CHAPTER – III
THEORETICAL BACKGROUND OF STUDIES
3.1 INTRODUCTION

Transient currents in dielectrics observed upon the application of a step voltage have been studied extensively to give an insight into the polarization processes in the materials undertaken for the study. It is generally accepted that the transient currents in an insulating material, on the application or removal of a step voltage, may be attributed to one or more of the following mechanisms: (i) electrode polarization, (ii) dipole orientation, (iii) charge storage leading to trapped space-charge effects, (iv) tunneling of charge from the electrodes to empty traps; (v) hopping of charge carriers through localized states. The above processes have been reviewed by several scientists and it has been established that the observed time dependence alone does not permit any discrimination to be made between various mechanisms. The argument for and against a particular mechanism is to be found by considering the variation of transient currents on various experimental parameters also, such as temperature, field and frequency. Polymers contain a large number of structural disorders and, therefore, contain discrete traps levels in their bulk. The role of various polarization processes and their relative contributions to the electret state of the polymer is not yet fully understood. Particularly, the space charge structure including the trap distribution of energy and also over the volume of the polymer, are still to be well understood. Such informations are also being obtained by carrying out the measurements of
absorption and short circuit isothermal desorption (discharging) currents at various temperatures. The d.c. step response technique in which the current response is measured as a function of time after d.c. voltage is applied to, or removed from the sample, is the isothermal analogue of TSDC measurement, as it determines the discharging current at constant temperatures instead of varying temperatures.

Polyvinyl formal (PVF) is a thermally stable and weakly polar polymer that exhibits excellent chemical resistance and good mechanical properties. Inspite of its activeness for many applications, the conduction mechanism is presently not well understood. In the present thesis, we have attempted to identify the nature of the transient conduction and thermally stimulated discharge currents in pure polyvinyl films by comparing the observed dependence on parameters such as electric field, electrode material, temperature, time and relation between the charge and discharge currents, in the light of characteristic features of various proposed mechanisms.

3.2 TRANSIENT CURRENTS IN CHARGING AND DISCHARGING MODES

The charging or absorption current is obtained immediately after the application of a step voltage on a dielectric specimen, while the discharging or desorption current is obtained on removal of the step voltage provided the temperature is kept constant. Both the charging and
discharging currents decay approximately as \( t^{-n} \), where \( t \) is the time elapsed after the application or removal of the step voltage, and the exponent \( n \) is a constant depending upon the properties of the material and the experimental conditions [1]. Charging current decays with time until a steady state current, usually known as conduction current, is reached. On the other hand isothermal discharging current decays for a long time depending upon the internal phenomenon taking place irrespective of the steady state current level.

The nature of transient charging and discharging currents differ from material to material depending upon the mechanism involved. The origin of these transient currents is still a subject of much controversy in the literature [2] and a large number of mechanisms have been proposed by various workers [3-10]. The combined effect of one or more may be responsible for the observed decay pattern of the transient currents. The discharging current is usually mirror image of charging current, provided that a steady state current does not occur. Hence, discharging currents can yield information about charging processes even when the corresponding charging current is masked by conduction current at charging. Quantitative as well as qualitative analysis can be made on comparing the experimental values of the decay exponent obtained under various experimental conditions [10]. The results of this technique can also be compared with those of some other electrical studies, like thermally stimulated
discharge current (TSDC) and isothermal surface charge decay, etc. to get clear and justified conclusions.

This technique is time consuming hence it is not very popular, but results of this long time technique are most consistent than any other technique because the electrical disturbances and instantaneous variations in other experimental parameters affect these experiments much less as compared to those involved in the fast discharge processes.

The origin of isothermal charging and discharging currents has not been clearly accounted for in most of the dielectric materials because of lack of experimental data covering an adequate range of experimental parameters, i.e., field, temperature, electrode material etc. However, the results are available for many materials although covering very few experimental conditions, which are insufficient to yield clear and firm conclusions.

In view of this it becomes worthwhile to undertake a detailed study of transient currents and to correlate the results obtained with those of other studies. This is expected to give a proper clarification of the transient response of charging and discharging in polymers, which is of prime importance for the analysis of the electret effect in polymer dielectrics.
3.3 MECHANISMS OF TRANSIENT CURRENTS

We find that there is a little consensus on the way absorption currents originate in polymers. This lack of agreement is evident from the fact that several mechanisms have been proposed to arrive at an explanation. But it has been seen that the applicability of each is limited and specific. The principal mechanisms are -

3.3-1 ELECTRODE POLARIZATION MECHANISM

Free charges are frequently available in the polymer bulk and have thermally activated mobilities. There is movement of these free charges towards electrodes of opposite polarities on application of a polarizing voltage and they start piling up near the electrode. We find that the electrode polarization or blocking mechanism (occurring in ionic materials) is characterised by linear dependence of the isochronal current on the field (though theory predicts a nonlinear region at low field), and a current that is thermally activated. It is also found that no definite confirmation exists on the dependence of the isochronal current at constant field with the specimen thickness. The current fall is initially proportional to $t^{-1/2}$ followed by a severe change, where $n$ is greater than 1. The charging and discharging currents are mirror images of each other [12,13].

3.3-2 DIPOLE ORIENTATION MECHANISM

If we have randomly distributed dipoles inside a
polymeric sample, they will not produce a net dipole moment. However, these dipoles possess a definite relaxation time and activation energy with the relaxation time being thermally activated. On application of an external electric field at an elevated temperature, the dipoles start orienting in the field direction. Image charges are induced on the metal electrode surface during the orientation of dipoles, causing a net current to flow in the external circuit. The value of this absorption current depends on the rate of dipole orientation and decreases gradually with time at a fixed temperature and time. After removal of the polarizing electric field, the dipoles start deorienting, producing the desorption current in the external circuit.

Dipole relaxation [12,13] can account for a $t^{-n}$ absorption current, if a wide distribution of relaxation times exist for the dipoles uniformly distributed through the bulk of the material. The distribution has been theoretically analysed by Cole and Cole [14]. These relaxations are thermally activated and the current temperature curves taken at a fixed polarization time (isochronals) give an activation energy $A(1-\alpha)$, where $A$ is the activation energy, and $\alpha$ is the distribution parameter, for times $t/\tau < 1$, where $\tau$ is the relaxation time. When $t/\tau > 1$, the current falls with increasing temperature, with an apparent negative activation energy $A(\alpha-1)$. In dipole orientation there is no contact effect, i.e., there is no dependence on the electrode
material. The current varies as $I \propto t^{-n}$, where $0 \leq n \leq 2$. The isochronal current at constant field is independent of the thickness and is directly proportional to the field. To apply the dipolar relaxation model to nonpolar polymers, we require a sufficient concentration of adventitious polar groups. Since the current being observed is small, we presume that this concentration is usually there.

3.3.3 CHARGE INJECTION LEADING TO TRAPPED SPACE CHARGE EFFECTS

There are usually a high concentration of trapping sites in the forbidden energy gap of polymers. These trapping sites are the outcome of impurities or due to the internal molecular arrangements in macromolecules. The application of an electric field to the polymer sandwiched between two metallic electrodes causes electrons or holes to be injected which get trapped in the trapping sites available, the distribution depending on the energy and trap depths. The charges which get trapped inside the bulk form a space charge which opposes further trapping of charge carriers. The trapping process causes the charging current to flow while removal of the external field produces the discharging current. The space charge model [12,13] needs a sufficiently high concentration of deep trapping levels to be present. Under this model, the isochronal current at constant field is independent of thickness.
3.3-4 THE HOPPING MECHANISM

Insulators have a wide energy band gap and low carrier mobility. The structure of these materials is such that the bonding between molecules is mainly due to Vander Waals or London forces and is rather weak, and also the overlap of the molecular orbitals and the intermolecular electron exchange are small which is not conducive for charge transport. These materials may have a large number of localized states within the bulk, with a wide distribution of activation energy and trap depths. These states may be filled with charge carriers like electrons, or holes. These states are separated from one another by potential barriers which prevent electrons or holes from moving from, say one molecule to a neighbouring molecule. Under application of an electric field, a carrier can move from one molecule to another by jumping over the potential barriers. This kind of charge transport by random jumps is known as the hopping model and will take place when $\tau_v < \tau < \tau_e$, where $\tau_v$ is the intramolecular vibration period, $\tau$ is the electron relaxation time and $\tau_e$ is the intermolecular vibration period [23].

In transient currents, the hopping model [11,13] will exhibit the following characteristic features. The isochronal current will be directly proportional to the field. At constant fields, the isochronal current will be independent of the thickness of the sample. The current will also be independent of the electrode material. The current will be
thermally activated and its time dependence will be of the form $t^{-n}$ with $0 \leq n \leq 2$. The charging and discharging currents will be mirror images of each other.

3.3.5 THE TUNNELLING MODEL

This model [15,12,13] assumes the presence of a trap level or trap levels in the dielectric. It may so happen that charge carriers may lack enough energy to surmount the potential barrier existing between these traps and hence take part in the current process. This model [16] assumes that an electron in a $\pi$-molecular orbital on one molecule, when excited to a higher energy level (in our case by application of an external field at elevated temperature) can tunnel through a potential barrier to a non-occupied state of a neighbouring molecule. Traps are an essential part of the tunnelling model. It has been observed that the current-time curve is mainly due to the trap level closest to the Fermi level of the injecting electrode, whereas trap level which are deep and located well inside the band gap have been postulated. Deep traps have been reported [17] in corona charged samples which in fact may be ion traps. The lack of substantial evidence on the presence of deep traps may be due to an inhomogeneous distribution leading to a weaker concentration of deep traps in the bulk as indicated by Davies [11].
The tunnelling model points to a field which is directly proportional to the isochronal current. Here, the isochronal current at constant field is inversely proportional to the thickness. The current is strongly dependent on the electrode material and is independent of the temperature. The current is dependent on time as \( I \alpha t^{-n} \) with \( 0 \leq n \leq 2 \).

### 3.4 THEORY OF TRANSIENT CURRENT IN POLAR DIELECTRICS

When an electric field is applied to a dielectric specimen kept between two plane metal electrodes, an absorption current flows in the external circuit. This current is composed of two components namely the polarization current component and the conduction current. Assuming that the polarization is due to dipoles of a single relaxation frequency \( \alpha(T) \), the polarization current can be written as

\[
\frac{dP_s(t)}{dt} + \alpha(T) P_s(t) = \varepsilon_0 (\varepsilon_s - \varepsilon_\phi) \alpha(T) E \quad \ldots (3.1)
\]

where \( T \) is the absolute temperature, \( t \) is the time, \( \varepsilon_0 \) is the permittivity of free space and \( \varepsilon_s \) and \( \varepsilon_\phi \) are the static and high frequency dielectric constants, respectively. The density of current generated by decay in polarization is given by

\[
i_p(t) = \frac{dP(t)}{dt} = -\alpha(T)P_s(t) + \varepsilon_0 (\varepsilon_s - \varepsilon_\phi) (T)E \quad \ldots (3.2)
\]

the conduction current \( i_c \) at a fixed temperature \( T \) and field \( E \) is defined as

\[
i_c = \sigma(T) E \quad \ldots (3.3)
\]
where $\sigma(T)$ is the conductivity of the material at a fixed temperature $T$. Thus, the total absorption current will be the sum of both the components, i.e.,

$$i_{ab} = i_c + i_p(t) = \left[ \varepsilon_o (\varepsilon_s - \varepsilon_phi) \alpha(T) + \sigma(T) \right] E - \alpha_s P_s(T) \quad \ldots (3.4)$$

The desorption current is obtained when the sample is short circuited and the field is made zero. Thus, from eq.(3.2) we have

$$\frac{dP_s(t)}{dt} + P(t) \alpha(T) = 0 \quad \ldots (3.5)$$

where $\alpha(T)$ is a time dependent parameter. The above equation is a differential equation with constant coefficients. Its isothermal solution can be written as

$$P_s(t) = P_o \exp \left[ - \int_0^t \alpha(T) \, dt \right] \quad \ldots (3.6)$$

The current generated during deorientation of dipoles is only due to polarization. There is no conduction current since the external field is zero. The desorption current is thus given by

$$i_d(t) = - \frac{dP_s(t)}{dt} = \varepsilon_o Ef(t) = \left[ \alpha(T) P_o \exp[-\alpha(t)t_o] \right] \quad \ldots (3.7)$$

where $E$ is the steady charging field, $f(t)$ is the dielectric response function, $P_o$ is the initial polarization and $\alpha(T)$ is the dielectric response loss peak in frequency domain.

