CHAPTER V

TRANSIENT CURRENTS
IN CHARGING
AND
DISCHARGING MODES
5.1 INTRODUCTION

If we take a polymeric sample and apply a step field to it, the field interacts with the bound and free charge causing their motion. The motion of charges manifests itself as a current flow in the external circuit. Generally, this current known as absorption or charging current, depends on the time elapsed after the application of potential to the electrodes; usually it falls off at first and then becomes steady. After the step voltage has been removed, there is still a current flowing in the external circuit, which is called desorption of discharging current. We find that under isothermal conditions both absorption as well as desorption currents decay approximately in most of the cases as $t^{-n}$, where $t$ is the time elapsed after the application of the step voltage and 'n' is an exponent whose value may be greater or less than 1, depending upon the properties of the material chosen and the experimental conditions [1-12]. The discharge current may be the mirror image of the charging current except that a steady state current is not reached. The isothermal desorption current decays for a long time, depending upon the internal phenomena taking place irrespective of the steady state current level.

Desorption currents can yield much useful information about the charging process even when the corresponding absorption current is masked by the conduction current during charging. The analysis of the experimental conditions can lead to a quantitative as well as qualitative idea of the mechanisms. The results can be compared with some other
studies like thermally stimulated discharge current (TSDC), etc., to arrive at coherent and cogent conclusion. Transient current measurements are tedious - on being carried out over a long time is not a regular study but nevertheless it is a very useful one, giving far more consistent results than the others. This being so on account of electrical and other perturbing influences affecting the charging process far less than in other experiments involving decay processes.

The fact that electronic conduction plays a role in polymers has been established experimentally by Seanor [13]. To discuss electronic condition, it is necessary to investigate the generation of free carriers and their transport through the material.

In polymers at low temperature, the density of free charge carriers is extremely low and with an electric field, non-equilibrium conditions can be achieved, which can be easily enhanced by injecting a charge through an ohmic contact. Current-voltage curves is generally non-linear on account of two basic causes. At high fields the charges are accumulated between the electrodes. The density, energy distribution and nature of the traps have a determining influence on current-voltage characteristics which also depend on type of charges involved in the conduction process.

Trapping sites exert strong influence on the current flow, i.e. the concentration of free carriers and their mobility if the activation energy values are low 0.2 to 0.3 eV, hopping is contacted with charge jumps
brought about by motion of chain elements while great values (0.5 eV) the so-called trap hopping mechanism is involved.

5.2 TIME DEPENDENCE CURRENT MODELS

Many scientists have attempted to explain the mechanisms of the charging and discharging in polymers. A number of models incorporating charging and discharging related processes have been evolved to explain the mechanism. The important ones are given in succeeding subsections.

(a) Electrode polarisation:

Free charge are frequently available in the polymer bulk and have thermally activated mobilities. These charges move towards electrodes of opposite polarities on application of a polarising voltage and start piling up near the electrode. 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 has been observed that the isochronal current at constant field does not depend upon the thickness on the sample. The current fall is initially proportional to $t^{-1/2}$ followed by a steep change where $n > 1$. The charging and discharging currents are mirror images of each other [14,15].

(b) Dipole orientation:

Randomly arranged dipoles in the polymer bulk do not contribute any definite dipole moment to the polymer specimen. They possess a
definite relaxation time and activation energy, however, relaxation time is a thermally activated parameter. On applying an external electric field and raising the temperature, relaxation of dipole is activated and they start orienting in the field direction. Fast polarisation responds immediately to the orientational effect of the field. The rate of orientation is thermally activated as the relaxation time gradually decreases on increasing the temperature. Like accumulation of space charges, orientation of dipoles is also field dependent as more and more electrostatic force is available for dipole alignment on increasing the polarisation field. Image charges are induced on metal electrode surface during the orientation of dipoles, causing a net current to flow in the external circuit. The value of this current depends on the rate of dipole orientation and decreases gradually with time at a fixed temperature and field, thus causing fall in the value of absorption current with time. The exact behaviour of the decay of absorption current depends upon relaxation time, activation energy, distribution function and the experimental conditions. The current density of absorption current is unaffected by the specimen thickness and this type of polarisation is polar dielectrics is a volume or bulk phenomenon.

After removal of the polarising field, dipoles start disorienting to acquire their original configuration. The fast dipoles are disoriented earlier than the slow dipoles. The rate of depolarisation also depends on the temperature, maximum charge attained and some inherent properties like activation energy and distribution function. This again causes a definite
amount of desorption current to flow in the external circuit, which is expected to be a mirror image of absorption current provided that the value of steady state conduction current is negligible and the experimental conditions are identical to those during polarisation.

