7. ELECTRICAL CONDUCTION

7.1 INTRODUCTION

The steady interest in the conduction properties of dielectric polymers in the last few decades reflects their technical importance. Thin films of polymeric materials are being considered for technical applications for insulation, isolation and passivation in microelectronics [1]. In such applications, the polymeric materials have to function in contact with semiconductor or metal films. The charge transport measurements in disordered insulators are of much interest because they provide information regarding the electronic structure of the material.

The study of a.c. conductivity also gives information about the type of conduction mechanism in the film. The chief advantage of a.c. conduction studies is that an investigation of the interior structure of the insulator is made possible. The second advantage is that, because of the low bias, the maximum field is kept to a minimum and there is little danger of more than one conduction process being active.

When thin films are subjected to low electric fields, they exhibit an ohmic behaviour. Under the influence of high fields, the thin films show much more interesting properties. According to the theory of band structure of solids, an insulator is characterised by a full valence band separated from an empty conduction band by a forbidden energy gap of a few electron volts. Strictly speaking, a well-defined energy gap is a property of a crystalline solid. However, the essential features of the band structure of a solid are determined by the short range order within the solid. Thus the general properties of the band structure of the crystalline state are carried over to the polycrystalline state. The lack of long-range order in a non-crystalline solid causes smearing of the
conduction and valence band edges so that the energy gap is no longer well defined. In the study of thin insulating films, it is assumed that this energy gap, to a first order approximation, can be represented by a well-defined energy gap which is a representative of perhaps an average value of the actual non-discrete energy gap. With this model, features of the band structure of thin film insulators can be estimated [2].

In order to measure the electrical conductivity of an insulator, electrodes are connected to its surfaces. The electrical conduction in such a Metal-Polymer-Metal (MPM) system is determined not only by the properties of the insulator but also by the contact of the insulator with the electrodes. There are three types of contacts, namely, (i) ohmic (ii) neutral and (iii) blocking contacts.

In general, most of the polymers are insulating because these polymers have a low conductivity. The conductivity depends on the thermally generated carriers and also on the suitable dopants [3-4]. Due to the complicated chemical and physical structures of the polymers, the role of dopants in the conduction process [5] is difficult to understand. However, a considerable amount of work has been reported on steady state electrical conduction in pure and impurity doped polymers [6-16]. In the present investigation, an attempt has been made to study the a.c and d.c. conduction behaviour of solution grown pure 4% CA and 0.05%, 0.1% and 0.15% nickel doped CA films.

7.2 THEORY

7.2.1 A.C.Conduction

The a.c.conductivity of amorphous materials gives an idea about the conduction mechanism in such materials. In a parallel plate capacitor, if $C_0$ is...
capacitance value in air and \( \varepsilon_r \) is the permittivity of the medium that fills the condenser, then, neglecting the fringing effects, the capacitance can be expressed as,

\[
C = \varepsilon_r C_0
\]  

(7.1)

When an alternating e.m.f. \( 'V' \) with an angular frequency \( \omega = (2\pi f) \) is applied across this condenser, the alternating current is given by,

\[
i = j \omega \varepsilon_r C_0 V
\]  

(7.2)

Substituting the values of \( C_0 \) as \( C_0 = \frac{A}{d} \), where 'A' is the common area of the plates, \( d \) the separation between them and the \( \omega \) angular frequency, equation (7.2) becomes

\[
i = j \omega (\varepsilon' - j \varepsilon'')(A/d) \varepsilon_0 V
\]  

(7.3)

where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of permittivity.

By definition the field strength is \( E = \frac{V}{d} \) where 'V' is the voltage applied and the current density is \( J = \frac{i}{A} \). Therefore,

\[
J = j \omega \varepsilon_0 \varepsilon' E + \omega \varepsilon_0 \varepsilon'' E
\]  

(7.4)

The conductivity (\( \sigma = \frac{J}{E} \)) is given by,

\[
\sigma = j \omega \varepsilon_0 \varepsilon' + \omega \varepsilon_0 \varepsilon''
\]  

(7.5)
In a dielectric, the imaginary part is accounted for the capacitance which involves the real part $\varepsilon'$ of the relative permittivity. Thus the dielectric conductivity is defined as the real part of the ratio $J/E$, that is,

$$\sigma_0 = \omega \varepsilon_o \varepsilon''$$  \hspace{1cm} (7.6)

The conductivity, $\sigma_0$ represents the sum of all the loss mechanisms in the material and is a measure of the performance of the dielectric as an insulator.

For the parallel equivalent circuit,

$$\tan \delta = 1/\omega C_p R_p$$  \hspace{1cm} (7.7)

where $C_p$ is the parallel equivalent capacitance and $R_p$ is the parallel a.c. resistance. Therefore the equivalent parallel conductance $G_p$ will be

$$G_p = 1/R_p = \omega C_p \tan \delta$$  \hspace{1cm} (7.8)

The frequency dependence of conductivity of different materials has been widely investigated by many researchers [17-21] because they can give information about the electronic structure of these materials. In all these cases the conductivity was found to be a non-decreasing function of frequency. Such a behaviour is suggestive of hopping conduction [22], either by electrons or ions. This theory is in line with Anderson’s theory [23], according to which, the localised states generally exist in disordered systems, and with Mott’s [24] model of the pseudogap in amorphous solids.

