Abstract: The polymer electrolyte based on polyeethylene oxide (PEO) complexes with conducting Polyaniline (PANI) and Sodium triflate salt (NaCF$_3$SO$_3$) has been prepared in different weight percentage (wt%) by in-situ polymerization method. The complexation is confirmed by Fourier transform infrared spectroscopy (FTIR) studies on PANI:NaCF$_3$SO$_3$:PEO complexes, and the peak at 1122 cm$^{-1}$ is considered to be measure of the degree of electron delocalization, 1487 cm$^{-1}$ is due to C=C stretching of benzonoid ring, 1558 cm$^{-1}$ is C=N quinonoid stretching mode of vibration. The ac conductivity has been studied in the frequency range of 50 Hz to 1 MHz and it is found that 30 wt% shows high conductivity compared to pure polyaniline and other complexes.

Keywords: Polyaniline, Sodium triflate salt, Polylethylene oxide, complexes, AC conductivity.

1. Introduction

Polymer electrolytes represent a relatively new class of ionic conductors with potential applications in rechargeable batteries and other electrochemical devices. The most investigated systems consist of poly (ethylene oxide), PEO, with dissolved salts. Ionic transport in these systems is highly coupled to the relaxation processes of the polymer backbone and has been determined to occur predominantly in the amorphous phase for a number of polymer-salt systems. The microscopic mechanism of ionic transport in these systems is not well understood, but certainly involves the breaking and reforming of cation-ether oxygen bonds and changes in the local conformation. The characterization of ion-ion and ion-polymer interactions further our molecular level understanding of ionic conductivity in these systems. In this work, the authors have studied the effect of Sodium triflate salt (NaCF$_3$SO$_3$) on the ionic dielectric behavior of the PANI-PEO-NaCF$_3$SO$_3$ polymer complexes [1-8].

Polymers have traditionally been considered as a good electrical insulators and a variety of their applications have relied on their insulating property [9]. However more than a decade now, researchers have shown that certain class of polymers which are conjugated, exhibit semi conducting behavior [10]. The discovery of doping has led to a further dramatic increase in the conductivity of such conjugated polymers to values as high as 10$^3$ S/cm.

Conducting polymers have become the foci of much research in materials science and among all; polyaniline and polypyrrole have received greater attraction due to their favorable economics, easy synthesis, environmental stability, and unique chemistry [11]. Applications of these polymers have begun to emerge as a new era. These include coating and blends for electrostatic dissipation and electromagnetic interface (EMI) shielding [12]. Electromagnetic radiation, welding (joining) of plastics, conductive layers for light emitting polymer devices and anti-corrosion for iron and steel [13]. In this paper, the authors have reported the Synthesis, characterization and studies on AC conductivity, dielectric constant and dielectric loss of PANI: NaCF$_3$SO$_3$:PEO complexes;
different polyaniline / NaCF$_3$SO$_3$ + PEO complexes with different weight percentages of NaCF$_3$SO$_3$ + PEO (10, 20, 30, 40 and 50 wt%) in polyaniline have been synthesized. All the complexes are crushed into fine powder in an agate mortar in the presence of acetone medium.

The powders of polyaniline and polyaniline – NaCF$_3$SO$_3$ + PEO complexes so obtained from synthesis techniques discussed in the early sections are crushed and finely in the presence of acetone medium in agate mortar. This powder is pressed to form pellets of 10 mm diameter and thickness which varies from 1 to 2 mm by applying pressure of 90 MPa in a hydraulic press. The pellets of polyaniline and its complexes so obtained from above mentioned techniques are coated with silver paste on either side of the surfaces to obtain better contacts.

3. Characterization

The FTIR spectra of all the samples are recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording FTIR spectra, powders are mixed with KBr in the ratio 1:05 by weight to ensure uniform dispersion in KBr pellets. The mixed powders are pressed in a cylindrical die to obtain clean discs of approximately 1 mm thickness. The Dielectric tangent loss and dielectric constant are studied by sandwiching the pellets of these complexes between the silver electrodes and is studied in the frequencies 10$^6$ Hz – 10$^9$ Hz, using LCR meter Newton Model PSM-1735.

4. Results and Discussion

4.1 FTIR

![Figure 1: FTIR Spectra of pure polyaniline.](image1)

![Figure 2: FTIR Spectra of Pure Polyethylene oxide.](image2)

Figure 1 shows FTIR spectra of pure polyaniline. The characteristic vibration of polyaniline is known to be in the region 1000 – 1500 cm$^{-1}$. The FTIR spectra of PANI shows vibrations around 814, 1024, 1122, 1240, 1300, 1487, 1556, 2860, 2924, 3447 cm$^{-1}$, 814 cm$^{-1}$ which corresponds to plane bonding of C-H bonding aromatic ring, 1024 cm$^{-1}$ corresponds to S-O vibration, 1122 cm$^{-1}$ is C-O-C stretching excess oxidant, 1240 is C-N stretching of benzonoid ring, 1303 cm$^{-1}$ is C-N aromatic amines, 1487 cm$^{-1}$ is C=C stretching of benzoid ring, 2860 cm$^{-1}$ and 2924 cm$^{-1}$ are C-H stretching, 3447 cm$^{-1}$ is N-H stretching vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline.

