

# Synthesis, Characterization, Dielectric Behavior and AC Conductivity of ZrO<sub>2</sub> Doped Polyaniline

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## ABSTRACT

The composites of polyaniline (PANI) with Zirconium dioxide (ZrO<sub>2</sub>) at different weight percentage are synthesized by insitu chemical oxidation polymerization method using Ammonium peroxydisulfate (APS) as an oxidizing agent. The composite formation and structural changes are studied using X-ray diffractometer to investigate amorphous or crystalline nature. From XRD it is found that polyaniline is amorphous in nature and composite is in crystalline in nature and ZrO<sub>2</sub> is uniformly distributed in the PANI. SEM images confirmed that size particles of PANI and its composite is in the range of 0.9-1 $\mu$ m. Further the dielectric constant, dielectric loss and AC conductivity are studied as a function of frequency at room temperature. The dielectric constant, dielectric loss decreased as frequency increased and after 1.5 KHz they almost remain constant. AC conductivity increased after 1.5 KHz as frequency increased.

**Keywords:** A C conductivity, Dielectric constant, Dielectric loss, polyaniline composite, SEM and XRD, ZrO<sub>2</sub> Composite.

## 1. Introduction:

Polyaniline is unique and most studied polymer among all intrinsically conducting polymers. The scientific, academic and technological interest in the polyaniline is increasing drastically because of the richness of their chemical and physical properties. There are many ways by which their chemistry, electrochemistry, electronic, magnetic and optical properties can be fine-tuned and tailored by the proper doping [1-2]. The conducting polymers have made significant impact in the field of material science due to their potential applications in many electronic devices [3]. Polyaniline is one of the promising conducting polymer 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 [4-8]. 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 [9-13], gas detection [14], adsorption [15], anticorrosive coating on iron [16], energy storage elements [17-19], organic light emitting diodes [20] etc.

In the present work the composites of polyaniline with ZrO<sub>2</sub> were synthesized at different weight percentage by chemical oxidation polymerization method using ammonium persulphate as an oxidizing agent [4]. Zirconium dioxide sometimes known as zirconia, is a white crystalline oxide of zirconium with chemical formula ZrO<sub>2</sub>, molecular Wt 123.218 gmol<sup>-1</sup>, density 5.68 gcm<sup>-3</sup> and melting point 2715<sup>o</sup>C.

Zirconium dioxide is one of the most studied ceramic materials. It naturally occurs in the form of mineral baddeleyite, with a monoclinic crystalline structure and band gap of  $ZrO_2$  is 5–7 eV, and is dependent on the phase and preparation methods.

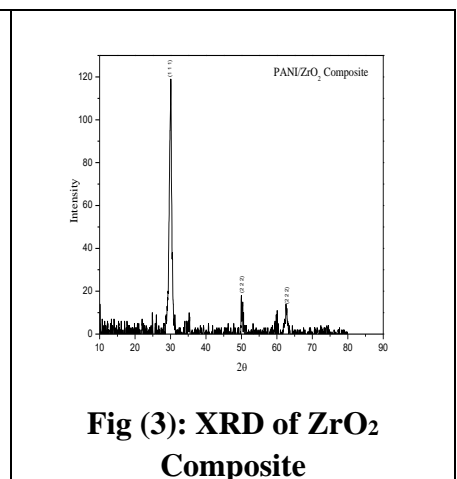
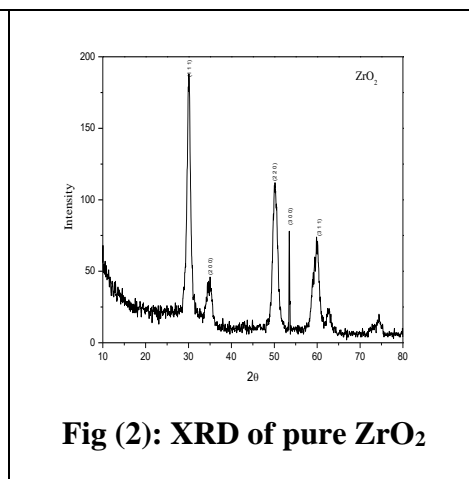
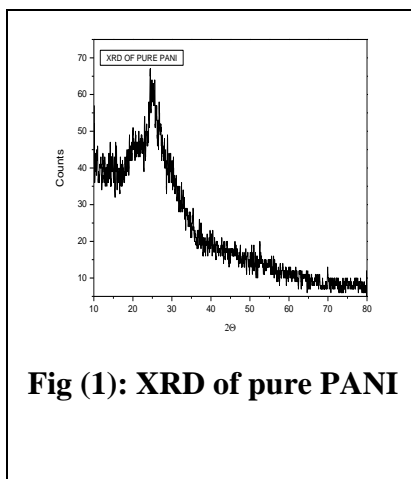
## 2. Experimental Measurements