Pollack and Geballe [25] have given a detailed interpretation of the frequency dependence of the electrical conduction in amorphous solids. The
a.c. conductivity should increase with frequency of the applied field and saturate at frequencies high enough to be comparable to the natural frequency of hopping between the centers. It has been pointed out that it is necessary to average conductivity over all hopping distances and activation energies for all pairs of occupied and empty centers [26]. This averaging process yields, for single or multiple hops, the a.c. conductivity \( \sigma(\omega) \) in amorphous solids depends on the angular frequency \( \omega \) obeying relation,

\[
\sigma(\omega) \propto \omega^n
\] (7.9)

where \( n \) decreases from 1.0 for single hops to 0.5 for multiple hops. This relation is in reasonable agreement with the observations [18-27]. The increase of \( n \) at low temperatures is due to the predominance of single holes. This indicates that the frequency dependence of a.c. conductivity saturates at very high frequencies.

However, there are a few cases where a square law dependence is observed [16,28]. This is explained on the basis of two center hopping as

\[
\sigma \propto \omega^2
\] (7.10)

i.e., the conductivity increases as the square of the frequency. The dielectric films that have high densities of localised levels in the forbidden gap also exhibit the hopping mechanism. The presence of compensated donors and acceptors in the crystalline dielectric also associates the hopping process with them. These properties could be expected in the case of amorphous substances. In these substances, electronic transitions between trapping levels suggest a more fundamental hopping mechanism which gives the Mott \( T^{-1/4} \) Law [29]. Jonscher has theoretically shown that the change in the character of transitions of the carriers is related to the slope of the log \( \alpha \) versus frequency curve.
7.2.2. D.C Conduction

In general, polymers are amorphous or semicrystalline substances. The transport mechanism in amorphous materials is more complicated than in crystalline materials, especially for monocrystals where a long range order exists. Thus the transport mechanism in dielectric solids can be better understood from modifications applied to the quantum mechanical theory of solids. Hence the band model of disordered materials has some of the gross features of crystalline structure but with significant difference concerning details.

If the concept of band models are directly applied to organic solids, we expect a large energy gap between the valence and conduction band, so that thermal activation in the normal temperature range is too small for transferring an electron from the valence band to the conduction band.

In amorphous substances there are many localised charge carrier levels and carrier mobility is very low. The low lying states may be treated as trapping sites (levels) but in comparison with crystalline substances, they are not related to the discrete activation energy values because they are situated in the broadened edges of the conduction band and valence band.

The electrons can be raised into conduction band in a number of ways [30-32]. If the forbidden gap, (energy gap) is small and temperature is high, the carriers can be excited thermally from valence band to conduction band by acquiring sufficient energy to cross over the energy gap, due to Schottky emission from the metal surface electrodes and by the thermal excitation of the electrons in the trapping levels.
Fig. 7.1. Diagram of the various conduction processes
7.2.2.1 Different conduction mechanisms proposed to explain the transport phenomenon in polymer films.

If one applies the concept of the band model directly to organic solids, even to non-crystals, one should expect a very large energy gap between the valence and conduction bands, so that thermal activation in normal temperature range is too small for transferring an electron from the valance to the conduction band. The phenomenon of dark electrical conduction in dielectrics consists of two basic processes of carrier generation and transport.

Different conduction mechanisms have been proposed to explain the transport phenomenon in polymer films. Fig 7.1 shows some of the conduction mechanisms which add to the ohmic conduction in polymers [33] at high fields i.e., above $10^4$ V/cm. The figure is valid only in case of dielectrics with well defined valence and conduction bands. Carrier generation i.e., the production of carriers responsible for conduction in the bulk of the dielectric is based either on injecting an adequate number of them from the electrodes by thermionic emission (Schottky mechanism) [34-35] thermionic field or field emission are on the dissociation of donor/acceptor centres in the bulk of the material (Poole-Frankel generation) [36-37] where the carriers can be transported through the bulk of the dielectric faster than they are generated. The dominant roll in the conduction phenomenon is played by the generation properties. In the opposite case the transport process decides the electrical conduction. Various other mechanisms such as tunnelling [38] and thermally activated hopping [39] etc., have also been proposed by various workers to explain the conduction behaviour of polymers. The various mechanisms are summarised briefly in the following pages.
Fig. 7.2: Schottky effect at a Neutral contact
(a) Schottky emission

Consider a metal-insulator metal sandwich structure. The potential step at the metal-insulator interface changes smoothly due to the image force which arises as the result of the metal surface becoming polarised by the escaping electron. Fig 7.2 shows the potential step (w.r.t. Fermi level) at a neutral barrier with attendant image potential as a function of distance. The barrier in the presence of image force is illustrated by the line AB.

