Analysis of uniaxial compression of vertically aligned carbon nanotubes

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Abstract

We carry out axisymmetric, finite deformation finite element analyses of the uniaxial compression of cylindrical bundles of vertically aligned carbon nanotubes (VACNTs) firmly attached to a Si substrate. A compressible elastic–viscoplastic constitutive relation with a piecewise, linear hardening–softening–hardening flow strength is used to model the material. Calculations are performed for VACNTs both with uniform properties and with axially graded properties. We show that, with uniform properties, sequential buckling initiates at the substrate and propagates away from it, in agreement with previous experimental findings. We investigate the dependence of the magnitude and wavelength of the buckles on characteristics of the function defining the flow strength. When a property gradient giving a more compliant response at the end opposite to the substrate is specified, we find that sequential buckling initiates at that end and propagates toward the substrate. Results of the analyses are compared with the experimental observations and capture many of the experimentally obtained stress–strain and morphological features. The proposed model serves as a promising foundation for capturing the underlying energy absorption mechanisms in these systems. Comparison of the model predictions with the experimental results also suggests directions for model improvement.

1. Introduction

Vertically aligned carbon nanotubes (VACNTs), referred to within the literature as carbon nanotube (CNT) forests, turfs, brushes, and mats, have shown promising mechanical properties for use in a variety of applications, for example, viscoelastic energy absorption (Cao et al., 2005; Gogotsi, 2010; Misra et al., 2009; Pathak et al., 2009; Xu et al., 2010; Zhang et al., 2010), compliant thermal interfaces (Cola et al., 2009; McCarter et al., 2006; Zbib et al., 2008), and biomimetic dry adhesives (Boesel et al., 2010). A fundamental understanding of their mechanical behavior is of paramount importance as it provides the basis for design in these applications as well as for in-use lifetime analysis in the various VACNT technologies in which mechanical properties may be of secondary importance. Several groups have published studies of the mechanical properties of VACNTs measured through nanoindentation (McCarter et al., 2006; Mesarovic et al., 2007; Pathak et al., 2009; Qiu et al., 2011), uniaxial compression (Cao et al., 2005; Hutchens et al., 2010; Raney et al., in press; Suhr et al., 2007; Tong et al., 2008; Zbib et al., 2008), and impact testing (Daraio et al., 2006; Misra et al., 2009). Variations...
in observed behavior and quantitative results in these publications illustrate that the wide variety of growth conditions that can, in turn, result in significant dissimilarities in the mechanical properties, including deformation morphology, the amount of post-deformation recovery, and the elastic modulus. In particular, some VACNTs display high recoverability after significant strain (Cao et al., 2005) while others have been observed to deform permanently (Hutchens et al., 2010; Yaglioglu, 2007; Zbib et al., 2008). This paper aims to provide insight into the largely irrecoverable deformation observed after uniaxial compression of the VACNT bundles observed by Hutchens et al. (2010) and others (Zbib et al., 2008; Zhang et al., 2010) as opposed to highly recoverable and/or viscoelastic behavior (Cao et al., 2005; Gogotsi, 2010; Pathak et al., 2009; Xu et al., 2010; Zhang et al., 2010), though many similarities exist between the two, particularly the localization of deformation via buckling under uniaxial compression (Cao et al., 2005; Hutchens et al., 2010; Yaglioglu, 2007; Raney et al., in press; Zbib et al., 2008). As illustrated in Fig. 1, this rich behavior is characterized by the accommodation of strain through the creation of a series of vertically localized folds or buckles, which form sequentially starting from the base (where CNTs grow from the substrate) and proceed toward the top (Cao et al., 2005; Hutchens et al., 2010; Yaglioglu, 2007; Zbib et al., 2008) (see Fig. 1c), and the initiation of buckles followed by their lateral propagation as revealed through in situ deformation of micron-sized cylindrical bundles, or pillars by Hutchens et al. (2010) (see Fig. 1b). Fig. 1a shows the overall foam-like stress–strain response gathered during testing. The response consists of elastic, plateau, and densification regimes typical of these materials (Cao et al., 2005). The plateau possesses a small hardening slope. Here, we plot nominal stress, \( \sigma_n = P/A_0 \), versus nominal strain, \( \epsilon_n = \Delta H/H \), where \( P \) is the applied load, \( A_0 \) is the initial area of the top of the pillar, \( H \) is the initial pillar height, and \( \Delta H \) is the displacement of the top. We find that immediately following the elastic loading the load drops sharply before reaching the sloped plateau characterized by periodic softening events shown to correspond to the appearance and evolution of individual buckling events (Hutchens et al., 2010). This correspondence is illustrated in the image series in Fig. 1b for strains denoted by the blue circles in Fig. 1a.

