Dielectric relaxation studies of $FeCl_3$ doped PVA Films

H K Mahavar
Department of Physics, M.S.J. Govt. P. G. College, Bharatpur 321001, Rajasthan, India

Abstract. Polyvinyl alcohol (PVA) and $FeCl_3$ doped films with different concentrations were prepared using solution grown technique, in order to investigate the effect of $FeCl_3$ doping (up to 10%) on dielectric properties of PVA host at microwave frequency and at room temperature. Measurements of the dielectric parameters such as dielectric permittivity, dielectric loss, loss tangent, a. c. conductivity and relaxation time were carried out. The changes in the dielectric parameters have been observed with doping concentration of $FeCl_3$ in PVA matrix. We have used dielectric data at microwave frequencies as a tool to evaluate optical constants, like extinction coefficient 'k' and refractive index 'n' of the films.

Keywords: PVA, dielectric permittivity, dielectric loss, relaxation time, loss tangent, a.c.conductivity, extinction coefficient, refractive index.

INTRODUCTION

In recent years, conjugated polymers have been the main focus of research laboratories for the studies of their various properties. They have very diverse structure and application ranging from domestic article to sophisticated scientific and medical equipments. The modern era can definitely be called a polymer era as we wear these manmade materials, sleep between them, build houses, pull switches with their help. We can see and hear the sights remote from us. The behaviour of polymeric films is of direct interest to both the basic studies of electrical conduction and their application in capacitors for microelectronics. Polymer films are being used as photoresist and electron beam resist for very large scale integration, photo conductors, printing and copying, liquid crystal displays and for surface modifications. 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]. 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 semi crystalline 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 phase[3-8].Recent studies have been done by Abdelaziz *et al*[4]., Bhattacharyya *et al*[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 at achieving better reflection, antireflection, interference and polarization properties. Different additives are usually added to polymer in order to modify and improve its properties. Inorganic additives such as transition metal have considerable effect on the optical and electrical properties of PVA polymer[13-15].

Considerable work at low frequencies in polymeric materials has been reported in recent years[2], but very little work has been done at microwave frequencies. The present work describes the results of our investigations on dielectric properties of pure PVA and $FeCl_3$ doped films at 9.02 GHz frequencies and at room temperature.

2. Experimental Techniques

2.1 Sample Preparation

PVA with average degree of polymerization and molecular weight 1,25,000 was obtained from Central Drug House (P) Ltd., New Delhi (India), while $FeCl_3$ was obtained from Qualigens Fine Chemicals, Mumbai. The films having thickness of the order of 100µm for virgin PVA and its composite with $FeCl_3$ were prepared by solution cast method[2,12]. The deionised water was used as a solvent. The films of virgin PVA and its composites with $FeCl_3$ were prepared in the laboratory by weight percentage method. Initially PVA was dissolved in deionised water then $FeCl_3$ was added in above solution for the preparation of composite films of varying weight percentage viz., 1%,3%,5%,7% and 9%. A magnetic stirrer was used for few hours ensuring maximum dispersion and homogenous mixing. The solution was poured in to a cleaned Petri dish and then placed in a dust free chamber to evaporate the solvent at room temperature for five days. The average thickness of prepared films was found of the order of 100µm. Micrometer (Mitutoyo, Japan, M120-25) with a least count of 1µm was used in order to measure the thickness of the prepared films.

2.2 Dielectric Measurements

The prepared films of pure PVA and its composites with $FeCl_3$ were subjected for the measurement of their dielectric constant at microwave frequencies using the techniques developed by Dube & Natarajan[1,2]. In this method the sample was mounted along the axis of the waveguide in such a way that electric field acts in the plane of the film. The advantage of this method is that the specimen is placed longitudinally at the centre of broad side of a hollow rectangular waveguide excited in the TE_{10} mode (figure 1), so that the entire specimen remains in the maximum electric field. Standing waves were produced in the rectangular waveguide by short circuiting the system and detected in the slotted line by means of a travelling wave

