CHAPTER IV

ELECTRICAL CONDUCTION
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Introduction:

For long, organic molecular solids have been viewed upon as insulators. Much interest in them has been created in an attempt, to understand conduction mechanism. In the last decade, there has been rapid increase in the work on structural properties of organic substances. Recently polymer composites\textsuperscript{1-7} have attracted wider attention of scientist, owing to their vital applications. Hence the understanding of the mechanism of electrical transport in thin polymeric films is of considerable importance. Interest in the mechanism of electrical conduction of polymers composite is due both to their technical importance, and to the fact that their conductivity is related to the physical structure as well as to their chemical nature. Though much work on electrical behaviour of polymers has been reported\textsuperscript{3,8-16} in reviews and books, the understanding of transport mechanism in them is far from clear, also not much information is available on the charge carrier generation and transport in composite.

The study of electrical conductivity is an important aid in the investigation of conduction mechanism in the solids. It is believed that the observed conductivity in thin insulating film is often due to extrinsic, rather than intrinsic carrier.
In order to understand completely, electrical conduction in any organic solid, following mechanisms are to be understood -

(a) Energy Band Structure of the Materials:

Polymers have a specific structure, which in its turn affects the conduction mechanism. Electrically any semi-conducting solid is characterized by crystal structure defects, the nature of the majority carriers, and by their mobility. The defect traps, known as localized levels where electrons and holes get localized, are the cause of high conductivity, high dielectric losses, aging of materials in electric field etc. Each polymer has very large number of giant molecules or macro molecules which have a large number of recurring structural unit called monomers and they are tightly bound together by strong covalent bonds. There are two types of bonds in a polymer, namely strong inter-molecular bonds with an activation energy of 4 to 8 ev and weak intermolecular bonds with very low activation energy. The intra molecular 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. The band gap, or the minimum energy required to create a pair of free carriers each in its lowest energy state, then involves the excitation of an electron from valence band to the conduction band and is determined by the optical absorption
FIG. 4.1 - ENERGY BAND STRUCTURE OF POLYMERS.
threshold. In contrast to this, the organic solids are held together by weak Van-der-Waals forces and the molecular properties are preserved to a high degree despite the binding of the molecules into a lattice. Consequently the weak, direct optical transitions between different molecules, or the energy bands, might well be obscured by the intermolecular absorption and thus the optical absorption spectra can not yield a value for the band gap. The much intramolecular bonds most 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.

However, from purely thermodynamic considerations, the estimates for the energy of the levels taking part in conduction in an organic solid can still be obtained, from a knowledge of the energies of the ionized state.

According to this scheme, the energy required to produce a pair of free carriers, where the electron is not attached to any molecule or to the positive hole is given by

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

where \( I_c \) and \( I_g \) are the ionization energies of the crystal and the gaseous molecule respectively.

(b) Carrier Generation or Modulation of Charges:

Carrier generation via low probability mechanism of
direct band to band transition can not be totally excluded. Carrier generation mechanism of charges is discussed here -

In Dark :

The dark conductivity data on most of the organic solids show an exponential temperature dependence of the form -

$$\sigma = \sigma_0 \exp \left(-\frac{E_a}{KT}\right) = \frac{A}{\exp \left(-\frac{E_a}{KT}\right)}$$ (4.2)

Carrier generation in dark, is possible by injection. Both holes and electrons can be injected into an organic solid. Free carriers can also be generated by exciting an electron from the valence band to the conduction band of the crystal. In Anthracene holes have been injected through iodine\textsuperscript{17} and O-chloranil\textsuperscript{16} while Grancher and Adolp and Buchner\textsuperscript{18} have reported electron injection in the same material.

By Contacts :

Though the injection (or emission) of charge carriers from contacts (electrodes) was realized many years ago, the importance of this process to explain the conduction in polymers has been realized only recently. The contact may inject carriers in to the solids, and if the carrier concentration in the solid itself is very low, then the injected carriers may swamp those originally present and may produce a completely
different type of majority carrier conduction. The carrier density within the material being tested, so that the contact may act as a reservoir of carriers.

With ohmic contact semiconductors exhibit an ohmic current - voltage characteristic at low applied voltages where other electrodes may cause blocking effects.

Ohmic carrier injection into solids has been accomplished either by applying suitable electrode material or by generating carriers in a surface layer with strongly absorbed light. The difficulties inherent in attempting to provide truly ohmic contacts might be avoided by a method given by Harman and Higier.

Satisfactory contacts for conductance measurement can often be applied by means of evaporated metal films, metallic paints, graphite layers and some organic liquids. Pressure contacts are also useful in some cases. Kallmann and Pope used electrolytic contacts throughout their investigations. Mark and Helfrisch, working on electrolytic contacts concluded that an electrolytic contact anode forms an ohmic contact to crystals of substances containing more than two ring structures per molecule. The steady state direct current, then is limited only by space charges and trap existing within the bulk of the solids.
In Light:

In contrast to inorganic semiconductors, there is no simple explanation for photo generation of carriers in organic solids. The optical properties of organic solids can be fully described in terms of Frenkel excitons only. The electrical conductivity of organic materials in the presence of light due to optical absorption has been investigated by various workers both theoretically\textsuperscript{32} and experimentally.\textsuperscript{33,34} The conclusion of these studies are:

(1). The energy of longer wave length absorption limit does not correspond to the band gap and is usually longer than it.

(2). The absorption of the light quantum by organic semiconductors, results in the creation of Frenkel excitons within the crystal. These excitons are coupled hole electron pairs which are highly localized.

Davydov\textsuperscript{35} while investigating the absorption of light by complex molecular crystal, found that the peculiar feature of the absorption of light and luminescence in molecular crystals are connected with the process of migration of energy in the crystal. This migration is caused by resonance interaction between the molecular excited states. Such excited states are called "Excitons." These excitons are localized within a volume of space small enough to be identified with a particular molecule.
The generation of charge carriers on breaking of the excitons into an electron hole pair can occur by autoionisation\textsuperscript{36} of excitons (induced by phonons). Photoionisation\textsuperscript{37,38} (induced by photons), or by an interaction with a suitable electrode\textsuperscript{39-43} at the surface of the crystal. It has been suggested by experimental studies\textsuperscript{30,44} on the dissociation of excitons at the organic crystal - metal interfaces that the electron affinity, or any other similar property of the electrode may affect the location of dissociation sites in the crystal.

The carrier may also be produced via exciton-exciton interactions between two singlet excitons, the some of whose energies, is sufficient to excite an electron-hole pair.\textsuperscript{45} This was reviewed by Jortner.\textsuperscript{46}

Carrier generation by dissociation of charge transfer excitons, has not been proposed in organic solids, although, it has been shown to occur in inorganic crystals. However, definite experimental evidence\textsuperscript{47-49} exists to indicate the existence of charge transfer state in anthracene. There are several suggestions to the involvement of triplet-exciton, also in the photo-carrier generation processes. Triplet excitons may interact to form an electron hole-pair.\textsuperscript{50} Alternatively, the carrier generation may proceed by the dissociation of singlet excitons formed in a triplet-triplet annihilation process.\textsuperscript{51}
Space-charge Limited Current:

If the electrode-insulator (Polymer) contact is ohmic and the insulator is trap free, the accumulation of carriers near the electrode results in the space charge build up in the conduction band or at trapping centres, which will oppose the applied voltage and impede the electron flow. At low applied biases, if the injected carrier density is lower than the thermally generated free carrier density, Ohm's law is obeyed. When the injected carrier density is greater than the free carrier density the current becomes space charge limited. The following two conditions must be satisfied.

(1) 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.

(2) The insulator should be free from trapping effects relatively.

The surface charges on the interface of a micro-crystalline solid and electrode may give rise to an apparent volume space charge. The space charge are certainly present near the electrodes, whenever, a field is present, and they decay when the field is switched off. Direct evidence for space charges in electrically organic materials, has been obtained by Forster and others.
At sufficiently high fields, the solid is unable to transport all the injected charge and a build up of charge begins within the solid. 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 the 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.

