Temperature dependent studies of electric and dielectric properties of polythiophene based nano composite

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The fabrication, characterization, electric, dielectric and ac conductivity measurement of polythiophene and carbon nanotube (CNT) composite are described. The polythiophene (PTh) and polythiophene/ multiwalled carbon nanotube (PTh/MWCNT) composite are prepared chemically by oxidative polymerization of thiophene(Th). The formation of PTh and incorporation of CNTs into PTh are confirmed by Fourier Transform – Infrared spectroscopy (FT-IR) and Energy Dispersive X-Ray analysis (EDAX) analysis. Scanning Electron Microscopic (SEM) analysis revealed the formation of polymer/CNT composite. SEM image of PTh shows a leaf like structure and image of PTh/MWCNT shows the incorporation of MWCNT into the PTh flakes. Atomic force microscopic (AFM) analysis shows the morphology of PTH and PTh/MWCNT. The structural features of Nanotube-Polymer association are observed by AFM studies. The electrical behaviour of prepared samples has been studied by measuring I-V characteristics at varying temperature. The dielectric properties of these samples have been studied at low frequencies (150-700 kHz) for varying temperature. The dielectric constant for PTh/MWCNT is found to be higher than PTh for all temperature ranges. Finally, the ac electrical conductivity (σac) and dielectric relaxation time calculations have been carried out by using the data available from dielectric measurements and by employing a simple relationship. Conductivity shows a linear dependence on temperature and is also higher for PTh/MWCNT.

Keywords: Dielectric constant, Carbon nanotubes, Polythiophene, ac conductivity, Relaxation time

1 Introduction

Conjugated polymers exhibit conducting or semiconducting properties and these polymers seem to be suitable candidates due to their optical and electrical properties such as dielectric constant, refractive index, impedance, permittivity, etc. Among these polymers, thiophene based materials have emerged as one of the most promising materials due to the ease in its synthesis, its environmental stability and the possibility to modify it with different chemical groups.1,2

Polythiophene in its original state is a non-conducting material. However, chemical treatment with oxidants or electrochemical oxidation followed by anion intercalation can result in the formation of conducting polythiophene. Carbon nanotubes (CNTs) have attracted a great deal of interest because of their unique structural, electrical, mechanical properties and their potential applications in various fields which include material chemistry, nanoscale devices, field emissions and scanning probe microscopy.3,4

Multi-walled carbon nanotubes (MWCNTs) have been used in composite materials to improve electrical properties while reinforcing the mechanical performance of the composites.5,10 In some special applications, such as space explorations, high-performance, lightweight structural materials are required and these can be developed by adding CNTs to polymers or other matrix materials. The superior properties of CNTs offer exciting opportunities for new composites. NASA has invested large sum of money to develop carbon nanotubes-based composites for applications such as the Mars mission.11

Recently, polymer/CNT composites have attracted considerable attention owing to their unique mechanical, surface and multi-functional properties and strong interactions with the matrix resulting from the nano-scale microstructure and extremely large interfacial area. The temperature dependent studies of conductivity and dielectric measurements of polythiophene (PTh) and polythiophene multiwalled carbon nanotube (PTh/MWCNT) nanocomposite, have been reported in the present paper.
2 Experimental Details

2.1 Materials
Thiophene (Th) (Merck) is double distilled prior to use. Anhydrous ferric chloride (FeCl₃) is purchased from Ranbaxy and used without further purification. Multiwalled carbon nanotubes (MWCNTs) are purchased from Aldrich.

2.2 Synthesis of PTh and PTh/CNT composite
The synthesis of PTh is done by taking known amount of anhydrous FeCl₃ (1 M) and this solution is added to 25 ml of chloroform (CHCl₃) in a conical flask. To this solution, thiophene monomer (1M) is dissolved in 25 ml of CHCl₃ and added to the conical flask dropwise using a burette. The reaction mixture is stirred continuously with magnetic stirrer at 0°C under controlled temperature conditions for 3 h and later allowed to reach the room temperature with continuous stirring for 1 h. The polymer mixture is diluted with CHCl₃ and filtered. The sample material collected by filtration is then washed several times with methanol and double distilled water for removing the unreacted oxidants and thiophene monomer until the solvent remains colourless. Finally, this polymer material is dried in a vacuum chamber. PTh/MWCNT nano-composite is synthesized in a manner similar to that of PTh in the presence of MWCNTs by keeping the ratio of PTh: CNT at 10:2.

2.3 Preparation of a polymer disk
The prepared materials namely PTh and PTh/MWCNT are taken in equal amount to form their pellets by subjecting to pressure at 2000 lbs/in² by hydraulic press (Spectra lab Model SL-89) for few minutes. The two pellets are then used for dielectric measurements.

