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Dielectric Characteristics of Nanoparticles Doped Polyvinyl Alcohol

Abstract: -A comparative study of structural characterization and dielectric properties of Polyvinyl alcohol, after insertion of Zinc oxide (ZnO) and Aluminum oxide (Al_2O_3) to form sample composite in the form of films at frequencies varying from 1Hz to 100 Hz and for several temperatures from 288k to 353k has been done. Structural characterization of PVA-Zn and PVA-Al done by x-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Field emission Electron Microscopy (FESEM). It is confirmed that ZnO and Al_2O_3 was well incorporated in PVA matrix. Together composites of ZnO and Al_2O_3 with PVA tested by electrical properties like dielectric constant (ε') and dielectric loss (ε") which shows the dispersed values at lower range of frequencies and seen to decreased at higher ranges at all temperatures, interprets the interfacial polarization. Imaginary part of electric modulus (M") has been determined by studying the dielectric relaxation properties of both composites. The modulus graph shows that the peaks position transfer near higher frequencies with rise in temperatures. The time of dielectric relaxation is determined from peak frequencies of M" plot; lessened with temperature rise.

Keywords:Dielectric Properties, XRD, FTIR, FESEM

I. INTRODUCTION

Polymer composite films have imperative applications in supercapacitors, sensors like gas sensors, batteries and many more as a result of their good thermal stability with better ionic conductivity. Now a days polymer incorporated with ceramic fillers improves electronic properties and thus opens for vast applications in fields like electronic packaging, angular acceleration accelerometers, integrated decoupling capacitors, etc.So, for the same probable technical applications, it is most imperative to study dielectric properties. It is significant to consider charge transfer mechanism in polymer composites for perspective of technological and fundamental mode. In highly doped polymers ions or charge carriers are localized, hence movement of the carriers happens by tunnelling or hopping mechanism among the localized states.One of the known charge transfer mechanisms is Variable Range Hopping (VRH), in which charge transfer happens in consecutive localized states by attaining phonon thermal energy[1-5]. Temperature dependent polymer is also called as polar polymer complex when insertedthrough metal salts in view to increase the ionic conductivity. The polymer composites can be easily process into films and also have electrochemical stability, hence received excessive attraction but coredownside is its low conductivity. It may improve the conductivity of polymer composites by incorporating the ceramic materials [6]. As Polyvinyl Alcohol (PVA) is compatible with each type of fillers so that it acknowledgeda lot of industrial applications like food, cosmetics, packaging, pharmaceuticalsetc as well as it is biocompatible, non-toxic, hydrophilic and semicrystalline polymer and hence preferred for present work [7].Present work emphasizes on the comparative structural and dielectric study of PVA with Al_2O_3 and ZnO to synthesize polymer composite by solvent casting technique for temperaturesvaries from 288 k to 353 k.

II. EXPERIMENTAL

The required polymer(PVA) of 86–89% degree of saponification, has molecular weight of 124000 mol^{-1}, analytical grade Zinc oxide (ZnO) of molecular weight 81.39 and Al_2O_3 of molecular weight 101.9 were together collected from SDFCL, Mumbai, India.

Films of pristine PVA, PVA-ZnO and PVA-Al_2O_3 composite were synthesised by simple and cost-effective solution casting method [8 -11]. As per method, first, 1g PVA powder is liquified in 30 mlhighly double distilled water. The transparent solution was prepared by stirring the solution continuously at ambient temperature. Vacuum dried ZnO of 10 weight percentage,was placed into the congruent solution bysimultaneous heating at 50°C for 1 h. The mixture after coolingtransportedon plane glass surface and left to evaporate at normal temperature and finallydehydrated at 40°C temperatures. Prepared layers of composite were then unwrapped from petri dishes which thenkept separately inthe vacuum chamber. Film thickness was measured by thickness profilometer, is found 114-120 μm. Similarly, PVA-Al_2O_3 composite is synthesized by the equalphenomenon and entitled asPVA-Zn, PVA-Al.

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Structural study of composites has been done by X-ray diffraction analysis, on Bruker D8 advance x-ray diffractometer, Germany of wavelength 1.5406 Å,FTIR of SHIMADZU 8400 spectrophotometer, Japan over the range of 400-4000 cm^{-1} and FESEM with EDAX of HITACHI S-4800. The dielectric properties were analysed on Novocontrol concept 80 with Alpha A high resolution Analyzerlinked to a computer of frequency starts from 0.1 Hz to 1 MHz and for temperature in between 288K to 353K.