When the potential barrier is too thick to permit tunnelling to occur, or at sufficiently high temperatures, the current flowing through the insulator is limited principally by the rate at which electrons are thermally excited over the interfacial potential barrier into the insulator conduction band. The current density expression in Schottky emission is,

$$J = AT^2 \left( \exp \left( \frac{e\beta_s F^{1/2} - \phi_0}{kT} \right) \right)$$  \hspace{1cm} (7.11)

where $A$ is the Richardson constant and $\phi_0$ is the barrier height at the metal - insulator interface in the absence of the field. $\beta_s$ and $\beta_{pf}$ are constants such that,

$$2 \beta_s = \beta_{pf} = 2\left(\frac{e}{4\pi\varepsilon\varepsilon_0}\right)^{1/2}$$  \hspace{1cm} (7.12)

where $\varepsilon$ is the dielectric constant of the polymer and $\varepsilon_0$ the permittivity in free space.

(b) Poole-Frenkel emissions

The Poole - Frankel effect (field assisted thermal ionisation) is the lowering of cumbolic potential barrier when it interacts with an electric field and is
Fig. 7.3 Poole-Frenkel Emission at a Donor centre
usually associated with the lowering of a trap barrier in the bulk of insulator as shown in figure 7.3.

When the electric field interacts with the coulombic potential barrier of a donor centre or trap, the height of the barrier is lowered. This trap depth/ barrier height, \( \phi_0 \), is given by either the difference in ionisation potential or electron affinities of trapped molecule and host matrix. The expression of current density takes the form

\[
\sigma = \sigma_0 \exp(\frac{e \beta_F F^{1/2} \phi_0}{kT})
\]

(7.13)

where \( \sigma_0 \) is the low field conductivity, the other terms representing quantities already mentioned. In this case the conductivity is not electrode limited.

(c) Tunnelling

According to quantum theory, the wave function of an electron has finite values within the classical forbidden barrier of the insulator separated by the two metal 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 of the potential barrier. Tunnelling may take place through barriers if effective thickness is reduced by a strong electric field.

I) Direct Tunnelling

For a very thin film in high field it becomes possible for electrons to tunnel directly from one electrode to the other. The current density associated with the processes, at high fields, is given by the Fowler Nordheim expression [38],

\[
J_T = \left( \frac{3.38 \times 10^{-10}}{\phi_T} \right) F^2 \exp \left[ 0.069 \frac{\phi_T^{3/2}}{F} \right]
\]

(7.14)
where $\phi_T$ is the height of the potential barrier.

ii) Thermally Assisted Tunnelling

Direct tunnelling involves transfer of electrons between the Fermi level of the electrodes. If, in the electrode, an electron raised above the Fermi level by thermal activation, it may tunnel into the insulator conduction band when a field is applied across the insulator. This is called thermally assisted tunnelling. The current density is computed as

$$J_{\text{tat}} = a \exp \left( \frac{b - \phi}{KT} + C \right) V^{1/2} / t^{1/2}$$

(7.15)

where $a = 6.8 \times 10^{-7}$ A Cm$^{-2}$, $b = 1.65 \times 10^{-24}$ Jm$^{1/2}$ V$^{-1/2}$, $C = 1.2 \times 10^{-4}$ m$^{1/2}$ and $t$ is tunnelling distance.

iii) Thermally assisted hopping

Conduction may also take place due to the electron hopping between the localised electron states. The condition for this conduction mechanism is that the average hopping distance $R$ should be such that $FR \ll KT$

Mott (39) showed that if the mean hopping distance is $R$, and the distance between the centres $R_0$, then

$$\Delta \omega = \Delta \omega_0 \left( \frac{R_0}{R} \right)$$

(7.16)

The hopping conduction mechanism is characterised low activation energies and a dependence of $\log \sigma$ on $T^{-1/4}$ as

$$\log \sigma \sim \left( \frac{T_0}{T} \right)^{\nu}$$

(7.17)

where $T_0 = 2.1 \left( \frac{\alpha}{KN(E_F)} \right)^\nu$

(7.18)
\( \alpha \) is the decay constant of the localised wave function, \( K \), the Boltzmann constant and \( N(\varepsilon_F) \) is the density of the states in the vicinity of the Fermi level.

**(d) Space charge limited conduction**

If the Schottky tunnelling and impurity processes are not rate limiting processes then there are fair chances for the space charge to build up and this will be the major source of impedance, which affects the applied voltage.

At low applied bias, if the injected carrier density is greater than the free carrier density, the current becomes space charge limited (Fig7.4). The two requirements that must be satisfied for SCLC flow to be observed are (1) At least one electrode must make ohmic contacts with the insulator. (2) The insulator must be relatively free from trapping effects. The current passing through the insulator is given by

\[
J = 10^{-13} \mu \varepsilon V^2 / t^3 \text{ A/cm}^2
\]

(7.19)

where \( V \) is the applied voltage, \( t \), the thickness of the insulator, \( \mu \), the drift mobility of the charge carriers and \( \varepsilon \) is the dielectric constant.

