

Nanoscale Weibull Statistics for Nanofibers and Nanotubes

N. M. Pugno¹ and R. S. Ruoff²

Abstract: In this paper a modification of the classical Weibull statistics is applied to nanostructures. A comparison is presented of “nanoscale” versus classical Weibull statistics in treating recent experimental results on the fracture strength of C nanofibers and nanotubes, and WS₂ nanotubes. “Nanoscale” Weibull moduli of 3.8 for electrospun and then heat-treated carbon nanofibers, 2.7 for arc-discharge synthesized multiwalled carbon nanotubes, 1.8 for chemical vapor deposited multiwalled carbon nanotubes, and 3.0 for multiwalled WS₂ nanotubes, are deduced.

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Introduction

One may question whether Weibull statistics [WS; Weibull (1951)] for strength of solids, and deterministic linear elastic fracture mechanics [LEFM; Griffith (1920)], apply properly at the nanoscale. For WS it is assumed that the number of critical flaws is proportional to the volume or to the surface area of the structure. However, single crystal nanostructures may either be defect free or perhaps have a small number of (critical) defects. Recently LEFM, which implicitly assumes infinite ideal strength of solids, as well as large (with respect to the so-called “plastic zone”) and perfectly sharp cracks, has been modified and quantized fracture mechanics [QFM; Pugno and Ruoff (2004)] has been presented. QFM treats defects of any size and shape (e.g., atomic vacancies, nanoholes). In this paper we describe and use a modification of WS for describing the strength of solids (also) at the nanoscale [recently published by Pugno and Ruoff (2006)], as a statistical counterpart of QFM. We will compare “standard” WS versus the modified form [nanoscale Weibull statistics (NWS); Pugno and Ruoff 2006] in fitting of fracture datasets for (1) high-temperature treated electrospun (PAN-based) carbon nanofibers (Zussman et al. 2005), perhaps of interest due to the extensive use of carbon fibers in the aerospace industry; (2) arc-discharge (AD) produced multiwalled carbon nanotubes (Yu et al. 2000); (3) chemical vapor deposited (CVD) multiwalled carbon nanotubes (Barber et al. 2005); and (4) WS₂ multiwalled nanotubes (Barber et al. 2005). The statistical data analyses suggest that a small number of critical defects determine fracture in such nanostructures.

Tensile Tests on Nanofibers and Nanotubes

High-Temperature Treated Electrospun (PAN-Based) Carbon Nanofibers (Zussman et al. 2005)

To perform failure tests, a single carbonized nanofiber was mounted on one end of an atomic force microscope (AFM) cantilever tip that served as a force-sensing element, and on the other end to the etched tip of a tungsten (W) wire. (The nanofiber was first glued on one end of a W wire tip using an optical microscope equipped with mechanical translators.) The free end of each nanofiber was clamped onto the AFM cantilever tip using electron beam-induced deposition (EBID). The W wire and the AFM cantilever were each mounted on a nanomanipulator [Yu et al. (1999); the device actually used is a third generation instrument, D. Dikin and R. S. Ruoff, unpublished results] located inside a scanning electron microscope (SEM). Tensile tests were conducted inside the SEM and the applied force was calculated from the measured AFM cantilever deflection (Fig. 1); the stress was calculated from the measured nanofiber geometry. The measured failure stress of each of the carbon nanofibers tested are shown in Table 1. The spread of fracture strengths, and that fracture occurred “randomly” in the gauge region for the 18 specimens tested (rather than always occurring close to the clamps where a stress concentration is expected to be present) suggests that there is a distribution of defects in these nanofibers. Is there a way of assessing if just one or a few critical defects is present for each? The comparison between WS and NWS will be shown to suggest the presence of only a few critical defects in such nanofibers, as discussed in the section “Application to Carbon Nanofibers, Nanotubes, and to WS₂ Nanotubes.”

