

Effect of ZnO particles on structural, morphological electrical and dielectric properties of polyaniline

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Abstract: In situ chemical oxidation route has been adopted to prepare polyaniline emeraldine salt (PANI) & zinc oxide doped Polyaniline (ZnO/PANI) with different additive weight percent of ZnO using ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant & HCL as catalyst. Composite of PANI with 10%, 20%, 30%, 40% & 50% of zinc oxide (ZnO) has been synthesized by adding zinc oxide powder gradually in the polymerization solution of aniline & APS. Further these composites were characterized by XRD & SEM techniques to investigate their structural and morphological studies. As a part of electrical studies, AC conductivity, dielectric constant of all the composites were studied as a function of frequency by using impedance analyser. DC conductivity was studied as a function of temperature.

Key Words: Polyaniline, XRD, SEM, AC, DC conductivity & dielectric constant.

1. Introduction:

Polyaniline is an organic conducting polymer that shows the behaviour of semiconductor or conductor. Polyaniline (PANI) is relatively popular and has unique properties due to easy synthesis route, good environmental stability, lightweight & controllable electrical conductivity. Polyaniline (PANI) can be found in one of three idealized oxidation states. Fully reduced leucoemeraldine base $(\text{C}_6\text{H}_4\text{NH})_n$ are the oxidation state of the polyaniline. These are colourless, poor conductor (even when doped with acids) and which are very reactive. Fully oxidised pernigraniline base $(\text{C}_6\text{H}_4\text{N})_n$ are another oxidation state of the polyaniline. They are blue/violet in colour, poor conductor and which is environmentally stable. Another most widely used oxidation state of the polyaniline are partially oxidised Emeraldine Base/salt $([\text{C}_6\text{H}_4\text{NH}]_2[\text{C}_6\text{H}_4\text{N}]_2)_n$ with green for the emeraldine salt, blue for the emeraldine base, which is

environmentally unstable and does not undergo any change in chemical structure [1-4]. Emeraldine base of the polyaniline is regarded as the most useful form of polyaniline due to its high stability at room temperature and the fact that, upon doping with acid, the resulting emeraldine salt form of polyaniline is highly electrically conducting [5].

Shamil M. Hammo reported that, we can observe increase in the electrical conductivity of the emeraldine when reacts with acids up to ten order of magnitude. The Undoped polyaniline has conductivities in the order of 6.28×10^{-9} S/m and it can be increased to 4.60×10^{-5} S/m by doping [6].

Usually almost metal oxides are crystalline in nature and it has attracted considerable interest for scientific research due to their potential applications in the field of polymer, optoelectronics and sensing devices [7]. Due to the enhancement of the physical and chemical properties of metal oxide shows the better in environmental remediation applications. (Peng, X. et al., 1998).

In the present work the composites of polyaniline with ZnO were synthesized at different weight percentage by chemical oxidation polymerization method using ammonium persulfate as an oxidizing agent [8]. 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 [9-10]. 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 1KHz to 1MHz at room temperature [11].

2. Materials and methods

2.1 Materials and Method:

Chemicals used to prepare polyaniline are aniline, hydrochloric acid (HCL), ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ of analytical grade and synthesized by employing chemical oxidative polymerization method using as monomer in the presence of hydrochloric acid as catalyst and ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant.

2.2 Preparation of Polyaniline

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction.

The solution of 0.2M of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) was added drop wise into the mixer. This reaction mixer was continuously stirred in magnetic stirrer for 8 hrs in room temperature. The precipitate formed and separated out by filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50°C for 24 hrs. The final product was grinded into powder.

2.3 Preparation of ZnO/Polyaniline:

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.2 M ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) was added drop wise into the mixer. Zinc oxide (ZnO) powder for different additive weight percentage (10%, 20%, 30%, 40% & 50%) is dissolved in the mass fraction to the above solution with vigorous stirring in order to keep the Zn O homogeneously suspended in the solution and stirring of final solution was continued for another 8 hours at room temperature. After 8 hrs the precipitate was separated out by filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50°C for 24 hrs. The final product was grinded into powder.

