Charge transport properties of water dispersible multiwall carbon nanotube-polyaniline composites

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The transmission electron microscopy images of *in situ* prepared multiwall carbon nanotubes (MWNTs) and polyaniline (PANI) composites show that nanotubes are well dispersed in aqueous medium, and the nanofibers of PANI facilitate intertube transport. Although low temperature transport indicates variable range hopping (VRH) mechanism, the dc and ac conductivity become temperature independent as the MWNT content increases. The onset frequency for the increase in conductivity is observed to be strongly dependent on the MWNT weight percent, and the ac conductivity can be scaled onto a master curve. The negative magnetoresistance is attributed to the forward interference scattering mechanism in VRH transport. © 2010 American Institute of Physics. [doi:10.1063/1.3374628]

I. INTRODUCTION

Carbon nanotubes (CNTs) owing to their excellent thermal stability and unique mechanical and electrical properties are of great interest for developing several types of multifunctional materials.^{1,2} The CNT-polymer composites have been extensively studied in recent years because of their importance in applied as well as basic sciences.^{2–4} The inclusion of CNTs in polymers can simultaneously provide enhanced electrical conductivity and mechanical reinforcement. The CNT-polymer composites find applications in organic photovoltaic cells,⁵ supercapacitors,⁶ field emission devices,⁷ etc.

As for the electrical properties of CNT-polymer composites, the high aspect ratio of CNTs helps to form a percolation network at relatively low loading percentages of the order of 1 wt % of nanotubes.^{8,9} However, as CNTs are usually insoluble in common solvents and polymers,¹⁰ they tend to aggregate, which makes their dispersion a significant challenge in host polymer matrices. Furthermore, the intrinsic hydrophobic nature of CNTs makes the production of water dispersion of CNTs even more difficult. These problems can be solved by the addition of surfactants¹¹ or stabilizers¹² or by chemical modification of CNTs.¹³ However, the most successful approach to prepare dispersions includes sonication of CNTs in presence of polymers that may attach to the nanotube surface by noncovalent interactions, and this often results in stable dispersions in water.¹⁴ Moreover, this method avoids the degradation of properties that chemical modification usually does to CNTs, also enables higher concentration of CNTs in dispersion.

Polyaniline (PANI), with its ease of synthesis, environmental stability, and high conductivity, is one of the most promising conducting polymers. The soluble form of PANI in water is of much interest due to environmental reasons. The water dispersion of PANI can be achieved through vari-

ous methods like chemical modification of PANI,¹⁵ using polyelectrolytic counterions,¹⁶ using hydrophilic polymer mixtures¹⁷ or through copolymerization.¹⁸ However, a more simple route involves synthesis of PANI nanofibers which form spontaneously during the early stages of the chemical oxidative polymerization of aniline.¹⁹ Because of the electrostatic repulsion between nanostructures, these nanofibers tend to form a homogeneous and stable dispersion in water. Long *et al.*²⁰ synthesized CNT-PANI composite through an *in situ* chemical oxidative polymerization method which showed enhanced conductivity. Recently we have combined the synthesis of PANI nanofibers and CNT polymer association through noncovalent interactions by *in situ* polymerization techniques to obtain CNT-PANI composite which contains well segregated CNTs partially coated by PANI nanofibers.²¹ In this method CNT-PANI composites of about 50 wt % CNT could be prepared. Moreover, the electrical conductivity and other properties have observed to be sensitive to the method of incorporation of CNTs in polymer, since the interfacial interactions between the matrix and CNTs are different.²²

In the present work we report the dc and ac charge transport properties of multiwall carbon nanotubes (MWNTs) and PANI composites that can be dispersed in aqueous solutions at high concentrations of MWNT. The temperature dependence of dc conductivity indicates hopping transport at low temperatures. The universality of ac conduction is demonstrated by the master scaling curve. The magnetoresistance (MR) and ac conductivity measurements show that the connectivity of network improves with MWNT loading. This detailed investigation is required to optimize the correlation among morphology and transport properties in MWNT-PANI composites toward applications in antistatic coating, electromagnetic shielding, etc.

