

The experimental determination of the onset of electrical and thermal conductivity percolation thresholds in carbon nanotube-polymer composites

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ABSTRACT

We show evidence of electrical and thermal conductivity percolation in polymer based carbon nanotube (CNT) composites, which follow power law variations with respect to the CNT concentrations in the matrix. The experimentally obtained percolation thresholds, *i.e.*, ~ 0.074 vol % for single walled CNTs and ~ 2.0 vol % for multi-walled CNTs, were found to be aspect ratio dependent and in accordance with those determined theoretically from excluded volume percolation theory. A much greater enhancement, over 10 orders of magnitude, was obtained in the electrical conductivity at the percolation threshold, while a smaller increase of ~ 100 % was obtained in the thermal conductivity values. Such a difference is qualitatively explained on the basis of the respective conductivity contrast between the CNT filler and the polymer matrix.

INTRODUCTION

Polymer composites containing conducting fillers [1] such as carbon black [2], carbon fiber, and metal fibers have been extensively investigated for various applications such as electromagnetic interference (EMI) shielding [3], electronic packaging [4], radar absorption [5], *etc.*, However, presently used composites require high filler to polymer loading ratios which deteriorates the overall mechanical properties, through a compromise of intrinsic matrix morphology [6]. A possible way to ameliorate the above problems, through using *low* filler volume fractions, incorporates carbon nanotubes (CNTs) in composites [7-10]. A concomitant large aspect ratio and tunable electrical conductivity would enable electrical percolation to be achieved at very small CNT volume fractions [9]. The use of small CNT volume fractions would also reduce the economic costs and clustering of the CNTs within the polymer matrix, important for large scale application. In this paper, we discuss the issue of the minimum volume fraction necessary, *i.e.*, the percolation threshold (ϕ_c) for the CNT-polymer composites to serve as electrically or thermally conductive materials through percolation theory [11]. Such a study could then lead to an understanding of the viability of such composites for a large number of applications.

EXPERIMENTAL DETAILS

We have sought to understand issues associated with the uniform dispersion of CNTs into polymer matrices through optimized synthesis/processing, involving enhanced nanotube-polymer interactions through chemical functionalization schemes. We chose for our initial experiments, a composite of CNTs and a Reactive Ethylene Terpolymer (RET: Elvaloy 4170) – Figure 1.

Both pristine and carboxyl functionalized SWNTs (average diameter 1-2 nm, and length 5-20 μm) and MWNTs (average diameter 40 nm, length 5-9 μm) were used and dispersed in toluene with sonication. The exact location of the functional groups would depend on the defect density on the nanotubes which can be manipulated [12]. If the defects are randomly dispersed, isotropic bonding of the nanotubes with the polymer matrix is implied and would yield uniform dispersion and mixing. It was typically seen that sonication reduced the average length of the SWNTs to $\sim 4.3 \mu\text{m}$, with a bundle diameter $\sim 4.8 \text{ nm}$, resulting in an aspect ratio of ~ 880 . On the other hand, the MWNTs have an average length of 1.4 μm , with a bundle diameter $\sim 40 \text{ nm}$, yielding an aspect ratio of ~ 33 .

The nanotube dispersion was added to the RET solution (in toluene), and then the mixture was ultrasonicated for 5 hours. To remove excess solvent, the mixture was stirred and evacuated in vacuum (10^{-3} Torr) for 12 hours. Subsequently, a hot press was used to press the composites into the desired thickness, of $\sim 2 \text{ mm}$, reported here.

The four-wire resistance method was used to measure the resistance (R) for the nanocomposites with $R < 1 \text{ G}\Omega$, while for higher resistance ($> 1 \text{ G}\Omega$) composites, two point measurements using the Agilent B1500A semiconductor device analyzer, with triaxial probes were used. The composites were treated with oxygen plasma and subsequently, 5-10 nm of Ti, along with $\sim 100 \text{ nm}$ of Au were sputtered for electrical contacts. The thermal conductivity (κ) was measured through the 3ω principle [13], using a Wheatstone bridge based methodology as shown in Figure 2.

