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Synthesis, characterization and DC Conductivity Studies of $NaCF_3SO_3$ -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 ($NaCF_3SO_3$) has been prepared in different weight percentage(wt%) by insitu polymerization method. The complexation is characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM), which confirmed the presence of polyethylene oxide complexes with conducting Polyaniline and Sodium triflate salt. DC conductivity studies show thermally activated behavior of all the composites. The conductivity was found to increase with the increase in temperature indicating the semiconducting behavior of all the complexes. Maximum conductivity was observed in 30 wt% of Sodium triflate salt complexes with conducting Polyaniline and polyethylene oxide.

***Keywords* -** Polyaniline, Sodium triflate salt, Polyethylene oxide, complexes, DC conductivity.

I. INTRODUCTION

The ionic conductivity in high molecular weight polyethylene oxide (PEO) doped with sodium and potassium salts were first reported by Wright [1]. The technological implications of these PEO based electrolytes, such as their use in lithium batteries were realized and suggested by Armand et.al [2]. These reports related to these solid electrolytes have been reported in reviews by many researchers [3-4]. In general, the polymer component of PEO based composite electrolyte is a mixture of crystalline and amorphous phases, ratio of which depends to a great extent on compositions of the electrolyte, temperature and thermal history. The solid polymer electrolytes, i.e., polymer salt complexes are of technological interest due to their possible application as solid electrolytes in different devices such as energy conversion units (batteries/fuel cells), electro-chromic display devices/smart windows and photo-electrochemical solar cells, etc., [5-7]. Subsequently studies on PEO-based polymer electrolyte complexes using alkali salts [8-10] were developed in this field.

A large number of lithium ion conductors have been developed because of the availability of insertion materials to realize high energy density solid state batteries. The present work is directed towards investigation of analogues or similar sodium systems. Lithium and sodium have similar physico-chemical properties. Sodium is much more abundant and lower priced than lithium. The softness of sodium metal is expected to promote good contact with the components in solid state ionic devices such as batteries, during repeated cycles [11-13]. In this paper, the authors have reported the Synthesis, characterization and studies on DC conductivity of PANI:$NaCF_3SO_3$:PEO complexes.

II. MATERIALS AND METHOD

All Chemicals used were analytical reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate (APS) ($(NH_4)_2S_2O_8$), Hydrochloric acid (HCl), and $NaCF_3SO_3$, 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°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°C to achieve the constant weight [14].

b) Synthesis of Polyaniline / $NaCF_3SO_3$ +PEO complexes

The 0.1 mole aniline monomer is dissolved in 1 mole nitric acid to form polyaniline hydronitride. Fine graded pre-sintered $NaCF_3SO_3$ +PEO (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 10,20,30,40 and 50 is added to the polymerization mixture with vigorous stirring in order to keep the $NaCF_3SO_3$: 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 5^0C. Polymerization of aniline takes place over fine grade $NaCF_3SO_3$ +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 60^0C for 24 hrs to achieve constant weight of resulting complexes [15]. In this way, five different polyaniline / $NaCF_3SO_3$ +PEO complexes with different weight percentage of $NaCF_3SO_3$ +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.

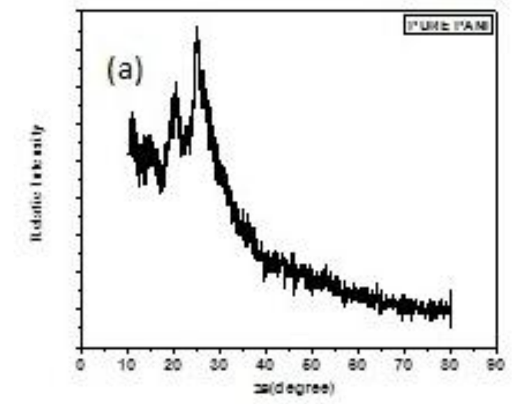
The powders of polyaniline and polyaniline – $NaCF_3SO_3$ +PEO complexes so obtained from synthesis techniques discussed in the early sections are crushed and finely in the presence of acetone medium in agate mortar. This powder is pressed to form pellets of 10 mm diameter and thickness which varies 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.