II. EXPERIMENTAL

MWNTs of 2–5 μm length and 20–50 nm in diameter were produced in an arc-discharge reactor by sublimation of

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FIG. 1. TEM images of (a) PANI and (b) 30 wt % MWNT-PANI composite.

pure graphite rods using a current of 60 A and a voltage of 25 V, under helium atmosphere of 66 KPa. PANI and its composites with MWNTs were produced via chemical oxidative polymerization of aniline. Aniline was dispersed and then polymerized in presence of different weight proportions of MWNTs (5, 10, and 30 wt %; no MWNTs in the case of pure PANI sample) as described elsewhere,²¹ so that the nanostructured MWNT-PANI composite is formed *in situ*, with PANI in its doped emeraldine chloride and conducting state. Transmission electron microscopy (TEM) was performed in JEOL JSM-6400 microscope after evaporating a dilute dispersion of the sample on a carbon coated copper grid. Samples were compressed in the form of 13 mm diameter pellets under a pressure of 5 tonnes, during 2 min, using polyvinylidene fluoride, (5 wt %) as a binder material.

The low temperature conductivity measurements are performed in a Janis continuous flow cryostat system. For dc conductivity measurements, current in the range 0.5–2 μ A is applied (using Keithley 224 current source), and the voltage measured through Keithley 6514 electrometer. Electrical contacts to the samples, in van der Pauw configuration, were made by conducting silver paint. ac conductivity measurements (100 KHz–8 MHz), down to 8 K, were carried out by Agilent 4285A precision LCR meter, in Janis continuous flow cryostat. The ac conductivity measurements were further extended to lower frequencies (down to 40 Hz) using a lock-in amplifier (SR-830). The low temperature MR measurements were carried out in a Janis variable-temperature cryostat, equipped with 11 T superconducting magnet.

III. RESULTS AND DISCUSSIONS

TEM images of PANI and MWNT-PANI composite, with 30 wt % MWNT loading, are shown in Fig. 1. TEM image of PANI reveals nanoscale morphology of elongated structures of average diameter 100 nm and length 300 nm. TEM image of MWNT-PANI composite shows [Fig. 1(b)] that MWNTs are partially covered with PANI nanofibrils, and this prevents the bundling of nanotubes. Figure 1(b) also shows that it is possible for PANI coatings to connect the well-separated nanotubes.

In order to examine the effect of MWNT content on charge transport properties, we present the temperature dependence of conductivity of MWNT-PANI composites at various MWNT loading, as in Fig. 2(a). Unlike in case of insulating polymer-MWNT blends, in which a sharp percolation threshold is observed, it is not possible to observe this feature in MWNT-PANI composites since the conduction

FIG. 2. (Color online) (a) Temperature dependence of conductivity of MWNT-PANI composites. (b) Reduced activation energy W vs T with linear fit.

TABLE I. Parameters describing the transport properties of MWNT–PANI composites.

Sample MWNT (wt %)	Resistivity ratio ($\rho_{5\text{ K}}/\rho_{300\text{ K}}$)	Exponent p	σ_0 at 20 K (S/cm)	ac conductivity onset frequency at 20 K (rad/s)
PANI	1.1×10^7	0.51	$\sim 2 \times 10^{-4}$	3.6×10^2
5	1.2×10^5	0.4	$\sim 10^{-3}$	4.8×10^3
10	1.8×10^4	0.37	$\sim 10^{-2}$	2.3×10^6
30	5.9×10^2	0.34	$\sim 10^{-1}$	3.2×10^7
MWNT	1.3	...	~ 2	$\geq 5 \times 10^7$

via PANI matrix smears out the onset of rapid increase in conductivity. The conductivity of pressed pellets of MWNT is nearly temperature independent, indicating its intrinsic metallic nature and high quality. The conductivity of MWNT–PANI blends shows strong temperature dependence especially at low temperatures, though it gets weaker as the MWNT content increases. Previously, Long *et al.*²⁰ have suggested a hopping model for low temperature transport in MWNT–PANI composites, with the stretched exponential form

$$\sigma(T) = \sigma_{0T} \exp \left[- \left(\frac{T_0}{T} \right)^p \right], \quad (1)$$

where T_0 is characteristic temperature and p depends upon the dimension of system. The value of p is determined from reduced activation energy^{23,24} $W(T) = -\partial \ln \rho / \partial \ln T$. The actual values of p are calculated from the slope of straight line in W versus T plot in log-log scale, at $T < 50$ K, as shown in Fig. 2(b). These values are presented in Table I. The T_0 values are also obtained from W -plot: $\ln W = -p \ln T + \ln(pT_0^p)$. A one-dimensional Mott's variable range hopping (VRH) mechanism with exponent close to 0.5 is observed in case of these PANI nanofibrils, and other composites nearly follow two dimensional Mott's VRH with exponent close to 0.33. The exponent ($p \sim 0.4$) in 5 wt % sample is bit higher [see Table I], and this is mainly due to the weaker inter-nanotube transport. The MWNTs are sparingly adhered with PANI coatings, and this facilitates intertube hopping at low temperatures. However, as the MWNT content increases its role in intertube transport increases, as shown by the weaker temperature dependence of conductivity.²⁰ Although the tunnel transport via PANI matrix is also expected to reduce the temperature dependence of conductivity, especially at $T < 20$ K, its role is observed to be rather minimal.

