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Abstract

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Comments

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Effect of nanotube alignment on percolation conductivity in carbon nanotube/polymer composites

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Percolation conductivity of a stick network depends on alignment as well as concentration. We show that both dependences exhibit critical (power-law) behavior, and study the alignment threshold in detail. The highest conductivity occurs for slightly aligned, rather than isotropic, sticks. Experiments on single wall carbon nanotube composites are supported by Monte Carlo simulations. These results should be broadly applicable to percolating networks of anisotropic conductors.

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Electrical and thermal transport in disordered systems, an active area of physics research for decades,[1] has become of prime importance with the advent of functional organic materials, nanomaterials, etc. The onset of percolation paths with increasing concentration is well understood for spheres and ellipsoids, while for high aspect ratio objects such as conducting polymer chains, nanotubes, and nanowires, the alignment of the conducting phase becomes paramount. Investigations to date of such systems focused on the effects of preferred orientation on conductivity anisotropy at a fixed alignment.[2,3] A recent calculation predicts concentration thresholds that vary with aspect ratio, treating the extreme cases of isotropic and perfectly aligned rods.[4]

In this paper we systematically address percolation conductivity as a function of alignment, varied in a controlled manner from isotropic to highly aligned. We employed single wall carbon nanotubes (SWNT) as the ideal paradigm for high aspect ratio, highly conductive objects. Variable extensional forces were applied to achieve various degrees of SWNT alignment in a polymer matrix.[5] Surprisingly, the electrical conductivity follows power-law dependence in *alignment* as well as concentration; we name this phenomenon the alignment percolation. Furthermore, the best electrical conductor at a fixed concentration and fixed aspect ratio is *not* the isotropic material. Both of these unanticipated results were reproduced in our Monte Carlo simulations.

Two phase systems with high aspect ratio, one-dimensional electrical conductors consistently exhibit lower concentration percolation thresholds than those with spherical fillers, as expected.[6–8] However, these systems exhibit contradictory results with respect to alignment.[5,9,10] The lowest percolation threshold and the maximum conductivity are believed to occur when the rodlike fillers are randomly oriented. This is consistent with our previous work[9] in which we measured room-temperature electrical conductivities σ from 2 wt % single wall carbon nanotube (SWNT)/poly(methyl methacrylate) (PMMA) composites of 10^{-10} and 10^{-4} S/cm for samples with highly aligned and unaligned SWNTs, respectively. Balberg *et al.*[11] investigated theoretically the percolation thresholds in a two-dimensional (2D) anisotropic system of conducting high aspect ratio rods, and found that the concentration threshold increased with increasing anisotropy. However, a careful inspection of their simulations suggests that the lowest threshold occurs when the distribution of rod orientations is slightly anisotropic, an observation that the authors attributed to the small sampling size. Also, counter to the prevailing understanding of SWNT alignment and electrical conductivity is a report by Choi *et al.*[10] in which σ increased slightly (from $\sim 10^{-7}$ to $\sim 10^{-6}$ S/cm) with nanotube alignment. Clearly the relationship among rod alignment, percolation threshold, and electrical conductivity requires renewed consideration.

The SWNT/PMMA composites were made by a coagulation method[9] that provides a uniform dispersion of small SWNT bundles. The resulting composites serve as a model system for the study of the influence of rodlike filler alignment, because the average length and diameter of the SWNT bundles are ~310 and ~6.9 nm, respectively, giving a mean aspect ratio of ~45.[12] Note that all the composites used in this study were prepared from the same batch of purified SWNT, so that the aspect ratio is fixed. The SWNT were aligned by melt fiber spinning, during which the extrusion speed (1–15 mm/min), the spinneret diameter (0.5, 1.5, 2.5 mm), and the fiber-drawing speed (1–31 m/min) were varied to control extensional flow and thereby produce various levels of SWNT alignment. "Isotropic" samples were made by hot pressing as-coagulated composites.

Electrical conductivities of composite fibers were measured at room temperature with a two-probe method using a high impedance electrometer (Keithley Model 616). The degree of SWNT alignment was characterized using small-angle x-ray scattering (SAXS) fiber diagrams.[12] SWNTs prepared by the HiPco process[13] do not form large crystalline bundles, so our texture analysis is derived from form factor scattering by isolated tubes and bundles in the range $0.01\ \text{Å}^{-1} < Q < 0.1\ \text{Å}^{-1}$, where $Q = 4\pi \sin(\theta/\lambda)$. From 2D scattering patterns, we integrated radially along the cited Q range, plotted this intensity as a function of azimuthal angle, and fit it by a Lorentzian function whose full width at half-maximum (FWHM) quantitatively describes the distribution of SWNT alignment. Increasing FWHMs from 0° (perfectly aligned) to 180° (isotropic) correspond to increasing SWNT isotropy. The hot-pressed control samples were verified by x ray to be completely isotropic.

