Effect of Microstructural, Optical and Electrical Properties of host PVA by Zinc Ferrite Nano Fillers

Thirumala Patil M[1,2]*, S.N.Lakshminarasimhan[1],

[1]*Department of Industrial Engineering and Management, Sri Siddhartha Institute of Technology, Tumkur-572105,Karnataka, India.*

[2] *Department of Mechanical Engineering, Government of polytechnic Hosadurga-577527, Karnataka,India*

---***---

Abstract - *Zinc ferrite nano fillers are synthesized via way of means of the usage of chemical precipitation technique. The length of the synthesized nanoparticles is decided from XRD result. The virgin and nano sized zinc ferrite doped PVA composite films had been organized via way of means of solvent casting technique. The organized polymer nanocomposite become characterised via way of means of XRD, UV-Vis and Electrical conductivity measurements. From XRD outcomes it's far discovered that the semicrystalline polymer get becomes crystalline shape upon doping. Using the discovered UV-Vis examine Molar extinction coefficient, dipole moment, dipole power, dipole duration and oscillator power had been expected via way of means of adopting fashionable technique and version of those parameters with doping stage are attributed to adjustments withinside the orientation of the crystallites in the composite. The optical power band hole and activation power had been additionally calculated the usage of absorption spectra and it's far discovered that the optical band hole decreases and activation power will increase with filler concentration. The lower withinside the band hole and advent of latest dipoles complements the electric conductivity of the composite films. The most conductivity of 6.52571×10^{-5} S/cm is completed for 2 wt% dopant concentration.*

***Key Words**: Nanoparticles, Semicrystalline, Dipole, Charge Transfer Complex, Dipole strength*

1. INTRODUCTION

In current years polymer composites are attracted the researchers due to the reality that the preference bodily and chemical properties of a polymer for a specific utility may be acquiring the use of doping. It is discovered that the extrade withinside the properties of a polymer upon doping relies upon at the chemical nature of the dopant, polymer and the manner wherein the dopant interacts with polymer. Among the dopants, the nanoparticles are critical due to their floor to quantity ratio, which isn't the same as the majority substances. If the nanoparticles are doped in to a polymer, one could assume the changed microstructure and consequently the macroscopic properties of the polymer composite. Here extrade withinside the properties of a polymer composite are exceptional for exceptional nano particles. Among many polymers, Poly (vinyl alcohol) (PVA) is

taken into consideration as top host polymer due to its specific bodily, chemical properties and dopant structured properties [1, 2]. Ferrite belongs to the family of magnetic substances which exhibits incredible magnetic properties. Their properties are in addition improved while particle length reaches to nanometer range. The nano sized zinc ferrite is utilized in stopping brought on eddy present day and performs an critical position in inspecting the perennial diseases, magnetic garage devices, magnetic resonance imaging, fueloline sensor etc. The zinc ferrite has spinel shape and is belongs to the everyday spinel ferrite own circle of relatives withinside the bulk form. These everyday spinel ferrite modifications to the cubic spinel ferrite while its length reduces to nanoscale region. The zinc ferrite nanoparticle is an n-kind semiconductor cloth with small band gap (1.9 eV) [3] and is beneficial in seen mild photocatalytic programs. These substances have an capacity to soak up seen mild withinside the sun spectrum and for that reason it's far a capacity candidate for the sun electricity conversion. Here the ratio of zinc metallic and iron performs a first-rate position in controlling the character of $ZnFe_2O_4$ nanoparticles [4]. These magnetic nanoparticles included polymers are beneficial in optoelectronic tool programs like sensors, electrochemical show devices, huge band microwave absorbers, sun cells, etc. It is predicted that the incorporation of magnetic nanoparticles right into a polymeric matrix will regulate the microstructure and consequently the optical and different properties of the composite. The present study aims to apprehend the impact of zinc ferrite doping on microstructural, optical and electric properties of PVA.