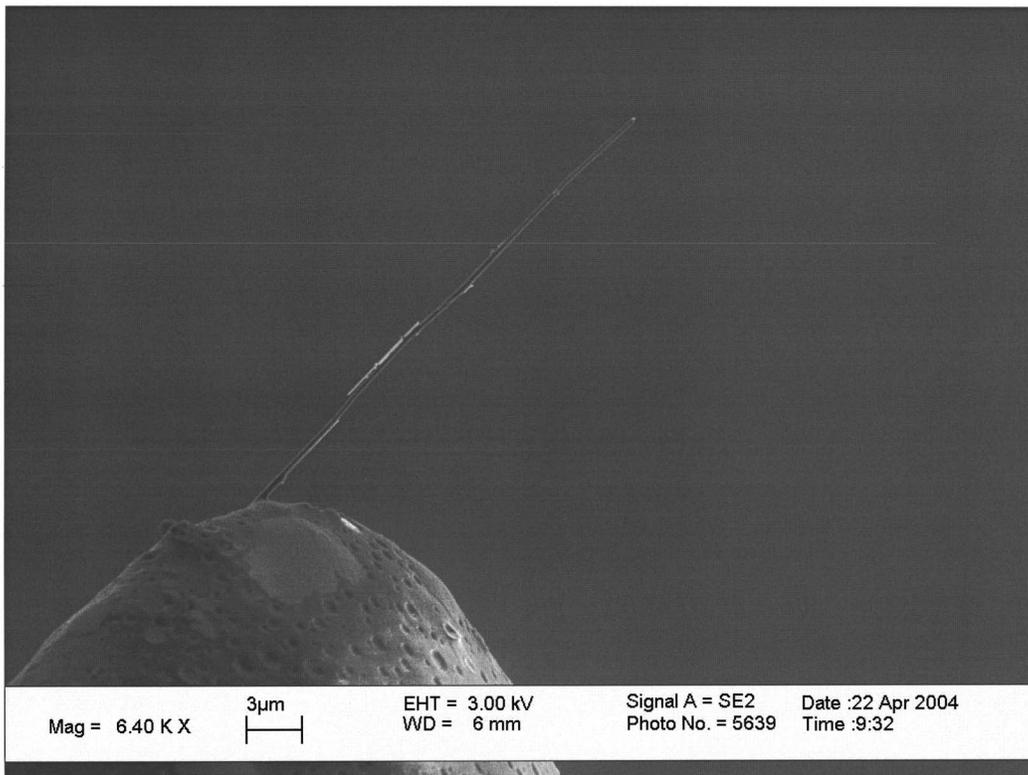
Arc-Discharge Produced Multiwalled Carbon Nanotubes (Yu et al. 2000)

Tensile loading of individual multiwalled carbon nanotubes (MWCNTs) were performed in an analogous approach to that used for carbon nanofibers discussed above. The method is described in detail by Yu et al. (2000); the MWCNT being tested was mounted by EBID on each end to separate AFM cantilever tips, with one cantilever significantly more rigid compared to the other. Tensile tests were conducted inside a SEM vacuum chamber using a home built nanomanipulator.

