CONDUCTIVITY AND THERMAL STABILITY OF PANI- Fe_2O_3 COMPOSITES SYNTHESIZED BY EX SITU POLYMERIZATION TECHNIQUE

Vijayalaxmi Reddy[1], Mahadevi Konin[1], Nirdosh Patil[*] and Anilkumar Bidve[1]
[1]Department of Physics, Appa Institute of Engineering and Technology, Kalaburagi, Karnataka-585 103 India
[*]Department of Chemistry, Appa Institute of Engineering and Technology, Kalaburagi, Karnataka-585 103 India

***Abstract:** In the present work we report the synthesis of PANI-Fe2O3 composites by ex situ polymerization technique. The Fe2O3 content in the composites was varied from 10 to 50 wt%. Morphological and structural characterization of the synthesized composites was carried out using scanning electron microscope and X-ray diffraction technique. The AC conductivity and dielectric constant of composites were studied as a function of frequency. With the increase in Fe_2O_3 content in composites from 10% to 50% the conductivity is found to increase at higher frequencies. The dielectric constant measurements showed that with the increase in Fe_2O_3 concentration the dielectric constant was found to be increasing and was highest for composite with 50% Fe_2O_3 content.*

***Keywords:** X-ray Diffraction, Dielectric, Conductivity, SEM.*

I .INTRODUCTION:

For wide variety of electronic and electric applications, conducting polymers with five membered heterocycles such as polyacetalene and polyaniline are quite popular as they can be substitute for semiconductors and conductors. Out of all these conducting polymers, polyaniline(PANI) is quite popular because of its ease in synthesis, good environmental stability, availability in film form and reversibility. Along with these properties this conducting polymer has very good electrical conductivity and its low cost make it probable candidate for many applications. Because of its low density, low operational voltage and high conductivity make PANI a good candidate material for actuator applications. These properties of PANI are mainly due to their unique structure composed of alternate arrangement of benzene ring and nitrogen atoms [1]. The polymer composites are synthesized by two general techniques which include direct compounding or known as ex situ and in situ technique. The PANI is usually synthesized by using either chemical or electrochemical techniques such as in situ polymerization [2], solution blending [3] or dispersion technique [4]. It is well known that PANI has three stable oxidation states which are referred as leucoemeraldine (fully reduced state), pernigraniline form (fully oxidized state) and emeraldine (partially oxidized state). Here the emeraldine base can be doped with protonic acid to obtain emeraldine salt whose conductivity can be increased by charge delocalization by doping with H^+. However PANI alone cannot be used for many applications and in order to use it, it must be incorporated with metal or metal oxide particles.

It is well known that the conductivity of PANI and its composites can be tuned with various dopants to meet the requirements of an application. In order to obtain better properties of PANI, metal and metal oxide particles are incorporated in many works. By incorporating such particles in PANI can be used in anticorrosion coatings, lithium ion batteries, electromagnetic shielding and dye sensitized solar cells [5-7]. On the other hand metal oxide particle like Fe_2O_3 are quite popular due to their electrochemical, magnetic and photo catalytic properties. It is available in large quantity at very low cost and is nontoxic in nature. This metal oxide is used as chemical sensors to detect the toxic gases as well as other gases like liquid petroleum gases and hydrogen. Apart from these, ferrite particles are added to conducting polymers so that the resulting composite material will have both electrical and magnetic properties. Likewise lot of work has been carried out on development of composites based on Fe_2O_3 and PANI for gas sensing and drug carrier applications. In addition to this PANI composites composing of ferrite particles are also being tried out for microwave shielding applications.

Much attention has been paid on development of PANI-Fe_2O_3 composites keep various properties like electrical, drug carrier and gas sensing properties in mind. In their work, Bashir et al [8] developed the polyaniline-Fe_2O_3 nanocomposites by chemical oxidative polymerization technique by varying the content of Fe_2O_3 from 5 and 30%.The X-ray diffraction analysis of $Fe_2O_3$and polyaniline-Fe_2O_3 showed an average size of 25 and 31 nm respectively. The dispersion of Fe_2O_3in PANI was uniform and had regular shape with an average size of 29-33 nm. Further the electrical conductivity of composites was found to be increasing with increase Fe_2O_3content up to 5% while it started decreasing beyond that. The increase in conductivity was attributed to alignment of PANI chains on the surface of Fe_2O_3 particles. Li et al [9] studied the gas sensing properties and sensing mechanism of Fe_2O_3/PANI nanocomposite. Initially the Fe_2O_3nanosheets were synthesized by combined method of electrospinning and hydrothermal techniques which was followed by coating these sheets with PANI. The developed composite displayed better response magnitude for NH3 concentration of as low as 0.5-10.7 ppm when compared to that of sensors of PANI and Fe_2O_3 alone. The excellent selectivity of the composite towards NH3 was mainly attributed to p/n heterojunction established between PANI and Fe_2O_3.

