

# Conductivity Study of Polyaniline-Nickel Oxide (NiO) Composites

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## ABSTRACT

*The Polyaniline-Nickel Oxide (NiO) composites were synthesized by in situ polymerization method. The FTIR studies on Polyaniline / NiO composites indicates the peak at 1122 cm<sup>-1</sup> is considered to be measure of the degree of electron delocalization, 1488 cm<sup>-1</sup> is C=C stretching of benzenoid ring, 1569 cm<sup>-1</sup> for C=N quinonoid stretching mode of vibration. XRD patterns of the PANI-NiO composite show sharp peaks characteristic of crystalline materials and suggest generally a semi-crystalline nature to all the PANI-NiO composite samples. The conductivity increases with increase in temperature. The DC conductivity has been studied in the temperature range from 40<sup>o</sup> to 200<sup>o</sup> C and it is observed that the conductivity increases with increase in temperature due to hopping of polarons. This is supported by one-dimensional variable range hopping (1DVRH) model proposed by Mott. The results obtained for these composites are of scientific and technological interest.*

**Keywords:** Polyaniline; Nickel Oxide; Composites; SEM; Conductivity

## INTRODUCTION:

The transition metal oxides have been investigated by several workers in the last few years. The study of these nano-particles has become of increasing interest due to the presence of unusual physical and chemical properties different from those observed in transition rare earth bulk oxide materials [1]. Besides their structural aspects, magnetic properties of the oxide particles are of particular interest. Nickel oxide (NiO) particles exhibit weak ferromagnetism or super paramagnetism for the fine particles. NiO particles are p-type semiconducting with band gap 3.51 eV. It is considered as promising electrode material for electrochemical capacitor and gas sensor for NO<sub>2</sub>, NH<sub>3</sub> and NiO has received a considerable amount of attention for its catalytic properties such as decomposition of ammonium per-chlorate, hydro-cracking reactions, reforming of hydrocarbons and methane for production of syngas. The removal of tar by the adjustment of gas composition in biomass pyrolysis/gasification in cellulose pyrolysis and so forth [2-4]. Several methods are reported for the preparation of NiO particles viz; biosurfactant-mediated microemulsion technique [5], sol-gel method [6], template-free synthesis.

Polyaniline (PANI) is one of the most promising electrically conducting polymer of particular interest because of its various structures, special doping mechanism, environmental stability, high conductivity and its wide applications in microelectronic devices [7], diodes [8], light weight batteries [9], super capacitors [10], sensors [11], corrosion inhibition [12], for electro-rheological [13] and magneto-rheological fluids [14]. Polymer composites constitute a class of hybrid materials composed of a polymer matrix and an inorganic component. The composites exhibit combination of properties like conductivity [15], electronic, electrochemical, catalytic and optical properties. To obtain materials with synergetic advantage between PANI and inorganic nanoparticles such as CeO<sub>2</sub>, TiO<sub>2</sub>, BaTiO<sub>3</sub>, MoO<sub>3</sub>, SnO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and NiO are reported [16-19]. Therefore, here we have an attempt to study of electric properties of the polyaniline – NiO composites prepared by in situ polymerization.

## EXPERIMENTS:

### Materials and Method:

All Chemicals used were analytical reagent (AR) grade. The monomer aniline (procured from Marck) was doubly distilled prior to use. Ammonium persulphate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), Hydrochloric acid (HCl) and Nickel Oxide (NiO) were procured from Sigma Aldrich and were used as received.

### Synthesis of Polyaniline:

5 ml of aniline is dissolved in 200 ml of 1 M HCL and stirred well, 11.4 gm of Ammonium persulphate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) is dissolved in 300 ml of 1M HCL and stirred well, both mixtures are cooled to 0-5<sup>o</sup>C in a freezing mixture. Ammonium persulphate + HCL solution to prevent the warming, with the continuous stirring using

a magnetic stirrer for about 2-4 hours. The polymerization was carried out by a maintain the temperature of about 0 -5°C in a freezing mixture to ensure the completion of polymerization reaction. Finally green color power of polyaniline is obtained.