(c) **Hopping mechanism:**

In certain materials, a large number of localised states are present inside their molecular arrangement, with a wide distribution in their activation energy or trap depths. These states are usually filled by the charge carriers, which are electrons in most of the cases. On applying an external electric field, some of the charge carriers may jump from one localised state to another causing disturbance in the internal charge distribution. Hopping of the charge carriers is thermally activated as their mobility and detrapping from the traps increase with the thermal energy. However, field can play an important role in detrapping of charge carriers causing field assisted thermal excitation of impurity centres. It can also provide a directive force to the charge carriers. Thus, the absorption current in the process is expected to be field and temperature dependent. However, it is independent of the electrode material and the specimen thickness as the trapped charge carriers are intrinsic and uniformly distributed in the polymer bulk. The absorption and desorption currents are expected to be the mirror image of each other as the trapping and detrapping are perfectly reversible mechanisms [16,17]. Farriera and Morena [18] observed that a time dependent, effective medium,
approximation essentially explains the time behaviour of the polarisation reversals obtained in doped copolymers of vinylidene fluoride and trifluoroethylene.

(d) **Tunnelling model**:

This model [14,15] assumes the presence of the trap level (s) in the dielectric. It may so happen that the charge carriers may lack enough energy to overcome the potential barrier existing between the traps and hence take part in the current process. This model [19] assumes that an electron in a π-molecular orbital on one molecule, when excited to a higher energy level (in our case by application of an external field at a higher 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 levels which are deep and located well inside the and gap have been postulated. Deep traps have been reported [20] 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.

The tunnelling model points to a field (up to $10^5$ V/cm) and which is directly proportional to the isochronal current at moderate field (up to $10^5$ V/cm) and is inversely proportional to the thickness. The current is
strongly dependent on the electrode material and is independent of the
temperature. It is dependent on time as $I \propto t^{-n}$ with $0 \leq n \leq 2$ and the
charging and discharging currents are mirror images of each other.

(e) **Charge injection leading to trapped space charge effects:**

There are usually a high concentration of trapping sites in the
forbidden energy gap of polymer. These trapping sites are the outcome of
impurities or 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, their distribution depending upon the
energy and trap depths. The charges which get trapped inside the bulk
form a space charge, further oppose trapping of charge carriers. The
trapping process causes the charging current to flow while removal of the
external field produces the discharging current. Nagashima and Faria [21]
have developed a model for space charge migration in discharge current
measurements.

The space charge model 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. We find that the transient
current shows a field dependence, temperature effect and electrode
material dependence which is related to the charge injection mechanism
prevalent. The transient current is proportional to $t^{-n}$, where $0 \leq n \leq 1$ and the charging and discharging currents are totally dissimilar to each other.

The process of charging and discharging a polymer sample is a complex process which is attributed to the generation of the charge carriers. The charging and discharging processes exhibit electrical properties of a polymer dielectric and thus help in its better understanding. The current across a polymer dielectric immediately after applying a field is called the transient charging or absorption current and the same immediately after removing the field is called transient discharge or desorption current. Under isothermal conditions, charging and discharging currents decay approximately as $t^{-n}$, where $t$ is the time elapsed after the application of the field and '$n$' is the constant depending upon the properties of the material and the experimental conditions. The discharge current may be the mirror image of the charging current except that a steady state current is not reached.

The discharge current can yield very useful information about the charging process even when the corresponding charging current is masked by the conduction current during charging. The analysis of experimental conditions can lead to a quantitative as well as a qualitative idea of the mechanisms at work. The result can then be compared with some other studies like TSDC etc. to arrive at some useful conclusions.

Although many transient measurements have so far been made [22-24] and subjected to detailed analysis, the origin of charging and discharging currents is still afflicted with doubts and controversies. This is
because more extensive study on the effects of various parameters like field, temperature and electrode material is still desired. To take a step forward, i.e. to reach a clear, irrefutable and concrete explanation for the mechanisms involved in transient charging and discharging current flow, the present work takes up the studies of PVDF.

5.3 EXPERIMENTAL

The sandwiched sample (metal-PVDF-metal) was placed in a specially designed cell. The temperature of the cell was controlled with an accuracy of ± 1 K by adjusting the input voltage from the variac for which the calibration has been made. The d.c. voltage 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 40-70 °C, respectively. A fresh sample is used for each set of observation.

