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Dielectric Studies in PTh-Ni Composites

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ABSTRACT

Polythiophene and Nickel nanoparticles were synthesized by chemical oxidation and modified polyol methods respectively. Both powders were mixed mechanically in different weight percentages and the composites were prepared. Dielectric properties for pure PTh and PTh-Ni nanocomposites have been measured as a function of frequency in the range from 1 kHz to 1 MHz and temperature in the range from 303 K to 473 K. Dielectric constant and dielectric loss both decreased with increase in frequency and increased with increase in temperature. Conductivity has been determined using dielectric data and all the samples have shown semiconducting nature. Intersecting frequency between real and imaginary parts of dielectric constant has been determined and its variation with temperature was analyzed. Motts SPH model has been fit to the conductivity data and activation energy has been calculated. Activation energy for ac conduction decreased with increase in frequency and Ni content.

1. Introduction

Ordered conjugation with extended pi electrons and large carrier concentrations, polymers such as polyaniline, polypyrrole, polythiophene etc exhibit electrical conductivity [1] hence they called conducting polymers. By proper doping it is possible to control conductivity of the polymers spanning from insulating to metallic [2]. The metal and metal oxide nanoparticles incorporation in the conducting polymer provides the new class of materials with novel properties. Therefore, organic-inorganic nanocomposites have drawn attention of many as they combines the advantages of inorganic materials such as mechanical strength, electrical, magnetic properties and processibility of organic materials [3-6]. Studying dielectric properties of conducting polymer-inorganic nanocomposites may lead to applications in the capacitor manufacturing. Few studies have been carried out on dielectric properties of such nanocomposites. An improvement in electrical conductivity and dielectric properties of PANI/Ag and PANI/Au nanocomposites has been noticed as compared to pure PANI [7, 8]. The observed decrease in ac conductivity with increase in weight percentage of Nb_2O_5 has been attributed to the increase in the disorderliness in the PANI/Nb_2O_5 composites [9]. Increase in dielectric constant and dielectric loss with increase in doping levels of V_2O_5 in PANI has been observed in reference [10]. Ac conductivity of PPy/Cu nanocomposites has been analysed by employing Motts SPH model. Activation energy calculated using the same was found to be decrease with increase in frequency and Cu nanoparticles content in the composites [11].

Polythiophene and its derivatives have been studied for various applications like light emitting diodes [12], super capacitors [13], field effect transistors [14], etc. Nickel is a transition metal having wide ranging applications in its nano form in the fields of magnetic fluids, magnetic recording media, solar energy absorption, fuel cell electrodes, catalysts, etc., [15].

Literature reveals that no work has done on dielectric properties of polythiophene–nickel nanocomposites as function of frequency and temperature. In this paper we report dielectric properties of PTh-Ni nanocomposites. Using dielectric data ac conductivity has been calculated. Conductivity analysed by Motts small polaron hopping model.

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2. Experimental Methods

Analytical grade chemicals were used to synthesize polythiophene and Nickel nanoparticles. Polythiophene (PTh) synthesized by chemical oxidation method using $FeCl_3$ as an oxidizing agent. The polymerization was carried out for 24 hours at 275 K. Black precipitate of polythiophene was filtered and washed with methanol and double distilled water and resulted powder has been dried in an oven.

Nickel (Ni) nanoparticles were prepared by modified polyol process by dissolving nickel (II) acetate tetrahydrate and sodium hydroxide in 1, 2 propandiol. Both the solutions were stirred and mixed. Hydrazine hydrate of 80% concentration was added drop wise to the mixed solution and reduction allowed for 1 hour at 353 K. Black coloured nickel powder separated from the solution, washed and dried in an oven [16].

As prepared PTh and Ni nanoparticles were mixed in the weight percentages defined as $PTh_{100-x}Ni_x$. Where, x = 10%, 20%, 30%, 40% and 50% and labelled as PTh-Ni1, PTh-Ni2, PTh-Ni3, PTh-Ni4 and PTh-Ni5 respectively. Pure PTh, Ni nanoparticles and their composites were investigated for structure, grain size and surface morphology using XRD and SEM. The results have been published [16]. Dielectric properties have been measured in Wayne kerr make Precession Impedance Analyzer (Model No 6500B) as a function of frequency in the range from 1 kHz to 1 MHz and temperature in the range from 303 K to 473 K. Using dielectric data ac conductivity has been determined as $\sigma_{ac} = \varepsilon'' \omega \varepsilon_o$ [11].