The reason for the interest in space-charge-limited currents in polymers lies in the wealth of information which can be obtained from the current voltage curves. Space charge limited current is independent of the mechanism of carrier generation and depends only on the transport and trapping of the carriers within the crystals. The character of the currents due to these injected charge carriers of a particular sign is defined by the density distribution of the trap levels in the band gap. Rose\textsuperscript{59} and Lampert\textsuperscript{60} developed the theory of unipolar SCLC. The values of slope coefficient M\textsuperscript{72} of current-voltage characteristics are typical of the continuous trap level distribution in the band gap of dielectrics.

The complete mathematical analysis of time-independent space-charge current is so complex that no explicit explanation has yet been obtained. Mott-Gurney\textsuperscript{59} 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:

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon \mu \frac{V}{d^3}
\]  

where \( \varepsilon_0 \) - permittivity of free space \( \varepsilon \) - dielectric constant of the sample, \( \mu \) - dipole moment, \( d \) - thickness of the sample and \( V \) - applied voltage.

If there are traps in the insulator, the space charge limited current may be decreased by several orders. Rose\(^{59}\) and Lampert\(^{60,61}\) modified the theory for SCLC independently. Rose\(^{59}\) 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:

\[
J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \theta \frac{V}{d^3}
\]  

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:

\[
\theta = \frac{n_{\text{eff}} \exp\left(-\frac{E_T}{kT}\right)}{N + n_{\text{eff}} \exp\left(-\frac{E_T}{kT}\right)}
\]  

where \( n_{\text{eff}} \) is the density of states in the conduction band and \( N \) is the density of traps.
Assuming \( N \gg n_{\text{eff}} \exp. \left( - \frac{ET}{KT} \right) \)

then \( \theta \) becomes

\[
\theta = \frac{n_{\text{eff}} \exp. \left( - \frac{ET}{KT} \right)}{N}
\]

substituting for \( \theta \) in equ (4.4)

\[
J = \frac{9}{8} n_{\text{eff}} \exp. \left( - \frac{ET}{KT} \right) \frac{\varepsilon_0 \varepsilon_n}{N} \cdot \frac{v^2}{d^3} \quad ---(4.6)
\]

The dependence of \( J \) on some higher power of \( v \) has been described as due to the existence of deep traps and continuous distribution of trapping in the forbidden gap.\textsuperscript{60,61}

Equ. (4.6) suggests that SCLC in solids depends on the carrier transport and trapping and is independent of carrier generation. The fact that only very few organic solids show ohmic conduction has, therefore led to the belief that conduction in organic solids is mainly extrinsic.

Despite the importance of the role of traps in influencing the transport processes very little work has been done on the study of the density and levels of traps in thin insulators. Ullman\textsuperscript{63} studied photo currents and thermally stimulated current.\textsuperscript{34} Recently, the existence of SCLC and the influence of temperature in many organic solids have been reported by Swarakowski,\textsuperscript{64} Szymanski et al.,\textsuperscript{65,66} and Thomas\textsuperscript{67} et al. The relationship of the number and depth of the traps to the pretreatment of the polymer, its molecular structure and
morphology are of prime importance in understanding the electrical behaviour of polymer.

Schottky Emission:

In the presence of an applied electric field the barrier profiles are altered. If the applied field is high enough and the electrode makes ohmic contact with insulator (polymer) then charge carriers are injected into the insulator by lowering the barrier of metal insulator interface. Such effect is referred to as Schottkey Richardson emission (S R emission). The well known Richardson-Schottky formula for Schottky emission has been applied to tunnel structure with well defined rectangular energy by Simmons, Gunlach and Mann. The specimen is a sandwiched system between two metal electrodes $M_1$ and $M_2$ of work function $\phi_1$ and $\phi_2$, with respect to insulator $I$ respectively. On application of voltage between the electrodes, the actual potential experienced by an electron, in passing from $M_1$ to $I$ is less than $\phi_1$ and is shown in Fig. (4.2) by the dotted line. It differs from conduction band level by virtue of the image forces between the electron in the insulator and metal. Image forces are created because the abrupt changes in potential at the metal insulator interface are unrealistic, since abrupt changes in potential, imply infinite fields. The actual fact is that the potential step changes smoothly as a result of the metal surface becoming
FIG. 4.2- SHOWING THE SCHOTTKY EMISSION FROM THE METAL OF NEGATIVE POTENTIAL INTO THE CONDUCTION BAND OF INSULATOR.
polarized (positively charged) by an escaping electron in turn exerts an attraction force on the electron. An electron in the metal with a forward energy greater than the potential maximum can enter the conduction band of the insulator and hence gives rise to a conduction current.

In a sandwich structure, it is necessary to add the thermonic current in both directions. Thus, since thermonic emission over a barrier is given by \( A T^2 \exp \left( -\frac{\Phi}{kT} \right) \), the current density is given by

\[
I(t) = A T^2 \left( \exp \left( \frac{\Phi_1}{kT} \right) - \exp \left( \frac{\Phi_2}{kT} \right) \right) \quad (4.7)
\]

where \( \Phi_1 \) and \( \Phi_2 \) are maximum barrier heights above Fermi level of negatively biased and positively biased electrodes respectively, when a potential \( V \) exists between electrodes so that

\[
\Phi_2 = \Phi_1 + eV
\]

\[
\therefore I(t) = A T^2 e^{-\frac{\Phi_1}{kT}} \left( 1 - e^{-\frac{eV}{kT}} \right) \quad (4.8)
\]

where \( A = \frac{120A}{cm^2} \) and \( K \) is the Richardson constant. If the barrier is symmetrical then by applying a parabolic image force correction for barrier we obtain Richardson-Schottky formula -

\[
I(t) = A T^2 \exp \left( -\frac{\Phi - (14.4 \text{ ev}/\epsilon s)^{1/2}}{kT} \right) \quad (4.9)
\]

Schottky emission was experimentally identified by Emstage and Tantraporn\(^7\) by Mead\(^7\), Standley and Maissel\(^7\), and Pollack\(^7\).
I - V characteristics are replotted as Schottky plots. It is generally possible at high temperatures and high field. Further barrier height $\theta$ can be calculated from the slope of $\log J/T^2$ vs $1/T$ and the slope $B_{RS}$ is given by:

$$B_{RS} = \frac{1}{kT} (\frac{\frac{e^3}{4\pi\epsilon\epsilon_0}}{\frac{e^3}{4\pi\epsilon\epsilon_0}})^{\frac{1}{2}} \quad (4.10)$$

where,

- $e$ = the electron charge,
- $T$ = absolute temperature,
- $\epsilon$ = the dielectric constant,
- $K$ = boltzmann constant

Recent observations of O'Dwyer,75 Landyel,76 Lilly and Mc Donell77 and Shrivastava and Tomar78 and others79-82 have shown existence of this mechanism in their respective studies.

**Poole-Frenkel (P-F) Effects:**

If the charge carrier gets trapped in a coulombic potential well then the charge carrier can be detrapped by lowering the trap depth on the application of an electric field. The current resulting from the charge carriers detrapped from these traps also has the same linear dependence on the applied voltage as the Schottky-Richardson emission. The effect is known as Poole-Frenkel (PF) effect. The current density in Poole-Frenkel type of emission is given by:

$$I_{(PF)} = \text{Const.} \exp. (\frac{-\theta}{kT}) \exp. \frac{1}{kT} (\frac{e^3}{\Pi\epsilon\epsilon_0})^{\frac{1}{2}} \quad (4.11)$$
where the constant term is free from field and temperature. The slope of log $\sigma$ Vs $E^2$ curves is given by:

$$B_{PF} = \frac{1}{KT} \left( \frac{e^3}{\pi \epsilon \epsilon_o} \right)^{1/2}$$  \hspace{1cm} (4.12)

PF mechanism is a bulk process and would be expected to exhibit symmetric I - V characteristics. The PF effect is more pronounced when donor like traps (electron liberating) are present in abundance in the bulk of the insulator which are neutral when occupied by an electron. Even if some holes are liberated from acceptor like centres, their contribution to the total current is usually very small to their much lower mobility and greater mass. These centres bind their carriers by long range coulomb forces and the resulting lowering of the potential barrier under the influence of an external electric field.

