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# INVESTIGATION OF THERMALLY STIMULATED DISCHARGE CURRENT ARISED DUE TO PURE AND DOPED ETHYL CELLULOSE

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**ABSTRACT**

*Thermally Stimulated Discharge Current (TSDC) has been carried out to study the relaxation phenomenon responsible for the formation of charge transfer complex in pure and iodine doped samples of ethyl cellulose at poling temperature 80 $^{o}$C. Thermograms of pure and doped samples have two peaks in lower and higher temperature range. Activation energy, charge released and relaxation times were calculated for pure and doped samples. Activation energy for first peak is approximately 0.2 eV and 0.4 eV for second peak. This energy decreases as doping concentration is increased but it increases as poling field is increased. Variation of different data explained on existing theories. With increase in polarizing field charges are released easily.*

***Keywords – Thermally stimulated discharge current, TSDC, Ethyl Cellulose, Iodine, doping, Charge Transfer Complex (CTC), Space charge, Trapping.***

## I. INTRODUCTION

The polymers have contributed a great deal in electrical insulation, but high fields yield these polymers causing electrical breakdown. Although the causes of breakdown have been attempted to be explained in a number of ways in terms of models, understanding of high field transport in polymers is far behind and needs to be studied in greater details. Of the many factors which cause the electrical breakdown, composition of polymers, electrical stress applied, charge transport in the bulk and temperature are some of the important factors. There are ways and means of improving the performance of a polymer by mixing or blending /doping of other suitable polymers.

EC is a weakly polar polymer that exhibits excellent chemical resistance and good mechanical properties. Ethyl Cellulose (EC) is an important member of the family of cellulose group. It is a thermally stable polymer that exhibits excellent chemical resistance and good mechanical properties. Because of its activeness it is used for many applications.

The Thermally stimulated discharge current (TSDC) technique is ideal for the investigation of the structure of polymers, semi-crystalline polymers and co-polymers because it is a more sensitive alternative than other thermal analysis techniques for detecting the transitions that depend on changes in mobility of molecular scale structural units [1-3]

TSDC is a general method for investigating the electrical properties of high solids via the study of thermal relaxation effects and as such offers an alternative scheme to the conventional bridge methods or current voltage temperature measurements. The method has special advantages of its own which are (i) conductivity does not interfere in the measurements, (ii) the motion of small chain segments whose processes have very low losses can be detected, (iii) since time and temperature can be and are simultaneously changed in TSDC method; therefore the phenomena which vary with time or temperature can be analyzed and (iv) low frequency behaviour of the dielectrics can be elucidated in a simple way.

Thermally stimulated discharge current (TSDC) is a conventional technique for investigation of charge storage and transport processes in high resistivity materials and devices. For many applications of polymers and doped polymers, it is necessary to know the dielectric properties of material (e.g. insulators and packaging substrates) [4].

The interpretation of charge storage and transport behaviour in polymers is not an easy task; this becomes still more difficult due to complexity of polymer relaxations which is further magnified in blends by the complex morphology. Thermally stimulated depolarization current (TSDC) is a well-known technique for investigating the various mechanisms in electrets formation and also the phenomenon of charge storage in electrets [5].

In the present work, the TSDC studies are reported and discussed to understand the polarization phenomena for pure and doped ethyl cellulose samples with iodine having different concentration.

## II. EXPERIMENTAL STUDIES

The material used in present study is Ethyl Cellulose (EC) and Iodine (I2) which was obtained from Glaxo Laboratory, Mumbai. Pure and doped samples were prepared using Solution casting technique which includes dissolving of EC and iodine in Benzene. To obtain homogeneous solution it was kept for 8 hours on magnetic stirrer. Then prepared solution was poured on an optically plane cleaned glass plate floating on mercury. Great care was taken to avoid air bubbles during the setting of polymer solution on the glass plates. The solvent was allowed to evaporate in an oven at 50ºC for 24h to yield the desired samples. The deposited films were then detached carefully form the glass plate using a sharp edge knife of blade.

The prepared samples were then inserted in between aluminium electrodes in an oven to heat them at polarization temperature 80 $^{o}$C. Then DC field i.e., polarization field Ep was applied for 30 min. The samples were then cooled to room temperature under the applied DC field. Then the field was removed and sample was short circuited to remove stray charges. Now, the thermoelectret obtained was reheated at the rate of 3 $^{o}$C per minute and the depolarization current was then recorded using Keithley 610C electrometer. The polarization was carried out by connecting a DC power supply (EC-HV 4800D) in series with the sample.

