Analysis of electrical percolation thresholds in carbon nanotube networks using the Weibull probability distribution

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We suggest a method for the *a priori* determination of the electrical percolation threshold in carbon nanotube (CNT) networks, of relevance in electronic devices, polymer composites, etc. The variability in the CNT lengths, commonly observed in practical processing and dispersion, was also considered and the resulting probability distribution function determined to be of the Weibull type. Subsequently, the predicted percolation threshold volume fractions for single-walled CNTs, ~0.000 73 and multiwalled CNTs, ~0.0193, were found to be in close correspondence to the experimentally determined values of 0.0011 and 0.0147, respectively. © *2010 American Institute of Physics*. [doi:10.1063/1.3452361]

It is of scientific and technological interest to analyze the minimal concentration of carbon nanotubes (CNTs) necessary to form a percolating network. From a practical perspective, CNT networks have been proposed as constituents of thin film transistors[1] for electronics and biosensors,[2] polymer composites for electromagnetic interference shielding,[3] etc. While variability in device characteristics was considered,[4] the widespread unpredictability in the intrinsic geometry, e.g., the length (L) of the CNTs, has not yet been modeled. Such issues with predictability of the geometry are typical of nanostructure synthesis processes and could strongly influence the electrical characteristics and device properties. The prediction of a threshold is also pertinent in the synthesis of CNT based composites, where the cost of the nanostructures is a major factor.

In this paper, we first use an excluded volume percolation theory based model[5,6] to estimate the theoretical critical volume percolation threshold, ϕ_c of the CNTs, as a function of L. For this, we assume that the i^{th} CNT has a volume, v_i, in a polymer/insulating matrix of unit volume. Now, if the percolation threshold corresponds to the connectivity of N_c CNTs, then the odds of *not* selecting any CNT (corresponding to a point in the matrix) would be:

$$(1-\phi_c) = (1-v_1)\left(\frac{1-v_1-v_2}{1-v_1}\right) \times \left(\frac{1-v_1-v_2-v_3}{1-v_1-v_2}\right) \cdots \left(\frac{1-v_1-v_2-v_{N_c}}{1-v_1-v_2-\ldots v_{N_c-1}}\right) = 1-N_c\sum_{i=1}^{N_c}\frac{v_i}{N_c},$$

implying that

$$\phi_c = N_c E[v], \tag{1}$$

$E[v]$ denotes the expected value or ensemble average of the CNT volume. It is to be noted that Eq. (1) is distinct compared to the critical percolation threshold extant in literature, which assumes that the percolating objects are penetrable, i.e., hitherto applied to pores in rock, etc. In deriving Eq. (1), we have assumed that the CNTs were impenetrable. We then use the identity, $E[v]=(E[V_{ex}]N_c/E[V_{ex}])(E[v]/N_c)$, where V_{ex} is defined as the excluded volume:[7] the space circumscribed around the CNT by the center of another CNT, whereby both CNTs contact each other but do not overlap. For isotropically oriented, spherically capped *stick like* objects of diameter "D" and random length "L," which we take to be akin to CNTs, $E[V_{ex}]=(4\pi/3)D^3+2\pi D^2E[L]+(\pi/2)DE[L^2]$. Also, for the CNT modeled as a capped cylinder, $E[v]=(\pi/6)D^3+(\pi/4)D^2E[L]$. Note that the CNT diameter is assumed to be constant. For infinitely thin cylinders of deterministic length, Monte Carlo simulations were used[6] to estimate $E[V_{ex}]N_c$ as ~1.4. This is an upper bound when the lengths vary randomly, as $E[V_{ex}]$ should be weighted to favor the longer CNTs. For a given D, the theoretical ϕ_c would be:

$$\phi_c(L) = \frac{E[V_{ex}]N_c}{\frac{4\pi}{3}D^3+2\pi D^2E[L]+\frac{\pi}{2}DE[L^2]} \times \left(\frac{\pi}{6}D^3+\frac{\pi}{4}D^2E[L]\right). \tag{2}$$

