

INVESTIGATION OF DIELECTRIC AND PYRO-ELECTRIC PROPERTIES OF AZO DYE (CHR): PVA COMPOSITE.

Raj Kumar¹, G.D.Sharma², M.S. Roy³

¹Rajasthan College of Engineering for Women, Jaipur, ²Molecular Electronics and Opto-Electronics Laboratory Department of Physics, J.N.V.University, Jodhpur, ³Solar Device Group Defence Laboratory, Jodhpur, INDIA.

¹ kulhariraj@yahoo.com

ABSTRACT

In this article, we present the thermally stimulated depolarization currents (TSDC), dielectric properties and pyro- electric investigations of electrically poled azo dye (chromotrope -2R (CHR) doped poly (vinyl alcohol) (PVA) thin films. Based on dielectric spectroscopy data, the pyroelectricity have been explained with reversible dipole density changes during thermal expansion, whereas increase in dielectric constant has been explained in terms of polarization caused by charge carriers, probably ions. The thermally stimulated depolarization currents (TSDC) in azo dye: PVA has been investigated in the temperature range 30 - 120 °C. Two distinct peaks of TSDC spectra were observed at approximately 65 °C (α -peak) and 110 °C (ρ -peak). The α -peak and ρ -peak in the TSDC spectra are originated from the dipolar process and space charge relaxation, respectively. The effect of azo dye (CHR) on dielectric and polarization properties of PVA was also investigated. Dielectric studies showed the relaxor behavior with diffuse phase transition. It is found that the dielectric dispersion in the film support the well known Vogel-Fulcher law. The pyroelectric coefficient of electrically poled PVA: CHR thin film goes upto 0.4 $\mu\text{C}/\text{m}^2 \text{K}$ at room temperature. It is concluded from the observations that the orientation of strong anisomeric side chain takes place with a degree of alignment of about 8 %.

Keywords: Polarization, Thermally stimulated discharge current, Dielectric constant, Pyroelectric coefficient, lipids, inflammation, atherogenic, elements, cardiovascular

INTRODUCTION

Pyroelectricity in polymers with orientated molecular dipoles has been investigated for more than twenty years. Many electronic and optical devices require materials that sustain mechanical displacement under controlled electrical excitation for actuators. In these studies, relaxation processes with non - destructive probing of spatial polarization distributions were of particular interest. Recent developments in the field of pyroelectric polymers and their applications have been investigated by Bauer [1, 2] and Lang and Bauer [3].

Polymers with azo -chromophores side chains have attracted considerable interest as a candidates for nonlinear optical applications [4, 5]. In this material, donor and acceptor groups are linked by its delocalized π - electron system and azo chromophores groups form strong dipoles (A- π -D dipole). The polymeric materials with azo chromophores may lead to the formation of dipole domains resulting in enhancement in dipole moment. Therefore, azo chromophore containing polymers are interesting materials for pyroelectric applications as well as the pyroelectricity may arise from the liberation of molecular dipoles or dipolar domains and from thermally induced expansion or contraction of the materials. In semi-

crystalline polymers, reversible changes of crystallinity as well as trapped charge carriers may also contribute to the pyroelectricity [6].

We have studied the pyroelectric and dielectric properties of azo dye (chromotrope -2R (CHR) composite with poly (vinyl alcohol) PVA. During the process of mixing, the azo groups of dyes get attached with the side groups in the polymer chain. In these composite materials, oxygen acts as electron donor and the dye with azo chromophores as electron acceptor leading to the formation of A- π -D dipole. The electro negativity difference of azo group with oxygen located at opposite sides of polymer chain results in large dipole moment perpendicular to chain direction. Our aim is to investigate the contribution of A- π -D dipoles to electrical polarization and to pyroelectricity as well. We have estimated the pyroelectric coefficient as well as polarization charges and its temperature and poling field dependence. A combination of dielectric spectroscopy and its dependence on temperature have been employed for the pyro- electric response in this material.

