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

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Abstract. 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 get turns in to 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 $6.52571 \times 10^{-5}$ S/cm is achieved for 2 wt% dopant concentration.

1. INTRODUCTION

In recent years polymer composites are attracted the researchers because of the fact that the desire physical and chemical properties of a polymer for a particular application can be obtaining using doping. It is found that the change in the properties of a polymer upon doping depends on the chemical nature of the dopant, polymer and the way in which the dopant interacts with polymer. Among the dopants, the nanoparticles are important because of their surface to volume ratio, which is different from the bulk materials. If the nanoparticles are doped in to a polymer, one would expect the modified microstructure and hence the macroscopic properties of the polymer composite. Here change in the properties of a polymer composite is different for different nano particles. Among many polymers, Poly (vinyl alcohol) (PVA) is considered as good host polymer because of its unique physical, chemical properties and dopant dependent properties [1, 2].

Ferrite belongs to the family of magnetic materials which exhibits remarkable magnetic properties. Their properties are further enhanced when particle size reaches to nanometer range. The nano sized zinc ferrite is used in preventing induced eddy current and plays an important role in examining the perennial diseases, magnetic storage devices, magnetic resonance imaging, gas sensor etc. The zinc ferrite has spinel structure and is belongs to the normal spinel ferrite family in the bulk form. This normal spinel ferrite changes to the cubic spinel ferrite when its size reduces to nanoscale region. The
zinc ferrite nanoparticle is an n-type semiconductor material with small band gap (1.9 eV) [3] and is useful in visible light photocatalytic applications. These materials have an ability to absorb visible light in the solar spectrum and thus it is a potential candidate for the solar energy conversion. Here the ratio of zinc metal and iron plays a major role in controlling the nature of ZnFe₂O₄ nanoparticles [4]. These magnetic nanoparticles incorporated polymers are useful in optoelectronic device applications like sensors, electrochemical display devices, broad band microwave absorbers, solar cells, etc. It is expected that the incorporation of magnetic nanoparticles into a polymeric matrix will modify the microstructure and hence the optical and other properties of the composite. The present study aims to understand the effect of zinc ferrite doping on microstructural, optical and electrical properties of PVA.

2. Experimental

2.1. SYNTHESIS OF ZnFe₂O₄ NANOPARTICLE

ZnCl₂ (0.1M) and FeCl₃ (0.2M) are dissolved in separate beakers A and B containing 75 ml of distilled water and stirred well until complete dissolution. Then, 2M of NaOH solution is added drop-wise to the solution B under continuous stirring. Finally the solution A is added to the solution B containing NaOH and the temperature is raised to 80°C. After 3h brown colour precipitate is obtained. This precipitation is collected by centrifuge method and then washed with distilled water and ethanol for several times. Then the final product of ZnFe₂O₄ nanoparticles was obtained by annealing at 75°C for 24h in a hot air oven and calcination at 500°C for 5h [4].

The ZnFe₂O₄ nanoparticle doped PVA films were prepared by solvent casting method using double distilled water as a solvent [1, 5]. The PVA films with different weight fraction of 0, 0.5, 1, 1.5 and 2 (wt%) of ZnFe₂O₄ nanoparticles were prepared. The polymer nanocomposite films are characterized using different experimental techniques. The structural studies were carried out using Rigakusmart Lab X-ray diffractometer with CuKα 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 sample is sandwiched in the configuration of Ag/PVA+ZnFe2O4/Ag.

3. Results and Discussion

3.1. XRD studies

The X-ray diffractograms of pure and ZnFe₂O₄ doped PVA nanocomposite films are shown in Fig. 1. (a). Figure shows a broad peak centered at 2θ=19.56° for pure PVA indicates the semicrystalline nature of the polymer. Using the scherrer’s equation the particle size of ZnFe₂O₄ has been calculated from the XRD results and is found to be 16.198 nm [5]. For composite films, it is observed that the main peak is slightly shifted to lower angle with decrease in the intensity and increase in the broadness of the halo with increase in the dopant concentration. Apart from this, many sharp peaks are appeared after 1 wt% of doping and these peaks are different from the pure ZnFe₂O₄. The intensity also increases with the dopant concentration on the higher angle side of the diffraction halo (2θ = 24.65°, 29.06° and 34.36° for 2 wt% of ZnFe₂O₄). This change indicates the crystal structure is disrupting in this region. It is interesting to note that the additional peak does not coincide with any peak of pure ZnFe₂O₄ at 2θ = 29.96°, 35.27°, and 42.90°). The observed shift and variations in the intensity of the sharp peak within the composite films shows that the nanoparticles are dispersed in the polymer matrix and crystalline nature of the dopant within the composite is different from that of free condition. To understand the effect of doping on crystal structure of the composite films the crystallinity is calculated using the area ratio method [1] and is increases with doping level (Fig. 1. (a)). More over the observed new peaks within the composite suggest the enhancement of crystalline nature of the composite films and all these results are attributed to the interaction of dopant with the polymer and formation of complexes within the composite.
3.2. UV-VIS studies