The electrical conductivities of the isotropic SWNT/PMMA composites show typical concentration percolation behavior with increasing SWNT loading [Fig. 1(a)]. To de-

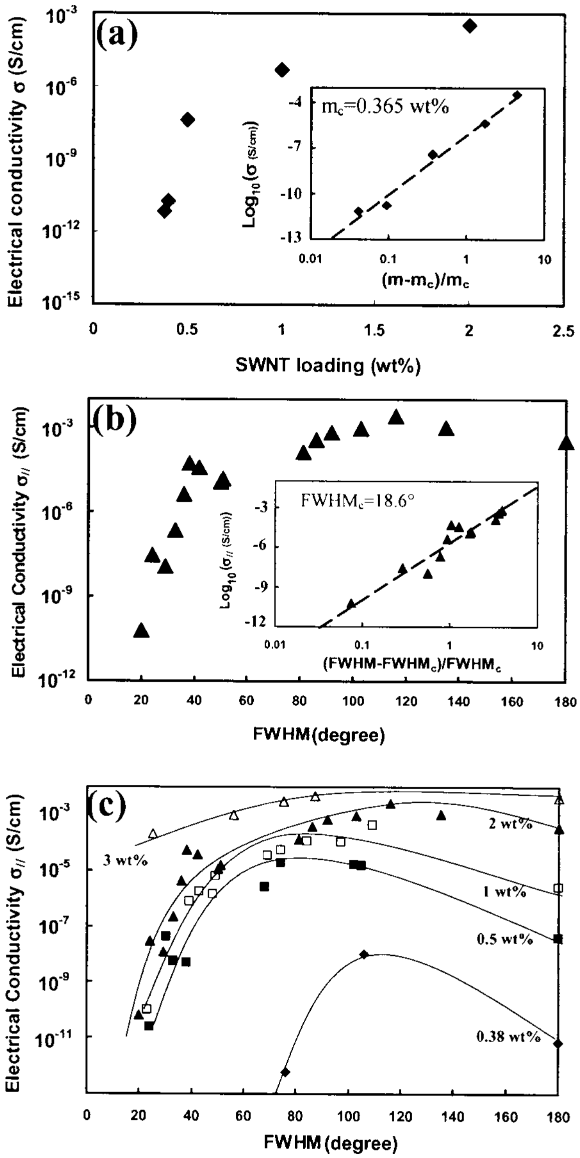

FIG. 1. (a) Electrical conductivity of isotropic SWNT/PMMA composites as a function of loading. Inset: a log-log plot of conductivity vs reduced mass fraction determines the critical composition, m_c. (b) Electrical conductivity of the 2 wt % SWNT/PMMA composite along the alignment direction as a function of alignment. Inset: a log-log plot of conductivity vs reduced FWHM determines the critical alignment, $FWHW_c$. (c) Electrical conductivity along the alignment direction as a function of SWNT alignment for composites with various loadings. △: 3 wt %; ▲: 2 wt %; □: 1 wt %; ■: 0.5 wt %; ◆: 0.38 wt %.

termine the concentration threshold m_c, a power-law relation is used[6]

$$\sigma \propto (m - m_c)^{\beta_m}, \qquad (1)$$

where m is the SWNT mass fraction and β_m is the critical exponent. A straight line with $m_c = 0.365$ wt % gives a good fit [Fig. 1(a), inset]. We conclude that there exists a conductive nanotube network in the composites, which allows macroscopic direct electron transport at loadings above m_c.

