CHAPTER 4

4. RESULTS AND DISCUSSION

4.1 PTh nanoparticles

The results of XRD, SEM, UV-VIS, electrical conductivity and dielectric measurement studies on PTh and PTh-composites are discussed below.

4.1.1 X-ray Diffraction (XRD)

A typical XRD pattern obtained for PTh1 is shown in Fig. 4.1. In the figure, we see no sharp peaks. This indicates that PTh1 is noncrystalline in nature [1, 2]. XRD patterns of other two samples also revealed same information.

4.1.2 Scanning Electron Microscopy (SEM)

To understand the surface morphology, samples were subjected to Scanning Electron Microscopy. The SEM images of three PTh samples are shown in Fig.4.2 (a-c). The Fig.4.2 (a) shows nanoparticles agglomerated with micropores in between. In Fig. 4.2(b), the size of the agglomeration is found to be increased. In Fig. 4.2(c), a tube like structure formed by the nanoparticles is observed. The average sizes of the nanoparticles are found to be 41 nm, 50 nm and 71 nm for PTh1, PTh2 and PTh3 respectively. It may be noted that SEM image shown in Fig. 4.2(c) correspond to the
sample prepared at 323K. This imply that PTh prepared at higher temperature produced tube like structure.

Fig 4.1. X-ray diffraction pattern of pure PTh1.
Fig 4.2. SEM images of (a) PTh1, (b) PTh2 and (c) PTh3 samples.
4.1.3 Optical Absorption: The UV-visible spectra of PTh samples in their colloidal form are shown in Fig.4.3. These spectra in the UV-visible region were recorded at room temperature. The spectra of PTh1 show two distinct bands at 306 nm and 377 nm. The band at 306 nm is associated with $\pi-\pi^*$ inter band transition and band at 377 nm is associated with $n-\pi^*$ transition [4-6]. For PTh2 and PTh3, the absorption bands are observed at 320nm and 360nm respectively. PTh3 also exhibited an additional weak band at 480nm. It is worth noting that the surface morphology and UV-Vis spectra of all the three samples are differing from one another. It may be due to the fact that they are prepared at different temperatures. This implies that temperature of preparation of the polymer affects the properties such as structure and optical properties.
Fig 4.3. UV-Vis. spectra of three systems of PTh.
4.1.4 DC Electrical conductivity

The measured room temperature conductivities for PTh1, PTh2 and PTh3 samples are $2.43 \times 10^{-5}$ (Ωm)$^{-1}$, $0.95 \times 10^{-5}$ (Ωm)$^{-1}$ and $1.65 \times 10^{-5}$ (Ωm)$^{-1}$ respectively. The room temperature conductivity of Polythiophene prepared by chemical oxidative method has been reported to be $1.67 \times 10^{-4}$ (Ωm)$^{-1}$ [5]. Conductivity of the present polymer samples increased with increasing temperature, indicating semiconducting nature of them (Fig 4.4) [7, 8]. The temperature variation of conductivity has been fit to conductivity expression derived by Mott in the case of Small polaron hopping (SPH) in noncrystalline semiconductor solids [4, 9, 10]. The plots of ln(σT) versus (1/T) were plotted according to Mott’s (SPH) conductivity expression and shown in Fig. 4.5. The linear lines were fit to the data in the high temperature region where the data appeared linear. The slopes were used to determine the activation energy, $E_a$ (Table.1). Activation energy is found to be highest for PTh2 and least for PTh1.

Table 1. Activation energy, $E_a$, of PTh nanoparticle systems.

<table>
<thead>
<tr>
<th>Systems</th>
<th>PTh-1</th>
<th>PTh-2</th>
<th>PTh-3</th>
</tr>
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<tbody>
<tr>
<td>$E_a$ (meV)</td>
<td>0.07±0.01</td>
<td>0.53±0.02</td>
<td>0.30±0.02</td>
</tr>
</tbody>
</table>

