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CHARGE STORAGE AND DECAY IN HIGH TEMPERATURE INSULATING MATERIALS

By

Mohamed Abdulbari A. Sussi

A Dissertation
Submitted to the Faculty of Graduate Studies and Research
Through the Department of Electrical Engineering
in Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy
at the University of Windsor

Windsor, Ontario, Canada
1992
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ABSTRACT OF THE DISSERTATION
CHARGE STORAGE AND DECAY IN HIGH TEMPERATURE INSULATING MATERIALS

by
Mohamed A. Sussi

Doctor of Philosophy in Electrical Engineering, 1992
University of Windsor, Windsor, Ontario, Canada, N9B 3P4.
Supervisor: Dr. G.R. Govinda Raju.

The demand for electrical power over the years has led to the generation of more power, and for developments of larger power equipment to sustain the demand. This leads to higher voltage stresses and higher operating temperatures, and the use of traditional insulating materials becomes uneconomical due to their bulkiness and lower operating limits of voltage and temperature. The development of high temperature polymeric insulating materials such as aromatic polyamides overcomes these temperature and voltage stress limitations to a certain extent. These materials exhibit excellent dielectric properties such as low conductivity, low dielectric constant, extremely low loss factor, high breakdown field strength and favourable mechanical and chemical properties. Several studies on their dielectric loss factor and dielectric strength have been carried out on various insulating materials. Yet little is known about the physical mechanisms responsible for the conduction, charge storage and decay processes.

This dissertation deals with the studies of charge storage and decay in aromatic and composite polyamide materials for the first time, along with an extended study of the conduction currents in Teflon (PTFE) at higher ranges of applied electric fields and temperatures, where the data obtained fills the gap in the published literature.

Different experimental techniques are employed to identify the mechanisms
responsible for conduction currents, charge storage, and decay in aromatic and composite polyamides. These techniques include the measurements of thermally stimulated polarization and depolarization currents and windowing polarization, which are employed to get insight into the molecular mechanisms of charging, relaxation process, dipolar orientation, and release of charges from trapping sites. Corona charging on the other hand is used to study the mechanisms of charge storage under isothermal conditions and the subsequent release of charges from the bulk of the material by employing the TSD current techniques. To evaluate the results further, wide angle X-ray diffraction and Infrared spectroscopy analyses are also conducted on aromatic polyamides which have been exposed to corona charging.

The insulating materials tested during the course of this dissertation are chosen because of their engineering importance and lack of published literature on them. Several studies reported in this dissertation on these materials are believed to have been carried out for the first time.

The results of the conduction current in Teflon (PTFE) indicated that the ionic space charge mechanism is operative at temperature $\leq 120 \, ^{\circ}C$, while electronic space charge at temperatures $> 120 \, ^{\circ}C$.

The low frequency dielectric loss factor in aramid paper shows two relaxation peaks due to dipolar reorientation at $T \leq 190 \, ^{\circ}C$, and no relaxation peak at $T=200 \, ^{\circ}C$ suggesting an interfacial polarization mechanism. A relaxation time of $6.3 \times 10^4 \, s$ at room temperature with an activation energy of 0.84 eV was obtained from the thermally stimulated polarization (TSP) current in aramid paper with total polarization of 1.73 $\mu$Cm$^{-2}$. 
at a heating rate of 2 Kmin
1. The X-ray diffraction results show an improvement in the polymer crystallization when exposed to higher annealing temperature of 300 °C.

The results of the low frequency dielectric loss factor in composite polyamide shows one broad relaxation peak at T ≤ 130 °C which is due to the dipolar polarization, while for T ≥ 140 no relaxation frequency was observed and the low frequency loss factor increases rapidly with decreasing frequency suggesting an interfacial polarization mechanism. The Pool-Frenkel and ionic hopping mechanisms were responsible for the conduction current in composite polyamide. The thermally stimulated depolarization (TSD) current results show that the fast dipoles are oriented at lower poling temperature while slow dipoles are at higher poling temperatures. The windowing polarization result shows that the distribution of the relaxation time of the dipolar process for T ≤ 130 °C is thermally activated with activation energies in the range of 1.01 to 1.55 eV in the temperature range of 70 to 130 °C.
To my loving parents, wife

and children

Ibrahim, Tasnim, and Idris Sussi
ACKNOWLEDGMENTS

The author would like to express his deepest gratitude and sincere appreciation to his supervisor Dr. G.R. Govinda Raju for his advice, help, financial support, and guidance through the progress of this dissertation, and for installing the data acquisition system and the experimental setup. Thanks are also due to the committee members, Dr. Alan Watson, Prof. Philip Alexander, and Dr. William Youdelis for their valuable discussions and comments on all the relevant topics of this dissertation. Thanks are also due to Dr. Reuben Hackam, previous member of the committee.

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Chapter 1

INTRODUCTION

1.1 An Overview

The demand for electrical insulating polymers has increased over the last two decades or so due to their high levels of electrical, chemical, and mechanical integrity which make them ideally suited as insulation materials in transformers, motors, generators, and electronic and microelectronics devices.

Some organic polymers are considered stable materials at high temperature, and have the capabilities of withstanding radiations, chemical attacks, high electric field strengths, and mechanical stresses. These properties make them very suitable for nuclear power plants and space applications. High mechanical flexibility enables them to be formed in different shapes. In contrast, inorganic insulating materials such as porcelain and mica can also be used as high temperature insulation, but they lack flexibility to be used in electrical motors, generators, or transformers.

These polymer materials have the capability to store charges when they are charged under the influence of applied electric fields. It is important to know the amount of charges that are stored under different temperatures and electric fields, and how fast these charges are released from the dielectric materials. If the amount of the stored
charges is large this could have quite an impact on the breakdown of the dielectrics and the study of charge storage and decay in these materials are very important. Such studies contribute not only towards a knowledge of the electrical properties but also for development of new materials.

This dissertation is concerned with the study of the charge storage/decay and the mechanisms which govern the conduction currents in high temperature dielectric materials such as Teflon (PTFE), Aromatic Polyamides, and Composite Polyamide. In view of the large number of parameters available for study the present studies are limited to specific materials with the objective of obtaining insight into the charge storage and decay phenomena.

1.2 Conduction Currents

Several techniques are available for the study of charge storage and transport in polymer insulating materials leading to information on polymeric structures and chain motions [1,2]. One of these is the measurement of conduction currents characterized by several processes: (1) Ionic conduction, (2) Schottky emission, (3) space charge limited currents, (4) tunnelling and internal field emission, and (5) impurity conduction.

Ionic conduction occurs due to the drift of defects, in the bulk of the material, under the influence of an applied electric field. Schottky emission mechanism corresponds to the thermal activation of electrons over the metal-insulator interface barrier with the added effect that the applied field reduces the height of this barrier. Poole-Frenkel effect mechanism, on the other hand, is based on the same lowering of a barrier height within
within the dielectric. For this mechanism to occur the polymer must have a wide band gap and must contain donors or acceptors. In this case the barrier in question is that for thermal excitation of trapped electrons into the conduction band of the insulator [2].

Several studies have been conducted towards identification of the electrical conduction mechanisms operating in organic polymers [3-10]. So far, however, much of the information obtained on the conduction mechanisms is still conflicting and contradictory. For example, Lilly and McDowell [4] favoured Schottky injection as the origin of conduction in Teflon (PTFE) films at high fields ranging from 3.54 to 14.2 MV/m at limited temperatures of 162.5, 181.5, and 200 °C. On the other hand, Vollmann and Poll [5] suggested the modified Poole-Frenkel effect. Several studies in materials such as polyethylene (PE), and polyethylene terephthalate (PET) suggest conflicting mechanisms. Amborski [11] provided evidence that the current in PET at 130 °C is due to thermal activation of ions with a jumping distance of 6.9 nm. However, Lengyel [12], Lilly and McDowell [4] suggested Schottky injection as the origin of electrical conduction in PET and PTFE films. Electronic conduction has also been suggested [2]. The Poole-Frenkel effect mechanism is discussed by Frank and Simmons [13] who extended the trapping effect into the region of emission limited current flow. Ieda et al. [14] also presented the extended Poole-Frenkel model which includes the variation of the barrier height with an electric field in directions both opposite and forward to the electric force on an electron. They claim that their equation also considers Ohm's law at low fields with the usual Poole-Frenkel equation at extremely high fields. A variation of the Poole-Frenkel effect model has also been considered by Pulfrey et al. [15].
The conflicting results in the conduction currents in polyethylene (PE) were also attributed to the space charge effect which distorts the internal electric field thus making it difficult to identify the conduction process [7]. Adamec and Calderwood [8] proposed a mathematical model for the conduction mechanism in polymer insulating materials based on a classical concept. In contrast to the models based on the Schottky and Poole-Frenkel effects several authors have made suggestions aimed at improving these mechanisms [3-6].

Evidence of ionic conduction mechanisms has been reported in several other polymers such as Polyvinyl Chloride [9], Kapton [10], aromatic polyamides [16], and linear polyamides [17,18]. The investigation of the conduction currents in Kapton [10] was carried out at high electric fields in the range of 50-450 kV/m in the temperature range of 100-200 °C. The conduction in Kapton confirms the ionic mechanism with an ionic jump distance in the range of 5 to 6 nm with a temperature dependence, higher temperatures yielding higher values.

Conduction currents in aromatic polyamides were recently investigated for the first time by Govinda Raju [16], who provided evidence of ionic mechanisms with a separation distance between traps in the range of 4.4 to 8.0 nm depending on the temperature, higher temperatures yielding higher values for both thicknesses investigated. In related polymers such as linear polyamides Baker and Yager [17] reported that the conduction mechanisms were protonic with an activation energy of 1.29 eV which is several times higher than the dissociation energy for the hydrogen bond of 0.22 eV and the energy required for self ionization is 0.75 eV.
In linear polyamide (Nylon-66) Seanor [18] reported that the dependence of conduction currents on temperature was observed in three temperature ranges. Below 80 °C the conduction current was observed to decrease continuously with time, whereas at higher temperatures up to 110 °C the conduction current remains constant over longer periods. Above 120 °C the conduction current was observed again to decrease with time. The mechanism below 120 °C was considered to be electronic and above 120 °C due to both electrons and protons. The reported activation energies varied in the range of 1.3 eV to 2.18 eV depending upon the temperature range. Baird [19] on the other hand reported that the conduction currents in linear polyamide (Nylon 610) is electronic at temperatures lower than 100 °C and probably ionic and electronic above this temperature.

Sacher [20] investigated the DC conductivity of polyimide film in the temperature range of 65 to 125 °C and observed it to be independent of the applied field (up to least 4 kVm⁻¹). The activation energy was 1.41 eV for both thicknesses of 25.4 and 127 μm films. The conduction mechanisms were investigated in dry and wet samples. In the dry sample the conduction current was reported to be due to protons ionized from unreacted polyamide acid, while for wet samples due to residual impurity ions. Sawa et al. [21] extended the investigation to a higher electric field strength of 4 to 500 kVm⁻¹ over a time range of 10 to 3600 s. His results supported the ionic mechanism with an ionic jump distance of 8.0 to 11.5 nm with the activation energy of 1.1 eV.
1.3 Charging and Discharging Currents

Upon application or removal of a DC field across the dielectric material inserted between two electrodes the current which flows in the external circuit is known in most cases to decay with time, approximately as $t^{-n}$. These currents have been studied by many authors [22-27]. Several possible mechanisms have been proposed to explain this behaviour, the most important of these are:

1. dipolar orientation (Atkinson et al. [28], Das-Gupta et al. [29])

2. electrode polarization (Lindmayer [23], Wintle [25])

3. carrier hopping between localized states (Govinda Raju [16], Taylor et al. [3], and Das-Gupta et al. [26])

4. charge injection leading to trapped space charge effect (Lindmayer [23], Wintle [25])

5. tunnelling of charge from the electrodes to empty traps (Wintle [30], Atkinson et al. [28])

A dipolar orientation mechanism has been reported in several polymeric insulating materials such as Teflon (PTFE), Polyethylene (PE), Polyvinylchloride (PVC), Polyethylene terephthalate (PET), and Polystyrene (PS) by Atkinson and Fleming [28] who measured the charging/discharging currents. The charging/discharging currents in these co-polymers probably originated in the dipole orientation or hopping motion of the charge carriers. Das-Gupta et al. [31] also favoured a dipolar orientation mechanism in discharging currents in PET. Two ranges of temperatures have been investigated, below and above room temperature. The results suggested that the low temperature isochronal
peak was due to structural motions (β-relaxation) whereas the peak at 117 °C may be due to either space charge accumulating at the crystalline-amorphous interfaces or to charge carrier hopping between localized states. Das-Gupta and Joyner [31], and Smith et al. [32] summarized the characteristic features of the conduction mechanisms in organic polymers in a tabulated form. This characterization provides the tools needed to choose the appropriate conduction mechanism in materials. Wintle [25] on the other hand gave a general review of these conduction mechanisms with the exception of the hopping mechanism, and discussed their applicability to polymers.

Discharging currents data have also been used to calculate the low frequency behaviour of polymers [26,31]. The dielectric theory presented in chapter 2 shows that DC discharging currents measured as a function of time can be interpreted in terms of their alternating voltage properties such as the dielectric loss factor [33] which is dependent on the frequency. Baird et al. [19,34] suggested that large values of dielectric loss factors arise from a mixture of relaxation processes, and DC conductivity is eliminated by using the discharging current to evaluate data of loss factor $\varepsilon''$ vs. $\log f$.

The process of time varying release of trapped electrons in amorphous polymers which leads to a time varying trap depth and to phenomena which could contribute to or compete with the polarization relaxation phenomenon were addressed by several workers [35-41]. In general amorphous materials possess a considerable degree of short-range order, resulting in a combination of bands extended states and tails of localized state extending into the energy gap. This means that the amorphous materials exhibit no energy gap since the electronic states are allowed to be exist at all energy levels, but charge
carrier mobility edge becomes vanishingly small at the mobility edge, and so the mobility gap can be regarded as equivalent in many respects to the band gap in the crystalline case.

Polymers are generally subdivided into two groups for the purposes of structure and property classifications [36]. These may be (1) linear and branched systems or (2) cross-linked into a network systems. There will be two conducting pathways in such a system. One is electronic and confined to the chains of mers comprising the polymer molecules or perhaps to pendant groups on the chains. The other is ionic hopping transport and confined to the free volume pathways between the chains along which neutral molecules will also diffuse. The charge transport in electronic conduction occurs via extended states where electrons can tunnel between localized state due to high density defects in amorphous solids. On the otherhand hopping transport and transport via extended states can therefore occur in parallel though clearly one mechanism will predominate.

The traps of electrons in localized states in polystyrene, for example have been studied by Keith Watson [35] by means of electron beam technique. A 2.2 kV beam is used to inject a short pulse of charge into the free surface of a thin film of the polymer, and a second electron beam monitors the surface potential is related to trapped charge density and to the depth of charge penetration. The surface potential in this case is monitored by using one-sided metallized sample the field is essentially directed toward the electrode. Thus, most electrons penetrate beyond the average range into regions where the RIC is still large enough to allow inward motion of electrons or outward motion of
holes. The release of electrons from traps is analyzed in terms of a time and temperature dependent demarcation energy $E_m$. The time dependence of charge decay is thus related to the energy distribution of traps in the amorphous polymers.

The process of time varying release of electrons in amorphous polymers were not considered to play an important role in the aromatic polyamides and composite polyamide polymers due to the following reasons:

(1) The predominant conduction mechanism in aramid and composite polyamide dielectrics is due to ionic hopping and hence the time and temperature dependence on the release of trapped electrons do not contribute to the conduction process. As mentioned above they might compete with the ionic hopping process but it is not the predominante process.

(2) Amorphous polymers do not posses an energy gap. The charges are trapped at all levels in contrast to the semicrystalline polymers where the energy gap can extend from about 0.4-10 eV.

(3) In the case of injected electrons by beam the measuring of the surface potential is carried out by one-side metallized sample (i.e. by an open circuits of the electrodes). The studies conducted on the polymers that we have used follow the short circuit techniques of both electrodes. Thus, the charge transport and decay are mainly due to the internal bulk charges and not due to the surface charge distribution.
1.4 Thermally Stimulated Polarization and Depolarization Currents

Thermally stimulated polarization currents are measured while the dielectric material, which is placed between two electrodes, is heated linearly at a constant rate in the presence of the applied DC electric field. Such a TSP current technique has several advantages; the charge build-up process is revealed in great detail and the search for optimum poling temperature is eliminated. Thus, excessive sample over-heating is avoided [35]. In addition, since the TSP current measurements are carried out in the presence of applied electric field the current consists of two components. The first is due to dipolar polarization and the second due to non-zero conductivity [16,42,43] which usually appears at high temperature.

A study of the TSP currents in aromatic polyamides [43] and composite polyamide polymeric materials are conducted for the first time in this dissertation. No other data are available on these two polymeric materials in the literature of which the author is aware. In comparison to the TSP currents, the thermally stimulated depolarization (TSD) currents, on the other hand, enable us to study the charge decay process in the bulk of the polymeric materials which are revealed by heating the dielectric at a linear rate after removing the charging DC field. Thus, the charge decay processes are revealed very quickly since they are examined as a function of temperature instead of time. Furthermore, the TSD current techniques provide additional information with regard to conduction mechanisms.

TSD current measurements have been conducted in Teflon (PTFE) with no agreement between them. Ginter and Bowlt [44] reported that the conflicting results in
PTFE suggest that the production methods of the polymers and the electrode arrangement influence the dielectric properties. Studies of the TSD currents were also made on electron-irradiated [45] and corona treated [46] Teflon; the temperatures of the current maxima were related to glass transition temperature. Camos [47] studied the current peaks in Teflon due to thermal gradient and related it to glass transition temperature. He reported that some of the current peaks observed without any external electric field but with temperature gradient are the same as those observed in measurements of TSD current with the application of an external field [48]. Moreover, the current peaks observed in the measurements of TSD current for Teflon are due to molecular motion and thermal excitation, in addition to the typical processes of space charge.

