

# Dielectric and AC Conductivity Studies of $\text{NaCF}_3\text{SO}_3$ -PEO Doped Polyaniline Complexes

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**Abstract:** The polymer electrolyte based on polyethylene oxide (PEO) complexes with conducting Polyaniline (PANI) and Sodium triflate salt ( $\text{NaCF}_3\text{SO}_3$ ) 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: $\text{NaCF}_3\text{SO}_3$ :PEO complexes, and the peak at  $1122\text{ cm}^{-1}$  is considered to be measure of the degree of electron delocalization,  $1487\text{ cm}^{-1}$  is due to C=C stretching of benzonoid ring,  $1558\text{ cm}^{-1}$  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, Polyethylene 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 furthers our molecular level understanding of ionic conductivity in these systems. In this work, the authors have studied the effect of Sodium triflate salt ( $\text{NaCF}_3\text{SO}_3$ ) on the ionic dielectric behavior of the PANI-PEO- $\text{NaCF}_3\text{SO}_3$  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  $10^5\text{ S/cm}$ .

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 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:  $\text{NaCF}_3\text{SO}_3$ : PEO complexes;

## 2. Materials and Methods

All Chemicals used were analytical reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate (APS) ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ), Hydrochloric acid (HCl), and  $\text{NaCF}_3\text{SO}_3$ , PEO were procured from sigma and were used as received.

### a) Synthesis of Polyaniline

The synthesis was based on mixing aqueous solutions of aniline hydrochloride and ammonium persulphate at room temperature, followed by the separation of polyaniline hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equi molar volumes of aniline and hydrochloric acid) was dissolved in distilled water in a volumetric flask to 100 mL of solution. Ammonium persulphate (0.25M) was dissolved in water also to 100 mL of solution. Both solutions were kept for 1 hour at room temperature ( $25^\circ\text{C}$ ), then mixed in a beaker, stirred with a mechanical stirrer, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter, washed with 300-mL portions of 0.2 M HCl, and similarly with acetone. Polyaniline (emeraldine) hydrochloride powder was dried in air and then in vacuum at  $60^\circ\text{C}$  to achieve the constant weight [14].

### b) Synthesis of PANI: $\text{NaCF}_3\text{SO}_3$ :PEO complexes

The 0.1 mole aniline monomer is dissolved in 1 mole nitric acid to form polyaniline hydronitride. Fine graded pre-sintered  $\text{NaCF}_3\text{SO}_3$  +PEO (AR grade, SD-Fine Chem.) powder in the weight percentages (wt%) of 10,20,30,40 and 50 wt% is added to the polymerization mixture with vigorous stirring in order to keep the  $\text{NaCF}_3\text{SO}_3$ :PEO powder suspended in the solution. To this reaction mixture, APS as an oxidant is added slowly with continuous stirring for the period of 4 hrs at temperature  $5^\circ\text{C}$ . Polymerization of aniline takes place over fine grade  $\text{NaCF}_3\text{SO}_3$  +PEO particles. The resulting precipitate is filtered and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any uncreated aniline. After washing, the precipitate is dried under dynamic vacuum at  $60^\circ\text{C}$  for 24 h to achieve constant weight of resulting complexes [15]. In this way, five

different polyaniline /  $\text{NaCF}_3\text{SO}_3$  + PEO complexes with different weight percentages of  $\text{NaCF}_3\text{SO}_3$ +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 –  $\text{NaCF}_3\text{SO}_3$  +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  $10^2\text{Hz}$ – $10^6\text{Hz}$ , using LCR meter Newton Model PSM-1735.

## 4. Results and Discussion

### 4.1 FTIR

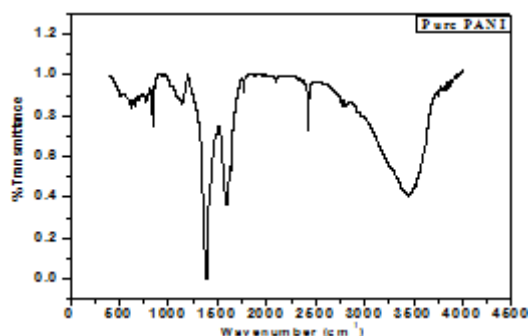


Figure 1: FTIR Spectra of pure polyaniline.

