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Impact on Structural, Optical, Impedance and Dielectric Properties of Polymer PVA Loaded with Nanofiller ZnO

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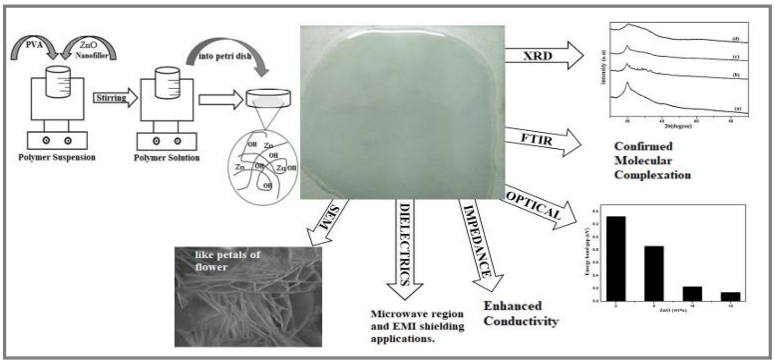
ABSTRACT

Incessant research curiosity has been shown to the fabrication of ZnO blended polymer nanocomposites owing to their extraordinary antimicrobial, catalytic, electrical, mechanical, optical, thermal and medical features. The Solution Casting Method is employed to fabricate PVA-ZnO nanocomposite film by incorporating the filler of ZnO nanoparticles which are synthesized by a novel starch-assisted combustion (SAC) method. XRD study revealed that increasing ZnO loading increases amorphous nature of the PVA-ZnO films. FTIR studies reveal the formation of molecular complex of PVA with ZnO filler. It was observed that ionic conductivity of the films as calculated from A.C. impedance studies tend to depend on the morphology and amorphousity of the films. The dielectric study observed the decreasing dielectric constant (Ɛ') with increasing frequency and it was its maximum for 15wt% ZnO filling in PVA. The band gap energy revealed from UV-Visible spectroscopic studies has revealed that on increasing the ZnO loading band gap of the films decreases. SEM studies illustrated distinctive morphology for each level of ZnO loading in the films which may be important for morphology dependant applications. Thus the study shows that by incorporating ZnO to PVA results in homogenous nanocomposite films with appropriate dielectric constant and conductivity values coupled with unique physical features, divulging their applications in microwave absorption and Electro Magnetic Induction (EMI) shielding in addition to the already known multifarious applications like in optics, sensors etc.

Graphical Abstract



Solution casting method for PVA-ZnO Nanocomposite films.

Keywords: PVA-ZnO, Polymer composites, Band gap, A.C. impedance, Dielectric properties.

INTRODUCTION

For over three decades, polymeric materials such as thermoplastics and thermosets have made a huge revolution in industries, electronics and optoelectronic devices and more specifically in household utilities [1, 2]. Later advancements in polymer technology have resulted in the most coveted, indispensable and a special class of engineering material namely *polymer nanocomposites* that has recently attracted a major market in food packing [3] and textile industries, flexible/foldable hand-held electronic gadgets and in very many fields of science, technology and engineering. Especially, polymer nanocomposites with polyvinyl alcohol (PVA) which is a water processable polymer [4] is bestowed with several interesting physiochemical features and thus undoubtedly the most frequently investigated matrix, occupying the niche within polymer family. Further reasons why PVA is a preferred matrix for fabricating composites are that it is a semi crystalline, water soluble material with low electrical conductivity, good optical property, biocompatibility and has excellent film forming and adhesive properties [5, 6] making it a suitable engineering material for combining with a diversified class of compounds for producing many luminescent materials [7], (bio)sensors, pharmaceuticals and biomedical [8-12], optoelectronic components [13], gas barrier [14] applications. Above all, PVA is biodegradable and imitates natural polymers and so it is vital in paper coating and textile sizing industries [15].

A quick scanning of literature reveals that PVA can accommodate many fillers, dispersants or additives to produce freestanding films for the afore-mentioned applications. A few studies with PVA as matrix are of importance and hence shown here. Anji Reddy Polu and Ranveer Kumar *et al* [16] has shown that ionic conductivity of PVA was high at room temperature when complexed with magnesium nitrate. Sivadevi *et al* [17] have investigated the properties of PVA-PAN blend and showed that charge carrier responsible for both d.c. conductivity and relaxation are the same. In addition to the above PVA has attracted incredible attention in solid-state electrochemical devices too [18]. Alkaline composite polyvinyl alcohol polymer electrolyte films synthesized using solution casting method for photovoltaic applications were also reported [19]. Polymer nanocomposite films PVA/PEO/In_2S_3 synthesized via solution casting method and concluded enhancement of photovoltaic effect [20].

Chun-Chen Yang and Shen-Jen Lin [21] have reported glass fiber-PVA polymer composite electrolyte and their studies suggest that PVA has potential use in solid state alkaline batteries systems. Therefore, PVA is considered versatile and research goes unabated as it can accommodate numerous other fillers such as ZnO [22], Ag [23], graphene oxide [24], iron oxide [25] for many important applications. In an interesting research by Obula Reddy and Chandra Babu [26], magnetic profile of PVA: $Gd3^+$ & PVA:Ho^{3+} were studied and the research summed up that these films can be used in electrochemical display systems. In another work, Al_2O_3 nanoparticles filled polymer gel electrolytes of PVA: DMSO: NH_4SCN was prepared by solution casting method and the authors have shown from XRD and CV studies that amorphousity and electrochemical current stability of PVA gel electrolytes was improved upon adding Al_2O_3 nanofiller [27]. ZnO nanoparticles prepared by sol-gel and a combined sol-gel and hydrothermal methods, it is a step forward towards the preparation of ZnO with enhanced activity like antibacterial activity [28, 29].

Many polymeric matrices blended with ZnO, a semiconductor with wide band gap, have been reported for enhanced electrical, mechanical, structural, optical and dielectric properties [30-32]. It is well established that ZnO based polymeric nanocomposite materials exhibit very interesting characteristics such as good transparency and high electron mobility and so it is very promising in applications like short-wavelength light emitting diodes, transparent conductors, dye-sensitized solar cells, gas sensors, as a high resistance semiconducting device and in fully transparent thin film transistors. Since there is an unabated interest in developing composite membranes with high dielectric constant fulfilling the criteria for harnessing many slim, foldable/flexible electronic and photonic gadgets or even in EMI absorbing, ZnO dispersed PVA film composites will be the choice in the future electronics as this combination always brings forth excellent physiochemical properties [33, 34].

Nevertheless, to the best of the authors' knowledge, not many reports are available on obtaining high dielectric polymer nanocomposites based on semiconductor nanoparticles for a wide band of frequency. To cite a few, in an interesting research by Hamza *et al* [35], PVA/Ag nanoparticles/ZnO nanofibers were synthesized and have shown to exhibit excellent antibacterial properties thus establishing its use in the biomedicine fields as well. Yet another report has shown that PVA/ZnO films exhibit photo luminescence (with 10 mol% of ZnO doped on PVA) and has been suggested for prospective use in optoelectronic devices [36] and for both d. c. & a. c. electronic devices [37].

On the light of the above, the present study uses ZnO nanoparticles as nanofiller because of its multidimensional applications like in environmental, food packaging, medical care, healthcare as well as construction and decoration. Further, ZnO is non-toxic and is compatible with human skin making it a suitable additive for textiles and surfaces that come in contact with human body. Thus to examine the effect and influence of various weight percentages of ZnO nanofiller loading in PVA polymer matrix on the essential properties like structural, optical, impedance and dielectric properties in PVA-ZnO nanocomposite pore free and freestanding films has been taken as the objective of the work and the observations are presented systematically. The study is expected to pay way for tuning the above-listed properties by way of loading ZnO in PVA matrix and thus leads to the development of new hybrid materials for electrical, optical, EMI shielding applications etc., and subsequently to unearth the potential of PVA in unexplored areas of Science & Technology.

