CHAPTER - I

INTRODUCTION
The electrical behaviour of film of all types of material—dielectric, semiconductor and metal has assumed a greater significance in the period following the second world war. After the discovery of the transistor, it rapidly became clear that the conventional vacuum tubes, resistors and capacitors could in many cases be replaced by thin film systems. Polymers are the dielectric material and form good thin films under controlled conditions. These films can bring persistent polarisation by importing preferential orientation to dipolar moieties within the polymer chains. The electrical properties of these films are very much structure sensitive. Workers in this field are fascinated to have deeper knowledge of the properties of thin film systems of polymers.

1.1 Relaxation Phenomena in Dielectrics

The relaxation process is defined as the approach to equilibrium of a system which is initially out of thermo-dynamic equilibrium. Dielectrics are, by definition, those materials with negligible or small electrical conductivity which possess the ability to be polarised in the presence of an external field.
Polarization of dielectric materials due to the application of electrical field can be due to four different processes, which are electronic, atomic, orientational and space charge:

(a) Electronic polarization is due to the displacement of the electrons relative to the nuclei in each atom.

(b) In atomic polarization, the applied field causes a displacement of atomic nuclei in a molecule, when its constituent atoms are of different types.

(c) In polar molecules the asymmetric (or unequal sharing of electrons) charge distribution between unlike constituents of a molecule gives rise to permanent dipole moment which exists even in the absence of an electric field. These dipoles tend to orient themselves in the field direction. Consequently, an orientational (or dipolar) polarization arises.

(d) Charge carriers do exist in dielectrics (charge density may be small) which are mobile and can migrate, at least for some distance through the dielectric. These carriers give rise to space charge or interfacial polarization, when trapped in the material or at interfaces or accumulated.
near the electrodes. Such a space charge polarization increases the capacitance of the sample and may be indistinguishable from a real rise of the dielectric permittivity.

Assuming that the four polarization mechanisms act independently of each other, the overall polarizability of a dielectric $\alpha_T$ is the sum of four terms

$$\alpha_T = \alpha_e + \alpha_a + \alpha_o + \alpha_s$$  (1.1)

where,

$\alpha_e$ - Electronic polarization, $\alpha_a$ - Atomic polarization, $\alpha_o$ - orientational polarization, $\alpha_s$ - Space charge polarization.

Relaxation time of a polarization process may be defined as the time in which the polarization decays to $1/e$ times to its original value, on the removal of the applied field$^9$.

Debye$^9$ gave the classical picture of relaxation of dipolar polarization with a single relaxation time. In his model, he considered a set of identical, non-interacting dipoles free to rotate against some viscous resistance in a fluid like medium.
Out of many models suggested to describe dielectric polarization, Frohlich's bistable model\textsuperscript{10} is most useful of all. In this model, charged particles (bistable dipoles) can jump between two preferred orientations separated by a potential barrier, by thermal excitation. The relaxation time is defined as the inverse of the frequency of jump, and has the temperature dependence

\[ \tau = \tau_0 \exp\left(-\frac{\epsilon}{kT}\right) \quad (1.2) \]

where,

\[ \epsilon \] is the barrier height, \( k \) is Boltzmann constant, \( T \) is absolute temperature and \( \tau_0 \) is characteristic relaxation time.

In the above treatments, it had been assumed that electronic interaction between the dipoles was negligible. Frequently the common dielectrics donot show simple behaviour.

A universal law of dielectric relaxation has been proposed recently by Janscher\textsuperscript{11} and others\textsuperscript{12} covering a wide range of solid dielectrics. This law is of the form

\[ \chi''(\bar{\omega}) = \omega^{n-1} \quad \text{with} \quad 0 < n < 1 \quad (1.3) \]

where,

\( \omega \) is the frequency and \( \chi'' \) is the imaginary part of the dielectric susceptibility.
This expression is valid up to GHz (Gamma Hz) frequencies and is based on many body interactions between its constituent parts - a common property of all condensed matter.

1.2 Relaxations in Polymers

Polymeric materials in solid state may exist in crystalline and amorphous form. These phases are not well defined in polymers, therefore, it is very difficult to decide which transition belong to which phase. Corresponding to various relaxation regions, various transitions are possible in polymers.