#### Synthesis of Polyaniline - NiO Composites:

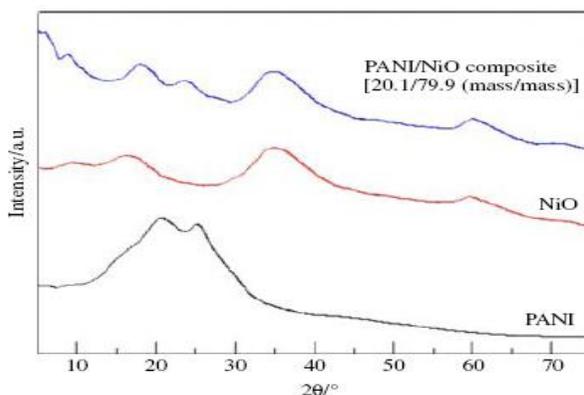
5 ml of aniline is dissolved in 200 ml of 1 M HCl, to this mixture nickel oxide (NiO) is added in the weight percent of 5, 10, 15, 20 and 25 and continuously stirred such that Zinc tungstate particles suspended in the solution. 11.4 gm of ammonium persulphate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  is dissolved in 300 ml of 1 M HCL, and is added very slowly drop wise to the aniline + HCL + NiO solution, with continuous stirring using a magnetic stirrer for about 2 – 4 hours. The polymerization was carried out by a maintaining reaction mixture at a temperature of about 0 – 5°C in a freezing mixture to prevent the warming. The precipitated powder recovered was vacuum filtered and washed with deionized water. Finally the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. In this way 5 different polyaniline-NiO composites with different wt% of NiO (05, 10, 15, 20 and 25) in polyaniline have been synthesized [20].

#### Characterization:

The IR spectra of all the samples are recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording IR spectra, powders are mixed with KBr in the ratio 1:25 by weight to ensure uniform dispersion in KBr pellets. The mixed powders are pressed in a cylindrical die to obtain clean discs of approximately 1 mm thickness. The X-ray diffraction patterns of the samples in this present study are obtained on Philips X-ray diffractometer using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The diffractograms were recorded in terms of  $2\theta$  in the range  $20^\circ - 120^\circ$  with a scanning rate of  $2^\circ$  per minute.

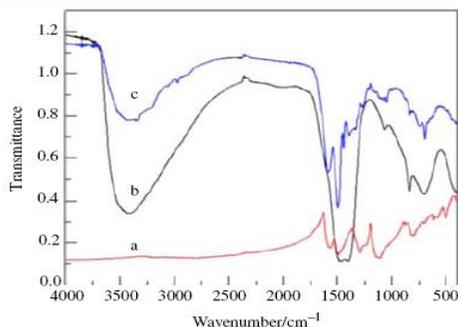
#### RESULTS AND DISCUSSION:

Figure-1 shows the XRD patterns of PANI, NiO nano-particles and PANI/NiO composite [20.1/79.9 (mass/mass)]. It can be seen that in the range of  $2\theta$  from 5 to  $75^\circ$ , the PANI exhibited two characteristic peaks at about  $20^\circ$  and  $26^\circ$ , which indicated that pure PANI had crystallinity to a certain extent. NiO nano-particles with hexagonal structure showed four broad peaks at about  $16^\circ$ ,  $35^\circ$ ,  $60^\circ$  and  $71^\circ$  for its nano-structure. The PANI/NiO composite [20.1/79.9 (mass/mass)] integrated peaks of PANI and NiO nano-particles. While, the characteristic peaks of PANI shifted to higher angles in the XRD pattern of PANI/NiO composite [20.1/79.9 (mass/mass)] for the interaction of PANI chains and NiO nano-particles.



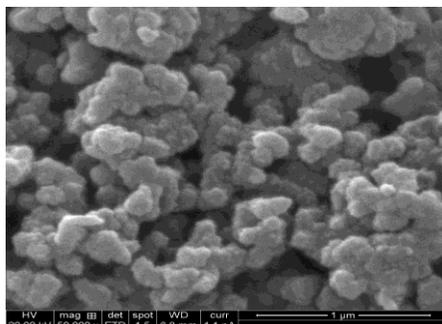
**Figure-1:** X-ray diffraction pattern of PANI, NiO and Polyaniline – NiO composite

Figure-2 shows the IR spectra of PANI/ NiO composite (25 % wt of NiO in PANI). The IR transmission spectra of powder using KBr pellets having different weight percentage of NiO in PANI were recorded in the range  $450 - 4000 \text{ cm}^{-1}$  to confirm polymerization of polyaniline. The spectra for all the samples showed strong bands in the region  $500 - 1600 \text{ cm}^{-1}$  that are the characteristics of PANI. Similar stretching frequencies can also be found in other composites but intensity of metal oxygen peak increases as the weight present of NiO is increased. The important peaks that are observed in this composite in IR spectra are observed at  $1648 \text{ cm}^{-1}$ ,  $1564 \text{ cm}^{-1}$ ,  $1488 \text{ cm}^{-1}$ ,  $1394 \text{ cm}^{-1}$ ,  $1303 \text{ cm}^{-1}$ ,  $1252 \text{ cm}^{-1}$ ,  $1118 \text{ cm}^{-1}$ ,  $882 \text{ cm}^{-1}$ ,  $804 \text{ cm}^{-1}$ ,  $595 \text{ cm}^{-1}$  and  $512 \text{ cm}^{-1}$ . It is found from the FTIR spectra that some of the characteristic stretching frequencies are considerably shifted towards higher frequency side. The typical peaks observed are at  $1564 \text{ cm}^{-1}$ ,  $1488 \text{ cm}^{-1}$ ,  $1303 \text{ cm}^{-1}$ ,  $801 \text{ cm}^{-1}$  and  $512 \text{ cm}^{-1}$ , which may be attributed due to the weak interaction between NiO and PANI chain.