The data deviated from SPH model has been fit to Mott’s 3D VRH model. Mott’s (VRH) model has been used earlier for analysing conductivity of polypyrrole and Polythiophene [11, 12]. The plots of ln(σ) versus $(T^{-1/4})$ were made according to this model and shown in Fig. 4.6. The linear lines were fit through the data. Certain range
of data appeared to be in agreement with the model fit. However, the data corresponding to lower temperature has deviated from Mott’s VRH model fit [13, 14]. Density of states \( N(E_F) \) were determined using slope and intercept and they were found to be \( 8.83 \times 10^{31} \text{ (eV}^{-1} \text{ m}^{-3}) \), \( 0.10 \times 10^{31} \text{ (eV}^{-1} \text{ m}^{-3}) \) and \( 3.80 \times 10^{31} \text{ (eV}^{-1} \text{ m}^{-3}) \) for PTh1, PTh2 and PTh3 respectively. The phonon frequency, \( \nu = 10^{13} \text{ Hz and } \alpha = 1.2 \text{ Å} \) were used to calculate \( N(E_F) \) [15]. These values of \( N(E_F) \) are much greater than that reported for elemental semiconductors and polymers. So, it can be concluded that though Mott’s (VRH) model fit appeared to be in agreement with data, the obtained results are far off from the expected values of \( N(E_F) \) and hence this model may be considered to be not suitable for explaining the present data.
Fig 4.4 Conductivity versus temperature for PTh systems.
Fig 4.5. Plots of $\ln(\sigma T)$ versus $(1/T)$ for PTh systems. Solid lines are linear fits as per Mott’s SPII model.
Fig 4.6. Plots of ln(σ) versus (T^{-1/4}) of PTh nanoparticles systems. Solid lines are linear fits as per Mott’s VRII model.
4.2 PTh-V$_2$O$_5$ Nanocomposites

Dopant anionic plays important role in polymerization [4,9, 16, 17]. PTh has been successfully combined with different metal nanoparticles and produced nanocomposites. Nanocomposites possess physical, chemical and biological properties which are very special can be used in making quantum electronic devices, magnetic recording materials, sensors, batteries etc [18-20]

4.2.1 X-ray diffraction

A typical XRD pattern obtained for pure V$_2$O$_5$ is shown in Fig 4.7. The XRD pattern of the PTh-VO$_5$ composite is shown in Fig.4.8. The Fig.4.8 reveals peaks at 2θ = 15.46, 20.38, 21.80, 26.21, 31.11, 32.46, 34.38, 41.31, 47.39, 51.27 and 55.69 degrees. The crystalline planes corresponding to these 2θ values were determined. They were found to be  d = 5.72 Å, 4.35 Å, 4.07 Å, 3.39 Å, 2.87 Å, 2.75 Å, 2.60 Å, 2.18 Å, 1.91 Å, 1.78 Å and 1.64 Å respectively.

Presently observed peak positions are comparable with those observed for pure V$_2$O$_5$ [21-23]. Using peak widths and by following Scherer Eqn given below [24].

\[
D = \frac{(0.98)\lambda}{\beta \cos \theta}
\]  

(4.1)

Where,

D is average diameter of particles
The grain sizes were determined to be 72.13nm, 55.56nm, 60.33nm, 60.92nm, 42.29nm, 46.29nm, 53.82nm, 72.81nm, 94.16nm, 117.8nm and 89.00nm, respectively.

\( \lambda \) is wavelength of radiation used

\( \beta \) is fullwidth half maximum of a peak observed

\( \theta \) is Bragg’s angle.
Fig 4.7. X-ray diffraction pattern of Pure V$_2$O$_5$. 
Fig 4.8. X-ray diffraction pattern of PTh-V$_2$O$_5$ composite.
4.2.2 Scanning Electron Microscopy

SEM images of the pure V$_2$O$_5$ and PTh-VO1 composites are shown in Fig 4.9 and 4.10 respectively. Agglomerated particles with micropores in between can be observed in Fig 4.9. In Fig 4.10, tubular structure along with grains can be observed. Here, grains may be due to V$_2$O$_5$ and tubular structure may be due to PTh in the composites. It may be noted that tubular structure of pure PTh has been reported to be the feature of the PTh particles synthesised at temperature 323K [25]. The average size of grains of pure V$_2$O$_5$ determined from Fig 4.9 is 85nm, which is in the range of sizes obtained from XRD patterns. Average grain size of the grains determined from Fig 4.10 is 70nm. The average grain sizes determined for PTh-VO2, PTh-VO3, PTh-VO4 and PTh-VO5 are 63nm, 71nm, 83nm and 81nm respectively. These grain sizes indicate nanocrystalline nature of the PTh-VO composites.
Fig 4.9 SEM image of pure V₂O₅ sample.