III. RESULT AND DISCUSSION

XRD spectra of PVA, PVA-Zn, PVA-Al sample compositeare revealed in Fig 1. XRD peak of PVA is wide retorting to (101) plane at $2\theta = 19^0$ suggesting semi crystalline form of PVA [12-14]. In PVA-Zn film(JCPDS Card No. 36- 1451 and 80-0075) the ZnO peaks had orientation from 100, 002, 101, 102, 110, 103, 110, 200, 112 and 201 planes for which the scattering angles are 31.6°, 34.4°, 36.16°, 47.52°, 56.48°, 61.56°, 62.88°, 66.24°, 67.84°, 68.96° respectively whichdesignates that ZnO has the structure of hexagonal wurtzite[15-17]. The generalPVA-Zn composite film XRD spectra reveals that Zinc Oxidekept its unique structure in composite film [18,12,17]. From XRD spectrum of PVA-Al composite film, it reveals that width of broad hump of PVA has been enlarged somewhat in size with lessened in height. Besides the intensity peak at 66.3^{o}, no other peaks and features are detected in PVA-Al composite film, which shows the amorphous structure of composite. This is occurred due to smaller crystallites and very strong interface of Al with PVA. Size of Crystallitesis calculated from Debye-Scherer formula, is nearly equal 3.16nm.

Fig. 2 shows FTIR spectra of PVA, PVA-Zn, PVA-Al composite films. Strong and broad hydrogen bond (O-H group) of alcohol in PVA is detectedin between 3617-2738 cm^{-1}, which is then shiftedto 3617-3451cm^{-1}inPVA-Zncomposite and 3635-3452cm^{-1} in PVA-Al composite, occurs because of adsorption of water during creation of PVA-Zn composite films.Existence of of hydrogen bond in PVA-Zn and PVA-Al composite confirmed by the occurrence of hydroxy group of PVA. For 2964 cm^{-1} and 2963 cm^{-1} medium stretching of C-H bond are seen in PVA-Al and PVA-Zn composite films. O-H bonding of acetyl group is occurred at 1131 cm^{-1} in PVA which thenswitched almost to 1139 cm^{-1}in PVA-Zn composite. Bending vibrations of O-H group is detected at 1270 cm^{-1} as aresult of vibrations at gas phase, next it isshiftedto 1288 cm^{-1}. The bending of C-H bond in $-CH_2$ group is at 1457 cm^{-1} and 620 cm^{-1}.The M-O bond of Zinc-oxide (Zn-O) isoccurred at 578cm^{-1} in PVA-Zn and of Al-O is formed at 765 cm^{-1} in PVA-Al composite film, which approves the presence of ZnO and Al_2O_3contentin composite film[19-23].

