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Nonlinear stress-strain behavior of carbon nanotube fibers subject to slow sustained strain rate

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Nonlinear stress-strain behavior of carbon nanotube (CNT) fibers is studied based on the test data where fiber strength can be modeled by the Weibull distribution. CNT fibers spun from vertically aligned arrays are tensioned at slow sustained strain rate (0.00001 1/s) to study the tensile strength resulting from sliding-to-failure effects. A model is developed to estimate the Weibull modulus which characterizes the dispersion of fiber strengths in terms of the maximum sustained stress and failure strain of the fibers. The results show that the sliding indeed has great influence on the stress-strain relation of CNT fibers at low strain rate. © *2013 AIP Publishing LLC*.
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Carbon nanotube (CNT) fibers spun from vertically aligned arrays, which was first reported in 2004, received more and more attentions in the recent years.[1–8] By assembling millions of interconnected individual CNTs and small bundles together, CNT fibers inherit excellent mechanical strength and, at the same time, possess excellent electrical and thermal conductivity, which make them ideal building blocks for high performance engineering materials and lead to large scale applications possible due to the simplicity in fiber spinning process.[9–12] For example, high electrical conductivity of pure CNT fibers in the range of 300–600 S/m has been demonstrated, which is much higher than that of buckypapers and CNT-based composites.[12,13] Their mechanical strengths were reported in the range of 0.25–3.3 GPa.[12] Compared to conventional fibers, CNT fiber exhibits some unique properties. For example, Li and his group reported a double-peak behavior of the tensile properties of CNT fibers as a function of twist angle; Zheng and his group found strain rate strengthening effect due to the complex scenarios in slippages and stress relaxation behavior of CNT fibers.[14,15] By combining experimental observations and modified Weibull distribution models, the failure mechanisms of CNT fibers are found that inter-tube slippage dominates at low strain rates.[16,17] So, it is still important to investigate the influence parameters on the unique mechanical performances of CNT fibers.

At low strain rate, due to the slippage generated during fiber tension, the total measured strain is composed by two parts: (1) strain of individual CNTs or small bundles and (2) strain generated by slippage

$$\varepsilon_T = \varepsilon_{CNT} + \varepsilon_\tau. \tag{1}$$

So, the strain of individual CNTs becomes even smaller, and the nonlinear elastic properties of individual CNTs could be neglected.[18] On the other hand, the tensile strength/strain of most defect-controlled materials can be adequately described by the Weibull distribution.[19–21] Weibull model, as one of the widely adopted mathematical descriptions of fracture statistic, has been utilized to predict the strength/strain distribution and failure mechanisms of CNT and CNT-based composite fibers.[17,22] The more precise calculation by taking relevant influence parameters into account will lead to a narrower distribution (bigger value for shape parameter m). In a strain controlled tensile test, the probability of survival $R(\varepsilon)$ of CNT interconnection inside the fiber with a length of L under an applied strain, ε, is

$$R(\varepsilon) = \exp\left[-L\left(\frac{\varepsilon}{\varepsilon_0}\right)^m\right], \tag{2}$$

where ε_0 is the characteristic strain and m the Weibull modulus (or shape parameter) which controls the dispersion of the distribution. Based on the understanding of Weibull model and our previous experimental observation, the purpose of this study is to develop a nonlinear model to estimate the influence of sliding and then give further prediction of future effort on developing more reliable CNT fibers for long term applications.

Vertical CNT arrays were synthesized at 750 °C by chemical vapor deposition with 46 sccm ethylene and 154 sccm Ar for 10 min. A layer of Fe film (0.8 nm) on the top of Si substrate, which was coated with Al_2O_3 (10 nm), was used as catalyst. All as-grown CNT arrays have a similar height of 0.4 mm. CNT fibers tensile tested in this study with the same gauge length, 6 mm, were spun from CNT arrays using a microspindle mounted on a motor with a speed of 340 rpm. Ethanol was applied during spinning for fiber densification. The detail experiments could be found in our previous studies.[23–25] A typical stress-strain curve at a strain rate of 0.00001 1/s is shown in Fig. 1. The diameters of tested fibers are 4 μm. The fiber exhibits ductile-like mechanical behavior, indicating that sliding happens inside the fiber.

