

Synthesis of PANI/ZnO Composite and Study of DC Conductivity

R. V. Bobade*, S. V. Pakade (Yawale), S. P. Yawale

*Department of Physics & Electronics, Govt. Vidarbha Institute of Science & Humanities, Amravati – 444604,
Maharashtra, India

ABSTRACT

In the present study, novel electrically conducting material polyaniline(PANI) and PANI/ZnO composite is synthesized by chemical oxidation method using ammonium persulfate as oxidizing agent. The Zinc Oxide (ZnO) nanopowder is synthesized by in-situ method by using Iron Nitrate and ammonium bicarbonate solution. Various PANI/ZnO composites are prepared by varying the amount of ZnO (5, 10, 15, 20 and 25 wt% of aniline monomer). In the study DC conductivity was measured and the results showed that the D.C. electrical conductivity increases with increasing concentration of ZnO. The X-ray diffraction technique is used to determine the amorphous nature of the sample.

Keywords: Conducting polymer, Polyaniline, ZnO, DC electrical conductivity

I. INTRODUCTION

Conducting polymers have been extensively studied for its wide range of technological applications [1-3]. Amongst the variety of conducting polymers, polyaniline (PANI) is one of the most prominent polymer due to its unique electrical properties, good environmental stability and easy synthesis. It is widely used in many applications such as electromagnetic interference shielding, rechargeable batteries, chemical sensors, corrosion protection coatings, and microwave absorbing materials [4-8]. Conducting polymers provide tremendous scope for tuning of their electrical conductivity from semiconducting to metallic region by way of doping [9]. In order to modify the transport, optical and mechanical properties of materials for certain applications, dopants are added into the host materials. Moreover nanocomposite material composed of conducting polymers and oxides have open more field of application such as drug delivery, conductive paints, rechargeable batteries, toners in photocopying, smart windows, etc [10, 11]. Attempts have been made to improve the mechanical strength of conducting polymer by combining it with the inorganic materials to form a composite. Among various inorganic materials ZnO is one of the attractive and extensively used material. The present study deals with the synthesis & characterization of PANI/ZnO composites and evaluation of dc conductivity for different wt. % of ZnO in PANI composites with an intension to know the formation of composite material and effect of doping ZnO in PANI material. Conductivity is a measure of electrical conduction and thus a measure of the ability of a material to pass a current. The characterization of the composites samples prepared has been done with the X-ray diffraction analysis techniques.

II. METHODS AND MATERIAL

PANI/ZnO composites were synthesized using chemicals such as, Aniline hydrochloride [C₆H₇N.HCL], Ammonium peroxydisulphate [(NH₄)₂S₂O₈] and double distilled water for synthesis of PANI. While, Zinc sulfate [ZnSO₄] and ammonium bicarbonate [NH₄HCO₃] for synthesis of ZnO powder. All chemicals used were of AR grade of high purity (LOBA Chemicals) in this work. The double distilled water and Acetone (AR grade 99.9% purity) was used as a solvent and washing reagent in the chemical reaction respectively

A. Preparation of polyaniline (PANI)

Aniline hydrochloride (purity, 2.59 g, 20 mmol) was dissolved in distilled water in a volumetric flask to 50 mL of solution. Ammonium peroxydisulfate (purity, 5.71 g, 25 mmol) was dissolved in water also to make 50 mL solution. Thus using above solutions 0.2 M aniline hydrochloride is oxidised with 0.25 M ammonium peroxydisulfate in aqueous medium. Both solutions were kept for 1 h at room temperature, then mixed in a beaker, briefly stirred, and left to rest in order to polymerize. Next day the PANI precipitate was collected on a filter, washed with 100 mL portions of 0.2 M HCl and similarly with acetone and then dried in air.