**2.1 Synthesis of Sample:** The chemicals of aniline monomer, Ammonium per sulfate (APS)  $(NH_4)_2S_2O_8$ , hydrochloric acid (HCl), and Zirconium dioxide ( $ZrO_2$ ) 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.  $ZrO_2$  was added in different wt% to the above solution with vigorous stirring to keep  $ZrO_2$  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 8hrs at 60 degree temperature. The dried powder of polyaniline with  $ZrO_2$  composite is used to make a pellet by applying 5-6 tons of pressure using a pellet making machine [Model-UTM]. The 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:

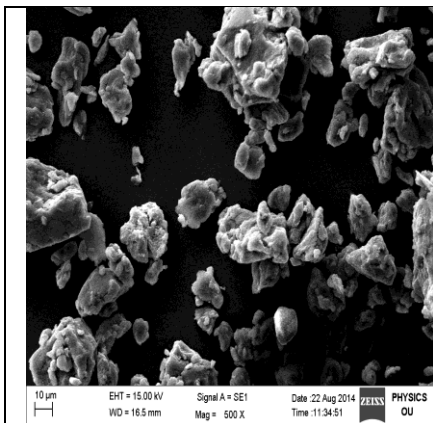
### 3.1 XRD Characterization:

The X-ray diffraction pattern of pure PANI,  $ZrO_2$  and the PANI/  $ZrO_2$  composite with 40 wt% is shown in Fig (1-3) . The XRD spectrum of polyaniline is shown in Fig 1. It is observed from the figure that the X-ray diffraction shows a broad and diffused peak at around  $2\theta = 25$  degree. This shows polyaniline is amorphous in nature. In Fig 2 The sharp peaks are occurred for  $ZrO_2$  at an angle of  $2\theta = 30.16, 35, 50.2, 53.4,$  and  $59.84$  degrees which shows the crystalline nature of  $ZrO_2$ . The XRD spectrum for the composite of polyaniline with  $ZrO_2$  is also shown in Fig 3. The peaks are occurred at an angle of  $2\theta = 30.32, 50.01, 62.74$  degree for the composite of polyaniline with  $ZrO_2$  which depicted the composite has crystalline in nature and hence there is modification in the structure of the composite.

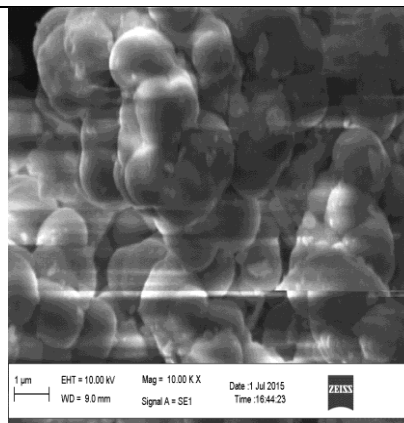


### 3.2 Scanning Electron Microscope (SEM)

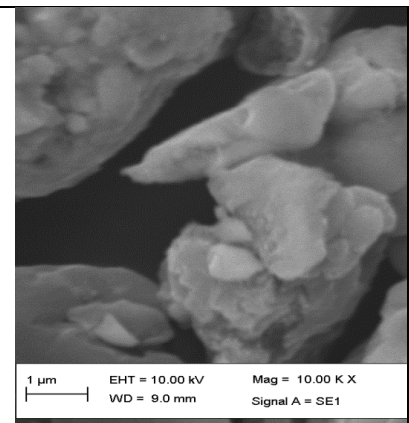
Morphological study is done using SEM. The SEM images of pure PANI, ZrO<sub>2</sub> and PANI/ ZrO<sub>2</sub> composite with 40 wt% of ZrO<sub>2</sub> in PANI are given in Figs 4, 5 and 6. SEM micrograph of polyaniline synthesized by chemical oxidative method is shown in Fig 4. It is seen clearly from the SEM micrograph of PANI that, it has highly agglomerated granular in shape. The grains are well interconnected with each other, which indicate that they have enough binding energy to combine with neighbor grains. The granular morphology of the polyaniline particle structure is measured from SEM photographs and is found to be 65 nm. It is observed from Fig 5. that the SEM image of ZrO<sub>2</sub> has spherical cluster like structure where, particles are arranged compactly. It is observed from the SEM photograph that the average particle size is in the range of 0.900 μm. SEM image of PANI/ZrO<sub>2</sub> reveals the homogeneous distribution of ZrO<sub>2</sub> in PANI. Polyaniline has retained its cluster and granular structure even after the addition of ZrO<sub>2</sub>. The mean grain size is found to be 1μm. It is observed from the images that grains are well resolved and some are circular in shape.



