CHAPTER - VI
CHARGING, DISCHARGING TRANSIENT CURRENTS AND
STEADY STATE ELECTRICAL CONDUCTION
6.1 INTRODUCTION

The subject of transport of carriers through thin insulating films has been the subject of intensive theoretical and experimental investigation. Inspite of large number of reports on it [1-5] the understanding of transport mechanism is far from clear. Transport mechanism in these films still requires a wide range of experimental investigations.

In comparison to well ordered covalent or ionically bonded inorganic materials, polymers are weakly bonded disordered [6] materials. These differences have profound effect on most of the properties of polymers. They are heat insulators and are usually soft and easily distorted. They are electrically insulating and are found with very low conductivity [7,8] which depends upon - thermally generated carriers within the material and the injection of charge carriers from electrodes at high field.

The intrinsic charge carrier generation, at room temperature, in polymer is very low. Polymers contain many impurities, additives and imperfections; their amorphous structure is complex. Due to these reasons not much information is available on the nature of charge carriers and the charge transfer mechanism [9-24] operating through the dielectric metal boundary. The study of electrical conduction has become important in the investigation of conduction mechanism in the solids [25].
Information on the dominant process of electrical conductivity in the polymer sandwiched between two metal electrodes can be obtained by studying current voltage (I-V) characteristics.

The charging current 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 current 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 [26]. 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 discharging currents differ from material to material depending upon the mechanisms involved. The origin of transient currents is still a subject of much controversy in the literature [27] and a large number of mechanisms have been proposed by various workers [28-35]. 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 [25, 25a]. The results of this technique can also be compared with those of some other electrical studies, like thermally stimulated discharge current (TSDC) [25b] and isothermal surface charge decay, etc., to get clear and justified conclusions.

This technique is time consuming, hence, it is not very popular, but the results of this long time technique are more 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 discharging currents has not been clearly accounted for in most of the dielectric materials including PVF 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 and steady state conduction 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 discharging in polymers, which is of prime importance for the analysis of the electret effect in polymer dielectrics. There are many processes expected during charging and discharging of a dielectric, however, the response of various processes is always combined and the resultant effect gives a particular mode to the transient and steady state conduction currents depending upon the material properties and experimental conditions.

6.2 CALCULATIONS

6.2-1 POWER LAW (m)

The variation of current with applied DC voltage is important because power law given below is obeyed.

\[ I = KV^m \] \hspace{1cm} (6.1)

m determines the degree of linear relationship between \( \log I \) and \( \log V \). Taking logarithms of the above equation

\[ \log I = \log K + m \log V \] \hspace{1cm} (6.2)

Putting \( \log I = y \), \( \log V = x \) and \( \log K = c \),

we have \[ y = mx + c \] \hspace{1cm} (6.3)

It is an equation of straight line. The problem has now reduced to the fitting a straight line to a set of points on
the XY plane and thus to a simple problem of least squares as follows:

\[ m = \frac{\Sigma X \cdot \Sigma Y - n \Sigma (XY)}{(\Sigma X)^2 - n \Sigma X^2} \]  \quad \ldots (6.4)

The values obtained from above equation are somewhat different from those obtained by solving original least square equation, but these differences are small.

6.2-2 CONDUCTIVITY

The conductivity is calculated by using the equation

\[ \sigma = \left( \frac{d}{a \times V} \right) \times I \]  \quad \ldots (6.1)

where \( d \) is the thickness of the sample,
\( a \) is the area,
\( V \) is the voltage applied across the materials, and
\( I \) is the conduction current.

6.2-3 ACTIVATION ENERGY

Relation between conductivity and temperature is governed by the equation \( \sigma = \sigma_0 \exp(-A/kT) \). On the basis of the equation, Activation energy can be calculated as

\[ A = \frac{K(\log_e \sigma_1 - \log_e \sigma_2)}{1/T_2 - 1/T_1} \]  \quad \ldots (6.6)

where, \( K \) is the Boltzmann constant = 8.617 x 10^{-5} eV, \( \sigma_1 \) and \( \sigma_2 \) are the values of conductivity at two points corresponding to temperature \( 1/T_1 \) and \( 1/T_2 \).
6.3 EXPERIMENTAL SET UP

