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Temperature Dependent Spectroscopic studies of HiPco SWNT composites.

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Abstract

Hybrid systems of the conjugated organic polymer poly(p-phenylene vinylene-co-2,5-dioctyloxy-m-phenylene vinylene)(PmPV) and HiPco SWNTs are explored using spectroscopic and thermal techniques to determine specific interactions. Vibrational spectroscopy indicates a weak interaction and this is further elucidated using Differential Scanning Calorimetry, Temperature Dependent Raman Spectroscopy and Temperature Dependent Infrared Spectroscopy of the raw materials and the composite. An endothermic transition is observed in the DSC of both the polymer and the 0.1% HiPco composite in the region of 60°C. Also observed in the DSC of the composite is a doubly peaked endotherm at -39°C and -49°C, which does not appear in the polymer film. The Raman of the polymer backbone upon increasing the temperature to 60°C shows diminished phenyl A_g modes at 1557cm^{-1} and 1575cm^{-1}, with an increase in the relative intensity of the vinyl mode at 1630cm^{-1}. This change in the Raman of the polymer is translated to the Raman of the composite upon increase to 60°C, where the spectrum becomes abruptly dominated by nanotubes. The Raman of the composite shows no change in the lower temperature regions, however infrared suggests that the transition at -39°C derives from an interaction with the polymer side chains. The composite at -39°C shows a change in the absorption of the polymer side chain aryl-oxide linkage at 1250cm^{-1}, while Raman suggests a change to the polymer backbone configuration at 60°C. Implications are discussed.

Keywords: Semi-conjugated polymers, SWNT Composites, Differential Scanning Calotimetry, Infrared and Raman Spectroscopy

1. Introduction

Carbon nanotubes exhibit many unique physical and chemical properties [1]. Due to the electronic and mechanical properties of nanotubes, polymer composites containing tubes have been recently investigated for improved electrical conductivity, optical devices and high strength fibers [2,3]. Thus much work has been done on the investigation of the nature of the interaction within polymer nanotube composites [4-7]. In one proposed system, specific interactions between PmPV and nanotubes have been reported [4-6]. The chemical structure of PmPV has been shown to allow solubility due to the presence of floppy side chains and conjugation along the polymers backbone [5]. The PmPV backbone reorganises into a relatively flat helical structure due to the m-phenelylene linkage and the repulsive interaction between the octyloxy side groups.

It has been shown that the exposure of the backbone plays an important role in facilitating dipolar binding between the polymer and the nanotube, allowing the polymer to π stack onto the nanotube backbone [5]. The trans linkage in the repeat unit is of particular importance, which inhibits polymer aggregation, as all cis conformations have been shown to cause polymer aggegation and inhibit interaction with the nanotube. In this paper to further investigate these systems films of 0.1%wt HiPco/PmPV are investigated using temperature dependent (TD-) vibrational spectroscopy and Differential Scanning Calorimetry (DSC).

2. Experimental

The HiPco SWNTs (obtained from CNI Houston) (0.1% by weight) were mixed in solutions of PmPV(1g/litre) in toluene as in reference 6. DSC measurements were made using a Perkin Elmer Pyris Diamond power compensated DSC. The samples, 0.1% HiPco/PmPV (~5mg) dry composite were placed in closed platinum iridium

crucibles and each sample was run twice (heat at 40°C/min). Raman spectra were obtained using an Instruments SA LabRam IB system. The confocal imaging system uses an argon ion source at 514.5nm. For infrared measurements, samples were drop cast onto slides and spectra were obtained in reflection mode using a Perkin Elmer Spectrum GX FT-IR microscope. Each system was fitted with a Linkam LNP cooling stage for temperature dependent measurements. Measurements were taken every 10 minutes at 5°C intervals from -100°C to 130°C. For Raman measurements the laser was switched off in between samplings. The system was cycled through twice in the same fashion as the DSC to ensure changes in the spectra were reversible or not where the case may be, as discussed in the following section.

