

Synthesis, Characterization and DC Conductivity of PANI/ZnFe₂O₄ Composites

Ajai Kumar S. Molakeri¹, Sangshetty Kalyane²Assistant Professor, Department of Physics, Guru Nanak Dev Engineering College, Bidar, Karnataka, India¹Associate Professor, Department of Physics, Bhemanna Khandre Institute of Technology, Bhalki, Karnataka, India²

ABSTRACT: The polyaniline-zinc ferrite (PANI/ZnFe₂O₄) composites have been prepared by an interfacial polymerization using ammonium persulphate as an oxidizing agent. The composites have been synthesized with different weight percentage (10, 30 and 50 wt %) of ZnFe₂O₄ in PANI. The composites are characterized by various methods such as Fourier transform infrared spectra (FTIR) and the dominant peaks confirmed the formation of PANI/ZnFe₂O₄ composites, X-ray diffraction (XRD) indicated the dispersion of ZnFe₂O₄ in PANI and scanning electron microscopy (SEM) images indicated morphological variation of particles aggregated in the composite as compared to the PANI. The temperature dependent DC conductivity of PANI/ ZnFe₂O₄ composites has been studied in the temperature range 30-160°C and supports the one-dimensional variable range hopping model proposed by Mott. The results of PANI/ ZnFe₂O₄ indicate interaction of PANI with ZnFe₂O₄ in the composites.

KEYWORDS: Polyaniline, Temperature, DC conductivity, Zinc ferrite, Composites.

I. INTRODUCTION

Intrinsically conducting polymers, also known as “synthetic metals”, are polymers with a highly π -conjugated polymer chain [1-3]. For the discovery of conducting polymers, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa were awarded the Nobel Prize in chemistry in 2000. Typical conducting polymers include polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly(para-phenylene) (PPP), poly(phenylenevinylene) (PPV), polyfuran (PF) etc., [4]. Among conducting polymers, polyaniline has become a particular focus of interest because of its environmental stability, controllable electrical conductivity [5]. The synthesis of polyaniline is very simple, properties can be tuned easily and it has numerous application possibilities [6]. Polyaniline has attracted considerable attention since then to prepare composites by incorporating inorganic particles like Nb₂O₅ [7], BaTiO₃ [8], V₂O₅ [9], TiO₂ [10], ZrO₂ [11], CdO [12], ZnWO₄ [13], NaVO₃ [14], inorganic salts [15] etc., Polyaniline-inorganic particle composites studied for applications as electro-rheological fluids [16] and in high density information storage devices [17] have been studied. In this paper authors report the synthesis, characterization and DC conductivity of polyaniline-zinc ferrite (PANI/ ZnFe₂O₄) composites.

II. EXPERIMENTAL DETAILS

MATERIALS AND METHODS

All the chemicals used were of AR grade. Double distilled water was used throughout the work. As prepared zinc ferrite is used for preparation of polyaniline composites. Ammonium persulphate was purchased from Qualigens. Aniline was double distilled before use and HCl was purchased from Aldrich chemicals. Zinc ferrite was synthesized by combustion route.

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SYNTHESIS OF PANI

The synthesis of PANI was based on mixing aqueous solutions of aniline hydrochloride and ammonium persulphate at room temperature, followed by the separation of polyaniline hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equimolar volumes of aniline and hydrochloric acid) was dissolved in double distilled water in a volumetric flask to 100 ml of solution. Ammonium persulphate (0.25M) was dissolved in water also to 100 ml solution. Both solutions were kept for 1 hour at room temperature (25°C), then mixed in a beaker, stirred mechanically and left at rest to polymerize. After 24 hours the PANI precipitate was collected on a filter, washed with portions of 0.2M HCl and similarly with acetone. PANI (emeraldine) hydrochloride powder was dried in air and then vacuum at 60°C to achieve a constant mass.

