



Unique Journal of Engineering and Advanced Sciences

Available online: www.ujconline.net

Research Article

SYNTHESIS, CHARACTERIZATION AND DC CONDUCTIVITY OF $ZnFe_2O_4$ DOPED POLYANILINE COMPOSITES

Chanshetty Vijaykumar B^{1*}, Sharanappa.G²

¹Department of Mechanical Engineering, Bheemanna Khandre Institute of Technology, Bhalki, Dist:Bidar, Karnataka, India

²Department of Mechanical Engineering, Reva Institute of Technology and management, Yelahanka, Bangalore, Karnataka, India

Received: 09-07-2013; Revised: 04-09-2013; Accepted: 02-10-2013

*Corresponding Author: Vijaykumar B Chanashetty
Email: vjchan2007@gmail.com, Phone: +919448446252

ABSTRACT

The Polyaniline/ $ZnFe_2O_4$ composites were prepared at different weight percentage using ammonium persulphate as an oxidant. The prepared composites were characterized by XRD for structural studies and SEM to studies the morphology of the composites. The dc conductivity indicates there was a strong influence on the conductivity of small dopant added to the conducting polymer. It is observed that conductivity is increases with increase in temperature for all composites. Among all composites 15 wt% show high conductivity due to the hopping of polarons and follow the mott theory.

Keywords: Polyaniline, Zinc ferrite, Composites, Scanning electron microscopy.

INTRODUCTION

Conducting polymers have been the subject of continuous research and development due to their potential applications in many technological areas. Conducting polymers offered the promise of achieving a new generation of polymers; materials which exhibit the electrical and optical properties of metals or semiconductors and which retain the attractive mechanical properties and processing advantages of polymer leading to wide range of technological applications¹⁻⁴. Amongst the family of conducting polymers, polyaniline (PANI) is unique due to its ease of synthesis, environmental stability, and simple doping/dedoping chemistry. Because of its rich chemistry, polyaniline has been one of the most studied conducting polymers of the past 20 years. Polyaniline (PANI) is a promising material because of its intrinsic electrical conductivity by doping with organic dopants⁵. The highly order structures such as crystalline or self assembled structures of ideal conducting polymer with p-conjugated structure is expected to have metal-like electrical conductivity⁶. To induce an ordered structure, other materials acting as filler for the composite are required⁷⁻¹⁴. Nano structurization of conducting polymers and their composites emerged as a new field of research and development, directed to creation of new materials for use in modern and future technologies. Recently,

conducting polymer/metal oxide nano particle composites have been considered as a new class of materials due to their improved properties when compared with those of pure conducting polymer and metal oxide¹⁵⁻¹⁷.

In this present paper authors reporting the synthesis of polyaniline/ $ZnFe_2O_4$ composite. The prepared samples were characterized by XRD and SEM. Dc conductivity studies shows that there are increases in conductivity with increase in temperature.

MATERIALS AND METHODS

All Chemicals used were analytical grade (AR). The monomer aniline was doubly distilled prior to use. Ammonium persulphate ($(NH_4)_2S_2O_8$, Hydrochloric acid (HCl), Lead oxide (PbO), were procured and used as received.

Synthesis of Polyaniline / $ZnFe_2O_4$ Composites:

0.1 mole aniline monomer is dissolved in 1 mole hydrochloric acid to form polyaniline hydrochloride. Fine graded pre-sintered $ZnFe_2O_4$ (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 5, 10, 15, 20 and 25 is added to the polymerization mixture with vigorous stirring in order to keep the $ZnFe_2O_4$ powder suspended in the solution. To this reaction mixture, APS as an oxidant is added slowly with continuous stirring for the period of 4 hrs at temperature 5°C. Polymerization of aniline takes place over fine grade zinc

ferrite particles. The resulting precipitate is filtered and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any unreacted aniline. After washing, the precipitate is dried under dynamic vacuum at 60°C for 24 hrs to get resulting composites [19]. In this way five different polyaniline/ ZnFe₂O₄ composites with different weight percentage of zinc ferrite (5, 10, 15, 20 and 25) in polyaniline have been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium.

