



## AC Conductivity Study of Polyaniline / Dysprosium Oxide (PANI / Dy<sub>2</sub>O<sub>3</sub>) Composites

### KEYWORDS

Polyaniline, Dysprosium oxide, AC conductivity

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**ABSTRACT** *The conducting polyaniline / Dysprosium oxide (PANI / Dy<sub>2</sub>O<sub>3</sub>) composites were synthesized by single step in situ polymerization technique by placing finely grinded powder of Dy<sub>2</sub>O<sub>3</sub> during the polymerization of aniline. The formation of mixed phases of the polymer together with the conducting emeraldine salt phase was confirmed by spectroscopic techniques like XRD, FTIR & SEM images indicated a systematic morphological variation of particles aggregated in the composite matrix as compared to the PANI. AC conductivity of these composites were investigated in the frequency range 50 Hz to 5MHz. It is found that AC conductivity obeyed the power law index and the variation of conductivity with wt% of Dy<sub>2</sub>O<sub>3</sub> could be related to conductivity relaxation phenomenon.*

### 1. Introduction

Conjugated polymers have attracted lot of attention due to their unique electrical properties and have been defined as "the polymers, which have a frame work of alternating single and double carbon-carbon (sometimes carbon-nitrogen) bonds" [1]. The transport properties of conducting polymers are highly dependent on the structural disorder arising from sample quality, doping procedure and aging. Conducting polymers generally display a wide variety in their morphology and being partially crystalline and partially disordered. Even if the polymer chains are well-ordered, macroscopic transport is not possible unless the charge carriers can hop to avoid chain break and defects. Localization occurs in the disordered regions due to one dimensional electronic nature of the polymer chains. The transport properties are then dominated by hopping, phonon-induced delocalization in the disordered regions or even tunneling between metallic islands, which depends on the morphology of the polymer [2]. The conducting polymers have wide applications such as solar cells, lightweight batteries, light emitting diodes, polymer actuators, corrosion protection agents, sensors and molecular electronic devices. Biosensors based on conducting polymers have found to have promising applications in various fields such as biotechnology, food and agricultural products processing, health care, medicine and pollution monitoring [3]. Conducting polymer composites, especially organic - inorganic composites have been in the extensive research for the past few years [4, 7]. Among the heterogeneous conducting polymers, polyaniline (PANI) is the most extensively studied, ever since its discovery. Hence the polyaniline is one of the most popular electro-conductive polymers and it also called as synthetic metals [8, 10]. Polyaniline has attracted considerable attention to prepare the composites by incorporating inorganic particle like BaTiO<sub>3</sub> [11], molybdenum trisulfide [12], V<sub>2</sub>O<sub>5</sub> [13], inorganic salts [14], montmorillonite [15], TiO<sub>2</sub> [16], ZrO<sub>2</sub> [17], etc. polyaniline - inorganic particle composites have been studied [18] and in high density information storage devices [19]. The understanding of charge transport mechanism in the composite materials is very important both from fundamental and technological point of view. The impedance measurement is one of the powerful techniques to characterize and realize the charge transport that process in the complex materials. The studies on electrical properties of new systems are useful for possible technical applications. Various theoretical models were developed for the description of charge transport in conducting polymers [20]. In spite of high doping of polymers, the charge carriers seems to be localized, so they should move in material by hopping over or tunneling through the potential barriers between the localized states. Variable range hopping (VRH)

is the most common charge transport mechanism and this model assumes that carriers tunnel through the energy barriers between the localized states with help of phonon thermal energy [21]. 3D-VRH occurs in disordered polymers with structures similar to the amorphous semiconductors, where charges can choose a most easy hop in any direction. Quasi-1D VRH occurs in the polymers where charges move along the polymer chain, with sudden inter-chain hops [22]. In some cases polymerization and protonation leads to creation of small conducting islands distributed in non-conductive matrix. In such case charges tunnel between these regions according to charged energy limited tunneling (CELT) mechanism [23]. In the present paper, the preparation of polyaniline / Dysprosium oxide (PANI / Dy<sub>2</sub>O<sub>3</sub>) composites, its characterization through XRD, FTIR & SEM, transport properties such as ac conductivity is reported.