To obtain mechanism responsible for the TSDC spectra of pure and doped samples, electric field Ep was applied on the samples. Pure Ethyl Cellulose (EC) was designated as P0, 0.004, 0.02 and 0.04 were designated as P2, P3 and P4 respectively.

## III. RESULTS

The thermally stimulated discharge current (TSDC) spectrum for ethyl cellulose (EC) samples polarized with poling fields (Ep) 125, 150, 175 and 200 kV at constant poling temperatures 80 °C is illustrated in Figure 1. The Thermally Stimulated Discharge Current spectrum have two peaks. The first peak is in lower temperature range i.e. 65- 75 $^{o}$C and second peak is in higher temperature range i.e. 150-162 $^{o}$C. The lower and higher temperature peaks are designated as α and ρ respectively. In general, both the peaks shift towards higher temperature and magnitude of first peak is less as compared to the higher temperature peak.

The TSDC thermograms for iodine doped ethyl cellulose samples with different fields (i.e. 125, 150, 175 and 200 kV) at constant Tp (i.e. 80 °C) shown in figures 2 – 4 respectively, shows two well resolved peaks as observed for pure samples in similar temperature ranges. The peak current increases and peak position shift towards higher temperature side with increase in polarizing field poling and temperature.

The depolarization kinetic data i.e. activation energy, charge released and relaxation times calculated using initial rise plots (not attached) for pure and iodine doped ethyl cellulose samples poled at various temperatures with different polarizing fields are listed in Table 1.

With the application of an electric field movement of charges occurs within the atoms of a dielectric and the negative electronic cloud get displaced relative to the positive nucleus and hence a small dipole moment is created. This effect occurs within very short times, its time scale cannot be changed from outside. Many dielectrics, including polymers, contain molecules that have an electric moment. An applied field tends to align these elementary dipoles along its own direction and thus produce an electric moment of the whole body giving rise to dipole polarization.

Depending upon the nature of the polymer, the polarization in a polymer can be attained by various mechanisms such as the orientation or the dipoles, trapping of the charge carriers at microscopic distances (Maxwell–Wagner effect) and space charge polarization i.e. trapping of charge carriers at macroscopic distances. Any one or more processes can contribute to the polarization. Thus the net polarization of an electret is generally due to the aligned dipoles and space charges (makes an electret non-neutral). However, before the formation of electret the polymer is neutral and contains free charges. When electric field is applied current is observed in the circuit, hence polymer contains free charges. The charges present in the electret do not contribute to the total polarization but they are responsible only for conduction current which varies linearly with the field and vice versa in TSD current due to space charges which will not vary linearly [6].

The TSDC spectra may arise due to various above said mechanisms. Dipole orientation is strongly temperature dependent. At high temperature the forces opposing rotation are lessened. Thus, a high degree of polarization can be achieved in a short time by application of an electric field at a high temperature if the dielectric is cooled and the field removed, only after a low temperature has again been reached, dipoles return to the original disordered state very slowly because rotation is hindered by strong viscous forces. The polarization is thus frozen-in. The decay of the charge of electrets during TSC results from dipole reorientation, excess charges motion and ohmic conduction. The first process will be clear, the thermal agitation will reorient the aligned dipoles at random. The motion of excess charges originates from space charge called drift and diffusion. The

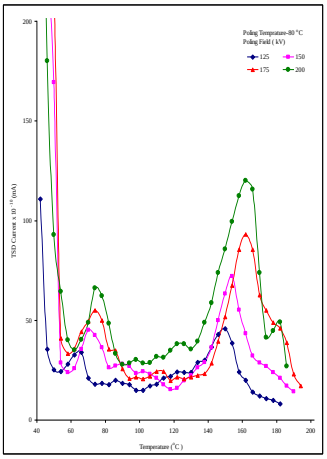

**Figure-1: Thermally stimulated discharge current thermogram of $P_0$ sample at 80°C with different Poling fields (i.e. 125, 150,175 and 200 kV)**

