AC CONDUCTIVITY AND DIELECTRIC PROPERTY OF ZNO DOPED POLYANILINE COMPOSITE

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ABSTRACT

The composites of polyaniline (PANI) with Zinc oxide (ZnO) at different weight percentage were synthesized by insitu chemical oxidation polymerization method using Ammonium peroxydisulfate (APS) as an oxidizing agent. The prepared samples were characterized using X-ray diffractometer to investigate amorphous or crystalline nature. The XRD spectrum shows that polyaniline is amorphous in nature but where as its composite is crystalline in nature. The SEM images confirmed that the size of particles in PANI and its composite is found to be in the range of 62-471 nm. The dielectric constant, dielectric loss and AC conductivity are studied as a function of frequency at room temperature. The dielectric constant and dielectric loss decreased as frequency increased and after 10 KHz they almost remain constant. The AC conductivity increased after 1MHz as frequency increased.

Key words: *Dielectric Constant, Dielectric Loss, A C Conductivity, Polyaniline Composite, Zinc Oxide.*

1. Introduction

The conducting polymers have made significant impact in the field of material science due to their potential applications in many electronic devices [1]. Polyaniline is one of the important conducting polymers among all other conducting polymers because of its stability in air, easy polymerization, low cost, good conductivity and solubility in some organic solvents. It is the type of conducting polymer whose properties can be changed by protonation state, oxidation state and also by the nature of dopant [3-6]. In general the change in properties makes polyaniline a versatile material. Particularly change in electrical properties of polyaniline with applications such as active electrode in batteries, in microelectronics, sensors, humidity sensing, gas sensing, chemical sensing [7-11], gas detection [12], adsorption [13], anticorrosive coating on iron [14], energy storage elements [15-17], organic light emitting diodes [18-21] etc. In the present work the composites of polyaniline with ZnO were synthesized at different weight percentage by chemical oxidation polymerization method using ammonium persulphate as an oxidizing agent [2]. Zinc oxide (ZnO) is n-type semiconductor and has wide band gap of energy (3.4 eV), large excitation binding energy, effective ultraviolet absorbance and good chemical stability. It shows great potential application in solar cell, gas sensor, varistor, cosmetic material etc. With this background of multifunctionality ZnO is used in preparation of composites [22-23]. The formation of PANI/ZnO composites were characterized using XRD and SEM. The properties such as dielectric permittivity, dielectric loss and AC conductivity of PANI/ZnO composites have been studied as function of frequency in the range of 50 Hz to 50 MHz at room temperature.

2. Experimental Measurements

Synthesis of Samples: The chemicals of aniline monomer, Ammonium per sulfate (APS) $(NH_4)_2S_2O_8$, hydrochloric acid (HCl), and Zink oxide (ZnO) were procured from Sd fine Chemicals Mumbai. The chemicals used were of analytical reagent (AR) grade. Aniline of 0.0548 mol was dissolved in 1M HCl to form aniline hydrochloride. ZnO was added in different wt% to the above solution with vigorous stirring to keep ZnO particles suspended in the solution. The oxidant solution which was prepared by dissolving 0.022mol APS in 50 ml of distilled water, added drop wise to this reaction mixture with continuous stirring for about 2 hrs and the resulting mixture is kept overnight to polymerize completely. After one day the resulting precipitate is filtered and washed repeatedly with deionized water and finally the resultant precipitate was dried in an oven for 8 hrs at temperature of 60 ^{0}C. The dried powder of polyaniline with ZnO composite is used to make a pellet by applying 5-6 tons of pressure using a pellet making machine [Model-UTM]. A silver paste is coated on both sides of surface of the pellet for providing electrical contacts. The pellets are used for experimental measurements of capacitance, dissipation, impedance and phase angle using computer interfaced LCR Q-meter [Model: HIOKI 3532-50].

3. Results and Discussion

3.1 Characterization

XRD: The ZnO in the form of powder is used for XRD measurements using powder method of X-ray diffractometer [Model: Regaku]. The XRD spectrum is shown in Fig 1. The peaks are occurred for ZnO at an angle of 2θ = 32, 34, 36, 48, 57, 63, 68 degrees which leads the crystalline nature. The XRD spectrum of polyaniline is shown in Fig 2. It is noticed from Fig 2 that a broad and diffused peak observed at around 2θ = 25 degree. This shows polyaniline is amorphous in nature. The XRD spectrum for the composite of polyaniline with ZnO is also shown in Fig 3. The peaks are occurred for the composite of polyaniline with ZnO at an angle of 2θ = 25, 38, 44, 65, 77 which depicted the composite has crystalline in nature and hence there is modification in the structure of the composite.