SYNTHESIS OF PANI/ZnFe₂O₄ COMPOSITES

PANI/ ZnFe₂O₄ composites were prepared with different weight percentage of ZnFe₂O₄ (10, 30 and 50%). One gram of aniline was dissolved in 40 ml of CHCl₃. 0.1M ammonium persulphate is dissolved in 1M HCl and the as prepared zinc ferrite is slowly added to the above mixture of aqueous phase and organic phase. After few minutes, darkgreen precipitate formed slowly at the interface and then gradually diffused into the aqueous phase. After 24 hours, the entire aqueous phase was filled homogeneously with darkgreen colour film, organic layer observed shows orange colour due to formation of aniline oligomers. The aqueous phase was then collected, washed with ethanol and water to remove the unreacted aniline. The residue of polymer thus obtained is purified and dried in vacuum oven at 40°C for 36 hours. The dried PANI/ZnFe₂O₄ composite sample is used for structural characterization.

PREPARATION OF PELLETS

The powders of polyaniline and PANI/ ZnFe₂O₄ composites so obtained are crushed finely in the presence of acetone medium in agate mortar. This powder is pressed to form pellets of 10 mm diameter and thickness varying from 1 to 2 mm by applying a pressure of 90 MPa in a hydraulic press. The pellets of PANI and its composites are coated with silver paste on either side of the surfaces to obtain better contacts.

CHARACTERIZATION

The FTIR spectra of all the samples were recorded on a ThermoNicolet, Avatar 370 spectrometer in KBr medium at room temperature. The XRD patterns were recorded on a X-ray diffractometer, Bruker AXS D8 Advance using CuK α radiation ($\alpha = 1.5418\text{\AA}$) in the 2θ range 20-80°. The surface morphology of the samples was investigated by scanning electron microscope Joel Model JSM-6390LV. The temperature dependence DC conductivity for the samples in a temperature range between 30-160°C were performed using a Keithley-6514 system electrometer.

III. RESULTS AND DISCUSSION

FOURIER TRANSFORM INFRARED SPECTROSCOPY

The molecular structure of the PANI and PANI/ ZnFe₂O₄ composites can be studied by FTIR spectra measurement. Figure 3.1 a shows FTIR spectra for pure polyaniline. The characteristic absorption peaks are found to be at 3425 cm⁻¹ is due to C-H stretching vibration, 1564 cm⁻¹ corresponds to C=C stretching of quinoid ring, 1478 cm⁻¹ corresponds to C=N bond stretching, 1478 cm⁻¹ corresponds to stretching vibration of benzenoid ring, 1301 cm⁻¹ corresponds to stretching vibration mode of C-H bonding of aromatic nuclei, 1244 cm⁻¹ corresponds to the stretching of C-N bonds of aromatic amines, 1137 cm⁻¹ considered to be the measure of degree of electron delocalization, 707 cm⁻¹ corresponds to the N-H out of plane bending 702 cm⁻¹ corresponds to the out of bending of C-H bond in aromatic ring respectively

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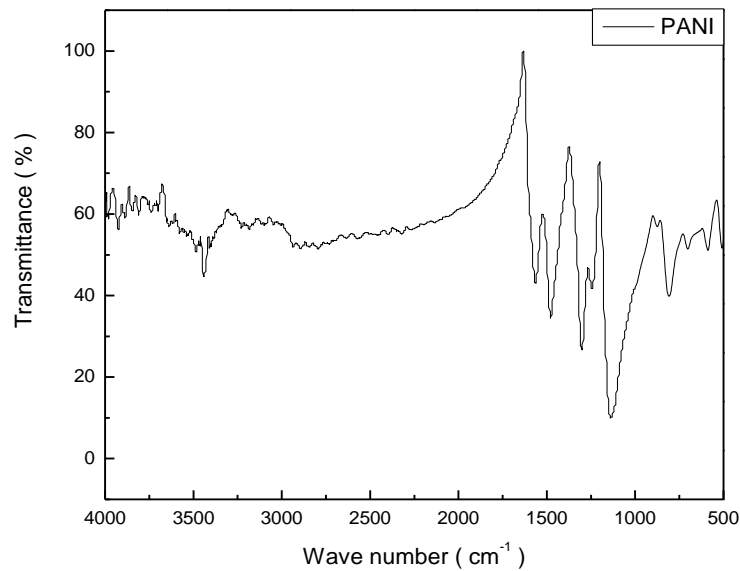


Figure 3.1 a FTIR spectra of pure PANI

. The characteristic peaks appears at 1564 cm^{-1} due to C=C stretching of quinoid rings, 1478 cm^{-1} due to stretching of the benzenoid ring, which confirms the formation of polyaniline.

