CHAPTER IV

ELECTRICAL CONDUCTION
4.1 INTRODUCTION

The subject of transport of carriers through thin insulating films has been the subject of intensive theoretical and experimental investigation. In spite of large number of reports on it\textsuperscript{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\textsuperscript{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\textsuperscript{7,8} which depends upon -
A- thermally generated carriers within the material and
B- 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\textsuperscript{9-24} operating through the dielectric metal boundary. As a consequence different workers have reported\textsuperscript{25-27} different conduction mechanisms for the same material\textsuperscript{28-30}. The study of electrical conduction has become important in the investigation of conduction mechanism in the solids\textsuperscript{31}. For a complete understanding of electrical conduction following mechanism are to be understood.
4.2 EXTRINSIC NATURE OF CONDUCTIVITY

It is believed that the observed conductivity in thin insulating films is often due to extrinsic rather than intrinsic carriers. This is implied from the fact that the insulators are characterised with a forbidden band gap of energy \( \geq 4.0 \text{ eV} \). The current density observed in insulators at any temperature on the application of an electric field is much higher than that expected from such a wide gap material. The activation energy associated with conduction of carriers is usually less than half the band gap.

In order to understand the nature of conduction following mechanisms are to be understood.

(A) Energy band structure of the material.
(B) Carrier generation or modulation of charges.
(C) Trapping and recombination.
(D) Mobility of the charge carrier.

(A) ENERGY BAND STRUCTURE OF THE MATERIAL

Polymers have a specific structure which in its turn affects the conduction mechanism. Effect of structural defect, for example, molecular weight, presence of side groups, degree of crystalinity etc. Each polymer has very large number of gaint molecules or macro molecules which have a large number of recurring structural unit called monomers that are tightly bound together by strong covalent bonds. The macro molecules are in the form of long chains and can change their relative orientations easily because relatively much weaker Vander Wall’s type of forces hold them together. Thus there are two types of bonds in a polymer, namely strong intramolecular bonds with an activation
energy of 4 to 8 eV and weak intermolecular bonds with very low activation energy. The intramolecular bonds give rise to a valence band that is full of electrons in the absence of an electron acceptor and a normally empty conduction band. Both these bands are expected to be wide; more than 1 eV in view of strong overlap of the wave-functions corresponding to intramolecular bonds. The much weaker intramolecular bonds must result in very narrow bands which need not be either completely empty or full. The separation of which is also much smaller than intermolecular band gap. In addition the structural disorders resulting from chain folding, chain terminations and from amorphous matrix between crystallites will produce localized states which may be distributed in space and energy and may get occupied by electrons.

Low conductivity and large activation energy is a result of intermolecular interaction which is supposed to give electron conduction. It is molecular orbital overlap. The orbital overlap is molecular structural dependent and semi-conduction arises from it. Then activation energy will also be structural dependent such as ionization energy, electron affinity and excitation energy of triplet-state transition (Figure 4.1).

Polymers have a specific structure, which in turns affects the conduction mechanism. The conduction mechanism in polymers can not be explained, on the basis of band theory because (i) Polymers are weakly bonded materials because the molecules are held together by weak Vander -Wall forces. The overlapping of molecular orbitals is very small. (ii) They are heterogenous in nature and their structure is not
periodic (figure 4.1).

Therefore, their energy bands are very narrow and there is a disorder in energy levels\textsuperscript{37,38}. For the trapping charge carriers, these disordered energy levels, lead to the localized states\textsuperscript{39}. The number of charge carriers which contribute to the conduction depends on the number of trapping sites between conduction and valance bands and also on the trap levels of these bands.

However, from purely thermodynamic considerations, the estimates for the energies of the levels taking part in conduction in organic solids can still be obtained\textsuperscript{40} from a knowledge of the energies of the ionised states. According to this scheme, the energy $E_c$ required to produce a pair of free carriers, where the electron is not attached to any molecule or to any hole, is given by

$$E_c = 2 I_c - I_g \quad \ldots \quad (4.1)$$

Where $I_c$ and $I_g$ are the ionisation energies of the crystal and the gaseous molecules respectively.

(B) CARRIER GENERATION OR MODULATION OF CHARGE

Frenkel excitons produced by absorption of light in semiconductor becomes a source of an electron-hole pair\textsuperscript{41}. This absorption of light energy is connected with migration of energy. The excitons thus formed are capable of hopping causing diffusion through the crystal. An electron hole pair can be generated from excitons by autoionization\textsuperscript{42} or excitation induced by phonons or photoionization\textsuperscript{43,44} induced by photons or by interaction with electrodes\textsuperscript{45-50} at the surface of the crystal. It is suggested on the basis of experimental studies\textsuperscript{51,52} carried out on the
FIG 4.1 - ENERGY BAND STRUCTURE OF POLYMERS
dissociation of excitons that at the organic crystal-metal interfaces the electron affinity may affect the location of dislocation sites in the crystal. Evidently conduction cannot take place in either the filled or the empty bands unless additional carriers are introduced because of large band gap of material. Thus one has to consider the possibility of generation of charge carriers in terms of injection from electrodes.

4.3 THEORIES OF ELECTRICAL CONDUCTION

Though the injection (or emission) of charge carriers from contacts (electrodes) was realized many year ago, the importance of this process to explain the conduction in polymers has been realized only recently. In the recent years there are a number of reviews and articles to explain the conduction mechanism in polymers.54-77 Several investigators invoked different type of mechanisms such as –

(i) Schottky Richardson emission.  (ii) Poole-Frenkel effect.
(iii) Space charge limited current.  (iv) Ionic conduction.
(v) Electronic conduction.  (vi) Tunneling current.
(vii) Hopping conduction.

4.3-1 SCHOTTKY- RICHARDSON EMISSION

In the presence of an electric field the barriers profiles are altered. When high electric field exists at a metal insulator interface, it interacts with the image force and lowers the potential barrier and Schoottky emission of electrons may occur from the metal contact of negative potential into conduction band of insulator[figure (4.2)]. It is called Schottky-Richardson current. Such effect is referred to as Schottky-Richardson
Fig. 4.2: The Schottky effect. Reduction in barrier height \((\Delta \phi_S)\) on application of the applied field \(\vec{F}\) due to the image charges operative in the distance \(x_0\).
emission (SR emission). The expression for current due to SR emission is given \(^70,71,73,78\) by

\[ I = A S T^2 \exp \left[ -\phi_s/kT + B_{SR} V^{1/2} \right] \]  \hspace{1cm} (4.2)

where \( B_{SR} \) is Schottky field lowering constant

\[ B_{SR} = 1/\left[ kT \left( e^3/(4\pi\varepsilon_0\varepsilon_r d) \right)^{1/2} \right] \]  \hspace{1cm} (4.3)

\[ e \text{ - Electronic charge} \quad \varepsilon_0 \text{ - Permittivity of free space.} \]
\[ A \text{ - Richardson's constant} \quad T \text{ - Absolute temperature} \]
\[ K \text{ - Boltzmann constant} \quad V \text{ - Applied voltage.} \]
\[ S \text{ - Surface area of the sample} \]
\[ \varepsilon_r \text{ - High frequency dielectric constant of the material.} \]

The first term of equation (4.2) represents the Richardson's equation.

\[ I = A S T^2 \exp \left[ -\phi_s/kT \right] \]  \hspace{1cm} (4.4)

**GRAPHICAL METHOD:**

The equation (4.2) predicts a linear relationship between \( \log I \) and \( V^{1/2} \) (or \( \log J \) and \( E^{1/2} \)). If the graphs shows linearity, one can expect Shottky emission. It is generally possible at high temperature and high field\(^71-74\). Further barrier height \( \phi_s \) can be calculated from the slope of \( \log I/T^2 \) Vs \( 1/T \) and the slope \( B_{SR} \) is given by equation (4.3).