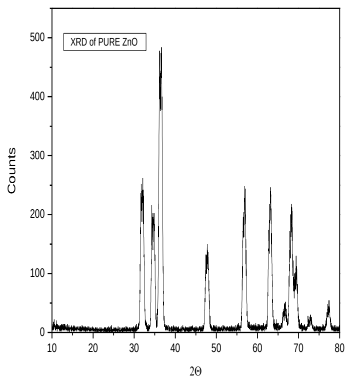

Fig 1: XRD Spectrum of ZnO

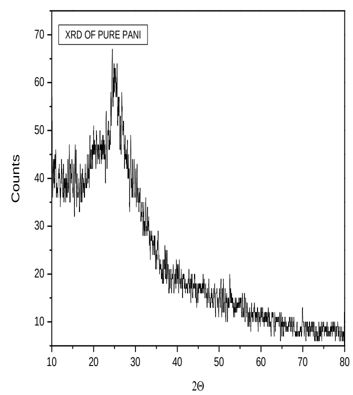

Fig 2: XRD Spectrum of PANI

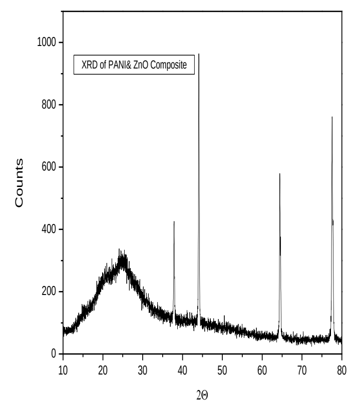

Fig 3: XRD Spectrum of PANI/ZnO Composite

The particle size could be easily estimated using the Debye Scherrer's formula given by

$$D = \frac{0.9\,\lambda}{\beta\,\cos\theta} \qquad (1)$$

Where D is the particle size (crystal size), β = FWHM of stronger peak (highest intensity peak) and λ is the wavelength of the X-ray. From high intensity peak the size of ZnO particle calculated is 12nm and PANI/ZnO composite particle size is14nm.

SEM: The SEM images of PANI, ZnO and composite of PANI/ZnO is shown in the Fig 4-Fig 6. It is observed from these figures that the size of the particles is obtained in nanometer range. The size of particles in polyaniline is around 62 nm and in composite of PANI/ZnO is around 471nm. The SEM image reveals the homogenous distribution of ZnO in polyaniline polymer matrix.

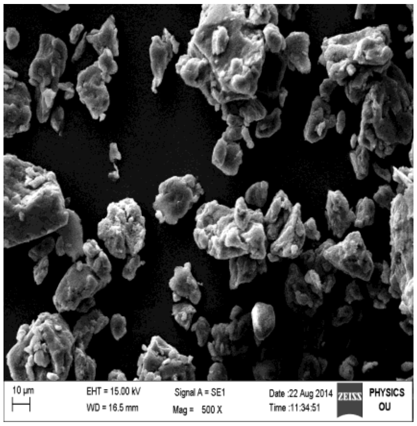

Fig 4: SEM Image of PANI

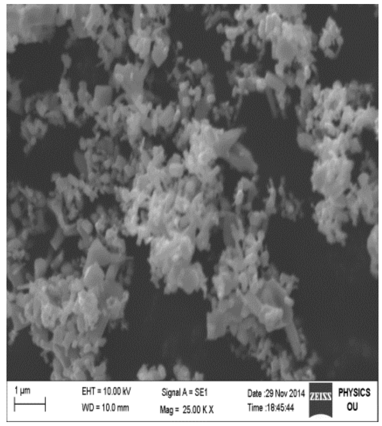

Fig 5: SEM Image of ZnO

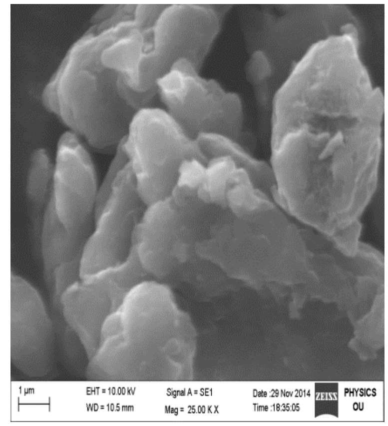

Fig 6: SEM image PANI/ ZnO Composite

3.2 Transport Properties

3.2.1 Dielectric Constant

The dielectric constant as function of frequency for PANI and the composites of PANI/ZnO for different wt% at room temperature is obtained using the equation given by