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MATERIALS AND METHODS

Materials: Polyvinyl alcohol powder with average molecular weight of 30000 (with degree of polymerization 1700-1800 and 98-99% hydrolyzed) used in this study was purchased from Sigma Aldrich. Zinc nitrate $[Zn(NO_3)_2.6H_2O]$ and starch $(C_6H_{10}O_5)_n.(H_2O)$ were also purchased from Sigma Aldrich. Doubly distilled water used for the experiments was produced in-house.

Synthesis of zinc oxide (ZnO) powder: One of the authors of the present communication had reported the synthesis of a few oxide based materials for use as cathode in lithium batteries through a very simple route namely starch assisted combustion (SAC) method [38]. In the present work also, the filler ZnO was synthesised by following the above method. In a representative example, starch solution was prepared by dissolving 3 g of starch in 50 mL of double distilled water at ~90^oC. Then 2 g of zinc nitrate $[Zn(NO_3)_2.6H_2O]$ crystals was dissolved in 2 mL double distilled water and added to the hot starch solution. This mixture was stirred well at the same temperature till homogenous slurry was formed. Later, the slurry was dried in an air oven at 100°C for 1h and finally heated in a furnace at 400°C for 2h to get the fine powder of white ZnO powder.

Fabrication of virgin PVA film: Virgin PVA film was fabricated by solution casting method following the procedure described in [39]. In a typical procedure, a known quantity of PVA (say 1g) and double distilled water (10ml) were taken in a glass beaker and heated at 80°C with continuous stirring until the polymer was completely dissolved and a clear viscous solution was obtained. This solution of PVA was poured on a clean and dry Petri dish and kept in a dust free chamber at room temperature for 4 to 5 days for drying, later peeled off and stored flat until further studies.

Preparation of PVA-ZnO nanocomposite films: To prepare free-standing PVA-ZnO nanocomposite films, ZnO powder prepared above was used as the nanofiller with wt% of 5, 10 and 15 for the PVA content fixed at wt% 95, 90, 85 respectively with water as a solvent by adopting solution casting technique as described above. The filler loading (wt%) in the film was calculated using the following equation:

Weight % of filler = [weight of filler / (weight of filler + weight of PVA)] * 100

Calculated quantity of PVA was dissolved in a required quantity of hot water and to this solution calculated amounts of ZnO filler for the desired wt% was added and the mixture was ultrasonicated for 15 minutes and subsequently stirred on a magnetic stirrer/hotplate until a homogenous viscous solution was obtained. Finally, nanocomposite films were cast as described in the above method. The dried films were peeled off from the Petri plates and stored flat in vacuum desiccators until further use. The thickness of the fabricated films was found to be 0.2 mm. The solution casting or solution blending method has proved good PVA-ZnO blending, resulting in mechanically stronger and stable films.

Characterization techniques: XRD patterns were recorded using PAN Analytical model X-ray diffractometer using Cu-K_α radiation as source (λ = 1.54060A°; V = 45KV; I = 40 mA). The FTIR spectra of virgin PVA, ZnO powder and PVA-ZnO nanocomposite films were recorded in the region 400-4000 cm^{-1} using JASCO spectrometer (Model: FT/IR-4700). UV-Visible absorption of nanocomposite films was recorded in the range 200-900 nm on JASCO UV-Vis spectrophotometer (Model: V-750). The morphology of the samples was examined by VEGA 3 TESCAN Scanning Electron Microscope. A. c. impedance and dielectric studies on PVA-ZnO nanocomposite films were done over the frequency range of 50 Hz-5MHz using HIOKI 3532-50 LCR HiTESTER which was interfaced to a personal computer.

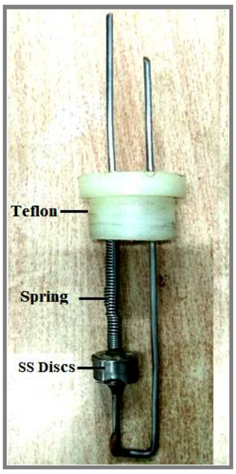

Figure 1. Photo of the sample holder.

For a. c. impedance studies, a sample holder with teflon and stainless steel as materials of construction was fabricated in-house and the model has been depicted in figure 1. Two stainless steel (SS) discs acting as blocking electrodes are included in the design between which the polymer films are tightly positioned and the springs ensure tight grip of the films between the SS discs. For the studies the fabricated films were cut into circles of 2cm diameter and placed between the discs of the sample holder.

RESULTS AND DISCUSSION

Phase analysis by X-Ray Diffraction: Figure 2 represents the XRD pattern of the virgin PVA film. A sharp peak at 23.1° associated with the (101) plane confirms the semi crystalline nature. This observation matches exactly with the earlier reports of Roy and Deepak *et al* [**39, 40**].

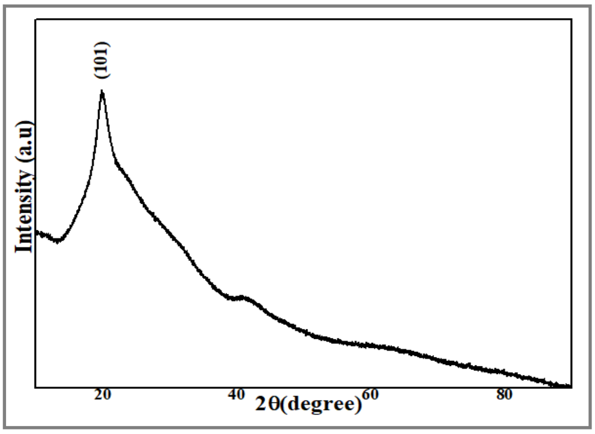

Figure 2. XRD pattern of virgin PVA film.

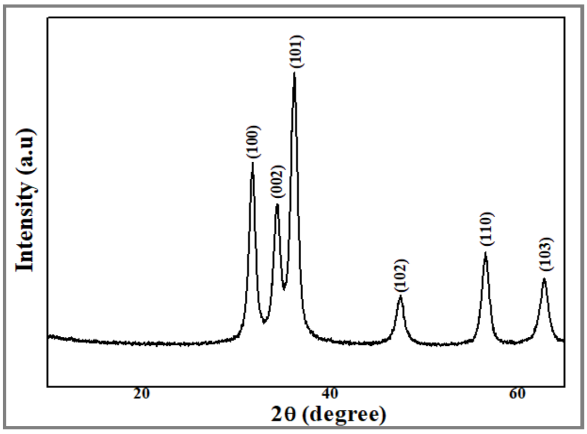

Figure 3. XRD pattern of virgin ZnO.

Figure 3 represents the XRD of the ZnO powder which can be indexed to the typical hexagonal wurtzite structure of ZnO (JCPDS no: 36-1451) and features a series of crystalline peaks appearing between 30° and 65°. A sharp peak appears at 31.7° (indexed as (100)) which is followed by a doublet appearing at 34.4° and 36.3° which may be indexed as (002) and (101) respectively. Further, sharp and well defined medium and short crystalline peaks appear at 47.0°, 56.5° and 62.8° which may be indexed as (102), (110) and (103) planes respectively which matches exactly with those reported by Mansour *et al* and Bouropoulos *et al* [41,42].