B. Preparation of ZnO powder

The ZnO nanopowder was synthesized by in-situ method. Initially 100 ml of (0.1M) Iron Nitrate solution and 126 ml of (2.5 M) ammonium bicarbonate solution was prepared in aqueous medium. The prepared solution of zinc sulfate was then added to the solution of ammonium bicarbonate with constant stirring keeping the reaction mixture at 45°C. After some time slurry of basic zinc carbonate (BZC) in the form of white precipitate was obtained. The obtained ppt is then filtered, washed and dried. Finally zinc oxide nanoparticle is prepared by heating the dried precipitate at 500°C for 1 hr. Thus fine powder of zinc oxide is obtained.

PANI and PANI/ZnO composite samples were synthesized by chemical oxidation method. Same procedure was used to synthesize the composite with an additional step of adding the ZnO into the prepared aniline hydrochloride solution. Different composites were obtained by varying the amount of ZnO (5, 10, 15, 20 and 25 wt% of aniline monomer) and named as PB1, PB2, PB3, PB4 and PB5 respectively.

III. RESULTS AND DISCUSSION

A. XRD Analysis

The XRD patterns of pure ZnO is shown in figure 1(a), while that of PANI/ZnO composites are shown in figure 1(b),1(c),1(d),1(e) and 1(f) respectively. The main peaks for pure ZnO were observed at different values of 2θ at 32.69°, 34.35°, 36.18, 47.46°, 58.42°, 63.78°, 67.98° and 69.09° corresponding to crystal planes (100), (002), (101), (102), (110), (103), (112) and (201) respectively. The pattern thus matches to the standard XRD pattern of pure ZnO which is confirmed from the JCPDS card no 36-1451. The peaks are similar to those observed by other researchers [12]