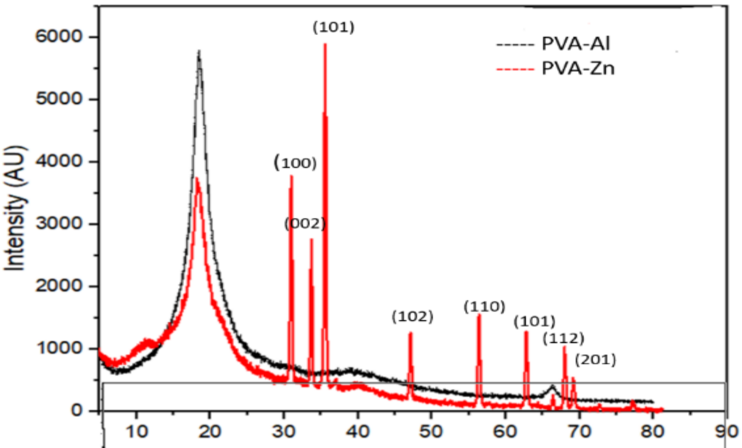

Figure 1. X Ray Diffraction of PVZn-10 and PVAl-10

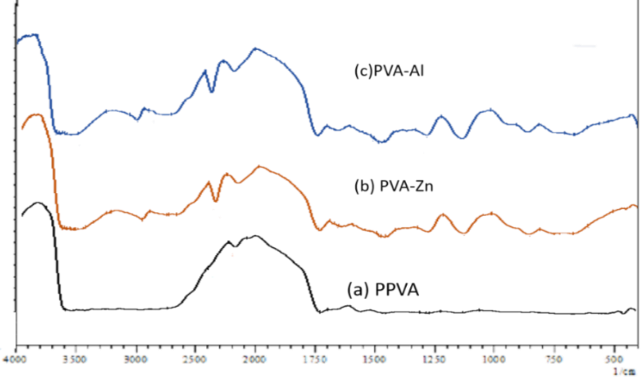

Figure 2. FTIR of PVA, PVZn-10 and PVAl-10

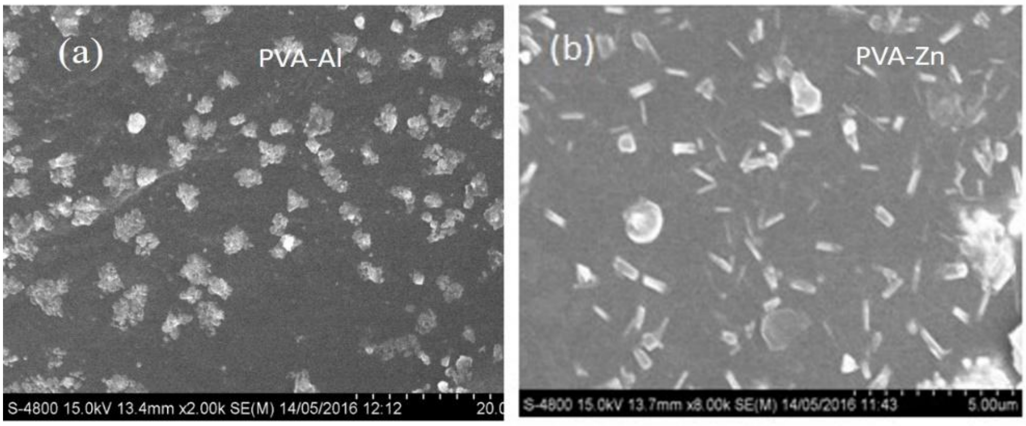

Figure 3.FESEM of a) PVZn-10 and b) PVAl-10

Figure 4: EDAX of PVZn-10 and PVAl-10

The FESEM imageofPVA-Al and PVA-Zn is revealed in Fig. 3a and 3b. From Figure 3a, it is predicted that PVA when inducedinZnO,particles weredispersed arbitrarily on thesurface and looks tube like constructions. The EDAX of PVA–Zn composite is depicted in Figure 4a shows presence of Zn and O element in composite film [24 -25]. Similarly, in PVA-Al micrograph the shape of Al_2O_3 particles becomes irregular and it spreads over the whole surface shows homogeneity of the filmdepicted in Figure 3b. The EDAX images of PVA-Al composite is shown in Figure 4b, specifies that energy of release of characteristics X-Ray spectrum for k-series of Al is 1.486keV and that of oxygen for k-series is 0.525 keV, directs the existence of Al and Oxygen in synthesized PVA-Al composite film [26-27].

The graph of (ε') of PVA, PVA-Al and PVA-Zn composite film with frequency from 100Hz to 1MHz is presented in Fig 4a. It isdepicted that value of ε'for both composites fall with rising log *f* valueand shows high values at low frequencies, because it gets enough relaxation time for the setback of ions with field arise as a result of interfacial polarization. It may arise due to electrode polarization in which charge carriers which are stored at electrodes easily follows with field reversal resulting in rised value of ε′. However, at higher frequencies, the charges not trails the field because of ionic and electronic polarization, which results in fall in ε′ [28-30].

Besides PVA has minimum value of ε′ which is formerly increased with doping of Al_2O_3 and ZnO into PVA due to oxide structure [23]. Fig. 4b shows the variance of ε′ for temperatures varying from 288k to 353k. It is detected from graph that ε′ grows with temperature for all composite films due to improvement in flexibility of polymer chain at high temperatures, thereby increases mobility of molecules. At low-temperature (288k), the polarization procedure slows down as of excess viscosity of polymer thus alignment of dipoles can't follow with the field setback results in lesser value of ε′. As temperature rises above 288k, the thick nature of polymer decreases, inscription of easier alternation of dipole with field thereby increase in ε′. Rise in density of charge carrier and mobility of molecules with temperature can be well explained by,

$$N= n_0\exp\left(-\frac{U}{\epsilon' k_B T}\right) \text{ ---------1}$$

Where, N is charge carrier Density, K_B is Boltzmann constant and U is the dissociation energy.Debye relaxation model is used to describe dielectric relaxation in polymer having only one relaxation time can be given by,

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_S - \epsilon_\infty}{1+i\omega_\tau}\text{------------2}$$

ε′ is given by,

$$\varepsilon' = \epsilon_\infty + \frac{\epsilon_S - \epsilon_\infty}{1+\omega^2\tau^2}\text{------------3}$$

Where, ε_∞ is the limiting value of the ε′ at high frequencies, ε_s is the static ε′, $\omega=2\pi f$ is the angular frequency and τ is the relaxation time. Polar and nonpolar polymers showdiversebehaviourof ε′ withtemperature. In polar polymer ε′ increases with temperature whereas remain independent of temperature in non-polar polymers [31].

