



Multimodal Daniels' theory: An application to carbon nanotube twisted strands

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ABSTRACT

In this paper a new extension of the Daniels' theory, which account for multiple modes of failure, is presented and applied to carbon nanotube (CNT) bundles. We developed a hierarchical statistical model for treating CNT twisted strands. The analysis allow us to rigorously characterize for the first time the weakest link, that is the CNT–CNT joint, in terms of Weibull size and shape parameter.

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1. Introduction

Research on carbon nanotube (CNT) synthesis and on CNT fibers are interdependent, and drive new discoveries in CNT catalysis and growth. Many of the key advances in CNT synthesis led immediately to new results in fiber production. Various synthesis techniques can produce either shorter nanotubes (including arc-discharge, laser oven, high-pressure CO conversion (HiPco), fluidized bed Chemical Vapor Deposition (CVD)) or longer nanotubes (substrate growth CVD, catalytic gas flow CVD).

The Weibull distribution has been widely used to describe the strength of brittle materials [1–5]. It is now well-known that a Weibull distribution of strength values necessarily arises, if the distribution of defects obeys the following three conditions [1,6]: (1) the defects are independent from each other, i.e. they are not interacting; (2) the material obeys the weakest-link hypothesis; i.e. the weakest link causes failure of the whole structure and (3) a critical defect density can be defined and the size of a critical defect is uniquely related to the strength.

The strength of a fiber is an extreme-value property, depending only on the strength of the weakest link. This is the basis of the so-called weakest link theory of brittle materials, which has been extensively discussed in the literature [7–9]. The most well-known one is due to Weibull [10]. The importance of weakest link theories is twofold: first, the theories are experimentally statistically predictive and verifiable and secondly, they provide a mechanism

for extrapolating fiber strength to experimentally inaccessible gauge lengths.

Carbon fiber strength distributions have been analyzed with single modal distributions, even though in many cases the measured distributions were clearly multimodal. Accordingly, we here extend the Daniels' theory [11] to multi-modal failure. As an example, we apply the theory to predict the strength of CNT twisted strands and of the related CNT–CNT junctions, complementary to previous analyses [12–16].

2. Multimodal Daniels' theory

Daniels [11] considered Z parallel fibers with given cross-sectional area, linear elastic constitutive law and single modal Weibull distribution. Tensile strength distributions having more than one mode of failure are now considered in extending the Daniels' theory. The presence of several modes in the strength distribution implies the existence of several distinct types of strength-limiting defects in the fiber structure. Accordingly, we consider a multimodal Weibull distribution for each fiber. For a multi-modal distribution, the probability function is given by:

$$F(\sigma) = 1 - ([1 - F_1(\sigma)][1 - F_2(\sigma)] \dots [1 - F_n(\sigma)]) \quad (1)$$

where $F_1(\sigma)$, $F_2(\sigma)$..., $F_n(\sigma)$ are the statistical probabilities of each modal failure.

The probability density for the strength of a fiber is illustrated in Fig. 1a. In a bundle, the fibers with strength larger than the applied stress, P , sustain the stress. On other hand, the fibers with the strength lower than P , will break and the stress of broken elements becomes zero.

