THINK INDIA JOURNAL

ISSN:0971-1260
Vol-22- Issue-04-October -2019

Synthesis, Ac Electrical Conductivity And Dielectric Properties Of Polythiophene-V_2O_5 Nanocomposite

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ABSTRACT

Polythiophene has been prepared by oxidation process. Polythiophene-V2O2 composites were prepared by mechanical mixing of PTh and V_2O_2 in different weight percentages.. The Polythophene has been synthesised at 323K by chemical route. The temperature dependence of electrical conductivity has been analyzed using Mott's SPH and 3D VRH models. Activation energy, E_a, for conduction were determined. Ea values were found to be 0.638 to 0.399 (meV). With increase in V_2O_5 content, E_a decreased and increased. The density of charge carriers at Fermi level was determined. The changes in dielectric properties with temperature and frequency were calculated over broad ranges. Dielectric constant decrease gradually with frequency up to 70KHz 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.

KEYWORDS: Polythiophene, nanocomposites, conductivity, pTh-V_2O_2

1. INTRODUCTION

1.1 POLYTHIOPENE

In specific, polythiophene and its derivatives (Figure 1) were the subject of numerous recent studies. Normally, polythiopene and derivatives were synthesized utilizing two techniques: chemical and electrochemical processes. Thiopene, furan, and selenphene were polymerized with

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various initiators: sulphuricacid, chloride iron (III) and catalyst Ziegler. Experimental data, however, show that polythiopene with an acidic pter comprises of alternating units of thiopene and tetrahydrothiopene. Yamamoto et al. synthesis of 2,5-dibromothiopene or 2,5-dihalogenothiopene by nickel salt catalytic coupling of the Grignard reagent. In fact, Kossmehl and Chatzitheodorou synthesized poly (five-membered hetrocycles) by mixing the monomer or dimer with the AsF5 compound. Many studies on polythiopene's electrochemical synthesis and its relative have been published.

Polythiopene and its derivatives are insoluble and infusible and their densities, determined by the flotation techniques, lie in the range 1.4-1.6 g/cm3. The oxidation potential values of substituted polythiopenes show a decrease when electron-donating groups are substituted on positions 3 and/or 4. These variations confirm that the polymer formation results from the coupling of radicals derived from the supporting salt. Polythiopene's ultraviolet visible absorption spectrum and its variants are typically defined by an extreme broad band with a limit that differs with the length of the polymeric chain, this duration being related to the monomer's structure and synthesis method Polyhetrocycles can be doped either with the donor group or with the acceptor group, but due to the high air sensitivity of the adduct; only polymers doped with acceptor groups have been studied extensively. In display devices, polythiopenes and their derivatives are widely used. The reversible polyhetrocycle doping-undoping processes make them a good candidate for secondary battery choice. They have been also used in photovoltaic applications: the conversion of solar energy in electricity with the undoped semiconducting polymers as the photoactive material, and protection against photo corrosion or photoelectrochemical cells by grafting thin conducting polythiopene films on the surfaces. These polymers are also used for protection of small band gap semiconductors against photodegradtion, also a lot of work has been devoted to the physicochemical properties of metallic clusters or aggregates, owing to their interesting applications in the field of catalysis.

Polythiopene [poly (2,5-thienylene)] (PT) is normally synthesized from di-halogenated thiopene utilizing dehalogenation polymerization catalyzed by transition metal. This process leads, however, to a polymer of quite low molecular weight, implying a chain length of only 6-15 monomer units.

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Polythiophene (PTh) has been extensively studied by many researchers. It is a conjugated polymer like polyacetylene (PA), poly (p-phenylene) (PPP) and polyaniliane (PANi). PTh has a heterocyclic structure similar to polypyrrole (PPY). PTh is obtained from the polymerization of thiophene a sulphur heterocycle that can be made into conducting by adding or removing an electron from the orbitals via doping process [1, 2]. PTh and its derivatives are attractive more due to their high electrical conductivity, environment and thermal stability. Conducting polymers are used in combination of other polymers or inorganic materials as composites or blends [2, 3]. PTh consist of alternating double and single-bonds in which each first and fourth carbon atom connected by sulphur atom forming a thionyl ring. The bond between the second and third carbon atoms therefore has more single bond character than the other C-C bonds and therefore the bonds linking the thionyl rings have more single bond character [4].