5.4 RESULTS AND DISCUSSION

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

The time dependence of the charging and discharging transient currents in polyvinylidene fluoride (PVDF) samples have been investigated over a period of time 1-80 min. The Figs. 5.1 to 5.30 show the variation of discharging transient currents with time at different temperatures, i.e. 40, 50, 60, 70 and 80 °C with polarizing fields of 10, 25, 50, 75, 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 discharging currents are, in general, characterized with two regions which are designated as the short-time and the long-time regions, respectively.

Figures 5.31 to 5.60 illustrate the charging characteristics of PVDF 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, 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.
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Al Electrode system.
Fig. 5.2

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 60, 70 and 80°C for Al-Al Electrode system.
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70, and 80°C for Al-Al Electrode system.
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 75 kV/cm with different polarization temperature i.e., 40, 50, 60, 70 and 80°C for Al-Al Electrode system.

Fig. 9.4

\[ E_P = 75 \text{kV/cm} \]  
[Al-Al SYSTEM]
Fig. 5.5
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70, and 80°C for Al-Al Electrode system.
Fig. 5.6

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Cu-Cu Electrode system.
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Cu-Cu Electrode system.

Fig. 5.7

$E_p = 25$ kV/cm

(Cu-Cu SYSTEM)
$E_p = 50 \text{ kV/cm}$

(Cu-Cu SYSTEM)

Fig. 5.8

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70, and 80°C for Cu-Cu Electrode system.
Fig. 5.9
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Cu-Cu Electrode system.
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Cu-Cu Electrode system.
Fig. 5.11
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Ag-Ag Electrode system.
Fig. 5.12
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Ag-Ag Electrode system.
Fig. 5.13
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μ m) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Ag-Ag Electrode system.
Fig. 5.14
Transient currents in Discharging mode for polvvinylidene fluoride sample (20 μm) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Ag-Ag Electrode system.
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Ag-Ag Electrode system.
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Sn-Sn Electrode system.
Fig. 5.17
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70.
Fig. 5.18

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Sn-Sn Electrode system.
Fig. 5.19
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Sn-Sn Electrode system.
$E_p = 100 \text{ kV/cm}$

(Sn-Sn SYSTEM)

Fig. 5.20

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Sn-Sn Electrode system.
Fig. 5.21

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Cu Electrode system.
**Fig. 5.2.2**

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Cu Electrode system.
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Cu Electrode system.
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) cooled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C.

Fig. 5.24
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Cu Electrode system.
Fig. 5.26

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al- Ag Electrode system.
Fig. 5.27
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Ag Electrode system.
Fig. 5.28

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70, and 80°C for Al-Ag Electrode system.
Fig. 5.29

Transient currents in Discharging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40°, 50°, 60°, 70° and 80°C for Al-Ag Electrode system.
Fig. 5.30
Transient currents in Discharging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al- Ag Electrode system.
Fig. 5.31
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Al Electrode system.
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Al Electrode system.
E_p = 50 (kV/cm)

(AL-AL SYSTEM)

Fig. 5.33
Transient currents in Charging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Al Electrode system.
Fig. 5.34
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Al Electrode system.

$E_p = 75 \text{kV/cm}$

(Al-Al SYSTEM)
Fig. 5.35
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Al Electrode system.
Fig. 5.36

Transient currents in Charging mode for polyvinylidene fluoride sample (20 \mu m) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Cu-Cu Electrode system.
Fig. 5.37

Transient currents in Charging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Cu-Cu Electrode system.
Fig. 5.38

Transient currents in charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40°, 50°, 60°, 70° and 80°C for Cu-Cu Electrode system.
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Cu-Cu Electrode system.
Fig. 5.40

Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Cu-Cu Electrode system.
$E_p = 10 \text{ kV/cm}$

(Ag-Ag SYSTEM)

**Fig. 5.41:** Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Ag-Ag Electrode system.
Fig 5.42.
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 25 kV/cm, with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Ag- Ag Electrode system.
E_P=50 kV/cm
(Ag - Ag SYSTEM)

Fig. 5.43
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Ag - Ag Electrode system.
$E_p = 75 \text{ kV/cm}$

(Ag-Ag SYSTEM)

Transient currents in Charging mode for polyvinylidene fluoride sample (20 $\mu$m) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Ag-Ag Electrode system.
Fig. 5.45

Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40°, 50°, 60°, 70°, and 80°C for Ag- Ag Electrode system.
$E_p = 10 \text{ kV/cm}$

(Sn-Sn SYSTEM)

 transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Sn-Sn Electrode system.
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Sn-Sn Electrode system.
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Sn-Sn Electrode system.
Fig. 5.49
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Sn-Sn Electrode system.
Fig. 5.50

Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Sn-Sn Electrode system.
Transient currents in Charging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al- Cu Electrode system.