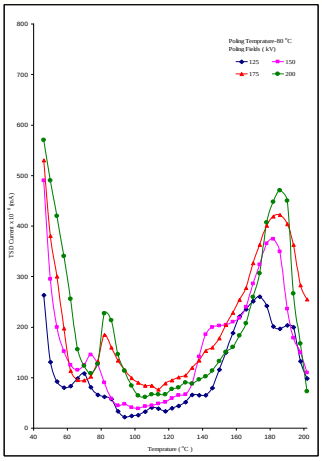

**Figure- 2: Thermally stimulated discharge current thermogram of $P_1$ sample at 80°C with different poling fields (i.e. 125, 150, 175and 200 kV)**

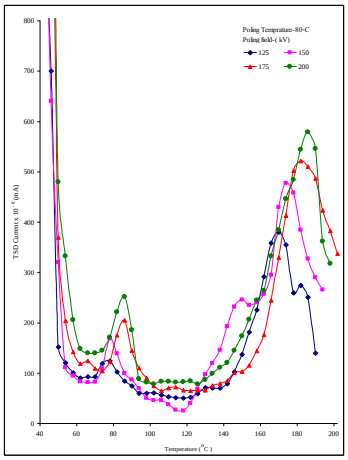

**Figure - 3: Thermally stimulated discharge current thermogram of $P_2$ sample poled at 80°C with different poling fields (I. e. 125, 150, 175 and 200 kV)**

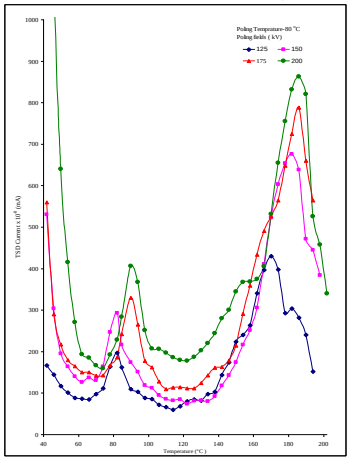

**Figure-4: Thermally stimulated discharge current thermogram of $P_3$ sample poled at 80°C with different poling fields (I. e. 125, 150, 175 and 200 kV)**

first motion is due to the local electric fields forcing the mobilized excess charges to drift towards opposite charges, whereby electric neutrality is restored [7].

The temperature dependence of the dipole orientation can be differed from the motion of excess charges. The latter will confirm closely to that of ohmic conduction, from which the charges often originated. In particular, we may expect the current maxima for dipole reorientation to occur at lower temperature than that of the excess charge motion. The first process requires only a rotational motion of molecular groups, whereas the latter process involves a motion of molecular groups (ions) over macroscopic distances. The activation energy predicted theoretically by Reddish and Wiseman [8-9] for the relaxation process resulting from the local twisting of the main chain or the orientation of the side groups in a polymer is about 0.2 eV. The relaxation process associated with the peak is the orientation of the side groups and or local twisting of the main chain.

