



e-ISSN: 2319-8753 | p-ISSN: 2320-6710

IJRSET

International Journal of Innovative Research in
SCIENCE | ENGINEERING | TECHNOLOGY

INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 10, Issue 1, January 2021

ISSN INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA

Impact Factor: 7.512

9940 572 462

6381 907 438

ijirset@gmail.com

www.ijirset.com

Some Studies on Synthesis and Characterization of Zinc Oxide (ZnO) Doped Polyaniline(PANI)

Vijayalaxmi Reddy¹, Mahadevi Konin², Dr. Anilkumar Bidve³, Dr. Sangshetty Klyane⁴

Research Student, Department of Physics, Appa Institute of Engineering & Technology, Kalburgi, Karnataka, India¹

Research Student, Department of Physics, Appa Institute of Engineering & Technology, Kalburgi, Karnataka, India²

Professor, Department of Physics, Appa Institute of Engineering & Technology, Kalburgi, Karnataka, India³

Professor, Bheemanna Khandre Institute of Technology, Bhalki, Bidar, Karnataka, India⁴

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.

I. INTRODUCTION

Polyaniline is also an organic conductive polymer that exhibits similar characteristic of semiconductor or conductor. Polyaniline are quite popular and has unique properties due to its ease in synthesis, reversibility easy synthesis route, good environmental stability, lightweight & availability in film form. Polyaniline (PANI) could be identified during 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 have drawn significant interest in scientific research due to their possible applications in the various field of polymer, optoelectronic devices including sensors [7]. Due to the enhancement of the chemical & physical properties of metal oxide shows the better in environmental remediation applications. (Peng, X. et al., 1998).

In the present research, polyaniline composites with ZnO have been synthesised at various weight fractions using a chemical oxidation polymerization process using ammonium persulphate as an oxidising agent [8]. Zinc oxide (ZnO) is an n-type semiconductor which has a large energy band gap (3.4 eV), high energy binding, effective ultraviolet absorbance and good chemical stability. It exhibits promising applications in solar panels, gas sensing, varistor, beauty products, etc. With all this perspective of multifunctionality ZnO will be used for the production of composite materials [9-10]. Its production of PANI/ZnO composites was characterized by XRD and SEM. Characteristics like dielectric permittivity, dielectric loss and AC conductivity of PANI/ZnO composites have been studied as material characteristics [11].

II. MATERIALS AND METHODS

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 oxidizing agent.

Preparation of Polyaniline

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixture 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 by drop into the mixture. This above mixture were continuously stirred in magnetic stirrer for 8 hrs in room temperature. The precipitate formed and separated out by filtering and rinse with de-ionised water with acetone. The obtained final suspension was dried in oven at 50° C for 24 hrs. The final product were grinded into powder.

Preparation of ZnO/Polyaniline

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixture 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.

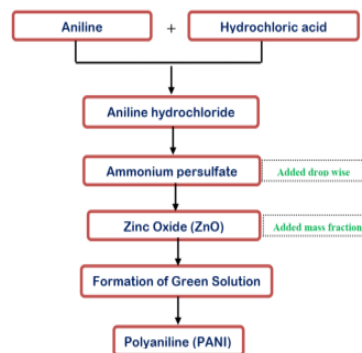


Figure-1: Flow chart of preparation composite

III. RESULT AND DISCUSSIONS

Structural Analysis

Composites characterized by powder XRD was done on an X-ray diffractometer with $\text{CuK}\alpha$ ($\alpha = 1.5406$) radiation. Fig-2(a) illustrate the XRD configuration of ZnO/PANI (10%, 20%, 30%, 40% & 50%) respectively. The broad peak of the sample illustrates the amorphous nature of the sample and as we increase the composition from 10% to 50% it illustrates that increasing crystallinity behaviour of the PANI might be because of the existence of ZnO in polyaniline. Fig 2(a) illustrate the prominent peak of pure polyaniline is in the range of 25-27°, it is distinctive peak of PANI. The XRD designs demonstrate that the composite are well crystalline and uncovers all diffraction peaks, which are completely analogous to the literature (JCPDS no. 751526). The experimental reflection planes take after the tetragonal ZnO nanostructure; it tends to be seen that the reflections are notably widened. The peaks are occurred for the composite of polyaniline with ZnO at an angle of $2\theta = 31.27, 34.65, 37.25, 46.10, \text{ and } 55.85$ which depicted the composite has crystalline in nature and hence there is modification in the structure of the composite. The normal crystalline dimension of the PANI was calculated from the expanding of the XRD by the ‘Debye Scherrer’s’ equation and got approximately in the range 10-20 nm. It is likewise seen from pattern that, the intensity of the peak expanding as doping expanded, suggests that ZnO are dispersed in the PANI matrix.