An amorphous polymer can exhibit five types of relaxation regions.6

(i) Motion of the entire chain as a unit.

(ii) Motion of chain segment of (perhaps) 50-100 carbon atoms, i.e. corresponding to the glass transition.

(iii) Motion of 2, 3, 4 carbon atoms moiety about the chain axis (i.e. the \( \gamma \) transition).

(iv) Motion of side group.

(v) Motion of moieties containing hetero - atoms in the main chain.
In amorphous polymers, the temperature transitions are of a relaxation nature. In crystalline polymers the thermodynamic phase transitions also relate to temperature ones.

Transitions attributed to the crystalline phase are -

(i) Crystalline melting temperature at which the long range order is destroyed.

(ii) The transitions corresponding to the mobility of the groups at the surfaces or at the lattice defects.

(iii) Transition of one crystal form into another.

(iv) Transitions involving local motion of groups of the main chain arranged in crystal lattice.

Relaxation processes cannot be generalized because their molecular origin is not the same for all polymers. Major physical and mechanical properties of polymeric materials are affected by changes in temperature. The specific volume of the material changes abruptly. Structural transitions are especially sensitive to thermal pre-treatment.
A critical temperature above which cooperative motion of relatively long segments of the molecular chains becomes possible, is known as glass transition temperature \( T_g \). Generally, glass transition \( T_g \) is the primary transition due to \( \alpha \)-relaxation region associated with major backbone chain movements. Below \( T_g \), majority of polymers exhibit multiple relaxations, known as secondary transitions. Following the practice of Deutsch, Hoff and Reddish,\(^\text{13}\) the various dispersion regions in an amorphous polymer are usually designated by greek alphabets, \( \alpha \)-representing the highest temperature transition observed at a fixed frequency, \( \beta, \gamma, \delta \) etc. representing other transition in decreasing order of temperature.

Secondary transitions usually involve the rotation of side groups attached to the main polymer chain.\(^\text{14}\) Another possibility is rotation of short segments without involving large scale rearrangements of the structure and is called Crank - Shaft type rotation of groups in the main chain.\(^\text{15-17}\) Near to the crystal melting temperature a variety of molecular motions are possible. Following four types of transitions may be observed -
(i) Pre-melting effects.

(ii) Interaction between crystalline and amorphous regions.

(iii) Transition involving rearrangements in crystalline phase.

(iv) Amorphous transition between one liquid state to another.

The polymeric relaxation time follow Arrhenious type of temperature dependence below $T_g$ and upto the temperature $T_g$. Activation energy $E$ is characteristic of each relaxation process. A wide spectrum of relaxation times is necessary to properly express the relaxation behaviour of a polymer at its $T_g$. Conformational changes in the shape of a molecule brought about by the ability of individual segments to rotate about the macromolecular axes are basically responsible for the observed character of the glass transition. In a condensed system in which molecules are in close proximity to one another, temporary binding may occur. Above $T_g$, the temperature dependence of the relaxation time is given by Williams - Landel - Ferry (W - L - F) empirical equation.\(^{19}\)

$$\log \left( \frac{T}{T_c} \right) = \frac{A (T - T_g)}{B + (T - T_g)} \quad \text{(1.5)}$$
where,

\[ A \text{ and } B \text{ are numerical constants exhibited by the experiment. ( } A = 17.44, \ B = 51.6) \]

This relation is based on the free volume theory of polymers established by Fox and Flory. A temperature above \( T_g \), the activation energy is highly temperature dependent. The WLF equation can also be used to find out the activation energy above \( T_g \).

The presence of relaxation processes can be investigated by the static or dynamic measurements. Dynamic methods, with a mechanical, electrical or thermal excitation of the sample, are more commonly used to investigate the secondary relaxation processes. It should be noted that each technique employed for the characterisation of relaxations in polymers influences the molecules of a polymer in a different way and thus the response of a system to different stimuli may be very different.

