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Synthesis and characterization of styrene grafted carbon nanotube and its polystyrene nanocomposite

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Abstract

Effective side wall functionalization of single-walled carbon nanotube (SWCNT) with 4-vinylaniline was carried out through solvent free functionalization. The functionalized SWCNT was characterized through FT-IR and NMR. Typical peaks to identify the functionalization were observed. Thermal analysis shows around 48% weight loss in functionalized SWCNT in comparison to the pure SWCNT. The ratio of disordered to order transition (I_D/I_G) in FT-Raman, indicated the generation of some surface defects due to functionalization. Near infrared spectrum of functionalized SWCNT also confirmed the functionalization of SWCNT. The polystyrene nanocomposite materials were prepared with functionalized SWCNT as fillers by solution casting from tetrahydrofuran. The functionalized SWCNT nanocomposite showed significant improvement in mechanical properties and electrical properties. The dispersibility of the carbon nanotube in the composite was investigated by using scanning electron microscopy.

Keywords: SWCNT; Functionalization; Composite; Electrical properties; TGA; FESEM

1. Introduction

Due to high mechanical strength, high aspect ratio, small diameter, light weight, high electrical and thermal conductivities, and high thermal and air stabilities [1–11], carbon nanotube (CNT) has been considered as ideal reinforcing fillers in nanocomposite materials. The mechanical properties of thermosets, such as epoxy resins [6,12–16], and thermoplastic polymers, such as poly(hydroxyaminoether) [17,18], polypropylene (PP) [19], and poly(methyl methacrylate) (PMMA) [20] have been enhanced significantly with the addition of CNT. CNT composites also show dramatic improvements in electrical conductivity with a percolation threshold below 1% of CNT concentration [21–25]. The addition of 1 wt% multi-wall carbon nanotubes (MWCNT) to polystyrene (PS) has been demonstrated to increase the elastic modulus and stress at break in comparison to pure PS [26]. Safadi et al. [27] also studied PS/MWCNT composites, showing a 40% increase of modulus with 1 wt% concentration and a percolation threshold

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for conductivity at concentrations below 1 wt%. Chang et al. [28] showed higher electrical conductivity and high mechanical properties (20–30% increment) for annealed single-wall carbon nanotube (SWCNT)/PS composites.

The development of CNT–polymer nanocomposite has been impeded by the lack of dispersibility of SWCNTs, which typically appears as ropes, in the polymer matrix due to the lack of chemical compatibility between the polymer and the SWCNTs [18,20,29]. A cursory summation of important areas for composites with SWCNTs would include homogeneity of dispersion, interfacial compatibility with the matrix, and the exfoliation of SWCNT ropes and bundles. Chemical functionalization of SWCNTs may help address all of these concerns by the attachment of appropriate moieties to the surface of SWCNTs. Tour et al. have shown that the electro chemical reduction of diazonium salts [30] and thermally generated diazonium compounds [31] readily functionalized SWCNTs. Later this group suggested a solvent free technique for functionalization of SWCNTs in large scale [32]. Recently authors reported MWCNT functionalization through atom transfer radical polymerization (ATRP) [33]. In ATRP method we have used solvent as well as some ATRP reagent which is required plenty of synthetic skill to handle those chemicals. So we have adapted here the solvent free as well as quick and simple functionalization scheme for chemical modification of SWCNT without damaging the nanotube structure.

The major goals of this work include (i) chemical modification of SWCNTs with styrene monomer in solvent free technique, (ii) characterization of the functionalized SWCNTs, (ii) preparation of polystyrene–SWCNTs polymer nanocomposite, and (iv) to study their mechanical and electrical properties.

2. Experimental

2.1. Materials

SWCNTs used for this study was produced via chemical vapor deposition (CVD) and purchased from Carbon Nanotechnology Inc. (CNI). Polystyrene (Mw $\sim$ 350,000), 4-vinylaniline, sodium nitrite, hydrochloric acid, dimethyl formamide (DMF), tetrahydrofuran (THF) were obtained from Aldrich Chemical Company.