### 2. Experimental

All Chemicals used are analytical grade (AR) and were procured, used as received. The monomer aniline was doubly distilled prior to use. Synthesis of Polyaniline / Dysprosium oxide (Dy<sub>2</sub>O<sub>3</sub>) composites has been carried out by single step in situ polymerization technique. 0.1 mol of aniline was dissolved in 1 M of Hydrochloric acid to form aniline hydrochloride. Finely grinded powder of Dysprosium oxide (Dy<sub>2</sub>O<sub>3</sub>) is added in the weight percent of 10, 20, 30, 40 and 50 to the above solution with vigorous stirring to keep Dysprosium oxide (Dy<sub>2</sub>O<sub>3</sub>) suspended in the solution. To this reaction mixture, 0.1 M of oxidizing agent ammonium persulphate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] in 1 M of Hydrochloric acid was added slowly with continuous stirring for 4 – 8 h at 0 – 5° C to polymerize. The precipitated powder was recovered, vacuum filtered and washed with deionised water. Finally, the resultant precipitate was dried in an oven for 24 h to achieve constant weight. In this way, five different PANI / Dy<sub>2</sub>O<sub>3</sub> composites with different weight of Dy<sub>2</sub>O<sub>3</sub> (10, 20, 30, 40 and 50) in PANI have been synthesized [24-33]. The pellets of 10 mm diameter are formed with thickness varying up to 2 mm by applying pressure of 10 Tons in a UTM – 40 (40 Ton Universal testing machine). For conductivity measurement, the pellets are coated with silver paste on either side of the surfaces. The characterization studies are employed on all the above synthesized PANI / Dy<sub>2</sub>O<sub>3</sub> composites to confirm the presence of Dy<sub>2</sub>O<sub>3</sub> in PANI. The frequency dependent AC conductivity of polyaniline / Dy<sub>2</sub>O<sub>3</sub> composites are studied in the frequency range 50 Hz to 5 MHz at room temperature using Hioki impedance analyzer, model 3532-50 (JAPAN) programmable LCR meter. In this experiment, five different samples of each composite varying in their weight percentage are investigated for their frequency dependent conductivity.

### 3. Results and discussions

Figure 1. Shows X-ray diffraction pattern of Polyaniline. Careful analysis of X-ray diffraction of polyaniline suggests that it has semi-crystalline nature with a broad peak centered around  $2\theta \approx 270$ . XRD spectra of pure PANI, shows a broad reflection at lower Bragg angle  $2\theta$  value of  $25.38^\circ$  corresponding to (200) diffraction plane of ES-I structure of HCl doped PANI (Joo et al 1998) .

Figure 2. shows the X – Ray diffraction pattern of Polyaniline -  $Dy_2O_3$  composite (50 wt %  $Dy_2O_3$  in PANI). By comparing the XRD pattern of composite with that of  $Dy_2O_3$  (JCPDS No. 22-0612) the prominent peaks corresponds to  $2\theta = 29.59^\circ$  i.e. first peak no change,  $31.09^\circ$  shifted to  $34.12^\circ$ ,  $48.55^\circ$  and  $58.64^\circ$  are due to (211), (222), (422) and (433) planes of  $Dy_2O_3$  respectively. By comparing the XRD patterns of the composite and  $Dy_2O_3$ , it is confirmed that  $Dy_2O_3$  has retained its structure even though dispersed in PANI during polymerization reaction. The semi sharp peak of PANI at  $27^\circ$  has widened this is due to doping  $Dy_2O_3$  in PANI

SEM micrograph of conducting polyaniline synthesized by chemical oxidative method is shown in figure 3. It can be clearly seen that the micrograph of polyaniline is smooth and homogeneous. Since Hydrochloric acid is used as protonic acid in the preparation of polyaniline, the presence of microcrystalline structure can be seen that is not homogeneously distributed through out. The presence of microcrystalline structures in polyaniline in this particular samples can be confirmed from XRD studies. Since conducting polymers are very sensitive to the temperature, due to the interaction between electron and the sample, considerable amount of heat is generated which causes the development of small crackening in the sample during SEM recording. A granular morphology of the microcrystalline structures is measured and is found to be about 200 – 600 Å in diameter for polyaniline which is consistent with other reports [10-15]. The contrast in the image is a result of differences in scattering from different areas of the surface as a result of geometrical differences.

Figure 4. Shows the SEM of polyaniline –  $Dy_2O_3$  composite (50 wt % of  $Dy_2O_3$  in polyaniline). Among the five composites that were synthesized using  $Dy_2O_3$  with different wt % (10, 20, 30, 40 and 50), a composite of polyaniline –  $Dy_2O_3$  with 50 wt % of  $Dy_2O_3$  in polyaniline is selected to obtain the SEM micrograph.

From SEM micrograph it clearly indicates highly branched chain structure (or fibrillar morphology). The presence of  $Dy_2O_3$  has a strong influence on various electrical parameters such as conductivity. The contrast in the image is due to the difference in scattering from different surface areas as a result of geometrical differences between polyaniline and  $Dy_2O_3$ .