The molecular origin of transitions is not the same for all the polymers. In chapter second transitions and corresponding relaxation regions in PMMA and PVAc are briefly described as these materials and their blends have been studied in the present work.
1.3 Response of Polymers to Electrical Stress

Synthetic organic polymers are as electrical insulating materials. A consequence of their low conductivity is that they readily become electrostatically charged. The poor reproducibility of conductivity causes difficulty. Both the micro and macro structures of these materials are sensitive to their thermal, mechanical and electrical history. In this section, electrical conduction, polarization and the influence of polymeric transitions on these properties are briefly discussed.

1.3.1 Conduction in Polymers

Conduction in polymers depends on the carrier generation and their transport. Conductivity of polymeric thin film is often due to extrinsic rather than intrinsic reasons. Charge carriers may transport within the molecule itself and also from molecule to molecule. First type of transport is known as intermolecular transport which depends to a large extent on the structure of molecule. The second type of transport is known as intermolecular and is generally poor as the interaction between polymer chains is weak. The intramolecular charge transport can be improved by an increase in degree of crystallinity. But the
polymeric materials are usually amorphous or partially crystalline, and therefore have a non-periodic structure, i.e., short range order exists. This gives rise to narrow conduction bands$^{24}$ and low electron mobility. Hauser$^{25}$ advocated an energy band model for polymer which is shown in figure 1.1.

In polymers recurring structural unit called monomers are tightly bound together by strong covalent bonds. The macro-molecules are in the form of chains and can change their relative orientations easily, because much weaker vander-Wall's type of forces hold them together. Strong intermolecular bonds have an activation energy of 4 to 8 ev and weak intermolecular bonds have very low activation energy. The intermolecular bonds give rise to a valence band which is full of electrons in the absence of an electron acceptor and a normally empty conduction band. Both these bands are expected to be wide; more than 1 ev in view of strong overlap of the wave functions.$^{26}$ The much weaker intermolecular bonds must result in very narrow bands which need not be either completely empty or full. The separation of which is also much smaller than intermolecular band gap.
FIG. 1.1 -

(A) ENERGY BAND DIAGRAM FOR POLYMERS; LOCALIZED STATES (TRAPS) ARE SHADED; $E_C$ AND $E_V$ MOBILITY EDGS (B) CARRIER TRANSPORT BY HOPPING; $T_E$ ELECTRON TRAPS AND $T_H$ HOLE TRAPS.
The conduction and the valence bands are narrow and each band may even split into individual energy levels, spaced closely with respect to location (intermolecular distance) and energy. Each level represents a whole molecular unit. The difference in energy are due to local differences in the overlap integrals, which, in turn result from difference in the local environments of each molecular unit. Conduction may take place only by hopping of electrons from one level to another under such conditions. Besides this intermolecular transport, the electrons can also make intermolecular jumps to molecules on neighbouring chains. As is clear from figure 1.1, the spread in energy in the conduction and valence levels is small as compared to the forbidden band gap width.

Two models, Tunnel model and Hopping model, are suggested to describe the transport mechanism in polymers. Current density for tunneling is given by Fowler-Nordheim equation

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

(1.6)

where,

\( \phi \) is the barrier height,

\( V \) is potential and

\( A \) is a constant.
The conductivity of polymers increases with temperature and follows the relation $^{29-32}$

$$\sigma = \sigma_0 \exp \left( - \frac{E_c}{kT} \right) \quad (1.7)$$

where,

$E_c$ is the activation energy of conduction dependent on temperature, and $K$ & $T$ have their usual meaning.

The carrier mobility obeys the relation $^{32,33}$

$$\mu = \mu_0 \exp \left( - \frac{E_\mu}{kT} \right) \quad (1.8)$$

where,

$E_\mu$ is the activation energy for charge carrier mobility.

The carrier mobilities in polymers (both electron and hole) are experimentally observed to be temperature activated, establishing the validity of Hopping model. $^{34-36}$ Magnitude of carrier mobility generally lies in the range $10^{-8} - 10^{-14}$ m$^2$ v$^{-1}$ s$^{-1}$. Low carrier mobility results from the absence of any long range order in polymers. The carriers, therefore, cannot move over long distances without being captured or scattered.

1.3.2 Polarization in Polymers

Mechanism responsible for the polarization of
polymer depends upon the properties of polymer, electrode material and technique of excitation.

