Supporting Online Material

Higher Recovery and Better Energy Dissipation at Faster Strain Rates in Carbon Nanotube Bundles: an *in-situ* Study.

Siddhartha Pathak [1*], Ee J. Lim [1], Parisa Pour Shahid Saeed Abadi [2], Samuel Graham [2,3], Baratunde A. Cola [2,3], Julia R. Greer [1]

[1] Materials Science, California Institute of Technology (Caltech), Pasadena, CA, USA
[2] George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, USA.
[3] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA.

[*] Contact author: - Materials Science, California Institute of Technology (Caltech), 1200 E. California Blvd., MC 309-81, Pasadena, CA 91125-8100, Phone: +1 (626) 395-8165, Fax: +1 (626) 395-8868, E-mail: pathak@caltech.edu, siddharthapathak@gmail.com

Viscoelastic Characterization

In addition to their distinctive buckling behavior and their ability to recover from large deformations, VACNTs have also been reported to demonstrate a unique viscoelastic response, which was reported by a subset of the current authors for two separate VACNT systems [1, 2]. The remarkable nature of the viscoelastic behavior of VACNTs was further demonstrated in [3], where the material was found to exhibit this behavior for a wide temperature range from -196°C to 1000°C – something no other material had shown previously. In the research conducted in our group viscoelastic behavior including storage and loss moduli over a range of frequencies was reported by Hutchens, et al [1]. Below we describe the results of our additional viscoelastic experiments performed on the described VACNT micro-pillars.

The viscoelastic properties of the VACNT film were measured using flat punch indentation following the procedure outlined in Ref [1]. In this method the indenter is loaded into the sample at a constant displacement rate of 10 nm/s up to a specified strain, where the indenter head is oscillated at ~8 nm amplitude across a range of frequencies from 1 to 50 Hz. This cut-off frequency (50 Hz) is an instrument limitation as detailed in Ref [1, 4]. The procedure was repeated at four different strains: ε = 0.18, 0.4, 0.62 and 0.84, which ensured visco-elastic characterization of the samples in both their pre and post-densification regimes.

Viscoelastic materials are commonly characterized by their storage (E') and loss (E'') moduli, where the former represents the stored energy or the elastic response, and the latter corresponds to the amount of energy dissipated or the viscous response, as well as their ratio – $\tan\delta$. Assuming linear viscoelastic behavior, these terms can be computed following the calculations described in Refs [4-7] as follows:

$$E' = k'\frac{\sqrt{\pi}}{2\beta}\frac{1-{\nu_s}^2}{\sqrt{A}},\ k' = \left|\frac{F_0}{u_0}\right|\cos\varphi - \left|\frac{F_0}{u_0}\right|_{air}\cos\varphi_{air},$$
$$E'' = k''\frac{\sqrt{\pi}}{2\beta}\frac{1-{\nu_s}^2}{\sqrt{A}},\ k'' = \left|\frac{F_0}{u_0}\right|\sin\varphi - \left|\frac{F_0}{u_0}\right|_{air}\sin\varphi_{air},$$
$$\tan\delta = \frac{E''}{E'} \quad (1)$$

Here k' and k'' are the storage and loss stiffnesses of the sample, obtained by finding the real and complex parts, respectively, of the stiffness differences between oscillating the indenter head on the sample at a fixed displacement and in air at the same raw displacement, β is a constant (=1 for a flat punch indenter), F_0 and u_0 are the load and displacement oscillation amplitudes respectively, and φ is the phase angle between the load and displacement oscillations. The accuracy in the values of E' and E'' in Eq. (1) can be affected by a couple of factors: uncertainties in the value of the Poisson ratio (since the Poisson's ratio can also be frequency dependent), and accuracy in the value of the contact area, especially at lower indentation depth where full contact may not have been established. On the other hand, calculation of $\tan\delta$ is independent of these parameters, and thus is ideally suited as a measure of the viscoelasticity of the indented material [2, 8].

The viscoelastic indentation response of the VACNT film, in terms of the measured values of their storage modulus (E'), loss modulus (E'') and $\tan\delta$ values, is shown below (Figure S1). Similar to the % recovery results discussed in the main manuscript, two distinct responses are seen in this figure depending on if the indenter is oscillated at levels corresponding to the (i) pre-densification regime (open symbols in Figure S1) or (ii) post-densification regime (filled symbols). While both E' and E'' are seen to increase by around 2-3 times after densification (Figures S1a and b), there is no difference in the values of $\tan\delta$ between the pre- pand post-densification regimes (Figure S1c). This indicates that both the values of E' and E'' have increased in equal proportions after densification.

The storage modulus values were found to be frequency independent over the range of frequencies used in this work. On the other hand the loss modulus (and the $\tan\delta$) values are strongly affected by the frequency, and they generally increase with increasing frequency, although a couple of local minimas can be indentified at 30 and 50 Hz respectively. Unfortunately the cut-off frequency (50 Hz) of our instrument prevents further study of this behavior at higher frequencies.

