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Synthesis, Characterization and DC Conductivity Studies of Polyaniline / Dysprosium Oxide Composites

KEYWORDS: Polyaniline (PANI); Dysprosium oxide (Dy_2O_3); composites; conductivity.

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ABSTRACT *In situ polymerization of aniline was carried out in the presence of Dysprosium oxide to synthesize polyaniline / Dysprosium oxide composites (PANI/Dy_2O_3) by chemical oxidation method. The composites have been synthesized with various compositions (10, 20, 30, 40 and 50 wt %) of Dy_2O_3 in PANI. The surface morphology of these composites was studied with scanning electron micrograph (SEM). The polyaniline/ Dy_2O_3 composites were also characterized by X-ray diffractometry (XRD) and infrared spectroscopy (FTIR). The dc conductivity has been studied in the temperature range from 40-2000C and supports the one-dimensional variable range hopping (1D-VRH) model proposed by Mott. The dimensions of Dy_2O_3 in the matrix have a greater influence on the observed conductivity values. The results obtained for these composites are of greater scientific and technological interest.*

Introduction

Polymers have traditionally been considered as a good electrical insulators and a variety of their applications have relied on their insulating property [1]. However more than a decade now, researchers have shown that certain class of polymers which are conjugated, exhibit semiconducting behavior [2]. 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 S/cm. The presence of an extended π conjugation in polymers, however, confers the required mobility to charges that are created on the polymer backbone (by the process of doping) and make them electrically conducting [3]. 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, envi ronmental stability and unique chemistry [4]. The electrical conductivities of the intrinsically and conducting polymer systems range from those insulators ($<10^{-5}$ and 10^{-10} S/cm) to those of typical semiconductors such as silicon ($\approx10^{-5}$ S/cm) and to those greater than 10^4 S/cm (nearly to that of a good metal such as copper $\approx5\times10^5$ S/cm) [5]. Applications of these polymers have begun to emerge a new era. These include coating and blends for electrostatic dissipation and electromagnetic interface (EMI) shielding [6, 7]. Electromagnetic radiation absorbs for welding (joining) of plastics, conductive layers for light emitting polymer devices and anti corrosion for iron and steel [8]. Many attempts in the preparation of polypyrrole composites with inorganic particles were also performed, such as with montomorrillonite and y-zeolite [9]. Polypyrrole inorganic particles were also investigated for their applications in electroheological (ER) fluid and high-density information storage [10].

2. Experimental

All chemicals used were analytical reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate ($(NH_4)_2S_2O_8$), hydrochloric acid (HCl), and Dysprosium oxide (Dy_2O_3) (sigma) were used as received. Aniline (0.1mol) was dissolved in 1M HCl to form aniline hydrochloride solution. Dysprosium oxide was added to the aniline hydrochloride solution with vigorous stirring to keep the Dysprosium oxide suspended in the solution. To this reaction mixture, 0.2M of ammonium persulphate [$(NH4)_2S_2O_8$], which acts as the oxidant was added slowly with continuous stirring at 0–5^{0}C. After complete addition of the oxidizing agent, the reaction mixture was kept under stirring for 24h [11]. The greenish black precipitate of the polymer was recovered by vacuum filtration and washed with acetone. The resultant precipitate was dried in an oven for 24 h to achieve a constant weight. PANI/ Dy_2O_3 composites were prepared in weight percent ratio, in which the concentration of Dysprosium oxide (10, 20, 30, 40, and 50 wt %) was varied. The test samples were prepared in pellet form (diameter: 10 mm; thickness: 3 mm) by applying pressure of 2-3 tones in hydraulic press. The contacts were made using silver paste on both sides.

3. Results and discussion

The FTIR spectra of the samples were recorded on a PerkinElmer 1600 spectrophotometer in KBr medium. X-ray diffraction studies were performed by using Philips X-ray diffractometer with Cu Kα as the radiation source. The morphology of the composites in the form of pellets was investigated using Philips XL 30 ESEM scanning electron microscope (SEM). Temperature dependent electrical conductivity was measured by four-probe technique using a laboratory-made setup.