The sandwiched sample (metal-PVF-metal) was placed in a specially designed cell. The temperature of the cell was controlled with an accuracy of ± 1K by adjusting the input voltage from the variac for which the calibration has been made. The d.c. voltages across the sample were fed from a regulated power supply (ECIL, India) and currents in the circuit were recorded by means of a Keithley Electrometer Model 610C. After making proper electrical connections, the sandwiched sample mounted on electrode assembly was placed inside the thermostat and allowed to attain required temperature. It took about 1.5 hours. When the sample attained the desired temperature, a dc voltage was applied. A sudden burst of current observed in the beginning decreases with time. Its initial as well as steady state value was recorded. At lower voltages and temperature it took longer period to reach the steady state while at higher voltages and temperatures steady state was obtained in considerable low period. The effect of voltage variation in current was noted by increasing the voltage at fixed temperatures while temperature variation was measured keeping voltage constant and increasing the temperature. Measurements were taken in the voltage and temperature ranges of 10-100 kV/cm and 30-70 °C, respectively. A fresh sample is used for each set of observation.
6.4 RESULTS AND DISCUSSION

The results of transient currents in charging and discharging modes and steady state conduction are analyzed and interpreted.

The time dependence of the charging and discharging transient currents in polyvinyl formal (PVF) samples have been investigated over a period of time 1-100 min. The Figures 6.1 to 6.10 show the variation of charging and discharging transient currents with time at different temperatures (i.e., 40, 45, 50, 55, 60, 65, 70 C with polarizing fields of 10, 25, 50, 75 and 100 kV/cm, respectively. It is evident from the figures that the current decays at a faster rate for a few minutes and then the decay rate slows down. Curves illustrating the time-dependence of transient charging and discharging currents are, in general, characterized with two regions which are designated as the short-time and the long-time regions, respectively.

Figures 6.11 to 6.18 illustrate the charging and discharging characteristics of PVF films at different temperatures (i.e. 40, 50, 60 and 70 C) with different polarizing fields (10, 25, 50, 75 and 100 kV/cm). From the above characteristics (Figures 6.1 to 6.18), it is clear that at least two distinct mechanisms should be responsible for the observed transient currents. One mechanism is operative in the short-time range with a particular value of decay constant and the other mechanism is operative in the range of long-time with a decay constant of different value.
Fig. 6.1 - Charging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.2 - Charging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.3 - Charging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.4 - Charging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.5 - Charging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.6 - Discharging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.7 - Discharging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.8 - Discharging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.9 - Discharging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.10 - Discharging characteristics of polyvinyl formal films with different temperatures at constant applied field.
Fig. 6.11 - Charging characteristics of polyvinyl formal films with different applied fields at constant temperature.
Fig. 6.12 - Charging characteristics of polyvinyl formal films with different applied fields at constant temperature.
Fig. 6.13 - Charging characteristics of polyvinyl formal films with different applied fields at constant temperature.
Fig. 6.14 - Charging characteristics of polyvinyl formal films with different applied fields at constant temperature.
Fig. 6.15 - Discharging characteristics of polyvinyl formal films with different applied fields at constant temperature.
Fig. 6.16 - Discharging characteristics of polyvinyl formal films with different applied fields at constant temperature.
Fig. 6.17 - Discharging characteristics of polyvinyl formal films with different applied fields at constant temperature.
Fig. 6.18 - Discharging characteristics of polyvinyl formal films with different applied fields at constant temperature.
The temperature dependence of the transient currents in charging and discharging modes are shown more clearly when the current measured at a constant time (isochronals) is plotted against temperature. Such isochronals for charging and discharging mode have been constructed for 01, 5, 10, 30 and 70 min are shown in Figures 6.19 to 6.28. From these plots, it may be concluded that the currents show thermal dependence. Such isochronals are characterized by a maxima around 65±5 C.

The time dependence of charging and discharging transient characteristic plotted with different fields at constant temperatue are shown in Figures 6.29 to 6.36. All the curves show almost similar characters. However, the charging and discharging currents at various time after the applications and termination of fields are found to follow the power-law dependence of fields. Log-log plots of charging and discharging currents and fields at different times (Figures 6.29 to 6.36) show that both charging and discharging currents reasonably follow a relationship, $V^m$, voltage dependence with the power lying between 1 and 2.

