

FTIR, DC Current Conduction, Ionic Conductivity, and Resistivity Studies of PEO Based Polymer Composite System

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Summary: Polymeric composites of Iron chloride (FeCl₃) doped Poly (ethylene oxide) fabricated in various weight fractions were subjected to FTIR, AC impedance test, DC conductivity and resistivity respectively. FTIR data confirms the complexation of FeCl₃. DC test and AC impedance results reveal that direct current (DC) carrying capacity and ionic conductivity of the fabricated composites increases with increasing FeCl₃ content, while reverse trend was observed for resistivity. The current findings are strongly supported by the decreasing trend in the energy band gap values for the FeCl₃ doped PEO composites.

Key words; Poly (ethylene oxide) (PEO), Iron Chloride (FeCl₃), Doping, DC conductivity, Resistivity, Ionic conductivity, Energy band gap

Introduction

The quest for improved materials has introduced a lot of new materials, polymers, though introduced in the material's field in meaningful manner only very recently; occupy a major place and key position in the materials field today. In performance uniqueness, application scenario and diversity, they offer novelty and versatility not found in any other kind of materials.

Compositing is a process somewhat similar to compounding and results in composite formation. Composite materials are engineered materials made from two or more constituent materials with significantly different Physical or chemical properties and which remain separate and distinct within the finished structure. Composite material is defined as a material having fibrous or particulate reinforcement supported by a binder or matrix material. Any such composition that comprises two or more materials as separate phases, at least one of which is a polymer can be called as polymer composite. By combining a polymer with another material, such as glass, carbon, or another polymer, it is possible to obtain unique combination or level of properties. In a polymer composite, the constituent polymer and composite components are usually present in significant weight or volume proportions with respect to each other, but seldom occurs in equal proportions [1, 2]. An obvious advantage of this approach is that it requires little or no extra capital expenditure relative to new polymers. It is also possible to produce materials with properties completely different from those of the composite constituents [3]. Composites are in growing demand from architects and construction engineers in the transport, sports, aerospace, defense, building,

household, recreation, industrial, and other sectors [4-7]. Composites have been developed because no homogeneous structural material could offer all the desired attributes for a given application. The search for electrometric and adhesive electrolytes with improved performances, especially room temperature conductivity, is of great interest since the ionic conductivity of anhydrous lithium polymer electrolytes generally made of poly(ethylene oxide) (PEO) and LiClO₄ or LiCF₃SO₃ salts lies in the range 10⁻⁷- 10⁻⁸ S cm⁻¹ at room temperature [8].

An extensive literature on the synthesis and characterization of different polymeric composites are available and many more are being in progress [9]. PEO is a commercial polymer available in a variety of molecular weights. It is soluble both in aqueous and organic solvent and forms yellow complexes with FeCl₃ showing photochromic effect under Ultra Violet (UV) irradiation [10]. Many studies have been reported on electrical and thermal properties of PEO-salt composites which might have a broad array of applications in industrial and consumer's end-products [11], however the data regarding the synthesis and characterization of iron chloride doped – PEO composite is scarce. In this paper an attempt was made to investigate the complexation of iron chloride with PEO by using FTIR, DC and AC impedance techniques.

Results and Discussion

IR Transmittance

Fig. 1 displays infrared absorption spectra for PEO filled with 0, 5, 10, 15 and 20 wt % of FeCl₃ in

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the transmittance mode. Fig. 1 depicts that spectra of all samples are nearly similar and illustrating characteristics peaks of PEO. This finding is in consistence harmony with already reported data [12]. Comparative graph given in Fig. 1 depicts distinct band from (-CH-) stretching vibrations of Methylene (CH_2) at 2878.19 cm^{-1} . It also shows simple wagging and wagging deformation of (- CH_2 -) group appearing in the frequency range of $1356\text{-}1466\text{ cm}^{-1}$. From the comparative spectra it is clear that the intensity of (- CH_2) goes on increasing with the increasing concentration of FeCl_3 , this may be due to the interaction of Fe cation (Fe^{+3}) with the (O) of the PEO, causing increase in the proportion of free (- CH_2 -) in the composites. Broader and stronger bands appearing at 1240 cm^{-1} and $1010\text{-}1040\text{ cm}^{-1}$ corresponding to C-O-C stretching are comparable to the earlier reported values [13]. The absorption peaks of PEO appearing at ($2878.19, 1466.56, 1278.96, 1241.60, 1341.04, 1143.47, 1094.02, 1059.40, 960.04$ and 841.09 cm^{-1}) were shifted and some new peaks at ($3389.20, 1647.79$ and 674.88 cm^{-1}) were observed in the FeCl_3 doped PEO composite. X-Ray diffraction (X-RD) analysis of pure PEO and FeCl_3 doped PEO composites also supports FTIR studies by showing complexation of FeCl_3 with PEO matrix. This suggests that addition of FeCl_3 causes structural variation in the polymeric network [10].