2. EXPERIMENTAL

SYNTHESIS OF $ZnFe_2O_4$ NANO PARTICLE

ZnCl2 (0.1M) and FeCl3 (0.2M) are dissolved in separate beakers A and B containing 75 ml of distilled water and stirred properly till entire dissolution. Then, 2M of NaOH solution is introduced drop-wise to the solution B under non-stop stirring. Finally the solution A is introduced to the solution B containing NaOH and the temperature is raised to 800 C. After 3h brown color precipitate is obtained. This precipitation is collected through centrifuge technique after which washed with distilled water and ethanol for numerous times. Then the final roduct of ZnFe2O4 nanoparticles

became acquired through annealing at 75oC for 24h in a warm air oven and calcination at 500oC for 5h [4]. The ZnFe2O4 nanoparticle doped PVA films were developed through solvent casting technique by using double distilled water as a solvent [1, 5]. The PVA films with varying weight fraction of 0, 0.5, 1, 1.5 and 2 (wt%) of ZnFe2O4 nanoparticles were prepared. The polymer nanocomposite films are characterised by using different experimental techniques. The structural research had been conducted by using the Rigakusmart Lab X-ray diffractometer with CuKa radiation of wavelength 1.5406 Å. The optical properties were studied using SHIMADZU UV-1800 UV-Vis spectrophotometer and DC conductivity measurements were carried out using Keithley-236 source measuring unit. For the conductivity measurements the samples were sandwiched withinside the configuration of Ag/PVA+ZnFe2O4/Ag.

3. RESULTS AND DISCUSSION

3.1 XRD studies: The X-ray diffractograms of virgin and ZnFe2O4 doped PVA nanocomposite films are shown in Fig. 1. Figure suggests a huge peak centered at 2θ=19.560 for virgin PVA suggests the semicrystalline nature of the polymer. Using the scherrer's equation the particle size of $ZnFe_2O_4$ has been calculated from the XRD effects and is found to be 16.198 nm [5]. For composite films, it is found that the main peak is barely shifted to lower attitude with decrease in intensity and increase in the broadness of the halo with increase in the dopant concentration. Apart from this, many sharp peaks are seemed after 1 wt% of doping and those peaks are unique from the virgin ZnFe2O4. The intensity additionally will increase with the dopant concentration at the higher angle side of the diffraction halo (2θ = 24.650, 29.060 and 34.360 for 2 wt% of ZnFe2O4). This alternate suggests the crystal structure is disrupting on this region. It is exciting to note that the extra peak does now no longer coincide with any peak of virgin ZnFe2O4 (at 2θ = 29.960, 35.270, and 42.900). The observed shift and variations in the intensity of the sharp peak within the composite films suggests that the nanoparticles are dispersed in the polymer matrix and crystalline nature of the dopant within the composite isn't the same as that of free condition. To understand the impact of doping on crystal shape of the composite films the crystallinity is calculated the use of the vicinity ratio method [1] and is will increase with doping level (Fig. 1). More over the observed new peaks within the composite propose the enhancement of crystalline nature of the composite films and a lot of these effects are attributed to the interaction of dopant with the polymer and formation of complexes within the composite.
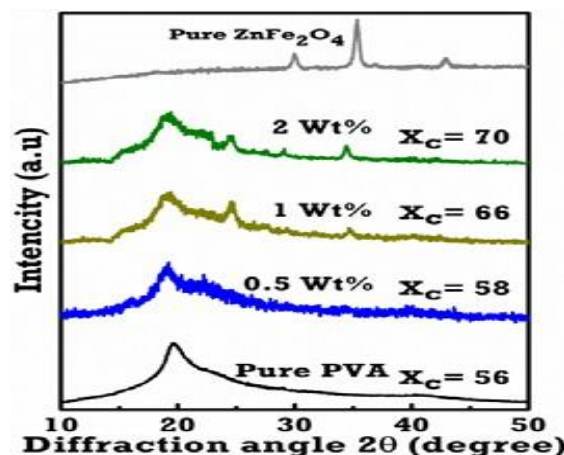

Fig -1: XRD diffractogram of pure and $ZnFe_2O_4$ doped PVA,

3.2 UV-Vis studies: The optical absorption spectra of virgin and ZnFe2O4 doped PVA nanocomposite films are displayed in Fig. 2. . From the figure, a sharp absorption peak at 196 nm (assigned to π-π* transition) with an absorption edge at 205nm is found for virgin PVA. The absorption of this peak will increase in conjunction with a shift (red shift) towards higher wavelength side (215 nm) with absorption fringe of 389 nm for 2 wt% of filler concentration. The different absorption peak found round 208 nm (associated with n- π*) with absorption fringe of 242 nm additionally shifts (red shift) to the higher wavelength facet around 320 nm with absorption edge at 570 nm for 2 wt% of dopant concentration. These adjustments imply the presence of intra/inter molecular hydrogen bonding and introduction of charge transfer complex (CTC). These CTCs are arises because of the interplay of dopant with the polymer. To recognize the impact of doping on optical properties of these films, other optical constants like transition dipole moment and oscillator energy have been anticipated the use of UV-Vis spectra. Here the incident UV light of a selected wavelength interacts with molecular dipoles of the material; emergent light offers records approximately the electricity ranges in ground state and as well as in excited states of the molecule. In such case it's far beneficial to understand the behavior of various dopant concentrations of PVA films through the use of transition dipole moment and Oscillator strength. Therefore, the use of UV-Vis information you can still estimate the transition dipole moment (μ), dipole strenght (M), dipole length (L), oscillator strength (G) and additionally molar extinction coefficient (Am) of virgin and doped polymer films the use of the strategies defined in the literature [6, 7] and anticipated parameters are indexed in the table 1. Fig. 3 indicates the variant of dipole moment (μ) and oscillator strenght (F) as a feature of ZnFe2O4 concentration and it's very clean that the dipole moment and the oscillator strength are at once varies with the dopant concentration shows the formation and variant of CTC in the composite.