Alternatively, this can also be expressed in terms of the frequency response of the complex dielectric constant, $\varepsilon(w)$,
\[ \varepsilon(w) = \varepsilon'(w) - i \varepsilon''(w) (1+iw)^{-1} \quad \ldots \quad (3.8) \]

where, \( \varepsilon'(w) \) and \( \varepsilon''(w) \) are the real and imaginary part of the dielectric constant.

Thus, isothermal depolarization current measurements differ an alternative technique for dielectric constant and dielectric loss measurements as a function of temperature and frequency.

Frequency dependence of dielectric loss factor can also be obtained using Hamon's approximation [18], i.e.,

\[ \varepsilon''(t) = \frac{i(t)}{2 \pi f C V} \quad \ldots \quad (3.9) \]

where \( i(t) \) is the magnitude of the transient current at time \( t \), \( C \) is the geometrical capacitance of the electrode assembly without the sample, \( V \) is the applied step voltage and \( f \) is Hamon's frequency (\( \approx 0.1/t \)). This approximate method gives good accuracy in calculation of dielectric loss provided there is a broad distribution of relaxation times.

The time dependence of transient currents can be expressed according to the Curie-von-Scheidler [19] law expressed in the following form

\[ i(t) = k t^{-n} \quad \ldots \quad (3.10) \]

In the optimum time range if the charging phenomena persists for a time \( t_p \), then according to the principle of superposition, time dependence of the transient currents can be expressed by the following equation
\[ i_d(t) \propto (T)(t) = i_p(t) - i_p[\alpha(T) + t] \quad \ldots (3.11) \]

Using eq. (3.11) we have,
\[ -i_d(t) \propto (T)(t) = -k t^{-n} \left[ 1 - \left( \frac{\alpha(T)}{t+1} \right)^{-n} \right] \quad \ldots (3.12) \]

which gives for \( t << 1/\alpha(T) \)
\[ i_d, \propto (T)(t) = -k t^{-n} \quad \ldots (3.13) \]

and
for \( t >> 1/\alpha(T) \)
\[ i_d, \propto (T)(t) = -n \alpha(T) k t^{-n-1} \quad \ldots (3.14) \]

where \( 0 < n < 1 \).

### 3.5 LAST DECADES' WORK

Transient charging and discharging currents in dielectrics have been studied extensively. Dasgupta and Joyner [20-22] observed the transient charging and discharging currents in polypropylene and PET films over a wide range of temperatures and electric fields as a function of electrode materials and sample thicknesses. Vanderschuren and Linkens [23] measured the transient charging and discharging currents in several polymers from room temperature to the glass transition temperature and the effect of varying parameters such as field strength, electrode material, sample thickness, method of polymer preparation and addition of impurities was investigated in some of them. The absorption currents in polystyrene (PS) and its donor-acceptor complex with chloranil (PS-CA) and in a blend of polycarbonate and polypropylene have
been observed [24,25]. Transient currents were measured in discharging [26] and charging mode [27] with ethyl cellulose foil samples. Ranjeet Singh and S.C.Datt [28] have also reported transient currents in polypropylene and concluded that the observed currents are governed by charge injection processes leading to space charge effect. Charging transient currents on ethyl cellulose foil samples have been measured by Dubey et al [29]. Transient (charging and discharging) currents in polyvinyl alcohol-polyvinyl pyrrolidone polymer blend films and polyethylene terephthalate were measured as a function of temperature, field strength and electrode materials by LakshmiNarayan et al [30] and Neagu and Neagu [31]. Recently, Khare [32,33] and his co-researchers [34-43] measured charging and discharging transient currents in various polymers as a function of electrode materials, sample thicknesses, poling fields and results have been interpreted on the basis of available theories.

3.6 THE ELECTRICAL CONDUCTION

The electrical conduction in polymeric dielectrics is mainly due to transport of free charge carriers present in the bulk of the polymer and from a number of different conduction processes taking place simultaneously depending upon the experimental conditions. The structure of these materials are sensitive to their electrical, mechanical and thermal history so that the mode of conduction differs from polymer to polymer and the sensitivity of measurement is different for different
materials. When a polymer is subjected to different conditions they often undergo structural transitions making charge carrier generation and transport phenomenon more complicated. No universally accepted theory has been propounded till date which can explain the conduction phenomenon in all the polymeric dielectrics. However, attempts have been made to explain the observed conduction behaviour on the basis of various existing theories.

Many workers have tried to explain the dark conduction in polymers in their own way, such as traps and their energy distribution [44-46], tunnelling of charge carriers [47-50], Schottky emission [51-55], avalanche breakdown [56], etc. Still, despite inconsistencies in understanding the conduction mechanism, one can conclude on the basis of various studies reported in the literature that some of the phenomena occurring during electrical conduction in polymers are similar and have physical origin similar to those observed in solids of poor electrical conductivity.

In general, polymers are amorphous or semicrystalline substances. The transport mechanism in amorphous bodies is more complicated than the crystalline materials, especially for monocystals where long range order exists. Thus, the charge transport mechanism in dielectric solids can be better understood from modifications applied to the quantum mechanical band theory of solids. Hence, band model of disordered materials has some of the gross features of that of
crystalline structure, but with significant differences concerning details. Electronic conduction may be due to the motion of free electrons in the conduction band or holes in the valence band or alternately due to the motion of quasi localized carriers.

If the concepts of band model are applied directly to organic solids, a very large energy gap between valence and conduction bands is expected, so that thermal activation in the normal temperature range is too small to transfer an electron from the valence band to the conduction band.

In amorphous substances, there are many localized charge carrier levels and carrier mobility is very low. The low lying states may be treated as trapping sites (levels) but in comparison with crystalline substances they are not related to the discrete activation energy values because they are situated in the broadened edges of conduction band and valence band. Hence, it is difficult to consider the transport behaviour of polymers in terms of a generalised theory. It is, therefore, not surprising to see controversies on transport theories in the literature [57-63] or no single mechanism is able to explain the entire conduction in these materials. However, the theories proposed for amorphous and polycrystalline inorganic solids are normally applied to describe the conduction behaviour of these materials with a few limitations.
3.6-1 GENERATION OF CHARGE CARRIERS

Most of the materials reveal in dark an exponential temperature dependence of conductivity ($\sigma$) of the form,

$$\sigma = \sigma_0 \exp(-A/kT)$$  \hspace{1cm} (3.15)

where $A$ is the activation energy, $k$ is the Boltzmann constant and $T$ is the temperature. This led the earlier workers to assume that carriers are intrinsic in nature and hence they equated the experimental activation energy to half the band gap.

The resistivity of polymers is high because both the mobility and carrier concentration are low. The concentration of carriers produced intrinsically by thermal ionization is also very low since the band gaps are several electron volts. Hence, it seems more likely that ionization of impurities is responsible for any outstanding concentration of carriers. Impurities may also provide carriers by internal field emission in the presence of gross doping.

The charge carrier generation through the injection of electrons and holes from the electrodes has been widely accepted and this is probably the main source of carriers in high polymers. It is important to note here that the carrier density within the material should be much greater than the material being treated, i.e., the contact should act as the reservoir of carriers. Carriers once injected have appreciable mobilities and life times. Several workers have studied the injection of charge carriers in polymer [64-66]. Hofman [67]
has shown that conduction in atactic polystyrene (PS) depends on the injection of excess of electrons from metals. Davies [68] studied injection in polyvinyl fluoride and has shown that injection continues for a long time and for both polarities of applied potentials, although some asymmetry is indicated.

Despite a great deal of work done, there are still plenty of unanswered questions about the origin of free charge carriers, which take part in conduction under electrical stream. It is still not evident whether the measured current is by the motion of charge carriers inherent to the polymers or those injected from the electrodes. Adamec and Calderwood [69] measured current in polymethyl methacrylate (PMMA) under two conditions; first when the specimen was in direct contact of the electrode, and second when an insulating air gap was present between the specimen and electrode. The finding that the conductivity determined by the experiment with contactless electrodes is the same as that obtained with evaporated electrodes supports the contention that the free charge carriers originate in the bulk of the polymeric dielectric.

Doping of polymers with donors and acceptors and blending of two or more polymers increases/decreases the conductivity by several orders of magnitude and also modifies the charge carriers response for conduction.
3.7 MECHANISMS RESPONSIBLE FOR CONDUCTION

Some important conduction mechanism are now discussed briefly:

3.7-1 OHMIC CONDUCTION

Ohmic conduction is attributed to a linear relationship between the conduction current and applied voltage at a constant temperature. The value of ohmic conductivity in polymer dielectric is given by:

\[ \sigma = e (n_+ \mu_+ + n_- \mu_-) \quad \ldots \quad (3.16) \]

where \( \mu_+ \) and \( \mu_- \) are trap modulated mobilities and \( n_+ \) and \( n_- \) are the concentrations of positive and negative charge carriers, respectively. Because of large energy band gap in polymers, the charge carriers concentrations, i.e., \( n_+ \) and \( n_- \) are very small as long as radiation effects are absent. The mobilities \( \mu_+ \) and \( \mu_- \) are also very small in electret forming materials. Thus, the ohmic conduction current can be regarded as a universal source of conduction current in polymers. The origin of free charge carriers in PMMA and other polymers also indicate some possibility of intrinsic charge carrier conduction in polymer dielectric [70].

3.7-2 SCHOTTKY-RICHARDSON EMISSION AND POOLE-FRENKEL EFFECT

In the presence of an applied field barrier profiles are altered. If the applied field is high enough and the electrode makes ohmic current with the insulator, the charge carriers are injected into the insulator by lowering of the barrier at
the metal-insulator interface. This effect is referred to as the Schottky-Richardson (SR) emission.

The expression for current due to SR emission is given by [55],

\[ I = ZST^2 \exp\left[\frac{-\theta_S}{kT} + \beta_{SR}E^{1/2}\right], \]  

... (3.17)

where \( Z \) is the Richardson-Dushman constant (120° A cm\(^{-2}\) in theory), \( S \) is the dielectric sample area, \( \theta_S \) is the Schottky potential barrier, \( k \) is the Boltzmann constant, \( T \) is the temperature and \( E \) is the applied field across the sample. \( \beta_{SR} \) is Schottky field lowering constant, which is given by

\[ \beta_{SR} = \frac{1}{kT} \left[ \frac{\varepsilon^3}{4\varepsilon'_0} \right]^{1/2}, \]  

... (3.18)

where \( \varepsilon \) is the charge on the electron, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon' \) is the high frequency dielectric constant of the material.

