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Synthesis and Characterization of Polyaniline / Al₂O₃ Nano Composites

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ABSTRACT: In the present work, the conducting polymer, namely Polyaniline was chosen. This research work performs mainly to a study of synthesis of polymer: polyaniline from conducting to poor conducting form (Emeraldine Base) and the preparation of composites with Al₂O₃ nano powder and the characterization techniques such as X-Ray Diffraction, Fourier Transform Infra-red Spectroscopy and Ultra Violet Visible spectroscopy. Further from the quantitative analysis of the conductivity data, the temperature dependence behaviour of electrical conductivity for all the samples is observed. In addition to that, the pH measurements also taken for all the samples. Finally it will be concluded that the insulation nature of Al₂O₃ influencing the chemical and electrical properties polyaniline emeraldine base. This work finds the optimum range of its electrical conduction with 1 D charge transport.

I. INTRODUCTION

Plastics and elastomers had always been considered as intrinsic insulators. The plastics would be made to conduct electricity. In general, polymers are insulating materials having conductivities ranging from 10⁻¹⁰ (ohm cm⁻¹) for polyvinyl chloride to 10⁻¹⁸ (ohm cm⁻¹) for poly (tetra fluoro ethylene).

A single polymer consists of a number of units linked together by covalent bonds to form a large molecule or macromolecule.

Chemical compounds are referred to as polymers if their molecules consist of numerous repeating structural elements. The individual unit that repeats to constitute a polymer is called the monomer

Characterization Techniques

1. X-Ray Diffraction
2. Fourier Transform Infra red Spectroscopy
3. Ultraviolet-Visible Spectroscopy

II. X-RAY DIFFRACTOMETRY

X-Ray Diffraction (XRD) is used to identify specific crystalline compounds, both mineral and inorganic, based on their crystal structure. In XRD, a powder made up of small crystals is irradiated with a monochromatic beam of X-rays with the assumption that the orientation of the crystallite is random. The beam is diffracted at angles determined by the spacing of the planes in the crystals and the type and arrangement of the atoms. A scanning detector or a CCD device records the diffracted beams as a pattern. The intensity and position of the diffractions are unique to each type of crystalline material.

FOURIER TRANSFORM INFRA-RED SPECTROSCOPY

In the present work, the IR spectra of doped samples were recorded using SHIMADZU 4800 spectrometer, MKU. Samples are finely ground along with about 100 times its weight of KBr. This mixture was then made into pellets by applying very high pressure. The resulting pellet which was transparent to IR, was run as such.

ULTRAVIOLET AND VISIBLE SPECTROSCOPY

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV/VIS) involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR)

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ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy.

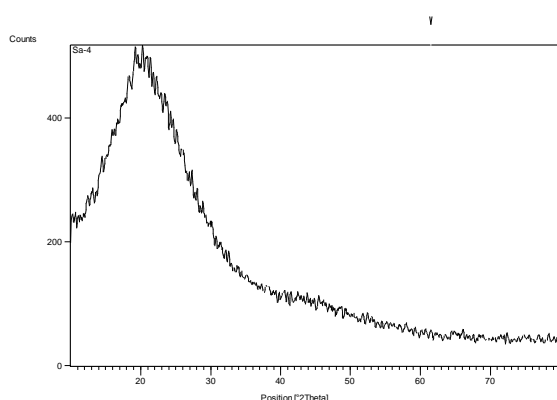
DC CONDUCTIVITY MEASUREMENTS

Measuring the temperature dependence of resistivity reveals some important differences between metals, insulators and semiconductors. There are a variety of factors that influence resistivity and thus its inverse, conductivity and identifying these materials such as the band gap energy or the temperature coefficient of resistance. There are two important factors that contribute to the conductivity of a material, i.e., the availability of free electrons and the ability of these electrons to move freely through a material. For a conducting metal with free valence electrons, the factor limiting conductivity is the lattice vibrations which scatter moving electrons: as temperature decreases, these vibrations and thus the resistivity also decreases. The temperature dependent DC resistivity measurements were carried out using two probe method.