Jonscher and Ansari$^{83}$ pointed out that the proper distinction to draw between the Poole-Frenkel and Richardson-Schottky mechanism is whether the effect is bulk or electrode dominated, there is no compelling reason to judge this from the magnitude of a factor in the exponent of the temperature dependent form.

(c) Traping and Recombination of Charge Carriers:

Carrier recombination in organic materials has been studied by variety of methods including fluorescence.$^{84}$
with in the classical forbidden barrier of the insulator, separated by two model electrodes. The wave function decays exponentially, with the thickness of the barrier, therefore, if the barrier is very thin, the electron has a finite penetration probability, which depends on the size and shape (area) of the potential barrier. Tunneling (field emission) may also take place through barriers whose effective thickness is reduced by a strong applied field. Several authors\textsuperscript{96-99} have discussed the formulation of tunnel equations. Frenkel\textsuperscript{99} attempted a solution. Sommerfield and Bethe,\textsuperscript{100} Holm and Krischstein\textsuperscript{101} and others\textsuperscript{102-106} simplified barrier height. Simmons\textsuperscript{104-106} generalized for symmetric and asymmetric potential barrier. The Fowler-Nordheim equation\textsuperscript{102} -

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

(4.13)

describes tunneling current for a simple case and predicts a linear relationship between -

\[ \log \left( \frac{I}{V^2} \right) \text{ and } \left( \frac{1}{V} \right) \]

where \( \phi \) is barrier height, \( V \) is potential and \( A \) is constant. The tunneling current is temperature independent.
electroluminescence, pulsed X-rays, field dependence of carrier generation and ionization by high energy particles. The hole-electron recombination cross section in anthracene found from fluorescence, due to recombination of simultaneously injected holes and electrons come out to be much too higher than in say Ge. In Sano's experiment carrier pair generation was attributed to injection and subsequent accelerations of electrons which in turn caused ionization of neutral molecules.

Kepler and Coppage studied recombination of carriers generated by pulsed X-rays and deduced the mean free paths of holes and electrons to be much less than 120 Å. If an electron gets closer to a hole than this critical distance, the possibility of its getting, trapped and eventually recombining with the hole increases markedly.

Trapping of carriers takes place because of discrete state present. The detrapping of charge carriers can take place from the traps depending on the trap depth and on the energy available for the detrapping. The detrapping may be purely thermal and depends on the molecular motion and molecular environment. The local field may assist in detrapping. Because of detrapping and subsequent trapping of charge carriers the time required for the charge transport is very high and the mobility is decreased. The number of charge carriers that contribute to the conduction depends on the
number of trapping sites between conduction and valence bands and also trap levels and these bands. Hoesterey and Lastson found anthraquinone and anthrone to trap electrons in anthracene substantially, even when present at a concentration of 10 ppm only. Sworakowsky has successfully calculated trap depths for holes and electrons in anthracene crystal doped with anthraquinone and tetracene. Discrete as well as exponentially distributed trapping levels are also present.

(d) Mobility of Charge Carriers:

Theoretical attempts to explain the mechanism of charge transport in organic solids have been based on two different observations—dark conductivity and mobility. Drift mobility is the fundamental property of a substance. Further modification of band models have been given to explain reasonably, the measured mobility values.

Tunnel Model of Conduction:

Eley and Parfitt suggested this type of tunneling. It is a quantum mechanical tunneling in which an electron possesses over the top of the barrier without acquiring enough energy. Later on Eley et al., proposed conduction mechanism in molecular crystals. For quantum mechanical tunneling the wave function of an electron has finite values.
Hopping Model :

Polymers have only crystalline or amorphous structure. In case of amorphous structure a limited short range order exists, so that the glass transition of the electronic band structure proposed by Block,¹⁰⁷ are maintained in amorphous state. Once an electron (or hole) acquires sufficient energy to get detrapped from its trapping sites to reach the conduction or valence band, it is free to move unhindered and unobstructed. But the concept of unhindered free conduction band electrons is incompatible with the low mobility of carriers observed in most of the polymers. 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. If the charge carrier spends more time in a lattice site, then the period of vibration of the molecule or atom, as would be the case for an extremely low mobility, the medium gets sufficient time to relax around the charge carrier.¹⁰⁸ This gives rise to a region of polarization around the charge carrier which is referred to as a "polaron". The entity carrier plus its region of polarization, is called a
"small polaron". 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 traps itself within the region of polarized dielectric when this occurs, the motion involves thermally activated hops and the mobility is given by -

\[ \mu = \mu_0 \exp\left( -\frac{W}{kT} \right) \]  (4.14)

where, \( W, k, T \) are the activation energy, Boltzmann's constant and absolute temperature respectively. The expression was presented by Mott\textsuperscript{109} and Boer\textsuperscript{110} separately with -

\[ U_0 = e \psi \phi \frac{a^2}{kT} \]

where \( \phi \) describes the wave function overlap, \( a = N^{-1/3} \) is the hop distance and \( e \) is the electronic charge and \( \psi \) is the lattice frequency. The localized trap states are thought to be randomly distributed in space and energy.

Electronic Band Model:

The much popular way of explaining the observed electrical conductivity is in terms of a modified
"electronic band model". Through this model one can calculate the width of energy bands by overlap integrals between electron molecular wave functions on adjacent molecules. The weak intermolecular crystals results in narrow conduction band and low carrier mobilities.

Small electrical conductivity and high activation energy of organic solid suggest that some kind of intermolecular interaction takes place, which in an electric field, gives rise to electronic conduction. It is suggested that this interaction is molecular orbital overlap. The extent of orbital overlap is a function of molecular structure and hence, if semiconduction arises from such overlap, it is not surprising that semiconduction activation energy correlates with the properties which are also a function of molecular structure, such as the molecular ionization energy, electron affinity and excitation energy of the ground triplet state transition. One of the entities which influences these properties is the number of more easily polarizable π electrons. As the number of these increases in a conjugated system, there is a trend toward smaller activation energies of conduction indicating that the probability of achieving overlap is enhanced by the presence of a large number of
\( \Pi \) electrons. However, if the overlapping of molecular orbitals gives rise to semiconduction, then some other factors which contribute to such overlapping should also encourage semiconduction, even if only few \( \Pi \) electrons are present in the individual molecule. Since intermolecular hydrogen bands may provide such overlap, it might be expected that the activation energy in hydrogen bonded compounds should be lower than anticipated solely on the basis of number of \( \Pi \) electrons.

4.2 : Factors Affecting Conductivity :

A brief review of factors which affect the electrical conductivity of polymers is given below -

(a) Pressure :

Akamotu and Inokuchi\textsuperscript{113} found that the conductivity increases with the pressure up to 80 atmosphere after that the conductivity remains constant.

(b) Field :

A number of mechanisms\textsuperscript{114,115} have been employed to explain increase of conductivity with field. Poole\textsuperscript{116} has observed exponential variation of conductivity with field strength. However, Joffe\textsuperscript{117} states that it is only
the steady state conductivity which increases with field and the true conductivity has been shown to be independent of field strength.

According to Gunn\textsuperscript{118} and Koenig\textsuperscript{119} the field affects, the electron mobility in the region of impurity. Zener\textsuperscript{120} suggests that the variation in conductivity is due to thermal activation of trapped electrons. Lindmayer et al.\textsuperscript{121} have reported electronic conductivity in insulators to be strongly controlled by trap sites. With the applied voltage, the variation of current has been generally given by

$$ I = aV^m $$

(4.15)

where, a and m are the constants. The values of "a" and "m" are very much dependent on electrode material and dielectric constant. The value of "m" is 1, when the behaviour is ohmic. A value of m = 2 is given by Rose,\textsuperscript{60} when a space charge limited current flows through a trap free insulator between plane parallel electrodes.

