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### Electrical and Optical Properties of Conducting Poly(3-hexylthiophene)/Multi-walled Carbon Nanotube System

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## Electrical and Optical Properties of Conducting Poly(3-hexylthiophene)/Multi-walled Carbon Nanotube System

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*Polymer multi-wall carbon nanotube (MWNT) composites were prepared and characterized as part of an effort to develop polymeric materials with improved combinations of properties for potential use in solar cell applications. Multi-walled carbon nanotube (MWNT) poly(3-hexylthiophene) nanocomposites were synthesized by in situ polymerization of monomers in the presence of different amounts of MWNTs. A process is reported to efficiently disperse multi-walled carbon nanotube (MWNT) bundles in a semiconducting polymer matrix. A uniform dispersion of the nanotubes in the polymer matrix was obtained. Characterization of the nanocomposites and the effects of MWNT concentration and dispersion on the structural, optical and electrical properties were discussed. FTIR and Raman spectroscopic investigations of nanocomposites indicate that the polymer is wrapped on the nanotubes, taking up a rigid orientation through  $\pi$ - $\pi$  stacking. The Hall voltage measurement is followed to monitor carrier concentrations and mobilities, instead of the device fabrication and hole mobility measurements.*

**Keywords:** conducting polymers, conjugated polymers, Hall effect

### INTRODUCTION

The in situ doping polymerization method with carbon nanotubes is relatively much easier than other template synthesis methods.

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Polymeric network-coated carbon nanotubes have wide potential applications in many fields such as nanowires and nanochannel-based devices. The structure and conductivity aspects of MWNT/poly(3-hexylthiophene) (P3HT) composite films, prepared through blending and sonication procedure, have been analyzed in the context of a general picture in the field of carbon nanotube/polymer composite materials for improvement in electrical conductivity [1]. The morphology, structure, thermal and mechanical properties, optical and conductivity measurements for MWNT/P3HT composites prepared through in situ polymerization method, with a probable explanation of the difference in physical properties as a function of MWNT concentrations, were presented [2]. This present work tries to throw further light on some of the unexplored properties of the composites.

## EXPERIMENTAL

### Materials

Multi-walled carbon nanotubes produced by the CVD process were purchased from Hanwha Nanotech (South Korea) (diameter: 10–15 nm, length: 10–20  $\mu\text{m}$ , purity: 95%). MWNT (diameter: 10~15 nm, purity: 95%), 3-hexylthiophene (3HT) monomer, chloroform, anhydrous  $\text{FeCl}_3$  (oxidant), and other organic solvents purchased from Aldrich as reagent grade, were used without further purification.

### Nanocomposites and Polymer Preparation

The in situ polymerization of 3-hexylthiophene monomer in the presence of MWNTS and of  $\text{FeCl}_3$  as oxidant in chloroform medium, was followed under continuous sonication and stirring following the procedure described earlier [3].

### Characterization

The FTIR spectra of the samples were recorded on a Thermo 5700 model instrument. The Raman spectra of the solid samples were taken using a Thermo Almega XR model. The UV-visible spectra were recorded using a Shimadzu Model UV-160 in a chlorobenzene solvent. The photoluminescence, PL, experiments of the samples were performed with a Hitachi instrument (FL-4500 fluorescence spectrometer) at excitation wavelengths of 450 nm. The dc conductivity of P3HT and P3HT-MWNT composite pellets were measured at room temperature,

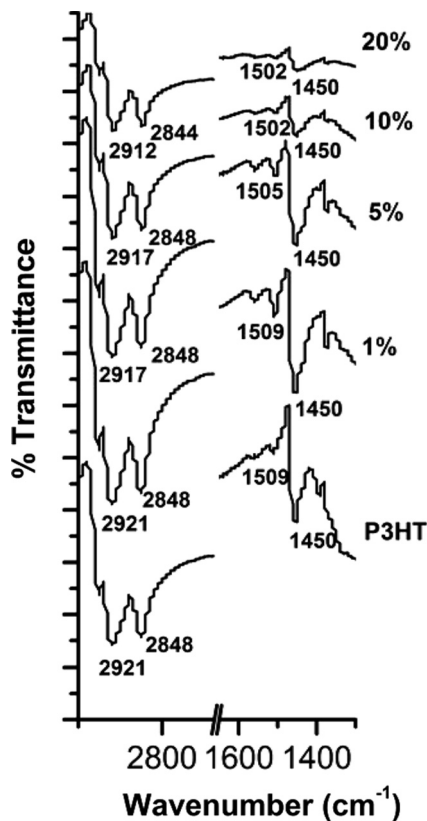
using a Keithley/Luft Semiconductor Device Analyzing System, by the van der Pauw method. The Hall voltage was measured for the composites using ECOPIA system (HMS-3000) with an applied magnetic field.

