# Synthesis and Characterization of Polymer-Inorganic composite thin films: Applications

Shri.Shivalingappa.S.Aland,

Associate Professor in Chemistry

Department of Chemistry,

S.V.P.V.V.Samstha's

Shri.S.B.Mamadapur Arts, Commerce & Science College,

Badami-587201

## Chemistry

**Abstract:**This work presents the results of the Polymer-Inorganic (PVA-ZnO) composite thin films were prepared by solution casting method, the samples were characterized by different characterization techniques by XRD, FTIR, UV– visible spectroscopy, Mechanical and Morphological. Also, we had studied the optical properties of PVA/ZnO composites based on ZnO as inorganic filler material and PVA as the main matrix.

**Keywords:** PVA-ZnO, XRD, FTIR, UV-Vis, SEM

**Introduction:**

Polymer based nanocomposites is a subject of considerable research due to their ability to combine the advantages of both polymers and filler components. There are several applications of polymeric nanocompositesbased on their optical, electrical, mechanical and magnetic properties [1, 2]. Polymeric ZnO nanocompositematerials have attracted large interest. In particular,introduction of ZnO filler into polymeric matrices canmodify the optical, electrical and mechanical properties [3–5].Poly(vinyl alcohol) (PVA) is a water-soluble polymer with many technological, pharmaceutical and biomedicalapplications. ZnO is one of the most important widebandgap materials (3.22 eV, at 300 K) and has superiorelectronic and optical properties. As a low cost II–VI semiconductor which is    friendly, itspromising applications in short-wavelength light-emitting,transparent conductors, dye-sensitized solar cells, piezoelectricmaterials, gas sensors varistors and fully transparentthin film transistor have initiated intensive research. Several physical and chemical methods have beenused for the fabrication of ZnO nanostructures. The aims of the present study are to investigate the opticaland the dielectric properties of ZnO/PVA membranes.ZnO nanocrystals of

different size were prepared withthermal decomposition of zinc acetate and embedded in aPVA matrix. The reflection and absorption spectra of ZnOpowders and ZnO/PVA nanocomposites, respectively.

### 3.1. X Ray Diffraction Study

X-ray diffractograms for pure and ZnO incorporated PVA films are given in Figure 3.1. The pure PVA/ZnO shows a single characteristic peak at $2\theta = 20.11°$. When theZnO were added, a peak corresponding to thePVA shifts towards the higher theta value and the diffraction peak becomes broader. This implies that the dispersed and induces changes in the structural properties of thePVA. Since the concentration of ZnO is very less (0.01-0.04 wt%), peaks corresponding to it are not observed, but for higher ZnO concentrations (0.04 wt%), we can observe all peaks at 31.70° and 37.20°. The changes in the structural properties of thePVA after ZnO incorporation, were quantified in terms of crystallite size ($L_{XRD}$), lattice strain ($\varepsilon_{av}$), and crystallinity ($X_c$) of the samples.
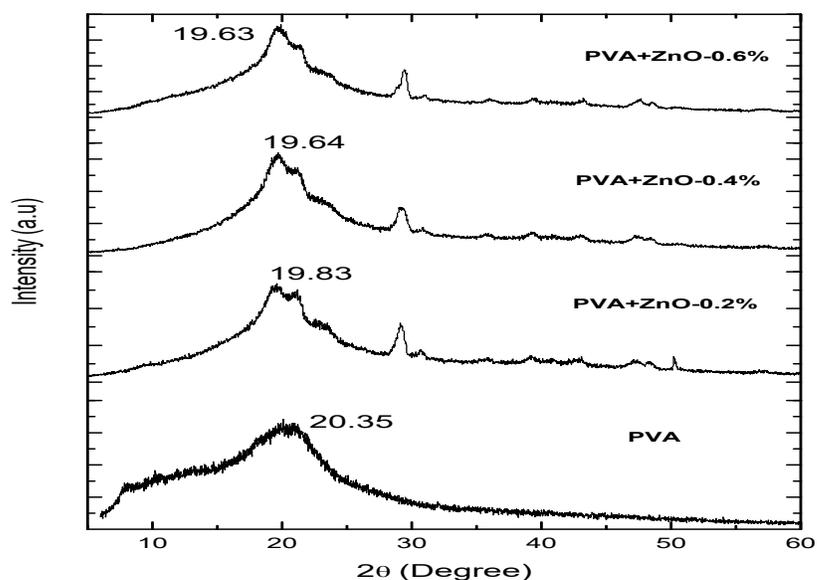