Fig. 5.51

$E_p = 10 \text{ kV/cm}$

(Al - Cu SYSTEM)
Fig. 5.52
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Cu Electrode system.
Fig. 5.53

Transient currents in Charging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Cu Electrode system.
Fig. 5.54.
Transient currents in Charging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Cu Electrode system.
Fig. 5.55
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al- Cu Electrode system.
Transient currents in Charging mode for polyvinylidene fluoride sample (20 µm) poled with polarization field 10 kV/cm with different polarization temperature i.e. 40, 50, 60, 70, and 80°C for Al-Cu Electrode system.
Fig. 5.57

Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 25 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al- Ag Electrode system.
Fig. 5.58
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 50 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Ag Electrode system.
Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 75 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Ag Electrode system.
Fig. 5.60

Transient currents in Charging mode for polyvinylidene fluoride sample (20 μm) poled with polarization field 100 kV/cm with different polarization temperature i.e. 40, 50, 60, 70 and 80°C for Al-Ag Electrode system.
and the other mechanism is operative in the range of long-time with a 
decay constant of different value.

The temperature dependence of the transient currents in 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 2, 6, 10, 20, 40 
and 70 min are shown in Figs. 5.61 to 5.90. From these plots, it may be 
concluded that the currents show thermal dependence. Such isochronals 
are characterized by a maxima around 70±5°C.

Figures 5.91 to 5.120 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.

The observed results can be discussed in the light of the existing 
models of transient currents.

The Curie-von Scheweilder type of time dependence has been 
observed for many polymers with the index close to 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
Isochronal Characteristics curves of figures No. 5.1

Fig. No. - 5.61

Ep = 10 kW/cm
(Al-Al system)

Isochronal Characteristics curves of figures No. 5.2

Fig. No. - 5.62

Ep = 25 kW/cm
(Al-Al system)
Fig. No. - 5.63
Isochronal Characteristics curves of figures No. 5.3

Fig. No. - 5.64
Isochronal Characteristics curves of figures No. 5.4
Fig. No. - 5.67
Isochronal Characteristics curves of figures No. 5.7

Fig. No. - 5.68
Isochronal Characteristics curves of figures No. 5.8
Fig. No. - 5.69
Isochronal Characteristics curves of figures No. 5.9

Fig. No. - 5.70
Isochronal Characteristics curves of figures No. 5.10
 Isochronal Characteristics curves of figures No. 5.12

Fig. No. - 5.72

Fig. No. - 5.71

Isochronal Characteristics curves of figures No. 5.11
Fig. No. - 5.73
Isochronal Characteristics curves of figures No. 5.13

Fig. No. - 5.74
Isochronal Characteristics curves of figures No. 5.14
Isochronal Characteristics curves of figures No. 5.16

Isochronal Characteristics curves of figures No. 5.17

$E_p = 25 \text{ kV/cm}$

$E_p = 10 \text{ kV/cm}$
Fig. No. - 5.78
Isochronal Characteristics curves of figures No. 5.18

Fig. No. - 5.79
Isochronal Characteristics curves of figures No. 5.19
Fig. No. 5.80

Isochronal Characteristics curves of Sn-Sn SYSTEM
**Fig. No. - 5.83**
Isochronal Characteristics curves of figures No. 5.23

**Fig. No. - 5.84**
Isochronal Characteristics curves of figures No. 5.24
Fig. No. - 5.87
Isochronal Characteristics curves of figures No. 5.27

Fig. No. - 5.88
Isochronal Characteristics curves of figures No. 5.28
Fig. No. 5.90
Isochronal Characteristics curves of figures No. 5.30

Fig. No. 5.89
Isochronal Characteristics curves of figures No. 5.29

Ep=100 kV/cm
(A1-Ag SYSTEM)

Ep=75 kV/cm
(A1-Ag SYSTEM)

Temperature (°C)

Discharging Currents (Amp)
Fig. No. 5.91
Initial rise plots of Fig. No. 5.61

Fig. No. 5.92
Initial rise plots of Fig. No. 5.62

Fig. No. 5.93
Initial rise plots of Fig. No. 5.63

\( E_p = 10 \text{kV/cm} \) (Al-Al SYSTEM)

