"Dielectric relaxation studies of PVA and PVA/$CuSO_4$ composite films"

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Abstract

Dielectric relaxation parameters on PVA and their composition with inorganic metal salt $CuSO_4$ have been carried out at microwave frequency 9.03 GHz and at 308K temperature. The values of different dielectric parameters viz. dielectric permittivity(ϵ'), dielectric loss (ϵ''), ac conductivity (σ'), relaxation time (τ), loss tangent ($\tan\delta$), extinction coefficient (k) and refractive index (n), carried out for PVA and PVA/$CuSO_4$ composite films. An increase in the dielectric permittivity was observed on doping of inorganic metal salt $CuSO_4$ into PVA lattice at different concentrations (up to 10%). Dopant present in the low concentration does not significantly affect the dielectric permittivity but as the dopant concentration increases, it creates additional sites for trapping and thereby, enhances the dielectric permittivity. PVA is a polar polymer in which each dipole can act as an electron trap, therefore the observed increment in the dielectric parameters is understood. In general, at microwave frequency the movement of network and modifying ions are held responsible for relative dielectric permittivity and the oscillations between them for losses.

Keywords: PVA, dielectric relaxation, dielectric loss, extinction coefficient, refractive index

DOI Number: 10.48047/nq.2015.13.2.822 **Neuroquantology 2015; 13(2): 253-260**

1. INTRODUCTION

In recent years, conjugate polymers have been the main focus of research laboratories for the studies of their various properties. The behaviour of polymeric films is of direct interest to both the basic studies of electrical conduction and their application in capacitors for microelectronics. In view of the application of the polymer films in microelectronics and optical waveguide systems, studies of the dielectric properties of the polymeric films are of considerable interest. In polymeric materials, the polarization and depolarization behaviour are related to the dielectric relaxation process [1,2].

Polyvinyl alcohol (PVA) is one of the most studied polymers due to its several interesting physical properties as observed by the researchers [3,4], which are very useful in technical applications [5-7]. The important feature of this semicrystalline polymer is the presence of crystalline and amorphous regions. These two regions are well separated by portions of an intermediate degree of ordering, which enhances the mobility of the molecule, producing several crystalline and amorphous phases [3-8]. Recent studies have been done by Abdelaziz and Abdelrazek [4], Bhattacharyya and Pal [9], Gupta *et al.* [10], Khan *et al.* [11] and Rawat *et al.* [12], on the electrical and optical properties of polymers have attracted much attention in view of their application in electronic and optical devices. Electrical conduction in polymers have been studied aiming to understand the nature of the charge transport prevalent in these materials, while the optical properties are aimed achieving better reflection, interference and polarization properties.

Doping with metal salts has significant effect on the physical properties of polymers [10,13-15], depends on the chemical nature of the dopant and the way in which they interact with the host polymer. Recently, PVA films are doped with multiple valance metal ions and show a strong dependence of donor-acceptor mechanism between the metal ions and polymer matrix. Various research groups have studied the optical, structural and other properties of PVA with different dopants like Iodine, $CuCl_2$, ZnSe,

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CdS, $NiCl_2$, $MnCl_2$ etc., using different techniques. These studies show the changes in the properties like crystalline, structural, optical and electrical behaviour etc. of the host polymer due to doping. PVA is normally a poor electric conductor, it can become conductive upon doping with some ionic dopant. The small conducting nature of doped PVA is thought to be due to interactions between polymer chain and dopant via hydrogen bonding with hydroxyl group as well as the complex formation [8, 16-20]. Considerable work at low frequencies in polymeric materials has been reported in recent years [14,15], but very little work has been done at microwave frequencies. The major aim of this study is to obtain a wide range of the dielectric properties of PVA films filled with different concentrations of dopants $CuSO_4$ in order to select the optimum conditions necessary for the required technical applications.