**Fig (4): SEM Image of pure PANI**



**Fig (5): SEM Image of pure ZrO<sub>2</sub>**



**Fig(6) :SEM image ZnO composite**

### 3.3 Transport Properties

#### 3.3.1 Dielectric constant

The dielectric constant as function of frequency for PANI/ZrO<sub>2</sub> composites at room temperature is studied using the equation

$$\epsilon' = \frac{C d}{\epsilon_0 A}$$

Where  $C$  is the capacitance,  $d$  is thickness of the sample,  $A$  is the area of the sample and  $\epsilon_0$  is the permittivity of free space. Fig7 shows the variation of dielectric constant with frequency at different wt%. The variation of dielectric constant as function of frequency for the composite PANI with 10, 20, 30, 40 and 50 wt% of ZrO<sub>2</sub> at room temperature is given in Fig 7. It is found that dielectric constant of PANI/ZrO<sub>2</sub> composites decreases exponentially upto 1 KHz of frequency and thereafter remains constant for higher frequency. This type of behavior is due to Debye like relaxation mechanism taking place in the material. From the Fig 7 it is noticed that, value of dielectric constant is high for 20 wt% and the dielectric constant decreases for 50, 30 and 40 wt% relatively among them. It is observed from Fig 7 that as wt% of ZrO<sub>2</sub> increased the dielectric constant decreased at lower frequency region except for 50 wt%. But the dielectric constant remained same at higher frequency. For composite of 10 wt% value of dielectric

constant is less than PANI. This is due additional contribution of hopping of polarons in the localized state.

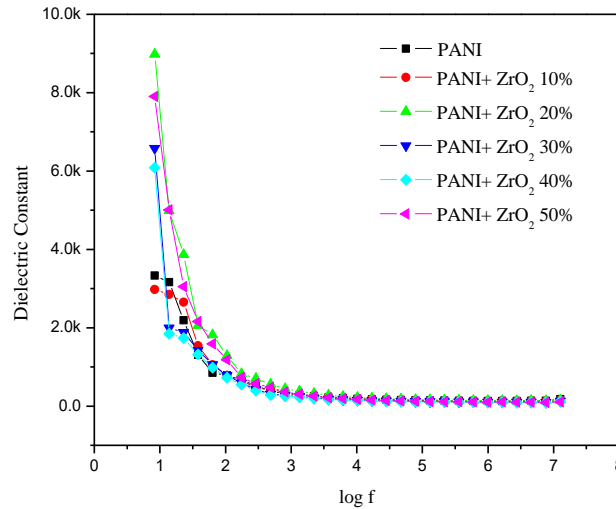


Fig (7): Variation of dielectric constant with frequency for PANI/ZrO<sub>2</sub> composites

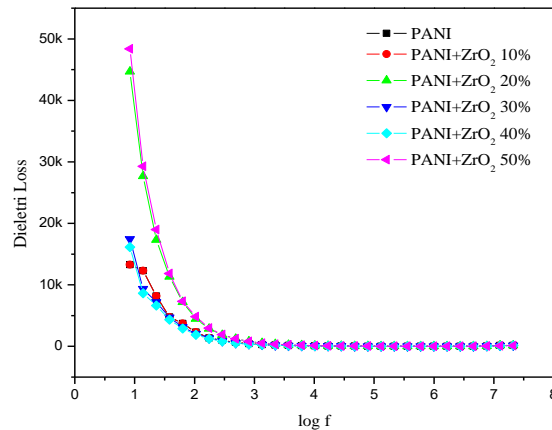
### 3.3.2 Dielectric loss

The dielectric loss as function of frequency for PANI/ZrO<sub>2</sub> composites at different weight percentages are obtained with help of the measured data of dissipation and the values of dielectric constant are calculated using the equation

$$\epsilon'' = \epsilon' \tan \delta$$

Where  $\epsilon'$ -dielectric constant of the PANI and its composites and  $\tan \delta$  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 the figure that the dielectric loss decreases exponentially in low frequency region of 50 Hz to 1 KHz, as frequency increases, after 1 KHz dielectric

loss remained constant irrespective of increase in frequency and behaves as lossless material. From the Fig 8 it is found that, value of dielectric loss for all the wt% of ZrO<sub>2</sub> is more than PANI. But it is greater for 50 and 20 wt% and goes on decreases for 40, 30, 10 wt%. The observed behavior of dielectric loss compared to PANI increases as doping of ZrO<sub>2</sub> increases.