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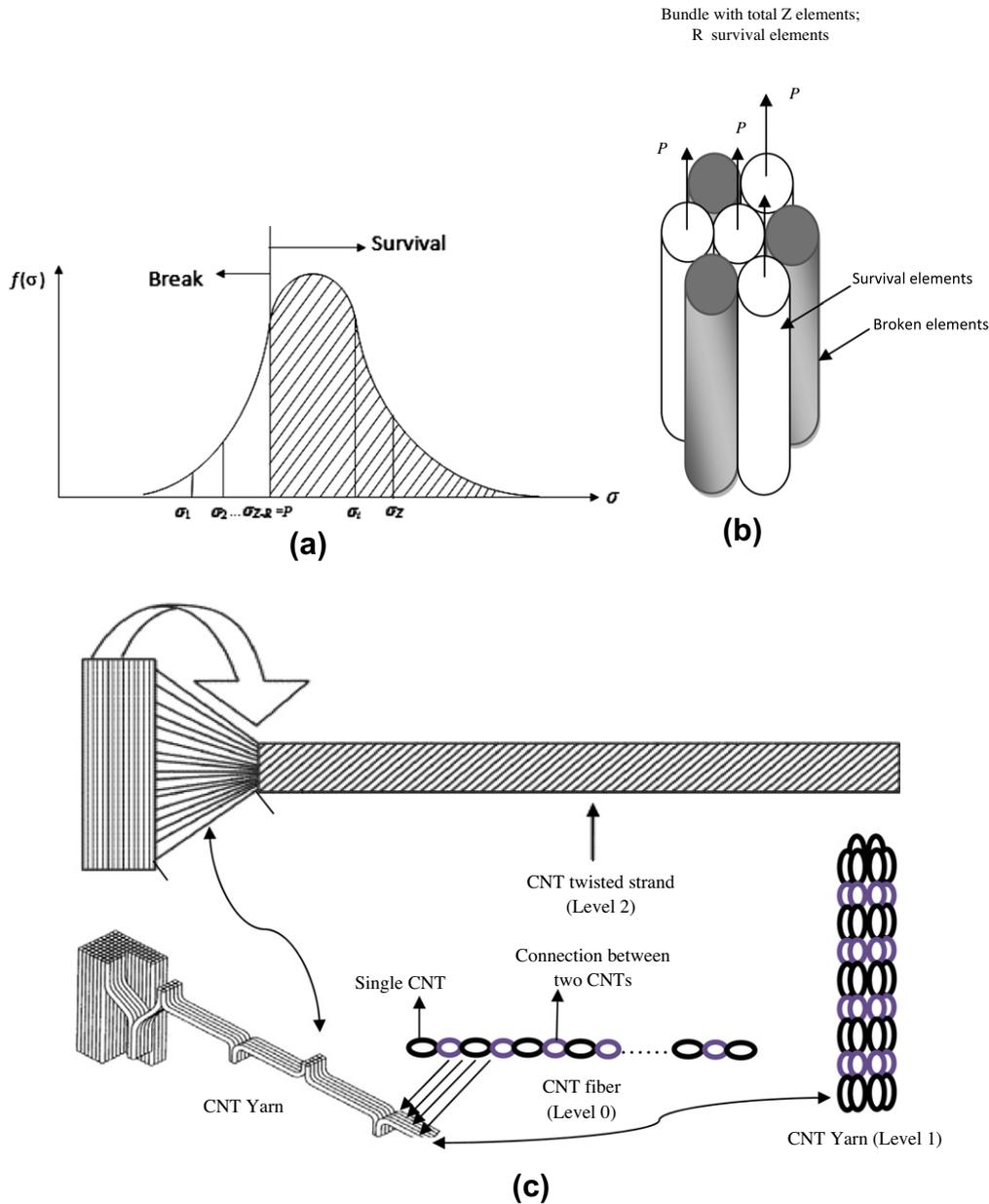


Fig. 1. (a) Probability density for the strength of each fiber in the bundle. (b) Stress condition of the bundle. (c) Hierarchical twisted strand CNT model.

Assuming $F_i(\sigma)$ of Weibull type, the cumulative probability function is thus given by:

$$F(\sigma) = 1 - \exp\left(-\sum_{i=1}^n \frac{l}{l_{0i}} \left(\frac{\sigma}{\sigma_i}\right)^{m_i}\right) \quad (2)$$

where l is the fiber length, l_{0i} is the characteristic length, σ is the stress applied in the longitudinal direction, whereas σ_i and m_i are the scale and shape parameters respectively.

Accordingly, the probability density is

$$f(\sigma) = \sum_{i=1}^n \frac{l}{l_{0i}} \left(\frac{m_i}{\sigma_i}\right) \left(\frac{\sigma}{\sigma_i}\right)^{m_i-1} \exp\left(-\sum_{i=1}^n \frac{l}{l_{0i}} \left(\frac{\sigma}{\sigma_i}\right)^{m_i}\right) \quad (3)$$

Fig. 1b shows the stress condition of the bundle. If R is the current number of surviving fibers in the bundle, then assuming the Equal Load Sharing (ELS), the average stress of the bundle is defined as

$$\bar{\sigma} = \frac{R}{Z} P \quad (4)$$

where P is the stress sustained by the survival fibers.

The maximum value of $\bar{\sigma}$ gives the strength of the bundle. Hence the strength of the bundle is obtained from $\frac{d\bar{\sigma}}{dP} = 0$.