7.3 MEASUREMENTS

Initially the solution grown CA (Pure and 0.05\%, 0.1\% and 0.15\% nickel doped) films were stabilised by repeated annealing. The a.c. conductivity have been evaluated from the values of (i) capacitance and loss factor which were measured by the methods described in section 6.3, (ii) the thickness of the film and (iii) area of the capacitor. For d.c. conduction studies the current across the capacitor was measured at different temperatures using an electrometer amplifier (ECIL – EA 815) as given in the block diagram Fig.7.5.
Fig. 7.4: Space charge limited conduction in insulating films with Ohmic contacts
(a) Under zero BIAS
(b) With voltage BIAS
Figure 7.5: Block Diagram of D.C. Conduction Measurement Setup

- Electro Meter Amplifier
- Thermocouple
- Film on Heater
- Rotary Pump
- Digital Multimeter
- Regulated Power Supply
- Power Supply for Heater
7.4 RESULTS AND DISCUSSION

7.4.1 A.C. Conduction

The a.c. conductivity for pure and nickel doped CA films were calculated at different temperatures using the equation.

\[ \sigma = \omega c_p \tan \delta \frac{d}{A} \]  \hspace{1cm} (7.20)

where

- \( \sigma \) = Conductivity
- \( \omega \) = Angular frequency
- \( c_p \) = Parallel capacitance
- \( d \) = Thickness of the dielectric film
- \( A \) = Area of dielectric film

The plots of a.c. conductivity versus frequency (10kHz-10MHz) for 4% CA and 0.15% nickel doped CA films are shown in the Fig. 7.6 (a and b). The conductivity of the pure and doped samples increases linearly with frequency for the entire temperature range (303 to 450 K). The variation of a.c. conductivity in the case of 0.05 and 0.1% of nickel doping is not appreciable, however some important results are discussed (Fig. 7.7 b and c). The a.c. conductivity is observed to be proportional to \( \omega^n \), where \( n \) is seen to vary depending on the frequency and temperature range studied.

From Fig.7.6 (a), at 303 K the conductivity of the pure film shows almost a linear variation with the average `n' value of 0.87 for the entire range of frequency and on increasing the temperature to 350 K, the n value is 1.7 upto 30 kHz, there after to 1.3. At 400 K the n value remains at 0.27 until 30 kHz and afterwards it changes to 1.25 (from 30 kHz to 1 MHz) and 1.83 (1 to 10 MHz)
Fig. 7.6 (a) Log $\sigma$ versus log $F$ of pure 4% CA film at various temperatures.
Fig. 7.6 (b) Log $\sigma$ versus log $F$ of 0.15% nickel doped CA film at various temperatures.
Fig. 7.7 (a) Log $\sigma$ versus $\frac{1}{T} \times 10^3$ of pure 4% CA film at various frequencies.
Fig. 7.7 (b) Log $\sigma$ versus $\frac{1}{T} \times 10^3$ of 0.05% nickel doped CA film at various frequencies.
Fig. 7.7 (c) Log $\sigma$ versus $\frac{1}{T} \times 10^3$ of 0.1% nickel doped CA film at various frequencies.
Fig. 7.7 (d) Log $\sigma$ versus $1 \times 10^3$ of 0.15% nickel doped CA film at various frequencies.
further increase of temperature to 450 K results with two regions of frequencies with \( n = 0.16 \) and 1.83.

On doping with 0.15% of nickel (Fig.7.6 b ) results with three frequency regions i.e., low, mid and high frequency regions, where the \( n \) values vary from 0.4 to 1.5, 1.00 to 1.4 and 1.83 to 2.0 for the temperature of 303, 350 and 450 K respectively.

The activation energies have also been calculated from the slopes of the log \( \sigma \) versus \( (1/T) \) plots of Fig 7.7 (a to d) for pure and nickel doped CA films.

The Fig. 7.7 a depicts the variation of conductivity with temperature of pure 4% CA films at different frequencies (10kHz to 10MHz). In this case two regions viz. low temperature and high temperature ( >375 K) were observed. In most of the cases the activation energy decreases with the increase of frequency was noticed. In the low temperature region the activation energy varies from 0.36 to 0.03 eV and in the high frequency region this value changes from 0.99 to 0.26 eV. Films at both the 300kHz and 1 MHz frequencies show a steady conductivity until 400 K.

Fig .7.7 (b and c) shows the variation of \( \sigma \) with temperature in 0.05 and 0.1% nickel doped CA films at 10 kHz and 10 MHz. In both the cases a slight variation in activation energy was observed in region I (low temp). In this region, activation energy varies from 0.07 to 0.03 eV. 0.05% nickel doped CA film and from 0.15 to 0.10 eV in 0.1% nickel doped CA films. The figures show three regions of frequencies, i.e. region I (low temp), region II (plateau region), where the conductivity almost remains same at this temperature range and region III (high temperature), where the sudden increase in conductivity is observed. In both the films the region III was observed at >400 K. In this region the activation
energy changes from 0.33 to 0.10 eV and 0.33 to 0.66 eV in 0.05 and 0.1% nickel doped CA films.

In most of the cases, in the first region (low frequency) the value of $n$ is found to vary up to 1. It has been observed that $n$ decreases as the temperature increases. In the other regions (II and III) this value varies from 1 to 2, i.e., in most of the cases, it shows a square law dependence.

The presence of two or three dispersive regions in the conductivity versus frequency plot suggests that there are two/three dissipation mechanisms operating in the frequency range studied. This behaviour suggests that the mechanism responsible for a.c. conduction is of the hopping type. It is consistent with the results reported on various hopping systems [17,40-41]. Jonscher [42] explained for this behaviour on the basis of easy and difficult hops of the carriers between possible sites. Though the high frequency dependence of the conductivity is accompanied by lead and electrode effects, they can be minimised by thick aluminium deposits.