Variation ofdielectric loss with frequency and temperature for PVA,PVA-Al and PVA-Zn is depicted in Fig.5a and 5b.It is observed from Fig.5a that at down frequencies, dielectric loss(ε”)illustrates scattered nature, while at upper frequencies its value decreases and reaches to zero. As at lesser frequencies charges contributes to field alignmentbecause ofsufficient time span but at up frequencies, ε” value decreases and therebylessening in ε”. Besides the rising of ε” value with the temperature because of increasedflexibility of charges with high thermal energy is described in Fig.5b.It trails the DC involvement which is temperature dependent, results in increment of both conductivity and the dielectric loss[32].

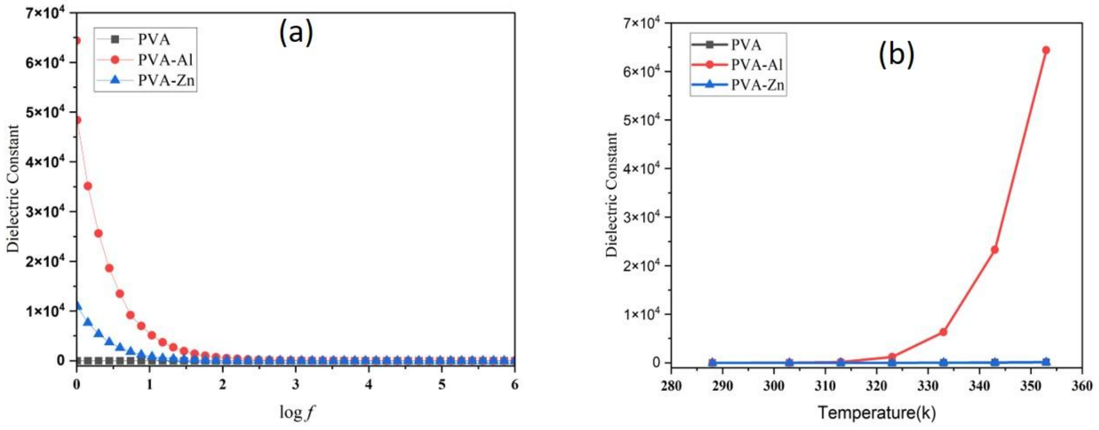

Figure 4. A plot of Dielectric constant of PVA, PVA-Al and PVA-Zn with (a) log f and (b) Temperature (k)

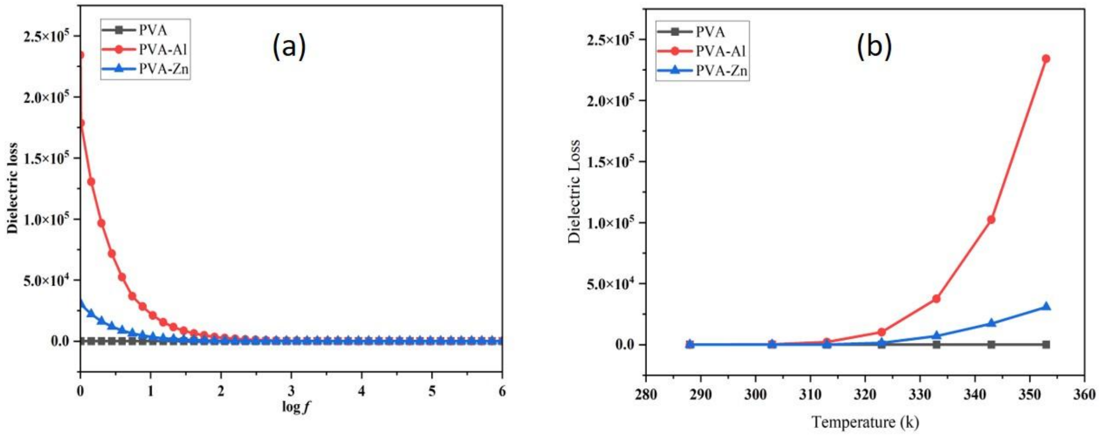

Figure 5. A plot of Dielectric loss (ε”) of PVA, PVA-Al and PVA-Zn with (a) log f and (b) Temperature k

