Multiscale Mass-Spring Model for High-Rate Compression of Vertically Aligned Carbon Nanotube Foams

We present a one-dimensional, multiscale mass-spring model to describe the response of vertically aligned carbon nanotube (VACNT) foams subjected to uniaxial, high-rate compressive deformations. The model uses mesoscopic dissipative spring elements composed of a lower level chain of asymmetric, bilateral, bistable elastic springs to describe the experimentally observed deformation-dependent stress–strain responses. The model shows an excellent agreement with the experimental response of VACNT foams undergoing finite deformations and enables in situ identification of the constitutive parameters at the smaller length scales. We apply the model to two cases of VACNT foams impacted at 1.75 ms$^{-1}$ and 4.44 ms$^{-1}$ and describe their dynamic response.

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Keywords: carbon nanotube foams, mechanical properties, high-rate compression, multiscale modeling, strain localization, hysteresis

1 Introduction

Macroscopic nanotube foam (CNT) foams have been synthesized from vertically aligned bundles of CNTs [1] or randomly oriented CNT fibers (sponges) [2]. Their exceptional mechanical properties and energy absorption characteristics make these stand-alone CNT-foams excellent candidates for various applications [3] including energy absorbing/protective packaging materials for electronics and mechanical systems [1,2], structural reinforcements in composites [4] and woven fibers for bulletproof tough textiles [5]. Bulk VACNT foams present a hierarchical fibrous microstructure with constituent features in various length scales [Ref. [1], Fig. 3 in Ref. [6]]: The individual multiwalled carbon nanotubes (MWCNTs) have a concentric tubular configuration with several walls in the nanoscale; the MWCNTs entangle with each other to form a forest-like system in the microscale; and the bundles of MWCNTs are aligned vertically in the mesoscale. When subjected to compressive loadings, they exhibit distinct deformation mechanisms at different length scales: A foam-like compression in the macroscale; collective sequential buckling of the aligned CNT bundles in the mesoscale; and bending and buckling of individual tubes in the microscale [1,7]. The bulk compression response of VACNT foams is identified with three distinct loading regimes: An initial linear elastic regime, a plateau regime governed by progressive buckles and a final densification regime [1]. VACNT foams exhibit different mechanical responses when subjected to different loading regimes. Macroscopic samples exhibit a viscoelastic response when subjected to long duration stress relaxation experiments in compression [8] or when tested for creep with nano-indentation [9]. The same material exhibits rate-dependent deformation mechanisms in quasi-static compression experiments [10]. However, few studies suggested dependence of VACNT foam’s unloading modulus and recovery on strain rate [11,12]. In the linear dynamic regime, VACNT foams subjected to torsional mode dynamic mechanical analysis exhibited a frequency invariant dissipative response [13]. The VACNT’s storage and loss moduli were shown to be independent of frequency in uniaxial linear vibration experiments [14]. VACNT foams impacted by a striker exhibit complex rate-effects: The loading response is rate-independent, whereas the unloading modulus increases with strain rate [7]. When VACNT foams are impacted at velocities higher than a critical velocity (∼6.5 ms$^{-1}$), they support shock formation [7].

Several models have been proposed to describe the rate-independent mechanical response of VACNT foams in the quasi-static regime. Analytical micromechanical models supported by finite element models have been used to describe the response of forests of VACNTs subjected to nano-indentation with a spherical indenter [15]. It has been shown that the indentation force during nano-indentation scales linearly with tube areal density, tube moment of inertia, tube modulus, and indenter radius, whereas the force scales inversely with the square of tube length [15]. Buckle formation and progression in VACNT micropillars under quasi-static compression has been modeled using a finite element formulation of an isotropic viscoelastic solid combined with piecewise hardening-softening-hardening function [16]. It revealed that the buckle wavelength decreases with increasing magnitude of “negative hardening slope” and the buckle wave amplitude increases with the increasing width of the flow strength function well [16]. It was also found that the buckles always initiated near the substrate due to the displacement constraint and sequentially progressed even in the absence of a property gradient along the height of the sample [16]. Recently, a Timoshenko beam model for an inelastic column in buckling has been used to predict the critical buckling stress of VACNT micropillars with transverse isotropy [17].

