Dielectric Properties and AC Conductivity Studies of PTh-Co Nano-Composites

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Abstract:*Polythiophene (PTh) and cobalt nanoparticles (Co-nps) were prepared by chemical oxidation and modified polyol processes respectively. Composites were made by mixing them in the proportions, PTh1-xCox; x = 0.1, 0.2, 0.3, 0.4, 0.5. Morphology of the samples was studied by SEM technique. Dielectric properties with temperature and frequency as variables were investigated. Dielectric constant and loss factor decreased with frequency and increased with temperature. AC conductivity was estimated from the dielectric data. Ac conductivity decreased with increase of Co-nps in the composites which indicates that electrically insulating effect has been induced by Co-nps. Small polaron hopping mechanism is found to be the conduction mechanism operated. Activation energy for ac conduction decreased with increase of frequency and weight percent of Co-nps in the composites. Electric modulus was determined and its analysis leads to the estimation of dielectric relaxation time. Relaxation time decreased with increase of temperature for all the five composites. For the first time PTh-Co nanocomposites have been reported for dielectric properties and ac conductivity as a function of frequency and temperature.*

Keywords: *Polythiophene, Cobalt, Conductivity, Electric modulus, Relaxation time.*

1. INTRODUCTION

The discovery of intrinsically conducting polymers like polyacetylene, polyaniline, polypyrrole, polythiophene, polyindole, etc. have emerged as a active materials lead to a wide range of applications [1-4]. The useful properties of these polymers are tunable by adding inorganic nanoparticles to them [5]. For example, increase of conductivity, dielectric constant and dielectric loss with increase of V2O5 was recorded in polyaniline-V2O5 composites [6]. A good thermal stability and noticeable crystallinity were observed in polyaniline-silver nanocomposites [7]. Increased conductivity with metal nanoparticles has been measured for polythiophene-nickel and polypyrrole-copper nanocomposites [8, 9]. Increase of magnetization and decrease of conductivity were noted for polyaniline-Iron nanocomposites [10]. The optical band gap decreased and electrical conductivity increased in polyaniline when doped with Ag nps [11]. These fundamental properties and their variations in different environments for polymer composites lead to the applications of the type gas sensors, super capacitors, microwave and electromagnetic wave absorbers, resistive switching devices etc [12-16]. On our extensive literature survey, it is learnt that polythiophene-cobalt nanocomposites have not been explored for dielectric and ac conductivity.

In the present paper the results on morphology, dielectric properties and ac conductivity of polythiophene-cobalt (PTh-Co) nanocomposites are presented.

2. EXPERIMENTAL PROCEDURE

AR grade chemicals were used to synthesize polythiophene and cobalt nanoparticles. By following chemical oxidation method polythiophene (PTh) has been synthesized using FeCl3 as an oxidizing agent. The reaction has been carried out for 24 hours at the temperature of 275 K. The precipitate so obtained was filtered and washed with methanol and distilled water and dried in an oven [17].

Cobalt nanoparticles were prepared by modified polyol process. Cobaltous chloride hexahydrate (CoCl2. 6H2O) and sodium hydroxide (NaOH) were separately dissolved in 1, 2 propandiol. Both these solutions were mixed and stirred and, then treated with hydrazine hydrate (N2H4. H2O) 80%. The reduction was allowed to take place in the temperature range from 328K to 333K. The dark grey colour cobalt particles formed were collected and washed with distilled water and acetone. The powder was dried [18].

As prepared PTh and Co particles were mechanically mixed in the proportions, PTh1-xCox. where, x = 0.1, 0.2, 0.3, 0.4, 0.5 and the composites obtained were labeled as PTh-CO1, PTh-CO2, PTh-CO_3, PTh-CO4 and PTh-CO5, respectively. The pure PTh, cobalt nano powder and the composites were investigated for structure by XRD method. These composites were investigated for surface morphology at various magnifications by Scanning Electron Microscope (SEM) (model JSM 6360) technique. Composites were pelletized using a hydraulic press using a pressure of 20 kg/cm2. Dielectric properties (dielectric constant, ε' and loss factor, ε'') have been measured in a Wayne kerr make Precession Impedance Analyzer [Model No. 6500B] for the frequency range from 1k Hz to 1M Hz and temperature from 303 K to 473 K [19]. Temperature was measured using Chromel-Alumel thermocouple with an accuracy of ±1K. Using dielectric loss factor, ε'', ac conductivity, σ_{ac} has been determined as $\sigma_{ac} = \varepsilon''\omega_{\varepsilon 0}$.