Fig 4.10 SEM image of PTh-VO1 sample.
4.2.3 DC Electrical Conductivity

Conductivity variation with temperature for the composite PTh-VO1 is shown in Fig 4.11. Conductivity increased with increasing temperature indicating semiconducting nature. Remaining composites of the present series behaved in the same way and, this result is in agreement with that reported for other similar systems [23, 7].
Fig 4.11. Temperature dependence of electrical conductivity of composite, PTh-VO1.
The measured room temperature conductivity for PTh-VO1, PTh-VO2, PTh-VO3, PTh-VO4 and PTh-VO5 composites are $8.147 \times 10^{-7} \ (\Omega m)^{-1}$, $6.555 \times 10^{-7} \ (\Omega m)^{-1}$, $7.262 \times 10^{-7} \ (\Omega m)^{-1}$, $9.779 \times 10^{-7} \ (\Omega m)^{-1}$ and $7.98 \times 10^{-7} \ (\Omega m)^{-1}$ respectively. These values are two orders of magnitude smaller than the reported values for pure PTh [25]. This implies that conductivity decreased with the incorporation of V$_2$O$_5$ in PTh. The decrease in conductivity with increase in V$_2$O$_5$ concentration up to 10% has been observed in PPy–V$_2$O$_5$ composites [26]. However, increase in conductivity with V$_2$O$_5$ content has been observed in PANI–V$_2$O$_5$ composites [27]. The conducting data with temperature has been fit to conductivity expression derived under Mott small polaron model.

According to this model, the conductivity in the non-adiabatic region is given by [9, 10].

\[
\sigma = \frac{\sigma_0}{T} \exp \left\{ -\frac{E_a}{K_B T} \right\}
\]  

(4.2)

Where, $E_a$ is the activation energy for small polaron hopping and $\sigma_0$ the pre-exponential factor.

The plots of ln($\sigma T$) versus (1/T) were made as per Eqn (4.2) for all the composites and shown in Figure-4.12(a–e). Least square linear lines were fit to the data in the high temperature region where the data appeared linear and slopes were extracted. Using slope of each line, activation energy, $E_a$ of the corresponding sample has been estimated.
Fig 4.12(a). Plot of $\ln(\sigma T)$ versus $(1/T)$ of PTh-VO1 composite. Solid lines are linear fit as per Mott’s SPH model.
Fig 4.12(b). Plot of $\ln(\sigma T)$ versus $1/T$ of PTh-VO2 composite. Solid lines are linear fit as per Mott’s SPH model.
Fig 4.12(c). Plot of $\ln(\sigma T)$ versus $(1/T)$ of PTh-VO3 composite. Solid lines are linear fit as per Mott’s SPH model.
Fig 4.12(d). Plot of $\ln(\sigma T)$ versus $(1/T)$ of PTh-VO4 composite. Solid lines are linear fit as per Mott’s SPH model.
Fig 4.12(e). Plot of $\ln(\sigma T)$ versus $(1/T)$ of PTh-VO5 composite. Solid lines are linear fit as per Mott’s SPH model.
Variation of activation energy, $E_a$, and conductivity, $\sigma$, at 400K as a function of wt% of V$_2$O$_5$ are plotted in Figs, (4.13). From the figure, it can be noted that $E_a$ decreased and conductivity increased with increase of wt% of V$_2$O$_5$ content. In PANI-V$_2$O$_5$ composites, the conductivity increased with increase in V$_2$O$_5$ concentrations up to 40% [27].

Increase in conductivity with increase in V$_2$O$_5$ content may be due to the fact that conduction process is made relatively easy by the presence of V$_2$O$_5$ grains in between PTh tubes or grains. Decrease in $E_a$ with increase in V$_2$O$_5$ concentration may be ascribed to the decrease in scattering rate of polarons with increase in V$_2$O$_5$ content. PANI and PANI-V$_2$O$_5$ composites conductivity increased with doping when compared to undoped sample [27].
Fig 4.13. Variation of activation energy, $E_a$ at 400K as a function of weight % of $V_2O_5$ in PTh-VO composites.
The conductivity data deviated from SPH model was considered under Mott’s 3D Varible Range Hopping (VRH) model. According to this model conductivity is given by

$$\sigma = A \exp \left\{ -BT^{-\frac{1}{4}} \right\}$$

(4.3)

Where

$$A = 4 \left[ \frac{2\alpha^3}{9\pi^2 N(E_F)} \right]^{\frac{1}{4}}$$

and

$$B = \left[ \frac{e^2}{2(8\pi^3)^{\frac{1}{2}}} \right] v_0 \left[ \frac{N(E_F)}{\alpha k_B T} \right]^{\frac{1}{2}}$$