**Figure 1:** XRD Scans of PVA/ZnOfor different concentrations of ZnO.

The XRD patterns of the polyvinyl alcoholand PVA/ZnO composites films at various weight percentages areshown in Fig. 1. It is suggests that the PVA is amorphous in nature.A peak maximum is observed to be around $20.35^0$ for polyvinyl alcohol,which may be assigned to the scattering between

polyvinylalcohol chains at interplanar spacing. Thehomogeneously distributed ZnO increases the high surfacearea of PVA/ZnOcomposites, leading to increase in the crystallinity ofthe polymer composites [3]. Therefore, the degree of crystallinityof polyvinyl alcohol increases and the diffraction peaksmerged into the zinc oxide peaks, which cannot be distinguished.By comparing the XRD patterns of PVA/ZnO composite withthat of ZnO, the observed that the plane oriented to(100), (002), (101), (102), (110), (103), (112) and (201) due tocorresponding to $2\theta = 29.25^0$, $30.63^0$, $36.04^0$, $40.35^0$, $43.02^0$,$47.20^0$ and $50.18^0$ which shows the presence of zinc oxide in polyvinylalcohol. The XRD patterns of pure polyvinyl alcohol, ZnOandits composite indicates that ZnO has retained its structure eventhough it is being capped with PVA after formation of composites.This is due to the weakening of the van der Waal's forces between the polymer molecules, 1) Increase in lattice strain with increase in ZnOconcentration, and 2) Decrease in crystallinity of PVA.These changes result in more broadening of the X-ray Bragg's reflections and hence, decrease in the microstructural parameters. On a macroscopic scale, these affect the mechanical parameters like tensile strength, Young's modulus, and percentage of elongation.
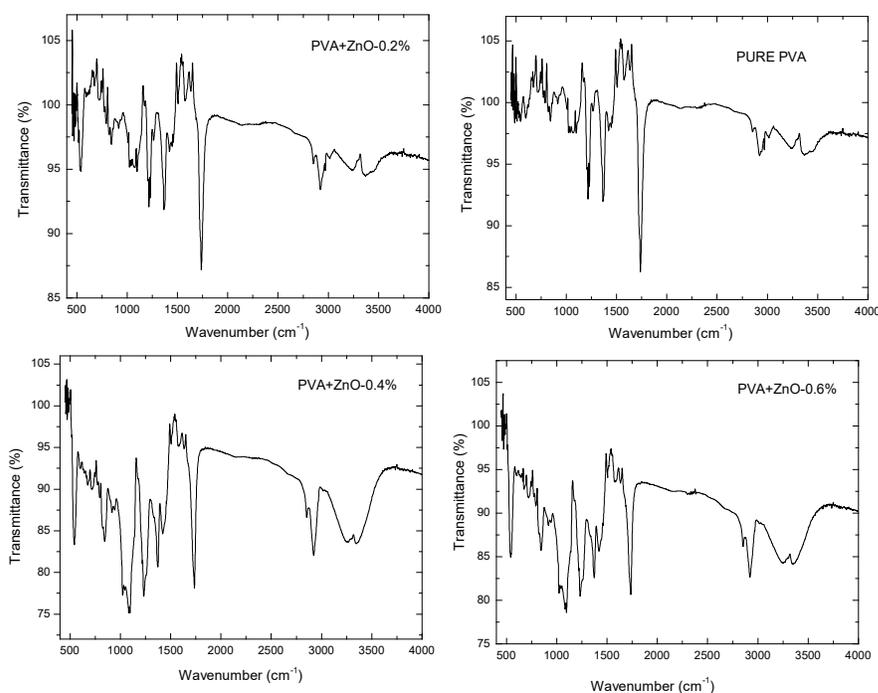
## 2. FT-IR spectra analysis