Remke and Muth [49] studied the TSD current measurements on Teflon (PTFE) film using three different testing methods: short-circuit TSD, open circuit TSD, and isothermal charge decay measurements, which was performed at a constant temperature of 150 °C with the electret held in open-circuit in shielded containers. The charge decay was monitored by measuring the equivalent voltage with an electrostatic voltmeter. Their work was aimed at understanding the initial charge movement in negatively corona charged PTFE and comparing their results with electron-beam charging techniques. They concluded that short-circuit TSD results depend on the charging techniques, because of the depth and character of the irradiated region through which the charge moves. Open-circuit TSD current results appear nearly independent of the charging technique but controlled by the material properties. Finally, the isothermal current and open-circuit TSD current decay results suggest that a combination of space charge limit drift and
trapping/retrapping model may be appropriate to interpret the open-circuit decay results.

Several other authors [47,50,51] reported on the TSD current studies of traps in electron irradiated Teflon (PTEF). Their results suggested that there are different structure locations in the material for the same types of traps, and the differences in peak positions are due to different degrees of the molecular motion. In addition thermal excitation seemed to play an important role in charge release.

In other polymeric materials, Perlman [52] investigated the thermal currents and internal polarization in Carnauba Wax electrets. His results show that the polarization is uniform and hence space charges, resulting from either charge injection from the electrodes or macroscopic ion displacement, are ruled out as possible causes of the heterocharge process. The dipole orientation mechanism is also investigated and ruled out due to the large number of dipoles that must interact with the applied electric field to produce this effect. The proposed heterocharge mechanism was the microscopic displacement of ions with trapping. The overlapping in the TSD current spectra shows activation energies of 1.7, 2.3, and 2.7 eV at temperature maxima of 47°, 54°, and 69 °C, respectively. These activation energies have been associated with ionic trap depth.

Studies of TSD currents in other polymeric materials, such as; Polyethylene terephthalate (PET) [53,54], Polyvinyl chloride (PVC) [55], Polyvinylidene fluoride (PVF₂) [56], and Polyimide [20] have been carried out. Their results show that there are different mechanisms associated with each specific material.

Recently, results of TSD currents in aromatic polyamides were reported for the first time in thermally charged [16] aramid paper. The study of thermal charging was
conducted on samples having thicknesses of 76 and 127 \( \mu m \) coated with silver and aluminum electrodes. The results of TSD currents in thermally charged samples show a peak at 135 °C for a heating rate of 1 Kmin\(^{-1}\) and a shift to a higher value when the rate of heating is increased. The reported relaxation time at room temperature was 5.3x10\(^5\) s.

1.5 Research Objective

The objective of this dissertation is to study for the first time the mechanisms responsible for the charge storage, transport, and decay in aromatic polyamides and composite polyamide dielectric materials using different charging methods such as thermal and corona charging.

The studies considered in this dissertation are outlined below:

i) The conduction currents in Teflon (PTFE) at higher ranges of applied electric fields and temperatures. The data obtained fill the gap in the published literature and are carried out in commercial samples as they are more relevant to practical applications.

ii) The charging and discharging currents, in aromatic polyamides and composite polyamides and the influence of various parameters such as electrode materials, sample thickness, and field polarities. This material is being used increasingly in a high temperature environment and fundamental data are not available in the literature.

iii) The polarization currents, in aromatic polyamides and composite polyamides, using the thermally stimulated polarization (TSP) techniques and the influence of various
parameters such as electrode materials, sample thickness, field polarities, and heating rate.

iv) The effect of corona charging on the charge storage and decay in the bulk of aromatic polyamides using the thermally stimulated depolarization (TSD) current techniques with the influence of poling times, poling fields, sample thickness, heating rate, annealing time, and electrode materials.

v) The effect of physical and chemical changes are investigated using the X-ray and Infrared spectrum of the corona charged aromatic polyamides with the view of supplementing the results of TSD results. The X-ray diffraction technique reveals the interatomic distance between the atoms in the molecules and reveals the amorphous and crystalline phase in the polymeric materials. Infrared spectra, on the otherhand, reveals the chemical changes and the type of the chemical bonding which can be obtained from the number and frequency of the infrared absorption bands.

vi) Low frequency dielectric loss factor in aromatic and composite polyamides are investigated using the results obtained from the discharging currents.

vii) Conduction currents, TSD current, and TSD windowing polarization currents are also measured in composite polyamides.

A study of the above mentioned dielectric materials is carried out for the first time in this dissertation, with the exception of conduction currents and TSD current studies carried out by Govinda Raju [16] in thermally charged aromatic polyamides and hence not considered in this dissertation. Of the large number of polymers which are available for
study aromatic polyamide is chosen because of its engineering importance and lack of published literature. The techniques employed in this study reveal the fundamental mechanisms more clearly rather than serving simply as a set of collection of data.

1.6 Organization of the Dissertation

Chapter 2 reviews some of the theory behind the thermally stimulated polarization (TSP) and depolarization (TSD) current techniques, and the phenomenological theory of dielectrics.

In chapter 3 the experimental techniques that are used in various dielectric materials are discussed while the details of experiment and sample preparation procedures are discussed in later chapters in later chapters under the section of experimental arrangements.

In chapter 4 the results of electrical conduction currents in Teflon (PTFE) film, with thicknesses of 50 and 130 μm and DC electric field strength up to 246 kV/m over a period of 1 hour are investigated in the temperature range of 40°-200 °C. The measured conduction currents in PTFE are examined in the light of the available theory of Schottky emission, Poole-Frenkel effect, and ionic hopping mechanisms.

In chapter 5 the results of charging/discharging currents, thermally stimulated polarization (TSP) currents, and low frequency dielectric loss in aromatic polyamides are discussed with the influence of the various parameters such as electrode materials, sample thickness, heating rate.

Chapter 6 presents the results of thermally stimulated depolarization (TSD)
currents for corona charged aromatic polyamides with the influence of various parameters. In this chapter the results of wide angle X-ray diffraction and the Infrared spectroscopy analysis in aromatic polyamides are also presented.

In chapter 7 the results of charging/discharging currents, loss factor, and the conduction currents in composite polyamide are discussed with various parameters and available theories in solids.

Chapter 8 presents the results of thermally stimulated polarization (TSP) and depolarization (TSD) currents, and TSD windowing polarization currents in composite polyamide with consideration of various parameters.

Chapter 9 summarizes the conclusions and suggestions for future work. References are listed at the end of the dissertation.
Chapter 2

THEORETICAL BACKGROUND

This chapter presents the theories of the thermally stimulated polarization and depolarization currents used during the course of study in this dissertation. First, the presentation of the TSD and TSP current theories, in thermally charged aramid paper and composite polyamides, will be discussed and then the theories of corona charged aramid paper and loss factor will be presented in the second and third section of this chapter respectively.

2.1 Theories of TSD and TSP Currents

During the TSD current measurements the electrodes are short circuited and the stored charges in the dielectric materials are released on reheating the dielectric at a constant rate. The measured TSD current in the external circuit will be due to the image of these charges escaping from the evaporated electrodes, where they were previously induced by the dipoles and space charges.

Bucci et al. [57] have developed a complete theory to account for the dipolar reorientation, with single relaxation time, under non-isothermal conditions. The outline of his theory which is pertinent to the TSP and TSD experiments are summarized herein.

During the TSD current measurements the dipoles reorient on reheating the dielectric and the rate at which the instantaneous polarization $P$ decays with time can
be expressed in terms of the polarization and relaxation time \( \tau \) by

\[
\frac{dP}{dt} = \frac{-P}{\tau}
\]

(2.1)

where \( \tau \) is the relaxation time which depends on temperature.

The solution to eqn. (2.1) is

\[
P = P_o \exp \left( -\int_0^t \frac{dt}{\tau}\right)
\]

(2.2)

The initial polarization \( P_o \) is formed during the charging period by the reorientation of dipoles. The polarization according to the Debye theory is given by

\[
P_o = \frac{N \mu^2 E}{3 k T}
\]

(2.3)

in which \( N \) is the number of dipoles, \( \mu \) the dipole moment, \( E \) is the applied electric fields, and \( k \) the Boltzmann constant. The temperature variation of the relaxation time may be represented by

\[
\tau(T) = \tau_o \exp \left( \frac{\xi}{k T} \right)
\]

(2.4)

where \( \tau_o \) is the characteristic time independent of \( T \) and \( \xi \) the characteristic energy.

If the heating rate is linear then

\[
T = T_o + \beta t
\]

(2.5)

in which \( T_o \) is the temperature at commencement of heating and \( \beta \) the heating rate.

The current density \( j \) generated by the decay in polarization is simply the rate of
change of polarization and is expressed by

\[ j(t) = \left( \frac{P_o}{\tau} \right) \exp \left( - \int_0^t \frac{dt}{\tau} \right) \]  

(2.6)

combining eqns. (2.2) to (2.6) the polarization current density may be expressed as [39]

\[ j = \frac{N \mu^2 E}{3 \tau_o k T} \exp \left\{ \frac{\xi}{k T} + \frac{1}{\beta \tau_o} \int_{\tau_o}^{\tau} \exp \left( - \frac{\xi}{k T} \right) dT \right\} \]  

(2.7)

Making the assumption that the term with the integral sign in eqn. (2.7) is negligible over the initial part of the TSP current curve [16], we may write eqn. (2.7) in the form

\[ j = C \exp \left( - \frac{\xi}{k T} \right) \]  

(2.8)

A plot of \( \ln (jT) \) against \( 1/T \) yields a straight line with a slope of \( -\xi/k \).

The total polarization can be found from the TSP and TSD current curves by integration of \( j(T) \)

\[ P(T) = \frac{1}{\beta} \int_{\tau_o}^{\tau} j(T') dT' \]  

(2.9)

where \( \tau_o \) and \( T \) are the initial and final temperatures.

The total charge released, \( Q \), by TSP and TSD techniques is given by
\[ Q = \int_{t(T)} \dot{j}(t') \, dt' \quad (2.10) \]

An inspection of equation (2.7) shows that the total charge released from traps is independent of the thickness provided that both the electric field E and temperature T are kept constant and \( Q \) is proportional to the applied field.

By differentiating eqn. (2.8) with respect to temperature we can show that the temperature at which the maximum current (i.e. set \( dj/dT = 0 \)) occurs is

\[ T_m = \sqrt{\frac{\tau \beta \xi}{k}} \quad (2.11) \]

in which \( T_m \) is the temperature at which the current peaks occur and \( \tau \) is the corresponding relaxation time.

For a more accurate analysis of the relaxation time, it is essential to use all the data in the ln \( j \) vs. \( T \) curves obtained from TSP or TSD studies to calculate the relaxation time at each temperature according to

\[ \tau(T) = \frac{1}{\beta \int_{T_o}^{T} \frac{d\tau'}{j(T')}} \quad (2.12) \]

\( \tau(T) \) being determined experimentally using eqn. (2.12) by simply finding the integral of the current density curve from temperature \( T_o \) to the final value at \( T \) and
dividing this area by the current density at $T_o$ gives the relaxation time at $T_o$. From eqn. (2.4) a plot of $\ln \tau$ vs. $1/T$ should give a straight line if a uniform process is operative and hence the activation energy can be determined from the slope of $(E/\kappa)$.

2.2 Theory of TSD Currents in Corona Charged Dielectric

We consider a polymer which is subjected to corona poling. Assuming a uniform charge density of free and trapped charge carriers the charge in an element of thickness $dx$ at a depth $x$ and unit area is

$$dQ = \rho \ dx$$

(2.13)

in which $\rho$ is the charge density. The contribution to the current in the external circuit due to release of this element of charge is [58]

$$dj = \frac{w}{s} \frac{dQ}{dx} = \frac{J(x) \ dx}{s}$$

(2.14)

where $s$ is the thickness of the material, $dj$ the contribution to the externally measured current of the element of charge, $w$ the velocity with which the charge layer moves and $J(x)$ the local current due to the motion of the charge carriers.

According to Ohm's law, the current density is

$$J(x) = \rho \ \mu \ E(x)$$

(2.15)
where \( \mu \) is the mobility and \( E(x) \) the electric field at a depth \( x \). The electric field is not uniform due to the presence of space charges within the material and it can be calculated by solving Poisson's equation

\[
\frac{d E}{d x} = \frac{\rho_r}{\varepsilon_o \varepsilon_r}
\] (2.16)

where \( \rho_r \) is the total charge density (free plus trapped) and \( \varepsilon_r \) is the dielectric constant of the material. If we denote the number of free and trapped charges by \( n_f \) and \( n_t \), respectively, the current density is

\[
J = \frac{\mu e^2 \delta^2}{2 \varepsilon_r s} n_f (n_f + n_t)
\] (2.17)

in which \( \delta \) is the depth of charge penetration, \( \delta \ll x \) and \( e \) the electronic charge.

In general, it is reasonable to assume that \( n_r \ll n_t \) and eqn. (2.17) may be approximated to

\[
J = \frac{\mu e^2 \delta^2}{2 \varepsilon_r s} n_f n_t
\] (2.18)

The released charge carriers may be retrapped again and for the case of slow retrapping Creswell and Perlman [48,58] have shown that
\[ J = \frac{\mu e^2 \delta^2 n_o^2 \tau}{2 \varepsilon_o \varepsilon_r s \tau_o} \exp \left\{ -\frac{E_a}{kT} - \frac{2}{\beta \tau_o} \int_{T_o}^{T} \exp \left( \frac{-E_a}{kT} \right) dT \right\} \] (2.19)

Where

- \( n_o \) = initial density of charges in traps,
- \( \tau \) = lifetime in traps
- \( 1/\tau_o = \nu \) = attempt to escape frequency
- \( \beta \) = heating rate
- \( E_a \) = trap depth below conduction band
- \( T, T_o \) = final and initial temperatures respectively of the TSD run, (°K)
- \( k \) = Boltzmann constant

and

\[ \tau = \tau_o \exp \left( \frac{E_a}{kT} \right) \] (2.20)

Equation (2.19) may be written in the form

\[ J = R \exp \left\{ -C + B \int_{C_o}^{C} \exp \left( -C \right) C^{-2} dC \right\} \] (2.21)

where

\[ R = \left\{ \frac{\mu e^2 \delta^2 \tau_n^2}{2 \varepsilon_o \varepsilon_r s \tau_o} \frac{\tau}{\tau_o} \right\} \] (2.22)
\[ B = \frac{2E_a}{k \beta \tau_c} \quad (2.23) \]

\[ C = \frac{E_a}{kT} \quad (2.24) \]

Differentiating eqn.(2.21) and equating it to zero yields

\[ B = C_{max}^2 \exp \left( C_{max} \right) \quad (2.25) \]

in which \( C_{max} \) is related \( T_{max} \) according to eqn. (2.24).

From the measured TSD currents, the activation energy may be calculated using the method suggested by Cowell and Woods [59] which is basically a curve fitting method. All the measured values of current at various temperatures are used to obtain \( E_a \) to a better accuracy. An alternative method is to use the procedure suggested by Garlick and Gibson [60] in which \( \ln j \) is plotted as a function of \( 1/T \) and the slope is evaluated by a least square error method.

The curves of current and temperature can also be used to evaluate the relaxation time of the material. The charge remaining in the sample at temperature \( T \) is given by

\[ Q = \int_{t(T)}^{\infty} J(t') \, dt' \quad (2.26) \]
and the relaxation time at $T$ is given by

$$
\tau (T) = \frac{\int_{t(T)}^{T} J(t') \, dt'}{J(T)} = \frac{Q}{J(T)}
$$

(2.27)

From eqn. (2.20) the relaxation time is related to $T$ according to

$$
\ln \tau (T) = \ln \tau_o + \frac{E_a}{kT}
$$

(2.28)

A plot of $\ln \tau(T)$ versus $1/T$ yields $E_a$. It is useful to note that the current due to depolarization of permanent dipoles in the material results in an equation similar to (2.19) except for the pre-exponential factor [16,43,55].
2.3 Phenomenological Theory of Dielectric Loss:

The method of charging/discharging currents is used to obtain the dielectric relaxations which occur in the low frequency range \(< 0.1\) Hz. The discharging current decay of a charged dielectric is defined by the function \(\phi(t) \propto t^a\).

The complex dielectric constant of a material under alternating fields is

\[
\varepsilon^* = \varepsilon' - j \varepsilon''
\]  
(2.29)

where

\(\varepsilon'\) is the dielectric constant

and \(\varepsilon''\) is the dielectric loss factor.

The current decay is governed by the angular frequency \((\omega)\) dependence of both dielectric constant \(\varepsilon'(\omega)\) and dielectric loss factor \(\varepsilon''(\omega)\) according to the relation below [24,75]

\[
\varepsilon'(\omega) = \left[ \frac{1}{C_a} \int_0^\infty \phi(t) \cos(\omega t) \, dt \right] + \frac{C_o}{C_a}
\]  
(2.30)

\[
\varepsilon''(\omega) = \left[ \frac{1}{C_a} \int_0^\infty \phi(t) \sin(\omega t) \, dt \right] + \frac{G}{\omega C_a}
\]  
(2.31)

where

\(C_a\) = the capacitance of the electrodes when the sample is replaced by air.

\(C_o\) = the capacitance of the sample at very high frequencies.

\(\omega\) = the angular frequency, \(2\pi f\).

\(\phi(t)=\) the current flowing in the sample after applying unit voltage at \(t=0\).

\(G\) = the steady-state d.c. conductance.
The value of $\phi(t)$ does not include the steady-state conduction current from which $G$ is calculated; thus $\phi(\infty) = 0$. The decay function $\phi(t)$ which is frequently called the relaxation function is observed to decay with time in many dielectric materials according to the relation

$$\phi(t) = A C_a t^{-n}$$

(2.32)

where $A$ and $n$ are constants for a given material.

Substituting the value of $\phi(t)$ in both equations (2.30) and (2.31) gives

$$\varepsilon'(\omega) = \{ \omega^{n-1} A \Gamma(1-n) \cos \left( \left(1-n\right) \frac{\pi}{2} \right) \} + \frac{C_a}{C_o} \quad 0 < n < 1, \quad (2.33)$$

and

$$\varepsilon''(\omega) = \{ \omega^{n-1} A \Gamma(1-n) \cos \left( \left(1-n\right) \frac{\pi}{2} \right) \} + \frac{G}{\omega C_a} \quad 0 < n < 2. \quad (2.34)$$

The integrals converge over the ranges given for $n$.