The ratio of the number of sustain fibers R to the total number of fibers Z , when Z is high and when fiber failures are equally probable events, is (Fig. 1a and b)

$$\frac{R}{Z} = \int_P^\infty f(\sigma) d\sigma \quad (5)$$

and, considering Eq. (3), becomes:

$$\frac{R}{Z} = \exp\left(-\sum_{i=1}^n \frac{l}{l_{0i}} \left(\frac{P}{\sigma_i}\right)^{m_i}\right) \quad (6)$$

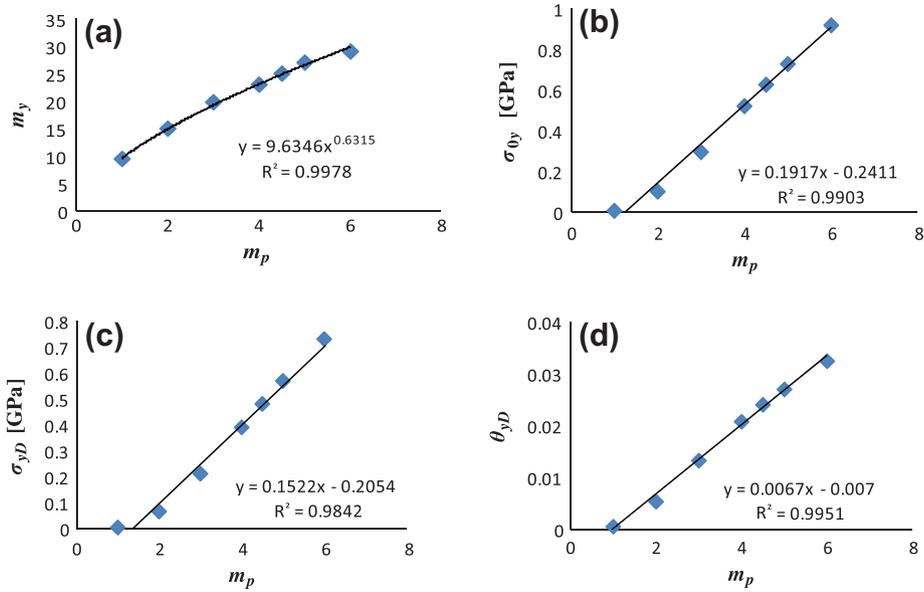


Fig. 2. Variation of CNT yarn (a) shape parameter, (b) scale parameter, (c) mean strength and (d) standard deviation, versus shape parameter of the connection between CNTs in the yarn.

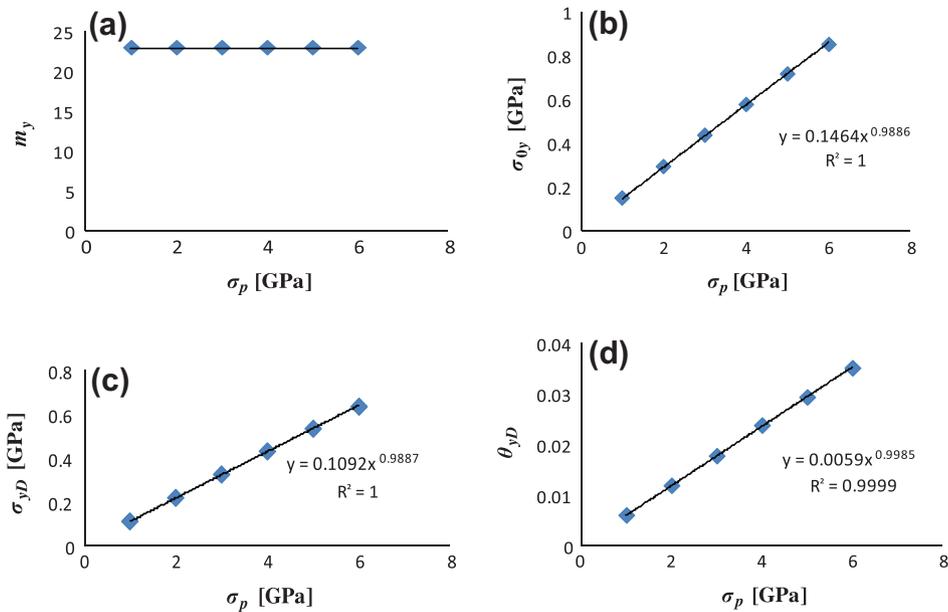


Fig. 3. Variation of CNT yarn (a) shape parameter, (b) scale parameter, (c) mean strength and (d) standard deviation, versus scale parameter of the connection between CNTs in the yarn.