EXPERIMENTAL DETAILS

The composite of PVA with dye having azo chromospheres were made by mixing PVA and dye (20 % wt) in common solvents. The thin films of azo dyes PVA were obtained by casting the solution containing PVA and azo dye and the thin film were dried about 12 hrs to remove the traces of solvent from the films. The thickness of the film was about 20 μm . The electrodes on both side of the film were developed by silver paint. Since, the prepared polymer thin film is isotropic, a preferential dipole orientation and pyroelectricity was achieved by means of thermal poling. A DC field at 2 - 20 MV /m was applied vertically to the plane of film at 80° C for one hour and subsequently the sample was cooled to room temperature under the field with a rate 5° C/min. The pyroelectric current was measured using direct method wherein, pre-polarised sample is heated with its electrode shorted and short circuit current is monitored with Keithley electrometer (model 6714) Three runs were carried out to obtain the pyroelectric current (reversible) because some charges were released during the first and second runs. The presence of space charge in the first run gives an unreal pyroelectric current. The dielectric data were taken in the frequency range of 40 Hz to 100 MHz range with impedance analyzer (HP).

RESULTS AND DISCUSSION

Fig. 1 shows the variation of dielectric constant (ϵ) with azo dye volume ratio at room temperature. The value for PVA is equal to 1.6, when the volume of fraction of azo dye in PVA increases, the value of dielectric constant attains the magnitude of 7.5 at 35 % of azo dye content. The increase in the dielectric constant with the contents of azo dye is due to the increase in conductivity. Frequency variation in dielectric constant and loss factor of the PVA and PVA: azo dye composite measured at room temperature are shown in Fig 2 (a) and 2 (b). It can be seen from the Fig. 2 (a) and 2(b) that the loss factor of composite is dominated by that of pure PVA. The dielectric losses for higher frequency of composite are lower than those of the pure PVA. The experiment revealed a relaxation process in the pure PVA and PVA: azo dye composite with a maximum at 12.8 and 15.6 KHz respectively. The dielectric absorption is dominated by the polymer. It can be seen from the Fig. 2 (b) that the imaginary part of dielectric constant (loss factor) of composite is dominated by that of the polymer phase. In low frequency range both the ionic conduction contribution and low frequency dispersion is observed. According to Jonscher several polymer show similar behavior [7 - 9]. For the azo dye -polymer composite, there is an evidence of peak around 15.6 KHz, which is due to the masking of electronic conduction by the ionic contribution.

This peak is more visible in PVA alone. The increase in dielectric constant in CHR: PVA composite is due to the increase in conductivity.

Fig. 3(a) and 3 (b) presents the dielectric properties (dielectric constant and loss factor) as a function of temperature for PVA and CHR: PVA film at different frequencies. The dielectric constant for PVA: CHR film is higher than pure PVA, which is consistent with the polarization results and arises due to the higher dipole orientation in the PVA-CHR film. These plots show broad maxima (diffuse phase transition DPT) in the region near room temperature and strong frequency dispersion, which indicates the relaxor behavior of PVA-CHR. It has been observed that the phase transition temperature (T_m) shifted to higher temperature side) from 65° C at 100 Hz to 75° C at 100 KHz) and the dielectric constant at phase transition temperature (ϵ_m) decreases from 9.7 at 100 Hz to 6.0 at 100 KHz (Fig 3 (a)) and the loss at the phase transition temperature ($\tan \delta_m$) increases from 0.23 at 100 Hz to 0.11 at 100 KHz. A sharp decrease in dielectric constant with the increase in frequency can be explained in terms of the interfacial polarization. Contribution from interfacial polarizability is due to the presence of two materials with different conductivity. In this case the motion of the charge carriers occurs readily in the higher conductivity phase (CHR), but is interrupted at the phase boundary due to the lower conductivity of second phase (PVA). The diffuse phase transition in Para electric phase of the PVA-CHR can be described by modified Curie –Wiess Law [10]

$$(1/\epsilon - 1/\epsilon_m) = A (T-T_m)^\gamma \text{ ----- (1)}$$

Where A is a constant and γ is the diffusivity parameter which can vary from 1 for normal ferroelectric to 1-2 for relaxor ferroelectric.

