

Conductivity Study of Polyaniline/ZnFe₂O₄ Composites

Vijaykumar.B.Chanshetty^{1,3}, Sharanappa.G² and Sangshetty Kalyane³

¹Research Scholar, JITU, Jhunjhunu, Rajasthan, India.

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

³Department of Physics, Bheemanna Khandre Institute of Technology, Bhalki, Karnataka, India.

ABSTRACT: The conducting polymer (PANI / ZnFe₂O₄) composites were synthesized by single step in situ polymerization technique by placing finely grinded powder of ZnFe₂O₄ during the polymerization of aniline. The formation of mixed phases of the polymer together with the conducting emeraldine salt phase was confirmed by spectroscopic techniques like X-Ray diffraction (XRD), Infrared (IR) spectra & Scanning Electron Microscopy (SEM) images indicated a systematic morphological variation of particles aggregated in the composite matrix as compared to the PANI. AC conductivity of these composites were investigated in the frequency range 100 Hz to 1MHz. It is found that AC conductivity obeyed the variation of conductivity with wt% of ZnFe₂O₄ could be related to conductivity relaxation phenomenon.

KEY WORDS: Polyaniline, AC conductivity,

1. INTRODUCTION:

Conducting polymers have become the foci of interest in materials science because of their specific electronic properties, which can be tailored via synthetic organic chemistry. The resulting electronic system has in general either quasi-one or two dimensional character, resulting in a specific electronic conduction ranging from insulating semi conducting to highly conducting phase. The multiplicity of intra and intermolecular vibrational modes in conjugated polymers are the key for the many exciting properties, leading to numerous technological applications, such as active electrode materials in energy storage [1]. Optoelectronic devices [2, 3], display devices [4, 5], corrosion inhibitors [6, 7], controller of electromagnetic radiations and electrostatic charge [8, 11].

The electrical transport in polymeric materials [12, 13] has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices. Similarly, conducting polymer composites attracted considerable interest in recent years because of their numerous applications in variety of electric and electronic devices. Conducting polymer composites with some suitable compositions of one or more insulating materials led to desirable properties [14-17]. These materials are especially important owing to their bridging role between the world of conducting polymers and that of nano particles. For applications of conducting polymers, knowing how these conducting polymer composite will affect the behavior in an electric field is a long-standing problem and is of great importance. The discovery of doping in conducting polymers has led to further dramatic increase in the conductivity of such conjugated polymers to values as high as 10⁵ Scm⁻¹.

Among all conducting polymers, Polyaniline (PANI) achieved widespread importance because of its unique conduction mechanism and environment stability. The survey of literature reveals that the detailed conductivity studies on PANI/ ZnFe₂O₄ are scarce. In the present study, PANI and PANI/ ZnFe₂O₄ composite have been synthesized and the ac conductivity of these samples are measured and studied.

2. EXPERIMENTAL:

All Chemicals used are analytical grade (AR) and were procured, used as received. The monomer aniline was doubly distilled prior to use. Synthesis of Polyaniline / ZnFe₂O₄ composites has been carried out by single step in situ polymerization technique. 0.1 mole of aniline was dissolved in 1 mole of Hydrochloric acid to form aniline hydrochloride. Finely grinded powder of ZnFe₂O₄ is added in the weight percent of 5, 10, 15, 20 and 25 to the above solution with vigorous stirring to keep ZnFe₂O₄ suspended in the solution. The precipitated powder was recovered, vacuum filtered and washed with deionized water. Finally, the resultant precipitate was dried in an oven for 24 hrs to achieve constant weight. In this way, five different PANI / ZnFe₂O₄ composites with different weight of ZnFe₂O₄ (5, 10, 15, 20 & 25 wt%) in PANI have been synthesized. The pellets of 10 mm diameter are formed with thickness varying up to 2 mm by applying pressure of 10 Tons in a UTM – 40 (40 Ton Universal testing machine). For conductivity measurement, the pellets are coated with silver paste on either side of the surfaces. The characterization studies are employed on all the above synthesized PANI / ZnFe₂O₄ composites to confirm the presence of ZnFe₂O₄ in PANI, The frequency dependent AC conductivity of Polyaniline / ZnFe₂O₄ composites are studied in the frequency range 100 Hz to 1 MHz at room temperature using Hioki impedance analyzer, model 3532-50 (JAPAN) programmable LCR meter. In this experiment, five different samples of each composite varying in their weight percentage are investigated for their frequency dependent conductivity.