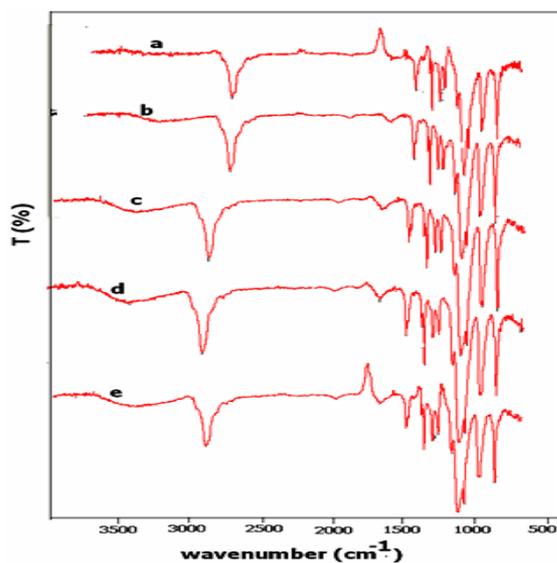


Fig. 1: FTIR spectra of (a) pure PEO (b) doped with 5 (c) 10 (d) 15 (d), and (e) 20 wt% of FeCl_3 .

Direct Current (DC) and Resistivity

Figure 2 and 3 illustrate the direct current and resistivity of pure PEO and PEO doped FeCl_3 vs. FeCl_3 concentration at room temperature at fixed

voltage of 0.3 kV respectively. The graph depicts that the DC current carrying capacity of FeCl_3 doped PEO composites increases with increasing FeCl_3 concentration while resistivity shows declining trend with increasing FeCl_3 content. The possible explanation is the decrease in the crystalline character of PEO with the increasing filler concentration, which in turn increases the mobility of the dopant ion. This result has been confirmed by the X-RD and optical energy band gap (E_{opt}) analysis with increasing FeCl_3 concentration [10].

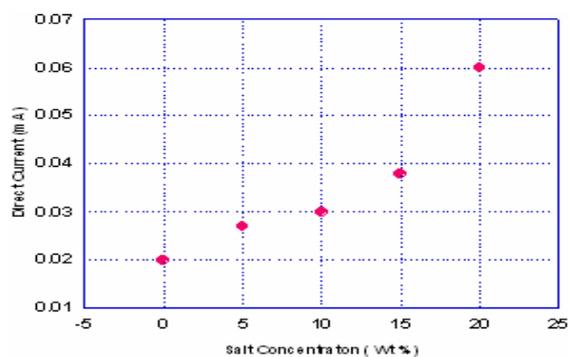


Fig. 2: Effect of FeCl_3 concentration on Direct Current of FeCl_3 doped PEO

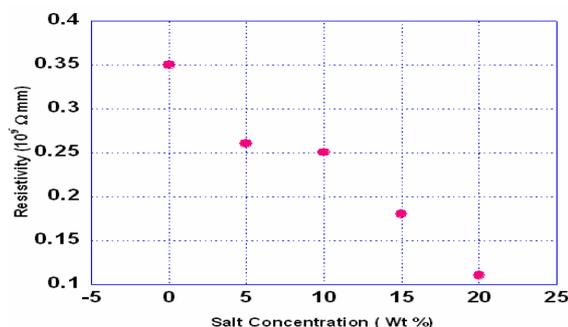


Fig. 3: Effect of FeCl_3 concentration on the resistivity of FeCl_3 doped PEO.

Alternating Current (AC) Impedance

Fig. 4 displays the typical complex impedance (CI) plot for FeCl_3 doped PEO films. The plot shows a semicircle at high frequency corresponding to the parallel combination of resistor and capacitor, reflecting single conduction mechanism and a spur at low frequency indicating deviation from ideal interface due to the roughness of electrode /electrode interface. The complex impedance plots showed decreasing bulk resistance with increasing salt loading. The variation of log of ionic conductivity (σ) as a function of FeCl_3 concentration is manifested in Fig. 5. exploring that conductivity of pure PEO at

