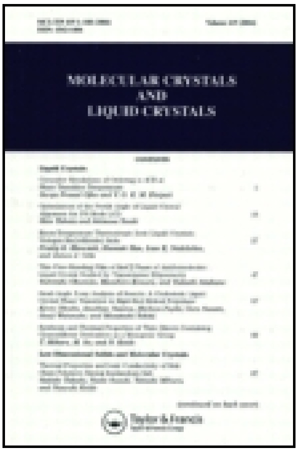

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Electrical Properties of Composites of Polystyrene and Multi-Walled Carbon Nanotubes

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Electrical Properties of Composites of Polystyrene and Multi-Walled Carbon Nanotubes

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The dependencies of electrical conductivity on the electrical field and temperature of high-resistivity polystyrene/carbon nanotube (CNT) composites were investigated. The electrical conductivity of the samples and their thermal activation energy were systematically dependent on the CNT doping level. Several unusual phenomena were observed which could be explained by the inhomogeneous distribution of CNTs in the polystyrene matrix. At higher levels of CNT doping, an interconnected conducting network is formed. If the amount of CNT is equal to or less than 0.6%, "islands" of CNT become separated by the layers of polystyrene, which limit charge transport. At low voltages, there is a sharper decrease in conductance as the voltage decreases.

Keywords Carbon nanotubes; composites; conductivity; polystyrene

Intorduction

Carbon nanotubes (CNTs) have been extensively studied since their discovery in 1991 due to their excellent mechanical, thermal and electrical properties [1,2]. The dispersion of functionalised nanotubes within a polymer matrix enables the production of polymer composites with enhanced physical properties, including mechanical strength and thermal and electrical conductivities [3,4]. Proposed applications for CNT-polymer composites include electromagnetic shielding [5], electronic fabrics [6], polymer electronics [7] and solar cells [8]. Both single-walled (SWNTs) and multi-walled (MWNTs) carbon nanotube polymer composites are being actively pursued in both fundamental and applied research. Multi-walled carbon nanotubes are currently receiving much attention for large-scale commercial applications due to their bulk availability via CVD or arc discharge production methods. Polymer materials doped with dispersed MWNTs represent a new class of conducting composite material in which the network of metallic MWNTs form percolative conducting pathways. Control over material properties such as resistivity and mechanical toughness can be achieved by varying the CNT doping level. Advanced materials engineering requires

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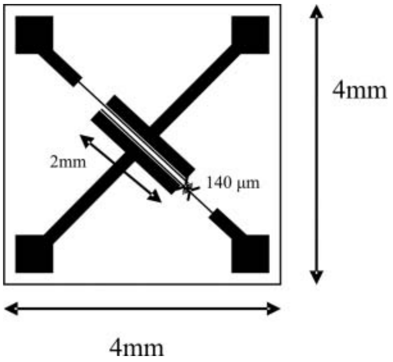

Figure 1. Sample layout.

detailed knowledge of the dependence of composite material behaviour on MWNT doping. This paper presents a systematic investigation of the electrical transport properties of high-resistivity polystyrene/CNT composites as a function of the MWNT doping ratio.

Samples and Experiments

We investigated the electrical conductivity of high-resistivity polystyrene/carbon nanotube composites. The uniform dispersion of individual carbon nanotubes within the polymer matrix is key to obtaining high conductivities and reproducible results from these experiments. The composites investigated here were formed following the gRAFT polymerisation process developed by Curran et al. [8]. Briefly, acid-treated MWNTs were functionalised to form dithiocarboxylic-ester linkages between nanotubes in a toluene solution. Styrene was then grafted onto the dithioester linkage and the resultant styrene/CNT solution was thermally polymerised. The resultant nanocomposite solution was then spin-coated onto sapphire substrates upon which gold electrode structures had been deposited. Four electrodes were arranged to perform four-point resistivity measurements (Fig. 1). The polymer/CNT films consisted of a thiol-bonded network of singly wrapped MWNTs within a polystyrene matrix. We investigated samples with CNT/polystyrene mass ratios ranging from 0 to 1%. The conductivity measurements were performed in a temperature range between 200 and 400 K. The lower temperature limit was set by the breakdown of the sample conductivity at about 210–220 K as described below.