To understand the optical behavior of the materials further, the optical energy band gap (E_g) and activation energy

(E$_a$) for pure and composite films were estimated by converting the observed UV- Vis spectra into Tauc's plots (E$_g$) and using Urbach rule (E$_a$) using the method explained in ref.6. Fig.4 gives the plot of (ahυ)$^{1/2}$ versus photon energy (hυ)
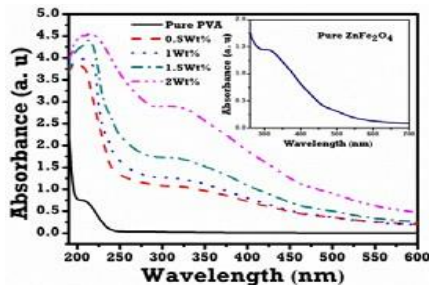

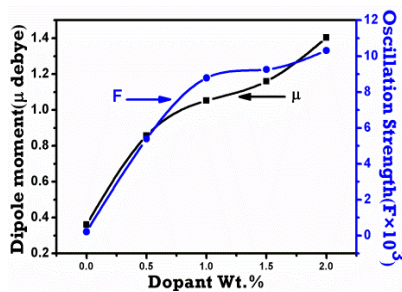**Fig-2:** UV-Vis absorption spectra of pure and ZnFe$_2$O$_4$ doped PVA,

Fig-3: Variation of dipole moment and oscillation strength with dopant concentration

(Tauc's plots) at room temperature, by extrapolating the linear portion of the curve upto (ahυ)$^{1/2}$ =0 gives the Eg Fig. 5.

3.3 DC Conductivity studies: Fig. 9 shows the measured DC Conductivity of pure and ZnFe$_2$O$_4$ doped PVA with different concentration. From the figure it is observed that the conductivity of the composite increases with increase of dopant concentration. Here the nano fillers enhances the ordering of the dipoles (observed from XRD results) within the polymer matrix via CTC formation and the polymer chains segmental motion provides a pathway for the ions to conduct. The majority of the conduction of charge carriers is due to the crystalline networks and interfacial interaction between the polymer chain and nanoparticles. The increase in filler concentration creates the new dipoles in the form of CTC within the conduction band and lives long life (confirmed from UV-Vis studies) in the form of C=C or C=O bands, which lowers the potential barriers between the charge carriers. Therefore, it clearly shows the enhancement of electrical conductivity in ZnFe$_2$O$_4$/PVA is due to the interaction of Zn-O with O-H group or Fe-O with O-H group of PVA [1, 5]. This interaction decreases the potential barriers between the charge transfer groups and provides the pathway between the hopping sites. Hence, the maximum conductivity of 6.52571X10^{-5} S/cm is achieved for 2 wt% dopant concentration.
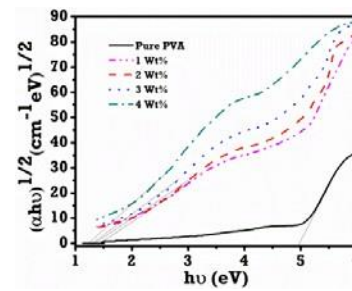

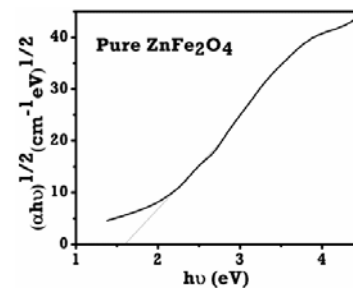**Fig-4:** Plot of (ahυ)$^{1/2}$ versus hυ of pure and ZnFe$_2$O$_4$ doped PVA