Here, $N(E_F)$ refers to density of states of the carriers at the Fermi level, $v_0$ the phonon frequency ($=10^{13}$ Hz) and $\alpha=$ 1.2 Å (size of the monomer unit) [15]. Mott’s VRH model has also been used previously for understanding conductivity behaviour of pure polypyrrole and Polyythiophene [14, 12]. The plots of $\ln(\sigma)$ versus $(T^{-1/4})$ made as per this model are shown in Fig.4.14(a-e). The linear lines were fit through the data. For each of the composite, only some range of data appeared to be in agreement with the model fit. The deviations of data from the VRH model fit below certain range of temperature have been reported previously in respect of other systems [25, 12-13].
Fig 4.14(a). Plot of \( \ln(\sigma) \) versus \( 1/T^{1/4} \) of PTh-VO1 composite. Solid lines are linear fit as per Mott’s VRH Model.
Fig 4.14(b). Plot of $\ln(\sigma)$ versus $(1/T^{1/4})$ of PTh-VO2 composite. Solid lines are linear fit as per Mott’s VRH Model.
Fig 4.14(c). Plot of $\ln(\sigma)$ versus $1/T^{1/4}$ of PTh-VO3 composite. Solid lines are linear fit as per Mott's VRH Model.
Fig 4.14(d). Plot of $\ln(\sigma)$ versus $(1/T^{1/4})$ of PTh-VO4 composite. Solid lines are linear fit as per Mott’s VRH Model.
Fig 4.14(e). Plot of \(\ln(\sigma)\) versus \((1/T^{1/4})\) of PTh-VO5 composite. Solid lines are linear fit as per Mott’s VRH Model.
Density of states of charge carriers at Fermi level, \(N(E_F)\), of PTh-VO composites have been determined using slopes and are tabulated in Table 2. \(N(E_F)\) values are found to be in the range from \(10^{28}\) eV\(^{-1}\)m\(^{-3}\) to \(10^{30}\) eV\(^{-1}\)m\(^{-3}\). These \(N(E_F)\) values are high as the values reported for PPY-Ag composites [21] were in the range from \(10^{28}\) eV\(^{-1}\)m\(^{-3}\) to \(10^{30}\) eV\(^{-1}\)m\(^{-3}\).

Table 2. Density of states at Fermi level, \(N(E_F)\) for PTh-VO composites

<table>
<thead>
<tr>
<th>Systems</th>
<th>PTh-VO1</th>
<th>PTh-VO2</th>
<th>PTh-VO3</th>
<th>PTh-VO4</th>
<th>PTh-VO5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N(E_F)) (eV(^{-1})m(^{-3}))</td>
<td>6.24x10(^{28})</td>
<td>1.086 x 10(^{30})</td>
<td>8.484 x 10(^{28})</td>
<td>3.566 x 10(^{30})</td>
<td>76.090x 10(^{28})</td>
</tr>
</tbody>
</table>

4.2.4 Dielectric Properties

Using the measured capacitance, \(C\) and dissipation factor, \(\tan\delta\) the dielectric parameters were determined for all the composites, using the expressions given in reference [28]. Figure 4.15 shows the variation of dielectric constant, \(\varepsilon'\) with frequency for all the three composites. From this figure, we note that, \(\varepsilon'\) decrease gradually with frequency upto 70 KHz and become constant for higher frequencies.

Dielectric loss factor, \(\varepsilon''\) variation with frequency for all the three composites is plotted in Fig.4.16. \(\varepsilon''\) varied with frequency in the same fashion as that of \(\varepsilon'\).
Temperature variation of $\varepsilon'$ for PTh-VO1 is shown in Fig.4.17. In this figure, we see that $\varepsilon'$ increases with temperature. Similar nature of variation of $\varepsilon'$ with temperature has been observed for the remaining composites. The change in $\varepsilon''$ with temperature for PTh-VO1 is shown in Fig.4.18(a). Similar behaviour of $\varepsilon''$ with temperature has been observed for the remaining composites.
Fig 4.15. Dielectric constant, $\varepsilon'$ versus ln(f) for PTh-VO nanocomposites at the temperature of 343K.
Fig 4.16. Dielectric loss, $\varepsilon''$ versus $\ln(f)$ for PTh-VO nanocomposites at the temperature of 343K.
Fig 4.17. Dielectric constant, $\varepsilon'$ versus $\ln(f)$ for PTh-VO1 nanocomposite for different temperatures.
Fig 4.18. Dielectric loss, $\varepsilon''$ versus $\ln(f)$ for PTh-VO1 nanocomposite for different temperatures.
AC Electrical conductivity

Conductivity, $\sigma_{ac}$, has been determined using dielectric data using the following equation [29].

$$\sigma_{ac} = \varepsilon'' \omega \varepsilon_0$$  \hspace{1cm} (4.4)

Where, $\varepsilon_0$ is free space permittivity which is equal to $8.85 \times 10^{-12}$ Fm$^{-1}$. Conductivity variation with temperature for different frequencies for the composite PTh-VO1 is shown in Fig.4.17. It can be seen in Fig.4.17 that conductivity increases with increasing temperature indicating semiconducting type of behaviour. It also increased with increasing frequency. Similar results have been reported for polyaniline doped with silver nanoparticles, polyaniline doped with cobalt and polyaniline doped with nickel oxide [30-32]. All the present composites behaved in the same way. Variation of conductivity of all the present composites was found to be within the same order of magnitude i.e, $10^{-4}$ ($\Omega^{-1}$m$^{-1}$).