Results and Discussion

The experimental data clearly show that the conductivity of the samples and their mechanisms depend strongly on the CNT doping level (Fig. 2). The sheet resistance of the samples with the highest content of CNTs (1% by mass) was $\sim 10^8\ \Omega\square^{-1}$, whereas samples containing less than 0.55% CNT doping exhibited sheet resistances above $10^{16}\ \Omega\square^{-1}$. At high biases conduction of the samples with doping levels above 0.5% was almost temperature independent in the range 250–400 K, with thermal activation energy values being as low as 0.013–0.016 eV. The dependence of the sample conduction on the CNT doping level is presented in Fig. 3, and the dependence of the effective thermal activation energy value on doping is shown in Fig. 4. It can be seen from these figures that two different conductivity

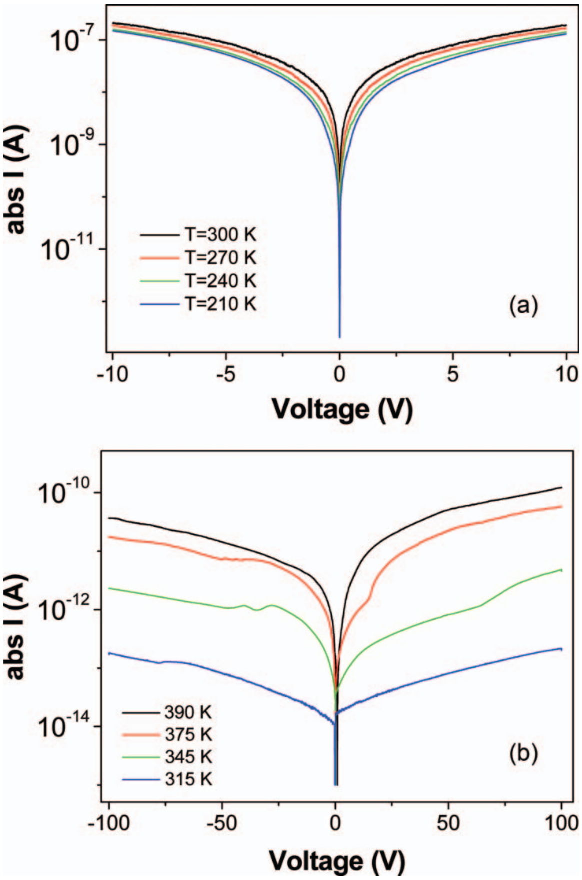

Figure 2. I–V dependencies at different temperatures of the samples, where (a) 0.7% CNT and (b) 0.4 % CNT.

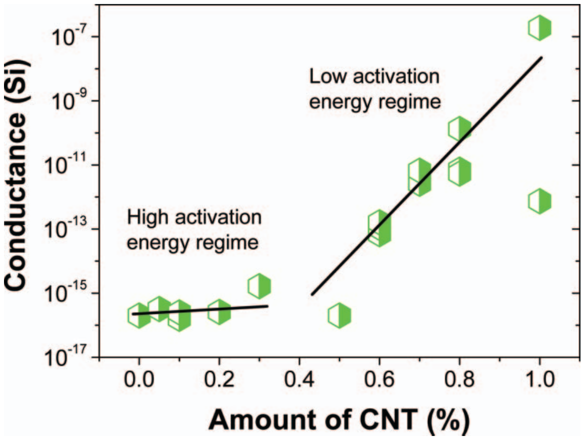

Figure 3. Dependence of the sample conduction on the amount of CNT. The marked lines indicate regions above and below the percolation threshold.

