Molecular Crystals and Liquid Crystals

Charge Carrier Mobility in Films of Carbon-Nanotube-Polymer Composites

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Charge carrier mobility in thin films of composites of single wall carbon nanotubes and poly-N-vinylcarbazole in the range of nanotube concentrations below that of the percolation threshold is studied. The drift mobility of electrons is found to range between $(1.2–4.5) \times 10^{-6} \, cm^2/(V \, s)$, which is by a factor of 5 higher than that for holes. The polymer is shown to provide the electron and hole transport in composite films.

INTRODUCTION

Single wall carbon nanotubes (SWCNTs) are of particular interest for applications in electronics [1]. SWCNT-polymer composites are studied due to their interesting properties and the potential for a wide range of applications such as light-emitting diodes [2], photovoltaic cells [3], photorefractive media [4], and conductive layers [5]. In this connection, the elucidation of the mechanism of charge carrier transport in composite films is of particular interest.

EXPERIMENTAL

The SWCNT material (AP-grade, the average diameter of 1.4 nm) produced by arc discharge was purchased from CarboLex, Inc. (USA).

SWCNTs included both semiconducting (2/3) and metallic (1/3) tubes. SWCNTs were further purified from catalyst impurities (Ni, Y) by treatment in 65% nitric acid for 26 h. The solution was then filtered through a PTFE filter with 0.2-μm pores leaving SWCNTs on the filter. SWCNTs were then dispersed in deionized water and washed in a centrifuge until the pH level of a solution was equal to 7. The impurities were left as a bottom sediment.

Poly-N-vinylcarbazole (PVK) as-received from Aldrich was used. For the PVK–SWCNT composite preparation, SWCNTs were dispersed in tetrachlorethane and sonicated for half an hour followed by addition of PVK to the solution. Finally, the blend was sonicated for 5 min. Just after the treatment, the composite solution was drop cast onto an ITO glass substrate and dried for 3 h at 60°C. Films of the PVK–SWCNT composite were 9 μm in thickness. The amount of SWCNTs in the blend was 0.26 and 0.43 wt.% to PVK.

The drift mobility of charge carriers was measured by a conventional time-of-flight method (TOF) technique in the small-current mode. Sandwich specimens of the ITO/polymer composite/Se/Al structure were prepared for the experiment. The Se and Al layers were deposited by thermal evaporation at a residual pressure of 10^{-4} Pa. Note that because the thickness of a selenium layer ($0.2 \pm 0.05 \mu m$) was by an order of magnitude lower than that of the polymer composite film, and the drift mobility of charge carriers in (vitreous) amorphous Se films is as high as $0.15 \, cm^2/(V \, s)$ [6], the Se layer does not affect the measured mobility values. In the TOF experiment, charge carriers were generated by illumination through the ITO glass with a 20-ns pulse of a xenon lamp (Xenon Corp., Model-437B) with a filter selecting the Se absorption band and excluding SWCNT-polymer absorption bands. All requirements for the small-signal mode of the TOF technique were fulfilled. The current transients were recorded with a digital oscilloscope (Tektronix TDS 3032B and ADA400A). The transit time, t_T, is related to the drift mobility as $\mu_d = L/(Ft_T)$, where F is the applied electric field strength and L the thickness of a polymer composite film. The current-voltage (I-V) characteristics of steady-state injection currents were measured in the same specimens. The surface area of the electric contact was $10 \, mm^2$. All measurements were carried out at room temperature and in air.

RESULTS AND DISCUSSION

At low nanotube concentrations, the nanotube bundles are not sufficiently close to one another to form a percolating conductive path along the nanotubes. The rheological and electrical properties of the

composite are thus comparable to those of the host polymer. Figure 1 shows the typical *I-V* characteristics of stationary injection currents at various pressures near the transition to the high-conductivity state in films of the PVK–SWCNT composites containing 0.26 (triangles) and 0.43 (squares) wt.% of SWCNT. The *I-V* characteristics can be closely approximated by the power function $J \sim U^n$. At low voltages (up to U_1), the *I-V* curves are well described by the Ohm's law. According to the space-charge-limited injection current model [7], at U_1, the concentration of thermally equilibrium free charge carriers becomes comparable to the concentration of injected charges, while the *I-V* curves obey the trap-related quadratic law