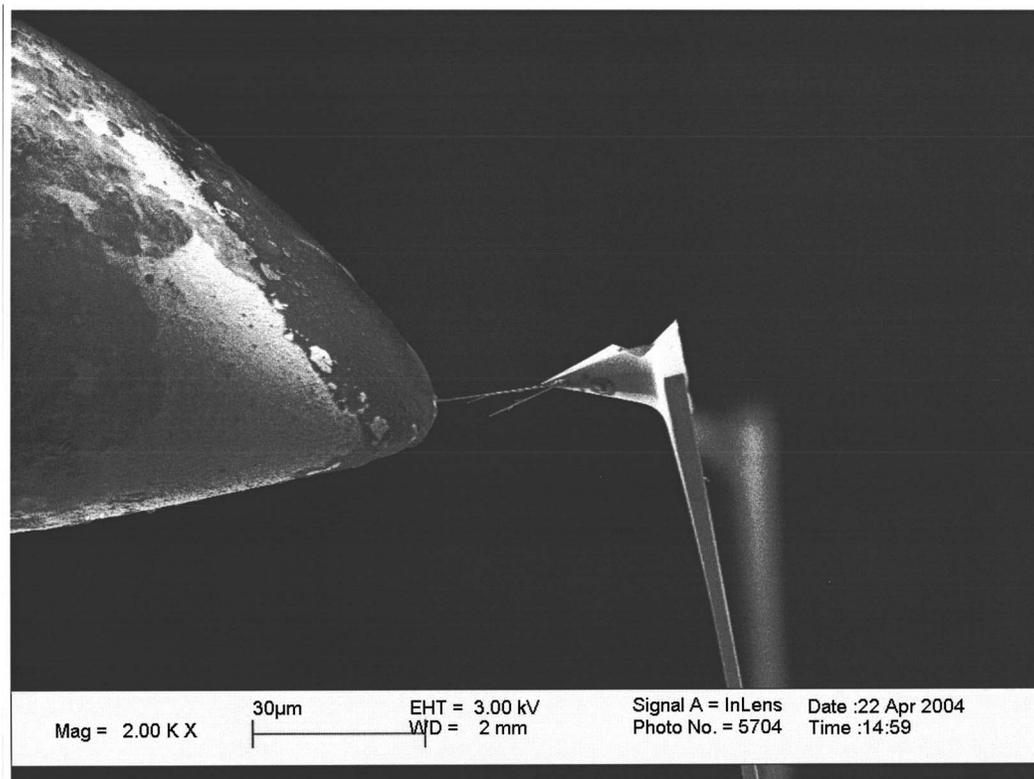
¹Dept. of Structural Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino 10129, Italy.

²Dept. of Mechanical Engineering, Northwestern Univ., Evanston, IL 60208-3111.

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(a)



(b)

Fig. 1. Nanotensile test, on a *C* nanofiber

Table 1. Nanofiber Length, Diameter, and Strength [Data Adapted from Zussman et al. (2005)]

Number	Length (μm)	Diameter (nm)	Strength (MPa)
1	16.5	150	294
2	177	224	340
3	23	340	343
4	359	500	369
5	9	155	400
6	52	300	430
7	13	169	467
8	374	300	550
9	23	280	567
10	12	160	569
11	21	120	575
12	33	120	586
13	30	157	625
14	5.5	83	637
15	12	167	684
16	35.5	182	721
17	20	145	752
18	21	128	920

Chemical Vapor Deposited Multiwalled Carbon Nanotubes and WS₂ Multiwalled Nanotubes (Barber et al. 2005)

The method used to test these nanostructures is similar in type to that of Yu et al. (2000), and the reader is referred to Barber et al. (2005) for discussion and prior references.

Classical and “Nanoscale” Weibull Statistics

Classical Weibull statistics (Weibull 1951) assumes the probability of failure F for a fiber of volume V under uniaxial uniform stress σ as

$$F(\sigma) = 1 - \exp\left[-V\left(\frac{\sigma}{\sigma_{0V}}\right)^m\right] \quad (1)$$

where σ_{0V} and m =Weibull’s *scale* and *shape* parameters, respectively; and V =fiber volume [see e.g., Bagdahn and Sharpe (2003)]. The surface-flaw based Weibull distribution replaces the volume V in Eqs. (1) with the surface area S of the specimen (and σ_{0V} with a new constant σ_{0S})

$$F(\sigma) = 1 - \exp\left[-S\left(\frac{\sigma}{\sigma_{0S}}\right)^m\right] \quad (2)$$

Note that σ_{0V} or σ_{0S} has dimensions of a stress times a volume (σ_{0V}) or a surface raised to the $1/m$ power (σ_{0S}); thus the exponents in Eqs. (1) and (2) are dimensionless.

