

## Synthesis and Transport Properties of Polythiophene Polymer Composite

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### ABSTRACT

Polythiophene-Polyethylene oxide (PTh-PEO) polymer composite was synthesized using Ferric Chloride (FeCl<sub>3</sub>) as oxidant by in situ chemical oxidative polymerization method. The polymerization was carried out at room temperature. Attempts were made to increase the electrical conductivity by using various concentration of Li<sub>2</sub>SO<sub>4</sub>. PTh-PEO polymer composite was characterized using FTIR for confirmation of successful polymerization of polymer composite. The transference numbers of PTh-PEO composite films, synthesized with different wt. % of Li<sub>2</sub>SO<sub>4</sub> were investigated by dc polarization techniques. The value of transference number of all polymer composite samples was found to be in the range of 0.80 to 0.89. This suggests that the charge transport in the PTh-PEO composite doped with different wt. % of Li<sub>2</sub>SO<sub>4</sub> is predominantly due to ions only.

**Keywords :** Ferric Chloride (FeCl<sub>3</sub>), Lithium sulphate (Li<sub>2</sub>SO<sub>4</sub>), and transference number

### I. INTRODUCTION

In recent three decades intrinsically conducting polymers were discovered and this discovery withdraw attention of researchers because of numerous applications of these polymers in scientific field. These are also called as synthetic metals as their electrical conductivity is very high analogous to those of metals. The examples of various conducting polymers (CPs) are: polyacetylene, poly furan, polypyrrole, polythiophene, which are in sulaters in their neutral state. The insulating behavior of polymers can be converted into conducting by carrying out doping of different salts by chemical and electrochemical redox reactions Among the conjugated polymers, Polythiophene (PTh) and its derivatives have been studied for various applications. Polymer composite

doped with lithium salts have attracted considerable attention due to the possibility of application in ambient and moderate temperature lithium or lithium ion batteries. Polythiophene (PTh) is one of the most studied polymers due to its flexibility, ease of doping , good thermal and electrical stability that exhibit some unique advantages of PTh for the development of various applications [1].

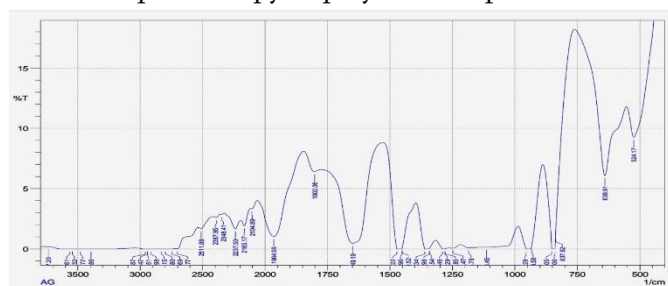
In the present work, Polythiophene-Polyethylene oxide (PTh-PEO) composite doped with Li<sub>2</sub>SO<sub>4</sub> were prepared by *in situ* chemical oxidative polymerization method. Polymerization was confirmed by FTIR spectroscopy. The effect of various concentrations of Li<sub>2</sub>SO<sub>4</sub> on the transport properties of the PTh-PEO composite films was investigated.

## II. EXPERIMENTAL

PTh-PEO composite doped with  $\text{Li}_2\text{SO}_4$  was synthesized at room temperature (303 K) by chemical oxidative method. Anhydrous  $\text{FeCl}_3$  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  $\text{FeCl}_3$  and  $\text{Li}_2\text{SO}_4$  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  $\text{Li}_2\text{SO}_4$  in this solution was changed from 1 to 6. For each wt. % of  $\text{Li}_2\text{SO}_4$ , 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.

## III. RESULTS AND DISCUSSION

Polythiophene-Polyethylene oxide (PTh-PEO) composite doped with different wt. % i.e. 10, 20, 30, 40 50 and 60 of  $\text{Li}_2\text{SO}_4$  were prepared by *in situ* chemical oxidative polymerization method. Figure (1) Shows the FTIR spectroscopy of polymer composite.



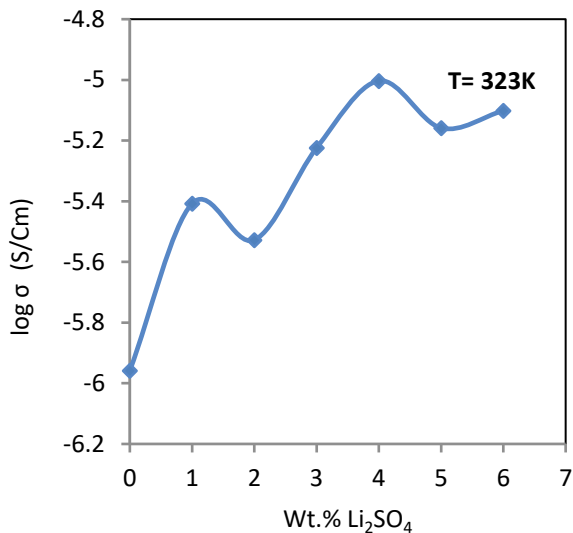
**Figure 1.** FTIR Spectroscopy of PTh- PEO Polymer Composite doped with of  $\text{Li}_2\text{SO}_4$ .