Figure 1 (a) & (b) shows the X – Ray diffraction pattern of (a) Dy_2O_3 (b) Polyaniline - Dy_2O_3 composite (50 wt % Dy_2O_3 in PANI). It is seen from the figure that the triclinic peak of Dy_2O_3 indicates the crystalline nature of the composite. By comparing the XRD pattern of composite with that of Dy_2O_3 (JCPDS No. 22-0612) the prominent peaks corresponds to 2θ = 29.59 ^{0} i.e. first peak no change, 31.09 ^{0} shifted to 34.12^0, 48.55 ^{0} and 58.64 ^{0} 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 [12]. The semi sharp peak of PANI at 27^0 has widened this is due to doping Dy_2O_3 in PANI

Figure 2 shows the scanning electron micrograph 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.

A very high magnification reveals the presence of Dy_2O_3 in polyaniline which is homogeneously distributed through out the polymer sample. From SEM micrograph it clearly indicates highly branched chain structure (or fibrillar morphology) [13-15]. The presence of Dy_2O_3 has a strong influence on various electrical parameters such as conductivity and dielectric behavior of these composites. 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.

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The IR spectra of pure Dy_2O_3 is shown in Fig. 3 (a). The important peaks observed in Dy_2O_3 are at 482 cm^{-1} and 587 cm^{-1} which are due to the presence of metal oxygen stretching frequencies. The IR spectra of polyaniline – Dy_2O_3 composite (50 wt % of Dy_2O_3 in PANI) is shown in Fig 3(b). The characteristic stretching frequencies are observed at 3450 cm^{-1},2919 cm^{-1} ,2845 cm^{-1} ,1739 cm^{-1} ,1647 cm^{-1} ,1573 cm^{-1} ,1486 cm^{-1} ,1387 cm^{-1} ,1295 cm^{-1} ,1245 cm^{-1} cm^{-1}, 1165 cm^{-1} cm^{-1},1140 cm^{-1} ,1116 cm^{-1} ,1011 cm^{-1} ,887 cm^{-1} ,819 cm^{-1} ,707 cm^{-1} ,618 cm^{-1} ,598cm^{-1} and 504 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 [16-18].

Figure 4 shows the variation of dc conductivity as a function of wt % Dy_2O_3 in polyaniline at two fixed temperatures viz., at 100^0 and 200^0 C. It has been observed that the values of DC conductivity of these composites increases till 20 wt % of Dy_2O_3 in polyaniline and for 30 wt % of Dy_2O_3 in polyaniline the DC conductivity decrease latter the conductivity increases with 40 wt % of Dy_2O_3 in polyaniline.

The initial increment in the conductivity values up to 20 wt % of Dy_2O_3 in polyaniline may be due to extended chain length of polyaniline in which the charge carriers possess sufficient energy to hopp between various favorable localized sites. At the 30 wt % of Dy_2O_3, the blocking of charge carrier hop takes place as a result the charge carriers are unable to hopp between favorable localized sites and hence the conductivity decreases. Further experimentally it is found that, there is an increases in the conductivity 40 wt % and 50wt % and this may be due to extended chain length.

5. 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 semicrystalline 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 semiconducting range.