In QFM (Pugno and Ruoff 2004) the assumed existence of a “fracture quantum” suggests that a very small defect can cause the failure of a nearly defect free structure. It is therefore, in principle, possible that regardless of its volume or surface area, a nanostructure may fail due to a single critical defect or due to a very small number of (critical) defects. The tensional analog of the energy based QFM suggests that not the stress σ , but rather its mean value σ^* “along a fracture quantum,” has to reach a critical value to cause the failure of the specimen. Replacing σ with σ^* in the Weibull approach removes the nonconvergence of the Weibull

integrals [that have to be considered in Eqs. (1) and (2) for non-uniform stress distribution, see Pugno and Ruoff (2006), for details] at stress intensifications, where the integral of σ^m diverges but the integral of σ^{*m} is finite. By using the number n of critical defects instead of the volume V or surface area S of the specimen, and σ^* instead of σ , one has

$$F(\sigma^*) = 1 - \exp\left[-n\left(\frac{\sigma^*}{\sigma_0}\right)^m\right] \quad (3)$$

where n =number of defects and σ_0 (dimensions of stress) and m (dimensionless)=two constants.

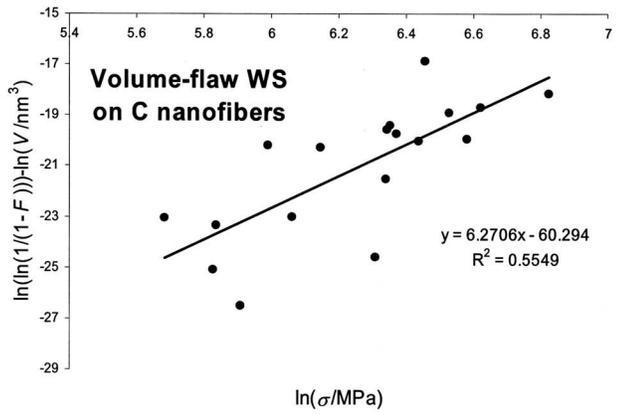
Note that WS (in the context of NWS) assumes $n=kD^\alpha L^\beta$, with $\alpha=2$ and $\beta=1$ if volume flaws are considered, or $\alpha=1$ and $\beta=1$ if surface flaws are considered (and k is a constant). For nearly defect free structures, one may make the assumption (for the purposes of testing a model) that failure occurs at $n=1$ (or equivalently at a value of n independent from the specimen size) for which $\alpha=0$, $\beta=0$. That is, it may be more appropriate to expect $0 \leq \alpha \leq 2$ and $0 \leq \beta \leq 1$. It is perhaps of interest that this corresponds to substituting the volume (or surface area) in the WS with a fractal volume (or fractal surface area), always intermediate between a geometrical point and a Euclidean volume (Carpinteri and Pugno 2005). NWS thus has to be considered, in general, with $n=kD^\alpha L^\beta$ with $0 \leq \alpha < 2$, $0 \leq \beta \leq 1$, or $n=kH^\alpha L^\beta W^\gamma$ for rectangular cross section areas $W \times H$, with $0 \leq \alpha, \beta, \gamma \leq 1$, e.g., nanowires, even if at atomic scale we suggest that $\alpha=0$, $\beta=0$.

The cumulative probability $F(\sigma_i)$ can be obtained experimentally as (Johnson 1983) $F(\sigma_i)=(i-1/2)/N$ where N =total number of tests and the observed strengths $\sigma_1, \dots, \sigma_N$ are ranked in ascending order.

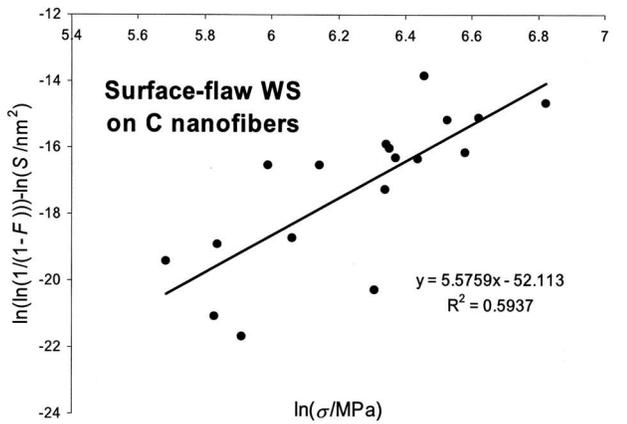
Application to Carbon Nanofibers, Nanotubes, and to WS₂ Nanotubes