3 Measurements
Dielectric properties of PTh and PTh/MWCNT have been studied at low frequency (150 to 700 kHz) by using HIOKI 3532 LCR Hi Tester by placing the prepared pellets into specially designed sample holder made up of brass. The sample holder along with pellets is placed one by one into a high precession oven (Universal, New India, Model No. 12/3). The two wires are taken out and connected to LCR meter probe. Dielectric parameters have been studied at different temperature conditions (25, 50, 75 and 100°C) by varying frequency from 150 to 700 kHz at individual temperature ranges. For each temperature range, the real and imaginary part of dielectric permittivity as well as its ac conductivity has been calculated. Electrical measurements are taken by connecting dc voltage power supply (Philips GP-4303D) and voltmeter (Kiethley-196) is placed parallel to the sample placed in sample holder and micro-ammeter (Simpson) is placed in series with the circuit.

4 Results and Discussion

4.1 FT-IR analysis
The chemically prepared PTh and PTh/MWCNT are analyzed by FT-IR spectroscopy by making pellets with KBr. The region in the range 500-1500 cm⁻¹ is a fingerprint region for PTh and the peaks at 2800-3100 cm⁻¹ are low intensity peaks attributed to aromatic C-H stretching vibrations and C=C characteristic band (1652.66 cm⁻¹). The peak at 787.80 cm⁻¹ is usually ascribed to the C-H out-of-plane deformation mode, whereas other peaks in this region are attributed to the ring stretching and C-H in-plane deformation modes. The C-S bending mode has been identified at approximately 694.13 cm⁻¹ and indicates the presence of a thiophene monomer. The PTh/MWCNT composite shows almost the same position of the peaks in the range 600-3200 cm⁻¹. The C-H stretching vibrations (2800-3100cm⁻¹) and C=C characteristic peaks (1647.52cm⁻¹) can be identified almost in the same range, respectively. The ring stretching and deformation modes are having a minor shift in the peaks because of polaron/π transition interaction between the PTh and MWCNT surface.

4.2 SEM-EDAX analysis
The scanning electron microscopy in Fig.1 shows leaf like structure of PTh while Fig. 2 shows the incorporation of MWCNTs into the PTh leafs. The SEM analysis revealed the interaction of MWCNTs with polymer matrix because the presence of a random network of interconnected bundles of MWCNT, packed underneath the polymer confirm formation of polymer nanocomposite. Elemental EDAX analysis shows the atomic and weight percentage of PTh and PTh/MWCNT. The Wt % of carbon in case of PTh is 56.78 and At% is 78.38 as shown in Table 1 while in case of PTh/MWCNT the W% and At% of both increase as presented in Table 2 which give an idea that increase in percentage of carbon is only due to the presence of MWCNTs. As FeCl₃ is used as an oxidant in polymerization and due to that traces of iron are left after washing.
4.3 AFM analysis

The morphology of PTh and PTh/MWCNT samples has been investigated using a AFM analysis. Figs 3 and 4 show 3-D image of an AFM scan of the surface of PTh and PTh/MWCNT having nodular structure. In case of PTh/MWCNT, nodular size is higher than PTh. Nodular structure is associated with the highly doped conducting samples in which nodules represent dopant rich highly conductive area\textsuperscript{15}. In our composite, we find the same nodular structures indicating that the polymer growth process is not affected significantly by the insertion of nanotubes. The insertion of thin bundles of these MWCNTs into the polymer matrix allows the formation of large shapeless nodules increasing the conductivity of the sample.

In case of PTh, the roughness of sample is 57 nm and particle size is 338 nm but after incorporation of MWCNTs during polymerization reduces the roughness and particle size to 13 and 61 nm and act as filler material, respectively. MWCNTs and thiophene (Th) monomer are polymerized simultaneously and it is found that the PTh has grown across the MWCNT, due to nano dimensions of CNTs it leads to smoothening of resulted PTh/MWCNT nanocomposite. The nanomaterials occupy interfacial sights and act like a filler material. The unpaired...
lattice defects on the surface of CNTs act as active centers for the interaction of PTh molecular chains on the surface of CNTs. The reduced roughness and particle size increase the polymer conductivity.

4.4 Electrical measurements

In order to make electronic measurements of PTh and PTh/MWCNT nanocomposite, the $I$-$V$ characteristics are measured at four different temperature ranges and comparison is seen between both the materials as shown in Figs 5 and 6. In case of PTh, the voltage is varied from 10 to 50 V in a step wise manner and the current is measured at varying temperature. $I$-$V$ characteristics show almost linear relationship and it is noticed that the value of current increases for every applied voltage with increase in temperature. The electrical behaviour of polythiophene sample is poor semiconducting.

