

TEMPERATURE DEPENDENCE ELECTRICAL PROPERTIES OF POLYTHIOPHENE POLYMER COMPOSITE

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Abstract: The electrical properties of Polythiophene polymer composite doped with Lithium Perchlorate were studied by *in situ* chemical oxidative polymerization method. dc conductivities as a function of temperature (303–338 K) were measured. An endeavour has been made to explore the effect of temperature and concentration of LiClO₄ on the conductivity of composite film. The conductivity of the prepared Polythiophene composite film was found to increase with the increase in LiClO₄ concentration. Which shows the conductivity behaviour follows Arrhenius type .

Keywords: Polythiophene, Polymer Composite, Lithium Perchlorate (LiClO₄)

1. Introduction:

Now a Days tremendous advancement has taken place in the development of Conducting Polymers (CPs) in recent years due to their interesting physical, electrical and chemical properties. Some of the applications of CPs include: rechargeable batteries, electrochromic display devices, sensors and photovoltaic devices [1, 2]. New classes of conducting polymers include polythiophene, polypyrrole, polyfluorene and polyaniline. while none have exhibited higher conductivity than polythiophene, these polymers have been useful in designing new structures that are stable and soluble in some cases. Its serves as a model for developing both the electronic and physical properties of electronically conducting polymer with unique properties [3, 4].

In the present work, Polythiophene-Polyethylene oxide polymer composite doped with LiClO₄ were prepared by *in situ* chemical oxidative polymerization method. The effect of various concentrations of LiClO₄ on the electrical properties of the PTh-PEO composite films was investigated, with an intension to exploit these composites for various applications such as solar and photovoltaic devices.

2. Experimental:

PTh-PEO polymer composite doped with LiClO₄ was synthesized at room temperature (303 K) by chemical oxidative method. Anhydrous FeCl₃ was used as an oxidizing agent. A solution of PEO was first prepared in methanol by stirring for 6 h and kept over a night. Appropriate amount of Anhydrous FeCl₃ and LiClO₄ were added and stirred for 15 min. When monomer thiophene was added drop by drop to the solution a dark brown homogeneous solution was obtained. The solution was then poured on a polypropylene dishes (Petri dishes), to prepare the composite films. The wt. % of LiClO₄ in this solution was changed from 1 to 6. For each wt. % of LiClO₄, quantity of thiophene was kept constant at 0.5 ml. The thiophene polymerization progresses because the evaporation of the solvent increases the oxidation potential of cast solution. After evaporation of the solvent, the composite films were formed [5, 6]. DC conductivity of the composite film was measured by using Ohms law. The resistance of the samples was measured.

3. Results And Discussion:

DC conductivity of the PTh-PEO polymer composite doped with different wt. % of LiClO₄ was measured in the temperature range 303 to 338K by using Ohms law. The resistance of the samples was measured. It is observed that the value of resistance depends on composition as well as on temperature.

The variation of ionic conductivity with different wt. % of LiClO₄ at constant temperature 323K is shown in figure 1. As compared to pure PTh-PEO polymer composite the conductivity increases with LiClO₄ wt. % except 3 and 5 wt. % LiClO₄. PTh-PEO composite doped with the 6 wt. % LiClO₄ shows the maximum value of ionic conductivity. Addition of LiClO₄ results in increase in the conductivity value due to the aggregation of excess LiClO₄ salt.

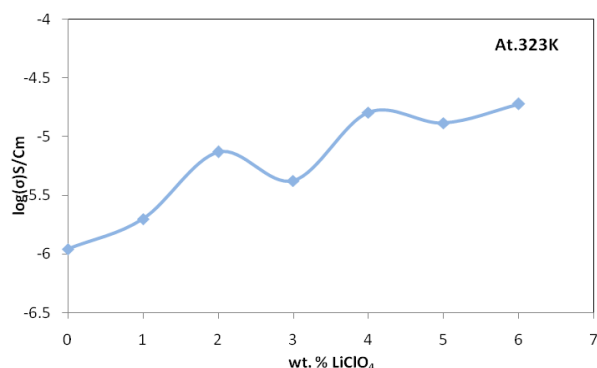


Figure 1: Variation of conductivity versus wt. % of LiClO₄ for PTh-PEO polymer Composite films.