The powders of polyaniline, polyaniline – ZnFe₂O₄ so obtained from synthesis techniques discussed in the early sections are crushed and finely in the presence of acetone medium in agate mortar. This powder is pressed to form pellets of 10 mm diameter and thickness which varies from 1 to 2 mm by applying pressure of 90 MPa in a hydraulic press. The pellets of polyaniline and its composites so obtained from above mentioned techniques are coated with silver paste on either side of the surfaces to obtain better contacts.

Characterization:

The X-ray diffraction patterns were recorded for these materials with CuK α radiation of wavelength $\lambda=1.5420 \text{ \AA}$ in the 2θ range 8-90°. The powder morphology of polyaniline and its composites sintered in the form of pellets are investigated using Philips XL30 ESEM scanning electron microscope (SEM).

Home made two probe dc conductivity set up is used to study the temperature dependent conductivity of prepared samples.

RESULTS AND DISCUSSION

Zinc ferrite and Polyaniline / ZnFe₂O₄ composites:

Figure shows the X-ray diffraction (XRD) patterns of the samples calcined at temperatures in the range of 300°C. At 300°C, in figure, the formation of a spinel crystal structure has been noted on the basis of diffraction peaks corresponding to Miller indices of (220) and (311), showing the presence of spinel phases of Fe₃O₄, γ -Fe₂O₃ and Zn-ferrite, not distinguishable by XRD.

Figure 1 shows the X-ray diffraction pattern of Polyaniline – ZnFe₂O₄ composite with 50 wt % of ZnFe₂O₄ in polyaniline. It is seen from figure that the peak of ZnFe₂O₄ indicates the crystalline nature of the composite. By comparing the XRD pattern of composite with that of PANI, the prominent peaks corresponds to $2\theta = 18.59^\circ, 30.09^\circ, 35.55^\circ, 56.43^\circ$ and 62.32° are due to (220), (311), (400) (422) and (333) planes of ZnFe₂O₄. By comparing the XRD patterns of the composite and PANI, it is confirmed that ZnFe₂O₄ (JCPDS 06-0696) has retained its structure even though it is dispersed in PANI during polymerization reaction¹⁰.

Figure 2(a) shows that Scanning Electronic Micrograph (SEM) image of pure Polyaniline. The highly agglomerated granular in shape and has amorphous nature is found. The average grain size is found to be 2 to 4 μm . The grains are well interconnected with each other indicating that they have enough binding energy to combine with neighbors grains or molecules.

Figure 2(b) show the 15 wt. % of PANI/ZnFe₂O₄ composite. The images shows a highly crystalline granular flake like

networking structure arranged in soccer shape and is well interlinked between each other. The average grain size is found to be 230 nm to 340 nm.