Pollack and Gabelle [25] have theoretically predicted that the relation for non-adiabatic condition is

$$\text{Re} \left[ \sigma_d (\omega) \right] \propto [14.8 - 1/2 \ln \omega]^4$$  \hspace{1cm} (7.21)

The slope of the $\ln[\sigma_d (\omega)]$ versus $\ln \omega$ curve is found to be 0.99 according to this theory. This is in agreement with the experimental value. Hence the dispersion in the low frequency region can be explained as due to non-adiabatic hopping of charge carriers between impurity sites. Pollack and Geballe have also explained that if hopping takes place between a random distribution of localised sites, then the value of $n$ lies between 0.5 and 0.1. Here the lower value of $n$ occurs for multiple hops and the higher values for single hops.
higher value of n at lower temperatures is attributed to the predominance of single hops. The square law dependence of conductivity at higher frequencies has been explained by Argall and Jonscher [17] based on two center hopping.

Since the structure of CA films is a mixture of amorphous and crystalline, there is a possibility for the change in the degree of crystallinity of polymer with increasing temperature, which has been well established by earlier workers [43,44]. This change in structure results in the re-orientation on molecules in the polymer matrix and this may be the case of the sudden variation in the conductivity at high temperatures. It is seen that the conductivity of doped films behaves similar to that of the undoped CA films but the conductivity values are increased on 0.05% doping and further doping results with a slight decrease in the conductivity at higher frequencies. The higher values of conductivity may be due to the formation of CTC between nickel and CA polymer matrix.

These charge transfer complexes may reduce the barrier height at the amorphous/crystalline interfaces and provide conducting paths for the charge carriers through these boundaries [45]. This suggests the formation of the charge transfer complexes due to the electrostatic interaction between the dopant and the polymer main chain which reduces the intermolecular interaction between the dipolar molecules. On further doping nickel (0.15%) the polymer acts predominantly as an intermolecular plasticizers where the nickel atoms are distributed in the inter-aggregate space. This may be attributed to the formation of molecular aggregates of the doped substance as the polymer matrix, there by decreasing the mobility of charge carriers.

Fig.7.7 (a to d) show that the temperature coefficient of electrical conductivity of these films increases suddenly after the glass transitions temperature (T_g) [see Table 8.2 of chapter 8]. This behaviour can be interpreted qualitatively as resulting from a remarkable increase in the mobility of
the amorphous chains [46,47] At $T_g$, the molecular motion of chain segment lowers the trap depth considerably and trapped charges are realised by thermal excitation. Above $T_g$, the life time of carriers in the conduction band is longer, which increases the conductivity rapidly.

The low activation energy observed in the low temperature region is only large enough to allow migration of atoms into vacancies. The higher activation energies observed in the high temperature region is the sum of the energies required for the generation of charge carriers and their motion into the vacancies.

The decrease of the activation energy at higher frequencies has been explained by Chopra and Bahl [18]. The total a.c. resistivity due to the conduction by intrinsic excitation ($\rho_1$) and by hopping which are parallel processes is given by the equation.

$$\frac{1}{\rho_{a.c}} = \frac{1}{\rho_1} + [A/\omega^n] \cdot e^{-\omega(T,\omega)/kT} \cdot (\Omega >> \omega)$$

Here $A$ is a constant, $\Omega$ is the characteristic hopping frequency and the activation energy $\omega$ for hopping is a function of both the temperature and frequency. The frequency dependence arises, since $\omega$ depends on the hopping path which will vary with the frequency. Thus as frequency increases, the activation energy decreases to a small value characteristic of thermally activated hopping.
7.4.2 D.C. Conduction

The electrical conductivity of pure and Ni-doped CA films was studied under different temperatures and bias field strengths. Various parameters used for the measurement of electrical conductivity are

- Film growth temperature: 303 K
- Film thickness: (a) 12,000 Å in electrical conductivity studies, (b) 10,000 Å in I-V studies.
- Bias Field Strength Range: 0.83 x 10^6 V/m to 33.3 x 10^6 V/m.
- Temperature range: 303 K to 423 K
- Voltage range: 40 - 200 V

The annealed films were subjected to the electrical conductivity studies. The general variation of conductivity was found to be similar to that of other polymers like polypropylene [48], polyethylene [49], polystyrene [50] and polyvinyl acetate [51].

7.4.2.1 Electrical conductivity

(A) Results

Electrical conductivity was studied as a function of temperature in the range of 303 to 423 K. The bias field strength applied to the films was in the range of 0.83 x 10^6 V/m to 33.3 x 10^6 V/m.