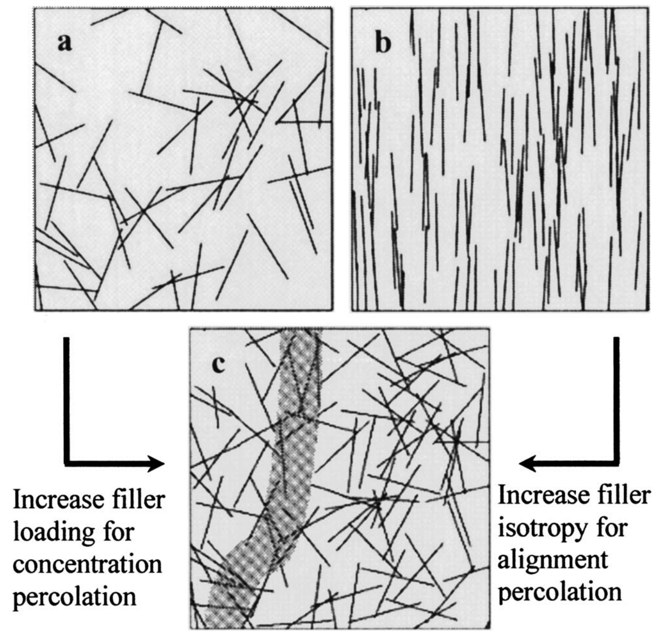

FIG. 2. 2D stick-in-unit-square simulations with stick alignment determined by a cutoff angle θ_μ. (a) 50 sticks with $\theta_\mu = 90°$ (randomly distributed) do not exhibit a percolation path; (b) 100 sticks with $\theta_\mu = 5°$ (highly aligned) do not exhibit a percolation path; (c) 100 sticks with $\theta_\mu = 90°$ (randomly distributed) exhibit a percolation path (the gray area). All sticks have $L = 0.255$ relative to the unit square.

More interestingly, at fixed 2 wt % loading the electrical conductivity parallel to the alignment direction, $\sigma_\parallel$, shows a sharp transition with respect to the degree of SWNT alignment [Fig. 1(b)]. $\sigma_\parallel$ increases dramatically, from 6.5×10^{-11} to 4.4×10^{-6} S/cm, as the FWHM varies from 20° to 36°. Percolation is also appropriate for describing this behavior. When the SWNT are highly aligned (small FWHM), they rarely touch each other and thus do not form conductive pathways at small loading (≤ 3 wt %). Upon increasing the isotropy (increasing FWHM), the SWNT start to contact one another as the FWHM approaches a critical value, $FWHM_c$, at which the SWNT form a conductive network. This produces the huge increase in $\sigma_\parallel$ that can be described quantitatively by a power law,

$$\sigma_\parallel \propto (FWHM - FWHM_c)^{\beta_{ori}}, \qquad (2)$$

where β_{ori} is the orientation critical exponent. A straight line with $FWHM_c = 18.6°$ gives a good fit for the 2 wt % composite [Fig. 1(b), inset]. Note that Eq. (2) only applies to $\sigma_\parallel$(FWHM) near the orientation threshold, specifically FWHM $< 120°$ for 2 wt %. Similar analyses were performed to obtain $FWHM_c$ for composites with 0.5 wt % and 1 wt % loading.

Figure 2 illustrates these two types of percolation behavior with respect to rodlike filler loading and alignment. A unit square containing 100 sticks placed randomly with respect to position and orientation exhibits a percolation pathway [Fig. 2(c)]. If the number of sticks is decreased to 50 [Fig. 2(a)], or if the 100 sticks are preferentially aligned [Fig. 2(b)], the

TABLE I. Electrical conductivities (σ_{max} and σ_{iso}) and nanotube alignments ($FWHM_c$ and $FWHM_{max}$) for the SWNT/PMMA composites shown in Fig. 1(c).

SWNT loading	$FWHM_c$	$FWHM_{max}$	σ_{max} (S/cm)	σ_{iso} (S/cm)	$\sigma_{max}/\sigma_{iso}$
0.38 wt %	~75°	116°	1.0×10^{-8}	7.0×10^{-11}	1400
0.5 wt %	23°	109°	1.9×10^{-5}	4.0×10^{-8}	470
1 wt %	22°	80°	1.2×10^{-4}	2.5×10^{-6}	46
2 wt %	19°	106°	2.7×10^{-3}	3.5×10^{-4}	8
3 wt %	<19°			4.2×10^{-3}	

percolation pathway is destroyed. Highly aligned sticks fail to create percolation paths because the sticks seldom intersect each other.

The alignment threshold $FWHM_c$ depends on SWNT loading, as shown in Fig. 1(c) for loadings from 0.38 to 3 wt % and recorded in Table I. $FWHM_c$ drops from ~75° to <19° (more anisotropy) as the SWNT loading increases. At higher loadings where there are more tube-tube connections, greater anisotropy is required to break the contacts and disrupt percolation.