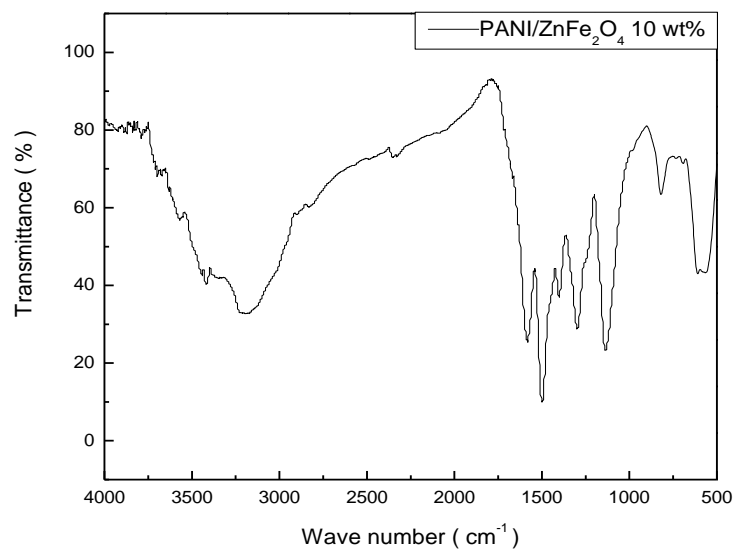


Figure 3.1 b FTIR spectra of PANI/ZnFe₂O₄ (10 wt%) composite

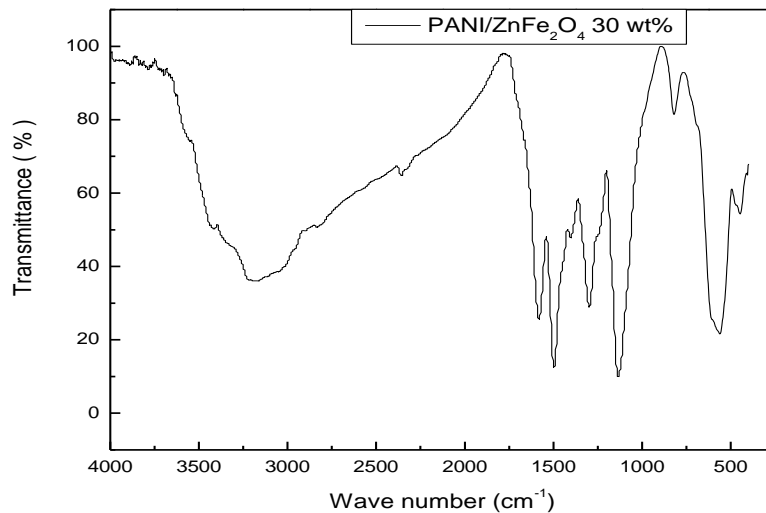


Figure 3.1 c FTIR spectra of PANI/ZnFe₂O₄ (30 wt%) composite

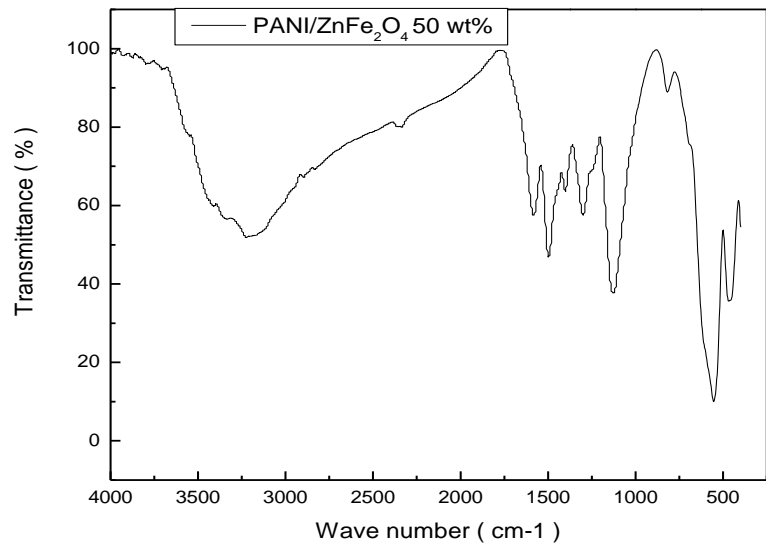


Figure 3.1 d FTIR spectra of PANI/ZnFe₂O₄ (50 wt%) composite

Figure 3.1 b-3.1 d shows FTIR spectra of PANI/ZnFe₂O₄ composites at different weight percentage (10, 30 and 50 wt%).The absorption peaks are found to be at 3195 cm⁻¹,3164 cm⁻¹ and 3224 cm⁻¹ corresponds to N-H stretching vibration, 1579 cm⁻¹, 1579 cm⁻¹ and 1583 cm⁻¹ corresponds to C=C stretching vibration of quinoid ring,1498 cm⁻¹,1479 cm⁻¹ and 1498 cm⁻¹ corresponds to stretching vibration of benzenoid ring, 1297 cm⁻¹, 1298 cm⁻¹ and 1299 cm⁻¹ corresponds to stretching