In the present we report the synthesis of polyaniline-Fe_2O_3 composites prepared by ex situ polymerization technique with varying Fe_2O_3 content. X-ray diffraction and Scanning electron microscopy studies were conducted on the developed composites. The AC conductivity and dielectric properties of composites as function of frequency with varying Fe_2O_3 concentration was also studied.

II. MATERIALS AND METHODS:

A. Synthesis:

Synthesis of the PANI–Fe_2O_3 composites was carried out by ex situ polymerization. Aniline (0.2 M) was dissolved in 1 M HCl and stirred for 2hrs to form aniline hydrochloride. Iron oxide was added in the mass fraction to the above solution with vigorous stirring in order to keep the Fe_2O_3 homogeneously suspended in the solution. To this mixture, 0.2 M of ammonium persulphate, which acts as an oxidant was slowly added drop-wise with continuous stirring at room temperature for 8 hrs to completely polymerize the monomer aniline. The precipitate was filtered, washed with demonized water and finally dried in a hot air oven for 24 hrs to achieve a constant mass. In this way, PANI–Fe_2O_3 composites containing various mass fractions of Fe_2O_3 (5%, 15%, 25%, 35% and 45%) in PANI were synthesized.

B. Characterization:

The as synthesized PANI–Fe_2O_3 composite powder morphology and the structures were studied using scanning electron microscopy (SEM, JSM-6360LV, Japan) and X-ray diffraction (XRD). The X-ray diffraction patterns of the powders were taken using Philips XPERT diffractometer using Cu Kα radiation (λ = 1.54 A˚). The AC conductivity of all the composites with different Fe_2O_3 content was studied in the frequency range of 0.2 to 10 MHz using LCR-Q meter (Wayne Kerr, 4300) analyzer. The thermal behavior of the polymer samples was examined by simultaneous differential scanning calorimeter (DSC) and thermo gravimetric analysis (TGA) up to 1000^{o}C using Thermal Analyzer STA PT 1600 (Linseis make, Germany) in nitrogen atmosphere at heating rate at 2 ^{o}C /min.

III. Results and discussion:

A. Characterization: SEM and X-ray diffraction:

SEM micrographs of PANI–Fe_2O_3 composites synthesized by ex situ technique with varying Fe_2O_3 content from 5% to 45% is shown in figure 1 a-e. From the SEM micrographs it can be observed that the composite is in the form of grains and have porous morphology. All Fe_2O_3 particles are embedded in the lumps in the polyaniline matrix of the composite. The dispersion of Fe_2O_3 particle is found to be uniform and all these particles are attached to the PANI chain. Further these composite particles seem to have capillary pores which can help in adsorption of gas due to their large surface area. On the other hand the composites with 5% and 35% Fe_2O_3 particles had crystalline flake like morphology. Similar observations were reported by Patil et al [10] in their work on polyaniline–zinc ferrite composite, where the composite had granular flake like networking structure.