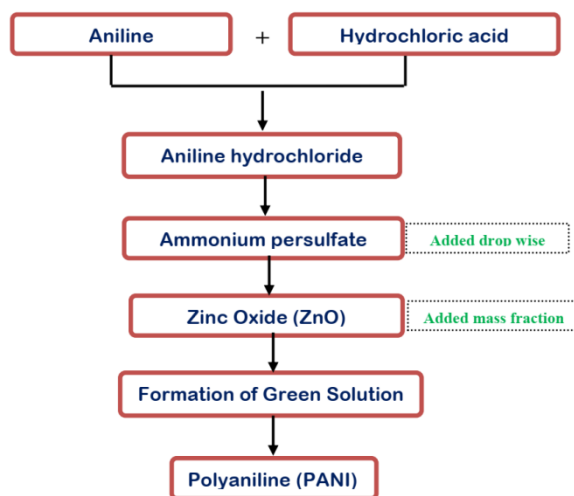


Figure-1: Flow chart of preparation composite

3. Result and Discussions

3.1 Structural Analysis:

Composites characterization by Powder XRD was carried out on a X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5406$) radiation. Figure-2 (a) shows the XRD pattern of pure polyaniline and Figure-2 (b-f) shows the

XRD pattern of ZnO/PANI (10%, 20%, 30%, 40% & 50%) respectively. The broad peaks of the sample illustrates the amorphous nature of the sample and as we increase the composition from 10% to 50% it shows that increasing crystallinity of the PANI may be due to the presence of ZnO in polyaniline. Figure-2(a) shows the prominent peak of pure polyaniline is in the range of 25-27°, which is characteristic peak of PANI. The XRD patterns indicate that the composites are well crystalline and reveals all diffraction peaks, which are perfectly similar to the literature (JCPDS no. 751526). The observed reflection planes resemble the tetragonal ZnO nanostructure; it can be seen that the reflections are markedly broadened. The peaks are occurred for the composite of polyaniline with ZnO at an angle of $2\theta = 31.27, 34.65, 37.25, 46.10, 55.85$ which depicted the composite has crystalline in nature and hence there is modification in the structure of the composite. The average crystalline size of the PANI was calculated from the broadening of the X-ray diffraction using the Debye Scherrer's formula and found approximately in the range 10-20 nm. It is also observed from pattern that, the intensity of the peak increasing as doping increased, suggests that ZnO are dispersed in the PANI matrix.