Hamon [75] reduced the expression for $\varepsilon''$ to a simple approximation by expressing $\varepsilon''$ in terms of the relaxation function $\phi(t_i)$ at a particular time $t_i$ as

$$\varepsilon'' = \frac{\phi(t_i)}{\omega C_a} + \frac{G}{\omega C_d}$$

(2.35)

provided that $\omega$ and $t_i$ are related by the equation (2.36)
\[ \omega t_1 = [ \Gamma (1-n) \cos \left( \frac{n \pi}{2} \right) ]^{-1} \quad (2.36) \]

The expression on the right-hand side of eqn. (2.36) is almost independent of \( n \) in the range \( 0.3 < n < 1.3 \), and, to an accuracy within \( \pm 3\% \), can be taken as having the mean value 0.63. To an approximation accurate within \( \pm 3\% \), eqn. (2.34) can now be written as

\[ \varepsilon'' = \frac{G + \phi \left( \frac{0.63}{\omega} \right)}{\omega C_a} \quad (2.37) \]

If \( i(t) \) is the total charging current as a function of time after the application of a step voltage \( V \), which is the sum of the charging current and direct conduction current, so that

\[ \frac{i(t)}{V} = G_o + \phi(t) \quad (2.38) \]

equation (2.37) takes the simple form

\[ \varepsilon'' = \frac{i \left( \frac{0.63}{\omega} \right)}{\omega C_a V} \quad (2.39) \]

or alternatively
\[ \varepsilon'' = \frac{i (0.1/f)}{2 \pi f C_a V} \]  \hspace{1cm} (2.40)

Hamon [75] also indicated that, even if the relaxation function \( \phi(t) \) departs considerably from the form in eqn. (2.32), the approximation in eqn. (2.40) is still reasonably accurate [24].
Chapter 3

EXPERIMENTAL TECHNIQUES

The various experimental techniques that have been used during the course of this investigation are presented in this chapter. The dielectric preparation will be discussed in detail in each chapter according to the experiment type and dielectric material used.

3.1 High Vacuum Evaporating Unit

The high vacuum evaporating unit used to coat the samples under study is supplied by Balzers company and is shown in Plate 3.1. It consists of three controlling units, one called the automatic pumping unit control (BSP 102) which contains the power supply and pumping switches. The others are the quartz crystal thin film monitor (QSG 201), which is used to measure the thickness of the coating, and the evaporation control unit. The latter consists of two operations, one is evaporation and the other is glow discharge formation.

Before evaporation is commenced the coating material is placed in a coating boat between two high current electrodes. The sample to be coated is placed on top of the coating boat with some clearing distance and the pumping unit is evacuated when the diffusion pump is ready for operation. The automatic control unit is then switched to heat position so the chamber is evacuated and heated to facilitate out-gassing. The high vacuum in the chamber is measured by the vacuum gauge. When the desired level of
Plate 3.1 High vacuum evaporating unit.

(1) Rotary pump.
(2) Diffusion pump.
(3) Quartz Crystal thin film monitor (QSG 201).
(4) Automatic pumping unit control (BSP 102).
(5) Evaporation control unit.
(6) Coating boat.
(7) Sample holder.
pressure is reached the evaporation control unit is switched on and then the quartz crystal thin film monitor (QSG 201) unit is adjusted to zero frequency before starting the coating. Increasing the current through the coating boat causes the coating material to melt and evaporation is achieved while the thickness is measured with the frequency meter.

3.2 Conduction Current

After the preparation of the dielectric to be used in the experiment, the dielectric is placed between two stainless steel electrodes inside an environmental chamber. Plate 3.2 shows the equipment used in the study of conduction current in dielectric materials and Figure 3.1 shows the schematic arrangement of the experimental set up. The temperature of the dielectric is controlled using an environmental chamber which is controlled by a microprocessor unit designed to operate over a temperature range of -80° to 200 °C. The temperature control and measurement is accurate to 0.1 °C. In addition, a thermocouple is attached to the sample to measure its accurate temperature. This thermocouple is connected directly to the strip chart recorder. The step voltage is applied using a variable stabilized DC power supply (Brandenburg, Alph Series II) and the current is measured using a Keithley 610 C electrometer which is connected through a DC amplifier (NEFF Instrument Co. Model 128) with variable gain to a strip chart recorder (Cole-Palmer Instrument Co. Model 8373-20) having a sensitivity of 4 μVmm⁻¹.
Plate 3.2  Equipment used in the studies of conduction currents in PTFE.

(1) Variable DC power supply.
(2) Two way switch.
(3) Current limiting resistor.
(4) DC amplifier with variable gain (not shown behind the electrometer).
(5) Environmental chamber.
(6) Sample holder.
(7) Electrometer.
(8) Strip chart recorder.
(9) Microprocessor unit.
Figure 3.1 *Schematic arrangement of the experimental set up.*

(1) Variable DC power supply.  
(2) Two way switch.  
(3) Current limiting resistor.  
(4) Top high voltage electrode.  
(5) Bottom current measuring electrode.  
(6) Guard ring.  
(7) Sample.  
(8) Thermocouple.  
(9) Environmental chamber.  
(10) Ground connection.  
(11) Electrometer.  
(12) DC amplifier.  
(13) Strip chart recorder.
For reproducibility of results Sawa et al. [21] introduced an experimental technique, a variation of which is adopted in this study. Figure 3.2 shows the schematic of the experimental procedure [21] used. The thermal protocol which the dielectric material goes through before measurements are carried out are as follows:

A-B increase the environmental temperature from 25° to 200 °C.

B-C hold temperature constant at 200 °C for 3 hours.

C-D lower temperature to the desired value.

D-E-F maintain constant temperature for 2 hours.

E-F apply the desired DC voltage for 1 hour and take the measurements of the conduction current.

The electrodes are kept short circuited throughout the thermal protocol, which start at A and ends at E. At the end of the conduction current measurements the electrodes are short circuited while the temperature is raised to 200 °C again until the current decreases to at most 0.3% of the previously established current before the next run is conducted. This procedure is thought to minimize the effects due to space charges caused by trapped charges [10].

3.3 Charging and Discharging Currents

Figure 3.3 shows the schematic experimental arrangement for the study of charging and discharging currents in high temperature dielectric materials and Plate 3.3 shows the instruments used. The currents are measured using a Keithley 610 C electrometer which is connected to the low voltage electrode from one side and to IBM-PC through a DC
Figure 3.2 Schematic arrangement of the experimental procedures.

Figure 3.3 Schematic experimental arrangement for the study of charging/discharging, TSP/TSD currents. The strip chart recorder of Fig. 3.1 is replaced by: (13) A/D converter and (14) IBM-PC.
Plate 3.3 Experimental set up.

(1) Variable DC power amplifier.
(2) Two way switch.
(3) Environmental chamber.
(4) Sample holder.
(5) Electrometer.
(6) IBM-PC.
(7) Strip chart recorder.
(8) Microprocessor control unit.
(9) DC amplifier (not shown behind the electrometer).
amplifier with variable gain and A/D converter from the other end. The data acquisition system is capable of handling 16 channels of input with individual control for each channel. The frequency of sampling can be adjusted up to 4 kHz, though most of the data reported in this study were acquired at 1 Hz. A block averaging scheme was employed in the acquisition of data, the number of readings in a block being related to the sampling frequency.

Figure 3.4 shows the thermal protocol adopted in the study of charging/discharging currents experiments which is similar to that adopted during the study of conduction current techniques. The periods of charging/discharging currents are 5 hours during which the temperature is kept constant. The thermal protocol from point A to E is similar to the thermal protocol described in the conduction current studies adopted in Fig. 3.2. The thermal protocol adopted in charging/discharging is described below.

A-B increase the environmental temperature from 25° to 200 °C.

B-C hold temperature constant at 200 °C for 3 hours.

C-D lower temperature to the desired value.

D-G maintain temperature constant for 11 hours.

E-F apply the DC voltage for 5 hours and measure the charging currents.

F-G remove the DC voltage and short circuit the electrodes for 5 hours and measure the discharging currents.
Figure 3.4 Schematic of the experimental procedures.
3.4 *Thermally Stimulated Polarization (TSP) Current*

Figure 3.3 represents also the schematic experimental set up used in the TSP current experiments. Figure 3.5 shows the TSP current techniques used which consist simply of raising the temperature linearly at a constant rate until the maximum desired temperature is reached while the voltage is applied.

3.5 *Thermally Stimulated Depolarization (TSD) Current*

The schematic of the experimental procedures adopted during the study of the TSD currents are shown in Fig. 3.6. The experimental technique consists of the following steps:

A-B  increase the environmental temperature from 25° to 200 °C.

B-C  hold the temperature constant at 200 °C for 3 hours.

C-D  lower the temperature to the desired value for charging.

D-F  maintain the temperature constant.

E-F-G apply the desired DC voltage for 1 hour.

F-G  lower the temperature to 0 ° while the DC voltage is applied. When the temperature reaches 0 °C at G short circuit the electrodes.

G-H  maintain constant the temperature at 0 °C for 30 minutes.

H-I  reheat the dielectric at a linear rate and measure the TSD current.
Figure 3.5 Schematic of the experimental procedures.

Figure 3.6 Schematic of the experimental procedures.
3.6 Thermally Stimulated Windowing Polarization (TSWP) Current

The schematic of the experimental procedure that is used during the TSWP experiment is shown in Fig.3.7, and consists of the following steps:

A-B increase the environmental temperature from 25° to 200 °C.

B-C hold the temperature constant at 200 °C for 2 hours.

C-D lower the temperature to the desired value for charging.

D-F maintain constant the temperature at T_p for 2 hours.

E-F-G apply the desired DC voltage at T_p for a time t_p (i.e. 1 hour).

F-G lower the temperature to T_d (10 °C below T_p); at point G the electrodes are short circuited.

G-H hold constant the temperature at T_d for a time t_d = t_p (i.e. 1 hour).

H-I lower the temperature to 0 °C.

I-J maintain constant the temperature at 0 °C for 30 min.

J-K reheat the dielectric at a linear rate and measure the TSWP currents.

The windowing polarization, storage, and TSWP periods are clearly shown in Fig.3.7.

In addition a large number of experiments were carried out to separate the polarization component of the current from the transport component (ch. 7). These techniques are described at the appropriate section of the dissertation.
Figure 3.7 Schematic experimental procedures for TSWP currents.
Chapter 4

CONDUCTION CURRENTS IN TEFLOM (PTFE)

4.1 INTRODUCTION

The insulating material commercially known as Teflon (PTFE) or Polytetrafluoroethylene, is a non-polar thermoplastic polymer, has excellent dielectric properties, such as, low dielectric constant of 2.0 and 2.1 at frequencies of 60 Hz and 1 kHz respectively and a low loss factor of $2 \times 10^{-4}$ over a wide range of frequencies [2]. Higher thermal stability, low conductivity, resistance to chemical attack, low coefficient of friction, are its general properties making it an excellent insulating polymer for microelectronics components.

There are a number of papers published with regard to the properties of PTFE [61-64] and only a few deal with the study of electrical conduction mechanisms [4,5] and thermally stimulated currents [65,66]. Information on the electrical properties of PTFE film, such as the electrical breakdown and conduction mechanisms, so far is incomplete.

Investigations of high field conduction current in PTFE film with a thickness of 254 μm has been carried out by Lilly and McDowell [4]. They measured the conduction currents at high fields in the range of 78.7 - 118.1 kVcm$^{-1}$ and at just three temperatures of 162.5, 181.5 and 200 °C using electrodes having an area of 45.6 cm$^2$. Their results are discussed in terms of the available theories of conduction mechanisms in solids and the measured current varied with the field as exp( $\alpha E^{1/2}$ ), where $\alpha$ is a geometric constant.
which is unity for absolutely plane parallel electrodes with no fringing effect. It was concluded that the conduction mechanisms were ionic and electronic, each dominant at different field levels and both influenced by space charge effect. Vollmann and Poll [7] however, investigated the conduction current in thin fluorocarbon films with thicknesses between 0.1 and 0.5 μm, deposited by different methods and different electrode materials over a wide range of electrical field strength at room temperature. Over the whole range of thickness and field strength investigated no dependency on the electrode material or noticeable influence of polymerization method was observed for the steady-state currents. In conclusion their results are interpreted by means of a modified Poole-Frenkel effect for insulators with high impurity density.

The conflicting results in PTFE [4,5] suggest different mechanisms that might be operative at different temperatures and electrical field strengths. These mechanisms perhaps are influenced by the method of polymerization.

The study of the steady-state conduction currents in other polymers such as aromatic polyamide [16] and Kapton polyimide [10], in the temperature range between 50 - 200 °C at electrical fields up to approximately 450 kV cm⁻¹, suggested that the ionic conduction mechanism is the operative mechanism of conduction even at high fields with an ionic jump distance in the range of 5-6 nm and increases with increasing temperatures. Sawa et al. [21] observed that the ionic jump distance, in polypyromellitimide, commercially known as Kapton, is inversely proportional to the temperatures. The reported values of the ionic jump distance range between 8-11.5 nm obtained in a temperature range of 120 - 180 °C and electrical fields up to 500 kV cm⁻¹.
Sawa et al. [21] reported that the difference in the reported values of the ionic jump distance is probably due to the different heat treatments which might lead to a change in the jump distance. The other reason was attributed to the time at which the conduction current was recorded since the current occasionally rises with time at higher temperatures and therefore the calculated values of the jump distance could easily be underestimated in connection with an underestimate of current at higher fields.

The objective of this work is to examine further the effect on conduction currents of various thicknesses as they are of interest in practical applications and to extend the studies over a wider temperature range and higher electrical field strengths.

Electrical conduction in PTFE films, with thicknesses of 50 and 130 μm, was studied under steady-state conditions in the temperature range of 40 - 200 °C and electrical field strengths up to 246 kVcm⁻¹. The measured conduction currents at various constant electric field strengths and temperatures are examined in the light of the theory of Schottky, Poole-Frenkel and ionic conduction mechanisms.
4.2 *EXPERIMENTAL PROCEDURE*

The currents were measured on specimens of PTFE film which were 50 and 130 μm thick. The electrodes were made of stainless steel with an outside diameter of 12 cm, and the low voltage electrode, which had a diameter of 8.8 cm and which was provided with a guard ring, was connected to a Keithley 610 C electrometer for measuring the current. The samples were coated with a silver conducting composition (DuPont 4817) on each side and left to dry at room temperature for 30 min. before placed between the electrodes. The temperature of the sample was controlled using an environmental chamber which was controlled by a microprocessor unit designed to operate over a temperature range of -80° to 200 °C.

The temperature control and measurement is accurate to 0.1 °C. In addition to the measured temperature by the thermocouple provided by the chamber, a thermocouple was attached to the PTFE film to measure its temperature accurately. The voltage was applied using a variable stabilized DC power supply (Brandenburg, Alpha Series II) and the current was recorded using a strip chart recorder (Cole-Parmer Instrument Co.) having a sensitivity of 4 μV mm⁻¹. The strip chart signal input was connected to the recording probe of the electrometer. Figures 3.1 and 3.2 show the schematic diagram of the experimental set up and procedures respectively.

In order to ensure that there are no thermal gradients across the sample thickness, several preliminary experiments were conducted. Figure 4.1 shows the thermocouple positions. The sample is placed between the two electrodes and four measuring thermocouples were attached at different places to the sample and electrodes.
Figure 4.1 Schematic arrangement of the thermocouple set up positions.
The observed results indicated that the thermal gradients across the sample were considered to be negligible and the temperature of the dielectric was about 2 °C lower than the set temperature of the environmental chamber unless the stabilization time was more than 20 min. Although, at a heating rate less than 2 °C min⁻¹ the difference between the dielectric temperature and the environmental temperature decreases requiring a lower stabilization time.

4.3 RESULTS AND DISCUSSION

The measured conduction currents were examined in the light of the available conduction theories in the solids. Four mechanisms have been generally put forward; they are tunnelling, Schottky emission, Pool-Frenkel effect, and space charge effect.

Figure 4.2 shows the conduction current as a function of the electrical field strength at various applied temperatures in PTFE film with a thickness of 50 μm. Two distinct regions were observed, one at an electrical field below 40 kVcm⁻¹ and a temperature lower than 100 °C where the transport current is ohmic, in agreement with [5] where the ohmic conductivity in radio frequency sputtered PTFE films at temperatures between 43° and 93 °C and with electrical field intensities up to 1.5 x 10⁵ kVcm⁻¹ was measured.

For electric fields greater than 40 kVcm⁻¹, the conduction currents deviate from ohmic behaviour and the plots of log I vs. E could be fitted to a straight line with reasonable justification. For ionic hopping the current density is given by [2].
Figure 4.2 Isochronal currents as a function of applied electric field at various constant temperatures for 50 μm thick film.
\[ J = 2 e N s \nu \exp \left( - \frac{\phi}{kT} \right) \sinh \frac{e s E}{2 kT} \]  \hspace{1cm} (4.1)

in which \( e \) is the charge of an ion, \( \nu \) is the attempt to escape frequency, \( s \) is the separation distance between traps, and \( \phi \) the barrier height.

In the high electric field region, eqn. (4.1) can be reduced to

\[ I = I_o \exp \left( \frac{esE}{2kT} \right) \]  \hspace{1cm} (4.2)

where

\[ I_o = 2A e \bar{N} s \nu \exp \left( - \frac{\phi}{kT} \right) \]  \hspace{1cm} (4.3)

and \( A \) is the surface area of the electrodes. From eqn. (4.2) a plot of \( \ln I \) vs. \( E \) yields a straight line having a slope \( (es/2kT) \) from which the separation distance \( s \) between traps can be obtained. The separation distance between traps appears to be influenced by two different regions of temperatures. In one region the separation distance increases with decreasing temperature from 200\(^\circ\) - 80 \(^\circ\)C, and in the other, decreasing for temperatures less than 80 \(^\circ\) C indicating different mechanisms.

Figure 4.3 shows the conduction currents as a function of the electric field at various temperatures for PTFE film having a thickness of 130 \( \mu \)m. Three distinct regions are observed at temperatures higher than 120 \(^\circ\)C. At an electric field below 15.4 kVcm\(^{-1}\) the conduction current was ohmic and for higher fields the current deviates from ohmic and the plot may be fitted to a straight line as shown in Fig. 4.3. For an electric field higher than 100 kVcm\(^{-1}\) the slope decreases further. The separation distance between traps
Figure 4.3 Isochronal currents as a function of applied electric field at various constant temperatures for 130 μm thick film.
at a field less than 100 kV cm\(^{-1}\) increases with increasing temperatures up to 120 °C. For a field higher than 100 kV cm\(^{-1}\) and temperature more than 120 °C, the separation distance decreases with increasing temperature. The calculated values of the separation distance between traps appear to be temperature and thickness dependent. Table 4.1 lists the calculated values of the separation distance in 50 and 130 μm PTFE films.

