effective moduli of a nanotube-reinforced polymer. In particular, the Mori–Tanaka solution for a multiphase composite with randomly orientated cylindrical inclusions is well suited for this analysis,[17] where each NT phase is modeled as an isotropic material of cylindrical shape with an effective reinforcing modulus E_{wavy} (see Fig. 2) based on its embedded geometry. Note that the Mori–Tanaka method accounts for the stress-field disturbance due to neighboring nanotube inclusions.

To highlight this procedure we have analyzed data for multiwalled nanotubes (MWNTs) (10 wt %) embedded in polystyrene[11] via shear mixing. Figure 3(b) compares the experimentally measured moduli with micromechanics predictions obtained assuming two- and three-dimensional random orientations of straight and wavy NTs. (For the former, the reported modulus is in the plane of random orientation.) The wavy NT calculations assumed the waviness distribution in Fig. 3(a), while the corresponding E_{wavy} values were deter-

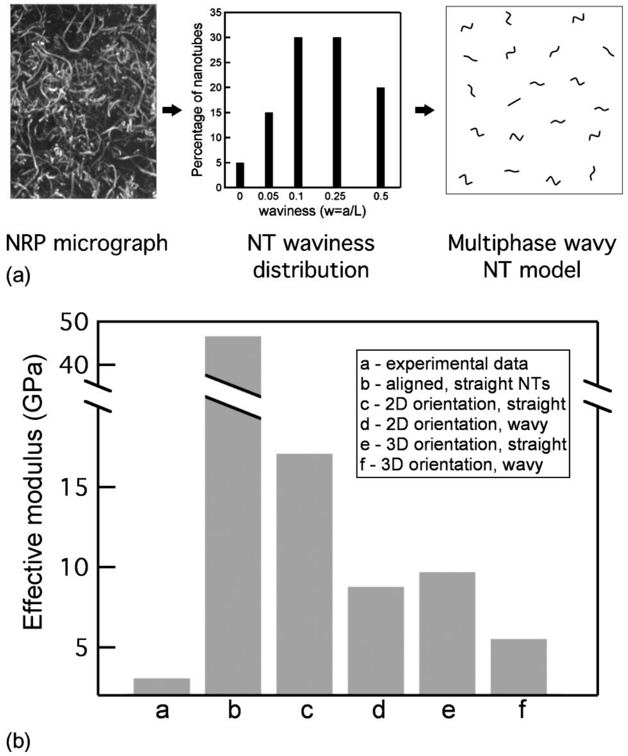

FIG. 3. (a) Schematic of the micromechanical approach to account for nanotube waviness. (b) Experimental data (10 wt % MWNTs in polysytrene) (Ref. 11) and micromechanical predictions (assuming straight and wavy nanotubes) of NRP effective moduli with different NT orientations. The modulus of the polystyrene matrix was 1.91 GPa, and the following parameters describe the discrete NT phases modeled in the wavy NT calculations: ($w=0$, $E_{\text{wavy}}=450$ GPa, NT fraction$=0.05$), (0.05, 377, 0.15), (0.1, 283, 0.30), (0.25, 91, 0.30), (0.5, 42, 0.20).

mined based on the results of Fig. 2 ($E_{\text{rat}}=200$) and an estimated (straight) MWNT modulus E_{NT} of 450 GPa.[18] The results first show that moving from a model of perfectly aligned, straight NTs to randomly orientated straight NTs can decrease the potential reinforcement of the NRP by more than a factor of 2. The micromechanics predictions for randomly orientated *wavy* NTs, assuming an appropriate distribution of NT waviness,[19] show that moderate NT waviness can further reduce the predicted effective modulus of the NRP by an additional factor of 2. While it is impossible to isolate the effects of NT waviness from those of bonding, alignment, NT dispersion, and other reinforcement-limiting mechanisms in the existing experimental data, our modeling results nonetheless demonstrate that NT curvature and alignment significantly influence the mechanical behavior of NRPs.

In summary, nanoscale imaging of various nanotube-polymer composites has consistently shown that nanotubes typically remain curved when embedded in polymer materials. Using finite element and micromechanics methods, we have shown that this waviness can greatly reduce the effective reinforcing modulus of the nanotubes, thus limiting the overall effective modulus of the NRP. Finally, a method to calculate the effective moduli of polymers with embedded wavy nanotubes has been developed. The nanotube inclusions in a given composite are partitioned into several discrete phases, where each phase represents the fraction of NTs with a given waviness. The effective reinforcing moduli E_{wavy} for each NT phase, based on this waviness, are then utilized within a micromechanical multiphase composite analysis to provide the overall effective modulus of the composite with wavy nanotubes. Such a model highlights nanotube waviness as one of several key mechanisms that may ultimately determine the effectiveness of nanotube materials as a reinforcement phase for structural applications.

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[13] While a sinusoidal shape was assumed here, it would be straightforward to extend this analysis for more complex embedded nanotube shapes.
[14] A dilute solution assumes no contribution from the cell boundaries and no interaction between inclusions.
[15] Note that due to the constraint of the surrounding matrix, E_{wavy} will be dependent on the matrix modulus for the case of an embedded nanotube.
[16] Poisson ratios of 0.30 were assumed for all simulations. This value is representative of a wide range of polymer materials, and while the Poisson ratio for nanotubes has been estimated to be slightly lower, the effect on E_{wavy} is small.
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[19] Lacking an appropriate image of the nanostructure of the material, this distribution was based on the NRP images shown in Fig. 1 and represents a nonunique, but reasonable, estimation of NT waviness.