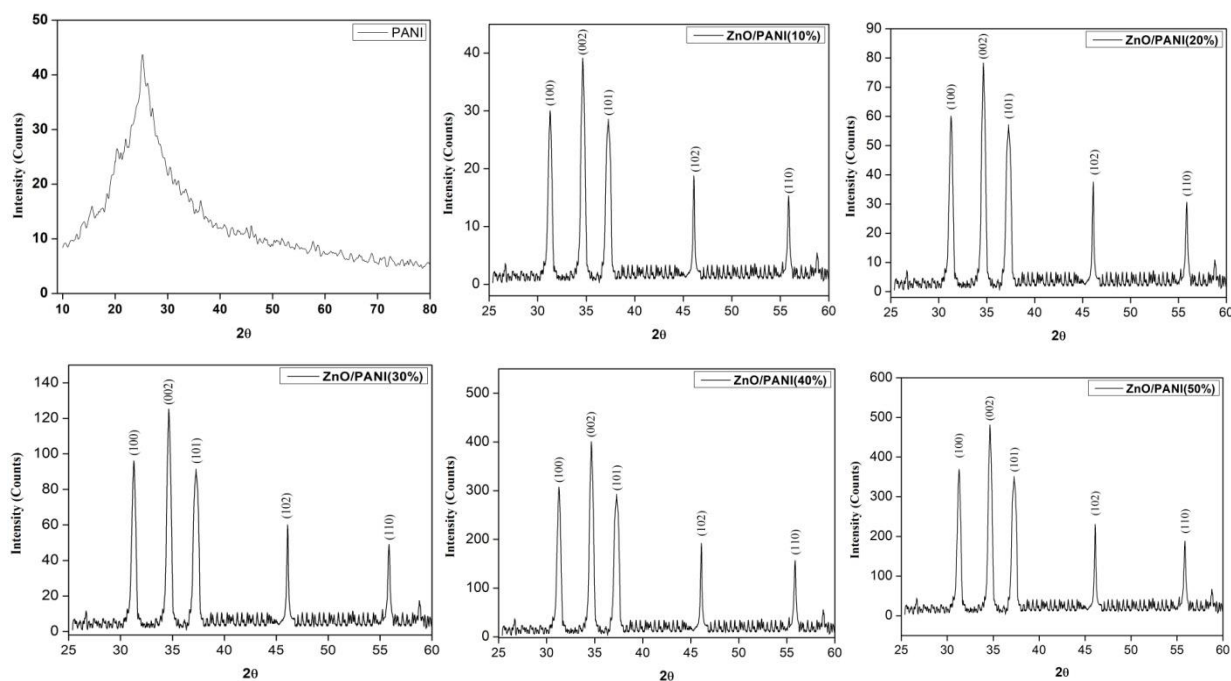


Figure-2: XRD pattern of (a) PANI, (b) ZnO (10%)/PANI, (c) ZnO (20%)/PANI, (d) ZnO (30%)/PANI, (e) ZnO (40%)/PANI, (f) ZnO (50%)/PANI

3.2 Morphological Study

Figure-3(a) illustrates the surface morphology of pure polyaniline and Figure-3 (b-f) are the surface morphology of ZnO/PANI (10%, 20%, 30%, 40% & 50%) respectively. SEM micrographs exhibit

agglomeration of particles having irregular shape and it is confirmed that the ZnO particles were equally distributed in the polymer matrix. High magnification of SEM image suggest the composition of ZnO affects morphological image considerably and reveals the presence of ZnO particles along with variation in the particle dimension of ZnO which is uniformly distributed in the sample. Since structure property correlation plays a significant role, a correlation between dimension of ZnO used for composite preparation and its effect on electrical properties. By comparing the figure 3(a) & Figure-3 (b-f), it can be conclude that the change in the morphological images of composites and variation of particle size may helps the transportation of charge particles through the carbon back -bone of polymer chains

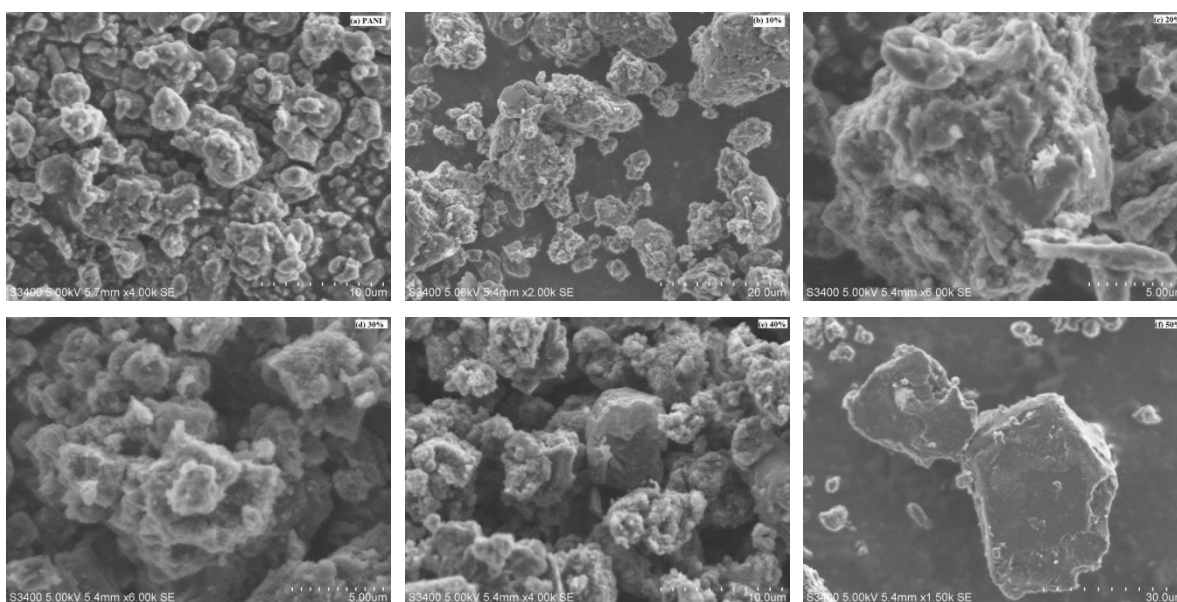


Figure-3: SEM image of (a) PANI, (b) ZnO (10%)/PANI, (c) ZnO (20%)/PANI, (d) ZnO (30%)/PANI, (e) ZnO (40%)/PANI, (f) ZnO (50%)/PANI