of C-N bonds of aromatic amines,1136 cm⁻¹,1135 cm⁻¹ and 1128 cm⁻¹ corresponds to C-H in plane of aromatic rings, other bands 819 cm⁻¹, 819 cm⁻¹ and 817 cm⁻¹ are corresponds C-H bond in aromatic ring due to the out of plan bending respectively.The composites show characteristic absorption bands of ZnFe₂O₄, the absorption bands 608 cm⁻¹, 561 cm⁻¹ and 553 cm⁻¹ and 575 cm⁻¹, 447 cm⁻¹ and 467 cm⁻¹, which confirms the formation of PANI/ZnFe₂O₄ composites of PANI/ZnFe₂O₄ of 10 wt%, 30 wt% and 50 wt% respectively.

X-RAY DIFFRACTION ANALYSIS

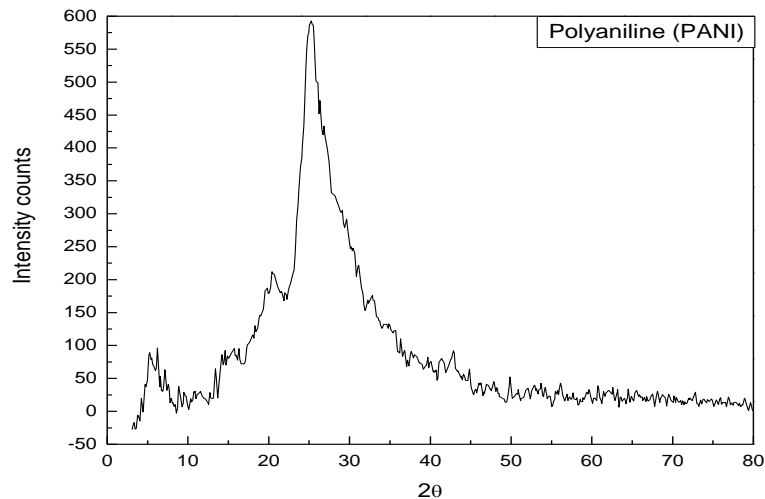


Figure 3.2 a XRD pattern of pure PANI

Figure 3.2 a shows the XRD spectra of PANI. The XRD pattern of PANI shows two broad peaks observed at 20° and 25.3° are similar to other research groups.