For a deterministic L, the variation in ϕ_c as a function of the aspect ratio ($=L/D$) is shown in Fig. 1. Such a depiction necessarily implies that a definitive ϕ_c is obtained at a given L. However, it is commonly observed both in our experiments[3] and in other examples from literature[8] that L is not a deterministic constant but should properly be considered a random variable, i.e., as $\underline{L}$, that could have considerable variation. For example, we have measured subsequent to ultrasonication—a procedure necessary[3] for dispersion of the CNTs into polymer matrices, that single-walled CNTs (SWNTs) have lengths ranging from 2.2–7.8 μm while multiwalled CNTs (MWNTs) vary in length from 3.0–8.4 μm. In another instance,[9] a batch of SWNTs syn-

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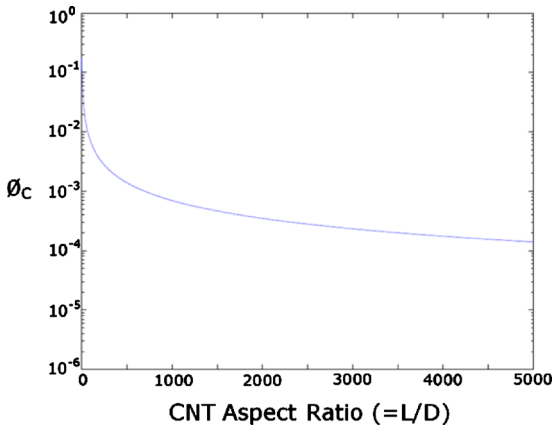

FIG. 1. (Color online) The theoretical variation in the critical percolation threshold (ϕ_c) plotted as a function of the CNT aspect ratio ($=L/D$) assuming a deterministic length and diameter.

thesized through arc-based methods had L in the 0.7–4.3 μm range. Such large variability clearly makes ϕ_c a function of $\underline{L}$ and would lead to uncertainties in obtaining an accurate percolation threshold.

The above issues also imply that a suitable stochastic model is necessary to evaluate the ϕ_c, e.g., for a CNT/polymer composite[10] or a CNT network transistor,[11] as $\phi_c(\underline{L})$ is not equal to the ϕ_c evaluated at the average CNT ensemble length, i.e., ϕ_c $(E[L])$. A proper expression for ϕ_c would account for variations in $\underline{L}$ and could be expressed through the correlation, i.e., $E[\underline{L}^2]$. The stochastic approach would then provide a theoretical value, i.e., a $\phi_c(\underline{L})$ that accounts for the mean and variance of $\underline{L}$. A theoretical value for ϕ_c can be found from Eq. (2) where the average CNT length is now $E[\underline{L}]$ with a variance, $VAR[\underline{L}]=E[(\underline{L}-E[\underline{L}])^2]=E[\underline{L}^2]-(E[\underline{L}])^2$. Both $E[\underline{L}]$ and $E[\underline{L}^2]$ can be evaluated by fitting empirical CNT length data to a probability density function (pdf). As the pdf cannot be *a priori* determined, we use the sample mean length μ_L and sample variance s_L^2 as unbiased estimates of the population mean and variance.[12]

For the practical application of the above principles and experimental verification, we first dispersed carboxyl (–COOH) group functionalized SWNTs and MWNTs into a polymer. A reactive ethylene terpolymer [(RET), Elvaloy 4170] constituted of an epoxide functional group was chosen for a polymer/insulating matrix, with the underlying rationale that the epoxide ring rupture[13] on the RET would be facilitated by the –COOH groups on the functionalized CNTs. The bonding between the –COOH and the epoxide group could help in the uniform dispersion. The exact location of the functional groups would depend on the defect density on the CNTs and can be manipulated.[14] However, if the defects are considered to be randomly dispersed, isotropic bonding of the CNTs with the polymer matrix is implied and yields uniform mixing. More details regarding the fabrication procedure and characterization of the composites have been reported elsewhere.[3,10]

The lengths of the CNTs in several composite samples were first measured using a scanning electron microscope (Phillips XL30). In the case of SWNTs, while the bundle diameters (D) were noted to be ~4.8 nm using atomic force

