Studies on Fourier Transform Infrared Spectroscopy, Scanning Electron Microscope, and Direct Current Conductivity of Polyaniline Doped Zinc Ferrite

Ramesh Patil,[1] Aashis S. Roy,[2] Koppalkar R. Anilkumar,[3] Srikant Ekhelikar[4]

[1]*Department of Physics, Dr. Babasaheb Ambedkar Marthwada University, Aurangabad, Maharashtra, India*
[2]*Department of Materials Science, Gulbarga University, Gulbarga, Karnataka, India*
[3]*Department of Physics, Materials Research Lab, S.S. Margol College, Shahabad, Gulbarga, Karnataka, India*
[4]*Materials Research Lab, Department of Physics, N.V. Degree College, Gulbarga, India*

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ABSTRACT: *In situ* polymerization of aniline was carried out in the presence of zinc ferrite to synthesize polyaniline/$ZnFe_2O_4$ composites (PANI/$ZnFe_2O_4$) by chemical oxidation method. The composites have been synthesized with various compositions (10, 20, 30, 40, and 50 wt %) of zinc ferrite in PANI. From the Fourier transform infrared spectroscopy (FTIR) studies on polyaniline/$ZnFe_2O_4$ composites, the peak at 1140 cm^{-1} is considered to be measure of the degree of electron delocalization. The surface morphology of these composites was studied with scanning electron micrograph (SEM). The dc conductivity has been studied in the temperature range from 40–160°C and supports the one-dimensional variable range hopping (1DVRH) model proposed by Mott. The results obtained for these composites are of scientific and technological interest. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 262–266, 2011

Key words: polyaniline; zinc ferrite; composites; conductivity

INTRODUCTION

Polymers have become increasingly attractive because of its large number of applications in applied and basic science. Conductive polymer composite (CPC) materials result from the mixture of conductive particles dispersed in an insulating phase. The filler is usually a metal powder, carbon black, fiber of carbon black, metal fibers, etc and the insulating phase can be a thermosetting resin, thermoplastic, elastomer, etc. The composite material combines both the intrinsic properties of the fillers (mechanical, electrical, magnetic, and thermal) and of the matrix (elasticity, easy to manipulate, low cost). The various conductive properties of CPC have allowed them to find a variety of industrial applications. They are used, for example, as protection devices against electromagnetic radiation and for the dissipation of electrostatic discharge[1]; they are used in microelectronics as electrical conductive adhesive for electrical connections.[2] The control of the conductivity of CPC is also interesting for applications including sensor, electrochromic devices, corrosion inhibitors, electrochemical actuators, electromagnetic shielding, polymeric batteries, etc.[3,4] The conductivity of these composites depends strongly on the nature and interaction of the filler with the polymeric matrix. Cobalt metal was selected as filler due to its interesting electric and magnetic properties, since it may exist in different structural forms i.e., tetrahedral, octahedral, and isolated forms.[5]

This article focuses on the effect of $ZnFe_2O_4$ addition on structural and transport properties of polyaniline.

EXPERIMENTAL

Synthesis of PANI/$ZnFe_2O_4$ composites

Aniline (AR grade) was purified by distillation before use and ammonium per sulfate [$(NH_4)_2S_2O_8$)], HCl were used as received. 0.1 mol aniline monomer is dissolved in 1 mol hydrochloric acid to form polyaniline. Fine graded pre-sintered $ZnFe_2O_4$ (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 10, 20, 30, 40, and 50 is added to the polymerization mixture with vigorous stirring to keep the $ZnFe_2O_4$ powder suspended in the solution. To this reaction mixture, [$(NH_4)_2S_2O_8$)], which is used as an oxidant, is added slowly drop-wise with continuous vigorous stirring for the period of 4 h at temperature 5°C. Polymerization of aniline takes place over fine grade zinc ferrite particles. The resulting precipitate is filtered under suction and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any unreacted aniline.

Correspondence to: S. Ekhelikar (shrikant_ek@yahoo.com).