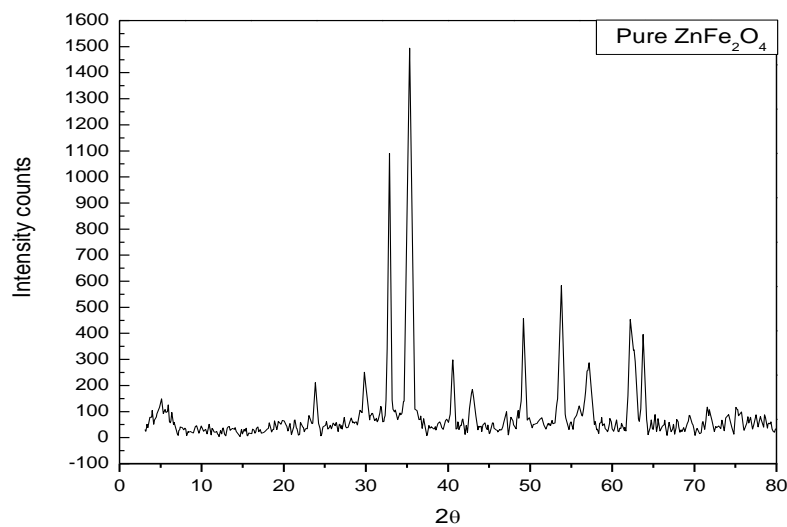


Figure 3.2 b XRD pattern of ZnFe₂O₄ particles

Figure 3.2 b shows the XRD spectra of pure ZnFe₂O₄ indicates the crystalline nature, the prominent peaks corresponding to 2θ are 32.85°, 35.32°, 40.58°, 53.81° and 63.75° are due to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes respectively.

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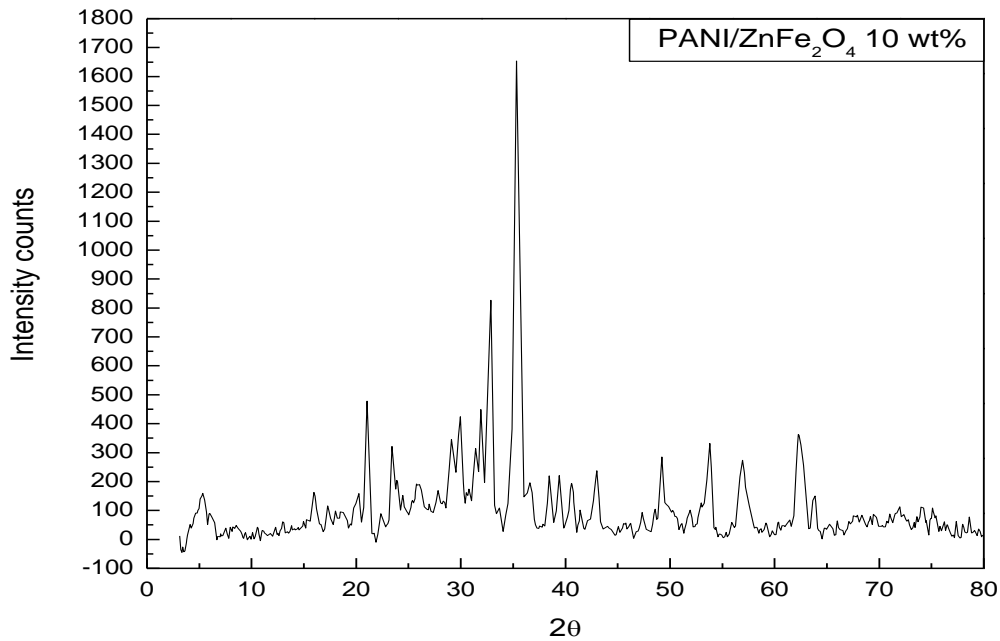


