



Measurement of Transference Number of Polythiophene - Poly(Ethylene Oxide) Polymer Composite

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ABSTRACT

A 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. In this present paper, Polythiophene-Polyethylene oxide (PTh-PEO) polymer composite were prepared by in situ chemical oxidative polymerization method with FeCl_3 as an oxidant in methanol. Their chemical structures were identified by a FTIR and SEM. dc conductivities as a function of temperature (303–338 K) were measured. An attempt has been made to investigate the effect of temperature and concentration of LiClO_4 on the conductivity of composite film.

Keywords: Conducting Polymers, Transference Number, Polymer composite etc.

I. INTRODUCTION

Conducting polymers (CPs) still remain a subject of intense investigation of many research groups worldwide. During the past decade, there have been many reports concerning fruitful investigations, leading to practical applications of CPs in various fields. A tremendous advancement has taken place in the development of conducting polymers in recent years due to their interesting physical, electrical and chemical properties. 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 and its derivatives are important conducting polymers, have attracted considerable attention over the past two decades due to their high mobility of charge carriers and other remarkable solid-state properties [1–3]. 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 [4].

In the present work, Polythiophene-Polyethylene oxide (PTh-PEO) composite doped with LiClO_4 were prepared by *in situ* chemical oxidative polymerization method. The effect of various concentrations of LiClO_4 on the transport properties of the PTh-PEO composite films was investigated, with an intension to exploit these composites for various applications such as batteries and sensors.

II. EXPERIMENTAL

PTh-PEO composite doped with LiClO_4 was synthesized at room temperature (303 K) by chemical oxidative method. Anhydrous 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 FeCl_3 and LiClO_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 LiClO_4 in this solution was changed from 1 to 6. For each wt. % of LiClO_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 [5,6].

III. RESULTS AND DISCUSSION

Figure 1 shows the morphology of PTh-PEO composite doped with LiClO_4 . The surface morphologies of these films are completely different as compared to the films prepared in the absence of dopant. From the SEM micrographs of the film doped with Lithium Perchlorate (LiClO_4). It is found that the films PS11 show certain types of crystallinity. The crystals that are found in the film may be due to the Lithium Perchlorate (LiClO_4). These crystals are scattered in all direction and found more in case of 4 wt. % of LiClO_4 . The average size of the particles is $0.5\mu\text{m}$ to 100 nm . However, several aggregated phases and separate phase domains can be detected.

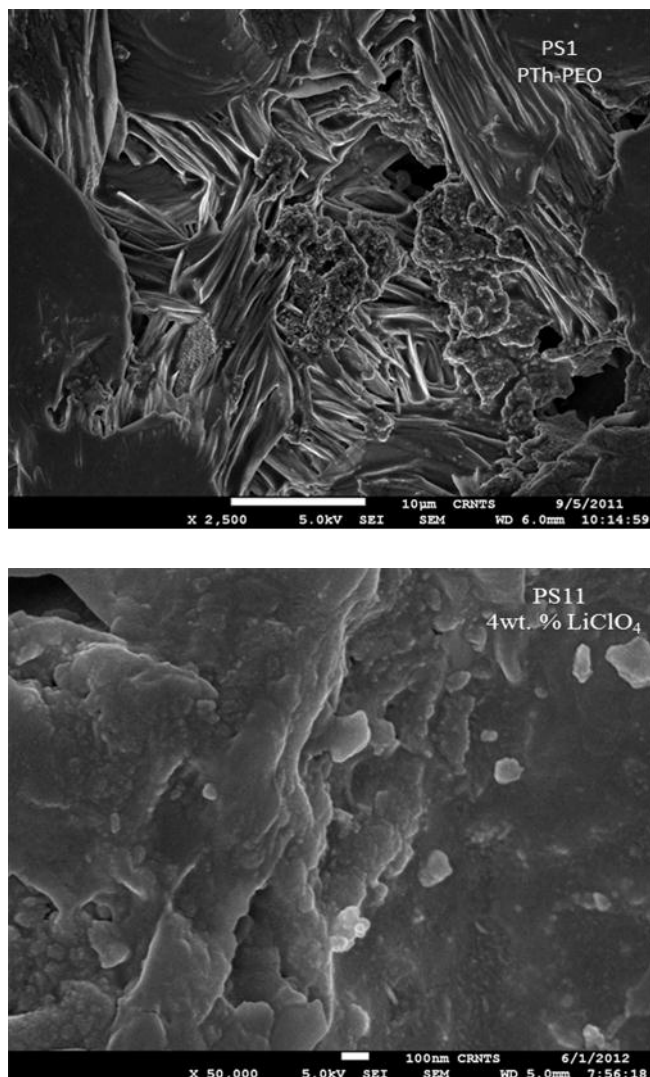


Figure 1. SEM Micrographs of PTh-PEO composite doped with Lithium Perchlorate (LiClO_4)

The transference number gives qualitative information of the extent of ionic and electronic contribution to the total conductivity.