2.2. Characterization

Thermogravimetric analysis of pure and functionalized carbon nanotube were done in the nitrogen environment using Perkin-Elmer thermogravimetric analyzer (TGA 7) in the temperature of 25–850 °C at a heating rate of 10 °C/min. Fourier transform infrared spectra (FT-IR) were recorded using Perkin-Elmer FT-IR 2000 spectrometer in the range of 400–4000 cm^{-1} at the resolution of 4.0 cm^{-1}. Structural characterization of styrene grafted CNT dispersed in $CDCl_3$ was done using 300 MHz ^1H NMR (JNM-AL 300, JEOL, Japan). Morphological characterizations of pure and functionalized CNTs were carried out using Stereoscan 440 field emission scanning electron microscopy (FE-SEM) (Leica Cambridge, England). The samples for FE-SEM were prepared by dip coating of a dilute solution of polymer grafted carbon nanotube in THF on silicon wafer. Raman spectra were recorded on RFS-100/S (Bruker, Germany) Raman spectrometer equipped with a charge coupled device (CCD detector) and 1064 nm laser excitation. Near infrared spectra (NIR) were obtained using V-550 near infrared spectrometer (Jasco co., Japan) in the range of 200–2500 nm. The samples for NIR were prepared by dip coating of a dilute solution of functionalized carbon nanotube in THF on glass slide.

Flexural modulus tests were carried out as ASTM D 790 using Instron universal testing machine (Model No. 5844) at a cross head speed of 10 mm/min at room temperature. The tensile property measurement was performed in an Instron tester (Model No. 5844) at a cross head speed of 50 mm/min at 25 °C as ASTM D 638. The average values of five test results are reported.

The morphology of the composites was studied by a scanning electron microscope (STEREOSCAN 440, LEICA, Cambridge Ltd., England) at an accelerating voltage of 3KV and in low vacuum mode. The images were taken at nitrogen pressure between 0.3 and 0.5 mBar.

The room temperature electrical conductivity of the composite films was measured using the two probe technique in KEITHLEY 2000 Digital Multimeter. The ohmic behavior was checked in each case.

2.3. Functionalization of SWCNT

0.1 g (8 mmol) of pure SWCNT with 3.97 g (4 equiv/mol of carbon) of 4-vinylaniline and

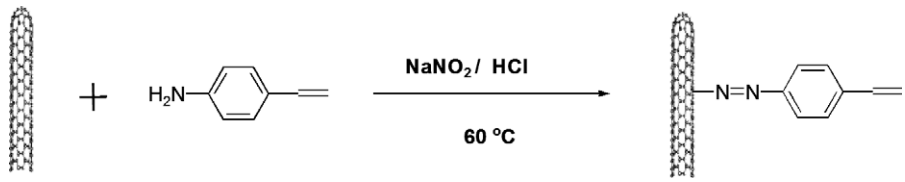

Fig. 1. Reaction scheme for functionalization.

50 ml of 1 M HCl were taken in a two neck round bottom flask equipped with a reflux condenser and a magnetic stir bar. 2.3 g (4 equiv/mol of carbon) of sodium nitrite was added and it is stirred at 60 °C for 12 h. The paste formed was diluted with DMF and then filtered. The collected solid was washed several times with DMF and water until the filtrate became colorless (see Fig. 1 for reaction scheme).

2.4. Preparation of polystyrene based nanocomposite films

The functionalized SWCNT was dissolved in THF and ultrasonicated for 5 min (Ultrasonic Processor, 20 kHz) to get a good dispersion. The SWCNT-THF solution was then mixed with THF solutions of 10% PS to yield the SWCNT/PS mixtures with different SWCNT/PS concentrations. These solutions were homogenized by mechanical stirring for 1 h. For comparison, the pure SWCNT/PS samples were made using same procedure mentioned above.

The so-obtained SWCNT solution was poured into a Petri dish and heated to 90–100 °C for solvent removal. These dishes were then placed into a low pressure (25 in. Hg) vacuum oven at 100 °C for 24 h for additional solvent removal. After drying, the material was cooled to ambient temperature and then broken into smaller pieces. These pieces were then pressed into sheets with a thickness of 0.5 mm for electrical and 2–3 mm for mechanical measurements.

3. Results and discussion

The SWCNTs are functionalized with 4-vinyl aniline using solvent free functionalization and the product is characterized by FTIR and NMR spectrum. Fig. 2 shows the representative FTIR spectra for pure SWCNTs and grafted SWCNTs. The peaks at 690, 1600, 3062 cm^{-1} are correspond to the styrene ring vibration, unsaturation sites in the benzene ring and –CH stretching of aromatic ring respectively. The diazoreaction mechanism is noticed by getting the peaks at 1265 and 1560 cm^{-1} which correspond to the C–N and N=N stretching vibrations, respectively.