Figure 3.2 c XRD pattern of PANI/ZnFe₂O₄ (10 wt%) composite

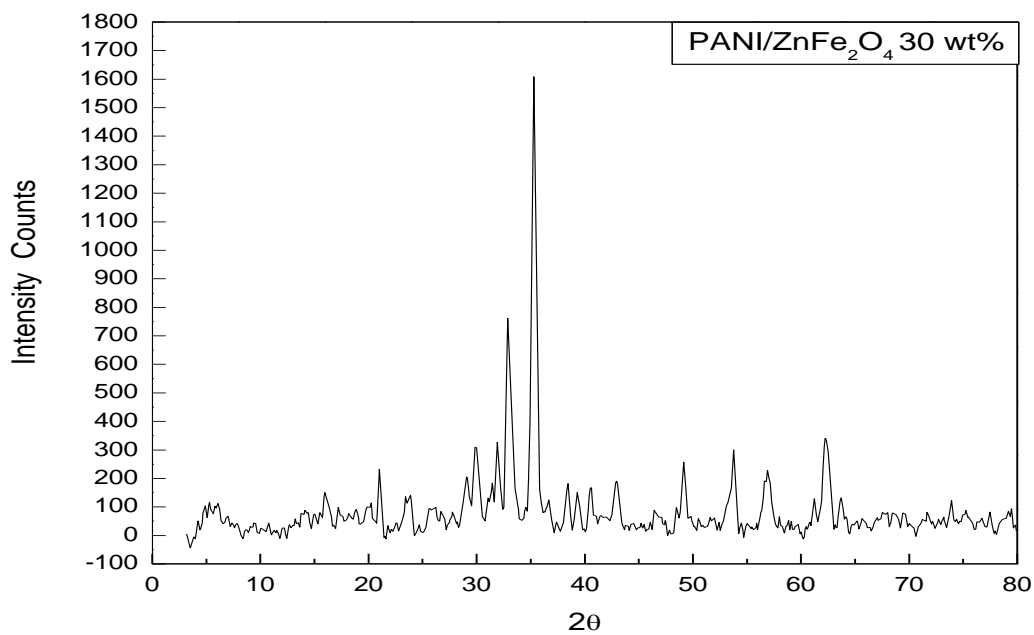


Figure 3.2 d XRD pattern of PANI/ZnFe₂O₄ (30 wt%) composite

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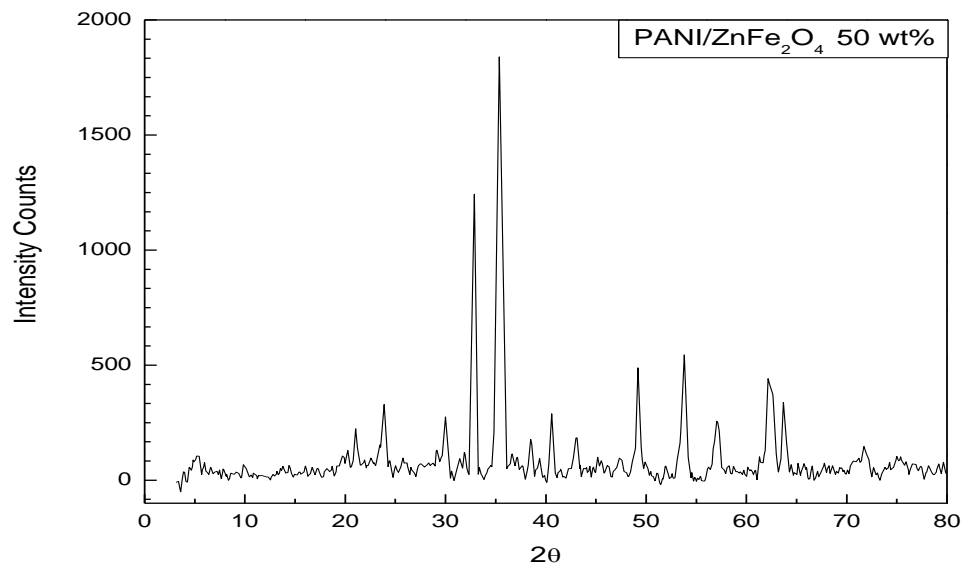


Figure 3.2 e XRD pattern of PANI/ZnFe₂O₄ (50 wt%) composite

Figure 2c-2e shows the XRD spectra of PANI/ ZnFe₂O₄ composites, by comparing the XRD pattern of the composites and that of PANI, it is confirmed that ZnFe₂O₄ is dispersed in PANI during polymerization reaction