With the addition of 5wt% ZnO to PVA, the peak at 23.1° due to virgin PVA presented in figure 4a is still observed. However, the intensity of the characteristic peaks due to ZnO have drastically been reduced and broadened as shown in figure 4b. This reduction in intensity and peak broadening of films suggest the increased amorphous nature of the PVA-ZnO nanocomposite film. At 10 wt% of ZnO (Figure 4c), the characteristic XRD peak of PVA at 23.1° gets further broadened with no visible trace of peaks corresponding to ZnO. This observation suggests that the crystalline nature of PVA reduces with higher loading of ZnO.

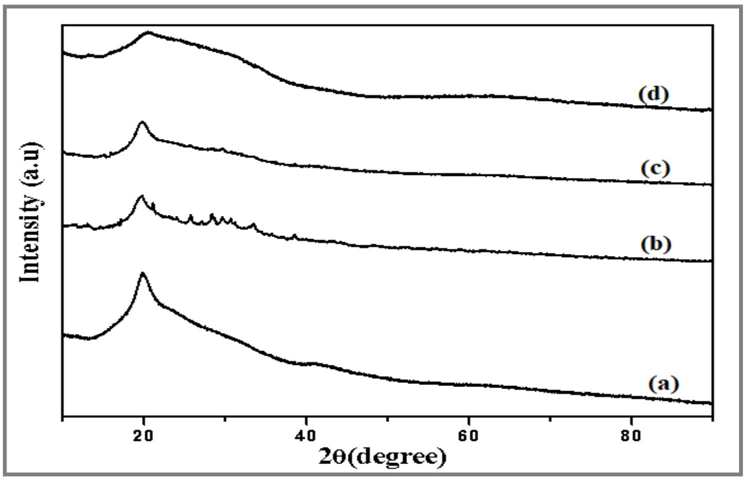

Figure 4. XRD pattern of (a) virgin PVA film, (b-d) PVA + [5,10,15wt% of] ZnO nanocomposite films.

At a still higher level of loading i.e. with 15wt% ZnO (Figure 4d) in the film, the characteristic peak at 23.1° ascribed to PVA still gets broadened and completely became amorphous, thus suggesting that increasing wt% of ZnO in the host matrix namely PVA decreases the crystalline nature or in other words, increases the amorphous nature of the composite films. This could be due to the increase in the intermolecular interaction between the PVA chains contributing to more amorphous nature, an observation which coincides with that of reported by Hemalatha *et al* and Muhammad *et al* [**36, 43**] from their work on composition dependant studies with hybrid PVA-ZnO nanocomposites. Therefore, an analysis of figure 4a-d would conclude that a higher ZnO loading would introduce amorphous character to the polymer films and it will be later shown in this article that increased amorphousity contributes to the enhancement in the conductivity of the nanocomposites films. With no additional or new XRD peaks observed further suggest that ZnO has excellently been capped in the PVA matrix in the %loading studied and also confirms phase purity of the films.

Fourier Transform Infrared Spectroscopic Analysis: Figure 5 depicts the FTIR spectrum of ZnO filler in which the peak observed around 432 cm^{-1} may be assigned to the stretching vibrations of Zn-O bond [**36, 44**]. FTIR spectrum of virgin PVA is given in figure 6a which shows the signatures at 837 cm^{-1} and 916 cm^{-1} respectively corresponding to C-C stretching and CH_2 rocking vibrations. Signature peak at 1329 cm^{-1} confirms CH_2 stretching and 1420 cm^{-1} signature refers to CH_3 bending. The broad band around 3257 cm^{-1} may be attributed to the OH stretching of PVA in the polymer backbone. In addition to the above signatures, the band in the frequency region 2921 cm^{-1} attributes to CH_2 asymmetric stretching, an observation which is in accordance to references [**41, 43**]. When 5 wt% of ZnO was loaded in PVA, the peaks appear with reduced intensity as evidenced from figure 6b. While further analyzing the wavelength region, a new peak appears at 1224 cm^{-1} corresponding to C-H wagging or C-C stretching with 10 wt% ZnO loading, as shown in figure 6c. Signatures of O-H stretching in PVA polymer backbone gets broadened further for higher loading of ZnO filling, as evidenced from figure 6d. The shifting of peak due to ZnO from 432 cm^{-1} to ~510 cm^{-1} in nanocomposite films might be related to the interactions between ZnO particles and PVA [**39, 44**] thus resulting in a new complexed structure through CH rocking, CH wagging and OH stretching.

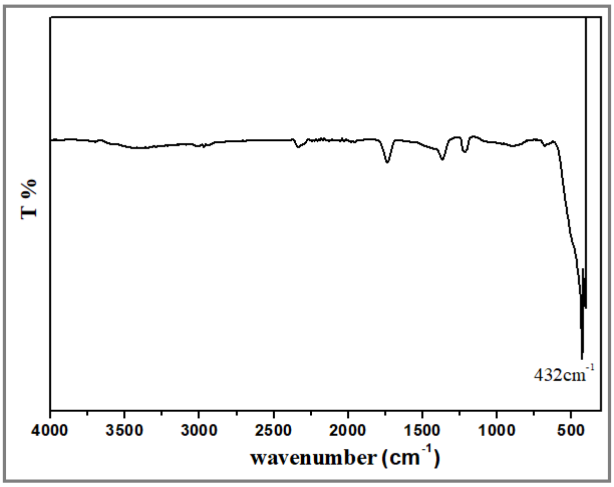

Fig. 5. FTIR spectra of virgin ZnO

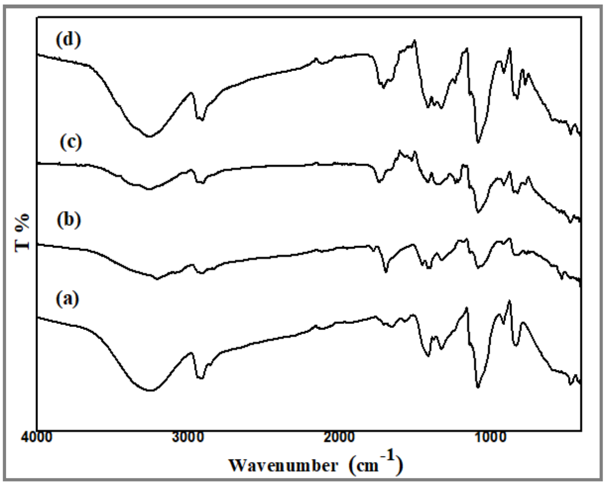

Fig. 6. FTIR spectra of (a) virgin PVA film, (b-d) PVA + [5,10,15wt% of] ZnO nanocomposite films.

From the foregoing description on the FTIR spectra establishes the interaction between Zn ions and OH group of PVA backbone which is effected through intra-/intermolecular hydrogen bonding thus resulting in a complex structure [**43, 45**].

Impedance Spectroscopic Analysis: Figure 7(a-d) shows the Nyquist plots of virgin PVA, PVA-ZnO nanocomposite films for the three wt% of ZnO respectively. All impedance spectra have convoluted with two regions, one is a semi circle at high frequency region and another is a linear region at low frequency inclined at 45° or little more with reference to the real part of the spectra.

All the ZnO laden PVA nanocomposite films have shown well defined semi circles which are followed by linear traces irrespective of the variation in ZnO loading in PVA. The semi-circle formation corresponds to the bulk resistance (R_b) of the film and the linear traces at the lower frequency are attributed to the blocking effect of the SS electrodes [34]. The R_b values of all the films are obtained at the intersection of the semi circles with the real axis. Further the conductivity of the films has been calculated using the formula given below [46],

$$\sigma = T/ R_b \text{ x } A$$

where, T is the Thickness of the polymer films, R_b is the bulk resistance and A is the surface area of the film ($A = \pi r^2$).