**Table 1:- TSDC parameters of pure and iodine doped ethyl cellulose samples at poling temperature 80 $^{o}$C.**

| Thermo-electret | Poling Field (kV) | Peak Position ($T_m$) ($^{o}$C) | | Peak Current (mA) | | Activation Energy (eV) | | Charge Released (Q) (Coul) | Relaxation Time ($\tau_0$) (Sec) |
|---|---|---|---|---|---|---|---|---|---|
| | | st I | nd II | st I | nd II | st I | nd II | | |
| $P_o$ | 125 | 66 | 150 | $33.9\times10^{-10}$ | $45.3\times10^{-10}$ | 0.231 | 0.491 | $3.785\times10^{-8}$ | $8.765\times10^{-10}$ |
| | 150 | 70 | 154 | $52.2\times10^{-10}$ | $72\times10^{-10}$ | 0.234 | 0.494 | $4.785\times10^{-8}$ | $7.453\times10^{-10}$ |
| | 175 | 74 | 162 | $54.9\times10^{-10}$ | $96\times10^{-10}$ | 0.235 | 0.497 | $5.063\times10^{-8}$ | $6.534\times10^{-10}$ |
| | 200 | 74 | 162 | $66.2\times10^{-10}$ | $120\times10^{-10}$ | 0.242 | 0.501 | $5.997\times10^{-8}$ | $5.887\times10^{-10}$ |
| $P_1$ | 125 | 70 | 174 | $107.9\times10^{-8}$ | $260\times10^{-8}$ | 0.229 | 0.484 | $4.785\times10^{-8}$ | $9.785\times10^{-11}$ |
| | 150 | 74 | 182 | $146.1\times10^{-8}$ | $374\times10^{-8}$ | 0.230 | 0.489 | $5.326\times10^{-8}$ | $8.876\times10^{-11}$ |
| | 175 | 82 | 186 | $184.2\times10^{-8}$ | $422\times10^{-8}$ | 0.234 | 0.491 | $6.475\times10^{-8}$ | $3.957\times10^{-10}$ |
| | 200 | 82 | 186 | $227.2\times10^{-8}$ | $470\times10^{-8}$ | 0.239 | 0.499 | $6.789\times10^{-8}$ | $2.476\times10^{-10}$ |
| $P_2$ | 125 | 78 | 170 | $122.4\times10^{-8}$ | $380\times10^{-8}$ | 0.222 | 0.480 | $5.397\times10^{-8}$ | $7.743\times10^{-11}$ |
| | 150 | 78 | 174 | $168\times10^{-8}$ | $477.5\times10^{-8}$ | 0.225 | 0.482 | $7.887\times10^{-8}$ | $6.478\times10^{-11}$ |
| | 175 | 86 | 182 | $205\times10^{-8}$ | $521.9\times10^{-8}$ | 0.230 | 0.489 | $9.956\times10^{-8}$ | $5.997\times10^{-11}$ |
| | 200 | 86 | 186 | $251\times10^{-8}$ | $579\times10^{-8}$ | 0.232 | 0.490 | $1.557\times10^{-7}$ | $4.876\times10^{-11}$ |
| $P_3$ | 125 | 82 | 170 | $197\times10^{-8}$ | $430\times10^{-8}$ | 0.219 | 0.474 | 7.653x10-8 | $8.765\times10^{-11}$ |
| | 150 | 82 | 182 | $293\times10^{-8}$ | $676\times10^{-8}$ | 0.220 | 0.480 | $9.987\times10^{-8}$ | $7.654\times10^{-11}$ |
| | 175 | 90 | 186 | $230\times10^{-8}$ | $788\times10^{-8}$ | 0.229 | 0.483 | $2.879\times10^{-7}$ | $6.457\times10^{-11}$ |
| | 200 | 90 | 186 | $406\times10^{-8}$ | $863\times10^{-8}$ | 0.230 | 0.489 | $4.593\times10^{-7}$ | $5.329\times10^{-11}$ |

One of the arguments advocated for distinguishing a dipolar polarization and space charge polarization is based on the field dependence of the TSDC properties; such as the peak current, peak temperature and charge released. The linear dependence of charge processed and the peak current on polarization field strength is a characteristic of dipolar origin whereas in the case of space charge polarization, the peak current and charge released will show a non-linear variation with polarizing field strengths. For a dipolar peak, the peak temperature will be independent of polarizing field strength and polarizing temperature whereas the peak temperature depends on the poling field and temperatures of the space charge polarization. The linear field dependence of peak current suggests that the TSDC spectra may be either due to dipolar origin or migration of charge carriers through microscopic distance with trapping [10].

The increasing value of peak current with poling field and the observed activation energy values indicate that the peak may be contributed significantly by dipolar and ionic polarizations. Also, the contribution from the migration of charge carriers through microscopic distance with trapping is possible. The linear dependence of

charge released from electrets on the polarizing field strengths suggest that the depolarization process throughout the volume of the electrets is uniform, which is a characteristic of dipolar origin or due to migration of charge carriers through microscopic distance with trapping [11]. Hence, the observed TSDC may not be completely due to alignment of dipoles. In addition to dipolar contribution care must be some contribution from the hetero-charge also.

The TSDC studies on iodine doped films were made in usual manner as that of pure EC sample. The peak current increases and peak position shift towards higher temperature side with increase in polarizing field and temperature.