Values of "m" is given by the equation

$$ m = -\frac{T_c}{T} + 1 $$

(4.16)

If the traps are present with in the insulator, where Tc is a temperature characteristics of distribution of
traps at room temperature T. Departure from Ohm's law at high fields occur as a result of perturbation of activation barriers. Conductivity then increase in high field region Frohlich,\textsuperscript{122} on the basis of interaction between trapped electrons suggests the following equations -

$$\sigma = \sigma_0 \exp \left( \frac{V}{\Delta V} + \frac{F^2}{eF_m^2} \right)$$ \hspace{1cm} (4.17)

where,

$\Delta V$ = potential barrier on the trapped electrons.

$F$ = Field and

$F_m$ = the intrinsic field.

O' Dwyer\textsuperscript{123} has modified Frohlich's theory and showed that the conductivity also depends on space charge. He gave a new expression -

$$\sigma = \sigma_0 \left( 1 + \frac{B}{n_0} \right) \exp \left( \frac{V}{\Delta V} + \frac{F^2}{eF_m^2} \right)$$ \hspace{1cm} (4.18)

where,

$n$ = density of conduction electrons.

$n_0$ = density of space charge of electrons.

(c) Temperature :

The nature of electrical conductivity very much depends on the temperature state of polymers. An
increase in electrical conductivity could be obtained with increasing temperature. The temperature dependence of electrical conductivity is often given by the formula -

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

where,

\[ E = \text{activation energy and} \]
\[ k = \text{Boltzmann's constant}. \]

If conductivity (\( \sigma \)) is plotted against inverse of temperature (\( 1/T \)), two regions, a high temperature region and the a lower temperature region are obtained. In both these regions the logarithm of conductivity is roughly a linear function of \( T^{-1} \) and the complete conductivity curve is a superposition of two lines corresponding to\(^{124,125}\) -

\[ \sigma = \sigma_1 \exp \left( -\frac{E}{kT} \right) \] and \( \sigma = \sigma_2 \exp \left( -\frac{E}{2kT} \right) \) (4.20)

where \( \sigma_1 \) and \( \sigma_2 \) are the constants \( \sigma_1 \) decreases with increasing purity whereas \( \sigma_2 \) is not sensitive to it. The low-temperature region is due to the varying number of lattice defects,\(^{126,127}\) that are frozen-in or due to lack of purity of the crystal, whereas, the high
temperature region (which involves large activation energy) called the intrinsic region may be due to the thermal generation of new defects. It is observed that curves found on increasing or decreasing the field or temperature are quite different showing a hysteresis which is a mark of the presence of space charges. In case of carnauba wax, polyethylene, sealing wax, polyvinyl chloride and Indian sugar can wax, hysteresis effect has been observed.

(d) Electrode Material:

Electrodes are considered ideal if they do not react chemically with the material and are unaffected by variations of temperature, field and should introduce no resistance to the flow of current. According to a study by Reucroft, the nature of the metal used in making a contact has no effect on the value of conduction current, on its temperature dependence. He deduced that any non-ohmic behaviour observed is independent of the work function of the contact metal at least.

The behaviour of electrolytic contacts has been studied by Mark and Helfrich. They concluded that an electrolytic anode formed an ohmic contact to crystals. The anode is ohmic if the electron affinity of the
electrolyte is greater than the ionization energy of the solid. Recently Kulshrestha et al.\textsuperscript{133} have reported no variation in electrical conductivity of polystyrene doped with chloranil as regards different materials of the electrodes. Srivastava et al.\textsuperscript{134} have also noted considerable effect of electrode materials in the conductivity of copper phthalocyanine doped polystyrene.

(e) Impurity Content:

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 materials is known. Atoms or molecules of an impurity present in the polymer act as a source of free electrons. Effect of known impurities on electrical properties have been observed by Northrop and Simpson\textsuperscript{135} Okamoto and coworkers\textsuperscript{136}. The conductivity will be given by the sum of two terms:

\[ \sigma = \sigma_1 e^{-\frac{E_1}{KT}} + \sigma_2 e^{-\frac{E_2}{KT}} \quad (4.21) \]

In this equation (4.21) one term has a large activation energy ($E_1$) and a large coefficient ($\sigma_1$), while the second term due to impurity has a smaller coefficient ($\sigma_2$). If log $\sigma$ is plotted against $1/T$, in the usual way, the curve will show a kink separating
two straight lines, the one with smaller slope corresponds to the structure sensitive region or to the extrinsic conductivity while that with greater slope corresponds to the structure insensitive region or the intrinsic conductivity.\textsuperscript{137}

In case of semiconductors where the number of impurity centres is greater than the number of electrons available (log $\sigma$, $1/T$) curve, again yields two straight lines with different slope separated by a knee. As the materials becomes purer the knee shifts to lower temperature side.\textsuperscript{138} Recently impurity incorporation in PS has been the subject of many workers.\textsuperscript{133,134,139} All of them have reported increase in conductivity with dopant.

(f) Humidity:

There are numerous reports of several workers\textsuperscript{114,115,140} regarding the dependence of conductivity on humidity. It was observed that impurity causes the conductivity to increase with field strength. Sorbed water molecules also acts as impurity molecule and increase the conductivity of polymer. Water molecules also affects the ionic conductivity.
Moisture affects\textsuperscript{141} the conductivity in two ways:

(i) It increases the dielectric constant and therefore, the concentration of ions by reducing the effective dissociation energy.

(ii) It brings about the departure from Ohm's law in high fields as a result of activation perturbation even in the absence of thermal and chemical effects. Manthia et al.\textsuperscript{142} have concluded the increase in conductivity with humidity.

(g) Thickness:

There are considerable evidences\textsuperscript{143,144} regarding the dependence of electrical conductivity on sample thickness. Wright found that the current varies as the inverse cube of thickness -

\[ I = a \left( \frac{1}{d^3} \right) \quad \text{(4.22)} \]

where \( a \) is the constant. In an insulator in which the traps are either absent or shallow, current varies as inverse cube of thickness (\( d \)) and when the traps are distributed uniformly in energy below the conduction band, current varies inversely as the square of the thickness, (\( d \)). Szymanski\textsuperscript{65} observed that the current decreases with increasing sample thickness. Sharma\textsuperscript{131}
has found a linear relationship between conductivity and thickness. With increasing thickness the space charge limited current also increases. 146

4.3: Present Investigation:

Before measuring the current or electrical resistivity of any material, it is necessary to have the sample of the material in a suitable form and also electrodes for it. Preparation of the sample depends upon the nature of material. For example, alkali halides can be taken in crystal forms while the substances in powder form may be taken in the shape of pressed disc pellets. But the probable chances of occurring internal cracks in the conductivity. Solution cast films133,147 in semi insulating materials are being used these days. They are preferred because of low probability of voids, pinholes and other like defects in them.

There are number of instruments148-153 available to measure dark current. The use of an instrument depends upon its sensitivity and the conductivity of the material under probe.
4.3 - 1 : Details of Measurement:

The study of steady state dark conductivity has been undertaken in the present investigation. Electrical conductivity of the material can be measured to any degree of accuracy by measuring current, voltage and dimensions of the specimen. It is also necessary that thermal and other physical treatment of the sample, should be the same, as it undergoes during other studies.