After washing, the precipitate is dried under dynamic vacuum at 60°C for 24 h to get resulting composites. In this way five different polyaniline/ $ZnFe_2O_4$ composites with different weight percentage of zinc ferrite (10, 20, 30, 40 and 50) in polyaniline have been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium. The composite powder is pressed to form pellets of 10 mm diameter and thickness varies from 2 to 2.5 mm. The electrical measurements on these samples were made using the silver paint as electrodes on both sides.

Infrared spectroscopy

The IR spectra of all the samples are recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording IR spectra, polyaniline and polyaniline composites were mixed with KBr in the ratio 1 : 25 by weight to ensure uniform dispersion. The mixed powders are pressed in a cylindrical dye to obtain clean discs of ~ 1 mm thickness.

Scanning electron microscopy

The surface morphology of PANI/$ZnFe_2O_4$ composites has been studied by employing Scanning Electron Microscopy (SEM) Model: Phillips XL 30 ESEM.

RESULTS AND DISCUSSION

Fourier transmission infra spectroscopy

The Fourier transform infrared spectroscopy (FTIR) spectra measurement was carried out to study the molecular structure of the polyaniline and polyaniline/$ZnFe_2O_4$ composites.

Figure 1(a) shows the FTIR spectra for pure Polyaniline. The characteristic absorption peaks are found to be at 2922 cm^{-1} is due to the C—H stretching, 1566 cm^{-1} is corresponds to C=C stretching quinoid ring, 1548 cm^{-1} for C=N bond stretching, 1494 cm^{-1} is corresponds to stretching vibration of benzonide ring, 1406 cm^{-1} is the characteristic vibration mode of C—H bonding of aromatic nuclei, 1302 cm^{-1} is assigned to the stretching of C—N bonds of aromatic amines, 1140 cm^{-1} is an strong band, which considered to be measure of the degree of electron delocalization 796 cm^{-1} corresponding to the N—H out of plane bending in rocking mode. 734 cm^{-1} and 684 cm^{-1} are due to the out of plan blending of C—H bond in aromatic ring, respectively.

Figure 1(b–f) shows the FTIR spectra of of polyaniline/$ZnFe_2O_4$ composites at different percentage (10, 20, 30, 40, and 50 wt %). The absorption peaks are found to be at 3441 is correspond for N—H stretching vibration, 1581 cm^{-1} is corresponds to C=C stretching vibration of quinoid ring, 1481 cm^{-1} is corresponds to stretching vibration of benzenoid ring, 1300 cm^{-1} is for the stretching of C—N bonds of aromatic amines, 1240 cm^{-1} for the C—N stretching of benzenoid ring, 1140–1145 cm^{-1} is correspond to C—H in plane of aromatic rings is found to be an strong band, which considered to be measure of the degree of electron delocalization, and other bands like 802, 738, and 686 cm^{-1} are due to the out of plan blending of C—H bond in aromatic ring, respectively. The samples show characteristic absorptions bands of Zinc ferrite, the absorptions bands at 507 cm^{-1} is due to the intrinsic vibration of Zn^{+2}, which is present in tetrahedral positions and around 415 cm^{-1} is corresponds to the vibration of octahedral group of $Fe^{+3}O^{-2}$, which confirm the formation of the polyaniline/Zinc ferrite composites.

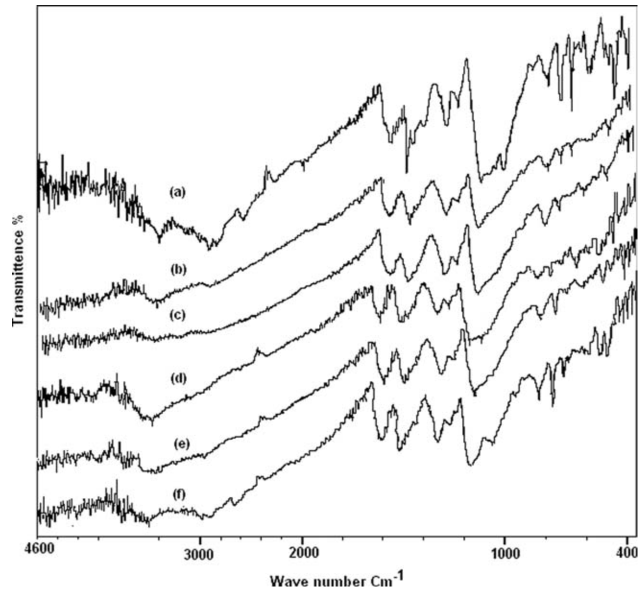

Figure 1 (a–f) Shows the FTIR spectra for pure polyaniline and polyaniline $ZnFe_2O_4$ composites.