4.1 Electrical properties

a. AC conductivity:

Figure-4 shows the variation of ac conductivity as a function of frequency for pure polyaniline and ZnO/PANI (10%, 20%, 30%, 40% & 50%) was carried out at 1KHz–1MHz frequency in room temperature. It is reported previously that, polyaniline has electrical conductivity ranges between 10^{-10} and 10^3 S/cm depending on the acid dopant and fillers [12]. It is observed that in all the cases of pure & composite, shows constant variation of ac conductivity up to 600KHz and it increases from the order 10^{-3}

to 10^{-2} S/m upto 1MHz frequency. Increase of σ_{ac} at higher frequencies is due to the charge motion in the amorphous region and this supports the presence of isolated polarons in this region [13].

Figure-5 shows the ac electrical conductivity of as function of composition at 1KHz and 1MHz frequency. It illstartes that, as the content of ZnO is increased in the PANI matrix, the conductivity of the higher composite always increasing at both 1KHz and 1MHz frequency. This may due to the presence of ZnO particles in the matrix. Also this increase in the conductivity for composites may be due to facilitation of hopping of charge in the PANI extended chain length [13].

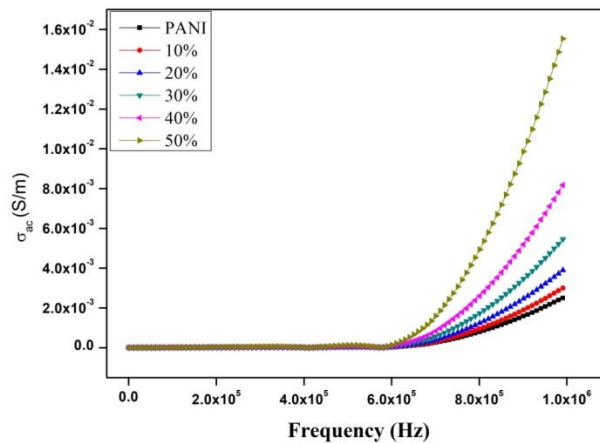


Figure-4: AC conductivity of PANI & ZnO/PANI composite

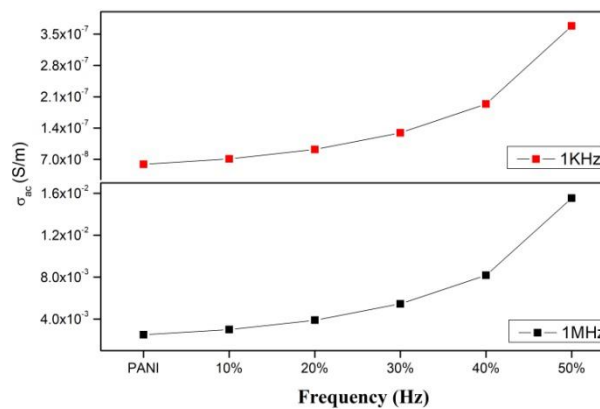


Figure-5: AC conductivity as function of composition at 1KHz & 1MHz frequency

b. DC conductivity:

Figure-6 shows the dc conductivity of the pure polyaniline & ZnO/PANI (10%, 20%, 30%, 40% & 50%) as a function of the temperature in the range 30° C to 180°C. It is found that there is increase in the

conductivity of the PANI & composite for the increase in temperature exhibiting semiconducting behaviour and it is the characteristic property of materials [14]. It is observed from figure that, conductivity of PANI & composite showing in two phase i.e., the conductivity in the range 30°C - 90°C, 100°C - 180°C. The first phase conductivity is almost constant may be due to inter-chain transport of charge carriers, i.e., hopping of charge carriers between the polymer chains and is usually observed at intermediate temperature. But, at high temperature region, (phase two) there is a sudden increase in the conductivity with increase in temperature due to intra-chain transport of charge carriers which can be described by the band conduction mechanism and is usually it is observed at high temperatures as reported by authors in their previous work [15-17]. Compared to the conductivity of PANI, the conductivity of MgO/PANI composites increased. This increase in the dc conductivity may due to the presence of MgO in polyaniline.

