

Electrical and Structural Properties of PTh-PEO Polymer Composite

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ABSTRACT: Polythiophene-Polyethylene oxide (PTh-PEO) polymer composite were prepared at room temperature by chemical oxidative polymerization method with FeCl_3 as an oxidant in methanol solvent. The characteristics of PTh-PEO polymer composite films are investigated by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The DC conductivity was investigated as a function of temperature (303–338 K). PTh-PEO composite doped with the 4 wt. % Li_2SO_4 shows the maximum value of ionic conductivity which is of the order of 1.12×10^{-5} S/cm. The temperature dependence of conductivity showed Arrhenius behaviour.

Keywords: Polymer composite, Polythiophene (PTh), Polyethylene oxide (PEO) and Lithium sulphate (Li_2SO_4), conducting polymers (CPs)

I. INTRODUCTION

Polythiophene and its derivatives are important conducting polymers, have attracted considerable attention over the past 20 years 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]. Polyethylene oxide (PEO) based polymer electrolytes have attracted great attention for high energy density and high power lithium-ion batteries because of its ease of formation of complex with lithium salt, flexibility, stable mechanical properties, comparatively high mobility of charge carriers, etc. Among the polymeric materials reported, polyethylene oxide (PEO) based polymer electrolytes are the most commonly studied [5–6]. Many researchers have studied the synthesis, electrical and structural characterization of polymer composite such as PEO-CO-PTh [7], PTh/ LiClO_4 [8], PTh/ LiPF_6 [9], PEO / LiClO_4 [10], PTh- PVAc [11], PPY-PEG [12]

In the present study, the Polythiophene-Polyethylene oxide (PTh-PEO) composite doped with Li_2SO_4 were prepared by chemical oxidizative polymerization method. The effect of various concentrations of Li_2SO_4 on the structure and electrical conductivity 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 Li_2SO_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 Li_2SO_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 Li_2SO_4 in this solution was changed from 1 to 6. For each wt. % of Li_2SO_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.

Prepared polymer composites were characterized by FTIR and SEM. The FTIR study of PTh- PEO polymer composites was studied on a SHIMADZU FTIR IR Affinity 1 spectrophotometer in the range 500 to 4000 cm^{-1} at room temperature (303 K) at Dept. of Physics and Electronics, Govt. Vidarbha Institute of Science and Humanities, Amravati. The morphology of the PTh- PEO polymer composites was observed by scanning electron microscopy (SEM) using JSM-7600F microscope at RSIC, Indian Institute of Technology, Powai, Mumbai. The thickness of the films was measured by digimatic micrometer (Japan), having a least count of 0.001mm. DC electrical conductivity of the samples was measured in the temperature range of 303-338 K using Ohms law method by two probe method.

III. RESULTS AND DISCUSSION

Figure 1 gives the FTIR spectrum in the frequency range 500–4000 cm^{-1} of PTh-PEO composite doped with Li_2SO_4 . The major peaks at 1084.42 cm^{-1} and 1645.82 cm^{-1} are due to the presence of C-S and C=C bonds in polythiophene respectively. The strong intensity of the 846.30 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 650-600 cm^{-1} shows the ion-ion interactions in PEO $-\text{Li}^+$ ions based polymer composite. Two medium peaks at 1474 and 1451 cm^{-1} are assigned to stretching vibrational modes of the thiophene ring [13]. The spectrum of PTh-PEO showed characteristic peaks in the range of 900 and 1200 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 [14, 15]. For PTh-PEO composite, it was observed that the triplet peak of PEO, C–O–C stretching slightly shifted to 1248, 1119 and 1072 cm^{-1} . Besides, one of the split in the CH_2 wagging mode band at 1341 cm^{-1} was observed in the composite.

The aliphatic CH stretching vibrational band (2900 cm^{-1}) shows a decrease in intensity and width by the addition of lithium salt. The shoulder peak at $\sim 635 \text{ cm}^{-1}$ is noticeable, which indicates presence of lithium salt in PTh-PEO polymer composite.