3. Result and Discussion

Dielectric data of PTh and PTh-Ni nanocomposites has been analysed as a function of frequency, temperature and composition. Fig. 1 shows the variation in the dielectric constant, ε' with frequency for pure PTh and all PTh-Ni nanocomposites. From this figure it can be seen that ε' decreased with increase in frequency. This is due to the fact that interfacial dipoles will not have sufficient time to orient themselves in the applied field direction. Therefore, the interfacial polarization decreases with increase in frequency and hence the dielectric constant [17].

The change in dielectric loss, ε'' of PTh and PTh-Ni nanocomposites with frequency is shown in Fig. 2. From the Fig it is clear that ε'' also decreased with frequency for PTh and PTh-Ni composites.

Change in ε' with frequency at different temperatures is shown in Fig. 3. It can be observed that ε' increases with temperature. Pure PTh and other PTh-Ni nanocomposites of the present series have shown the same nature of variation.

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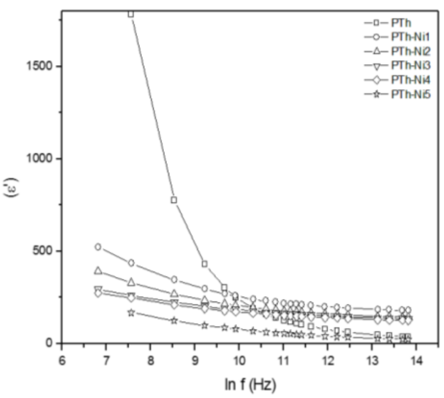

Fig. 1 Dielectric constant, ε' versus ln(f) for PTh and PTh-Ni nanocomposites at 393K

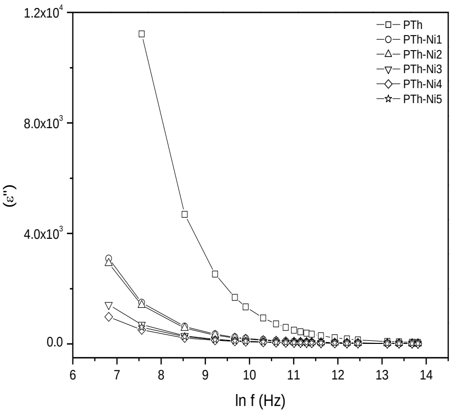

Fig. 2 Dielectric loss, ε'' versus ln (f) for PTh and PTh-Ni nanocomposites at 393 K

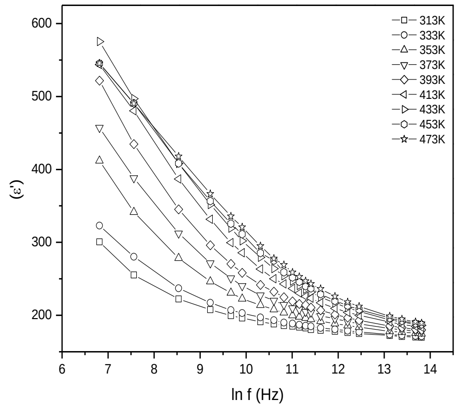

Fig. 3 Dielectric constant, ε' versus ln (f) for PTh-Ni1 at different temperatures

The variation of ε'' with frequency at different temperatures is shown in Fig. 4. We note from Fig. 4 that ε'' increased with increase in temperature. The similar trend has been observed for the remaining composites and pure PTh. Increase of ε' and ε'' with temperature has also been reported for PTh/V_2O_5 composites [18].

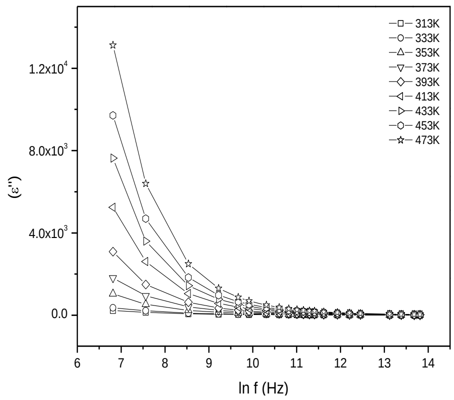

Fig. 4 Dielectric loss, ε'' versus ln (f) for PTh-Ni1 at different temperatures

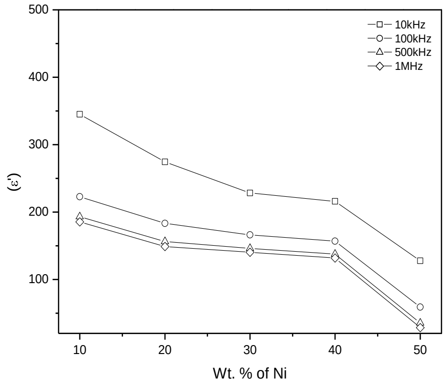

Fig. 5 Variation of ε' with weight percentage of Ni at 423 K for different frequencies

Variation of ε' and ε'' with Ni content in PTh at 423 K for different frequencies is plotted in Fig. 5 and Fig. 6 respectively. Both ε' and ε'' have shown decreasing trend with increase of Ni content. Decrease in ε' and ε'' with copper content in polypyrrole has been reported for PPy/Cu nanocomposites in reference [11].