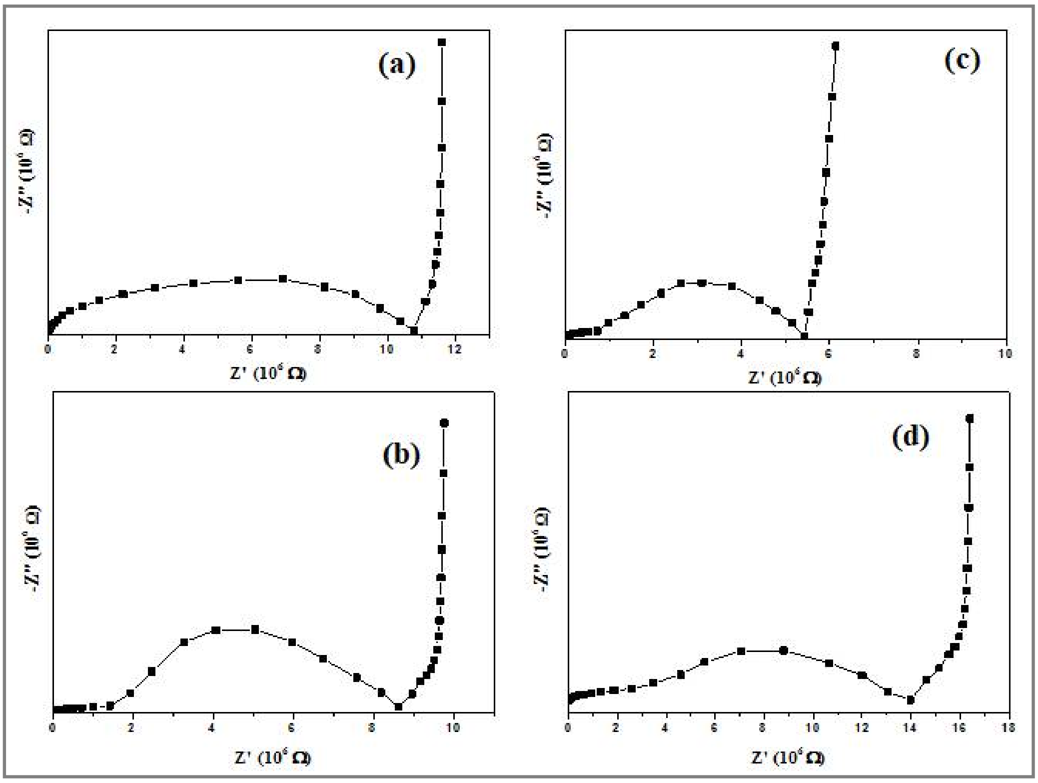

Figure 7. A.C Impedance plot for (a) virgin PVA film, (b-d) PVA + [5,10,15wt% of] ZnO nanocomposite films.

The conductivity values of various films calculated using the above formula is shown in table 1.

Table 1. Conductivity values of PVA-ZnO films at 303K.

Sample description	**Bulk resistance R_b (10^6) Ω**	**Conductivity σ (Sm^{-1})**
PVA + 0% ZnO	10.7744	0.027×10^{-6}
PVA+ 5wt% ZnO	8.6363	3.687×10^{-6}
PVA+ 10wt% ZnO	5.4452	5.848×10^{-6}
PVA+ 15wt% ZnO	13.9665	2.280×10^{-6}

It is observed from table 1 that of all the PVA-ZnO films with 10 wt% ZnO has exhibited enhanced conductivity of 5.848×10^{-6} Sm^{-1} at ambient temperature (303 K). The enhancement in conductivity with increase in ZnO loading in the fabricated polymer films may be explained due to the interaction between polymer chains and ZnO leading to complexation and also the transition from semi-crystalline phase to an amorphous phase of the polymer complexes due to the dispersion of ZnO. The deviation in conductivity (increased impedance) observed for 15% ZnO loading is assumed to be due to the heavy loading of the film with the filler which might have resulted in high R_b when compared to the other films. Again, it can be later shown from the SEM studies that morphology has also a definite say on the conductivity of the films in addition to the crystalline or amorphous nature of the films.

Dielectric property analysis: For understanding the properties of the films for future prospects in the development of microwave antennas and EMI shielding, an investigation of dielectric properties in the range of GHz was undertaken. Figure 8 shows the variation of dielectric constant (Ɛ') with frequency and ZnO loading in PVA composite films fabricated for the present study.

From the plots it is understood that the value of Ɛ' decreases with increasing frequency and reaches a constant value at higher frequencies as observed by Hemalatha *et al* and Roy *et al* [37, 39] from their work similar to the present study wherein the decrease in Ɛ' with increasing frequency and increased addition of ZnO in PVA the matrix has been reported. This could be explained by the fact that at higher a. c. frequencies the charge carriers may not follow the fast alternating electric field [47]. But at low frequencies, large dielectric constant values are observed and the reason may be associated with an enormous increase in the storage of the electric charges per unit volume of the film leading to enormous and strong ionic polarization due to Zn^{2+} and O^{2-} in the polymer, as explained in reference [48].

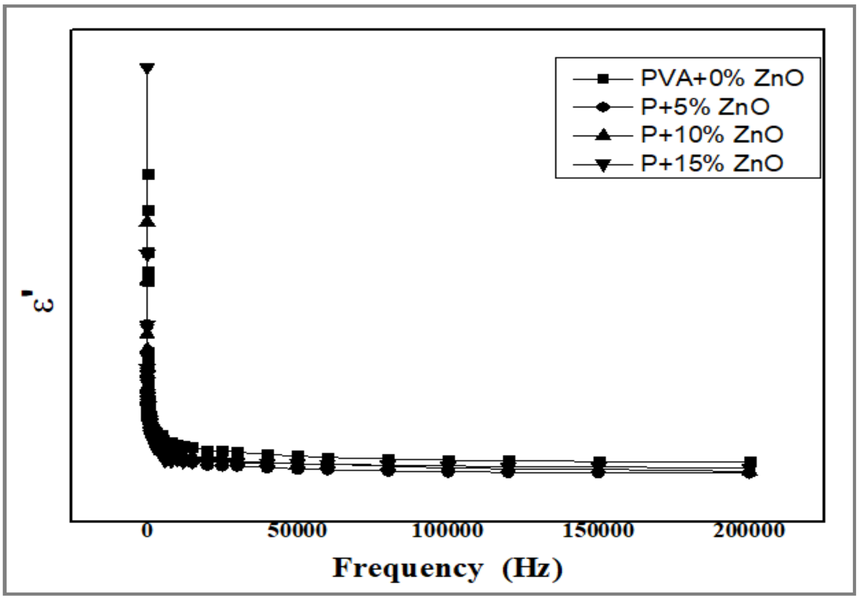

Figure 8. Variation in dielectric constant of PVA upon ZnO loading.

Moreover, interfacial polarization also exists due to the variation in permittivity between ZnO and PVA, a generally observed nature of the polymer nanocomposite dielectric materials. The observed trend in the dielectric constant of the nanocomposite films which is due to the introduction of semiconducting ZnO in the PVA host matrix would be more attractive in electronic and electrical gadgets than the virgin PVA film. At low frequencies the composite films thus may facilitate devices operating in the microwave region and for EMI shielding.