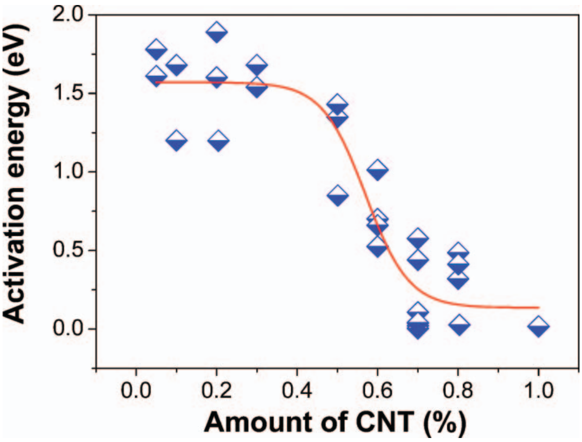

Figure 4. Dependence of the effective thermal activation energy on the amount of CNT. The dashed curve is an approximation by a Boltzmann sigmoid and serves as an eye guide.

modes can be singled out which have different activation energy values. This inference coincides qualitatively with the conclusions of Curran et al. [8]. If the actual activation energy is constant for the sample containing only closely linked material or very dilute material, conduction should be a power law with doping as predicted from percolation theory. However, for our more complex inhomogeneous composites, such laws cannot be verified since experimental results are significantly scattered in the transition region.

In the highly doped samples the I–V characteristics were usually symmetric in both directions of the applied bias and were only weakly dependent on the temperature. Figures 5(a) and (b) show that at high bias (>4 × 10^4 V/cm) the samples exhibited ohmic conduction, while at low bias non-linear I–V dependencies were observed. For highly doped samples, the high bias behaviour was found to fit the fluctuation-assisted tunnelling model [9–11]. This model describes tunnelling across a small barrier driven by electric fields associated with thermal fluctuations in metallic regions to either side of the barrier. It is found to be most pronounced in 1D systems (such as carbon nanotubes) and is described by the equation:

$$G = \frac{I}{V} = G_0 \exp\left(\frac{-T_1}{T + T_0}\right) \frac{\exp(V/V_0)}{1 + h[\exp(V/V_0) - 1]} \tag{1}$$

where G_0, T_1, T_0, V_0 and h are positive constants. In the high temperature limit considered here, the constant T_0 can be approximated to zero and T_1 represents the activation energy associated with this transport mechanism.

The properties of the samples changed significantly with the reduction of CNT doping below 0.5% (Figs 2(b), 3 and 4). It is important to note that these highly resistive samples exhibited non-regularities in their I–V dependence that were generally not repeatable in detail (as is demonstrated in Fig. 2(b)). As a result, the calculated thermal activation energy values for each sample were averaged from the results of several repeated experiments. Below 0.5% CNT doping, the effective activation energy grew to 1.2–1.8 eV. Nonetheless, these samples did show increased conductivity compared to a blank polystyrene matrix. It is believed that conduction is facilitated by field-driven transport through the polystyrene

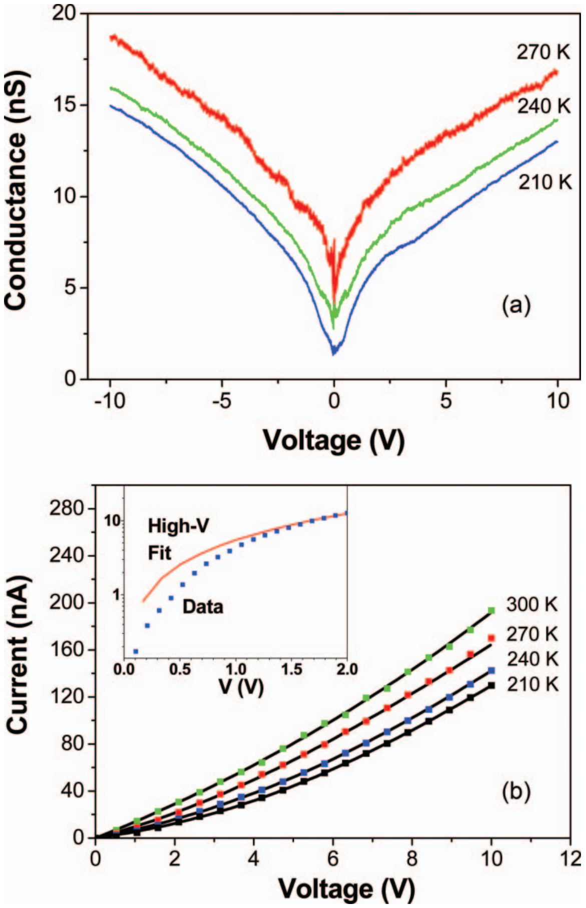

Figure 5. (a) I–V dependences at different temperatures for a sample with 0.7 % CNT; (b) Fits of FAT conduction model to this sample (only a few points are shown for clarity). Inset: Log scale showing the zero bias anomaly as the data decrease below the fit to the higher-voltage data.

matrix across small gaps in the CNT network, i.e. the conduction-limiting mechanism is attributed to impurity conduction through the polystyrene matrix.