Fig. 3 (c) shows the variation of $\log (1/\epsilon - 1/\epsilon_m)$ with $\log (T - T_m)$ for PVA:CHR at 1 KHz. This graph shows a linear behavior with temperature. To estimate the value of γ , the experimental data at $T > T_m$ were fitted to Eq. (1), by the method of least square. The value of γ obtained is 1.45, which clearly indicates the diffuse phase transition. Fig. 3 (d) shows the variation of inverse of temperature T_m with $\ln (f)$. It can be seen from this figure that the frequency derivative of $1/T_m$ is smaller at lower frequencies. This indicates that as $f \rightarrow 0$, a static freezing temperature (T_f) is approached. This frequency dependence of T_m can be modeled using Vogel –Fulcher empirical relation [8, 9]

$$f = f_0 \exp [-U/k(T_m-T_f)] \text{ ----- (2a)}$$

where T_m is the dielectric constant peak temperature, U is the activation energy, f is corresponding frequency and k is the Boltzmann's constant. This relationship was employed by various authors [11, 12] to explain the frequency dispersion of phase transition temperature in bulk and thin film relaxor ferroelectrics. Excellent fitting of Vogel –Fulcher relation with U, f_0 and T_f using nonlinear fit to Eq. (2a) are found to be 0.56 eV, 1.23×10^{10} Hz and 39° C respectively which are consistent with earlier reports on similar systems [13,14]. The value of f_0 is found to be in the optical frequency range of lattice vibration. In PVA-CHR film the dielectric peak shifts towards the higher temperature in comparison to pure PVA film. In addition, the dielectric peak in CHR-PVA film become narrower and exhibit less frequency dependence. The shifting of dielectric peak to lower temperature with decreasing frequency (dielectric relaxor) behavior is observed.

Fig. 4 shows the typical thermally stimulated discharge current (TSDC) of CHR : PVA thin film for both polarization (charging) fields and it was observed that there are two relaxation peaks located approximately at 70°C and 106°C, respectively. The first relaxation peak observed at 70° C is related to the transition temperature and denoted as α peak [18] and

second peak, observed at higher temperature of 106°C, is ρ peak related to the formation of space charge. It is also observed that the peak at higher temperature depends on the poling conditions also. It is observed that the peak value of α -relaxation process is identical for both polarities of charging field and that the shape of the relaxation spectrum is symmetric. However, the magnitude of the ρ peak shows a weaker dependence on the polarity of the charging field. The magnitude of second peak shows a weak dependence on the polarity of charging voltage. This suggests that the formation of a blocking schottky barrier at Ag - polymer interface may affect the space charge peak for different poling fields and times. Detrapping of charges is also related to the polymer chain motion.

Fig. 5(a) Shows the behavior of the α peak as a function of poling time τ_p at 70° C at a constant field 20 MV/m for 20 μ m thick films. The Fig. 5(b) shows a significant dependence of magnitude of the peak on τ_p and that of α -peak, originating from a dipolar process. As can be seen from Fig. 5 (b) that the current value at α peak may not reach near saturation level of polarization at poling time ($\tau_p < 20$ min) at 80° C at field 30 MV/m. Fig.6 (a) show the TSDC spectra of PVA: CHR film for different poling voltage and Fig. 6 (b) shows the dependence of α -peak value on the poling voltage. A linear dependence of the value of α -peak on the poling voltage is observed, which is generally expected with dipolar processes. This linear dependence of α -peak on poling voltage suggests that the -peak is due to the dipolar processes. This is further confirmed by the linear dependence of current density on poling field.

Fig. 7 shows TSDC spectra of CHR: PVA films obtained for the case $T_p < T_g$ and $T_p > T_g$, where T_p is the highest temperature at which the poling fields are initially applied. It is observed that at $T_p > T_g$, the ρ - peak starts to dominate in comparison with the α peak. The α -peaks shifts towards the higher temperature which is originated from the chemical reaction of dye with polymer and increase in dc conductivity due to the incorporation of CHR dye leading to an increase in the density of dipole concentration. The electronegativity difference of (-N = N-) and OH substituent located at the opposite sides of polymer chains results in large dipole moments perpendicular to chain direction. These dipoles are aligned in randomly oriented domains. After the poling, the polymer exhibits the pyroelectric properties. This can be attributed to the permanent orientation of dipoles resulted through poling process. The similar type of pyroelectric response in PVDF polymer has also been reported [17].