3. Results and Discussion

Differential Scanning Calorimetry (DSC) was used to probe the SWNT-PmPV interaction. In fig 1, a broad endotherm is observed in the PmPV thermogram at 51°C in the temperature range of -60°C to 130°C, showing PmPV is semi-crystalline with some degree of order [8]. Introduction of nanotubes shows a similar transition although an increase in the peak temperature to 53°C is observed, which has been reported previously using MWNT composites [8]. Here it has been suggested via spectroscopic analysis as well as microscopy that the nanotubes can act as a template upon which the polymer can self-assemble, consequently increasing the crystallinity of the polymer film at ambient temperatures.
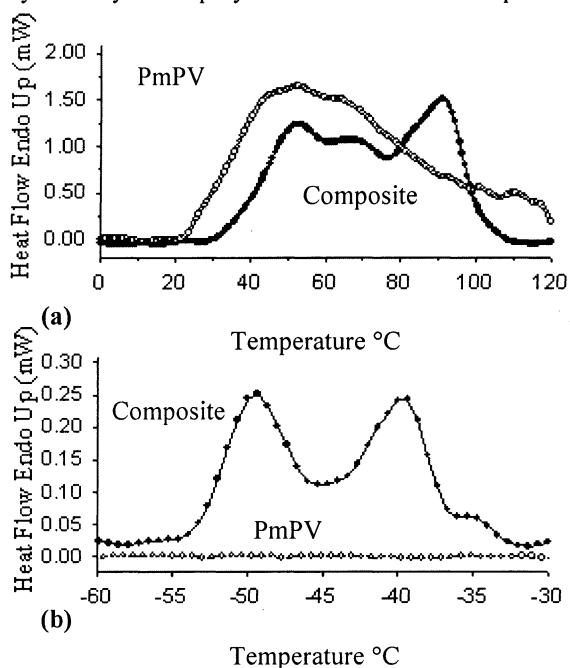

(a)

(b)

Fig 1 Thermogram of the SWNT composite film and the PmPV film for first run at (a); the high temperature regions and (b); the low temperatures regions.

The changes however to the polymer observered in the DSC seem to suggest a strong temperature dependence of this polymer-nanotube coupling. In addition to the changes in the high temperature regime a doubly peaked endotherm at -49°C and -39°C is observed in the composite as shown in fig 1(b), which is not present in the first run of the pristine PmPV film. These transitions are of lower energy than that of the higher temperature transition. It has been previously suggested using atomistic molecular dynamic simulations that the polymer backbone provides the strongest binding to the nanotubes compared to the octyloxy side chains, which is around four times smaller in binding energy [5]. Hence it may be suggested that these lower temperature features arise from the influence of the nanotubes on the polymer side chains i.e. the floppy octoloxy side chains in the composite gain some additional degree of order when dispersed in nanotubes. It is proposed that investigation of the polymer interaction using TD-spectroscopy in particular FTIR and Raman spectroscopy may help to distinguish changes in the side chains from those of the backbone as a consequence of the nanotube polymer environment. It should be noted that the DSC of raw nanotubes shows no transitions within these temperature regions.

In fig 2 the observed structure of the Raman G-line is a result of the superposition of both metallic and semiconducting type nanotubes with different diameters, which has been reported previously for HiPco tubes [9]. The high frequency component of the G line has been fitted using Lorentzian line shapes describing semiconducting tubes [10]. The shape of the lower frequency metallic mode has been described by the Breit-Wigner-Fano (BWF) function ($I(\omega) = I_o\{1+(\omega-\omega_o)/q\Gamma\}^2/\{1+[(\omega-\omega_o)/\Gamma]^2\}$, where I_o, ω_o, Γ, and q are intensity, the BWF peak frequency, broadening parameter, and the asymmetry parameter respectively [11]. As the temperature is increased the line shapes broaden and downshift, which has been reported previously for all modes in the Raman spectrum [12]. The frequency downshift has been mainly attributed to softening on the C-C bond, which results in thermal expansion of the material upon temperature increase [13]. There are no other strong changes in the raw nantoube G-line spectra and shifting is reversible, in this temperature range.

Fig 2(c) presents the PmPV sample, fitted with 6 Lorentzian line shapes at -35°C and 60°C. The vibrational spectroscopy of PmPV is dominated by multiple modes around 1600cm^{-1},where the dominant mode at 1592cm^{-1} has been assigned to stretches within the phenyl ring [4]. The most dramatic change in the polymer upon increase in temperature is the broadening of the frequency distribution and decrease in relative intensity of the A_g phenyl stretch modes at 1555cm^{-1} and 1573cm^{-1}, which is also observed in the PmPV spectra at excitation wavelength 632.8nm (not shown) [14]. Subsequently a change in the relative intensity of the C=C vinyl stretch on the backbone at 1626cm^{-1} [15], which up shifts to 1630cm^{-1} is also observed. On cooling the pristine PmPV

sample does not replicate its original spectrum and in particular the *cis* to *trans* ratio decreases, showing an increase in crystallinity of the polymer sample as a consequence of heating [14].