Coarse-grained molecular dynamic simulations of VACNT foams [18] have found that the frequency-independent viscoelasticity in shearing [13] arises from rapid unstable attachment/ detachment among individual CNTs induced by the van der Waals forces and contributes to constantly changing microstructure of the CNT network. This rate-independent dissipation was also

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described using triboelastic constitutive models and it has been shown that the increased adhesive energy significantly increased the overall stiffness of the network compared to the tension-, bending-, and torsion-stiffnesses. This suggests that the van der Waals interaction not only contributes to energy dissipation but also influences the elasticity of the network [18]. A phenomenological multiscale mass-spring model with bistable elements has been used to describe the rate-independent quasi-static compressive response of macroscopic VACNT foams [19]. This model also enabled in situ material parameter identification in multilayered CNT arrays, and allows modeling experimentally observed local deformations accurately [20]. It has been extended later to describe a few experimentally observed phenomena, such as preconditioning [20], loading history, and loading direction dependency [10] and permanent damage [21]. However, numerical models of high-rate, uniaxial, finite deformation of VACNT foams have not yet been developed.

In this article, we propose a phenomenological mass-spring model that uses rate-independent, dissipative spring elements in association with phenomenological damping devices [22] to describe dynamic response of bulk VACNT foams. We use this model to describe the global dynamic response observed in experiments and then to identify the deformation-dependent microscale mechanical parameters in situ. In the following sections, we provide a detailed description of the experimental methods and observations (Sec. 2), a detailed description of the generalized mechanical model (Sec. 3) and the application of this model to describe the dynamic response of VACNT foams with in situ parameter identification (Sec. 4).

2 Brief Overview of Experimental Methods and Observations

Dynamic experiments were performed on an impact testing setup using a flat plunge striker as the loading apparatus. The complete description of the experimental setup and the data analysis methodologies can be found in Ref. [6]. The VACNT foam samples were attached to a striker and launched at controlled velocities on a frictionless guide to directly impact a force sensor. A rigidly mounted force sensor recorded the transmitted force–time histories to prescribe load-histories in the model, and we calculate the dynamic responses during the time the sample is in contact with the force sensor. In Sec. 3, we present the numerical model in details.

3 Mechanical Model

We use a one-dimensional, multiscale, phenomenological model to numerically describe the dynamic response observed experimentally (and summarized in Sec. 2). The model describes the response of VACNT foams at the mesoscopic scale, through the discretization of the foams into a collection of lumped masses connected by dissipative springs [19]. Each mesoscopic spring represents the continuum limit of a chain of infinitely many microscopic bistable elastic springs. The bistable springs are characterized by two stable phases (prebuckling loading and postbuckling densification) and an intermediate unstable phase (buckling phase). The dynamic snapping of the microscopic springs and the subsequent snapping back induce hysteretic energy dissipation via “transformational plasticity” [19,24]. Our model comprises two different timescales: An external timescale, which controls the evolution of the applied loading and the response at the mesoscale; and an internal timescale, which governs the dynamic relaxation of the system at the microscale, for a fixed external time. The constitutive behavior is viscous at the microscale, and rate-independent at the mesoscale [19,24]. Eventually, the overall response of a CNT structure can be described through a single dissipative element (macroscopic mass-spring model [10,25]). This multiscale model has been previously applied to describe the quasi-static response of CNT structures [10,19,20,21,25]. Here, the same model is applied to describe the mechanical response of VACNT foams under high-rate loading in association with the phenomenological damping devices [22]. The constitutive parameters are assigned depending on the applied strain rate. Alternatively, rate-dependent models that accounts for the evolution laws of material parameters as a function of strain rate can be formulated, and we leave such an extension of the model for the future work.

We briefly summarize the analytic formulation of the model at the mesoscale, which is detailed in Ref. [19]. Let us introduce a chain of \( N+1 \) lumped masses \( m_0, m_1, \ldots, m_N \), connected by \( N \) springs. The constitutive parameters are assigned depending on the applied strain rate. Alternatively, rate-dependent models that accounts for the evolution laws of material parameters as a function of strain rate can be formulated, and we leave such an extension of the model for the future work.