Figure 5. Shows the IR spectra of Polyaniline where the transmittance is plotted as a function of wave number ( $cm^{-1}$ ). Careful analysis of the spectra from the figure 5 reveals the presence of intensity peaks  $1578\text{ cm}^{-1}$ ,  $1486\text{ cm}^{-1}$ ,  $1300\text{ cm}^{-1}$ ,  $1239\text{ cm}^{-1}$ ,  $1140\text{ cm}^{-1}$  and  $880\text{ cm}^{-1}$ ,  $819\text{ cm}^{-1}$ ,  $707\text{ cm}^{-1}$ ,  $516\text{ cm}^{-1}$ . The spectra show the presence four intense bands at  $1578\text{ cm}^{-1}$ ,  $1480\text{ cm}^{-1}$ ,  $1300\text{ cm}^{-1}$  and  $1239\text{ cm}^{-1}$ . The intense peaks at  $1578\text{ cm}^{-1}$  and  $1486\text{ cm}^{-1}$  may be attributed due to the presence of quinoid rings. This is further supported by the FTIR spectra of vacuum-deposited polyaniline thin film. The characteristic signature of polyaniline structure is visible in the FTIR spectra of the thin film. The FTIR spectra of the thin film confirmed the presence of amino group .

The IR spectra of polyaniline –  $Dy_2O_3$  composite (50 wt % of  $Dy_2O_3$  in PANI) is shown in Fig 6. The characteristic stretching frequencies are observed at  $3450\text{ cm}^{-1}$ ,  $2919\text{ cm}^{-1}$ ,  $2845\text{ cm}^{-1}$ ,  $1739\text{ cm}^{-1}$ ,  $1647\text{ cm}^{-1}$ ,  $1573\text{ cm}^{-1}$ ,  $1486\text{ cm}^{-1}$ ,  $1387\text{ cm}^{-1}$ ,  $1295\text{ cm}^{-1}$ ,  $1245\text{ cm}^{-1}$ ,  $1165\text{ cm}^{-1}$ ,  $1140\text{ cm}^{-1}$ ,  $1116\text{ cm}^{-1}$ ,  $1011\text{ cm}^{-1}$ ,  $887\text{ cm}^{-1}$ ,  $819\text{ cm}^{-1}$ ,  $707\text{ cm}^{-1}$ ,  $618\text{ cm}^{-1}$ ,  $598\text{ cm}^{-1}$  and  $504\text{ cm}^{-1}$ . By comparing the IR spectra of polyaniline and

polyaniline –  $Dy_2O_3$  composite, it is observed that in the composite the characteristic stretching frequencies are shifted toward higher frequency side which may be attributed due to the Vander walls kind of interaction between  $Dy_2O_3$  and polyaniline chain .

Figure 7. Show the variation of ac conductivity as a function of frequency for polyaniline –  $Dy_2O_3$  composites (for different weight %). It is observed that in all the cases,  $\sigma_{ac}$  remains constant up to  $10^4$  Hz. In case of composites with 10, 20, and 30 wt % of  $Dy_2O_3$  in PANI, the conductivity slightly increases after  $10^5$  Hz and in case of composites with 40 and 50 wt % the conductivity increase after  $10^4$  Hz. The anomaly in the conductivity behavior of these composites is due to the variation in the distribution of  $Dy_2O_3$  in PANI i.e. weight % of  $Dy_2O_3$  in PANI.

Figure 8. Show the variation of  $\sigma_{ac}$  as a function of wt% of  $Dy_2O_3$  in polyaniline at three different frequencies at room temperature. It is observed that in all the composites the conductivity increases up to 40wt % of  $Dy_2O_3$  in polyaniline and then decreases rapidly for 50wt %. This may be due to the extended chain length of polyaniline, which facilitate the hopping of charge carriers when the content of  $Dy_2O_3$  is up to 40wt %. Further the decrease in conductivity for 50wt % is attributed due to the trapping of charge carrier hop.

### 4. Conclusion

Polyaniline composites with different weight percentages of  $Dy_2O_3$  in PANI were synthesized by chemical oxidative polymerization of monomer aniline. Detailed characterizations of the composites were carried out using XRD, SEM and IR techniques. The result of XRD and SEM reveals the semi crystalline nature of the PANI /  $Dy_2O_3$  composites. The signature of  $Dy_2O_3$  has been observed in the PANI /  $Dy_2O_3$  FTIR spectra. The results of ac conductivity show a strong dependence on the weight percent of  $Dy_2O_3$  in polyaniline. The values of conductivity of these composites are found be in the semi-conducting range.

