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Formation and Properties of ZnO Nanoparticle Dispersed PVA Films

R. Divya[1], M. Meena[2], C. K. Mahadevan[2] And C. M. Padma[1]
[1] Department of Physics, Women's Christian College, Nagercoil – 629001, Tamilnadu, India.
[2] Physics Research Centre, S.T. Hindu College, Nagercoil – 629002, Tamilnadu, India

Abstract:- We report here the preparation and properties of ZnO nanoparticle dispersed polyvinyl alcohol (PVA) films. X-ray diffraction measurement carried out on the five prepared films (pure and 4 different ZnO concentrated) shows an increase in crystallinity with ZnO content. Field emission scanning electron microscopic analysis shows an increase of dispersion stability with the increase in ZnO content. In order to understand the change in some physical properties of PVA film due to ZnO dispersion, the prepared films were subjected to UV-Vis-NIR spectral, photoluminescence spectral and electrical (both DC and AC) measurements. Results obtained in the present study indicate an increase of optical extinction coefficient, UV absorption, absorption edge wavelength, PL wavelength and electronic conductivity and a decrease of refractive index, optical band gap and dielectric constant due to ZnO dispersion.

1. INTRODUCTION

Polymer matrix based nanocomposites with embedded nanoparticles have become a prominent area of current research and development in both nanotechnology and polymer territory. Nanocomposites based on semiconductor nanoparticles and polymer matrix are prospective materials for application in optoelectronics [1], for creation of luminescent materials [2], sensor electronics [3], etc. Introducing semiconductor nanoparticles into polymer matrix volume changes physicochemical properties of the system. The properties of the obtained structures depend on a semiconductor particle type, dimensions of particles, etc. The polymers modified by metal oxide nanoparticles have been prepared by sol-gel process, by polymerization of monomer containing nanoparticles and by dispersing of nanoparticles in a polymeric matrix [4-7]. The presence of nanoparticles in polymer improves the mechanical, electrical and optical properties of the material and it is possible to control these properties, including the refractive index, by concentration and size of the particles [8-11].

Polyvinyl alcohol (PVA) is a material with technological potential as a water processable polymer. It is produced through the hydrolysis of polyvinyl acetate. It is strong, durable and possesses high crystalline structure [12].

Zinc oxide is a wide band gap material that can crystallize in a cubic zinc blende or wurtzite structure with many promising properties for blue/UV optoelectronics, transparent electronics, spintronic devices and sensor applications. The importance of ZnO is due to its unusual physical properties such as high conductance, chemical and thermal stability [13], wide and direct band gap of 3.37 eV [14], and a high excitation binding energy of 60 MeV [15]. Moreover, it has good radiation resistance [16], and is harmless to the environment [17]. The ZnO nanostructure has great potentiality for being used in preparing solar cell, acoustic, electrical and optical devices, chemical sensors, catalysts, pigments, cosmetics, varistors and gas sensors [18, 19]. Nanoparticles filled polymers provide advantages over micron-filled polymers because they provide resistance to degradation [20] and improvement in thermo-mechanical properties without causing a reduction in dielectric strength.

Recently, the polymer inorganic nanocomposites with high dielectric permittivity have been considered to be potential candidates for integration into electronic devices. Owing to the continuous development towards the miniaturization of electronics, newer dielectric materials were sought which would enable to achieve high energy density for capacitor applications. As a white powder, ZnO finds extensive use today as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g., car tires), lubricants, paints, ointments, adhesives, sealants, pigments, foods (as a source of Zn nutrient), batteries, ferrites, fire retardants, first aid tapes, etc [21-23]. On the basis of this knowledge, this study aims to disperse ZnO in different concentrations in a PVA matrix to develop new hybrid materials for electrical and optical applications. The results are reported herein.

2. PREPARATION OF PURE AND ZNO DISPERSED PVA THIN FILMS

Polyvinyl alcohol, dimethyl sulfoxide (DMSO), demineralised water, zinc acetate and urea were purchased from Aldrich. Pure PVA thin film was prepared by dissolving 2.5 g of PVA in a mixed solvent of DMSO and water at 40 ^{o}C and stirred continuously for about 1 hour. The thin film was made by evaporating the excess solvent by pouring the solution in petri dish and dried in sunlight. For ZnO dispersed PVA films, the above prepared PVA solution was modified by adding 2.5 wt% of zinc acetate and urea solution. The same procedure was followed for the remaining three concentrations (5.0, 7.5 and 10 wt%) also. Pure and four ZnO dispersed PVA thin films were prepared and characterized by X-ray diffraction (XRD), field effect scanning electron microscopic (FESEM), thickness, UV-Vis-NIR spectral, photoluminescence (PL) spectral and electrical (both DC and AC) measurements using the available standard procedures. The polymer films prepared in the present study are represented as: Pure PVA for the pure PVA polymer film and 2.5 % ZnO, 5.0 % ZnO, 7.5 % ZnO and 10 % ZnO respectively for the 2.5 wt%, 5.0 wt%, 7.5 wt% and 10 wt% ZnO dispersed PVA polymer films.