Injected charges are also important for the polarization behavior during poling of PVA: CHR film with fields in opposite direction. Not only polarization development occurs during poling but also polarization stability is affected strongly by injected charges. Fig.8 shows comparison between dielectric displacement during poling and the remnant polarization measured afterwards of two differently contacted PVA: CHR film at identical field strengths. One sample was directly contacted with metal electrodes, and the field was applied via blocking electrodes made with insulator. As shown in Fig.8, the dielectric displacement during poling is same for both samples indicating equal field strengths. But after removing the external field the polarization in the sample with blocking electrodes decay much more rapidly to nearly zero remanant depolarization. This shows that injected charges are needed for stabilization of the polarization in polymer film. The charges injected during the polling processes must be trapped some how at the boundaries of the polarized region and thus play an important role for generating permanent polarized states.

In this case, a time delay between immediate dipole orientation and polarization stabilization can be expected because of the limited charge injection at electrodes. In contrast to this polarization stabilization by a pure dipole -dipole interaction should results in an immediate

correspondence of momentary and permanent polarization. But in fact a significant time delay has been observed in short time polarization experiment with un-poled and pre-poled polymer films.

The binding energies have been examined by thermally stimulated discharge currents (TSDC) spectra and is observed that the films poled at low field strength exhibit binding energy about 1.4eV whereas the film poled at higher fields have binding energy about 2.1eV. These measurements show that the poling conditions have strong influence on the formation of charge traps. At high polling fields, the dipole orientation is completed before a significant amount of charge is injected which results in trapping near the sample surface with high binding energies. In this case the dipoles in the centre of the sample are not locally neutralized by trapped charges and therefore easier to depolarize. At low poling field strength, a local field enhancement by charge penetration into the bulk of the material is necessary in order to reach the coercive field needed for dipole orientation. This results in strong charge injection and in trapping at lower binding energies at less complete oriented dipole. The injected charges trapped at the boundaries of the polarized crystallites play a crucial role for the polarization stabilization in polymer films.

The pyroelectric coefficient p (T) is calculated by using well known relationship [14]

$$P(T) = I / [A (dT/dt)] \text{ ----- (2b)}$$

where I is the pyroelectric current, A is the electrode area of the sample and (dT/dt) is the heating rate which is 2°C/min for present investigation.

Fig. 9 shows the pyroelectric coefficient of pure PVA and azo dye PVA composite films. It can be seen from the Fig. 9 that the pyroelectric coefficient of PVA with azo dye film is much higher than that of PVA film alone. Further more, the composite is very sensitive in the temperature range of $60 - 80^\circ \text{C}$, where pyro-electric coefficient changed from 0.48 to $2.58 \times \mu\text{C/m}^2\text{K}$ i.e. for small temperature variations there is a large change in pyro-electric current.

The variation of pyroelectric coefficient with the poling field is shown in Fig. 10. In amorphous glassy polymeric materials the pyroelectric activity is mainly caused by changes in dipole density upon thermal expansion and contraction as proposed by many researchers in literature. In this case proportionality between the pyroelectric coefficient and polarization follow the Langevin function. It is observed that the pyroelectric coefficients tend to saturate at high field. This saturation may be due to the accumulation of charges at the internal boundaries of the film.

The poled samples show a pyroelectric effect; however magnitude and temperature stability strongly depends on the poling temperatures and doping of chromophores unit. The pyroelectric coefficient (p) is

$$p = (1/A) (\partial Q / \partial T) = \alpha (\epsilon + 2) P/3 \text{ ----- (3)}$$

where A is the electrode area, ∂Q is the accumulated charge on the electrodes for a temperature variation ∂T , α is the thermal expansion coefficient of the material and P is the frozen in polarization, ϵ is the dielectric constant of the polymer at the frequency and temperatures where the dipole orientation does not relax and nor follow the electric field. Eq.(3) considers reversible changes of the polarization due to thermal expansion. The pyroelectric coefficient of PVA: CHR is about $0.4 \mu\text{C/m}^2\text{K}$ at room temperature. Taking the dielectric constant (ϵ) of PVA: CHR as 7.8 and the thermal expansion coefficient (α) as $70 \times 10^{-6} \text{K}^{-1}$ the value of polarization (P) have been evaluated as $1.7 \mu\text{C/m}^2$. The polarization (P) can be related to molecular polarization [15]