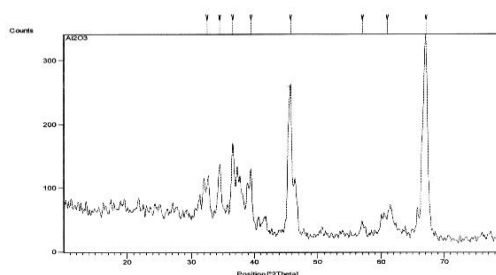
III. RESULTS AND DISCUSSION

X-RAY DIFFRACTOMETRY

XRD is used to characterize polyaniline, Al_2O_3 and polyaniline/ Al_2O_3 nanocomposite. Fig shows the XRD pattern of PANI-EB which clearly indicates that PANI emeraldine base is amorphous. The broad peaks at about 19.9° and 24.1° are characteristics peak of PANI. Fig shows the XRD pattern of Al_2O_3 nano particles. Here the broad peaks at about 45.82° and 67.17° are characteristics peak of Al_2O_3 . In the pattern, the 2θ values are $32.52, 34.53, 36.55, 39.48, 45.82, 57.05, 61.00$ and 67.17° . The XRD patterns of PANI/ Al_2O_3 composite is shown in the Fig. Here the broad peaks are obtained at and for the sample 1, (Al_2O_3 -5 mg, PANI-380 mg) and the 2θ values are . For the sample 2, (Al_2O_3 -10 mg, PANI-380 mg) the broad peaks are obtained at and and the 2θ values are . For the sample 3, (Al_2O_3 -15 mg, PANI-380 mg) the broad peaks are obtained at and and the 2θ values are . For the sample 4, (Al_2O_3 -20 mg, PANI-380 mg) the broad peaks are obtained at and and the 2θ values are . Fig shows the XRD patterns of Al_2O_3 protonated PANI-EB which significantly shows that the crystalline Al_2O_3 mixed with base and make it partly crystalline. These results indicate that the PANI/ Al_2O_3 composite dispersions contain two different phases of the Fe_2O_3 particles, and the PANI is amorphous in the composite.



XRD Spectrum of PANI

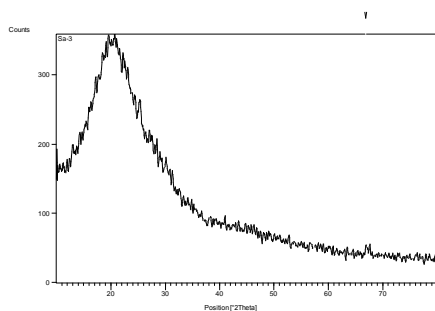


XRD spectrum of Al_2O_3

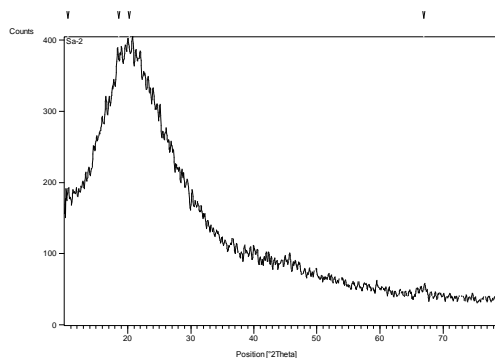
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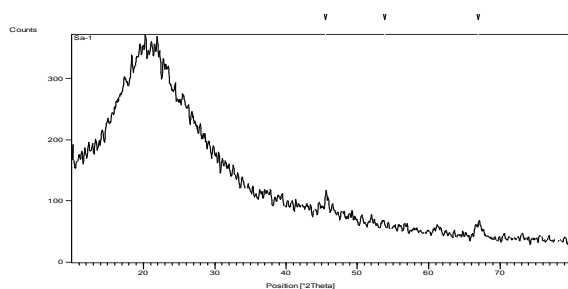
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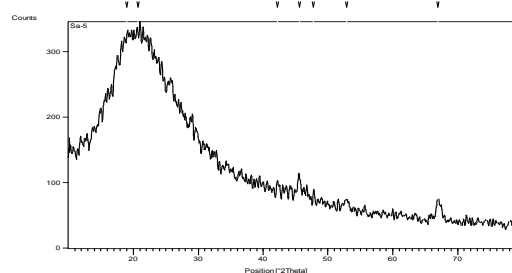
XRD Spectrum of sample-PANI/Al₂O₃ (1.3 wt %)