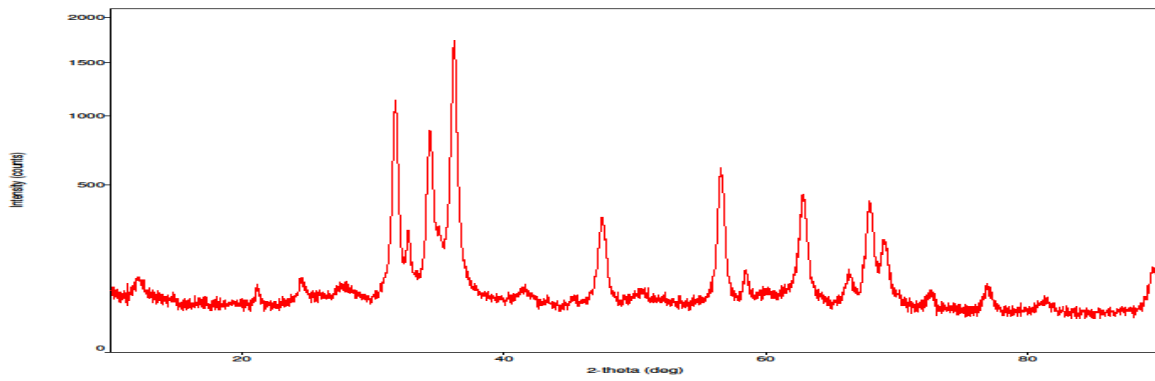


Fig.1(a) XRD spectra of ZnO sample

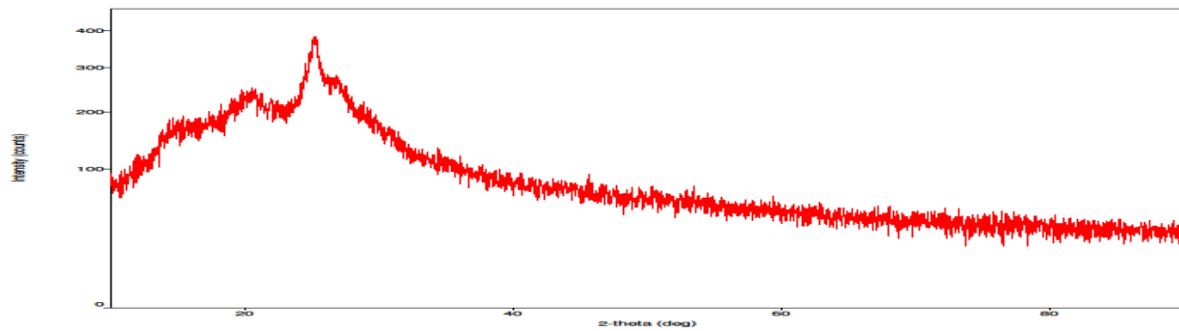


Fig.1(b) XRD spectra of PB1

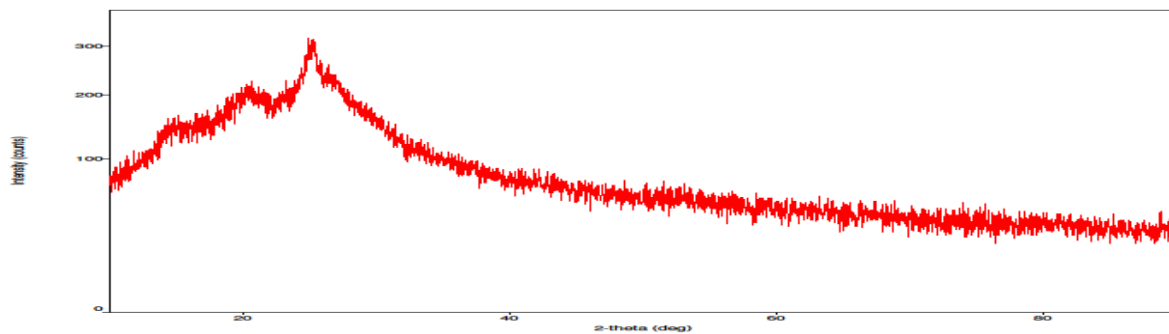


Fig.1(c) XRD spectra of PB2

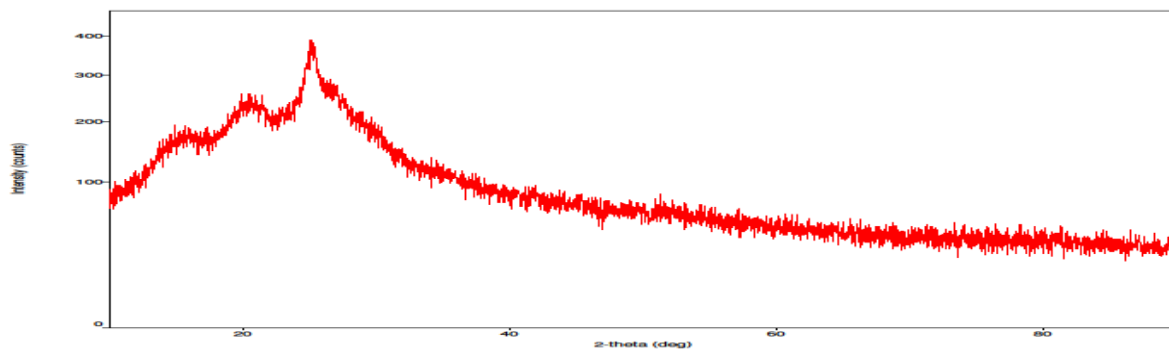


Fig.1(d) XRD spectra of PB3

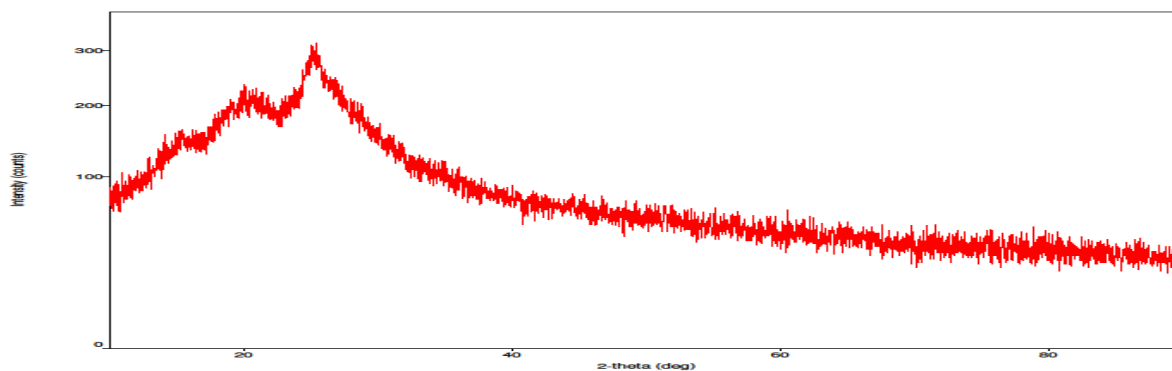


Fig. 1(e) XRD spectra of PB4

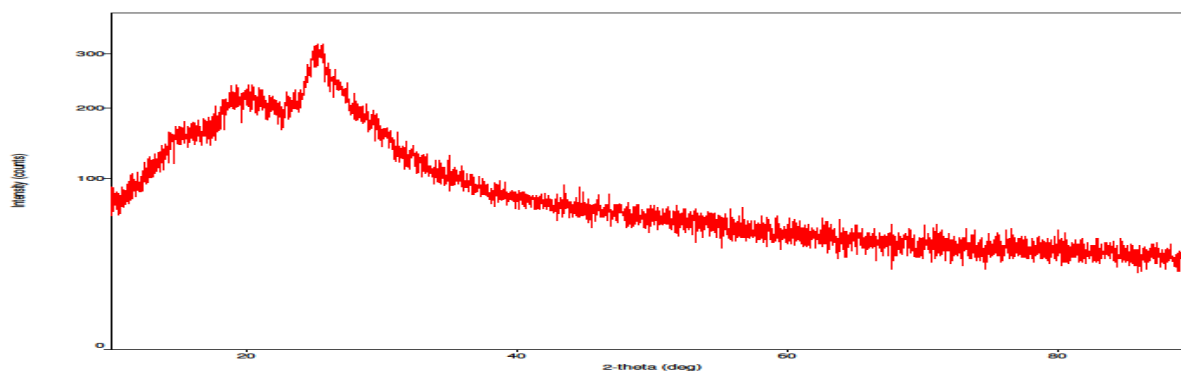


Fig.1(f) XRD spectra of PB5

The peak at $2\theta=25^\circ$, is present in all five prepared composites, indicates that the PANI retains its identity in composite phase also. Formation of composites was confirmed with lower crystallinity.

B. DC conductivity

Conducting polymers are unique, their conductivity depends strongly on their redox state. In its oxidized state CPs can exceed the upper limit of the semiconducting range, while the polymer in its reduced state it conducts poorly [13]. Doping is a process of oxidizing (p-doping) or reducing (n-doping) a neutral polymer and providing a counter anion or cation (i.e., dopant), respectively. The process of doping introduces charge carriers in the form of polarons or bipolarons into the polymer.

Conductivity mechanism:

A mechanism often used to explain the dc conductivity of conducting polymers is Mott's polaron hopping model [14]. This mechanism describes a phonon-assisted quantum-mechanical transport process in which a balance is obtained between the thermodynamic constraint on a charge carrier moving to a nearby localized state of different energy, and the quantum mechanical restraint on a carrier moving to a localized state of similar energy, but spatially separated. This description is equally applicable to charge carriers such as electrons, holes, polarons or bipolarons provided that the appropriate wave function is incorporated. The temperature dependence of the dc conductivity according to Austin et al[15] and Mott[16] is given by:

$$\sigma = n e \mu = \left(\frac{\nu_0 N e^2 R}{kT} \right) C(1-C) \exp(-2 \alpha R) \exp\left(-\frac{W}{kT}\right) \quad (1.1)$$

Where N is the number of metal ions sites per unit volume and C is the ratio of concentration of ion in low valance state to total concentration of metal ion; the term $\exp(-\alpha R)$ represents electron overlap integral between sites. R is the hopping distance and W is activation energy. Assuming that a strong electron lattice interaction exists, the activation energy W is the result of polaron formation with binding energy W_p and any energy difference WD which might exist between the initial and final sites due to variation of the local arrangements of ions. Austin et al[5] has shown that

$$W = W_H (1/2)W_D$$

$$\text{for } T > \theta_D/2 = W_D \quad \text{for } T < \theta_D/4 \quad (1.2)$$