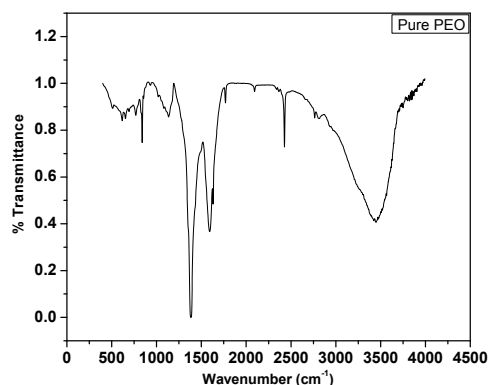


Figure 2: FTIR Spectra of Pure Polyethylene oxide

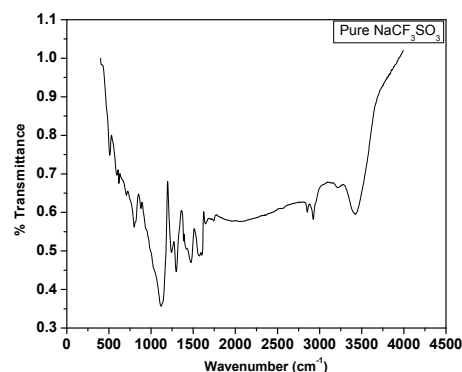


Figure 3: FTIR Spectra of Sodium triflate salt.

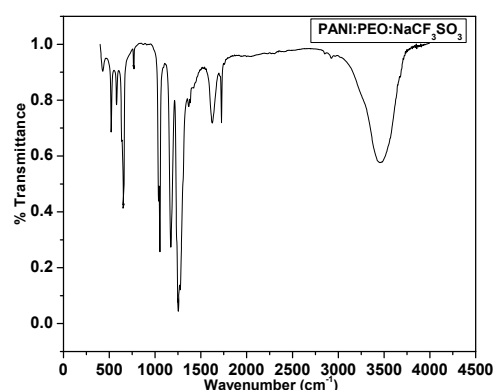


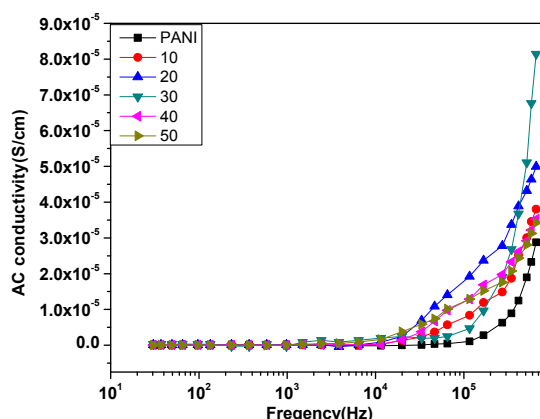
Figure 4: FTIR Spectra of PANI: $\text{NaCF}_3\text{SO}_3$ :PEO complexes

Figure 1 shows FTIR spectra of pure polyaniline. The characteristic vibration of polyaniline is known to be in the region  $1000 - 1500 \text{ cm}^{-1}$ . The FTIR spectra of PANI shows vibrations around  $814, 1024, 1122, 1240, 1300, 1487, 1556, 2860, 2924, 3447 \text{ cm}^{-1}$ .  $814 \text{ cm}^{-1}$  which corresponds to plane bonding of C-H bonding aromatic ring,  $1024 \text{ cm}^{-1}$  corresponds to S-O vibration,  $1122 \text{ cm}^{-1}$  is C-O-C stretching excess oxidant,  $1240$  is C-N stretching of benzonoid ring,  $1303 \text{ cm}^{-1}$  is C-N aromatic amines,  $1487 \text{ cm}^{-1}$  is C=C stretching of benzonoid ring,  $2860 \text{ cm}^{-1}$  and  $2924 \text{ cm}^{-1}$  are C-H stretching,  $3447 \text{ cm}^{-1}$  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  $3442 \text{ cm}^{-1}$ . 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  $\text{CH}_2$  stretching between  $2950$  and  $2840 \text{ cm}^{-1}$ . However, the band is split into two at  $2922 \text{ cm}^{-1}$  and  $2359 \text{ cm}^{-1}$  corresponding to asymmetric  $\text{CH}_2$  stretching ( $n(\text{CH}_2)_a$ ) and symmetric  $\text{CH}_2$  stretching ( $n(\text{CH}_2)_s$ ), respectively.