$$P = [(\epsilon + 2)/3] (N/V) \mu [\cos \theta] \text{ ----- (4)}$$

N/V is the density of chromophores and $\mu (\cos \theta)$ is the average of projections of molecular dipole moments on the poling field axis, Taking $N/V = 10^{27} \text{ m}^{-3}$, $\mu = 7\text{D}$ and $\epsilon = 7.8$ $\cos \theta = 0.023$. The average cosine of angle θ between dipole axis and poling field axis is related to poling conditions as follows

$$\langle \cos \theta \rangle = \mu E_{\text{eff}} / 3kT_p \text{ -----(5)}$$

E_{eff} is the effective field for the chromophores during poling (including the local fields), k is the Boltzmann constant and T_p is the poling temperature. Using Eq. (5) and the value of $\langle \cos \theta \rangle = 0.023$, we have estimated the effective poling field as about 1.5 MV/m. This field is considerably lower than that field which we have applied during the poling (5- 30 MV/m). This indicates that the some part of applied poling field may be shielded in side the polymer film due to the trapped charges present in the material. This shows that the degree of orientation of the dipoles depends strongly on the poling field.

With Eq. (4), the maximum dipole polarization P_s (all dipoles are fully aligned along the field direction) can be estimated from the concentration of dipoles and the effective dipole moments of the intrinsic dipolar groups. It is assumed that the polarization arises mainly from the A- π -D dipoles and from hydroxyl groups, therefore

$$P = (\epsilon_{\infty} + 2) (N_{\text{OH}} \mu_{\text{OH}} + N_{\text{A-}\pi\text{-D}} \mu_{\text{A-}\pi\text{-D}}) / 3 \text{ ----- (6)}$$

Where N_{OH} and $N_{\text{A-}\pi\text{-D}}$ are dipole densities and μ_{OH} and $\mu_{\text{A-}\pi\text{-D}}$ dipoles, respectively. The dipole moments for A- π -D dipole and OH groups are taken as 3.9 D and 1.67 D respectively as reported in literature [16]. With $\epsilon_{\infty} = 7.8$, $N_{\text{OH}} = 2.4 \times 10^{26} \text{ m}^{-3}$ and $N_{\text{A-}\pi\text{-D}} = 1.36 \times 10^{27} \text{ m}^{-3}$, a maximum polarization of $P_s = 1.5 \times 10^{-5} \text{ C/m}^2$ is calculated, which is about one order magnitude smaller than the experimentally determined value at 70°C. This discrepancy indicates that the dipole process can not be the main cause of large polarization measured. The observed polarization may be an effect of charge accumulation at internal boundaries inside the film. It is observed that the current saturates at relatively low field of about 5 MV/m, whereas a dipolar current saturates at higher fields. This is due to the fact that the pyroelectric coefficient is field dependant. Therefore, it can be concluded that the pyroelectric effect in the sample is not related to the main component of the polarization.

CONCLUSIONS

We have investigated TSDC, dielectric properties and pyroelectric coefficient of electrically poled PVA containing CHR -2R (an azo dye). The observed TSDC spectra in PVA: CHR thin film confirms the presence of both dipolar and space charge relaxations. The dielectric studies showed the relaxor behavior with diffuse phase transition. Modeling of dielectric data using Vogel-Fulcher relationship exhibits strong evidence for static freezing temperature of thermally activated polarization in PVA: CHR thin films. The observed pyroelectricity indicates a field induced orientation of A- π -D dipoles. However, the observed pyroelectricity is essentially a secondary one because it is very unlikely that the A- π -D dipoles can liberate during heating. The large polarization in the material originates essentially from a displacement of charge carriers, probably ions, between internal phase boundaries. The internal field of the polarization charge partially compensates the externally applied field. This is probably the reason for the fact that pyroelectric coefficient at low field is very small. The measured pyroelectric coefficient of electrically poled PVA-CHR is about 0.4 C/m² K at room temperature. From this the degree of orientation that the chromophores have (~ 8 %) is determined.

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