While there are several experimental studies showing this highly localized commencement of structural collapse, models describing the mechanical response of VACNTs are few and past efforts have focused on capturing only the one-dimensional stress–strain or load–displacement response. For example, the load–displacement response has been modeled energetically as well as in a standard linear solid framework and compared with nanoindentation testing results

![Fig. 1. In situ mechanical compression results using methods presented in Hutchens et al. (2010). (a) Nominal stress–strain response. Blue circles and red squares denote the strains at which the images in (b) and (c) were taken. (b) Illustrates buckle initiation and evolution. (c) Illustrates bottom-to-top sequential buckling. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
by Mesarovic et al. (2007). In addition, Euler buckling criteria were applied to uniaxial compression tests (Cao et al., 2005; Deck et al., 2007; Tong et al., 2008; Zbib et al., 2008) as well as nanoindentation testing (Mesarovic et al., 2007; Pathak et al., 2009) in order to predict a threshold stress corresponding to the onset of buckling of the CNT struts. The most detailed of these models by Zbib et al. (2008) predicts a functional relationship between the sample height and this transition stress. These predictions are limited to capturing the behavior at relatively small overall strains. More recently, compressions of large VACNT mats were modeled as a one-dimensional series of mesoscopic springs that are themselves limiting cases of infinite bi-stable springs in series (Fraternali et al., 2011). This model captures the elastic recoverability and energy dissipation seen in many VACNTs. Bi-stable springs are characterized by a hardening–softening–hardening behavior that we also utilize here, as will be presented in Section 2. Our model attempts to capture the permanent, rather than the recoverable, deformation and includes the two-dimensional deformational changes associated with the overall pillar stress–strain response through an axisymmetric finite element formulation, thereby enabling the analysis of buckle evolution and morphological characteristics.

We begin by discussing the physical foundation for our choice of constitutive law. We then outline the well-established finite element framework and specify the parameters used in the simulations. We compare results from our simulations with the experimentally obtained uniaxial microcompression results from 50 μm diameter VACNT pillars and examine the influence of model parameters on buckle evolution and morphology. An examination of the parameter space of our model indicates the roles of various experimental factors affecting the mechanical response. Finally, we show the effect of influencing of model parameters on buckle evolution and morphology. An examination of the parameter space of our model
deformation tensor is taken to be the sum of elastic,

\[ d = \frac{1}{E} \frac{\partial 
abla \cdot \nabla F}{\partial t} - \frac{v}{F} \text{tr}(\dot{F}) \mathbf{I}, \]  

(1)

where \( E \) is Young’s modulus, \( v \) is Poisson’s ratio, \( \text{tr}(\cdot) \) denotes the trace, \( \mathbf{I} \) is the identity tensor and \( \dot{\mathbf{F}} \) is the Jaumann rate of Kirchhoff stress.

In the experiments of Hutchens et al. (2010) (summarized in Fig. 1), little recovery of deformation was observed so that a material model framework allowing for irrecoverable deformation was used. Also, material rate dependence is taken into account both for numerical reasons as well as in accordance with the observations in Zhang et al. (2010). We model the plastic response by a modification of the relation for an isotropic, hardening viscoplastic solid to account for the compressibility of the VACNTs. We write

\[ \dot{d} = \frac{3}{2} \hat{\epsilon}_p [\mathbf{I} + B \text{tr}(\sigma)] \]  

(2)

with

\[ \hat{\epsilon}_p = \hat{\epsilon}_0 \left( \frac{\sigma_e}{\dot{\sigma}_0} \right)^{1/m} \]  

(3)