3. RESULTS AND DISCUSSIONS

3.1. XRD

The XRD patterns of pure PTh, Cobalt nano particles and PTh-Co composites were thoroughly examined. It was found that XRD patterns of Pure PTh, cobalt nano powder and PTh-Co composites exhibited amorphous nature with an exemption of two small peaks observed for pure PTh and composites at 2θ values of 33.18° and 35.55° [17-18, 20]. These peaks may be due to the residual FeCl3 particles left in the polymerization process. Typical XRD patterns for cobalt nano powder and PTh-CO5 are shown in Fig.1 (a) & (b) for inspection.

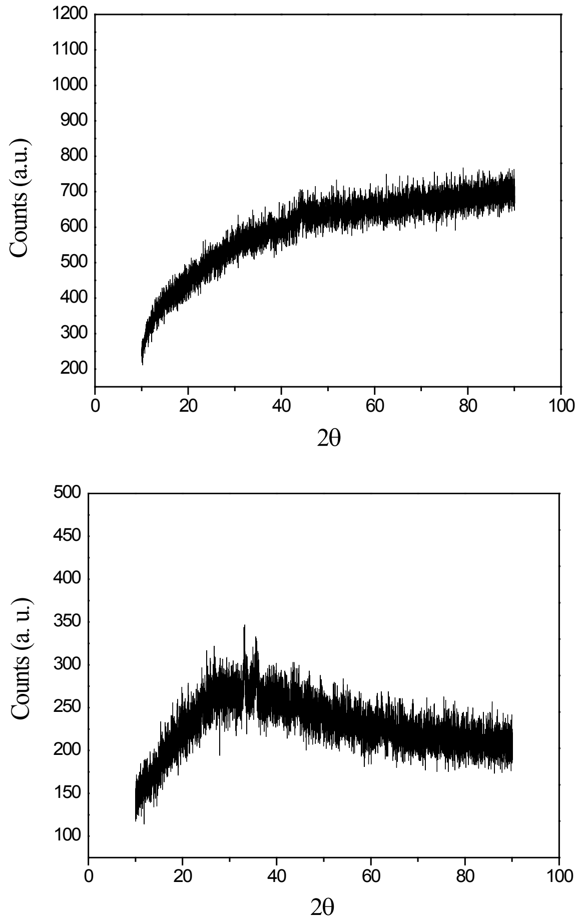

Fig. 1. XRD patterns of
(a) Co-nanoparticles (b) PTh-Co5 composite.

3.2. SEM

From the SEM images shown in Fig. 2 (a) & (b) respectively for pure PTh [17] and composite PTh-Co5, presence of cobalt nanoparticles in polythiophene host matrix can be confirmed. A good degree of mixing of the PTh and Co-nps can also be judged. Similar types of images for the present four composites have been observed. Average particle size calculated from SEM image of the composite is 32 nm. No other experimental facilities such as particle size analyzer, TEM etc were available to determine accurately the degree of mixing of PTh and cobalt nano particles.

