E-ISSN: 2321–9637
Volume 2, Issue 1, January 2014
International Journal of Research in Advent Technology
Available Online at: http://www.ijrat.org

SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYMER – TRANSITION METAL OXIDE COMPOSITE

R. Bhuvaneswari, G. Dhanu, V. Divya Preethi, K.P. Bhuvana*, K .Palanivelu, S.K. Nayak
Central Institute of Plastics Engineering & Technology, Guindy, Chennai, India
kpusha27@gmail.com

ABSTRACT:
An attempt towards the realization of magnetism in polymers has been made by inducing transition metal oxide particles into the polymer matrix. Composite of Polyaniline and ferric oxide (50% by weight) was prepared by solid state reaction method. Composite was subjected to X-ray diffraction, UV-Visible spectroscopy and Vibrating sample magnetometry in order to investigate its structural, optical and magnetic properties. The composite exhibits excellent ferromagnetism at room temperature with the saturation magnetization of 0.136 emu. The irreversible hysteretic loop of B-H curve was obtained with the remenance field of 0.826 emu/g and Coercivity of 569.7 G respectively. The optical constants like electronic band gap and refractive index of the composite were also determined to be around 2.37 eV and 1.40 – 1.41 in the visible region respectively.

Keywords: *Polymeric Composites, Optical properties, X-ray techniques.*____

1. INTRODUCTION

Conducting polymers have attracted a great interest in applied and fundamental research. From the discovery of high electrical conductivity in doped polyacetylene, huge amount of research is going on towards the understanding of electronic and transport properties in conjugated polymers for the applications including rechargeable batteries, coaxial cable, thin film transistor, electromagnetic shielding, smart window, and light emitting diodes [1–6].
In the recent years, the development of carriers for controlled drug delivery is a challenge for researchers. Synthesize and characterization of magnetic polymer constitutes a new topic of research rapidly developing in last 10 years. The magnetic behavior of a polymer benefits the features of both magnetic particles and the conducting polymer [7]. Drug targeting can be achieved by magnetic control. In this technology, targeted drug is binded with magnetic particles, which facilitate to concentrate drugs in the focused area of interest by means of magnetic fields [8-10]. Various inorganic or polymeric materials have been proposed as carriers of magnetic materials. A considerable advantage of the polymeric carriers is the presence of a variety of functional groups, which is able to modulate the carrier properties for the desired applications [8]. The use of natural polymers also attracts much more interest due to their availability from abundant renewable resources and due to their biocompatibility and biodegradability.

In this work, a composite of a magnetic particle is embedded into a polymer matrix to realize magnetism in a polymer. A composite of Polyaniline (conducting polymer) and Ferrous oxide (transition metal oxide, a magnetic particle) was synthesized and characterized for its magnetic properties.

E-ISSN: 2321–9637
Volume 2, Issue 1, January 2014
International Journal of Research in Advent Technology
Available Online at: http://www.ijrat.org

2. SAMPLE PREPARATION AND CHARACTERIZATION TECHNIQUES

Pure Polyaniline and Polyaniline / Fe_2O_3 composite were prepared and characterized for its structural, optical, electrical and magnetic properties.

2.1 Synthesis of Polyaniline

Prescribed amount of aniline (2.78g) is dissolved in 1N Hydrochloric acid under constant stirring for 1 hour. Calculated amount of Potassium persulphate, K2S2O8 (1.62g) in 20 ml distilled water is added to aniline in HCl solution and constantly stirred for 1 hour under a temperature of 0 – 5°C. The polymerization solution results with the formation of dark green precipite and it is kept under room temperature for 24 hours. The precipitate is then filtered and dried in oven at 110°C to get Polyaniline powder [11].

2.2 Synthesis of Polyaniline / Fe2O3 composite by solid state reaction

Equal amount of polyaniline and Fe2O3 is taken and crushed in a mortar for uniform mixing. The mixture was subjected to heat treatment at 150°C for 5 hrs. The mixture was grinded into fine particles and annealed at 250°C for 4 hrs. The process of composite synthesis is depicted in a flow chart (Fig. 1). PANI / Fe2O3 composite was obtained as dark brown powder. Composite was subjected to XRD diffraction, UV-Visible spectroscopy, Scanning electron microscopy and Vibration sample magnetometry in order to study the structural, optical, morphological and Magnetic properties of the composites respectively.