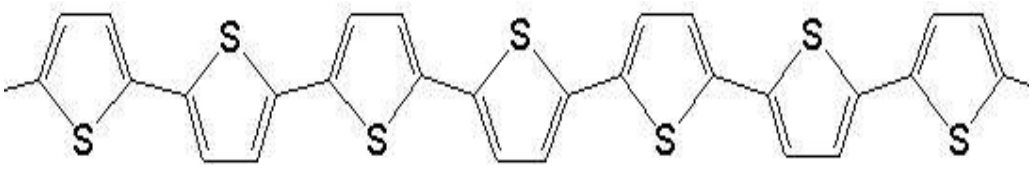

Fig 1 Structure of Polythiophene.

1.2 DIELECTRIC PROPERTIES

The functional dependence of complex dielectric function, $\varepsilon^*(\omega)$ temperature orginiates from the following different processes such as 1) Microscopic fluctuation of molecular dipoles (rotational diffusion), 2) propagation of cell charging carriers (translation of electrons, holes or ions) and 3) isolation of charges at interfaces resulting in further polarization [5]. The later can take place at inner dielectric boundary layers (Maxwell/Wagners/Sillers polarization) on a microscopic scale or at the external electrodes contacting the sample (electrode polarization) on a macroscopic scale [6, 7]. Because of molecular functions, its contribution to the dielectric loss is of several orders of magnitude greater than the dielectric reaction.

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It has specific characteristics for each of the above-mentioned processes in the temperature and frequency dependency of the real and imaginary parts of ε*. The relaxation mechanisms are defined by increases in the imaginary part, ε' and step like decrease in the real part, ε*(ω) with increasing frequency of the dynamic dielectrical feature ε*.In pure ohmic conduction, the real part of ε* is independent of frequency where as in non-ohmic conduction its real part increases with decrease in frequency [8]. Alternate representation of the dielectric properties of the materials are the complex conductivity, σ'(ω) or complex modulus M*(ω).

In disordered systems, the charge transport is possible due to hopping of carriers [9]. In addition, electrical relaxation accompanies the motion of charge in these systems: an ionic or electronic charge is surrounded by positive or negative counter charges. A load carrier hop to a new location that can only result in a good load transport if the polarization cloud follows. Otherwise, with a high probability, the charge carrier would jump back. The mutual movement of the load carrier and the surrounding polarization cloud needs an average electrical relaxation time t its impact on the load transport. the polarization cloud relaxation is in accordance with the ambient electrical field. Because of this, the field supports charging propagation. This form of electrical relaxation leads to the complex dielectric mechanism, which rises with reduced frequency. It is the essence of the Debye/Huckel/Falkenhagen theory [10-16]. This explains the experimental observation that for electrolytes the real part ' increases with decreasing frequency [17-20].

Literature survey upto now revealed that PTh-V2O2 nano composites have not been investigated by anyone for dielectric properties and ac conductivity as a function of frequency and temperature. Therefore, we report on dielectric results obtained for PTh-V2O2 nanocomposites. AC conductivity has been determined using dielectric data. Frequency and temperature dependence of dielectric and conductivity data has been thoroughly analyzed.

2. EXPERIMENTAL

Here samples were prepared using a chemical method. The chemicals used for the sample preparation were analytical grade Thiophene, Ferric chloride, Methanol and Chloroform. The PTh nanocomposites were prepared by mechanical mixing analytical grade vanadium pentaoxide V2O5.

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Thiophene and chloroform solution was prepared and stirred well. Chloroform and ferric chloride solution were prepared and magnetic stirred for half an hour. To the homogeneous PTh solution, the chloroform , ferric chloride solution was added in drop wise. For 24 hours, the whole mixture was stirred magnetically and the black precipitate was obtained. It was first chloroform washed and then methanol washed. Throughout this procedure, the precipitate became brown indicating the formation of Polythiophene [21-24].

The collected precipitate was filtered and washed repeatedly with double distilled water and methanol for removing unreacted oxidants and thiophene monomer until the filtrate was colourless. The powder was dried and grinded. The synthesis was carried out at three different temperatures of 278K, 305K and 323K and the products so obtained were labelled as PTh1, PTh2 and PTh3 respectively.