It is possible to distinguish injection current from detrapping phenomenon, by using electrodes of different work function. Recent observations \(^79-86\) have shown existence of this mechanism in their respective studies.

**4.3-2 POOLE-FRENEKEL EFFECT**

Poole-Frenkel \(^87-91\) effect is similar to Schottky emission. The only difference is that the electrons are excited thermally \( (F_{4.3}) \) from traps in the conduction band of the insulator. The PF effect...
Fig. 4.3: The Poole-Frenkel effect. Reduction in coulombic potential ($\Delta \phi_{PF}$) on application of the applied field ($F$). Here $E_d$ is the trap depth below the conduction band.
is more pronounced when donor like traps (electron liberation) are present in the bulk of the insulator which are neutral when occupied by an electron. Even if some holes are liberated from acceptors like centres, their contribution to the total current is usually very small owing to their much lower mobility and greater mass. Due to immobility of the positive charges associated with the trap, barrier lowering in Poole-Frenkel is twice than that in case of Shotky effect.

The expression for the current due to Poole-Frenkel effect is given by

\[ I = A S T^2 \exp \left[ \frac{\phi_{PF}}{kT} + B_{PF} V^{1/2} \right] \]  \hspace{1cm} (4.5)

where \( B_{PF} \) - field lowering constant, \( \phi_{PF} \) - Trap depth

Other notation have the same significance as in (4.1.1).

For a simple process - \( B_{PF} = 2 \beta_{SR} \) \hspace{1cm} (4.6)

However, certain reports have shown that \( B_{PF} \) becomes comparable to \( \beta_{SR} \). The distinction between the two processes may be using different electrodes because SR emission is electrode dependent whereas PF effect is not. PF effect has made important contribution in pure and doped polymeric systems. It has some basic drawback of not recognizing the details of the shape and range of the potential well and microscopic mechanism of the carrier escape. It also predicts linear relationship between \( \log J/V \) and \( V^{1/2} \).

4.3-3 SPACE CHARGE LIMITED CURRENT

The surface charges on the interface of a micro-crystalline solid and electrodes may give rise to an apparent volume space
charge\textsuperscript{107}. The space charges are certainly present near the electrodes whenever a field is present and they decay when the field is switched off \textsuperscript{108-109}. These charges oppose the applied voltage and impede the electron flow. Mutual repulsion between the individual charge limits total charge injected into the sample and thus resulting current is said to be space charge limited current (SCLC). The following two conditions must be satisfied.

I- One electrode must make ohmic contacts with insulator out of two electrodes. By a suitable choice of electrodes, the type of carriers injected can be controlled.

II- The insulator should be free from trapping effects relatively.

A second cause of space charge is the existence of traps within the solid. The traps may be any localized state within the energy gap associated with impurities, disorder or molecular nature of the polymer. Space charge may also accumulate for other reasons, such as partially blocking electrodes or because one type of carrier is much more mobile than the other.

Space charge limited current is independent of the mechanism of the carrier generation and depends only on the transport and trapping of the carriers within the crystals. The complete mathematical analysis of time-independent space-charge current is so complex that no explicit explanation has yet been obtained. Mott-Gurney\textsuperscript{24} were the first to emphasize the importance of an injecting contact between a metal and an insulator. They provided an expression relating current density $J$ and applied voltage $V$ for a trap-free insulator which is given by

100
\[ J = \frac{9}{8} \varepsilon_0 \varepsilon' \mu \frac{v^2}{d^3} \quad (4.7) \]

Where \( \mu \) is depole moment and remaining quantities have the same significance as in (4.3.1).

If there are traps in the insulator, the space charge limited current may be decreased by several orders. Rose and Lampert 110-113 provided a modified equation, with a trap limiting factor (\( \Theta \)) which is the ratio of trapped charge to free charge.

The expression for current density is given by

\[ J = \frac{9}{8} \varepsilon' \varepsilon_0 \mu \Theta \frac{v^2}{d^3} \quad (4.8) \]

Assuming that the carriers are trapped at shallow traps of average depth \( E_T \) that remain in the thermal equilibrium state with the concerned band and \( \Theta \) is given by

\[ \Theta = \frac{n_{\text{eff}} \cdot \exp(-E_T/kT)}{N + n_{\text{eff}} \cdot \exp(-E_T/kT)} \quad (4.9) \]

Where \( n_{\text{eff}} \) is the density of states in the conduction band and \( N \) is the density of traps. Assuming \( N \gg \exp (-ET/kT) \) then \( \Theta \) becomes

\[ \Theta = \frac{n_{\text{eff}} \cdot \exp(-E_T/kT)}{N} \quad (4.10) \]

Substituting \( \Theta \) in equation (4.8)

\[ J = \frac{9}{8} n_{\text{eff}} \cdot \exp(-\frac{E_T}{kT}) \cdot \frac{\varepsilon_0 \varepsilon' u}{N} \frac{v^2}{d^3} \quad \ldots \ldots \ldots \quad (4.11) \]

This equation suggests that SCLC in solids depends on the carrier transport 114-115 and trapping and is independent of carrier generation.

Muller 116 solved the theory of SCLC without taking any
assumptions of blocking electrodes. Also other reports are available for existence of SCLC in sugar can wax\textsuperscript{117}, Naphthalene\textsuperscript{118} Xanthene\textsuperscript{119} and photosensitive SCLC in Teracene\textsuperscript{120} Recently, the existence of SCLC and the influence of temperature in many organic solids have been reported by Swarakowski\textsuperscript{120}, Szymanski et al\textsuperscript{121-123} and Khare et al\textsuperscript{124}.

4.3.4. IONIC CONDUCTION

Ionic conduction occurs in polymers which contain ionic groups or to which ionic materials have been added. In these materials absorption and / or adsorption of water plays a dominant role because water may act as a source of ions, as a high dielectric impurity or as a local structure modifier. In amorphous polymers it can also occur due to the drift of defects on the application of an electric field. Though the phenomenon is best understood only in alkali-halides\textsuperscript{29} the process has been invoked to expalin the high field and high temperature effects in organic molecular solids\textsuperscript{125-126} and polymers\textsuperscript{127}. The special features of ionic conduction are\textsuperscript{128}.

I- activation energy being very large in comparison to electronic activation energy.
II-noticeable polarisation effect (current decay) under d.c.field
III-transport of ionic species from one electrode to the other (this being a microscopic effect need not be experimentally detectable).
IV- the large transit time for the ions. (It should, however be noted that the transit time of holes and electrons are equally large in organic materials).
Like in the electronic conduction in materials with defects centres, the ionic conduction also exhibits different slopes in the $\log J$ Vs $1/T$ or $\log J/T^2$ Vs $1/T$ plots. Activation energies at higher temperatures are higher than at lower temperatures.