E-ISSN: 2321–9637
Volume 2, Issue 1, January 2014
International Journal of Research in Advent Technology
Available Online at: http://www.ijrat.org

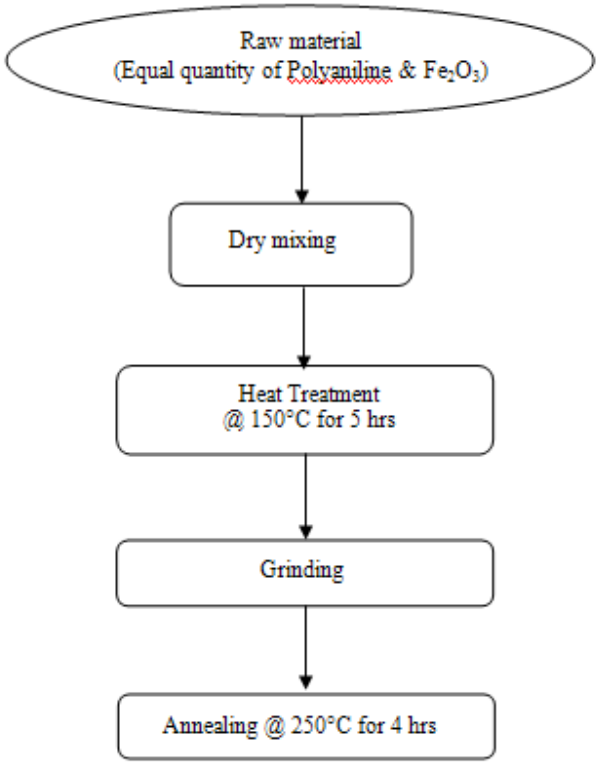

Fig. 1. Flow Chart for the synthesis of Polyaniline / Fe_2O_3 composite by solid state reaction method

E-ISSN: 2321–9637
Volume 2, Issue 1, January 2014
International Journal of Research in Advent Technology
Available Online at: http://www.ijrat.org

2.3 Analytical Characterization

The structural characteristic of composite was analyzed using X-Ray Diffraction pattern. The pattern was obtained in Shimadzu diffractometer, using the Cu Kα radiation, λ = 1.5406 Å with 40 KV and 20 mA, at a 0.04° scan rate. The measurements were made at room temperature with the diffraction angle (2θ) ranging from 10 to 70 degrees. The surface morphology of the composite was studied using scanning electron microscopy (Make: Carl Siezz, Model: EVO MA 15) at the resolution of 3 nm and the magnification of 1000 x. The absorption spectrum of the composite was observed using UV-Visible spectrometer (CARY 5E UV-VIS-NIR) at room temperature within the wavelength ranges from 300 nm to 1100 nm in steps of 1 nm. The magnetic behavior of the composite was investigated using Vibrating Sample Magnetometer (Lakeshore, Model 7404) having 1.0% accuracy of magnetic field and moment.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

The XRD pattern of PANI and PANI/Fe2O3 composite is depicted in Fig. 2. The pattern reveals the strong disordered chain of PANI with a broad is amorphous in nature due to the strong disordered chain formation. However PANI/Fe2O3 is polycrystalline with the preferential orientation of (104) plane. The XRD pattern of PANI/Fe2O3 composites also indicates the diffraction peaks of Fe2O3 centered at 24.25°, 33.11°, 35.73°, 40.75°, 49.36°, 54.16°, 57.71°, 62.53°, 64.0°.

