6. THERMALLY STIMULATED DISCHARGE CURRENTS

6.1. INTRODUCTION

Persistent electrical polarisation in polymeric solids may arise from an alignment of dipoles, a migration of charge carriers over macroscopic distances with subsequent accumulation near the electrodes, and an interfacial or Maxwell-Wagner polarisation [1]. Charges can also be introduced into polymers by means of charged particle injection and even by photo irradiation [2]. Charges, once inside the sample, dissipate slowly after termination of the charging, and in many cases persist over a long period of time. Thermally stimulated discharge current (TSDC) measurement technique is a technique which has contributed significantly to the recent understanding of the charge-storage and charge-decay processes in electrodes and moreover it forms a useful tool to study molecular motions in polymers.

6.2 THEORY

In general, polymers are good dielectrics which are capable of storing charge in them permanently when subjected to a field-temperature treatment. Such dielectric materials bearing persistent charge are called thermo electrets. When these electrets are subjected to a programmed heat treatment, they give rise to a current in the external circuit called 'thermally stimulated discharge current'. Whenever a solid dielectric is subjected to an external field, the polarisation may occur in the dielectric by processes such as,

1. Electronic polarisation
2. Atomic polarisation
3. Orientation or dipolar polarisation
4. Space charge polarisation.
5. Interfacial polarisation.
All these effects are related to an internal polarisation phenomena i.e., they are produced by the rotation or migration of charges originating from and remaining within the dielectric. However, space charge polarisation may also be originated due to injection from electrodes.

By heating a polarised sample up to or above the polarisation temperature, the release of charges is gradually speeded up giving rise to a current in the external circuit which increases with increasing temperature and decays when the supply of charge is depleted. The different steps involved in the charging and discharging processes in an electret are shown in Fig. 6.1. A current peak is observed at a temperature when dipolar disorientation, ionic migration or carrier release from traps, is activated. The total polarisation, in general, may result from a combination of several such effects with various relaxation times. This thermally stimulated discharge current is, therefore similar to a dielectric loss curve plotted as a function of temperature.

Bucci and Fieschi [3] developed a dipolar theory to explain thermally stimulated conductivity and thermoluminiscence in ionic crystals. As the shape of the peaks and parameters involved in thermally stimulated conductivity and thermoluminiscence are same as those of thermally stimulated discharge currents, this theory has been generalised and extended by Gross [4], Perlman [5] and Turnhout [6] to the electret effect in polymers.

In a dielectric, the dipolar polarisation at any temperature and instant is a result of simultaneous orienting action of the field and randomising action of thermal vibrations. According to Debye, the built up polarisation 'P', in a unit volume of the material during time 't' after the application of electric field 'E_p' at a temperature 'T_p' is given by,

\[ P(t) = \frac{P_e}{1 - \exp(-t/\tau)} \]  

\[ (6.1) \]
Fig. 6.1: Schematic representation of processes of Polarization and TSD Current formation
where 'τ' is the dipolar relaxation time and 'P_e' is the equilibrium polarisation, which is given by

\[ P_e = \frac{(S N_d \mu^2 E_p)}{(K T_p)} \]  \hspace{1cm} (6.2)

where 'S' is a geometrical factor which depends on the possible dipolar orientation (for freely rotating dipoles \( S = 1/3 \)), 'N_d' the concentration of dipoles, \( \mu \) the electrical dipole moment, \( K \) the Boltzmann constant and 'E_p' is the local directing electric field operating on the dipoles.

If we assume that the relaxation times for polarising and depolarising the electret are equal, the decay of polarisation after removal of the field at \( t = \infty \) is given by

\[ P(t) = P_e \exp(-t/\tau) \]  \hspace{1cm} (6.3)

and the corresponding depolarisation current may be written as

\[ i = \frac{-dP(t)}{dt} = \frac{P(t)}{\tau} \]  \hspace{1cm} (6.4)

When the electret is subjected to a linear temperature programme, increasing from an initial temperature such that

\[ T = T_0 + \beta t \]  \hspace{1cm} (6.5)

where \( \beta \) is the heating rate, then equation (6.3) can be written as

\[ P(t) = P_e \left[ \exp \left( - \int \frac{dt}{\tau} \right) \right] \]  \hspace{1cm} (6.6)
Here it is assumed that (i) Equation (6.6) holds good for varying temperatures (ii) Initially frozen-in polarisation is equal to the equilibrium value at the polarising temperature (iii) The temperature variation of ‘\( \tau \)’ is given by

\[
\tau (T) = \tau_0 \exp \left( \frac{U}{KT} \right)
\]