**Figure 2:** FT-IR Transmittance curve of PVA/ZnO composite for various wt%

Fig. 2 shows Fourier transform infrared spectra of pure PVA film, and PVA–ZnO polymer composite samples where the interactions between dopant and the host PVA polymer matrix are clearly seen. Figure. 2. For the spectra of the PVA film, astrong and broad absorption band at 3334 cm$^{-1}$ is attributed tothe O–H stretching vibration. The bands at 2912 and2940 cm$^{-1}$are assigned to the C–H stretching vibration of –CHand –CH2, respectively. The peak at 1422 cm$^{-1}$is designatedas a CH2 scissoring mode, while the peaks at 1374 and1329 cm$^{-1}$are attributed to the CH2 deformation, and thebands at 1093 cm$^{-1}$and 916 cm$^{-1}$are due to the C–O and C–Cstretching vibrations. The band at 850 cm$^{-1}$is due to theCH2 rocking mode [2]. The moderate absorption peak at1658 cm$^{-1}$is assigned to the O–H bending mode of the –OH groupsin the PVA [3]. The band at 1235 cm$^{-1}$is due to the C–O–C vibration in the vinyl acetate group [4]. Notably, the peak at 1143 cm$^{-1}$, which is related to the C–O stretching vibration ingroups at the surface of the ZnO.The stretchingvibration of the N–H and the O–H on the surface ofthe ZnO is located at 3200–3600 cm-1. For thecombined action of the N–H, the O–H on the surface of the ZnOand the O–H in the PVA, the peak at 3334 cm$^{-1}$in the spectra of the PVA/ZnO is far broader than that in the PVA spectra.

## 3. UV-visible analysis

### Optical properties

The UV–Visible absorption spectroscopy is a widely usedtechnique to examine the optical properties of nano sized particlesand hence nanocomposite films. The UV–Visible absorption spectra of pure PVA, nanoZnO and PVA–ZnOnanocompositesover the range 200–800 nm were recorded using a double beamCary 5000 UV–Visible spectrometer and are shown in Fig. 3.The absorption spectrum of pure PVA shown in Fig. 3a ischaracterized by a sharp absorption edge at 241 nm [5] whichmay indicate either an un-hydrolyzed acetate group in the PVAback bone [6] or the semi crystalline nature of PVA [7].The optical absorption spectrum of nanoZnO is shown inFig. 3b. The absorption edge in this occurs at 371 nm (3.318 eV)which is blue shifted with respect to characteristic bulk ZnO(380 nm, 3.268 eV) at room temperature [8]. This shift may bedue to the quantum confinement effect i.e., due to the reduction in the crystallite size. The absorbance spectrum of PVA–ZnOnanocomposite films is shown in Fig. 3c–f. As indicated in thefigure, doping of nanoZnO into PVA matrix has enhanced the

absorbance of the PVA host in the UV–Visible region. It is clear thatthe absorption edge shifts systematically to the higher wavelengthor lower energy corresponding to blue–green region of the visiblespectral range with increasing concentration of ZnOnanoparticles.The observed red shift in energy may be due to the development ofmicrostrain in PVA–ZnO composite matrix due to the incorporationof dopant ZnO. This strain results in variation in energy band

structure of the dopant ZnO and is reflected in the absorption edgeshift. Formation of more defect states in the energy gap due to thedopant nanoZnO[8–9] is also another possible mechanism thatmay be contributing to the shift.
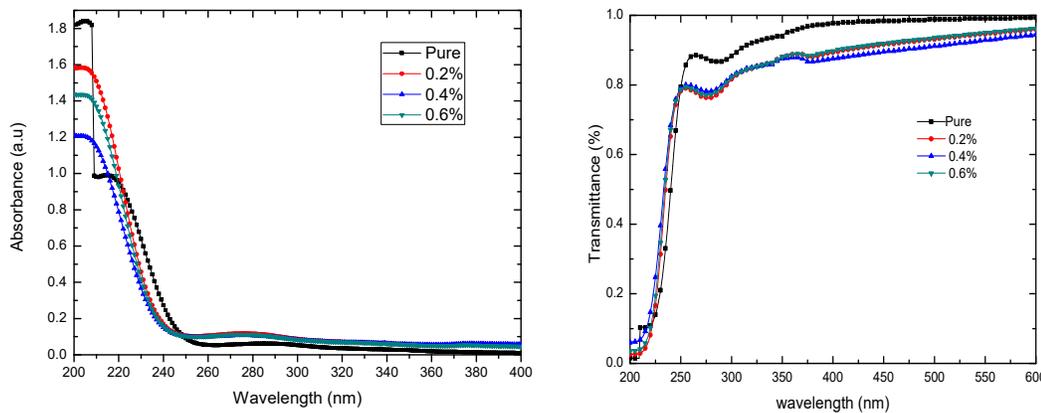