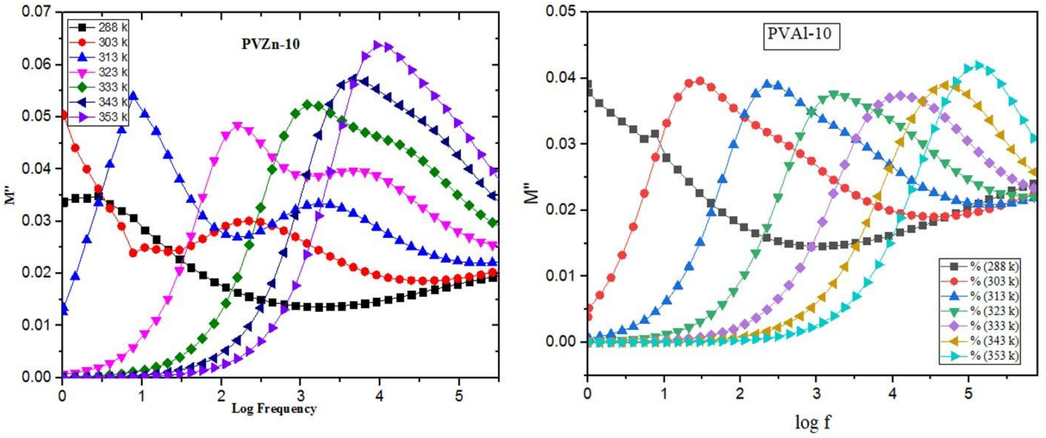

Figure 6 A plot of M" of PVAl-10 and PVZn-10 with log *f* for different Temperature (k)

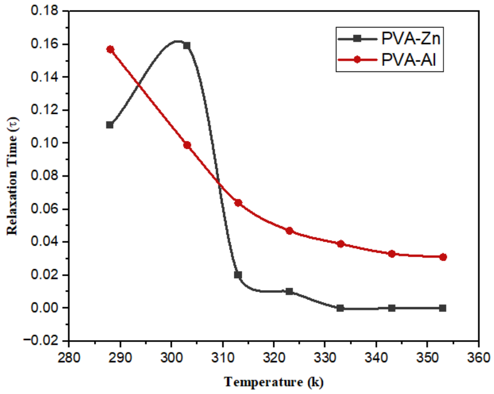

Figure 7 Variation of relaxation time with temperature of PVA-Zn and PVA-Al composite films

Dielectric relaxation can likewise be explored by studying electric modulus M" of samples composite. M" is stated in terms of ε",

$$M = \frac{1}{\epsilon} \text{------------}4$$

$$M^{*} = M' + M'' \text{ ------------}5$$

Where M' is real part and M" is the imaginary part of the electric modulus and it can likewise inscribed as,

$$M' = \frac{\epsilon'}{\epsilon'^{2} + \epsilon''^{2}} \quad and \quad M'' = \frac{\epsilon''}{\epsilon'^{2} + \epsilon''^{2}} \text{----------}6$$

A plot of electric modulus *M*" for PVZn-10 and PVAl-10 composite verses frequency for temperaturechanges from 288k to 353kis shown in Figure (a)and (b) respectively. Both plots shows the peaks at each temperatures which suggests the dielectric relaxation process in which peaks are transferring towards upside frequencies with rise in temperatures. The shifting of peaks nearto higher frequency sides depicts that ions are responsible for electric conduction. This is because at higher temperatures, carriers become thermally activated thereby decreases the relaxation time. The relaxation time for PVZn-10 and PVAl-10 composites is calculated from the M" Vs frequency plot is depicted in Figure, by using the relation,

$$\tau = \frac{1}{2\pi f_{max}} \text{ ---------------}7$$

Where, $f_{\max}$frequency of a peak for all temperatures.

Figure shows the relaxation time varieswith rise in temperature from 288k to 353k. It clearly confirms that for both PVZn-10 and PVAl-10 composite relaxation time decreases sharply with increase in temperature which result in increasing conductivity of composites[33-34].

IV. CONCLUSIONS

PVA-ZnO and PVA-Al_2O_3 composite films were synthesized and characterized by structural and dielectric characterization that are dielectric constantε', dielectric loss ε" and electric modulus M"at temperaturesstarts from 288k to 353k. FESEM of both composites indicates well dispersion of dopant into PVA matrix. Values of ε'and ε" for both dopantvaries with temperature and frequency, might be due to viscosity of polymer. The electric modulus graph with frequency for both fillers show peaks for every temperature, was shifts with rising temperature to higher frequency range, depictsions are the charge carriers. The time of dielectric relaxation, was calculated from electric modulus plot,decreased with temperature. This is happeneddue to charge carriers becomesthermally activated at upper temperatures.Improved dielectric properties of PVA-ZnO and PVA-Al_2O_3 composite are applicable in fields like thin film transistors for high k dielectric layer, capacitors, optoelectronics devices etc.

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