The PTh-V_2O_5 composites were prepared by mixing with the prepared Polythiophene and analytical grade V_2O_5 in different wt% defined as, $(PTh)_{100-X}$ $(V_2O_5)_X$, where X=5%, 10%, 15%, 20% and 25% labelled as PTh-VO1, PTh-VO2, PTh-VO3, PTh-VO4 and PTh-VO5 respectively. In a hydraulic press, the pellets of suitable size were prepared.

3. RESULTS AND DISCUSSIONS

3.1 STUDIES ON PTH-V_2O_5 NANOCOMPOSITES

Dopant aonic plays important role in polymerization [25-28]. 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

3.2 DIELECTRIC PROPERTIES

The dielectric parameters were calculated for all composites using the calculated capacitance, C and dissipation factor, tanδ using the expressions given in reference Figure-2 displays the dielectric constant variance, ε' with frequency of all three composites. We note from this figure that the ε' gradually decreases to 70 KHz and becomes constant for higher frequencies.

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Dielectric loss factor, ε'' variation with frequency for all the three composites is plotted in Fig.3 ε'' varied with frequency in the same fashion as that of ε'.

Temperature variation of ε' for PTh-VO1 is shown in Fig.4. We can see in this figure that ε' increases with temperature. For the remaining composites, identical properties have been found of variability of of ε' with temperature. The change in ε''with temperature for PTh-VO1 is shown in Fig.5. For the remaining composites, similar behavior of the of ε'' with temperature was observed.

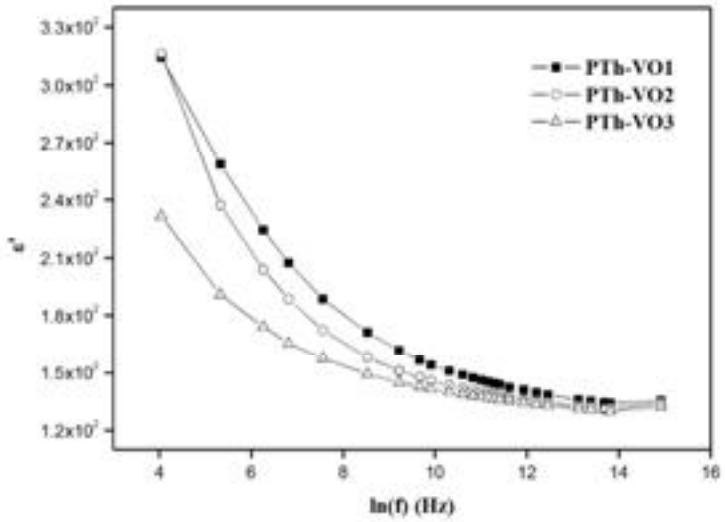

Fig 2 Dielectric constant, ε' versus ln(f) for PTh-VO nano composites at the temperature of 343K.

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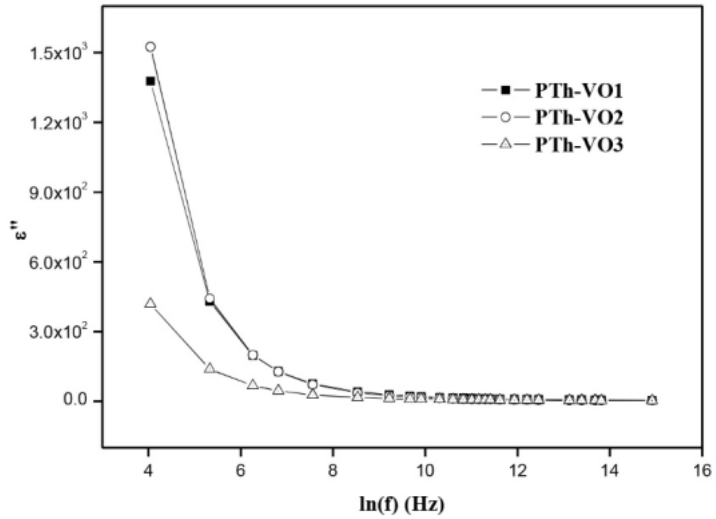

Fig 3. Dielectric loss, ε'' versus ln(f) for PTh-VO nanocomposites at the temperature of 343K.