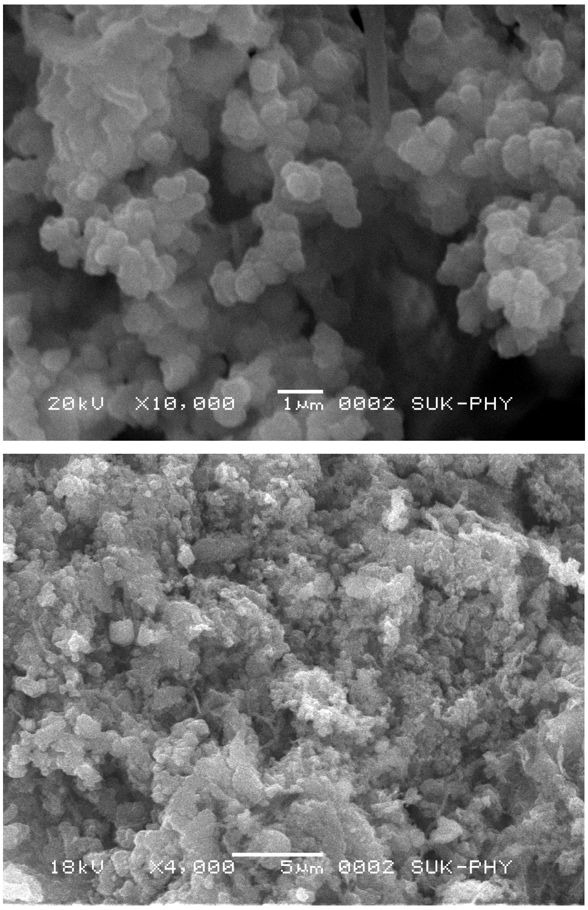

Fig. 2. SEM images of
(a) pure PTh [17] (b) PTh-Co5 composite.

3.3. Dielectric Properties

Fig. 3 shows variation of dielectric constant as a function of frequency at different temperatures for the sample PTh-CO1. From this figure, it can be noted that, ε' was high at lower frequencies and decreased fast with increase in frequency. It increased with increase of temperature. This is due to the various polarization effects such as electronic, ionic, orientational, interfacial space charge polarization, which have different relaxation frequencies [21]. Dielectric loss factor, ε'' also exhibited similar trend as that of ε' with respect to frequency and temperature as shown in Fig. 4 for PTh-CO1. Decrease of ε' and ε'' with increase of frequency may be due to decrease of ionic component to the total polarization with frequency. Further, increase of ε' and ε'' with temperature may be due to weakening of atomic bonds with increase of temperature. The same nature has been observed in the remainining four composites. Variation of ε' and ε'' with Co-content at different frequencies have been observed and found that both of these parameters decrease with Co-content (Figs. 5 and 6). This implies that dipoles are loosing freedom of orientation with respect to applied field with increase of Co-content. This is similar to the electric dipoles getting pinned by the Co-particles in the composites. Similar nature of variation of ε' and ε'' are seen in polythiophene sample [22].

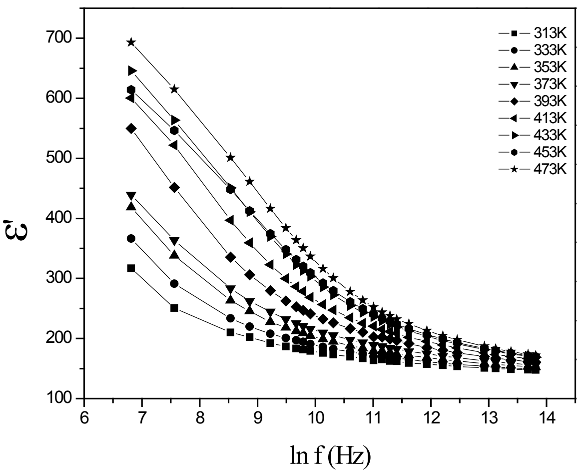

Fig. 3. Dielectric constant, ε' versus ln(f) for PTh-Co1 nanocomposite at different temperatures.

Conductivity, σ_{ac} has been determined using dielectric data using the expression, $\sigma ac = \varepsilon'' \omega \varepsilon o$.Where, ω is the angular frequency and εo the permittivity of free space which is equal to 8.85x10-12 Fm^{-1}. Change in conductivity, σ_{ac} versus frequency for different temperatures are plotted in Fig. 7 for PTh-Co1 nanocompoiste. Here, it can be seen that conductivity increased with increase in frequency and temperature. Increase in conductivity with increase in temperature indicates electrically semiconducting behavior of the composite. Remaining composites of the present series have behaved in the same fashion. Fig.8 shows a decrease in conductivity, σ_{ac}, with increase of cobalt nanoparticles. The decrease in σ_{ac} with increase of cobalt particles may be due to the barrier offered to the motion of charge carriers. AC conductivity as a function of temperature has been fit to Mott's Small Polaron Hopping (SPH) model. According to this model, conductivity is given by,

$$\sigma = \frac{\sigma_o}{T} \exp\left(-\frac{E_a}{k_B T}\right)$$

where, σ_o is the pre - exponential factor and E_a is the activation energy for small polaron hopping.