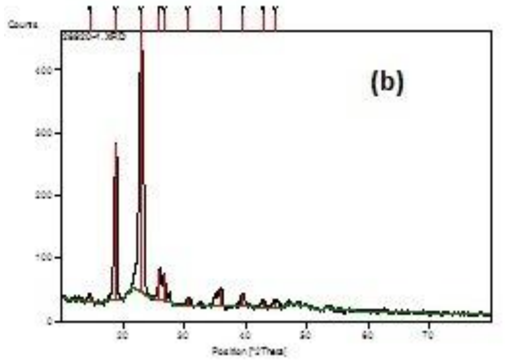
III. RESULTS AND DISCUSSION

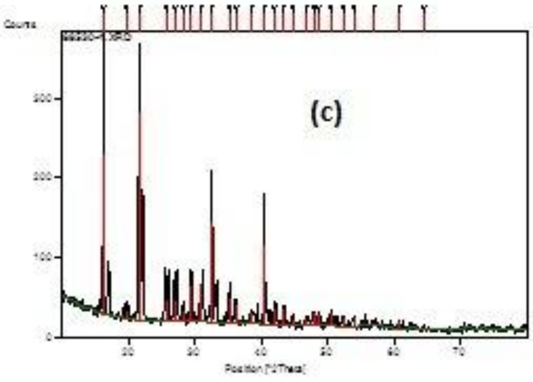
A) X - Ray diffraction

The Figure 1(a) shows X-ray diffraction pattern of Polyaniline. The broad peak is observed at $2\theta = 26.31^0$, which clearly indicates complete amorphous nature. These results clearly indicate the dominant amorphous nature which causes high mobility of the ions in the material. Figure 1(b) shows the X-ray diffraction pattern of the pure Polyethylene oxide. The sharp peaks are observed at $2\theta = 18.31^0$ and 24.01^0 which confirms the crystallinity of the pure Polyethylene oxide. This XRD data of Polyethylene oxide indicates the low ion mobility. Figure 1(c) Shows the X-ray diffraction pattern of the pure sodium triflte salt these peaks have been observed at $2\theta = 8.5^0$, 9.95^0, 16.8^0, 22.15^0, 26.25^0, 32.9^0, 35.6^0, and 40.9^0 [16].

Figure 1(d) Shows the XRD patterns of polyaniline – $NaCF_3SO_3$+PEO complexes include the character- ristic peaks of both PANI and $NaCF_3SO_3$ +PEO with the crystalline structure, which confirms the formation of complexes with lower crystallinity. It has been suggested by XRD study that PANI undergoes interfacial interaction with $NaCF_3SO_3$ +PEO crystallites and loses its own morphology by its mixing with $NaCF_3SO_3$ +PEO. PANI- $NaCF_3SO_3$ +PEO complexes show peaks of $NaCF_3SO_3$ +PEO as well as polyaniline indicating that $NaCF_3SO_3$ +PEO crystallites have been uniformly mixed within the polymer chain. It also shows that PANI interacts with $NaCF_3SO_3$+PEO particles and the molecular chains of the PANI are stretched leading to decrease in crystallinity.







