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Sinead Keogh

Technological University Dublin

Theresa Hedderman

Technological University Dublin, Theresa.Hedderman@tudublin.ie

A. Maguire

Trinity College Dublin

See next page for additional authors

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Authors

Sinead Keogh, Theresa Hedderman, A. Maguire, M. G. Ruther, Elizabeth Gregan, Gordon Chambers, and Hugh Byrne

The Physical Interactions between HiPco SWNTs and Semi-Conjugated Polymers

¹S.M. Keogh, ¹T.G. Hedderman, ¹A. Maguire, ²M.G. Rüther, ¹E. Gregan, ¹G. Chambers, ¹H.J. Byrne.

¹*Facility for Optical Characterisation and Spectroscopy (FOCAS), School of Physics, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland*

²*Materials Ireland, Physics Department, Trinity College Dublin, Dublin 2, Ireland*

Abstract. Hybrid systems of the conjugated organic polymer poly (p-phenylene vinylene-co-2,5-dioctyloxy -m-phenylene vinylene) (PmPV) and HiPco SWNT 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 and Temperature Dependent Raman Spectroscopy. Two distinct transitions in region of -60°C and + 60°C are investigated.

INTRODUCTION

Single walled carbon nanotubes (SWNTs) exhibit many unique physical and chemical properties [1]. Although there are many different methods for SWNT synthesis, none have been successful in producing 100% pure SWNTs in large quantities. HiPco samples contain a high amount (90%) of high purity (99%) SWNTs [2]. The diameter distribution is predominantly 0.7nm-1.2nm (average diameter of 1nm[2]). Specific interactions between arc-discharge SWNT within polymer composites have been documented [3][4]. This proposed system for purification uses the organic semi-conjugated polymer poly (p-phenylene vinylene-co-2,5-dioctyloxy-m-phenylene-vinylene) (PmPV). 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, which allows wrapping of the polymer around the nanotubes [3]. Although the exact nature of interaction has not yet been clearly defined, in this proposed system the polymer maps onto the nanotube lattice in a periodic and well-defined manner [4]. In this study hybrid systems of the organic conjugated polymer PmPV (provided by Trinity College, Dublin), and HiPco from toluene solution are explored in order to further elucidate the specific nature of the interaction. Temperature dependent Raman (T.D.Raman) spectroscopy at 514.5nm in conjunction with Differential Scanning Calorimetry (DSC) are employed to obtain thermal measurements of the composite.

EXPERIMENTAL

Composites of HiPco SWNTs (0.1% by weight) were mixed in 1g/L of PmPV in toluene. The composites were sonicated for 10 hours, left to stand for 48 hours and then decanted. Films were made by drop casting onto glass slides and characterised by the (Instruments S.A Labram 1B) Raman system and a Pyris Diamond DSC from Perkin Elmer.

RESULTS

Differential Scanning Calorimetry (DSC) was used to study the thermal properties of the composites by monitoring the thermodynamics of the system as it passes through phase transitions. Fig 1(a) shows a thermogram of the nanotube composite and pristine polymer from the temperature range of -55°C to -30°C . Fig 1(b) shows thermograms of the nanotube composite and pristine polymer from the temperature range of 30°C to 60°C . These broad features between 30°C and 60°C are due to the melting of the polymer backbone and are present in both the composite and pristine polymer thermograms. The composite shows a new doubly peaked endotherm between -30°C and -50°C , which is not present in the pristine polymer thermogram, and as there are no distinct features in the thermogram of raw tubes this new feature is proposed to be due to an interaction between the polymer and the nanotubes. Therefore there are three distinct regions of interest in the composite. **A**: this is before the composite peaks occur in the thermogram. **B**, this is after the composite peak and before the melting of the polymer backbone, and **C**, this is after the polymer backbone has melted. These three regions were further investigated using temperature dependant Raman spectroscopy at 514.5nm in order to gain a greater understanding of the changes that occur in the thermograms. Figure 2 presents temperature dependant Raman spectrum at 514.5nm for the 0.1% HiPco composite. The spectra correspond to points labeled **A**, **B** and **C** in the thermograms.