4.3-5. ELECTRONIC CONDUCTION

Higher activation energy and small electrical conductivity of organic solids suggest that some kind of intermolecular interaction takes place within solids. It gives rise to electronic conduction in presence of an electric field. This interaction is molecular orbital overlap which is a function of molecular structure. The properties of molecular structure correlates with activation energy of those semiconductor which arises from such overlap. The properties are molecular ionization energy, electron affinity and excitation energy of the ground triplet state transition, and one of the entities which influences these properties is the number of more easily polarizable electrons.

4.3-6 TUNNELING CURRENT

If the electrode contact is ohmic, the applied field is very high and thickness of the film is less than $100\,\text{Å}$, then the width of the potential barrier decreases to such an extent that the probability of finding an electron on the other side of the potential barrier by quantum mechanical tunneling increases.

The Fowler-Nordheim equation.

$$I = AV^2 \exp\left(-\frac{\phi}{V}\right)$$

(4.12)

Describes tunneling current for a simple case and predicts a
linerar relationship between log (I/V^2) and (1/V). The tunneling current is temperature independent.

Eley and Parfitt where the first to suggest this model and later on Eley et al proposed semiconduction mechanism in molecular crystals. Several authors have discussed the formulations of tunnel equations. Sommerfield and Bethe, Holm and Krischstein and others simplified barrier height. Simons generalised it for symmetric and asymmetric potential barrier.

4.3-7 HOPPING CONDUCTION

The process in which a charge carrier crosses the potential barrier between two molecules by moving over the barrier through an activated state is called Hopping. Such a mechanism is well known in 3-d transition metal oxides which have a very little mobility that increases exponentially with temperature.

According to this, the conduction in polymeric systems should be interpreted as the conduction by localized carriers which undergoes hopping like motions from one localized state to the next and are supposed to spend most of their time in localized states. The carriers may be electrons or polarons (the carriers plus its region of polarization). If the charge carrier spends more time in a lattice site, than the period of vibration of the molecule or atom, the medium gets sufficient time to relax around the charge carriers. The effect is to reduce the mobility of charge carriers and to increase the effective mass. Depending upon the coupling between the electrons and lattice phonons, the effective mass may be increased so greatly that the electron trap itself within the region of polarized dielectric.
When this occurs, the motion involves thermally activated hops and mobility is given by

$$\mu = \mu_0 \exp \left( -\frac{w}{kT} \right) \tag{4.13}$$

where $\mu$ is the activation energy for charge carriers mobility. The expression was presented by Mott $^{146}$ and Boer $^{147}$ separately with

$$\mu_0 = e \psi a^2 / kT \tag{4.14}$$

where $\psi$ describes the wave function overlap $a = N^{-1/3}$ is the hop distance ($N$ is density) and $e$ is the electronic charge $\nu$ is the lattice frequency.

4.4. FACTORS AFFECTING CONDUCTIVITY

The factors which affect the electrical conductivity of polymers are given below:

4.4-1 PRESSURE

Akamotu and Inokuch $^{148}$ found that conductivity increases with increase in pressure up to 80 atmosphere after that the conductivity remains constant.

4.4-2 FIELD

Poole $^{149}$ has reported exponential variation of conductivity with field, while Joffe $^{150}$ states that it is only the steady state conductivity which increases with field and the true conductivity is independent of field. According to power law

$$I = a \nu^m \tag{4.15}$$

where $a$ and $m$ are constants, depends upon electrode material and dielectric constant. When $m = 1$, the conduction is ohmic and when $m = 2$ $^{151}$, a SCLC flows through a trap free insulator. Values of "$m$" are given by equation.

$$m = T_c / T + 1 \tag{4.16}$$
If the traps are present within the insulator, where $T_c$ is a temperature characteristic of distribution of traps at room temperature $T$. Departure from Ohm's law at high field occurs as a result of perturbation of activation barriers. Conductivity then increases in high field region. Frohlich\textsuperscript{152} on the basis of interaction between trapped electrons suggests the following equation.

$$\sigma = \sigma_0 \exp \left[ \frac{V}{\Delta V} \left( \frac{F^2}{eF_m^2} \right) \right] \quad (4.17)$$

where $V$ - Potential barrier of trapped electrons.

$\Delta V$ - Energy barrier of the average exited trapped electrons

$F_m$ - Intrinsic field strength, $F$ - Field.

The measurements on soda glass\textsuperscript{153-164} and varnish films\textsuperscript{155} are in qualitative agreement with this theory.

O'Dwyer\textsuperscript{156} has modified Frohlich's theory and showed that the conductivity also depends on space charge. He gave a new expression -

$$\sigma = \sigma_0 \left( 1 + \frac{n}{n_o} \right) \exp \left( \frac{V}{\Delta V} \cdot \frac{F^2}{eF_m^2} \right) \quad (4.18)$$

where - $n$ - Density of conduction electrons

$n_o$ - Density of space charge electrons

4.4-3 TEMPERATURE

Organic polymers being semiconductors show a rise in their electrical conductivity with increase of temperature and in most of the cases\textsuperscript{72,74-76} exhibit an exponential temperature dependence of the form\textsuperscript{157}

$$\sigma = \sigma_0 \exp \left( -\frac{E}{kT} \right) \quad (4.19)$$

where, $E$ - activation energy of conduction, $\sigma$ - conductivity

$\sigma_0$ - pre-exponential factor, $k.T$ - have their usual meaning
When \( \log \sigma \) Vs 1/T curves are plotted they show two regions one at high temperature which depends upon the material. The whole conductivity curve is a superposition of two or more curves \(^{158}\) given by

\[
\sigma = \sigma_1 \exp(-E_1/kT) + \sigma_2 \exp(-E_2/kT) \tag{4.20}
\]

where \( \sigma_1 \) and \( \sigma_2 \) are pre-exponential terms. The first term has a small co-efficient and small activation energy and predominate at low temperature, while the other has large co-efficient and high activation energy and is predominant at high temperature.

### 4.4-4 THICKNESS

There are considerable evidences \(^{159-160}\) regarding the dependence of electrical conductivity of sample thickness. Wright\(^{161}\) found that current varies as the inverse cube of the thickness.

\[
I = a \left( \frac{1}{d^3} \right) \tag{4.21}
\]

where (a - constant, d - thickness)

Bashara and Dotty\(^{162}\) suggested that space charge limited currents increases with thickness.

### 4.4-5 HUMIDITY

Many workers\(^{163-167}\) have found that humidity cause the conductivity to increase with field strength. Moisture affects\(^{168}\) the conductivity in two ways.

1. It increase the dielectric constant.
2. It brings about the departure from ohm's law in high fields.

Manthia et al\(^{169}\) have concluded the increase in conductivity with humidity.
4.4-6 IMPURITY

The electrical conductivity of organic compounds is extremely sensitive to the presence of impurities. The conductivity itself could be used as a measure of purity provided the absolute value for a given material is known. It was found that the presence of two slopes in log rVs 1/T plots is indicative of an impure specimen since further purification gives rise to single slope. Pick and Wissmann showed for naphthalene that the activation energy depends on the presence of the impurity. Impurity incorporation in PS has been the subject of many workers. All of them have reported increase in conductivity with dopant.