2. EXPERIMENTAL

Sample Preparation

The films of pure polyvinyl alcohol (PVA) and doped PVA with inorganic dopants, were prepared in the laboratory by solution cast method, [2,12,21,25]. To prepare $CuSO_4$ doped films, the $CuSO_4.5H_2O$ was taken in the percentage weights viz., 2%, 4%, 6%, 8% and 10%. The average thickness of all prepared films were of the order of 100 µm.

Dielectric Measurements

For the measurement of dielectric parameters at microwave frequencies, we have used the technique developed by Dube and Natarajan [1]. The dielectric permittivity ϵ' and dielectric loss $\epsilon"$ were calculated by measuring the shift in minima and voltage standing wave ratio (VSWR) without and with the specimen. These microwave data so collected was employed to determine relaxation time (τ) and loss tangent ($\tan\delta$) respectively, using the following equations:

$$\tau = \frac{\epsilon"}{\omega\epsilon'} \quad \text{... (1)}$$

$$\tan\delta = \frac{\epsilon"}{\epsilon'} \quad \text{... (2)}$$

and the conductivity of the specimen was determined using the relations

$$\sigma' = \omega\epsilon_0\epsilon" \quad \text{... (3)}$$

$$\sigma" = \omega\epsilon_0\epsilon' \quad \text{... (4)}$$

where σ' and $\sigma"$ are, respectively the real and imaginary part of the conductivity, $\sigma = \sigma' + i\sigma"$. The real part of conductivity (dielectric conductivity) shows the features of ac conductivity in composite materials [21,22]. The optical constants like extinction coefficient (k) and refractive index (n) have been calculated for the specimen using the relations [23-25]

$$\tan\delta = \frac{2k}{1-k^2} \quad \text{... (5)}$$

$$\epsilon" = 2n^2k \quad \text{... (6)}$$

The significance of k is given by the fact that after the wave has travelled over a distance equal to the wavelength of wave in the dielectric material, its amplitude decays by a factor $e^{-2\pi k}$ [23].

3. RESULTS AND DISCUSSION

In Table 1, dielectric permittivity (ϵ') , dielectric loss ($\epsilon"$), loss tangent ($\tan\delta$), ac conductivity (σ'), extinction coefficient (k) and refractive index (n) have been listed for pure PVA and its composite with $CuSO_4$ at 9.03 GHz frequency and at room temperature (308K) for the films of varying concentrations. The variation of dielectric permittivity (ϵ') with dopant concentration depicted in Figure 1. The figure shows an increasing trend in the dielectric permittivity with the increment of $CuSO_4$ content into PVA matrix. The ϵ' obtained for pure PVA is 3.07 and for the presence of $CuSO_4$ (2 -10 wt%), ϵ' varies from 3.18-3.27. Generally, the dielectric properties of a polar polymer will depend on whether the dipoles are attached to the main chain or not and the dipole polarization will depend on segmental mobility, which is low at temperature below the glass transition temperature. In view of this, the observed variation in the dielectric properties are understood by invoking the Maxwell-Wagner-Sillars (MWS) effect of polarization [26]. Accordingly, the enhancement in the dielectric properties is attributed to the interfacial polarization: a phenomenon that appears in heterogeneous media consisting of phase with different dielectric permittivity and conductivity and is mainly due to the accumulation of charges at the interfaces. The presence of $CuSO_4$ complex in the PVA matrix acts as charge clusters and these clusters increases with dopant concentrations, which enhances the

Table 1:- Dielectric parameters, dielectric permittivity (ϵ′), dielectric loss (ϵ"), ac conductivity (σ′), relaxation time (τ), loss tangent (tanδ), extinction coefficient (k) and refractive index (n), carried out for PVA and PVA/$CuSO_4$ composite films at 9.03 GHz frequency and at room temperature (308K)