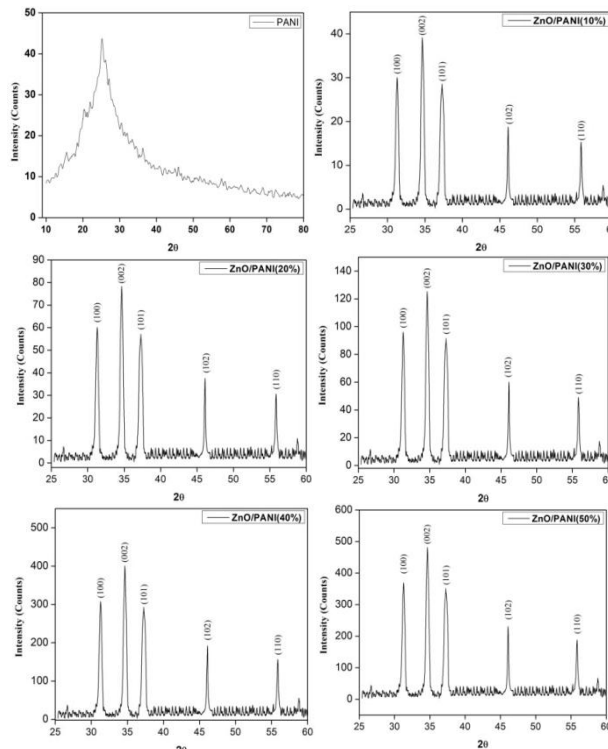
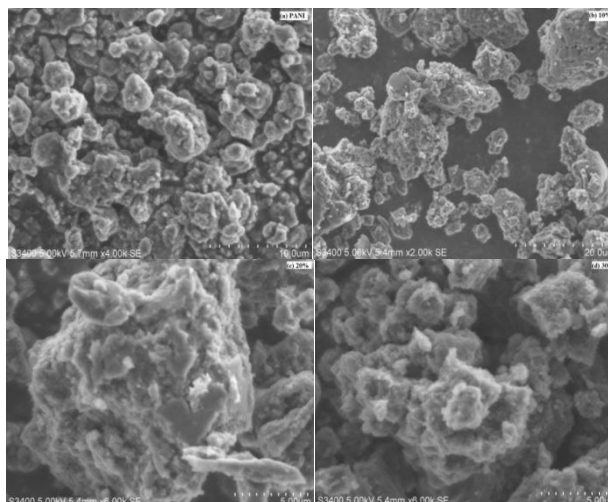


Figure-2: XRD pattern of (a) PANI, (b) ZnO (10%)/PANI, (c) ZnO (20%)/PANI, (d) ZnO (30%)/PANI, (e) ZnO (40%)/PANI, (f) ZnO (50%)/PANI

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.



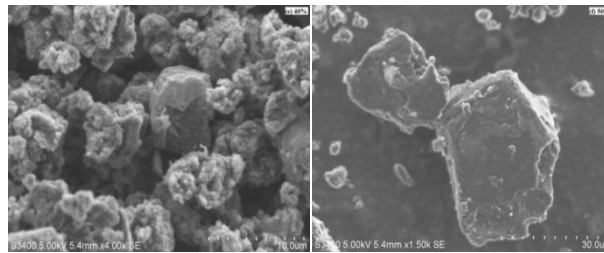


Figure-3: SEM image of (a) PANI, (b) ZnO (10%)/PANI, (c) ZnO (20%)/PANI, (d) ZnO (30%)/PANI, (e) ZnO (40%)/PANI, (f) ZnO (50%)/PANI

IV. ELECTRICAL PROPERTIES

AC conductivity:

The measurement of AC conductivity for all composite materials with respect to change in frequencies of different weight percent was carried out at 1KHz–1MHz frequencies at room temp was seen in figure:5.4. Polyaniline has previously been reported to have electrical conductivity between 10^{-10} and 10^3 S/cm, on the basis of both acid doping as well as additives [12]. It can be seen that in all the cases of pure composite, exhibit constant variation of ac conductivity up to 600 KHz and it increases from the order 10^{-3} to 10^{-2} S/m up to 1MHz frequency. The change in σ_{ac} at specific frequencies was related to only the transition of charges in the amorphous phase but this stimulates the creation of isolated polarons in this phase [13].