Dipolar polarization is observed in polar polymers, i.e., those polymers which have polar groups. In some non-polar polymers, dipolar polarization is observed because dipoles may arise due to impurities and oxidation of the polymer surfaces.\textsuperscript{37,38} This polarization may be observed below $T_g$, if the secondary relaxation involves motion of the polar group. Polymers in which polar side group is rigidly attached to the main chain or polar group is in the main chain itself, dipolar orientation cannot occur without cooperative motion of the main chain segments.

Maxwell - Wagner - Sillars (MWS)\textsuperscript{8} polarization is due to the heterogeneous structure of polymers. In polymers, conductivity of the two amorphous and crystalline regions is different. MWS polarization is expected to contribute to polarization of all polymers.\textsuperscript{39}

Space charge polarization occurs in polymers due to accumulation of charges near the electrodes and capturing of charge carriers at various localized trapping levels. Space charge polarization involves migration of charge carriers over certain distance before they are trapped.
1.4 Persistent Internal Polarization

Dielectric material which can persist the polarization for a considerable long time after removing the field is known as electret. The study of the phenomenon of Persistent Internal Polarization (PIP) in the hydrocarbon is important because it provides the lifetime of the static electric field generated due to the formation of an electret. An electret exhibits a quasi-permanent electric charge. The quasi-permanent means that the time constant characteristics for the decay of the charge are much longer than the time-periods over which studies are performed with the electret.

Electret properties originate from dipole polarization, from charge displacement within molecular or domain structures, from space charge effects from surface charging. Induced or instantaneous polarization does not contribute to PIP. Knowledge of the properties of a specific material and the physics of the charging process often allows one to distinguish between these possibilities. These charging processes and properties of the specific material may be modified for the persistancy.

The electret charge may consist of real charges, such as surface charge layers or space charge, it may be
a true polarization, or it may be a combination of these. The true polarization is usually a frozen—in alignment of dipoles, while the real charges comprise layers of trapped positive and negative carriers, often positioned at or near the two surfaces of the dielectric. The electret charges may also consist of carriers displaced within molecular or domain structures throughout the solid, resembling a true dipolar polarization. If the charges are displaced to domain boundaries, they are referred to as Maxwell—Nernst—Sillars Polarization. Mostly the net charge of an electret is zero or close to zero and its fields are due to charge separation and not caused by a net charge.

The permanent dipole polarization and charge retention achievable in various electret—forming materials depends to a large degree on material properties and environmental conditions. To be useful for electret studies, substances have to show either suitable properties or extremely low conductivity due to a large number of deep trapping centers.

The decay of permanent dipole polarization is controlled by the dipole relaxation frequency \((\gamma T)\), valid for the case of single \((\gamma T)\). In the absence
of an applied voltage \( E = 0 \) and for isothermal conditions

\[
P_p (t) = P_p (0) \exp (-\gamma T) = \cdots \quad (1.4)
\]

where,

\( P_p \) is the saturation polarization.

Oftentimes, observed decays are non-exponential with increasing 'time constant', including a distribution of relaxation frequencies. These distributions may in general be due to a distribution of activation energies or a distribution of pre-exponential factors.\(^{41}\)

Many models\(^{45-48}\) have been suggested for the decay of charge phenomena, but actual decay phenomena are usually more complex, because of involved trapping effects, field dependent mobilities, etc.

The charge stability of electrets can be improved by application of heat during charging.\(^{42}\) It is probably due to retrapping of carriers in energetically deeper levels. The charge stability can also be increased by annealing after charging.\(^{42}\)

Retention of charges in polymers mainly refer to the trapping sites. Number of structural anomalies,
such as impurities, \(^{49-52}\) defects of the monomeric units, \(^{53}\) chain irregularities \(^{54}\) and imperfections of the crystallities \(^{55}\) are responsible for the trapping sites. Charges may also be stored in the highly ordered crystalline regions \(^{56}\) of polymers or at crystalline-amorphous interfaces. \(^{56}\) Little is known about the nature of surface traps \(^{41}\), although chemical impurities, \(^{49-52}\) specific surface defects caused by oxidation products, \(^{57}\) broken chains \(^{55}\) and absorbed molecules \(^{58}\) are believed to be responsible for the capture of charges.

