Study on electrical behaviour of polyaniline doped with various weight percentage of ZnO

K B Raulkar

Department of Physics, Vidya Bharati Mahavidyalaya, Camp, Amravati (M.S.)-444 602, India

Corresponding author e-mail : kbraulkar2016@gmail.com

Abstract: The composites of polyaniline doped with various weight percentage such as 10%, 20%, 30%, 40%, 50%, 60% and 70% of ZnO had been prepared by in-situ polymerization method. The synthesized composites were characterized by x-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Infrared Spectroscopy (FTIR). The DC conductivity of the samples was measured as a function of temperature in the range 300°C to 2100°C. The DC and AC conductivities showed strong dependent of ZnO wt % doping in PANI and were found best for 40 wt % of ZnO. DC conductivity was found to be 7.25 x 10-5 S/cm at 2100°C temperature and that of AC conductivity was 3.68 x 10-2 S/cm at room temperature (270°C).

1. Introduction:

Among the CPs, polyaniline (PANI) is one of the most studied intrinsically CPs because of its interesting electrical conductivity, novel electronic structure and mechanism of electrical conductivity as well as the possibility for application as a new electronic material [1-6]. CPs have recently emerged as a new class of potentially useful materials. A great deal of work is being done by many groups all over the world to understand and engineer their exceptional electrical, optical and chemical properties. Recently nano-composite materials are the most extensively studied materials all over the world as they have found to possess several technological applications such as effective quantum electronic devices, sensors in magnetic recording materials, etc. As polyaniline (PANI) is widely used for various applications such as in solar cells, sensors, electromagnetic shields and rechargeable battery electrodes, it is one of the most interesting CPs. Additionally, it is also known for its easy preparation methods and environmental stability [7-8].

As PANI has unique properties, it has attracted very special attention among all the CPs in the recent years. Suitable doping significantly modifies the electrical conductivity of the PANI. For example, when molanic acid is doped in PANI, its conductivity can be enhanced by significant order of magnitude. Similarly, nanocomposites made of PANI and montmorillonite show a variation in room-temperature conductivity as much as eight to nine orders of magnitude depending on the PANI content [9]. Semiconductor material has been received great attentions. Because of
ZnO properties such as mechanical, electrical, optical, magnetic and chemical sensing properties, ZnO is a versatile material among the various semiconductors oxide nanomaterials. It has a wide band gap of 3.3 eV and it is used in various applications of electronic devices, biomedical field, variety of sensors, etc [10]. In this work, PANI/ZnO composites were synthesized by in-situ polymerization method. These composites were characterized by using Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD) analysis, Scanning Electron Microscopy (SEM) and also studied the electrical properties of synthesized composites.

2. Preparation of Polyaniline-ZnO composites:

PANI–ZnO nano-composites containing various weight percentages of ZnO (10 %, 20 %, 30 %, 40 %, 50 %, 60% and 70%) in PANI were synthesized by in-situ polymerization method. 0.1M Aniline was mixed in 1M HCl and stirred for 20 min to form aniline hydrochloride. ZnO particles were added in the mass fraction to the prepared solution with vigorous stirring in order to keep the ZnO homogeneously suspended in the solution. To this solution, 0.1 M of ammonium persulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at 5°C for 5 h to completely polymerize. Finally the precipitate was filtered, washed with acetone and de-ionized water and air heated for 24 h to get constant mass. Finally PANI–ZnO nano-composites were obtained.

3. Result and Discussion:

3.1. x-ray Diffraction:

XRD studies were performed using Philips x-ray diffractometer with CuKα as the radiation source.

![XRD spectra of PANI, ZnO, and PANI-ZnO composite](image)
As shown in figure (1), diffraction pattern of poly aniline is represented by figure (a). A broad peak is obtained at 25.62° which may be assigned to the scattering from the polyaniline chains at interplanar spacing and it clearly exhibits the amorphous nature of polyaniline. It shows (200) pure Poly aniline diffraction planes. XRDs patterns for ZnO and PANI-ZnO composite are shown by figures (b) and (c) respectively. The ZnO powder XRD diffraction peaks are found in a good agreement with hexagonal structure reported (ICPDS File Card No.05-0664). For PANI-ZnO composite, the intensity of diffraction peaks are lower than that for zinc oxide. Due to the presence of amorphous PANI, percentage ratio of ZnO reduces and it weakens diffraction peaks of ZnO.