Sample	Dielectric constant ϵ′	Dielectric loss ϵ"	ac conductivity σ′ (Sm^{-1})	Relaxation time τ (10^{-12}) Sec.	Loss tangent tanδ	Extinction coefficient k	Refractive index n
PVA	3.07	0.72	0.36	4.1	0.23	0.11	1.76
PVA+2%$CuSO_4$	3.18	0.76	0.38	4.2	0.24	0.12	1.79
PVA+4%$CuSO_4$	3.20	0.84	0.42	4.7	0.26	0.13	1.81
PVA+6%$CuSO_4$	3.22	0.96	0.48	5.3	0.30	0.15	1.82
PVA+8%$CuSO_4$	3.25	1.07	0.54	5.8	0.33	0.16	1.83
PVA+10%$CuSO_4$	3.27	1.18	0.59	6.4	0.36	0.17	1.84

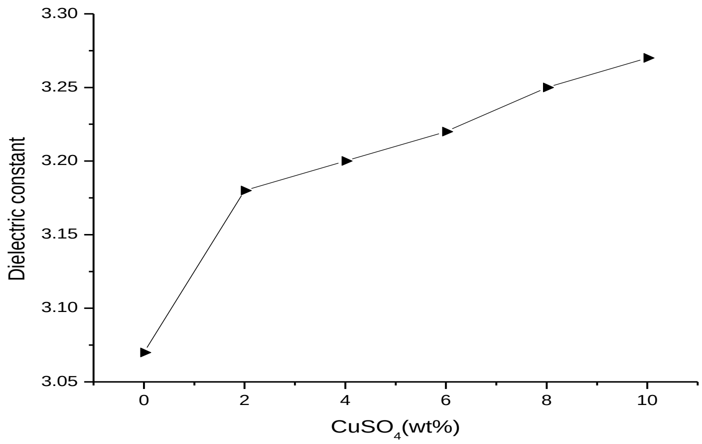

Figure 1:- Variation of dielectric permittivity (ϵ′)with doping percentage of $CuSO_4$ in PVA

average polarization, where the mobile ions and electrons may be responsible for the enhancement of the dielectric permittivity (ϵ′).

The XRD scan of PVA and PVA/$CuSO_4$ composite films (Fig. 2a-2c) justified the effect of $CuSO_4$ concentration in PVA lattice.