$$\varepsilon' = \frac{C\ d}{\varepsilon_0\ A} \qquad (2)$$

Where C is capacitance of the sample, d is thickness of the sample, A is area of the sample and ε_o is the permittivity of free space. The variation of dielectric constant with frequency at different wt% of ZnO with PANI is shown in Fig7.The dielectric constant of polyaniline decreased exponentially as frequency increased upto 10 KHz and afterwards it shows independent of frequency behavior because of electrical relaxation process. Further it is observed from Fig7 the doping of ZnO with the PANI the dielectric constant at lower frequency is increased compared to polyaniline and exponentially decreased up to 10 KHz after that it shows independent of frequency.

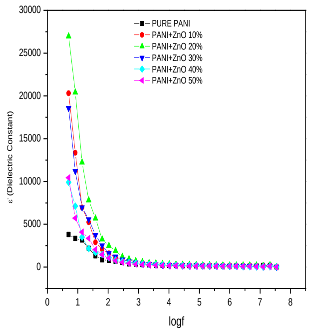

Fig 7: Variation of dielectric constant with frequency for PANI/ZnO composite

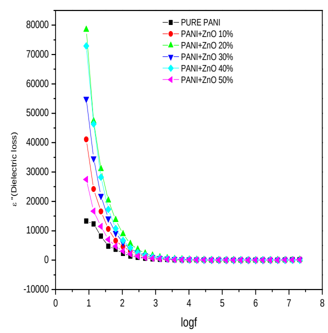

Fig 8: Variation of dielectric loss with frequency for PANI/ZnO composite

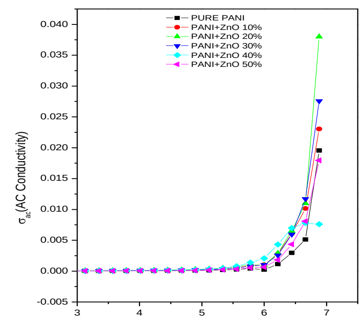

Fig 9: Variation of AC conductivity with frequency for PANI/ZnO composite

3.2.2 Dielactric Loss.

The dielectric loss as function of frequency for PANI and composite of PANI/ZnO 10,20,30,40 and 50 percentages of ZnO are obtained with help of the measured data of dissipation and the values of dielectric constant using the relation given by

$$\varepsilon'' = \varepsilon' \tan\delta \qquad (3)$$

Where ἑ is the dielectric constant of the PANI and its composites and tanδ is dissipation factor. The variation of dielectric loss as a function of frequency at room temperature is shown in Fig 8. It is observed from Fig 8 that the dielectric loss decreased exponentially as frequency increased up to 10 KHz and afterwards it is independent of frequency. It is also observed that the dielectric loss in PANI is lesser compared to its composites at lower frequency region. Further it is noticed that as weight percent of ZnO increased the dielectric loss increased at lower frequency region except for 50 wt% of ZnO in PANI.

3.2.3 AC Conductivity.

The electrical property of AC conductivity (σ_{ac}) as function of frequency for the polymer of PANI and for its composites with ZnO at different weight percentages are obtained using values of the dielectric constant and dielectric loss through the relation given by

$$\sigma_{ac} = \varepsilon_0 \varepsilon' \omega \tan \delta \qquad (4)$$

Where ε_0 is the permittivity of free space, ω is angular frequency and έ is the dielectric constant. The variation of AC conductivity as a function of frequency at room temperature is shown in Fig 9. It is seen From Fig 9 that conductivity remains constant up to 1MHz after that it increased exponentially. Further it is observed that the doping of ZnO increased the AC conductivity and for 20wt% of ZnO conductivity is found to be higher. The exponential increase in AC conductivity at higher frequency is due to various factors that may influence the conductivity which may be the number of charge carriers available for conduction, all the dipoles are aligning in one direction and also the extension of chain length of PANI where the polarons get sufficient energy to hop between favorable localized sites.

4. CONCLUSION

Polyaniline and its composite with ZnO at different weight percent have been synthesized by in situ polymerization using chemical oxidation method. The XRD spectrum for the composite of polyaniline with ZnO reveals that the PANI/ZnO composite is crystalline in nature. The peak positions differs from the ZnO compared to that of PANI/ZnO composite and this indicates the occurrence of modification in the structure of the composite. The values of dielectric constant and dielectric loss have been increased as weight percent of ZnO decreased at lower frequency region. A remarkable increase is observed in AC conductivity after the doping of ZnO. The size of the particle is in nanometer range which can found by the SEM images and XRD.

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