XRD Spectrum of sample- PANI/Al₂O₃ (2.6 wt %)



XRD Spectrum of sample- PANI/Al₂O₃ (3.8 wt %)



XRD Spectrum of sample- PANI/Al₂O₃ (5 wt %)

FOURIER TRANSFORM INFRA RED SPECTROSCOPY

Figure shows the FTIR assignment of the samples, Al₂O₃ doped PANI-EB for different molecular weights. For the sample 1, (Al₂O₃-5 mg,PANI-380 mg), the peak at 1589cm⁻¹ and 1499cm⁻¹ was due to C=C stretching of quinoid and benzenoid rings. The peak at 1300cm⁻¹ was due to C-N stretching. The peak at 826cm⁻¹ was due to C-H out of plane deformation.

For the sample 2, (Al₂O₃-10 mg,PANI-380 mg), the peak at 1589cm⁻¹ and 1498cm⁻¹ was due to C=C stretching of quinoid and benzenoid rings. The peak at 1300cm⁻¹ was due to C-N stretching. The peak at 827cm⁻¹ was due to C-H out of plane deformation.

For the sample 3, (Al₂O₃-15 mg,PANI-380 mg), the peak at 1589cm⁻¹ and 1498cm⁻¹ was due to C=C stretching of quinoid and benzenoid rings. The peak at 1300cm⁻¹ was due to C-N stretching. The peak at 827cm⁻¹ was due to C-H out of plane deformation.

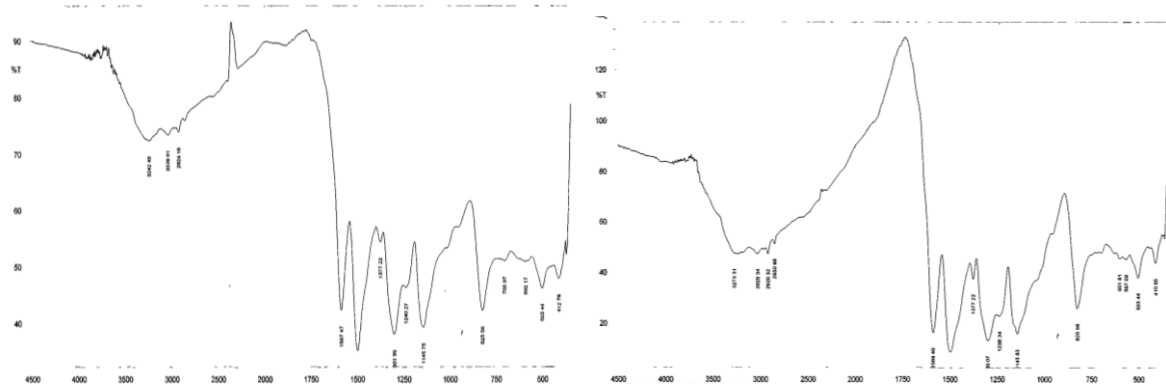
For the sample 4, (Al₂O₃-20 mg,PANI-380 mg), the peak at 1589cm⁻¹ and 1500cm⁻¹ was due to C=C stretching of quinoid and benzenoid rings. The peak at 1300cm⁻¹ was due to C-N stretching. The peak at 825cm⁻¹ was due to C-H out of plane deformation.

From this we can conclude that when the Al₂O₃ particles present in the composite, the intensity at the peak at 1587 cm⁻¹ is decreased and shift to 1589 cm⁻¹, which represents the decrease of doping UV-VIS absorption band of composite, to have a red shift. These observations indicate that Al₂O₃ was doped with PANI-EB.