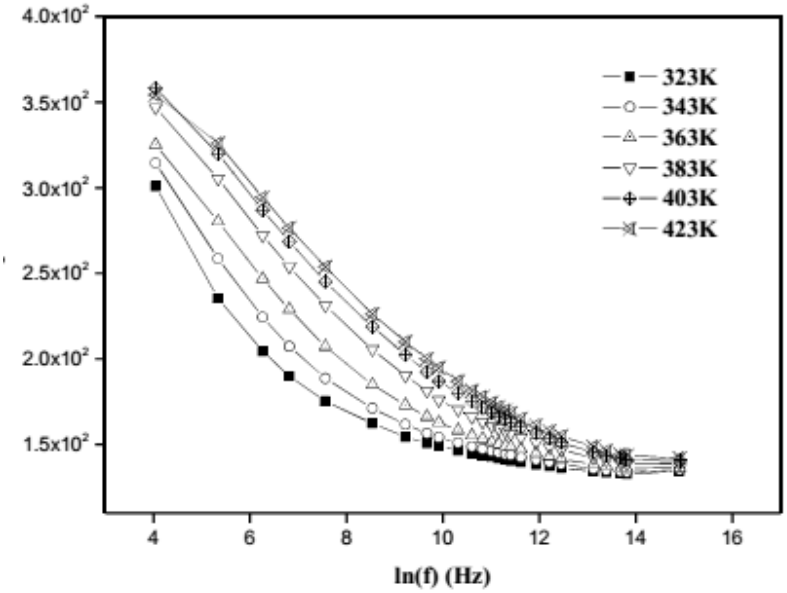

Fig 4. Dielectric constant, ε' versus ln(f) for PTh-VO1 nanocomposites at the temperature of 343K.

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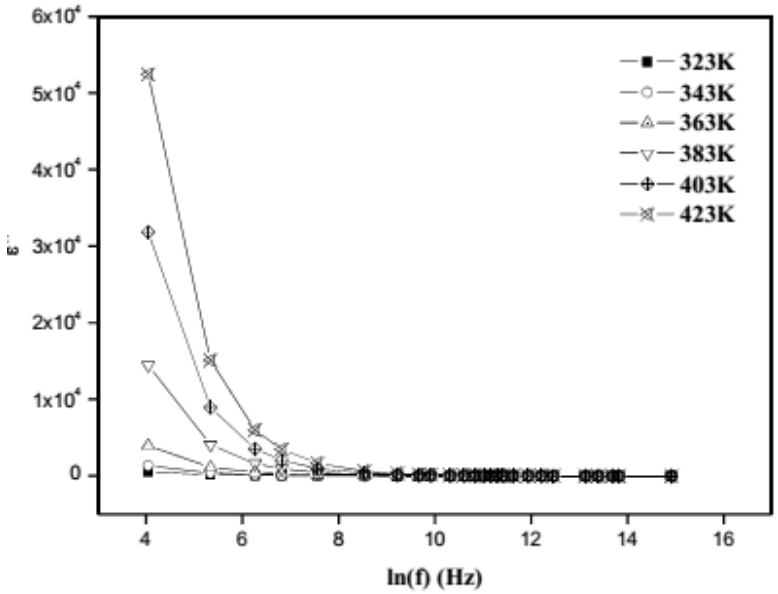

Fig 5. Dielectric loss, ε" versus ln(f) for PTh-VO1 nanocomposites at the temperature of 343K.

3.3 AC ELECTRICAL CONDUCTIVITY

Conductivity, σac, has been determined using dielectric data using the following equation [29].

$$\sigma_{ac} = \varepsilon'' \omega \varepsilon_0 \quad \ldots\ldots 1$$

Where, ε_0 is free space permittivity which is equal to 8.85 x 10^{-12} Fm^{-1}. The variance in conductivity with temperature for the composite PTh-VO1 for different frequencies is shown in Fig.6. Fig.6 indicates that conductivity rises with increasing temperature showing the type of behavior that is semiconducting. With increasing frequency, it also increased. Similar results for polyaniline doped with silver nanoparticles, cobalt-doped polyaniline and nickel oxide-doped polyaniline [30-32] have been reported. The behavior of all the present composites was the same. The conductivity variation of all the present composites was found to be in the same order of magnitude, i.e. 10^{-4} ($\Omega^{-1}m^{-1}$).

