

# Structural and Conductivity Studies of Poly(Ethylene Oxide)—Silver Triflate Polymer Electrolyte System

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## ABSTRACT

Films of PEO containing  $\text{AgCF}_3\text{SO}_3$  were prepared by the solution casting technique. Fourier transform infrared (FTIR) spectroscopy has been carried out on a series of complexes containing poly(ethylene oxide) PEO and silver triflate ( $\text{AgCF}_3\text{SO}_3$ ) salt. Spectral analysis of all the samples has revealed the complexation of silver ions with oxygen in PEO. The ac conductivity and electrical modulus of the prepared samples have been analyzed. The ac conductivity was observed to obey the Universal power law. The temperature dependence of the power law exponent  $n$  is reasonably interpreted by the overlapping large polaron tunneling (OLPT) model. The imaginary part,  $M''$  of electrical modulus shows the formation of dispersion peak. The plot of log conductivity relaxation times and log conductivity as a function of salt concentration was in accordance with each other.

**Keywords:** PEO- $\text{AgCF}_3\text{SO}_3$ , FTIR, Conductivity, Modulus

## 1. Introduction

Polymer based solid electrolytes are one of the most extensively studied systems. PEO is widely used as host polymer because of its ability to dissolve a wide variety of metal salt, good mechanical properties compared with those of other polymer host [1,2]. Interestingly, silver ion-conducting polymer electrolytes based on PEO appear to be the most appropriate choice for various electrochemical applications [3]. As stated by most experimental work, cation mobility occurs in the amorphous phase and its diffusion occurs through a complex mechanism involving the PEO segmental mobility. For that, crystallization has to be avoided by modifying the polymer structure or by adding salts to inhibit regular packing. Moderate conductivity in amorphous materials is then a direct consequence of PEO features where high salvation is counterbalanced by the energetic complexation of cations. Suthanthiraraj *et al.* reported enhancement in conductivity in silver based PEO polymer electrolytes due to incorporation of nano-fillers [4]. There was an increased thrust during the last decade towards investigating new matrices for improving ion-conducting characteristics as well as their detailed structural characterization by means of

fourier transform infrared (FTIR) spectral features. In the present work we intend to study the effect of silver salt concentrations in PEO-based polymer electrolytes by means of vibrational spectroscopy and complex impedance analysis.

## 2. Experimental

The solution was prepared by dissolving weighted percentage of PEO {with an average molecular weight of M.W 1,000,000, Sigma-Aldrich} and various concentration of Silver trifluoromethane Sulphonate ( $\text{AgCF}_3\text{SO}_3$ ) [( $x = 2$  wt%, 3.5 wt%, 5 wt%, 7 wt%, 11 wt%) {purity > 99%, Aldrich}] in an acetonitrile solution {used as solvent obtained from MERCK}. This mixture was constantly allowed to stir for 48 hours at ambient temperature. Any contamination with the external ambient was carefully avoided by performing all the preparation steps in a controlled environment. The homogenous and viscous solution was cast in PTFE plates. Solvent evaporation was carried out in closed apparatus for 24 to 30 hours at ambient temperature. Next, the dried film so obtained was hot-pressed in a polymer press by specially made stainless steel die (20  $\mu\text{m}$  - 50  $\mu\text{m}$  thickness) by applying

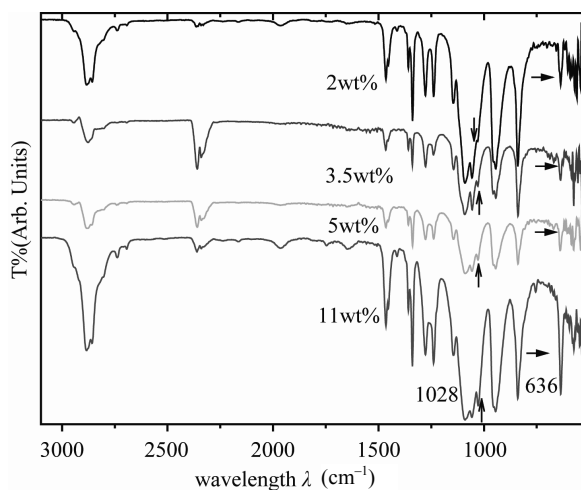
10 tons pressure at  $65 \pm 5^\circ\text{C}$  (338 K) for 10 min. Semi-transparent homogeneous membranes having thickness ranging from 10 - 30  $\mu\text{m}$  and good mechanical strength were obtained.