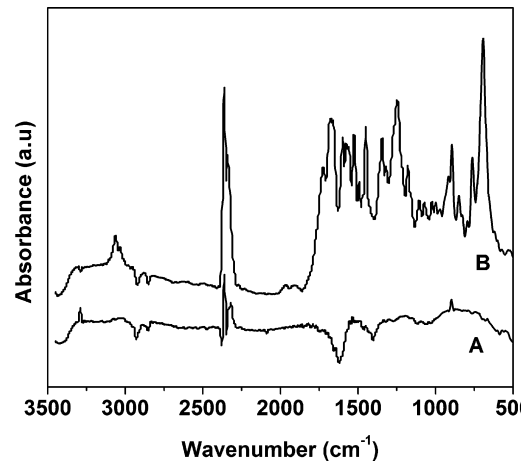

Fig. 2. FTIR spectra for (A) pure SWCNT and (B) functionalized SWCNT.

The grafting reaction is further confirmed by ^1H NMR spectrum. Fig. 3 shows the representative ^1H NMR spectrum for grafted SWCNT. The vinyl proton of the styrene group appears at 5.7 (–CH=CH_2)

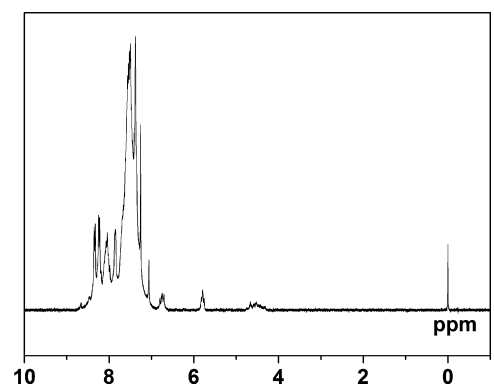

Fig. 3. ^1H NMR spectrum of functionalized SWCNT.

and 6.9 (–C*H*=CH_2). The aromatic proton appears in between 7.1 and 7.5.

The TGA analysis provides further evidence for the functionalization (Fig. 4). A minimum of 5% weight loss is observed up to 850 °C for pure SWCNT where as 48% of weight loss is observed for functionalized SWCNT, confirming the grafting of 4-vinylaniline monomer onto the carbon nanotube surface.

Fig. 5 shows Raman spectra for pure SWCNT and functionalized SWCNT. The characteristic peaks such as tangential mode (G band) appears at ~1590 cm^{-1} and disorder mode (D band) sp3 modes appear at 1295 cm^{-1}. The ratio of disordered to order transition (I_D/I_G) in FT-Raman gives valuable information regarding the effectiveness of the functionalization. The I_D/I_G value increases from 0.3 (SWCNT) to 0.49 in functionalized SWCNT indicating the generation of some surface defects due to functionalization which also confirm the covalent modification.

Qin et al. [34] showed that functionalization of CNT could alter the electronic properties. Near infrared spectroscopy provides useful information about the electronic structure of the SWCNTs. The near IR absorption spectrum contains peak due to Van Hove singularities, which are band gap transitions in semiconducting nanotubes from about 800 to 1400 nm. If the nanotubes modified with covalent functionalization, creating much larger compounds, these bands recede with smoother curve appears in the NIR spectra [32,34]. Fig. 6 shows NIR absorption spectra for pure and functionalized SWCNTs. The peak in the range of 800–1400 nm is weaker in case of functionalized SWCNTs indicating small change in electronic structure due to functionalization.

Fig. 7 shows the FESEM images of pure and functionalized SWCNTs. The functionalization of SWCNTs significantly alters the surface roughness of the nanotube surface. The length of the nanotube is significantly decreased due to functionalization. Increase in diameter of the SWCNT also confirms the functionalization.

For brittle material such as polystyrene, flexural measurement is an appropriate method to test the mechanical property. Fig. 8 shows the flexural moduli of PS/SWCNT nanocomposite and PS/functionalized SWCNT nanocomposite with different SWCNTs concentration. Compared with the pure PS/SWCNT composites, the flexural modulus of

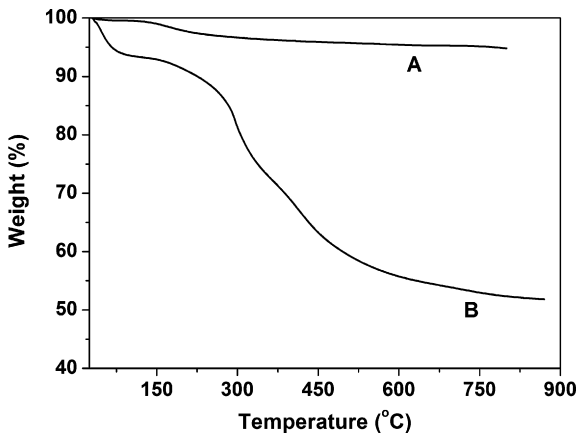

Fig. 4. TGA analysis for (A) pure SWCNT and (B) functionalized SWCNT.