Figure 2(a) shows that SEM image of pure Polyaniline highly agglomerated granular in shape and has amorphous nature. The average grain size was found to be 2–4 μm. The grains are well interconnected with each other, which indicate that they have enough binding energy to combine with neighbor grains or molecules.

Figure 2(b) show the SEM of 10 wt % of PANI/ $ZnFe_2O_4$ composite were highly agglomerated cube like structure are seen. The crystallinity of the $ZnFe_2O_4$ decreases with the addition of PANI in it. It is clearly observed that ferrites were homogeneously distributed throughout polyaniline matrix. The average grain size is found to be 600 nm.

PANI/$ZnFe_2O_4$ composite of 20 wt % is shown in Figure 2(c). The composite is highly clustered,

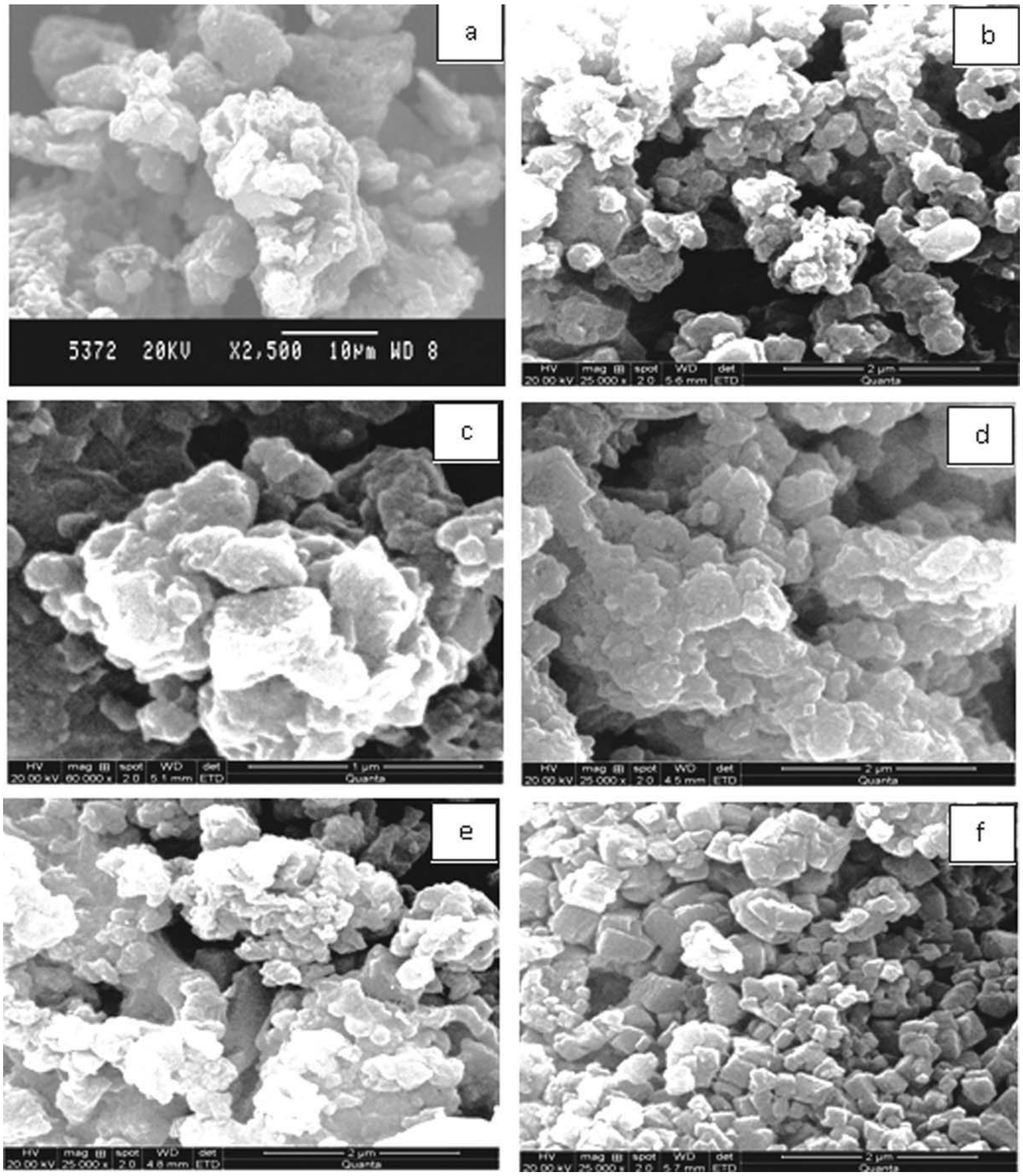

Figure 2 (a–f) Shows SEM image of pure polyaniline and polyaniline/$ZnFe_2O_4$ composites.

spherical in shape, and have interlinked to each other which decreases the intergranular distance. The decrease in the intergranular distance between the grains helps to the charge transfer mechanism from one grain to another grain. The average grain size is found to be 1.5 μm.