Figures 6.37 to 6.46 gives the log I vs 1000/T (where T is the absolute temperature) plots (constructed from linear portion of isochronal current and temperature plots). The value of activation energy is calculated from the slope of these characteristics.
Fig. 6.19 - Charging currents versus temperature curves for different times at constant applied field.
Fig. 6.20 - Charging currents versus temperature curves for different times at constant applied field.
Fig. 6.21 - Charging currents versus temperature curves for different times at constant applied field.
FIELD
$E_p = 75$ kV/cm

CHARGING CURRENTS (AMP)

$10^7$
$10^6$
$10^5$
$10^4$

TEMPERATURE (°C)

40 45 50 55 60 65 70 75

$1$ min
$10$ min
$70$ min
$10$ min
$5$ min

Fig. 6.22 - Charging currents versus temperature curves for different times at constant applied field.
FIELD
$E_p = 100 \ \text{kV/cm}$

Fig. 6.23 - Charging currents versus temperature curves for different times at constant applied field.
Fig. 6.24 - Discharging currents versus temperature curves for different times at constant applied field.
Fig. 6.25 - Discharging currents versus temperature curves for different times at constant applied field.
Fig. 6.26 - Discharging currents versus temperature curves for different times at constant applied field.
\[ E_p = 75 \text{ kV/cm} \]

Fig. 6.27 - Discharging currents versus temperature curves for different times at constant applied field.
Fig. 6.28 - Discharging currents versus temperature curves for different times at constant applied field.

FIELD
$E_p = 100$ kV/cm
Fig. 6.29 - Charging currents versus applied field for different times at constant temperature.
Fig. 6.30 - Charging currents versus applied field for different times at constant temperature.
Fig. 6.31 - Charging currents versus applied field for different times at constant temperature.
Fig. 6.32 - Charging currents versus applied field for different times at constant temperature.
Fig. 6.33 - Discharging currents versus applied field for different times at constant temperature.
Fig. 6.34 - Discharging currents versus applied field for different times at constant temperature.
Fig. 6.35  - Discharging currents versus applied field for different times at constant temperature.
Fig. 6.36 - Discharging currents versus applied field for different times at constant temperature.
Fig. 6.37 - Charging currents versus $10^3/T$ curves for different times at constant applied field.
Fig. 6.38 - Charging currents versus $10^3/T$ curves for different times at constant applied field.
Fig. 6.39 - Charging currents versus $10^3/T$ curves for different times at constant applied field.
Fig. 6.40 - Charging currents versus $10^3/T$ curves for different times at constant applied field.
Fig. 6.41 - Charging currents versus $10^3/T$ curves for different times at constant applied field.
Fig. 6.42 - Discharging currents versus $10^3/T$ curves for different times at constant applied field.
Fig. 6.43 - Discharging currents versus $10^3/T$ curves for different times at constant applied field.
Fig. 6.44 - Discharging currents versus $10^3/T$ curves for different times at constant applied field.
Fig. 6.45 - Discharging currents versus $10^3/T$ curves for different times at constant applied field.
Fig. 6.46 - Discharging currents versus $10^3/T$ curves for different times at constant applied field.
The steady state conduction current-field characteristics are shown in Figure 6.47 at 40, 50, 60, 65 and 70°C. The effects of dissimilar electrodes (i.e. Al-Cu and Al-Ag) on the current-field characteristics at a fixed temperature 50°C is also given in the same figure.

Figure 6.48 represents the variation of conduction currents vs field for different thicknesses (i.e., 10, 15, 20, 25 and 30 μm) of PVF samples at constant temperature 60°C. It is evident from the figure that with the decrease in thickness of the sample, conduction current increases.

The Schottky plots (log J vs $\sqrt{E}$) for PVF samples with similar (Al-Al electrode combination) and dissimilar electrode combination are shown in Figures 6.49 and 6.50. The plot (Figure 6.49) exhibit two regions at the lower and higher fields. The isothermal reveals almost ohmic behaviour initially, which gradually becomes non-ohmic. The slope values in the lower field region lie between 1.04 to 1.11 and slope of 1.71 to 1.92 are observed at higher field strength. It is evident from the Figures 6.47 and 6.50 that no regular variation of conduction currents on electrode materials is seen.

The observed results can now be discussed in the light of the existing models of transient currents and steady state conduction currents.