Fig-5: Plot of (ahυ)$^{1/2}$ versus hυof pure ZnFe$_2$O$_4$,
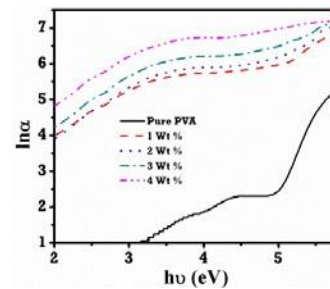
Fig-6: Plot of lna versus hυ of pure and ZnFe$_2$O$_4$ doped PVA.
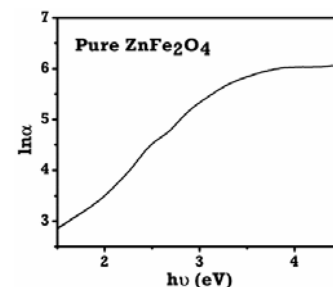
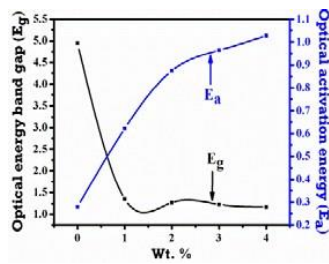**Fig-7:** Plot of lna verses hυ of pure ZnFe$_2$O$_4$

Fig-8: Optical band gap and Activation energy of pure and $ZnFe_2O_4$ doped PVA,
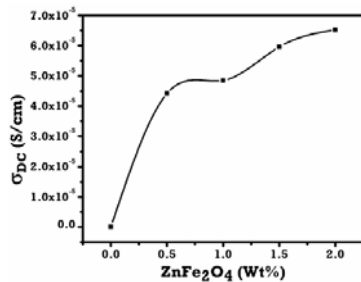

Fig-9: DC Conductivity of pure PVA and $ZnFe_2O_4$ doped PVA with different wt%.

Table -1: Molar extinction coefficient (Am), Dipole strength (M), Transition dipole moment (μ), Dipole length (L), Oscillator strength (F) of pure and $ZnFe_2O_4$ doped PVA films

Wt.%	A_m (10^6)	M (D^2)	μ (D)	L (nm)	F (10^3)
0	41.4160	0.13	0.3605	0.0749	0.2185
0.5	60.3508	0.7347	0.8571	0.1782	5.3870
1	61.6366	1.1066	1.0519	0.2188	8.7835
1.5	68.2713 1.3446		1.1596	0.2412	9.2567
2	70.7854	1.9684	1.4029	0.2918	10.311

3. CONCLUSION

Zinc ferrite nano fillers are synthesized by using chemical precipitation method. The size of the synthesized nanoparticles is determined from XRD result. The pure and nano sized zinc ferrite doped PVA composite films were prepared by solvent casting method. The prepared polymer nanocomposite was characterized by XRD, UV-Vis and Electrical conductivity measurements. From XRD results it is found that the semicrystalline polymer gets turns into crystalline form upon doping. Using the observed UV-Vis study Molar extinction coefficient, dipole moment, dipole strength, dipole length and oscillator strength were estimated by adopting standard method and variation of these parameters with doping level are attributed to modifications in the orientation of the crystallites within the composite. The optical energy band gap and activation energy were also calculated using absorption spectra and it is observed that the optical band gap decreases and activation energy increases with filler concentration. The decrease in the band gap and creation of new dipoles enhances the electrical conductivity of the composite films. The maximum conductivity of 6.52571×10^{-5} S/cm is achieved for 2 wt% dopant concentration.

REFERENCES

[1] Mahantesha B K, Ravindrachary V, Padmakumari R, Sahanakumari R, Ganesh Sanjeev, Verma V P 2018 Indian J. Pure Appl. Phys. **56** 616

[2] Padmakumari R, Ravindrachary V, Mahantesha B K, Rohan N Sagar, Sahanakumari R, Bhajantri R F 2018 AIP Conf. Proc. 1953 030248

[3] Thalkappiyan R, Vishista K 2014 Solar Energy **106** 118

[4] Annaie Vinosha P, Ansel Mely L, Emima Jeronsia J, Krishnan S, and Jerome Das S 2017 Optik **134** 99

[5] Praveena S D, Ravindrachary V, Bhajantri R F, and Ismayil 2016 Polym. Compos. **37** 987

[6] Harish A, Ravindrachary V, Bhajantri R F, Sanjeev G, Poojary B, Dutta D, Pujari P K 2008 Polym. Degrad. Stab. **93** 1554

[7] Radwan R M 2009 J. Phys. D: Appl. Phys. **42** 015419