The first term of eq.(3.17) shows a linear relationship between \( \ln(1/T^2) \) and \( 1/T \) and the slope of the curve represents the Schottky potential barrier. Equation 3.17 also shows a linear relationship between \( \ln I \) and \( E^{1/2} \) with a slope \( \beta_{SR} \) for a given temperature.

Apart from the Schottky-Richardson emission [71], the linear dependence of \( \ln I \) on \( E^{1/2} \) is also predicted by the Poole-Frenkel effect. If a charge carrier gets trapped in a Coulombic potential well, then it can be detrapped on lowering
of the trap depth by an applied electric field. The current due to the Poole-Frenkel [72] effect is given by,

\[ I = ZST^2 \exp\left[ \frac{-\Theta_{PF}}{kT} + \beta_{PF} E^{1/2} \right], \]  

(3.19)

where \( \beta_{PF} \) is the field lowering constant and \( \Theta_{PF} \) is the trap depth, which is given by

\[ \beta_{PF} = \frac{1}{kT} \left[ \frac{e^3}{\pi \epsilon \epsilon_0} \right] \]  

(3.20)

Thus from eqs. (3.20) and (3.19),

\[ \beta_{PF} = 2 \beta_{SR} \]  

(3.21)

The main difference between the Poole-Frenkel and the Schottky-Richardson models is that in the former the conductivity is bulk-limited whereas in the later it is electrode-limited.

3.7.3 SPACE CHARGE LIMITED CURRENT (SCLC)

If the electrode-insulator contact is ohmic and the insulator is trap free, the accumulation of carriers near the electrode results in the space charge build up. Mutual response between individual charge limits the total charge injected into the sample. The resulting current is said to be Space charge limited current (SCLC).

A complete mathematical analysis of time-independent space-charge current is so complex that no explicit explanation has yet been obtained. Mott and Gurney [73] were the first to emphasize the importance of an injecting contact.
between a metal and an insulator. The expression relating the current density $J$ to the applied voltage $V$, for a trap-free insulator is given by,

$$J = \frac{q}{8} \varepsilon_0 \mu \varepsilon' \frac{V^2}{d^3}, \quad \ldots \quad (3.22)$$

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon'$ is the dielectric constant of the sample, $\mu$ is the dipole moment, $d$ is the thickness of the sample and $q$ is the elementary charge on the charge carrier.

If traps are present in the insulator, the space-charge-limited current is decreased by several orders. Rose [74] and Lampart [75] modified the theory of SCLC independently. Expression, given by Rose [74], for a trap dependent current density is

$$J = \frac{q}{8} \varepsilon_0 \mu \theta \frac{V^2}{d^3} \quad \ldots \quad (3.23)$$

where $\theta$ is the ratio of trapped charge to free charge, and is called the trap limiting factor.

Assuming that the carriers are trapped at shallow traps of average depth $E_t$, that remain in the thermal equilibrium state with the concerned band, $\theta$ is given by,

$$\theta = \frac{n_{eff} \exp\left(-E_t/kT\right)}{N + n_{eff} \exp\left(-E_t/kT\right)} \quad \ldots \quad (3.24)$$

where $n$ is the density of states in the conduction band and $N$ is the density of traps.

Assuming $N \gg n_{eff} \exp\left(-E_t/kT\right)$, $\theta$ becomes,
\[ \theta = \frac{1}{N} \left[ n_{\text{eff}} \exp \left( -\frac{E_r}{kT} \right) \right] \] \quad \ldots (3.25)

and,

\[ J = \left( \frac{q}{8} \right) n_{\text{eff}} \exp \left[ -\frac{E_r}{kT} \left( \frac{\varepsilon \varepsilon_0 \mu V^2}{N d^3} \right) \right] \] \quad \ldots (3.26)

Deviation from eq.(3.26) due to the dependence of the current density \( J \) on powers of \( V \) greater than 2 has been observed. This is explained on the basis of existence of deep traps and continuous distribution of trapping sites in the forbidden gap. Space charge limited currents (SCLC) in solids depend on the carrier transport and trapping and is independent of carrier generation. The fact that only very few organic solids show ohmic conduction has led to the belief that the conduction in organic solids is mainly extrinsic.

3.7-4 IONIC CONDUCTION

Ionic conduction occurs in materials which contain ionic groups or to which ionic materials have been added. In these materials, adsorption of water plays a dominant role because it can act as a source of ions, as a high dielectric impurity or as a local structure modifier. In amorphous polymers, ionic conduction can also occur due to the drift of defects on the application of an electric field. In various polymers, particularly those with halogens in their molecular structure conduction has been proved to be qualitatively ionic. Based on a model of diffusion of lattice defects or ions and a carrier hopping process [76], the expression for steady state current \( (I_s) \) at high fields is given by,
\[ I_s = I_0 (-A/kT) \exp(e^*. L/kT), \quad ... (3.27) \]

where \( L \) is the hopping (jump) distance and \( A \) is the activation energy. Eq. (3.27) show a relationship between \( \ln(I) \) and \( A \).

Ionic conduction is characterized by a high activation energy, noticeable polarization and a large transit time for ions. For materials with defect centres, the ionic conduction also exhibits different slopes in \( \ln(I) \) vs \( (1/T) \) or the \( \ln(I/T^2) \) vs \( (I/T) \) plots [77]. Activation energies are larger at higher temperatures than at lower temperature.

Studies of the structure of the polymer its physical and chemical properties and electrical properties will characterise the polymer and given an insight into the various mechanisms responsible for the different properties exhibited by it. Here an attempt has been made to characterise the polymer, polyvinyl formal, in thin film form.

3.8 LAST DECADE'S WORK ON D.C. ELECTRICAL CONDUCTION

The studies of electrical conductivity of these polymer films would enable us to understand their behaviour with temperature and the nature of conduction mechanism prevalent in them. A number of workers have investigated the nature of conduction mechanisms in a variety of polymers. Excellent reviews dealing both theoretical and experimental results have appeared in the literature [78-81]. A brief review of the work reported in the literature is given below.
Bashara and Doty [82] studied the current voltage characteristics and resistivity measurement in very thin polybutadiene films of thickness range 100 to 500 Å. It was found that the space charge limited conduction mechanism was the dominant mechanism in their films. It was also observed that the tunnelling takes place through the interface partly.

Lengyel [83] studied the voltage-current characteristics and conductivity measurements of polyethylene-terephthalate and polyvinyl formal films prepared by vacuum evaporation method, in the temperature range 40 C to 120 C. The above two material films displayed the familiar Richardson-Schottky characteristics for fields between 20 to 200 kV/cm and temperatures 25 to 100 C.

Lilly et al [84] studied the high field (2-1400 kV/cm) conduction in Mylar and teflon films of thickness ranging from 1 to 10 mils as a function of temperature (70-163 C). In the above films, the Schottky theory was found to be responsible for conduction mechanism by two space charges, ionic and electronic, each dominant at a different field level.

Davies [85] studied the carrier transport in iodine doped polythene films which were sandwiched between two metal electrodes, the film thickness was approximately 1 mm. It was observed that the presence of iodine increases the carrier mobility over the pure film.
Babcock and Christy [86] studied the electrical capacitance, conductance and photo conductance of tetramethyl tetraphenyl trisiloxane thin films of thickness 150 A\(^0\) formed by electron bombardment, on glass substrates in the sandwich configuration. They have successfully explained the conduction mechanism by field assisted thermal ionization of donors heavily compensated by acceptors.

Gupta and Barbarez [87] measured the D.C. conductivity of polyethylene films over a thickness range 25-75 \(\mu\)m in sandwich configuration. The results were applied to a model proposed by Adachi et al [88] and good agreement was found between experimental results and the model.

Gazso [89] studied the variation of electrical conduction with applied voltage in vacuum deposited polyethylene films of 2000 A\(^0\) thick, in the sandwich configuration. He also studied the effect of irradiation by gamma rays on the conduction of polyethylene films.

Boonthanom and White [90] studied D.C. and A.C. electrical conductivities in the polyethylene polymer films with copper dispersed in its matrix. They observed the large increase in electrical conductivity due to doping with copper. The results were explained by the mechanism of hopping traps in localised states close to fermi level.

Kryzewski and Swiatek [91] studied the current voltage

88
characteristics of polyvinyl carbazole and polystyrene films prepared by glow-discharge method. The studies were made over a temperature range 290-373 K. They found that above room temperature, conduction was controlled by surface limited and bulk limited depending on the electrical field strength.

Suzuki et al [92] studied the electrical conductivity and Hall effect on vacuum deposited thin films of polyacrylonitrile and made them semi-conductive by heat-treatment in nitrogen atmosphere. The results suggested that the conduction should be understood in terms of hopping transport of charge carriers in the localised states.

Rastogi and Chopra [93] studied the current-voltage characteristics of pure and iodine doped polyvinyl chloride thin films prepared by solution growth technique, both in sandwich and surface configuration over a temperature range 120-400 K. In the case of pure films, the conduction was ascribed to hopping mechanism at low temperatures and at high fields and at high temperatures to Schottky emission mechanism. The electrical resistivity of polyvinyl chloride films decreases considerably by the addition of iodine. They also found that the activation energy depends upon the type of configuration in which the studies were made.

Vollmann and Poll [94] studied the current-voltage characteristics at thin polymer fluoro-carbon films with thickness between 0.02 and 1.5 μm deposited by different
methods and with different contact materials. They observed the uniform conduction mechanism over the entire field strength not depending upon the method of preparation and the contact materials. The results were interpreted by means of a modified Poole-Frenkel effect for insulators with high impurity density.

Desbarax et al [95] studied the electrical conductivity of polysiloxane thin films formed by glow-discharge method. They observed that in the steady state, Poole-Frenkel mechanism seems to be mainly responsible for the conduction.

Mahendru et al [96] studied the electrical conduction in polypropylene films and found that the Schottky field assisted by thermionic emission was the dominant conduction mechanism in the temperature range 390-440K.

Electrical conductivity studies in pure and iodine doped polyvinyl acetate films were made by Mahendru et al [97]. They prepared the films by solution growth technique and studies were made in the sandwich configuration. The electrical conductivity of polyvinyl acetate films was found to be increased by large amount due to doping of iodine. The results were interpreted in terms of Poole-Frenkel charge transfer mechanism.

Gupta et al [98] carried the conductivity measurements of pure and doped polyvinyl fluoride thin films, prepared by solution growth technique, whose thickness was about 50 µm.
Conductivity measurements on pure and doped PVF films in the temperature range 300-500K have been reported. Here, vanadyl ions were found to affect the mode of conduction in the PVF matrix by contributing two additional activation energies of conduction. In unannealed films, the conduction was a thermally activated process while in annealed films the conduction was the combination of more than one thermally activated process.

Jain et al [99] studied the temperature dependence of electrical conductivity of solution grown films of pure and doped polyvinyl alcohol. The thickness of these films was of the order of 100 microns and they were doped with different impurities, viz., CuSO\(_4\), CuCl\(_2\), FeCl\(_3\), ZnCl\(_2\), NaCl and rhodamine. These impurities found to affect the electron traps in the forbidden band of dielectric and modulate the current flow.

Phadke et al [100] studied the electrical conduction mechanism in polyferrocene films prepared by plasma polymerization. They found that space charge limited conduction was the dominant mechanism.

