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Electrical Characterization of Polythiophene Composite Thin Films with Iodine as Dopant

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ABSTRACT

Synthesis of polymer composites poly (vinyl acetate) (PVAc) and polythiopene (PTh) was done by chemical oxidative method using ferric chloride oxidant in methanol with Iodine as a dopant. The dc conductivity as a function of temperature (313-363 K) was measured by two probe method. The maximum value for dc electrical conductivity was found for 10.4 wt % (σ = 9.78x10-10 S/cm).The decrease in conductivity for more Iodine concentration may be due to reduced segmental motion. The temperature dependence conductivity shows percolative behavior and clear cross over from Vogel-Tamman-Fulcher (VTF) to Arrhenius behavior. Ionic conduction was found to be decreased with increase in concentration of Iodine which shows ionic charge transport.
Keywords: Poly(vinyl acetate) (PVAc), Polythiophene (PTh), Iodine, dc.

I. INTRODUCTION

Polythiphene(PTh) is found to be a better conducting polymer and a leading field of investigation in the field of conducting polymers and the research still continues. Study of polythiophenes started in 1981 [1] but the field is still in exploration stage. Numbers of applications have been proposed for PThs such as field effect transistors, electroluminescent devices solar cells, photochemical resists, nonlinear optic devices, batteries, diodes and chemical sensors [2] but none has been commercialized. Roncali [3,4] surveyed electrochemical synthesis of PThs in 1992 and the electronic properties of substituted PTs in 1997.The overall review on chemical synthesis of PThs and applications as chemical sensors, organic memory devices, photo conductivity etc. is given by many researchers[5-8]. The temperature dependent conductivity, in case of ionically conducting solid electrolytes, is more completely explained by VTF (Vogel-Tamman-Fulcher) [9-11] rather than other models.

Ryu et al [12] and Yildiz et al [13]predicted that PTh powder prepared by electrochemical performance shows better results than that prepared by fast oxidation method. Barde et al [14] and Bobade et al [15] observed the variation in ionic conductivity in Polypyrrole (PPy)-poly(vinyl acetate)(PVAc) films synthesized by oxidative polymerization method. The present paper focuses on the synthesis and characterization of PTh-PVAc composite films using $FeCl_3$ oxidant and Iodine as a dopant with an aim to know the structural behavior and conduction mechanism.

II. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

PTh was synthesized at room temperature (301K) by mixing monomer Thiophene (Lobachemie Pvt. Ltd.,India) (AR grade) with solution of (oxidizing agent) anhydrous $FeCl_3$ (E.Merck,Germany) and PVAc (Lobachemie Pvt. Ltd.,India) in methanol (AR grade). Films with different wt% of Iodine were synthesized (5.5,10.4,14.9,18.9 and 22.5 wt % of Iodine).

2.2 dc conductivity measurement

The dc conductivity of the samples was measured by two probe method [16-18] in the temperature range of

313-363K. The heating rate of the sample was 1^{O}C/min.

III. RESULTS AND DISCUSSION

3.1 dc conductivity

The dc conductivity of the samples of Iodine wt % (5.5 to 22.5 wt. %) was measured in the temperature range 313 to 363 K by measuring the resistance of the samples. From figure 1 initially the conductivity increases, reach to 9.78 X 10^{-10} S/cm for 10.4 wt % of Iodine and then rapidly decreases with Iodine concentration. Many researchers [14, 20, 21] reported a similar conductivity isotherm. In case of PTh composites [20-24] percolation behavior was reported even for low concentration of PTh. The temperature dependence of conductivity for different Iodine wt % is shown in fig 8. From this plot it is observed that the conductivity increases with increase in temperature due to increase in mobility of the ions. The ionic conductivity for 10.4 wt % of Iodine show maximum conductivity. Also the formation of PTh-PVAc-I^- has much contribution to the ionic conductivity.