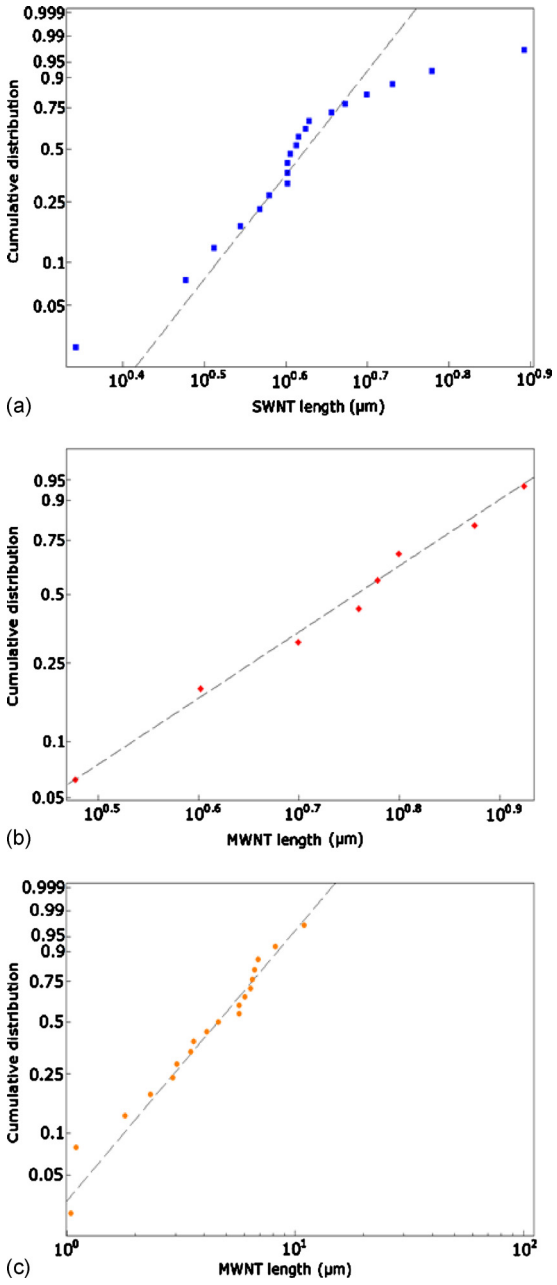

FIG. 2. (Color online) The lengths of (a) SWNTs, (b) MWNTs dispersed into the polymer matrix in the present study, and (c) MWNTs from another study in literature (Ref. 8), plotted on Weibull probability paper. Nonlinearities in (a) indicate a poor fit to a Weibull pdf while excellent fits were obtained for (b) and (c).

microscopy, the length variation did not fit Gaussian, exponential, Rayleigh, log-normal, or Weibull—Fig. 2(a), distributions. The poor fit is attributed to a mixture of different pdfs of the SWNT lengths within the composite. We then used our mean sample SWNT length ($\mu_L \sim 4.28$ μm) as an estimate of $E[\underline{L}]$ and the sample variance of $s_L^2 \sim 1.364$ μm^2 for estimating $E[\underline{L}^2]$ $(=VAR[\underline{L}]+E[\underline{L}]^2 \sim s_L^2 + \mu_L^2)$. Using the upper bound of $N_c E[V_{ex}]$, ~1.4, and substituting sample statistics, μ_L and s_L^2 in Eqs. (1) and (2) yields a theoretical percolation threshold of $\phi_c(\underline{L})=0.000\,73$.

On the other hand, for the case of MWNT bundles (with $D \sim 188$ nm) the lengths were fit very satisfactorily to a Weibull distribution—Fig. 2(b). For example, the value of

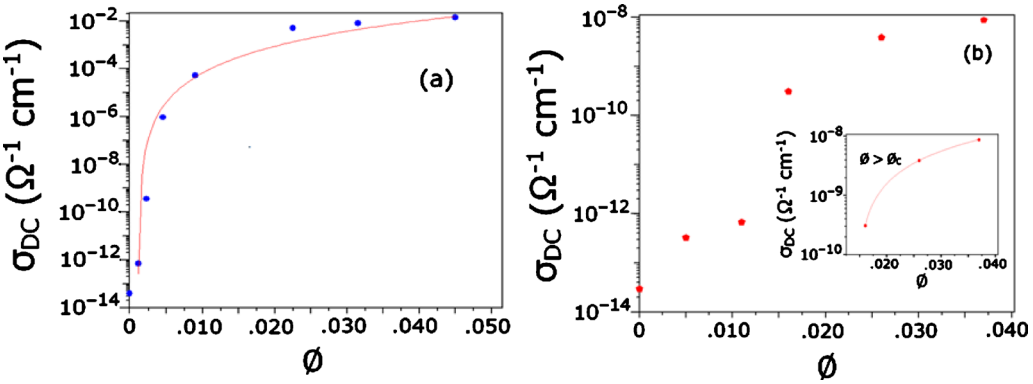

FIG. 3. (Color online) The variation in the dc electrical conductivity (σ_{dc}) with volume fraction (ϕ) for (a) SWNTs and (b) MWNTs dispersed in a polymer matrix, was used to determine the percolation threshold (ϕ_c). The inset in (b) indicates the fit of σ_{dc} to an expression of the form $\sigma_{dc} \sim \sigma_0(\phi - \phi_c)^t$ for $\phi > \phi_c$.