Hanscomb and Kaahwa [101] studied the high temperature electrical conduction in polyethylene terephthalate in the temperature range 10-180 C at field strengths extending to 2.4 \times 10^8 \text{ V m}^{-1}. The data was found to be well fitted to electronic or hole, Poole-Frenkel conduction or ionic conduction resulting from field assisted dissociation of protons.
Takai et al [102] studied the high field conduction in poly(p-xylylene) thin films. The dark currents under fields upto 6 MV/cm were investigated for a poly(P-xylylene) film with Au and Al as electrode materials.

Audenaert et al [103] studied the D.C. electrical conductivity of poly(2-vinyl pyridine)-iodine films of thickness 80-100 μm as a function of iodine concentration and temperature in the range 200-300K. The electrical conduction mechanism was governed by electronic hopping between random localised states.

Rao and Chopra [104] investigated the electron transport properties of Cu doped polyvinyl chloride films. D.C. conductivity, A.C. conductivity, dielectric relaxation and thermally stimulated discharge current measurements were made on Cu doped PVC films as function of Cu concentration upto 12%. The results were explained in terms of tunnelling mechanism. The A.C. conductivity of these films favoured the hopping conduction.

The electrical properties of thin films of glow discharge polymerized hexamethylcyclotrisilazane were investigated by Tyezkowski et al [105] in order to determine the mechanism of electrical conduction. The I-V characteristics were studied at room temperature and measurements of activation energy were made in temperature range 300-370K. The results of field dependence, temperature
dependence and film thickness on the conductivity supported by the results of TSC measurements, suggested electrode limited conduction in the material investigated.

**Staryga and Swiatek** [106] studied the electrical conductivity of polycrystalline p-terphenyl films as a function of electric field, temperature and film thickness. The experimental data was interpreted in terms of hopping process between localised sites through potential barrier lowered by the electric field according to the modified Poole-Frenkel equation.

**Bahri and Singh** [107] investigated electrical conduction mechanism in the metal-polyvinyl chloride (1500 A)-metal sandwich structure using Al, Ag and Cu electrodes. Two kinds of switching properties were found. The symmetric sandwich with Al electrodes exhibited voltage controlled negative resistance (VCNR) with memory, while asymmetric structures displayed current controlled negative resistance (CCNR) with memory. The VCNR mechanism was explained on the basis of high field domains and the CCNR phenomenon was explained on the basis of filamentary model.

**Sawa et al** [108] studied the electrical conduction mechanism in polypyrromellitimide films in the temperature range 120-180 C as function of electric field. An attempt was made to fit the experimental results to the theoretical values for the ionic hopping conduction.
Miyairi and Ieda [109] observed new type of I-V characteristics in polyethylene teraphlate films of thickness 6 μm as function of different electrode materials. In the case of Au electrodes, two current peaks were observed around 5V and 20V at higher temperatures 160 and 170 C, whereas in Al electrodes single peak was observed at 160 C.

Kulshrestha and Srivastava [110] studied the electrical conduction of solution grown polystyrene films of thickness about 15 μm in the field and temperature ranges of about 6 X 10⁵ to 3 X 10⁷ Vm⁻¹ and 300-400 K respectively. The results showed that the Poole-Frenkel (PF) mechanism as modified by Jonscher and Ansari was the dominant conduction mechanism.

Bahri and Singh [111] studied the conduction mechanism and I-V characteristics of pure polyvinyl chloride films of thickness range 500-1500 Å obtained by the isothermal immersion technique. The conduction process was examined in a broad temperature range 260-507 K, with applied electric fields ranging from 4.6 X 10⁵ to 1.5 X 10⁷ V cm⁻¹. At low temperature (below 325K) and at high fields (> 1.5X10⁶ V cm⁻¹) the current transport was ascribed to a tunneling mechanism. At high temperatures (above 325K) and at high fields (> 1.5 X 10⁶ V cm⁻¹) it was concluded that although the analytical form of I-V characteristics was similar to that obtained for both Schottky emission and Poole-Frenkel effect the experimental value of \( \beta_{\text{exp}} \) was incompatible with the theoretical values of
$\beta_{RS}$ or $\beta_{PF}$. The resistivity of the PVC films was about $10^{13}$ Ω cm at room temperature and at a field of $10^7$ V cm$^{-1}$. The activation energy was 0.60 eV at temperatures above 325K and at a field $1.5 \times 10^6$ V cm$^{-1}$. Finally the annealing of PVC films at temperatures around 500K resulted in increased resistivity.

Cros-Lee Gloan and St-Onge [112] studied the electronic conduction in polyethylene films in a high electric field. A study was made on the effects of applied voltage, temperature, electrode materials and polyethylene density. The results were interpreted in the light of existing physical models of space charge and electron trapping.

The electrical conduction of Nylon was studied by Nakamura et al [113]. The results were interpreted in terms of the migration of a fixed number of ions existing in the polymer towards counter electrode. Lipinski et al [114] studied the electrical conductivity of p-terphenyl TCNE structures. The increase in conductivity by two orders was explained by the existence of charge transfer complex formation. Sharma and Pillai [115] studied the electrical conduction in kapton polyimide films at high electric fields and results were interpreted in terms of ionic conduction. Bahri [116] studied the D.C. electrical conduction in pure and iodine doped polystyrene films and the results were interpreted on the basis of charge transfer complexes. The effect of iodine on electrical conduction in polyvinyl fluoride films was studied
by Chand et al [117] and the results were explained on the basis of charge transfer. Tyszkowski et al [118] studied the Poole-Frenkel centres in dielectrics of plasma polymerized organosilicon films. Jayarama Reddy and Syrajuddin [119] studied the electrical conduction in pure and iodine doped polyvinylfluoride films. The results were explained on the basis of charge transfer between polymer and iodine. The D.C. electrical measurements on evaporated thin films of copper phthalocyanine was studied by Gould [120]. Lee et al [121] studied the conduction phenomenon of the polypropylene films. Four regions of conducting currents were observed and were attributed to ionic conduction a Poole-Frenkel region, a Schottky region and a negative resistance region. Kojima et al [122] studied the electronic conduction in polyethylene terephthalate at high electric fields. The results were explained by the impact ionization. The electrical conduction phenomena in polyimide (Kapton) films was studied by Sessler et al [123] with a particular attention to the separation of interface and bulk phenomena. The current-voltage characteristics were found to be ohmic at low fields while space charge characteristics were found to be ohmic at low fields and space charge limited at high fields.

Tawanski et al [124] investigated the D.C. electrical conduction in polyvinyl alcohol films. The ohmic type of conduction was found to be operative below 303 K whereas space charge limited above 303 K.
Narasimha Rao et al [125] studied the electrical conduction mechanism in pure and doped polyvinyl formal films. The results were attributed to the Poole-Frenkel conduction mechanism. Das Gupta and Doughty [126] studied the dielectric and conduction processes in polyether ketones. It was suggested that several mechanisms may be relevant and may all be involved in the conduction mechanism in a complicated manner. Narasimha Rao and Kalpalatha [127] studied electrical conduction mechanism in polyvinyl pyrrolidone films. The results were interpreted in terms of Poole-Frenkel type conduction mechanism. Electrical conduction in polyacrylic acid was studied by Narasimha Rao et al [128] and, two conduction regions were observed. Basha et al [129] studied the electrical transport in polyvinyl alcohol films containing transition metal halides. The transport of carriers was attributed to hopping mechanism between localized states.

Narasimha Rao and Subba Rao [130] studied the electrical conduction in polyacrylamide polymer films in the temperature range 300-450K and field strengths ranging from $0.48 \times 10^6$ - $24.1 \times 10^6 \text{ V m}^{-1}$. The electrical conduction was explained as due to the simultaneous action of Richardson-Schottky and Poole-Frenkel mechanisms. Narasimha Rao et al [131] studied the electrical conduction mechanism in polyvinyl alcohol films in the temperature range 300-450K and was found Richardson Schottky mechanism operating over the entire range. Sathyanarayana et al [132,133] studied the electrical conduction mechanism in polyacrylamide films.
3.9 EFFECT OF VARIOUS PARAMETERS ON ELECTRICAL CONDUCTION IN INSULATORS

The electrical conductivity has been found to vary with various experimental parameters. However, the extent and the nature of variation differs from material to material. A brief description about the variation of electrical conductivity with various parameters, in general, is as follows.

3.9-1 ELECTRIC FIELD

The dc conductivity has been found to increase with the applied electric field and is generally attributed to the Schottky-Richardson and Poole-Frenkel emissions. Kramer [134] have studied the field dependence of conductivity over a number of plastic films.

3.9-2 TEMPERATURE

The temperature dependence of the conductivity can be emphasized considering insulating and semiconducting behaviour of the materials. At absolute zero, most of the semiconducting properties are brought about by thermal excitation of trapped charges or thermally stimulated charge carrier generation. Therefore, a rise in temperature is always associated with an increase in conduction current.

Current-voltage or current-temperature curves are sometimes not identical during increase and decrease of the field or temperature. This type of hysteresis effect has been
observed in case of carnuba wax, sugarcane wax, polyethylene and many other compounds. The temperature dependence of conductivity has been studied by various scientists. Conductivity variation with linear temperature increase has been studied by Adamec [135].

3.9-3 PRESSURE

DC conductivity has also been found to increase with pressure. Akamatu and Inokuchi [136] have found that the resistivity of the isoviolanthrone power decreases with pressure. Increase in conductivity followed by lowering of activation energy [137,138]. At highest pressure it was found to be about 6 times the atmospheric value. The pressure dependence of conductivity has been studied by many workers [139] and the materials studied include pentacene [140,141], ferrocene [142], and many other materials [143-147].

3.9-4 MOISTURE

Conductivity is also affected by the presence of moisture in the insulator. Inokuch and Shirotani [139] have studied in detail the effect of moisture on pellets of organic solids. Barker and Tomar [148] have reported that humidity affects the steady state conduction in two ways: first being the increase in dielectric constant with the increase of humidity which gives rise to a net increase in ion concentration by reducing the effective dissociation energy and second being the increase in effective conductivity with
moisture. At higher fields departure from the other law was observed as a result of activation perturbation. Increase in dc conductivity with humidity has also been studied by Manthia et al [149].

3.9-5 ELECTRODE MATERIAL

The conductivity is also affected by the electrode material as the metal-insulator contact plays a genuine role in deciding the various conduction mechanisms. The injection of holes or electrons from the electrode material to the insulator is governed by the electrode material and insulator work function. Effects of electrode material over electrical conduction in a large number of insulators have been studied by various workers [150-161].

3.9-6 IMPURITY

The presence of impurity content in the insulators has also been found to increase the conductivity of materials. The effect of impurity over electrical conductivity is so pronounced that the conductivity can be indicated as a characteristic of the sample purity. In the opposite way, the addition of limited impurity can be used to alter the dc conductivity in a desired proportion. It has been observed that the conductivity always increases with dopants even when the dopants are more resistive to the host materials.
3.10 SPONTANEOUS CURRENT EMISSION (SCE)

On heating most of the polymers [162-173] sandwiched between two like or unlike metallic electrodes, an electric current known as short-circuit current or spontaneous current ($I_s$) is generated. Sawa et al [165] have reported the possible mechanisms of origin of $I_s$ during heating. On heating cellulosic and hygroscopic substances, an electric current $I_s$ is produced [170-173] as sorbed moisture get desorbed. The absorbed water may be present in loosely and/or strongly bound states, within samples and on their surfaces [174-177]. The desorbed water molecules or a particular fraction of them dissociate into $H^+$ or $OH^-$ ions under the influence of voltaic potential difference between the two electrodes [171,172].