The frequency dependence of normalized conductivity [$\sigma(\omega)/\sigma_0$], for various MWNT–PANI composites at 20 K, is shown in Fig. 3(a), along with the data for PANI and MWNT samples. All the curves exhibit two different regions, in the low frequency plateau region, the conductivity maintains a constant value up to a characteristic onset frequency ω_0 , and at $\omega > \omega_0$ the conductivity increases; which is usually observed in many disordered systems.^{25,26} This frequency dependence of conductivity follows the extended pair approximation model:²⁷

FIG. 3. (Color online) (a) Frequency dependence of normalized conductivity for various MWNT loading at 20 K. Inset: onset frequency vs dc conductivity of MWNT–PANI composites at 20 K. Solid line shows a linear fit. (b) Frequency dependence of normalized conductivity for 5 wt % of MWNT at various temperatures. Inset: onset frequency vs T on a log-log scale. Solid line shows a linear fit.

$$\sigma(\omega) = \sigma_0 \left[1 + k \left(\frac{\omega}{\omega_0} \right)^s \right], \quad (2)$$

where k is an arbitrary constant, and s (values in range 0–1) is an exponent dependent on both frequency and temperature. It is interesting to observe how this frequency dependence of conductivity evolves as the MWNT content increases. In pure MWNT hardly any frequency dependence can be observed, and rather similar in 30 wt % sample too, due to the dominance of coherent intertube transport. Although the 10 wt % sample is expected to have adequate intertube transport, an onset of the increase in conductivity can be observed at $\omega \sim 10^5$ Hz. Also this onset frequency shifts to higher frequencies as the MWNT loading increases. The onset frequency ω_0 , can be defined as the frequency at which $\sigma(\omega_0) = 1.1\sigma_0$, where σ_0 is the dc conductivity value.²⁷ The value of ω_0 increases with dc conductivity, and it increases by several orders of magnitude as the MWNT content increase, which is usually the scenario in frequency assisted transport in percolative systems. The log-log plot of onset frequency and dc conductivity suggests a linear relation [$\omega_0 \propto \sigma_0$], as shown in the inset of Fig. 3(a).²⁸ The onset frequency and dc conductivity values of various composites, at 20 K, are summarized in Table I.

A detailed temperature dependence of $\sigma(\omega)$ has been

carried in 5 wt % sample to understand the charge transport mechanism, since the ac conductivity of 5 wt % sample shows substantial frequency dependence. The $\sigma(\omega)$ of 5 wt % sample, at various temperatures, is shown in Fig. 3(b). The conductivity data are normalized by appropriate dc conductivity values at each temperature. At low temperatures, the ac conductivity is strongly frequency dependent, and the data show onset frequencies shift to lower values as temperature decreases. The onset frequency is plotted as a function of temperature in the inset of Fig. 3(b). The log-log plot, for $T < 50$ K, suggests a form $\omega_0 \sim T^q$, where $q \sim 3.5$.²⁹ In any disordered system a correlation length λ can be defined which corresponds to the distance between connections (e.g., junctions and nodes) in the system.²⁷ At the onset frequency ω_0 , carrier travels a distance $\sim \lambda$. It has been shown for disordered systems that the onset frequency scales inversely to some power of this correlation length. Above the onset frequency, carriers travel shorter distance within a well-connected region that does not involve the difficult hopping processes. A higher value of the onset frequency implies smaller correlation length and shorter connections in the system.³⁰ The increase in onset frequency with MWNT loading implies that the connectivity improves with MWNT loading in the composite.²⁷ The significant decrease in onset frequency, as temperature is lowered, indicates that transport via the links in network is reduced at low temperatures; and the value of ω_0 is a useful parameter to probe the extent of connectivity in the system. This investigation in turn can be used for identifying the morphological factors that play a major role in charge transport properties, and to optimize the performance of MWNT composites.