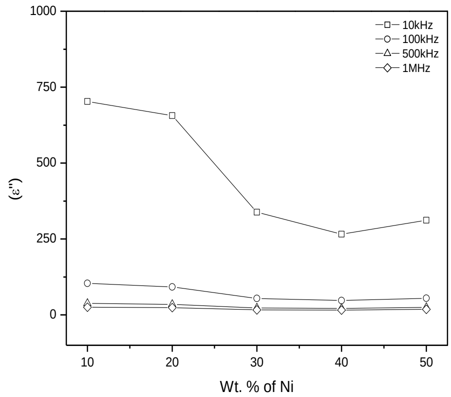

Fig. 6 Variation of ε'' with weight percentage of Ni at 423 K for different frequencies

The plots of ln (ε') and ln (ε'') versus ln (f) at different temperatures for PTh-Ni1 is shown in Figs. 7(a-e). From Figs. 7(a-e), it can be observed that ln (ε') and ln (ε'') curves intersects at a particular frequency, f_c. It is noticed that f_c increases with increase in temperature. Increase in f_c with increase of temperature indicates increasing trend of loss with temperature. Similar behavior has been observed for the remaining composites of the present series. Shift in the f_c towards higher frequency with increase in temperature observed in the iodine doped PHEPB also [19].

The intersecting frequency, f_c at different temperatures for PTh-Ni1 is shown in Fig. 8(a). A graph of f_c at 353 K for PTh-Ni nanocomposites is shown in Fig. 8(b). For pure PTh, f_c at 353 K is 807.3 kHz.

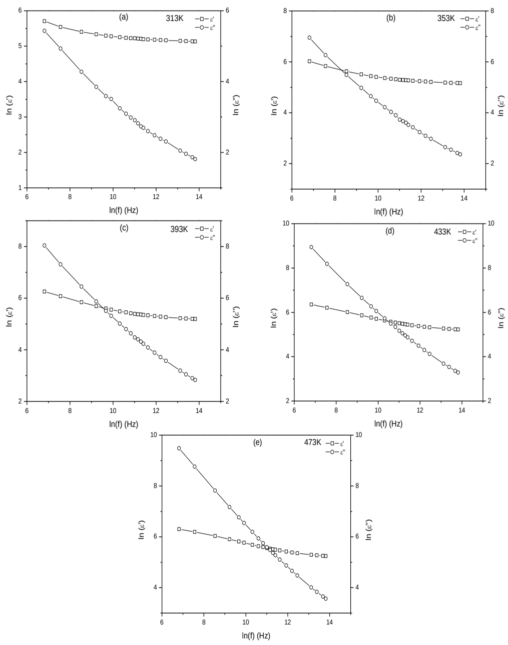

Fig. 7 a-e) Frequency dependence of ε' and ε'' at different temperatures for PTh-Ni1

Conductivity, σ was estimated using dielectric data. Temperature dependent conductivity for four different frequency values of PTh-Ni1 nanocomposite is shown in Fig. 9. One can see from the Fig. 9 that the conductivity increases with temperature revealing semiconducting nature. It can also be noticed that conductivity increases with increase in frequency. Electrical conductivity was also found to be increased with increase in temperature and frequency for PANI/Ag [1], PPy/Cu [11] and PTh/V_2O_5 [18] composites.

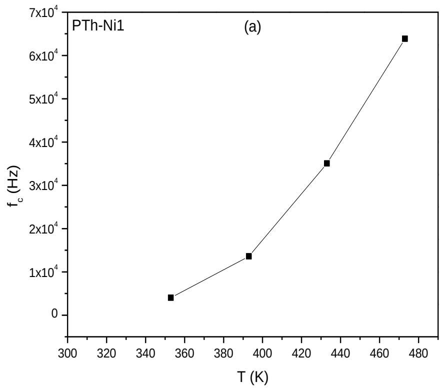

Fig. 8a Intersecting frequency, f_c for PTh-Ni1 at different temperatures

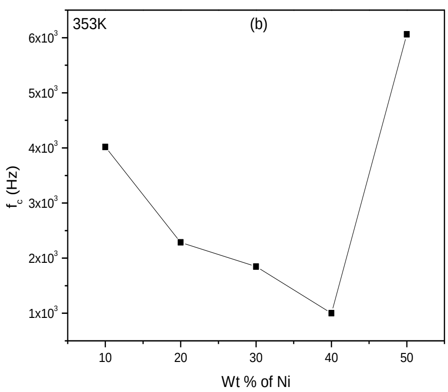

Fig. 8b Intersecting frequency, f_c as a function of weight percent of Ni in PTh at 353K

Fig. 10 shows the variation in σ with Ni content in the PTh at 423 K for different frequencies. It is clear that the conductivity decreases with Ni content in the PTh. It is also seen that as frequency increases conductivity also increased in PTh-Ni composites. Frequency response observed for pure PTh is similar to that of composites.