In the case of field assisted thermionic emission from the cathode the current density \(J_c\) may be expressed by the Schottky equation

\[
J_c = A_c T^2 \exp \left\{ - \frac{\Phi_s - \beta_s E^{1/2}}{k T} \right\} \tag{4.4}
\]

where \(\beta_s\) is the Schottky Coefficient given by

\[
\beta_s = \sqrt{\frac{e^3}{4 \pi \varepsilon_o \varepsilon_m}} \tag{4.5}
\]

The zero electric field emission current density according to eqn. (4.4) is given by

\[
J_o = A_c T^2 \exp \left( - \frac{\Phi_s}{k T} \right) \tag{4.6}
\]

and is obtained by the y-axis intercept in Figs. 4.5 and 4.6 from which the emission constant \(A_c\) is obtained. It is observed to be temperature dependent in the range of 0.027 x 10\(^{-7}\) to 44.96 x 10\(^{-7}\) A cm\(^{-2}\)K\(^{-2}\) in 50 μm and 6.495 x 10\(^{-12}\) to 1.913 x 10\(^{-8}\) A cm\(^{-2}\)K\(^{-2}\) in 130 μm PTFE film respectively. They are about 6 and 3.5 order of magnitude lower than the expected value of 120 A cm\(^{-2}\)K\(^{-2}\) for Schottky emission [6]. Table 4.2 shows the calculated values of the emission constant \(A_c\) for 50 and 130 μm PTFE films.
Figure 4.4 Plot of $\ln I_0$ as a function of $1000/T$
A plot of $\ln I_o$ vs. $1/T$ according to eqn. (4.6) also yields a reasonably straight line as shown in Figure 4.4. From the slope, the effective work function between the Fermi level of the metal cathode and the conduction band of insulator, can be easily calculated and it is found to be between 0.72 and 0.86 eV for 130 and 50 $\mu$m respectively. This is in good agreement with [46] in which the TSC spectra in PTFE film shows considerable peaks below room temperature when charged by an electron beam. The obtained activation energies were in the range of 0.4 to 1.2 eV. Above room temperature PTFE changes considerably due to thermal expansion [50] and hence different phase changes in the morphology of the polymer were observed to occur at a different temperature levels in PTFE [63].

When donor like states exist in the insulator the current density may be expressed by the Poole-Frenkel effect as [68]

$$J_{pf} = BE \exp \left\{ - \frac{\left( \phi_{pf} - \beta_{pf} E^{1/2} \right)}{kT} \right\}$$

(4.7)

where $\phi_{pf}$ is the zero electric field ionization energy of the donor and $\beta_{pf}E^{1/2}$ is the reduction in this energy due to the application of the electric field.

Both equations (4.4) and (4.7) show that a plot of log I vs. $E^{1/2}$ also yields a reasonably good straight line as shown in Figs. 4.5 and 4.6. For Schottky emission from the slope, which is equal to $\beta_s/kT$, $\beta_s$ can be calculated and hence $\varepsilon_{\infty(0)}$ from eqn. (4.5). The calculated dielectric constant at high frequencies $\varepsilon_{\infty(0)}$ was observed in the range of 8 to 588 and 2.6 to 0.4 in 50 and 130 $\mu$m film respectively, as shown in Table 4.2 at the end of this chapter. For the Pool-Frenkel effect, however, the dielectric constant
Figure 4.5  Log I vs. $E^{1/2}$ at various constant temperatures in 50 μm thick film.
at high frequencies $\varepsilon_{\text{w/p}}$ would be four times these values [6] and obviously too high when compared with the static permittivity of 2.0 at room temperature. Hence, both Schottky emission and Poole-Frenkel effect mechanisms are definitely not acceptable.

Muller [69] and Lilly et al. [4] observed that the electrical field can be written as $E = \gamma V/d$, where $d$ is the distance between electrodes and $\gamma$ is a geometrical constant which is unity for absolutely plane parallel electrodes with no fringing effects. Muller [69] indicated that the value of $\gamma$ is greater than unity and he observed values as high as 139. Values less than unity, however, have been reported by Lilly and McDowell [4] in Mylar film with a thickness of 35.4 $\mu$m. Moreover, values of $\gamma$ were also reported, in PTFE [4], in the range of 13.4 to 25.6 and they were increasing with increasing temperature.

The computed values of $\gamma$ in this work are to overcome any deviation in the log $I$ vs. $E$ plots due to the accumulation of the space charge. We choose the value of $\gamma$ as unity at the temperature of 40 $^\circ$C and accordingly calculate the other values. The observed values of $\gamma$ were temperature dependent and higher than unity up to a temperature about 100 $^\circ$C and less then unity at higher temperatures. Table 4.1 presents the computed values of the geometrical constant $\gamma$ at various temperatures in 50 and 130 $\mu$m PTFE films.

The observed values of the geometrical constant $\gamma$ greater than unity suggest an increase in the field due to ionic space charge [4] while, values less then unity suggest a reduction in the field due to electronic space charge.
Figure 4.6  Log I vs. $E^{1/2}$ at various constant temperatures in 130 μm thick film.
### Table 4.1  Summary of the conduction current results in PTFE.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Ionic Jump Distance (nm)</th>
<th>Correlation Factor</th>
<th>γ</th>
<th>Ionic Jump Distance (nm)</th>
<th>Correlation Factor</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>3.42</td>
<td>0.997</td>
<td>1.00</td>
<td>3.02</td>
<td>0.996</td>
<td>1.0</td>
</tr>
<tr>
<td>60</td>
<td>3.91</td>
<td>0.998</td>
<td>1.48</td>
<td>5.70</td>
<td>0.986</td>
<td>2.55</td>
</tr>
<tr>
<td>80</td>
<td>4.55</td>
<td>0.996</td>
<td>1.17</td>
<td>9.00</td>
<td>*2.69</td>
<td>*0.971</td>
</tr>
<tr>
<td>100</td>
<td>4.09</td>
<td>0.989</td>
<td>1.03</td>
<td>5.57</td>
<td>*1.22</td>
<td>*0.975</td>
</tr>
<tr>
<td>120</td>
<td>1.78</td>
<td>0.962</td>
<td>0.13</td>
<td>*0.470</td>
<td>*0.978</td>
<td>1.59</td>
</tr>
<tr>
<td>140</td>
<td>1.07</td>
<td>0.979</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>0.68</td>
<td>0.993</td>
<td>0.017</td>
<td>*2.69</td>
<td>*0.971</td>
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<tr>
<td>180</td>
<td>0.56</td>
<td>0.989</td>
<td>0.011</td>
<td>*1.22</td>
<td>*0.975</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.30</td>
<td>0.999</td>
<td>0.014</td>
<td>*0.470</td>
<td>*0.978</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4.2  Summary of dielectric constant at high frequencies and Schottky emission constant in PTFE films.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\varepsilon_\infty$ (s)</th>
<th>$A_\varepsilon x 10^7$ (Acm$^{-2}$K$^{-2}$)</th>
<th>$\varepsilon_\infty$ (s)</th>
<th>$A_\varepsilon$ (Acm$^{-2}$K$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>13.4</td>
<td>44.959</td>
<td>9.4</td>
<td>19.129x10$^{-9}$</td>
</tr>
<tr>
<td>60</td>
<td>8.0</td>
<td>14.753</td>
<td>3.7</td>
<td>1.014x10$^{-9}$</td>
</tr>
<tr>
<td>80</td>
<td>9.0</td>
<td>9.165</td>
<td>2.8</td>
<td>6.431x10$^{-12}$</td>
</tr>
<tr>
<td>100</td>
<td>9.2</td>
<td>0.027</td>
<td>6.495x10$^{-10}$</td>
<td>*7.287x10$^{-9}$</td>
</tr>
<tr>
<td>120</td>
<td>67.0</td>
<td>0.027</td>
<td>6.166</td>
<td>3.223x10$^{-10}$</td>
</tr>
<tr>
<td>140</td>
<td>74.6</td>
<td>13.647</td>
<td>2.6</td>
<td>*4.757x10$^{-9}$</td>
</tr>
<tr>
<td>160</td>
<td>414.1</td>
<td>2.080</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>588.2</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>411.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* For field regions > 100 kVcm$^{-1}$. 
Chapter 5

ABSORPTION AND THERMALLY STIMULATED
POLARIZATION CURRENTS IN ARAMID PAPER

5.1 INTRODUCTION

Aramid paper which is an aromatic polyamide polymer, also known as Nomex (manufactured by E.I. DuPont De Nemours & Co. Inc.) is a high temperature insulating material and finds increasing applications in electrical equipments such as motors, generators, transformers and other high energy devices. There are a growing number of uses of this material in nuclear power and space applications due to its ability to withstand intense levels of radiation such as beta, gamma and X-rays [1]. The dielectric properties of this polymer, particularly the conduction currents due to an applied electric field and the discharging currents following the removal of an applied step voltage are obviously of engineering importance. A study of these currents also yields valuable information with regard to the fundamental processes enhancing a designer's ability for optimum choice of operating conditions.

Upon application of a step voltage to an insulating material the current which flows in the external circuit decays with time and this current has been termed variously as charging, conduction, resorption or poling current [42] depending upon the duration of application of the voltage. We shall adopt the first of these. If the applied step voltage
is removed and the two electrodes are short circuited, a discharging or absorption current flows and the time variation of this current is according to a well known power law [25,29,32]

\[ I(t) = A(T) t^{-n} \]  

(5.1)

where \( I \) is the current in ampere, \( A(T) \) a factor dependent upon the temperature \( T \), \( t \) the time in seconds and \( n \) the decay constant. The mechanisms responsible for the generation of absorption currents have been variously identified [31] as (i) electrode polarization, (ii) dipolar orientation, (iii) charge injection leading to space charge effects; (iv) hopping of charge carriers between trapping sites and (v) tunnelling of charges from the electrodes into the traps. Recently, Wintle [25] reviewed the above mentioned mechanisms, and discussed their applications to polymers, with the exception of the hopping mechanism. An attempt to identify the mechanism involves a study of the absorption currents by varying several parameters such as the electrical field applied during charging, the temperature, sample thickness and electrode materials. A summary of the above mentioned mechanisms responsible for the charging currents have been provided by Das-Gupta et al. [31] and Smith et al. [32] in a tabular form which may help to identify and eliminate those mechanisms not responsible for the transient currents.

Absorption currents also enable one to calculate the low frequency behaviour of a polymer [26,31]. Dielectric theory shows that d.c. absorption currents measured as a function of time can be interpreted in terms of its alternating voltage properties such as the dielectric loss factor [33] which is dependent on the frequency.

A variation of the technique for measurement of charging current isothermally is
to measure the current as a function of the temperature of the material which is allowed to increase linearly while a constant electric field is applied. Measurement of these currents, also known as thermally stimulated polarization (TSP) currents, has several advantages [35], one of which is that the measured current reveals how the orientation of the dipoles is proceeding. A search for an optimum poling temperature is eliminated and overheating of the specimen is avoided.

In this study the absorption currents which arise after a sudden application or removal of a step d.c. voltage in aromatic polyamide are reported over a temperature range of 70°-200 °C. The effect of varying parameters such as field strength, electrode material which is formed by vapour deposition and sample thickness were investigated. The dielectric loss factors at low frequencies (<0.1 Hz) were evaluated from the discharging current measurements. Moreover, the thermally stimulated polarization (TSP) currents were also measured and the influence of the various parameters as above were investigated. In addition, the rate of heating of the sample was also varied.

5.2 EXPERIMENTAL PROCEDURE

Measurements of charging and discharging currents were carried out on aramid paper (grade 410) having a radius of 44 mm and thicknesses of 76 and 127 µm. Before using the samples they were heat treated for 5 hours at 260 °C to remove any moisture content and to improve reproducibility of results. Two different electrode materials, aluminum and silver of 50 nm thickness were vacuum deposited on the specimens at pressure of 10^-6 Torr. The low voltage electrode was provided with a guard ring which was also vapour
deposited to reduce effects due to stray fields. The low voltage electrode was connected to a Keithley 610 C electrometer for measuring the currents in the dielectric materials. A step voltage was applied to the sample and the charging current monitored for a period of 5 hours. The step voltage was then removed and the sample short circuited for the same period of time during which the discharging currents were recorded. The temperature was then increased in steps of 10 °C and the procedures repeated at each temperature for different applied voltages. Before each measurement a blank run was performed in order to free the sample from extraneous charges. This run consisted of raising the temperature of the sample at a constant rate to 200 °C with the electrodes short-circuited. At this temperature the samples were kept short-circuited for a further period of about 12 hours until the current decreased to about 3% of the previously established current before the next step voltage is applied to minimize the effects of the space charge build up.

Figures 3.3 and 3.4 show the schematic arrangement of the experimental set up and procedures respectively.
5.3 RESULTS AND DISCUSSION

5.3.1 Charging and Discharging Currents

(a) Time Dependence and Effect of Sample Thickness

Figures 5.1 and 5.2 show typical charging currents in aramid paper for a 76 and 127 \( \mu \)m sample respectively, with silver electrodes, at a constant temperature of 200 °C and various poling electric fields for a time duration of 5 hours. The charging currents decay very slowly with time according to eqn. (5.1) with the value of index \( n \) in the range of 0.01 - 0.04 for both thicknesses with no polarity dependence and no appreciable dependence on the sample thickness or electrode material was observed. A similar time dependence of charging current has been reported for other insulating materials, such as SiO\(_2\) and SiO with aluminum electrodes [23], solid n-octadecane [70] and polycarbonate [27] above its glass transition temperature of 150 °C. Lindmeyer [23] suggests that a slow filling of traps by charge carriers in conjunction with a space charge effect is responsible for the slow decay of current with respect to time. Recently, it has been suggested that a high electric field can induce traps in polymers [71] with the trap creation rate being proportional to applied electric field. This theory also possibly explains the reason for not being able to observe a steady current under certain experimental conditions even after times of the order of \( 10^5 \) s.
Figure 5.1  Charging currents at various electric fields at 200 °C with silver electrodes and a thickness of 76 μm aramid paper.
Figure 5.2  Charging currents at various electric fields at 200 °C with silver electrodes and a thickness of 127 μm aramid paper.
Figures 5.3 and 5.4 show the discharging currents as a function of time at a constant temperature of 200 °C after poling at various electrical fields in the range of 1.32 - 6.58 MVm$^{-1}$ for 76 μm and 0.08 - 8.0 MVm$^{-1}$ for 127 μm thick paper with silver electrodes. The current decays fast for a time up to 10$^3$ s where the power law holds with a value of $n = 1$. For times longer than 10$^3$ s the discharging current tends to flatten out, the current decay is much less pronounced, and the decay constant $n$ ranges between 0.1 to 0.4 (see inset). Both charging and discharging currents showed no appreciable dependence on the sample thickness or polarity.

The difference between charging and discharging currents is defined as the transport current [32]. Figures 5.5 and 5.6 show typical transport currents in aramid paper with a thickness of 127 μm and 76 μm deposited with silver electrodes. Similar results were obtained in 76 μm film with aluminum electrodes. As the discharging currents decrease faster with time, the transport currents are observed to increase up to a time of 100 s and then flatten out with a slope almost similar to the charging currents slope at times greater than 100 s. Similar results are observed in polyimide (PMDA-ODA) film [32]. However, in polyimide the transport current was decreasing with time up to 100 s due to the mirror image, of the charging and discharging currents, to one another. In aramid paper, however, the data for 76 and 127 μm thick paper, shown in Figs. 5.1 and 5.4 demonstrated that the charging and discharging currents are dissimilar for the investigated periods of time. There is no strong evidence of the dependence of charging and discharging currents on the thickness of samples as shown in Figs. 5.1 - 5.4.
Figure 5.3 Discharging currents at various electric fields at 200 °C. Sample thickness=76 μm; electrode material-silver.
Figure 5.4  Discharging currents at various electric fields at 200 °C. Sample thickness=127 μm; electrode material-silver.
Figure 5.5  Transport currents at various electric fields at 200 °C. Sample thickness=127 μm; electrode material-silver.
Figure 5.6 Transport currents at various electric fields at 200 °C. Sample thickness=76 μm; electrode material-silver.
The inset of Fig. 5.4 shows the range of values of $n$ obtained under various experimental conditions. Such dissimilarities have been observed previously in other polymers [23,27,70] and there is no complete agreement on the processes responsible for it. Lindmayer [23] discussed these dissimilarities with the aid of energy diagrams and attributed the initial transient during charging to empty traps. The current can be as large as allowed by the injecting barrier. As the traps become filled the current reduces to the space charge limited current with traps. In the discharging period, on the other hand, the trapped carriers will be discharged toward both electrodes showing a smaller current in the external circuit.

Das Gupta and Brockley [72] on the other hand concluded that the dissimilarity between the charging and absorption current is probably due to the onset of a quasi steady state conduction current which is superimposed on the transient current.

The influence of temperature on the charging and discharging currents for a 76 μm sample with silver electrodes as a function of time at a constant electric field of 6.6 MVm$^{-1}$ and various poising temperatures from 70 to 170 °C are shown in Figs. 5.7 and 5.8 respectively. The decay of currents during charging are observed to be more rapid at lower temperatures in the range of 70 - 170 °C. Seanor [18] has also observed a similar behaviour in linear polyamides in which the conduction currents in the ranges of 25 - 80 °C and 120 - 155 °C decay with time more rapidly than currents in 80 - 110 °C range. Obviously there is a change of conduction process above 180 °C in aramid paper. The discharging currents shown in Fig. 5.8 indicate that at a lower temperature of 90 °C the current decays up to $3 \times 10^3$ s and for longer periods the rate of decay is much higher.
Figure 5.7  Charging currents at various temperatures and constant electric field of 6.6 MVm\(^{-1}\); sample thickness=76 \(\mu\)m; silver electrodes.
Figure 5.8  Discharging currents at various temperatures and constant electric field of 6.6 MVm$^{-1}$; sample thickness=76 µm; silver electrodes.
However, at the highest temperature of 200 °C the initial rate of current decay is higher than that at times longer than $10^3$ s. The behaviour observed at 200 °C for the 76 μm paper is consistent with that of 127 μm (Figure 5.4) at the same electric field. The relaxation phenomenon at 90 °C appears to be quite different from that at 200 °C with a gradual transition at intermediate temperatures.

