iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL
FOR RESEARCH
IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 2 Issue: XI Month of publication: November 2014

DOI:

Electrical conductivity of multi-walled carbon nanotubes doped conducting polythiophene

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***Abstract:** To improve the functions of conducting polymers, the fabrication of multifunctional conducting polymer Nano composites has attracted a great deal of attention with the advent of carbon nanotubes (CNTs). Addition of CNTs in the matrix of conducting polymers changes their behaviour mostly towards the electrical conductivity. In this paper we report the influence of functionalized multi-walled carbon nanotubes (MWCNTs) on conductive properties of conducting polymer polythiophene (PTH). Nano composites based on multi-walled carbon nanotubes were synthesized by in-situ oxidative polymerization of thiophene monomer in the presence of functionalized CNTs. These Nano composites have been characterized by UV-VIS, FTIR, XRD and SEM to study the effect of incorporation of MWCNTs on the morphology, structure and crystalline of the conducting polythiophene. Addition of functionalized CNTs to the polymer matrix helps the polymer material to settle down on the walls of CNTs. The interaction between the quinoid ring of PTH and the MWCNT causes PTH chains to be adsorbed at the surface of MWCNT, thus forming a tubular core surrounding the MWCNT. Nano composites show high electrical conductivity compared to pure PTH. The enhancement in conductivity of the Nano composites is due to the charge transfer effect from the quinoid rings of the PTH to the MWCNT. The effect of MWCNT on the transport parameters of PTH was also studied. By comparing the transport parameters of PTH and PTH-CNT Nano composites, charge localization length (α^{-1}) and most probable hopping distance (R) were found to be decreased with high wt % of CNT in PTH-CNT Nano composites, whereas the charge hopping energy (w) was found to be increased. These results show that the addition of CNT in PTH matrix, improved the electrical properties of PTH and such Nano composites are most suitable advanced materials for electronic devices.**