Conductivity variation with V2O5 content for two different frequencies at the temperature of 403K is shown in Fig.7. From Fig.7, it is clear that conductivity decreased with increasing V_2O_5 content.

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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. (1) [10].

The plots of ln(σT) versus (1/T) were made as per Eqn(1) for the composite PTh-VO and shown in Fig.8. The linear lines fit the data in the high-temperature area where the data was linear. Activation energy, Ea for ac conductivity was calculated using the slopes of the fit linear lines.

Activation energy, Ea versus V_2O_5 content determined for the present composites for different frequencies are plotted in Fig.9.

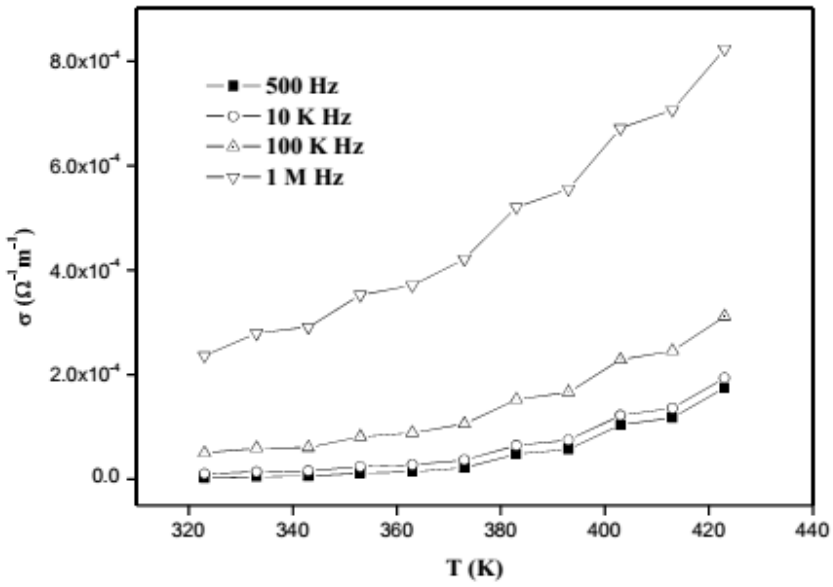

Fig 6 Temperature dependence of electrical conductivity, σ, of PTh-VO1 composite nanoparticles at different frequencies.

From the Fig.6 indicates that Ea rises with V_2O_5 content rise and decreased with the increase of frequency. Ea increase with V_2O_5 concentration increase may be that introducing V_2O_5 content to the PTh network adds more to the polarons scattering. Similar results were published for V_2O_5 -doped polyaniline, CeO_2-polyniline and Ag -doped polypyrole..

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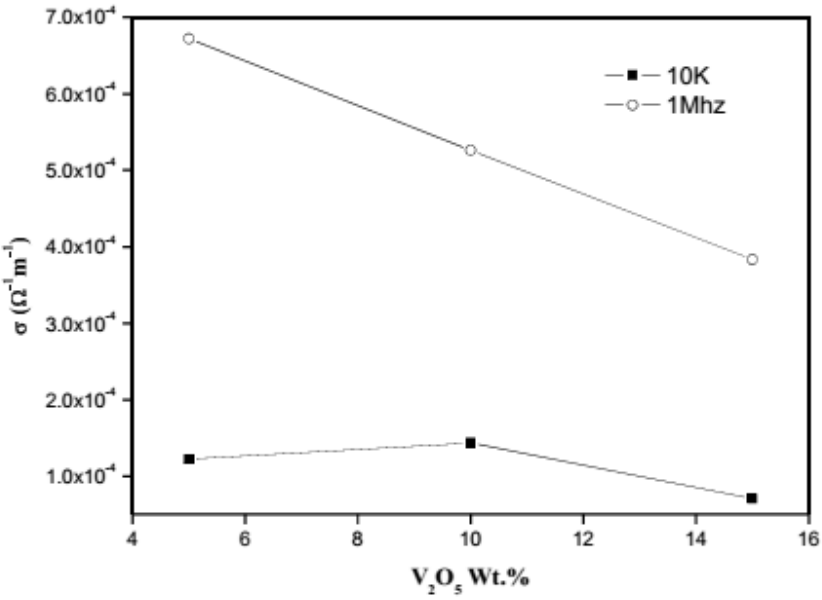