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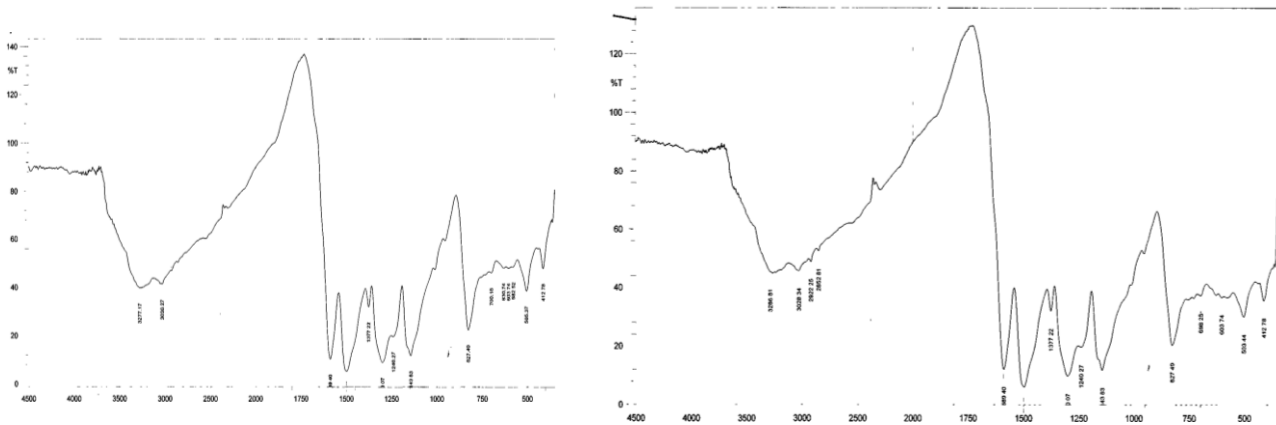
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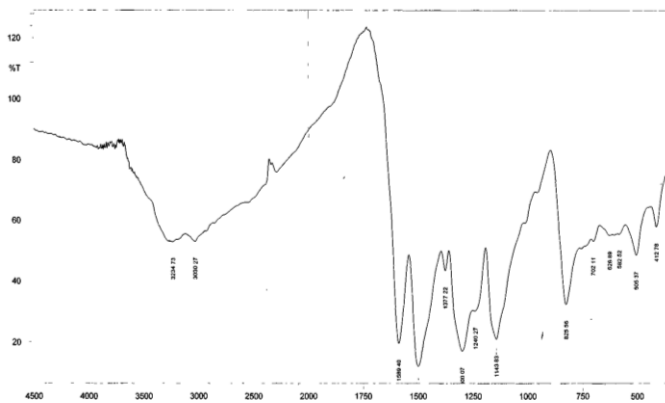


FTIR spectrum of PANI

FTIR Spectrum of sample- PANI/Al₂O₃(1.3 wt %)



FTIR Spectrum of sample-PANI/Al₂O₃ (2.6 wt %) FTIR Spectrum of sample-PANI/Al₂O₃(3.8 wt %)



FTIR Spectrum of sample-PANI/Al₂O₃ (5 wt %)

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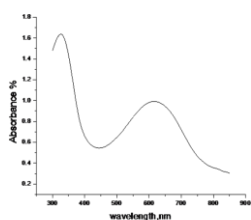
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UV-VIS SPECTROSCOPY

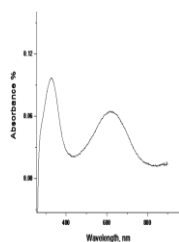
The UV-VIS absorption spectra of PANI is shown in the figure. A typical absorption spectrum of PANI dispersions has three distinct absorption peaks at 351, 436, 757 nm respectively. The peak at 351 nm arises from $\Pi-\Pi^*$ electron transition from benzenoid segments. The peak at 436 nm is due to the polaron state and the wide peak at 757 nm is related to the doping level. The UV-VIS absorption spectra of PANI/ Al_2O_3 for different molecular weights is shown in the figure. Compared to the PANI dispersions, UV-VIS absorption peak of PANI/ Al_2O_3 composite dispersions show little difference, for example, the peak at 351 nm shifts to 326 nm. The shift may be originated from the decreasing doping level by the addition of Al_2O_3 .

UV absorption values of PANI/ Al_2O_3 composites.