The increase in depolarization currents and decrease in activation energy (Table 1) of ethyl cellulose samples on iodine doping may be explained by the formation of charge transfer complexes. The addition of dopant has a strong effect on the activation energy of the discharge process. The molecular motion obviously assisted by the presence of charge transfer complexes, hence activation energy decreases due to the increase in mobility of charge carriers. Also this indicates that the presence of dopants between polar molecules reduces of interaction and these results in a reduction of activation energy. Swan [12] proposed four mechanisms for the charge transfer complex processes involved between the strong electronegative acceptors present in the polymer molecular chain-(i) the electron may go back to the polymer molecule from which it originates (ii) the electron may be retained by the dopant and may move as a stable negative ion (iii) the electron may transfer from the negative dopant into another polymer molecule without motion of the dopant molecule and (iv) a charge exchange may occur between the negative dopant ion and a neutral dopant molecule.

The formation of CTC will result in the reduction of the crystalline amorphous interface and provide conducting paths through the amorphous regions and thus interconnect the crystallites. Due to the reduced barrier at the interfaces the mobility of the dipoles and/or charge carriers will increase. The low temperature relaxation occurs due to orientation of the side groups and or local twisting of the main chain.

Incorporation of iodine in ethyl cellulose form strong complexes, iodine develops following properties in the newly formed aggregates (i) tightens the side chains so strongly that their orientation / de-orientation even on thermal treatment (ii) prevents the trapping of the charge carriers. (iii) enhance the conductivity perhaps by enhancing the mobility of the carriers and (iv) develops excess of charge of certain nature that overwhelms the other type of charge at higher temperature . The possibility of (i) stage (i.e. the return of possibility of electron to the polymer sites from where it originates) is less marked in strong complexes like the one under study while the probabilities mentioned earlier as (ii), (iii) and (iv) are very high as iodine is a strong acceptor. Hence the creation of a space charge cloud in the CTC matrix is very much probable.

The shifting of peak to higher temperature region may be because of the tightening of the main chain of the complex so the dipoles get fully relaxed (de- oriented)/induced on supplying higher thermal energy. Increase in current magnitude may be due to the increase in mobility of carriers. Inclusion of iodine in polymer matrix has developed, perhaps, a space charge cloud by filling all the traps present in the polymer matrix.

Khare et al [13] studied TSDC of pure and doped films. The peak temperature and charge retaining capacity was found to alter with the different dopants. The results are explained in terms of the energy levels created by the

dopants and charge transfer through a tunnelling mechanism. Ionic conduction currents in homogeneous dielectrics usually lead to the formation of space charge clouds in the electrode regions.

An increase in activation energy observed with the increase in polarizing field suggest that the broad peak is not due to discrete level having a single relaxation, but is a complex one having distributed activation energies (Table 1).

Distribution of relaxation time in polymers arises due to the different size and shape of the polar groups/dipoles originated during a polarization and this depend on the poling temperature. The relaxation time decreases with increase of polarization temperature. This can easily be explained from the fact that relaxation phenomenon is due to the internal friction of the polymer which depends exponentially on temperature. The time lag corresponding to the motions of permanent dipoles (ions, free and trapped charges) changes markedly with temperature.

As the temperature is increased more charges are trapped in shallow traps. This larger amount of trapped charge on release gives a higher current and a higher sharp peak [14].

For a trapping level to contribute to the charge motion in the sample during charging, Ti has to be smaller than the charging time Tc. This means that with increasing temperature the number of "active" (contributing to charge motion) trapping levels N(T) increases whereas the number of inactive (not contributing to the charge motion) levels [NO-N(T)] decreases, These inactive levels store the charge delivered to the sample during charging process. In view of the above, the higher temperature peak is expected to shift toward higher temperature with increase in poling temperature which is experimentally observed in the present case [15].

## IV. CONCLUSION

From the above discussion, we can draw following inference.

(i) α peaks occur due to the disorientation of the back bone chain and side chains of EC, (ii) ρ peaks may be a result of the diffusion of space charges either at the electrons or due to their thermal release at high temperatures from the defect levels, (iii) Increase in polarizing field helps in releasing and mobilizing the charge easily, (iv) introduction of iodine in EC forms strong complexes.

I2 develops following properties in the newly formed aggregates (a) tightens the side chain so strongly so that their rotation/disorientation disappear even on the treatment, (b) prevents the trapping of carriers, (c) enhances the conductivity perhaps by enhancing the mobility of the carriers and (d) develops excess of charge of certain nature that overwhelms the other types of charge at higher temperature, to yield a current of negative polarity.

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