Transition 1: Changes in composite only

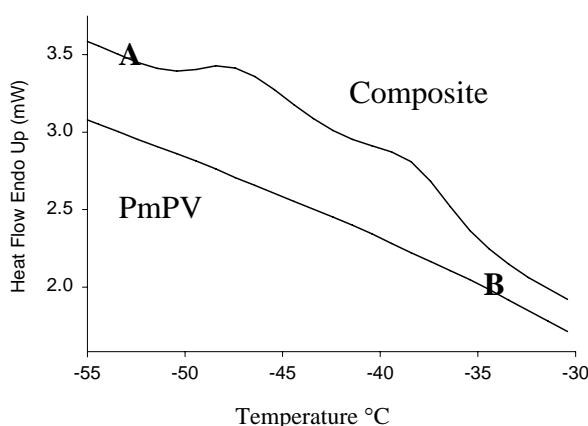


Figure 1(a). Thermogram of the SWNT Composite showing low temperature regions

Transition 2: Broad features occur in composite and Polymer

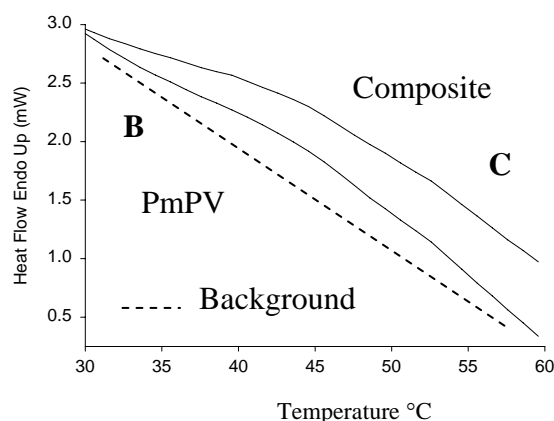


Figure 1(b). Thermogram of the SWNT Composite showing high temperature region

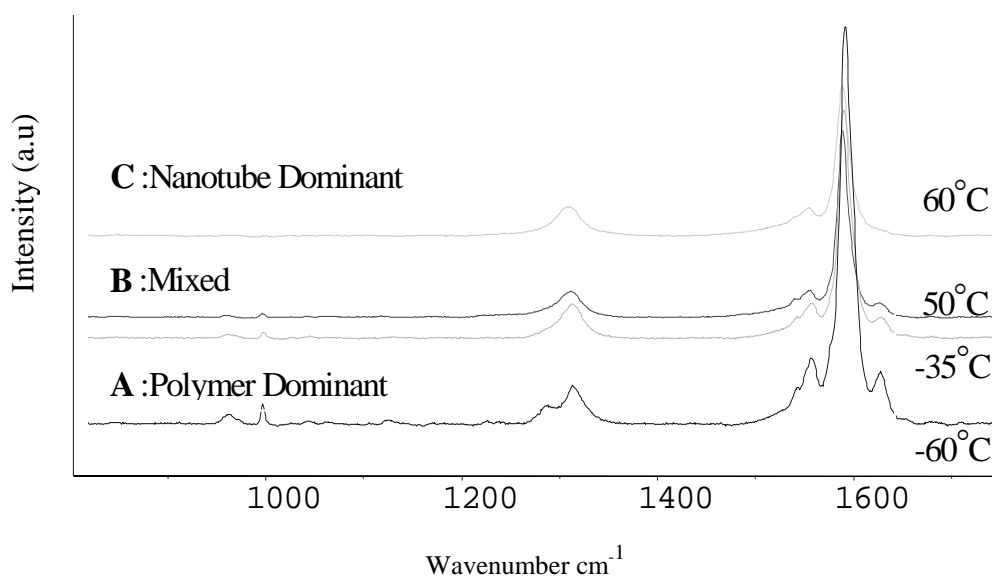


Figure 2. Temperature Dependant Raman spectra at 514.5 nm of the HiPco SWNTs in polymer composites