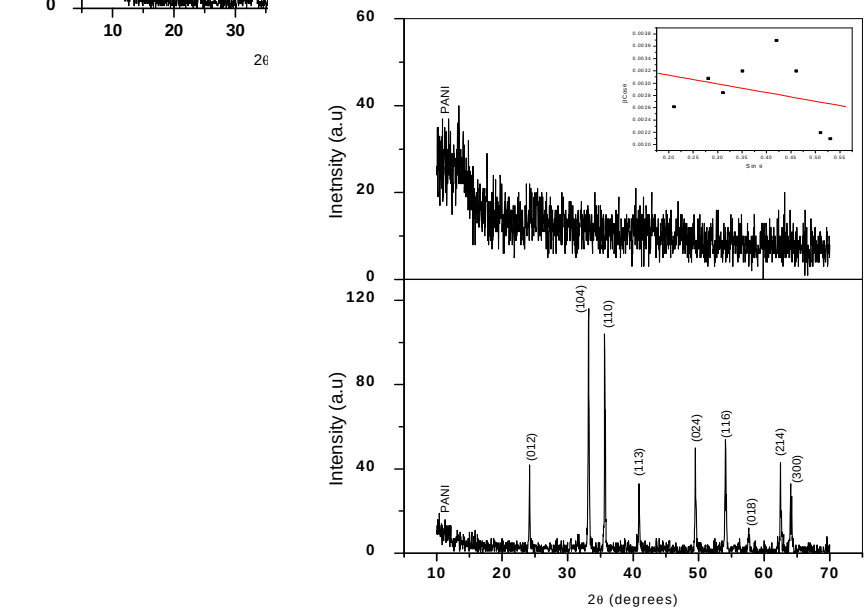

Fig 2: XRD pattern of PANI and PANI / Fe_2O_3 composite

E-ISSN: 2321–9637
Volume 2, Issue 1, January 2014
International Journal of Research in Advent Technology
Available Online at: http://www.ijrat.org

Inset of Fig. 2 shows the Williamson Hall plot of the polycrystalline composites. The plot is further interpreted to determine the particle size and the strain using de-Bye Scherrer's formula (eqn. 1),

$$\beta \cos\theta = \frac{A\lambda}{D} + 4\varepsilon \sin\theta \quad (1)$$

The particle size and the strain induced in the composite are determined to be 126 nm and -0.00341 respectively. The lattice constants a and c is determined as 3.114 Å and 5.393 Å respectively using eqn. 2 and 3 respectively.

$$a = \frac{\lambda}{\sqrt{3}\sin\theta} \quad (2)$$

$$c = \frac{\lambda}{\sin\theta} . \quad (3)$$

3.2 Optical Absorbance studies

UV-Visible absorption spectrum of the composite is depicted in Fig. 3. The absorption spectra posses two absorption peaks at 248 nm and 352 nm. The peak at 352 nm is associated with the electronic transitions from highly occupied molecular orbital (HOMO) π-band to lowly unoccupied molecular orbital (LUMO) π*-band of electronic states [12,13]. The peak at 248 nm is due to the charge transfer of ferric ions [14].