## RESULTS AND DISCUSSION

### Structural Investigation

The FTIR results indicate that the aromatic C-H stretching (weak) appearing at  $3050\text{ cm}^{-1}$  for the polymer is present in the composites also. The aromatic C-H out-of-plane stretch has not shown any significant shift for the composites. The methyl rock stretch is absent with 10 and 20 wt% composites [1,4]. This may indicate the presence of CH- $\pi$  interaction in the P3HT/MWNT system with C-H stretching frequency region ( $\sim 2850$  to  $2916\text{ cm}^{-1}$ ) for the polymer and the composites, showing a shift to higher frequency, while the frequency at  $1415\text{ cm}^{-1}$  decreases both in intensity and peak position [2]. The situation in the present investigation is presented clearly with regard to aliphatic C-H stretch and aromatic ring stretch in Figure 1, and intensity variation for the  $\nu_{\text{sym}}(\text{C}=\text{C})$  ( $1450\text{ cm}^{-1}$ ) with carbon nanotube contents in the composites in Figure 2. The transmittance intensity decreases with increasing concentration of nanotubes in the polymer matrix. This is quite possible when the polymer is wrapped on to the nanotubes, taking up a rigid orientation through  $\pi$ - $\pi$  stacking. Such observation has been reported for the blend composite involving the moieties [1].

The Raman spectra of MWNT, polymer and its composites are shown in Figure 3. In the case of MWNT, the peak at  $1582\text{ cm}^{-1}$  corresponds to  $E_{2g}$  modes (G line) which are often designated as single-crystal graphite. The additional lines at  $1312$  and  $1611\text{ cm}^{-1}$  are designated as D line and D' line corresponding to disordered carbon [5]. The frequency position of the thiophene ring mode at about  $1462\text{ cm}^{-1}$  has been observed to depend on the conjugation of the poly(alkylthiophene)s, being sensitive to deviation from coplanarity of the chain segments [6]. The shift of G and D line frequencies is seen as a direct consequence of interaction between carbon tubes and the polymer. With no shift, the ratio of D to G line intensities has also been used to predict the interaction. In the case of P3HT, Raman lines are observed at  $1450$  and  $1380\text{ cm}^{-1}$  as dominant peaks. In 1 and 5 wt% composites only polymer peaks are observed with  $1$ – $2\text{ cm}^{-1}$  shift to lower wavenumbers. With 10 and 20 wt% composites, the G and D line frequencies appear altered in position and intensity, besides the polymer peaks. Thus, in the lower percentage of CNTs (up to 5 wt%), the Raman spectrum is more reflective of the polymer rather

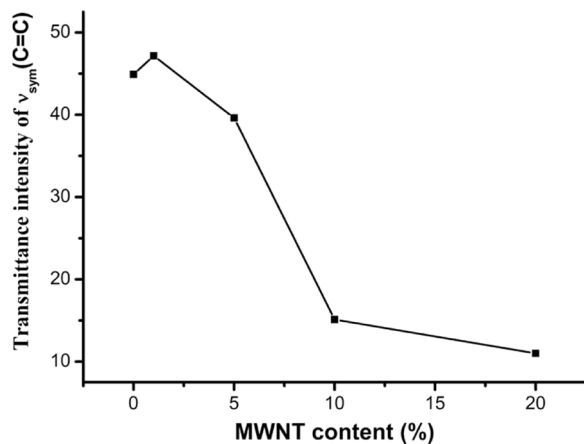


**FIGURE 1** FTIR spectra of P3HT and composites.

than the nanotubes. However with higher concentrations of the CNTs, the presence of the D and G-lines become distinct. The presence of the CNTs in the polymer matrix without much of chemical interaction can be inferred from the Raman results.

