Research Journal of Physical Sciences ISSN 2320–4796
Vol. **3(5),** 6-10, July **(2015)** *Res. J. Physical Sci.*

Frequency dispersion and Temperature variation of Dielectric properties in PPy-Cu Nanocomposites

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Available online at: www.isca.in
Received 21th May 2015, revised 29th June 2015, accepted 1st July 2015

Abstract

Nanocomposites of Polypyrrole-copper (PPy-Cu) were synthesized by mixing independently prepared Polypyrrole and copper nanoparticles, in different weight percentages. Dielectric properties were measured as a function of temperature in the range from 300K to 550K and frequency in the range from 50Hz to 1MHz. Dielectric constant decreased with increase in frequency and temperature. Dielectric loss decreased as the frequency and temperature are increased. Using dielectric data, ac conductivity has been determined. Conductivity was found to be in the order of 10^{-3} ($\Omega^{-1}m^{-1}$) and exhibited semiconducting behavior with respect to temperature. Using Mott's polaron hopping model to the conductivity data, activation energy for conduction has been obtained. Activation energy was found to be in the order of a meV and it has increased with increase in frequency and Cu nanoparticles content. It is for the first time PPy-Cu nanocomposites were investigated for dielectric properties with frequency and temperature as variable over wide ranges and data analyzed thoroughly.

Keywords: Polypyrrole, copper nanoparticles, dielectric constant, conductivity, activation energy.

Introduction

Polymers containing metal particles are attractive systems as they exhibit properties that are of practical interest[1-6]. Polypyrrole (PPy) and copper (Cu) are two different types of conductors. PPy is an organic polymer exhibiting semiconducting behavior and Cu is a metal. Mixture of PPy and Cu particles are called hybrid composites because they combine different electrical features of the parent constituents. Both PPy and Cu display a variety of morphologies on nanoscale.

The metal nanoparticles such as copper have applications in catalytic activities and in various electronic components[7]. The composites made of a metals and organic semiconductors are known to exhibit enhanced conductivity and tunable physical and chemical properties[8]. Of these, the composites made of polypyrrole (PPy) and copper nanoparticles are the best example. Synthesis and size control of PPy nanoparticles have been studied and proposed that due to large surface areas PPy nanoparticles can be efficiently dispersed and such systems exhibit sizable conductivity[9-11].

Copper nanoparticles have attracted considerable attention of the researchers as copper is an inexpensive and good conducting. Using copper nanoparticles of sizes less than 50nm, dispersed low viscous conductive ink was prepared. The ink-jet printed copper pattern exhibited conductivity of 5.8×10^6 ($\Omega^{-1}m^{-1}$)[12]. The band gap energy of copper nanoparticles was determined using photoluminescence spectrum of aged nanoparticles[13]. PPy-CuS nanocomposites were produced by an in situ chemical oxidative polymerization method and their frequency dependent electrical properties have been investigated. These composites exhibited improved stability and enhanced conductivity[14]. The room temperature electrical conductivity of PPy-Cu nanocomposites was measured by four probe technique and the value was 4.13 ($\Omega^{-1}m^{-1}$)[15]. From the above literature it is clear that PPy-Cu nanocomposites have not been investigated for dielectric properties with frequency and temperature as variables. In this communication, we present results on dielectric measurements carried out on PPy-Cu nanocomposites. Using dielectric data, ac conductivity has been determined. Measured conductivity has been viewed in terms of small polaron hopping model due to Mott[16].

Material and Methods

Analytical grade Pyrrole, Ammonium Peroxidisulphate, Methanol, Acetone, Copper sulfate (penta hydrated) and Sodium Borohydride were used in the preparation of PPy nanoparticles and copper nanoparticles. Preparation of PPy nanoparticles was carried out at a temperature of 277K. Aqueous Ammonium persulphate (APS) solution has been added drop wise to a homogeneous pyrrole solution. After addition of few drops of APS, the solution became greenish revealing PPy nanoparticles formation in the colloidal solution. Further addition of APS, the solution became black. The reaction has been carried out for eight hours. The colloidal solution was filtered and washed with double distilled water, methanol and acetone several times to remove unreacted pyrrole and ammonia. The powder was collected, dried and grinded[17].

Copper nanoparticles were prepared by following chemical reduction procedure in which ice cooled solution of sodium borohydride ($NaBH_4$) was added drop wise to the aqueous solution of Copper sulfate ($CuSO_4.5H_2O$). During the process of reaction the solution was stirred vigorously. The solution was filtered, thoroughly washed using distilled water and acetone. The collected powder was dried and grinded.