4.4-7 ELECTRODE MATERIAL

Values of the measured current have a great dependence on the nature of the electrodes. Electrodes are considered ideal if they do not react chemically with the material and are unaffected by variations of temperature, field. It should introduce no resistance in the flow of current. Improper matching of the electrode-semiconductor contact causes spurious results due to unsuitable work function. The I-V characteristic of a semiconductor depends on the electrode-semiconductor work function. The properties of contacts are governed by surface states which determines the work function between the contact and the substance. It also determines that whether a charge carrier would pass from the contact into the surface and vice-versa. In case of SR mechanism electrode play an important role, while in case of PF mechanism, most of the carriers are generated within the bulk of the material and therefore electrode effects.
become insignificant.

4.5. PRESENT AND LAST DECADE'S WORK

Electrical conduction behaviour of a variety of polymers has been investigated in the last decade by several workers 177-184. A wide range of electrical behaviours of polymers has been encountered which shows the complexity of the conduction mechanism.

The studies of electrical conductivity of these polymer films would enable us to understand their behaviour with temperature and the nature of conduction mechanism prevalent in them. A number of workers have investigated the nature of conduction mechanisms in a variety of polymers. Excellent reviews dealing both theoretical and experimental results appeared in the literature 185-187. A brief review of the work reported in the literature is given below.

Bashara and Doty 188 studied the current voltage characteristics and resistivity measurement in very thin polybutadiene films of thickness range 100 to 500 Å. It was found that the space charge limited conduction mechanism was the dominant mechanism in them. It was observed that the tunneling takes place through the interface partly.

Lengye 189 studied the voltage-current characteristics and conductivity measurements of polyethyleneterephthalate and polyvinyl formal films prepared by vacuum evaporation method, in the temperature range 40 °C to 120 °C. The above two material films displayed the familiar Richardson Schottky characteristics for fields between 20 to 200 kV/cm and temperatures 25 to 100 °C. Lilly et al 190 studied the high field (2-1400 kV/cm)
conduction in mylar and teflon films of thickness range from 1 to 10 mils as a function of temperature (70 -163 C). In the above films, the Schottky theory was found to be responsible for conduction mechanism by two space charges, ionic and electronic, each dominant at a different field level.

Davies\textsuperscript{191} studied the carrier transport in iodine doped polythene films which were sandwiched between two metal electrodes, the film thickness was approximately 1 mm. It was observed that the presence of iodine has increased the carrier mobility over the pure film.

Babcock and Christy\textsuperscript{192} studied the electrical capacitance, conductance and photo conductance of tetramethyl tetraphenyl trisiloxane thin films of thickness 150Å\textsuperscript{O} formed by electron bombardment, on glass substrates in the sandwich configuration. They have successfully explained the conduction mechanism by field assisted thermal ionization of donors heavily compensated by acceptors.

Gupta and Barbarez\textsuperscript{193} measured the D.C. conductivity of polyethylene films over a thickness ranges 25-75 μm in sandwich configuration. The results were applied to a model proposed by Adachi et al\textsuperscript{194} and good agreement was found between experimental results and the model.

Gazso\textsuperscript{195} studied the variation of electrical conduction with applied voltage in vacuum deposited polyethylene films 2000 Å\textsuperscript{O} thick, in the sandwich configuration. He also studied the effect of irradiation by gamma rays on the conduction of polyethylene films.
Boonthanom and White\textsuperscript{196} studied D.C. and A.C. electrical conductivities in the polyethylene polymer films with copper dispersed in its matrix. They observed the large increase in electrical conductivity due to doping with copper. The results were explained by the mechanism of hopping traps in localized states close to Fermi level.

Kryszewski and Swiatek\textsuperscript{197} studied the current voltage characteristics of polyvinyl carbazole and polystyrene films prepared by glow-discharge method. The studies were made over a temperature range 290-373K. They found that above room temperature, conduction was controlled by surface limited and bulk limited depending on the electrical field strength.

Suzuki et al\textsuperscript{198} studied the electrical conductivity and Hall effect on vacuum deposited thin films of polyacrylonitrile and made them semi-conductive by heat-treatment in nitrogen atmosphere. The results suggested that the conduction should be understood in terms of hopping transport of charge carriers in the localized states.

Rastogi and Chopra\textsuperscript{199} studied the current-voltage characteristics of pure and iodine doped polyvinyl chloride in films prepared by solution growth technique, both in sandwich and surface configuration over a temperature range 120-400 K. In the case of pure films, the conduction was ascribed to hopping mechanism at low temperatures and at high fields and at high temperatures to Schottky emission mechanism. The electrical resistivity of polyvinyl chloride films decreases considerably by the addition of iodine. They also found that the activation
energy depends upon the type of configuration in which the studies were made.

Vollmann and Poll\textsuperscript{200} studied the current-voltage characteristics in thin polymer fluoro-carbon films with thickness between 0.02 and 1.5 pm deposited by different methods and with different contact materials. They observed the uniform conduction mechanism over the entire field strength and does not depend on the method of preparation and the contact materials. The results were interpreted by means of a modified Poole-Frenkel effect for insulators with high impurity density.

Desbarax et al\textsuperscript{201} studied the electrical conductivity of current-voltage characteristics of polysiloxane thin films formed by glow-discharge method. They observed that in the steady state, Poole-Frenkel mechanism seems to be mainly responsible for the conduction.

Mahendru et al\textsuperscript{202} studied the electrical conduction in polypropylene films and found that the Schottky field assisted by thermionic emission was the dominant conduction mechanism in the temperature range 390-440K.

Electrical conductivity studies in pure and iodine doped polyvinyl acetate films were made by Mahendru et al\textsuperscript{203}. They prepared the films by solution growth technique and studies were made in the sandwich configuration. The electrical conductivity of polyvinyl acetate films was found to be increased by large amount due to doping of iodine. The results were interpreted in terms of Poole-Frenkel charge transfer mechanism.

Gupta et al\textsuperscript{204} carried the conductivity measurements of pure
and doped polyvinyl fluride thin films, prepared by solution growth technique, whose thickness was about 50 pm. Conductivity measurements on pure and doped PVF films in the temperature range 300-500 K have been reported. Here Vanadyl ions found to affect the mode of conduction in the PVF matrix by contributing two additional activation energies of conduction. In annealed films, the conduction was a thermally activated process while in annealed films the conduction was the combination of more than one thermally activated process.

Jain et al\textsuperscript{205} studied the temperature dependence of electrical conductivity of solution grown films of pure and doped polyvinyl alcohol. the thickness of these films was of the order of 100 microns and they were doped with different impurities, viz., CuSO\textsubscript{4}, CuCl\textsubscript{2}, FeCl\textsubscript{3}, ZnCl\textsubscript{2}, NaCl and thodamine. These impurities found to aflect the electron traps in the forbidden band of dielectric and modulate the current flow.

Phadke et al\textsuperscript{206} studied the electrical conduction mechanism in polyferrocene films prepared by plasma polymerization. They found that space charge limited conduction was the dominant mechanmism.

Hanscomb and Kaahwa\textsuperscript{207} studied the high temperature electrical conduction in polyethylene terephthalate in the temperature range 10 - 180 C at field strengths extending to $2.4 \times 10^8 \text{ V m}^{-1}$. The data was found to be well fitted to electronic or hole, Phoole-Frenkel conduction or ionic conduction resulting from field dissociation of protons.
Takal et al\textsuperscript{208} studied the high field conduction in poly (p-xylylene) thin films. The dark currents under fields up to 6 MV/cm were investigated for a poly (P - xylylene) film with Au and Al as electrode materials.