It could be supposed that irregularities of the I–V characteristics at different temperatures could be related to the polarisation-related phenomena evidenced in Fig. 6. These figures present current dependencies on temperature measured with and without applied biases. It can be seen that even without applied external voltage, significant current is induced both in low and high-resistivity samples (Figs 6(a) and 6(b)). In the experiment the samples were cold-finger oriented to avoid any temperature gradients between the contacts, so the appearance of such currents can be attributed to the polarised charge-trapping effects near the glass-transition temperature. The bulk glass-transition temperature (T_g) of polystyrene (PS) measured by DSC was found to vary from about 350 K up to 380 K depending on the molecular weight of PS films [12]. Moreover, the surface T_g proved to be much lower than the bulk T_g for the entire M_n range (260 K–360 K), and was strongly affected by the chain length of PS. The activation of the thermal molecular motion at the PS film surfaces was explained in terms of an excess free volume induced by the enriched chain end groups at

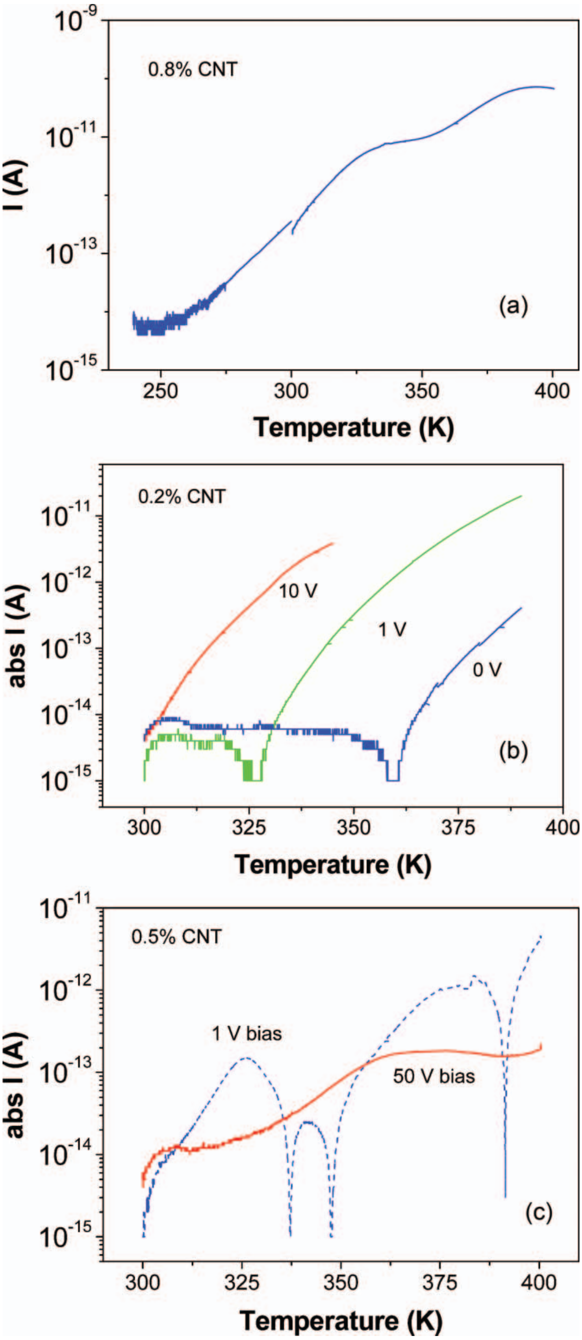

Figure 6. Temperature dependencies of the currents through the samples with different amounts of CNT. (a) Short-circuit current of the sample with 0.8% CNT without applied bias; (b) current of the sample with 0.2% CNT with different applied biases; (c) current of the sample with 0.5% CNT with different applied biases. Maxima and minima on the curve measured with 1 V bias indicate changes of the current direction.

