

Synthesis, Characterization and DC Conductivity Studies of CaCl_2 -PEO Doped Polyaniline Complexes

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Abstract: *The polymer electrolyte based on polyethylene oxide (PEO) complexes with conducting Polyaniline (PANI) and Cobalt Chloride (CoCl_2) has been prepared in different weight percentage (wt%) by in situ 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 Cobalt Chloride 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 Cobalt Chloride salt complexes with conducting Polyaniline and polyethylene oxide.*

Keywords: Polyaniline, Cobalt Chloride salt, Polyethylene oxide, complexes, DC conductivity

I. INTRODUCTION

Conducting polymers have been extensively studied in the last 20 years and used for technological applications in electrochromics, batteries, biosensors, gas separation membranes, enzyme immobilization matrices and metal protection against corrosion [1-3].

Polyaniline (PANI) has received much attention as a popular kind of conducting polymer with various exceptional [2]. Since the discovery of high electrical conductivity from blending poly(ethylene oxide) PEO with potassium salts by Fenton et al [3]. Polymer electrolytes have attracted a lot of interest, especially because of their potential use in thin film batteries [3]. Polymer electrolytes consist of polar polymer and ionizable salts. PEO is the most popular polymer used, due to its high solvating power with metal ions, good processability, and outstanding mechanical properties [4-8].

II. MATERIALS AND METHOD

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 Cobalt Chloride salt (CoCl_2), PEO were procured from sigma and were used as received.

2.1 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].

2.2 Synthesis of PANI: CoCl_2 : PEO Complexes

The 0.1 mole aniline monomer is dissolved in 1 mole HCl to form aniline hydrochloride. Fine graded pre-sintered CoCl_2 +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 CoCl_2 :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 50°C. Polymerization of aniline takes place over fine grade $\text{CoCl}_2 \cdot \text{PEO}$ particles. The resulting precipitate is filtered and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any unreacted aniline. After washing, the precipitate is dried under dynamic vacuum at 60°C for 24 h to achieve constant weight of resulting complexes [32]. In this way, five different PANI: $\text{CoCl}_2 \cdot \text{PEO}$ complexes with different weight percentages of $\text{CoCl}_2 \cdot \text{PEO}$ (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 – $\text{CoCl}_2 \cdot \text{PEO}$ 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 60 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 DISCUSSIONS