The Curie-Von Schweidler type of time dependence has been observed for many polymers with the index n close to
Fig. 6.47 - Conduction currents versus field plots for PVF samples.
Fig. 6.48 - Conduction currents versus field plots for different thickness of PVF samples.
Fig. 6.49 - Log of current density versus under root of field plots of polyvinyl formal samples at different temperatures (For Al-Al System).
Fig. 6.50 - Log of current density versus under root of field plots of polyvinyl formal samples at temperature 50°C for dissimilar electrode combination.
unity. A number of mechanisms may be used to explain such time
dependence. It is, therefore, not possible to specify the
origin of transient currents from the analysis of time
dependence alone. At temperatures much lower than the glass
transition temperature and for the low to moderate fields
used, several of the concepts previously postulated to account
for the transient conduction phenomenon can be ruled out on
the basis of the experimental facts. The various results
summarized here may help to distinguish between various
processes. The polarization of polymeric materials may be due
to dipolar orientation, space charge formation, trapping in
the bulk, tunnelling of charges from the electrodes to empty
traps, or hopping of charge carriers from one localized state
to another. The most probable mechanism responsible for the
observed currents in the dielectric can in principle be
determined by considering the variation of such currents with
temperature, time, fields and electrode materials, etc [36-41].

In fact, the charging and discharging currents observed
in most of the polymers investigated show the expected
behaviour of a dipolar relaxation mechanism in all aspects,
i.e., linear dependence on field strength and independence of
thickness, field polarity, electrode material, method of
sample preparation and additives, non-interfering with the
macromolecular motions. The observed time dependence is also
compatible with such a dipolar process since the relaxation
phenomena in polymers are generally characterized by a
distribution in relaxation times leading in the usual formation of Cole and Cole [41] to a $t^{-n}$ transient current.

So far as the nature of the trapping sites are concerned, there is, and has been much speculation on this topic, but at present, it is generally concluded that charge trapping is primarily due to the basic polymer structure consisting of various traps. This, one can envisage physical traps in cavities due to defects and free volume inerhents in the bulk polymer structure, in bonding energy resulting from a polarization of the surrounding molecules. Another type of trap or hopping site may be due to chemical heterogeneities in the polymer structure, such as C=O groups may represent at least a major fraction of the localized centres by which the transport of the injected electrons takes place. The above consideration indicates that the observed discharging current in the present case may be partially be due to dipole orientation and partially due to space charge mechanism [25].

The current in the time domain for the short time region is characterized by the relation

$$I(t) \propto t^{-n}, \quad 0 < n < 1; \quad t << 1/W_p \quad \ldots \quad (6.7)$$
i.e. the frequencies which are larger than the loss peak frequency $W_p$, and for the long time region

$$I(t) \propto t^{-1-P}, \quad 0 < n < 1; \quad t >> 1/W_p \quad \ldots \quad (6.8)$$

with logarithmic slope steeper than unity. The two power laws determine the time domain response of dipolar system in which
a loss peak is seen in the frequency domain. Similarly, behaviour is observed in carrier dominated systems, however, low frequency dispersion below a frequency \( W_c \), which corresponds to long time region is described by the above power laws with small value of \( n \).

Let \( n = 1 - p \), with \( p \) close to unity for low frequency dispersion region. The long time response of charge carrier system will then be denoted by

\[
I(t) \propto t^{-1-p}, \quad p = 1, \quad t \gg 1/W_p \quad \ldots (6.9)
\]

which corresponds to a very slow time varying current.

The complete representation of the universal dielectric response in the time domain covering both dipolar loss peaks and strong low frequency dispersion associated with the charge carrier dominated system may be represented by

\[
I(t) \propto t^{-n}; \quad 0 < n < 2 \quad \ldots (6.10)
\]

with the exponent \( n \) taking value in different ranges at long and short time respectively [43]. There appears a process of thermal activation over the whole range of temperature. It is evident from Figures 6.11 to 6.18 that both charging and discharging currents obey the well known expression.

\[
I_a(t) = A(t) t^{-n} \quad \ldots (6.11)
\]

where \( I_a \) is the absorption current, \( t \) the time after application or removal of the external field and \( A(t) \) a temperature-dependent factor. It is found that discharging current has been characterized with logarithmic slope smaller in magnitude than 1 (\( n < 1 \)) during the range of short times, and
then goes to the longer time region (where the slope is steeper, with $n$ lying between 1 and 2). Similar to discharging, the charging current has also been found to be characterized with $n<1$, in short time region, however, at longer times this current tends to approach the steady state conduction current.