***Keywords:** Multi-walled carbon nanotube, conducting polymer, polythiophene, Nano composites, conductivity.*

I. INTRODUCTION

Nano composites based on conducting polymers and carbon nanotubes have gained great interest for their unique physical chemistry properties. An interesting application can be the embedding of little quantity of CNTs inside the polymer matrix of conducting polymers for the fabrication of nanocomposites which can be carried on by polymerizing the monomer in the presence of a dispersion of CNTs, is very simple **[1]**. In 1977, the discovery of semiconducting and metallic properties of polyacetylene by A.G. MacDiarmid, A. J. Heeger, H. Shirakawa and coworkers **[2, 3]** elicited a tremendous research activity. Many researchers in the field chemistry, physics, materials science, and electrical engineering extended their participation in the field. The conducting polymers were found to be suitable for gas sensor **[4]**, functional hybrid **[5]**, as pH switching electrical conducting biopolymer hybrid for sensor applications **[6]**, as an electrically active redox biomaterial for sensor applications **[7]**. The concept of conducting polymer was then no longer restricted for polyacetylene but extended to all other conjugated hydrocarbon and aromatic heterocyclic polymers such as polyaniline (PANI), polythiophene (PTH), poly (*p*phenylene) (PPP), poly (phenylene sulfide) (PPS), polypyrrole (PPY), polypyridin (PPyr). From molecular structure point of view, a highly delocalized π-conjugation system is found to be possessed by conducting polymers. Upon oxidative doping (oxidation reactions) with oxidants, an electron is removed from the π-system of polymer backbone producing a free radical and a spinless positive charge. The radical and cation are coupled to each other via local resonance of the charge and the radical. The structural distortion site has higher energy level than the rest of polymer chain. This combination of the charged site and paramagnetic defect site is viewed as a polaron, and it creats a new localized energy state in the gap with a single electron occupies the lower energy state. Upon further doping (oxidation), the bipolaron (two separated charged defects) can be produced through either removing free radicals from polarons or recombination of polarons. Thus at higher doping level, polarons are replaced with bipolarons. The bipolaron states are located in a band gap of 0.71eV from the edge of conduction band and 0.61eV from the edge of valence band for conducting polymers respectively. Upon continuous doping, bipolaron states will gradually form a continuous bipolaron bands. Theoretically, at 100% doping level, the upper and the lower bipolaron bands will merge with the conduction and the valence bands respectively to produce partially filled bands and metallic conductivity **[8].** Conduction by polarons or bipolarons is now generally accepted as the dominant mechanism of interchain transport. Charges on the polymer backbone must hop from chain to chain, as well as move along the chain, for bulk conductivity to be possible. After the report of preparation of carbon nanotubes and conducting polymer composites, there have been efforts to combine carbon nanotubes and polymers to produce functional composite materials with desirable electrical and mechanical properties **[9].** Since the discovery by Iijima **[10],** carbon nanotubes (CNTs) have received much attention for their possible use in fabricating new classes of advanced materials, due to their unique structural, optical, mechanical and electronic properties [**11-13]**. Introducing CNTs into a polymer matrix improves the properties of the original polymer [**14-17**]. Thiophene-based conducting polymers have attracted considerable attention during the past two decades due to a wide range of unique optical, electrochemical and electronic applications. Especially low band gap thiophene-based polymers are very promising materials with high conductivities, high degrees of optical transparency, and enhanced nonlinear response. Other important factors that determine polythiophene (PTH) could be one of the most likely candidates for commercial applications because of the high stability of both its doped and undoped states, ease of structural modification of polymer backbone, and very good solubility of 3-substituted polythiophene derivatives. Because polythiophene posses so many unique properties for possible wide range of applications, structural modifications of polythiphene are of great importance. Polythiophene based polymers are currently, and will in the future be, applied in many fields such as polymeric light-emitting diodes, conducting polymer-based actuators, supercapacitor, corrosion protection, antistatic coatings, transparent electrodes for inorganic electroluminescent devices, sensors, rechargeable batteries, electrochromic windows, and photovoltaic devices, etc. **[18].** Wang et al and Du et al studied the thermoelectric properties of polythiophene/multiwalled carbon nanotube composites **[19, 20].** Electrochemical and Raman spectro-electrochemical investigation of single-wall carbon nanotubes–polythiophene hybrid materials was studied by Pokrop et al **[21].** Solid state heating method was used to study electrochemical properties of the poly(3,4-ethylenedioxythiophene)/single-walled carbon nanotubes composite **[22].** Looking to the tremendous scope for carbon nanotubes based polythiophene nanocomposites, we report the synthesis and characterization of multifunctional materials based on polythiophene and carbon nanotubes to study their transport properties in the light of application of such materials in nanodevices. We have systematically studied the effect of incorporation of CNT on the electrical and transport properties of polythiophene. The transport properties of polythiophene based conducting polymer nanocomposites have been reported first time in this paper **[23, 24].**

II. EXPERIMENTAL

A. *Materials*

Thiophene (99% purity) (Merck) was purified by distillation under reduced pressure. The oxidant, ferric chloride ($FeCl_3$) (99% purity), chloroform ($CHCl_3$, 98.5% purity) and methanol (CH_3OH, 95.5% purity) were also purchased from Merck and used as received. High purity MWCNTs of diameter 30-40 nm prepared by CVD method was made available from NPL, New Delhi, India. Other supplement chemicals were of AR grade and used as received.

B. *Methods*

UV-Vis spectra were recorded between the range 200-800 nm using Model UV-1800 Spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded on Model 8101A Spectrophotometer in the wavelength range of 400–4000cm^{-1} with 4 cm^{-1} resolution. Rigaku Mini Flex-II a bench top X-ray Diffraction instrument was used to study XRD patterns. SEM images were taken on JEOL JSM-6360 analytical scanning electron microscope. Direct current (dc) electrical conductivity was measured using standard four probe instrument and the pallets were prepared using hydraulic press (Ki-maya Engineers, India) by applying a pressure of 5000 kg/cm^2.