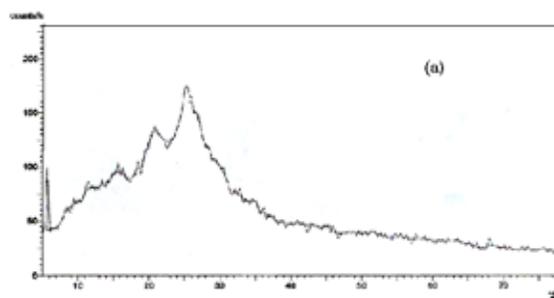


Figure 1. X – Ray diffraction pattern of Polyaniline

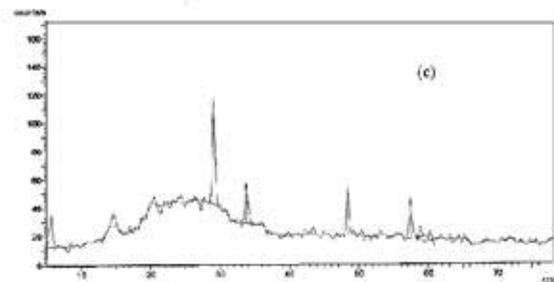


Figure.2 X – Ray diffraction pattern of PANI/  $Dy_2O_3$  (50 wt%)

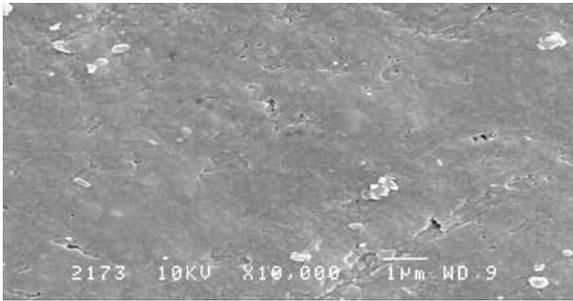


Figure 3 SEM Micrograph of Polyaniline

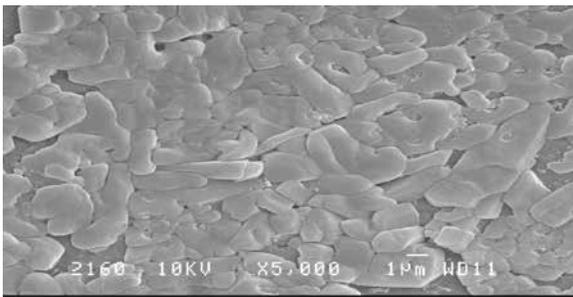


Figure 4 SEM Micrograph of Polyaniline - Dy<sub>2</sub>O<sub>3</sub> (50 wt %)

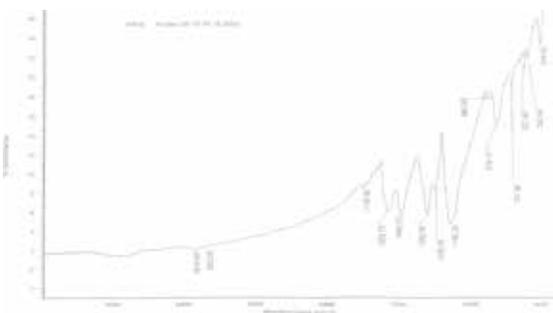


Figure 5 FTIR spectra of pure PANI

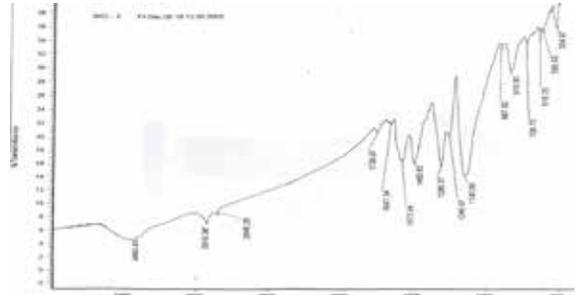


Figure 6 FTIR spectra of PANI /Dy<sub>2</sub>O<sub>3</sub> composite (50 wt %)

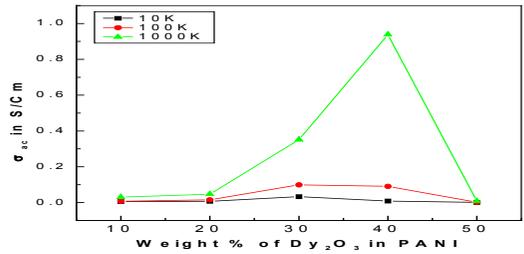


Figure 7 Variation of ac conductivity as a function of frequency for Polyaniline Dy<sub>2</sub>O<sub>3</sub> Composites

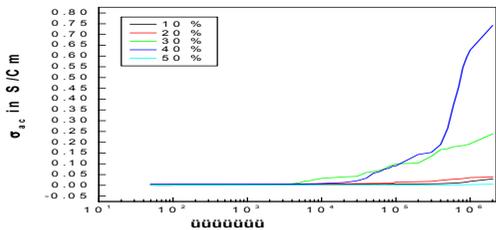


Figure 8 Variation of ac conductivity as a function of wt % for Polyaniline Dy<sub>2</sub>O<sub>3</sub> at different frequencies

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