However, in case of PTh/MWCNT nanocomposite, the voltage is applied from 10 to 80 mV and large variation in current is noticed in comparison to PTh and in a similar manner, there is also increase in current for every applied voltage with increase in temperature. The incorporation of MWCNTs into the PTh matrix converts its electrical behaviour from poor semiconducting to semiconducting and increase in value of current with increase in temperature which is due to thermal expansion and rapid increase in ion mobility.

4.5 Dielectric measurements

Dielectric response of chemically prepared PTh and PTh/MWCNT has been studied in the range 150-700 kHz using a HIOKI-3532 LCR Hi-tester at four different temperature ranges. At a particular temperature range, the frequency is changed on LCR Bridge in equal intervals and the values of $C$, $C_p$, $D$ ($\tan \delta$), $G$ (conductance) have been observed. Here both $\varepsilon'$ (real part) and $\varepsilon''$ (imaginary part) of the permittivity have been calculated. Finally, the real part is expressed as:

$$\varepsilon' = \frac{c_p d}{\varepsilon_0 A}$$  \hfill (1)

where $d$ is the thickness of the sample, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m (permittivity of free space), $A$ (effective area) = $\pi r^2$ (m$^2$) and imaginary part is given by:

$$\varepsilon'' = \varepsilon' \tan \delta$$  \hfill (2)

As shown in Fig. 7, the value of dielectric permittivity for PTh varies from 5 to 8 and is dependent on temperature as well as on frequency. The increase of dielectric permittivity with respect to temperature could be related to the well-known phenomenon that the polarization increases with temperature, which was found to be valid in a wide range of materials.

In case of PTh/MWCNT composite as shown in Fig. 8, the value of permittivity varies from 11 to 16 with increasing temperature at different frequencies. The dielectric permittivity increases with temperature at all measured frequencies and decreases with increase in frequency. This decrease in dielectric constant at higher frequency is due to increase in dielectric dispersion.
The dielectric constant \( \varepsilon' \) of PTh/MWCNT composite is higher than PTh for all temperature and frequencies. This increase is because of the fact that, dielectric permittivity of the material depends on the polarizability of the molecules; higher the polarizability of the molecules, higher is the permittivity of the material. In case of polymers and their composite materials, the orientation polarization and interfacial polarization play an important role. Interfacial polarization arises for electrically heterogeneous materials where two phases differ from each other in dielectric constant and conductivity. These two phases are mentioned in AFM analysis as in case of PTh/MWCNT nano composites, the grains are also observed. In case of CNT polymer composite, conductivity of the polymer matrix and that of the CNTs is different. In such materials, the mobility of the charge carriers occurs more easily and randomly through one phase and therefore, is constricted at phase boundaries. Finally, interfacial polarization results in an increase in the permittivity due to the random mobility of charge carriers which gets trapped at the interface of a multiphase material with different conductivity\(^{18}\). The nanocomposites consist of two materials having quite different conductivities and permittivity. The interface across the PTh and MWCNT may be a source of the large dielectric constant.

It has been observed that the dielectric permittivity increases by dispersing conducting particles e.g. carbon nanotubes/nanoparticles in the polymer material. The increased dielectric permittivity in such composites arises from the conducting particles isolated by very thin dielectric layers to form micro capacitors. However, dielectric loss is very high and difficult to control, because the particles can easily form a conductive path in the composite as the filler concentration nears the percolation threshold.

The decrease in dielectric constant with increasing frequency is due to the fact that the interfacial dipoles do not have sufficient time to orient themselves in the electric field direction; therefore, with the increase in frequency, the tendency for the interfacial polarization is expected to decrease resulting in the decrease of dielectric constant.

Figure 9 shows the temperature dependent behaviour of dielectric for both the samples at different temperatures so that one can perform comparison.

Figures 10 and 11 show the dielectric loss \( \varepsilon'' \) for PTh and PTh/MWCNT at varying temperature and different frequencies. The dielectric loss decreases with increase in frequency and increases for every frequency with increase in temperature. Fig. 12 shows the variation of dielectric loss with the temperature for both the materials from 25 to 100°C.