### Work Function

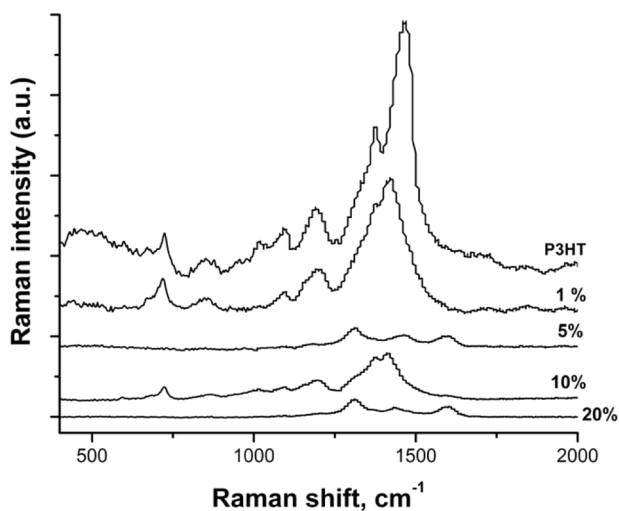
The photoelectron emission (PEE) measurements were carried out for MWNT, the polymer and 20 wt% composite and was found to be 4.72, 4.79, and 4.90 eV, respectively. There is an 0.11 eV increase in work function value when the polymer is wrapped onto the nanotubes, suggesting some weak  $\pi$ - $\pi$  interactions between them in the absence of a strong ground state interaction [7].



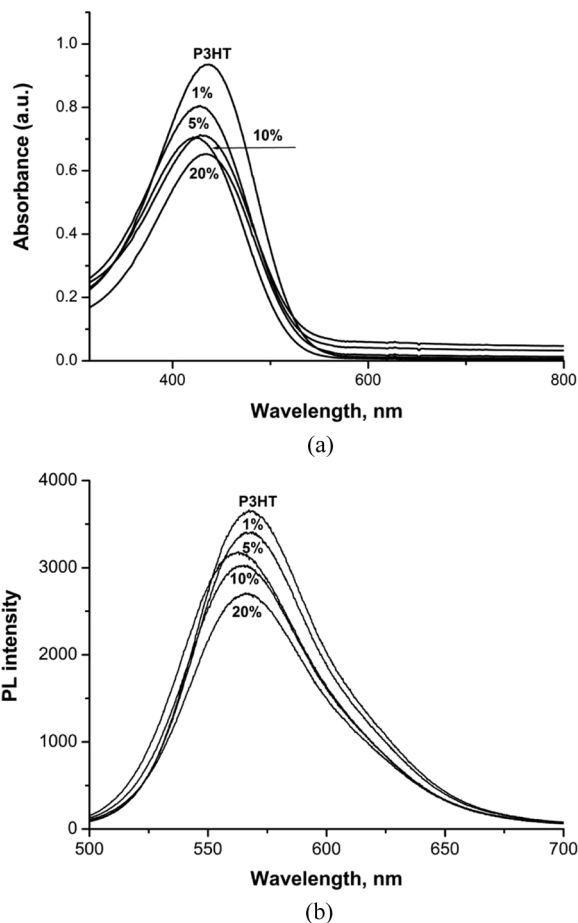
**FIGURE 2** The transmittance intensity variation for the  $\nu_{\text{sym}}(\text{C}=\text{C})$  with carbon nanotube contents in the composites.

### Optical Properties

The UV-vis absorption spectra of P3HT and P3HT/MWNT composites in chlorobenzene are presented in Figure 4a. The  $\lambda_{\text{max}}$  of P3HT was measured to be 435 nm and is as per the literature value [8]. The  $\lambda_{\text{max}}$  values for the composites are found to be shifted by 5 nm at the maximum to the lower wavelength side, except in the case of 10 wt%