It is relatively easier to interpret the results of Fig. 5.8 in terms of the universal dielectric theory of Jonscher [73] who proposes that the time domain response of the current has two slopes or two values for $n$. An increase in the value of $n$ at longer periods is due to a dipolar mechanism whereas a decrease in $n$ at longer periods is due to interfacial polarization. Figure 5.8 shows that a transition occurs from a dipolar mechanism at 90 °C to an interfacial polarization at 200 °C. Aramid paper is manufactured out of aromatic polyamide in the form of fibres which are amorphous and flocs which are crystalline, the finished product having a crystallinity of approximately 50 % [74]. The material abounds with boundaries between the crystalline and amorphous regions. Both the number of distributed trap levels and the mobility of charge carriers are likely to be higher resulting in a higher conductivity in the amorphous region in comparison with the crystalline parts. This difference in conductivity is possibly the origin of the observed interfacial polarization at higher temperature of 200 °C.
(b) Temperature dependence

Figure 5.9 shows typical results of discharging currents at prescribed times (isochronal) over a temperature range of 90 - 200 °C at an applied step voltage of 500 volts. The isochronal currents are obtained from the measured values of the discharge currents shown in Fig. 5.8. The currents show no significant peaks and increase with temperature smoothly. The slope of the curves yield an activation energy of $0.21 \pm 0.05$ eV.

(c) Field Dependence

Figure 5.10 shows the electric field dependence of the charging currents obtained at a constant temperature of 200 °C with sample thickness of 127 μm. The observed relationship is

$$I(t) = k(t) E^p$$  \hspace{1cm} (5.2)

where $k$ is a constant independent of $E$ and $p = 1$. Gupta and Joyner [31] and Das Gupta et al. [26] observed the same linear relation in polyethylene terephthalate (PET) at a temperature of 173 K. However, the current magnitudes were different depending upon the time lapsed at a constant electric field. Figure 5.10 shows that in aramid paper the time duration has only a marginal influence on the currents due to the fact that the current decays slowly with time (Figs. 5.1 and 5.2).
Figure 5.9  Temperature dependence of the discharging currents at prescribed times (i.e. isochronal). Pre-applied field of 6.56 MV/m; sample thickness=76 μm; charging time=5h; electrode material-silver.
Figure 5.10  Field dependence of isochronal charging currents at a temperature of 200 °C. Sample thickness=76 μm; charging time=5h; electrode material-silver.
(d) Effect of Electrode Material

The charging and discharging currents obtained at a constant temperature of 200 °C for a sample of 76 μm thickness with aluminum electrodes are shown in Fig. 5.11. Comparing these results with those of Figs. 5.1 and 5.3 it is observed that the charging currents and the value of index n are higher for silver electrodes when compared with those of aluminum electrodes. However, the discharging currents do not show any significant dependence on the electrode material.
Figure 5.11 Time dependence of charging/discharging currents at various applied fields and constant temperature of 200 °C. Sample thickness=76 μm; electrode material-aluminum. Top curves are for charging, bottom four are for discharging currents.
5.3.2 Low Frequency Dielectric Loss Factor ($\varepsilon''$)

The discharging currents after the removal of a step voltage can be used to obtain information on the dielectric loss factor $\varepsilon''$ of a solid insulating material at low frequencies using the Hamon approximation [75]

$$
\varepsilon''(f) = \frac{I(t)}{2\pi V C_o} \frac{I(0.1/f)}{2\pi V C_o}
$$

where $I(t)$ is the discharging current at time $t$, $C_o$ the geometric capacitance of electrode assembly in air, $V$ the magnitude of the step voltage and $f$ is known as the Hamon frequency $= 0.1/t$. Figure 5.12 shows the calculated values of $\varepsilon''$ at low frequencies in the temperature range of 100 - 190 °C. In the temperature range 100 - 190 °C, two relaxation frequencies are observed at each temperature. These correspond to relaxation times of $1.6 \times 10^3$ s and $2 \times 10^4$ s. Data are not available for comparison, but Govinda Raju [16] has calculated from thermally stimulated discharge (TSD) currents a relaxation time of $10^4$ s at 150 °C, which differs only by a factor 2 from the higher value observed in this study. Baird et al. [19,34] suggest that large values of dielectric loss factors arise from a mixture of relaxation processes and d.c. conductivity. In these studies the influence of d.c. conductivity is eliminated by using the absorption current to evaluate the data shown in Fig. 5.12. Govinda Raju [16] has shown that dipolar mechanism is responsible for the TSD currents in this temperature range, and the observed peak at the higher frequency is attributed to this mechanism. From Fig. 5.12 we note that the low frequency peak in the $\log f$ vs. $\varepsilon''$ curves are more pronounced at higher temperatures.
Figure 5.12 Frequency dependence of dielectric loss factor $\varepsilon''$ at various temperatures. Pre-applied field of 6.56 MVm$^{-1}$; sample thickness=76 $\mu$m; charging time=5 h; electrode material-silver.
We can examine whether the low frequency peak observed is possibly due to interfacial polarization according to the Maxwell-Wagner equation [2].

\[
\varepsilon'' = \frac{1}{\omega C_o \left( R_1 + R_2 \right)} + \frac{\varepsilon_x - \varepsilon_\infty}{1 + \omega^2 \tau^2} \omega \tau
\]

in which \( \omega = 2\pi f \) is the angular frequency in rad/s. \( R_1 \) and \( R_2 \) are the equivalent resistances of the amorphous and crystalline regions respectively. \( \varepsilon_\infty \) the high frequency dielectric constant. \( \varepsilon_x \) the dc (\( \omega = 0 \)) dielectric constant and

\[
\tau = \frac{\tau_1 R_2 + \tau_2 R_1}{R_1 + R_2}
\]

\[
\tau_1 = C_1 R_1
\]

\[
\tau_2 = C_2 R_2
\]

\( C_1 \) and \( C_2 \) are the capacitances of the amorphous and crystalline regions respectively. Assuming that \( C_1 = C_2 \), \( R_1 \ll R_2 \), and \( \tau_1 \ll \tau_2 \) eqn. (5.5) simplifies to

\[
\tau = 2 \tau_1
\]

Eqn. (5.4) shows that the dependence of \( \varepsilon'' \) on frequency is similar to that on dipolar relaxation though the peak for interfacial polarization occurs at much lower frequencies. Using eqn. (5.4) and measured conductivity, the relaxation time for interfacial polarization has been calculated and shown in Table 5.1.

At 200 °C the dielectric loss factor, \( \varepsilon'' \), increases very rapidly with decreasing frequency which is another manifestation of interfacial polarization.
Table 5.1 Summary of the dielectric loss factors, conductivity, and relaxation time in Nomex 410

<table>
<thead>
<tr>
<th>$T , (^\circ \text{C})$</th>
<th>$\varepsilon''$</th>
<th>$\sigma , (\Omega\text{m})^{-1}$</th>
<th>$\tau , (s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(a) High Frequency Peak:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>0.76</td>
<td>$1.75 \times 10^{15}$</td>
<td>$1.6 \times 10^3$</td>
</tr>
<tr>
<td>130</td>
<td>1.14</td>
<td>$5.48 \times 10^{15}$</td>
<td>$1.1 \times 10^3$</td>
</tr>
<tr>
<td>140</td>
<td>1.31</td>
<td>$1.20 \times 10^{14}$</td>
<td>$6.3 \times 10^2$</td>
</tr>
<tr>
<td>150</td>
<td>2.14</td>
<td>$2.62 \times 10^{14}$</td>
<td>$5.5 \times 10^2$</td>
</tr>
<tr>
<td>160</td>
<td>2.03</td>
<td>$4.38 \times 10^{14}$</td>
<td>$3.1 \times 10^2$</td>
</tr>
<tr>
<td><strong>(b) Low Frequency Peak:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>0.98</td>
<td>$7.0 \times 10^{16}$</td>
<td>$5.6 \times 10^3$</td>
</tr>
<tr>
<td>140</td>
<td>1.70</td>
<td>$2.3 \times 10^{15}$</td>
<td>$5.0 \times 10^3$</td>
</tr>
<tr>
<td>160</td>
<td>2.27</td>
<td>$4.0 \times 10^{15}$</td>
<td>$4.0 \times 10^3$</td>
</tr>
</tbody>
</table>
5.3.3 *Thermally Stimulated Polarization (TSP) Current*

(a) *Influence of Time Duration*

While the charging and discharging current measurements are carried out at a constant temperature (i.e., isothermal), thermally stimulated polarization (TSP) currents are measured with the temperature of the sample being raised at a linear rate in the presence of an electric field. This technique has several advantages; the charge build-up process is revealed in greater detail and excessive heating of the sample is avoided [42]. In these experiments the influence of poling electric field, heating rate and voltage polarities on TSP currents are reported for the first time.

Figure 5.13 shows typical TSP currents at various electric field strengths. The currents increase with temperature, the rate of increase being small up to 100 °C and more rapid at higher temperatures. At 200 °C the environmental chamber is switched to an isothermal mode and the current is observed to increase with time for a periods as large as 60 minutes. The upper curves of Fig. 5.13 show these isothermal measurements. Typically at an electric field of 7.9 MVm⁻¹ the current at 105 °C is 7.1 x 10⁻¹⁰ A, increasing to 7.9 x 10⁻⁸ A at 200 °C. The current measurements are continued in the isothermal mode for a period of about forty-five minutes during which time the current increased from 7.9 x 10⁻⁸ A to 3.2 x 10⁻⁷ A, a factor of about four. The same qualitative behaviour is observed at other electric fields and to determine the origin of these currents a number of experiments were carried out. Each experiment commenced with the sample at room temperature and the microprocessor programmed to rise the temperature at a constant heating rate of 2 Kmin⁻¹. When the temperature reached 200 °C, it is switched
Figure 5.13 Typical TSP currents at various electric fields up to 200 °C. Upper curves show isothermal currents at 200 °C. Sample thickness=127 μm; electrode material-silver.
to isothermal mode keeping the temperature constant for the remaining duration of the measurements. Fig. 5.14 shows the experimental arrangements in each run. In run 101 the voltage was applied at room temperature, in run 102 the voltage was applied at 200 °C and in run 103 a negative polarity voltage was applied at 200 °C. No significant difference is observed in the measured currents in these three runs. In run 104 a reduced electric field of 3.9 MVm⁻¹ was applied at 200 °C. Though the initial current was lower the current build up was larger during the first few minutes and then there was a much slower increase. Run 105 shows the results when the applied electric field is reduced from 7.8 MVm⁻¹ to 3.9 MVm⁻¹ at the instant the isothermal mode becomes operative. Except for the initial part the results of run 104 and 105 are considered to be repeated.

The differences in the initial part of the isothermal currents in all these runs can be explained on the basis of the fact that a reduction in applied field as was done in run 105 does not reduce the current to its final steady value instantly. These experiments show that the observed current increase with time under isothermal conditions is independent of the electrical field strength, and is attributed to the behaviour of the material at higher temperatures. A large number of experiments were performed to make sure that thermal lag and other extraneous factors are not responsible for the observed effects. Consistent with the results of the discharging current measurements, interfacial polarization is the most likely mechanism for the current growth. Other manifestations of the ionic conduction currents are the dependence of $\varepsilon^-$ on time lapsed after the removal of a previously applied electric field [76], and a sharp increase in $\varepsilon^-$ at higher temperatures [77].
Figure 5.14 Experimental arrangements during each run of the isothermal currents at 200 °C. Sample thickness=127 μm; electrode material-silver.
(b) Separation of Polarization and Conduction Current

The technique of TSP current measurements can also be used to separate the current due to polarization from the conduction current. The experimental technique is to measure the current as the sample is linearly heated to the highest temperature, 200 °C in this study. With the field still applied the temperature of the sample is held constant at 200 °C for a period of one hour to allow for the interfacial polarization current to reach its maximum value. The sample is then rapidly cooled to room temperature and reheated again, during which time the currents are measured. This forms the second cycle. The procedure is repeated again during the third cycle.

Figure 5.15 shows the results of a typical run with a sample thickness of 127 μm coated with silver electrodes and an applied electric field of 7.9 MVm⁻¹. The current during the second cycle is considerably smaller than during the first cycle at lower temperatures, the difference between the two currents decreasing as the temperature increases. At 200 °C the two currents are almost identical. These results clearly demonstrate that at lower temperatures the currents observed during the second cycle are lower because the dipoles are already oriented during the first cycle and therefore the measured currents which are lower in magnitude are conduction currents. The difference in currents during the second and third cycle is attributed to the disorientation of dipoles that occurs as the temperature is increased. The polarization currents which are obtained from subtracting the currents of the second cycle from those of the first cycle are also shown in Fig. 5.15 These results are in agreement with the discharging current data (Fig. 5.4) and the TSD currents results [16].
Figure 5.15 Separation of TSP and polarization currents in aramid paper. Electric field=7.9 MVm$^{-1}$; sample thickness=127 μm; electrode material-silver.
Application of the theories discussed in section 2.1 (chp. 2) yields the following quantities; \( P = 1.73 \ \mu \text{Cm}^2 \) from eqn. (2.9) and \( \tau = 610 \ \text{s} \) at 173 °C from eqn. (2.11). The only available data are those from TSD current measurements in this material [16]. It should be pointed out that these results should be treated with caution since they are arrived at by a single value of the temperature at which a peak is observed. A different value of \( \beta \) results in another value of \( T_m \) depending upon the distribution of relaxation times. For a more accurate analysis it is therefore essential to use all of the experimental data in the \( \ln I \) vs. \( T \) curve (Fig. 5.15) and calculate the relaxation time at each temperature according to eqn. (2.12). The results of these calculations are shown in Fig. 5.16. From the slope we derive an activation energy of 1.2 eV, and a room temperature relaxation time of \( 6.3 \times 10^4 \) s, which are in closer agreement with those of thermally stimulated discharge (TSD) current measurements in this material [16].

The following comments are appropriate with regard to the polarization currents. The electrical dipole moment, \( \mu_p \), is calculated in Nomex 410 using the Debye eqn.

\[
\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N \mu_p^2}{9 \varepsilon_o k T} \quad (5.9)
\]

where \( \varepsilon_r = 2.5 \) is the dielectric constant of the material, \( \varepsilon_o \) permittivity of free space \( \mu_p \) the permanent dipole moment and \( N \) the number of monomers/m\(^3\). The molecular weight is 242.3.

The number of monomers per unit volume is calculated to be \( 2.4 \times 10^{27} \text{ m}^{-3} \), using
\[ N = N_o \left( \frac{D}{W} \right) \]  

(5.10)

where \( N_o \) is the Avogadro number, \( D \) density (kg\( m^{-3} \)), and \( W \) the total molecular weight, and the density provided by the data sheet is 960 kg\( m^{-3} \).

The dipole moment obtained from eqn. (5.9) at \( T = 446.15 \, ^\circ K \) is \( 8.377 \times 10^{-30} \) coulomb-meter which is 2.5 Debye. To determine the bond which the observed dipole moment may be attributed to values of the bond moment must be known. The reported values of the bond moment [61] for C = O, C-N, H-N, and H-C are 2.4, 0.4, 1.3 and 0.4 Debye, respectively. From these reported values the C = O bond which has 2.4 Debye dipole moment and which is located in the side group is the most likely responsible for the obtained value of 2.5 Debye.
Figure 5.16 Relaxation time of polarization currents in aramid paper. Sample thickness=127 µm; electrode material-silver.
(c) Influence of Rate of Heating ($\beta$)

Figure 5.17 shows the influence of rate of heating on TSP currents. The conduction currents are not sensitive to the rate of heating and the dependence of current on $\beta$ provides additional evidence for the suggested dipolar mechanism. The results of varying $\beta$ show that a higher $\beta$ yields higher currents. $T_m$ is related to $\beta$ according to eqn. (2.11) which shows that a higher $\beta$ yields a higher $T_m$. However, as already stated, complete agreement between theory and experiment cannot be achieved due to the reason that eqn. (2.11) involves the assumption that the material possesses a single relaxation time. In fact most polymers have a distribution of relaxation times and additional experiments are required to determine these.
Figure 5.17 Effect of heating rate on TSP currents in aramid paper. Electric field=7.9 MVm$^{-1}$; sample thickness=127 μm; electrode material=silver.
Chapter 6

THERMALLY STIMULATED DISCHARGE CURRENTS
IN CORONA CHARGEDaramid PAPER

6.1 INTRODUCTION

Measurement of thermally stimulated discharge (TSD) currents is a powerful technique that has been used to gain insight into the molecular mechanisms of charging of polymer dielectrics [21]. It also provides considerable information with regard to the relaxation processes that occur in polymers such as disorientation of dipoles and release of charges from trapping sites and impurity locations.

Several techniques are available for poling a dielectric material such as thermal, electron beam and corona poling. The latter consists of exposing the surface of the material to a corona discharge between point-plane electrodes with the point electrode being maintained at a high voltage. During measurement of the TSD currents the polymer is heated linearly at a constant rate and a thermogram which is a plot of current as a function of temperature is obtained.

Thermally stimulated discharge (TSD) currents were measured in corona charged aramid paper to study the mechanisms of charge storage and its subsequent release from the bulk of the material. Studies were carried out on paper thicknesses of 76 µm and 127 µm using a point-plane gap in air at atmospheric pressure. TSD currents were measured over a temperature range of 0° - 200 °C and the influence of various parameters
such as the poling voltage, rate of heating and effect of electrode materials are investigated.

The current shows a number of peaks to reveal processes which are related to molecular relaxation and delocalization of charges injected into the polymer bulk during poling [49-51].

The results of investigation into TSD currents of aramid paper (grad 410) using corona charging techniques are reported in this chapter, with the results of both X-ray diffraction and Infrared spectroscopy analysis, for the first time.