4.6 ac Conductivity Measurement

The ac conductivity of the material is measured using a simple relation:

\[
\sigma_{ac} = \omega \tan \delta \varepsilon' \varepsilon_r
\]  

\[\text{where } \omega = 2\pi f \text{ and } \varepsilon' = \varepsilon_r \varepsilon_0, \varepsilon_0 \text{ is the permittivity of the free space and } \varepsilon_r \text{ is the relative permittivity. So:}\]

\[
\sigma_{ac} = 2\pi f \tan \delta \varepsilon'
\]  

... (4)
The general trend of conductivity is to increase according to increase in frequency. It is seen in Fig. 13 that the conductivity of the PTh increases linearly with temperature and frequency while as shown in Fig. 14 the \( \sigma_{ac} \) conductivity of PTh/MWCNT composite increases largely in comparison to PTh. It is noticed that by incorporation of multiwalled carbon nanotubes inside the polymeric matrix, there is an increase in charge transport and by heat treatment the conductive grains of CNT expand due to which mobility of carriers increases between the grains and hence \( \sigma_{ac} \) conductivity increases almost 10 times. So in the present experiment, it is considered that polymer material is used as a host matrix and MWCNT are expected to act as bridges which efficiently connect the conductive domains of PTh and thus, facilitates the total charge transport. The conductivity obeys the empirical law\(^\text{19}\) for frequency dependence and is given by the relation of the form:

\[
\sigma_{ac}(\omega, T) = A(T) \omega^s 
\]

where \( A(T) \) is a constant, generally, dependent on temperature and \( s \) is the frequency exponent and generally lies in the range \( 0 \leq s \leq 1 \). The plot of \( \sigma_{ac} \) conductivity versus frequency at various temperatures
indicates that the slopes of the curves remain similar for the reported temperature range (25-100°C). Therefore, the value of $s$ does not change much in the entire frequency range. This agrees with the reported model as predicted.

The increase of ac conductivity with respect to temperature reveals the conductive behaviour of the prepared composite with respect to PTh.

4.7 Dielectric relaxation

Dielectric relaxation is the exponential decay with time of the polarization in a dielectric when an externally applied field is removed. The relaxation time may be defined as the time in which this polarization is reduced to $1/e$ times its original value, $e$ being the natural logarithmic base. Dielectric relaxation is the cause of anomalous dispersion in which the dielectric constant decreases with increasing frequency. In terms of the theory of this phenomenon as developed by Debye\textsuperscript{20}, dielectric relaxation is the lag in dipole orientation behind an alternating electric field. The dielectric relaxation time $\tau$ for both PTh and PTh/MWCNT nanocomposite has been calculated and found to be temperature dependent. The plot of dielectric relaxation time with respect to frequency at varying temperature for PTh and PTh/MWCNT is shown in Figs 15 and 16, respectively.

In both the cases, PTh and PTh/MWCNT the relaxation time increases with increase in temperature and relaxation time for PTh/MWCNT increases in comparison to PTh.
5 Conclusions
In the present study, we synthesized polythiophene/MWCNT nanocomposite by using a monomer that undergoes oxidative polymerization in the presence of multiwalled carbon nanotubes. Following this chemical route, it is possible to generate polymer-based composites in which the nanotubes are not simply mixed up with the polymer, but are also in intimate contact with the polymer through specific chemical interactions and this formation is confirmed by SEM images. The above described synthesis proves to be a feasible pathway for the fabrication of a very important class of materials based on nanotube/polymer systems.

The electrical measurements for both PTh and PTh/MWCNT are taken by analyzing I-V parameters. The electrical behaviour of PTh/MWCNT changes from basic poor semiconducting polythiophene. This drastic change increases the quality of material and creates an idea for large view point of applications in commercial and industrial use.

The dielectric measurements are performed on PTh and PTh/MWCNT composites. The presence of MWCNTs enhances the dielectric constant for all temperature range and frequency as both interfacial polarization and nanosize of MWCNTs plays an important role to magnify the dielectric properties. However, the large dielectric constant of the nanocomposite provides promising materials for the applications in the fields of micro actuators, dynamic random access memory and metal oxide semiconductor devices.

The ac electrical conductivity of the polymer material and its composite has been calculated by using a simple relationship of the form $\sigma_{ac} = 2\pi \tan \delta \varepsilon^*$, with the data available from dielectric measurements. The result suggests that the ac electrical conductivity is directly proportional to the frequency and temperature. We conclude that incorporating MWCNTs into a polymer matrix to form nanocomposite, increases the conductivity by 10 times. It is observed that incorporating MWCNTs into PTh modifies the electrical behaviour and almost metallic type of behaviour of these nanotubes gives rise to a conducting polymer nanocomposite material. This increase in conductivity of polymer by incorporating MWCNTs can be used for solar cell applications.

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References
20 Debye P, Polar Molecules (Chemical Catalog, New York) 1929, Chap 5.