3. RESULTS AND DISCUSSIONS:

SEM technique is applied primarily for the visualization of the sample surfaces, especially for the study of surface morphology, domains, pin hole defects and patterns. The images are formed by the interaction of electrons with samples in vacuum.

3.1 Polyaniline and Polyaniline / ZnFe₂O₄ composites:

Figure 3.1(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 4µm. The grains are well interconnected with each other indicating that they have enough binding energy to combine with neighbors grains or molecules.

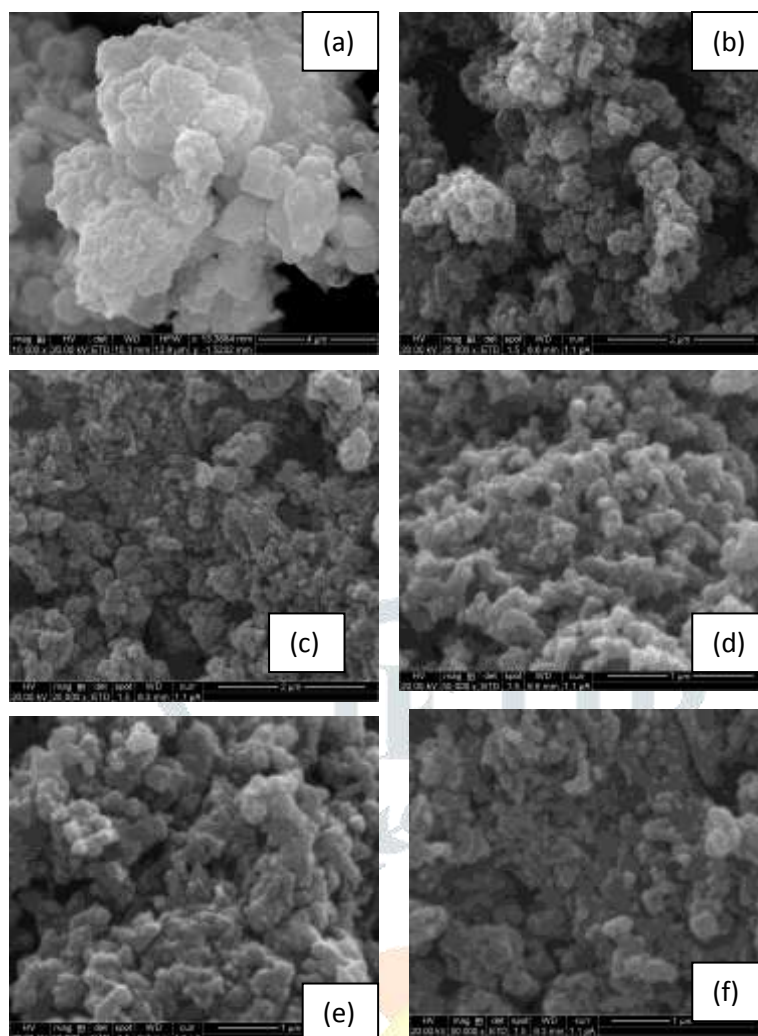


Figure 3.1: show the SEM image of PANI and PANI/ZnFe₂O₄ composites of different weight percentage (5, 10, 15, 20 and 25 wt%)

Figure 3.1(b) shows the Scanning Electron Micrograph of 5 wt. % of PANI/ZnFe₂O₄ composite where highly agglomerated cube like structure are seen. The crystallinity of the ZnFe₂O₄ decreases with the addition of PANI in it. It is found that zinc ferrite particles were homogeneously distributed throughout polyaniline matrix. The average grain size is found to be 600 nm. PANI/ZnFe₂O₄ composite of 10 wt. % is shown in **Figure 3.1(c)**. The composite is highly clustered, spherical in shape and have interlinked to each other. The decrease in the inter-granular distance between the grains helps in charge transfer mechanism. The average grain size is found to be 1.5µm. **Figure 3.1(d)** 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 3.1(e)** show that the 20 wt. % of PANI/ZnFe₂O₄ composite which is highly agglomerated and spherical in shape of about 0.5µm in granular size. PANI/ZnFe₂O₄ composite of 25 wt. % is shown in **Figure 3.1(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 3.1(a) to 3.1(f)**, 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 / ZnFe₂O₄ composites [17-18].