As the stress-strain curve is nonlinear and the Young's modulus decreases gradually while the loading strain increases, thus the strain-dependent Young's modulus could be expressed by a nonlinear model as

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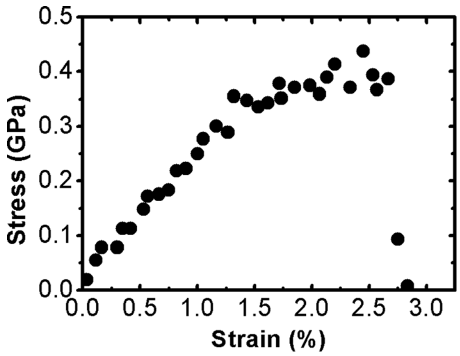

FIG. 1. Typical stress-strain curve of CNT fiber at a strain rate of 0.00001 1/s.

$$E = E_0(1 - \alpha\varepsilon + \beta\varepsilon^2 + \gamma\varepsilon^3 + \ldots), \qquad (3)$$

where E is the strain-dependent elastic modulus, E_0 the initial elastic modulus, and α, β, and γ are the strain dependent coefficients.

The CNT fiber as a unit is formed by interconnected CNTs loaded in the longitudinal direction. Assume that each CNT has the same probability of sliding when tensioned, and the total tensile stress (σ_t) sustained by the remaining unbroken CNT interconnections at strain ε is

$$\sigma_t = E_0(1 - \alpha\varepsilon + \beta\varepsilon^2 + \gamma\varepsilon^3 + \ldots)\varepsilon R(\varepsilon). \qquad (4)$$

If we take the first order nonlinear model as an example, then the nominal fiber stress σ is

$$\sigma = E_0(1 - \alpha\varepsilon)\varepsilon R(\varepsilon). \qquad (5)$$

The tensile strength of a CNT fiber is defined as the maximum of the stress-strain curve

$$\frac{\partial\sigma}{\partial\varepsilon} = 0. \qquad (6)$$

Using Eq. (5) into Eq. (6) gives

$$\varepsilon_0^m - mL\varepsilon^m = \alpha\varepsilon(2\varepsilon_0^m - mL\varepsilon^m). \qquad (7)$$

Setting $\alpha = 0$ and introducing ε_1, the linear solution of the failure strain, as referential strain,

$$\varepsilon_1 = \varepsilon_0(mL)^{-1/m}. \qquad (8)$$

Equation (7) becomes

$$\left(\frac{\varepsilon}{\varepsilon_1}\right)^m = \frac{1 - 2\alpha\varepsilon}{1 - \alpha\varepsilon}. \qquad (9)$$

Equation (9) is a transcendental equation that can be solved by a fixed-point iteration scheme. The failure strain of the CNT fiber ε_b is expressed as

$$\varepsilon_b = \varepsilon_1(1 - \alpha_k\varepsilon_k)^{1/m}, \qquad (10)$$

where coefficient α_k and ε_k are from Ref. 20.[21] The maximum tensile stress of CNT fiber is

$$\sigma_{max} = E_0(1 - \alpha\varepsilon_b)\varepsilon_b \exp\left[-L\left(\frac{\varepsilon_b}{\varepsilon_0}\right)^m\right]. \qquad (11)$$

Substituting Eq. (10) into Eq. (11) and using Eq. (8), we have

$$1 - \alpha_k\varepsilon_k = m \ln\frac{E(1 - \alpha\varepsilon_b)\varepsilon_b}{\sigma_{max}}. \qquad (12)$$

From Eq. (9) we get

$$\varepsilon_1 = \left(\frac{1 - \alpha\varepsilon}{1 - 2\alpha\varepsilon}\right)^{1/m}\varepsilon_b. \qquad (13)$$

Substituting Eqs. (12) and (13) into Eq. (10), we can solve for the Weibull modulus in terms of the measurable quantities E_0, ε_b, and σ_{max}

$$m = \left(\frac{1 - 2\alpha\varepsilon_b}{1 - \alpha\varepsilon_b}\right) \Big/ \ln\frac{E_0(1 - \alpha\varepsilon_b)\varepsilon_b}{\sigma_{max}}. \qquad (14)$$