3.1 X - Ray diffraction

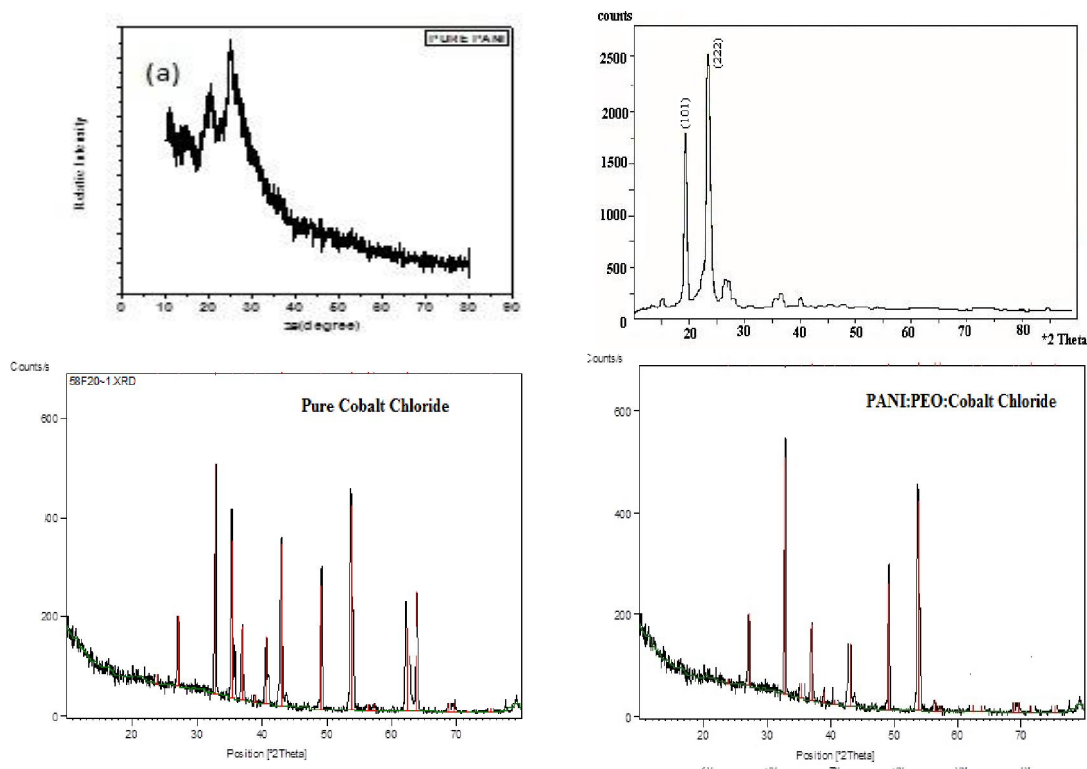


Figure 1: X-ray diffraction pattern of (a) Pure Polyaniline, (b) Pure PEO (c) CaCl_2 (d) 50wt% of $\text{CaCl}_2 + \text{PEO}$ in polyaniline.

The Figure 1(a) shows X-ray diffraction pattern of Polyaniline. The broad peak is observed at $2\theta = 26.31^\circ$, 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 $2\theta = 18.31^\circ$ and 24.01° 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 Cobalt Chloride salt and the peaks have been observed at $2\theta = 26.5^\circ, 32.95^\circ, 33.8^\circ, 36.15^\circ, 41.25^\circ, 43.9^\circ, 49.6^\circ,$ and 63.9° .

Figure 1(d) Shows the XRD patterns of polyaniline – $\text{CaCl}_2 + \text{PEO}$ complexes include the characteristic peaks of both PANI and $\text{CaCl}_2 + \text{PEO}$ 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 $\text{CaCl}_2 + \text{PEO}$ crystallites and loses its own morphology by its mixing with $\text{CaCl}_2 + \text{PEO}$. PANI- $\text{CaCl}_2 + \text{PEO}$ complexes show peaks of

CaCl₂+PEO as well as polyaniline indicating that CaCl₂+PEO crystallites have been uniformly mixed within the polymer chain. It also shows that PANI interacts with CaCl₂+PEO particles and the molecular chains of the PANI are stretched leading to decrease in crystallinity. Cobalt Chloride salt PEO doped with polyaniline complex and the peaks have been observed at $2\theta = 26.5^{\circ}, 32.95^{\circ}, 33.8^{\circ}, 36.15^{\circ}, 41.25^{\circ}, 43.9^{\circ},$ and 49.6° has retained its structure even though it is dispersed in Pani during polymerization reaction.