In fig 2(b) the temperature dependence of the Raman spectrum of the composite is illustrated. Similar to the raw HiPco spectra, metallic and semiconducting contributions are observed at both temperatures. At -35°C strong contributions from the polymer backbone are observed, especially with the presence of the intense mode at 1630cm⁻¹. However the fwhm of each mode has decreased compared to the raw sample, which has been reported previously and is due to the decreased interaction between individual tubes [4][6].
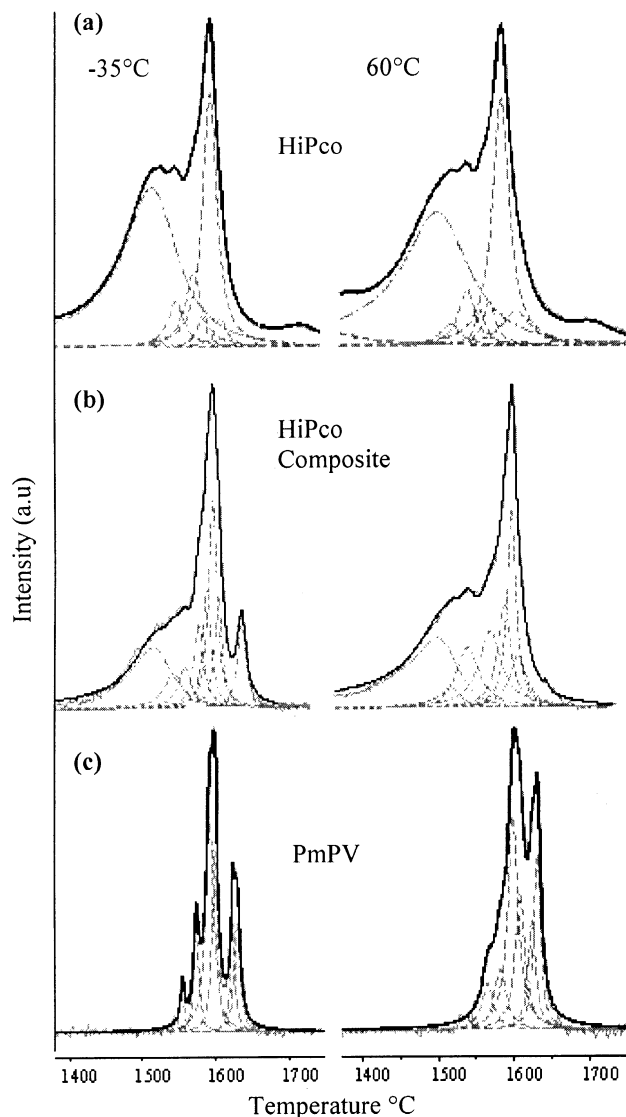
Upon increase in temperature to 60°C the polymer phenyl modes around 1555cm⁻¹ and 1573cm⁻¹ become damped and the Raman spectrum is dominated by nanotubes. The vinyl mode at 1630cm⁻¹ broadens and decreases in intensity. Changes appear to be governed by the disruption to the polymer backbone, which is also observed at laser excitation 632.8nm (not shown) at this temperature [14]. This disruption permits an increase in the tangential vibration of the nanotube backbone, thus altering the spectral properties of the composite upon temperature increase.

In fig 3 the relative intensity of the BWF mode divided by the vinyl mode at 1630cm⁻¹ in the composite was graphed as a function of temperature. It is assumed that only nanotubes contribute to the BWF mode in the composite and only the polymer contributes to the "vinyl" mode in the composite. Upon increase in temperature above 40°C the spectral contribution from the nanotube increases substantially, where at 60°C the ratio of spectral contribution of tube to polymer is roughly 8:1. This abrupt rise is similar to the transition in the DSC at ~60°C. This abrupt change in the relative contribution is interpreted as a dissociation of the polymer from the tube, reducing the damping of the nanotube tangential modes. Although the relative contributions from the *cis* and *trans* modes of the polymer are not discernable in the more complex composite spectrum, upon cooling the relative intensities do not return to their original positions [14]. This indicates that the nanotube-polymer backbone binding has been altered upon cooling. If the composite is governed by the behaviour of the polymer at a specific temperature this indicates an increase in crystallinity of the polymer within the composite as all *trans* PmPV has been shown to facilitate polymer-tube binding while all *cis* conformations cause polymer aggregation which inhibits polymer-tube interaction [5]. No significant changes in relative intensities to the composite backbone appear to occur in the lower temperature region.
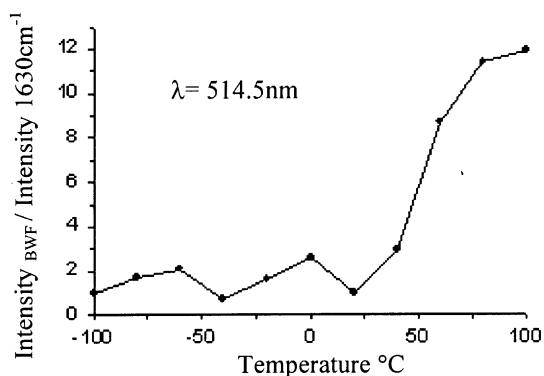