The principle involves the periodic heating of metal/contact lines (10 mm long, 90 μm wide) which serve as both the heater and thermometer, deposited on the composites through alternating current modulated at a frequency ω which induces a change in the resistance through a 2ω dependence. The κ can then be interpreted through measurement of the third harmonic component of the voltage, $V(3\omega)$.

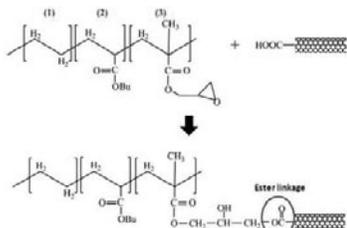


Figure 1. Schematic of reaction between CNT functional groups with epoxy groups on the RET constituted from (1) polyethylene, (2) methylmethacrylate, and (3) epoxide groups. While (1) and (2) contribute to mechanical robustness, (3) is used for forming ester linkages to $-\text{COOH}$ groups on the CNTs for enhanced bonding and dispersion.

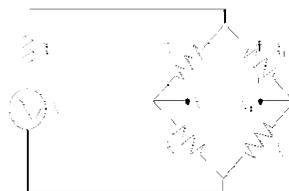


Figure 2. Schematic of the Wheatstone bridge based apparatus for the measurement of the thermal conductivity (κ) of the polymer composites. The 3ω component of across the sample (R_s) was obtained from measuring the voltage difference ($V_A - V_B$) using a Lock-in amplifier, SR830. The bridge serves to nullify the larger first harmonic component, $V(\omega)$.

RESULTS AND DISCUSSION

We indeed observed a *more uniform dispersion* for both *low* - Figure 3 (a) and *high*- Figure 3 (b) COOH-CNT filling fractions, as seen in the fracture surface images of the composites, in comparison to the clumped fillers observed for pristine CNT based composites in Figure 3 (c).

The DC conductivity (σ_{DC}) of the polymer composites as a function of the CNT (SWNT and MWNT) filler concentration (ϕ) is shown in Figure 4. It is immediately apparent that there is a much greater enhancement in the electrical conductivity (over ten orders of magnitude) compared to the approximately two-fold increase in the thermal conductivity values. The σ_{DC} were fit to the relations of the following form, where ϕ_c is the threshold volume fraction for electrical percolation, while s and t are critical exponents at the subcritical and overcritical region, respectively.

$$\sigma_{DC} \sim \begin{cases} (\phi_c - \phi)^{-s}, & \phi_c < \phi \\ (\phi - \phi_c)^t, & \phi > \phi_c \end{cases} \quad (1)$$

Given that the aspect ratio (r) was ~ 880 for the SWNTs and ~ 33 for the MWNTs, the theoretical ϕ_c was calculated from excluded volume percolation theory [14], to be ~ 0.08 and ~ 1.9 vol %, respectively, using

$$\phi_c(r) = \frac{1.4}{\frac{4\pi}{3}r^3 + 2\pi r^2 + \frac{\pi}{2}r} \left(\frac{\pi}{6}r^3 + \frac{\pi}{4}r^2 \right). \quad (2)$$

We have also shown how the variability in CNT lengths on the aspect ratio and the electrical percolation threshold could be dealt with through using statistical analyses [14]. Such modeling

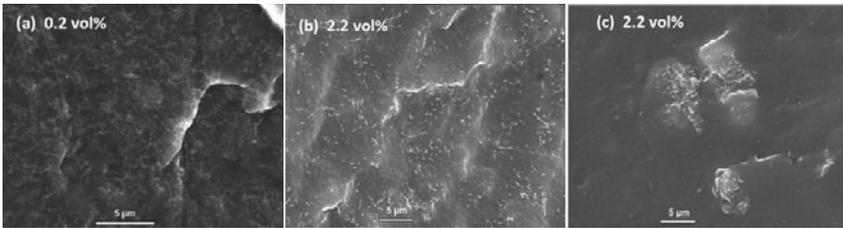


Figure 3. Scanning Electron Microscope (SEM) micrographs illustrating uniform dispersion of functionalized SWNTs in the RET polymer at (a) 0.2 and (b) 2.2 volume % CNT filling fractions while (c) non-functionalized SWNTs exhibit clumping.