(6.7)

where ‘\( \tau_0 \)’ is the relaxation time at infinite temperature and ‘\( U \)’ is the activation energy for dipolar orientation. Solving for the current during TSDC experiment, we have,

\[
l(T) = \left( \frac{P_0 T_p}{\tau_0} \right) \exp \left( -\frac{U}{KT} \right) \exp \left[ -\frac{1}{\beta \tau_0} \int \exp \left( -\frac{U}{KT} \right) dT \right]
\]

(6.8)

The first exponential, which dominates in the low temperature range, is responsible for the initial increase of current with temperature, while the second exponential dominates at high temperatures. Differentiating equation 6.8 and setting \( \frac{di}{dt} = 0 \), the temperature ‘\( T_m \)’ at which maximum current occurs is,

\[
T_m = \left[ \frac{(U/K) P_0 \exp (U/KT_m)}{\beta \tau_0} \right]^{1/2}
\]

(6.9)

Garlic and Gibson [7] have paid attention to the low temperature tail of equation (6.8) which can be written as

\[
\log i(t) = \text{constant} - \frac{U}{KT}
\]

(6.10)

from which activation energy can be evaluated.

A special characteristic of equation (6.8) is that, the activation energy can be evaluated not only from the low temperature tail but also from the whole curve. Simplification of equation (6.8) gives

\[
\log \tau(T) = \log \tau_0 + \frac{U}{KT} = \log \left[ \int \frac{i(T)}{i(T_0)} dT \right] - \log i(T)
\]

(6.11)
The integral in the above equation can be estimated by graphical integration of the curve. By plotting \( \log \tau(T) \) as a function of \( 1/T \), \( U \) can be evaluated.

6.3 MEASUREMENT

The TSD currents were measured in a sandwich configuration of Al-PI-Al obtained on glass slides. The block diagram of the circuit employed is shown in Fig.6.2. The films were annealed in an air oven by keeping them at 373 K for 2 hours. Films annealed in this manner showed stable properties. The samples were then polarized for 1 hour by keeping them in a specially constructed jig. The jig in turn was placed in an electrostatically shielded vessel which was evacuated to a vacuum of \( 10^{-3} \) Torr.

The film was kept inside the jig and the ends of the film were connected to a power supply (Aplab 7641 dual d.c.power supply, India). The discharge current was measured using an electrometer amplifier (EA 815, ECIL, India). During the polarisation process, the film was heated to a constant temperature (polarizing temperature) at a constant rate of heating. When the film attained the polarizing temperature, a known constant voltage (polarizing field) was applied for about one hour (polarizing time). Then the film was cooled under the same conditions. The two electrodes were then short circuited at room temperature for about 5 minutes. Then the film was warmed at a constant rate and depolarization or discharge current was detected using an electrometer amplifier. TSDC spectra were then plotted for temperature versus depolarization current for various fields.
Figure 6-2 Block Diagram of TSDC Measurement Setup
6.4. RESULTS AND DISCUSSION

The TSDC spectra of a pure PI film polarised at 323 K for different polarising fields for different thicknesses 2, 2.9 and 3.2\(\mu m\) are given in Figs 6.3 (a to c) respectively. Two peaks, one at a temperature of 340 K and the other at temperature 400 K were observed in all the figures. The TSDC spectra of 0.8\% iodine doped PI film polarised at 323 K for different polarising fields for different thicknesses 2.2, 2.52 and 3.4\(\mu m\) are given in Figs 6.4 (a to c) respectively. Only one peak at a temperature of 393 K is observed in the doped films.

The activation energy for the charge transport mechanism is calculated using the "initial rise method" of Garlic and Gibson [7] by isolating the individual peaks from the composite curves. The slopes of log \(I\) Vs \(1/T\) plot from the initial rising portions of the individual peaks were used to calculate the activation energies (Fig. 6.5 (a to c) for undoped PI films, and Fig 6.6 (a to c) for iodine doped PI films). Using these activation energies the characteristic relaxation parameters \(\tau_0\), \(\tau_{300}\) and \(\tau_m\) were evaluated. These represent the relaxation times at 0 K, 300 K and at peak temperatures. Tables 6.1 and 6.2 give the summary of the above results for undoped and iodine doped PI films respectively.

In the present study two peaks were observed in undoped PI films and one peak was observed in doped films. The first peak (340 K) which occurs at relatively low temperatures, may be attributed to dipolar orientation because of several factors. The peak position is independent of the polarizing field. Also the maximum of the peak current is proportional to the polarizing field. All the factors support the dipolar orientation theory for the first peak. Since PI is a strongly polar substance, and in view of the above fact, it appears that the dipolar orientation is largely responsible for the occurrence of the first peak.
The second peak (400 K for undoped and 393 K for doped films) occurs at higher temperature may be attributed to space charge polarization due to the trapping of electrons injected from the metal electrodes to the vicinity of the polymer surface. Similar observation was made by Tanaka et al [8] in polypyromellitimide film and Pillai and Rashmi [9] in polystyrene-chloranil complex and Daly et al [10] in epoxy resin coatings.