The major peaks at  $1084.42\text{ cm}^{-1}$  and  $1645.82\text{ cm}^{-1}$  are due to the presence of C-S and C=C bonds in polythiophene respectively. The strong intensity of the

$846.30\text{ cm}^{-1}$  band which is characteristic of 2,5-disubstituted thiophene rings indicates that the coupling of thiophene ring occurs preferentially at 2,5 positions. The absorption band at the region of  $650\text{--}600\text{ cm}^{-1}$  shows the ion-ion interactions in PEO -Li<sup>+</sup> ions. Two medium peaks at  $1474$  and  $1451\text{ cm}^{-1}$  are assigned to stretching vibrational modes of the thiophene ring [2]. The spectrum of PTh-PEO shows characteristic peaks in the range of  $900$  and  $1200\text{ cm}^{-1}$  due to the C-O-C symmetric and asymmetric stretching and C-O-C deformation modes that confirmed the crystalline phase of PEO by the presence of triplet peak of C-O-C stretching [3, 4].

The electric conductivity of PTh- PEO polymer composite was measured by tow probe method at different temperature It can be observed that ionic conductivity for all the compositions of PTh-PEO composite doped with the different wt. %  $\text{Li}_2\text{SO}_4$  increases with increasing temperature for the entire range. The ionic conductivity increases with increasing lithium salt concentration due to the increase in the carrier density [5]. However, the formation of ion-pairs becomes more in the case of high salt concentration than in the case of low concentration, leading to a drop in the ionic conductivity.

The variation of conductivity with  $\text{Li}_2\text{SO}_4$  wt. % is shown in figure 2. As compared to PTh-PEO composite the conductivity increases with  $\text{Li}_2\text{SO}_4$  wt. % except 2 and 5 wt. %  $\text{Li}_2\text{SO}_4$  samples. PTh-PEO composite doped with the 4 wt. %  $\text{Li}_2\text{SO}_4$  shows the maximum value of ionic conductivity. Addition of  $\text{Li}_2\text{SO}_4$  results in increase in the conductivity value due to the aggregation of excess  $\text{Li}_2\text{SO}_4$  salt.



**Figure 2.** Variation of ionic conductivity as a function of wt. % of  $\text{Li}_2\text{SO}_4$

The transference number gives quantitative information of the extent of ionic and electrical contribution to the total conductivity. The ionic/ electronic transference number can be given as:

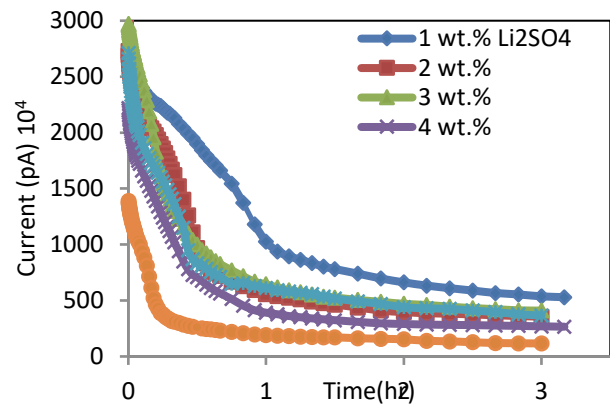
$$t_{\text{ion}} = \sigma_{\text{ion}} / \sigma_{\text{T}} = I_{\text{ion}} / I_{\text{T}} \quad (2)$$

$$t_{\text{e}} = \sigma_{\text{e}} / \sigma_{\text{T}} = I_{\text{e}} / I_{\text{T}} \quad (3)$$

Where  $\sigma_{\text{ion}} / \sigma_{\text{e}}$  and  $I_{\text{ion}} / I_{\text{e}}$  are the conductivity and current contribution due to ions/electrons, respectively. The ionic / electronic transference number ( $t_{\text{ion}}/t_{\text{e}}$ ) was measured using polarization technique [6].

Figure (3) shows the variation of polarization current as a function of time for PTh-PEO Composite doped with different wt. % of  $\text{Li}_2\text{SO}_4$ . As seen from figure (3) the total current becomes nearly constant at some non zero value after some time. The final residual current is mainly due to electrons/holes. The ionic and electronic transference numbers were calculated separately from the polarization current versus time plot using the Equations (2) and (3). The values of transference number, for sample synthesis with different wt. % of  $\text{Li}_2\text{SO}_4$  are found to be in the range of 0.80 to 0.89. This suggests that the charge transport in the PTh-PEO

composite doped with different wt. % of  $\text{Li}_2\text{SO}_4$  is predominantly due to ions only.



**Figure 3.** Variation of polarization current as a function of time for PTh-PEO Composite

#### IV. CONCLUSION

PTh-PEO polymer composites were prepared successfully by in situ chemical oxidative polymerization of thiophene doped with  $\text{Li}_2\text{SO}_4$ . FTIR study confirms the successful polymerization of polymer composite. The value of transference number of all polymer composite samples was investigated by dc polarization techniques and found to be in the range of 0.80 to 0.89. This suggests that the charge transport in the PTh-PEO composite doped is predominantly due to ions only.

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