temperature of 30 °C is $1.53 \times 10^{-10} \text{ S cm}^{-1}$ [14] and increases dramatically to $3.1 \times 10^{-7} \text{ S cm}^{-1}$ for 5wt% addition of salt. The graph shows linear increase in conductivity with salt concentration. This reveals that the addition of the ionic Fe^{+3} salts to the PEO crystal created an interaction between the Fe^{+3} ions and ether oxygen of the PEO. This is fully supported by FTIR analysis, which shows that the intensity of $(-\text{CH}_2-)$ goes on increasing with increasing salt content due to the interaction of Fe^{+3} with the (O) of PEO causing increase in the proportions of free $(-\text{CH}_2-)$ in the composites. X-ray scans also confirmed complex formation. The charge transport in PEO composites involves dissociation of the cation from its coordinating oxygen to move to adjacent site. The increase in ionic conductivity of electrolyte with increasing salt concentration is due to increasing ionic mobility and concentration of ionic charge carriers with increasing salt content. The motion of ions in solid polymer electrolytes seems to be liquid-like behavior augmented by the segmental motion of the polymer backbone [15-17]. It is clear from Fig. 5 that conductivity enhancement is sharp up to 20wt% of salt, beyond which it shows a very gradual change, which is in close agreement with the SEM observation. This means if we increase salt concentration beyond 20wt% it will deteriorate conductivity due to salt agglomeration and association resulting in ions clusters. AC conductivity is higher than DC, this is because conductivity is frequency dependant, and at higher frequency it is generally larger than DC conductivity. This behavior in conducting polymers (CPs) is caused by the high conductivity Islands resulted from localized doping surrounded by less doped insulating regions. DC conductivity varies with temperature while AC conductivity is strongly dependent on temperature and frequency [18].

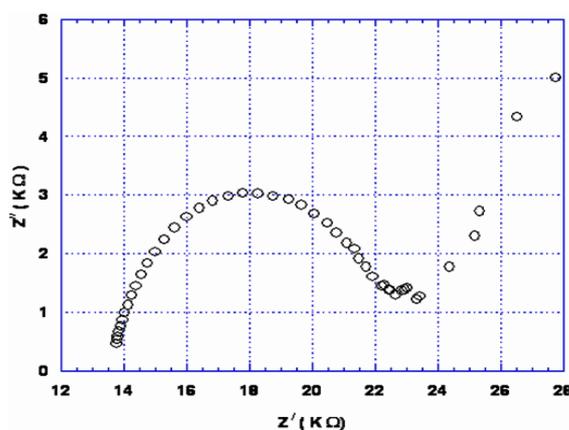


Fig. 4: Typical Complex Impedance plot of PEO/ 15 wt% FeCl_3 composite film.

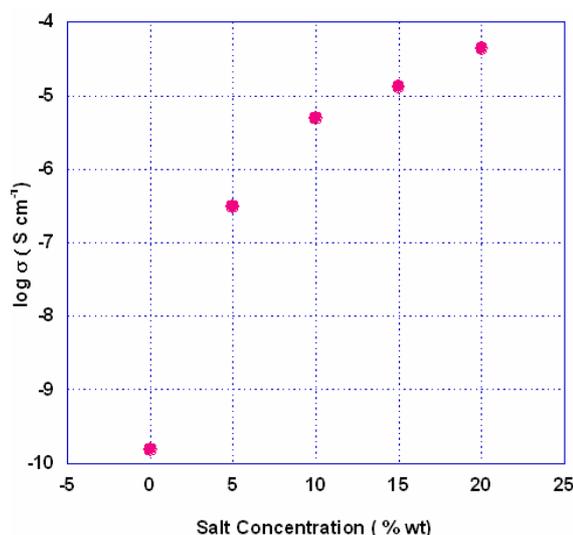


Fig. 5: Bulk Ionic conductivity (σ) of the FeCl_3 doped PEO against FeCl_3 concentration at 30 °C.

Experimental

Thin films of PEO/ FeCl_3 were prepared by following the procedure already reported in the literature [10]. FTIR spectra ranging from 500-40000 cm^{-1} were obtained using Nicolet 380 (FT-IR) (Thermoscientific) UK. DC current measurement was done with DC HV tester of Biddle Company. The impedance measurements were carried with Autolab 302 Potentiostat/ Galvanostat electrochemical instrument. The bulk resistance (R_b) was determined from the equivalent circuit analysis using frequency response analyzer (FRA software) at a frequency range of $1-10^7$ Hz with signals amplitudes of 100 mV. The R_b allows us to obtain the ionic conductivity using Equation 1

$$\sigma = \frac{l}{R A} \quad (1)$$

- σ - The conductivity (S/cm)
- R - The resistance (Ω),
- l - The thickness (cm),
- A - The area of the electrode (cm^2)

All measurements were carried out at temperature of 30 °C.

Conclusion

On the basis of the results obtained from various spectroscopic techniques, it can be concluded

that FeCl₃ incorporation into PEO results in complex formation and causes structural variation in the polymeric network of PEO. Increasing dopant concentration causes enhancement in DC and ionic conductivity and suppression in resistivity. This suggests that higher filler loading decreases crystallinity and viscosity of PEO, causing subsequent increase in mobility of dopant ions. The fabricated composites showing maximum ionic conductivity ($4.4 \times 10^{-5} \text{ S cm}^{-1}$) at room temperature and higher thermal stability are promising candidates for applications in electrochemical devices.

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