Polypyrrole-Copper (PPy-Cu) composites were prepared by mixing of Polypyrrole and Copper nanoparticles in the weight percentages defined as $(PPy)_{100-x}$ $(Cu)_x$, where x = 10%, 20%, 30%, 40% and 50% and are labeled as PPy-CU1, PPy-CU2, PPy-CU3, PPy-CU4 and PPy-CU5 respectively. These composites were investigated for structure and grain size using XRD and SEM. The results have been communicated to the journal[18]. Dielectric properties as a function of temperature and frequency have been determined by measuring capacitance and dissipation factor[19] in Wayne kerr make Precession Impedance Analyzer [Model No. 6500B] for the frequency range from 50 Hz to 1M Hz and temperature in the range from 300K to 550K. Temperature was measured using Chromel-Allumel thermocouple with an accuracy of ±1K.

Results and Discussion

Dielectric properties: The dielectric properties have been analyzed in terms of frequency, temperature and compositions. Figure-1 displays the changes in dielectric constant, ε' with respect to frequency for all the five composites. Form this figure, we can note that ε' decreased with increase in frequency. Dielectric loss factor, ε'' variation with frequency for all the five composites is plotted in Figure-2. The nature of variation of ε'' with frequency is same as that of ε' with frequency. Figure-2 shows that dielectric loss, ε'' decreases with increase in frequency and become almost zero at higher frequencies. This indicates lossless nature of samples for higher frequencies. Moreover, it is also known that dielectric loss depends on other factors such as stoichiometry[20]. Temperature variation of ε' for PPy-CU1 is shown in Figure-3. From Figure-3, we note that ε' decreased with increase in temperature. Remaining composites of the present series showed similar nature of variation of ε' with temperature. The change in ε'' with temperature for PPy-CU1 is shown in Figure-4. From Figure-4, we note that ε'' increased as temperature is increased. Increase of ε'' with increase in temperature has also been reported for nano alumina poly vinyl alcohol composites[21]. Similar type of variation in ε'' with temperature is observed for other samples of the present series.

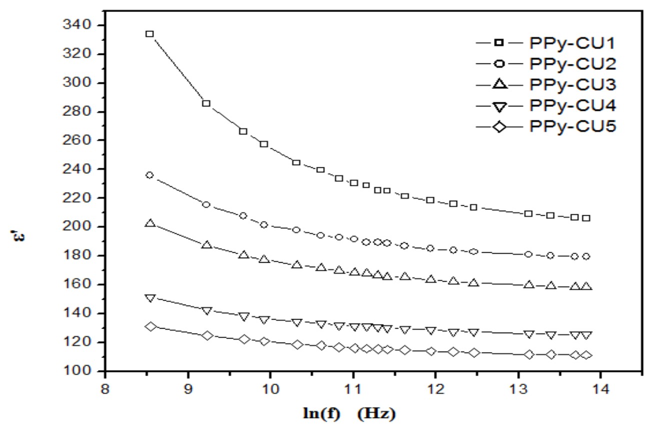

Figure-1
Dielectric constant, ε' versus ln(f) for PPy-Cu nanocomposites at the temperature of 323K

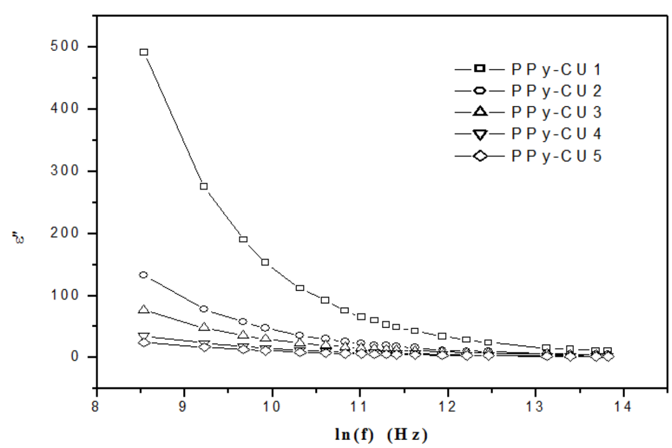

Figure-2
Dielectric loss, ε'' versus ln(f) for PPy-Cu nanocomposites at the temperature of 323K

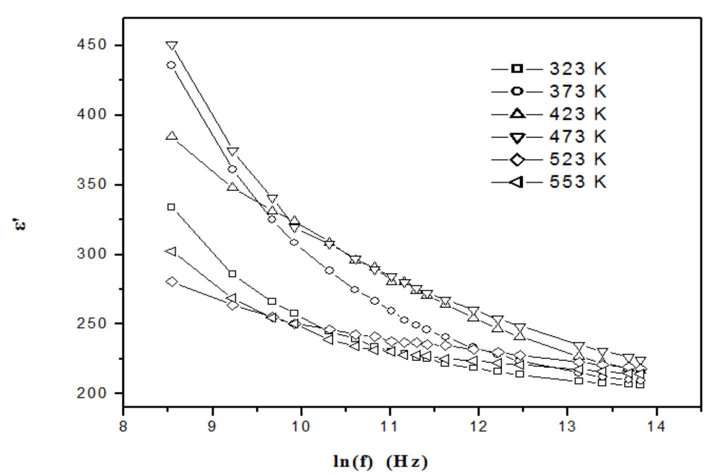

Figure-3
Dielectric constant, ε' versus ln(f) for PPy-CU1 nanocomposites for different temperatures