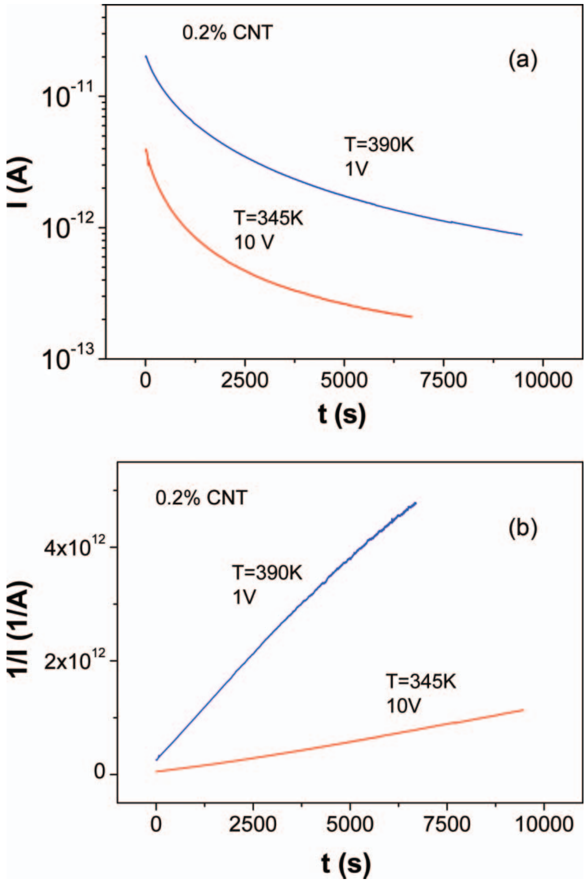

Figure 7. (a) Relaxation of the current after heating the sample containing 0.2% CNT up to the temperatures indicated in the figure. The biases were kept constant during heating and relaxation; (b) Plot of $1/I$ vs. time showing carrier re-trapping behaviour.

the surface [12]. This is in agreement with the value of 107°C reported for high molecular weight PS [13].

Some unusual current behaviour was observed in the samples with a medium level of CNT doping, corresponding to the percolative threshold and the transition regime for activation energy (Fig. 6(c)). At low biases of 1V, its sign could change several times under heating through the range from 300 to 400 K and, moreover, its value exceeded values of the current measured at 50 V, indicating the appearance of high thermal EMFs.

After the sample was heated and the temperature stabilised, very long and non-exponential current relaxations were observed, as shown in Fig. 7. Qualitatively these relaxations were independent of the applied bias or temperature. In the less conductive samples, thermal current relaxations took place over several thousands of seconds, following a reciprocal decay whereby $1/I \sim t$ (Fig. 7(b)). Similar behaviour is observed in persistent photocurrent decay in semiconductors where it has been attributed to multiple re-trapping of carriers that are excited from deep-level traps [14]. This implies that the long-lasting current relaxations cannot simply be ascribed to the effects of ohmic conductivity and geometric capacitance, but are related to trap states present within the inhomogeneous

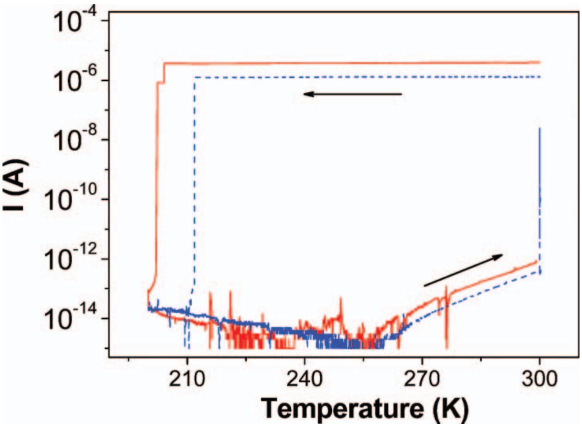

Figure 8. Destruction of the conductive network of the CNT by cooling down the samples with more than 0.6 ÷ 0.7% CNT. The arrows indicate the temperature change direction. Two repetitive heating and cooling cycles are demonstrated, confirming repeatability of the results and restoration of the sample conductivity at room temperature.