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 - 2 hours. When the sample attained the desired temperature following observations were taken -

Field and temperature are the two important parameters in the present investigation. Electric field is varied from $2.5 \times 10^3$ V cm$^{-1}$ to $2 \times 10^4$ V cm$^{-1}$ in eight steps, while temperature from 333 - 383 °K in six steps. Measurements are taken in two ways -

 Variation of Current With Field:

To observe this variation of current the temperature is kept constant and the field, is varied. Then the
temperature is changed to next value and process reported. At each temperature, the assembly is allowed to remain in thermostat for one hour, before the field is applied. This period is sufficient for the specimen to attain equilibrium. In all cases, where the field is applied before attainment of thermal equilibrium, the current always takes a very long time before it settled down to its steady state. When the field is applied under suitable conditions, it is observed that, at lower temperature, immediately after the application of the field a large burst of current is obtained which decays quite rapidly and in about 15 to 30 minutes settles down to its steady state value. At higher fields particularly at higher temperatures, this period is found to be comparatively less. The current is observed while increasing or decreasing voltage in same steps. Temperature of the specimen is always measured by the help of a thermocouple, & for arrangement; and each temperature, fresh specimen is used.

Variation of Current With Temperature:

The effect of temperature at constant field is measured. The field is kept fixed and the temperature varied. Different values of field are applied and the same process repeated. While observing this variation
of current with temperature, care is taken so that the thermal equilibrium of the specimen is obtained in about one hour at each temperature. Increasing or decreasing order of current are recorded for different temperatures, as in the previous case. For each fresh value, fresh specimen is used.

4.4 : Calculations :

Representative curves of variation of current with field at different temperatures on a log - log plot are shown in fig. 4.3. The curve show an approximate linear relationship in two regions, one in higher field, another in lower field. This suggests that a power law is obeyed, as -

\[ I = k V^m \]  

(4.22)

The degree of linear relationship between log I and log V is determined by computing the power "m".

Power "m" :

The calculation of power"m" involves the introduction of new variables, so as to arrive at a more tractable relationship. Thus taking a logarithm of equ. (4.22) -
\[ \log I = \log K + m \log V \quad (4.23) \]

Considering \( \log I = Y, \log V = X \) and \( \log K = C \), we have

\[ Y = mx + c \quad (4.24) \]

which is an equation of a straight line. The problem has now been reduced to the problem of fitting a straight line to a set of points on the \( X \) plane and thus to a simple problem of least squares as follows -

\[ m = \frac{\sum X \cdot \sum Y - n \sum X Y}{(\sum X)^2 - n \sum X^2} \quad (4.25) \]

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

**Activation Energy** \( (E) \):

Variation of conductivity with temperature in \( \log \sigma \) vs \( \frac{1}{T} \) plots (fig. 4.6) straight portion of the graph is governed by the equation -

\[ \sigma = \sigma_0 e^{\left( -\frac{E}{kT} \right)} \quad (4.26) \]

where

\[ E = \text{activation energy, and} \]

\[ K = \text{Boltzman's constant.} \]
Same type of straight lines with different slopes showing high temperature and low temperature regions, are obtained in log $\sigma$ Vs 1/T plots as has been said earlier. Activation energy $E_1$ and $E_2$ corresponding to higher and lower temperature regions have been calculated from the equation -

$$E = \frac{K}{(\frac{1}{T_2} - \frac{1}{T_1})} \text{ (4.27)}$$

where log $\sigma_1$ and log $\sigma_2$ are the values at two points corresponding to $\frac{1}{T_1}$ and $\frac{1}{T_2}$.

4.5: Present and Last Decade's Work:

Polymers have been known to be amorphous or semicrystalline materials, which makes their electrical properties to be more complicated and conduction mechanism more complex as compared to single crystalline materials.

Several workers$^{148-156}$ have investigated the electrical conduction in polymers. A wide range of electrical behaviour of polymers has been encountered which shows the complexity of conduction mechanism in these materials. A variety of mechanisms such as ohmic conduction,$^{156}$ Poole-Frenkel effect,$^{157,158}$ Schottky effect,$^{159,160}$ space charge limited current, Ionic
conduction,\textsuperscript{59,62,161} and even more complex than these have been invoked to explain the observed conduction phenomenon. The conduction mechanism in polymer films may depend upon the method of preparation of the sample and their history. As a consequence different investigators have reported different conduction mechanisms for the same material.\textsuperscript{162}

Conduction phenomena have been investigated in a large number of high polymers such as polyethylene,\textsuperscript{163,164} polystyrene\textsuperscript{165,166} poly vinyl chloride,\textsuperscript{167-169} polypropylene,\textsuperscript{163} polytetrafluoroethylene,\textsuperscript{77} polyvinyleadene fluoride,\textsuperscript{170,171} polyethylene terephthalate,\textsuperscript{76,77} poly \(\text{N}\)-vinyl carbazole.\textsuperscript{172} Cellulose acetate,\textsuperscript{173} polymethyl methacrylate\textsuperscript{174} and carbon filled polyethylene.\textsuperscript{155}

The conduction mechanism in polyethylene and poly tetrafluoroethylene films\textsuperscript{76} has been reported to be as Schottky emission type. Mylar\textsuperscript{175} films was governed by O' Dwyer theory of a space charge conduction. In polystyrene films\textsuperscript{176} explained in terms of a space charge formed by the injection of electrons into the film over Schottky emission. In poly vinyl acetate\textsuperscript{177} films is P-F effect, in poly vinyl chloride\textsuperscript{167} is ionic and in
thin films of polyferocene is space charge limited current.\textsuperscript{178} Polymers having desirable conductivity are very much required in electrothermography and related applications. The transport properties of polymeric materials can be modified by doping.\textsuperscript{179,184} Gill\textsuperscript{185} investigated in detail the transport properties of trinitrofluorenone dispersed in poly vinyl carbazole. Iodine doping has improved the conductivity of the polymers like polystyrene,\textsuperscript{172-186} polyethylene,\textsuperscript{187} cellulose acetate\textsuperscript{188} and polyacetylene.\textsuperscript{189} This has been attributed to the formation of charge-transfer complexes,\textsuperscript{190,191} between iodine and the main molecular chain of polymer. The mechanism is very well discussed by Swan.\textsuperscript{192} Sometimes doping cause reduction in trapping of charge carriers and increase in mobility.\textsuperscript{193,194}

An efficient control over electrical properties of polymers is achieved by doping the polymer with suitable dopant, which form a donor-acceptor complexes, with the host molecule.\textsuperscript{195,196} The spectroscopic studies of the polymeric donor-acceptor complexes have been reviewed by Rao et al.,\textsuperscript{197} and Tadkora et al.\textsuperscript{198}
4.6: Transient Current:

Transient charging and discharging currents were measured in several polymers, from room temperature to the glass transition temperature and the effect of some of the varying parameters such as field strength, electrode material, addition of impurities was investigated. Some limited comparative studies of the isochronal characteristics (i.e. current temperature plots at fixed times) with the thermally stimulated depolarization and polarization currents were also carried out in order to test possible correlations between the phenomena observed by different methods.

There are various methods of studying a.c. conduction, surface voltage decay, trapped charge decay, radius induced conduction and photo conduction. In all these methods, there are certain uncertainties, it is therefore, essential to have a better method of studying conduction processes. Time dependent dielectric absorption or deabsorption current which flow during the application or removal of a voltage, is an important tool of studying various processes of conduction. The origin of these dielectric absorption and resorption currents is still the subject of much controversy, in the literature and
a number of mechanisms have been proposed. The most important of which are dipolar relaxation, tunneling to empty traps, charge injection leading to trapped space charge effects, hopping of charge carriers and electrode polarization. The theoretical involvements of these different processes in view of their possible applicability to polymers were recently reviewed and discussed by Wintle,\textsuperscript{199,200} Dasgupta and Joyner.\textsuperscript{201,202}

The relaxations are thermally activated so that double logarithmic current-time plots are translated along a direction slope, as the temperature changes current temperature curves taken at a fixed polarising time yield an apperent activation energy (E\(\cdot\)1-\(\alpha\)), where E is the thermal activation energy and \(\alpha\) is the distribution parameter. This is applicable only at \(t/\tau\) is \(<0.1\), where \(\tau\) is the relaxation time. Since the dipolar orientation occurs with-in the material itself, there should be no contact effects. If the material is homogeneous the current at constant field will be independent of thickness. If the dipolar region is confined to the surface, the measured current will fall inversely with thickness (d).