For second order nonlinear model,

$$\sigma = E_0(1 - \alpha\varepsilon + \beta\varepsilon^2)\varepsilon \exp\left[-L\left(\frac{\varepsilon}{\varepsilon_0}\right)^m\right], \qquad (15)$$

$$\varepsilon_0 = \varepsilon_1(mL)^{1/m}, \qquad (16)$$

$$\varepsilon_1 = \left(\frac{1 - \alpha\varepsilon_b + \beta{\varepsilon_b}^2}{1 - 2\alpha\varepsilon_b + 3\beta{\varepsilon_b}^2}\right)^{1/m}\varepsilon_b, \qquad (17)$$

$$m = \left(\frac{1 - 2\alpha\varepsilon_b + 3\beta\varepsilon_b^2}{1 - \alpha\varepsilon_b + \beta\varepsilon_b^2}\right) \Big/ \ln\frac{E_0(1 - \alpha\varepsilon_b + \beta\varepsilon_b^2)\varepsilon_b}{\sigma_{max}}. \qquad (18)$$

For third order nonlinear model,

$$\sigma = E_0(1 - \alpha\varepsilon + \beta\varepsilon^2 + \gamma\varepsilon^3)\varepsilon \exp\left[-L\left(\frac{\varepsilon}{\varepsilon_0}\right)^m\right], \qquad (19)$$

$$\varepsilon_0 = \varepsilon_1(mL)^{1/m}, \qquad (20)$$

$$\varepsilon_1 = \left(\frac{1 - \alpha\varepsilon_b + \beta{\varepsilon_b}^2 + \gamma{\varepsilon_b}^3}{1 - 2\alpha\varepsilon_b + 3\beta{\varepsilon_b}^2 + 4\gamma{\varepsilon_b}^3}\right)^{1/m}\varepsilon_b, \qquad (21)$$

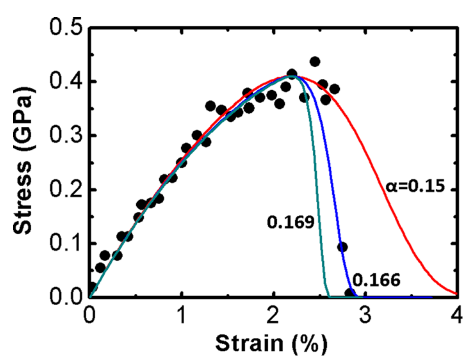

FIG. 2. Stress-strain curves for CNT fibers. The solid circles are experimental results; the solid lines are the curves for the first order nonlinear model with $\alpha = 0.15$, 0.166, and 0.169. The corresponding Weibull moduli are 36.49, 19.62, and 6.712, respectively.

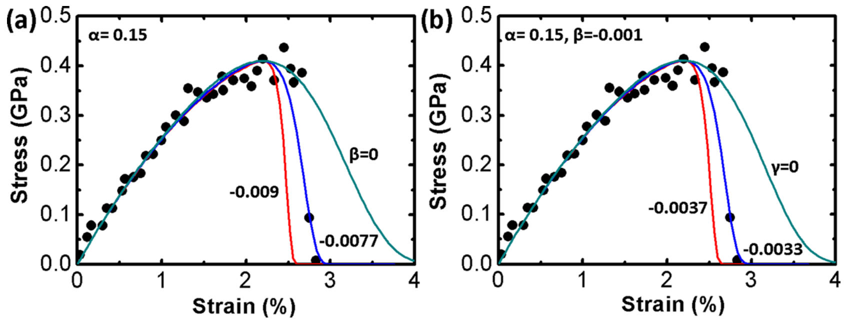

FIG. 3. Stress-strain curves for CNT fibers using second and third order fittings. The solid circles are experimental results; the solid lines are the curves for the nonlinear models. (a) The second order fitting: $\alpha = 0.15$ and $\beta = -0.009, \ -0.0077, 0$. The corresponding Weibull moduli are 39.87, 19.63, and 6.71; (b) the third order fitting: $\alpha = 0.15$, $\beta = -0.001$, and $\gamma = -0.0037, -0.0033, \ 0$. The corresponding Weibull moduli are 36.76, 20.84, and 7.159, respectively.