Figure 7.8.a shows the dependence of Log I as a function of inverse temperature for undoped films for different bias field strengths. From the figure two clear regions of activation energy are observed. A rapid increase of log I with 1000/T at above 363 K was noticed. The activation energies responsible for the conduction process were evaluated by fitting these values to relation.
Fig. 7.8 (a) Log $I$ versus $\frac{1000}{T}$ of pure 4% CA film at various bias fields.
Fig. 7.8 (b) Log I versus $\frac{1000}{T}$ of 0.05% nickel doped CA film at various bias fields.
Fig. 7.8 (c) Log I versus $\frac{1000}{T}$ of 0.1% nickel doped CA film at various bias fields.
Fig. 7.8 (d) Log I versus $\frac{1000}{T}$ of 0.15% nickel doped CA film at various bias fields.
<table>
<thead>
<tr>
<th>Film</th>
<th>Activation Energy (U)</th>
<th>Trap depth (φ)</th>
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<tbody>
<tr>
<td></td>
<td>Region I</td>
<td>Region II</td>
</tr>
<tr>
<td></td>
<td>U (eV)</td>
<td>φ(eV)</td>
</tr>
<tr>
<td>Pure</td>
<td></td>
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<tr>
<td>4%CA</td>
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<tr>
<td>Ni-doped CA</td>
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</table>

<table>
<thead>
<tr>
<th>Field x 10^6 V/m</th>
<th>Pure</th>
<th>4%CA</th>
<th>Ni-doped CA</th>
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<th>Ni-doped CA</th>
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Field activation energy (U) and metal-insulator work function/trap depth (φ) for different films.
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<tr>
<th>Film</th>
<th>Field x 10^6 V/m</th>
<th>Activation Energy (U) and Metal - Insulator Work function/trap depth (φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Region I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>U (eV)</td>
</tr>
<tr>
<td>0.1% Ni-doped CA</td>
<td>0.83</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>33.3</td>
<td>0.35</td>
</tr>
<tr>
<td>0.15% Ni-doped CA</td>
<td>0.83</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>33.3</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Log I = constant - U/KT

Where 'U' is the activation energy and 'K', the Boltzmann constant. The results are given in Table 7.1. The activation energies corresponding to the two regions suggesting that two different mechanisms are responsible for conduction in the two temperature ranges i.e., below and above 363 K.

The nature of the potential barriers can be determined from the log (I/T²) versus 1000/T plots drawn for various field strengths (shown in fig 7.9 (a)). These plots also indicate two clear regions of activation corresponding to the two temperature ranges. The parameter φ, called the metal insulator work function/trap depth, was calculated from the above plots using the Schottky equation (eqn 7.11).

The values of φ are found to increase with the increase in bias field strength. This value is approximately equal to the activation energy when the lower bias field (0.33 x 10⁶ V/m) is applied. On increasing the bias field, the difference between the activation energy and the value is also widened and for the bias field 33.3 x 10⁶ V/m, the value of φ = 1.13 eV where as the corresponding activation energy is only 0.29 eV. In order to differentiate between these two, further studies were done on I - V characteristics (see section 7.4.2.2 of this chapter). These studies reveal that this potential barriers corresponds to the metal insulator work function is associated with the Schottky conduction mechanism.

On doping 0.05% of nickel with CA, the behaviour of log I Verses 1000/T plots show interesting changes, which is shown figure 7.8 (b). The entire temperature region is now divided into three regions; the first and third regions on the low and high temperature sides showing sharply increasing conductivity,
Fig. 7.9 (a) Log $\frac{1}{T^2}$ versus $\frac{1000}{T}$ of pure 4% CA film at various bias fields.
Fig. 7.9 (b) Log $\frac{1}{T^2}$ versus $\frac{1000}{T}$ of 0.05% nickel doped CA film at various bias fields.
Fig. 7.9 (c) Log $I$ versus $\frac{1000}{T}$ of 0.1% nickel doped CA film at various bias fields.
Fig. 7.9 (d) Log $I$ versus $\frac{1000}{T}$ of 0.15% nickel doped CA film at various bias fields.
separated by a region of weakly temperature-dependent conductivity (plateau region). The electrical conductivity at room temperature showed a slight decrease when comparing with their undoped counterpart where as, there is an increase in activation energy values is observed. At high temperature, however the activation energies showed a decreasing trend. When the dopant concentration is increased to 0.1 and 0.15% (shown in Fig 7.8(c) - (d)), results with spreading of the plateau region. The activation energies slowly decreasing with the increase in dopant concentration. But, the conductivity values are found to increase with the increase in dopant concentration.

From the slopes of log I Vs 1000/T plots as shown in figures 7.8(b) to 7.8(d), activation energies corresponding to different biasing fields are evaluated and tabulated in Table 7.1-7.2. The values of $\phi$ are evaluated from log ($I/T^2$) versus 1000/T plots (shown in Figs 7.9 (b) to 7.9 (d)). The $\phi$ showed the same trend as in the case of their undoped counterpart.