**FIGURE 3** Raman spectra of P3HT and composites.

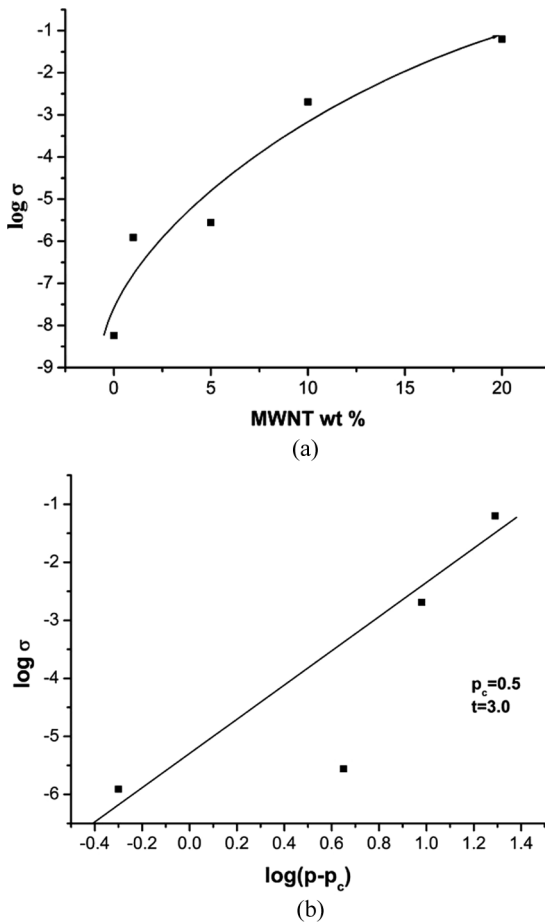


**FIGURE 4** UV-vis (a) and PL (b) spectra of P3HT and its composites.

composite. From the absence of new additional peaks for the composites compared to those of the polymer and with the marginal shift of  $\lambda_{\max}$  values, a lack of any strong ground state interaction may be inferred. Such observations have been reported in the case of P3OT/SWCNT blend composites [9]. The optical band-gap energy value, measured from optical absorbance results for the polymer, is 2.35 eV, and for the composites it is increased by a maximum of 0.1 eV, similar to the trend of work function results.

The PL spectra of P3HT and its composites in chlorobenzene for an excitation wavelength of 450 nm are presented in Figure 4b. The  $\lambda_{\max}$  of PL intensities for the polymer and the composites appear around

$565 \pm 2$  nm. There is about 25% photoluminescence quenching in the 20 wt% composite. The reason for the photoluminescence quenching of the composites may be attributed to  $\pi$ - $\pi$  interactions of P3HT with the nanotubes that form additional decaying paths for the excited electrons. The lack of a maximal luminescence peak shift for the composites from that of the polymer, suggests that the extended molecular packing between the polymer and MWCNT is of a physical nature, and not related to any important configurational relaxation in the excited state [10].



**FIGURE 5** (a) Plot of  $\log \sigma$  vs MWNT contents. (b) Plot of  $\log \sigma$  vs  $\log(p - p_c)$  for P3HT/MWCNT composites at room temperature.



**TABLE 1** Hall Effect Measurement Results

System	Carrier bulk concentration, cm <sup>3</sup>	Carrier sheet concentration, cm <sup>2</sup>	Mobility, (μ <sub>H</sub> ) cm <sup>2</sup> /Vs	Conductivity, S/cm
P3HT	1.962 * 10 <sup>11</sup>	3.923 * 10 <sup>8</sup>	8.850 * 10 <sup>-1</sup>	2.781 * 10 <sup>-8</sup>
P3HT/MWNT (10 wt%)	7.279 * 10 <sup>10</sup>	3.203 * 10 <sup>8</sup>	2.013 * 10 <sup>2</sup>	2.347 * 10 <sup>-6</sup>
P3HT/MWNT (20 wt%)	1.318 * 10 <sup>14</sup>	2.241 * 10 <sup>11</sup>	3.463 * 10 <sup>2</sup>	7.313 * 10 <sup>-3</sup>

## Electrical Properties

The DC electrical conductivity results of P3HT and its composites are presented in Figure 5a. The conductivity of the polymer increases with successive loading of the MWNT in the limits of 1–20 wt %, showing a five-fold increase. In the present case with the as-procured MWNT, the percolation threshold ( $p_c$ ) from DC conductivity measurements is noted to be  $p_c = 0.5$  wt% and  $t = 3.0$ , following model conductivity in the form  $\sigma = \sigma_0(p - p_c)^t$  for  $p > p_c$  (Figure 5b). A value in the range of 2–3 for the exponent is reported for CNT-coated polymer samples, indicating electron transfer by hopping mechanism between isolated polymers and tunneling through the nanotubes for a three-dimensional percolation system [11].

Hall effect measurements are important to semiconductor material characterization because from the Hall voltage, the conductivity type, carrier density and mobility can be derived. The Hall effect measurement results for the polymer and 10 and 20 wt% composites are presented in Table 1. The carrier mobility values were found to increase with increasing carbon nanotube contents in the polymer matrix. This is mainly because of the magnetically assisted enhancement of conductivity due to negative magnetoresistance of the multi-walled carbon nanotubes.

## CONCLUSION

Through the process of insitu polymerization, P3HT/MWNT composites have been prepared with FeCl<sub>3</sub> oxidant in chloroform medium. The prepared composites have good dispersion of the nanotubes, evident from the concurrent dc conductivity values measured for the pellet form of the substance and Hall measurement values measured for the film in 20 wt% compositions. In the absence of any clear tangible shift in the aromatic and C-H stretch frequencies from FTIR results and G and D lines in the Raman spectra, one can infer a weak

$\pi$ - $\pi$  ground state interaction between the polymer and the carbon nanotubes. The UV-vis measurements also support this view. The effective photoluminescence quenching for the composites suggest the formation of an active donor-acceptor interface. The Hall voltage measurements, and the consequent parameters derived from them indicate the usefulness of the semiconducting material in terms of conductivity and carrier mobility of the composites.

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