Conductivity variation with V$_2$O$_5$ content for two different frequencies at the temperature of 403K is shown in Fig.4.18. From Fig.4.18, it is clear that conductivity decreased with increasing V$_2$O$_5$ content.

The conductivity data as a function of temperature has been fit to the Mott Small Polaron Hopping (SPH) theory. This theory gave the conductivity expression as per Eqn. (4.2) [10].
Fig 4.17. Temperature dependence of electrical conductivity, $\sigma$, of PTh-VO1 composite nanoparticles at different frequencies.
The plots of $\ln(\sigma T)$ versus $(1/T)$ were made as per Eqn(4.2) for the composite PTh-VO and shown in Fig.4.19. The linear lines were fit to the data in the high temperature region where the data appeared linear. Activation energy, $E_a$ for ac conductivity was calculated using the slopes of the fit linear lines.

Activation energy, $E_a$ versus $V_2O_5$ content determined for the present composites for different frequencies are plotted in Fig.4.20.

From the Fig.4.20 one can note that $E_a$ increases with increase of $V_2O_5$ content and decreased with increase of frequency. Increase in $E_a$ with increase in $V_2O_5$ concentration may be that addition of $V_2O_5$ content to the PTh network contributes more to the scattering of polarons. Similar results have been reported for polyaniline doped with $V_2O_5$, polyanilinedoped with CeO$_2$ and polypyrrole doped with Ag [24, 33, 34].
Fig 4.18. Conductivity versus wt % of V$_2$O$_5$ in PTh-VO nanocomposites for two different frequencies at T=403K
Fig 4.19. Plots of $\ln(\sigma_{ac}T)$ versus $(1/T)$ for PTh-VO1 composite for four different frequencies. Solid lines are linear fits as per Mott’s SPH model.
Fig 4.20. Activation energy, $E_a$ versus wt. % of V$_2$O$_5$ for PTh-VO nanocomposites at two different frequencies.
4.3 PTh-CoO Nanocomposites

4.3.1 X-ray diffraction

A typical XRD pattern obtained for pure CoO and PTh-CO5 composite are shown in Fig. 4.21 and Fig. 4.22 respectively. The Fig. 4.22 reveals peaks at $2\theta = 18.98^\circ$, $31.26^\circ$, $36.84^\circ$, $44.80^\circ$, $59.36^\circ$ and $65.22^\circ$ corresponding to $d = 4.67 \text{ Å}$, $2.85 \text{ Å}$, $2.43 \text{ Å}$, $2.02 \text{ Å}$, $1.55 \text{ Å}$ and $1.42 \text{ Å}$ respectively.

These observed peak positions are comparable with those observed for pure cobalt oxide nanoparticles [35, 36]. Using peak widths and by following Scherer equation [24], the grain sizes were determined as $27.06 \text{ nm}$, $10.21 \text{ nm}$, $18.58 \text{ nm}$, $13.47 \text{ nm}$, $19.39 \text{ nm}$ and $22.19 \text{ nm}$, for PTh-CO1, PTh-CO2, PTh-CO3, PTh-CO4 and PTh-CO5 respectively.

4.3.2 Scanning Electron Microscopy

The SEM images of pure CoO and PTh-CO composites are shown in Fig. 4.23 and Fig. 4.24 respectively. Fig.4.23 shows nanoparticles agglomerated with micropores in between. In Fig. 4.24, tubular structures along with grains can be observed. Here, grains may be due to CoO and tubular structure may be due to PTh in the composites. It may be noted that tubular structure of pure PTh has been reported to be the feature of the PTh synthesised at temperatures above 323K [25], and no such features were observed in [1]. The average sizes of pure CoO in SEM image shown in Fig. 4.23 is determined to be $24nm$ which is in the range of sizes obtained from XRD patterns. Average grain size determined on SEM images shown in Fig. 4.24 are $48nm$. The
average grain sizes determined for PTh-CO2, PTh-CO3, PTh-CO4 and PTh-CO5 are 72 nm, 63 nm, 50 nm and 59 nm respectively.

Fig. 4.21 X-ray diffraction pattern of pure CoO.
Fig. 4.22 X-ray diffraction pattern of and PTh-CO5 composite.
Fig. 4.23 SEM image of pure CoO.

Fig. 4.24 SEM image of PTh-CO1 composite.
4.3.3 DC Electrical Conductivity

Conductivity versus temperature plot of the PTh-CO1 composite is shown in Fig. 4.25. Conductivity increased with increasing temperature indicating semiconducting nature. All the present composites behaved in the same fashion [23, 24]. Variation of conductivity with wt% of CoO has not followed any systematic trend.