Chemical and/or thermal degradation [164-178] may also generate $I_s$. The spontaneous current is expected to be reproducible [165-170] in successive hearings.

3.10-1 VIJH MODEL

ELECTROCHEMICAL EFFECTS AS THE SOURCE OF ELECTROMOTIVE FORCE (EMF) IN METAL(1)-POLYMER-METAL(2) SYSTEMS

In order to investigate the electrical behaviour of polymeric materials, one needs to apply metallic electrodes, i.e., the metal(1)-polymer-metal(2) system is essential for investigation. The existence of $V_o$ in $M_1$-PET-$M_2$ systems and $I_s$ during heating can only arise if the system behaves as a battery [174,181], with the associated electrode reactions at
the two metallic electrodes. This is supported by the fact that the magnitude of $V_o$ changes drastically with the change in the material of the electrodes. Although Ieda et al [162] suspected the paramount importance of the electrode oxidation-reduction processes as the source of electromotive force (EMF) in their system, they did not provide a detailed analysis based on the conceptual framework of modern electrochemistry. Vijh [182] has proposed a model to explain the problem of electrode effects in metal-polymer-metal systems at high temperatures. He has tried to explain the data reported by Ieda et al [162] on the basis of the electrochemical phenomena occurring at the metal-polymer interfaces. He suggested that the negative electrode of the battery reacted with the ambient moisture to form metal oxide by a reaction.

$$xM + yH_2O \longrightarrow M_{xO_y} + 2yH^+ + 2ye^-$$

Thus, at the negative electrode (M), the electrode potential was modified due to existence of a metal-metal oxide (M-MxOy) couple instead of metal only. Vijh suggested the correction of the EMF values observed in metal-PET-metal systems [183] due to formation of a metal-metal oxide couple. The protons thus released were expected to be injected into PET as a conducting species.

3.10-2 CORRECTION PROPOSED BY VIJH

Vijh [182] has selected the reference electrode of the
metal gold in this model and suggested the subtraction of -0.4V (i.e. to add +0.4V) from the observed EMF values of Ieda et al [163]. This -0.4V was ascribed to the internal resistance of PET in series with the EMF. The corrected EMF values were found to be quite near the metal-metal oxide potentials for all the cases except Al, Zn and Ag.

The abnormality of Ag was explained on the basis of formation of multiple of oxides on oxidation, e.g., AgO - Ag₂O₃. The abnormality of Al and Zn was also explained on the basis of protons released in battery reaction and their tendency to discharge back on the oxidized surface. The hypothesis of the oxidation of the negative electrode (M₂) in the suggested battery Au-PET-M₂ was further confirmed by obtaining a straight line plot between EMF values and the heats of formation per equivalent ΔHₑ values of the oxides of M₂. The -ΔHₑ values are a direct measure of the thermodynamic tendency of oxide formation on a metal.

3.10-3 WORK FUNCTION OF ELECTRODE MATERIAL AND M₁-Polymer-M₂ SYSTEMS

In certain metal-polymer-metal systems, experimental open circuit voltages can be correlated with the work function difference of the metals between which an insulator may be sandwiched [184-186].

Shareef et al [169] have reported open circuit voltages during the first heating run of virgin Al-Polyvinyl alcohol -
Cu/Ag/Pb/Zn/Al samples. They plotted the values of open
circuit voltages against the work function difference of the
 corresponding electrodes and obtained a straight line.

When the same kind of metal was evaporated on both sides
of the film, the magnitude of $I_s$ was relatively small and its
direction varied from sample to sample [162]. On the other
hand, when different kinds of metals were evaporated on each
side of the film, the magnitude of $I_s$ was larger and the
direction was determined solely by the combination of $M_1$ and
$M_2$. For example,

In $M_1$(Al)-PET-$M_2$(Au) .... $I_s$ is negative
and in $M_1$(Au)-PET-$M_2$(Al) .... $I_s$ is positive.

In the open-circuit voltage, the electric potential of
Au was always positive against Al [185]. The $I_s$ from the
Au-Polymer-Al system flowed in such a direction as a positive
charge carrier moved from Al to Au through the polymer. The
direction of $I_s$ and $V_o$ has been clearly reported by Nakamura
et al [185].

On the other hand, Vijn [182] has reported that there
was no correlation between EMF values (observed in his model)
and the work function of the metals involved. Barker [186] has
also pointed out the contradictory results for $V_o$ obtained by
Ieda et al. [162]. These values for $V_o$ were much smaller when
$M_1$ and $M_2$ were the same metal. However, Crine et al [187] have
commented on Vijn’s model, and reported that the metal-oxide
potentials themselves are important.
3.10-4 "COMMENTS" AND "ANALYSIS OF COMMENTS" ON VIJH'S MODEL

Crine et al [187] have commented on the Vijh model [182] and raised some points which cannot be explained by this model. According to them, the model was unable to explain the presence of voltage in a vacuum, the influence of different polymers upon this voltage and its temperature dependence. They argued that these observations can be understood if protons are released from residual acid groups in the polymer and not by the electrochemical reaction itself.

In a separate paper [183], Vijh tried to answer the objections raised by Crine et al. [187] to his model, and supported the validity of the model.

3.11 EFFECT ON $V_o$ DUE TO THE NATURE OF THE POLYMER

Sawa et al. [188] measured the following voltages: -1.0 V for Au-PE-Al, -1.4 V for Cu-Nylon 6-Al and -0.7 V for Au-Ethylvinyl-Al. Crine et al. [189] observed +0.27 V with Au-Kapton-Ag but almost nothing with Au-Teflon-Ag. Crine et al [189] have used the samples of equal thicknesses (25µm).

This shows clearly that the polymer has an effect upon the magnitude of the open circuit voltage. Vijh [183] has mentioned that the nature of the polymer will influence the measured voltage in two ways: (i) by changing the magnitude of the "series resistance" of the battery, i.e., the different polymers will have different internal resistances of the
specimen inspite of equal thicknesses; (ii) by changing the properties of the "electrolytes" (i.e., polymer) of the $M_1$-PET-$M_2$ battery. Since this polymer is a reservoir of traces of moisture, oxygen, conducting ionic species, and oxygenated active groups originating from the polymer; all of them provide the solutes for the surface oxidation of electrodes.

3.12 DETERMINATION OF PREDOMINANT CARRIER SPECIES IN ORGANIC POLYMERS BY A GALVONIC CELL

A new approach to the determination of carrier species in organic polymers was presented [190], using a galvanic cell consisting of Au-polymer-Al system. It was concluded that the ionic conduction was predominating, provided the following conditions are satisfied.

(i) The open-circuit voltage was almost independent of temperature, and

(ii) The conduction current under an external field and the short circuit current was found to have identical temperature dependence.

This analysis was presented by Sawa et al [190] and it can be applied only to low-field conduction corresponding to an electromotive force (EMF) of a galvonic cell. On the other hand, when these conditions were not fulfilled, it was not possible to determine predominant carriers solely with this analysis.
Nakamura et al [185] have also reported an interfacial phenomenon in polymers and their application for determining carriers species. The polymers used were ten in number. They described the temperature region of ionic conduction for each polymer at low electric field, which was determined by a galvanic cell system consisting of polymer.

Sawa et al [165] classified the polymers into two groups, A and B, depending on the behaviour of direction of the current. In the case of group A polymers, the direction of the current remains the same during heating as well as cooling. In the case of group B polymers, the direction (or sign) of the current during cooling is opposite to that during heating.

3.13 LAST DECADE'S WORK ON SPONTANEOUS CURRENT EMISSION

Systematic work on thermo-induced spontaneous current emission was first made by Ieda et al [191] who measured short circuit current and open circuit voltage (potential difference) of metal poly ethyl tetraphthalate metal system. The magnitude of current was of the order of $10^{-12}$ to $10^{-9}$ A. They suggested that the spontaneous current is due to electromotive force probably associated with oxidation reduction at electrodes. In their opinion the $M_1$-PET-$M_2$ system forms a galvanic cell generating an emf at certain high temperature and this phenomenon may be useful in developing a dry cell. Later on they studied other polymers [192] also
viz., PE (poly ethylene), PS (polystyrene), PVAC and Nylon (6,6). Similarly, a spontaneous current of the order of $10^{-12}$ to $10^{-7}$ A was observed by Radhakrishna and Haridass, while working on PVAC [193-194] samples, Pillai and Mollah [195,196], while working on cellulosic materials obtained the current of the order of $10^{-9}$ to $10^{-6}$ A. According to them some cellulosic plant cells when sandwiched in between different metals generate spontaneous current even at room temperature. They also observed that the magnitude of spontaneous current from the sample depends on the amount of water absorbed by the sample. The SCE increases with the increase in the amount of moisture in the polymer film. In similar and dissimilar electrode systems of metals with PVA films, a similar SCE effect due to absorbed moisture has been observed [197]. Stupp and Carr [198] have suggested, in PAN films, that some unidentified space charges are responsible for polarization of samples, even in unpolarized condition (in the absence of any external field). The SCE of iodine doped PVAc has been observed by Mahendru et al [199]. The order of current reported with these polymers lies between $10^{-14}$ to $10^{-8}$ A. PH, PVC, PS and PET were also studied by Radhakrishana et al [193-194]. Reports on the SCE from cellulosic materials, polyvinyl alcohol (PVA) and polyacrylnitrate (PVN) have also appeared in the literature [200-205]. Recently, spontaneous current in many polymers with $M_1$-Polymer-$M_1/M_2$ electrode configuration have been reported by Khare et al [206-209].
3.14 THERMALLY STIMULATED DISCHARGE CURRENTS (TSDC)

The thermally stimulated depolarization current (TSDC) is a general method for investigating the electrical properties of high resistivity 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 methods, therefore, the phenomena which vary with time or temperature can be analysed, and (iv) low frequency behaviour of the dielectrics can be elucidated in a simple way.

The TSDC technique involves measuring with a definite heating scheme, the currents generated by the release of a polarized state in a solid dielectric sandwiched between two electrodes. We find that TSDC being used for studying the fundamental mechanisms of charge storage and release in non-metallic solids and hence the present stage of experimental and theoretical development of TSDC is such that we have a vast number of theoretical models formulated to clarify the experimental data obtained on various types of charge storage mechanisms. But it can be seen that the proposed mathematical expressions rely on much simplified and unrealistic assumptions leading to similar descriptions of the
polarization process. We find that the immeasurability of the microscopic parameters lead to glaring discrepancies between the propounded theory and the experimental data. It can be observed that one of the major problems of the measurements is to unequivocally determine the physical origin of the observed current peaks.

The microscopic origin of a given current spectrum is obtained by comparing the predictions of the general theories related to the main polarization process with the available experimental data. Workers in the field ascribe the polarization of a solid dielectric - subjected to an external electric field - to a number of mechanisms involving either microscopic or macroscopic charge displacement. The mechanisms are (i) electronic polarization resulting from the deformation of the electronic shell requiring about $10^{-15}$ seconds, (ii) atomic polarization occurring from the displacement in molecules with heteropolar bonds requiring $10^{-14}$ to $10^{-12}$ seconds, (iii) dipolar or orientational polarization which can occur in pico seconds or months and occurs in materials containing permanent molecules or ionic dipoles, (iv) or space-charge polarization which occurs in materials containing intrinsic free charges (ions or electrons or both) and can take place in millisecond or years, (v) interfacial polarization also known as Maxwell-Wagner-Sillars (MWS) polarization happens in systems with a heterogeneous structure within the time range of millisecond to years [210]. The
present thesis highlights the theories of dipolar, space-charge and MWS polarization with special emphasis on the much discussed dipolar mechanism.