Here, \( \hat{\epsilon}_0 \) is a reference strain rate, \( m \) is the rate hardening exponent, \( \mathbf{s} \) is the deviatoric Kirchhoff stress tensor, \( \mathbf{s} = \mathbf{I} - \text{tr}(\sigma) \mathbf{I}/3 \), and \( \sigma_e \) is the effective stress conjugate to \( \dot{\epsilon}_p, \sigma_e = \sqrt{\mathbf{J}/2[\mathbf{s} + B \text{tr}(\sigma)^2]} \). The compressibility parameter \( B \) is specified in terms of a plastic Poisson’s ratio, \( \nu_p \), by

\[ B = \frac{1}{3} \left[ \frac{1 - 2\nu_p}{1 + \nu_p} \right]. \]  

(4)
Motivated by structural load-deflection responses that give rise to periodic folds (e.g., Bardi and Kyriakides, 2006; Bardi et al., 2003, 2006), we characterize the flow strength or hardening function, \( g(\epsilon_p) \), as consisting of a hardening range followed by softening and then subsequent re-hardening. A simple form that embodies these features is

\[
\frac{g(\epsilon_p)}{\sigma_0} = \begin{cases} 
1 + h_1 \epsilon_p & \text{if } \epsilon_p < \epsilon_1 \\
1 + h_1 \epsilon_1 + h_2 (\epsilon_p - \epsilon_1) & \text{if } \epsilon_1 < \epsilon_p < \epsilon_2 \\
1 + h_1 \epsilon_1 + h_2 (\epsilon_2 - \epsilon_1) + h_3 (\epsilon_p - \epsilon_2) & \text{if } \epsilon_p > \epsilon_2
\end{cases}
\] (5)

and is depicted in Fig. 2. Parameters \( h_1, h_2, \) and \( h_3 \) determine the hardening and softening slopes and \( \epsilon_1 \) and \( \epsilon_2 \) are the strains at which the hardening–softening and softening–hardening transitions occur, respectively, and \( \sigma_0 \) is a reference stress. The simplified piecewise nature of the flow strength curve lends itself well to a systematic study of changes in behavior with variations in its shape as discussed in Section 3. It is worth noting that the presence of a material rate dependence acts to regularize the governing equations in the softening regime (Needleman, 1988). A similarly shaped stress–strain relation, that of a bi-stable spring, was used in Fraternali et al. (2011) as a microscale element of a one-dimensional model that captured the quantitative aspects of a reversible deformation response in uniaxially loaded bulk VACNT samples (Cao et al., 2005). Attention is restricted to axisymmetric deformations, which eliminates the ability of the model to capture the nucleation and lateral buckle propagation seen in the experiments (Fig. 1b), but still allows for local sequential buckling and significantly reduces the computational time.

The finite element formulation is based on the dynamic principle of virtual work, which can be written as

\[
\int_V \tau : \delta \mathbf{d} \, dV = \int_S \mathbf{T} \cdot \delta \mathbf{u} \, dS - \int_V \rho \delta \mathbf{u} \, dV,
\] (6)

where \( V \) and \( S \) are, respectively, the volume and surface of the body in the initial configuration, \( \mathbf{T} \) is the traction vector, and \( \mathbf{u} \) is the displacement vector.

We perform calculations for a cylinder of height \( H \) and radius \( R \). With the assumption of axisymmetric conditions in a cylindrical coordinate system \((r,\theta,z)\) all field quantities are independent of \( \theta \). A velocity \( \dot{u}_z(t) \) is imposed at the top of the pillar, \( z=H \), with

\[
\dot{u}_z(r,H,t) = \begin{cases} 
t \tau_{\text{rise}}^{-1} & \text{for } t < \tau_{\text{rise}} \\
-\frac{\tau_{\text{rise}}}{2} & \text{for } t > \tau_{\text{rise}}
\end{cases}
\] (7)

and \( \tau_{\text{rise}}(r,H) = 0 \). Here, \( \tau_{\text{rise}} \) is the time interval over which the velocity is ramped up to avoid shock loading the system. The bottom of the pillar is presumed fixed to the substrate so \( \dot{u}_z(r,0,t) = \dot{u}_z(r,0,0) = 0 \). The outer surface of the pillar is taken to be traction free, \( T_t(R,z) = 0 \). We do not account for possible contact between the folds that develop due to buckling. The calculations are terminated prior to any material contact.