The tunneling process involves the presence of traplevel or levels in the dielectric. Such trap levels
are located in the band gap. The existence of such trap levels is evident from the thermoluminescence studies. Blake et al.,203 and others have shown that room temperature excitons leads to the thermoluminescence above room temperature which shows that there may be shallow electron traps. Deeper traps have also been reported for corono discharge materials but they may be ion traps rather then electron traps. The tunneling current should be independent of temperature and proportional to the field of the surface layer of the material is homogeneous and the current should also vary inversely with thickness.

The space charge model again postulates the presence of deep trapping levels in a high field concentration. At fixed time the transient current exhibits a field dependence but this is not the same as that for the charge injection mechanism. The characteristic time constant is also dependent upon the applied field, varying approximately inversely with initial current densities.

The electrode polarization occurs in ionic materials and it is characterised by linear dependence of field and the current which is thermally activated.204 The polarization phenomena accompanied by large increase in low frequency capacitance.
A systematic analysis\textsuperscript{200} of transient currents has helped in the explanation of injection mechanism and charge trapping mechanism. The study of transient current has helped very much in understanding the polarization process in dielectric materials.\textsuperscript{200-202,205-208} The transient current measurements correlate the dielectric relaxation processes studied by dielectric loss measurements with those obtained by thermally stimulated current measurements. Therefore, it becomes essential to undertake the time dependent transient current, studies systematically. In the present investigation time dependent and field dependent current studies were done with poly methyl methacrylate + Malachite Green samples.

It is well known that the transient currents are observed, upon the application of step voltage or after the removal of the field in two ways -

(1) Either at several fixed temperatures, after the d.c. field application to the specimen until the steady state value are drawn, or, until the steady state conductivity values are drawn, or,

(ii) After the field application, the temperature is steadily increased and simultaneously the current is measured and recorded with the help of 600 B electrometer.
In conductivity measurement the dependence of the "equilibrium current" on time is also an important factor. The equilibrium current is not observed immediately upon applying the d.c. voltage. A large current observed further as absorption current caused by relaxation process of dipole orientation, interferes with the conduction current in the polymer as a result the equilibrium current drops off first rapidly then slowly.

J. Vanderchueren and A. Linkens\textsuperscript{209} report, the result of such studies performed on several polymers including polyethyl methacrylate (PEMA), poly t-butyl methacrylate (PtBM), poly phenyl methacrylate (PPhMA), poly cyclohexyl methacrylate (PCHMA), polydiancarbonate (PDC), polystyrene, (PS) and polyethylene terephthalate (PET). They also compared in some cases, the results, with thermally stimulated current data and the possible mechanisms responsible for the transient behaviour are discussed.\textsuperscript{209}

\section*{4.7: Results:}

The Current Transient:

An Aluminium-composite-aluminium sandwich sample was kept in the thermostat, whose temperature was set to
a constant value and after allowing it to attain thermal equilibrium a field of $2.5 \times 10^3 - 2 \times 10^4 \text{ V cm}^{-1}$ (in steps of 5 volts) was applied to the electrodes of the sample through the electrometer amplifier. Current was noted after some time interval for 30 minutes.

Fixed time was taken, because the time required by the current to become steady is generally too long, sometimes (specially at high, temperatures and voltages) it is several hours. Kamisako et al., $^{176}$ have recommended a method to obtain study current at shorter time. According to them at first, a field/temperature higher than the desired one should be applied on the sample for some time then, after short circuiting the electrodes, lower (desired) field/temperature is established, keeping other parameters constant. The samples were annealed also at 373$^\circ$K for one hour to remove absorbed moisture. Current Vs time curves are presented in fig. 4.1 a and b, and 4.2a and b, Initially a large current is observed which drops off first rapidly then slowly before settling down to a steady value. Time required by the current to become steady is short at higher temperatures/voltages, but it becomes longer and longer with decrease in temperatures/voltages.

Variation of Current with Field:

After having achieved the thermal equilibrium at
CURRENT VS TIME CURVES (CURRENT TRANSIENTS), (a) AT VARIOUS TEMPERATURES AND (b) AT VARIOUS FIELDS FOR PURE POLYMETHYL METHACRYLATE FILMS. (ALUMINIUM - ALUMINIUM SYSTEM) (SCHER-MONTROLL PLOTS).

FIG: 4.1
CURRENT VS TIME CURVES (CURRENT TRANSIENTS), (a) AT VARIOUS TEMPERATURES AND (b) AT VARIOUS FIELDS FOR COMPOSITE (PMMA + MALACHITE GREEN) FILMS, (SCHER-MONTROLL PLOTS).

FIG: 4.2
a constant temperature, the $M_1$–composite – $M_1$, and $M_2$–composite – $M_2$ sandwiches, were subjected to various fields, ranging from $2.5 \times 10^3$ – $2 \times 10^4$ V cm$^{-1}$ in steps of 5 volt. Steady state current was noted at each step and current Vs field curves are plotted. The isothermal $I$ – $V$ characteristics, plotted in the form of log $i$ – log $v$ curves for Al–composite–Al, Al–composite–Cu and Al–composite–Ag, are shown in fig. 4.3. They exhibit almost similar nature for all the temperatures from 363°K – 383°K. These curves suggest that the current–voltage characteristics follow a relationship of the type –

$$I = KV^m,$$

where $K$ and $m$ are the constants.

or,

$$\log I = m \log V + \log K.$$

Thus, the slope of log $i$ – log $v$ plots would give the value of $m$, which in turn will be of help to understand the nature of conduction process. It is therefore, better to plot log $i$ Vs log $v$ graphs. It is seen from the curves that –

(i) Curves have two regions, a low field region approximately upto $1 \times 10^4$ V cm$^{-1}$ and a high field region above it.

(ii) Current depends upon the choice of electrode metals, being higher in case of dissimilar electrodes.
LOG I VS LOG V PLOTS FOR PMMA + MALACHITE GREEN FILMS

FIG. 4.3
Variation of Current with Temperature:

For this study the temperature of the thermostat was increased in step of 5°C (between the range 363°K to 383°K). After allowing the thermostat and the sample to attain thermal equilibrium, a particular field was applied at each constant temperature and steady state current is noted. The curves (fig. 4.4 a, b and c) exhibit also two regions, a lower field region and a higher field region and have similar nature as observed in fig. (4.3). It is found that current is higher in case of dissimilar electrode combination. Fig. (4.5) shows log J Vs $E^z$ for Al-composite-Al, Al-composite-Cu, Al-composite-Ag combinations, (each obtained at 383°K). It is clear that the value of current is higher in case of dissimilar electrodes. Variation of conductivity (σ) with inverse of temperature (10³/T) at different field values is shown in fig. (4.6)a, b and c, for different electrode combinations. All the curves are of similar nature with nearly similar slopes. The values of activation energy in different regions of temperature, are computed from these slopes.

Derived Graphs:

Charge carriers may be supplied by Richardson -
LOG I VS INVERSE OF TEMPERATURE FOR PMMA + MALACHITE GREEN FILMS.

FIG. 4.4

(a) ALUMINIUM - ALUMINIUM ELECTRODE SYSTEM

(b) ALUMINIUM - SILVER ELECTRODE SYSTEM

(c) ALUMINIUM - COPPER ELECTRODE SYSTEM

FIELD (E)

- 2.00 x 10^4 VOLTS CM^{-1}
- 1.75 x 10^4 VOLTS CM^{-1}
- 1.50 x 10^4 VOLTS CM^{-1}
- 1.25 x 10^4 VOLTS CM^{-1}
- 1.00 x 10^4 VOLTS CM^{-1}
- 7.50 x 10^3 VOLTS CM^{-1}
- 5.00 x 10^3 VOLTS CM^{-1}
- 2.50 x 10^3 VOLTS CM^{-1}
LOG J VS. $E^{1/2}$ PLOTS FOR PMMA + MALACHITE GREEN FILMS (FOR DIFFERENT ELECTRODE MATERIAL AT 383°K).