Results of optical studies (UV-Visible spectroscopic studies): UV-Visible spectroscopic studies were carried out to understand the effect of ZnO loading in PVA matrix on UV absorption and band gap energy and the results are presented in figure 9 (a-d) and inset figure 9(e-h) respectively. It is well established that PVA absorbs UV radiation strongly in the wavelength 200-250 nm region [49].

Figure 9(a-d) illustrates the shift in both absorption bands and the band edges towards the higher wavelengths with different absorption intensities for different increments of ZnO in PVA host polymer. The shift in the absorption band gives an insight on the formation of inter-/intramolecular hydrogen bonding between Zn ions with the adjacent OH groups of the PVA matrix. The increasing ZnO concentration would tend to cause more and more inter-/intra hydrogen bonding and also increased UV absorption, as expected from Beer's law. The observed shift in the absorption edge of the various ZnO doped PVA composite films is presumed to be due to the transition of phase (i.e. from crystalline to amorphous phase) upon ZnO loading, which ultimately may reflect in the energy band gap [50].

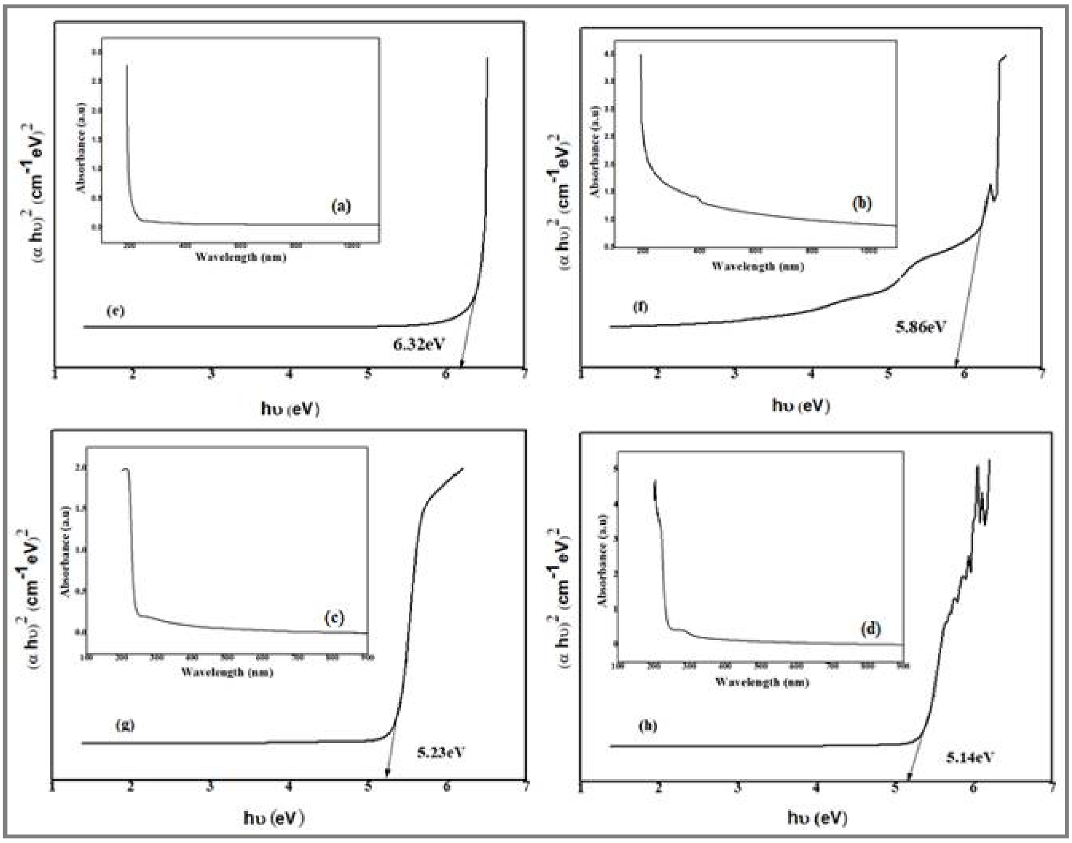

Figure 9. Energy band gap of (a) virgin PVA film, (b-d) PVA + (5, 10, 15 wt% of) ZnO nanocomposite films, UV Visible spectra of (e) virgin PVA film, (f-h) PVA + (5, 10, 15 wt% of) ZnO nanocomposite films.

It is well known that the band gap of a material is an important factor that explains the optical transitions, which may be either direct or indirect. Also, it is well established that the band gap has a direct relationship with the electrical and optical conductivities of the films [43]. The absorption coefficient (α) is the fractional power absorbed per unit length of the medium, and determined by Beer's equation, $\alpha = 2.303A/t$, where A is the absorbance observed from the UV-Visible absorbance spectra and t is the thickness of the film. The optical band gap determined by Tauc's plot correlates α with photon energy (hν) by the equation [51],

$$\boldsymbol{\alpha h\nu = \beta(h\nu - E_g)^r}$$

where α, hν, β, E_g and r are the absorption coefficient, incident photon energy, band tailing constant, band gap energy respectively. For the direct band gap material like ZnO, the r value is taken as ½ [52, 53]. Using the above equation, $(\alpha h\nu)^2$ was plotted against hν to calculate E_g of virgin PVA and other composite films and the results are presented as figure 9(e-h), which evinces the linear behaviour of $(\alpha h\nu)^2$ against hν in the absorption band, indicating the direct transition nature [43, 54].

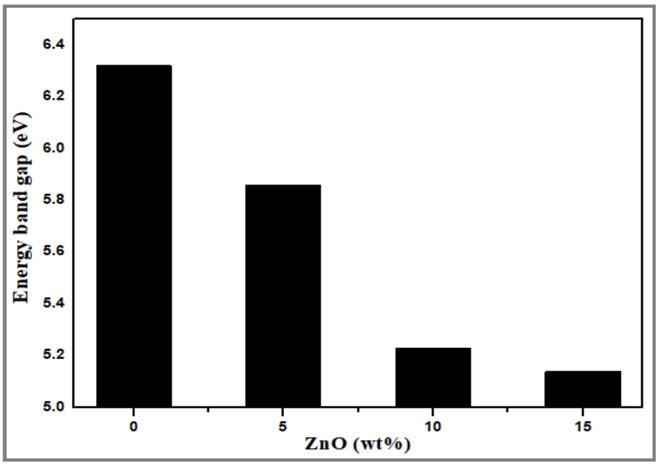

Figure 10. Variation of the energy band gap of the virgin PVA film and PVA-ZnO nanocomposite films.

The E_g value calculated for various ZnO loading in the composite films as well as pure ZnO are collectively presented in figure 10. It is obvious from the graph that when ZnO loading increases the E_g value decreases and the observed decrease in the polymer films could be due to the local cross-linking within the non-crystalline phase of the polymer. This increase in the local cross-linking may further increase the degree of ordering in PVA backbone thereby decreasing the E_g values [50]. Interestingly, Mansour *et al* and Elizabeth *et al* [41, 55] have also observed a decrease in the energy band gap with increasing ZnO loading. Mansour *et al* [41] explain this phenomena of ZnO concentration dependant energy gap to be due to the creation of new energy levels in the band gap, facilitating the crossing of electrons from the valence band to the newly created local energy levels and finally to the conduction band. As a consequence, a decrease in the band gap energy with simultaneous increase in the conductivity is expected [56, 57]. It is also given to understand that high concentration of the filler only leads to close aggregation of the filler particles thereby affecting UV absorption and this means scattering of visible light.