The measured room temperature conductivity for PTh-CO1, PTh-CO2, PTh-CO3, PTh-CO4 and PTh-CO5 composites are $1.16 \times 10^{-7} \ \Omega^{-1} \text{m}^{-1}$, $1.18 \times 10^{-7} \ \Omega^{-1} \text{m}^{-1}$, $1.15 \times 10^{-7} \ \Omega^{-1} \text{m}^{-1}$, $1.206 \times 10^{-7} \ \Omega^{-1} \text{m}^{-1}$ and $1.879 \times 10^{-7} \ \Omega^{-1} \text{m}^{-1}$, respectively. These conductivity values are two orders of magnitude smaller than those measured for pure PTh [25]. This implies that conductivity decreased with the incorporation of CoO with PTh. The temperature variation of conductivity has been fit to conductivity expression derived by for small polaron hopping (SPH) in noncrystalline semiconducting solids. According to this model, the conductivity in the non-adiabatic region is given by as per Equ. (4.1) [7, 10, 24].

The plots of \( \ln(\sigma T) \) versus \( 1/T \) were made as per Eqn. (4.2) and shown in Fig. 4.26(a-e). The linear lines were fit to the data in the high temperature region where the data appeared linear. The slopes were used and activation energy, \( E_a \) was calculated.
Variation of $E_a$ as a function of wt% of V$_2$O$_5$ composites are plotted in Fig. 4.27. From the figure, it is clear that $E_a$ decreased with increase of wt% of V$_2$O$_5$ content.

Variation of $\sigma$ as a function of wt% of V$_2$O$_5$ composites are plotted in Fig. 4.28.
Fig. 4.25 Temperature dependence of electrical conductivity, $\sigma$, of PTh-CO1 composite.
Fig. 4.26(a) Plot of ln(σT) versus (1/T) for PTh-CO1 composite. Solid line is a linear fit as per Mott’s SPH model.
Fig. 4.26(b) Plot of \( \ln(\sigma T) \) versus \((1/T)\) for PTh-CO2 composite. Solid line is a linear fit as per Mott’s SPH model.
Fig. 4.26(c) Plot of $\ln(\sigma T)$ versus $(1/T)$ for PTh-CO3 composite. Solid line is a linear fit as per Mott’s SPH model.
Fig. 4.26(d) Plot of \( \ln(\sigma T) \) versus \( (1/T) \) for PTh-CO4 composite. Solid line is a linear fit as per Mott’s SPH model.
Fig. 4.26(e) Plot of \( \ln(\sigma T) \) versus \( 1/T \) for PTh-CO5 composite. Solid line is a linear fit as per Mott’s SPH model.
Fig. 4.27 Variation of $E_a$ at 345K as a function of weight % of CoO in PTh-CO composites.
Increase in conductivity with increase in CoO content may be due to the fact that conduction process becomes relatively easy by the presence of CoO grains in between PTh tubes or grains. Decrease in $E_a$ with increase in CoO concentration may be attributed to the decrease in the scattering rate of polarons with increase of CoO content. Similar results have been reported for polyaniline doped with camphor sulphonlic acid and blended with tetrameric cobalt phthalocyanine and polyaniline-Co3O4 [37, 38].

The conductivity data deviated from SPH model line has been fit to Variable Range Hopping (VRH) model expression given by Equ.(4.3). Mott’s VRH model has also been used previously for understanding conductivity variation in polypyrrole and Polythiophene [39, 12]. The plots of ln($\sigma$) versus ($T^{-1/4}$) were made according to this model and shown in Fig. 26(a-e). The linear lines were fit through the data. From the figure, it can be noted that for each sample, still there is some data deviating from the fit line. Similar deviations of data from the VRH model fit have been reported previously also [25, 12-14].
Fig. 4.28 Variation of $\sigma$ at 345K as a function of weight % of CoO in PTh-CO composites.
Fig. 4.29(a) Plot of $\ln(\sigma)$ versus $(1/T^{1/4})$ for PTh-CO1 composite. Solid line is a linear fit as per Mott’s VRH model.
Fig. 4.29(b) Plot of $\ln(\sigma)$ versus $(1/T^{1/4})$ for PTh-CO2 composite. Solid line is a linear fit as per Mott’s VRH model.
Fig. 4.29(c) Plot of $\ln(\sigma)$ versus $(1/T^{-1/4})$ for PTh-CO3 composite. Solid line is a linear fit as per Mott’s VRH model.
Fig. 4.29(d) Plot of $\ln(\sigma)$ versus $(1/T)^{-1/4}$ for PTh-CO4 composite. Solid line is a linear fit as per Mott’s VRH model.
Fig. 4.29(e) Plot of $\ln(\sigma)$ versus $(1/T^{1/4})$ for PTh-CO5 composite. Solid line is a linear fit as per Mott’s VRH model.
Density of states at Fermi level, $N(E_F)$ of PTh-CO composites have been determined using the slopes and they are tabulated in Table.3. These $N(E_F)$ values are in the range from $10^{28}$ eV$^{-1}$ m$^{-3}$ to $10^{30}$ eV$^{-1}$ m$^{-3}$. These $N(E_F)$ values appears to be high compared to the values reported for PPY-Ag composites [24].