The Thermally Stimulated Depolarization Current (TSDC) is an useful and powerful technique to understand charge storage and charge decay processes in electrets. Now-a-days this technique is being utilized widely to investigate the molecular relaxation mechanism, trapping parameters and charge storage behaviour of insulating materials including polymers. The method consists of mainly two parts: Polarization of a specimen under the specified conditions of electric field, and temperature for a stipulated period. The poled sample (Thermoelectret) is afterward depolarized through a current recording device under stimulation of linear heating.

As an inherent property of regaining charge neutrality, electrets discharge by means of various processes. Depending upon the nature of polymer electret, any one or two or even more than two processes can play a prominent role in the discharging process. In the electrets made from the polar materials, the disorientation of dipoles plays a prominent role. The disorientation of dipoles involves the rotation of a coupled pair of positive and negative charges, and requires a certain energy which in solids may amount to a few eV per dipoles.
Often the disorientation energy (activation energy) differs for different dipoles (or charges). Therefore, the low activation energy dipoles respond at low temperature, while the high activation energy dipoles at high temperature. Consequently, TSC (thermogram) generally consists of many peaks. If the difference of activation energy is not large, these peaks overlap and merge into a broad peak (β-peak).

Such broad peaks are often seen as a result of disorientation of polar-side groups in polymers at low temperature. Another possible cause for the appearance of broad peak is a difference in the rotational mass of the dipoles. These differences occur in a polymer when it is heated to its softening temperature, where the dipoles are disoriented by the motion of main chain segments. This disorientation is responsible for the α-peak, which responds at glass-rubber transition temperature, $T_g$.

Polarization of dielectric can also occur due to any shift-of-ion from its equilibrium to a new position; the shift may be in the form of trapping at the position slightly away from their equilibrium position. Heating of dielectric provides activation of any such trapped ions to be detrapped and return to their original positions which results in the decrease of total polarization in the form of a peak of TSDC thermograms.
In addition to dipoles and trapped ions, polarization appears in an electret (dielectric) in the form of nonuniformly stored immobilized space charges, usually stored densely near electrodes [211-213]. Heating mobilizes them, which results in neutralization of such mobilized ions either at electrodes or in the sample by recombination with charges of opposite sign. In general, at higher temperature field controlled self drift persuades driving (motion) of any such charges. Space-charge peaks (referred as β peaks) appear at high temperatures [211,213-216] because disorientation of dipoles, merely involves a flip from one position to other while neutralization of space charges requires them to move over many atomic distances. In polymers, at very high temperature (near and above T_g), the self motion of space charges usually is accompanied with a second neutralization mechanism; namely, recombination with thermally generated carriers. These carriers are generated uniformly in the entire specimen by dissociation of neutral entities. These carriers may be electronic or ionic in nature and are responsible for conductivity of material. In polymers these seem to be impurity ions which contribute most of the ohmic conduction, because polymers show an appreciable conduction only above glass-transition temperature when enough free volume is available for ions to move. In the TSD of shorted electrets it passes completely unnoticed, the net conduction current being zero because there is no voltage across the sample.
Self motion of the space charges can be described in two ways. If the charges are ions, they are generally considered to be free to move with a thermally activated mobility. This can also be visualized as hopping from one vacancy to another across a potential barrier equal to the activation energy. If, however, the charges are electrons or holes, it is more appropriate to visualise them as being immobilized in local traps from which heating releases them into a band of energies in which they can freely diffuse to the electrodes.

In heterogeneous systems consisting of amorphous and crystalline phases, another kind of trapping known as interfacial trapping occurs [211,213-216]. The interfacial charges are due to difference in conductivity of phases. During polarization, these carriers will either accumulate or be depleted near a particular interface in the form known as Maxwell-Wagner effect depending on whether the incoming local conduction current is greater or smaller than the outgoing one. The difference in local conduction current are also responsible for the dissipation of the charges in the subsequent TSD, because the current then flow in the opposite direction.

Polarization in a dielectric also arises from charges injected from electrodes [205,206,210], when the material is sandwiched between two electrodes bearing high electric field. Injected charges may either be trapped or form space charge.
This injection takes place due to Richardson-Schottky emission of electrons or holes from the metal electrodes. Such charges can be captured in the dielectric at different sites. Perlman [217] based on his observation of TSDC of corona charged electrets containing no aligned dipoles, has classified the charge storage sites into three structural levels. The primary levels are atomic sites of molecular chains, secondary levels are the cages between adjacent molecules where charges can be trapped and the tertiary level trapping involves charge storage in the region where material changes its phase, i.e., interfaces. The charge released from the primary levels depend upon the motion of the group of atoms. The charge released from the tertiary level depends upon the main chain motion on their drift under space charge limited conduction [218,212-229]. Release of trapped charges takes place in two stages, first is detrapping while second is related with transportation of released ones.

The magnitude of the TSDC current depends on the charge retained by the electret. However, the time interval of current cannot be equal to the charge originally present, because all the decay processes do not contribute fully to the external current, e.g., charge neutralisation by ohmic conduction in shorted electrets does not contribute to the external current at all. Self drift of charges, particularly when neutralization requires them to move over relatively short distances, is also an inefficient current generating
process. Diffusion is likewise an inefficient current generating process. With ohmic electrodes the charges diffuse systematically outwards and no current is generated at all. The only process whose efficiency is 100% is the disorientation of dipoles.

3.15 TECHNIQUES AND THEORIES OF TSDC

Thermally stimulated decay of an electret can be studied by any one of the following four techniques -

(i) Current TSDC with shorted electrodes,
(ii) Current TSDC with an air gap,
(iii) Charge TSDC by transferring the charge induced on the upper electrode to a sensitive electrometer, and
(iv) Charge TSDC by field cancelling technique.

3.15-1 CURRENT TSDC WITH SHORTED ELECTRODES

The method was developed for bimetallized specimens by Freis [230] and subsequently successively applied by other workers. The particular name is derived from the fact that the voltage drop across the electrodes is zero. Owing to the virtual short circuit, the main electric field \( E_p \) and the mean ohmic conduction current within the electret are so small that only a displacement current makes observable influence. Therefore, the resultant external current is due to the image charges escaping from the evaporated electrodes which are induced by dipoles and space charges.
3.15-2 CURRENT TSDC WITH AN AIR GAP

To study the decay of unilaterally metallized homoelectrets, Turnhout [224] has modified Freis method [230] by introducing an air gap between non metallized side of the specimen and adjacent metal electrode. When such a assembly is heated, a displacement current is generated by image charge released from the noncontacting electrodes as the air gap prevents the electret charges from recombining with the image charges of the upper electrode. Since, the electret itself is not shorted, the electric field within the electret is no longer zero and in fact becomes quite large. Consequently, the ohmic conduction current flowing through the electret produces an appreciable displacement current, whereas it remains obscured in current TSD of shorted electrodes.

3.15-3 CHARGE TSD BY TRANSFERRING THE INDUCED CHARGE TO AN ELECTROMETER

Various methods have been developed to investigate charge TSD by employing an air gap between nonmetallized side of the dielectric and adjacent electrode. A common method is to move the nonadhering electrode periodically away in order to transfer the image charges induced on it to an integrating electrometer. However, no continuous record of the decaying charge can be obtained and hence it is difficult to determine accurately the temperature of the fastest decay.
3.15-4 CHARGE TSDC BY FIELD CANCELLING METHOD

Current TSDC measurements have been found to be unfavourable in case of one side metallized homoelectret foils for which the ratio between the air gap and electret thickness cannot be made small. In such a case, the decaying electret induces most of its image charge on the grounded adhering electrode instead of the probing electrode. A novel version of the air gap charge TSD developed by Turnhout [224]. The method which also allows a continuous monitoring of decaying charge is based on the field cancelling technique, according to which the external field of the foil is nullified by driving the noncontacting electrode with an adjustable bias voltage $V_s$ of the same value and polarity as the equivalent voltage of the electret. Since the upper electrode in such a system is virtually floating, the external current is zero and hence the method is referred to as the charge TSD in open circuit.

The discharge of a shorted electret usually takes place either due to dipole relaxation or space charge relaxation. These two processes are described by separate theories which have been discussed in the following sections.

3.15-5 THEORY OF TSDC DUE TO DEORIENTATION OF DIPOLES

Consider a polar material containing $N$ dipoles per cubic metre with a dipole moment $P$. The dipole will be oriented during the charging by field $E$, and produce a final polarization, $P_f$. 

118
\[ P_0 = N P \sqrt{\cos \theta} \quad \ldots (3.28) \]

where \( \theta \) is the angle the dipole makes with the direction of the field. The alignment that is forced on the dipoles by the charging field \( E \) is counteracted by their thermal motion. For non-interacting dipoles, i.e., when the dipolar concentration is sufficiently low, we have for the average orientation,

\[ \cos \theta = \frac{\varepsilon_o P \varepsilon}{3 k T} \quad \ldots (3.29) \]

where \( \varepsilon \) is the dielectric constant of the medium, \( \varepsilon_o \) is the dielectric constant of free space and \( T \) is the temperature.

During subsequent TSDC, the aligned dipoles will randomly deorient at a rate proportional to the number of dipoles still aligned. The polarization will, therefore, decay according to the Debye rate equation,

\[ \frac{dP(t)}{dt} + \alpha(t) P(t) = 0 \quad \ldots (3.30) \]

where \( P(t) \) is the dipolar polarization at a given time \( t \) and \( \alpha(t) \) is the reciprocal relaxation time or relaxation frequency which is assumed to be the same for all dipoles. The current density generated by the decay in polarization may then be expressed as

\[ I(t) = -\frac{dP(t)}{dt} = -\alpha(t) P(t) \quad \ldots (3.31) \]

where \( P(t) \) follows from eq.(3.30) after integration

\[ P(t) = P_0 \exp\left[ -\int_0^t \alpha(T) \, dT \right] \quad \ldots (3.32) \]

Since the temperature is raised linearly with time, the
current density may also be written as a function of temperature,

\[ I(T) = -\alpha(T) \rho_0 \exp\left[ - \int_{T_0}^{T} \alpha(T) \, dT \right] \]  \quad \ldots (3.33)

Here, \( h \) is the inverse heating rate \( dt/dT \). Because \( \alpha(T) \) is small at low temperature, the electret will retain its charge for a long time when stored at room temperature. During heating, \( \alpha(t) \) increases strongly following Arrhenius equation,

\[ \alpha(T) = \alpha_0 \exp(-A/kT) \]  \quad \ldots (3.34)

where \( \alpha_0 \) is the natural relaxation frequency and \( A \) is the activation energy required to disorient a dipole.