the correlation coefficient for the MWNT lengths, r^2 (=0.9833), exceeds the tenth percentile of r^2 (=0.85) established from Monte Carlo simulations using random numbers known to fit a Weibull distribution.[15] We also considered published literature from other groups on MWNT length data,[8] where again a satisfactory fit to a Weibull distribution was obtained—Fig. 2(c).

Generally, the n^{th} moment for a Weibull distribution is given by $E[\underline{L}^n]$, where

$$E[\underline{L}^n] = \theta^n \Gamma\left(\frac{n}{\beta} + 1\right), \tag{3}$$

Γ denotes the Gamma function. A two parameter Weibull pdf is then completely described by a shape parameter, β and the scale parameter θ. For Fig. 2(b), β=3.97 and θ=6.3525 were calculated from the slope and intercept and were then used to find the statistical moments, e.g., mean, correlation, skewness, kurtosis, etc., of the Weibull distribution.[15] To interpret these numbers, it is noted that for β=3.6, the distribution of lengths would be symmetrical about the mean. A $\beta > 3.6$ implies a left-hand skewness of the MWNT length pdf, i.e., more CNTs are shorter rather than longer, while a $\beta < 3.6$ suggests the MWNT lengths have a right-hand skewed distribution. Furthermore, θ denotes the value below which ~63% of the NT lengths are smaller, i.e., ~63% of the CNT lengths are less than 6.3525 μm. Additionally, a high r^2 on a Weibull plot suggests that the length distributions arise from a single pdf instead of a mixture of different pdfs. An r^2 of ~0.9833, in Fig. 2(b), then suggests that a single, particular mechanism could determine the length distribution, e.g., a uniform mode of fracture at particular defects, due to the CNT processing. A poor fit, as with the SWNT lengths in Fig. 2(a), would indicate that the length distribution arises from a mixture of two or more distributions where each distribution is the outcome or consequence of a different event, e.g., CNT fracture could occur at both defect-prone and defect-free sites, or could be mediated through multiple varieties of defects.

From the calculation of the moments, we determined for the case of Fig. 2(b) with MWNTs, that μ_L=5.756 μm and s_L^2=2.643 μm^2. The substitution of these μ_L and s_L^2 values into Eq. (2) then yields a theoretical $\phi_c(\underline{L})$=0.0193.

To experimentally analyze and correlate the influence of statistical variation on electrical percolation thresholds, we measured the electrical conductivity; σ. A four-point probe was used to measure the electrical resistance, R, for composites with $R < 1$ GΩ, using the Keithley 487 picoammeter and the Keithley 2400 Sourcemeter. For higher resistance (>1 GΩ) composites, two point measurements using the Agilent B1500A semiconductor device analyzer with triaxial probes were employed. For these measurements, samples with sputtered gold contacts were used. The experimental ϕ_c for electrical percolation was then determined by fitting the measured σ of the CNT dispersed composites to the conductivity power law equation,[16] $\sigma = \sigma_0 (\phi - \phi_c)^t$. Subsequently, for the SWNT samples—Fig. 3(a), we obtained from the fit to the σ variation, a ϕ_c of 0.0011 which is quite close to the theoretical mean (~0.000 73). In the case of MWNT dispersed polymers, the ϕ_c was found to be 0.0147 which, is again close to the theoretical mean of ~0.0193, predicted from stochastic theory.

We conclude by positing that statistical analysis using a stochastic approach can be used to describe the impact of random CNT lengths on the electrical percolation thresholds. Such modeling could be used to *a priori* determine the thresholds while accounting for realistic process variability. The proposed methodology can be extended to other mutable CNT characteristics such as diameter, agglomeration, curvature, etc.

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