In Fig. 1(c), there exist maximum electrical conductivities σ_{max} for composites with loadings <3 wt %, which are greater than the conductivity of isotropic composites, σ_{iso} (Table I). The physical origin of σ_{max} is that at fixed loadings near the concentration threshold, slightly anisotropic composites form more percolated pathways than isotropic composites. This finding is consistent with analytical results from Munson-McGee who calculated the probability of one cylinder intersecting any number of others in an ensemble of cylinders ($L/D=20$).[14] He found that the maximum intersecting probability occurred when the cylinders were partially aligned, which simply corresponds to σ_{max} in our composites. Our experimental results indicate that this maximum conductivity is most pronounced at lower loadings. The difference between σ_{iso} and σ_{max} decreases with increasing loading, and the ratio, $\sigma_{max}/\sigma_{iso}$, decreases from 1400 to 8 as the loading increases from 0.38 to 2 wt % (Table I). Furthermore, the 3 wt % composite does not exhibit a σ_{max}; instead, σ remains constant for FWHM >75°. At high loadings the SWNT form extensively interconnected percolated clusters, such that with small changes in alignment (from isotropic to slightly anisotropic), tube-tube connections are broken without significantly reducing the size of the percolated clusters. In contrast, percolated clusters in composites with low loadings experience significant changes with small variations of alignment, because they have fewer tube-tube connections. The loss of isotropy adds SWNT to the percolated clusters so that more SWNT contribute to the conductivity and σ_{max} is achieved below 180° FWHM.

Note that the curves in Fig. 1(c) are intended to qualitatively guide the eye. The data in Fig. 1(c) is insufficient to conclude that the maximum conductivity does or does not vary monotonically with respect to loading. This is particularly true because there are fewer samples with alignments between 90° and 180°, which are more difficult to prepare. In our simulations below, there are more data near the isotropic condition, and the position of the maximum conductivity varies only slightly. Thus, we have not commented how the alignment at which the maximum conductivity is observed varies with respect to loading.

To augment our experimental results, 2D Monte Carlo simulations were performed by adopting the method of Balberg and Binenbaum.[11] A unit square is filled with sticks having zero diameter and fixed length L, the latter specified as a fraction of the unit length. The centers of the sticks are randomly placed within the square. Angles θ with respect to the y axis are generated randomly within the interval $-\theta_\mu \leq \theta \leq \theta_\mu$, where $0 \leq \theta_\mu \leq 90°$, to provide variable stick alignment. When θ_μ is 90° the sticks are isotropic; smaller values of θ_μ correspond to preferred alignment in the y direction. Two sticks are considered to be touching when the algebraic expressions for their positions intersect within the square. Percolation occurs when opposite sides of the unit square are connected by a continuous stick cluster. Representative simulations are shown in Fig. 2 to illustrate the importance of both filler concentration and alignment on percolation. We define the percolation probability P as the fraction of 1000 independent simulations with percolated clusters. We use P as an estimate of the composite electrical conductivity, because a larger P indicates more percolated pathways.

Figure 3 shows P as a function of the stick alignment where the stick length is fixed ($L=0.108$) and the stick number varies from 420 to 900. At a fixed stick number, P exhibits a sharp transition with respect to alignment, θ_μ, corresponding to the alignment percolation behavior in electrical conductivity. We estimate a critical angle θ_c for each case by applying a similar power law, $P \propto (\theta-\theta_c)^{\beta_\theta}$, where β_θ is the critical exponent. θ_c decreases with increasing stick number, indicating that increasing loading shifts the alignment threshold to a more anisotropic state, consistent with our experimental results.