The energy \( A \) can be considered as a potential barrier, which the dipole has to surmount before it can readjust its direction [222,231,232]. Equation (3.34) broadly applies to relaxations involving the rotation of small molecular groups. However, this equation fails in the case of major relaxations in polymers, which occur when the polymer passes from the glassy to rubbery state. This glass rubber transition involves the configurational rearrangement of various parts of long main chains. Their relaxation in this case obey Wagner-Landle-Ferry (WLF) equations [222,233-239].

\[ \alpha(T) = \alpha_0 \exp\left[ C_1(T-T_g) (C_2 + T - T_g)^{-1} \right] (T>T_g) \] \quad \ldots (3.35)

For most amorphous polymers

\[ \alpha_0 = 7 \times 10^{-3} \text{ s}^{-1}, \quad C_1 = 40 \text{ and } C_2 = 52 \text{ K}. \]

Often the activation energy of dipoles is not the same. Dipoles with low activation energy orient at low temperature
while those with high activation energy respond at high temperatures. Apart from the distribution in activation energy, there may be a distribution in rotational mass of dipoles which will then lead to distribution in the pre-exponential factor $\alpha$, in eq.(3.34). These distributions are described by the following relations,

$$\alpha_i(T) = \alpha_0 \exp(-A_i/kT) \quad \cdots (3.36)$$

and

$$\alpha_i(T) = \alpha_0', \exp(-A/kT) \quad \cdots (3.37)$$

In the case of distribution in natural frequency $\alpha_0'$, the polarization is given by,

$$P(t) = P_0 \int_0^\infty F(\alpha_0') \exp\left[-\alpha_0 \int_0^t \exp(-A/kT) \, dT\right] d\alpha$$

$$\quad \cdots (3.38)$$

and in the case of distribution in activation energy, the same is given by,

$$P(t) = P_0 \int_0^\infty g(A) \exp\left[-\alpha_0 \int_0^t \exp(-A/kT) \, dT\right] d\alpha \quad \cdots (3.39)$$

where $F(\alpha_0')$ and $g(A)$ are the distribution function in natural frequencies and activation energies. These functions represent the contribution between $\alpha_0' \rightarrow \alpha + d\alpha$ and $A \rightarrow A+dA$ to total dipolar relaxation strength $\varepsilon_s - \varepsilon_\infty$. Actually, they are relative contribution to $\varepsilon_s - \varepsilon_\infty$ because they are normalised, so that

$$\int_0^\infty F(\alpha_0') \, d\alpha_0 = \int_0^\infty g(A) \, dA = 1. \quad \cdots (3.40)$$

121
The corresponding expressions for TSDC are obtained by differentiation of Eq. (3.38) and (3.38),

\[
i(t) = P_0 \exp(-A/kT) \int_0^\infty \alpha \exp[-A/kT] \exp(-A/kT) d\alpha
\]

... (3.41)

\[
i(t) = P_0 \exp \alpha \int_0^\infty g(A) \exp[-(A/kT) - \alpha] \exp(-A/kT) d\alpha
\]

... (3.42)

### 3.15-6 THEORY OF TSDC BY SELF MOTION OF CHARGES

Apart from the dipolar polarization, the polarization can also arise due to space charge formation in the sample. As we know that a dielectric never insulates perfectly, particularly, not at high temperature when an increasing number of thermal carriers are generated. During polarization these carriers move in the applied field and when the dielectric is cooled, some of them are trapped in various available traps existing in the sample. Owing to this process thermally formed electrets usually contain a space charge polarization. Space charges can also be injected from the electrodes, specially at high field strengths [211, 214-216].

At low temperature the space charges remain frozen in, but when the temperature is raised, these charges get thermally activated and remobilized. During heating in short circuit these space charges move under the influence of the internal field of the electret, giving rise to thermally
stimulated discharge current in the external circuit. Some of the mobilized space charges move to the electret [222,214-216] and recombine with their image charges while some of them recombine with their counter parts within the electret.

In the case of space charge TSDC, the current obtained in the external circuit is thus given by,

\[ I(t) = C \exp(-A/kT) - (\beta \tau_0)^{-1} \int_{T_0}^{T} \exp(-A/kT) \, dt \quad \ldots \quad (3.43) \]

where \( A \) is the activation energy, \( C \) is a constant, \( \beta \) is heating rate, \( k \) is the Boltzmann constant and \( \tau_0 \) is the pre-exponential factor of relaxation time.

3.16 EFFECT OF DIFFERENT FACTORS ON TSDC SPECTRA

(a) Polarizing Field (\( E_p \)) :

In order to form electrets, specimen is subjected to electric field, known as polarizing field \( E_p \). In the TSDC spectra, the peak due to dipolar or volume polarization increases linearly with \( E_p \), whereas the space charge polarization varies non linearly with polarizing fields [240].

(b) Polarizing Temperature (\( T_p \)) :

The temperature at which sample is polarized, is polarizing temperature. The polarizing temperature \( T_p \) affects the position and magnitude of peak current significantly. For a process with single relaxation time, the peak in the TSDC spectra remains unaltered while its magnitude increases with increasing (\( T_p \)). In a distributed relaxation process, both the position and magnitude of peak current depend on \( T_p \).

123
(c) **Polarizing Time** \( (T_p) \):  
The position and intensity of peak current in the TSDC spectra depend on the polarizing time. According to Turnhout [140], \( (T_p) \) should change logarithmically to obtain charges of the same magnitude as with the charge of \( T_p \).

(d) **Electrode Material**:  
Effect of electrode material on TSDC spectra of thermoelectrets has been studied and it has been shown that a good correlation exists between the charge acquired by the thermoelectret and the work function of the metal electrode used during polarization [241, 242-244]. Shrivastava et al [241] studied effect of electrode material on TSDC of poly(styrene) (PS) films and concluded that the first stage of charging of PS films, as a result of contact with the metal, is charge injection which decreases with the increase in metal work function. The second stage is entrapment of these charges in the border layer. Mahendru et al [244] observed that thermally stimulated discharge current is negative with electrode metals of lower work function, whereas it is positive when the metals used as electrodes are of higher work function during the depolarization of identically polarised specimen of polyvinyl acetate.

(e) **Specimen Thickness**:  
The charge on an electret has been found to depend upon its thickness [245].

124
(f) **Heating Rate**

When the heating rate is slow, the polymer responds sooner in giving a current at a lower temperature. Its intensity is lowered by a factor equal to the ratio of the increase in heating rate. The current is decreased because the final charge released is the same. The peak temperature and heating rate are related according to the following equation for dipolar relaxation processes,

\[ \tau = \frac{kT_m}{\beta A_a} \]

where \( k \) is the Boltzmann's constant, \( T_m \) is the peak temperature, \( \beta \) is the rate of heating, \( A_a \) is the activation energy and \( \tau \) is the relaxation time at peak temperature.

Variation in heating rate provides information regarding the nature of traps and type of relaxation mechanisms in an insulator. This method has been recently exploited by a large number of workers [246-249].

(g) **IMPURITY**

Whenever, a polymer matrix is impregnated by an impurity, a Charge Transfer Complex (CTC) is formed. CTC formation sometimes changes the structure of polymer. The magnitude and shifting of a current maximum has been observed by many workers in polyethylene [250-252].

(h) **Humidity**

Humidity also affects the TSDC thermogram. At different
pH values the absorption of moisture is different. Some polymers form complexes also with water [253].

3.17 EVALUATION OF TSDC DATA

3.17-1 ACTIVATION ENERGY

Now, we discuss the various methods for evaluation of activation energies from the observed TSDCs thermograms.

(A) INITIAL RISE METHOD

In this method, suggested by Garlick and Gibson [254], the activation energy A is obtained from the straight line portion of I(t) vs 1/T curves in the range where the TSDC current rises initially.

If we differentiate the TSD current over initial rising part with respect to 1/T, we have

\[
\frac{\text{dln } I(t)}{\text{d}(1/T)} = -\frac{A}{k}
\] ... (3.44)

(B) BUCCI-FIESSHI AND GUIDI (BFG) METHOD

According to this method [255], the activation energy A can be calculated from the relation

\[
\alpha(T) = \frac{I(t)}{P(t)} = \frac{I(t)}{\beta} \int_{T}^{\infty} I(t) \, dT
\] ... (3.45)

where \( \alpha(T) \) is the reciprocal relaxation time of relaxation frequency, \( \beta \) is the heating rate and \( T \) the absolute temperature.

126
(C) **HALF CURRENT PEAK-WIDTH METHOD**

Using this method, the activation energy $A$ can be evaluated from the relation

$$\frac{\Delta T}{T_m} \approx 2.47 \frac{k T_m}{A} \quad \ldots \quad (3.46)$$

where $\Delta T$ is the half width of the current peak and $T_m$ is the peak temperature.

(D) **HEATING RATE VARIATION METHOD**

Activation energy can also be estimated by changing the heating rate of the electret. If heating is changed, the activation energy can be deduced by observing the shift of the peak temperature from $T_1$ to $T_2$. On differentiating Eq.(3.42) we find that the current maximum occurs when

$$\frac{d}{dT} \left[ \frac{1}{\alpha(T)} \right] = -\beta \quad \ldots \quad (3.47)$$

which, for an Arrhenius type $d-T$ relation, transforms into

$$\frac{\alpha(T_m) \beta k T_m^2}{A} = 1 \quad \ldots \quad (3.48)$$

For the two heating rates, we then have

$$\beta_1 T_1' \alpha(T_1) = \beta_2 T_2' \alpha(T_2) = \text{constant} \quad \ldots \quad (3.49)$$

If the heating rate is changed more than twice, it is advantageous to find $A$ from $\beta T_m^2$ vs $1/T_m$ plot [165]. Such a plot need not be based solely on the TSDC maxima. The other points of the TSDC peaks may also be involved. This is done in the method suggested by Solunov et al [257,258].

127
3.17-2 RELAXATION TIME \((\tau_o)\)

The low temperature tail of equation 3.43 is given by

\[
\log i(T) = \text{Const} \left(- \frac{A}{kT} \right) \quad \ldots (3.50)
\]

Thus, from equation (3.50) the activation energy \(A\) of the discharge process responsible for the peak can be obtained from a plot of \(\log I\) versus \(1/T\).

On differentiating equation (3.43) with respect to temperature and equating it to zero \(\left(\frac{di}{dt} = 0\right)\), one obtains the temperature \((T_m)\) were maximum current occurs. \(T_m\) is given by

\[
\tau_o = \frac{k T_m^2}{\beta A \exp \left( \frac{A}{k T_m} \right)} \quad \ldots (3.51)
\]

Finding \(T_m\) from current versus temperature plots, one can calculate \(\tau_o\). Knowing \(\tau_o\) we can easily calculate the relaxation time at \(T_m\) and at any temperature, i.e.

\[
\tau(T_m) = \tau_o \exp \left( \frac{A}{k T_m} \right) \quad \ldots (3.52)
\]

Calculations of \(\tau(T_m)\) from equation (3.52) requires the value of \(\tau_o\) one can, however, calculate \(\tau(T_m)\) without knowing \(\tau_o\). From equation (3.51), we have

\[
k T_m^2 = \beta A \tau_o \exp \left( A/k T_m \right)
\]

\[
= \beta A \tau(T_m)
\]

\[
\text{or}, \quad \tau(T_m) = \frac{k T_m^2}{\beta A} \quad \ldots (3.53)
\]

128
Knowing $T_m$ from experimental plots $\tau_{(T_m)}$ can be obtained directly from 3.53.

3.17-3 CHARGE RELEASED ($Q$)

Charge released ($Q$) during the discharge was calculated by integrating the current versus temperature/time curves using Simson's rule.

3.18 LAST DECADE'S WORK ON TSAD

Polymers are generally good dielectrics which are capable of storing the charge in them permanently when subjected to field temperature treatment. Such dielectric materials bearing persistent charge are called thermoelectrets. When thermoelectrets are subjected to a programmed heat treatment, they give rise to a current in the external circuit and this is called thermally stimulated discharge current (TSAD). Thermally stimulated discharge current technique is a convenient and sensitive method for studying the charging and discharging process in dielectrics. These currents are due to dielectric relaxation behaviour and motion of free charges in the polymer. Hence the TSAD technique can be used to understand the low frequency dielectric relaxation in solids and the relaxation between dielectric behaviour and process on the atomic scale. Because of the high sensitivity of this technique, it is also used to investigate the low concentration of dipolar impurities,
formation and aggregation of impurity vacancy complexes, phase transitions, photographic response of silver halides etc.