SCANNING ELECTRON MICROSCOPY

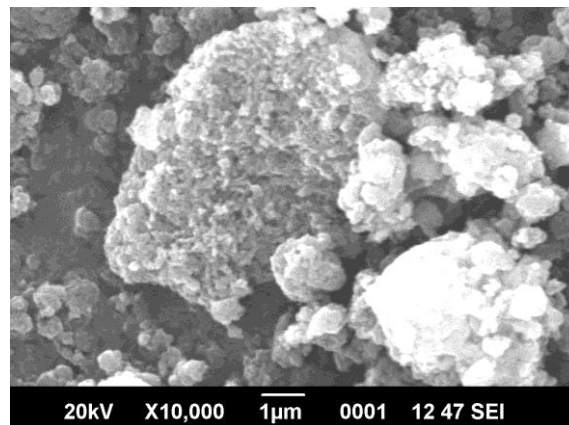


Figure 3.3 a SEM image of pure polyaniline

Figure 3.3 a shows that scanning electron micrograph image of pure polyaniline. The highly agglomerated granular in shape and has amorphous nature. The average grain size is found to be 2-5µm.

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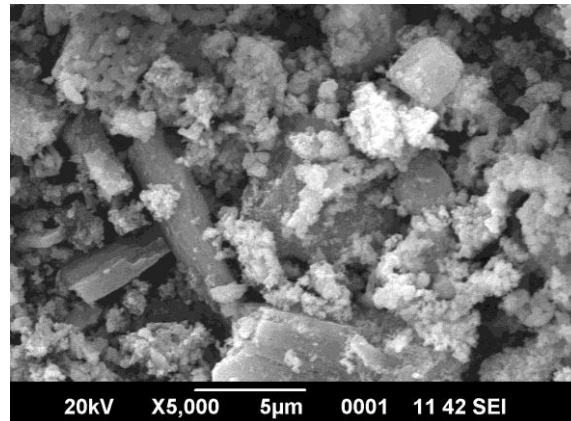


Figure 3.3 b SEM image of pure $ZnFe_2O_4$ particles

Figure 3.3 b shows SEM image of pure $ZnFe_2O_4$ particles, the particles are highly crystalline and roughly spherical in nature. The average grain size is found to be 200 nm to 400nm.

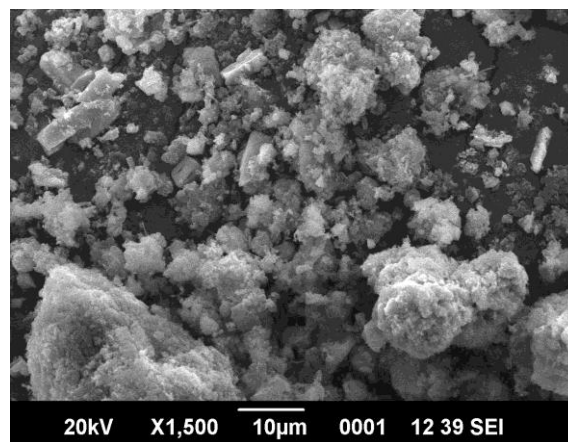


Figure 3.3 c SEM image of PANI/ $ZnFe_2O_4$ composite (30 wt%)

Figure 3.c shows SEM image of PANI/ $ZnFe_2O_4$ (30 wt%) composite, the image shows a highly crystalline and spherical nature of the composites. The average grain size is found to be 400 nm to 500 nm .From the figures 3.3 a-3.3 c it is found that, there is change in the morphology due to various weight percentage of $ZnFe_2O_4$ in PANI matrix's. The change in the morphology is favorable for the transport mechanism in PANI/ $ZnFe_2O_4$ composites.

DC CONDUCTIVITY

Figure 3.4 a shows the variation of DC conductivity ' σ_{dc} ' as a function of temperature for PANI and figure 3.4 b shows that for PANI/ $ZnFe_2O_4$ composites in the temperature range from 30°C to 160°C. From the figures it is observed that the DC conductivity remains almost constant up to 45°C and thereafter it increases with an increase in temperature 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. The conductivity varies directly with temperature, according to an expression proposed by Mott[18] and is as follows,

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

Where σ is the conductivity, T is the temperature, σ_0 is the conductivity at the characteristic temperature T_0 . It is observed that the conductivity increases for 30 wt% of $ZnFe_2O_4$ in PANI. This is due to the hopping of charge carriers from one localized states to another localized states and decreases for 50 wt% of $ZnFe_2O_4$ in PANI due to partial blocking of charge carriers.