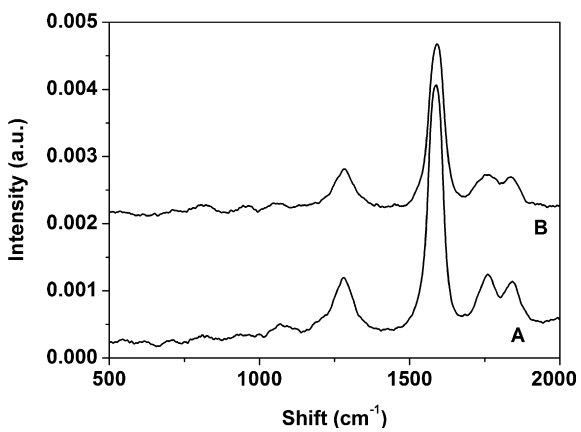

Fig. 5. Raman spectra (1064 nm excitation) of (A) pure SWCNT and (B) functionalized SWCNT.

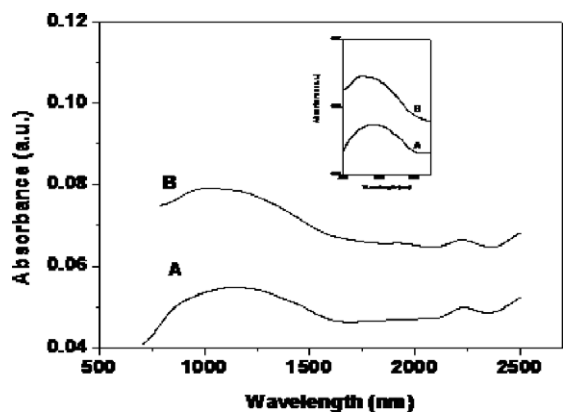

Fig. 6. Near IR spectra of (A) pure SWCNT and (B) functionalized SWCNT; inset is the same figure within the range 800–1800 nm.

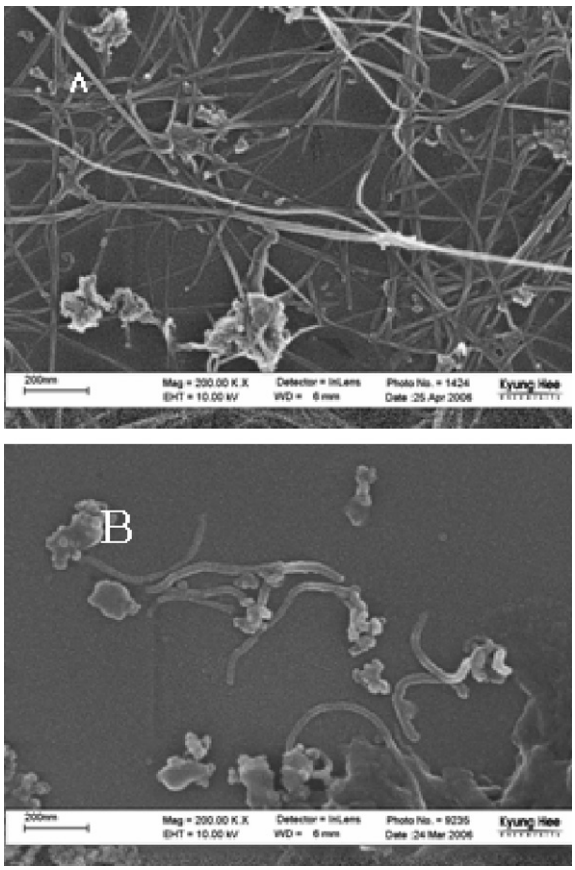

Fig. 7. FE-SEM images of (A) pure SWCNT and (B) functionalized SWCNT.