3. CHARACTERIZATIONS MADE

The XRD measurements were carried out on all the five films prepared in the present study using an automated X-ray powder diffractometer (XPERT PRO PANalytical) with CuKα radiation of wavelength 1.54056 Å. The FESEM images were obtained by using a FESEM-SUPRA 55 microscope (CARL ZEISS, GERMANY). The thickness of the films were measured using a US Mprobe VIS spectroscopic reflectometer. The UV-Vis-NIR spectral analysis was carried out in the wavelength range 190 – 900 nm using a Jasco V– 630 spectrophotometer. Optical band gap, extinction co-efficient and refractive index were determined from the UV-Vis-NIR absorption spectrum. The PL measurement was carried out by using a ―perkin Elemer spectrophotometer‖. The DC electrical conductivity measurement was carried out at various temperatures ranging from 30-90 °C by the two probe method [24-27] using a million megohm meter. The AC electrical (dielectric) measurements were performed (capacitance, C and dielectric loss factor, tan δ were measured) by the parallel plate capacitor method [28-31] using an impedance analyzer (Agilent 4284A LCR meter) at room temperature with various frequencies ranging from 20 to 1×10^6 Hz. Real and imaginary parts of the dielectric constant (ε' and ε”) and AC electrical conductivity (σ_{ac}) were determined from these measurements by adopting the procedures available in the literature [32]. For the electrical measurements, the film samples were cut into circular pieces of diameter 13 mm and coated with silver paste (to establish a good ohmic contact) and mounted between the electrodes of the parallel plate capacitor.

4. RESULTS OBTAINED

4.1 XRD patterns

The XRD patterns of as-prepared pure and ZnO dispersed PVA polymer films (composites) observed in the present study are shown in Figure 1. XRD pattern of pure PVA compares well with that reported earlier [33].

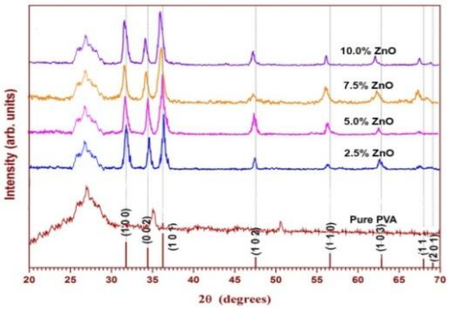

Fig 1: XRD patterns of the as-prepared pure and ZnO dispersed PVA films

In patterns for the ZnO-PVA nanocomposites, the peaks of both components remain for all ZnO concentrations, without any appreciable change in peak positions or widths for those peaks assigned to the ZnO phase [JCPDS File # 36-1451]. Moreover, the peak related to PVA at 27° of the composites becomes greatly intensified compared to that of pure PVA indicating an increase in crystallinity.

4.2 Thickness of films

The thickness was measured at different places in every film and the average values were determined and given in Table 1. The thickness measured in various places of the film does not vary much indicating the uniformity of the films prepared in the present study.

Table 1: The average thicknesses of the as-prepared pure and ZnO dispersed PVA thin films

Sample name	**Thickness (x 10^{-10} m)**
Pure PVA	1758
2.5 wt % ZnO	1782
5.0 wt % ZnO	1745
7.5 wt % ZnO	1825
10.0 wt % ZnO	1810

4.3 FESEM photographs

Field emission scanning electron microscopy has been used to study the compatibility between various components of the polymer composites through the detection of phase separations and interfaces. It has great influence on the physical properties of the polymer composite. Figure 2 shows the FESEM photographs of the as-prepared pure and ZnO dispersed PVA polymer composites. The films exhibit uniform density of grain distribution in the surface at lower concentrations of ZnO. At higher concentrations of ZnO, the surface morphology of the ZnO dispersed PVA polymer composite films shows many aggregates or chunks randomly distributed on the top surface. The results indicate that the nanosized ZnO particles tended to form aggregates and dispersed into the PVA polymer matrix. In effect, the FESEM analysis shows an increase of dispersion stability with the increase in ZnO content in the as-prepared ZnO dispersed PVA polymer films.