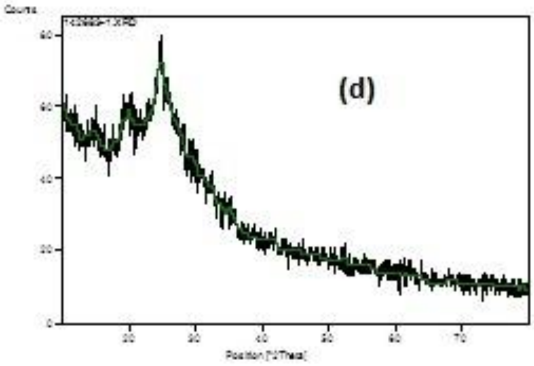
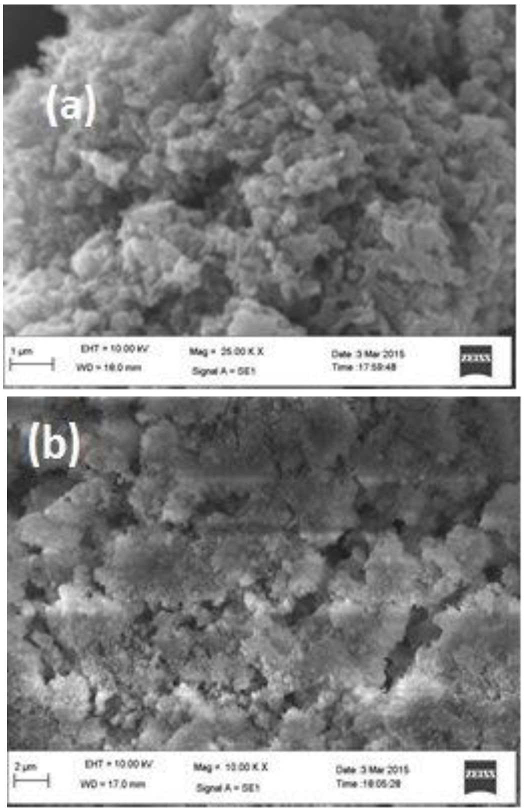


Figure 1: X-ray diffraction pattern of (a) pure polyaniline, (b) pure PEO (c) $NaCF_3CO_3$ (d) 50wt% of $NaCF_3CO_3$+PEO in polyaniline.

B) Scanning electron micrographs

The higher resolution SEM micrograph of conducting polyaniline (PANI) synthesized by chemical oxidative method is shown in figure 2 (a). It can be clearly seen that the micrograph of polyaniline is mesoporous with highly agglomerated granular shaped. The grains are well interconnected with each other, which indicate that they have enough binding energy to combine with neighbor grains or molecules.



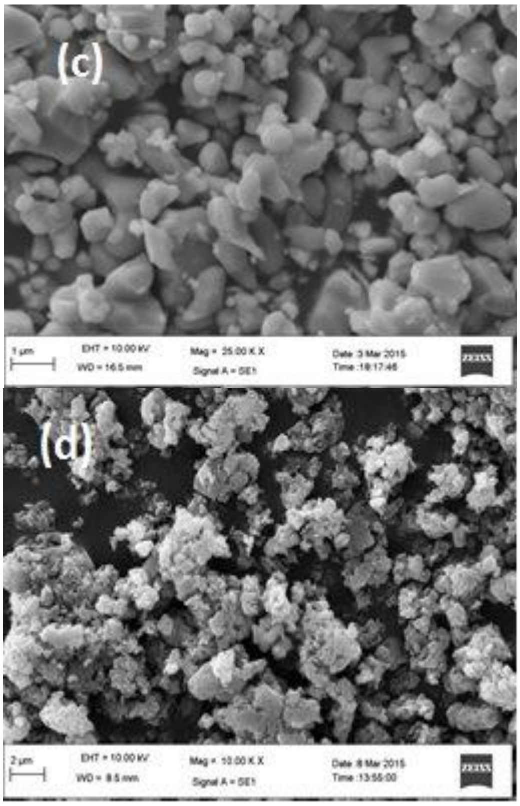


Figure 2: SEM image of (a) pure polyaniline, (b) pure PEO (c) $NaCF_3CO_3$(d) 50wt% of $NaCF_3CO_3$+PEO in polyaniline.

Figure 2(b) shows that Scanning Electronic Micrograph (SEM) image of pure polyethylene oxide and it is found to be highly macro-crystalline like structure. The grains are found to be well interconnected with each other which indicate that they have enough binding energy to combine with neighbour grains or molecules.

Figure 2(c) shows the SEM micrograph of pure $NaCF_3SO_3$, from this figure, it is observed that, they are highly crystalline, mesoporous, clustered and has granular morphology. Figure 2(d) show the SEM image of PANI- $NaCF_3SO_3$+PEO complexes. The complexes are softened after the addition of PANI into $NaCF_3SO_3$+PEO matrix and it is also well understood that the $NaCF_3SO_3$ salts are homogeneously distributed and greatly intercalated within the matrix. The crystallinity of the $NaCF_3SO_3$ +PEO is seen to decrease with the addition of PANI into it.