3.2 Zinc ferrite and Polyaniline / ZnFe₂O₄ composites:

Figure 3.2 Shows X-ray diffraction pattern of Polyaniline. Careful analysis of X-ray diffraction of polyaniline suggests that it has amorphous nature with a broad peak centered on $2\theta \approx 26.40^\circ$. **Figure 3.3** 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 3.4 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 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 reaction [22].

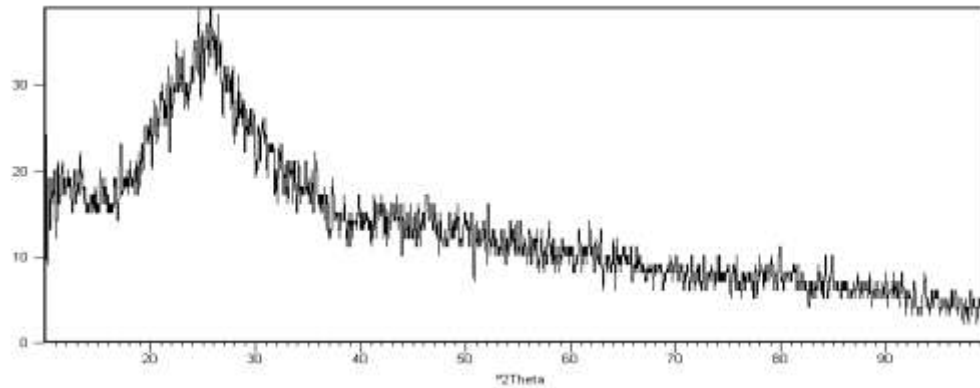


Figure 3.2: X-ray diffraction pattern of polyaniline

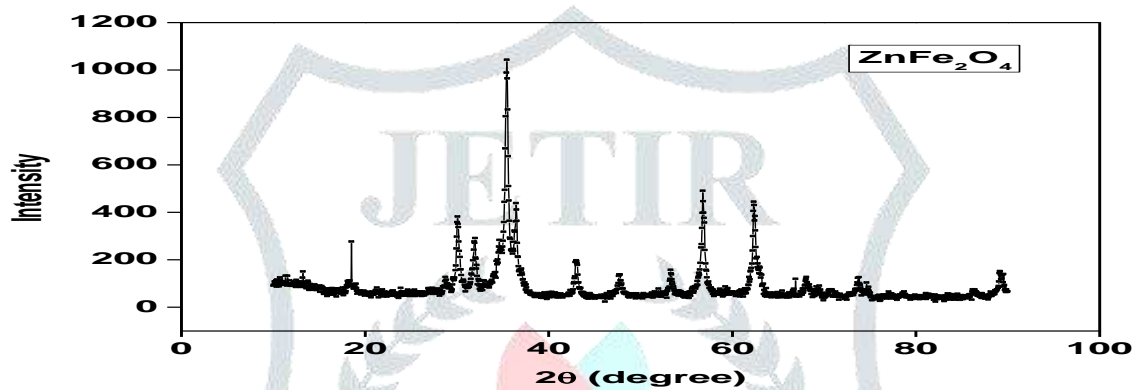


Figure 3.3: X-ray diffraction pattern of ZnFe₂O₄ composite

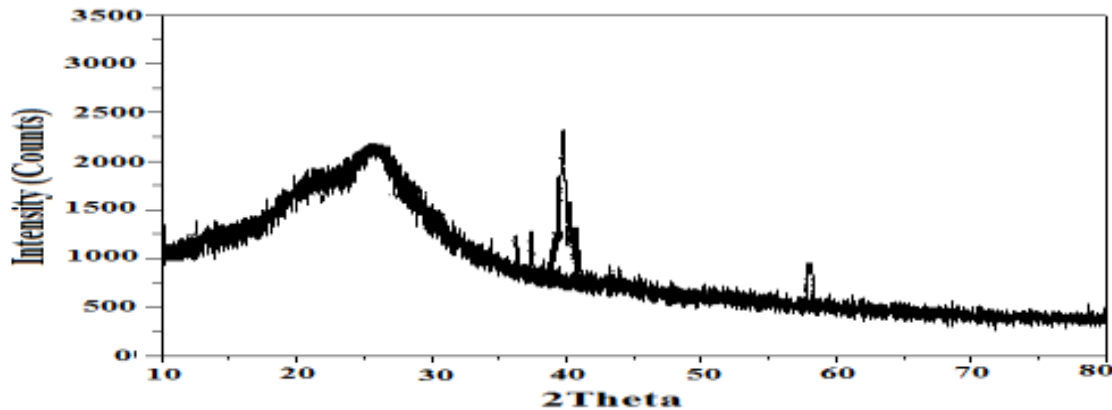


Figure 3.4: X-ray diffraction pattern of Polyaniline – ZnFe₂O₄ composite

Figure 3.5 (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 corresponds to C = C stretching vibration of quinoid ring, 1548 cm⁻¹ for C=N bond stretching, 1494 cm⁻¹ corresponds to stretching vibration of benzenoid ring, 1406 cm⁻¹ is the characteristic vibration mode of C - H bonding of aromatic