Where, W_H is the polaron hopping energy, W_D is the disorder energy arising from the energy difference between two neighbouring hopping sites and θ_D is Debye temperature. The polaron hopping energy W_H is given by,

$$W_H = W_p/2 \quad (1.3)$$

Where W_p is polaron binding energy. The polaron hopping energy W_H calculated from the theory of Austin et al [5] is given by,

$$W_H = \left(\frac{e^2}{4 \epsilon_p} \right) \left(\frac{1}{r_p} - \frac{1}{R} \right) \quad (1.4) \quad \text{Where} \quad \frac{1}{\epsilon_p} = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}$$

ϵ_s and ϵ_∞ are the static and high frequency dielectric constants of the material respectively, ϵ_p is the effective dielectric constant [17], r_p is the polaron radius estimated from the site spacing R (for crystal like solids). The most general expression to calculate the polaron binding energy given by Holstein [18] is:

$$W_p = (1/2N) \sum_q |v_q|^2 \omega_q \quad (1.5)$$

Where $|v_q|^2$ is the electron-phonon coupling constant, ω_q is the frequency of optical phonons of wave number q and N is the site density. Another method has been given by Mott [19] which gives a direct estimate (for polar lattices[19], if the distance R through which the electron must be transferred is not large compared to r_p) of the polaron binding energy:

$$W_p = \left(\frac{1}{2} \right) \left(\frac{e^2}{\epsilon_p r_p} \right) \quad (1.6)$$

In generalized polaron model, the activation energy is

$$W = W_H - J \quad (1.7)$$

Where, J is polaron band width which is related to the electron wave function overlap on adjacent sites.

Temperature dependence of conductivity:

The conductivity of conducting polymers shows temperature dependence. They have room temperature conductivity as high as those of traditional metals. However, typical organic conducting polymers and their composites exhibits non-metallic sign (conductivity increases with temperature) [20-22], which is a challenge for conventional ideas of metallic transport.

Mott's law of variable range hopping (VRH) is usually used to interpret the temperature dependence of conductivity of the electrically conducting polymers. The model was derived for amorphous semiconductors in which charge carriers such as electrons, holes and ions move between localized states having energies compatible to the Fermi energy [23]. The localized energy states correspond to structural disorder arising from imperfect crystallinity, lower degree of conjugation, and the presence of impurities. As temperature decreases, thermal energy kT decreases, and there are fewer neighbouring states with accessible energies, so the mean range of hopping of charge carriers increases. This leads to the following expression for the conductivity:

$$\sigma = \sigma_0 \exp \left\{ - \left(T_0 / T \right)^{1/(n+1)} \right\} \quad (1.8)$$

Where σ_0 is the pre-exponential factor, T_0 is the characteristic temperature of thermally assisted hopping and n ($= 1, 2, \text{ or } 3$) is the dimensionality of the process. The electron normally jump to a site for which the activation energy W is as low as possible, and is given as:

$$W = 3 / 4 \pi R^3 N(E_F) \quad (1.9)$$

Where $N(E_F)$ is the density of states at the Fermi energy. The probability of a hop per unit time can be given as:

$$P = \nu_0 \exp \left[-2 \alpha \bar{R} - \frac{W}{kT} \right] \quad (1.10)$$

Where, ν_0 is a jump rate factor and k is Boltzman's constant. Here α is defined so that $\exp(-\alpha r)$ is the rate at which the atomic wave function on a single potential well falls off with distance r . The conductivity will be obtained by:

$$\begin{aligned} \sigma &= e^2 N(E_F) \bar{R}^2 P \\ &= K_0 T^{-1/2} \exp \left[- \left(\frac{T_0}{T} \right)^{1/4} \right] \end{aligned} \quad (1.11)$$