C) DC Conductivity Studies:

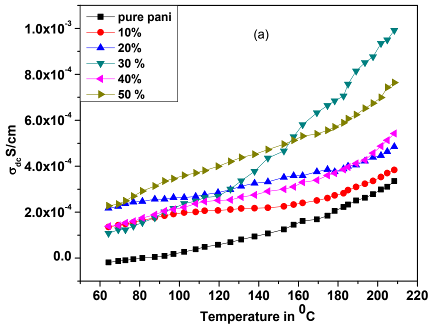
Figure: 3(a) shows the σ_{dc} conductivity as a function of temperature for PEO-$NaCF_3SO_3$ –PANI polymer complexes at various weight percentages. It is observed that the conductivity of the composites increases with increase in temperature ranging from 30^0C to 180^0C. Among all the PANI-PEO-$NaCF_3SO_3$ polymer complexes, 30 wt% shows higher conductivity. This clearly indicates that the conductivity is not only the motion of ions ($NaCF_3SO_3$) but also hopping of charge carriers like polarons and bipolarons from one island to another.

It is also suggested here that the thermal curling effects of the chain alignment of the polyaniline leads to the increase in conjugation length and that brings about the increase of conductivity. Also, there will be molecular rearrangement on heating which makes the molecules favorable for electron delocalization. The conductivity varies directly with the temperature obeying an expression of the following form.

$$\sigma(T) = \sigma_0 \exp[-(T^0/T)^{1/4}] \quad \ldots\ldots\ldots\ldots\ldots(1)$$

Where σ is the conductivity, T is the temperature, and σ_0 is the conductivity at characteristic temperature T^0.Conductivity varying with various values of the exponent (e.g.$T^{-1/4}$, $T^{-1/3}$and $T^{-1/2}$) has been reported and different models have been used to interpret this data.

Figure 3(b) shows the variation of dc conductivity as a function of different weight percentages of PANI-PEO-$NaCF_3SO_3$ polymer complexes at three different temperatures (50, 100 ,150 and 180^{0}C). It is observed that for 10 wt%, 20 wt% and 40 wt% of PANI-PEO-$NaCF_3SO_3$ polymer complexes, the conductivity decreases. However in 30 wt% and 50 wt% of PANI-PEO-$NaCF_3SO_3$ polymer complexes, conductivity increases which is due to the variation in distribution of PANI which may be supporting for more number of charge carriers to hopp between favorable localized sites causing increase in conductivity. The decrease in conductivity may be attributed due to the trapping of charge carriers. This can be well supported by VRH model.



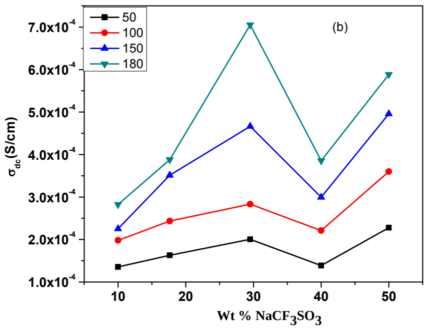


Figure3: (a) shows the σ_{dc} conductivity as a function of temperature, (b) shows the variation of dc conductivity as a function of different weight percentages

IV. CONCLUSION

The alkyl salt $NaCF_3SO_3$: PEO doped polyaniline complexes has been prepared at different weight percentages (10, 20, 30, 40 and 50 wt %) where synthesized by insitu polymerization method. The SEM image reveals the presence of PEO-$NaCF_3SO_3$ particles which are uniformly distributed throughout the composite sample. The temperature dependence of the conductivity of the composites exhibits a typical semiconductor behavior and hence can be expressed by the 1D-VRH model proposed by Mott. The decrease in the conductivity of the composites may be due to the trapping of charge carriers in the matrix, which may be confirmed by the percolation theory. This result indicates that the $NaCF_3SO_3$: PEO doped polyaniline complexes has an electrochemical stability and is thus suitable for application in solid-state batteries. Maximum conductivity was observed in the composite of 30 wt% of $NaCF_3SO_3$: PEO doped polyaniline complexes.

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