Thus:

$$\bar{\sigma} = P \exp \left(\sum_{i=1}^n -\frac{l}{l_{0i}} \left(\frac{P}{\sigma_i} \right)^{m_i} \right) \quad (7)$$

The maximum value of σ is given by:

$$\frac{d\bar{\sigma}}{dP} = 0 \quad (8)$$

namely:

$$\exp \left(\sum_{i=1}^n -\frac{l}{l_{0i}} \left(\frac{P}{\sigma_i} \right)^{m_i} \right) + P \sum_{i=1}^n -\frac{l}{l_{0i}} \left(\frac{m_i}{\sigma_i} \right) \left(\frac{P}{\sigma_i} \right)^{m_i-1} \times \exp \left(\sum_{i=1}^n -\frac{l}{l_{0i}} \left(\frac{P}{\sigma_i} \right)^{m_i} \right) = 0 \quad (9)$$

This equation can be solved numerically yielding P_f , which gives the mean strength of the bundle as:

$$\bar{\sigma} = P_f \exp \left(\sum_{i=1}^n -\frac{l}{l_{0i}} \left(\frac{P_f}{\sigma_i} \right)^{m_i} \right) \quad (10)$$

The standard deviation of the strength is predicted to be:

$$\theta = \sqrt{\frac{(\bar{\sigma})^2 Z^{-1}}{\exp \left(\sum_{i=1}^n -\frac{l}{l_{0i}} \left(\frac{P_f}{\sigma_i} \right)^{m_i} \right)} \left(1 - \exp \left(\sum_{i=1}^n -\frac{l}{l_{0i}} \left(\frac{P_f}{\sigma_i} \right)^{m_i} \right) \right)} \quad (11)$$

Eqs. (10) and (11) for $n = 1$ correspond to the results of the classical single modal Daniels' theory.

3. An application to carbon nanotube ropes

CNTs are an extremely interesting type of material due to their unique one dimensional structure, and their excellent mechanical properties [17,18]. To exploit their excellent physical properties at a macroscopic level, it is desirable to create CNTs with macroscopic length. However, it has been very challenging to grow arbitrarily long CNTs [19]. An alternative approach is to create long nanotube structures with many of them aligned into continuous yarns or ropes [20–25].

Due to the high-strength constituent CNTs and their twisted nanostructure, CNT yarns can potentially be made much stronger and tougher than Kevlar. When the twisted yarn is pulled, the CNTs attempt to straighten, invoking a locking mechanism used to make ropes stronger. CNTs have a finite length, l , but twisting prevents a bundle of CNTs (much longer than l) from falling apart. Like most advanced fibers, it has been shown that CNT strength can also be described by a Weibull distribution [26,12,13]:

$$F(\sigma) = 1 - \exp\left(-\frac{l}{l_0}\left(\frac{\sigma}{\sigma_0}\right)^m\right) \quad (12)$$

where l_0 is the length of the individual CNT, σ is the applied fiber axial stress, m and σ_0 are the Weibull shape and scale parameter, for a given fiber length l .

The mean strength $\langle\sigma_W\rangle$ is given by:

$$\langle\sigma_W\rangle = \left(\frac{l}{l_0}\right)^{\frac{1}{m}} \sigma_0 \Gamma\left(1 + \frac{1}{m}\right) \quad (13)$$

whereas the standard deviation is:

$$\theta_W = \langle\sigma_W\rangle \left(\frac{\Gamma\left(1 + \frac{2}{m}\right)}{\Gamma^2\left(1 + \frac{1}{m}\right)} - 1\right)^{1/2} \quad (14)$$

The situation can additionally turn out to be still more complex, if the strength distribution is not unimodal. Moreover, bimodal Weibull distributions were observed for carbon [27] and silicon carbide fibers [28] and for certain ceramics [29].