Audenaert et al\textsuperscript{209} studied the D.C. electrical conductivity of poly (2- vinyl pyridine) iodine films of thickness 80-100 pm as a function of iodine concentration and temperature in the range 200-300 K. The electrical conduction mechanism was governed by electronic hopping between random localised states.

Rao and Chopra\textsuperscript{210} investigated the electron transport properties of Cu doped polyvinyl chioride films. D.C. conductivity, A.C. conductivity, dielectric relaxation and thermally stimulated discharge current measurements were made on Cu doped PVC films as function of Cu concentration upto 12\%. The results were explained in terms of tunneling mechanism. The A.C. conductivity of these films favoured the hopping conduction.

The electrical properties of thin films of glow discharge polymerized hexa-methylcyclotrisilazane were investigated by J.Tyekowski et al\textsuperscript{211} in order to determine the mechanism of electrical conduction. The I-V characteristics were measured at room temperature and measurements of activation energy were made in temperature range 300-370K. The results of field dependence, temperature dependence and film thickness on the conductivity supported by the results of TSC measurements, suggested electrode limited conduction in the material investigated.

Staryga and Seiatek\textsuperscript{212} studied the electrical conductivity
of polycrystalline P-terphenyl films as a function of electric field, temperature and film thickness. The experimental data was interpreted in terms of hopping process between localised sites through potential barrier lowered by the electric field according to the modified Poole-Frenkel equation.

Bohri and Singh\textsuperscript{213} investigated electrical conduction mechanism in the metal-polyvinyl chloride (1500A)-metal sandwich structure using Al, Ag and Co electrodes. Two kinds of switching properties were found. The symmetric sandwich with Al electrodes exhibited voltage controlled negative resistance (VCNR) with memory, while asymmetric structures displayed current controlled negative resistance (CCNR) with memory. The VCNR mechanism was explained on the basis of high field domains and the CCNR phenomenon was explained on the basis of filamentary model.

G. Sawa et al\textsuperscript{214} studied the electrical conduction mechanism in polypyrromellitimide films in the temperature range 120-180 C as function of electric field. An attempt was made to fit the experimental results to the theoretical values for the ionic hopping conduction.

Miyairi and Ieda\textsuperscript{215} observed new type of I-V characteristics in polyethylene teraphthalte films of thickness 6 pm as function of different electrode materials. In the case of Au electrodes, two current peaks were observed around 5V and 20V at higher temperatures 160 and 170 C, whereas in Al-electrodes single peak was observed at 160 C.

Kulshrestha and Srivastava\textsuperscript{216} studied the electrical conduction of solution grown polystyrene films of thickness
about 15 Pm in the field and temperature ranges of about $6 \times 10^5$
 to $3 \times 10^7$ Vm$^{-1}$ and 300-400 K respectively. The results showed
that the Poole-Frenkel (PF) mechanism as modified by Jonscher and
Ansari was the dominant conduction mechanism.

Bahri and Singh$^{217}$ studied the conduction mechanism and I-V.
Characteristics of pure polyvinyl chloride films of thickness
range 500-1500 A$^0$ obtained by the isothermal immersion technique.
The conduction process was examined in a broad temperature range
260-507 K, with applied electric fields ranging from $4.6 \times 10^5$
 to $1.5 \times 10^7$ V cm$^{-1}$. At low temperature (below 325 K) and at
high fields ($>1.5 \times 10^6$ V cm$^{-1}$) the current transport was ascribed to
a tunneling mechanism. At high temperatures (above 325 K) and at
high fields ($> 1.5 \times 10^6$ V cm$^{-1}$) it was concluded that although
the analytical form of I-V characteristics was similar to that
obtained for both Schottky emission and Poole-Frenkel effect the
experimental value of $B_{\exp}$ was in compatible with the theoretical
values of $B_{RS}$ or $B_{PF}$. The resistivity of the PVC films was about
$10^{13}$ ohm cm at room temperature and at a field to $10^7$ V cm$^{-1}$. The
activation energy was 0.60 eV at temperatures about 325 K and at
a field $1.5 \times 10^6$ V cm$^{-1}$. Finally the annealing of PVC films at
temperatures around 500 K resulted in increased resistivity.

Cros-Lee Gloan and St-Onge$^{218}$ studied the electronic
conduction in polypropylene films in a high electric field. A
study was made on the effects of applied voltage, temperature,
electrode materials and polyethylene density. The results were
interpreted in the light of existing physical models of space
charge and electron trapping.

The electrical conduction of Nylon was studied by Nakamura
et al. The results were interpreted in terms of the migration of fixed number of ions existing in the polymer toward counter electrode. Lipinski et al. studied the electrical conductivity of p-terphenyl TCNE structures. The increase in conductivity by two orders was explained by the existence of charge transfer complex formation. Sharma and Pillai studied the electrical conduction in kapton polymeide films at high electric fields and results were interpreted in terms of ionic conduction. Bahri studied the D.C. electrical conduction in pure and iodine doped polystyrene films and the results were interpreted on the basis of charge transfer complexes. The effect of iodine on electrical conduction in polyvinyl fluoride films was studied by Chand et al. and the results were explained on the basis of charge transfer. Tyezkowski et al. studied the Poole-Frenkel centres in dielectrics of plasma polymerized organosilican films. Jayarama Reddy and Syrajddin studied the electrical conduction in pure and iodine doped polyvinylfluorode films. The results were explained on the basis of charge transfer between polymer and iodine. The D.C. electrical measurements on evaporated thin films of copper phthalocyanine was studied by Gould. Lee et al. studied the conduction phenomenon of the polypropylene films. Four regions of conducting currents were observed and were attributed to ionic conduction a Poole-Frenkel region, a Schottky region and a negative resistance region. Kojima et al. studied the electronic conduction in polyethylene terephthalate at high electric fields. The results were explained by the impact ionization. The electrical conduction phenomena in polymide
(kapton) films was studied by Sessle et al\textsuperscript{229} with a particular attention to the separation of interface and bulk phenomena. The current-voltage characteristics were found to be ohmic at low fields and space charge limited at high fields.

Tawanski et al\textsuperscript{230} investigated the D.C. electrical conduction in polyvinyl alcohol films. The ohmic type of conduction was found to be operative below 303 K whereas space charge limited above 303 K.

Narasimha Rao et al\textsuperscript{231} studied the electrical conduction mechanism in pure and doped polyvinyl formal films. The results were attributed to the Pool-Frenkel conduction mechanism. Das Gupta and Doughty\textsuperscript{232} studied the electric and conduction processes in polyether ketones. It was suggested that several mechanisms may be relevant and may all be involved in the conduction mechanism in a complicated manner. Narasimha Rao and Kalpalatha\textsuperscript{233} studied electrical conduction mechanism in polyvinyl pyrrolidone films. The results were interpreted in terms of Poole-Frenkel type conduction mechanism. Electrical conduction in polyacrylic acid was studied by Narasimha Rao et al.\textsuperscript{234} and two conduction regions were observed. Basha et al.\textsuperscript{235} studied the electrical transport in polyvinyl alcohol films containing transition metal halides. The transport of carriers was attributed to hopping mechanism between localized states.