In the present case, $n$ values for shorter time region were observed to vary from 0.5-0.8 and for long time region these values are observed to vary from 1.53-1.78. Also, discharging currents vary linearly with the field strength characteristic of dipolar mechanism. These findings indicate that the dipolar polarization is operative in the present case. The dipolar polarization is further supported if the polar nature of PVF is considered. In PVF, CO group is rigidly attached to the main chain. The nature of current in the observed temperature range may thus be attributed to a dipole process involving structural units with a small dipole moment and a broad distribution of relaxation times, this predominates over any hopping mechanism. The partial dipolar nature of sample is expected to manifest itself in the form of a peak in the isochronals. The isochronals constructed from current-time characteristics are found to be characterized with a peak located at 65°C (Figures 6.19 to 6.28). It is expected that the current peak observed in the Tg range, of PVF corresponds to dipolar orientations due to molecular motions associated with the side chains.
Although the dielectric response is commonly associated with orientation of permanent dipoles, it is undesirable that hopping charges of either electronic or ionic nature may give rise to a very similar dielectric behaviour. The important distinction lies in the degree of localization of these carriers. An electron or an ion confined to hopping between two preferred positions is indistinguishable from a dipole, while a distinctly different situation arises where the carrier is free to execute hops over finite paths, some of which may eventually extend all the way from one electrode to the other. We have to consider four components of the current in such a system, (a) the current controlled by various polarization mechanisms, (b) the current controlled by the charging of the capacitor through a resistance, $R$, (c) the conduction current, which a hundredth of a second. The third component is due to formation of space charge. The residual former current is referred to as bulk current, which may be ionic, electronic or both [36]. Struik [44] showed that solid like polymers are not in thermodynamic equilibrium at temperatures below their glass transition. For such materials, free volume enthalpy and entropy are greater than they would be in equilibrium state. The gradual approach to equilibrium affects many properties, for example the free volume of the polymer may be decreased. The decrease in free volume lowers the mobility of chain segments and also charge carriers. The decrease in mobility may be expected to reduce DC conductivity. At higher electric
fields, the change in mobility may take place faster than at lower fields and recombination of charge carrier may be more.

The electrode polarization predicts the strong dependence of the electrode material on the decay of transient currents [45]. Moreover, uniform and electrode polarizations require the charging and discharging currents at a particular instant to vary linearly with charging field [46-48]. Furthermore, the superposition principle according to which the charging and discharging currents should be equal but opposite at equivalent instants is supposed to be valid in such type of polarization. However, in the case of space charge polarization the superposition principle is not obeyed and the charging and discharging currents depend more strongly on the applied field [37]. The convincing criterion of the validity of the superposition principle can be provided by the discharging and charging currents ratio of various times, where the charging current value is obtained by subtracting the steady state component [39]. A value of unity throughout the transients would indicate the origin of the transients due to uniform or electrode polarization. In the present case, the charging current continued to decay although slowly, even at the end of charging process. Under such circumstances, accurate estimation of steady state current was not possible and hence the reliable evaluation of discharging/charging ratio could not be made. However, the charging and discharging at various times after the application or termination of
charging field are found to follow the power law dependence on field. Log-log plots of charging and discharging currents and fields at different times (Figures 6.29 to 6.36) show that both charging and discharging currents reasonably follow a relationship $V^m$, voltage dependence with the power $m$ lying between 1 and 2. The log $I_d$ versus log fields plots for pure PVF at five different times show that the $I_d$ versus $V^m$ relationship, with $1 > m > 2$, is reasonably obeyed. The divergence from Ohm's law and failure of the superposition principle indicates the space charge formation. Thus, the observed currents can be best described in terms of space charge mechanisms [48].