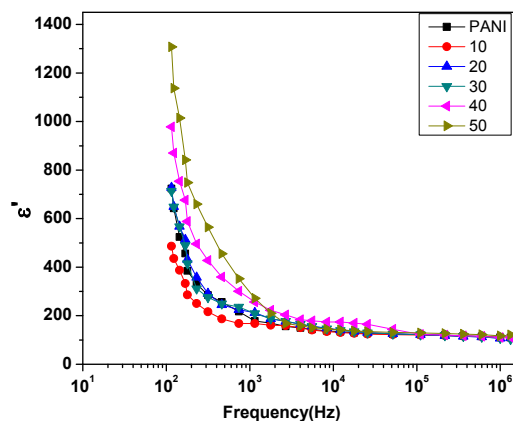
Two clear  $\text{CH}_2$  vibrational modes also appear in PEO at  $1467 \text{ cm}^{-1}$  which, corresponds to asymmetric  $\text{CH}_2$  bending ( $d(\text{CH}_2)_a$ ) and  $1344 \text{ cm}^{-1}$  which corresponds to symmetric  $\text{CH}_2$  wagging and some C-C stretching ( $w(\text{CH}_2)_s +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

## B) AC Conductivity



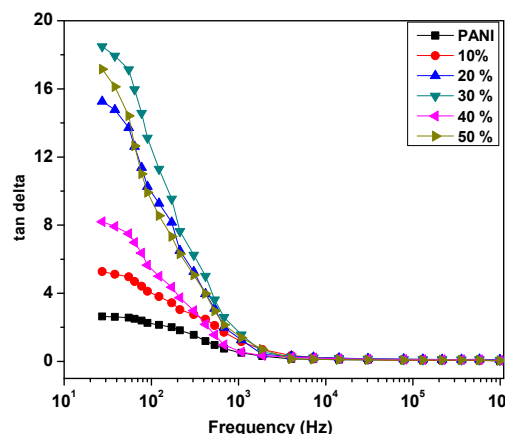
**Figure 5:** shows the variation of ac conductivity as a function of frequency for Polyaniline – NaCF<sub>3</sub>SO<sub>3</sub> + PEO complexes (different wt %).

Figure 5 shows the variation of ac conductivity as a function of frequency for PANI: NaCF<sub>3</sub>SO<sub>3</sub>:PEO complexes (different wt %). It is observed that in all the cases,  $\sigma_{ac}$  remains constant up to  $10^4$  Hz. Among all complexes, 30 wt% of PANI: NaCF<sub>3</sub>SO<sub>3</sub>: 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<sub>3</sub>SO<sub>3</sub> : PEO particles in polyaniline.



**Figure 6:** shows the variation of  $\epsilon'$  as a function of frequency for PANI:NaCF<sub>3</sub>SO<sub>3</sub>:PEO complexes (different wt %).

Figure 6 shows the variation of  $\epsilon'$  as a function of frequency for Polyaniline :NaCF<sub>3</sub>SO<sub>3</sub>: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<sub>3</sub>SO<sub>3</sub>: 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<sub>3</sub>SO<sub>3</sub>:PEO complexes (different wt %).

The variation of dielectric loss as a function of frequency for PANI:NaCF<sub>3</sub>SO<sub>3</sub> :PEO complexes (different wt %) is represented in figure 7. Even though NaCF<sub>3</sub>SO<sub>3</sub> :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  $10^4$ Hz [18].

## 5. Conclusion

The alkyl salt NaCF<sub>3</sub>SO<sub>3</sub>: PEO doped polyaniline complexes has been prepared at different weight percentages (10, 20, 30, 40 and 50 wt %) were synthesized by insitu polymerization method. From the Fourier transform infrared spectroscopy (FTIR), studies confirm the formation of PANI: NaCF<sub>3</sub>SO<sub>3</sub>: 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  $8.1 \times 10^{-6}$  S/cm has low dielectric constant compared to pure polyaniline and other complexes.

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