The finite element discretization of Eq. (6) is based on a convected coordinate representation of the governing equations with linear displacement crossed triangles as in a number of previous analyses, e.g., Needleman (1982) and Tvergaard et al. (1981). Time integration is carried out by the explicit Newmark \( \beta \)-method (Belytschko et al., 1976) using lumped masses. The rate tangent method of Peirce et al. (1984) is used for the constitutive update.

![Fig. 2](image-url) A plot of the hardening function, \( g(\epsilon_p) \), for \( \epsilon_1 = 0.005, \epsilon_2 = 0.1, h_1 = 5.0, h_2 = -5.0, \) and \( h_3 = 1.5 \) illustrating its general shape as defined in Eq. (5). The Maxwell stress for this relation is approximately \( 0.7\sigma_0 \).
2.1. Simulation parameters

The calculations are carried out with $E/\sigma_0 = 100$, $m=0.02$ (on the order of experimentally measured values of rate sensitivity in VACNTs, Zhang et al., 2010), $\dot{\epsilon}_0 = \dot{\epsilon}_{\text{ref}}$, $v = 0.25$, $v_p = 0.25$. The mesh geometry is that of a circular cylindrical pillar with an aspect ratio, $H/R$, of $3$. The imposed velocity, $v_z$, in Eq. (7) is fixed at $k\dot{\epsilon}_{\text{ref}}H$ with $k = 0.004$ and the ramp time $t_{\text{rise}} = 5/\dot{\epsilon}_{\text{ref}}$. The initial hardening portion of Eq. (5) was fixed at $\dot{\epsilon}_1 = 0.005$, $h_1 = 5$ throughout this study. Results are presented for variations in $\dot{\epsilon}_2$, $h_2$, $h_3$.

The finite element mesh in all calculations consists of a uniform $80 \times 240$ mesh of quadrilateral “crossed triangle” elements each of which is $H/240 \times H/240$.

If the analyses were quasi-static, these dimensionless parameters would be sufficient to characterize the formulation. However, dynamic, rather than quasi-static, analyses are carried out because, even though the response is generally quasi-static, dynamic snapping can occur due to the up-down-up shape of $g(t_p)$ (see Fig. 2). Hence, a density needs to be specified and is taken to be $\rho = 6.3\sigma_0/(\dot{\epsilon}_{\text{ref}}H)^2$ non-dimensional form.

For $\sigma_0 = 0.1$ MPa, $H = 75$ μm and $\dot{\epsilon}_{\text{ref}} = 25$ s$^{-1}$, we have $E = 10$ MPa and $\rho = 1.79 \times 10^{11}$ MPa$^2$/m$^2$ ($\rho = 179$ g/cm$^3$). Also, $v_z = 7.5$ μm/s and $t_{\text{rise}} = 0.2$ s, which corresponds to the applied velocity achieving its constant value when the overall strain, $u_z(r,H,t)/H$, reaches 0.01. All of these values are of a similar order to those in the experiments with the exception of the density.

Axial gradients in $E$ and $\sigma_0$ are incorporated into the material through multiplication of these variables by a dimensionless function $Q(z)$, where $Q(z)=1$ corresponds to the case in which there is no gradient with $z$ evaluated at the center of the element for which the rescaled $E$ and $\sigma_0$ values are being calculated.

3. Results and discussion

Implementation of the model, outlined in Section 2, and subsequent exploration of the parameter space resulted in capturing many of the qualitative features of CNT pillar deformation seen in the experiments (Fig. 1). Interpretation of the parameters that lead to sequential periodic buckling in axisymmetric pillars enables the generation of hypotheses regarding buckle characteristics (e.g., wavelength and amplitude) given a relationship between the CNT microstructure and the hardening function. The qualitative results from an example set of parameters are summarized in Fig. 3 in which an experimental nominal stress, $\sigma_n = P/A_0$, versus true strain, $\epsilon_t = \ln(1+\epsilon_t)$, response from a uniaxial compression experiment (Hutchens et al., 2010) is shown in Fig. 3a for reference. We plot the analogous response from a simulation (Fig. 3b) in terms of the nominal stress, $\sigma_n = P/|xR^2|$, and true strain, $\epsilon_t = -\ln[H+u_z(r,H,t)/H]$, where $P$ is the sum of the nodal forces in the z-direction at the top of the pillar. In both the experiment and the simulation, the area of the top of the pillar is nearly constant during the process of sequential buckling so that the difference between nominal and true stress is negligible over the majority of the range during which buckling occurs.