The variation of ionic conductivity as a function of inverse temperature for PTh-PEO polymer composite doped with the different wt. % LiClO₄ is shown in Figure 2, over the temperature range 303 to 338K. It can be observed that the ionic conductivity for all the compositions of PTh-PEO composite doped with the different wt.% LiClO₄ increases with increasing temperature for the entire range. All the curves had a turning point around 328–333K, corresponding to the transition from the crystalline state of PEO to the amorphous phase [7]. This used to increase PTh-PEO ionic conductivity because a Li⁺ ion is only transferred in amorphous phase [8].

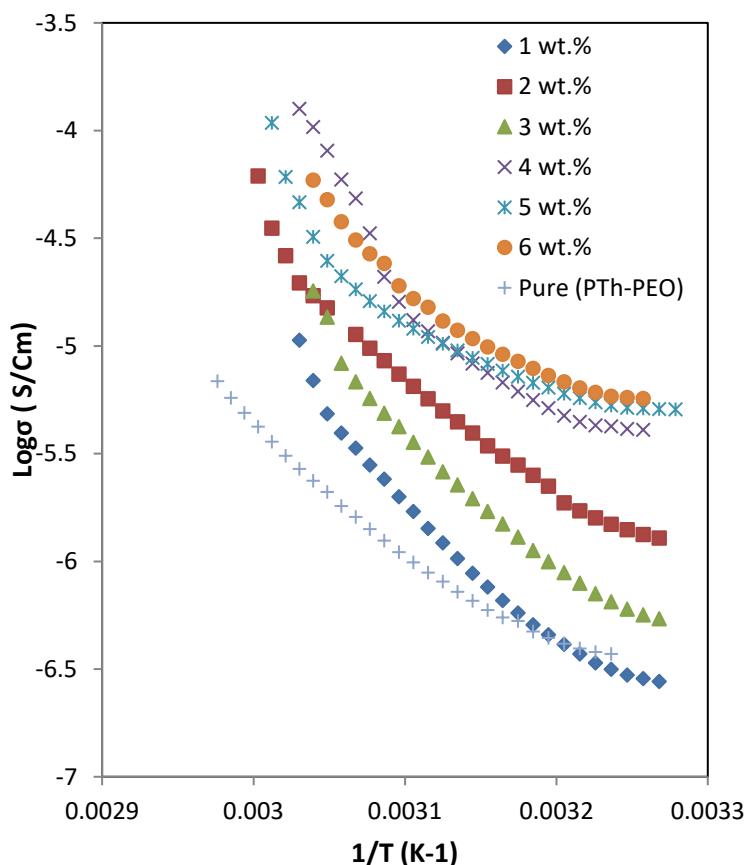


Figure 2: Arrhenius plots of the ionic conductivity of PTh-PEO composite for different wt. % of LiClO₄

The ionic conductivity increases with increasing lithium salt concentration due to the increase in the carrier density. However, the formation of ion-pairs becomes more in case of high salt concentration than the low concentration, leading to a drop in the ionic conductivity. Many researchers [9] reported a similar Arrhenius conductivity isotherm. It can be seen that the Arrhenius plots for all the samples display a similar behaviour. This type of ionic conductivity behaviour follows Arrhenius behaviour [10].

As the temperature increases, mobility of the ions increases, which results the rise in conductivity. Uppermost curve belong to 4 wt % of LiClO₄ for which conductivity is maximum. The conductivity versus temperature curves of all

synthesized samples shows that the increase in conductivity. The rate of increase of conductivity is linear for the composite; which may be due to the segmental motion of the ions in the polymer [11].