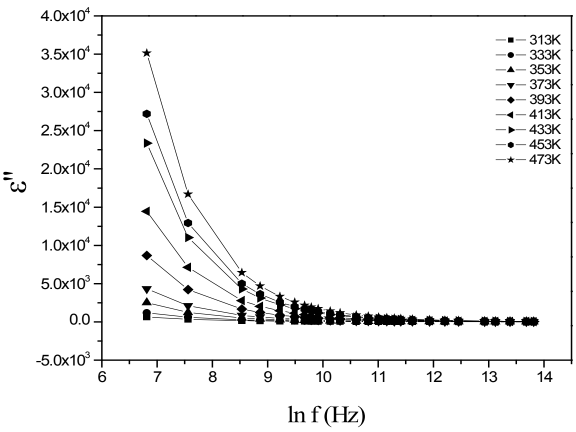

Fig. 4. Dielectric loss, ε'' ,versus ln(f) for PTh-Co1 nanocomposite at different temperature.

In the Fig. 9, the plots of $\ln(\sigma_{ac}T)$ versus (1/T) for the PTh-CO1 nanocomposites for four different frequencies are shown. The data of all the composites appeared linear for the entire experimental range of temperature. This reveals that Mott's Small Polaron Hopping (SPH) is the prevalent conduction mechanism in these composites for the temperature range studied. The linear lines were fit to the data and slope of these linear fits has been used to estimate activation energy, E_a, for conduction. It is found that E_a decreased with increase of frequency. Similar results have been reported in PTh-V2O5 and PPy-Cu composites [23, 24]. Same behavior is observed for the remaining present samples (Fig. 10). E_a decreased with increase of cobalt content. The values obtained are in close agreement with the PTh-CoO composites [25].

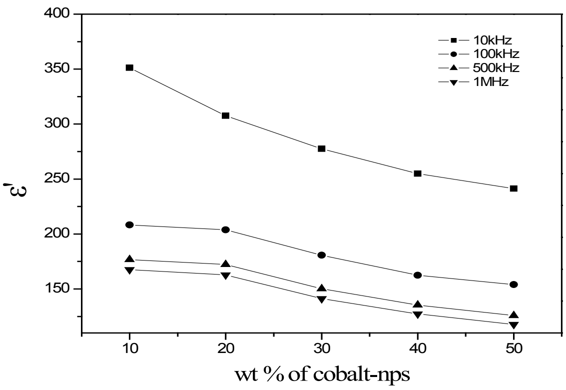

Fig. 5. Variation of dielectric constant, ε' with wt % of a cobalt nanoparticles content in polythiophene for different frequencies.

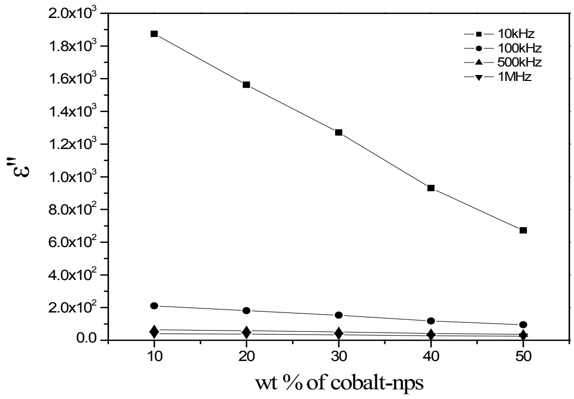

Fig. 6. Variation of dielectric loss, ε'' ,with wt % of cobalt nanoparticles content in polythiophene for different frequencies.

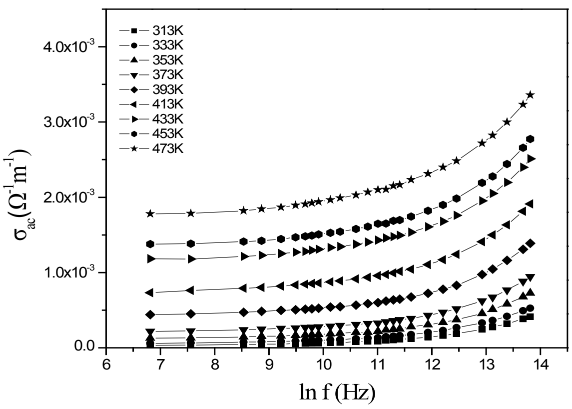

Fig. 7. Variation of conductivity, σ_{ac} with logarithmic frequency, ln(f) for PTh-Co1 nanocomposites at different temperatures.