Figure 3 clearly shows that for stick numbers less than 600, there exists a P_{max} at $\theta_\mu=70°-90°$, corresponding to slightly anisotropic systems. P_{max} statistically proves that at small loadings it is more probable to maximize percolation with slightly anisotropic filler distributions rather than with perfectly isotropic filler orientations. Similarly, the experimental σ_{max} occurs with partially aligned SWNT. To mimic the difference between σ_{max} and σ_{iso}, we calculate the ratio P_{max}/P_{iso}. With 600 or more sticks this ratio is 1, showing that there is no alignment effect on the number of percolated clusters unless the fillers are highly aligned ($\theta_\mu<50°$). However, this ratio becomes much larger as the stick number decreases; the ratios are 1.01, 1.19, and 1.22 for 500, 450,

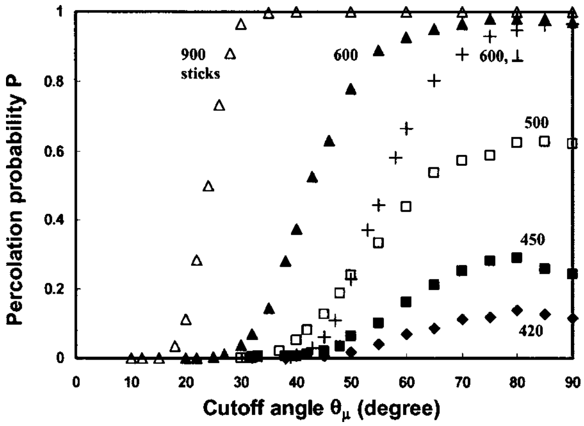

FIG. 3. Percolation probability, P, along the stick alignment direction from 1000 simulations as a function of the stick alignment (θ_μ) for various numbers of sticks (420–900) as indicated. The critical angles, θ_c are △: 11°; ▲: 21°; □: 31°; ■: 33°; ◆: 37°. In addition, P was found perpendicular to the alignment direction for 600 sticks (+) and exhibits θ_c=31°. All sticks have L=0.108 relative to the unit square.

and 420 sticks, respectively. At low loadings, even slight anisotropy significantly increases the number of percolating clusters relative to the isotropic case, as we observed in SWNT/PMMA composites

The 2D stick model clearly shows trends that agree with our conductivity data from SWNT/PMMA composites. This approach could be extended to three dimensions in order to more accurately represent the SWNT orientation distribution. Also, the assumed uniform alignment distribution within $-\theta_\mu \leqslant \theta \leqslant \theta_\mu$ could be replaced by the experimentally determined Lorentzian distribution. While more realistic simulations might provide additional insights about filler alignment effects on the properties of systems with anisotropic fillers, a quantitative comparison will remain elusive until the size distribution and morphology of the SWNT in composites are available.

Finally, we have also explored the electrical conductivity perpendicular to the alignment direction. Melt spun fibers (~50 μm diam) were hot pressed together to provide a sufficiently wide sample for electrical and SAXS measurements. In the 2 wt % composite, the electrical conductivities perpendicular to the alignment direction, $\sigma_\perp$, are 5.0×10^{-10}, 1.6×10^{-7}, and 3.8×10^{-7} S/cm for the anisotropic samples with FWHM of 33°, 42°, and 51°, respectively. This dramatic increase with a small increase in isotropy suggests that $\sigma_\perp$ also exhibits alignment percolation behavior having a threshold of ~30°. This value is ~11° larger than the alignment threshold for $\sigma_\parallel$, 19°, as expected due to the shorter effective tube length perpendicular to the alignment direction as compared to the parallel direction. Therefore, SWNT require more isotropy to reach the alignment threshold for $\sigma_\perp$. In addition, $\sigma_\perp$ of the 2 wt % composites are approximately two or three orders of magnitude lower than $\sigma_\parallel$ with the same level of alignment, because there are fewer conductive paths perpendicular to the alignment direction. Using our simulations, P was determined perpendicular to the stick alignment direction for 600 sticks (Fig. 3). The lower value of P and the higher value of θ_c for perpendicular percolation are consistent with our experimental results.

We studied two-phase systems of high aspect ratio, one-dimensional conductors with controlled levels of alignment as determined by x-ray scattering. The electrical conductivity exhibits percolation behavior with increasing FWHM corresponding to increasing isotropy. Alignment thresholds shift to lower FWHM (more anisotropic) as the loading increases. Near the concentration threshold, the highest conductivity, σ_{max}, occurs in slightly anisotropic composites with $FWHM_{max}$ of ~80°–120°. The difference between σ_{max} and σ_{iso} decreases as the loading increases. Percolation probabilities as a function of stick alignment, based on 2D Monte Carlo simulations, are in good agreement with the data. We have extended our experimental work to other one-dimensional conductors (multiwall carbon nanotubes and carbon nanofibers) and found the same correlations between loading, alignment, and electrical conductivity. We therefore believe that the results presented here are generally applicable to networks of discrete, high aspect ratio, one-dimensional conductors.

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