CNT network. These thermal current peculiarities could be explained by the inhomogeneous distribution of CNT in polystyrene matrix at doping levels below the percolation threshold. At higher doping levels, CNTs form an interconnected percolative network. However, below the 0.6% doping level, "islands" of CNT become separated by the layers of polystyrene, which limit charge transport. The unconnected CNT network has a very high surface area, and we attribute the observed high thermal EMFs to high sample capacitance coupled with deep-level traps. This leads to history-dependent *I-T* curves during thermal ramping, whereby previously injected electron hole pairs exit the sample as they are thermally excited from their capacitively coupled deep-level trap states.

An additional feature of the role of the CNT network is demonstrated by the characteristic behaviour that was observed when the samples were cooled below 210–200 K (Fig. 8). At this temperature a sharp drop of the current by several orders of magnitude took place. After the samples were heated back to 300 K and left to relax for about one day, the initial conductivity could be restored, indicating that the cycle was reproducible, as is demonstrated in Fig. 8 by two traces obtained in subsequent measurements on the same sample. It appears that at this critical temperature of ~210 K reversible mechanical changes occur within the samples such that percolative pathways formed by the CNT network through the PS are broken. One possible explanation for this would be the presence of a phase change at the CNT-PS interface, possibly mediated by the thiol bond leading to increased PS wrapping of the CNT below this value. Another simple assumption could be that thermal deformation leads to the entire film lifting off the contacts. However, this breakdown would not be restorable. On the other hand, it could also be supposed the thermal deformation of the PS may introduce excess tension into network until it breaks, but PS should surely shrink, not stretch.

Summary and Conclusions

The polymer/CNT films with CNT/polystyrene mass ratios from 0% to 1% that we measured consisted of a thiol-bonded network of singly wrapped MWNTs within a polystyrene matrix.

They were spin-coated onto sapphire substrates, and gold electrodes were deposited for four-point resistivity measurements. The sample conductivities measured in the temperature range from 200 K up to 400 K depended strongly on the CNT doping level. The resistance of the samples with the highest content of CNTs was $\sim 10^7\ \Omega\Box^{-1}$. These samples exhibited nearly temperature independent conduction with thermal activation energy values as low as 0.013–0.016 eV. The sample properties changed drastically with the reduction of the CNT doping below the percolation threshold of $\sim 0.5\%$. The resistance of these samples at 300 K increased to $\sim 10^{16}\ \Omega\Box^{-1}$, and the thermal activation energy values increased up to 1.2–1.8 eV.

Following temperature ramping, slow current relaxations took place that lasted several thousands of seconds. These relaxations followed a reciprocal decay with t proportional to $1/I$. This provides strong evidence that the observed effects cannot simply be ascribed to ohmic conductivity and geometric capacitance, but are related to percolation and polarisation phenomena in the inhomogeneous media formed by "islands" of CNT in the polystyrene matrix.

A number of unusual thermal currents observed in the high-resistivity samples could be explained by the presence of isolated CNT "islands" in the polystyrene matrix. It was found that the most homogeneous distribution occurred in the samples with 0.7% CNT. At a higher percentage CNT forms interconnected clusters. Meanwhile, if the amount of CNT is equal to or less than 0.6%, "islands" of CNT become separated by the layers of polystyrene, which govern charge transport.

Our conduction measurements of carbon nanotubes in polystyrene show similar results to those of other researchers on some low-conductivity polymers, namely an approximately exponential increase in conductance with voltage which starts to saturate at higher voltages. The I–V characteristics are consistent with fluctuation-assisted tunnelling through barriers between metallic regions (the carbon nanotubes in the present case) for medium and high voltages. However, at low voltages there is a sharper decrease in conductance as the voltage decreases, which could arise from small conduction barriers that only limit conduction at low voltages.

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