Experimentally [22,30], CNT yarns are peeled off from the super-aligned arrays, thanks to a strong binding force between the fibers. Also, the bundles were joined end to end forming a continuous yarn, Fig. 1c. Intrinsic nanotube fracture, and nanotube sliding at the fronts suggest a bimodal failure. Accordingly, Eq. (12) becomes:

$$F(\sigma) = 1 - \exp\left(-N_{CNT}\left(\frac{\sigma}{\sigma_{CNT}}\right)^{m_{CNT}} - N_p\left(\frac{\sigma}{\sigma_p}\right)^{m_p}\right) \quad (15)$$

where σ_{CNT} , m_{CNT} are the scale and shape parameter of single carbon nanotube whereas σ_p , m_p are the scale and shape parameters of the peeling joint failure.

The hierarchical structure of CNT strand is shown in Fig. 1c. It starts from level 0, a CNT fiber; this fiber consists of carbon nanotubes connected together end by end. We consider level 1 as a bundle of parallel CNT fibers. In level 2, a CNT strand, is a twisted bundle of CNT yarns. We model this complex hierarchical structure with our theory.

By differentiating Eq. (13), the probability density function is derived as

$$f(\sigma) = [N_{CNT}\alpha_{CNT}m_{CNT}\sigma^{m_{CNT}-1} + N_p\alpha_p m_p \sigma^{m_p-1}] \times \exp(-(N_{CNT}\alpha_{CNT}\sigma^{m_{CNT}} + N_p\alpha_p \sigma^{m_p})) \quad (16)$$

where $\alpha_{CNT} = (1/\sigma_{CNT})^{m_{CNT}}$ and $\alpha_p = (1/\sigma_p)^{m_p}$.

Accordingly,

$$\frac{R}{Z} = \exp(-(N_{CNT}\alpha_{CNT}P^{m_{CNT}} + N_p\alpha_p P^{m_p})) \quad (17)$$

By substituting Eq. (15) into (4), the average stress of CNT yarn is calculated as

$$\bar{\sigma} = \exp(-(N_{CNT}\alpha_{CNT}P^{m_{CNT}} + N_p\alpha_p P^{m_p}))P \quad (18)$$

The maximum value of $\bar{\sigma}$ is given by:

$$\frac{d\bar{\sigma}}{dP} = 0 \quad (19)$$

namely:

$$\exp(-(N_{CNT}\alpha_{CNT}P^{m_{CNT}} + N_p\alpha_p P^{m_p})) \times \left[-\left[N_{CNT}\alpha_{CNT}m_{CNT}P^{m_{CNT}-1} + N_p\alpha_p m_p P^{m_p-1} \right] \right] = 0 \quad (20)$$

i.e.:

$$1 - [N_{CNT}\alpha_{CNT}m_{CNT}P^{m_{CNT}} + N_p\alpha_p m_p P^{m_p}] = 0 \quad (21)$$

Eq. (21) can be solved numerically to obtain P_f ; by substituting P_f into Eq. (18), the strength of CNT yarn, σ_{yD} , is finally calculated:

$$\sigma_{yD} = \exp(-(N_{CNT}\alpha_{CNT}P_f^{m_{CNT}} + N_p\alpha_p P_f^{m_p}))P_f \quad (22)$$

whereas the standard deviation, θ_{yD} , of the strength is

$$\theta_{yD} = \sqrt{\frac{(\sigma_{yD})^2 Z^{-1}}{\exp(-(N_{CNT}\alpha_{CNT}P_f^{m_{CNT}} + N_p\alpha_p P_f^{m_p}))} (1 - \exp(-(N_{CNT}\alpha_{CNT}P_f^{m_{CNT}} + N_p\alpha_p P_f^{m_p})))} \quad (23)$$

where Z is the number of the CNT fibers in the CNT yarn, level 1.

In the case of a hierarchical rope [31] we can use our recently developed theory [32], implying:

$$\sigma_{yW} = \sigma_{yD} \quad (24)$$

$$\theta_{yW} = \theta_{yD} \quad (25)$$

where σ_{yW} and θ_{yW} are the mean strength and standard deviation of the CNT yarn in the Weibull form; σ_{yD} and θ_{yD} are the mean and standard deviation of CNT yarn in Daniels' form.