Figure 2(d) show the 30 wt % of PANI/$ZnFe_2O_4$ composite is highly crystalline granular flake like networking structure arranged in soccer shape is well interlinked between each other. The average grain size is found to be 230–340 nm.

Figure 2(e) show that the 40 wt % of PANI/$ZnFe_2O_4$ composite is highly agglomerated and spherical in shape of about 0.5 μm in granular size.

PANI/$ZnFe_2O_4$ composite of 50 wt % is shown in Figure 2(f). 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–f), it is found that, there is lots of change in the morphology of various wt % of $ZnFe_2O_4$ in PANI matrix's. The changes in the

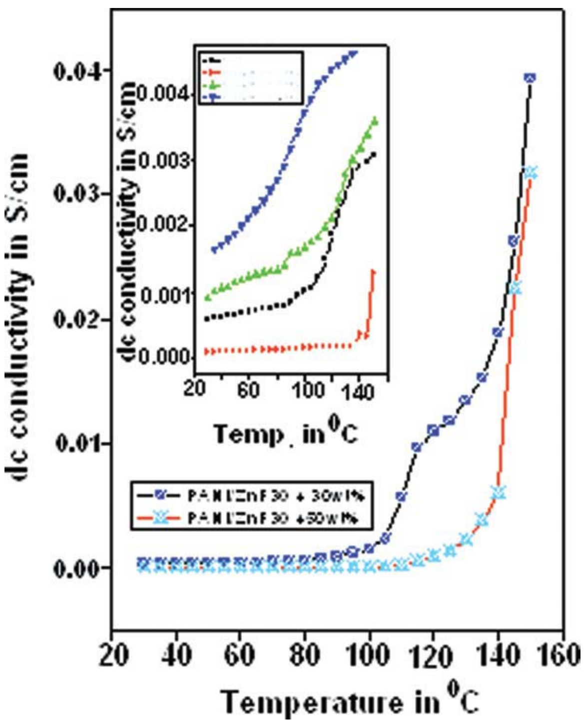

Figure 3 Shows the variations of dc conductivity as a function of temperature for PANI and PANI/$ZnFe_2O_4$-composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

morphology were favorable for the transport mechanism in PANI/$ZnFe_2O_4$composites.