Figure 1 shows the spectra of pure polyethylene oxide. In the pure PEO spectrum, a large broad band appears centered at 3442 cm$^{-1}$. This is possibly due to the hydration of PEO. It was known that the PEO is highly hydrophilic, thus it absorbs water vapor and gets hydrated. Pure PEO shows a large broad band of CH$_2$ stretching between 2950 and 2840 cm$^{-1}$. However, the band is split into two at 2922 cm$^{-1}$ and 2359 cm$^{-1}$ corresponding to asymmetric CH$_2$ stretching (n(CH$_2$)a) and symmetric CH$_2$ stretching (n(CH$_2$)s), respectively.

Two clear CH$_2$ vibrational modes also appear in PEO at 1467 cm$^{-1}$ which, corresponds to asymmetric CH$_2$ bending (d(CH$_2$)a) and 1344 cm$^{-1}$ which corresponds to symmetric CH$_2$ wagging and some C-C stretching (w(CH$_2$)s + n(CC)) [16].

![Figure 3: FTIR Spectra of Sodium triflate salt.](image3)

![Figure 4: FTIR Spectra of PANI:NaCF$_3$SO$_3$:PEO complexes](image4)
B) AC Conductivity

Figure 5: shows the variation of ac conductivity as a function of frequency for Polyaniline – NaCF\textsubscript{3}SO\textsubscript{4} + PEO complexes (different wt %).

Figure 5 shows the variation of ac conductivity as a function of frequency for PANI: NaCF\textsubscript{3}SO\textsubscript{4}: PEO complexes (different wt %). It is observed that in all the cases, \(\sigma_{ac}\) remains constant up to 10\textsuperscript{4} Hz. Among all complexes, 30 wt% of PANI: NaCF\textsubscript{3}SO\textsubscript{4}: PEO complexes shows high conductivity due to interfacial polarization. However, in case of polyaniline and other complexes 10, 20, 40, and 50 wt% the conductivity value is low because of dipole polarization. This behavior of these complexes may be due to the variation in the distribution of NaCF\textsubscript{3}SO\textsubscript{4}: PEO particles in polyaniline.

Figure 6: shows the variation of \(\varepsilon'\) as a function of frequency for PANI:NaCF\textsubscript{3}SO\textsubscript{4}:PEO complexes (different wt %).

Figure 6 shows the variation of \(\varepsilon'\) as a function of frequency for Polyaniline :NaCF\textsubscript{3}SO\textsubscript{4}:PEO complexes (different wt %). In all the cases, it is observed that, the dielectric constant is quite high at low frequency and decreases with increase in applied frequency. The observed behavior may be due to Debye like relaxation mechanism taking place in these materials. Among all complexes, 50 wt% of PANI: NaCF\textsubscript{3}SO\textsubscript{4}: PEO complexes shows high permittivity due to relaxation mechanism and may be also as it exceeds critical contraction [17].

Figure 7: shows the variation of tan delta as a function of frequency for PANI:NaCF\textsubscript{3}SO\textsubscript{4}:PEO complexes (different wt %).

The variation of dielectric loss as a function of frequency for PANI:NaCF\textsubscript{3}SO\textsubscript{4} : PEO complexes (different wt %) is represented in figure 7. Even though NaCF\textsubscript{3}SO\textsubscript{4} : PEO is added up to 30 wt% in polyaniline, the behavior of dielectric loss with respect to frequency follows the same trend as that of pure polyaniline. At higher frequencies these complexes exhibit almost zero dielectric loss which suggests that these complexes are loss less materials at frequencies beyond 10\textsuperscript{5}Hz [18].

5. Conclusion

The alkyl salt NaCF\textsubscript{3}SO\textsubscript{4}: PEO doped polyaniline complexes has been prepared at different weight percentages (10, 20, 30, 40 and 50 wt %) were synthesized by in situ polymerization method. From the Fourier transform infrared spectroscopy (FTIR), studies confirm the formation of PANI: NaCF\textsubscript{3}SO\textsubscript{4}: PEO complexes. The ac conductivity has been studied in the frequency range of 50 Hz to 1 MHz and shows 30 wt% high conductivity of 8.1x10\textsuperscript{-6} S/cm has low dielectric constant compared to pure polyaniline and other complexes.

References