Narasimha Rao and Subba Rao\textsuperscript{236} studied the electrical conduction in polyacrylamide polymer films in the temperature range 300-450 K and field strengths ranging from $0.48 \times 10^6$ - $24.1 \times 10^6$ V m\textsuperscript{-1}. The electrical conduction was explained as due to the simultaneous action of Richardson Schottky and Poole-
experimental conditions. 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 and a large number of mechanisms have been proposed by various workers. 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. The results of this technique can also be compared with those of some other electrical studies, like thermally stimulated discharge current (TSDC) and isothermal surface charge decay, etc., to get clear and justified conclusions.

This technique is time consuming hence it is not very popular, but 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
Frenkel mechanisms. Narasimha Rao et al. studied the electrical conduction mechanism in polivinyl alchol films in the temperature range 300-450 k and was found Richardson Schottky mechanism operating over the entire range. Sathyanarayana et al. studied the electrical conduction mechanism in polyacrylamide films. The electrical conduction of pure doped polymers and polyblend was also studies by Khare et al.

4.6 CALCULATIONS

4.6-1 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} (4.22)

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

\[ \log I = \log K + m \log V \]  \hspace{1cm} (4.23)

Putting \( \log I = v; \log V = x \) and \( \log K = c; \)
we have \( y = mx + c \)  \hspace{1cm} (4.24)

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

\[ m = \frac{\sum X \cdot \sum Y - n \sum (XY)}{(\sum X)^2 - n \sum X^2} \]  \hspace{1cm} (4.25)

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

4.6-2 CONDUCTIVITY

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The conductivity was calculated by using the equation

$$\sigma = \frac{d}{A \times V} \quad (4.26)$$

Where \(d\) is the thickness of the sample, \(A\) is the area, \(V\) is the voltage applied across the material and \(I\) is the conduction current.

4.6-3 ACTIVATION ENERGY

Relation between conductivity and temperature governed by the equation (4.19). On the basis of the this equation, Activation energy can be calculated as

$$E = \frac{K \left( \log_e \sigma_1 - \log_e \sigma_2 \right)}{1/T_2 - 1/T_1} \quad (4.27)$$

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

4.7. TRANSIENT CURRENT

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 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
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 EC and PMMA because of lack of experimental data
covering an adequate range of experimental parameters, i.e.,
field, temperature, electrode material, etc. However, the results
are available for many materials although covering very few
experimental conditions, which are insufficient to yield clear
and firm conclusions.

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

4.7-1 VARIOUS PROCESSES INVOLVED IN TRANSIENT CURRENTS

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 currents depending upon the
material properties and experimental conditions. Different
processes and their individual responses are described in the
following sections.

1. Electrode polarization
2. Dipole orientation
3. Charge injection leading to trapped space charge effects
4. Hopping of charge carriers from one localized state to another
5. Tunnelling of charge carriers from electrode to empty traps

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4.8 EXPERIMENTAL SET-UP

The block diagrams of an experimental set-up for the measurement of I-V characteristics in shown in Figure 4.4. The sample sandwiched between two electrodes, 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 current in the circuit were recorded by means of a Keithley Elecrometer Model 610C. After making proper electrical connections as shown in Figure 4.4, 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 lower temperature region it took longer period to reach the steady state while at higher voltages and higher 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 30-80°C respectively. A fresh sample was used for each set of observation. The following observations were taken

(a) Voltage variation at fixed temperatures.
FIGURE 3.22: PEAK CURRENT VS. POLING FIELD FOR POLY BL ND SAMPLES ($P_1, P_2, P_3$) WITH TEMPERATURES FOR (e) PEAK.
Fig 3.9 - TSDC Spectra of P samples at different polarizing temperature ($T_p$)
Ep=100 kV/cm.

**Figure 3.10-T**: S D C Spectra of P Samples at different polarizing temperature (Tp)

**Figure**: Initial Rise Plots of TSDC Spectra
**FIG:3.11-T S.D.C Spectra of P Samples at different polarizing fields (Ep)**

**FIG: INITIAL RISE PLOTS OF TSDC SPECTRA**
FIG: 3.12-T S D C Spectra of P. Samples at different polarizing fields (Ep)

FIG - INITIAL RISE PLOTS OF TSDC SPECTRA
FIG: S.13 - T S D C Spectra of P$_2$ Samples at different polarizing temperature (T$_p$)

FIG: - INITIAL RISE PLOTS OF TSDC SPECTRA
Fig. 8.14 - T S D C Spectra of P Samples at different polarizing temperature (T_p).

Fig. 9 - Initial rise plots of TSDC spectra.
Fig: 3.15 - TSC Spectra of P Samples at different polarizing fields (Ep)

Fig: Initial rise plots of TSCD spectra
Fig. 3.16 - TSDC Spectra of P Samples at different polarizing fields (Ep)

Fig. - Initial RISE plots of TSDC spectra
FIG. 8.17-T S D C Spectra of P₂ samples at different polarizing temperatures (T₀).

FIG. - INITIAL RISE PLOTS OF TSDC SPECTRA
FIG: 3.18 - T S D C Spectra of P₃ samples at different polarizing temperatures (T_p)

FIG: - INITIAL RISE PLOTS OF TSDC SPECTRA
FIG. 3.19 - T S D C Spectra of P samples at different polarizing field (Ep)

FIG.- INITIAL RISE PLOTS OF TSDC SPECTRA
FIG: 3.20-T SDC Spectra of R Samples at different polarizing field (Ep)

FIG: INITIAL RISE PLOTS OF TSDC SPECTRA
Fig. 4.4: A block diagram of the set-up for the conductivity measurement.
(b) Temperature variation at fixed voltages.
(c) Electrode variation at fixed temperature with varying voltages

4.9 RESULT AND DISCUSSION (CONDUCTION)

The time dependence of the transient discharging current in pure EC and PMMA and polyblend films was investigated over a period of 1-100 min in the temperature range 30-80 C. The discharge current transients for pure EC PMMA and polyblends (P1, P2 and P3) films for various poling fields (i.e. 10, 50 and 100 kV/cm) at 30, 40, 60 and 80 C have been shown in figures 4.5-4.8. It may be observed from the curves that the magnitude of discharging current transients shows a marked increase with temperature. There appears to be a process of thermal activation over the whole range of temperature. It is evident from figures that discharging current obeys the well-known expression 248a.

$$I_a(t) = A(T)t^{-n} \quad \text{(4.28)}$$

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, within lying between 1 and 2).

There is a departure from straight line and knee appear in all the curves. The isothermal I-V characteristics for EC, PMMA and polyblend reveal almost ohmic behavior (I-V) initially in a limited field region, which gradually becomes non Ohmic at higher fields. The slope values ($$m$$) in lower field region lie between
FIG: 4.5 TRANSIENT DISCHARGING CURRENT FOR Al-EC-Al SAMPLES FOR VARIOUS FIELDS AT CONTANT (T_p).
FIG. 4.6: TRANSIENT DISCHARGING CURRENT FOR Al-PMMA-Al SAMPLES FOR VARIOUS FIELDS AT CONTANT (Tp).
FIG: 4.7- TRANSIENT DISCHARGING CURRENT FOR Al-Pi-Al SAMPLES FOR VARIOUS FIELDS AT CONANT (Tp).
FIG: 48. TRANSIENT DISCHARGING CURRENT FOR Al-Pz-Al SAMPLES FOR VARIOUS FIELDS AT CONTANT (T_p).
FIG:4.9  TRANSIENT DISCHARGING CURRENT FOR Al-P3-Al SAMPLES FOR VARIOUS FIELDS AT CONSTANT (Tp).
1.0-1.2, and a slope of about 2 at higher field is observed.