From Eqs. (22) and (23), we deduce:

$$\frac{\Gamma\left(1 + \frac{2}{m_y}\right)}{\Gamma^2\left(1 + \frac{1}{m_y}\right)} = \left(\frac{\theta_{yD}}{\sigma_{yD}}\right)^2 + 1 \quad (26)$$

where m_y is the shape parameter of the CNT yarn and can be calculated numerically. Then σ_{0y} , the scale parameter of the CNT yarn, can be calculated as:

$$\sigma_{0y} = \frac{\langle\sigma_{yD}\rangle (l_y)^{\frac{1}{m_y}}}{\Gamma\left(1 + \frac{1}{m_y}\right)} \quad (27)$$

where l_y is the length of the CNT yarn.

According to Daniels' theory, the mean strength and standard deviation, σ_{st} and θ_{st} , of the CNT strand (level. 2), based on the shape and scale parameter of the CNT yarn, are predicted to be:

$$\sigma_{st} = (l_y m_y)^{-1/m_y} (\sigma_{0y}) \exp\left(\frac{-1}{m_y}\right) \quad (28)$$

$$\theta_{st} = \sqrt{\frac{\langle\sigma_{st}\rangle^2}{\left[\exp\left(\frac{-1}{m_y}\right)\right]^2} \left[1 - \exp\left(\frac{-1}{m_y}\right)\right]} K^{-1} \quad (29)$$

where K is the number of yarns inside the CNT strand.

The most commonly analyzed geometry of a twisted strand is the one in which the yarns lie in concentric cylindrical layers. Within each layer, yarns follow ideal helical paths with the same helix angle but the angle differs from layer to layer. In this idealization, yarns in different layers necessarily must have different

lengths to be strain-free yet without slack. This implies that between two strand cross-sections, yarns will have lengths when straight equal to their helical path lengths, and thus, will be longer than the distance between these cross-sections.

Here, we model the twisting with the approach by Porwal et al. [33] averaging the yarn helical paths across the strand. In doing so, a mean helix angle for the ideal helical structure is given as:

$$\bar{\psi} = \cos^{-1} \left(\frac{\sum_i z_k \cos \psi_k}{Z} \right) \quad (30)$$

where z_k is the number of elements in the k concentric layer, so that $\bar{\psi}$ is weighted by the fraction of all the yarns in each layer with respect to the total z_k/Z , which increases when traveling from the center to the surface of the strand.

Let us consider that any level of the hierarchical structure of CNT strand is made of a large number, K , of twisted CNT yarn of Weibull type. Based on Porwal et al. [33], the mean strength, $\sigma_{st}^{(\psi)}$, is given by:

$$\sigma_{st}^{(\psi)} = \sigma_{st} \cos^2 \bar{\psi} \quad (31)$$

whereas the standard deviation, $\theta_{st}^{(\psi)}$, becomes:

$$\theta_{st}^{(\psi)} = \theta_{st} \cos^2 \bar{\psi} \quad (32)$$

4. Characterizing the nanotube–nanotube joint

Now, we calculate the scale and shape parameters of the junctions between carbon nanotubes in the yarn, shown in Fig. 1c. We apply a reverse process, from the experimental data, which allow us to extract these two values. The mean strength and standard deviation of dry-draw CNT strand are 0.35 GPa and 0.023 GPa respectively [34] (level 2). The scale and shape parameter of CNT are $\sigma_{CNT} = 34$ GPa and $m_{CNT} \approx 2.7$ [13]. The characteristic number of CNT fibers in a yarn is of the order of 100 and $N_{CNT} \approx N_p = 500$. Accordingly, solving Eqs. (21)–(23) we deduced $m_p = 3.86$ and $\sigma_p = 3.36$ GPa. These two parameters play a fundamental role in characterizing the statistical properties of the CNT fiber, yarn and strand. Figs. 2 and 3 show the effect of m_p and σ_p on the overall performances, suggesting that our model is a new useful tool for design CNT strands.

5. Conclusions

In this paper, a new extension of the Daniels' theory, which account for multiple modes of failure, has been presented and applied to carbon nanotube (CNT) bundles. We have developed a hierarchical statistical model for treating CNT twisted strands. The analysis allow us to rigorously characterize the weakest link, that is the CNT–CNT joint, in terms of Weibull size and shape parameter. These joints are defects because the intermolecular interaction between CNTs at the joints is much weaker than the chemical bonds within a single molecule. Decreasing the density of joints should yield CNT yarn with higher tensile strength. Thus, producing super long carbon nanotubes (with defect density less than proportional to CNT length) is crucial in this context.

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