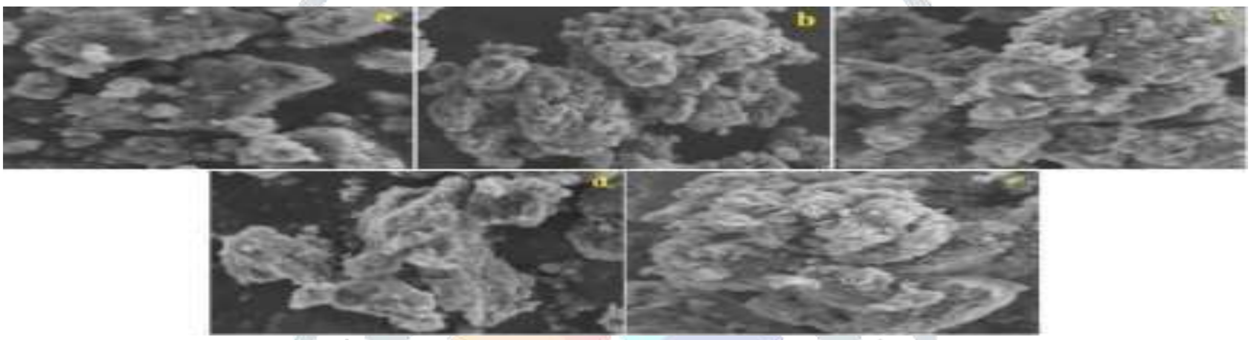
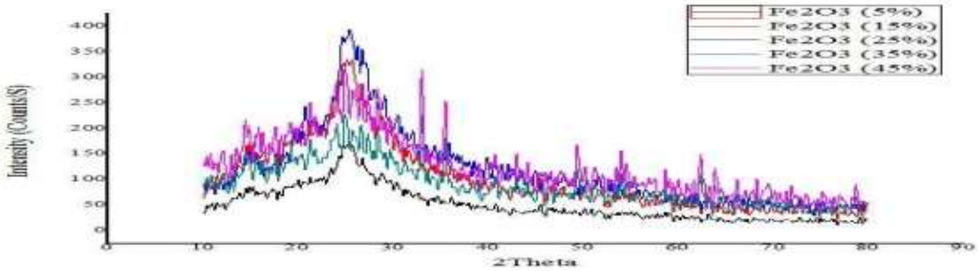


Figure 1: SEM micrographs of PANI-Fe_2O_3 composites with different Fe_2O_3 content: (a) 5, (b) 15, (c) 25, (d) 35 and (e) 45 wt%.

Figure 2 shows the X-ray diffraction patterns of PANI–Fe_2O_3 composites with different Fe_2O_3 content. Here the broad peak observed in between the 2θ = 20° to 30° is related to PANI exhibiting the amorphous behavior. The other sharp peaks observed at 2θ = 32.78°, 35.66°, 48.92°, 53.62°, 62.16° and 64.28° were related to reported values for α-Fe_2O_3 as according to JCPDS No. 89-596. It can be observed the sharp peaks are more in case of the composites which has more than 25% of Fe_2O_3 content. These sharp peaks refer to crystalline nature of the composites while no such peaks were observed for the composites having Fe_2O_3 content less than 25%. The suppressed peak intensity in these composites is mainly due to formation of PANI on the surface of Fe_2O_3 particles [11].

Figure 2: X-ray diffraction patterns of PANI-Fe_2O_3 composites with different Fe_2O_3 content.



B. AC conductivity of PANI-Fe_2O_3composites:

The AC conductivity of PANI-Fe_2O_3 composites as a function of frequency with varying Fe_2O_3 content is shown in figure 3. It can be observed that the composites show similar behavior up to a frequency of 6×10^5 Hz and after that the conductivity increases significantly for composite with 45% of Fe_2O_3content. The increase in the conductivity of composites with 5, 10 and 15% of Fe_2O_3 was minimal while in case of composites with 35 and 45% it was very high. The increase in AC conductivity with respect to the frequency can be attributed to the presence of various types of in homogeneities in the PANI-Fe_2O_3 composites. Along with this the hopping of the charge carriers from one localized state to another also contribute to the high conductivity values in the composites. This implies that the composites obey the universal power law which is in line with the other work carried out on polyaniline composites [12, 13]. On the other hand the low conductivity in case of composites with 5, 15 and 25% Fe_2O_3content can be due to the blockage of charge carriers because of large interface.

C. Thermal analysis:

Figure 4 shows the thermo grams of synthesized PANI-Fe_2O_3 composites with varying Fe_2O_3 content. The thermo grams were obtained from room temperature to 1000°C to study the thermal stability of all the composites using thermo gravimetric analysis. It can be seen that there is decrease in weight loss from room temperature to 200°C of the all composites. Most of the water molecules are entrapped in the PANI matrix. So at this temperature range the formation of water vapour and evaporation of moisture takes place which is reflected in the weight loss. For the temperature range of 200 to 600°C, the weight loss is not so significant but thereafter we can see the degradation of composite. Here the weight loss in this temperature range can be due to oxidative degradation of PANI matrix. The decomposition rates of composites with Fe_2O_3 content of 35% and 45% were slower than that of composites with 5% to 25%Fe_2O_3. In general the weight loss reaches a maximum of 7% of total weight of the composite samples with low Fe_2O_3 content (5 & 15%) [14].