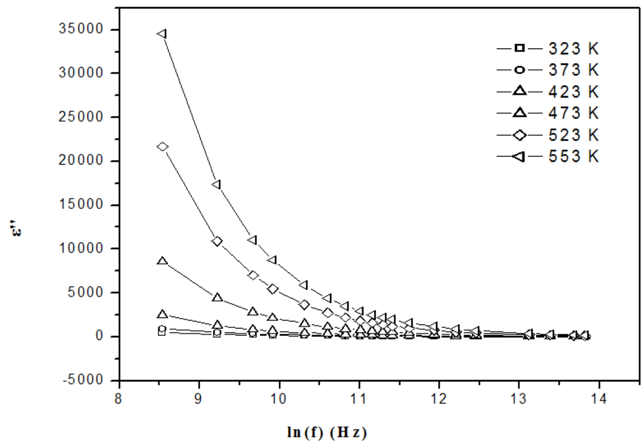

Figure-4

Dielectric loss, ε'' versus ln(f) for PPy-CU1 nanocomposites for different temperatures

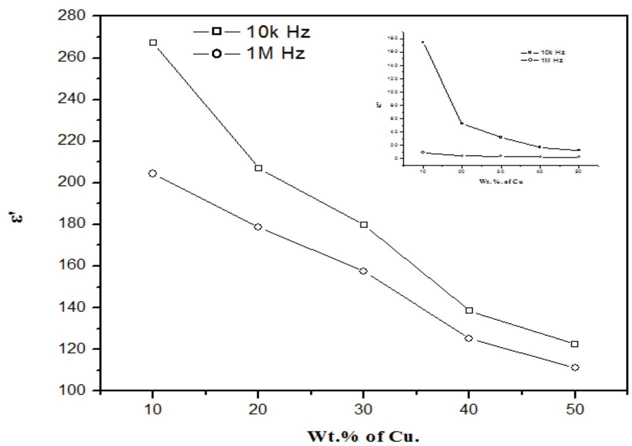

Figure-5

Variation of dielectric constant, ε' and dielectric loss, ε'' (inset) with copper content in polypyrrole nanocomposites

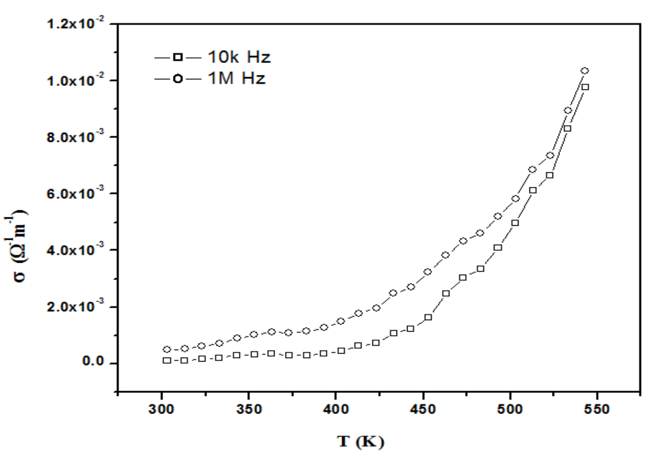

Figure-6

Temperature dependence electrical conductivity of PPy-CU1 nanocomposites at different frequencies

In Figure- 5 it can be observed that both ε' and ε'' decreases (inset) with increase of copper content in polypyrrole matrix.

Electrical conductivity: Conductivity, σ was estimated using dielectric data as per the following expression[19].

$$\sigma_{ac} = \varepsilon'' \omega \varepsilon_o \qquad (1)$$

Conductivity variation with temperature for two different frequencies (low and high) of PPy-CU1 is plotted in Figure-6. In Figure-6, it can be seen that conductivity increases with increase in temperature indicating semiconducting type of behavior. It also increased with increasing frequency. All the present composites behaved in the same fashion. Conductivity was found to be of the order of 10^{-3} ($\Omega^{-1}m^{-1}$) in the entire range of temperature of interest.