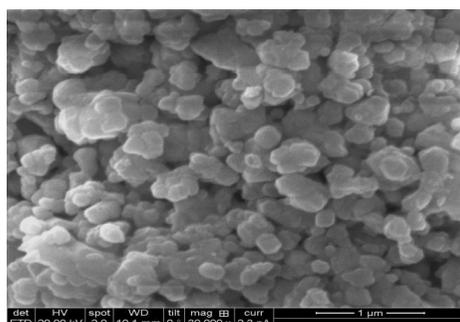


**Figure-2:** FTIR spectra of (a) Polyaniline, (b) NiO, (c) Polyaniline – NiO composite (25 wt%)

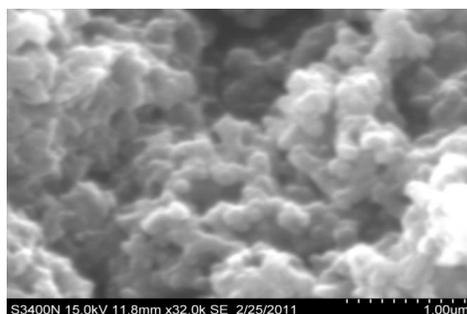
SEM micrograph of conducting polyaniline synthesized by chemical oxidative method is shown in Figure-3(a). It can be clearly seen that the micrograph of polyaniline is branched and homogeneous. Since Hydrochloric acid is used as proteomic acid in the preparation of polyaniline, the presence of microcrystalline structure can be seen. The presence of microcrystalline structures in polyaniline in this particular sample 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 mall crackening in the sample during SEM recording. A granular morphology of the microcrystalline structures of polyaniline which is consistent with other reports. 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-3(a):** SEM Micrograph of Polyaniline



**Figure-3(b):** SEM Micrograph of NiO

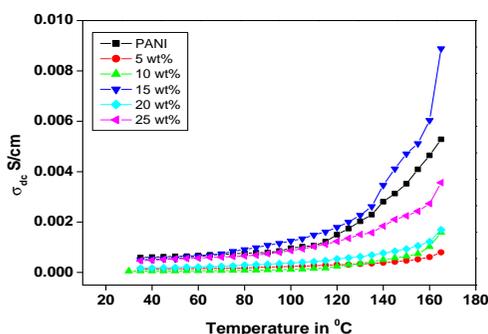


**Figure-3(c):** SEM Micrograph of Polyaniline – NiO composite

The SEM image of pure NiO is shown in Figure-3(b) and it is observed to have the rectangular like shape. The average length is found to be of 392.1 nm. These structures play an important role in enhancing the electrical property of the composites.

The SEM micrograph of polyaniline / NiO composite with 25 wt% in polyaniline is shown in Figure-3(c). High magnification SEM image reveals the presence of NiO particles uniformly distributed throughout the composite sample. A small variation in the particle dimensions of NiO so dispersed in polyaniline has been observed. Also fibrillar morphology is observed in the composite. 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 NiO.

Figure-4 shows the variation of dc conductivity as a function of temperature for NiO in polyaniline. It is observed that the value of dc conductivity of these composites increases exponentially with temperature. It remains nearly constant up to 100°C and there after it increases exponentially. The conductivity behavior is the characteristic of amorphous materials. The initial increase in the values of conductivity is due to the extended chain length of polyaniline due to which the charge carriers can hop between the favorable localized sites. The decrease in the values of conductivity at 25 wt % of NiO is due to partial blocking of charge carriers. Further, gradual increase in conductivity is noticed due to the variation in distribution of NiO particles in PANI.



**Figure-4:** shows the DC conductivity of polyaniline – NiO composites

## CONCLUSION:

Polyaniline-NiO composites were synthesized by in situ polymerization method using hydrochloric acid as proton donor agent. The FTIR studies on polyaniline/NiO composites indicates the peak at  $1124\text{ cm}^{-1}$  is considered to be measure of the degree of electron delocalization. This confirms the formation of polyaniline – NiO composite. XRD patterns of the PANI – NiO composite show sharp peaks characteristic of crystalline materials and suggest generally a semi-crystalline nature to the entire PANI – NiO composite samples. The surface morphology of these composites was studied with SEM and observed that particles are completely agglomerated with matrix. The DC conductivity has been studied in the temperature range from 20–200°C and it is observed that the conductivity increases with increase in temperature due to hopping of polarons. This is supported by one-dimensional variable range hopping (1DVRH) model proposed by Mott. The results obtained for these composites are of scientific and technological interest.

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