The effect of temperature on I-V characteristics may be explained as follows:

With the increase of temperature, the probability of thermal ionization of the trapping centers increases causing a shift in the quasi Fermi-level which gives rise to a lowering of the barrier across which the carriers have to be transported and the conduction becomes more or less ohmic. The ohmic behavior can be understood on the basis of the reasonable assumption that at lower fields the injection of carriers from the contact is less and the initial current is governed by the intrinsic free carriers in the material. The current will be ohmic until the injected free carrier density becomes comparable with the thermally created carrier density. However, at sufficiently higher fields the current is dominated by space charge limited conduction and is mainly due to injected pace charge 249.

The faster decay of current in long time region for different samples indicates the existence of energetically distributed localized traps in the sample. Trapping of charges can take place at various trapping sites-surface states, chain foldings and molecular disorder 250. Small irregularities observed in some cases may be due to presence of charge domains inside the material 251. The polyblend is a heterogeneous mixture and as such has a very large number of trapping sites. It seems that at lower charging temperatures only shallow traps are involved which get emptied at these temperatures. But as the temperature rises, more and more deeper traps are involved. The trapping of charge carriers (holes and electrons in the deep trap levels may lead to
induced dipole formation. The energy required for their disorientation and the release of charge carriers from these trapping sites will be high and as such the discharge current is small.

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 to 0.8 and for long time region these values are observed to vary from 1.03 to 1.78. Also, discharging current various linearly with the field strength which is 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 PMMA is considered. The structure of EC is such that it is a weakly polar polymer having a small dipole moment. In EC ethoxy group is rigidly attached to the main chain. The nature of current in the observed temperature range may thus be attributed to a dipolar 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 60 C (figures 4.1A and 4.2A). It is expected that the current peak observed in the \( T_g \) range of EC and PMMA corresponds to dipolar orientations due to molecular motions associated with the side chains. Moreover, at any fixed time the activation energy value
FIG:4.1A- ISOCRONAL CHARACTERISTICS OBTAINED FROM FIG:4.1
FIG 4.2A - ISOCHRONAL CHARACTERISTICS OBTAINED FROM FIG 4.2
FIG:4.3A- ISOCHRONAL CHARACTERISTICS OBTAINED FROM FIG:4.3
FIG: 4.4A - ISOCHRONAL CHARACTERISTICS OBTAINED FROM FIG: 4.4
FIG:4.5A- ISOCHRONAL CHARACTERISTICS OBTAINED FROM FIG:4.5
increases with increasing concentration of polymer. Increasing concentration of PMMA in the polymer matrix is considered to play an important role in modifying the trap structure in the sample causing more and more deeper traps. The broadness of the peak in the present case is however, most likely to be distribution in relaxation time, because the peak is occurring near $T_g$ of the two polymers, where the side groups move in unison with the main chain, differing in masses$^{253,254}$. Because the distribution of dipoles in the amorphous phase is most likely to be random, it is expected therefore, this complex process involving both the distribution of the activation energy and relaxation time.

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 electrodes causing a decrease in current. The charge injection from electrodes with subsequent trapping of injected charges in near surface region giving 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.

Addition of PMMA in EC produces heterogeneous structure and plasticization effect$^{255}$. Because of the heterogeneous structure, charge carriers injected in the bulk may pile at the phase
boundaries. Plasticization causes loosening of the structure and
greater mobility of charge carriers resulting in the increase of
current. In EC:PMMA matrices containing different percentage at
least two phases coexist and discontinuity of structure at such
boundary increases. Further, the dipoles may also originate due to
trapping of both positive and negative charge carriers in the
deep traps in such a way as to form induced dipoles. Such trapped
charge carriers may be generated in the bulk from the impurities
thus they lead to induced dipole polarization in the polyblend
films$^{256}$. It is also possible that contribution of a permanent
dipole of the host material is masked due to induced dipoles. In
the blends, dipoles of the polar compound are so constrained that
under the field, they either do not orient or their contribution
to the total polarization is almost negligible as compared to the
contribution of induced dipoles, which are formed in the bulk by
the deep trapping of charge carriers originating in the bulk.
The large value of activation energy may be taken as an
indication of induced dipole formation because in this case the
energy required to disorient them and subsequently release
charge carriers from the trapping sites is expected to be
higher$^{255-257}$.

More direct confirmation of the dipolar hypothesis may be
found, correlating the temperature dependence of the the
transient currents with thermally stimulated depolarization
currents for which and essentially dipolar origin is generally
accepted.

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 in distinguishable 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 resistor $R$,
(c) the conduction current, which is time dependent.

The former components gradually fall off to zero within 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. Struik 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 Curie-Von Schweidler type of time dependence has been observed for many polymers with the index enclose 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 conduction phenomenon can be ruled out on the basis of the experimental facts.

The electrode polarization predicts the strong dependence of the electrode material on the decay of the transient currents. Moreover, uniform and electrode polarizations require the discharging currents at a particular instant to vary linearly with charging field.

In fact, the d.c. step response measurements, in which the current response is measured as a function of time after a d.c. voltage is applied to or removed from the sample, are quite similar to TSDC measurements except for the temperature being constant. However, when the measurements are made at various temperatures, it is possible to collect the d.c. step data at a specific time and plot them as a function of temperature. In various cases, such collection of d.c. step data has been found to resolve the different relaxation peaks.
The discharging currents observed in EC, PMMA and blends are also expected to show the behaviour of dipolar relaxation mechanism. However, the possibility of weak carrier injection at such field values cannot be ruled out. In the case of transients governed by space charge, the peak in the current time curve should occur at a time

\[ t_m = \frac{0.786a}{\mu F} \]

Where \( F \) is the applied field, \( a \) 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 \( a, F \) and \( \mu \) to be 25 \( \mu \)m, 100 kV/cm and \( 10^{-11} \) cm\(^2\)/V. It was found that \( t_m \), should approximately be 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 dipoles.

The thermal dependence of the discharging current for pure and polyblend samples is seen clearly when the current is plotted against temperature (figures 4.5-4.5). The observed temperature dependence (i.e. thermal activation) and the absence of any significant effects (i) electrode materials and (ii) sample thickness, makes tunneling unlikely as a possible mechanism to explain the nature of transient currents. The process of electrode polarization is also unlikely because of the absence of electrode effects and also because the observed "n" values are significantly different from the theoretically predicted mode. 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. The hopping mechanism, such as the one described by Lewis\textsuperscript{265} required the existence of localized carrier trapping states which had a distribution of energies. The observed time dependence of the transient current would not be incompatible of such a process. In addition to the dipolar contribution, there must be some contribution from the heterocharges which may be injected into the dielectric from the electrode. These may be trapped subsequently and form a pair of opposite charges which act as dipoles and oriented by the applied field. The activation energy is in fairly good agreement and in samples, the value of E agrees well with the activation energy obtained for TSDC peak in the present case.

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\textsuperscript{266}. 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 carriers is not expected in the present case.

Electronic conduction in polymer films at higher fields may occur by a number of processes. The carriers may be injected into the conduction band by Schottky emission over the metal-insulator interface. Other methods of conduction are Poole-Frenkel (P-F) emission, field ionization of impurity or traps, ionic conduction, space charge limited conduction and tunneling of carriers into or via traps. Tunneling as the possible mechanism
can be excluded in view of the strong temperature dependence of the current as found in the present case. Further, the ionic conduction also seems unlikely as the observed activation energy values do not fit well with this mechanism. 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 is decreased by the applied electric field. The potential barrier can be one of two types:

(i) barrier between electrodes and dielectric taking the classic image force into consideration (Schottky emission) and
(ii) barriers due to trapping centers in the dielectric (P-F effect).