6.2 EXPERIMENTAL ARRANGEMENT

Aramid paper samples having a radius of 44 mm with thicknesses of 76 μm and 127 μm were employed in this study. Prior to the experiments they were heated for 5 hours at 260 ºC to remove absorbed moisture. One side of the sample was vapour deposited with aluminum or silver electrode of 20 nm thickness at a pressure of 10⁻⁴ torr. Following the vapour deposition the sample was placed between a needle shaped high voltage electrode and a planar backing electrode with the metallized side of the sample being attached to the planar backing electrode. The gap length was 4.5 cm. For corona charging a potential of 16.83 kV or 33 kV was applied to the high voltage electrode in air at atmospheric pressure for a period of 10 or 20 minutes.

Figure 6.1 shows the schematic set up of the corona charging equipment. After charging, a second aluminum electrode of the same thickness was vapour deposited on the other side. The sample was then placed between the measuring electrodes and kept
Figure 6.1 Schematic set up of the corona charging equipment.

(1) Variable DC power supply
(2) Current limiting resistor
(3) Point electrode
(4) Sample
(5) Current measuring electrode
(6) Electrometer
(7) Gap distance (4.5 cm)
short circuited for 1 hour to remove any stray charges before it was cooled to 0 °C.

The TSD currents were measured by heating the sample at a constant rate of 2 Kmin\(^{-1}\). An environmental chamber which was provided with a microprocessor was used to control the heating rate and the temperature range. The currents were recorded using a Keithley 610 C electrometer and a strip chart recorder of 4 μV/mm sensitivity.

6.3 RESULTS AND DISCUSSION

6.3.1 Influence of Poling Time and Voltage

Figure 6.2 shows the TSD currents in aramid paper for a thickness of 127 μm at a voltage of 16.83 kV and 33 kV. The negative polarity currents are normal TSD currents and the positive polarity currents are referred to as abnormal currents in this paper. In Fig. 6.2, the abnormal TSD currents flow in the circuit in the temperature range of 0° - 40 °C, with a peak centred at 20° - 25 °C. Curve (1) which is obtained for a poling duration of 10 minutes at 16.83 kV shows a peak in the normal TSD current at 62 °C. Increasing the poling duration to 20 minutes at the same voltage results in curve (2) which shows two peaks, one at 72 °C and the other at 112 °C. A similar behaviour is observed for a higher voltage of 33 kV as shown by curves (3) and (4). Similar results obtained for 76 μm paper are shown in Fig. 6.3 in which curves (1) and (2) are for poling duration of 10 and 20 minutes respectively.

Two observations are noted with regard to the effect of duration of poling. (i) As the poling duration increases the low temperature peak around 72 °C shifts to a higher temperature (curves (3) and (4) of Fig. 6.2), (ii) the current magnitude at this peak is
Figure 6.2 Thermally stimulated discharge (TSD) currents for positively charged aramid paper with Al electrodes.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(1)</th>
<th>(2)</th>
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<th>(4)</th>
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<tbody>
<tr>
<td>Charging voltage, kV</td>
<td>16.83</td>
<td>16.83</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Charging time, min.</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>
higher than that of the subsequent peak at about 110 °C. A similar behaviour is reported by Von Seggern [56] and Sessler et al. [57] for positive corona charged Teflon and electron injected FEP respectively. The various peaks are assumed to be due to different trapping levels. As the poling time increases, the charges are trapped possibly in deeper traps and this will cause the peaks to shift to a higher temperature during release of charges.

Figure 6.2 also shows the influence of poling voltage on the TSD currents. The currents are higher for higher poling voltage. Furthermore, with an increasing poling voltage the low temperature peak at 72 °C becomes more pronounced (curves (1) and (3) of Fig. 6.2) than those at higher temperatures. Neagu et al. [49] have observed a similar effect in Tefzel and suggest that the shallow trap density is probably greater than that for deeper traps.

The second peak in the normal TSD current occurs at 112 °C at 16.83 kV and shifts to 144 °C when the poling voltage is increased to 33 kV. Sessler and West [57] have also observed a similar shift with electron injected Teflon-FEP. They attributed the peak shift to the time dependence of radiation induced conductivity generated during electron injection. The observed effect in aramid paper is probably ionic in nature, which is consistent with the fact that higher energy ions are generated in the discharge and they are trapped in deeper traps as suggested earlier.

The calculated activation energies ranged from 0.5 to 0.98 eV for 76 μm and 0.5 to 2.0 eV for 127 μm samples and observed to be dependent on the poling voltages and independent of the poling time. Similar values of activation energies were reported in
Figure 6.3  Thermally stimulated discharge (TSD) currents for positively charged 76 μm aramid paper with Al electrodes.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(1)</th>
<th>(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charging voltage, kV</td>
<td>16.83</td>
<td>16.83</td>
</tr>
<tr>
<td>Charging time, min.</td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>
corona charged Mylar [50].

6.3.2 Influence of Heating Rate (β)

The influence of rate of heating on TSD currents is shown in Fig. 6.4. These results are obtained with a thickness of 76 μm. Curves (1) and (2), and 127 μm, curves (3) and (4), with aluminum electrodes for a time duration of 10 minutes and for a poling voltages of 33 kV and 16.83 kV respectively. The observed curves indicated that the current peak tends to shift to lower temperature as β decreases. This is in general agreement with the theory [21] and the results of Creswell and Perlman [50] in corona charged Mylar film. Figure 6.4 also shows that lower heating rate gives lower currents as expected.

The calculated activation energies were found to be also independent of the heating rate β. For instance, in Fig. 6.4, the activation energy obtained for curves (1) and (2) at β = 1 and 2 Kmin⁻¹ is 0.75 eV for 16.85 kV, while, for curves (3) and (4) at the same values of β and 33 kV, the activation energy is 0.97 eV.

6.3.3 Influence of Sample Thickness

Figure 6.5 shows the results obtained with two thicknesses for a poling duration of 20 minutes for curves (2) and (4), and 10 minutes for curves (1) and (3), at a poling voltage of 16.83 kV. The current magnitude is inversely proportional to the thickness of the film, thicker samples yielding lower currents with higher activation energy of 2.0 eV.

There is no appreciable dependence of the temperature at which the peak occurs on the sample thickness.
Figure 6.4 Influence of heating rates for 127 μm aramid paper with Al electrodes charged for 10 min.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charging voltage, kV</td>
<td>16.83</td>
<td>16.8</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Heating rate $\beta$, Kmin$^{-1}$</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 6.5  Influence of sample thickness on TSD currents in aramid paper with Al electrodes and charged with 16.83 kV.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charging time, min.</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Sample thickness, μm.</td>
<td>127</td>
<td>127</td>
<td>76</td>
<td>76</td>
</tr>
</tbody>
</table>
6.3.4 Influence of Annealing Time

Annealing time is the time interval during which the charged sample is kept short
circuited before commencement of TSD (step G-H in Fig. 3.6).

The influence of annealing time on TSD currents is shown in Fig. 6.6. These
results are obtained for aramid paper, with aluminum electrodes, having a thickness of
127 µm for a charging voltage of 16.83 kV and a poling duration of 10 minutes. The
results are shown for annealing times of 1, 6 and 48 hours. The peaks tend to shift to
higher temperatures as the annealing time increases with decreasing magnitude. Similar
results were reported by Sessler et al. [58] for Teflon FEP charged with an electron
beam, and the results were attributed to ohmic compensation of the primary electrons by
secondary holes and the population shift depended on the total number of the holes
available. The calculated activation energies were observed to be inversely dependent on
the annealing time, the longer the annealing time the lower the activation energy required
to liberate the trapped charges. Curves (1) to (3) in Fig. 6.6 provide activation energies
of 1.77, 0.94 and 0.56 eV for annealing time of 1, 6 and 48 hours respectively.

The observed effect is possibly due to the fact that the degree of crystallinity
changes with annealing time, higher annealing times resulting in greater crystallinity. The
trap depths are larger and their concentration is possibly smaller explaining the shift of
the peaks to higher temperatures as the annealing time is increased. Support for this
conclusion is based on X-ray diffraction studies described in section 6.5.
Figure 6.6  Influence of annealing time on TSD currents in aramid paper of 127 µm thick with Al electrodes charged with 16.83 kV.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing time, Hour</td>
<td>1</td>
<td>6</td>
<td>48</td>
</tr>
</tbody>
</table>
6.3.5 Influence of Electrode Materials

The influence of electrode materials on the TSD currents for a thickness of 76 μm film at a charging voltage of 16.83 kV is shown in Fig. 6.7. Curves (1) and (3) represent the TSD currents with aluminum electrodes at a poling time of 10 minutes while curves (2) and (4) represent the TSD currents with silver electrodes. The results indicate that the TSD currents obtained with aluminum electrodes are much higher than those of silver electrodes and it appears that the lower peak in curves (1) and (3), aluminum electrodes, disappeared in curves (2) and (4), silver electrodes. However, the position of the higher temperature peaks, in both materials, appear to be around the same temperature range of 90° - 120 °C. No results are available in other materials for comparison, since the effect of the electrode materials, in the case of corona charging, has not been studied. However, in the case of aramid paper the results indicated a dependency on the electrode materials with silver electrodes showing some kind of, and undetermined as yet, blocking process.

6.3.6 Activation Energy

The activation energy is determined for normal TSD current peaks at lower temperatures by using the initial rise method of Garlick and Gibson [60]. Typical values of activation energies obtained in this study from Fig. 6.8 are shown in Table 6.1. No data are available for comparison. Sessler [58] found an activation energy in Teflon FEP in the range of 0.7 to 1.0 eV for the positive carrier peaks and 1.8 eV for the negative carrier peaks. However, Creswell and Perlman [50] reported several values of activation energies in positively corona charged Mylar of 0.55 and 0.85 eV to be due to electronic traps and
Figure 6.7  Influence of electrode materials on TSD currents in aramid paper of 76 μm thick charged with 16.83 kV.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charging time, min.</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Electrode material</td>
<td>Al</td>
<td>Ag</td>
<td>Al</td>
<td>Ag</td>
</tr>
</tbody>
</table>
Figure 6.8  Influence of charging voltage and charging time on the activation energy for 127 µm thick aramid paper with Al electrodes.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Charging voltage, kV</th>
<th>Charging time, min.</th>
<th>Activation energy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>16.83</td>
<td>10</td>
<td>1.77</td>
</tr>
<tr>
<td>(2)</td>
<td>16.8</td>
<td>20</td>
<td>1.99</td>
</tr>
<tr>
<td>(3)</td>
<td>33</td>
<td>10</td>
<td>0.98</td>
</tr>
<tr>
<td>(4)</td>
<td>33</td>
<td>20</td>
<td>0.49</td>
</tr>
</tbody>
</table>
1.4 eV for either electronic trap with a coulomb barrier, or ionic. For a higher value of activation energy of 2.2 eV, the trap is identified to be either ionic, interfacial or involves dissociation of a complex with subsequent release of an electron to the conduction band. They also indicated that the transport during conduction is perhaps the only real distinguishing criterion.

The activation energy obtained in this study for the low temperature peak shows that the carriers are probably electronic. They are possibly generated with the bulk of the material by the intense radiation produced in the corona. Supporting evidence is that puncture of the sample was observed to occur if very high voltages are adopted for poling. Neagu and Das-Gupta [79] reported that with positive corona charging in air at atmospheric pressure, hydrated versions of $\text{H}^+$, $\text{NO}^+$ and $\text{NO}_2^+$ ions are produced, which could induce polarization in the polymer, whereas for negative corona charging $\text{CO}_2^-$ ions are generated. These ions may dissociate on the polymer surfaces to produce chemical changes in the polymer through the formation of double bonds and carbonyl groups [16].

Table 6.1 summarizes the results obtained. The activation energies presented in Table 6.1 were calculated for the first prominent peak in the normal TSD current thermogram. There is also dependency on the poling time (i.e., charging time) in general, the longer the poling time the higher the activation energy as shown in Table 6.1.
6.3.7 Relaxation Time ($\tau$)

The relaxation times calculated in aramid paper (eqn. 2.12) with thicknesses of 76 $\mu$m and 127 $\mu$m are shown in Fig. 6.9 for silver and aluminum electrodes. The plot of $\ln \tau$ vs $1/T$ does not yield a straight line as indicated by eqn. (2.20), which is formed on the basis of a single relaxation time. However, polymers, in almost all cases, have a distribution of relaxation times, the experimental manifestation of which is a nonlinear curve as in Fig. 6.9. Typical values of relaxation time for a sample with silver are in the range of 40° to 192 °C is $1.1 \times 10^5$ to 120 s. For aluminum $\tau$ ranges between $35 \times 10^2$ to 24 s. in the range of 38° to 86 °C.

6.3.8 Concentration of Charge Carriers ($n_c$)

The total charge $Q_t$ released during the TSD current spectrum, obtained using eqn. (2.26), are given in Table 6.1. $Q_t$ was observed to increase with increasing poling time.

The concentration of charge carriers $n_c$ captured by traps, for both cases of mono-molecular and bimolecular recombination with weak and strong retrapping, is given by [59], for mono-molecular retrapping

\[ n_t = \frac{2.7 J_m k T_m^2}{e L \beta E_a} \]  

(6.1)

where $J_m$ is the maximum current density, $T_m$ temperature at which maximum current occurs, and $L$ the depth of the space charge layer. In the case of strong bimolecular recombination, the above equation differs only by a factor of 1.48 [59]. Table 6.2 shows the list of the values of $n_t$ obtained in both cases.
Figure 6.9  Plot of \( \ln \tau \) vs \( 1/T \) for samples charged at 16.83 kV for 10 min.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Sample thickness, ( \mu m )</th>
<th>Electrode material</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>76</td>
<td>Ag</td>
</tr>
<tr>
<td>(2)</td>
<td>127</td>
<td>Al</td>
</tr>
</tbody>
</table>
The mobility of the charge carriers can be calculated using eqn. (2.18) and the
derived values of $n_t$. The penetration depth of the space charge layer is assumed to be at
the mid-point of the sample thickness and $n_t / n_i$ is assumed as 0.5. The mobility of the
charge carriers calculated for the conditions listed in Table 6.2 is in agreement with [60].
Two possible models have been suggested [60] for the charge-carrier transport in
molecular crystals. The first model deals with the conventional band theory with
mobilities greater than $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which vary as $T^n$, where $n$ is in the range of 1.5, and
the second deals with the hopping polaron model mobilities for which it is less than $1
\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and varies according to $\exp(-E/T)$. Also, higher mobilities which lie between
1 and $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and obey a $T^n$ temperature law have been reported in pure molecular
crystals. Aramid paper, as already stated, is manufactured out of aromatic polyamide in
the form of fibres which are amorphous and flocs which are crystalline, the finished
product having a crystallinity of approximately 50% [16]. An increasing mobility is
thought to indicate an increasing predominance of the amorphous region in the conduction
process.
Table 6.1 Summary of results obtained from corona charged aromatic polyamide paper (Nomex 410), \( Q \) is the total charge.

<table>
<thead>
<tr>
<th>Corona Voltage (kV)</th>
<th>Poling Time (°C)</th>
<th>Film Thickness (µm)</th>
<th>Electrode Material</th>
<th>Temp. For Maxm. Current ( T_m(°C) )</th>
<th>( Q \times 10^6 ) (coul.)</th>
<th>( E_s ) (eV)</th>
<th>Fig. No.</th>
<th>Curve No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.83</td>
<td>10</td>
<td>76</td>
<td>Al</td>
<td>72,113.6</td>
<td>3.469</td>
<td>0.66</td>
<td>6.7</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>76</td>
<td>Al</td>
<td>80,120</td>
<td>4.340</td>
<td>0.55</td>
<td>6.7</td>
<td>(3)</td>
</tr>
<tr>
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<td>10</td>
<td>76</td>
<td>Ag</td>
<td>113.6</td>
<td>1.263</td>
<td>0.71</td>
<td>6.7</td>
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<td></td>
<td>20</td>
<td>76</td>
<td>Ag</td>
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<td>0.906</td>
<td>0.82</td>
<td>6.7</td>
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</tr>
<tr>
<td>16.83</td>
<td>10</td>
<td>127</td>
<td>Al</td>
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<td>1.77</td>
<td>6.2</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
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<td>1.529</td>
<td>1.99</td>
<td>6.2</td>
<td>(2)</td>
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<tr>
<td>33.00</td>
<td>10</td>
<td>127</td>
<td>Al</td>
<td>70.4,96</td>
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<td>0.98</td>
<td>6.2</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>127</td>
<td>Al</td>
<td>96,144</td>
<td>3.012</td>
<td>0.49</td>
<td>6.2</td>
<td>(4)</td>
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Table 6.2  Typical values of the concentration of charge carrier and its mobility with monomolecular and bimolecular recombination mechanism from TSD current measurements
(a) monomolecular  (b) bimolecular

<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Curve Number</th>
<th>(a) ( n_t ) ( \times 10^{18} \text{ m}^{-3} )</th>
<th>(b) ( n_t ) ( \times 10^{18} \text{ m}^{-3} )</th>
<th>(a) ( \mu ) ( \text{cm}^2\text{V}^{-1}\text{s}^{-1} )</th>
<th>(b) ( \mu ) ( \text{cm}^2\text{V}^{-1}\text{s}^{-1} )</th>
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<tbody>
<tr>
<td>6.2</td>
<td>(1)</td>
<td>3.37</td>
<td>4.99</td>
<td>8.29</td>
<td>3.78</td>
</tr>
<tr>
<td>6.2</td>
<td>(2)</td>
<td>3.00</td>
<td>4.44</td>
<td>9.90</td>
<td>4.51</td>
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<tr>
<td>6.2</td>
<td>(3)</td>
<td>10.13</td>
<td>15.01</td>
<td>1.48</td>
<td>0.68</td>
</tr>
<tr>
<td>6.2</td>
<td>(4)</td>
<td>25.05</td>
<td>37.11</td>
<td>0.25</td>
<td>0.11</td>
</tr>
<tr>
<td>6.7</td>
<td>(1)</td>
<td>29.87</td>
<td>44.25</td>
<td>0.33</td>
<td>0.15</td>
</tr>
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<td>19.36</td>
<td>28.68</td>
<td>0.44</td>
<td>0.20</td>
</tr>
<tr>
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<td>(3)</td>
<td>71.09</td>
<td>105.32</td>
<td>0.09</td>
<td>0.04</td>
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<td>(4)</td>
<td>13.78</td>
<td>20.41</td>
<td>0.75</td>
<td>0.34</td>
</tr>
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</table>
6.4- X-RAY DIFFRACTION ANALYSIS

X-ray diffraction is a powerful technique that has been used extensively to investigate the crystallinity arrangements of atoms or molecules via the interference effects of X-rays with structures comparable in size to the wavelength of the radiation [62]. These interferences are sharpened in the case of an orderly (i.e. crystalline) array or lattice arranged structures. Two X-ray techniques are often used; (i) The low-angle X-ray scattering which is used to detect larger periodicities that might arise from lamellar crystallites or from voids, and (ii) The wide-angle X-ray scattering which gives information on the interatomic distances in crystals, since the wavelengths of X-ray are comparable to interatomic distances in crystals.