Where e is electronic charge

DC conductivity analysis:

The dc electrical conductivity of the samples for different molar concentration of ZnO is measured in the temperature range 303 – 353K by measuring the resistance of the samples. It was found that the value of the conductivity depends upon the composition of the sample as well as its temperature as shown in Fig.2 (a) and Fig.2 (b)

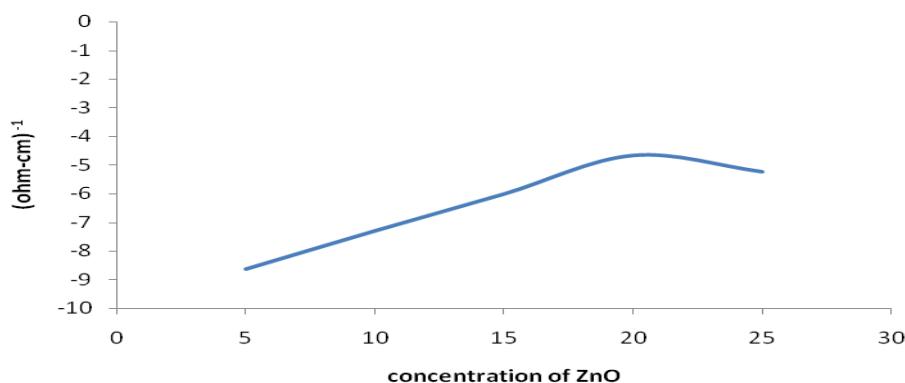


Fig. 2(a): Variation of dc conductivity with concentration of ZnO

The increase in conductivity of composite films with molar concentration of ZnO can be explained on the basis of formation of conducting Pani/ZnO network in the structure of composite films. While the decrease in the conductivity can be due to over oxidative reaction and formation of poor conducting Pani/ZnO with low bulk density.

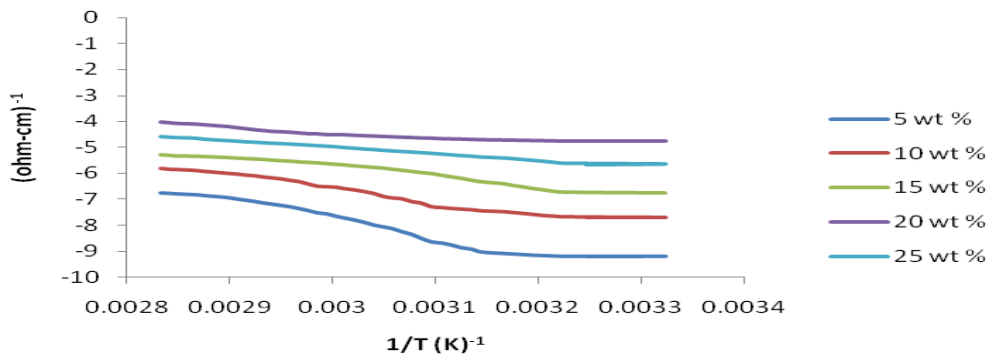


Fig 2(b):Variation of $\log \sigma$ with inverse temperature PANI- ZnO composite polymer

The increase in conductivity is due to increase in number of charge carriers with increase of ZnO content. This might be due to delocalization effect associated with doping in the composite structure [24-27]. The temperature dependence of conductivity fits the Arrhenius equation for the given temperature range and is given by, $\sigma = \sigma_0 \exp \left[\frac{-E_a}{kT} \right]$

Where 'Ea' is the activation energy and σ_0 is the pre-exponential factor.

The DC electrical conductivity of PANI/ZnO nanocomposite is significantly higher in (20 wt % ZnO) and lower in (5 wt % ZnO) nanocomposite.

IV. CONCLUSION

From the study of XRD pattern of PANI and ZnO with PANI/ZnO composite, it is confirmed that ZnO has retained its structure and the ZnO particles are uniformly distributed within polymer chain. While the DC conductivity studies shows that the conductivity of the PANI/ZnO composite increases with an increase in concentration of ZnO, the doping of ZnO in PANI produces polarons and/or bipolarons into the composite material which in turn enhances the conductivity. While the increase in conductivity with increase in temperature is attributed to polymer chain mobility and activation of dopant.