In both stress–strain responses in Fig. 3 there is a noticeable transition from the linear elastic region to the (slipped) plateau region. An inset of the experimental data is given in Fig. 3a in order to facilitate comparison with Fig. 3b. The model gives similar behavior as illustrated by a comparison of the ratio of the stress at a strain of 0.2 to the stress at the beginning of the buckling regime ($\epsilon_t = 0.05$) in Fig. 3a to the same ratio for strains of 0.2 and 0.015 in Fig. 3b. These ratios are around 1.3 in both cases. Periodic, local softening events occur within the plateaus and each corresponds to the formation of a new buckle. For the simulations, this finding is illustrated by a collection of curves showing the evolution of the outer surface, $u_z(R,z)/R$ versus $z/H$ (Fig. 3c) at several discrete values of the overall pillar strain, $\epsilon_t$, that immediately follow a softening event. These strain values are indicated by arrows in Fig. 3b where both nominal and true (force/current area) stress values are shown. The outer displacement profiles clearly identify sequential buckle formation beginning at the bottom and progressing to the top. As in the experiments, nearly all of the deformations are accommodated through the formation and evolution of localized buckles with the topmost region of the pillar remaining undeformed throughout, as evidenced in the strain contour plots in Fig. 4. All the simulation results in Figs. 3 and 4 correspond to the parameters defined in the caption of Fig. 2 and include a linear gradient, $Q(z)$, that gives values of $\sigma_0$ and $E$ at $z=H$ that are of 40% of their values at $z=0$. Subsequently, we discuss the effect of an applied gradient on the overall pillar hardening.

The responses shown in Fig. 3 are approximately quasi-static since the total kinetic energy of the system remains around 2% of the input work throughout the short rise time discussed in Eq. (7), during which the structural response is largely elastic, and then drops to less than 1% for the remainder of the calculation.

A parameter study on the effect of strain rate is not carried out here. However, we have carried out calculations in which the strain rate is increased from the imposed value in Fig. 3 by a factor of 2 and decreased from that value by a factor of 1/2 (with all other parameters fixed). As expected with a strain rate exponent of $m=0.02$, the effect of changes in strain rate on the stress magnitude is small. The main effect is that the average stress drop that occurs with each buckling event is somewhat greater when the strain rate is doubled and somewhat less for the case when the strain rate is halved. This trend is in agreement with experiments carried out over 3.5 orders of magnitude in strain rate (Hutchens et al., 2010) where it was observed that the magnitude of the stress undulations during buckling was greater at larger strain rates.

In exploring the model’s parameter space, we found that the range in which buckle formation occurs, and where the energy absorption is the most effective, is limited. Within that buckling domain, we explore the separate contributions of the flow strength function’s ‘well’ width, formed by the intersection of the softening and re-hardening slopes, and magnitude of the softening slope, $h_2$, changes in buckle morphology. Some calculations are carried out for a homogeneous pillar. However,
Fig. 3. Summary of buckle formation phenomena captured by simulations utilizing the proposed constitutive relation. (a) Experimental data from a pillar microcompression (Hutchens et al., 2010). Inset shows a close-up of the strain region from 0 to 0.3. (b) The overall nominal stress, force/original area, and true stress, force/current area, versus true strain response from a simulated pillar undergoing periodic sequential buckling. Arrows mark the strains at which the outer displacement profiles are plotted in (c). (c) Outer displacement profiles corresponding to strains directly following a softening event and illustrating simultaneous buckle emergence.