The natures of the curves are consistent with Arrhenius type charge conduction in polymer composites and the conductivity relationship follows the equation,

$$\sigma = \sigma_0 \exp (-E_a/kT) \quad 1$$

Where σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann's constant. The slope of each straight line gives the activation energy which lies between 0.34 and 0.55eV. From the figure 2, DC parameters for the curves are calculated and noted in table 1

Table1 : DC parameter for the PTh -PEO composite doped with LiClO₄

Sr.No.	LiClO ₄ wt %	Activation Energy E _a (eV)	Pre-exponential factor (SK ^{1/2} cm ⁻¹)
1	Pure PTh-PEO	0.43	11.86x10 ³
2	1	0.55	12.15 x10 ⁵
3	2	0.50	34.80 x10 ⁴
4	3	0.54	14.54 x10 ⁵
5	4	0.38	77.54 x10 ³
6	5	0.34	22.37 x10 ³
7	6	0.39	11.11 x10 ³

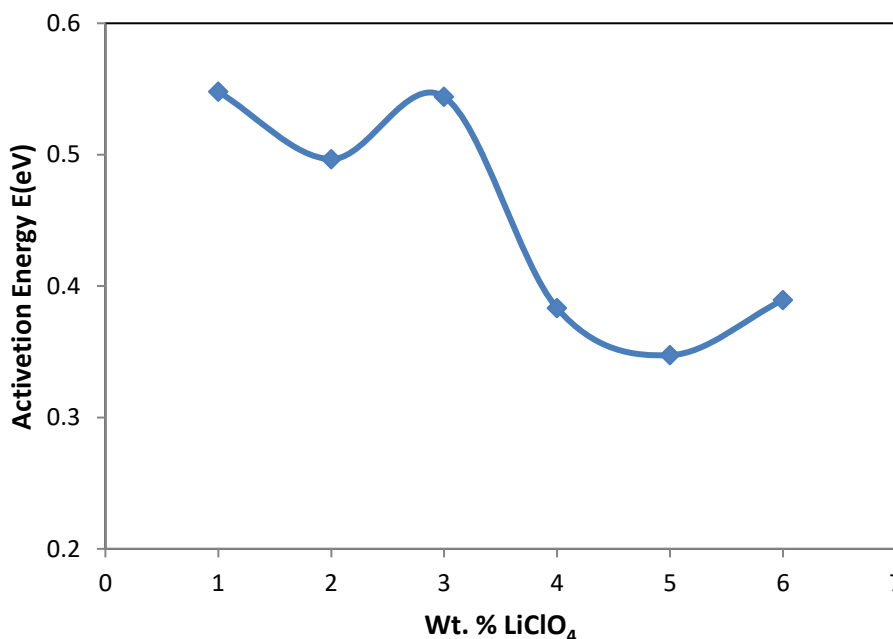


Fig 3 Variation Activation Energy as a function of wt. % of LiClO₄

Plot of activation energy with different wt. % of LiClO₄ is illustrated in figure 3 and it is similar to mirror image of conductivity plot. Activation energy is large for lower conductivity and is small for higher conductivity [12]. Which shows that activation energy E_a found to be maximum for the 1 wt % of LiClO₄. The value of activation energy varies with wt. % and DC conductivity respectively

4. Conclusion

Polythiophene polymer composites doped with LiClO₄ were prepared successfully by *in situ* chemical oxidative polymerization method. FTIR spectra confirm the successful polymerization of thiophene and formation of Polythiophene polymer composite. The temperature dependence of conductivity showed Arrhenius behaviour. PTh-PEO composite doped with the 4 wt. % LiClO₄ shows the maximum value of ionic conductivity which is of the order of 1.12 x10⁻⁵ S/cm. Plot of activation energy with different wt. % of LiClO₄ is similar to mirror image of conductivity plot. Activation energy is large for lower conductivity and Vice versa.

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