We apply the volume-flaw WS, Eq. (1) to the set of fracture strengths of C nanofibers of Table 1. Fig. 2(a) shows that the correlation coefficient is poor, $R^2=0.55$, thus the Weibull modulus cannot be considered statistically significant. Fig. 2(b) shows the analysis assuming surface flaws, Eq. (2), for which $R^2=0.59$. Considering length instead of the volume or surface yields $R^2=0.63$. With NWS, Eq. (3), and simply assuming $\sigma^* \equiv \sigma$ (since we are not considering prenotched specimens), and $n=1$ (i.e., a constant value independent from the geometry), the correlation coefficient is $R^2=0.95$; this is shown in Fig. 2(c). This suggests a small number of critical defects in nanostructures (perhaps just one critical defect), and that failure is more strongly dependent on them (or it) than on the volume or surface area of the specimen. The “nanoscale” Weibull modulus m , an index of the dispersion of the distribution, is 3.8 [the slope m in Fig. 2(c)], whereas σ_0 , an index of the mean value of the distribution, is 604 MPa (from the other negative term q in the best fit equation, as $\sigma_0=e^{q/m}$).

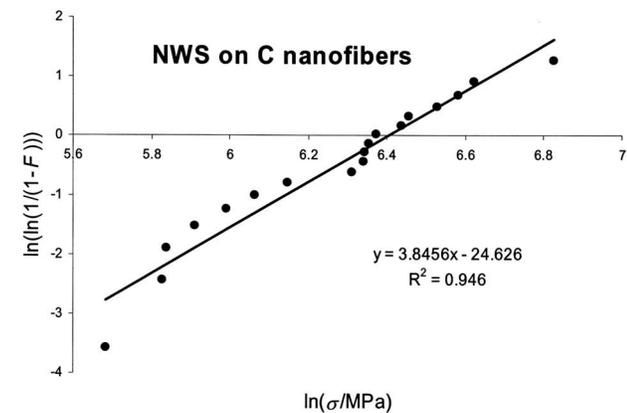
We turn now to the fracture strengths of the outer shell of arc-grown MWCNTs obtained by Yu et al. (2000). The volume- and surface-based approaches become identical for the case of fracture of the outer shell (external wall) of MWCNTs under nearly uniform tension, such as for the 19 MWCNTs tested. This is true because $V=St$, where t =nearly constant spacing between nanotubes of 0.34 nm which is thus considered as the shell thickness. WS yields a correlation coefficient of $R^2=0.67$ [for details, see Pugno and Ruoff (2006)]. With NWS we find $R^2=0.93$, m 2.7, and $\sigma_0 \approx 31.2$ GPa, as shown in Fig. 3.



(a)



(b)



(c)

Fig. 2. (a) Volume-flaws based Weibull statistics for strength of C nanofibers; (b) surface-flaws based Weibull statistics for strength of C nanofibers; and (c) nanoscale Weibull statistics for strength of C nanofibers

Finally we consider fracture strength distributions for CVD-grown MWCNTs and WS₂ MWNTs presented by Barber et al. (2005). By applying NWS to the first data set of MWCNTs (Fig. 4) we deduce $R^2=0.97$, m 1.8, and $\sigma_0 \approx 108.0$ GPa; but note that here interactions between nanotube walls have been postulated (Barber et al. 2005), and we would agree that this assumption is reasonable, due to the unrealistically high value of σ_0 . Furthermore, considering WS₂ MWNTs (Fig. 5) m 3.0 and $\sigma_0 \approx 13.3$ GPa (which may be close to the ideal material