Fig. 4. (Color online) Series of strain contour plots and deformed meshes clearly showing sequential deformation and the relatively undeformed upper region of the pillar.
based on images taken along the VACNT pillar height, there is reason to believe that there is an axial density gradient. Therefore, we investigate the effect of gradients in the onset of irreversible flow, \( \sigma_0 \), and elastic modulus, \( E \), for a single set of parameters. In order to illustrate the range of and reason for the limited buckling domain, a typical series of responses corresponding to selected flow strength functions, \( g(\epsilon_p) \), are shown in Fig. 5. All have fixed hardening slopes, \( h_1 = 5 \) and \( h_3 = 1.5 \), with \( \epsilon_1 = 0.005 \), but vary in the location of their minima, marked by the symbols in Fig. 5a. For example, a hardening function corresponding to a minimum at \( \epsilon_2 = 0.1 \) and 55\% of \( h/h_0 (h_2 = 5.0) \) exemplifies the buckling domain (filled circles) through the series of outer displacement profiles given for overall pillar strains of \( \epsilon_t = 0.05, 0.10, 0.15, \) and \( 0.20 \) (Fig. 5a). Outside of this buckling regime there are several types of behavior that can be roughly categorized into four groups. First, the instability domain (open circles) occurs where minima are located at similar strains but at a greater depth than that for the buckling domain, i.e., they possess a large softening slope \( h_2 \). Here, periodicity is completely lost and the deformation is dominated by local instability arising from the large magnitude of \( h_2 \). Diagonally upward, at greater strain from the buckling domain, lies the

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**Fig. 5.** (Color online) Influence of the ‘well’ minimum position on the formation and morphology of buckles \( (h_1 = 5, h_3 = 1.5, \epsilon_1 = 0.005) \). (a) Minima locations tested. Domains are denoted by (closed circles) buckling, (pluses) base-only buckling, (open circles) instability dominated, (diamond) base flow, and (squares) bulk flow. (b)–(f) Representative displacement profiles at \( r=R \) for overall strain levels of \( \epsilon_t = 0.05, 0.10, 0.15, \) and \( 0.20 \) for each of the domains.
base-only buckle domain (pluses). Here, the local instability due to softening is somewhat preserved, as evidenced by the small waves localized at the pillar base, however, the depth of the minimum has decreased so much that the behavior begins to approach that of a typical foam, i.e., a hardening function in which the softening region is replaced by a flat line, $h_2 = 0$. Continuing toward minima at larger strain but similar depth, there is a bulk flow domain (open squares) where the magnitude of ($|h_2|$) has considerably decreased to the point that the presence of a local minimum has no noticeable contribution. Here, local flow is large and, as a result, the pillar undergoes extensive plastic flow in a manner that is nearly identical to that seen for typical foam-like simulations ($h_2 = 0$). Finally, holding the magnitude of $h_2$ approximately constant while extending minima to greater strains we enter what we call the base flow domain (open diamonds). In this domain, the large strain occurs only at the base of the pillar. Periodic buckles do not form as the extensive deformation, due to the large strain position of the minima, damps out any surface fluctuations that would form. It is noteworthy that all of the simulations shown in Fig. 5 were generated with no gradient, $Q(z) = 1$.

As a result of these observations of the different morphological domains and their dependence on the character of the flow strength, $g(e_p)$, it becomes clear that a balance between the magnitude of $h_2$ and the size of the ‘well’ in $g(e_p)$ must exist in order to obtain the experimentally observed buckle morphology. In particular, it is evident that the local flow due to the ‘well’ size (i.e., width) must be limited enough that it does not wash out the undulations that form. Another way to state this is that the material must be strain constrained. We interpret this within the known morphology of VACNTs by noting that the inter-tube interactions (entanglement, van der Waals, etc.) limit the local strain that can be experienced by the material. The local softening captured by $h_2$ arises from the high aspect ratio of the CNT struts which individually undergo a large drop in stiffness by buckling in uniaxial compression. We propose then that local strain constraint, combined with the high aspect ratio of the CNT struts, gives rise to the complex buckling behavior seen in so many VACNT compression experiments. It should be noted that only a variation in the extent of these domains is seen for changes in the value of the hardening coefficient $h_3$ in Eq. (5) as variations in $h_3$ give rise to similar domains that have the same relative positions with respect to each other.