The change in σ_{ac} of polyaniline with respect to different composition of 1KHz, 10KHz & 1MHz frequency is shown in Figure-5.5, 5.6& 5.7. It illustrates that, as the content of ZnO is expanded in the PANI Chain, the conductivity of the higher composite with the frequency increases in particular contents. Maybe this is directly related to the existence of Zinc-oxide particles throughout the extended chain of PANI phase. Additionally this expansion in the conductivity for composites might be because of assistance of bouncing of charge in the PANI broadened chain length.

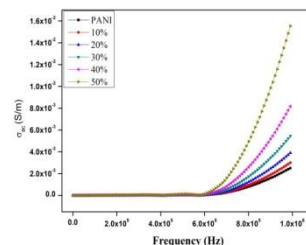


Figure-4: AC conductivity of PANI & ZnO/PANI composite

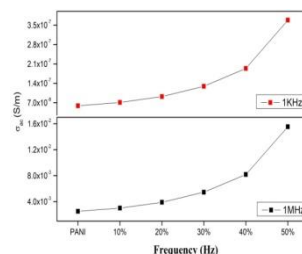


Figure-5: AC conductivity as function of composition at 1KHz & 1MHz frequency

DC CONDUCTIVITY:

The temperature dependence of dc-conductivity confirms (σ_{dc}) for PANI, ZnO/PANI (10%, 20%, 30%, 40% & 50%) composites in a temperature range around 30 to 180 °C are represented in Figure-5.15. It had been found that, there has been exponential rise in the conductivity of the PANI and composite for increasing temperature showing semiconducting behaviour and it is the characteristic property of materials [14]. It is seen from figure that, conductivity of PANI and composite appearing 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 because of movement of the charge carriers across polymer network, i.e., jumping of charge transporters between the polymer lattice and is typically seen at transitional temperature. In any case,

at high temperature region, (phase two) there is an abrupt increment in the conductivity with an increased temperature due to intra-chain transport of charge carriers that could be explained by the band conductive phenomenon and is normally it is seen at high temperatures as reported by authors in their past work [15-17]. The conductivity of ZnO / PANI composites increased compared with PANI conductivity. This expansion in the dc conductivity may be because of the existence of ZnO in polyaniline.

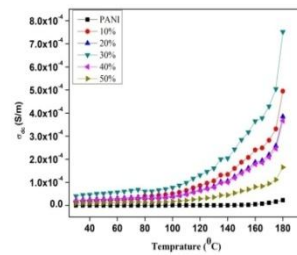


Figure-6: DC conductivity of PANI & ZnO/PANI composite

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].

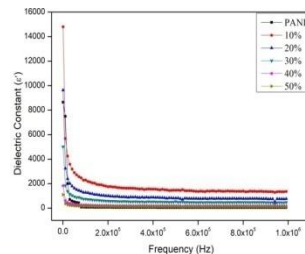


Figure-7: Dielectric constant PANI & ZnO/PANI composite

V.CONCLUSION

PANI/ZnO composites with varying doping percentage of ZnO was processed using in situ chemical oxidative polymerization at room temperature. The structural and morphological studies of PANI/ZnO confirm the effective interaction of PANI/ZnO particles. XRD could be attributed to the substantial internalization of PANI/ZnO particles. The SEM observations led to the hypothesis that the doping of ZnO would have an interaction on PANI morphology, also with enhanced ZnO substance, the composite materials demonstrated a transition in morphology of standard granular and nonporous PANI particles. Increased conductivity were due to the existence of a stronger charge transfer network in the comparatively insulating PANI matrix. The PANI/ZnO composites investigation has confirmed their durability and acceptability for solar cells and optoelectronics devices. The dielectric characterization shows that ZnO particles had a strong effect on the dielectric properties of the resulting PANI/ZnO composites. The dielectric constant is due to the creation of a stronger network of charges transport in a comparatively insulated polyaniline matrix. Dielectric measurements revealed about the strong interactions between Polyaniline and Zinc Oxide particles causing a beneficial effect on stability of the composites.



ACKNOWLEDGEMENT

The authors are thankful to Poojya Dr. Sharanabaswappa Appaji, President, Sharnbasveshwar vidya vardhak sangha, Kalburagi. & Prof. Dr. V.D Mytri, Principal Appa Institute of Engineering and Technology, Kalburagi, Karnataka, Dr. Sangshetty Kalyane Professor, VGST Research Centre of Bhalki by providing Basic Work, Bhalki, for encouragement during the process of carrying out this work.