C. Synthesis of polythiophene (pth)

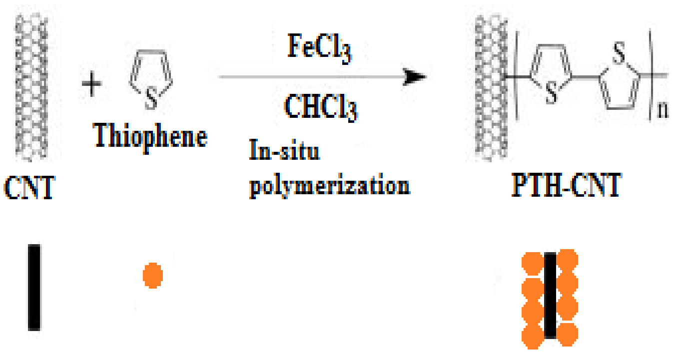
0.049 mol (0.2 ml) monomer thiophene was mixed with 50 ml of chloroform in a reaction vessel containing a magnetic stirring bar. 0.149 mol of anhydrous $FeCl_3$ was dissolved in 50 ml of chloroform and added drop wise to the stirred monomer solution. The molar ratio [oxidant] / [monomer] was kept at 3:1. Polymerization was carried out for 24 h at 0-5 ^oC temperature. The dark-brown precipitate of polythiophene (PTH) was collected by filtration and washed with $CHCl_3$. The PTH was further washed with methanol to remove the residual oxidant. During this procedure, the color changed from dark-brown to brown. The PTH powder was then dried in a vacuum oven at 60 ^oC for 24 h.

D. Synthesis of Pth-Mwcnts Nano composites

Due to van-der Waals forces, tight bonding of CNT limits their applications. Therefore in this study MWCNTs surface was functionally modified by ultra-sonication using H_2SO_4 and HNO_3 to provide specificity for improved interaction between CNT and polymer matrix which enhances the processability and properties of composites. For the Functionalization of CNTs, the solution of 6M H_2SO_4 and 6M HNO_3 in 3:1 ratio was stirred for 10 minute. CNTs were added to it and then solution was sonicated for 4 hours at 50 ^oC. After centrifugation CNTs was filtered, washed and dried to get functionalized MWCNTs. Functionalized MWCNTs (5 and 10 wt %) were then dissolved in $CHCl_3$. Sonicated for 2 hrs and added to the monomer just before addition of oxidant to the thiophene monomer to get PTH-MWCNTs nanocomposites. The schematic view of the process for CNTs coated with conducting PTH and representation of the formation of PTH-CNT nanocomposites is shown in **scheme 1.**

III. RESULTS AND DISCUSSION

The comparison of the FTIR spectrum of PTH with those of PTH-CNT nanocomposites is presented in **Fig. 1.** Bands at 1544 and 1514 cm^{-1} belong to C=C asymmetric and symmetric stretching vibrations of thiophene ring, respectively. At 1101 and 783 cm^{-1}, the in-plane and out-of-plane C–H aromatic bending vibrations of substituted thiophene ring are situated. The band at 853 cm^{-1} may be assigned to C–S stretching vibration **[25-27].** Band near 650 cm^{-1} represents the ring deformation of C–S–C in PTH. In PTH nanocomposites bands slightly shifted compared to those of PTH, some peaks are overlapped by the peaks of MWCNTs. Additional new bands belonging to surfactant appear in the FTIR spectrum of PTH nanocomposites. The presence of functionalized MWCNTs in the PTH matrix is confirmed by the FTIR spectra. The observed peak shifts reveal interactions between PTH and the MWCNTs.