Vibrational spectroscopy was carried out using JASCO 4100 series FTIR spectrophotometer in the wave number ranging from 500 to 3000  $\text{cm}^{-1}$ . For the impedance measurement, the polymer electrolytes film was sandwiched between two silver blocking electrolytes with diameter 1 cm, under spring pressure. Impedance spectroscopy was taken using the Solartron 1260 Impedance Gain/Phase Analyser in the frequency range of 10 MHz to 10 Hz frequency range. The cell temperature was controlled using a thermometer in the temperature range of 303 K to 328 K.

### 3. Result and Discussion

#### 3.1. FT-IR

**Figure 1** represents the FTIR spectra for pure PEO, and PEO- $\text{AgCF}_3\text{SO}_3$  films. For pure PEO, C-H stretching mode can be observed at 2876  $\text{cm}^{-1}$ ,  $\text{CH}_2$  scissoring mode at 1466  $\text{cm}^{-1}$ ,  $\text{CH}_2$  wagging mode at 1360 and 1341  $\text{cm}^{-1}$ ,  $\text{CH}_2$  twisting mode at 1279  $\text{cm}^{-1}$ , C-O-C stretching at 1104,  $\text{CH}_2$  rocking and C-O-C vibration mode at 960  $\text{cm}^{-1}$ ,  $\text{CH}_2$  rocking at 841  $\text{cm}^{-1}$  while C-O-C bending at 528  $\text{cm}^{-1}$ . The semi-crystalline phase of PEO is confirmed by the presence of triplet peak of C-O-C stretching [5,6]. C-O-C stretching vibrations are observed at 1145, 1095 and 1059  $\text{cm}^{-1}$  with maximum intensity at 1095  $\text{cm}^{-1}$  [7]. Complexation of silver salt with PEO can be confirmed on the appearance of the peaks at 636  $\text{cm}^{-1}$  which may be assigned to the  $\delta_s$  ( $\text{SO}_3$ ) mode of free triflate ion. It is also evident that the formation of the associated peak at 1028  $\text{cm}^{-1}$  corresponds to the  $\text{SO}_3$  symmetric mode [3]. The spectral features observed in the range of 945