3.2 Scanning Electron Micrographs

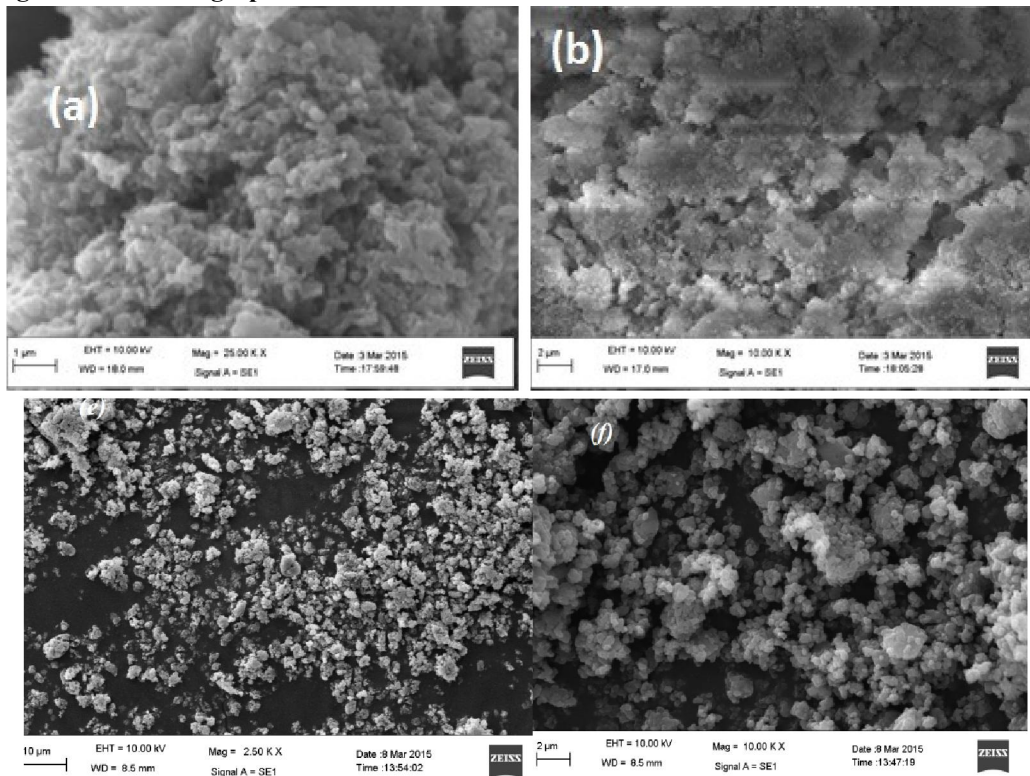


Figure 2: SEM image of (a) Pure polyaniline, (b) Pure PEO (c) Pure CaCl₂ (d) 50wt% of CaCl₂+PEO in Polyaniline. The higher resolution SEM micrograph of conducting polyaniline (PANI) synthesized by chemical oxidative method is shown in figure 2(a). It can be clearly seen that the micrograph of polyaniline 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(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 image of Pure CoCl₂, it is clearly observed that the particles are spherical and agglomerated one another to form a small bunch of particles. Figure 2 (d) shows the SEM image of PANI- CoCl₂+PEO complexes. The complexes are softened after the addition of PANI into CoCl₂+PEO matrix and it is also well understood that the NaCF₃SO₃ salts are homogeneously distributed and greatly intercalated within the matrix. The crystallinity of the CoCl₂+PEO is seen to decrease with the addition of PANI into it.

3.3 DC Conductivity Studies

Figure: 3(a) shows the σ_{dc} conductivity as a function of temperature for PEO-CoCl₂-PANI polymer complexes at various weight percentages. It is observed that the conductivity of the composites increases with increase in temperature ranging from 30^oC to 180^oC. Among all the PANI-PEO-CoCl₂ polymer complexes, 30 wt% shows higher conductivity. This clearly indicates that the conductivity is not only the motion of ions (CoCl₂) but also hopping of charge carriers like polarons and bipolarons from one island to another.

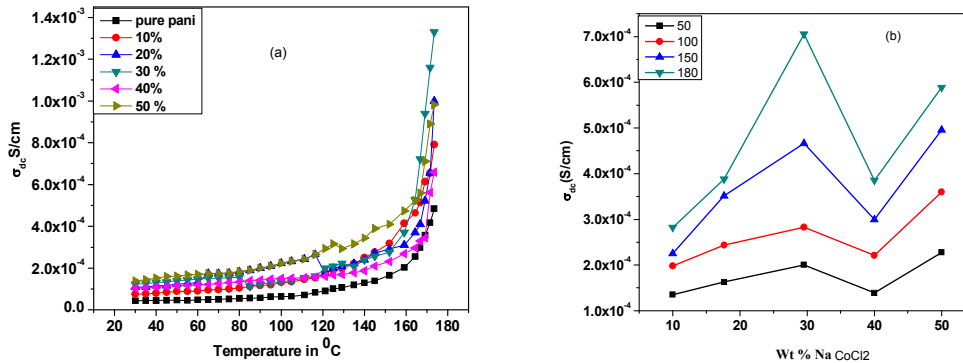


Figure 3: (a) shows the σ_{dc} conductivity as a function of temperature,

(b) shows the variation of dc conductivity as a function of different weight percentages

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.

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

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-CoCl₂ polymer complexes at three different temperatures (50, 100, 150 and 180°C). It is observed that for 10 wt%, 20 wt% and 40 wt% of PANI-PEO-CoCl₂ polymer complexes, the conductivity decreases. However in 30 wt% and 50 wt% of PANI-PEO-CoCl₂ 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 hop 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.

IV. CONCLUSION

The alkyl salt CoCl₂: 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-CoCl₂ 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 CoCl₂: 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 CoCl₂: PEO doped polyaniline complexes.

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