Since the slopes of I-V plots (figures 4.14-4.14) in the case of EC, PMMA and blends are in general, less than 2, the observed characteristics of the dark conduction current can not be explained on the basis of the space charge limited conduction current. Further, tunnelling as the possible mechanism of charge transport can be excluded because of strong temperature dependence of the current as observed in the present case.

The Schottky-Richardson (S-R) plots for EC, PMMA and blends are shown in Figures 4.15 and 4.16. The isothermals reveal almost Ohmic behaviour initially in a limited field region. It is also evident that the current values deviate from straight line behaviour at higher fields. This deviation from the linearity can be understood in terms of space charge build up at the electrodes due to the charge carriers normally present in the
FIG: 4. CONDUCTION CURRENT VERSUS FIELD PLOTS AT DIFFERENT TEMPERATURE FOR EC SAMPLES.
FIG: 4. CONDUCTION CURRENT VERSUS FIELD PLOTS AT DIFFERENT TEMPERATURE FOR PMMA SAMPLES.
FIG. 4: CONDUCTION CURRENT VERSUS FIELD PLOTS AT DIFFERENT TEMPERATURES FOR PI SAMPLES.
FIG. 45: CONDUCTION CURRENT VERSUS FIELD PLOTS AT DIFFERENT TEMPERATURE FOR P₂ SAMPLES.
FIG: 4.14 - CONDUCTION CURRENT VERSUS FIELD PLOTS AT DIFFERENT TEMPERATURE FOR P₃ SAMPLES.
FIG 4.18: CONDUCTION CURRENT VERSUS $\sqrt{E}$ PLOTS AT DIFFERENT TEMPERATURE FOR $P_1$, $P_2$, $P_3$ SAMPLES
bulk of the dielectric. This enhances the effective field at the
electrodes leading to higher value of the slope of log I- E
curves.

Taylor and Lewis\textsuperscript{267} have assumed a more generalized form of
the potential barrier rather than the Coulombic barrier usually
employed in treatment of the R-S effect. They concluded that the
potential barrier chosen referred to the cathode dielectric
interface and probably is determined by a space charge layer in
the dielectric. Such space charge layers are charged up by the
absorption curent.

The P-F mechanism is applied to the thermal excitation of
electrons from traps into the conduction band of the insulator.
An increase in electric field reduces the coulombic potential of
trapped charge carriers in its direction and increases the
possibility of the thermal excitation of charge carriers into the
conduction band of the insulator giving rise to non ohmic
characteristics. The classical Richardson-Schottky equation is
usually expressed in the form

\[ J = AT^2 \exp \left( -\frac{X}{kT} \right) \exp \left\{ \frac{P_{RS}}{kT} \right\}^{1/2} \]

with

\[ P_{RS} = \left( \frac{e}{kT} \right) \left( \frac{e}{4\pi \varepsilon \varepsilon_0 d} \right)^{1/2} \]

where \( e \) is the electronic charge, \( V \) the voltage, \( d \) the film
thickness, \( (\varepsilon) \) the dielectric constant and \( (\varepsilon_0) \) is the
permittivity of the free space. However in the case of a low
mobility material, the diffusion limited, Richardson -Schottky
effect must be considered.
\[ J = \left( \frac{\sigma V}{d} \right) \exp \left\{ - \frac{X_{PF}}{kT} \right\} \exp \left\{ \frac{B_{RS} V^{1/2}}{kT} \right\} \]

Where \((\sigma)\) is a constant.

A similar equation describes the bulk limited Poole-Frenkel effect.

\[ J = \left( \frac{\sigma V}{d} \right) \exp \left\{ - \frac{X_{PF}}{kT} \right\} \exp \left\{ \frac{B_{PF} V^{1/2}}{kT} \right\} \]

Where \(X_{PF}\) is now the barrier associated with the promotion of an electron from a donor level to the conduction state, or, alternately, the promotion of an electron from a valence state to an acceptor level and \(B_{PF}=2B_{RS}\) in the simple model usually considered.

The theoretical values of \(B_{RS}\) and \(B_{PF}\) along with the experimental values of \(B\) obtained from the slope of plot between current and square root of applied field \(E\) are shown in Table 2. The experimental values of \(B\) are in close agreement with the theoretically calculated values of \(B_{PF}\). This suggests that perhaps the P-F mechanism is the important mechanism of conduction at higher fields, though the evidence may not be conclusive, since \(B\) depends on a number of experimental conditions. Further, there are a number of shortcomings in theories and suffers from large deviation in its constants which may not give rise to agreement between theoretical and experimental results.

If we take 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. But it remains practically unchanged in the case of P-F effect, since it does not depend on potential barrier at the interfaces. This way
of distinguishing between the P-F and Schottky mechanism was
suggested by Jonscher and Ansari\textsuperscript{268}. Thus, the effect of nature of
electrode materials of different work functions on the I-V
characteristics has to be considered for deciding conduction
mechanism. Figures 4.10-4.14 also exhibit the I-V characteristics
at 30 C for EC, PMMA and polyblend for electrode metals
(aluminium, copper, silver), the other electrode being of
aluminium in each case. A single straight line is obtained with
in the limits of experimental error. It indicates that the effect
of electrodes on the I-V curve is weak and the contribution of
the induced charges from the electrodes to the conduction process
is small. So far we have restricted our attention to the
conventional P-F mechanism, which assumes that the charge
carriers are thermally detrapped from their trapping sites with
the assistance of an applied external field, they are free to
move unhindered within the conduction band of the insulator. The
modified P-F model\textsuperscript{269} assumes that the electrons produced as a
result of the field assisted thermal ionization of donor-like
centers perform thermally activated hopping between localized
states. The effect of an external electric field is to lower the
potential barrier between the hopping states from the initial
value $W_o$ to a value $W_o - \psi E^{1/2}$, where $\psi=(\sigma^3/\pi\epsilon \epsilon_o)^{1/2}$ and has the
same value as in the classical P-F mechanism.

Figure 4.13 shows a plot of log I versus $10^3/T$ at different
applied fields. The activation energies were calculated from the
slopes of these lines. The modified P-F mechanism predicts an
activation energy which is decreasing with the square root of the

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FIG. 4.17: CONDUCTION CURRENT VERSUS 1/T PLOTS AT DIFFERENT TEMPERATURE FOR EC & PMMA SAMPLES
applied field. Figure 4.16 shows the plots between Log I and $10^3/T$ at different applied fields. The values of activation energy calculated from the slopes of these curves. Assuming vacant trapping sites to be charged, the trap depth may be expressed by the relation

$$E_t = E_{to} - \beta_{PF} E^{1/2}$$

where $E_{to}$ is the depth when bias is zero and $E$ is the applied field. The various characteristics suggest that the dominant charge carrier mechanisms in the pure and polyblends is the Poole-Frenkel mechanism.
FIG: 4.1B. CONDUCTION CURRENT VERSUS 10^3 \( \frac{1}{T} \) PLOTS AT DIFFERENT TEMPERATURE FOR P1 & P2 SAMPLES.
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