The disappearance of the low temperature peak in the doped films may be attributed to shallow trapping of mobile charges and formation of molecular aggregates. A similar behaviour, has been reported by Jain et al [11] on copper doped polyvinyl acetate films and by Mahendru and Suresh Chand [12] on poly vinyl fluoride films.

No appreciable change observed in pure and iodine doped PI films with respect to thickness.
References


Fig. 6.3 (a) TSDC Spectra of Undoped PI film of thickness 3.2 μm polarised at 323 K for different polarising fields.

- \( E_p = 1.5 \times 10^6 \text{ V/m} \)
- \( E_p = 0.93 \times 10^6 \text{ V/m} \)
- \( E_p = 0.31 \times 10^6 \text{ V/m} \)

\( d = 3.2 \mu m \)
\( T_p = 323 \text{ K} \)
\( \beta = 0.913 \text{ K/s} \)
Fig. 6.3 (b) TSDC Spectra of Undoped PI film of thickness 2.9μm polarised at 323 K for different polarising fields.

- $d = 2.9\mu$m
- $T_P = 323K$
- $\beta = 0.913\ K/s$

Current $I \times 10^{-4}(A)$

Temperature(K)

- $E_p = 1.72 \times 10^6\ V/m$
- $E_p = 1.03 \times 10^6\ V/m$
- $E_p = 0.34 \times 10^6\ V/m$
Fig. 6.3 (c) TSDC Spectra of Undoped PI film thickness 2µm polarised at 323 K for different polarising fields.

- \(d = 2\mu m\)
- \(T_p = 323K\)
- \(\beta = 0.913K/s\)
- \(E_p = 2.5 \times 10^6 \text{ V/m}\)
- \(E_p = 1.5 \times 10^6 \text{ V/m}\)
- \(E_p = 0.5 \times 10^6 \text{ V/m}\)
Fig. 6.4 (a) TSDC Spectra of 0.8% iodine doped PI film of thickness 2.2μm polarised at 323 K for different polarising fields.

- \( d = 2.2\mu m \)
- \( T_p = 323K \)
- \( \beta = 2.283K/s \)

Current \( I \) (\( 10^{-10} A \))

Temperature (K)

- \( 0.45 \times 10^6 \) V/m
- \( 1.36 \times 10^6 \) V/m
- \( 2.27 \times 10^6 \) V/m
Fig. 6.4 (b) TSDC Spectra of 0.8% iodine doped PI film of thickness 2.5μm polarised at 323 K for different polarising fields.
Fig. 6.4 (c) TSDC Spectra of 0.8% iodine doped PI film of thickness $3.4\mu m$ polarised at 323 K for different polarising fields.

- $d = 3.4\mu m$
- $T = 323K$
- $\beta = 2.283K/s$

Current $I (10^{-10}A)$ vs Temperature (K)
Fig. 6.5 (a) Log(\sigma) Vs 1000/T of Undoped PI film for peak 1.
Fig. 6.5 (b) Log($\sigma$) Vs 1000/T of Undoped PI film for Peak 1
Fig. 6.5 (c) Log(\(\sigma\)) Vs 1000/T of Undoped PI film for peak 1
Fig. 6.6 (a) Log\(\sigma\) Vs 1000/T of Undoped PI film for peak2
Fig. 6.6 (b) Log I vs 1000/T of Undoped PI film for peak2
Fig. 6.6 (c) Log\(\alpha\) Vs 1000/T of Undoped PI film for peak2
Fig. 6.7(a) Log$_\sigma$ Vs 1000/T of 0.8% iodine doped PI film for peak1.
Fig. 6.7(b) Log $\sigma$ Vs $1000/T$ of 0.8% iodine doped PI film for peak1.
Fig. 6.7(c) Log I (Amps) Vs 1000/T of 0.8% iodine doped PI film for peak1
Table 6.1
Undoped PI film (First Peak)

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<th>THICKNESS D</th>
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<th>ACTIVATION ENERGY eV</th>
<th>RELAX TIME CORRESPONDING TO ZERO TEMP. $t_0$ s</th>
<th>RELAX TIME CORRESP TO TEMP. MAX $T_m$ s</th>
<th>RELAX TIME CORRESP TO ROOM TEMP $T_{300}$ s</th>
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Table 6.2
Undoped PI film (Second Peak)

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<th>RELAX TIME CORRESP TO TEMP. MAX ( T_m ) s</th>
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### Table 6.3
0.8% Iodine doped PI film

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