V. REFERENCES

- [1]. A. G. MacDiarmid, *Angewandte Chemie International Edition*, 40 (2001), pp. 2581-2590.
- [2]. S. Bhadra, D. Khastgir, N. K. Singha and J. H. Lee, *Progr. Polymer Sci* 34, (2009), pp. 783-810.
- [3]. J. R. Ellis. In *Handbook of Conducting Polymers*; T. A. Skotheim. Ed; Marcel Dekker: New York, Vol. 1, chap. 14, (1986), p. 501.
- [4]. T. Makela, S. Pienimaa, T. Taka, S. Jussila and H. Isotalo, *Synthetic Metals*, 85, (1997), pp. 1335-1336.
- [5]. K. Ghanbari, M. F. Mousavi. M. Shamsipur and H. Karami, *J. Power Sources*, 170, (2007), pp. 513-519.
- [6]. J. Q. Kan, X. H. Pan and C. Chen, *Biosens. Bioelectron*, 19, (2004), pp.1635-1640.
- [7]. N. Ahmed and A. G. MacDiarmid, *Synthetic. Metals* 78, (1996), pp.103- 110.
- [8]. T. L. Rose, S. D. Antonio, M. H. Jillson, A. B. Kron, R. Suresh and F. Wang, *Synthetic Metals*, 85, (1997), pp. 1439- 1440.
- [9]. Wessling B, *Handbook of conducting polymers* [New York, Marcel Dekker Inc Press] P, 1998, 471
- [10]. Jarjayes O, Fries P H and Bidan G, *Synthetic metals*, 1995, 69,343

- [11] . Butter worth M D, Corradi R, Johal J, Lascelles S F, Maeda S, and Armes S.P , J Colloid Interface sci., 1995, 174,510.
- [12] . S. M. Giripunje, J. Ghusha, Journal of Nano Research, 24, (2012),123-132.
- [13] . Saunders, B.R., Fleming, R.J., Murray, K.S., Chemistry of Materials ,7 ,(1995)1082-1094.
- [14] . Mott, N.F., Davis, E.A., 'Theory of Electrons in a Non-Crystalline Medium', Second Ed., Clarendon Press, Oxford, (1979)28, 50, 81, 205.
- [15] . Austin, I. G., Mott, N. F., Adv.Phys., 18,(1969)41
- [16] . Mott, N. F., J. Non-Cryst. Solid,1,(1968)1.
- [17] . Bogomolov, V. N.,Kudinov, E.K.,Firsov, A.,Fiz.Tvrđ. Tela.,9,(1967) 3175.
- [18] . Holstein, T., Ann. Phys., 8,(1959)243.
- [19] . Mott, N. F.,Phil. Mag.,9, (1969) 835.
- [20] . Kaiser, A. B.,Reports on Progress in Physics, 64 , (2001)1-49.
- [21] . Kaiser, A.B., Advanced Materials ,13(12-13) , (2001)927-941.
- [22] . Bobade, R.S., Pakade (Yawale), S.V., Yawale, S.P., J. Non- Cryst.Solids, 355 , (2009) 2410–2414.
- [23] . Saunders, B.R., Fleming, R.J., Murray, K.S., Chemistry of Materials, 7,(1995)1082-1094.
- [24] . Pawar S.G., Patil S.L., Chougule M.A., RauB.T.,Shashwati Sen and Patil V.B., International Journal of Polymeric Materials, 60, (2011), 979–987
- [25] . Maminya YP., Davydenko VV., Pissis P. and Lebedev EV., Eur Polym J, 38, (2002), 1887-1897.
- [26] . Huang JC, Adv Polym Technol, 21(4), (2002),299–313.
- [27] . Asif Ali Khan, Mohd. Khalid, Journal of Applied Polymer Science, 117, (2010), 1601–1607