**Fig (8): Variation of dielectric loss with frequency for PANI/ZrO<sub>2</sub> composite**

### 3.3.3 AC Conductivity

The electrical property of AC conductivity ( $\sigma_{ac}$ ) as function of frequency for the polymer of PANI and for its composites with ZrO<sub>2</sub> at different weight percentages are obtained with help of values of the dielectric constant and dielectric loss using the below equation

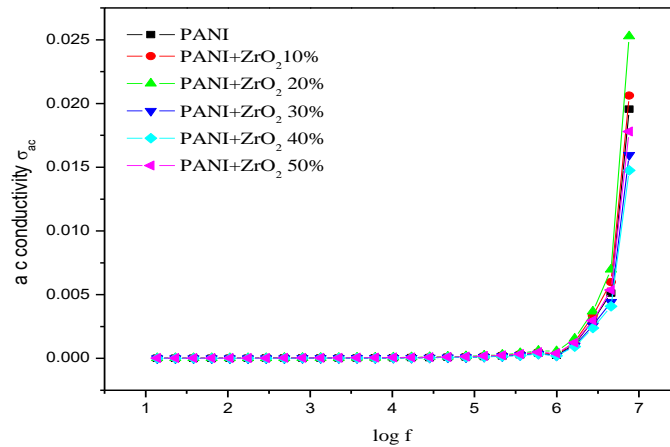
$$\sigma_{ac} = \epsilon_0 \epsilon' \omega \tan \delta$$

Where  $\epsilon_0$  is permittivity of free space,  $\omega$  is angular frequency. The variation of AC conductivity as a function of frequency at room temperature is shown in Fig 9.

It is observed from Fig 9 that the AC conductivity of PANI and its composite with ZrO<sub>2</sub> remained constant in the lower frequency range of 50Hz to 1MHz, and afterwards it increases exponentially at higher frequencies for all the composites. At higher frequencies, beyond 10 KHz, the conductivity increases because of the contribution of the polarons, which are moving along shorter distances in the polymer chain. The increase in AC conductivity at higher frequencies is attributed to charge motion in the crystalline

regions and this supports the presence of isolated polarons and bipolarons in this region [21].

It is noticed from the Fig 9 that, among all composites of ZrO<sub>2</sub> in PANI, the value of AC conductivity is greater than PANI for 20 wt% of ZrO<sub>2</sub> in PANI and less for 30, 40 and 50 wt% of ZrO<sub>2</sub> in PANI. It is clear that AC conductivity for 10 and 20 wt% of ZrO<sub>2</sub> is higher than those for the other composites. This may be a critical concentration for which the conductivity has the maximum value, and for other concentration the conductivity decreases. The decrease in conductivity may be due to the particals of ZrO<sub>2</sub> blocking the conduction path in the PANI matrix [22]. In case of the increase in the wt% of ZrO<sub>2</sub> leads to a larger number of polarons where the inter polaron coupling becomes progressively stronger, even though disorder is present, leading to severe pinning of polarons, thus restricting their contribution and hence a reduction in AC conductivity.



**Fig (9): Variation of ac conductivity with frequency for PANI/ZrO<sub>2</sub> composite**

#### 4. CONCLUSION

The conducting polyaniline and its composite with ZrO<sub>2</sub> at different wt% have been synthesized successfully by in situ polymerization using chemical oxidation method. The XRD spectrum for the composite of polyaniline with ZrO<sub>2</sub> reveals that the PANI/ ZrO<sub>2</sub> composite is crystalline in nature. The peak positions differs from the pure ZrO<sub>2</sub> compared to that of PANI/ ZrO<sub>2</sub> 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 wt% of ZrO<sub>2</sub> decreased at lower frequency region. A remarkable increase is observed in AC conductivity with the addition 10 and 20 wt% of ZrO<sub>2</sub>. From the SEM images it can be confirmed that the size of the particle is in micrometer range and it also reveals that homogenous distribution of ZrO<sub>2</sub> in polyaniline.

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