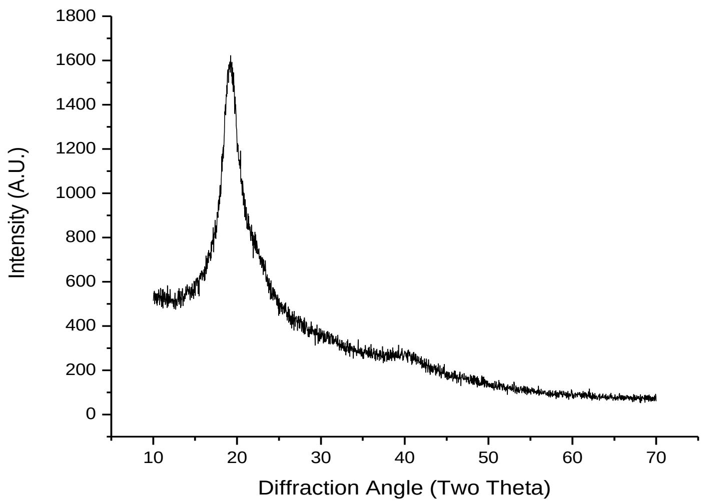

Figure 2a:- XRD pattern of pure PVA film

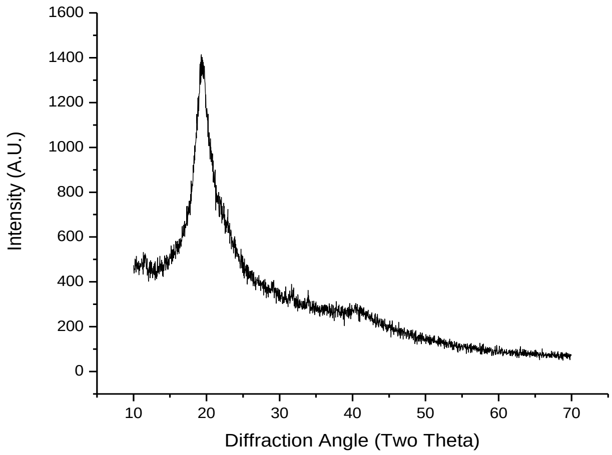

Figure 2b:- XRD pattern of PVA film doped with 2% $CuSO_4$

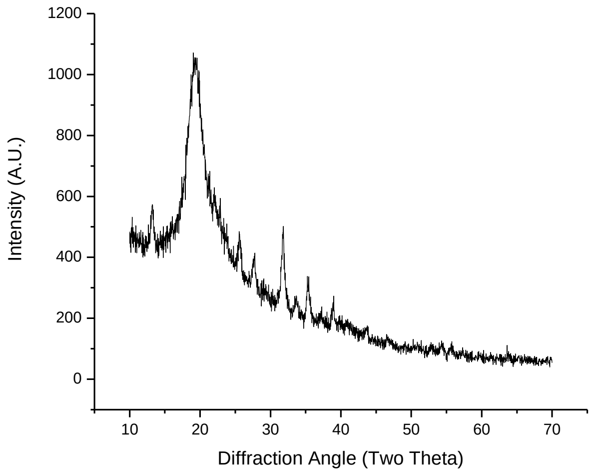

Figure 2c:- XRD pattern of PVA film doped with 6% $CuSO_4$

Figure 3 depicted variation in the dielectric loss (ϵ") versus dopant concentration. From the figure we observed an increasing trend for higher concentration (2-10 wt%) of $CuSO_4$ into PVA matrix.

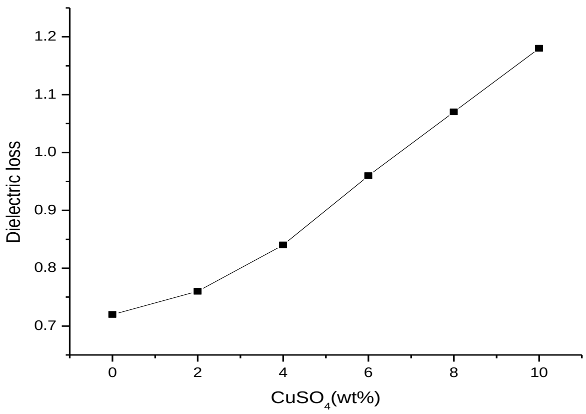

Figure 3:- Variation of dielectric loss (ϵ") with doping percentage of $CuSO_4$ in PVA

The ϵ" for PVA is found 0.72 and for its $CuSO_4$ composite films, ϵ" lies within the range 0.76-1.18. The origin of microwave dielectric loss in polymers is attributed to dipole absorption dispersion in both crystalline and amorphous polymers. The higher value of the dielectric loss for higher $CuSO_4$ concentration can be understood in terms of ac conductivity, which is associated with the dielectric loss ϵ" (Eq. 3). The ac conductivity σ′, obtained 0.36 Sm^{-1} for PVA and ranging from 0.38 Sm^{-1} to 0.59 Sm^{-1} for its $CuSO_4$ composite films (Fig. 4).

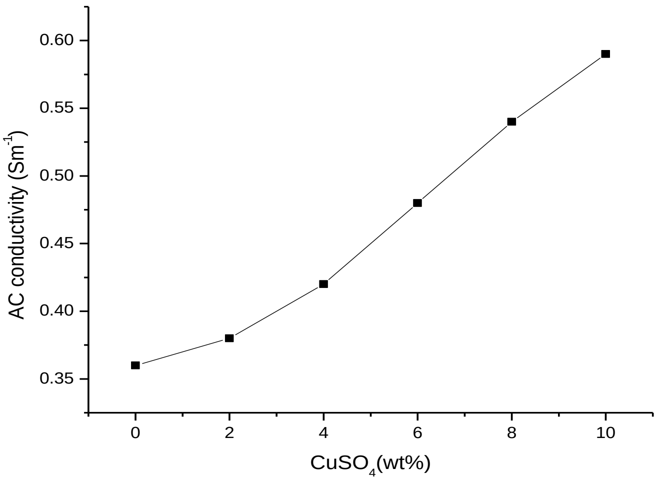

Figure 4:- Variation of ac conductivity (σ′) with doping percentage of $CuSO_4$ in PVA