The variation of conductivity with temperature has been fit to Motts Small Polaron Hopping (SPH) model. According to SPH model the 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 ac conduction [11].

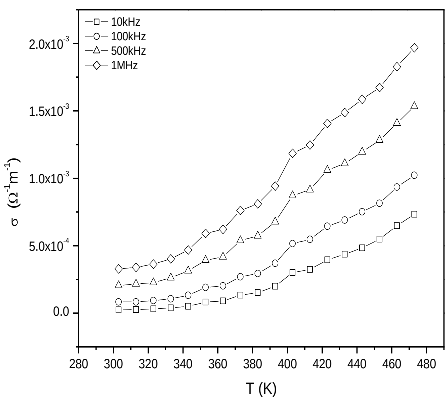

Fig. 9 Temperature dependence of σ for PTh-Ni1 at different frequencies

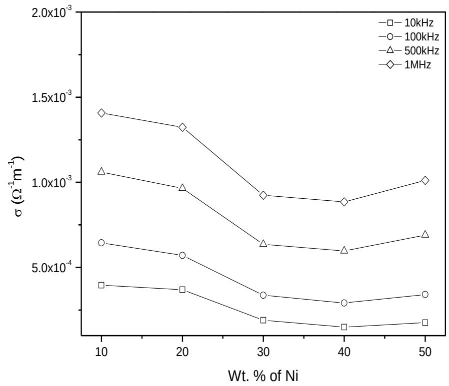

Fig. 10 Conductivity, σ variation with Ni content in PTh for different frequencies at 423 K

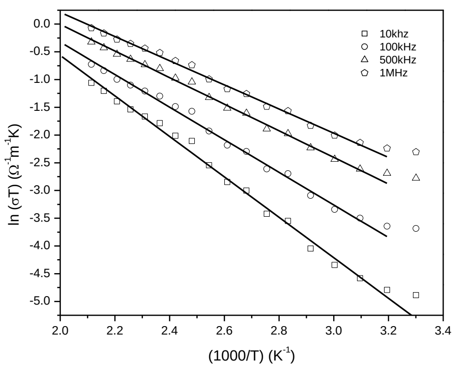

Fig. 11 The plot of ln (σT) versus (1/T) for PTh-Ni1at different frequencies, Solid lines are the linear fits to the data

The plot of ln(σT) versus (1/T) for PTh-Ni1 nanocomposite at different frequencies is shown in Fig. 11. The linear lines were fit to the data and using slope, activation energy, E_a is calculated. Similarly, activation energy, E_a has been determined for all the PTh-Ni nanocomposites and pure PTh.

From Fig. 12, one note that E_a decreased with increase in Ni nanoparticles content and frequency. For pure PTh, E_a decreased with increase in frequency.

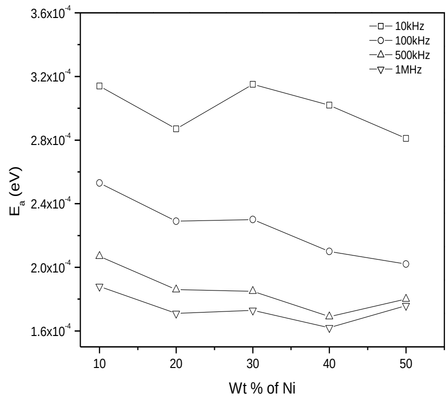

Fig. 12 Variation of E_a with Ni content in PTh for different frequencies

4. Conclusion

Polythiophene and nickel nanoparticles were synthesized and their composites were prepared by mechanical mixing in different weight percentages. Dielectric properties were measured as a function of frequency and temperature. Dielectric constant and dielectric loss both decreased with increase in frequency and Ni content and increased with increase in temperature. Intersecting frequency between dielectric constant and loss factor was determined for all the composites and found that it decreases with increase of Ni content up to 40% and increased for higher amounts of Ni. Conductivity has been determined using dielectric data. AC conductivity increased with increase in frequency and temperature and, decreased with increase of Ni content. Activation energy for ac conduction has been determined by applying small polaron hopping model to the data and it was found that activation energy decreases with increase in Ni content in the composites.

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