Scheme 1: The schematic view of the process for CNT coated with conducting PTH and representation of the formation of PTH-CNT nanocomposites

From UV-VIS spectra of PTH and PTH-CNT Nano composites as shown in **Fig. 2**, in PTH there are three absorption peaks one at 290nm which shows $\pi \rightarrow \pi^*$ transition the other near 400nm regards to $n \rightarrow \pi^*$ and the third near 600nm is due to inter ring charge transfer associated with the excitation from benzenoid to quinoid moieties. The characteristic absorption band of PTH at approximately 400 nm is attributable to the transition from the valence bond to the antibonding polaron state, indicating that the resultant PTH is in the doped state **[28].**

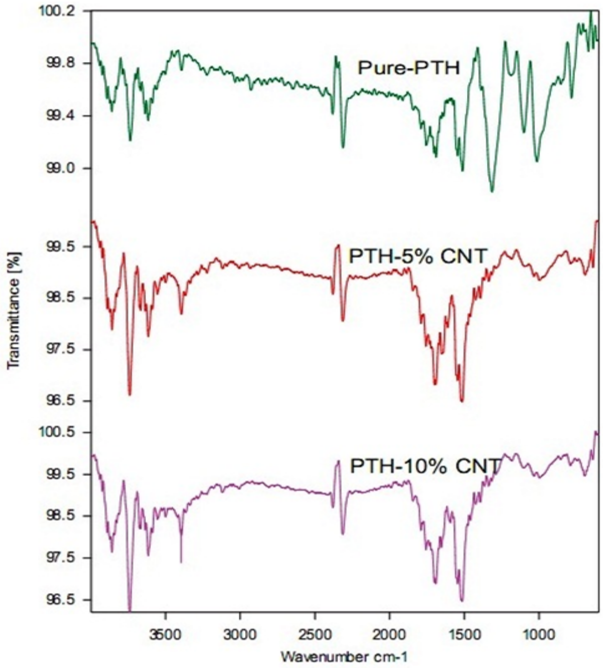


Figure 1: FTIR spectra of PTH and PTH-CNT

The peak intensity of $\pi \rightarrow \pi^*$ transition increases in PTH-CNT nanocomposites confirmed the addition of CNT into the PTH matrix. Peaks near 400 remain unchanged as they are associated with transition from loan pair of electrons. Addition of MWCNTs to the PTH matrix creates a layer of PTH polymer on MWCNTs.

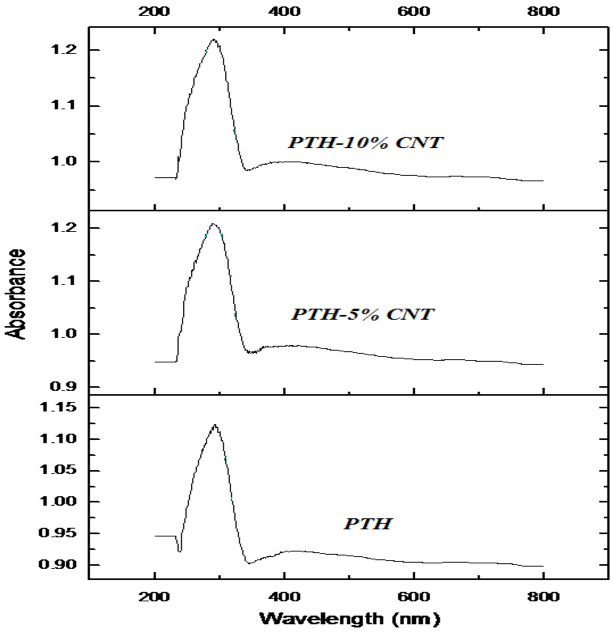


Figure 2: UV-VIS spectra of PTH and PTH-CNT

The SEM micrographs of PTH and PTH-CNT nanocomposites are shown in **Fig. 3.** PTH shows a multilayer structure where as nanocomposites shows porous in comparison. This porous structure may be helping in storage of charge and hence capacitive property of PTH may be increased by adding MWCNTs. The homogeneous coating of PTH onto the CNTs was observed from PTH-CNT indicating that CNTs were well dispersed in polymer matrix.