Moreover, PVA exhibits flexible polar side groups with polar bond as the bond rotating having intense dielectric α–transition [27]. Thus there is a change in the chemical composition of the polymer repeated unit due to the formation of hydrogen bonds with hydroxyl groups in the polymerization process, which in turns makes the polymer chain flexible and hence enhances the electrical conductivity as well as dielectric losses. Accordingly, the present increase in the conductivity upon doping suggests that the polymer-dopant interaction will increase the charge carrier concentration on mobility within the microcystalline domain of PVA. The loss tangent (tanδ), obtained by using equation 2 are illustrated in Figure 5, for pure PVA and its composite films with $CuSO_4$, tanδ comes out in the range 0.23-0.36. The variation in the loss tangent in polymers may be attributed to dipolar losses due to impurities and photon-phonon absorption, corresponding to density of states in amorphous regions of polymer [28].

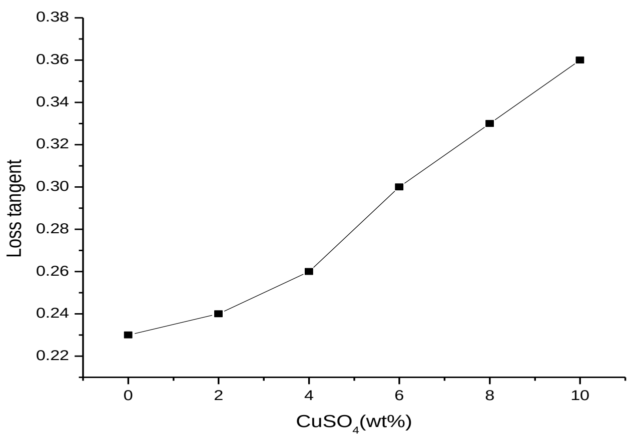

Figure 5:- Variation of loss tangent (tanδ)with doping percentage of $CuSO_4$ in PVA

eISSN: 1303-5150

The relaxation time (τ) for virgin PVA and PVA/$CuSO_4$ composite films, was calculated using equation 1. The relaxation time obtained for all the samples under investigation, comes out of the order of Pico second (10^{-12} second) and found in the range of 4.1-6.4. These values are in accordance with Tanwar *et al.* [25] and Khare *et al.* [29]. The variation in the τ values for PVA and doped PVA films with $CuSO_4$ (Fig. 6), may be due to the intermolecular interactions between PVA and $CuSO_4$ molecules.

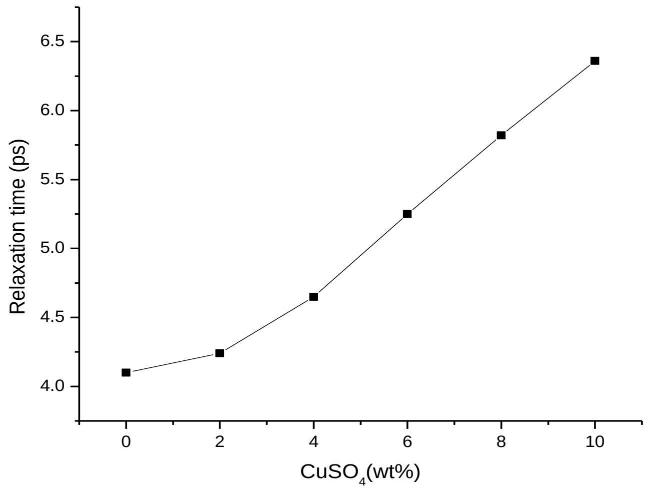

Figure 6:- Variation of relaxation time (τ) with doping percentage of $CuSO_4$in PVA

The optical constant viz., extinction coefficient (k) and refractive index (n) have been calculated using the equations 5 and 6 respectively. For pristine PVA, k comes out to be 0.11 and for PVA/$CuSO_4$ composite films k varies in the range 0.12-0.17. The values of refractive index (n) are found to be in the range 1.76-1.84 for PVA and PVA/$CuSO_4$ composite films.