Results of SEM analysis: PVA-ZnO polymer nanocomposite films have been examined by scanning electron microscope (x500 magnification) to demonstrate the changes brought about in the morphology of the virgin PVA as ZnO is dispersed at various chosen wt% and the same have been depicted in figure 11(a-e).

Figure 11a represents the SEM of SAC derived ZnO powder whose morphology appears to be somewhat quasi-hexagonal in shape. Figure 11b illustrates the homogeneous surface morphology of the virgin PVA. But the matrix surface has acquired an entirely different morphology when 5 wt% of ZnO was loaded. To be specific, ZnO particulates emerge with a stretched rod like structure with a centre of symmetry as it is dispersed in the PVA matrix (Figure 11c). Interestingly, at 10 wt% of ZnO, the rod like structure has swollen up and appeared like petals of a flower (Figure 11d). A still higher loading of ZnO i.e.15 wt% has introduced several folding of the host PVA matrix (figure 11e) leading to an enormous volume expansion which would impart increased amorphous character to the heavily loaded composite film, as evidenced from XRD studies. Folded morphology of the heavily loaded film would also mean hindered charge migration with a consequent decrease in conductivity as supported by impedance studies (Table 1). As a consequence the authors expect that the films would be attractive in applications where morphology is the tuning factor.

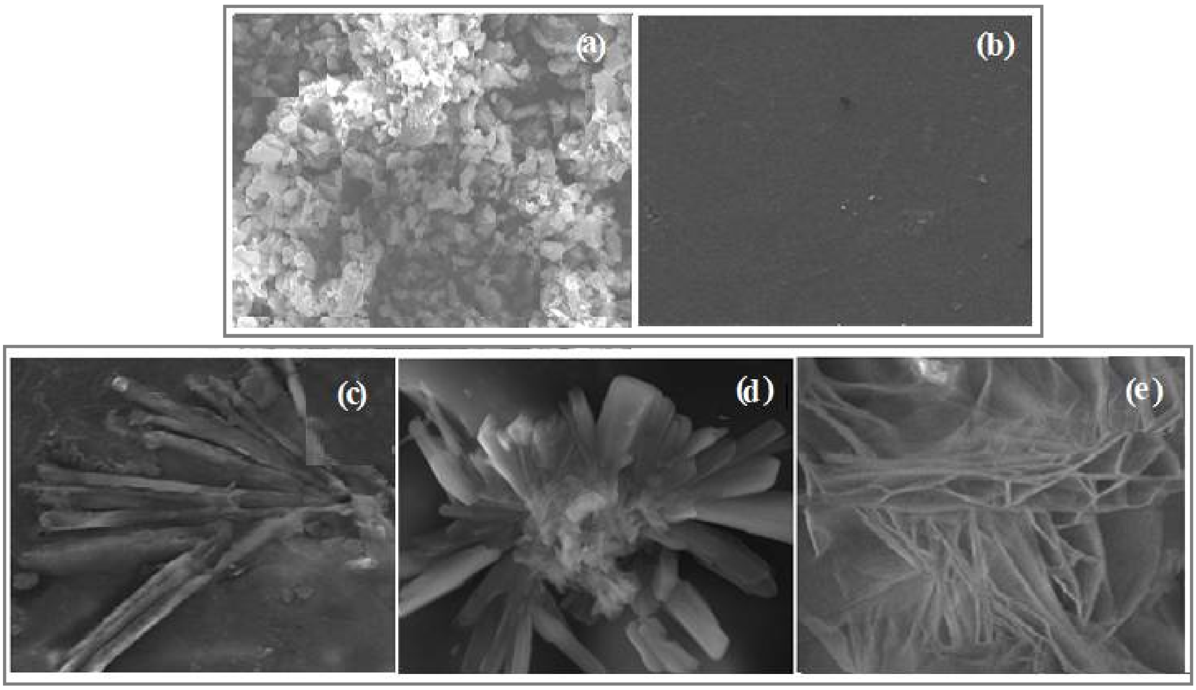

Figure 11. SEM image of (a) virgin PVA film, (b) virgin ZnO (c-e) PVA + [5,10,15wt% of] ZnO nanocomposite films.

Though several researchers [**36, 43, 50**] have described very interesting morphological features of their PVA films with ZnO dispersed to various wt% ranges, the features what the authors of the present communication observed are indeed distinctive which could possibly explain the amorphous character, optical character (e.g. opacity) and trend in conductivity values, the parameters which decides the final applications of the films. To conclude, SEM studies substantiate the changes in the morphology of virgin PVA with the dispersion of ZnO.

APPLICATION

PVA-ZnO nanocomposite films were prepared via a simple solution casting technique. Optical studies, dielectric constant and conductivity values of PVA-ZnO nanocomposite films reveal that these films have prospects in optical devices microwave absorption and EMI shielding applications. The nanocomposite films are expected to play an important role in the future microsensors, UV shielding flexible nanodielectrics, surgical aprons, microelectronic devices etc.

CONCLUSION

Novel Starch Assisted Combustion (SAC) method has successfully been adopted for synthesizing ZnO crystalline powder (Wurzite structure), the filler used for our studies. The above-prepared ZnO filler has been loaded/dispersed in PVA polymer matrix at various loading levels (wt% of 5, 10 and 15) to fabricate pore free, freestanding and multifunctional PVA-ZnO nanocomposite films using solution casting method. Interesting results obtained with the composite films are highlighted below.

1. XRD study identifies that 15wt% of ZnO doped PVA has reduced the crystalline structure of PVA. In fact, XRD has revealed an increase in the amorphous nature of the films with the addition of ZnO.
2. FTIR study has confirmed the molecular complexation of ZnO with PVA.
3. Impedance study has confirmed enhanced conductivity up to lower ZnO loading levels in PVA solution. The anomaly in conductivity (increased impedance) observed for 15% ZnO loading is

assumed to be due to the heavy loading of the film with the ZnO filler which might have resulted in enormous R_b build up when compared to the other films.

4. Optical studies have confirmed the decrease in the band gap energy with increase in ZnO loading, giving us a scope that the films can be utilized for optical devices.
5. SEM studies demonstrate the distinctive shapes of PVA matrix for each level of loading of ZnO and also ZnO nanoparticles are homogenously dispersed in the polymer matrix thus rendering itself for morphology dependant applications.
6. The observed trend in the dielectric constant which is due to incorporating ZnO in the PVA host matrix would be more attractive in electronic and electrical gadgets than the virgin PVA film. Moreover, from the conductivity and dielectric studies we may anticipate that at low frequencies these composite films may be a choice compatible for microwave region and EMI (Electro Magnetic Induction) shielding applications, the studies of which have been reserved for the near future.

Hence the results of the studies confirm the strong dependence of ZnO filler loading on the structural, optical, impedance and dielectric properties in PVA-ZnO nanocomposite films and evince a potential pathway for utilizing these composite films in multifarious areas of future science, technology and engineering like in reinforcement fillers and many novel applications indicated in the earlier sections. An in-depth study will be undertaken to explore the temperature dependent behavior of PVA nanocomposites with various fillers and to realize the applications of the films. The studies obviously support for the multi dimensional applications of the PVA based ZnO nanocomposite films and thus the films are anticipated to transform or redesign the entire polymer technology by widening the requirements and applications as well, especially towards flexible, ultrathin and wearable gadgets in the near future. Nevertheless, commercialization of nanocomposite films needs further investigation related to toxicity, structural deformation on continuous usage etc.

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REFERENCES

[1]. L. Beecroft, C. K. Ober, Nanocomposite Materials for Optical Applications, *Chem. Mater.*, **1997**, 9(6), 1302-1317.