### Table 1 Physical properties of the VACNT foam samples

<table>
<thead>
<tr>
<th></th>
<th>VACNT foam-1</th>
<th>VACNT foam-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>5.56</td>
<td>5.05</td>
</tr>
<tr>
<td>Diameter (mm)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Height (mm)</td>
<td>1.190</td>
<td>1.106</td>
</tr>
<tr>
<td>Bulk density (g cm(^{-3}))</td>
<td>0.238</td>
<td>0.232</td>
</tr>
</tbody>
</table>

121006-2 / Vol. 81, DECEMBER 2014 Transactions of the ASME
nonlinear spring elements ($N \geq 1$). The mass $m^0$ is clamped at the bottom (fixed-boundary), at position $x^0 = 0$, and the mass $m^N$ is free at the top (free-boundary), at position $x^N = l$. Spring 1 is at the bottom and connects masses $m^1$ and $m^0$ while spring $N$ is at the top and connects $m^N$ and $m^{N-1}$. The scalar quantity, $\varepsilon'$ characterizes the total strain at the ith spring

\[ \varepsilon' = \frac{u'}{h'} \]  

where $u'$ is the axial displacement of the mass $m^i$ relative to its initial position and $h' = x' - x''$. The constitutive equations for each mesoscopic spring are

\[
\begin{align*}
\sigma &= \begin{cases}
\sigma^{(a)} = \sigma^{(c)} + \Delta \sigma^i + k^i_2 (\varepsilon' - \varepsilon^i) & \text{for } (\varepsilon' \leq \varepsilon^i & \leq \varepsilon'^i) \text{ and } (\text{flag}^{(k-1)} = c); \\
\sigma^{(c)} = k^i_1 (\varepsilon' - \varepsilon^i) / (1 - (\varepsilon' - \varepsilon^i)) & \text{for } (\varepsilon' > \varepsilon^i) \text{ or } (\varepsilon' < \varepsilon^i) \text{ and } (\text{flag}^{(k-1)} \neq a) \\
\end{cases}
\end{align*}
\]

Here, $\sigma'$ is the stress at each time step $t = t_k$ ($k = 1, \ldots, M$) and

\[ \text{flag}^{(k)} = \begin{cases}
(a) & \text{if } \sigma' = \sigma^{(a)}, \\
(c) & \text{if } \sigma' = \sigma^{(c)}, \\
\text{flag}^{(k-1)}, & \text{otherwise}
\end{cases} \]  

The constitutive parameters $k_1^i, k_2^i, \Delta \sigma^i, \varepsilon^i, \varepsilon'^i, \varepsilon^i, k_{h_i}^i$, and $k_{h_f}^i$ in Eq. (2) are seven independent quantities, while $\dot{\varepsilon}_a$ and $\dot{\varepsilon}_c$ are computed by solving the following Eqs. (4) and (5) for $\varepsilon'$, respectively,

\[ \sigma^{(a)} = \sigma^{(c)} \]  

\[ \sigma^{(c)} = \sigma^{(c)} \]  

The stiffness parameters $k_1^i$ and $k_2^i$ represent the initial slopes $d\sigma'/d\varepsilon'$ at $\sigma' = 0$, of the bilateral branches $OA_1$ and $C_1C_2$ (Fig. 1). These two branches represent the initial elastic regime and the final densification regime of each spring, respectively. The $k_{h_i}^i$ is the slope of the unilateral branch $A_1C_1$, describing the snap

Fig. 1  Schematic diagram showing the response of a generic mesoscopic dissipative spring element and the relevant constitutive parameters

Fig. 2  Description of the model for the sample impacted at 1.75 ms$^{-1}$. (a) Schematic of the experiment showing the sample being compressed by the striker against the rigidly mounted force sensor. (b) Three different models considered for the sample. (c) Optical images showing the pristine and deformed states of the sample [7]. Markers are used to highlight the deformed and undeformed sections of the sample.
buckling and the consequent hardening during the loading phase. The $k_{h}^+$ is the slope of the unilateral branch $C_2A_2$, describing the snap-back recovery of the buckles during unloading phase. When $k_{h}^+$ and $k_{h}^-$ are zero, the unilateral branches describe a perfectly plastic behavior. The $\Delta \sigma' = \sigma' - \sigma''$, where the $\sigma'$ and $\sigma''$ are the stresses corresponding to the points $A_1$ and $C_2$.