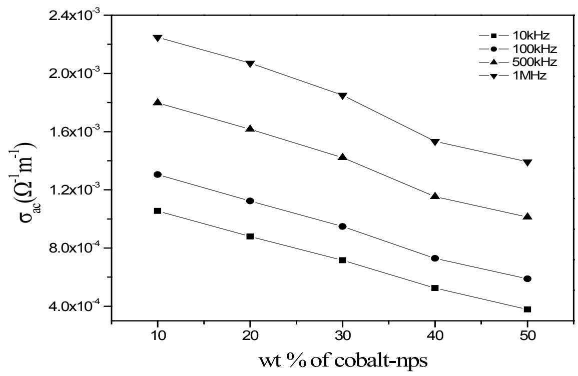

Fig. 8 Change in conductivity, σac with wt % of Co-nps in the composites for different frequencies.

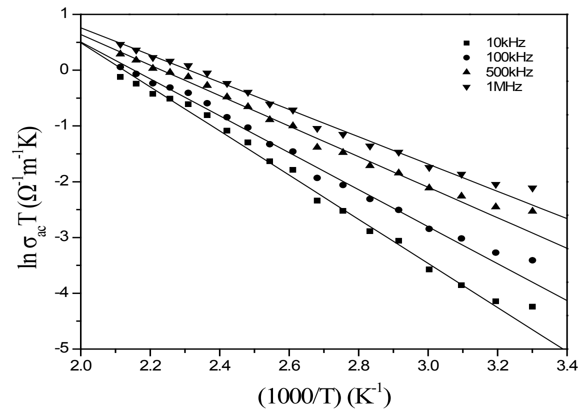

Fig. 9 Plots of ln(σacT) versus (1/T) for PTh-CO1 composite for four different frequencies. Solid lines are linear fits as per Mott's SPH model.

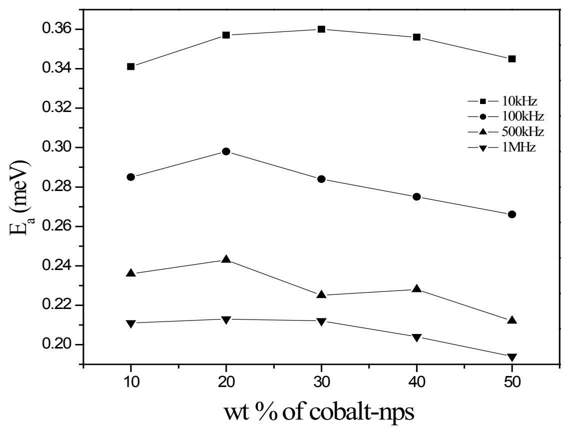

Fig. 10 Activation energy versus wt. % of cobalt for PTh-Co nano composites at four different frequencies.

To understand the dielectric process in detail, the complex electric modulus was determined and analyzed. Measured dielectric data was transformed to electric modulus. The electric modulus, M* represents real dielectric relaxation process which is reciprocal of complex permittivity, ε*. That is [26],

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + jM''$$

where, M' and M'' are the real and imaginary parts of the electric modulus respectively.

Table 1. The frequency, fmax and relaxation time, τmax for PTh-Co nanocomposites

Sample	T(K)	f_{max} (Hz)	τ_{max} = ½π f_{max} (μs)
PTh-CO1	313	5063.24	198.00
	353	19113.61	52.30
	393	61147.72	16.40
	433	176464.31	5.67
	473	257835.69	3.88
PTh-CO2	313	4703.21	213.00
	353	16236.22	61.60
	393	59041.74	16.90
	433	154507.82	6.47
	473	251450.14	3.98
PTh-CO3	313	1883.71	531.00
	353	10582.95	94.50
	393	48581.59	20.60
	433	128797.92	7.76
	473	257043.34	3.89
PTh-CO4	353	7966.49	126.00
	393	38832.00	25.80
	433	126247.55	7.92
	473	205458.63	4.87
PTh-CO5	353	6124.17	163.00
	393	37873.23	26.40
	433	104506.02	9.57
	473	154662.40	6.47