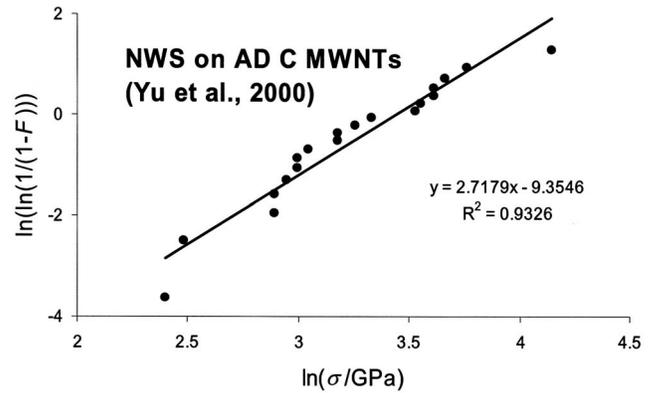


Fig. 3. Nanoscale Weibull statistics for strength of AD C nanotubes [data adapted from Yu et al. (2000)]

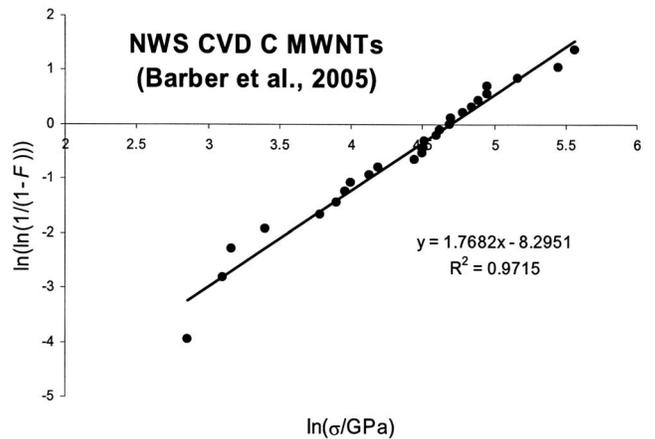


Fig. 4. Nanoscale Weibull statistics for strength of CVD C nanotubes [data adapted from Barber et al. (2005)]

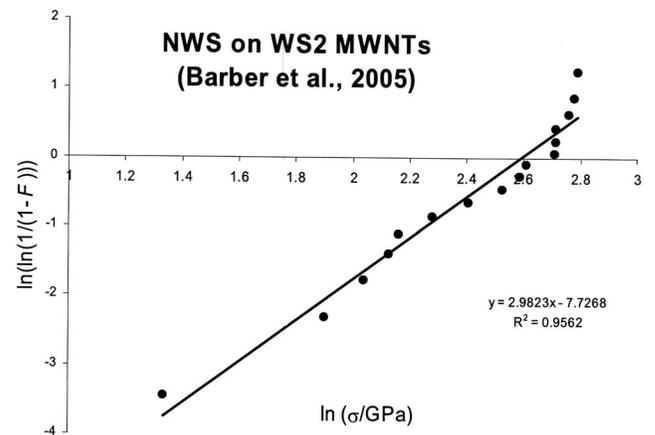


Fig. 5. Nanoscale Weibull statistics for strength of WS₂ nanotubes [data adapted from Barber et al. (2005)]

strength). Also in this case the correlation coefficient for NWS is close to the unit, i.e., $R^2=0.96$. Thus, we conclude that our extension of the Weibull statistics can work also at the nanoscale.

Conclusions

The comparison between classical and nanoscale Weibull statistics applied to datasets available for the fracture strength of C nanofibers and C and WS₂ nanotubes shows that the “nanoscale” Weibull statistics model presented here yields a much better fit to the spread of fracture strengths for each set of data. The values obtained for “nanoscale” Weibull moduli of 3.8 for heat-treated, PAN-based electrospun C nanofibers 2.7 for arc-discharge multiwalled carbon nanotubes, 1.8 for chemical vapor deposited multiwalled carbon nanotubes, and 3.0 for multiwalled WS₂ nanotubes. Note the role of the fracture “quantization” in the new statistics: It is crucial to treat stress intensifications in prenotched specimens (for which the classical Weibull integrals do not converge) with “nanoscale” Weibull statistics. We suggest that a small number of defects and perhaps simply one critical defect in each of the different nanofibers or nanotubes that were loaded to failure, was responsible for their breaking.

Acknowledgments

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