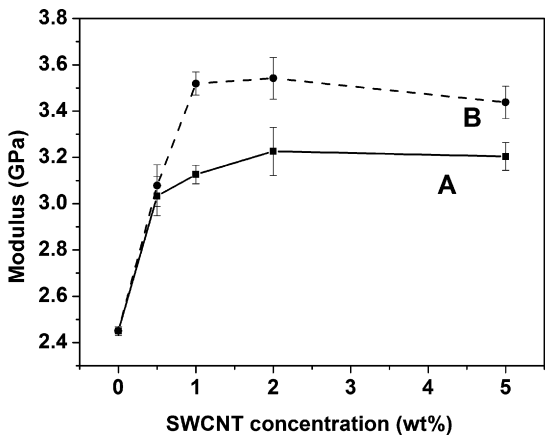

Fig. 8. Dependence of the flexural modulus on the concentration of the (A) pure SWCNTs and (B) functionalized SWCNTs.

the PS/functionalized SWCNTs composite increases by about 35–45% by the addition of 1 wt% functionalized SWCNTs. Surface functionalization of carbon nanotube by introducing styrene group on the SWCNT surface leads to the improved adhesion between SWCNT's and polystyrene matrix and thereby leads to the stress transfer from the weaker polystyrene matrix to the stronger nanotubes and thereby results in higher flexural strength of the resultant composites.

Fig. 9 shows the tensile strength of the PS/SWCNT nanocomposite as a function of SWCNTs loading. The tensile strength of the polystyrene/SWCNT and polystyrene/functionalized SWCNT nanocomposite increases with increase in filler loading and it tends to level off after 2 wt%. However, it is interesting to note that around 60% enhancements in tensile strength are observed for functionalized SWCNTs over pure SWCNTs nanocomposites. Earlier reports on the molecular dynamics simulation studies of PS/SWCNT nanocomposites reveal that the aromatic rings in the side chain rotate away from the CNT surface and the aromatic rings align parallel to each other that leads to the small non-bond interactions consists of electrostatic and van-der Waals interaction. This results in slight improvement of tensile strength of the PS/CNT nanocomposites. The introduction of styrene groups on the surface of CNT leads to the parallel alignment of aromatic rings in the PS chains and thereby providing higher interfacial adhesion between the functionalized SWCNT and polystyrene matrix [35] that leads to the effective load transfer between the CNT surface and PS matrix and thereby results in higher tensile strength over the range of CNT loading.

The SEM image for the tensile fractured surfaces of 2 wt% pure and functionalized SWCNT–PS nanocomposite films has been taken and is included

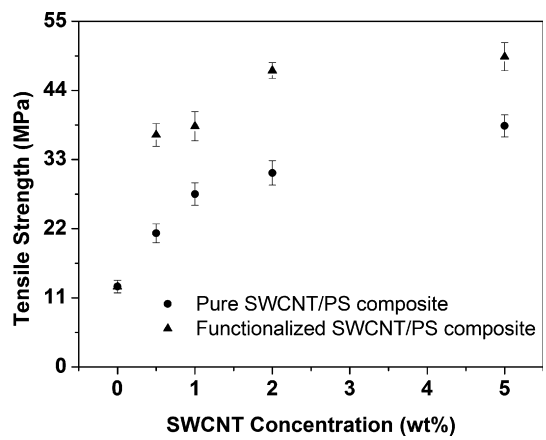

Fig. 9. Dependence of the tensile strength on the concentration of the pure SWCNTs and functionalized SWCNTs.

in Fig. 10. The bright dots present in the fractured surface are the ends of broken SWCNTs, demonstrating that the nanotubes break apart rather than just be pulled out from the fracture surface; similar observations are also noticed elsewhere [36,37]. The bright dots are more prominent and uniformly distributed in functionalized SWCNT–PS composite as compared to pure SWCNT–PS composite, which gives confirmation of the better dispersion of nanotube in the polymer matrix.