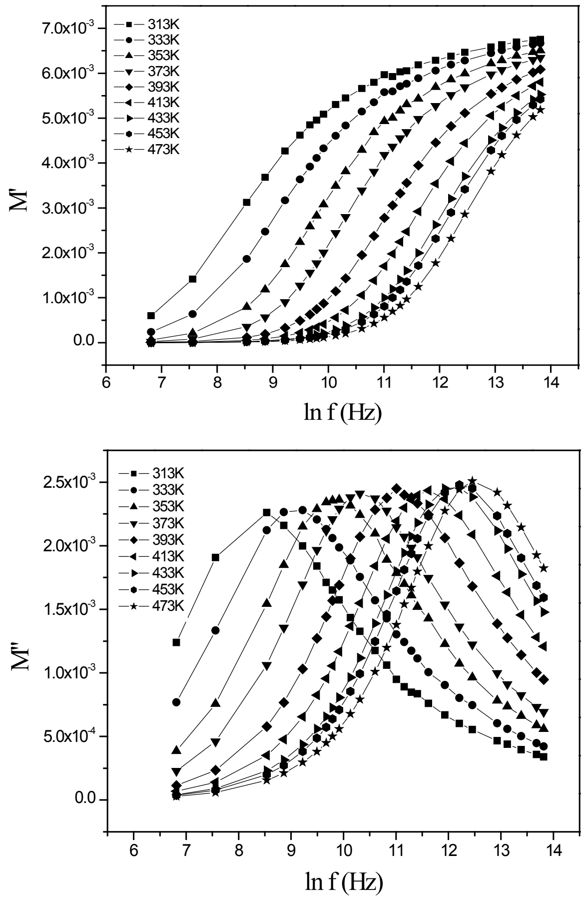

Fig. 11. Frequency dependence of real (a) M' and imaginary (b) M'' parts of electric modulus, M for PTh-CO1 nanocomposite at various temperatures.

Figs. 11 (a) and (b) depicts M' and M'' versus frequency at different temperatures respectively. From the spectrum of M'' versus frequency shown in Fig.11 (b), it can be observed that the relaxation peak fmax shifts towards higher frequency as the temperature increased which indicates that relaxation rate increases with increase in temperature [27]. Similar result was reported in reference [28]. The frequency fmax of the peak is assumed to represent a characteristic frequency of the conductivity relaxation. The inverse of the frequency fmax of the maximum peak position can be taken as characteristic relaxation time, τmax. i.e., τmax = (½)πfmax. The τmax versus temperature for the sample PTh-CO1 is shown in Fig. 12. The relaxation time decreased with increase in temperature. The remaining four composites have shown the same trend of variation of relaxation time with temperature (Table 1).

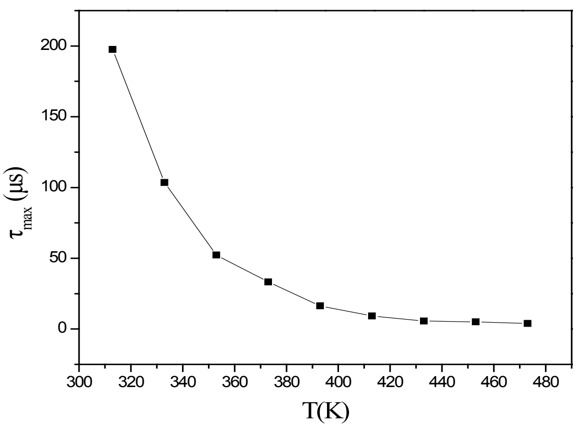

Fig. 12. Relaxation time, τmax versus temperature, T of PTh-CO1.

4. CONCLUSIONS

Polythiophene and cobalt nanoparticles were synthesized separately and their composites were prepared by mixing them mechanically. Scanning Electron Microscopy (SEM) technique has been used to understand the morphology. Dielectric measurements were carried out with temperature and frequency as input variables. AC conductivity variation with temperature indicated semiconducting behavior. Conductivity decreased with increase of cobalt nanoparticles content in the polythiophene matrix revealing the insulating effect getting induced in the composites with increase of cobalt content. Small polaron hopping is found to be the conduction mechanism in these composites. Activation energy for conduction decreased with increase of Co-content. Dielectric data was transformed to electric modulus and from which dielectric relaxation times were estimated. Relaxation time decreased with increase of temperature. This is for the first time that PTh-Co nanocomposites have been thoroughly investigated for dielectric properties and ac conductivity.

5. AKNOWLEDGMENT

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