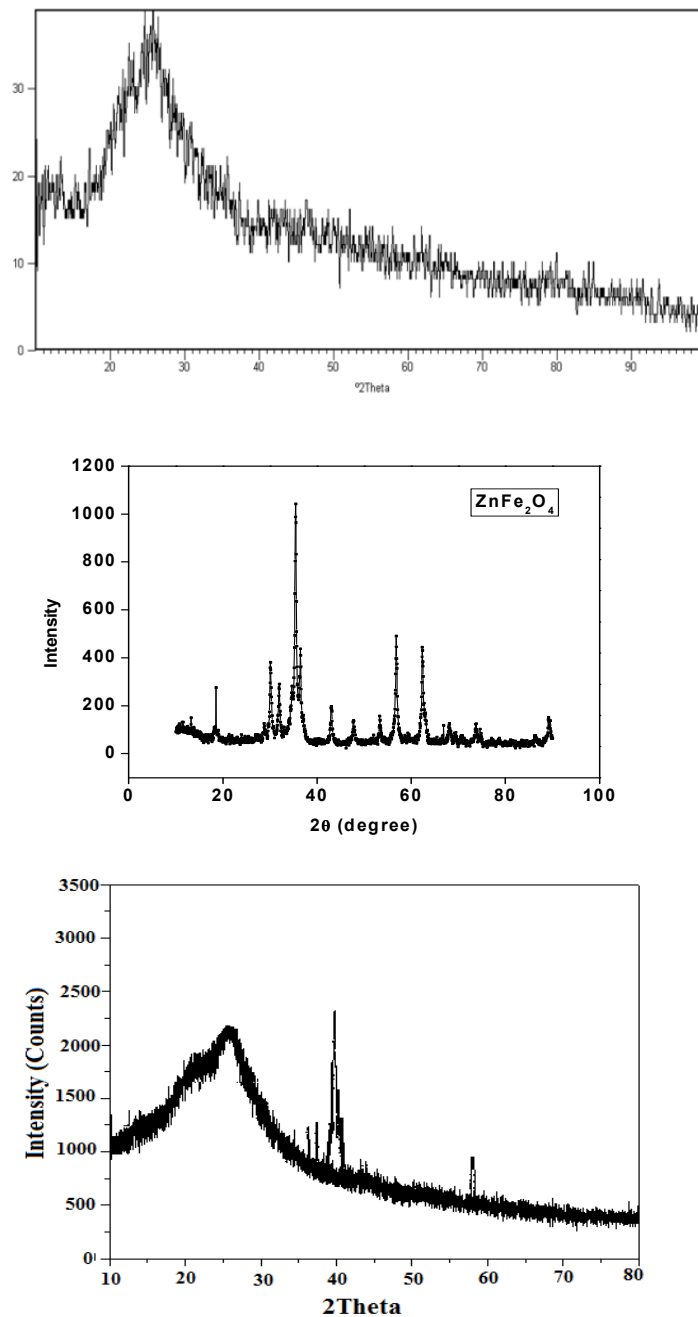


Figure.1: X-ray diffraction pattern of PANI ZnFe₂O₄, and PANI/ZnFe₂O₄ composite.

PANI/ZnFe₂O₄ composite of 25 wt. % is shown in figure 2(c). It is clearly seen that the ferrites particles are not well bonded with the polyaniline due to increasing in the percolation limit to the ratio of filler concentration of the matrix.

From the figure 2(a) to 2(c), it is found that, there is lots of change in the morphology of various wt% of ZnFe₂O₄ in PANI matrix's. The changes in the morphology were favorable for the transport mechanism in PANI / ZnFe₂O₄composites.

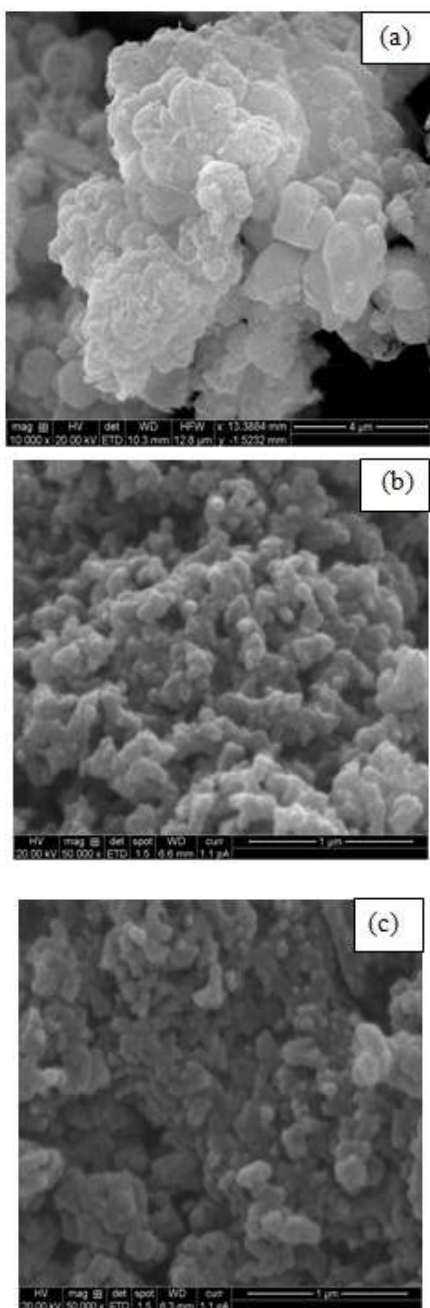


Figure.2: SEM image of (a) PANI (b) 15 wt% of PANI/ZnFe₂O₄ composite (c) 25 wt% of PANI/ZnFe₂O₄ composite.