7.4.2.2 Current - voltage characteristics

(A) Results

The current - voltage measurements were made on the samples in the voltage ranges 40 to 200 V at different temperatures and fields. The average thicknesses of films are 10000 Å. Fig 7.10 (a) shows the variation of log I as a function of square root of voltage at different temperature of 303, 333, 363, 393 and 423 K. The current was found to increase sharply with voltage at lower fields than at higher fields. The sharp increase in current at low fields, observed in the log I versus $V^{1/2}$ plots for undoped films could be due to space charge effects. The magnitudes of current and the slopes of log I versus $V^{1/2}$ plots were found to increase with increasing film temperature. The variation in the high field region was essentially linear at all temperatures. This linear behaviour of Log I versus $V^{1/2}$ plots in the high field region suggests either Schottky type or Poole - Frenkel
Fig. 7.10 (a) Log I versus $V^{1/2}$ of pure 4% CA at various temperatures.
Fig. 7.10 (b) Log I versus $V^{1/2}$ of 0.05% nickel doped CA at various temperatures.
Fig. 7.10 (c) Log I versus $V^{1/2}$ of 0.1% nickel doped CA at various temperatures.
Fig. 7.10 (d) Log I versus $V^{1/2}$ of 0.15% nickel doped CA at various temperatures.
type mechanism, both of which are electronic processes. In order to distinguish between the two mechanisms, slopes of log \( I \) versus \( V^{1/2} \) were equated to \( e\beta/\kappa T d^{1/2} \), from which experimental value of \( \beta \) was evaluated. The theoretical value of \( \beta \) for either Schottky (or) Poole-Frenkel mechanism could be calculated using the relation.

\[
\beta_{RS} = \left( \frac{e}{4\pi \varepsilon \varepsilon_0} s \right)^{1/2} \quad \text{for Schottky emission}
\]

and \( \beta_{PF} = 2 \beta_{RS} \quad \text{for Poole-Frenkel emission} \)

Taking \( \varepsilon \), the dielectric constant of the material as 4.5 [52]. The experimental and theoretical values of \( \beta \) for Schottky mechanism as well as Poole - Frenkel mechanism are shown in table 7.3. It is seen that \( \beta_{exp} \) values are nearest to \( \beta_{RS} \) theoretical value than indicating Schottky emission. In this mechanism, the elections are injected from the electrodes into the bulk of the polymer over a potential barrier corresponding to the polymer - electrode interface.

The current- voltage measurements made on doped samples of average thicknesses of 10000 \( \AA \) are presented in figs. 7.10 (b) - (d) for 0.05%, 0.1% and 0.15% Ni doped films at different temperatures. When the polymer was doped with 0.05 and 0.1% of the dopant the slopes of Log \( I \) Vs \( V^{1/2} \) plots at high fields, showed a increase while at low fields there was no appreciable variation. On further doping of 0.15% results with a linear variation of current at higher fields started appearing as in the undoped films.

To determine the actual conduction mechanism, the value of \( \beta \) at different temperatures, deduced from the plots of log \( I \) versus \( V^{1/2} \) are compared with the theoretical values (Table 7.3-7.4). It is seen that \( \beta_{exp} \) values are closer to \( \beta_{RS} \), thereby indicating the Schottky emission.
<table>
<thead>
<tr>
<th>Film</th>
<th>Temperature (K)</th>
<th>Experimental value of $\beta \times 10^3$ ($V^{1/2} \text{ m}^{1/2}$)</th>
<th>Theoretical $\beta_{rs} \times 10^3$ ($V^{1/2} \text{ m}^{1/2}$)</th>
<th>Theoretical $\beta_{pt} \times 10^3$ ($V^{1/2} \text{ m}^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure 4% CA</td>
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</tr>
<tr>
<td>303</td>
<td>1.26</td>
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<tr>
<td>333</td>
<td>1.3</td>
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<td>363</td>
<td>0.79</td>
<td>1.78</td>
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<td>393</td>
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<tr>
<td>423</td>
<td>1.59</td>
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<tr>
<td>0.05% Ni-doped CA</td>
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<td>3.56</td>
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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>423</td>
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<td></td>
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</tr>
<tr>
<td>Film</td>
<td>Temperature (K)</td>
<td>Experimental value of $\beta \times 10^{-5}$ $(V^{1/2} m^{1/2})$</td>
<td>Theoretical value of $\beta_{RS} \times 10^{-5}$ $(V^{1/2} m^{1/2})$</td>
<td>Theoretical value of $\beta_{PF} \times 10^{-5}$ $(V^{1/2} m^{1/2})$</td>
</tr>
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<td>--------------------------</td>
<td>----------------</td>
<td>---------------------------------------------------------------</td>
<td>---------------------------------------------------------------</td>
<td>---------------------------------------------------------------</td>
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</tr>
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<td>1</td>
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<td>423</td>
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<tr>
<td>0.15% Ni-doped CA</td>
<td>303</td>
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<td>0.9</td>
<td>1.78</td>
<td>3.56</td>
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<td>393</td>
<td>0.9</td>
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<tr>
<td></td>
<td>423</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 7.4
7.4.2.3. Discussion

The electronic conduction mechanisms, commonly discussed for insulating films in different temperature and field regions are tunneling, Schottky emission, Poole Frenkel emission, field ionisation of impurities or traps, ionic conduction or space charge limited conduction. A knowledge of the activation energies of the relevant region gives substantial information about the nature of the conduction mechanism operating in the materials.