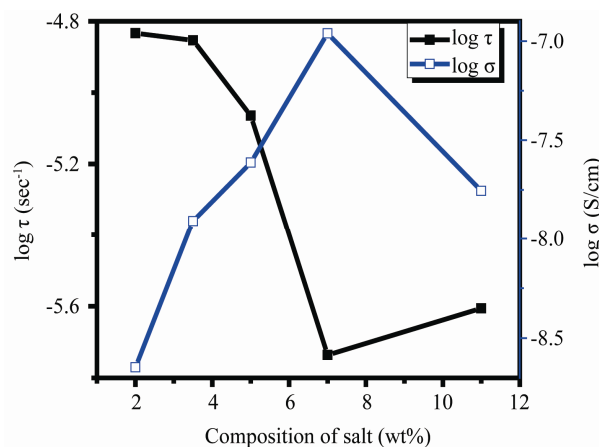


**Figure 1.** IR spectra at room temperature.

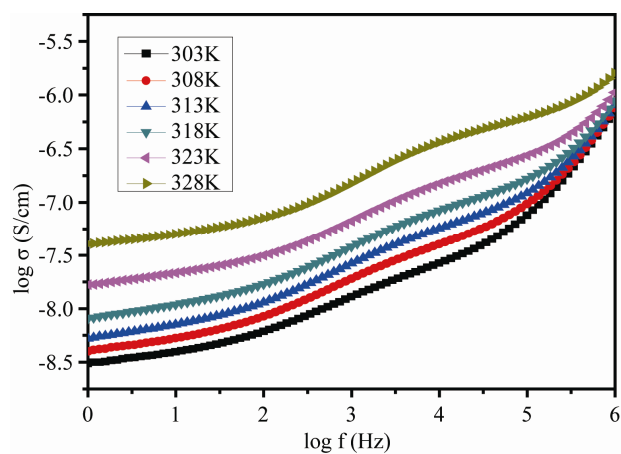
- 836  $\text{cm}^{-1}$ , for all the samples including pure PEO, suggest that the symmetrical rocking mode of  $\text{CH}_2$  group has not been affected by complexation with  $\text{AgCF}_3\text{SO}_3$ .

#### 3.2. Frequency Dependent Conductivity

It can be observed from **Figure 2** that the ionic conductivity of the polymer electrolyte increases with increasing salt content up to 7 wt% and thereafter the conductivity decreases. The increase in conductivity with salt concentration could be attributed to the increase in the number of mobile ions as a result of salt concentration [8]. Addition of salt increase the amorphous structure of the polymer (as evident from the FTIR) through favorable free volume and therefore, ion migration takes place easily [9]. However, with the further increase in salt concentration, these ions come closer to one another which are attributed to salt re-association and hence conductivity decreases [10]. A typical plot of ac conductivity as a function of frequency for 5 wt%  $\text{AgCF}_3\text{SO}_3$  is shown in **Figure 3**. Ac conductivity is observed to increase with



**Figure 2.** Variation of  $\log(\sigma)$  and  $\log(\tau)$  for different salt concentration.



**Figure 3.** Plot of ac conductivity (5 wt%  $\text{AgCF}_3\text{SO}_3$ ).

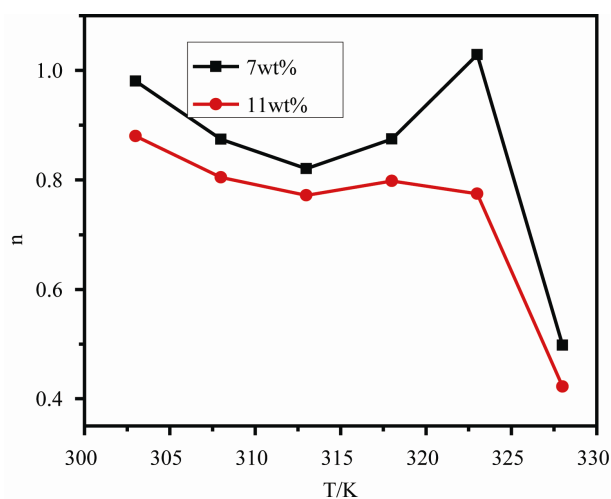
temperature and its flattened portion curve also increases with temperature. At the mid frequency region, the conductivity increases continuously because at that frequency, the charge carrier gets excitation energy from the electrical signal. Due to this excitation energy, the mobility of the charge carrier increases which in turn, decreases the relaxation time and thus, the conductivity increases. The nature of conductivity behavior observed can be explained using Jonscher's Universal power law [11]

$$\sigma(\omega) = \sigma_{dc} + A\omega^n \quad (1)$$

where,  $\sigma_{dc}$  is the *dc* conductivity of the sample,  $A$  is a constant for a particular temperature and  $n$  is the power law exponent. The value of  $n$  was calculated from the slope of the  $\log(\sigma' - \sigma_{dc})$  vs.  $\log\omega$ , which is a straight line. The values of exponent  $n$  were ranging from 0.5 to 0.9, *i.e.*, less than 1 and were observed to decrease with temperature for all  $\text{AgCF}_3\text{SO}_3$  concentration. It means that the increase in conductivity can also be ascribed to the increase in degree of disorder in the materials on complexation with salt. It is observed (**Figure 4**) that exponent  $n$  decreases with increasing temperature, exhibits a minimum at a certain temperature after which it begins to increase. This may due to breaking of internal correlation between the sites and relaxing ions and relaxing species become independent of each other which results in tunneling process rather than hopping. Therefore the overlapping large polaron tunnelling (OLPT) model is best suitable to explain the conduction process in the present study [12-14].