Table.3. Density of states at Fermi level, $N(E_F)$ for PTh-CO composites

<table>
<thead>
<tr>
<th>Systems</th>
<th>PTh-CO1</th>
<th>PTh-CO2</th>
<th>PTh-CO3</th>
<th>PTh-CO4</th>
<th>PTh-CO5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N(E_F)$</td>
<td>$2.75 \times 10^{28}$</td>
<td>$2.22 \times 10^{28}$</td>
<td>$0.11 \times 10^{30}$</td>
<td>$1.17 \times 10^{30}$</td>
<td>$1.87 \times 10^{30}$</td>
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</table>

### 4.3.4 Dielectric Properties

Using the measured capacitance, $C$ and dissipation factor, $\tan \delta$ the dielectric constant, $\varepsilon'$ and dielectric loss, $\varepsilon''$ were determined for all the composites, using the expression given in [28]. Fig.4.30 shows the variation of dielectric constant, $\varepsilon'$ with frequency for all the five composites. From this figure, we can note that, $\varepsilon'$ decrease gradually with frequency up to 70 KHz and become constant for higher frequencies for all the samples. Dielectric loss factor, $\varepsilon''$ variation with frequency for all the five composites is plotted in Fig.4.31. $\varepsilon''$ varied with frequency in the same fashion as that of $\varepsilon'$. The temperature variation of $\varepsilon'$ for PTh-CO3 composites is depicted in Fig.4.32. In this figure, we see that $\varepsilon'$ increases with temperature. Similar nature of variation of $\varepsilon'$ with temperature has been observed for the remaining composites. The change in $\varepsilon''$ with temperature for PTh–CO3 is shown in Fig.4.33. Similar behaviour of $\varepsilon''$ with temperature has been observed for the remaining composites.
Fig 4.30. Dielectric constant, $\varepsilon'$ versus $\ln(f)$ for PTh-CO nanocomposite at the temperature of 323K.
Fig 4.31. Dielectric loss, $\varepsilon''$ versus $\ln(f)$ for PTh-CO nanocomposite at the temperature 323K.
Fig 4.32. Dielectric constant, $\varepsilon'$ versus $\ln(f)$ for PTh-CO3 nanocomposite for different temperatures.
Fig 4.33. Dielectric loss, $\varepsilon''$ versus $\ln(f)$ for PTh-CO3 nanocomposite for different temperatures.
AC Electrical Conductivity

AC conductivity, \( \sigma_{ac} \), has been determined using dielectric data using Equ.(4.4) [29]. Conductivity variation with temperature for different frequencies for the PTh-CO composite is shown in Fig.4.34. It can be seen in Fig.4.34 that conductivity increases with increasing temperature indicating semiconducting type of behaviour. It also increased with increasing frequency [31]. All the present composites behaved in the same way. Conductivity variation in the entire range of temperature is found to be within the same order of magnitude i.e, \( 10^{-4} \, (\Omega^{-1}\, \text{m}^{-1}) \).

Conductivity variation with CoO content for two different frequencies at the temperature of 313K is shown in Fig.4.35. From Fig.4.35, it is clear that conductivity increases with increasing CoO content. This result reveals that more number of polarons (electrons) are getting added to the conducting pool in the composites as the cobalt oxide content is increased. Also, conduction mechanism in these composites appeared to be getting expedited with increasing frequency. This could be due to the fact that increase in frequency enhances polaron hopping frequency. The temperature variation of conductivity has been fit to an expression derived by Mott originally for Small Polaron Hopping (SPH) in noncrystalline semiconductor solids. As there are no good theories for explaining conduction mechanism in conducting polymers and their composites, we use Mott’s SPH model. According to this model, the conductivity is given by Eqn.(4.2) [10],
Fig 4.34. Temperature dependence of ac conductivity of PTh-CO1 composite nanoparticle at different frequencies.
Fig 4.35. AC conductivity versus wt % of CoO in PTh-CO nanocomposites for two different frequencies at T=313K.
The plots of ln(σ_a T) versus (1/T) were made as per Eqn. (4.2) for the PTh –CO1 composite and shown in Fig. 4.36. The linear lines were fit to the data in the high temperature region where the data appeared linear. The slopes were used to determine the activation energy, E_a.