In the present study, undoped films showed two clear regions of activation, below and above 363 K. The activation energies ranging from 0.17 to 0.29 eV in the low temperature region and 0.50 to 0.83 eV in the high temperature region. In the low temperature region, as the activation energies are lower, one can assume electronic conduction mechanism for conductivity behaviour while in the high temperature region one can assume either electronic or ionic conduction as the higher value activation energy can be associated with both the processes. If the ionic conduction is to be responsible for conductivity in the high temperature region, then according to rate theory [53], the plots of log I versus V^{1/2} show a sharp rise at high temperatures from their linear behaviour. Since such behaviour is not predominant in the present study, ionic conduction seems unlikely. It appears that electronic conduction continues to operate even at high temperatures. In the low temperature region, the conduction may be caused by the thermal detrapping of the electrons from the traps in the polymer. As the activation energies are of the order of 0.25 eV, it may be suggested that shallow traps are responsible for the conduction. In the high temperature region, it is believed that the conduction is caused by the electrons injected from the electrodes into the bulk of the polymer through a potential barrier corresponding to the metal insulator interface (Schottky mechanism). A behaviour similar to the present investigation has been reported by Sinha and Srivastava on polystyrene
films [54]. Pillai and Gupta [55] also observed two slopes in the conductivity behaviour of polystyrene doped with leucomalacate green.

The doped films in contrast to the undoped films showed three regions in log I versus 1/T plots; two regions of sharp activation separated by a weak plateau region. The plateau region is mainly confined to the glass transition (\(T_g\) from to \(T_g\) to \(T_g\) to ) temperature region of CA (given in table 8.2 chapter 8). A behaviour, similar to this, has been reported by several authors on various polymer with different dopants. Jain et al [56] have observed three regions of conductivity on pure and doped polyvinyl alcohol films. While the conductivity in the low and high temperature regions was attributed to electronic and ionic conduction respectively, no definite reasons were given for it as it occurred in the glass transition temperature region of the polymer. Gupta [57] has observed a similar behaviour on pure and vanadyl doped films of polyvinyl fluoride. No reason was forwarded for the occurrence of the plateau region whose activation energy was reported to 0.23 eV as compared to 1.2 eV and 1.35 eV as compared to 1.2 eV and 1.35 eV for the other regions. The results Sharma and Rukmini [58] on Fe-doped polyvinyl acetate films also showed similar behaviour. They have explained the conduction in the plateau regions in terms of conduction occurring between dopant ions. In the present study, while it is difficult to assign any particular reason for this behaviour, the authors feel that it is a combined behaviour of the dopant in a polymer matrix which is relatively in a fluid state is glass transition region, where the exchange and transport of charge carriers is facilitated. Further studies are necessary to understand the exact nature of this mechanism.

The decrease in conductivity and increase in activation energies in doped films may be explained in terms of formation of molecular aggregates [59] of the dopant material in the polymer matrix. The molecular aggregates which are formed in between the molecular chain of the polymer, impede the movement of
charge carriers thereby decreasing their mobility and increasing the activation energy. An essential feature of the formation of molecular aggregates is the occurrence of additional bands in the absorption spectrum. In the present study an additional peak around 370 nm, which is the characteristic of the nickel doped CA has been observed in all the doped samples (See fig 3.9 of chapter III). Hence it is reasonable to assume the formation of molecular aggregates of the dopant in the host CA matrix.

To confirm whether the observed results are due to any changes in the chemical structure of the polymer, infrared absorption spectra were taken. The undoped, as well as doped specimens showed identical characteristics corresponding to different functional groups of CA, showing that there is no change in the chemical structure of CA (fig. 3.9 - 3.12).

In order to find the charge transport mechanism in these materials, Schottkey's field assisted thermionic emission equation [60 to 62]

\[ I = A ST^2 \exp \left( \frac{\phi/K - C (U/kT)^{1/2}}{T} \right) \]

may be employed. If the temperature of the film is maintained constant, then the plot of log I versus \( V^{1/2} \) would yield the required information regarding the charge transport mechanism. Figs. 7.9(a) - 7.9(d) show the log I versus \( V^{1/2} \) plots for undoped and doped films.

The linear behaviour of these plots points to an electronic type conduction mechanism. Here the charge carriers are released by thermal activation over a potential barrier. The physical nature of such a potential barrier can be interpreted in two ways. It can be the transition of electrons over the barrier between the cathode and the dielectric (Schottky emission). Alternatively, Charge carriers can be released from the traps of the dielectric (Poole - Frenkel
effect). In order to differentiate between these two, the values of $\beta$ at different temperatures were calculated from the slopes $\log I$ versus $V^{1/2}$.

The theoretical values of $\beta$ for both Schottky and Poole - Frenkel mechanisms and the experimental values are shown in Tables 7.3-7.4. From the tables it is observed that $\beta_{\text{exp}}$ is not matching with neither $\beta_{\text{PF}}$ or $\beta_{\text{RS}}$. But, when comparing these three values, $\beta_{\text{exp}}$ is falling closer to $\beta_{\text{RS}}$ than that to $\beta_{\text{PF}}$. From this observation, it can be concluded that, the predominant mechanism which is responsible for the conduction is Schottky mechanism. Also it has been noted that the $\phi$ value is not coinciding with the corresponding activation energy, also the $\phi$ increases with the increase in bias field. This could be due to the presence of multiple traps which are expected to present in the dielectric.
References