Results obtained in the XRD and FESEM analyses and thickness measurement indicate that the simple chemical method adopted in the present study along with zinc acetate, urea and PVA as the precursors favors the formation of films of proper ZnO-PVA nanocomposites.

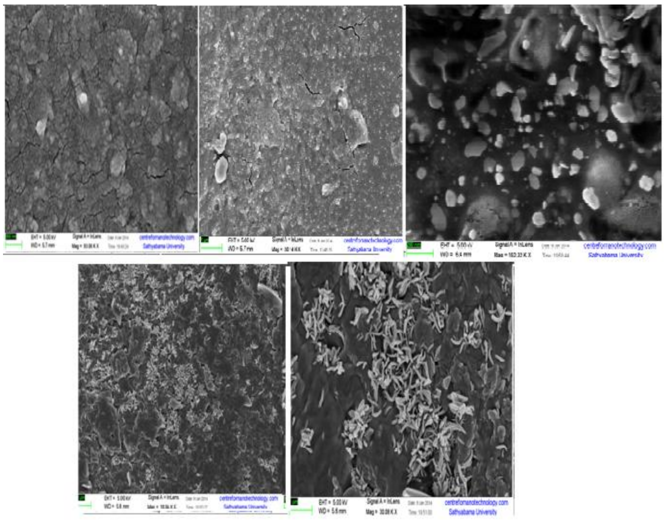

Fig 2: FESEM images of as-prepared pure and ZnO dispersed PVA films [a) Pure PVA, b) 2.5% ZnO, c) 5.0% ZnO, d) 7.5% ZnO and e)1.0% ZnO]

4.4 UV-Vis-NIR spectra

The spectroscopic behavior of materials is utilized to determine their optical parameters, viz. optical band gap (E_g), refractive index (n) and extinction coefficient (K). The variation of optical absorption with wavelength observed for all the as-prepared films is shown in Figure 3. Addition (dispersion) of ZnO in PVA produces red shift in the absorption edge. Moreover, the observed spectra indicate that the dispersed ZnO nanoparticles enhance the optical absorption of the PVA host. This further indicates that the lower concentrated ZnO dispersed PVA film may act as an ultraviolet shield and can be expected to be useful in sunscreen devices.

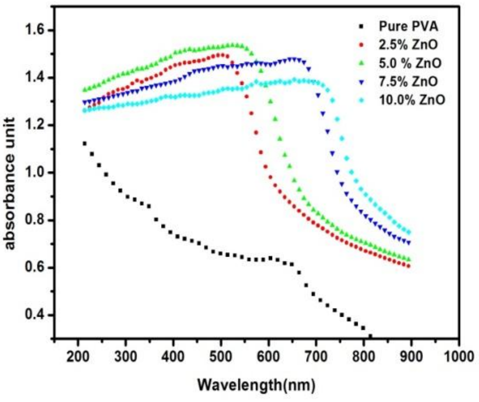

Fig 3: UV-Vis-NIR absorption spectra of the as-prepared pure and ZnO dispersed PVA films

The plot of energy versus $(\alpha h\nu)^2$ (Tauc plot) for the present experimental data near the absorption edge gives a linear fit over a wide range of energy (shown in Figure 4). This linearity suggests the presence of indirect allowed transitions in the investigated films filled with different concentrations of ZnO. Extrapolation of the linear portion of the plots to the abscissa yields the optical energy band gaps. The optical band gap observed for the pure PVA polymer film in the present study (3.474 eV) is comparable with that reported in the literature (3.37 eV) [14]. Figure 4 reveals that ZnO dispersion decreases the optical band gap of PVA polymer although not systematically with ZnO concentration. Minimum optical band gap has been obtained for the 5.0 wt % ZnO dispersed PVA film. The decrease in the optical energy band gap with filling may be explained on the basis of the fact that the incorporation of small amounts of dopant forms charge transfer complexes in the host matrix [34, 35]. These charge transfer complexes increase the electrical conductivity by providing additional charges, resulting in a decrease of the optical energy gap. As the dopant concentration is increased, the dopant molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carriers between two localized states [36].