Activation energy, E_a versus CoO content determined for the present composites for different frequencies are plotted in Fig.34. From Fig.4.37, it can be noted that E_a decreases with increase in frequency and CoO content. It may be attributed to the decrease in scattering rate of polaron orbitals with increase in CoO content. Similar results have been reported for polyaniline doped with camphor sulphonic acid and blended with tetrameric cobalt phthalocyanine and polyaniline-Co_3O_4 [37, 38].
Fig 4.36. Plots of $\ln(\sigma T)$ versus $(1/T)$ for PTh-CO1 composite for four different frequencies. Solid lines are linear fits as per Mott’s SPH model.
Fig 4.37. Activation energy, $E_a$ versus wt. % of CoO for PTh-CO nanocomposites at two different frequencies.
REFERENCE


CONCLUSIONS

(i) Pure PTh
Polythiophene samples have been synthesised at three different temperatures and their non-crystalline nature have been confirmed by XRD. Small differences in particle sizes have been noted between the samples made at different temperatures. SEM images showed tubular structure for PTh sample made at 323K. UV-visible spectra of all the three samples revealed the characteristic peaks of polythiophene in colloidal solution. The sample made at 323K exhibited additional peak at 480nm. The temperature dependent electrical conductivity has been measured and analyzed using Mott’s SPH and 3D VRH models. Activation energies for conduction were determined. The density of states of carriers at Fermi level were found to be quite high.

(ii) PTh-V₂O₅ composites
The Polythiophene has been synthesised at 323K by chemical route. The nanoparticles of Polythiophene-V₂O₅ (PTh-VO) composites were prepared by mechanical mixing of Polythiophene and V₂O₅ in different weight percentages. The compositions chosen were in different weight percentages of V₂O₅ the XRD patterns of the composites exhibited peaks corresponding to V₂O₅. SEM image of pure V₂O₅ showed nano size grains. Whereas SEM images of PTh-VO composites exhibited nano size grains and some tubular structure. The temperature variation of conductivity, σ, has been measured and found it to be semiconducting type. Range of σ was found to be 2.309 x 10⁻⁵ to 1.246 x 10⁻⁴ (Ω⁻¹m⁻¹). The temperature dependence of electrical conductivity has been analyzed using Mott’s SPH and 3D VRH models. Activation energy, Eₐ, for
conduction were determined. \( E_a \) values were found to be 0.638 to 0.399 (meV). With increase in \( V_2O_5 \) content, \( E_a \) decreased and \( \sigma \) increased. The density of states of charge carriers at Fermi level was determined.

The changes in dielectric properties with temperature and frequency were measured over broad ranges. Dielectric constant decrease gradually with frequency up to 70 KHz and become constant for higher frequencies. Dielectric constant decreased with increase in frequency and increased with temperature. Dielectric loss decreased with increase in frequency and increased with temperature. Conductivity increased with increase of both temperature and frequency. By employing Mott’s Small Polaron Hopping Model’s conductivity expression, activation energy for ac conductivity has been obtained. AC activation energy was found to be 0.462 to 0.49 (meV) at 10 KHz and 0.207 to 0.263 (meV) at 1MHz respectively. Activation energy was found to be decreased with increase in frequency and increased with \( V_2O_5 \) content and it may be attributed to increase in the scattering rate of polarons with increase in \( V_2O_5 \) content.

(ii) PTh-CoO composites

Polythophene has been synthesised at 323K by chemical route. PTh-CoO composites were prepared by mechanical mixing of Polythiophene and CoO in different amounts. The wt% of CoO were taken 5% to 25%. XRD patterns of the composites confirmed incorporation of CoO with PTh. SEM images of PTh-CO composites exhibited nano size grains and tubular structures. Changes in conductivity with temperature revealed semiconducting nature. Activation energy \( E_a \) for conduction has been determined by analysing data and using small polaron hopping model. The \( E_a \) was found to be in the range of 0.816 to 0.757 (meV). \( E_a \) decreased with increase in CoO. The density of
states of charge carriers at Fermi level were determined. They were found to be $2.75 \times 10^{28}$ to $1.87 \times 10^{30}$ (eV$^{-1}$m$^{-3}$).

Dielectric properties as a function of temperature and frequency have been measured for the frequency range 200Hz to 5MHz and temperature range of 323K to 423K. Dielectric constant decreased with increase in frequency and increased with temperature. Dielectric loss decreased with increase in frequency and increased with temperature. Using dielectric data, conductivity has been deduced. Conductivity was found to increase with increase in temperature and frequency and this may be due to the fact that conduction process is made relatively easy by the presence of CoO content. By employing Mott’s Small Polaron Hopping Model expression for conductivity, activation energy for AC conductivity has been obtained. Activation energy was found to be decreased with increase in frequency and CoO content and it may be attributed to the decrease in the scattering rate of polarons with increase in CoO content.