FIG: 4.5
VARIATION OF CONDUCTIVITY (\(\sigma\)) WITH INVERSE OF TEMPERATURE (ARRHENIUS PLOTS).

FIG: 4.6
Schottky emission\textsuperscript{210} process by the electrodes as defined by the formula:

\[ J = A T^2 \exp\left( -\frac{\varphi}{kT} \right) \exp\left( \frac{e}{kT} \left( \frac{eE}{4\pi\varepsilon} \right)^{\frac{1}{2}} \right) \] \hfill (4.28)

and, further carriers may also be generated by field emission process within the bulk of the polymer as described by Poole and Frenkel,\textsuperscript{157} in accordance with relation:

\[ \frac{J}{E} = \sigma = A \exp\left( -\frac{\varphi}{2kT} \right) \exp\left( \frac{e}{kT} \left( \frac{eE}{\pi\varepsilon} \right)^{\frac{1}{2}} \right) \] \hfill (4.29)

so as to ascertain whether any of these processes is operative, Schottky plots (log \( J \) Vs \( E^{\frac{1}{2}} \)) and Poole - Frenkel plots (log \( \sigma \) Vs \( E^{\frac{1}{2}} \)) should be plotted. Linearity of a graph would be the evidence in favour of the concerning process.

Schottky plots for Al-composite-Al, Al-composite-Cu, Al-composite-Ag, at different temperatures are presented in fig. 4.7 a, b and c, and the corresponding PF-plots are shown in fig. 4.8 a, b and c.

Further, the dielectric constant (\( \varepsilon \)) of the material can also be computed from the slopes of the above graphs as -
LOG J VS $E^{1/2}$ PLOTS FOR PMMA + MALACHITE GREEN FILMS
(SCHOTTKY PLOTS)

FIG: 4.7
\[ \sqrt{E} = \sqrt{V/D} \text{ (VOLTS}^{1/2} \text{ CM}^{-1/2}) \]

LOG $\sigma$ VS $\sqrt{E}$ PLOTS FOR PMMA + MALACHITE GREEN FILMS (POOLE - FRANKEL PLOTS).

FIG: 4.8
slope of Schottky plot -

\[ \delta_s = \left( \frac{e^3}{4 \pi \varepsilon \varepsilon_0} \right)^{\frac{1}{2}} \frac{1}{KT}, \text{ and} \]

slope of PF - plot -

\[ \delta_{PF} = \left( \frac{e^3}{\pi \varepsilon \varepsilon_0} \right)^{\frac{1}{2}} \frac{1}{KT}. \]

A comparison of the calculated value of with the experimental value may further provide a proof in favour/against, of a particular mechanism.

Values of as calculated by "Schottky" and "Poole - Frenkel" plots have been shown in table 4.1 and experimental values are also tabulated.

Furthermore, to find out whether transport of carriers is assisted by quantum mechanical tunneling, Fowler - Nordheim plots (log \( \frac{J}{\sqrt{V}} \) Vs \( \frac{1}{V} \)) have also been plotted in accordance with formula -

\[ J = AV^2 \exp \left( - \frac{\phi}{V} \right) \]

where,

\[ J = \text{current density}, \phi = \text{work function and} \]

\[ K = \text{Boltzmann's constant}, \]

and they have been shown in fig. (4.9). All the curves display similar nature showing an increasing trend. They do
LOG \( \frac{J}{V^2} \) VS INVERSE OF VOLTAGE FOR PMMA + MALACHITE GREEN FILMS (FOUNDER-NORDHEIM PLOTS).

FIG. 49
LOG \( \frac{J}{T^2} \) VS 1/\( KT \) PLOTS FOR PMMA + MALACHITE GREEN FILMS (RICHARDSON - PLOTS). FIG. 4.10
not yield linear portions in higher field region.

\[
\log \left( \frac{J}{T^2} \right) \text{ Vs } \left( \frac{1}{KT} \right),
\]
plots at different field values, resembles "Richardson type" plot (fig. 4.10 a, b and c).

4.8 : Discussion :

Transient Current :

When a d.c. field is applied on the specimen, the current in the beginning is very high and it subsides to a low steady value after some time. The possible reason for this phenomena may be that the application of the field, forces the space charge in the sample in the form of free charges. The initial high current might be due to these free charges.

If the substance is free from traps, the current would continue as steady current. If the sample contains traps, the forced free charges may get trapped in-to these traps and the decay of current is observed. The time required for the transient current to come down to a steady value depends on capture cross section of the traps for charge carriers. The fall of current with time is due to the gradual trapping of charge carriers in the traps. As the traps are filled, the current becomes steady.

The second reason for the decay of current may be the
relaxation of electric field by dipole orientation in the bulk of the sample. As the polarization increases, the absorption current will decrease and hence the equilibrium current tends to attain steady values.

The time dependence of charging currents observed in polymethyl methacrylate (PMMA) at different temperatures are shown in fig. 4.1 a and b. It can be seen clearly that the time in which the steady state conductivity is obtained is very much affected by temperature. At Tg (368°K), the steady state conductivity is obtained in about 300 seconds after the application of field. At higher temperatures ( Tg ), it takes less time to reach the steady state conductivity.

Fig. 4.2 a and b represent similar type of results for PMMA added with "Malachite Green". It appears that the time dependence of the transient currents is determined by the position of the measuring temperature with respect to the glass transition temperature. Some type of results have been reported by Vanderschuren et al.,209 for various polymers.

The charging current which flows on an application of a step field may be written as -
\[ J_c (t) = J_a (t) + J_s \quad (4.30) \]

where,

\[ J_c (t) = \text{charging current density}, \]

\[ J_a (t) = \text{absorption current density}, \]

\[ J_s = \text{steady state current density}, \text{ and} \]

\[ t = \text{the time after the application of the field}. \]

The charging current flowing in an insulator after the application of d.c. voltage, is known in most cases to decay approximately following the Curie-von Schweidler law -

\[ i (t) = A (T) t^{-n} \quad (4.31) \]

where \( i \) is the current, \( A (T) \) is a temperature dependent factor, \( t \) is the time after application of the external voltage, and \( n \) is a constant often observed to be close to unity.

A number of mechanisms have been proposed for the origin of these dielectric absorption currents, the most important of which are dipolar orientation tunneling of charge from the electrodes to empty traps, charge injection leading to space charge effects, hopping of charge carriers from one localized state to another, and electrode polarization. The charging current is a sum of time dependent absorption current and steady state conduction current.
The isothermal log I - log V plots at different temperatures for composite are shown in fig. 4.3. In these isothermals an ohmic nature is observed in the low field region $2.5 \times 10^3 - 1 \times 10^4$ V cm$^{-1}$ and above this current increases rapidly with voltage. An abrupt rise in the current is observed between 373 - 383°K, which may be attributed to some phase transition in the polymer matrix. The values of slopes are different at different voltages. This suggests that different conduction must be operative. The "$m$" values are of the order of 1 to 1.3 for lower voltages and 1.4 to 1.7 for higher voltages. At lower fields the isothermal exhibits almost ohmic behaviour in the lower field region. The "$m$" values for higher and lower temperatures at higher fields are in between 1.4 to 1.7. This is suggestive of non ohmic behaviour of current voltage relationship in this region, because the slope values in case of space charge limited current mechanism must be greater then 2. $^{60,62}$ Thus, these results can not be explained on this mechanism. The other possible mechanisms are -

(1) Charge carrier injection into the film from the contact via field assisted lowering of metal - insulator potential barrier (i.e.) Schottky - Richardson (SR) mechanism, and
(ii) Release of charge carriers from traps via field-assisted lowering of trap depth (i.e.) Poole-Frenkel (PF) effect. Both the processes bear a current voltage relationship of the form \( I \propto \exp(\beta V^{1/2}) \).