Studies on thermoelectretts started as early as 1922 by Eguchi on Carnuba wax. Since then various dielectrics both plastic and ceramics have been studied extensively by different workers. Excellent reviews on this subject both theoretical and experimental have appeared in the literature [259]. Some of the work recently reported in literature on polymer thermoelectretts is briefly reviewed below to get a comprehensive picture of the present state of research on this subject.

Thermally stimulated discharge currents (TSDC) in carnuuba wax electretts were studied by Perlman [260] using a linear heating rate for various polarizing fields, temperatures, times and thicknesses of the sample. Three peaks were observed at 47, 59 and 69 C respectively. Microscopic displacement of ions with trapping was proposed as the possible mechanism for the TSDC.

Caserta and Serra [261] have made simultaneous measurements of current voltage characteristics, isothermal discharge currents and thermally stimulated discharge currents to determine the mechanism of formation of electretts in carnuaba wax. Homocharge from the electrodes and hetero charge with the material are found to be responsible for TSDC.
The electret effect in shellac wax was investigated by TSD current (TSDC) by Pillai et al [262] prepared under different polarizing conditions. They observed only one peak for the TSDC spectra. They have attributed the TSDC spectra to the dipolar orientation and microscopic displacement of charges with trapping.

Jain et al [263] studied TSD currents in solution grown polyvinyl butyral films as a function of the polarization field (750 to 25000 V/cm) and iodine dopant concentration. Polarized PVB films exhibited two glow discharge peaks one at 350K (β) and the other at 430K (α) corresponding to activation energies of 0.19 and 0.53 eV respectively. It was observed that the β-peak disappeared at low polarizing fields (750 V/cm). The α-peak was attributed to the depolarization of the aligned dipoles connected to the main chain whereas the β-peak due to the local motion or twisting of the side groups connected to main chain. On doping with iodine, both un-polarized and polarized films exhibited TSD currents. This is attributed to the formation of charge complexes.

Mahendru et al [264] studied TSD currents in polyvinyl acetate thin films as a function of polarizing field (0-9 kV/cm) and thickness (1000-7000 Å). They reported three peaks at 326, 389 and 468K. The peaks at 326 and 389K were attributed to the motion of the side groups and the orientation of the dipoles of the main polymer chain.
respectively, whereas the peak at 368K was related to the relaxation process which was due to the release of the trapped space charges.

Mahendru et al [265] studied electret effects in polyvinyl fluoride thin films. They observed only one peak in the TSDC spectra. The results of these studies were explained in terms of the disorientation of dipoles and/or the migration of charges over microscopic distances with trapping.

Thermally stimulated discharge currents from polyacrylonitrile were studied by Comstock et al [266]. Electrically polarized films of stretched and unstretched polyacrylonitrile were studied with the thermally stimulated discharge technique. Preferential orientation of nitrile side groups in polarized specimens was inferred from birefringence and X-ray diffraction experiments but the contribution of observed persistent electrical polarization appeared to be small. The major contribution was found to be due to trapped space charges, some of which was found to be due to trapped space charges, some part of which was associated with residual solvent molecules. Small ordered regions within polyacrylonitrile were expected to play a role in development of each contribution to the final persistent electrical polarization.

Thermostimulated currents from polychlorotrifluoroethylene electrets were studied by Latour and Murphy [267].
Thermostimulated current profiles were obtained for electrets of chlorotrifluoroethylene poled under various conditions of field strengths, temperature and electrode contact. The principal current peak was located at 145 C for electrets poled at an elevated temperature (100-178 C) and at 125 C for electrets poled at room temperature (20 C). Increase in the poling field from 3 to 300 kV/cm produced continuous variations in the discharge current profile consistent with a transition from hetero-charge to homo-charge. Both hetero-charge and homo-charge appeared to be released simultaneously at the principal current peak. Similar curves were obtained for samples poled with corona.

Studies on electron traps in polyethylene terephthalate by thermally stimulated current and photostimulated detrapping current analysis was made by Takai et al [268]. A broad peak of TSDC was observed around 100 C at which the motion of the COO group was released and a plateau was observed around 0 C. The apparent activation energy of the former peak was estimated to be about 0.23 eV by the partial heating technique. On the other hand, TSDC spectra at 185 C showed an existence of deep traps at 2.3 eV, which could be thermally cleaned by heating only upto 70 C. These facts clearly showed the effect of molecular motions on the carrier detrapping process during heating.

Thermally stimulated depolarization studies of PVC polymer electrets were made by Talwar and Sharma [269].
Thermally stimulated depolarization (TSDC) of polyvinyl chloride thermoelectrets prepared at polarizing temperatures of 80, 100 and 120 C with field strengths of 10, 12.5 and 14 kV/cm was studied. A sharp peak appeared at 97 C and was associated with the activation energy of the trap at a depth of 0.44 ± 0.03 eV.

Miyairi and Yanagisawa [270] studied thermally stimulated current in polyethylene terephthalate in the high temperature region. Electrical conduction in polyethylene terephthalate (PET) at high temperature was dominated by ionic process.

Thermally stimulated depolarization current (TSDC) of polypyromellitimid was measured by Tanaka et al [271] in order to obtain knowledge of the charging and discharging mechanisms of carriers in polypyromellitimid. Two peaks were observed one at 173 C (α) and the other at 50 C (β) in the dried film. The β peak was attributed to dipole orientation polarization. The α-peak showed non-linear dependence on polarization electric field $E_p$. The peak showed electrode material dependence. The α-peak was considered to be due to space charge polarization due to trapping of electrons injected from the cathode in the vicinity of the polymer film surface.

Kojima and Maeda [272] studied thermally stimulated currents from polyethylene terephthalate due to injected charges. Thermally stimulated currents from polyethylene
terephthalate (PET) electrets was investigated in the
temperature range from -190 to +120 C. Both dependence of TSC
on electrode metals (Au, Al) and the polarity of an applied
field were remarkable in the temperature range above -40 C.
The results indicated that electrons injected from the Al
cathode greatly contributed to the TSC above -40 C and that
the TSCs below -40 C for Al electrode and at all temperatures
for Au electrodes were mainly induced by the depolarization of
dipoles.

Bhargava and Srivastava [273] investigated thermally
stimulated discharge currents in polystyrene thin films grown
by the solution growth technique. Films in the thickness range
(2000-10000 A°) were polarised at 130 C under the influence of
different field strengths (2-10 kV/cm). Two relaxation peaks
were observed at 77 C and 112 C. The occurrence of 112 C peak
was explained in terms of space charge injection from
electrode and ionic effect. The occurrence of 77 C peak was
shown to be due to release of trapped charges due to local
movements of polystyrene molecular chains.

TSDC study of pyrene picrate charge transfer complex was
made by Srivastava and Mathur [274]. They observed two peaks.
The first peak was attributed to bulk polarization whereas the
second peak due to Maxwell-Wagner charging. Iqbal and Hogarth
[275] studied the trap depth in evaporated polypropylene from
measurements of thermally stimulated currents. The occurrence
of thermally stimulated currents in thin evaporated films of
polypropylene was demonstrated and an analysis of the curve gave an electron trap depth of 0.33 eV to this material.

Jain et al [276] studied the charge storage properties in solution-grown polyvinyl butyral (PVB) thin films as a function of poling field (2.50 \times 10^4 - 2.00 \times 10^6 \text{ V/m}), temperature (333-398 K), time (5.40 \times 10^3 - 1.44 \times 10^4 \text{ sec}), thickness of the films (0.8-4.5 \text{ m}\mu) and heating rates of depolarization (2.8-10 K/min) by the TSDC technique. Two relaxation processes one at 347K and the other at 423K were observed having activation energies of 0.36\pm0.02 \text{ eV} and 0.66\pm0.02 \text{ eV} respectively. The peak at 347K was found to be due to the deorientation of the aligned dipoles involving the acetate/hydroxyl groups. The peak at 423K was attributed to the release of trapped electrons/holes. The increase in the activation energy associated with the peak at 423K and the shift in its position towards higher temperatures with increase in the poling time and temperature suggested that the peak was associated with a distribution of relaxation times.

Srivastava et al [277] studied electrical polarization in polystyrene films of thickness 20 \text{ m}\mu by measuring the TSDC at different polarizing fields, temperatures and heating rates. One peak was observed at 105 C which was unaltered by a change in the field. The occurrence of peak was due to a mechanism involving dipole orientation process.
Narasimha Rao and Narsingh Das [278] studied the TSDC in polyacrylic acid polymer films. Polyacrylic acid films of thickness 15 μm were grown by the solution growth technique. Thermally stimulated discharge currents (TSDC) were studied on these polymer films as a function of polarizing field strength and polarizing temperature at a constant heating rate of 0.08 KS⁻¹. In all these studies, one TSDC peak was observed and the temperature corresponding to this peak was found to shift to higher temperatures as the polarizing temperature increases. But for given polarizing temperature, the temperature corresponding to the peak was independent of polarizing field strength. The activation energies and relaxation parameters were evaluated. The origin of the TSDC was attributed to the dipolar orientation process.

Narasimha Rao and Kalpalatha [279] studied thermally stimulated discharge currents in polyvinyl pyrrolidone polymer films. Polyvinyl pyrrolidone films of thickness 17.6 μm were grown by the isothermal solution growth technique. Thermally stimulated discharge currents were studied on these films as a function of polarizing field strength and polarizing temperature at a constant heating rate of 0.15 KS⁻¹. In all these studies only one TSDC peak was observed and it was attributed to the space charge process.

Verma and Sinha [280] studied TSDC in bakeline (polyphenol formaldehyde) thermoelectrets. α and β peaks were
obtained for different poling temperatures and fields. **Dou-Yol Kang et al** [281] studied TSC in polypyrromellitimide (polyimide). They observed three peaks A, B and C. The C peak was shown to be due to the polarization of ionic space charge which was measured as a function of forming time, forming temperature, forming voltage. **Chand and Kumar** [282] studied the effect of doping on TSD relaxation in polyvinylidene fluoride (PVF₂) films. TSD spectra of both pure and methylene blue dye doped PVF₂ films showed two relaxation peaks, however, in the latter case the peak positions, peak currents and charges depend strongly on the concentration of the dopant. TSC peaks in undoped poly(p-phenylene vinylene) were observed by **Onoda et al** [283]. **Akuey and Hirch** [284] reported TSD and TSC measurements of PVK films over the temperature range 85-530K. The only peak reported was found to lie at 250K and the corresponding activation energy was deduced to be 0.55±0.05 eV. Thermally stimulated depolarization current (TSDC) spectra of polychlorotrifluoroethylene with relatively low crystallinity were studied by **Shimizu and Nakayama** [285]. These TSDC peaks were observed in the range of 85 to 400K.

**Narasimha Rao and Subba Rao** [286] studied the thermally stimulated depolarization currents in polyacrylamide polymer films between polarizing field strengths 0.48 X 10⁶ Vm⁻¹ to 24.1 X 10⁶ Vm⁻¹ and temperature range from 305 to 368K for different heating rates and polarizing times. The spectra
showed only one peak at low polarization temperatures whereas two peaks at high polarization temperatures. The origin of first TSDC peak was attributed to the dipolar orientation and peak II was attributed to the space charge polarization with the injection of charge carriers from the electrode and subsequent trapping and detrapping.

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145


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