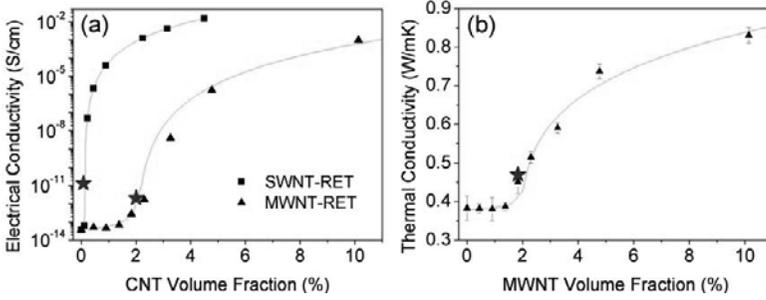


Figure 4. The enhancement of the (a) electrical conductivity of SWNT and MWNT based composites, and (b) the thermal conductivity of MWNT based composites, with increasing CNT volume fractions could be fit (solid lines) to expressions based on excluded volume percolation theory. The effective electrical and thermal conductivities (represented by *) at the threshold were estimated based on a percolation theory with the CNTs and the polymer being modeled as resistive elements [15].

could be used to *a priori* determine the threshold and considers realistic process variability which could then be extended to other mutable CNT characteristics such as diameter, agglomeration, curvature, *etc.* Consequently, for the carbon nanotube-polymer composites, both $\phi < \phi_c$ and $\phi > \phi_c$ regimes were accessible and fit, resulting in a $\phi_c \sim 0.074$ and 2.0 vol % of SWNT and MWNT filling fractions of the percolation threshold, respectively. For $\phi < \phi_c$, the s was ~ 0.7 for the both SWNT and MWNT based composites, while for $\phi > \phi_c$ t was determined to be ~ 3.5 and ~ 5.2 for the SWNT and MWNT based composites, respectively. We see a remarkable correspondence of the experimentally observed ϕ_c with the theoretically computed values from Figure 4. We then attempted to fit the thermal conductivity (κ) variation in the case of MWNT-RET composites, using expressions similar in form to (1),

$$\kappa \sim \begin{cases} (\phi_c - \phi)^{-p}, & \phi < \phi_c \\ (\phi - \phi_c)^q, & \phi > \phi_c \end{cases} \quad (3)$$

where ϕ_c is now the threshold volume fraction for the onset of thermal percolation, and p and q are critical exponents in the respective regimes. We obtained, experimentally, $\phi_c \sim 1.83$ vol %, which is quite close to the theoretically expected value ~ 1.9 vol % using equation (2), where $p \sim 0.02$ and $q \sim 0.17$.

The much larger variation in the increase of the electrical conductivity of the CNT-polymer composites compared to the thermal conductivity may be tentatively attributed to the greater contrast in the conductivity values of the matrix and the filler in both cases. In the former case, one has to consider the much lower electrical resistance of the CNTs compared to the polymers, while there is a much smaller variation in the κ between disparate materials. Invoking a model to determine the critical exponents [15], where the filler (R_f) and matrix (R_m) are

represented as individual resistors, it has been determined that the effective conductivity (σ/κ) at the percolation threshold fraction, could be related to $R_f^u R_m^{1-u}$, where $u = t'/t+s$ or $u = q'/p+q$ for σ/κ , respectively, and the computed value have been indicated (through * in Figure 4).

CONCLUSIONS

We have shown that the onset of electrical and thermal conductivity in nanotube-polymer composites, as determined through the percolation thresholds, can be fitted with power law equations. The close correspondence of the experimental values to those determined from theory is quite remarkable and suggests that similar processes are operative in two widely differing phenomena. Further research should probe the relationships between the exponents, the influence of the respective conductivity contrast ratio of the fillers (nanotubes) and the matrix (polymer), etc. Our investigations could yield better insight into percolation phenomena, of wide importance in the theory of networks, and the optimal conditions for nanotube connectivity and dispersion for wide scale application.

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