### 3.3. Modulus

To study the electrode effect in the system, we have analyzed the dielectric spectra by complex electric modulus



**Figure 4.** Variation of exponent  $n$  with temperature for  $\text{AgCF}_3\text{SO}_3$  7 wt% and 11 wt%.

$M_{(\omega)}^*$  [15]. The complex electric modulus can be evaluated from the following relations.

$$M_{(\omega)}^* \cdot \varepsilon_{(\omega)}^* = 1 \quad (2)$$

where

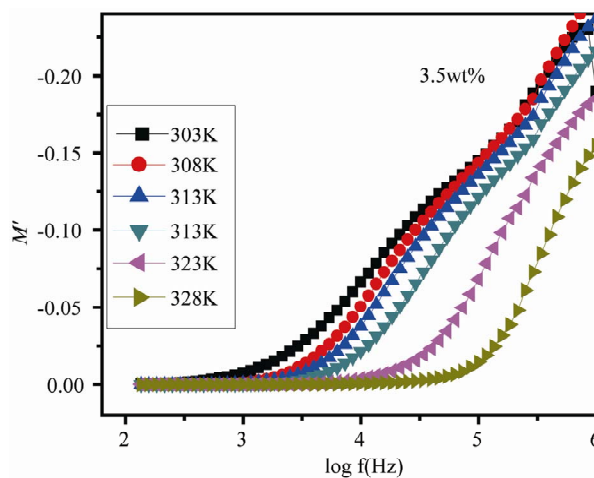
$$M_{(\omega)}^* = M'_{(\omega)} + iM''_{(\omega)}$$

$$M'_{(\omega)} = \frac{\varepsilon'_{(\omega)}}{\varepsilon'_{(\omega)^2} + \varepsilon''_{(\omega)^2}}$$

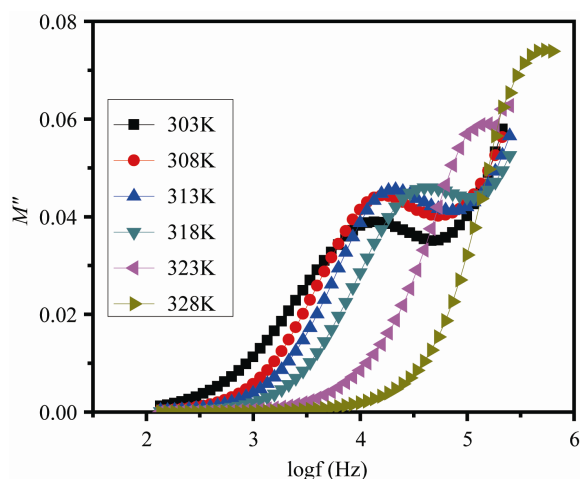
and

$$M''_{(\omega)} = \frac{\varepsilon''_{(\omega)}}{\varepsilon'_{(\omega)^2} + \varepsilon''_{(\omega)^2}}$$

The frequency dependence of  $M'$  and  $M''$  for PEO- $\text{AgCF}_3\text{SO}_3$  3.5 wt% is shown in **Figures 5** and **6** respectively. The plot shows the features of ionic conduction (an S shaped dispersion in  $M'$  and a peak in  $M''$  [16]. The peak in  $M''$  can be assumed to be related with the translational ion dynamics and mirrors the conductivity relaxation of the mobile ions. It is worth noticing that the relaxation peak which is responsible for fast segmental motion. This fast segmental motion of polymeric chain reduces the relaxation time and increases the transport properties. From the condition  $\tau = 1/2\pi f_{\max}$ , where  $\tau$  is the relaxation time for the ionic charge carrier is estimated [17]. The variation of conductivity  $\log \sigma$  and relaxation time  $\log \tau$  as a function of salt  $\text{AgCF}_3\text{SO}_3$  at 313 K is given in **Figure 2**. The conductivity increases nonlinearly till 7 wt% of  $\text{AgCF}_3\text{SO}_3$  and then decreases at 11 wt% of the salt. This anomaly is also observed for the variation of relaxation time,  $\log \tau$  where the relaxation time ( $1/f_{\max}$ ) is observed to decrease and suddenly increases for 11 wt% of  $\text{AgCF}_3\text{SO}_3$ .