The observed divergence from Ohm's law at moderate high electric fields and the thermal activation of discharge current at various prescribed times indicates the space charge formation. Polyvinyl formal is known to be weakly polar. The charging and discharging currents observed in PVF are also expected to show the behaviour of dipolar relaxation mechanism. In the case of transients governed by space charge, the peak in the current time curve should occur at a time

$$t_m = \frac{0.786d}{\mu E}$$

where $E$ is the applied field, $d$ is the sample thickness and $\mu$ the carrier mobility. To have a rough estimate of the time at which this peak should occur, we used the values of $d$, $E$ and $\mu$ to be $20 \, \mu m$, 100 kV/cm and $10^{-11} \, cm^2/V$. It was found that $t_m$ is approximately equal to $3.782 \times 10^3$ s. Thus, there is
possibility of space charge relaxation occurring at sufficiently longer times. The above considerations indicate that the observed currents in the present case may partially be due to dipolar orientation and partially due to space charge mechanism.

Discharging current measured at various prescribed times versus temperature plots are shown in Figures 6.19 to 6.28. It is clearly seen that the various isochronals are characterized by a single peak located at ≈ 65 °C. However, no shift is observed in the peak temperature with time of observation. It is observed that the peak temperature decreases with increasing time and is a characteristic of relaxation process. Similar qualitative behaviour is observed in the other samples. The isochronal peak is broad and probably it contains several minor processes, one of which may be associated with the glass transition of the polymer and the other may be due to thermal release of trapped carriers.

It is rather difficult to specify the origin of charging/discharging currents unambiguously from the time dependence alone. However, the various facts including the weak polar structure of polyvinyl formal, power law dependence of current on field, observed values of n, and thermal activation of current over a certain temperature range as observed in the present case indicate that the space charge due to accumulation of charge carriers near the electrodes and trapping in the bulk may be supported to account for the
observed current. The decay of current in the long time region for different samples indicate the existence of energetically distributed localized trap levels in the sample [23]. It seems that at shorter times only shallow traps get emptied contributing to stronger current. However, at longer times deeper traps with long detrapping times release their charges and the current decays at longer times. As temperature increases, mobility of carriers also increases, hence, all the deeper traps are filled. Release of a large number of charge carriers from the traps during the process may then result in high return rate of carriers leading to blocking of electrode causing a decrease in current. The charge injection from electrodes with subsequent trapping of injected charges in near surface region gives rise to homospace charge and the thermal release of charge carriers from the traps. Before the trapped space charge injected at higher fields is thermally released, a space charge barrier is presented to the electrode which suppresses the entrance of charge carriers into the sample. Thus, the observed current remains smaller than its corresponding value.

The bulk of the measurement of the transient currents in pure and iodine doped PVF samples were made with 20 μm thickness. A limited number of measurements, however, were made with samples of 5, 10 and 25 μm thickness over a temperature range.
The activation energy values for such isochronal peak are found to vary from 0.37 to 0.49 eV. The activation energy are found to decrease with time of observation. The value of activation energies agrees well with the activation energy obtained for TSDC peaks in the present case (Chapter 5) and is also reasonably compares with the activation energy value reported in the literature [41].

The polymer films are known to be a mixture of amorphous and crystalline regions. The presence of localized states may lead to the localization of injected charge carriers giving rise to the accumulation of trapped space charge [49]. The hopping mechanism is considered to lead to the increase in activation energy. However, in the present case, the activation energy is observed to decrease with increase in time. Such behaviour suggests that hopping of charge carrier is not expected in the present case.

As PVF is a weakly polar polymer, the probability that charge carries are present in it, the only charges could come from those injected through the electrodes. The injected charges are trapped at different trapping sites leading to a space charge which fundamentally influences all the transport phenomena and the effects at the electrode [40] space-charge-limited currents may also determine the transient behaviour, such as a large burst of current immediately after the application of voltage followed by a steady decline in

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current on standing. In the present study, the large currents obtained just after the application of voltage subsided to much smaller steady values after a certain length of time. When a metal, the work function of which is lower than that of dielectric, is brought into contact with it, a layer of electrons accumulates on the dielectric surface together with a positive charge on the electrode, giving rise to a space charge near the electrode. The space-charge layer accumulated will depend upon the relative difference between the work function of metal electrodes and the dielectric. The space-charge layers may further be modified because of surface states. On application of an electric field at a fixed temperature, the current was found to increase and then decrease with time, and finally attain a steady value [50].

Similarly, during the discharge cycle, at shorter time an instantaneous strong internal field will act on the sample giving a discharging current which decays at a faster rate. On the other hand, at longer times, when most of the absorbed charge has already decayed, the internal field becomes weak, giving a discharge current which decays at a slower rate.