This model does not allow for accumulation of permanent strains that is often found in the compression experiments of VACNT foams, both in their quasi-static [1] and dynamic [7] responses. However, it can be modified to prevent snap-back recovery of springs and allow permanent damage [21]. Similarly, the model can be generalized to describe pre-conditioning effects found in cyclic loading, by introducing initial strains, $\varepsilon_0 \geq 0$ and elastic strains $\varepsilon' = \varepsilon - \varepsilon_0$ for each spring as described in Ref. [20]. In this article, we will not attempt to extend these features in dynamics.

4 Experimental Fit and In Situ Parameter Identification

We model the striker as a rigid particle with lumped mass equal to the mass of the striker (7 g) and the force sensor as a rigid fixed wall (Figs. 2(a) and 2(b)). We apply the experimental stress–time history to the particle that represents the striker (top particle), and determine the stress–time and the displacement–time histories at the base of the VACNT foam (force sensor side) using the numerical model described in Sec. 3. The whole sample is assumed to be in dynamic equilibrium throughout the experimental duration [6]. Figure 2(c) shows selected snap-shots obtained from the high-speed image sequence, corresponding to the pristine state of the VACNT foam-1 at the instance of impact ($V_{\text{striker}} = 1.75 \text{ms}^{-1}$) and the deformed state at maximum compression ($V_{\text{striker}} = 0$). A visualization of the dynamic deformation of the sample can be found in the supplementary video of Ref. [7]. As shown on Fig. 2(c), collective buckles nucleate at the bottom of the sample during impact and progressively compress the sample to the height of $h_c = 0.490 \text{mm}$. The remaining section of the sample with height, $h_i = 0.700 \text{mm}$ undergoes infinitesimal compressive strains. As a first approximation (model-1 in Fig. 2(b)), we represent the whole height (1.190 mm) of the sample as a single effective spring (macroscopic dissipative element) that connects the striker particle to the rigid wall (force sensor). In addition, we neglect the mass of the VACNT foam (5.56 mg) in comparison to the large striker mass (7 g). The seven independent parameters

<table>
<thead>
<tr>
<th>Model</th>
<th>$k_0$ (MPa)</th>
<th>$\Delta \sigma / \sigma$</th>
<th>$\eta$ (Pa s)</th>
<th>$\varepsilon_a$</th>
<th>$\varepsilon_c$</th>
<th>$h$ (mm)</th>
<th>$k_{h+}/k_0$</th>
<th>$k_{h-}/k_0$</th>
<th>$k_c/k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model-1</td>
<td>5.50</td>
<td>-0.20</td>
<td>—</td>
<td>0.14</td>
<td>0.31</td>
<td>1.190</td>
<td>2.60</td>
<td>0.450</td>
<td>15</td>
</tr>
<tr>
<td>Model-2</td>
<td>5.50</td>
<td>-0.20</td>
<td>$1 \times 10^4$</td>
<td>0.14</td>
<td>0.31</td>
<td>1.190</td>
<td>2.60</td>
<td>0.425</td>
<td>15</td>
</tr>
<tr>
<td>Model-3</td>
<td>S1</td>
<td>60</td>
<td>—</td>
<td>3 $\times 10^4$</td>
<td>0.35</td>
<td>0.71</td>
<td>0.490</td>
<td>3.40</td>
<td>0.525</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>2</td>
<td>-0.32</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

The definition of these parameters in shown in Fig. 3. In model-3, S1 is the linear spring and S2 is the nonlinear, bistable spring.

![Fig. 3](http://appliedmechanics.asmedigitalcollection.asme.org/ on 10/31/2014 Terms of Use: http://asme.org/terms)
that define the nonlinear spring of model-1 are listed in Table 2. Figure 3(a) (top panel) shows the stress- and displacement-time histories and the stress-strain diagram obtained with model-1 (and superimposed to the experimental data). The overall results show a good agreement with experiments. The time histories of stress and displacement, however, exhibit significant oscillations that arise from numerical instabilities. These instabilities are particularly evident when the model transitions between adjacent branches of the dissipative spring element—for example, see the inset of stress-time history in Fig. 3(a). To ensure stability during the dynamic transitions between phases, we introduced an onsite damper with damping coefficient 0.01 MPa s to the striker mass (model 2 in Fig. 2(b)). The damping ratio between the adopted damping coefficient and the critical damping coefficient associated with the unloading branch (2$\sqrt{p_{c}}k_{d}$) is calculated to be 0.894. As shown in the middle panel of Fig. 3(b), the damper reduces the numerical instabilities significantly and facilitates smooth dynamic transitions.