At the first hand let us subjects SR and PF emission on trial. Equation (4.8) predicts a linear relationship between \( \log I \) and \( V_{\text{f}} \) and the slope \( \beta_{\text{SR}} \) should vary inversely with temperature. Poole-Frenkel mechanism also predicts a linear relationship between \( \log I \) and \( V_{\text{f}} \) but the difference between the two mechanisms may be better understood on the basis of fundamental difference between them. This difference is that "SR" mechanism is electrode dependent whereas PF is electrode independent.\(^8\text{3}\) The SR mechanism is similar to Richardson emission of thermal electron whereas PF mechanism is concerned with the field assisted thermal ionization of traps into the conduction band. The traps may be of two types - first, donor like and, second, acceptor like. The effect is remarkable when donor like traps are more in number in the bulk of the insulator. These traps become neutral when occupied by electrons. Though there might be some acceptors like centres which liberate holes but the contribution to the total current by such holes will be quite small, because the mobility of the holes is much lower. Because of
these facts, it is essential to test the mechanisms on the basis of fundamental difference between them.

Lilly et al., 77 have shown that $\beta$ values for both the mechanisms remain the same, therefore it is not sufficient to explain the results simply by comparison of the theoretical and experimental values of $\beta$ only. The linearity of Schottky plots should not be only assigned to Schottky emission. Therefore, P–F plots were also put to trial. These plots are also linear in high field region but the linearity is comparatively lesser as compared to that of Schottky plots.

Log $J$ Vs $E^2$, at different temperatures for the composite is shown in fig. 4.5. The higher slope values for higher field region can be explained on the basis of space-charge build up at the electrodes from the charge carriers normally present in the dielectric (composite) which enhances the field at the electrode and leads to the higher slope. This is supported by the observations in Teflon and Mylar. 77 At high fields, the electrode–insulator potential barrier is lowered, therefore, the injection of charge carriers is facilitated. These charge carriers are trapped at the trapping sites of polymer phase boundaries, chain folding etc. This phenomena reduces the field at the electrode and thereby, the slope of
log J Vs $E^2$ approaches theoretical value. The value of $\beta$ calculated experimentally from the slope of log J Vs $E^2$ & theoretically calculated values of $\beta_{SR}$ and $\beta_{PF}$ are given in table 4.3.

The $\beta$ exp. values calculated from SR and PF plots have also been listed in table 4.1. It is clear from the theoretical and experimental values of $\beta$ that nothing can be said definitively about the charge carrier generation mechanism in the composites.

To confirm the charge carrier generation mechanism in the composite conductivity measurements were also made with copper and silver electrodes. If we treat the contact between the electrode and insulator as a large source of free charges the I - V characteristics should not depend on the manner in which the charges are generated, but are strictly connected with the manner the charge is transported. As pointed out earlier the contacts may be of two types -

(i) Ohmic, in which the charges are supplied and removed without the space charge and,

(ii) Non-ohmic, in which the charge carriers are injected or blocked and so they give rise to space charge effects.
The ohmic contact is the one, in which the contact potential difference, between the metal and insulator is less, and this contact may also become injecting at high fields whereas the blocking contact has a high potential difference because of the accumulation of the charge carriers in the interfacial states.

Electronic conduction in thin films may take place by a number of processes. For thick film electron conduction may take place by quantum mechanical tunneling process in which an electron can pass through a potential energy barrier without having sufficient energy to pass over the top of the barrier. Fowler-Nordheim\textsuperscript{102} have pointed out a relation for tunneling -

\[ J = A V^2 \exp\left(-\frac{\phi}{V}\right) \]

If the current obtained is due to tunneling process \( \log (J/V^2) \) Vs \( 1/V \) plots should yield a straight line of negative slope. In the present study the Fowler-Nordheim plots are found to be non-linear in high field region. Thus the tunneling process is ruled out in the present investigation.
At high temperatures ionic conduction becomes probable. The main characteristics of the ionic conduction are -

(i) Large activation energy as compared to electronic activation energy.

(ii) Large transient times

(iii) Polarization effect under d.c. field and

(iv) Transport of matter from one electrode to the other.

In the present study the results suggest that the charge carriers get injection, particularly at high fields by the electrodes in the polymer. This effect is more pronounced in case of dissimilar electrodes. The plots of \( \log J \) vs \( E^2 \) for Al, Cu and Ag electrodes are shown in fig. 4.5. From this figure it is clear that the conductivity of the composite is electrode dependent to a large extent which favours SR mechanism. It is also evident that the charge carrier generation is basically from the electrodes. The other process of charge carrier generation mechanism in the composite might be the release of injected charges from the traps following PF mechanism.

It is also found (fig. 4.5) that the current value increases with increasing electrode metal work function.
(except in case of copper). This is possible if the effective electrode composite potential barrier increases with decreasing electrode metal work function. This effective metal electrode - composite barrier for different electrodes at a constant field of $2.5 \times 10^3 \, V \, \text{cm}^{-1}$ was calculated from the slope of $\log (J/T^2) \, Vs \, (\frac{1}{KT})$ plot (Richardson plot, fig. 4.10) and given in table 4.2.

It is worthwhile to note that these plots are straight line in agreement with $SR$ mechanism. (Fig. 4.10) shows the temperature dependence of conductivity of the composite measured at different fields. Straight lines are observed for all the electrode materials for all the field values. This indicates that any thermodynamic transition taking place in the composite in this temperature range is absent because in case of any thermodynamic transition, we would have expected at least two straight lines with different slopes. The activation energy values for all the electrode materials used were calculated from the slope of $\log \sigma \, Vs \, 10^3/T$ plot (fig. 4.6) and are given in table 4.2. These activation energy values are very close to the experimentally determined metal insulator effective potential barrier (fig. Table 4.2) obtained for different electrode materials. This again suggest that the dominant charge carrier mechanism in this case, is Schottky - Richardson type. The possibility of trapping
of charge carriers in shallow traps can not be ruled out because the activation energy found out is slightly higher than the effective metal insulator potential barrier.

Conclusion:

It can be concluded that the dominant charge carrier generation in the present study is Schottky - Richardson mechanism. It also seems that some of the injected charge carriers get trapped in the shallow traps of the composite, and the subsequent release is controlled by Poole - Frenkel mechanism. The deviation in log $J$ vs $E^{1/2}$ plot might be due to space charge build up near the electrode.
Table 4.1: Theoretical and Experimental Values of β.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>ε'T</th>
<th>βSR</th>
<th>βPF</th>
<th>βexp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>363</td>
<td>2.50</td>
<td>.135</td>
<td>.270</td>
<td>.019</td>
</tr>
<tr>
<td>368</td>
<td>2.55</td>
<td>.166</td>
<td>.332</td>
<td>.017</td>
</tr>
<tr>
<td>373</td>
<td>3.00</td>
<td>.152</td>
<td>.304</td>
<td>.014</td>
</tr>
<tr>
<td>378</td>
<td>3.30</td>
<td>.143</td>
<td>.286</td>
<td>.014</td>
</tr>
<tr>
<td>383</td>
<td>3.70</td>
<td>.133</td>
<td>.266</td>
<td>.012</td>
</tr>
</tbody>
</table>

ε'T = value of dielectric constant at different temperatures.

Table 4.2: Effective Potential Barrier and Activation Energy of the Composite with Different Electrodes.

<table>
<thead>
<tr>
<th>Metal electrodes</th>
<th>Metal Function Φ (eV)</th>
<th>Effective Potential Barrier Φ' (eV)</th>
<th>Activation Energy E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>4.73</td>
<td>0.41</td>
<td>0.58</td>
</tr>
<tr>
<td>Aluminium</td>
<td>4.71</td>
<td>0.70</td>
<td>0.88</td>
</tr>
<tr>
<td>Copper</td>
<td>4.48</td>
<td>0.95</td>
<td>1.13</td>
</tr>
</tbody>
</table>
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