It is known that the frequency dependent ac conductivity in disordered systems follows a master scaling curve by choosing the appropriate scaling factors.^{28,31} The scaling properties of MWNT-PANI composites as a function of MWNT loading and temperature are shown in Figs. 4(a) and 4(b), respectively. In both graphs the reduced conductivity $\sigma(\omega)/\sigma_0$ has been plotted against reduced frequency ω/ω_0 . The experimental data exhibit universal behavior, and all the

FIG. 4. (Color online) (a) Scaling of ac conductivity for various MWNT weight percent, at 20 K. Solid line is fit to the extended pair approximation model [Eq. (2)]. (b) Scaling of ac conductivity for 5 wt % of MWNT at different temperatures. Solid line is fit to the extended pair approximation model.

FIG. 5. (Color online) Magnetoresistance of composites of 5, 10, and 30 wt % of MWNT, at 10 K. The solid lines are fit to Eq. (3).

data fall onto a master curve, as described by the extended pair approximation model [Eq. (2)]. This scaling as function of both weight percent and temperature indicates that varying the weight percent of MWNT shows a one to one correspondence to the variation in charge transport through the connections in network, as the temperature is varied. The solid lines in Figs. 4(a) and 4(b) are master curves obtained from the fits to Eq. (2), and the fit parameters are: $k=0.85$, $s=0.54$ and $k=0.89$, $s=0.55$, respectively.

Further to explore the role of MWNT in low temperature transport, we have measured the MR in these samples. At low temperatures, a positive MR is observed in pure PANI,³² because the application of magnetic field causes a shrinkage of the wave functions of localized states, and this reduces the average hopping length.³³ Whereas due to the extended states (larger localization lengths) in MWNTs, the wave function shrinkage effect (positive MR) is not that significant, and the observed negative MR is interpreted in terms of forward interference effects among many possible hopping paths in a magnetic field.³⁴ Nguyen, Spivak, and Shklovskii (NSS) (Ref. 35) and Sivan, Entin-Wohlman, and Imry (SEI) (Ref. 36) have evaluated the effects of quantum interference in VRH transport. In low magnetic field, NSS model predicts a negative MR linear with field, whereas SEI model indicates a quadratic dependence. The MR data for 5, 10, and 30 wt % samples, at 10 K, are shown in Fig. 5. With increasing MWNT concentration, the negative MR increases. The data show a linear dependence at low field region ($B < 3$ T). The average localization length of composites enhances with MWNT loading, as a result the negative MR increases.²⁰ So the negative MR of MWNT-PANI composites supports that the electronic transport at low temperatures is dominated by MWNT network, which is consistent with dc and ac conductivity measurements. The negative MR tends to saturate at high fields, and a competing contribution due to the wave function shrinkage effect (positive MR) in VRH transport is observed.³⁷ The net MR by taking into account the negative and positive contributions is given by the expression³⁸

$$\ln \left[\frac{\rho(B)}{\rho(0)} \right] = -a_1 B + a_2 B^2 + a_3, \quad (3)$$

where a_1 is the coefficient of forward interference effects, a_2 is the coefficient of wave function shrinkage term, and a_3 accounts for the contribution from scattering effects at very low fields.³⁹ However, the minor deviations in the fits as field tends to zero can be explained due to the complex nature of scattering processes at very low fields.³⁹ This model fits quite well for both 5 and 10 wt % samples. However, the significant deviation of the fit at $B > 5$ T, in 30 wt % sample, indicates that the positive MR due to the contribution from electron–electron interactions could as well play a role, since the intrinsic metallic transport in MWNT starts to dominate at high fillings of MWNT.⁴⁰

IV. CONCLUSIONS

In summary, we have synthesized a nanoscale composite of PANI and MWNT, which can be easily dispersed in aqueous solutions at high concentrations of MWNT, via an *in situ* polymerization process. TEM images show that nanotubes are well segregated due to the presence of PANI coatings and nanofibrils. The charge transport measurements in MWNT–PANI composites indicate VRH mechanism and the transport parameters are summarized in Table I. The ac conductivity and MR measurements at low temperatures show that the role of disorder in charge transport properties decreases with increasing content of MWNT. The onset frequency alters by several orders of magnitude as MWNT weight percent varies, hence it is a quite sensitive probe to find the extent of connectivity in the system. These transport parameters are quite useful in optimizing the electronic properties of MWNT–PANI composites.

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