Fig 2. Temperature Dependent Raman spectra at 514.5nm at -35°C and 60°C of (a); Raw HiPco (b); 0.1% HiPco Composite and (c); PmPV

Fig 3. Intensity BWF/ Intensity 1630cm⁻¹ as a function of temperature for HiPco composite at 514.5nm

Temperature dependent infrared spectroscopy was carried out on all samples. The FTIR spectrum of

carbon nanotubes (not shown) agreed with literature [16] three main features at 1600cm^{-1}, 1400cm^{-1} and 1180cm^{-1} which have been attributed to the C-C and C=C stretching along the hexagonal array of the nanotube backbone, were observed [16]. In fig 4 the composite IR spectrum is dominated by the polymer and the nanotube modes within this wavelength range are overshadowed. Strong contributions from the polymer octyloxy side chains are seen. In particular the aryl-oxide stretch between 1230cm^{-1} and 1270cm^{-1} and the alkyl-oxide stretch between 1020cm^{-1} and 1075cm^{-1} are observed. For both the polymer and the composite these peak positions shift to a lower wavenumber as the temperature increases [14].
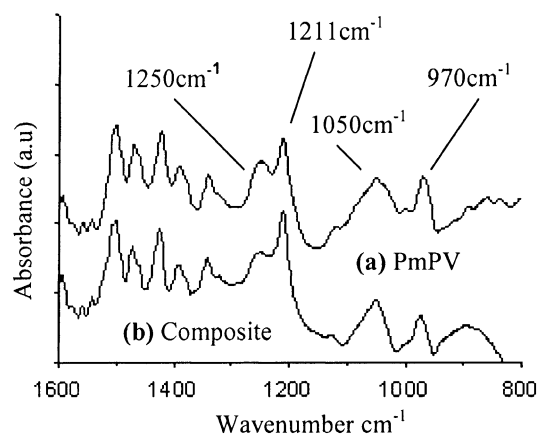

Fig 4. Infrared spectrum at ambient temperatures for (a) PmPV, (b) 0.1%HiPco composite.

In fig 5 the absorbance of the aryl-oxide stretch is graphed as a function of temperature for both PmPV and the composite for the first heating cycle at the lower temperatures. The side chains shows no changes for the polymer, however the composite graph shows an abrupt decrease in absorbance at about -40°C. This further suggests that transitions in the DSC at the lower temperatures originate from the side chains
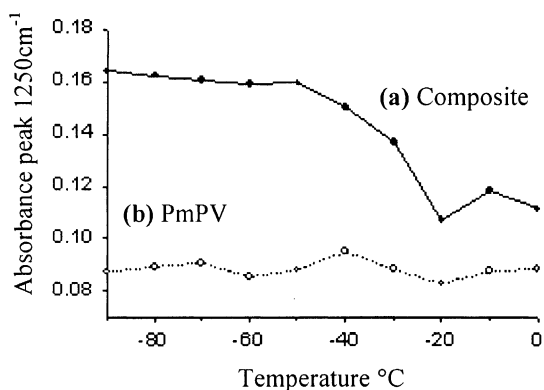

Fig 5. Absorption of the aryl-oxide stretch around 1250cm^{-1} as a function of temperature for (a); the composite and (b); PmPV for first heating cycle only.

4. Conclusions

Modifications to the vibrational spectra of the polymer and composite are observed with a change in temperature. The IR of the composite shows an abrupt change in the absorbance of the octyloxy side chains at -40°C, and such modifications may help to explain the doubly peaked transitions in the DSC at the lower temperatures. Upon heating the composite from -35°C to 60°C the Raman of the composite becomes abruptly dominated by nanotubes, suggesting that the polymer backbone dissociates and the nanotube tangential modes are no longer damped. The irreversibility of the process supports proposals that temperature cycling increases the crystallinity of the polymer seeded by the binding to the nantube [8].

Acknowledgments

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