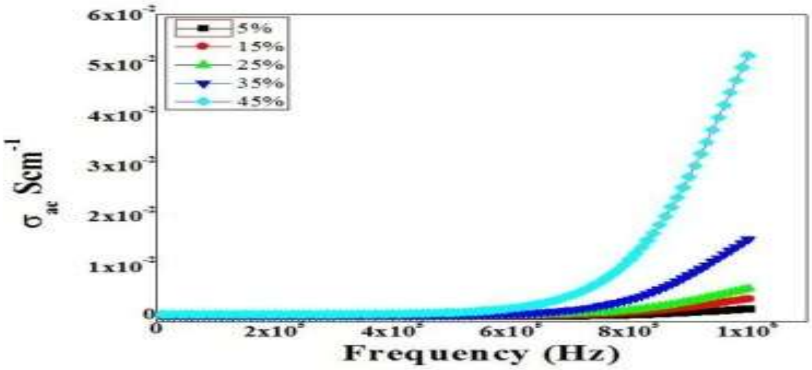


Figure 3: AC conductivity of PANI-Fe_2O_3 composites with varying Fe_2O_3 content.

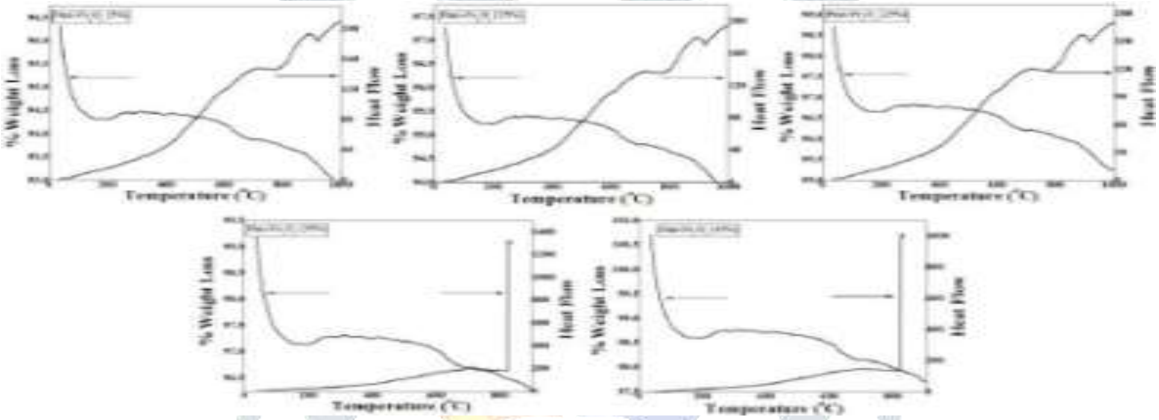


Figure 4: Thermo grams of PANI-Fe_2O_3 composites: (a) 5, (b) 15, (c) 25, (d) 35 and (e) 45 wt% -Fe_2O_3 content.

D. Dielectric behavior of PANI Fe_2O_3composites:

Figure 5 shows the dielectric behavior (ε') as a function of frequency for PANI-Fe_2O_3 composites with varying Fe_2O_3 content. It can be observed that the dielectric constant ε' up to 4×10^5 Hz for all the composites is constant. Later the dielectric constant tends to increase with the increase in frequency as well as with the increase in Fe_2O_3 content. Incorporation of Fe_2O_3 resulted in significant increase in dielectric constant of the composite and 35 wt% is showing higher than the other doped concentration. The deviation in the dielectric constant is mainly due to the concentration of Fe^{3+} ions in the composites.

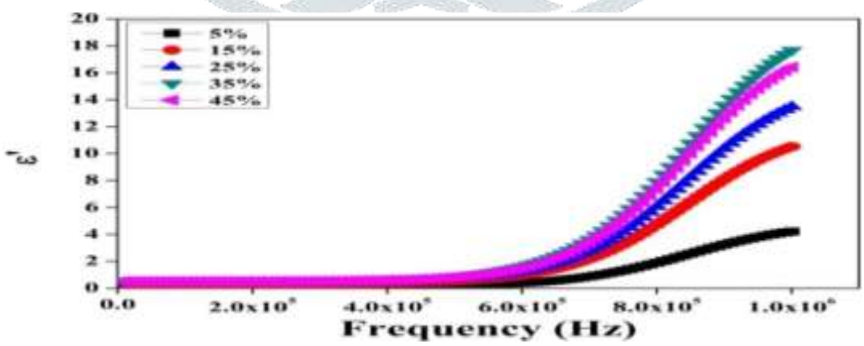


Figure 5 Variation of ε' for PANI-Fe_2O_3 composites as a function of frequency for different Fe_2O_3 content.