Fig 7 Conductivity versus wt % of V_2O_5 in PTh-VO nanocomposites for two different frequencies at T=403K

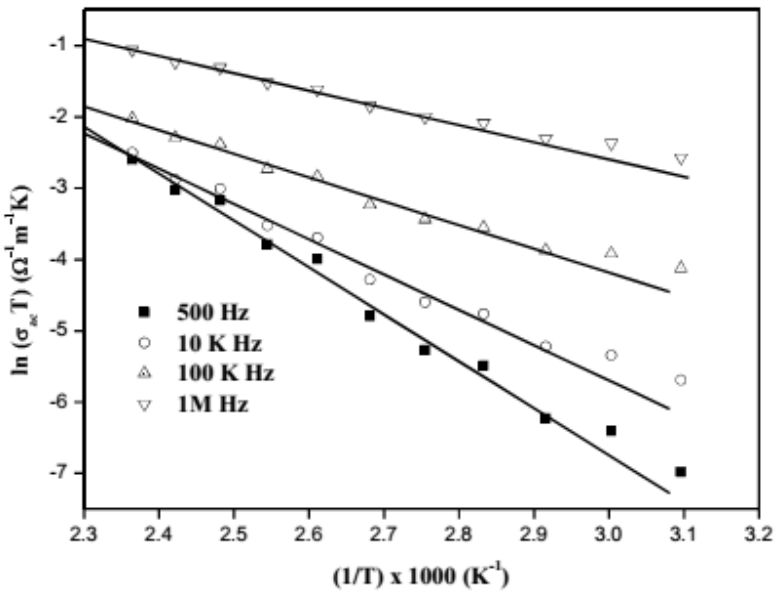

Fig. 8 Plots of $\ln(\sigma_{ac}T)$ versus (1/T) for PTh-VO1 composite for four different frequencies. Solid line are linear fits as per Mott's SPH model.

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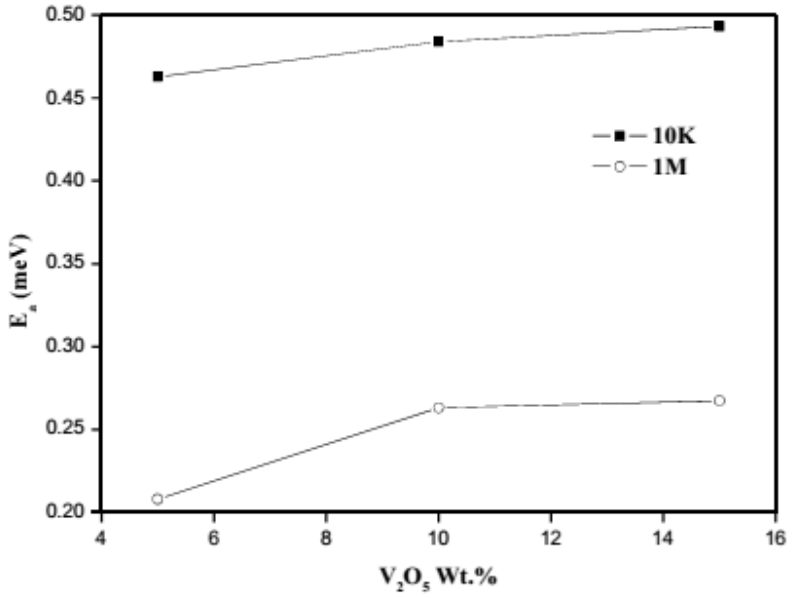

Fig. 9 Activation energy, ε_a versus wt.% of V_2O_5 for PTh-VO nano composites at two different frequencies.