nuclei, 1302 cm⁻¹ assigned to the stretching of C-N bonds of aromatic amines, 1140 cm⁻¹ an strong band which considered to be the measure of 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 3.5 (b-f) shows the FTIR spectra of polyaniline/ZnFe₂O₄ composites at different percentage (5, 10, 15, 20 & 25 wt. %). The absorption peaks are found to be at 3441 cm⁻¹ correspond for N-H stretching vibration, 1581 cm⁻¹ corresponds to C = C stretching vibration of quinoid ring, 1481 cm⁻¹ 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 to 1145 cm⁻¹ corresponds to C-H in plane of aromatic rings found to be an strong band which considered to be the measure of degree of electron delocalization, and other bands like 802 cm⁻¹, 738 cm⁻¹, 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 which corresponds to the vibration of octahedral group of Fe⁺³O⁻², which confirm the formation of the polyaniline / Zinc ferrite composites [23].

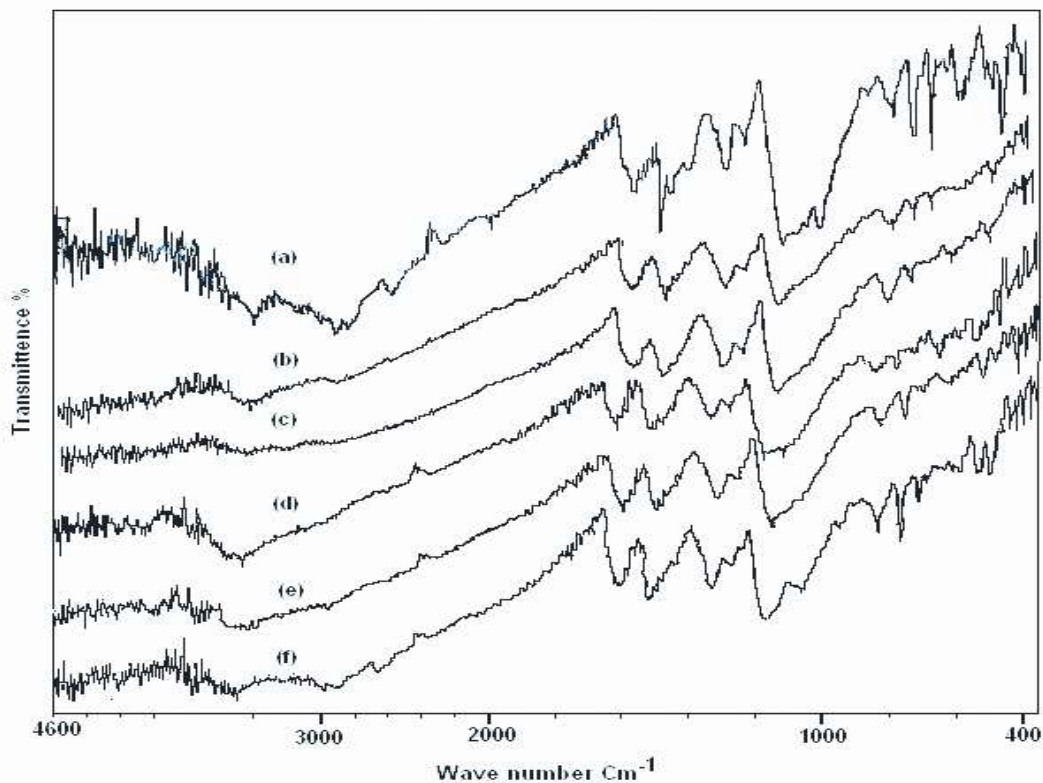


Figure 3.5: shows the FTIR spectra of PANI/ZnFe₂O₄ composites of different weight percentage.