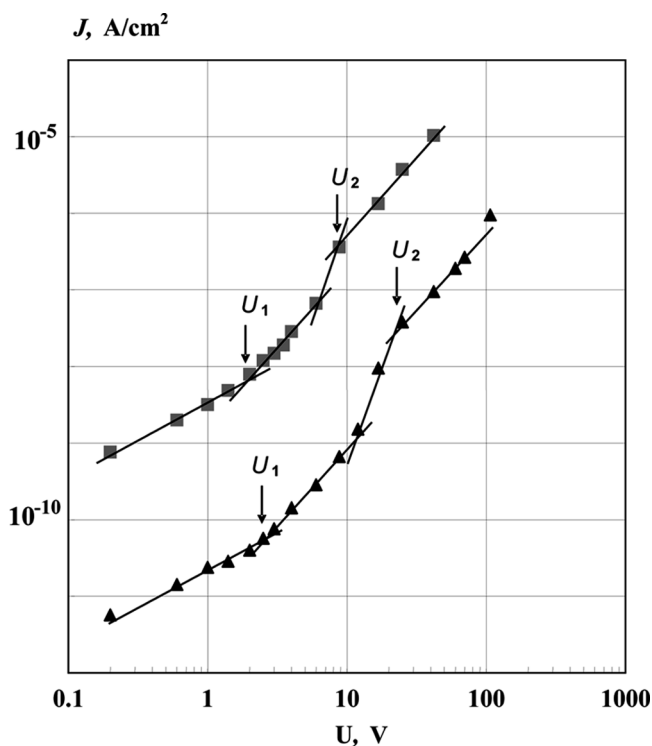$$J = \theta \varepsilon \varepsilon_0 \mu \frac{U^2}{L^3},$$ (1)

FIGURE 1 *I-V* characteristics of the steady-state currents in films of the PVK composite containing 0.26 (triangles) and 0.43 (squares) wt.% of SWCNTs. Arrowheads depict a voltage U_1 separating the ohmic and non-ohmic behaviors and U_2 corresponding to the trap-free mode of the current.

where J is the current density, ε the relative permittivity, ε_0 the permittivity of vacuum, θ the fraction of free charges, and μ the effective mobility. Then the steep segment of the curves ($n > 2$) is followed by the next quadratic law range at U_2 which corresponds to the trap-free current mode with $\theta = 1$. Based on expression (1), one can estimate the effective mobility of charge carriers:

$$\mu = \frac{J_2 L^3}{\varepsilon \varepsilon_0 U_2^2}.$$

In calculations, we used $\varepsilon = 3$ and J_2 at U_2. The mobilities for the composites containing 0.26 and 0.43 wt.% of SWCNT are 1.7×10^{-7} and $1.3 \times 10^{-5}\,\text{cm}^2/(\text{V s})$, respectively. The conductivities of composite films estimated at the ohmic range equal 2.9×10^{-14} and $4.9 \times 10^{-12}\,\text{S/cm}$ for the SWCNTs concentration of 0.26 and 0.43 wt.%, respectively. The conductivity of PVK was $2.7 \times 10^{-15}\,\text{S/cm}$.

The TOF experiment in the low-current regime allows carrying out a detailed study of the charge carrier transport. The field dependence of the drift mobility, μ_d, of charge carriers in the PVK–SWCNT (0.26 wt.%) composite and pure PVK films is presented in Figure 2. TOF transients demonstrated the dispersive behavior in the composite films. TOF transients could not be measured for the PVK–SWCNT (0.43 wt.%) composite because the conductivity of its films was too high for the TOF experiment. Nevertheless, the concentration dependence of the effective mobility allows one to expect that the drift mobility in PVK–SWCNT (0.43 wt.%) can be as great as $10^{-3}\,\text{cm}^2/(\text{V s})$. The data on mobility obtained from *I-V* (effective mobility) and TOF (drift mobility) measurements are listed in Table 1.

The drift mobility increases with the electric field strength and can be described by the relation $\mu_d \sim \exp(F^{1/2})$, so the dependence is linearized in the appropriate plot (Fig. 2). It is anticipated that the mobility of holes in the PVK–SWCNT composite may be higher than that in PVK. However, the fact that the electron mobility in the composite is higher than the hole mobility was not evident in advance, since no mobile electrons were observed in PVK. In the well-known composite of PVK and trinitrofluorenone (TNF), the hole transport is due to the hopping via uncomplexed carbazole states, while the electron transport is due to the hopping between TNF which may be complexed or uncomplexed [8].