1.5 **Electret Behaviour of Polymers**

Electret properties were first described by Gray \(^{58}\) in 1732's when he mentioned the 'perpetual attractive power' of a number of dielectrics in particular waxes, resins and sulphur. Systematic research into electret properties began in 1919's by Sugchi. \(^{59}\) Sugchi's electrets were made of a molten mixture of wax and resin which was allowed to cool in a strong electric field.

The dielectric polarized by the field-temperature treatment is called 'Thermo-electret'. A scheme for the formation of thermo-electret is shown in figure 1.2.
FIG. 1.2 -
FIELD AND TEMPERATURE PROGRAMME FOR THE FORMATION OF POLYMER ELECTRETS.
The polymer is heated to above $T_g$, by which the permanent dipoles and free charges are mobilized. A high electric field, for time $T_0$ is applied, which causes an alignment of permanent dipoles, and a drift of free charges to the electrodes. The forming field drives the positive charges to the cathode and the negative charges to the anode. After time $t_x$ the charged polymer is cooled to room temperature $T_x$ by which the main chains of the polymer are immobilized, so that most of the permanent dipoles and charges are frozen in. They do not respond when the field is switched off at $t_x$; only instantaneously part of the polarization disappears. The stored charges are released when they are thermally activated. The depolarization current is recorded as a function of temperature. The analysis of Thermally Stimulated Discharge (TSD) current thermograms provides a lot of information for the identification and evaluation of dipole reorientation processes and of trapping and recombination levels.

Aguchi\textsuperscript{59} pointed out, when the field was removed, the sample exhibited internal electric polarization, with the end of the sample originally facing the anode being charged negatively and the end facing the cathode charged positively. This type of electric charge was later named
The heterocharge of an electret decays during the first few days after polariization and then becomes practically constant (its further decay proceeds very slowly). In some cases initial heterocharge after decaying to zero reverse its polarity grows to some maximum value and then decays slowly. According to Gemant's terminology this charge of the electret which is of the same sign as that of the polarity of adjacent electrode is called the 'homo-charge'. The net surface charge density of an electret is the combine effect of hetero- and homo-charges.

Later on two charge theory was advanced by B. Gross and got eminent success. After this various phenomenological theories have been proposed to explain the electret phenomena by numerous workers as Addam, Thiesse-Winkel and Hermann, Gross, Swann, Baldus, Gerrson and Hurbangh, Wisman and Peaster, Perlman and Meunier, Henderek and Piech, Gross and Hart. The results followed were recognised to constitute a confirmation and extension of the B. Gross theory.

In 1911 Photoelectret was discovered by Golmen and Kalandyk. Photoelectrets are the dielectrics in which polarization is achieved by electric field-e.m. radiation. Later on Kurrelmeyer, Mankov and
Coworkers, Kallmann and Rosenberg also contributed a lot on it.

The dielectric may also be polarized by other treatment, to give rise to Auto-photo electret (e.m. radiation only), Thermo-photo electret (electric field - e.m. radiation, temperature), Magneto electret (magnetic field - temperature) Radio-electret (α, β, radiation - with and without electric field and temperature) and Electro-electret (corona discharge or electron beam irradiation).

The existence of electrets as electrical analogue of magnets was first postulated by Oliver Heaviside in the later part of the 19th century. As a magnet produces a static magnetic field, an electret produces a static electric field. This analogy fails as electret phenomena can be caused by dipolar and mono-polar charges while magnetic properties are only due to magnetic dipoles.

In recent years, a large number of polymers have attracted considerable interest due to their characteristic properties. They have high concentration of deep traps, besides being very good insulating materials. They can be easily obtained in the form of
thin films as well as of any desired shape. Therefore, it allows to choose a desired material depending on the requirement.

Polymeric electrets have been utilized in a variety of applications. These include biological and medical fields and are in various states of research, development or production. A number of applications of electrets have been investigated and these have been reviewed by Outtman, Turnhout and Pillai et al. Electrets are used in microphones, transducers, electret motors, dosimetry, electrophotography, particle collecting surfaces in intravascular thrombosis, pollution studies and electro-static precipitators. Electrometers, electro-static generators for focusing electronic beams, relay switches, motors, optical display systems, light detectors and vidicons etc.