![Fig. 6. Variation in buckle wavelength and amplitude as a function of changes in $\Delta e_w$ and in the magnitude of $h_2$. (a) Schematic indicating the variations in the hardening function, $g(e_p)$, considered for 25% changes in $\Delta e_w$ (red/squares = decreased, blue/circles = increased). (b) A series of displacement profiles at $r=R$ corresponding to the hardening functions in (a). An increased value of $\Delta e_w$ leads to increased buckle amplitude. (c) Schematic indicating the variations in the hardening function for 25% changes in the magnitude of $h_2$ (red/squares = decreased, blue/circles = increased). (d) A series of displacement profiles at $r=R$ corresponding to the hardening functions in (c). An increased magnitude of $h_2$ leads to decreased buckle wavelength. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
Within the buckling domain, variations in buckle wavelength and amplitude can be decoupled from one another through control of specific characteristics of the hardening function. These findings are summarized in Fig. 6. We define $\Delta e_w$ as the plastic strain range from the value of $e_p$ at which the function $g(e_p)$ in Eq. (5) first attains a maximum to the value of $e_p$ at which $g(e_p)$ attains that value again as illustrated in Fig. 6a. $\Delta e_w$ characterizes the width of the ‘well’ in the flow strength function, $g(e_p)$. We find that with the depth of the minimum in $g(e_p)$ and the value of $h_2$ held constant while varying $\Delta e_w$, the wavelength of the buckles remains the same and the amplitude increases (Fig. 6b). We quantify the changes in amplitude through a sine wave fit of the buckling region and define the relative change in amplitude, $\Delta a$, as

$$\Delta a = \frac{a_1 - a_0}{a_0} \tag{8}$$

where $a_0$ and $a_1$ are the amplitudes determined from fits of the results from the reference parameters and from $\pm 25\%$ changes in $\Delta e_w$, respectively. An analogous expression was used to quantify the relative changes in wavelength, $\Delta \lambda$.

A relative change in amplitude of $-16\%$ was obtained for a $25\%$ decrease in $\Delta e_w$ and a relative change of $12\%$ was obtained for a $25\%$ increase. The respective variations in wavelength of the buckles, $\Delta \lambda$, were $-2\%$ and $3\%$. Analogously, holding the depth of the minimum of $g(e_p)$ and $\Delta e_w$ constant while varying $h_2$, the amplitude of the buckles is much less affected while the wavelength decreases (Fig. 6d). A sine wave fit revealed relative changes in $\Delta \lambda$ of $7\%$ and $-4\%$ for a $25\%$ decrease and a $25\%$ increase in $h_2$ with $\Delta s$ varying by $-2\%$ and $0.5\%$, respectively. If $h_2$ is fixed and $\Delta e_w$ varied (or vice versa), while the depth of the minimum in $g(e_p)$ is allowed to change, the wavelength and amplitude variations are much more strongly coupled, and the buckle morphology varies in a way that precludes extracting a simple trend.

These correlations between the changes in $h_2$ and $\Delta e_w$ and the resulting variations in buckle wavelength and amplitude can be qualitatively related to real VACNT materials as follows. If we presume that the ability of a VACNT material to flow is constrained by the tube-to-tube interactions, we expect that a more dense (number of tubes per unit volume) material would produce smaller amplitude buckles due to its increased number of interactions and therefore decreased deformability. If the magnitude of the negative slope, $h_2$, is correlated with CNT strength in compression (i.e., smaller...
diameter tubes soften with a greater slope than larger diameter tubes), we expect that a material made with smaller tubes would have shorter wavelength buckles.