**Figure 3.**Absorption and transmittance spectra of (a) pure PVA; (b) PVA–ZnOcomposite films.

### 3.1. Determination of optical band gap

The optical transitions in nanocomposite films can be easilyunderstood by determining the optical band gap by translating the. UV–Visible spectra into Tauc's plot [10,11]. The frequencydependent absorption coefficient is given by

$$\alpha(h\nu) = B(h\nu - E_g)^r / h\nu$$

where a is the absorption co-efficient, hυ is the incident photonenergy, B is the parameter that depends on the inter bandtransition probability, Eg is the optical band gap and r is an index

Characterizing the nature of the electronic transitions causing theoptical absorption 'r' can take values 1/2, 3/2, 2, and 3 for directallowed, direct forbidden, indirect allowed and indirect forbiddentransitions, respectively.
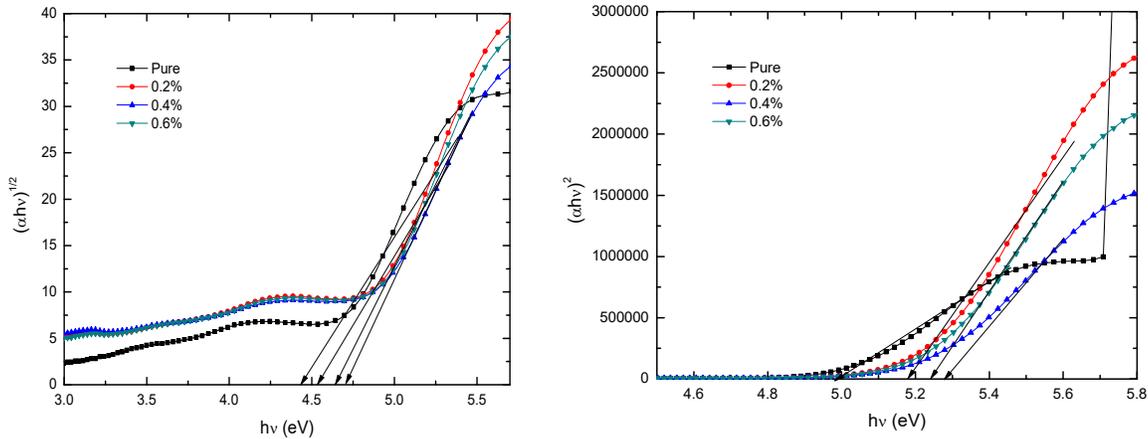
**Figure. 4.**Direct and Indirect band gap of pure PVA and PVA–ZnO composite films.

Influence of indirect transitions in nanocomposite films due toincorporation of filler PVA-ZnO into polymer matrix is understoodby estimating indirect band gap values from the plots of $(\alpha h v)^{1/2}$ versus$(h v)$ as shown in Fig. 4a. Extrapolating the linear portion ofthe graphs to $(h v)$ axis determines the respective optical energy gap.From Fig. 4a it is clear that the values of indirect band gapincreases in energy (from 4.43 eV to 4.70 eV) with increase indoping level. This decrease in band gap may be the result of twomechanisms.

The first is the formation of donor levels at the bottom of theconduction band resulting from the tensile strain induced inthe composite films. The second is the formation of defects inthe polymeric matrix.These defects produce localized states in theoptical band gap and these localized states are responsible for increasing energy band gap when dopant (filler) is increased in thepolymer matrix [12]. Variation of optical band gap andmicrostrain with different dopant concentration are given in Fig. 4b.The increase in band gap is directly correlated with increase in strainupto 10mol%, whereas at 20 mol% the increase in energy gap islarger and both the strain factor as well as the formation of the defectstates may be contributing to the observed gap.

## 4. SEM analysis

The scanning electron micrographs of pure PVA film, ZnOnanopowder and ZnO doped PVA films are shown in Fig. 3. SEM of purePVA at high magnification (Fig. 3a) shows uniformly processedsmooth PVA matrix and at low magnification (Fig. 3b) the semicrystalline nature of PVA supporting the observations of XRDanalysis. The micrographs of pure ZnOnano powder (Fig. 3c) showthat the particles are made up of