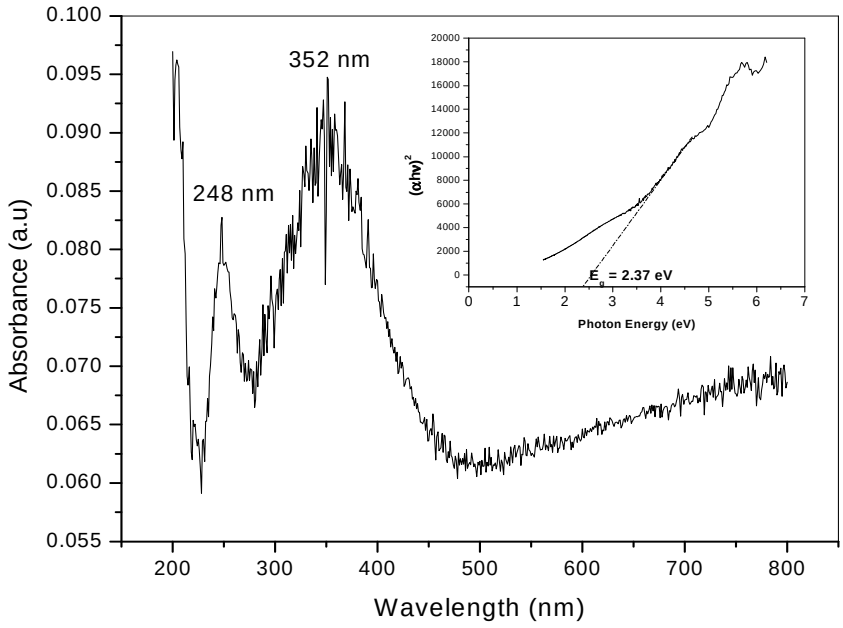

Fig. 3: UV visible spectrum of PANI / Fe_2O_3 composite

E-ISSN: 2321–9637
Volume 2, Issue 1, January 2014
International Journal of Research in Advent Technology
Available Online at: http://www.ijrat.org

3.2.1 Determination of Optical band gap

To determine the optical band gap of the composites, Tauc's plot for pure Polyaniline and Polyaniline/Fe2O3 composites were plotted and depicted in inset of Fig. 3. Tauc's plot is plotted between $(\alpha h\nu)^{1/2}$ and hν. The band gap is determined by extrapolating the linear region of the curve. The energy gap for pure polyaniline is observed to be 2.8 eV. The optical band gap of polyaniline was already determined and reported as 2.7 eV by Reda et al [15]. The higher value of optical band gap is due to the reduction in particle size of the synthesized Polyaniline powder. Composites with 50wt% of Fe_2O_3 in Polyaniline posses the energy gap of 2.37 eV. The reduction of band gap in the composite may be due to reduction in the disorder of the system and increase in the density of defect states. The widening of band gap in case of heavily doped semiconductors is due to the blocking of the low-energy transitions by the donor electrons occupying the states at the bottom of the conduction band which is known as the Burstein-Moss effect.

3.2.2 Determination of refractive index

Reflectance, Transmission and absorption from any material depend upon the refractive index of that material. Reflectance is given as,

$R = \frac{(n-1)^2}{(n+1)^2}$, from this relation, the refractive index as a function of wavelength in terms of reflectance have been derived and reported earlier [16] as,

$$n(\lambda) = \frac{-(R+1) \pm \sqrt{(-3R^2+10R-3)}}{2(R-1)}.$$

The reflectance of the samples was extracted from the transmittance and absorbance data. Fig. 4 depicts the relationship between the wavelength and refractive index. The refractive index of the composite in the visible range (300 – 700 nm) is determined as 1.40 to 1.41.

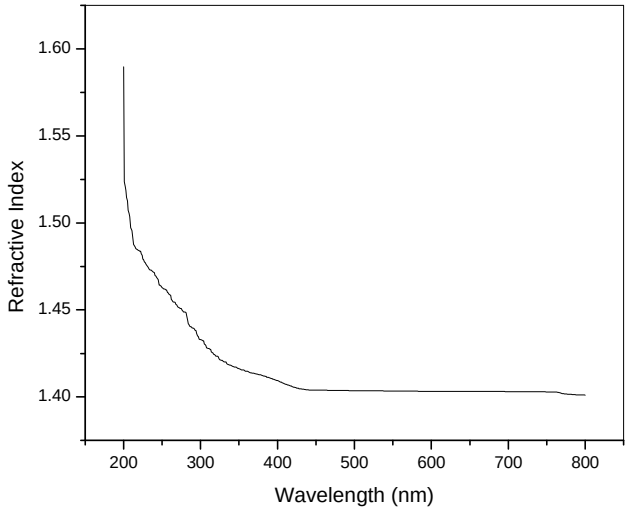

Fig 4: Refractive index Vs wavelength

E-ISSN: 2321–9637
Volume 2, Issue 1, January 2014
International Journal of Research in Advent Technology
Available Online at: http://www.ijrat.org

3.3 Magnetic Characteristics

Fig. 5 shows the typical magnetization curve of the magnetic composite. From the magnetization curve it is understood that the composite exhibits ferromagnetism with remanence magnetization (M_r) of 0.0413 emu (0.826 emu/g) and the coercive field of 590.78 gauss. The saturation magnetization (M_S) was around 0.139 emu (2.78 emu/g). The relative saturation remanence, $m_r = M_r/M_S$ is 0.297. The sensible value of M_r/M_s ratio also supports the better hysteresis behavior of the composite.