$$\mathrm{m} = \left(\frac{1 - 2\alpha\varepsilon_b + 3\beta\varepsilon_b^2 + 4\gamma\varepsilon_b^3}{1 - \alpha\varepsilon_b + \beta\varepsilon_b^2 + \gamma\varepsilon_b^3} \right) \Big/ \ln \frac{\mathrm{E}_0(1 - \alpha\varepsilon_b + \beta\varepsilon_b^2 + \gamma\varepsilon_b^3)\varepsilon_b}{\sigma_{\max}}. \tag{22}$$

Fitting the data with a cubic function, we obtain slope $E_0 = 0.30$ and $\sigma_{\max} = 0.41$ at $\varepsilon_b = 2.2$. Substituting these numbers and $\alpha = 0.15, \ 0.166,$ and 0.169 into first-order nonlinear model, we get the Weibull modulus $m = 6.712$, 19.62, and 36.49, respectively. The fitting curve is shown in Fig. 2

$$\sigma = 0.3(1 - 0.15\varepsilon)\varepsilon \exp[-3.804 \times 10^{-4}\varepsilon^{6.712}], \tag{23}$$

$$\sigma = 0.3(1 - 0.166\varepsilon)\varepsilon \exp[-4.112 \times 10^{-9}\varepsilon^{19.62}], \tag{24}$$

$$\sigma = 0.3(1 - 0.169\varepsilon)\varepsilon \exp[-3.585 \times 10^{-15}\varepsilon^{36.49}]. \tag{25}$$

Comparatively, the blue curve fits the experimental data the best with a Weibull modulus of 19.62. We also tried second and third order nonlinear models, and the results are shown in the following (Figs. 3(a) and 3(b)) with m of 19.63 and 20.84 for best fitting, respectively.

Furthermore, when α, β, and γ all equal to 0

$$\sigma = 0.255\varepsilon \exp[-5.26 \times 10^{-2}\,\varepsilon^{2.46}], \tag{26}$$

where Weibull modulus of m equals to 2.46, which is similar to our previous result with $m = 2.4$.[17]

At present, there are a few experimental datasets available in the literature for the strength distribution analysis of individual CNTs, bundles, and fibers. A Weibull modulus $m = 1.7$ is obtained from data for 26 multi-walled CNT (MWNT) specimens, $m = 2.6$ for 19 MWNT specimens, and $m = 2.5$ and 2.72 for 15 single-walled CNT (SWNT) rope specimens.[26–28] These m values are close to 2.4 reported for CNT fibers tested at low strain rate in our previous study,[17] suggesting a similar dispersion. Experimentally, the nonlinear stress-strain behavior was attributed to the sliding of CNTs inside the fiber during tension.[16] When we take the nonlinear behavior of CNTs inside the fiber into consideration, the Weibull modulus increases tremendously. The calculated m value (19) is also higher than experimental result in our previous study (7.1), where we used high loading strain rate to eliminate the influence of CNT sliding inside the fiber. The reason is probably due to that, in practical situation, sliding is unavoidable. It indicates that the sliding of CNTs inside fibers indeed has effect on the strength distribution, which dominates the failure mechanism under low strain rate. In addition, no matter how α, β, and γ are changed, as long as the fitting is the best, the Weibull modulus almost keeps constant at around 19, thus the first order nonlinear model is sufficient to estimate the stress-strain relation of CNT fiber.

In summary, based on the observed trend that the strength of CNT fibers follows the Weibull distribution and considering the sliding behavior of CNTs, a nonlinear model for describing stress-strain relationship of CNT fibers with interconnected CNTs has been developed. Comparison with experimental results shows that the model can characterize the nonlinear stress-strain relation of CNT fibers leading up to complete failure. The sliding of CNTs inside the fibers does have significant effect on the strength distribution of CNT fibers.

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