In the present study, with the addition of SWCNTs to PVK, the charge transfer complexing can take place forming a positive charge on PVK and a negative charge on SWCNTs. However, the concentration

TABLE 1 Charge Carrier Mobility in PVK–SWCNT (0.26 wt.%)

I-V curves	TOF experiment	
	μ_d, cm^2/(V s) at 258 (V/cm)$^{1/2}$	
μ_eff, cm^2/(V s) at 166 (V/cm)$^{1/2}$	Holes	Electrons
1.7×10^{-7}	3.38×10^{-7}	1.7×10^{-6}

of SWCNTs used in the work is below a threshold of percolation, so the probability of the electron hopping between adjacent SWCNTs is negligible. This suggests that PVK also provides the electron transport. It can come about the following way. In the TOF measurements, electrons are injected into the composite film and sites on SWCNTs forming charged particles (process 1 in Fig. 3). The charged particles facilitate the dissociation of neighbor charge transfer complexes of PVK–SWCNT (process 2 in Fig. 3) and the drift of holes via PVK carbazole states (process 3 in Fig. 3) toward the neighbor negatively charged SWCNTs forming complexes or recombining with electrons on SWCNTs (process
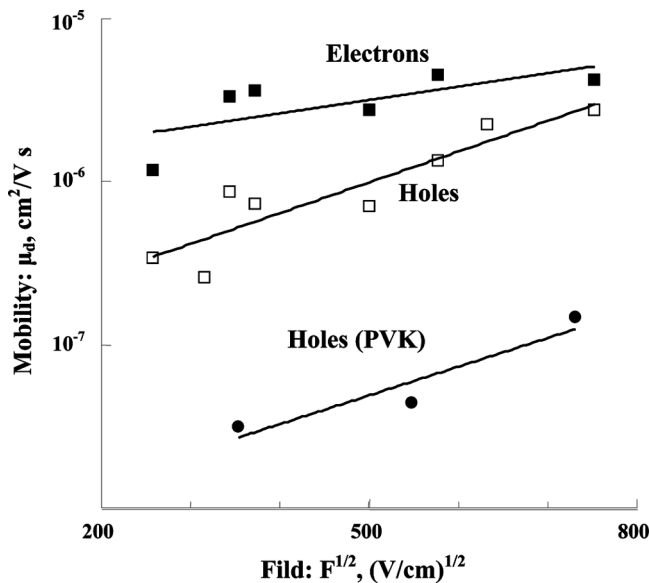

FIGURE 2 Electric field dependence of the drift mobility of electrons and holes in films of the PVK–SWCNT (0.26 wt.%) composite, as well as the hole drift mobility in pure PVK films.
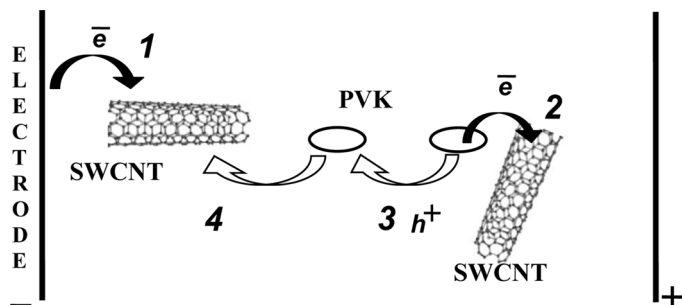
FIGURE 3 Sketch of charge transport processes in the electrode/ composite/electrode structure: electron injection from an electrode on SWCNTs (1), dissociation of the PVK–SWCNT charge transfer complex (2) and the hopping of holes via PVK (3) toward negatively charged SWCNTs followed by the recombination with electrons (4).

4 in Fig. 3). Electrons are moved to the next SWCNT towards the counter electrode by this process. It is worth to note that PVK, similarly to PMMA [5], may promote the transfer of SWCNTs from the semiconducting (*p*-type) to the metallic state. The latter can provide the enhanced electron transport.

In conclusion, we have studied the charge carrier mobility in thin films of PVK–SWCNT composites in the range of the SWCNT concentrations below that of the percolation threshold. The conductivity of the composite including 0.43 wt.% of SWCNT is found to be two orders of magnitude more than that for the 0.26-wt.% SWCNT composite. This small rise of the SWCNT concentration is believed to lead to the formation of a more efficient charge transport network resulting in the increased hole and electron mobilities. PVK is shown to provide not only the hole transport but also the electron transport in the composite films.

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