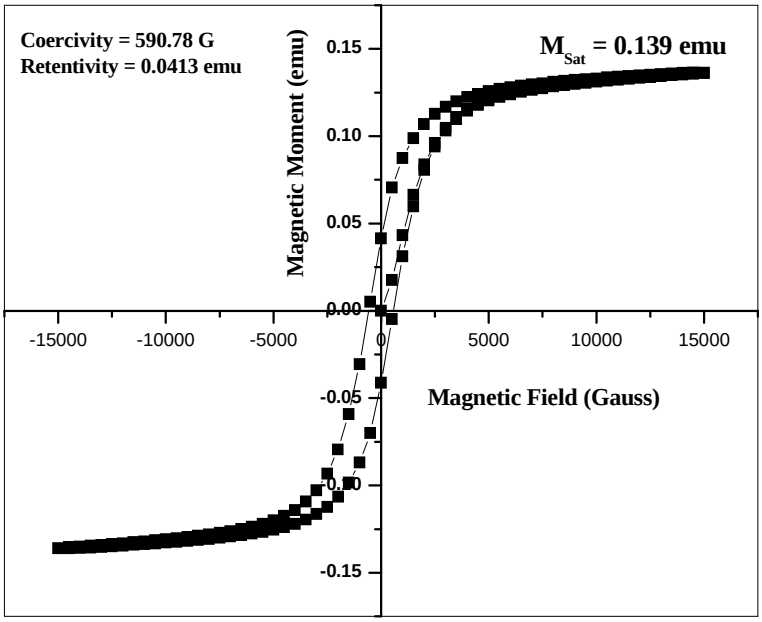

Fig. 5: M-H curve of PANI / Fe_2O_3 composite

E-ISSN: 2321–9637
Volume 2, Issue 1, January 2014
International Journal of Research in Advent Technology
Available Online at: http://www.ijrat.org

3.4 SEM analysis

PANI/Fe_2O_3 composite was subjected to SEM imaging. The image was observed at the magnification of 5000 x. The magnified SEM image was depicted in Fig. 6. The image shows the uniform distribution of PANI and Fe_2O_3 in the composite. There is no agglomeration of particles was observed.

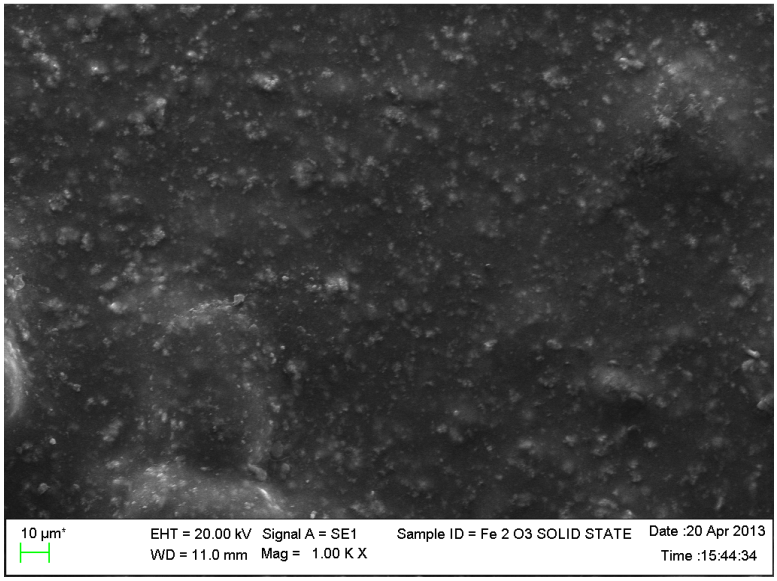

Fig. 6: SEM image of PANI / Fe_2O_3 composite

CONCLUSION

Composite of PANI and Fe_2O_3 was prepared by solid state reaction route. Composite were subjected to XRD, SEM, UV-Visible spectroscopy and Vibration sample magnetometry in order to study the physical characteristics of the composite. XRD pattern of the composite depict the polycrystalline nature and the lattice parameters was determined. The optical parameters like optical band gap and refractive index are established from the absorption spectrum of the composite.