As shown in the figures of the main manuscript (Figures 1 and 2), the VACNT microstructure starts getting densified at strain levels of $\varepsilon \geq 0.65$-0.7. Thus the higher values of E' obtained in the post-densification regime indicate that the material is capable of storing a higher amount of energy in this state, with the excess energy presumably being stored in the buckled/densified regions. A correspondingly higher proportion of energy is also dissipated in this regime, as indicated by a similar increase in the values of E'' . However, the overall visco-elastic response of the VACNT material still remains unaffected, as seen in Figure S1c. These results match well with the loss coefficient measurements shown in Figure 6 (main manuscript), which also show similar values of loss coefficient between the pre- and post densification regimes. An analogous response was also noted by Xu et al. over a much wider temperature range of -196°C to 1000°C [3]. In addition the unloading modulus values shown in Figure 3 (main manuscript) are also are also found to match well with that of E' in Figure S1a.

Characterization of Material Damping Response

The loss coefficient, η, (a dimensionless quantity) measures the degree to which a material dissipates energy and is calculated in two different ways as shown below [9]

$$\eta = \frac{\Delta U_i}{2\pi U_1}\ , \ U = \int_0^{\sigma_{max}} \sigma d\varepsilon\ , \ \Delta U = \oint \sigma d\varepsilon \tag{2}$$

$$\eta = \frac{\Delta U_i}{2\pi U_i}\ , \ U = \int_0^{\sigma_{max}} \sigma d\varepsilon\ , \ \Delta U = \oint \sigma d\varepsilon \tag{3}$$

where U_1 and U_i are the elastic energy stored in the material when it is loaded elastically to a stress $\sigma_{\max}$ in the 1st and the ith cycle respectively, and ΔU_i is the energy dissipated in the ith load-unload cycle (see Fig. S2). The main difference between the above two equations is that in Equation (2) the normalization is done with respect to the area of the 1st loading cycle, while in Equation (3) it is done w.r.t. the area of the ith cycle respectively. In other words, the denominator in Equation (2) is a constant while that of Equation (3) changes with every cycle. Each definition shows a different trend in the values of η as shown in the figure below.

As seen from the figure below, use of Equation (2) results in sharp drop in the values of η after the 1st cycle (Figure S2a), but there is no such drop when using Equation (3). Note that the values of η for the 1st cycle are exactly the same in both figures (Figure S2a and S2b). After the 1st cycle, both figures show a similar drop in the values of η for increasing cycle number. In both cases, η also appears to be strain dependent, and is maximized at the fastest 1000 nm/sec rate, similar to the trends noted for modulus and recovery. As in the case of the tan δ values described earlier, no significant different difference is seen between the pre- and post-densification regimes.

1. Hutchens, S. B.; Hall, L. J.; Greer, J. R., In situ Mechanical Testing Reveals Periodic Buckle Nucleation and Propagation in Carbon Nanotube Bundles. *Advanced Functional Materials* 2010, 20, 2338-2346.
2. Pathak, S.; Cambaz, Z. G.; Kalidindi, S. R.; Swadener, J. G.; Gogotsi, Y., Viscoelasticity and high buckling stress of dense carbon nanotube brushes. *Carbon* 2009, 47, 1969-1976.
3. Xu, M.; Futaba, D. N.; Yamada, T.; Yumura, M.; Hata, K., Carbon Nanotubes with Temperature-Invariant Viscoelasticity from-196 degrees to 1000 degrees C. *Science* 2010, 330, 1364-1368.
4. Herbert, E. G.; Oliver, W. C.; Pharr, G. M., Nanoindentation and the dynamic characterization of viscoelastic solids. *Journal of Physics D: Applied Physics* 2008, 41, 074021-1.
5. Herbert, E. G.; Oliver, W. C.; Lumsdaine, A.; Pharr, G. M., Measuring the constitutive behavior of viscoelastic solids in the time and frequency domain using flat punch nanoindentation. *Journal of Materials Research* 2009, 24, 626-37.
6. Wright, W. J.; Maloney, A. R.; Nix, W. D., An improved analysis for viscoelastic damping in dynamic nanoindentation. *International Journal of Surface Science and Engineering* 2007, 1, 274-92.
7. Wright, W. J.; Nix, W. D. In *Storage and loss stiffnesses and moduli as determined by dynamic nanoindentation*, 506 Keystone Drive, Warrendale, PA 15086, United States, Materials Research Society: 506 Keystone Drive, Warrendale, PA 15086, United States, 2009; pp 863-871.
8. Pathak, S.; Gregory Swadener, J.; Kalidindi, S. R.; Courtland, H.-W.; Jepsen, K. J.; Goldman, H. M., Measuring the dynamic mechanical response of hydrated mouse bone by nanoindentation. *Journal of the Mechanical Behavior of Biomedical Materials* 2011, 4, 34-43.
9. Ashby, M. F., *Materials Selection in Mechanical Design*. Butterworth-Heinemann; : 2005 (3 ed.).