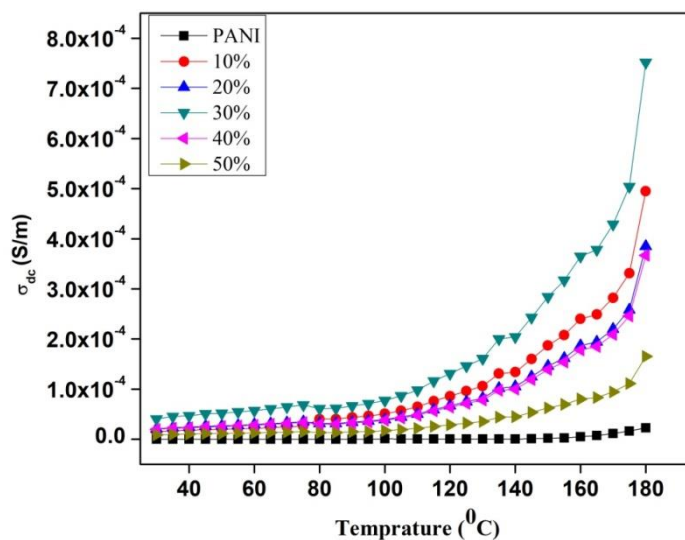


Figure-6: DC conductivity of PANI & ZnO/PANI composite

4.2 Dielectric properties:

Figure-7 show the variation of real dielectric constant (ϵ') as a function of frequency for polyaniline and polyaniline composites at room temperature (RT) in the frequency range of 1KHz to 1MHz. It is observed that, obtaining higher value of dielectric constant at low frequency range. Debye type relaxation mechanism may be responsible for higher value of dielectric constant at low frequency. Dielectric constant of polyaniline and polyaniline composites decreases as frequency increases over the measured

frequency range 1KHz to 1 MHz, which is a typical characteristic of disordered conducting polymer. The degree of polarization inside the nanocomposite system is thought to be increased with increasing ZnO concentration for 10% to 50%, which in turn enhances the dielectric constant of the composite. The ϵ' values matches to previously reported values i.e., the dielectric constant of polyaniline found to be 122.83 at room temperature for 1KHz and 85.68 for 500 KHz [18]. Also reported that, the ϵ' values for composite (wt.2% of EGf) found to be 7.92×10^6 at 1KHz [19].

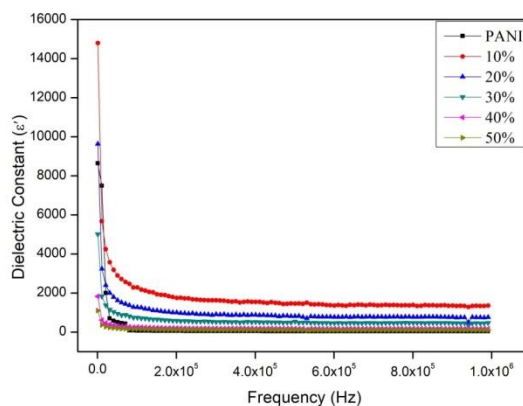


Figure-7: Dielectric constant PANI & ZnO/PANI composite

5. Conclusion:

PANI/ZnO composite samples with various dopant percentages of ZnO were synthesized using in situ chemical oxidative polymerization method at room temperature. The structural and morphology studies of PANI/ZnO support the efficient interaction of PANI/ZnO particles. XRD can be attributed to the substantive internalization between PANI/ZnO particles. The SEM images helped to draw the conclusion that the doping of ZnO had a effect on PANI morphology, and with increased ZnO content, the composites showed a transformation in morphology from typical granular and nonporous PANI particles. The increased conductivity was attributed to the formation of a better charge transport network in the relatively insulating PANI matrix. The investigation of PANI/ZnO composites confirmed their stability and suitability for solar cells and optoelectronics devices. Dielectric characterization demonstrated that ZnO particles exhibit a strong effect on the dielectric properties of resultant PANI/ ZnO composites. The dielectric constant is attributed to the formation of a better charge transport network in the relatively insulating polyaniline matrix. Dielectric measurements revealed about the strong interactions between PANI and ZnO particles causing a beneficial effect on stability of the composites.

6. References:

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