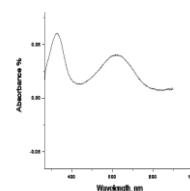
Al_2O_3 (wt %)	WAVELENGTH
0	326, 616
1.3	325, 616
2.6	325, 628
3.8	325, 619
5	325, 616



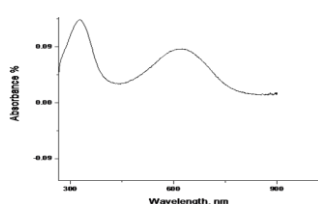
UV spectrum of PANI



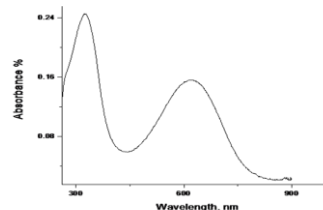
UV Spectrum of sample-PANI/ Al_2O_3 (1.3 wt%)



UV Spectrum of sample-PANI/ Al_2O_3 (2.6 wt %)



UV Spectrum of sample-PANI/ Al_2O_3 (3.8 wt %)



UV Spectrum of sample PANI/ Al_2O_3 (5 wt %)

pH MEASUREMENTS

From this table, it is inferred that , as the concentration of Al_2O_3 increases, the pH value also increases respectively.

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Tabular column for the pH value of PANI-Al₂O₃ composites

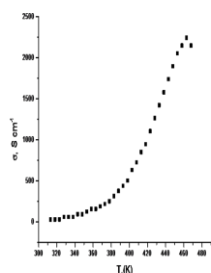
Al ₂ O ₃ (wt %)	pH value
0	7.61
1.3	9.36
2.6	9.38
3.8	9.64
5	9.64

DC CONDUCTIVITY MEASUREMENTS

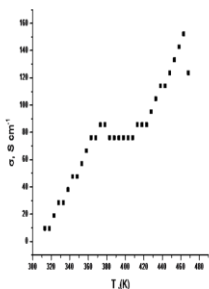
Figure show the temperature dependent DC conductivity curve for PANI / Al₂O₃ composites. All the samples, show the decreasing in conductivity as the temperature increases. This clearly indicates the figures, were used to calculate the activation energy in each case. The calculated activation energy values for PANI and its composites are tabulated in the table. A plot of conductivity versus concentration of Al₂O₃ is shown in the figure. This figure shows that the conductivity decreases, as the content of Al₂O₃ increases. A plot of activation energy versus concentration of Al₂O₃ is shown in the figure. This figure shows that as the content of Al₂O₃ increases, the activity energy increases.

Tabular column for the activation energy of PANI/Al₂O₃ composites

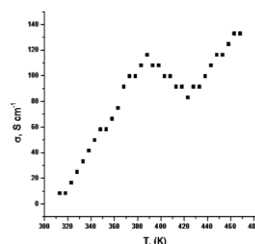
Al ₂ O ₃ (wt %)	Activation energy (eV)
0	0.3444
1.3	0.3042
2.6	0.3214
3.8	0.2440
5	0.3449



Temperature dependent DC Conductivity curve for PANI



Temperature dependent DC Conductivity curve for PANI/Al₂O₃(1.3 wt %)

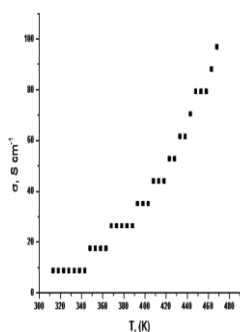


Temperature dependent DC Conductivity curve for PANI/Al₂O₃(2.6 wt %)

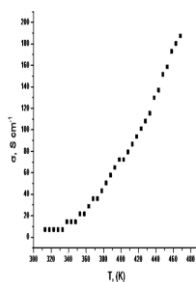
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Temperature dependent DC Conductivity curve for PANI/Al₂O₃(3.8 wt %)



Temperature dependent DC Conductivity curve for PANI/Al₂O₃(5 wt %)

IV. CONCLUSION

Emeraldine form of polyaniline (PANI) was synthesized by using chemical method. The dopant Al₂O₃ has been mixed with PANI in terms of wt % (0, 1.3, 2.6, 3.8 and 5). The samples were characterized by XRD, FT-IR and UV-VIS.

XRD pattern of Polyaniline/Al₂O₃ nano composites show the semicrystalline nature whereas the PANI synthesized was amorphous in nature.

FTIR spectrum show that the mixture of Al₂O₃ with PANI affect the benzenoid group and cause to appear other new broad peaks in the region 750-500 cm⁻¹. Also the Transmittance (%) also decreases due to the presence of Al₂O₃. The DC conductivity measurements were carried out for all the samples with the temperature range(313-468 K). The temperature dependent conductivity was observed. The activation energy was calculated.

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