3.2. Fourier Infrared Spectroscopy:

![Figure (2) FTIR spectra of a) PANI, b) Zinc oxide and c) PANI-ZnO composites.](image)

The molecular bonding of PANI, ZnO and PANI-ZnO composites (ZnO 70 wt % in PANI) was carried under ambient conditions out by FTIR spectra measurement. In the FTIR of PANI, due to C=C stretching of quinoid rings, characteristic peaks appear at 1892 cm\(^{-1}\), due to stretching of the benzenoid ring, the peak appears at 1468 cm\(^{-1}\) and it gives the confirmation of formation of polyaniline [9]. In the ZnO FTIR spectra, the peaks occur at 2412 cm\(^{-1}\) and 1588 cm\(^{-1}\) which confirm the formation of ZnO.

PANI-ZnO composite spectra broad peak at 3432 cm\(^{-1}\) which is due to the O-H stretch because of water molecule absorption, the peaks 1532 cm\(^{-1}\) corresponds to C-N stretching of quinoid rings, 1439 cm\(^{-1}\) is due to C-N-stretching of benzenoid rings. The peaks at 1095 cm\(^{-1}\) is due to vibration band of the dopant anion.
3.3. Scanning electron microscope analysis:

Figure (3) SEM image PANI

Figure (4) SEM image of ZnO
The SEM performed under ambient conditions on PANI, ZnO and PANI-ZnO composite samples indicate that the transformation of highly branched-like polyaniline which have granular-like structure were ZnO particle is highly agglomerated ZnO in PANI (10, 20, 30, 40, 50, 60 and 70 wt % of ZnO in PANI), increases the granular size and decreases the porosity (figure 5). The presence of ZnO in PANI is revealed by SEM image and showed throughout the polymer sample; it is homogeneously distributed [9-10]. The average porous size of PANI is 0.12 μm (figure 3), that of ZnO is 0.23 μm (figure 4) and it is 0.094 μm for PANI-ZnO composite (figure 5).

3.4. DC conductivity:

![Figure (6) Variation of DC conductivity of PANI-ZnO composites with temperature](image)
There is a direct relation of conductivity with temperature by the relation
\[ \sigma(T) = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{1/4} \]  
Where: \( \sigma \) is the conductivity, \( T \) is the temperature and \( \sigma_0 \) is the conductivity at characteristic temperature \( T_0 \). It is exhibited that the charge transport properties of conjugated polymers strongly dependent of the processing parameter. A very high chemical flexibility is imparted by the polymer chain flanked on either side by a phenylene ring as PANI has reactive N-H group. Protonation and deprotonation is occurred in addition to the adsorption through nitrogen, having lone pair of electrons which shows interesting technologies in chemistry and physics.

From figure (6), it is manifested that with increase in wt % of ZnO with PANI, conductivity increases, becomes maximum for 40 wt% of ZnO and then further decreases. The DC conductivity of 40 wt % ZnO doped with PANI showed best conductivity which is \(7.25 \times 10^{-5} \) S/cm at 210°C temperature among the prepared composites. Due to increase of efficiency of charge transfer between the polymer chains and the dopant with increase in temperature, the conductivity could be increased. The conjugation length might have been increased which caused the increase in conductivity as thermal curing affects the chain alignment of polymer.

3.5. AC conductivity:

![Figure (7) Variation of AC conductivity of PANI-ZnO composites with frequency at room temperature](image)

Figure (7) shows the variation of AC conductivity of PANI-ZnO composites as a function of the frequency at room temperature. As shown in figure (7), it is exhibited that:
- with increase in frequency, AC conductivity increases and becomes maximum at around 85 MHz.
- with increase in dopant wt % of ZnO with PANI, AC conductivity increases and becomes maximum for 40 wt % and with further addition of wt % of ZnO, conductivity decreases.
- Increase of conductivity obeys the universal power law but, at high frequency region, there is an sudden increase in the conductivity with increase in frequency which is the characteristic property of disordered materials.
- Maximum value of AC conductivity for 40% wt ZnO is found to be \(3.68 \times 10^{-2} \) S/cm at room temperature (27°C).
4. Conclusion:

PANI-ZnO composites were prepared by in-situ polymerization method and prepared materials were characterized by XRD, FTIR and SEM. The DC and AC conductivities showed strong dependent of ZnO wt % doping in PANI and were found best for 40 wt % of ZnO. DC conductivity was found to be $7.25 \times 10^{-5}$ S/cm at 210°C temperature and that of AC conductivity was $3.68 \times 10^{-2}$ S/cm at room temperature (27°C). Hence these materials are promising for electrical applications as in the enhancement of potentials.

Acknowledgments:
The author is grateful to Vidya Bharati Mahavidyalaya, Amravati for providing facilities to do the characterization and research work.

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