DC Conductivity:

The conduction mechanism in poly-conjugated systems can be described by the inter chain solution and bipolar hopping. But these models cannot explicitly describe the temperature dependence of conductivity in entire temperature range. Besides, MOTT's Variable Range Hopping (VRH) mechanism is not applicable in the entire doping and temperature range. In highly doped Narmann polyacetylene, the temperature dependence of conductivity could be explained by the Ping Sheng model, even though in all poly-conjugated systems conduction is basically due to delocalized π -electrons. Due to the complicated morphology of such

systems, a unified model for conduction process is yet to be proposed.

The total conductivity is the sum of the hopping and tunneling contributions.

$$\sigma_{\text{total}} = \sigma_{\text{hopp}} + \sigma_{\text{tunn}}$$

The tunneling contribution to conductivity is dominant only at low temperatures. The intrachain and interchain hopping depends on conjugation length. It is observed in many conducting polymer systems that as the chain length increases, conductivity increases and the temperature dependence of conductivity becomes weaker.

Various expressions for temperature dependence of conductivity in different temperature regions are given below

$$\sigma(T) = \exp[-(T_0/T)^{1/4}] \text{ at higher temperature}$$

$$\sigma(T) = \exp[-(T_0/T)^{1/2}] \text{ at lower temperature}$$

For very low temperatures, the conductivity follows the relation:

$$\sigma(T) = \sigma_0 [-(T/T_0)^{-1/3}]$$

Where,

$$T_0 = 15.1 K_2 / k_B u_w \text{ and } \sigma_0 \propto f_2(\infty) u_w^2 / T$$

Where u_w is the weight average conjugation length, K_2 is a constant for each polymer depending on the oxidation potential, the reduction potential and band gap of polymer, $f_2(\infty)$ is a interchain hopping frequency per unit volume. The Mott type temperature dependence can also result from the effect of finite conjugation length on the frequency of nearest neighbor interchain hopping. The nearest neighbor hopping process with a distribution of activation energies can give same type of exponential temperature dependence for conductivity as obtained for VRH. The fit parameter T_0 is a function of conjugation length (u_w) and σ_0 is proportional to u_w^2 . The effect of conjugation length on hopping frequency depends upon the effect of conjugation length on ionization potential and electron affinity of the polymer. The value of K_2 lies between 1.5 and 4 eV/electron for known conducting polymers. The value of K_2 does not vary as a function of the doping level.

The specific electrical conductivity of a solid ' σ ' $\Omega^{-1}\text{cm}^{-1}$, is defined as the current, in amps, flowing through a centimeter cube of the material under unit electrical potential

$$\text{i.e., } \sigma = \frac{IL}{AV}$$

Where the sample length is ' L ' (cm), its area is ' A ' (cm^2), and potential is ' V ' (volts).

A typical experiment setup used for the measurement of dc conductivity consists of following components:

1. A sample holder consisting of sample, electrodes, leads and a means of securely locating the sample.
2. A means of controlling the ambient atmosphere
3. A heater capable of giving a variable but linear rate of temperature increase over a broad range of temperatures.
4. A current detector capable of measuring currents from as small as 10^{-10} A to as high as 10^{-4} A,
5. A source of controlled, low-rippled dc potential and
6. A means of recording the current and temperature such as XY recorder.