DC conductivity

Figure 3 shows the variations of dc conductivity as a function of temperature for PANI and PANI/$ZnFe_2O_4$ composites in the temperature range from 40 to 200°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 Davis[6] 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 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.[7]

Figure 4 shows the variation of dc conductivity as a function of wt % of $ZnFe_2O_4$ in PANI at different temperatures. It can be observed that in all the composites the conductivity increase with respect to temperature forming multiple phases of conductivity. It can be seen that the value of conductivity increases up to 30 wt % of $ZnFe_2O_4$ in PANI and then decreases there after. This may be due to the extended chain length of PANI, which facilitates the hopping of charge carriers when the content of $ZnFe_2O_4$ is up to 30 wt %. This point is a percolation threshold and the composites obey percolation theory. Further the decrease in conductivity is observed after 30 wt %, which may be attributed due to the distribution of $ZnFe_2O_4$ particles of larger grain size, which are partially blocking the hopping of charge carriers, since charge trapping in PANI, and its blends is a general universal feature of these materials.[8,9]

CONCLUSIONS

Polyaniline composites with different weight percentages of $ZnFe_2O_4$ in PANI were synthesized by chemical oxidative polymerization of monomer aniline. Characterizations of the composites were

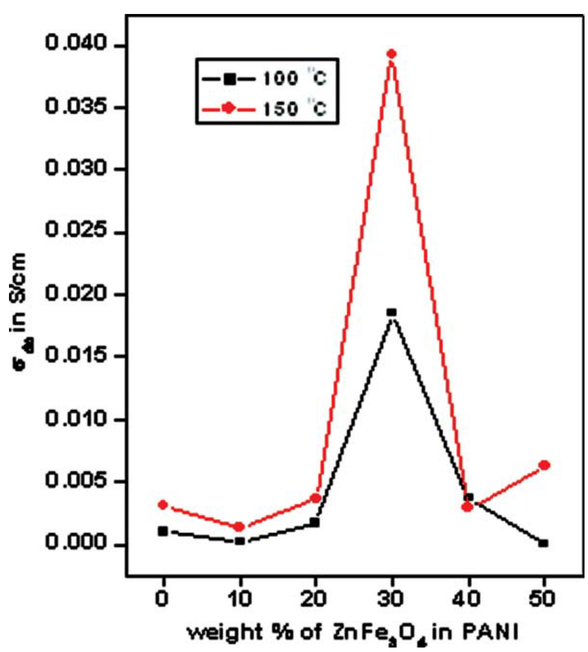

Figure 4 Shows the variation of dc conductivity as a function of wt % of $ZnFe_2O_4$ in PANI at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

carried out using IR and SEM techniques. From the FTIR studies on polyaniline/$ZnFe_2O_4$ composites, the peak at 1140 cm^{-1} is considered to be measure of the degree of electron delocalization and also the Vander walls interaction between polymer and Zinc ferrite. The results of dc conductivity show a strong dependence on the weight percent of $ZnFe_2O_4$ in polyaniline. At higher temperatures, conductivity (σ_{dc}) increases because of hopping of polarons from one localized states to another localized states. It is observed from the electrical conductivity studies that the 30 wt % of $ZnFe_2O_4$ in the polymer matrix shows the enhancement of the conductivity of the conducting polyaniline and their values are found to be in the semiconducting range.

References

1. Kumar, G. N. H.; Rao, J. L.; Gopal, N. O.; Narasimhulu, K. V.; Chakradhar, R. P. S.; Rajulu, A. V. Polymer 2004, 45, 5407.
2. Michaeli, W.; Pfefferkorn, T. G., Polym Eng Sci 2009, 49, 1511.
3. Bard, W. S.; Pakade, S. V.; Yawale, S. P. J Non-Cryst Solids 2007, 353, 1460.
4. Bhargav, P. B.; Mohan, V.; Sharma, A. K.; Rao, V. V. R. Current Appl Phys 2009, 9, 165.
5. Abdelaziz, M.; Abdelrazek, E. M. Phys B 2004, 349, 84.
6. Mott, N. F.; Davis, E. A. Electronic processes in nanocrystalline materials; Clarendon Press: Oxford, UK, 1979.
7. Tkaczyk, S. W.; Kityk, I. V.; Schiffer, R. J Phy D Appl Phys 2002, 35, 563.
8. Prakash, R. S.; Marimuthu, R.; Mandale, A. B. Polymer 2001, 42, 261.
9. Anilkumar, R. K.; Parveen, A.; Badiger, G. R.; Ambika Prasad, M. V. N. Physica B 2009, 404, 1664.