Figure 6.47 shows the current-voltage (I-V) characteristics of PVF films at temperatures ranging from 40-70 °C. The observed increment in the current was approximately the same throughout the studied range of temperature. For all the temperatures, the thermograms, though non-linear, were similar. A slope of \( \approx 2 \) generally indicates
shallow trapping, although the possibility for the presence of deep traps in the present case, cannot be excluded. The log I-V plots showed the slope in the lower field region, upto 25 kV/cm, as 1. In contrast, in the higher field region, the value of slopes was greater than 1, but not exceeding 2. The slope value of 1, in the low-field region indicates that the electrical conduction in this region obeys Ohm's law. However, since the complete I-V characteristics were nonlinear, they indicate the presence of other modes of electrical conduction as well. The observed non-linearity could be due to build up of a space charge resulting in nonuniformity of field distribution between the electrodes. Moreover, the linearity of I-V curves in the high-field region indicates that either of the mechanisms, Schottky-Richardson or Poole-Frenkel, may be operative. However, the slope value ($\approx 2$) also indicates that space charge limited currents may also take part in this region.

On the basis of the various factors governing the variation of current with temperature, i.e. (i) nature of trap distribution in the sample, (ii) presence of impurity in the sample, and (iii) production of defects due to thermal excitation, O'Dwyer [52] suggested the presence of numerous isolated shallow traps covering an energy range $\Delta W$ below the continuum of free electron levels. Presence of deep traps, whose energy $W$ is between the conduction and valency levels, is also a possibility. While at sufficient low temperature
(absolute zero), all the trapped electrons would be in deep traps, at a finite temperature, and the presence of an applied field, some of these electrons can be excited into the shallower traps (or conduction levels), either thermally or due to action of the applied field. Under the influence of the applied field, these electrons participate in electrical conduction.

Our results indicate that with increasing temperature, the probability of thermal ionization of the trapping centres also increases, resulting thereby in a shift in the quasi Fermi level. This shift lowers the barrier across which electrons are transported, and the electrical conduction is ohmic. At low energy fields, fewer carriers are injected from the electrodes, and therefore the initial current is governed by the intrinsic free carriers in the materials. At higher-energy fields, the change of slope is suggestive of deviation from Ohm’s law based conduction to the space charge limited conduction. This mode of electrical conduction continues until the injected free carrier density. However, at sufficiently higher energy fields, the current is dominated by space-charge limited conduction and the conduction is mainly due to injected space charge [53]. The departure from Ohm’s law in high-energy fields is due to perturbation of active barrier even in the absence of thermal and chemical effects. Since, for our studies, the film thickness was very high (20 μm), the conduction mechanism by tunnelling is ruled out, which requires the film thickness to be very small.
The observed relation between the current and voltage points to a conduction mechanism in which the charge carriers are released by thermal activation over a Coulombic potential barrier that decreases with the applied electric field. The physical nature of such a potential barrier can be interpreted in two basic ways: (i) barrier between the electrodes and dielectric taking the classic image force into consideration (Schottky emission), and (ii) barriers due to trapping centres in the dielectric Poole-Frenkel (P-F) effect.

While the expression for the current density in Schottky emission is

\[ J_{SR} = A^* T^2 \exp(-\phi/kT) \exp\left[ e/kT \left( eE/4\pi\varepsilon \right)^{1/2} \right] \quad \ldots (6.12) \]

where \( J \) is the current density, \( e \) the electronic charge, and \( E \) the field applied at \( T \) (in K) and \( A^* \) and \( \phi \) are the Richardson constant and potential barrier, respectively at the metal-insulator interface in the absence of a field, the current-voltage relationship in Poole-Frenkel (P-F) mechanism is given by:

\[ J_{P-F} = CE \exp(-\phi/2kT) \exp\left[ e/kT \left( -eE/\pi\varepsilon \right)^{1/2} \right] \quad \ldots (6.13) \]

where \( C \) is the constant independent of field and temperature, and \( \phi \) is the barrier height.