Another group of applications, namely those relating to biophysics, promise to have great future potential. It was shown that foil electrets placed in contact with bones of animals, accelerate the growth of callus necessary for fracture healing. Moreover, electret bandages put on skin incisions considerably improve the tensile strength of the wound over a given period of time and thus speed up the healing process.
1.6 Present Work: Aim and Scope

Blending of polymers promises a new material of useful properties for desired applications. In the present work the blending of the two polymers is taken as sensitization of one from another. The polyblend can be tailored to suit specific usage and thus a better and commercially viable product can be obtained by polyblending. Many reports are available on individual polymers, Poly (Methyl methacrylate)\textsuperscript{125-127} and Poly (Vinyl acetate)\textsuperscript{128-131} Both are amorphous and polar in nature, they are structurally related and form a compatible system.\textsuperscript{132} These two polymers differ strongly in their glass transition temperature and weatherability. It is expected that the polyblends of these polymers may incorporate the best of the individual polymers and give better characteristics for practical applications. In the present work conduction and relaxation behaviour of this polyblend are studied with different weight ratios, for the dedicated balance of the properties of individual polymers. Studies are also conducted on their composites with Ferrocene, Malachite-Green and Aceto-naphthene to search for a suitable material for specific usages.

The chapter-II gives the details of materials used.
Sample preparation and the details of measuring instruments employed in the studies undertaken are given in chapter-III. The results of differential thermal analysis, Infra-red and Ultra-violet spectroscopy and photopolarization studies have also been included in this chapter.

In chapter-IV relaxation phenomena have been analysed using Thermally Stimulated Discharge Current Technique. This study throws light on the nature of stored charge and mechanism of charge decay.

Background current of the sample is studied in chapter-V, by Spontaneous Current Emission technique.

In chapter-VI, carrier transport, trapping and injection mechanisms have been studied by the measurement and analysis of the conductivity.

Dielectric properties (dielectric constant, loss factor and relaxation temperature) are studied with different parameters using A.C. bridge measurement technique in chapter-VII.

The conclusions drawn from the different studies are correlated in chapter-VIII.
REFERENCES


5. A.C. Lilly Jr, R.M. Handerson and P.S. Sharp,


7. P. Hedvig, 'Dielectric Spectroscopy of Polymers',

8. C.P. Smith, 'Dielectric Behaviour and Structure',

9. P. Debye, 'Polar Molecules', Dover Publications,
   London (1945).

10. H. Frohlich, 'Theory of Dielectrics', Oxford University


    2475 (1979).


42. A.U. Shareef, Ph.D. Thesis 'Study of Spontaneous Current Emission, Isothermal and Thermostimulated Discharge in Doped Polymeric Systems', Dr. H.S. Gour University, Sagar (M.P.) 1984.


58. S. Gray; Philos. Trans. R. Soc. London, Ser A; 37, 235 (1732).


60. A. Gemanit, Phil. Mag., 20, 929 (1935).


63. A.I. Froiman and V.M. Fridkin, Kristallografiya, 1, 342 (1956).

64. R.P. Adams; J. Franklin Inst., 204, 469 (1927).


67. B. Gross, 'Electrot Research; Stages in its Development'


Phys. 45, 2841 (1974)


     Ibid 255, 513 (1953)
     Ibid 256, 167 (1953).


     (3) 521 (1957).

76. M.M. Perlman and J.L. Meinier, J. Appl. Phys. 36,
     420 (1965);
77. (a) J. Handerek and T. Piech, Acta Physica Polonica, 24, 3 (1963);
ibid, 27, 259 (1965).


81. R.C. Ahuja, Investigations of the photoelectret and 
electrophotographic Characteristics of 
Hg I<sub>2</sub>, ed. Binder Layers, Ph.D. Thesis, 


83. R. Nath, 'Studies on the Photoinduced Electronic and 
Dielectric Processes in Organic Photo- 
conducting Systems', Ph.D. Thesis, 


86. Mankov, N.A. Zh. Ekspert Teor. Fiz. 6, 1031 (1936).


ibid 4, 335 (1966)
ibid 17, 575 (1979).