Figure 3.6 shows that the AC conductivity of pure polyaniline and polyaniline/ZnFe₂O₄ composites (5, 10, 15, 20 & 25 wt%) at room temperature with respect to frequencies. The conductivity of pure polyaniline and its composites increases with increasing frequencies, obeys universal power law. The conductivity is almost constant up to 10⁵ Hz and then suddenly increases with increasing in frequencies are the characteristic property of disordered materials. Among all composites 20 wt % shows high conductivity, due to dipole polarization where the rotation of dipoles between two equivalent equilibrium positions is involved. It is the spontaneous alignment of dipoles in one of the equilibrium positions that give rise to the nonlinear polarization behavior of these composites [20].

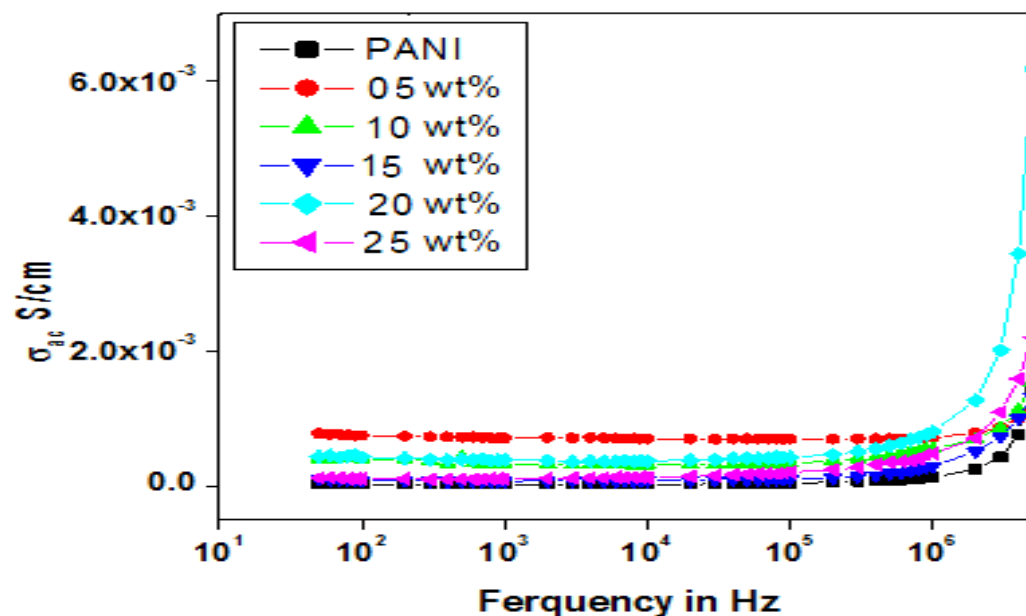


Figure 3.6: shows AC conductivity as a function of frequency for polyaniline – ZnFe₂O₄ composites

4. CONCLUSION:

In this present study, it has been synthesized successfully the conducting polymer, Polyaniline and its composites i.e. PANI / ZnFe₂O₄ in 5, 10, 15, 20 and 25 weight percentages. The structural morphology is studied using the various characterization techniques, i.e., SEM, XRD and

FTIR and found that Zink Ferrite $ZnFe_2O_4$ is well distributed in PANI. On the basis of results of electrical properties, so obtained in polyaniline – Zink Ferrite composites, they can be used as microwave absorbing materials and also in the fabrication of capacitors in high electric circuits.

5. ACKNOWLEDGMENT:

Thank you VGST and BKIT for providing facilities to conduct the tests at VGST, Department of Physics, BKIT – Bhalki.