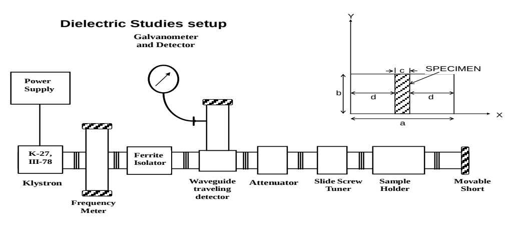

FIGURE 1. Schematic diagram of the experiment setup in X-band.

detector for the measurement of dielectric parameters. The dielectric permittivity (ε') and dielectric loss (ε") were calculated by measuring the shift in minima and VSWR with and without the specimen. These microwave data so collected was employed to determine relaxation time and loss tangent respectively, using the following equations.

$$\tau = \frac{\varepsilon"}{\omega\varepsilon'} \quad \text{------ (1)}$$

$$\tan\delta = \frac{\varepsilon"}{\varepsilon'} \quad \text{------ (2)}$$

and the a.c. conductivity of the specimen was determined using the relation.

$$\sigma = \omega\varepsilon_o\varepsilon" \quad \text{------ (3)}$$

3. Results And Discussions

In Table 1, dielectric permittivity (ε'), dielectric loss (ε"), loss tangent (tan δ), ac conductivity, extinction coefficient (k), relaxation time (τ) and refractive index (n) have been evaluated for pure PVA and its composite with $FeCl_3$ at 9.02 GHz frequency and at room temperature (35^0C) for the film of varying concentrations. Dielectric permittivity (ε') for pure PVA and its composites with $FeCl_3$ has been obtained in the range 3.07-3.33. The increase in the value of ε' on increasing dopant concentration may be attributed to the fact that doping of $FeCl_3$ in PVA affect its chemical as well as physical properties e.g. density, composition, stability, conductivity etc. The doping in PVA clearly showed the presence of Fe ions by change in colour i.e. transparent to yellowish. It is expected that Fe ions were well dispersed in the PVA lattice. Our dielectric parameters followed by Raja et al[16]. The ε" for pure PVA is found to be 0.72 and for its $FeCl_3$ composite films it ranging from 1.99-2.92. the higher value of the ε" for higher concentration of dopant can be understood in terms of electrical conductivity (σ), which is associated with ε" (Eq. 3). The σ obtained for neat PVA to be 0.36 Sm^{-1} and its $FeCl_3$ composite films, σ varies from 1.00-1.46 Sm^{-1}. PVA exhibits flexible polar side groups with polar bond, as the bond rotating having intense dielectric α-trasition[17]. 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 turn makes the polymer chain flexible and hence enhances the electrical conductivity.

Loss tangent (tan δ) for pure PVA and its composite films with $FeCl_3$ has been obtained in the range 0.23-0.88. The origin of microwave dielectric loss in polymer are attributed to dipole absorption dispersion in both crystalline and amorphous polymers, dipolar losses due to impurities and photon-phonon absorption spectra corresponding to the density of states in amorphous regions of polymer[18].The optical constants viz., extinction coefficient (k) and refractive index (n) have been calculated by using the relations, $\tan\delta = 2k/(1-k^2)$ and $\varepsilon" = 2n^2k$. For pure PVA, k comes out to be 0.11 and for its composite films with $FeCl_3$, k varies in the range 0.29-0.38. The values of n are found to be in the range 1.76-1.97 for pure PVA and its composite films with $FeCl_3$.

TABLE 1. Dielectric parameters carried out at 9.02 GHz. frequency and at room temperature (35^0C) for pure PVA and PVA/$FeCl_3$ composite films

Composition	ε'	ε"	σ (Sm^{-1})	τ (10^{12})sec.	tan δ	k	n
Pure PVA	3.07	0.72	0.36	4.10	0.23	0.11	1.76
PVA+1% $FeCl_3$	3.10	1.99	1.00	11.36	0.64	0.29	1.84
PVA+3% $FeCl_3$	3.22	2.20	1.10	12.05	0.68	0.31	1.89
PVA+5% $FeCl_3$	3.26	2.43	1.22	13.15	0.75	0.33	1.91
PVA+7% $FeCl_3$	3.29	2.74	1.38	14.72	0.83	0.36	1.95
PVA+9% $FeCl_3$	3.33	2.92	1.46	15.46	0.88	0.38	1.97

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