IV. Conclusions

The following conclusions were drawn from the current study, PANI-Fe_2O_3 composites with varying Fe_2O_3 content from 5% to 45% (in the steps of 10%) have been successfully synthesized by ex situ polymerization technique. X-ray diffraction results suggest the mixture of crystalline Fe_2O_3 phase and amorphous phase of PANI in composites. The composites showed increase in AC conductivity values with the increase in frequencies which is mainly attributed to hopping of the charge carriers from one localized state to another. The thermal analysis revealed that the composites with lower Fe_2O_3 content (5 & 15%) showed higher decomposition rates when compared to that of composites with higher Fe_2O_3 content.

V. Acknowledgement

The authors are thankful to Poojya Dr. Sharanbasvappa Apaa, President Sharanbasveshwar Vidya vardhak Sangha, Kalaburagi, Prof. Dr. V D. Mytri, Principal, Appa Institute of Engineering and Technology, Kalaburagi, Karnataka, for encouragement during the process of carrying out this work.

References:

[1] H. Shirakawa, Int. Ed. 40, 2001, The discovery of polyacetylene film: the dawning of an era of conducting polymers (Nobel Lecture). Angew. Chem2574-2580.

[2] N.V. Bhat, N.V. Joshi, 50, 1993 Investigation of the properties of polyacrylamide-polyaniline composite and its application as a battery electrode. J. Appl. Polym. Sci. 1423-1427.

[3] M. Thangarathinavelu, A.K. Tripathi, T.C. Goel, I.K. Varma, 51, 1994, Preparation and characterization of polyaniline–PVC polymer composite film. J. Appl. Polym. Sci. 1347-1349.

[4] M. Gill, J. Mykytiuk, S.P. Armes, J.L. Edwards, T. Yeates, P.J. Moreland, C. Mollett, 1992, Novel colloidal PANI–silica composites. Chem. Commun. 108-109.

[5] S. Sathiyanarayanan, S. Syed Azim, G. Venkatachari, 157, 2007, Preparation of polyaniline–Fe_2O_3 composite and its anticorrosion performance, Synth. Met. 751–757.

[6] S. Wang, L. Hu, Y. Hu, S. Jiao, 146, 2014, Conductive polyaniline capped Fe_2O_3 composite anode for high rate lithium ion batteries, Mater. Chem.Phys. 289-294.

[7] L. Saad, M. Y. Feteha, Sh. Ebrahim, M. Soliman, T.M. Abdel-Fattah 3, 2014, Dye Sensitized Solar Cell Based on Polyaniline-Carbon Nanotubes/Graphite Composite, ECS J. Solid State Sci. Technol.

[8] T. Bashir, A. Shakoor, E. Ahmad, M. Saeed, N.A. Niaz, S.K. Tirmizi, 57, 2015, Structural, Morphological, and Electrical properties of polyaniline–Fe_2O_3 nanocomposites, Polym. Sci. 257-263.

[9] Y. Li, H. Zhao, H. Ban, M. Yang, 245, 2017, Composites of Fe_2O_3nanosheets with polyaniline: Preparation, gassensing properties and sensing mechanism, Sens. Actuators B Chem. 34–43.

[10] R.Patil, A.S. Roy, K.R. Anilkumar, K.M. Jadhav, S.Ekhelikar, 43,2012, Dielectric relaxation and ac conductivity of polyaniline–zinc ferrite composite, Compos. Part B3406–3411.

[11] R. Suresh, K.Giribabu, R.Manigandan, A.Stephen, V.Narayanan, 128(2014) Fe_2O_3@polyaniline nanocomposite: Characterization and unusual sensing property, Mater. Lett. 369–372.

[12] G. Chakraborty, K. Gupta, A.K. Meikap, R. Babu, W.J. Blau, 2011, Anomalous electrical transport properties of polyvinyl alcohol-multiwall carbon nanotubes composites below room temperature, J.Appl. Phys. 109, 03,3707.

[13] J. Appl. Phys., 109, 2011 properties of polyvinyl alcohol-multiwall carbon nanotubes composites below room temperature, 033707.