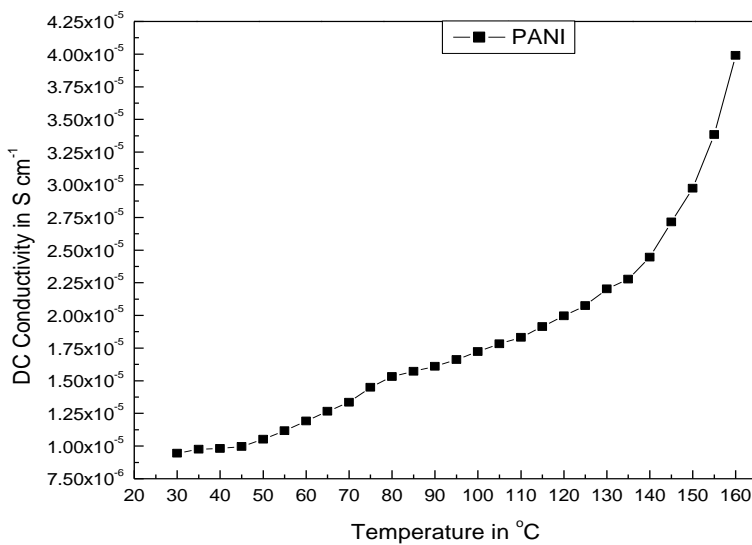


Figure 3.4 a Variation of DC conductivity with temperature of pure PANI

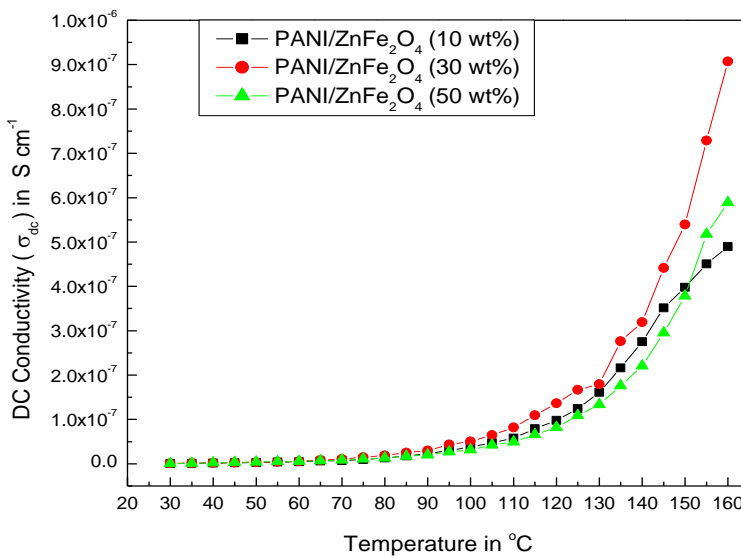


Figure 3.4 b Variation of DC conductivity with temperature of PANI/ $ZnFe_2O_4$ composites

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IV. CONCLUSION

The PANI/ZnFe₂O₄ composites with different weight percentages of ZnFe₂O₄ in PANI were synthesized by interfacial polymerization. Detailed characterizations of the composites were carried out using the techniques such as FTIR, XRD and SEM. The results of XRD and SEM reveals that the crystalline nature of the PANI/ZnFe₂O₄ composites. FTIR spectra of the composites show the characteristic absorption bands of ZnFe₂O₄ at 608 cm⁻¹, 561 cm⁻¹, 553 cm⁻¹ and 575 cm⁻¹, 447 cm⁻¹, 467 cm⁻¹, which confirms the formation of PANI/ZnFe₂O₄ composites. The DC conductivity as a function of temperature for PANI and PANI/ZnFe₂O₄ composites was studied in the temperature range from 30°C-160°C. At higher temperatures, DC conductivity increases because of hopping of polarons from one localized state to another localized state. The DC conductivity of the composites increases with an increase in temperature, which is characteristic behavior of semiconducting materials.

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