Region A: Polymer Dominant Composite Spectrum

Spectrum A (-60°C) corresponds to region A in the thermogram. Two distinct polymer peaks are present at 960cm^{-1} and at 1000cm^{-1} , which are also present in the pristine polymer Raman spectrum. These peaks are more dominant at lower temperatures and are attributed to the vibration of the side chains of the polymer. It is noted that at -35°C the peak at 960cm^{-1} has almost vanished, suggesting that the polymer side chains have melted. The D-line region of the composite has a peak at 1312cm^{-1} and a shoulder at 1283cm^{-1} . This doubled peak feature is due to the combination of the polymer's phenyl ring and double bond stretching and occurs also in the pristine polymer Raman spectrum. The shoulder at 1283cm^{-1} is no longer present at 50°C . In the G-line region of the composite six peaks are present at 1541cm^{-1} , 1557cm^{-1} , 1577cm^{-1} , 1591cm^{-1} , 1627cm^{-1} and 1653cm^{-1} . This is similar to the pristine polymer, but the relative intensities have changed. The peaks at 1627cm^{-1} and 1577cm^{-1} are less intense in the composite than in the pristine polymer.

Region B: Mixed Composite Spectrum

Traditionally presented Raman spectra occur between the temperatures of -35°C and 50°C , labeled B in figure 2. This corresponds to the temperature after which the composite peaks occur in the thermogram. Composite A differs from composite B, as the polymer is no longer dominating the spectrum. Here the G-line region presents peaks at 1627cm^{-1} , 1589cm^{-1} and 1555cm^{-1} and shows a mixed polymer/tube contribution. The composite peak at 1627cm^{-1} is less intense. The D-line region shows

a peak present at 1312cm^{-1} , the shoulder at 1283cm^{-1} is no longer present. Also there is a decrease in intensity of the polymer peak at 1000cm^{-1} .

Region C: Nanotube Dominant Composite Spectrum

Spectrum C corresponds to region C in the thermogram, which is dominated by changes in the pristine polymer. The composite spectrum is dominated by nanotubes, suggesting that the nanotubes tangential modes are no longer restricted due to change in the pristine polymer. The polymer peaks at 960cm^{-1} , 1000cm^{-1} , and at 1283cm^{-1} are no longer present and the D-line is symmetrical. This is similar to a raw nanotube Raman spectrum, however the composite peak at 1627cm^{-1} is still present but less enhanced.

CONCLUSION

From the DSC and Raman results obtained, it is clear that as the temperature of the composite changes so does its interaction properties. It can be concluded that three different composite types occur between the temperature ranges of $-60\text{ }^{\circ}\text{C}$ and $+60\text{ }^{\circ}\text{C}$. At $-60\text{ }^{\circ}\text{C}$, the composite presents a Raman spectrum which is dominated by the polymer. This suggests that the polymer is restricting the nanotubes tangential modes from vibrating. At $-35\text{ }^{\circ}\text{C}$, after the first transition in the thermogram, which only appears in the composite, the Raman spectra becomes mixed, suggesting that the polymer has a weaker interaction with the tubes than at $-60\text{ }^{\circ}\text{C}$. Raman spectroscopy suggests side chains are involved in this interaction as they are not as intense in the Raman spectrum at $-35\text{ }^{\circ}\text{C}$. At $60\text{ }^{\circ}\text{C}$, after the second transition, the composite is influenced by the melting of the polymer. The Raman spectrum of the composite is dominated by nanotubes, suggesting that the polymer backbone is also involved in this interaction. Raman spectroscopy suggests that both the polymer side chains and the polymer backbone are involved in composite formation, but as the temperature is increased the interaction becomes weaker.

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