The reflectance (R) can be estimated from the observed values of transmission (T) and absorbance (A) using the relationship:

$$R+T+A=1$$

For normal reflectance, the refractive index can be determined from the relation [37]:

$$n=\frac{(1+R)}{(1-R)}+\sqrt{\frac{4R}{(1-R)^2}-K^2}$$

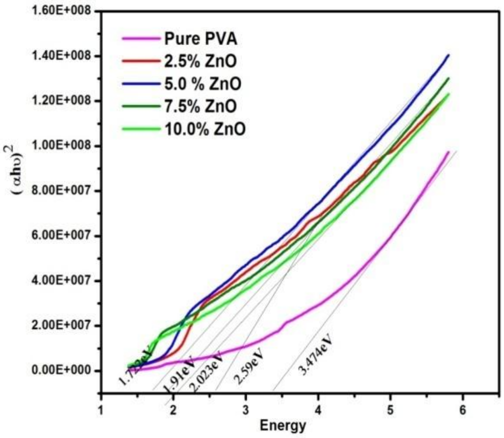

Fig 4: Plots of energy versus $(\alpha h\nu)^2$ observed for the as-prepared pure and ZnO dispersed polymer films

The extinction coefficient (K) is related to the absorption coefficient by the relation:

$$K=\frac{\alpha\lambda}{4\pi}$$

Here, λ is the incident photon wavelength.

Variations of refractive index and extinction coefficient with wavelength obtained using the above relations are shown in Figure 5. Embedding of ZnO nanoparticles in the PVA host matrix increases the extinction coefficient and decreases the refractive index. This is due to the increase in optical absorption due to ZnO dispersion in the PVA polymer matrix.

The increase in refractive index observed due to ZnO dispersion proves the presence of ZnO in the PVA matrix, because ZnO has higher refractive index (n =2.004). Moreover, it can be seen that the refractive index increases almost in proportion with the increase in ZnO concentration considered for the preparation of films.

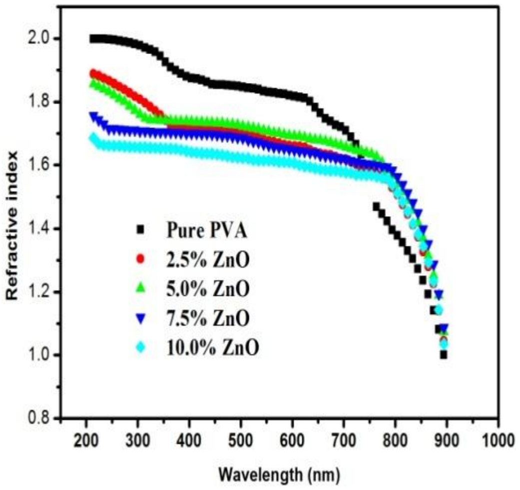

Fig 5: Variations of refractive index with wavelength obtained for the as-prepared pure and ZnO dispersed PVA films

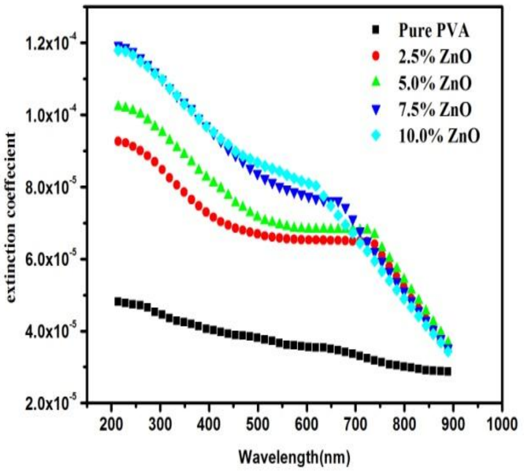

Fig 6: Variations of extinction coefficient with wavelength obtained for the as-prepared pure and ZnO dispersed PVA films

4.5 PL spectra

The PL spectra observed for the as-prepared nanocomposite films with the excitation wavelength of 280 nm are shown in Figure 6. PL emission is mainly attributed to the presence of vacancies or impurities. Vacancies may be zinc or oxygen vacancies while the defects may be interstitial zinc or anti-oxygen sites [20]. Vacancies present in the material induces the formation of new energy levels in the band gap and as a result emissions will arise from these trap levels while exciting the sample. Emission occurs due to radiative recombination of a photo-excited hole with an electron and the emission peaks are commonly referred to as deep level or trap site emission due to oxygen vacancies [21]. The observed PL spectra show clearly violet and green emissions. The ZnO dispersion in PVA matrix increases the wavelength of lights emitted almost in proportion with the concentration of ZnO.