We refine the model further to account for the elastic properties of the deformed section of the CNT foams (model-3). The refined model employs a dissipative spring element (S2), with height $h_{2} = 0.490$ mm, to describe the response of the heavily deformed state ($\sigma_{e}$) (Fig. 2(b)). The damping ratio between the adopted damping coefficient and the critical damping coefficient associated with the unloading branch (2$\sqrt{p_{c}}k_{d}$) is calculated to be 0.894. As shown in the middle panel of Fig. 3(b), the damper reduces the numerical instabilities significantly and facilitates smooth dynamic transitions.

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Table 3 Parameters of the model of VACNT foam-2, impacted at a velocity of 4.44 ms$^{-1}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{0}$ (MPa)</td>
<td>250</td>
</tr>
<tr>
<td>$\Delta \sigma$</td>
<td>$1 \times 10^{4}$</td>
</tr>
<tr>
<td>$\eta$ (Pa s)</td>
<td>0.70</td>
</tr>
<tr>
<td>$h$ (mm)</td>
<td>0.350</td>
</tr>
<tr>
<td>$k_{0}/k_{1}$</td>
<td>0.200</td>
</tr>
<tr>
<td>$h_{2}/h_{1}$</td>
<td>40</td>
</tr>
</tbody>
</table>

The definitions of these parameters are shown on the Figure 3. S1 is the linear spring and the S2 is the nonlinear bistable spring.

We apply a similar two-spring model to the VACNT foam-2 that was impacted at 4.44 ms$^{-1}$ (Fig. 4). Similar to the previous case, we use a dissipative element as an effective spring for the buckled section of the sample ($h_{2} = 0.756$ mm) and represent the infinitesimally strained section ($h_{1} = 0.350$ mm) with a unilateral linear spring. An onsite damper with damping coefficient of $1 \times 10^{4}$ is used to ensure stability during numerical simulation. The damping ratio required for such numerical stability is 0.525.

Figure 4(b) shows the comparison of numerical and experimental results. The model captures the global dynamics, while identifying the constitutive parameters at a lengthscale that is much smaller than the sample size. The bulk response of the sample is the effective response of these two elements, masses and the associated damping device.
significantly higher in VACNT foam-2 than in VACNT foam-1, the stiffness constant $k_0$ of VACNT foam-2 (5.75 MPa) is appreciably higher than $k_0$ of VACNT foam-1 (2.00 MPa). This increase in stiffness is explained by the increase in the intrinsic density of CNTs along the height [7].

5 Conclusions

We introduced phenomenological models to describe the dynamic response of VACNT foams under high-rate compression. The models use a one-dimensional mass-spring system containing an effective dissipative spring element, which describes either the entire sample (single-spring model), or its buckled (heavily deformed) section (two-spring model). We have shown that the models allow us to characterize the bulk dynamic response of the VACNT foams and their dissipation properties. The adopted spring models employ the concept of rate-independent, transformational plasticity, as opposed to more conventional, rate-dependent and/or plastic models. We showed that such models could be generalized to high-rate compression responses when they are used in association with damping devices, and the material parameters are modulated according to the applied strain rate. We introduced numerical viscosity through the phenomenological approach proposed in Ref. [22]. The two-spring model enables the identification of the VACNT foams’ deformation-dependent mechanical parameters, at lengthscales smaller than the sample height, which cannot be obtained alone from the experimental measurements. Even though we use our model to describe the VACNT foam’s dynamic responses, the model can be extended to other hierarchical materials, with fibrous morphology. Additional future research lines include the formulation of evolution laws of the material parameters as a function of the applied strain rate, and the numerical modeling of large-scale problems through the quasi-continuum method and local maximum-entropy schemes [26, 27].

Acknowledgment

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