The study of wide angle X-ray diffraction patterns in aramid paper with a thickness of 127 µm, charged with the corona charging technique were investigated for the first time in this study. The charging voltages were 16.83 and 33 kV, annealed at 200 °C for 5 hours. For purposes of comparison diffraction studies on uncharged samples were also carried out.

Aramid paper possesses two different phases; one is crystalline and the other is amorphous with about 50% ratio [10]. Both phases scatter radiation when X-ray diffraction technique is employed. The crystalline phase produces the well defined Bragg peaks which are characteristic of the spacings between the crystal phases, whereas the amorphous phase gives a diffused peak [63].
6.4.1 Experimental Procedures

To obtain the X-ray diffraction profile in Nomex 410 paper a step-scanning technique was employed using graphite monochromated CuKα radiations at 40 kV and 20 mA, and a Phillips X-ray diffractometer (Model PW 1050) using a proportional counter detection head which moves at a rate of 2 θ° min⁻¹. A chart recorder was utilized to record the diffracted beams.

6.4.2 Results and Discussions

(a) Influence of Corona Poling Voltages on the X-Ray Spectrum

Figure 6.10 show the results of typical diffraction profiles of aramid paper, with a thickness of 127 μm, charged using the corona charging technique at poling voltages of 16.83 and 33 kV for 10 min. The profile of an "as received" sample is also shown for comparison. Four peaks were observed in Figure 6.10, two of these peaks are less pronounced at a Bragg-angle (2θ) of ~ 12° and 19° for the "as received" sample and sample poled at a voltage of 16.83 kV respectively. The peaks at 2θ ~ 15° and 19° are for the sample poled at 33 kV. The other two peaks are at 2θ ~ 23° and 27°.

The sharp peak at 2θ ~ 27° is associated with the crystalline regions of three-dimensional order of aramid paper, whereas the more broad and diffused peaks at 2θ < 25° are associated with either small crystallite size or defects in the lattice parameters [64]. Data on the crystal plane structures for this polymer are not available, to the author's knowledge so far, which makes the identification of the phase plane for aramid paper difficult.
Figure 6.10 Influence of corona poling voltages on the X-ray diffraction spectrum in aramid paper with 127 μm thickness.
Figure 6.10 also shows no peak shift in 2θ position as corona voltage increased. However, the peak at 2θ = 18° becomes less pronounced as the corona voltage increased to 33 kV. The peak values of the diffracted intensities at 2θ ranging from 7° to 13° decreased with increasing poling voltages. A similar observation was obtained by Das-Gupta [65] in X-ray diffraction study of Polyvinylidene Fluoride where the peak of form 2 structural phase (100) and (020) was observed to decrease with increasing poling fields. In aramid paper, however, the peaks at 2θ > 15° were continuously increasing as the poling voltage increased. It has been suggested [65] that the increase in the intensity of form 1 composite peak (110)+(200), in Polyvinylidene Fluoride, was due to a change in the orientation and alignment in the lower-field region, whereas the behaviour of the form 2 peaks (100), (020), and (110) (i.e. the more diffused peaks) was explained by a modification of form 2 peaks due to an orientation of the resultant dipole moments of individual chains in the low-field region.

The X-ray diffraction profiles in aramid paper shown in Figure 6.10 are similar to the X-ray profile obtained by Kyotani et al. [66] in Nylon 6 with two crystalline forms; α and γ were observed with two α-form peaks at 2θ = 19° and 25° and one γ-form at 2θ = 22°. The fourth peak at 2θ = 11° was not assigned any form. Since, aramid paper is closely related to Nylon and the X-ray diffracted profiles are similar, the same crystalline form could exist in aramid paper. However, until some studies are conducted to determine the structural planes in aramid paper, it is difficult at this stage to confirm this point.
(b) Influence of Annealing Temperatures on the X-Ray Spectrum

Figure 6.11 shows the effect of annealing temperatures on the X-ray diffraction profile obtained from aramid paper, with a thickness of 127 μm vapour deposited with an aluminum electrode on one side, after they were annealed at different temperatures of 200, 260, and 300 °C for 5 hours. The diffraction pattern of an "as received" sample is also shown for comparison. In general, the diffracted pattern obtained in both Figures 6.10 and 6.11 are similar. However, the effect of increased annealing temperatures is very clear. The observed profiles indicated that the peak intensities increased with increasing temperatures up to 200 °C and then decreased at temperatures of 260 and 300 °C at 2θ < 15 °C. Moreover, the peak intensity at 2θ = 27° increased with increasing temperatures above 260 °C, while the peaks between 2θ of 15° and 25° becomes more pronounced and their intensities increased with increasing annealing temperatures above 200 °C with no peaks shift in the values of 2θ.

The interpretation of the increasing peaks intensities with increasing annealing temperatures is related to the improvement in the polymer crystallization. As the annealing temperatures increase beyond 200 °C the thermal motion plays an important part in the orientation and folding of the polymer molecules or chains [62]. Similar results were obtained by Kyotani et al. [66] in Nylon 6, for an annealed sample at 200 °C for 10 hours. The diffracted peaks in Nylon 6 of the two crystalline forms (i.e. α and γ) become sharper, with increased peak intensities, and the crystallinity increased on annealing.

Table 6.3 shows the results of the calculated values of the distance d between successive planes for the X-ray diffracted peaks in Figures 6.10 and 6.11 using the well
known Bragg equation

\[ n \lambda = 2d \sin \theta \] (6.2)

where \( n = 1 \) and \( \lambda = 1.5418 \) Å is the graphite monochromated (CuKα) wavelength which is incident on the set plane.

The results in Table 6.3 shows that the distance \( d \) between the planes is almost constant. The crystalline phase at \( 2\theta = 27.2^\circ \) shows the smallest distance between the planes of approximately 3.27 Å, while the other peaks at \( 2\theta = 23.3^\circ \) and \( 18.1^\circ \) have values of 3.8 and 4.8 Å.

As the annealing temperature increases the distance between planes is observed to decrease in general as listed in Table 6.3. However, in the case of corona charging voltage the distance between planes did not indicate any significant changes.

**Table 6.3**  Influence of corona voltage and annealing temperature on the distance between the crystal planes in aramid paper.

<table>
<thead>
<tr>
<th>V (kV)</th>
<th>Influence of Corona voltage</th>
<th>T (°C)</th>
<th>Influence of Annealing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 2\theta )</td>
<td>( d ) (Å)</td>
<td>( 2\theta )</td>
</tr>
<tr>
<td>0°</td>
<td>18.10</td>
<td>4.8478</td>
<td>18.10</td>
</tr>
<tr>
<td></td>
<td>23.30</td>
<td>3.8338</td>
<td>23.30</td>
</tr>
<tr>
<td></td>
<td>27.20</td>
<td>3.2784</td>
<td>27.10</td>
</tr>
<tr>
<td>18.83</td>
<td>18.10</td>
<td>4.9009</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>23.30</td>
<td>3.8176</td>
<td></td>
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<td>27.20</td>
<td>3.2784</td>
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<td>33</td>
<td>18.10</td>
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<td>300</td>
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<tr>
<td></td>
<td>23.30</td>
<td>3.8176</td>
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</tr>
<tr>
<td></td>
<td>27.25</td>
<td>3.2725</td>
<td></td>
</tr>
</tbody>
</table>

* As received sample.
Figure 6.11 Influence of annealing temperatures on the X-ray diffraction spectrum in aramid paper with 127 µm thickness.
6.5 INFRARED SPECTROSCOPY ANALYSIS

The infrared emission or absorption which arise from atomic vibrations, when molecules undergo transition between quantum states corresponding to two different internal energies, have taken a leading position among those physical methods which have been so widely used in the last two decades for investigating polyatomic molecular structures and properties.

Significant information such as the identification of chemical groups, mechanical properties and the geometry of molecules, and the type of chemical bonding can be obtained from the number and frequency of the infrared absorption bands.

The usual sources of radiation in infrared spectrometers are electrically heated silicon carbide or rare earth oxide rods which emit infrared radiation as black bodies [79].

6.5.1 Experimental Procedures

The infrared spectroscopy was obtained, for aramid film of 127 µm in thickness, using Nicolet 5DX Fourier Transform Infrared (FTIR) spectrometer with an Attenuated Total Reflection (ATR) attachment using KRS-5 which is a synthetic optical crystal, containing about 42% Thallium Bromide and 58% Thallium Iodide [62], with an approximate transmission limit in wave number of about 250 cm\(^{-1}\). The crystal dimension is 5 cm in length and 1 cm in width. The infrared spectra covered the range of the wave number from 20000 to 250 cm\(^{-1}\). The KRS-5 crystal is thoroughly cleaned with Methanol agent after each infrared test. This cleaning agent does not harm the crystal.

Before placing the two pieces of the aramid paper, which are cut to the same size
as the crystal, on the two sides of KRS-5 crystal between the sample holder shown in Plate 6.1, a background reading of the infrared is taken first. The KRS-5 crystal is separated from the stainless steel plates with a gap of about 2 mm. Spectra were obtained with and without the sample.

6.5.2 Results and Discussion

Figure 6.12 shows the chemical structure of the aramid paper which basically consists of two aromatic benzene rings and the amide group. The chemical name for this polymer is Poly-m- Phenylendiamineisophthalamide, which is formed from the combination of meta-Phenylendiamine and Isophthalic acid. This material is evolved from Nylon 66.

The infrared spectrum shown in Figure 6.13 demonstrates a large number of peaks, in the as received aramid paper; however, most of these peaks do not exhibit sharp bands and their intensities are low, as in most of the polyamides [63]. Knowing the chemical structure of aramid film, the absorption frequencies responsible for the molecular reactions, and the shape of these peaks, the determination of the molecules responsible for these peaks becomes easier.

Before discussing different aspects of the infrared spectra, it is interesting to identify the peaks in as received aramid paper first; and then consider the effect of both corona charging voltages and different annealing temperatures on the infrared spectra.

Referring to Fig. 6.13 the observed peaks at 3500 - 2852 cm\(^{-1}\) band region are identified to be due to NH band bending frequency [63], since they disappear when the
Plate 6.1  Set up of the sample holder and the arrangement of the instrument used in Infrared spectroscopy.

(1) Sample  
(2) KRS-5 Crystal  
(3) Sample holder  
(4) Reflecting mirrors.
Figure 6.12 Chemical structure of (a) Nylon 66 [2] from which the aromatic polyamide paper (Nomex 410) is evolved, (b) Nomex 410 [97].
amino hydrogen is removed, and they are typical of polyamides [63,64]. Tobin et al. [63] pointed out that the region of 3500 - 2800 cm$^{-1}$ is responsible for NH frequency. However, the frequency covered by Tobin et al. [63] in terms of NH band is discussed only in the band range of 3420 - 3077 cm$^{-1}$. Other sources [62] identified the band region of 3000 - 2800 cm$^{-1}$ due to Aliphatic CH stretching; where the band at 2930 cm$^{-1}$ is considered to be due to CH$_2$ asymmetric stretching while 2852 cm$^{-1}$ due to CH$_2$ symmetric stretching. The bands ranging from 3000 - 2800 cm$^{-1}$ are also observed in Polyalkylene Oxides [65], Polythene and Vinyl Polymer [67], and they are all assigned to CH$_2$ stretching.

The bands in the region of 4000 - 3600 cm$^{-1}$ have not been identified since there are no data on the molecular vibration frequencies in this region and the peak broadness is considered to be probably due to the background noise frequencies.

The broad band at 2600 - 2300 cm$^{-1}$ has not appeared in any of the linear polyamides discussed in the literature [62]; however, this band could be due to NH$_2$ stretching. Ambrose et al. [67] have given spectra of Nylon 66 under high resolution in the 3600 - 2800 cm$^{-1}$ region where they confirm that the NH stretching vibration is operative. The band at 1743 cm$^{-1}$ is due to C = O stretching, the Carboxylic salt C = O also absorbs near 1600 cm$^{-1}$ band. Tobin et al. [63] pointed out that the perpendicular band at 1650 cm$^{-1}$ and parallel band at 1550 cm$^{-1}$ in both Nylon 6 and 11 are due to NH frequency and they indicated that when the Hydrogen bonding is relaxed, the NH and CO stretching frequencies go to shorter wavelengths, whereas in the bending case the frequency goes to longer wavelengths. Accordingly, the band at 1645 cm$^{-1}$ is assigned to
Figure 6.13 Infrared spectrum of as received sample of aromatic polyamides (Nomex 410). Sample thickness = 127 μm.
both C = O and NH$_2$ stretching; while, the band at 1600 - 1519 cm$^{-1}$ is considered to be due to HNC stretching were N and H atoms move in the same direction relative to the Carbon. Tobin et al. [63] assigned the perpendicular bands at 1480 - 1420 cm$^{-1}$ to CH$_2$ bending and the parallel bands at 1370 - 1200 cm$^{-1}$ to CH$_2$ twisting and wagging in Nylon 6 and 11. Kawasaki et al. [65] also assigned the band at 1481 cm$^{-1}$ to CH$_2$ bending mode in Polypropylene Oxide. The absorption bands at 1102 - 911 cm$^{-1}$ are probably due to C - C motions. Tobin et al. [63] reported this finding for Nylon 6 and 11 for the absorption bands at 1100 - 800 cm$^{-1}$. The absorption at 853 - 500 cm$^{-1}$ bands are assigned to the out-of-plane NH deformation frequency (i.e. NH perpendicular bending). The NH wagging are also present in this band’s region. Moreover, the NH perpendicular bending and CH$_2$ rocking were not ruled out and both might be present in Nylon 6 and 11 [63] at 800 - 650 cm$^{-1}$ band regions.

(a) Infra-Red Spectra of Corona Charged Samples

The effects of various corona charging voltages in aramid paper, having a thickness of 127 µm are presented in Figure 6.14.

Plot A in Fig. 6.14 represents the spectrum of as received paper; while plot B and C show the infrared spectrum for samples exposed to corona charging voltages of 16.83 and 33 kV, for a poling time of 10 minutes respectively.

The intensities of the absorption bands at 2925 and 2852 cm$^{-1}$, owing to the NH stretching vibration, decrease as the corona charging voltage increases and finally disappear when the voltage is increased to 33 kV as shown in plot C Fig. 6.14. This
behaviour is attributed to the NH bond bending by the hydrogen bonding forces, since the NH bond lies in a plane perpendicular to the chain, absorption is stronger. The disappearance of this band, in samples exposed to higher corona voltage, is shown [63] to be due to the removal of the amino hydrogen from aromatic polyamides. Ambrose et al. [67] demonstrated this behaviour and compared it with the position when one is looking along the chains, where the absorption is stronger with the electric vector parallel to the sheet. This gives change in the dipole moment as the NH deformation frequencies take place in the direction parallel to the chain. This is also the cause of the C = O vibration, which occurs at the 1743 cm$^{-1}$ absorption band and disappears completely in the parallel position. This also confirms the earlier finding that the C = O bond bending, which is the cause for the large dipole moment, found using equations (5.9) and (5.10).

The absorption at 1645 cm$^{-1}$ and the shoulder at 1655 cm$^{-1}$ were observed to increase in intensities as the poling voltage increases and they shift to lower wave numbers of 1638 cm$^{-1}$ and 1645 cm$^{-1}$ respectively. The rest of the infrared spectra did not show any major changes except the intensities of these absorption bands become sharper.

(b) Influence of Various Annealing Temperatures

The infrared spectra of aramid paper of a thickness of 127 \( \mu \)m at various annealing temperatures are shown in Figure 6.15. The samples were annealed for 5 hours. Plot A in Fig. 6.15 represents the spectrum of as received film while plots B and C show the spectra exposed to annealing temperatures of 260 and 300 °C respectively.

Comparing plots A and B in Figure 6.15, the absorption bands at 2925 - 2850 cm$^{-1}$
Figure 6.14 Effect of different poling corona voltage on infrared spectra in aromatic polyamide sample with a thickness of 127 μm. A; as received paper, B; sample exposed to 16.83 kV, C; sample exposed to 33 kV.
which are responsible for the NH frequency band are observed to decrease in intensity as the annealing temperature increases to 260 °C. However, when the temperature increased to 300 °C the intensity increased, as shown in plot C. This could be due to the effect of bending and twisting of the NH bond. The broad absorption band at 2600 - 2300 cm⁻¹ shows steadily an increase in its intensities as the annealing temperatures increased up to 300 °C. Furthermore, the absorption band at 1743 cm⁻¹, which is assigned to C = O stretching, also shows an increase in intensities as the annealing temperature increases and the peak observed to become sharper at an annealing temperature of 300 °C (plot C).

The decrease of the intensity in the band at 1230 cm⁻¹, in the exposed to higher annealing temperature, is attributed to the CH₂ twisting and wagging frequency. As mentioned earlier, Tobin et al. [63] assigned this band to CH₂ twisting and wagging in Nylon 6 and 11. The band originated at 1080 - 1023 cm⁻¹ shows a steadily an increase in its intensity, with samples exposed to higher annealing temperature, this band is assigned to CH₂ rocking frequency. However, Tobin et al. [63] suggested the band could be due to C-C motions in Nylon 6 and 11.

In aramid paper the infrared studies show an increase in the absorption band intensities at 1743 cm⁻¹ as the annealing temperature increased to 300 °C. This behaviour could be due to the improvement in the sample crystallinity where the C = O bond bending stretches in the direction of the plane perpendicular to the chain where the absorption is stronger.
Figure 6.15 Effect of different poling temperatures on infrared spectra in aromatic polyamide sample with a thickness of 127 µm.
Chapter 7

CHARGING AND DISCHARGING CURRENTS IN
COMPOSITE POLYAMIDES

7.1 INTRODUCTION

The electrical and mechanical properties of aramid paper can be improved by using other materials in conjunction. Such materials are termed composite polyamides in this dissertation. For example Nomex-Polyester-Nomex (N-P-N), consists of three layers of equal thicknesses of 50.8 μm each. N-P-N is suitable as an electrical insulating material for electrical equipment which operate at temperatures up to 200 °C. This limitation of temperature range is due to the presence of polyester, between the two layers of Nomex, which has a glass transition temperature of 69 °C and a melting point of 250° to 265 °C [1]. Polyester increases the mechanical strength of Nomex paper which is a distinct advantage in practical applications.