The ionic and electronic transference number can be defined as:-

$$t_{ion} = \sigma_{ion}/\sigma_T = I_{ion}/I_T \quad (1)$$

$$t_{e,h} = \sigma_e/I_T \quad (2)$$

where σ_{ion}/σ_e , and I_e/I_T are the conductivity and current contributions due to ions/ electrons respectively. The ionic / electronic transference number was measured by using dc polarization technique [7] in which PTh-PEO composite film is sandwiched between blocking (graphite) and non blocking (silver) electrodes. A constant dc voltage (0.5V) is established across the sample and the resultant current was measured as a function of time.

Figure 2 shows the variation of polarization current as a function of time for PTh-PEO Composite doped with different wt. % of LiClO_4 . As seen from figure (2) 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 (1) and (2). The values of transference number, for sample synthesis with different wt. % of LiClO_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 LiClO_4 is predominantly due to ions only.

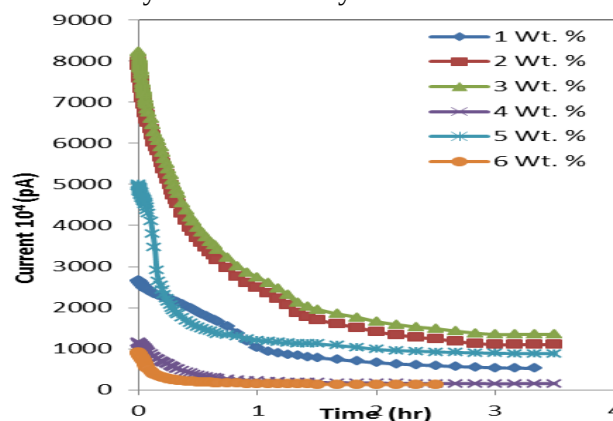


Figure 2. Variation of polarization current as a function of time for PTh-PEO Composite

Figure 3 shows the variation of ionic transference number (t_{ion}) with different wt. % of LiClO_4 . It shows that ionic transference number (t_{ion}) increases with increasing the LiClO_4 concentration, obviously it is due to the increase of lithium ion concentration in the PTh-PEO composite. Up to 2 wt. % of LiClO_4 it increases then slightly decreases and again increases. The ion mobility depends on segmental motion of polymer chain. In this case due to increase in wt. % LiClO_4 , PTh-PEO composite become more rigid this ultimately reduces the segmental motion.

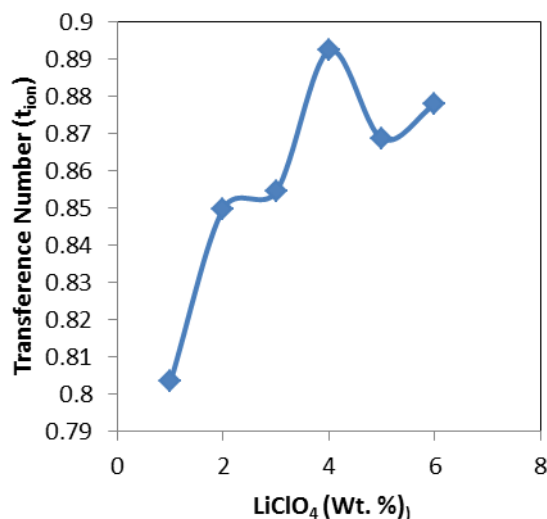


Figure 3. Variation of ionic transference number with different wt. % of LiClO_4

IV. CONCLUSION

PTh-PEO polymer composites were prepared successfully by in situ chemical oxidative polymerization of thiophene doped with LiClO_4 . The temperature dependence of conductivity showed Arrhenius behaviour. The value of transference number suggests that the charge transport in the PTh-PEO composite doped is predominantly due to ions only.

V. REFERENCES

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