[2]. R. V. Kumar, R. Elgamiel, Y. Diamant, A. Gedanken, Preparation and Characterization of Nanocrystalline Copper Oxide Embedded in Poly(Vinyl Alcohol) and Its Effect on Crystal Growth of Copper Oxide, *Langmuir*, **2001**, 17(5), 1406-1410.

[3]. S. Tripathi, G. K. Mehrotra, P. K Dutta, Physicochemical and bioactivity of cross-linked chitosan-PVA film for food packaging applications, *Int. J. Biol. Macromo.*, **2009**, 45(4), 372-376.

[4]. Tetsuo Hino, TakumiNamiki, Noriyuki Kuramoto, Synthesis and characterization of novel conducting composites of polyaniline prepared in the presence of sodium dodecylsulfonate and several water soluble polymers, *Synth. Met.*, **2006**, 156 (21-24), 1327-1332.

[5]. A. M. M. Gomes, P. L. da Silva, C. de L. e Moura, C. E. M. da Silva, N. M. P. S. Ricardo, Study of the Mechanical and Biodegradable Properties of Cassava Starch/Chitosan/PVA Blends, *Macromol. Symp.*, **2011**, 299–300(1), 220–226.

[6]. N. A. Nik Aziz, N. K. Idris, M.I.N. Isa, Solid Polymer Electrolytes based on methylcellulose: FTIR and Ionic conductivity Studies, *IJPAC*. **2010**, 15(5), 319–327.

[7]. M. B. Muradov, The Influence of the Type of Polymer Matrix on the Photoluminescence from Cadmium Sulfide Nanoparticles, *OAM-RC*, **2008**, 2(2), 85-88.

[8]. C. M. Hassan, N. A. Peppas, Structure and applications of poly(vinyl alcohol) hydrogels prod uced by conventional crosslinking or by freezing/thawing methods, *Adv. Polym. Sci.*, **2000**, 153, 37- 65.

[9]. M. Kokabi, M. Sirousazar, Z. Hassan, PVA-clay nanocomposite hydrogels for wound dressing, *Eur. Polym. J.* **2007**, 43, 773- 781.

[10]. M. Nagura, T. Hamano, H. Ishikawa, Structure of poly(vinyl alcohol) hydrogel prepared by repeated freezing and melting, *Polym*., **1969**, 30, 762-765.

[11]. C. A. Scotchford, M. G. Cascone, S. Downed, P. Giusti, Osteoblast responses to collagen-PVA bioartificial polymers in vitro: the effects of cross-linking method and collagen content, *Biomaterials*, **1998**, 19, 1-11.

[12]. Rajesh, T. Ahuja, D. Kumar, Recent Progress in the Development of Nano-Structured Conducting Polymers/Nanocomposites for Sensor Applications, *Sens, Actuator B-Chem.*, **2009**, 136(1), 275-286

[13]. T. P. Nguyen, Polymer-based nanocomposites for organic optoelectronic devices. A review, *Surf. Coat. Technol.* **2011**, 206 (4), 742-752.

[14]. Sudhir K. Kisku, Niladri Sarkar, Satyabrata Dash, Sarat K. Swain, Preparation of Starch/PVA/$CaCO_3$ Nanobiocomposite Films: Study of Fire Retardant, Thermal Resistant, Gas Barrier and Biodegradable Properties, *Polym-Plast Technol*., **2014**, 53, 1664-1670.

[15]. M. Liu, B. Guo, M. Du, D. Jia, Drying induced aggregation of halloysite nanotubes in polyvinyl alcohol/halloysite nanotubes solution and its effect on properties of composite film, *Appl. Phys. A Mater. Sci. Process*., **2007**, 88, 391–395.

[16]. Anji Reddy Polu and Ranveer Kumar, AC impedance and dielectric spectroscopic studies of Mg2+ ion conducting PVA–PEG blended polymer electrolytes, *Bull. Mater. Sci.*, **2011**, 34(5), 1063-1067.

[17]. S. Siva devi, S. Selvasekarapandian, S. Karthikeyan, N. Vijaya, F. Kingaslin Mary Genova and C. Sanjeeviraja, Structural and AC Impedance Ananlysis of Blend Polymer Electrolyte Based on PVA and PAN, *IJSR* **2013**, 2(10), 1-3.

[18]. S. Kumar, G. K. Prajapati, A. L. Saroj, P. N. Gupta, Structural, electrical and dielectric studiesof nano-composite polymer blend electrolyte films based on (70-x) PVA-x, PVP-NaI-SiO_2, *Physica B.*, **2019**, 554, 158–164.

[19]. Mingqing Wang, Yanqing Lian, Xiaogong Wang, PPV/PVA/ZnO nanocomposite prepared by complex precursor method and its photovoltaic application, *Curr. Appl. Phys*., **2009**, 9, 189-194.

[20]. Hosaholalu Balakrishna Uma, Sannaiah Ananda, Siddaramaiah Basavarajaiah, Synthesis and Characterization of PVA/PEO/In_2S_3 Polymer Nanocomposite Films and Study of their Optical, Electrical and Thermal Properties, *J. Applicable Chem*., **2019**, 8(3), 1123-1134.

[21]. Chun-Chen Yang and Shen-Jen Lin, Preparation of composite alkaline polymer electrolyte, *Mate*r, 2002, 57, 873-881.

[22]. Tapas Kumar Kundu, Nantu Karak, Puspendu Barik and Satyajit Saha, Optical Properties of Zno Nanoparticles Prepared by Chemical Method Using Poly (VinylAlcohol) (PVA) as Capping Agent, *IJSCE*, **2011**, 1, 19-24.

[23]. Mahshad Ghanipour and Davoud Dorranian, Effect of Ag-Nanoparticles Doped in Polyvinyl Alcohol on the Structural and Optical Properties of PVA Films, *J. Nanomater*., **2013**, 1-10.

[24]. Bhasha and Prunima Jain, Effect of Nanofiller on the Properties of PVA nanocomposites thin film, *Proceeding of NCGE*, **2017**, 1-6.

[25]. Mohan Lal, S. R. Verma, Synthesis and Characterization of Poly Vinyl Alcohol Functionalized Iron Oxide Nanoparticles, *Macromol. Symp.*, **2017**, 376,1-5.

[26]. M. Obula Reddy and B. Chandra Babu, Structural, Optical, Electrical, and Magnetic Properties of PVA:Gd^{3+} and PVA:Ho^{3+} Polymer Films, *IJMS*, **2015**, 1-8.

[27]. Navin Chand, Neelesh Rai, S.L agrawal, S. K. Patel, Morphology, thermal, electrical and electrochemical stability of nano aluminium-oxide-filled polyvinyl alcohol composite gel electrolyte, *Bull. Mater. Sci*., **2011**, 34, (7) 1297-1304.

[28]. M. G. Liman, A. H. Abdullah, M. Z. Hussein, Z. Zainal, Characteristics of ZnO Synthesized by Combined Sol-Gel and Hydrothermal Methods for the Removal of Nitrobenzene, *J. Applicable Chem.*, **2018**, 7(2), 426-435.

[29]. H. C. Charan Kumar, R. Shilpa, Sannaiah Ananda, Synthesis and Characterization of Al-Doped ZnO Nanoparticles by Electrochemical Method: Photodegradation Kinetics of Methylene Blue Dye and Study of Antibacterial Activities of Al-Doped ZnO Nanoparticles, *J. Applicable Chem*, **2020**, 9(1), 9-21.