The electrical conductivity of the polystyrene/functionalized SWCNT nanocomposite has been measured using digital multimeter and the results are represented in Fig. 11. The electrical conductivity of the polystyrene/SWCNT nanocomposites have been increased with filler loading. The volume conductivity of 2% loaded polystyrene/functionalized SWCNT composite is 3.67×10^{-6} S/cm, in comparison with 1×10^{-7} S/cm for polystyrene/pure SWCNT composite (not shown in the figure). This result also confirms the well dispersion of functionalized SWCNTs in PS polymer matrix. The introduction of nanotubes increases the conductivity of the composite by up to six orders of magnitude, being the measured conductivity of the pure polystyrene 10^{-7} S/cm. Earlier reports reveal that the 1.5 wt% loading of SWCNT in polymer matrix exhibits the percolation threshold [38]. However, in the present investigation, filler loading has been varied as 1.0 and 2.0 wt% SWCNT and it is observed that the composite conductivity displays a dramatic increase. This is clearly understood by the sudden rise in electrical conductivity from 0.77×10^{-6} S/cm (1 wt% functionalized SWCNT) to 3.67×10^{-6} S/cm (2 wt% functionalized SWCNT). This indicates that for weight fractions of SWNTs below 1.0 wt%, the nanotubes are almost isolated and the electrical conductivity governed by the electrical characteristics of the polymer. As the fraction of SWCNTs increases further, the average distance between the nanotubes becomes sufficiently small for electrons to tunnel through the polymer or by contact between nanotubes that result in drastic increase in electrical conductivity of the polystyrene nanocomposites.

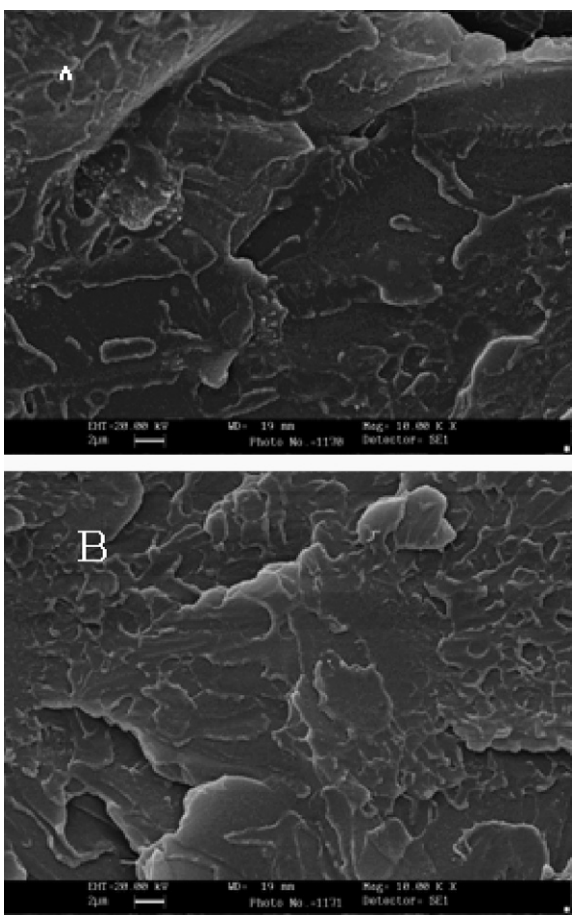

Fig. 10. SEM images of tensile fracture surface of 2% (A) pure SWCNT–PS composite and (B) functionalized SWCNT–PS composite.

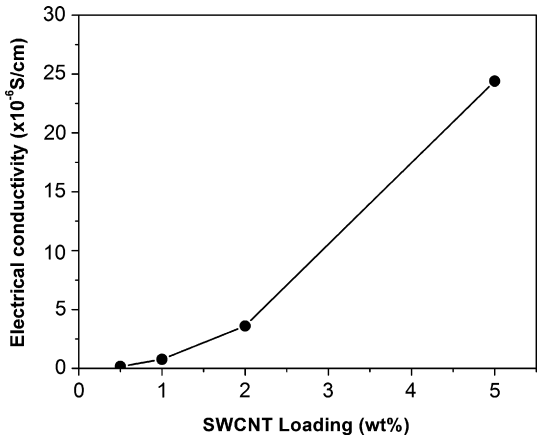

Fig. 11. Room temperature PS–functionalized SWCNT composite volume resistivity as a function of SWCNT concentration.

4. Conclusion

Functionalized SWCNTs is prepared by solvent free technique and is confirmed by FTIR and NMR. Significant weight loss in TGA for functionalized SWCNTs also give indication for graft of 4-vinylaniline onto surface. Higher degree of disorderness in Raman spectra also justifies the

covalent modification. FESEM images give qualitative indication for functionalization of the SWCNTs. Higher flexural modulus, tensile strength and electrical property is observed for functionalized SWCNT polymer nanocomposite and those confirm the improved compatibility and dispersibilty between SWCNT and PS due to the presence of 4-vinylaniline on the surface.

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