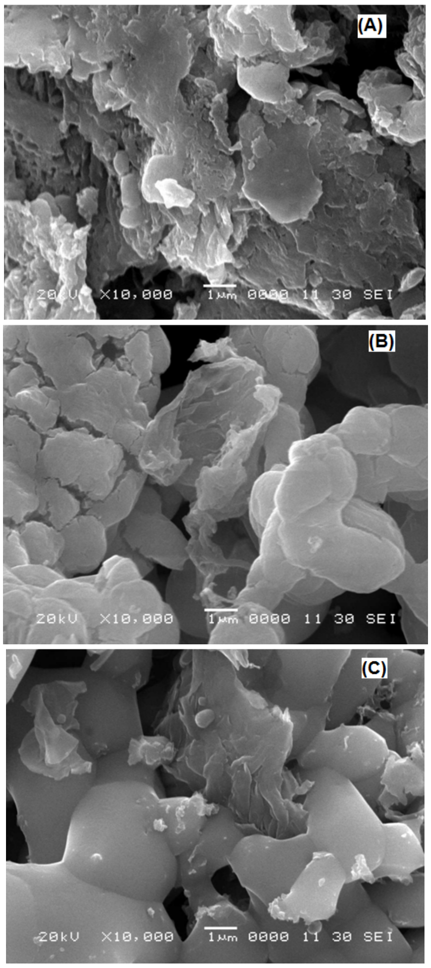


Figure 3: SEM images of PTH (a), PTH-5%CNT (b) and PTH-10%CNT (c)

The XRD pattern of PTH and PTH-CNT nanocomposites are shown in **Fig. 4.** When carbon nanotubes were incorporated into the PTH matrix, the sharp and strong diffraction peak of CNT was observed and peak near 30° in PTH splits up to dive more crystalline structure. Intensity of all the peaks in PTH seems to increase in its composites. This result shows that the homogeneous coating of PTH onto the CNTs indicating that CNTs were well dispersed in polymer matrix as seen from their SEM also.

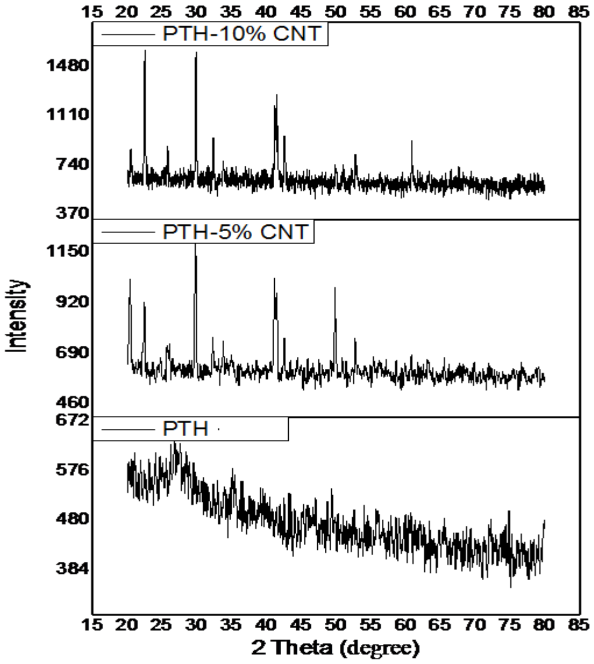


Figure 4: XRD pattern of PTH and PTH-CNT

Fig. 5 shows the variation in electrical conductivity of PTH and PTH-CNT nanocomposites with temperature. The room temperature conductivity of PTH was found to be 0.011 S/cm which enhanced to 0.023 S/cm by addition of 10% functionalized MWCNTs. The increase in conductivity with temperature was observed for PTH-CNT nanocomposites confirmed the semiconducting nature indicated the "thermal activated" behavior as that of pure PTH. The interaction between PTH and CNT could facilitate the charge transfer process between them and influence the charge transport properties of composites.