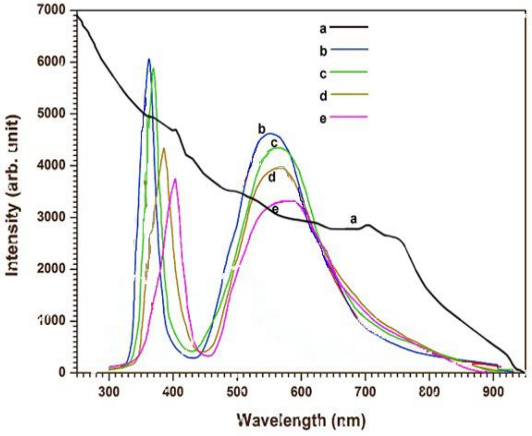

Fig 7: PL spectra of the as-prepared pure and ZnO dispersed PVA films

Results of optical (UV-Vis-NIR and PL spectral) measurements indicate that the ZnO dispersed PVA polymer films prepared in the present study are expected to be more useful in photonics applications.

4.6 DC electrical conductivities

The DC electrical conductivities observed in the present study are shown in Figure 8. It is found that the DC conductivity increases with the increase in temperature. ZnO dispersion increases it but not systematically with ZnO concentration. Maximum DC electrical conductivity is obtained for the 5.0% ZnO film. This indicates that the electronic conduction is increased significantly by dispersing ZnO in the PVA polymer matrix. It is expected that the addition of ZnO may result increase in localization of charge carriers density causing higher conductivity. This result shows that the space charge contribution may play an important role in the charge transport process [38-40].

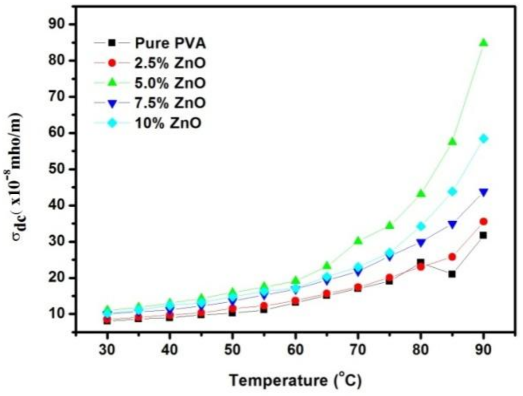

Fig 8: DC electrical conductivities observed for the pure and ZnO dispersed PVA films

4.8 Dielectric property of the composites

Variations of real and imaginary parts of dielectric constant (ε'and ε") as a function of frequency for various weight percentages of ZnO nanoparticles in polyvinyl alcohol at room temperature are shown in Figure 9. It is found that the increase in frequency decreases the real part of the dielectric constant (ε') due to the electrical relaxation processes which may be due to the dipolar contribution of charge carriers between isolated states. Therefore, it is expected that the space charge contribution may play an important role in the polarizability process also.

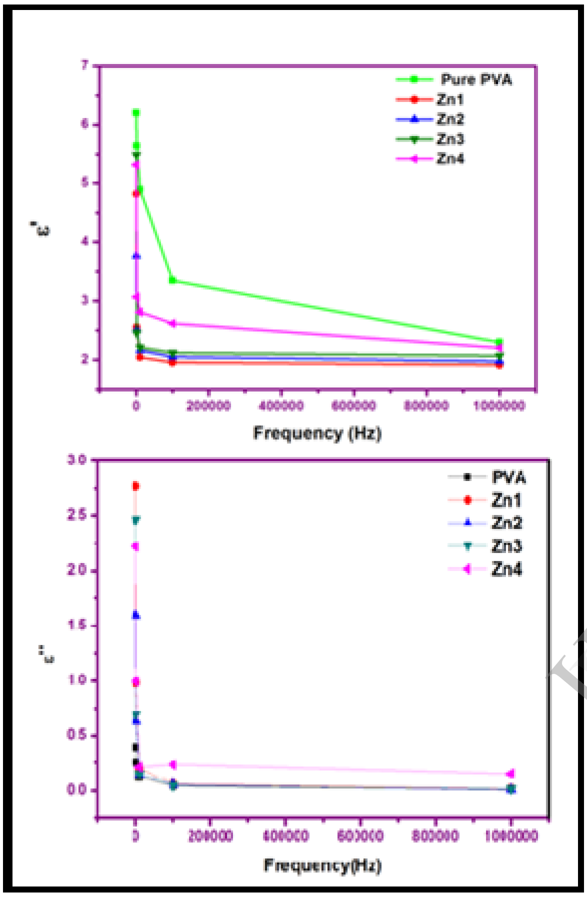

Fig 9: Variations of ε' and ε'' with frequency observed for the pure and ZnO dispersed PVA films