From the figure 2 it is observed that initially the rate of increase of conductivity is fast and after certain temperature the rise is slow. Thus it leads to two activation region (I and II as shown in figure 2) giving two different activation energies. The samples synthesized by concentration of Iodine (5.5, 10.4, 14.9 and 22.5 wt %), show the curvature type behavior below a certain temperature Tc, called knee temperature, and above which the curves are nearly linear in nature. The non-linearity in Arrhenius plot for samples synthesized at 5.5, 10.4, 14.9 and 22.5 wt % of Iodine indicates the ionic transport facilitates by the segmental motion of polymer chains. Thus Vogel-Tamman-Fulcher (VTF) [9-11] equation may more effectively represent the results. And the sample with 18.9 wt % of Iodine indicates straight line nature to which VTF equation could not be applied.

$$\sigma = \frac{A}{T^{1/2}} \exp\left[-\frac{B}{k(T-T_0)}\right] \text{ ..... (1)}$$

where T is the absolute temperature; 'A', 'B' and T_0 are the fitting constants and 'k' is Boltzmann constant. 'A' is the pre-exponential factor, which is related to the number of charge carriers. 'B' is the pseudo activation energy related to activation energy of the ion transport. It is related to critical volume for displacement in free volume model [11] and to the energy barrier for rotational motion of polymer segment in configuration entropy model [25]. T_0 is the critical (ideal glass transition) temperature, usually it is 30-50 K below 'Tg'. It is the temperature at which configuration entropy or free volume disappears.

The exploration of equation (1) gives the VTF fit parameters (figure 9) which are summarized in Table 1. It is evident that the activation energy value 'B', for the sample prepared with 5.5 wt % of Iodine is minimum. The values of T_0 increases with rise in concentration of Iodine. Such dependence of T_0, with respect to concentration of salt, has been reported in polymer electrolytes [26]. In high temperature region (figure 2) the curves no longer fits the VTF equation. The cross over from VTF to Arrhenius is clearly visible in the high temperature region. This type of cross over in conductivity behavior generally observed in polymer electrolyte systems [9-11].

Arrhenius equation is,

$$\sigma = \sigma_0 \exp\left[-\frac{Ea}{kT}\right] \text{ ..……..(2)}$$

Where Ea is the Activation energy and σ_o is the pre-exponential factor.

Below Tc the curves follows VTF equation. When the ionic conduction follows the VTF equation, a linear relation between log ($\sigma T^{1/2}$) and l/ (T- T_0) is expected as shown in figure 3.

IV. CONCLUSION

Temperature dependant conductivity for the samples 5.5, 10.4, 14.9 and 22.5 wt % of Iodine dopant follows the VTF equation [9-11] except 18.9 wt % sample. The cross over from VTF to Arrhenius observed in present system may be due to some sort of transition in energetic of local ion motion and reduction in effective ion density on undergoing order-disorder transition at temperature Tc. Thus Tc can be linked to order-disorder temperature. Below Tc the curves follows VTF equation. When the ionic conduction follows the VTF equation, a linear relation between log ($\sigma T^{1/2}$) and l/ (T- T_0) is expected as shown in figure 3.

V. REFERENCES

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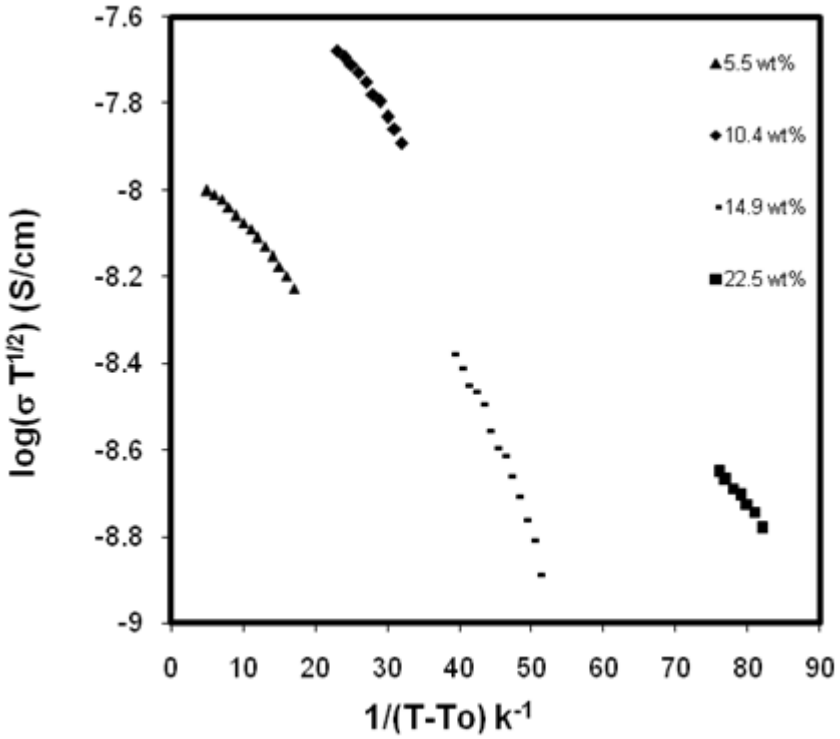