6. REFERENCES:

- [1] A.J. Heeger, (Nobel Lecture) *Angew. Chem. Int. Ed.*, 40, (2001), 2591.
- [2] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A.J. Heeger, *Chem. Commun.*, (1977) 578.
- [3] A.G. MacDiarmid, (Nobel Lecture), *Angew. Chem. Int. Ed.*, 40, (2001) 2581.
- [4] C.K. Chiang, C.R. Fincher Jr., Y.W. Park, A.J. Heeger, H. Shirakawa and E.J. Louis, *Phys. Rev. Lett.*, 39, (1977) 1098.
- [5] H. Shirakawa, (Nobel Lecture), *Angew. Chem. Int. Ed.*, 40, (2001) 2574.
- [6] J.L. Bredas and R. Silbey, *Conjugated polymers*, (Kluwer Dodrecht, 1991).
- [7] A.J. Heeger, S. Kivelson, Schrieffer and W.P. Su, *Rev. Mod. Phys.*, 60, (1988) 781.
- [8] W.R. Salaneck and J.L. Bredas, *Solid State Comm.*, Special issue on highlights in condensed matter physics and material science, 92, (1994) 31.
- [9] J.Y. Shimano and A.G. MacDiarmid, *Synth. Met.*, 123, (2001), 251.
- [10] E.M. Genies, A. Boyl, M. Lapkowski and C. Trintavis, *Synth. Met.*, 36, (1990), 139.
- [11] Y. Cao, A. Andretta, A.J. Heeger, P. Smith and *Polymer*, 30, (1989), 2305.
- [12] J.-C. Chiang and A.G. MacDiarmid, *Synth. Met.*, 13, (1986), 193.
- [13] J.L. Cadenas and H. Hu, *Solar Energy Mate. Sol. Cells*, 55, (1998), 105.
- [14] A.G. MacDiarmid, J.-C. Chiang and A.F. Richter, *Synth. Met.*, 18, (1987), 317.
- [15] A.G. Green and A.E. Woodhead, *J. Chem. Soc.*, (1910), 1117.
- [16] A.G. Green and A.E. Woodhead, *J. Chem. Soc.*, (1910), 2388.
- [17] Y. Cao, A. Andretta and A.J. Heeger, *Polymer*, 67, (1998), 1863.
- [18] Salunkhe. R. R, Shinde, V. R, Lokhande. C. D., *Sens Actuators B*, 133 (2008) 296.
- [19] Aashis S. Roy, Koppalkar R. Anilkumar, M. V. N. Ambika Prasad, *J. App. Poly. Sci.*, (2011); DOI 10.1002/app.34696
- [20] Aashis. S. Roy, Koppalkar.R. Anilkumar and M.V.N. Ambika Prasad; *J. Appl. Poly. Sci.*, 121(2011) 675.
- [21] S.C. Raghavendra, Syed Khasim, M. Revanasiddappa, M.V.N. Ambika Prasad and A.B. Kulkarni, *Bull. Mater. Science.*, 26 (7) (2003) 733.
- [22] Narsimha Parvatikar, Syed Khasim, M. Revansiddappa, Shilpa Jain, S V Bhoraskar, and M V N Ambika Prasad *Sens and Actuators B* 114 (2006) 599.
- [23] K. Cheah, M. Forsyth, V. -T. Truong; *Synth. Metals* 94 (1998) 215. Irkhin Yu P and Turov E A. *Phys. JEPT*, 33 (1957) 673.
- [24] A. Kodge, S. Kalyane, A. Lagashetty, *Synthesis, characterization and thermal study of poly (methyl methacrylate)-Co3O4 nanocomposite film*, Volume 3, Issue 1, Summer 2012, Page 53-57.
- [25] Divakar S.J and Sangshetty Kalyane, *AC CONDUCTIVITY STUDY OF POLYANILINE / Nicufe2o3 COMPOSITES*, Volume 5, Issue 11, November (2014), pp. 10-12.
- [26] Mahantappa Limbitot, Sangshetty Kalyane, Nagbasavanna Sharanappa and Kamalakanth Lagali, *Synthesis and Characterization of Ag2O Doped Polyaniline*, (Special Issue on ICRIET-2016) 7(2); 207-211(2016).
- [27] Sangshetty Kalyane and U V Khadke, *AC conductivity of Polyaniline/Mixed metal oxide (Pani/NiCoFe2O3) Composites*, ISSN 0973-1776 Volume 13, Number 2 (2017), pp. 201-209.
- [28] Sangshetty Kalyane, *Synthesis, Characterization and ac conductivity Study of Polyaniline/ MgSnO3 Composites*, ISSN 0973-4589 Volume 12, Number 2 (2017), pp. 175-180.
- [29] Molakeri, Ajai Kumar S., Kalyane, Sangshetty, *Electrical and Magnetic Properties of Polyaniline-Zinc Ferrite Nanocomposites*, Volume 6, Number 2, June 2017, pp. 223-228(6).