The imaginary part of dielectric constant (ε") has low value at higher frequency which may be due to the motion of free charges through the nanocomposites and above 10^4 Hz, **ε''** remains almost constant throughout the frequency region. The dielectric property depends on the conductivity of nanocomposites which may cause a decrease in the dielectric constant. The measured imaginary part of dielectric constant is contributed by two phenomena: the dipolar orientation as well as interfacial polarization of surface charges between the electrode and ZnO-PVA nanocomposite surface [37].

The variation of dielectric loss factor with frequency observed for the pure and ZnO dispersed PVA films in the present study (shown in Figure 10) also suggests that the relaxation process in desired films depends on the characteristic properties of dipolar relaxation. The variation of AC electrical conductivity with frequency observed is also shown in Figure 9. It is found that the AC electrical conductivity increases with the increase in frequency. Also, it increases due to ZnO dispersion. Among all nanocomposites prepared, 10 wt.% ZnO-PVA shows high conductivity when compared to others. The lower AC conductivity at lower frequency may be due to all types of polarization, but where the dipole polarization is observed more dominant after the frequency range of 10^4 Hz which may be due to the rotation of dipoles between two charge carriers with same axes of symmetry positions.

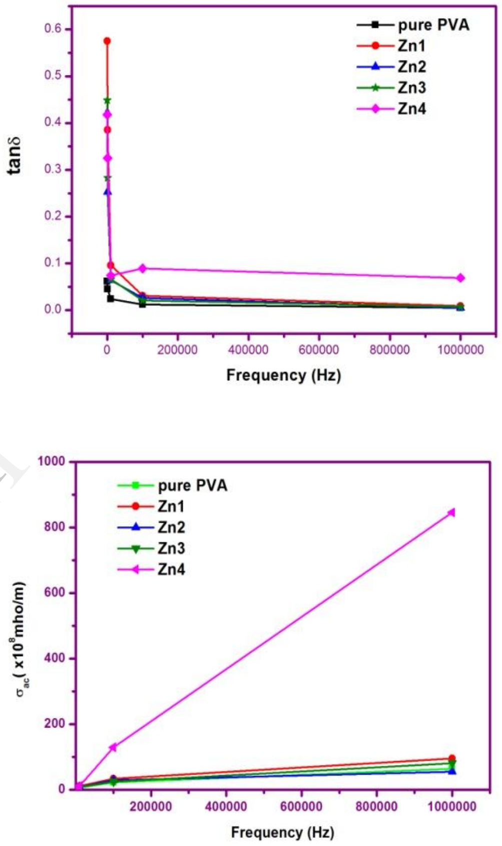

Fig 10: Variations of tan δ and AC electrical conductivity with frequency observed for the pure and ZnO dispersed PVA films

Results observed in the present study through electrical (both DC and AC) measurements indicate an increase of electronic conductivity and decrease of the real part of dielectric constant due to ZnO dispersion in the PVA polymer matrix. This leads to an expectation that the ZnO dispersed PVA polymer films prepared in the present study will find more utility in electronic and other related electrical devices than the pure PVA polymer film.

5. CONCLUSIONS

Pure and ZnO dispersed PVA polymer films have been prepared successfully by a simple chemical method and characterized chemically, structurally, optically and electrically. The XRD and FESEM analyses and thickness measurement indicate that the simple chemical method adopted in the present study favors the formation of good quality films of proper ZnO-PVA nanocomposites. Results of optical measurements indicate a decrease of optical band gap and refractive index and an increase of optical extinction coefficient, UV absorption, absorption edge wavelength and PL wavelength due to ZnO dispersion. Results of electrical measurements indicate a decrease of dielectric constant and an increase of electronic conductivity with ZnO dispersion. The present study indicates that ZnO dispersion tunes significantly the optical and electrical properties of the PVA polymer film making the ZnO- PVA nanocomposites (films) prepared in the present study expected to be more useful in photonic and electronic device applications.

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