\( E_p = 25 \text{kV/cm} \) (Al-Al SYSTEM)

\( E_p = 50 \text{kV/cm} \) (Al-Al SYSTEM)

DISCHARGING CURRENTS [AMP]

TEMP. \((10^7 T) K^{-1}\)

(min)

2

6

10

20

40

70
Fig. No. 5.94  
Initial rise plots of Fig. No. 5.64

Fig. No. 5.95  
Initial rise plots of Fig. No. 5.65

Fig. No. 5.96  
Initial rise plots of Fig. No. 5.66
Fig. No. 5.97
Initial rise plots of Fig. No. 5.67

Fig. No. 5.98
Initial rise plots of Fig. No. 5.68

Fig. No. 5.99
Initial rise plots of Fig. No. 5.69
Fig. No. 5.100
Initial rise plots of Fig. No. 5.70

Ep = 100 kV/cm (Cu-Cu SYSTEM)
(min) 2 6 10 40 70

Fig. No. 5.101
Initial rise plots of Fig. No. 5.71

Ep = 10 kV/cm (Ag-Ag SYSTEM)
(min) 2 6 10 40 70

Fig. No. 5.102
Initial rise plots of Fig. No. 5.72

Ep = 25 kV/cm (Ag-Ag SYSTEM)
Fig. No. 5.103
Initial rise plots of Fig. No. 5.73

Temp (10^3/T) K'

Discharging Currents (Amp)

Ep = 50 kV/cm
(Ag-Ag SYSTEM)
(min)
2
6
10
20
40
70

Fig. No. 5.104
Initial rise plots of Fig. No. 5.74

Temp (10^3/T) K'

Discharging Currents (Amp)

Ep = 75 kV/cm
(Ag-Ag SYSTEM)
(min)
2
6
10
20
40
70

Fig. No. 5.105
Initial rise plots of Fig. No. 5.75

Temp (10^3/T) K'

Discharging Currents (Amp)

Ep = 100 kV/cm
(Ag-Ag SYSTEM)
Initial rise plots of Fig. No. 5.82

Initial rise plots of Fig. No. 5.83

Initial rise plots of Fig. No. 5.84
Fig. No. 5.118
Initial rise plots of Fig. No. 5.88

Fig. No. 5.119
Initial rise plots of Fig. No. 5.89

Fig. No. 5.120
Initial rise plots of Fig. No. 5.90
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, tunneling 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.

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 [25] 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 inherents 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.

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

\[ I(t) \propto t^{-n}, \quad 0 < n < 1; \quad t << 1/W_p \]  \hspace{1cm} \text{(5.1)}

i.e. the frequencies which are larger than the loss peak frequency \( W_p \), and for the long time region

\[ I(t) \propto t^{-1-p}, \quad 0 < n < 1; \quad t >> 1/W_p \]  \hspace{1cm} \text{(5.2)}

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

$$I(t) \propto t^{-1-p}, \quad p = 1; \quad t \gg 1/W_p$$

... (5.3)

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

$$I(t) \propto t^{-n}, \quad 0 < n < 2$$

... (5.4)

with the exponent $n$ taking value in different ranges at long and short time respectively [26]. There appears a process of thermal activation over the whole range of temperature. It is evident from Figs. 6.11 to 6.18 that both charging and discharging currents obey the well known expression.

$$I_a(t) = A(t) \cdot t^{-n}$$

... (5.5)

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 nature of current in the observed temperature range may attribute 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 around 75°C.

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. Struijik [27] 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 [28]. Moreover, uniform and electrode polarization require the charging and discharging currents at a particular instant to vary linearly with charging field [29-31]. 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 [32]. 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 [33,34]. 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 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.

The charging and discharging currents observed in PVDF 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

\[ t_m = \frac{0.786 d}{\mu E} \]  \hspace{2cm} \ldots (5.6)

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 \( d, E \) 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 $3.782 \times 10^{-4}$ 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 Figs. 5.10 to 5.30. It is clearly seen that the various isochronals are characterized by a single peak located at $\sim 75^\circ$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 polyvinylidene fluoride, 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. 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 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 [35]. 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 PVDF is a polar polymer, the probability that charge carriers 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 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 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 [36].

Similarly, during the discharging 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 [37].

The activation energy values for such isochronal peak are found to vary from 0.57 to 0.69 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 4).
REFERENCES