Figure 3 shows the variations of dc conductivity as a function of temperature for PANI and PANI/ZnFe₂O₄ composites in the temperature range from 40°C to 160°C. It is observed from figure 3 that the dc conductivity remains almost constant up to 80°C and thereafter it increases steadily up to 160°C, which is the characteristic behavior of semiconducting materials. At higher temperatures, conductivity is found to increase because of hopping of polarons from one localized states to another localized states. Temperature dependence of conductivity of the composites exhibits a typical semiconductor behavior and it can be expressed by the one-dimensional variable range hopping (1D-VRH) model proposed by Mott and is as follows,

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/2}]$$

$$T_0 = 8\alpha / Z N(E_F) K_B$$

where α^{-1} is the localization length, $N(E_F)$ the density of states at Fermi level, K_B the Boltzman constant and Z the number of nearest neighbor chains. It is observed that the transport mechanism observed in figure 4.3 may be due to the principal role of the polymer composites at the interface of nanosheets forming the trapping levels, further it is also due to the electron-phonon interaction.

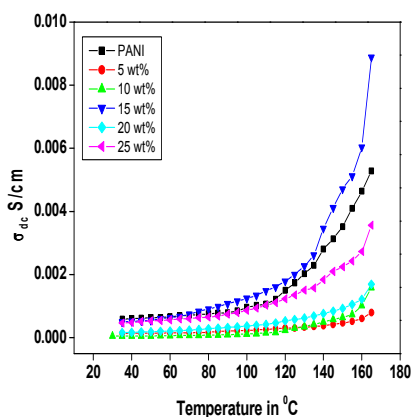


Figure.3: shows the σ_{dc} conductivity of PANI and PANI/ZnFe₂O₄ composites as function of temperature of various weight percentages.

CONCLUSION

The composites were doping ZnFe₂O₄ in polyaniline at different weight percentage using ammonium persulphate as an oxidant. The prepared composites were characterized by XRD for structural studies and SEM to studies the

morphology of the composites. The dc conductivity indicates there was a strong influence on the conductivity of small dopant added to the conducting polymer. It is observed that conductivity is increases with increase in temperature for all composites. Among all composites 15 wt% show high conductivity due to the hopping of polarons and follow the mott theory.

REFERENCES

1. Sexena V, Malhotra BD, Curr. Appl. Phys., 2003; 3: 293-305.
2. Srinivasan S, Pramanik P, Synth. Met., 1994; 63: 199-204.
3. Jing X, Wang Y, Zhang B, J. Appl. Polym. Sci., 2005; 98 (5): 2149-2156.
4. Cai Z, Geng M, Tang Z, J. Mater. Sci., 2004; 39 (12): 4001-4003.
5. Jang J, Ha J., Kim S., Macromol. Res., 2007; 15: 154-159.
6. Luzny W, Banka E, Macromolecules, 2000; 33: 425-432.
7. Kim DK, Oh KW, Kim SH, J. Polym. Sci. Part B, 2008; 46: 2255-2266.
8. Pud A, Ogurtsov N, Korzhenko A, Shapova IG., Prog. Polym. Sci., 2003; 28: 1701-1707.
9. Gangopadhyay R, De A., Chem. Mater., 2000; 12: 608-613.
10. Mittal H, Kaith B, Jindal R, Advances in Applied Science Research, 2010; 1(3): 56-66.
11. Ramaswamy V, Vimalathithan RM, Ponnusamy V. Advances in Applied Science Research, 2010; 1 (3): 197-204.
12. Igwe HU, Ugwu EI., Advances in Applied Science Research, 2010; 1 (3): 240-246.
13. Tomar AK, Mahendia S, Kumar S, Advances in Applied Science Research, 2011; 2 (3): 327-333.
14. Lanje AS, Sharma SJ, Ponde RB, Ningthoujam RS., Advances in Applied Science Research, 2010; 1 (2) 36-40.
15. Kondawar SB, Thakare SR, Khati V, Bompilwar S. J. Modern. Phys. B, 2009; 23 (15): 3297-3304.
16. Chaudhari S, Mandate, AB, Patil, KR, Sainkar, SR, Patil, PP, J. Appl. Polym. Sci., 2007; 106: 220-229.
17. Novak BM, Adv. Mater., 1993; 5: 422-433.

Source of support: Nil, Conflict of interest: None Declared