It has been speculated that the initiation of the sequential buckling phenomena observed experimentally by several research groups was due to an axial density gradient in the material (Cao et al., 2005; Hutchens et al., 2010). This is motivated by the observations of a lower CNT number density base of similarly grown VACNTs (Bedewy et al., 2009; Hutchens et al., 2011). An axial gradient in the number of load-bearing members is expected to give rise to a corresponding inhomogeneity in stiffness and yield stress. Since the precise correlation between the stiffness and the tube number density remains to be determined, we refer to it hereafter as a property gradient. We explore the effects of such a property gradient within the simulation framework by multiplication of density remains to be determined, we refer to it hereafter as a property gradient. We explore the effects of such a property gradient within the simulation framework by multiplication of $E$ and $\sigma_0$ by the function $Q(z)$, where $Q(z)=1$ corresponds to the case in which there is no gradient. We find that changes in Young’s modulus, $E$, have very little effect on the shape of the stress–strain curve or the overall buckle morphology, but are included for completeness. We present the results of simulations with no gradient (black), 20% and 200% linear increases (blue/circles, red/squares), and a 10% linear decrease (green/triangles) in $Q(z)$ in Fig. 7. Here, in Fig. 7b we plot curves of true stress, $\sigma_\text{t} = P/(\pi (R + u_r(R,H,t))^2)$ versus true strain, $\varepsilon_\text{t} = -\ln[(H + u_z(r,R,H,t))/H]$. Simulations with no property gradient give rise to sequential periodic buckling (Fig. 7(b)), implying that buckle formation is robust against local density variations, and propagation occurs at about the Maxwell stress. The fixed constraint of the rigid substrate, as is the case for as-grown CNT bundles, we model by the fixed displacement boundary conditions at $z=0$. This constraint induces non-uniform deformation which promotes buckle initiation at the base of the pillar. The gradient in $\sigma_0$ has a marked effect on the hardening plateau of the overall applied stress–strain response as illustrated by the curves corresponding to 20% and 200% increases (Fig. 7a). Here, it is clear that the property gradient directly correlates with the overall pillar hardening as a $10 \times$ increase in property gradient yields an approximately $5 \times$ increase in overall strain hardening. For property gradients that are sufficiently large, $\sim 400\%$, periodic buckling is no longer obtained. In our calculations, even a small reverse gradient can cause the sequential buckling to occur in the reverse direction (Fig. 7c), suggesting that a plausible explanation for variation in top-first versus bottom-first buckling (Pathak et al., 2011; Qiu et al., 2011) is the difference in the spatial location of the least number of load-bearing members within the sample.

Although our model captures some of the key qualitative features of VACNT pillar buckling, there are also some discrepancies between the model predictions and the experimental observations. One marked difference concerns the number and size of buckles. This could be due to a number of idealizations including, for example: isotropy and the simple characterization of compressibility, such as the assumption of a constant value of the compressibility parameter, $B$, in Eq. (4). In addition, contact between buckles is not modeled.

4. Conclusions

We report that a dynamic finite element implementation of an isotropic, viscoplastic solid combined with a piecewise positive–negative–positive hardening function within an axisymmetric pillar mesh geometry captures the main qualitative features seen in experimental microcompression tests on 50 µm VACNT pillars. These include sequential, periodic buckling initiated at the base of the pillar and progressing to its top, strain accommodation nearly entirely through the formation of localized buckles, a stress–strain response characterized by an elastic loading followed by a low-hardening plateau, local softening events within the plateau corresponding to buckle formation, and strain hardening within the buckle region due to an axial property gradient. We explore the parameter space which we use to define a window in which buckle formation occurs, thereby providing understanding of the microstructural mechanism behind buckle formation. Through this exploration, we find that the buckle wavelength decreases with an increased magnitude of the negative hardening slope and its amplitude increases with an increased width of the ‘well’ in the flow strength function. Agreement with multiple experimental observations provides evidence that the proposed constitutive relation is a reasonable starting point for developing a full three-dimensional anisotropic constitutive relation for VACNTs. In addition, exploration of the parameter space within the simple isotropic model provides insight into the mechanisms governing VACNT deformation. Specifically, it is the strain-constrained nature of VACNTs combined with the loss of load carry capacity accompanying the buckling of the CNT struts that gives rise to the sequential periodic buckling that characterizes these materials in uniaxial compression. The model also reveals bottom-to-top buckling, even in the case of homogeneity (no axial property gradient). However, we find that this buckling sequence can be reversed (top-to-bottom) with a small inverse property gradient (having lower strength at the top). Finally, we show that the value of the slope of this property gradient directly correlates with a post-buckling increase in the overall pillar stress level.

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