agglomeration of many primarycrystallites with irregular size and shape which is due to theenormous heat generated during the combustion reaction. Further,the images reveal the presence of voids and pores on the surface ofZnO sample.
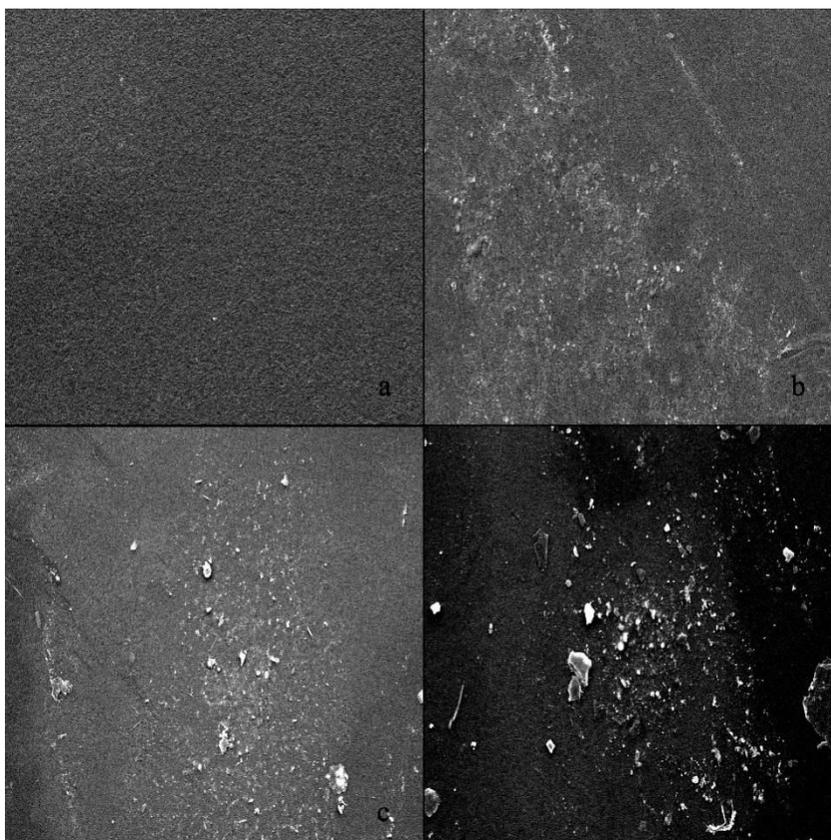


Fig. 5. SEM micrographs of (a) pure PVA (b) PVA–ZnO(0.2%) (c) PVA–ZnO(0.4%) (d) PVA–ZnO(0.6%) composite films.

These pores are attributed to the inherent nature ofcombustion derived products due to the large amount of gasesliberated during the combustion process. The micrograph at highermagnification (Fig. 5d) shows the hexagonal pyramid formassociated with quasi platelet structures and the formation ofquasi-spherulitic polycrystalline aggregates are also noticed. SEMimage of PVA–ZnO composites (Fig. 5e–h) confirm the changes inthe morphology of pure PVA with dispersion of ZnO into thepolymer matrix. SEM shows uniformly dispersed ZnO, wheremore compactness exists as concentration of dopant increasesindicating more crystalline nature of the sample and the surface isrough compared to pure PVA. [13]

## Conclusions

The bionanocomposite is prepared successfully by incorporating ZnO materials on PVA polymer matrix by simple solution casting technique. The interaction between the polymer is more physical by the formation of hydrogen bonds between the polymer chain and the surface oxygen atoms of theZnO. The addition of ZnO rearranges the fringed micell structure of the PVA by increasing the crystallite size and crystallinity.

The basic optical properties and optical constants of the PVA/ZnO composite films have been investigated by means of absorbance and transmittance spectra. The optical constants such as the optical band gap (Eg), of PVA/ZnO composite films were determined. PVA/ZnO composite films has been investigated as a potential technique of refractive index modulating optical elements.The PVA-ZnO Bio-composite films improve the mechanical properties compared to the pure PVA film. Hence, PVA/ZnO Bio-composite films is a promising candidate for packaging materials in the food.The solution casted PVA/ZnO composites containing various wt% of ZnO were prepared and characterized by FTIR and XRD techniques. FTIR peak at 558 cm$^{-1}$ showed the presence of ZnO in the composites. The infrared spectrometry confirmed the presence of ZnO in PVA matrix.XRD showed the crystal structure of ZnO did not altered after preparation of the composites. The surface morphology and morphology of the PVA/ZnO composites films elucidated by SEM observed that PVA film surface is smoother than other composite films.

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