[30]. J. Lee, D. Bhattacharyya, A. J. Easteal, J. B. Metson, Properties of nano-ZnO/poly(vinyl alcohol)/poly(ethylene oxide) composite thin films, *Curr. Appl. Phys*., **2008**, 8, 42-47.

[31]. X. M. Sui, C. L. Shao, Y. C Liu, White-light emission of polyvinyl alcohol/ZnO hybrid nanofibers prepared by electrospinning, *Appl. Phys. Lett*., **2005**, 87, 113115(1-3).

[32]. M. Xiong, G. Gu, B. You, and L.Wu, Preparation and Characterization of Poly (styrene butylacrylate) Latex/Nano-ZnO Nanocomposites, *J. Appl. Polym. Sci*., **2003**, 90, 1923-1931.

[33]. Y. W. Heo, D. P. Norton, L. C. Tien, Y. Kwon, B. S. Kang, F. Ren, S. J Pearton, J. R LaRoche, ZnO nanowire growth and devices, *Mater. Sci. Eng. R Rep*, **2004**, 47(1-2), 1-47.

[34]. E. M. C Fortunato, P. M. C Barquinha, A. C. M. B. G Pi-mentel, A. M. F. Goncalves, A. J. S. Marques, L. M. N. Pereira, R. F. P. Martins, Fully transparent ZnO thin-film transistor produced at room temperature, *Adv Mater.*, **2005**, 17, 590.

[35]. Ammar M. Hamza, E. D Alhtheal, Ali K. Shakir, Enhancement the Efficiency of ZnO nanofiber mats antibacterial Using Novel PVA/Ag nanoparticles, *Energy Procedia*, **2017**, 119, 615-621.

[36]. K. S. Hemalatha, K. Rukmani, N. Suriyamurthy, B. M. Nagabhushana, Synthesis Characterization and optical properties of hybrid PVA-ZnO nanocomposite: A composition dependent study, *Mater. Res. Bull*., **2014**, 51, 438-446.

[37]. K. S. Hemalatha, G. Sriprakash, M. V. N Ambika Prasad, R. Damle, K. Rukmani, Temperature dependent dielectric and conductivity studies of polyvinyl alcohol-ZnO nanocomposite films by impedance spectroscopy, *J. Appl. Phys*, **2015**, 118, 154103-1-14.

[38]. P. Kalyani, N. Kalaiselvi, N. Muniyandi, A new solution combustion route to Synthesize $LiCoO_2$ and $LiMnO_2$, *J. Power Sources*, 2002, 111, 232-238.

[39]. Aashis S. Roy, Satyajit Gupta, S. Sindhu, Ameena Parveen and Praveen C. Ramamurthy, Dielectric Properties of novel PVA/ZnO hybrid nanocomposite films, Compos, *B. Eng*., **2013**, 47, 314-319.

[40]. Deepak Kumar, Suraj Karan Jat, Pawan K. Khanna, N. Vijayan, Shaibal Banerjee, Synthesis, Characterization and Studies of PVA/Co-Doped ZnO Nanocomposite Films, *Int. J Green Nanotechnol.*, **2012**, 4, 408-416.

[41]. A. F. Mansour, S. F. Mansour, M. A. Abodo, Improvement Structural and Optical Properties of Nanocomposites, *IOSR J. Appl. Phys*, **2015**, 7(2), 60-69.

[42]. N. Bouropoulos, G. C. Psarras, N. Moustakas, A. Chrissanthopoulos, S. Baskoutas, Optical and dielectric properties of ZnO-PVA nanocomposites, *Phys. Status Solidi A*, **2008**, 205(8), 2033-2037.

[43]. Muhammad Aslam, Mazhar Ali kalyar, and Zulfiqar Ali raza, Investigation of Zinc Oxide-Loaded Poly(Vinyl Alcohol) Nanocomposite Films in Tailoring Their Structural, Optical and Mechanical Properties, *J. Electron. Mater*., **2018**, 1-15.

[44]. Elham Gharoy Ahangar, Mohammad Hossein Abbaspour-Fard, Nasser Shahtahmassebi, Mehdi Khojastehpour and Parisa Maddahi, Preparation And Characterization Of PVA/ZnO Nanocomposite, *J. Food Process*. 2015, 39(6), 1442-1451.

[45]. B. Karthikeyan, T. Pandiyarajan, R.V. Mangalaraja, Enhanced blue light emission in transparent ZnO:PVA nanocomposite free standing polymer films, Spectrochim, *Acta Mol. Biomol. Spectrosc.*, **2016**, 152, 485-490.

[46]. R. Padma Suvarna, K. Raghavendra Rao, Subbarangaiah, A simple technique for a.c. conductivity measurements, *Bull. Mater. Sci*., **2002**, 25(7), 647-651.

[47]. You Kok Yeow, Zulkifly Abbas, Kaida Khalid and Mohamad Zaki Abdul Rahman, Improved Dielectric Model for Polyvinyl Alcohol-Water Hydrogel at Microwave Frequencies, *Am. J. Appl. Sci.*, **2010**, 7(2), 270-276.

[48]. I. Latif, Entisar E. AL-Abodi, Dhefaf H. Badri, Jawad Al Khafagi, Preparation, Characterization and Electrical Study of (Carboxymethylated Polyvinyl Alcohol/ZnO) Nanocomposites, *Am. J. Polym. Sci.*, **2012**, 2(6), 135-140.

[49]. M. A. El-Ahdal, Radiation effect on the molecular structure of dyed poly (vinyl alcohol), *Int. J. Polym. Mater*, **2002**, 86(5), 1219-1226.

[50]. N. B Rithin Kumar, Vincent Crasta, B. M. Praveen, Advancement in Microstructural, Optical and Mechanical Properties of PVA (Mowiol 10-98) doped by ZnO Nanoparticles, *Phys. Res. Int.*, **2014**, 1-9.

[51]. J. Tauc, A. Menth, D. Wood, Optical and Magnetic Investigations of the Localized States in Semiconducting Glasses, *Phys. Rev. Lett*., **1970**, 25, 749-752.

[52]. S. B. Aziz, H. M. Ahmed, A. M. Hussein, A. B. Fathulla, R. M. Wsw, R.T. Hussein, Tuning the absorption of ultraviolet spectra and optical parameters of aluminum doped PVA based solid polymer composites, *J. Mater. Sci. Mater. Electron*, **2015**, 26, 8022-8028.

[53]. Brian D. Viezbicke, Shane Patel, Benjamin E. Davis, and Dunbar P. Birnie, Evaluation of the Tauc method for optical absorption edge determination: ZnO thin films as a model system, *Physica Status Solidi, B*, **2015**, 252, 1700-1710.

[54]. O. G. Abdullah, Synthesis of single-phase zinc chromite nano-spinel embedded in polyvinyl alcohol films and its effects on energy band gap, *J. Mater. Sci. Mater. Electron*, **2016**, 27, 12106-12111.

[55]. Elizabeth Jeessa James, Shweta Mishra, Joice Jose, Arunendra Kumar Patel, Kallol Das, Preparation & Optical Studies on Zinc Oxide: Poly Vinyl Alcohol (PVA) Composite, *IJSRD*, **2016**, 4, 1042-1044.

[56]. E. M. Abdul Razek, A. M. Abdugany, A. H. Oraby, G. M. Asnag, Investigation of Mixed Filler Effect on Optical and Structural Properties of PEMA Films, *J. Eng. Technol., IJET-IJENS,* **2012**, 12, 98-102.

[57]. Sreetama Dutta, Bichitra N. Ganguly, Characterization of ZnO nanoparticles grown in presence of Folic acid template, *J. Nanobiotechnol.*, **2012**, 29, 10- 29.