REFERENCES

- [1]. Kerileng M. Molapo, Peter M. Ndingili, et al, Electronics of Conjugated Polymers (I): Polyaniline, Int. J. Electrochem. Sci.,7(2012)11859 -11875
- [2]. C.K. Chiang, M.A. Druy, S.C. Gau, A.J. Heeger, E.J. Louis, A.G. MacDiarmid, Y.W. Park and H. Shirakawa, J. Amer. Chem. Soc., 100 (1978) 1013-1015.
- [3]. P.J. Kaveeta, R.G. Prasad, S.J. Venkata, R.S. Aparna and A.R. Phani, Nano Biomed. Eng., 4 (2012) 144-149.
- [4]. Srinivasan Palaniappan, Amalraj John, Polyaniline materials by emulsion polymerization pathway, Prog. Polym. Sci. 33 (2008) 732-758
- [5]. MacDiarmid, Alan G. (2001). "Synthetic Metals": A Novel Role for Organic Polymers (Nobel Lecture)". *Angewandte Chemie International Edition*. 40 (14): 2581
- [6]. Hammo, Shamil M. (2012). "Effect of Acidic Dopants properties on the Electrical Conductivity of Poly aniline". *Tikrit Journal of Pure Science*. 17 (2).
- [7]. T. Jintakosol, P. Singjai, *Curr. Appl. Phys.* 9, 2009, 1288-1292.
- [8]. Ehsan Nazarzadeh zareh, Peyman Nazafi Moghadam, Elham Azariyan and Iman Sharifian Iranian Polymer Journal 20(4), (2011), 319-328.
- [9]. Aizuddin Abdul Rahman M, Shahrom Mahmud, Abdul Karim Alias and Abdul Fauzi Mohd Nor. *Journal of Physical Science* 24(1), (2013), 17-28.
- [10]. Shahid Pervez Ansari and Faiz Mohammad. *IUP Journal of Chemistry* 3, (2010), 4.
- [11]. Manjula V T et al., "AC conductivity and dielectric property of ZnO doped polyaniline composite", *International Research Journal of Natural and Applied Sciences*, Volume - 2, Issue- 6 (June 2015), ISSN: (2349-4077).
- [12]. Y. Long, Z. Chen, N. Wang, J. Li, M. Wan, "Electrical transport in Polyaniline - CSA/Polyaniline - DBSA polyblends", *Physica B: Condensed Matter*, 344 (2004), pp. 82-87.
- [13]. Chaturmukha V. S. et al "Influence of compositional variation on electrical properties of PANI/SnO₂ nanocomposites, International Conference on Condensed Matter and Applied Physics (ICC 2015), AIP Conf. Proc. 1728, 020348-1-020348-4; doi: 10.1063/1.4946399, AIP Publishing. 978-0-7354-1375-7.
- [14]. S. D. Thakre, U. B. Mahatme, A. A. Dani, "Preparation and Characterization of Polyaniline/Zinc Oxide Composites via Oxidative Polymerization", *ijcm*, 2014, 4(1): 14-20.
- [15]. N. Chandrakanth and M. A. Careem, *Polymer Bulletin*, 44 (2000) 101.
- [16]. M. Ghosh, A. Barman, A.K. Meikap, S.K. De, S. Chattejee, *Phys. Lett. A*, 260 (1999) 138.
- [17]. Thesis "Synthesis and characterization of polyaniline doped with some nanoferrites, Prasanna, G D, <http://hdl.handle.net/10603/80975>, Shodhganga@ INFLIBNET.
- [18]. Saxena Dinesh, Dwivedi Vivek and Mishra Pankaj Kumar, "Dielectric Study of Polyaniline in Frequency Range 100Hz to 500 KHz at Temperature 200C and 300C", *Research Journal of Chemical Sciences*, Vol. 3(2), 16-19, February (2013), ISSN 2231-606X.
- [19]. Prasanna B P, Avadhani D N, Muralidhara H B, Revanasiddappa M, "Synthesis, Characterization and Enhanced Dielectric Constant of Polyaniline-Exfoliated Graphite Flakes Composites", *IJLTEMAS*, Volume III, Issue V, May 2014, ISSN 2278 - 2540.



INNO  **SPACE**
SJIF Scientific Journal Impact Factor

**Impact Factor:
7.512**

ISSN INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA



INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

 **9940 572 462**  **6381 907 438**  **ijirset@gmail.com**



www.ijirset.com

Scan to save the contact details