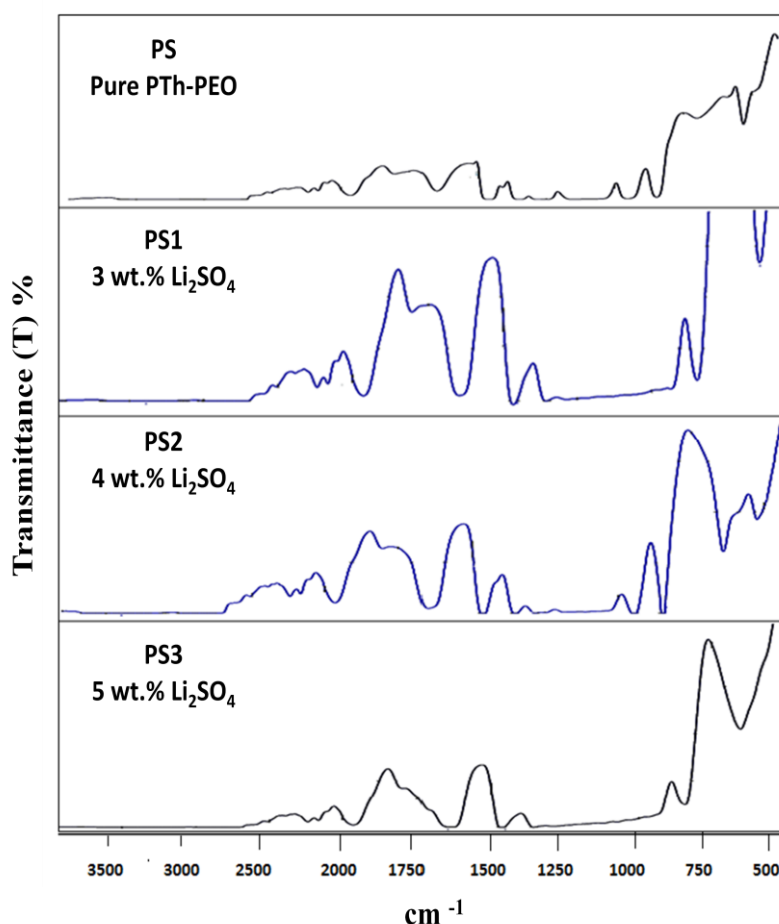


Fig 1: FTIR spectra of PTh-PEO composite doped with Li_2SO_4 .

Fig. 2 shows the morphology of PTh-PEO composite doped with Li_2SO_4 . The surface morphology changes severely from rough to smooth as shown in Fig. 2(b). PTh-PEO composite doped with Li_2SO_4 shows further drastic improvement of surface morphology as appears in Fig. 2(c) and (d) in which clusters of particles and voids are observed. The average size of the particles is 2–10 μm , as seen in Fig. 2(b). From the PTh-PEO composites image, the clusters of particles resulting from the aggregation of the composite particles can be seen. It is seen that clusters of particles consist of crystals which nearly shows a hexagonal structure [fig.2(c)]. The crystals are arranged in different layers. However, several aggregated phases and separate phase domains can be detected. The rough and porous morphology [Fig. 2(d)] could result from the aggregations of excess lithium salt.