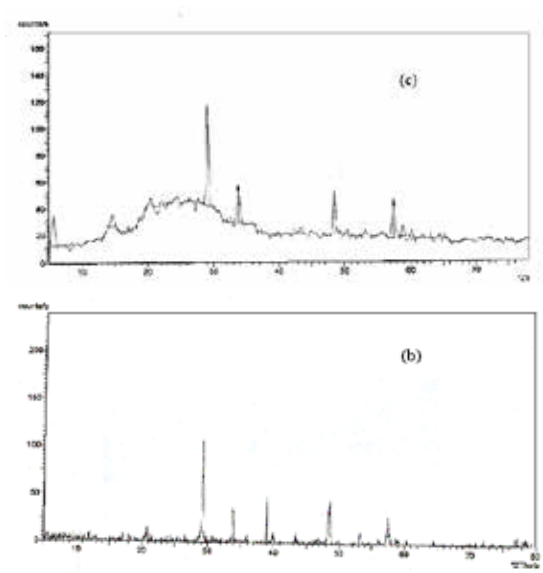

Figure 1 X – Ray diffraction pattern of (a) Dy_2O_3 (b) Polyaniline - Dy_2O_3 composite (50 wt %)

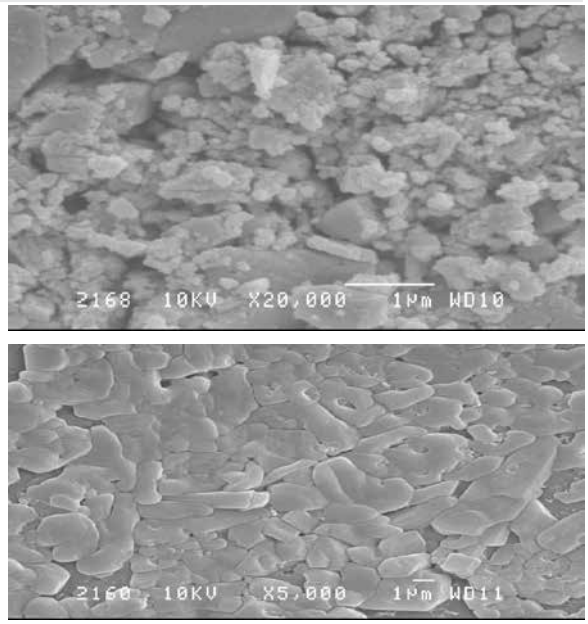

Figure: 2 SEM Micrograph of (a) Dy_2O_3 (b) Polyaniline - Dy_2O_3 (50 wt %)

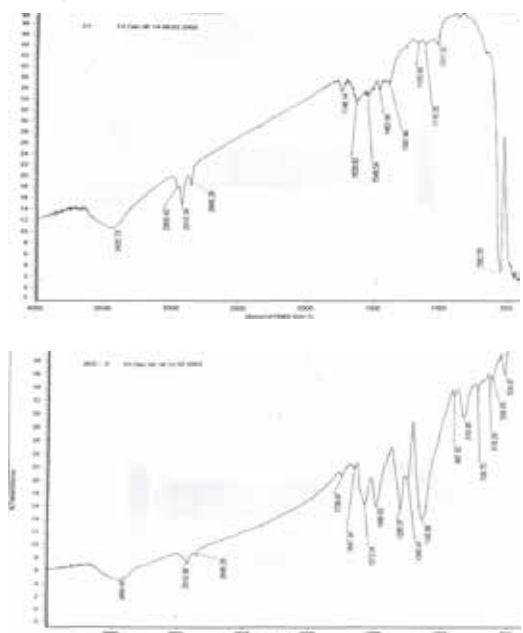

Figure: 3 FTIR spectra of (a) Dy_2O_3 (b) PANI /Dy_2O_3 composite (50 wt %)

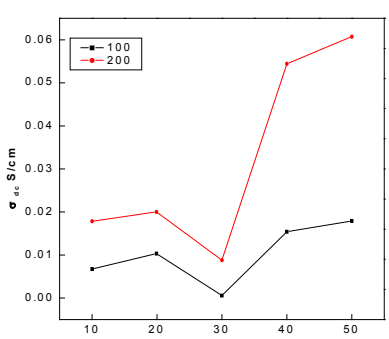

Figure 4. Variation of σ dc as a function of weight % of Dy_2O_3 in PANI at different temperature

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