Figure 3. VTF plots for PTh-PVAc films for different wt % of Iodine

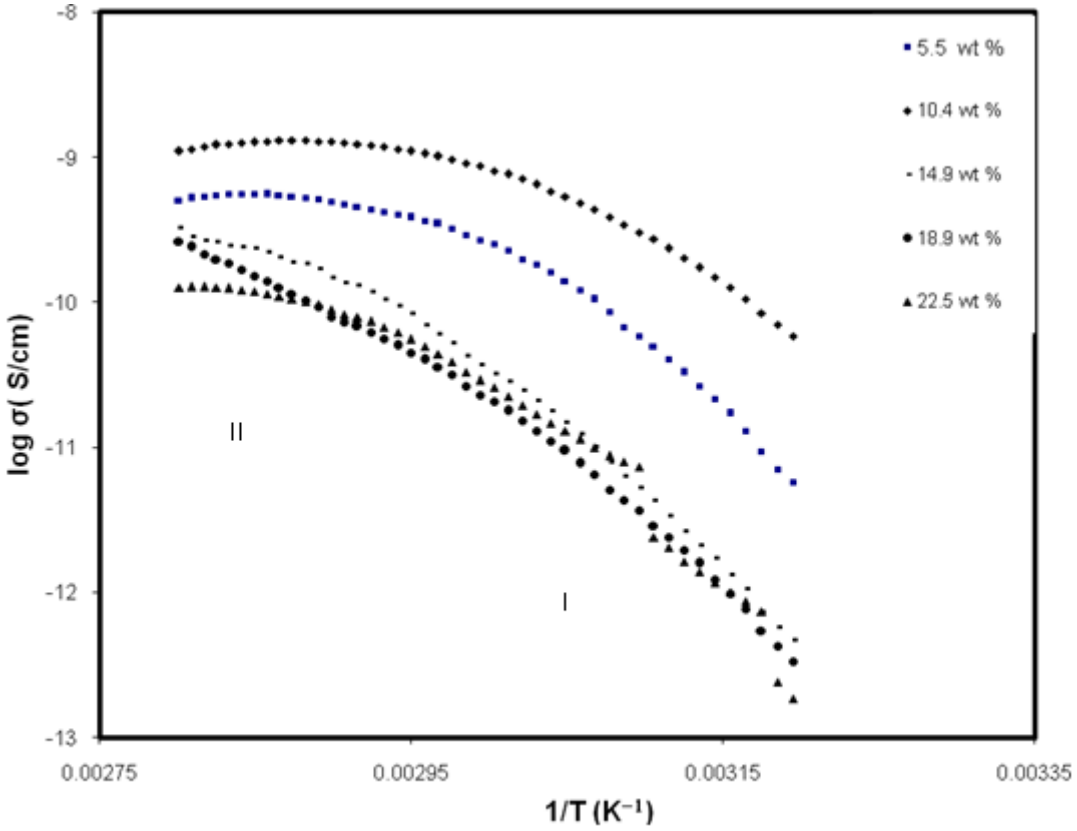

Figure 2. Variation of logσ with 1/T for different wt. % of Iodine

Table 1. VTF equation fitting parameters for the PTh-PVAc films for different Iodine wt %

	Ionic Transference number (tion)	**Energy Ea (eV)**	**Temperature T_c(K)**	**Pre-exponential factor A (SK1/2 cm-1)**	**Pseudo activation energy B(eV)**	**Ideal glass transition temperature T_o(K)**
5.5	0.96	0.149	388	2.3319×10^{-7}	0.00009	327
10.4	0.94	0.188	385	1.6538×10^{-7}	0.00019	330
14.9	0.95	0.420	362	1.0124×10^{-8}	0.00058	332
22.5	0.87	0.150	380	1.7047×10^{-8}	0.00010	341