4. CONCLUSION

The Polythophene has been synthesised at 323K by chemical route. The nanoparticles of Polythiophene-V_2O_5 (PTh-VO) composites were prepared by mechanical mixing of Polythiophene and V_2O_5 in different weight percentages. The compositions chosen were in different weight percentages of V_2O_5 the XRD patterns of the composites exhibited peaks corresponding to V_2O_5. The temperature variation of conductivity, σ, has been calculated and found it to be semiconducting type. Range of $\sigma$was found to be 2.309×10^{-5} to 1.246×10^{-4} ($\Omega^{-1}m^{-1}$).The temperature dependence of electrical conductivity has been analyzed using Mott's SPH and 3D VRH models. Activation energy, E_a, for conduction were determined. Ea values were found to be 0.638 to 0.399 (meV). With increase in V_2O_5 content, E_a decreased and increased. The density of charge carriers at Fermi level was determined.

The changes in dielectric properties with temperature and frequency were calculated 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

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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.

5. REFERENCES

1. F. Mohammad, J. Phys., D: Appl. Phys., 31, 951 (1998).
2. N. S. Wadatkar, S. A. Waghuley, International Journal of Basic and Applied Research, 51 (2012).
3. Jacek Nowaczyk, Kornelia Kadac, Ewa Olewnik-Kruszkowska, Advances in Science and Technology Research Journal, 9, 27, 118 (2015).
4. V. Gupta, N. Miura, Electrochem. Commun. 7, 995 (2005).
5. C. J. Bottcher, P. Bordewijk, Theory of electric polarization, vol 2. Dielectrics in time dependent fields, Elsevier (1978).
6. R. W. Wagner, Arch Elcktrotech, 02, 371 (1941).
7. R. W. Sillars, Inst. Elect Eng, 80, 373 (1937).
8. A. K. Jonscher, Dielectric relaxation in solids, Chelsa Dielectric press, London (1983).
9. H. Boettger, V. V. Bryskin, Hopping conduction in solids, Akademie, Berlin (1985).
10. P. Debye and H. Falkenhagen, Phys.Z., 29, 121 (1928).
11. P. Debye and H. Falkenhagen, Phys.Z., 29, 401 (1928).
12. P. Debye and I. Huckel, Phys.Z., 24, 185 (1923).
13. J. M. Hyde, M. Tomozawa and M. Yoshiyagawa Phys.,Chem.Glasses, 28, 174 (1987).
14. A. S. Nowick and B. S. Lim, J. Non-Cryst. Solids, 172, 1389 (1994).
15. P. B. Macedo, C. T. Moynihan and R. Bose, Phys.Chem.Glasses, 13, 171 (1972).
16. W. H. Mayer, Adv. Mater., 10,439 (1998).

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Vol-22- Issue-04-October -2019

17. I. J. A. Mertens, M. Wubbenhorst, W. D. Oostebaan, L. W. Jenneskens and Van

18. Tturnhout, Macromolecules, 32, 8663 (1999).

19. F. Kremer, L. Dominguez, W. H. Meyer and G. Wegner, Polymer, 30, 023 (1989).

20. D. L. Sidebottom, B. Roling and K. Funke, Phy. Rev., B 63, 02430 (2000).

21. Kowsar Majid . R. Tabassum . A. F. Shah .S. Ahmad .M. L. Singla, J Mater Sci: Mater Electron 20:958 (2009).

22. D C Tiwari, Vikas Sen & Rishi Sharma, Indian Journal of Pure & Applied Physics, 50, 49-56 (2011).

23. Sandip V Kamat, Vijaya Puri and R. K. Puri, 84, 1-5 (2011).

24. O. Yunus Gumus, H. Ibrahim Unal, Ozlem Erol, Bekir Sari, Polymer Composites -10. 1002,418 - 426 (2011).

25. S. V. Kamat, S. H. Tamboli, Vijaya Puri, J. B. Yadav, Oh Shom Joo Arch. Phy. Res., 1 (4):119 (2010).

26. S. V. Kamat, S. H. Tamboli, Vijaya Puri, R. K. Puri, J. B. Yadav, Oh Shom Joo, Journal of optoelectronics and advanced materials,12(11), 2301 (2010).

27. V. Sen, D. C. Tiwari, Appld. Phy. 3, 54 (2013).

28. D. Aradilla, F. Estrany, S. D. Azambuja, T. M. Casas, J. Puiggali, A. C. Ferreira, C. Aleman, Europ. Polymer J, 46, 977 (2010).