The significance of the increased refractive index is that, as the wave penetrates the specimen, it got attenuated causes decay in the wavelength, hence refractive index increased for pure PVA as compared to the air (which is around of 1). On addition of $CuSO_4$ into PVA matrix, further damping in the wavelength resulting increase in the value of refractive index. The variation in the values of k and n with respect to $CuSO_4$ concentrations were illustrated in Figures 7 and 8 respectively.

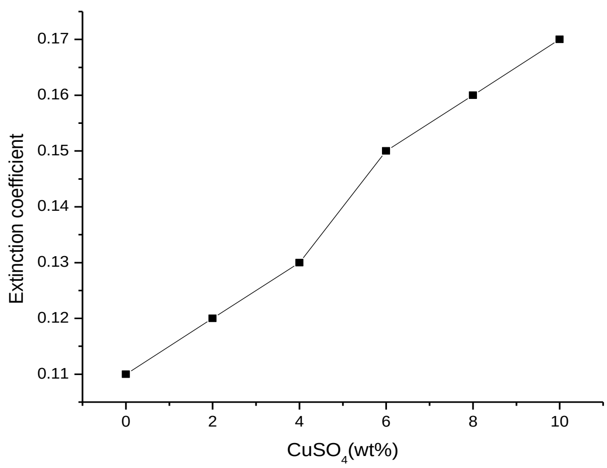

Figure 7:- Variation of extinction coefficient (k) with doping percentage of $CuSO_4$ in PVA

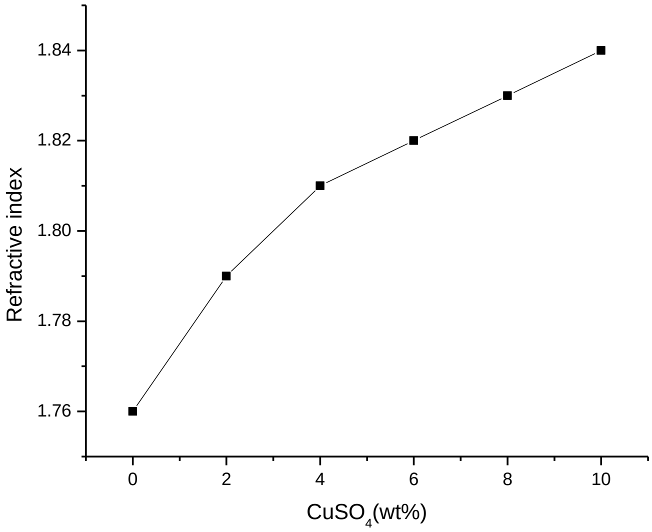

Figure 8:- Variation of refractive index (n) with doping percentage of $CuSO_4$ in PVA

4. CONCLUSION

- The dielectric parameters of virgin PVA and doped PVA films with different concentrations of $CuSO_4$ and thickness of the order of 100 μm have been investigated at 9.03 GHz frequency and at room temperature (308K).
- The study revealed the significant effect of doping on dielectric properties of PVA films.
- An increase in the dielectric permittivity was observed on doping of inorganic metal salt into PVA lattice at different concentrations. Dopant present in the low concentration does not significantly affect the dielectric permittivity but as the dopant concentration increases, it creates additional sites for trapping and thereby, enhances the dielectric permittivity.
- In this study the host polymer PVA is a polar polymer in which each dipole can act as an electron trap, therefore the observed increment in the dielectric parameters is understood. In general, at microwave frequency the movement of network and modifying ions are held responsible for relative dielectric permittivity and the oscillations between them for losses.
- The refractive index of PVA was modified through the addition of inorganic materials and showed values between 1.76 and 1.84 depending on the composition of the polymer. PVA with these new light sensitive compositions can be easily spin coated on to variety of semiconductor substrate.

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