References

[1] J.M. Ko, D.Y. Park, N.V. Myung, J.S. Chung, K. Nobel, (2002) *Electrodeposited conducting polymer–magnetic metal composite films*, Synth. Met.; **128,** pp. 47 – 50
[2] A.F. Diaz, J.A. Logan, (1983) *Electrodeposited conducting polymer – ferromagnetic compsites***,** J. Electroanal. Chem. **111**, pp.111-115
[3] J.C. Chiang, A.G. MacDiarmid, (1986) *A Novel Role for Organic Polymers*, Synth. Met., **13,** pp. 193 - 196.
[4] W.S. Huang, B.D. Humphrey, A.G. MacDiarmid, (1986) *Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes*. J. Chem. Soc.,Faraday. Trans. 1986; **82**, pp.2385.
[5] E.M. Gennies, M. Lapkowski, J.F. Pennean, (1988) *Cyclic voltammetry of polyaniline: interpretation of the middle peak*, J. Electroanal. Chem. **249,** pp. 97.
[6] A.J. Esptein, A.G. MacDiarmid, (1995) *Polyanilines: From solitons to polymer metal, from chemical currosity to technology*, Synth. Met. **69,** pp.179.
[7]. Olga Philippova, Anna Barabanova, Vyacheslav Molchanov, Alexei Khokhlov, (2011) *Magnetic polymer beads: Recent trends and developments in synthetic design and applications*, Euro. Poly. Journal, **47**, pp.542 - 559.

E-ISSN: 2321–9637
Volume 2, Issue 1, January 2014
International Journal of Research in Advent Technology
Available Online at: http://www.ijrat.org

[8] Yan Wu, Jia Guo, Wuli Yang, Changchun Wang, Shoukuan Fu, (2006) *Preparation and characterization of chitosan–poly(acrylic acid) polymer magnetic microspheres*, Poly., **47**, pp. 5287–5294.
[9] Wu Yan, Yang WL, Wang CC, Hu Jianhua, Fu Shoukuan, (2005) *Chitosan nanoparticles as a novel delivery system for ammonium glycyrrhizinate*, Int J Pharm, **295**, pp.235.
[10] J. Stehr, J. Crewett, F. Schindler, R. Sperling, et al, (2003) *A Low Threshold Polymer Laser Based on Metallic Nanoparticle Gratings*, Adv Mater, **15**:1729
[11] J. Stejskal, R.G. Gilbert, (2002) *Polyaniline. Preparation of a conducting polymer(IUPAC Technical Report)*, Pure Appl. Chem., **74,** pp. 857–867.
[12]. Y. Tan, Y. Zhang, J. Kan, (2009) *Synthesis and properties on polyaniline in the presence of nickel chloride***,** Express Poly. Let. **3**, pp. 333–339.
[13] M.A. Ali, Elias Saion, N. Yahya, A. Kassim et al, (2007) Synthesis of Conducting Polyaniline Nanocomposites by Radiation Doping J. of Engg. Sci. and Tech.**2**, pp.111-118.
[14] F.A. Moustaffa, F.H. El-Batal, A.M. Fayadd and I.M. El-Kashef, (2010) *Absorption Studies on Some Silicate and Cabal Glasses Containing NiO or Fe_{2}O_{3} or Mixed NiOi + Fe_{2}O_{3}, Acta Physica Polonica A*, **117**, pp. 471 – 477.
[15] Safenaz M. Reda, Sheikha M. Al-Ghanna, Synthesis and Electrical Properties of Polyaniline Composite with Silver Nanoparticles, (2012) Adv. in Mat. Phy. Chem., **2**, pp. 75-81.
[16] Bhuvana.K. P., R.S. Jebas, N. Gopalakrishnan and T. Balasubramanian, (2007) Development of NLO tunable band gap organic devices for optoelectronic applications, Mat. Lett. **61**, pp. 4246.