**Figure 5.** Variation of real part of electric modulus ( $M'$ ) with  $\log f$  at different temperature for  $\text{AgCF}_3\text{SO}_3$  3.5 wt%.

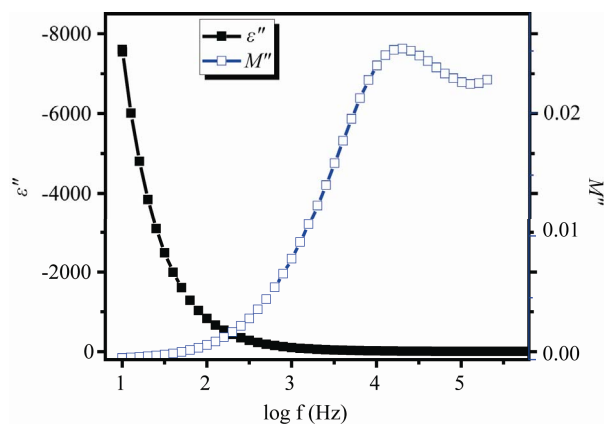


**Figure 6.** Variation of imaginary part of electric modulus ( $M''$ ) with  $\log f$  at different temperature for  $\text{AgCF}_3\text{SO}_3$  3.5 wt%.

The plotting of ac data in terms of impedance, electric modulus and dielectric permittivity simultaneously is extremely advantageous for distinguishing the different relaxation processes occurring inside the materials. The comparison of the experimental data in the  $M''$  and  $\epsilon''$  formalism is, therefore, useful to distinguish long-range conduction process from the localized dielectric relaxation. To visualize this, we have plotted the imaginary part of complex dielectric permittivity ( $\epsilon''$ ) and modulus ( $M''$ ) as a function of frequency for PEO- $\text{AgCF}_3\text{SO}_3$  (7 wt%) polymer electrolyte (Figure 7). Dielectric relaxation is a result of the reorientation process of dipoles in the polymer chains, which show a peak in  $\epsilon''$  spectra. For electrolyte with higher ion concentration, the movement of ions from one site to another perturbs the electric potential of the surroundings. Motion of the other ions in this region will be affected by perturbed potential. This type of cooperative motion of ions exhibits non-exponential decay, or a conduction processes with distribution of relaxation time [18]. In the imaginary part of modulus spectra, a relaxation peak is observed (for the conductivity processes), whereas no peak was seen in the dielectric spectra. This suggests that ionic and polymer segmental motion is strongly coupled and hence manifesting as a single peak in the  $M''$  spectra with no corresponding feature in dielectric spectra [19].

#### 4. Conclusions

PEO- $\text{AgCF}_3\text{SO}_3$  samples are principally ionic conductors. Even a small dispersion of the silver salt causes an enhancement in the conductivity in comparison to pure polymer. The complexation of salt with polymer has been confirmed using FTIR studies. The electrical modulus representation of the same data shows a loss feature in the



**Figure 7.** Plot of the imaginary part of  $\epsilon''$  and modulus ( $M''$ ) as a function of frequency for  $\text{AgCF}_3\text{SO}_3$  7 wt% at 313 K.

imaginary component. The relaxation associated with this feature shows a stretched exponential decay. The analysis of frequency dependence of dielectric and modulus formalism suggests that the ionic and polymer segmental motion are strongly coupled manifesting as a single peak in the  $M''$  spectra with no corresponding feature in dielectric spectra. The frequency dependent of ac conductivity follows Jonscher's power law feature and the low frequency dispersion indicating the presence of electrode polarization phenomena in the materials.

#### 5. Acknowledgements

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