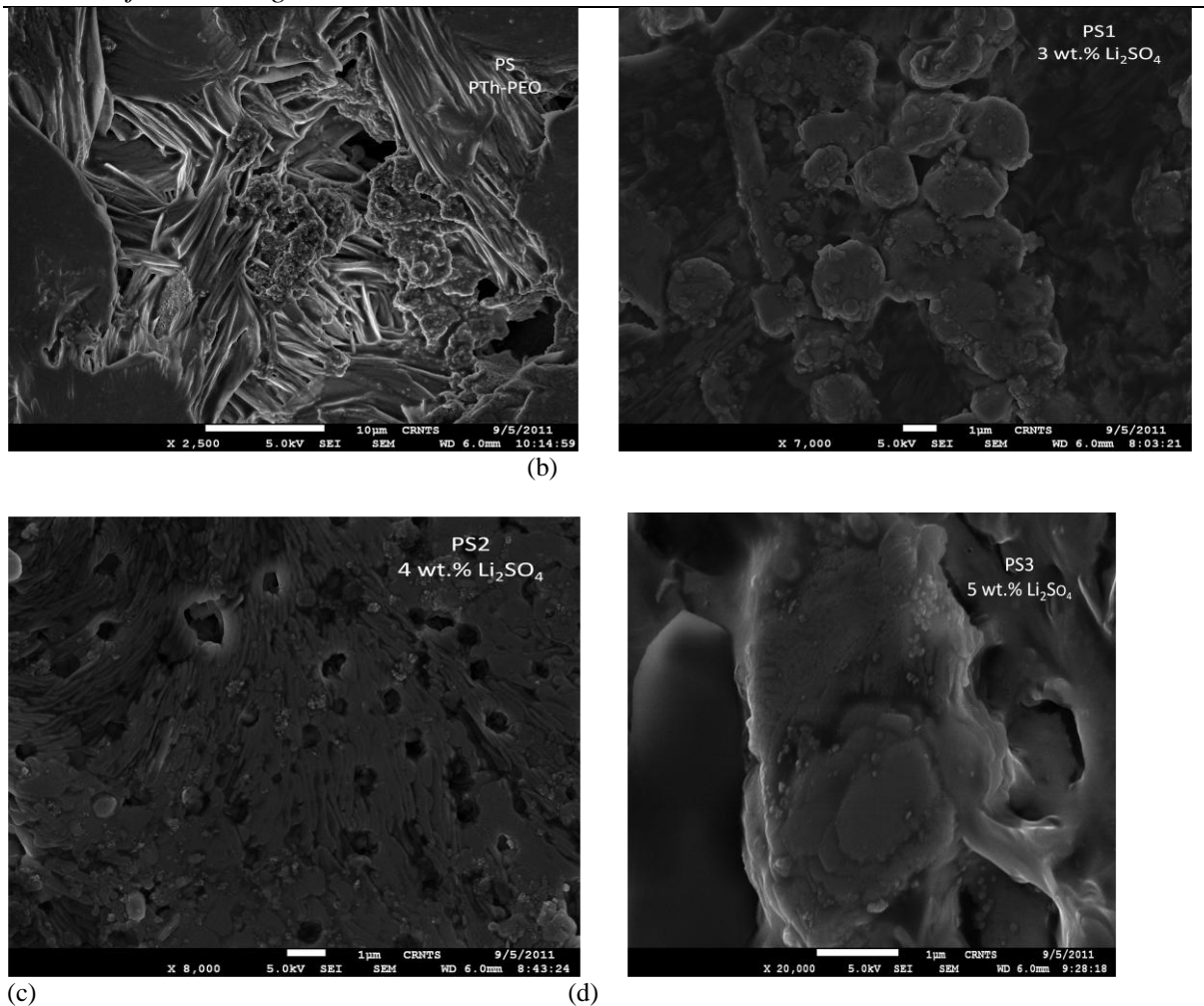


Fig (2) SEM Micrographs of PTh-PEO composite doped with Li_2SO_4 .

Figure 3 shows the variation of ionic conductivity as a function of inverse temperature for PTh-PEO polymer composite doped with the different wt.% of Li_2SO_4 . It can be observed from Figure 3 that the ionic conductivity for all the compositions of PTh-PEO composite doped with the different wt. % Li_2SO_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. 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 natures of the curve are consistent with Arrhenius type charge conduction in polymer composites and the conductivity relationship follows the equation,

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (3)$$

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 0.15 and 0.53 eV.

It can be seen that the Arrhenius plots for all the samples display a similar behaviour. The ionic conductivity value increases with the different wt. % Li_2SO_4 at different temperatures.

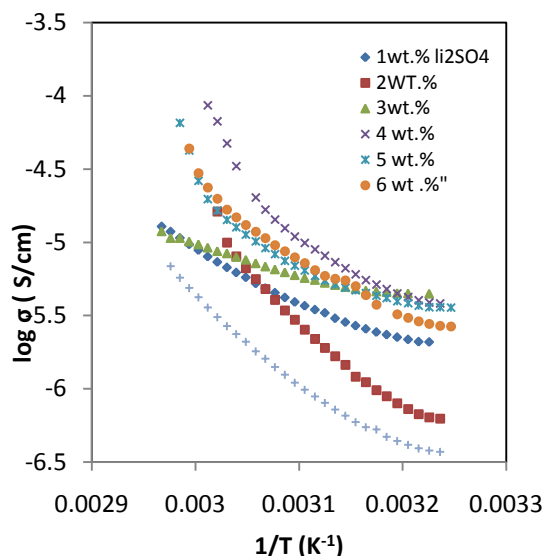


Fig. 3: Arrhenius plots of the ionic conductivity of (PTh-PEO) Composite for different wt. % of Li_2SO_4

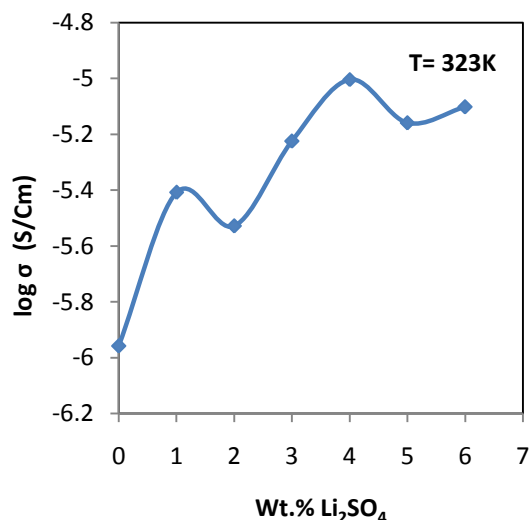


Fig 4: Variation of ionic conductivity as a function of wt. % of Li_2SO_4

The variation of conductivity with Li_2SO_4 wt. % is shown in figure 4. As compared to PTh-PEO composite the conductivity increases with Li_2SO_4 wt. % except 2 and 5 wt. % Li_2SO_4 samples. PTh-PEO composite doped with the 4 wt. % Li_2SO_4 shows the maximum value of ionic conductivity. Addition of Li_2SO_4 results in increase in the conductivity value due to the aggregation of excess Li_2SO_4 salt.

IV CONCLUSION

PTh-PEO polymer composites were prepared successfully by *in situ* chemical oxidative polymerization of thiophene doped with Li_2SO_4 . FTIR spectra confirm the successful polymerization of thiophene and formation of PTh-PEO composite. SEM micrograph shows the semi crystalline morphology. Also the addition of Li_2SO_4 improves the surface morphology of composite. The temperature dependence of conductivity showed Arrhenius behaviour. PTh-PEO composite doped with the 4 wt. % Li_2SO_4 shows the maximum value of ionic conductivity which is of the order of 1.12×10^{-5} S/cm.

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