To determine the actual conduction mechanism, the value of \( \beta \)-factor, at different temperatures, calculated from the slope of the plots of log \( I \) versus \( \sqrt{E} \) (Figure 6.49), were
compared with the theoretically calculated value of $\beta$, based on the assumption that one of the mechanisms was operating. The experimental values of $\beta$ (Table 6.1) in the present case, were close to the theoretically observed values of $\beta_{PF}$ based on the premise that P-F was the particular mechanism that was operating. Jonscher and Ansari [51] pointed out that instead of basing the distinction between the two mechanisms, on the magnitude of $\beta$, it should be based on studies taking an asymmetric M-I-M structure with two electrodes of different work functions. The current in the case of Schottky effect will be asymmetrical when polarities are reversed. On the other hand, it will remain practically unchanged in the case of P-F effect. Since it does not depend on potential barrier at the interfaces, i.e. the basic difference between them is: one is electrode-dependent and the other is not. This can be further substantiated by a study of thermally stimulated discharge currents as a function of polarizing field strength, to determine the actual conduction mechanism. Consequently, a graph of log I versus $\sqrt{E}$ was plotted for different electrode materials (aluminium, silver and copper) at 50 C, the other electrode being of aluminium in each case (Figure 6.47). Since a single straight line was obtained within the limits, RS mechanism can perhaps be ruled out.

But in the present investigation, the P-F model of conduction, in its conventional model assumes a field assisted thermal excitation of electrons from traps situated in the
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\beta_{RS}$ $\times 10^{-23}$</th>
<th>$\beta_{PF}$ $\times 10^{-23}$</th>
<th>$\beta_{exp}$ $\times 10^{-23}$</th>
</tr>
</thead>
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<tr>
<td>30</td>
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<td>7.898</td>
</tr>
<tr>
<td>40</td>
<td>4.376</td>
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<tr>
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<td>6.756</td>
</tr>
<tr>
<td>70</td>
<td>3.712</td>
<td>7.424</td>
<td>6.377</td>
</tr>
</tbody>
</table>
conduction band of insulators. Once the electron has acquired sufficient energy for reaching the conduction band, it is free to move unhindered and unobstructed. But Mott and Davis [54] pointed out that a drift mobility, less than about 1 cm²V⁻¹s⁻¹, can not correspond to this unhindered free-hand conduction. Taking this into account, a modified model for conduction was, therefore, proposed by Jonscher and Ansari [51] for substances of low mobility. This model involves the use of a large number of localized trap states, randomly distributed in space and energy. Mott and Davis [54] too conjectured the presence of trap states in disordered structures. In polymers, these traps may be a result of regular chain folding, their (chain) termination, the presence of crystalline-amorphous interfaces, chain entanglements, etc.

The low value of activation energy (< 1 eV) indicates the predominance of electronic conduction in the present case. The activation energy values decrease with the applied field, suggesting that the potential barriers are lowered due to the applied field. This suggests that the applied field interacts with the field of the ionizable centre so that the energy required for an electron to escape in a direction opposite to the field direction (i.e. in the field-assisted or 'forward' direction) is reduced by an amount [55,56].

The new model furthermore suggests that the process of field-assisted ionization of donor-like carriers, which is the basis of P-F mechanism, does not produce free carries in a
Fig. 6.51 - Activation energy verses square root of the applied field.
conduction band, as is normally considered to be the case, but merely causes hopping like movements of localized carriers in the trap levels. This process of hopping is assisted by the presence of an external field which reduces 'hop behaviour' by $\nu E^{1/2}$, where $\nu = (e^3/\pi \varepsilon \varepsilon_o)^{1/2}$, as given in the conventional P-F model. The revised expression can thus be written as:

$$I = I_0 \exp E(W_o - \nu E^{1/2})kT], \quad \ldots \quad (6.14)$$

where $W_o$ is the average barrier height of 'hops', $I_0$ the pre-exponential coefficient that may be defined as the current at an infinite temperature, $e$ the electronic charge, $\varepsilon$ the high-frequency dielectric constant and $\varepsilon_o$ the permittivity of space charge [57].

The activation energy values have been plotted against the square root of the field (Figure 6.51). The activation energy decreases with the applied field suggesting that the potential barriers are lowered with the applied field. A straight line is obtained. The intercept of the line at zero field gives the values of $W_o$ of $1.89 \times 10^{-19}$ J (1.18 eV). The slope yields value equal to $8.567 \times 10^{-23}$ J m$^{1/2}$ V$^{-1/2}$ which is in fair agreement with the theoretical value of $\beta_{PF}$. 

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REFERENCES