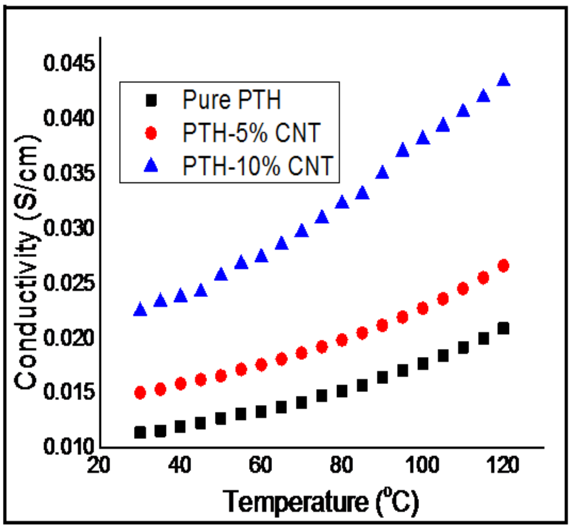


Figure 5: Variation in electrical conductivity of PTH and PTH-CNT nanocomposites with temperature.

MWCNT may serve "conducting bridge" connecting the PTH conducting domain. Thus functionalized MWCNT embedded in the PTH matrix have better conductivity with enhanced solubility and processability as compared to that of pure PTH.

Table 1: Transport parameters of PTH and PTH-CNT nanocomposites

Composition	**σ(S/cm) at 303K**	**Band Gap E_g (eV)**	***To* (K)**	**α^{-1} (nm)**	***R* (nm)**	***W* (eV)**
PTH	0.011	0.25	6488	9.71	35.69	0.14
PTH- 5% CNT	0.015	0.22	7502	8.39	33.19	0.16
PTH- 10% CNT	0.023	0.21	9554	6.59	29.41	0.21

The transport parameters of PTH and PTH-CNT have been computed from the data of electrical conductivity using equation 1 and summarized in table 1.

$$\sigma(T) = \sigma_o . e^{\left(\frac{T_o}{T}\right)^{1/2}} \text{------- (1)}$$

The plot of *log* $\sigma(T)$ versus $T^{1/2}$ was found to be linear for pure PTH and PTH-CNT nanocomposites, hence $T_o$was determined from the slope of the line. T_o, the characteristic temperature, can be used to calculate the transport parameters such as charge localization length (α^{-1}), most probable hopping distance (*R*) and charge hopping energy (*w*) using the equations (2), (3) and (4) respectively.

$$T_o = \frac{8\alpha}{N(E_f)Zk} \quad \text{-------- (2)}$$

$$R = \left(\frac{T_o}{T}\right)^{1/2} \left(\frac{\alpha^{-1}}{4}\right) \quad \text{------- (3)}$$

$$w = Zk\frac{T_o}{16} \text{ ------- (4)}$$

In these equations, *Z* is the number of nearest neighbouring chains (~4), *k* is Boltzmann constant and $N(E_F)$ is the density of states per electron **[16, 17].** By comparing the transport parameters of PTH and PTH-CNT nanocomposites, charge localization length (α^{-1}) and most probable hopping distance (*R*) were found to be decreased with high wt % of CNT in PTH-CNT nanocomposites, whereas the charge hopping energy (*w*) was found to be increased. These results show that the addition of CNT in PTH matrix, improved the electrical properties of PTH and such nanocomposites are most suitable advanced materials for electronic devices.

IV. CONCLUSIONS

Polythiophene (PTH) and PTH-CNT nanocomposites were successfully prepared by using an in-situ chemical oxidation polymerization of thiophene in the presence of functionalized MWCNTs. The results show that the MWCNTs have been well interacted with PTH. The PTH-CNT nanocomposites show semiconducting behavior as that of pure PTH with improved electrical conductivity and transport properties useful for electronic devices.

V. ACKNOWLEDGEMENTS

The authors gratefully acknowledge UGC, New Delhi (India) for financial assistance provided to carry out this work through major research project file F No.39-540/2010 (SR).

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