The data of conductivity variation with temperature has been fit Mott's expression that was derived for Small Polaron Hopping (SPH) in noncrystalline semiconductors. As there is no good quantitative theory for explaining conduction mechanism in conducting polymer composites, here we use Mott's SPH model. According SPH model, the conductivity is given by[16].

$$\sigma = \frac{\sigma_0}{T} \exp\left\{-\frac{E_a}{K_B T}\right\} \qquad (2)$$

Where, E_a is the activation energy for small polaron hopping. The plots of ln(σT) verses (1/T) were made as per Eqn.(2) for sample PPy-CU1 and shown in Figure-7. The least square linear lines were fit to the data in the high temperature region where the data appeared linear. Activation energy, E_a for each sample was determined using their respective slopes.

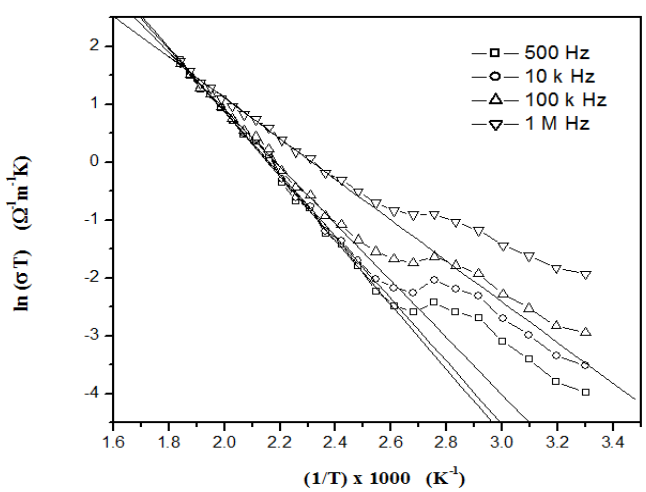

Figure-7

The plots of ln(σT) versus (1/T) for the nanocomposite PPy-CU1 for different frequencies, Solid lines are the linear fits to the data

Conductivity variation with Cu content for different frequencies at the temperature of 473K is shown in Figure-8. It can be noted that conductivity decreased with increasing copper content. In addition to this conduction mechanism in these composites gets expedited with increasing frequency. This could be due to the fact that increase in frequency enhances polaron hopping frequency. Activation energy, E_a versus Cu content for different frequencies are plotted in Figure-8. From Figure-8, one note that E_a decreased with frequency. Also, E_a increased as the Cu nanoparticles content is increased. It may be that addition of Cu nanoparticles to the PPy network contributes more to the scattering of polarons such as grain boundary scattering.

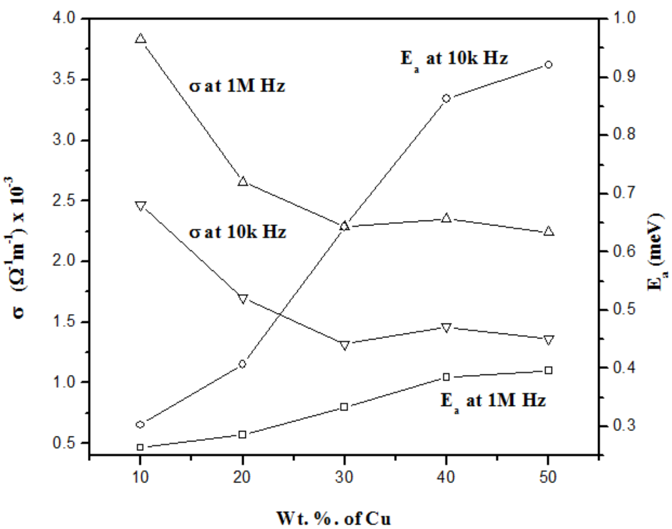

Figure-8

Variation of Conductivity, σ, at 473K and Activation energy, E_a, with Copper content in PPy-Cu nanocomposites at different frequencies

Conclusion

Polypyrrole and copper nanoparticles have been synthesized at 277K by chemical route. PPy-Cu nanocomposites were prepared by mixing Polypyrrole and copper nanoparticles in different weight percentages. Dielectric parameters were measured as a function of temperature and frequency over wide ranges. With increase in frequency and temperature, dielectric constant decreased. Whereas dielectric loss decreased with frequency and, increased with temperature. AC conductivity has been deduced using dielectric data. Conductivity was found to increase with temperature and frequency. By employing Mott's Small Polaron Hopping Model, activation energy for ac conduction has been obtained. Activation energy was found to be decreasing with increase in frequency and increased with Cu nanoparticle content. Based on this result, it is concluded that polaron scattering rate increases with the addition of Cu nanoparticles to PPy matrix.

Acknowledgement

One of the authors, K. Praveenkumar acknowledges the financial support from UGC, New Delhi under UGC-BSR fellowship.

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