The optical absorption spectra of pure and ZnFe$_2$O$_4$ doped PVA nanocomposite films are displayed in Fig. 1. (b). From the figure, a sharp absorption peak at 196 nm (assigned to π-π* transition) with an absorption edge at 205 nm is observed for pure PVA. The absorption of this peak increases along with a shift (red shift) towards higher wavelength side (215 nm) with absorption edge of 389 nm for 2 wt% of filler concentration. The other absorption peak observed around 208 nm (related to n- π*) with absorption edge of 242 nm also shifts (red shift) to the higher wavelength side around 320 nm with absorption edge at 570 nm for 2 wt% of dopant concentration. These changes indicate the presence of intra/inter molecular hydrogen bonding and creation of charge transfer complex (CTC). These CTCs are arises due to the interaction of dopant with the polymer.

To understand the effect of doping on optical properties of these films, other optical constants like transition dipole moment and oscillator strength were estimated using observed UV-Vis spectra. Here the incident UV light of a particular wavelength interacts with molecular dipoles of the material, emergent light gives information about the energy levels in ground state as well as excited states of the molecule. In such case it is useful to understand the behavior of different dopant concentration of PVA films by using transition dipole moment and Oscillator strength. Therefore, using UV-Vis data one can estimate the transition dipole moment (μ), dipole strength (M), dipole length (L), oscillator strength (F) and also molar extinction coefficient (Am) of pure and doped polymer films using the methods explained in the literature [6, 7] and estimated parameters are listed in the table 1. Fig. 1. (c) shows the variation of dipole moment (μ) and oscillator strength (F) as a function of ZnFe$_2$O$_4$ concentration and it is clear that the dipole moment and the oscillator strength are directly varies with the dopant concentration indicates the formation and variation of CTC within the composite.

![Figure 1](image-url)

**Figure 1:** (a) XRD diffractogram of pure and ZnFe$_2$O$_4$ doped PVA, (b) UV-Vis absorption spectra of pure and ZnFe$_2$O$_4$ doped PVA, (c) Variation of dipole moment and oscillation strength with dopant concentration.

**Table 1:** Molar extinction coefficient (Am), Dipole strength (M), Transition dipole moment (μ), Dipole length (L), Oscillator strength (F) of pure and ZnFe$_2$O$_4$ doped PVA films.

| Wt.% | Am ($10^6$) | 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     |
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. 2. (a) gives the plot of (ahv)^1/2 versus photon energy (hv) (Tauc’s plots) at room temperature, by extrapolating the linear portion of the curve upto (ahv)^1/2 =0 gives the E_g (Fig. 2. (b)). It shows that the band gap decreases (4.9446eV - 1.1666 eV) by increase in the filler concentration (E_g for pure ZnFe_2O_4 is 1.5343eV). Fig. 2. (c) shows the relationship between the logarithmic variation of the absorption coefficient (a) and the photon energy (hv), slope of the line gives the activation energy. The figure shows that the activation energy increases with increases in dopant concentration (0.28 to 1.02883eV) (for pure ZnFe_2O_4 the E_a is 0.7225eV, Fig. 3. (a)). From the Fig. 3. (b) it is observed that the band gap (E_g) decreases and activation energy (E_a) increases with increase in the dopant concentration. The decrease in the band gap is due to creation of large number of defects within the polymer nanocomposite. The increase in the activation energy may be due to the ordering of molecules to the particular direction with dopant concentration.

3.3. DC Conductivity studies

Fig. 3. (c) shows the measured DC Conductivity of pure and ZnFe_2O_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

Figure 2: (a) Plot of (ahv)^1/2 versus hv of pure and ZnFe_2O_4 doped PVA, (b) Plot of (ahv)^1/2 versus hv of pure ZnFe_2O_4, and (c) Plot of lnα versus hv of pure and ZnFe_2O_4 doped PVA.

Figure 3: (a) Plot of lnα versus hv of pure ZnFe_2O_4, (b) Optical band gap and Activation energy of pure and ZnFe_2O_4 doped PVA, (c) DC Conductivity of pure PVA and ZnFe_2O_4 doped PVA with different wt%.
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 ZnFe₂O₄/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 6.52571×10⁻⁵ S/cm is achieved for 2 wt% dopant concentration.

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5. References
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