In this chapter the results of studies on charging and discharging currents, the dielectric loss factor at very low frequencies ( <0.1 Hz ), and conduction currents are presented for the first time in N-P-N.

Upon removal of the step voltage and short circuiting the two electrodes, a discharging current flows in the external circuit which decays with time according to a
power law \([1,2,73]\). However, in the case of application of a step voltage, the charging current in general consists of two components \([1,2,16,21]\), especially in the polar polymers. The first component is due to polarization current which usually decays with time according to \(I=I_0 t^{-n}\). The second component is the transport current which is due to the motion of charge carriers in the bulk of the material \([1,2,32,78]\). The polarization current is usually the dominant component of the charging current for short times and low temperatures \((<100 \, ^\circ \text{C})\), while the transport current, which has the tendency to increase with temperature, becomes dominant for longer times \((>10^3 \, \text{s})\) and higher temperatures \((>100 \, ^\circ \text{C})\) \([16]\).

The charging and discharging currents in composite polyamide dielectrics were evaluated over a wide range of temperatures ranging from 70 to 200 \(^\circ\)C in steps of 10 \(^\circ\)C at a constant electric field strength of 6.56 MVm\(^{-1}\), and at a limited number of constant temperatures of 70\(^\circ\), 100\(^\circ\), 140\(^\circ\), and 200 \(^\circ\)C at various electric fields in the range of 0.23 to 9.84 MVm\(^{-1}\).

Several mechanisms \([6,23,25,29,32]\) were examined, with only one thickness of 152.4 \(\mu\)m, and different electrode materials in order to identify the mechanisms responsible for the discharging currents from the following possibilities: (i) dipolar orientation, (ii) electrode polarization, (iii) space charge effects, (iv) tunnelling of charge carriers from the electrodes, and (v) hopping of charge carriers through localized states.

The low frequency dielectric loss factors are obtained from the discharging current data at various temperatures using the Hamon approximation \([75]\). Comparing these results with the previously obtained results in chapter 5 in aramid paper, the effect of the
presence of polyester between the two layers of aramid paper on the increasing interfacial polarization phenomena is presented.

Finally, the results of conduction current in composite polyamide are also presented in this chapter with one thickness of 152.4 μm. The influence of the electrode materials on the conduction current, are also investigated at two limited temperatures of 140° and 200 °C.

7.2 EXPERIMENTAL PROCEDURE

Studies of charging and discharging currents were conducted on samples heat treated for a period of 12 hours at a temperature of 200 °C to remove moisture from the material and to improve the reproducibility of the results. Two types of measuring electrodes were used, one aluminum and the other silver with a thickness of 50 nm, vacuum deposited on either side at a pressure of 10⁻⁶ torr. The experimental procedures and arrangement are described in chapters 3 and 5.
7.3 RESULTS AND DISCUSSION

7.3.1 Charging and Discharging Currents

(a) Time Dependence of Isothermal Currents

The time dependence of charging and discharging currents in N-P-N with aluminum electrodes is shown in Figures 7.1 and 7.2 at a constant applied step field of 6.56 MVm\(^{-1}\), and a wide range of poling temperatures ranging from 70° to 200 °C for time periods up to 5 hours.

The charging currents shown in Fig. 7.1 are observed to decay faster, at lower poling temperatures than higher temperatures, according to the power law equation. The value of the exponent \( n \) is observed to be in the range of 0.48 to 0.08 in the temperature range of 70 to 200 °C.

A comparison of Figs. 7.1 and 7.2 shows that the charging and discharging currents were dissimilar and these dissimilarities increase with increasing temperatures. A similar behaviour was observed by Das Gupta and Brockley [72] in low-density polyethylene, where charging and discharging currents were a mirror image of each other at low temperatures, and then departed from being mirror images at higher temperatures. They attributed this behaviour to the onset of a steady-state current in polymers at higher temperatures.

Figure 7.2 shows that the rate of decay depends both on time duration and temperature. Two slopes are observed one being at time \( t < 10^{-3} \) s and the other at \( t > 10^{3} \) s. The mechanisms at \( T < 130 \) °C appear different from that at higher temperatures where the change has been identified by Jonscher [73] as discussed in chapter 5.
Figure 7.1 Time dependence of the charging currents at an electric field of 6.56 MVm\(^{-1}\); 152.4 \(\mu\)m sample with aluminum electrodes.
Figure 7.2  Time dependence of discharging currents for temperatures ranging from 70°-200 °C. The pre-applied field is 6.56 MVm⁻¹; 152.4 μm sample with aluminum electrodes.
At \( t < 10^3 \text{s} \) the value of \( n \) decreases with increasing temperature where \( n \) is in the range of 0.7-0.4. At \( t > 10^3 \text{s} \) and \( T \leq 130 \text{ °C} \) \( n \) is in the range of 1.0-0.97 and for longer times and temperature higher than 130 °C the value of \( n \) is smaller in the range of 0.5-0.2. A discussion of change of slope of discharging currents has already been presented in chapter 5. The behaviour shown in Fig. 7.2 confirms Jonscher's [73] interpretation in which, at longer periods of time, the change from dipolar to interfacial mechanisms occurs at a temperature of 140 °C.

In aramid paper (Nomex 410) by itself, the onset temperature for interfacial polarization has been found at a temperature of 200 °C, as discussed in chapter 5, and the observed lower value of 140 °C in composite polyamide dielectric must be attributed to the presence of polyester material between two layers of aramid papers. Although the glass-transition temperature \( T_g \) of polyester is at 69 °C, it is likely to be higher in N-P-N since it is sandwiched between the two layers of aramid papers.

(b) Temperature Dependence of Isochronal Currents

Figure 7.3 shows typical results of discharging currents at prescribed times (i.e. isochronal) over a temperature range of 70° to 200 °C at pre-applied field of 6.56 MVm⁻¹. The isochronal currents are obtained from the measured values of discharge currents shown in Fig. 7.2 at constant times of 10, 600, 1200, and 10200 s, with a peak observed in the range of 80 to 100 °C. The position of this peak tends to shift to a higher temperature with decreasing times, thus suggesting the presence of thermal activation processes [31].
Figure 7.3  Temperature dependence of the isochronal discharge current at prescribed times. The field is 6.56 MVm\(^{-1}\); 152.4 \(\mu\)m sample with aluminum electrodes.
The observed peaks at these low temperature regions could be attributed to a dipolar polarization that might be caused by the glass-transition temperature of the polyester (i.e. $T_g = 69$ °C) which is embedded between the two layers of aramid papers, causing $T_g$ to be higher. For a temperature higher than 130 °C the isochronal discharge currents are observed to increase at longer times almost linearly which suggests that the conduction currents are due to interfacial polarization.

The influence of the presence of polyester can be demonstrated by comparing Fig. 7.3 with Fig. 5.9 the latter being isochronal currents in aramid paper.

(c) Field Dependence

The influence of electric field on both charging and discharging currents was investigated in N-P-N at limited temperatures of 70°, 100°, 140°, and 200 °C at electric fields ranging from 0.13 to 9.84 MVm$^{-1}$. Typical results of charging and discharging currents with aluminum electrodes are shown in Figs. 7.4 and 7.5 at 140 °C. The charging and discharging currents are observed to be dissimilar at all temperatures and electric fields measured. The charging currents at temperatures lower than 140 °C were decaying at a much faster rate than the charging currents at much higher temperatures over the range of electrical field. The charging currents at 70 °C were observed to decay with $n$ in the range of $0.65 \pm 0.1$ for $t \leq 320$ s. For longer times $n$ varied from 0.5 to 0.3. However, these currents for $T > 100$ °C and in the range of fields measured, were decaying at a much slower rate with $n$ in the range of 0.03 and 0.01 at $140 \leq T \leq 200$ °C respectively. This possibly suggests that the fast decrease in the charging currents at $T < 100$ °C could
Figure 7.4  Time dependence of charging currents at a constant temperature of 140 °C and various electric fields. Sample thickness=152.4 μm; electrode material-Al.
Figure 7.5  Time dependence of discharging currents at a constant temperature of 140 °C and various pre-applied fields. Sample thickness=152.4 μm; electrode material-Al.
be attributed to the dipolar polarization since the relaxation time of the dipolar polarization is usually independent of the electric fields [72]. This is more evident as shown in Fig. 7.4 where the shape of Log I vs. Log t curve were independent of electric fields.

Figure 7.5 shows the discharging currents at constant temperatures of 140 °C and various pre-applied electric fields ranging from 0.13 to 9.84 MVm⁻¹ in a sample with aluminum electrodes. The discharging currents obtained in N-P-N were observed to be dissimilar to corresponding charging currents at all electric fields. Such dissimilarities were observed previously in other polymers [23,27,70] and there is no complete agreements on the processes responsible for it. The decay constant n is in the range of 0.3 to 0.8 up to a time of $10^3$ s at longer times it is in the range of 0.12 - 0.17 at pre-applied electric fields of 0.13 to 9.84 MVm⁻¹.
(d) Effect of Electrode Materials

The influence of electrode materials is investigated using aluminum and silver at a temperature of 140 °C, and various applied electric fields of 0.13 to 9.84 MV m\(^{-1}\).

The charging currents for both electrode materials show no significant dependency. Comparing the discharging currents obtained in a sample with aluminum electrodes shown in Fig. 7.5 with that obtained with silver electrodes (Fig. 7.6) some dependency on the electrode materials were observed at times longer than 10\(^3\) s. The discharging currents were decaying at a much faster rate, for the same pre-applied electric fields, with silver electrodes than aluminum electrodes. This phenomenon could be due to electrode polarization that might be caused by surface oxidation, of the silver electrodes, creating dipolar molecules [2,48]. The discharging currents for this phenomenon to be operative decrease inversely with thickness and increase linearly with electric fields. Since only one thickness of the N-P-N was investigated the inverse dependency could not be verified. But a dependency on the electric field is clearly seen in Fig. 7.6.
Figure 7.6  The discharging currents with silver electrodes at a constant temperature of 140 °C and various pre-applied fields. Sample thickness=152.4 μm.
(e) Effect of Electric Field Polarities

The influence of the polarity of the applied electric field on the charging and discharging currents in a sample with aluminum electrodes is shown in Figs. 7.7 and 7.8 respectively.

The charging currents shown in Fig. 7.7 with positive polarities at applied electric fields of 2.63 and 6.56 MVm\(^{-1}\) are observed to be much higher in magnitude than with negative polarities under the same fields. Similar results were observed during discharging under the same pre-applied field. The results for discharging currents are shown in Fig. 7.8. The behaviour of the discharging currents were similar for both polarities up to a time of \(10^3\) s. For greater times the discharging currents with positive polarity tends to flatten out with much smaller slope than the negative polarity. This is possibly due to the large release of charges under the positive polarity, whereas during the negative polarity the charges seem to re-trap in the trapping sites.
Figure 7.7  Effect of the polarity of the applied electric field on the charging currents in N-P-N sample with a thickness of 152.4 µm; electrode material-Al.
Figure 7.8  Effect of the polarity of the applied electric field on the discharging currents in N-P-N sample with a thickness of 152.4 μm; electrode material-Al.
7.3.2 *Low Frequency Dielectric Loss Factor* (*ε''*)

The low frequency dielectric loss factor in N-P-N is obtained from the results of the discharging currents discussed in section 7.3.1.

The time dependence of the discharging currents, following the removal of the step applied field, and short circuiting the two electrodes, can be used to calculate the low frequency dielectric loss factor using Hamon’s approximate equation [75] provided there is a broad distribution of relaxation times [31,34]. Equation (5.3) represents the dielectric loss factor *ε''* at very low frequencies (f < 0.1 Hz).

Figures 7.9 and 7.10 show the results of the calculated values of loss factor *ε''* at low frequencies for 70° ≤ T ≤ 130 °C and 180° ≤ T ≤ 140 °C respectively.

Figure 7.9 shows one broad peak at each temperature up to 130 °C, while in aramid paper (Nomex 410) by itself there were two peaks up to a temperature of 190 °C. This is more evidence that in N-P-N a change of mechanism occurs at temperature greater than 130 °C. It is observed that the maximum frequencies, *f_m*, shift to higher values (i.e. shorter time) as the temperature increases, possibly due to dipolar polarization. Figure 7.10 shows that the magnitude of loss factor *ε''* is higher by at least an order of magnitude when compared with Fig. 7.9. Moreover, the values of loss factor *ε''* increase with increasing frequency, suggesting that a peak, if it exists at all, possibly occurs at very low frequencies. This is considered to be a further evidence for interfacial polarization within the N-P-N at temperatures greater than 140 °C.
Figure 7.9 Frequency dependence of dielectric loss $\varepsilon''$ in N-P-N sample with silver electrodes at various temperatures ranging from 70°-130 °C. Pre-applied field = 6.56 $\text{MVm}^{-1}$; charging time = 5 h.; sample thickness = 152.4 $\mu\text{m}$.
Figure 7.10 Frequency dependence of dielectric loss $e''$ in N-P-N sample with silver electrodes at various temperatures ranging from 140°-180 °C. Pre-applied field=6.56 MVm$^{-1}$; charging time=5 h.; sample thickness=152.4 μm.
The loss peak in dipolar polarization according to the Debye equation [2] occurs at

$$\omega \tau = 1$$  \hspace{1cm} (7.1)

where $\omega$ is the angular frequency and $\tau$ is the relaxation time. Knowing the peaks at which the maximum frequency $f_m$ occurs, from the plots of $\varepsilon''$ vs. log $f$ at each temperature, the relaxation time can be calculated using

$$\tau = \frac{1}{2\pi f}$$  \hspace{1cm} (7.2)

Table 7.1 shows the values of the calculated relaxation time at each temperature in the range of 70 to 130 °C. From the plot of $\ln \tau$ vs. $1/T$, as shown in Fig. 7.11, using eqn. (5.11). The slope obtained from the plot shows an activation energy of 0.38 eV. Das Gupta [31] obtained a value of 0.65 ± 0.15 eV from the plot of $\ln f_m$ vs. $1/T$ in Polyethylene terephthalate (PET), which is in agreement with our results in N-P-N Material. No data are available in this material for comparison.

Lilly et al. [53] also investigated the thermally stimulated currents in Mylar at various fields ranging from 8 to 236 kV/cm, and at temperatures of 27° and 142 °C. Their results obtained from the initial rise method at temperature of 27 °C indicated that as the forming voltage increases the relaxation time increases from $4.64 \times 10^3$ to $1.30 \times 10^9$ s. At a higher temperature of 142 °C the relaxation time, however, was observed to decrease from 701 to 131 s, while the activation energy increased from 0.22 to 1.42 eV as the forming voltage increased from 8 to 236 kV/cm.
Table 7.1  Summary of the loss factor and relaxation times in N-P-N.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\varepsilon''(\text{max.})$</th>
<th>$f_m$ (Hz)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.397</td>
<td>$9.52 \times 10^6$</td>
<td>16711.3</td>
</tr>
<tr>
<td>80</td>
<td>0.518</td>
<td>$1.075 \times 10^5$</td>
<td>14801.4</td>
</tr>
<tr>
<td>90</td>
<td>1.028</td>
<td>$1.282 \times 10^5$</td>
<td>12414.1</td>
</tr>
<tr>
<td>100</td>
<td>1.268</td>
<td>$1.961 \times 10^5$</td>
<td>8116.9</td>
</tr>
<tr>
<td>120</td>
<td>1.365</td>
<td>$3.333 \times 10^5$</td>
<td>4774.7</td>
</tr>
<tr>
<td>130</td>
<td>1.537</td>
<td>$6.667 \times 10^5$</td>
<td>2387.3</td>
</tr>
</tbody>
</table>
Figure 7.11 Relaxation time as a function of $1000/T$ in 152.4 $\mu$m thick paper of N-P-N sample; electrode material-Ag.
7.3.3 Conduction Current in Composite Polyamide

The conduction currents in composite polyamide are investigated using the results obtained from the charging and discharging currents at limited constant temperatures of 70°, 100°, 140°, and 200 °C.

The difference between charging and discharging currents is defined as transport or conduction currents [32]. Figure 7.12 shows typical conduction currents in N-P-N dielectric at a temperature of 200 °C and electric fields in the range of 6.56 to 9.84 MVm⁻¹ deposited with aluminum electrodes. The conduction current is observed to decay with time, and does not reach steady state even after 5 hours. As the discharging current decreases faster with time, and the difference between the charging and discharging currents becomes smaller, the conduction currents are observed to be almost equal to the charging currents at longer times. Similar findings are observed in polyimide (PMDA-ODA) film [32] and in a polyethylene (PE) [29]. Hence, taking the isochronal currents at longer times of 5 x 10³ s with different temperatures of 70°, 100°, 140°, and 200 °C the conduction current as a function of the applied electric fields can be obtained.

Figure 7.13 shows the isochronal conduction currents at 5 x 10³ s with aluminum electrodes as a function of various poling electric fields and temperatures. Two distinct regions were observed, one at electric fields below 4 kVcm⁻¹ where the conduction current is ohmic. The other at electric fields greater than 4 kVcm⁻¹, where the conduction currents deviate from ohmic behaviour, and the plots of Log I vs. E could be fitted to a straight line with reasonable justification. Sawa et al. [21], and Govinda Raju [16] provided
Figure 7.12 Typical conduction currents in N-P-N sample at a constant poling temperature of 200 °C and various poling fields ranging from 1.31-9.84 MVm⁻¹; sample thickness = 152.4 μm; electrode material-Al.
Figure 7.13 Isochronal currents as a function of applied electric field at various constant temperature for 152.4 µm thick paper of N-P-N; electrode material-Al.
evidence that the electrical conduction in polyimide and aramid paper dielectric respectively is due to ionic hopping. Since the ionic conduction holds good at lower electric field strengths it is not likely to be dismissed in composite polyamide dielectrics. For ionic hopping the current density is given by Wintle [2] as shown by equations (4.1) to (4.3) in chapter 4.

From eqn. (4.2) a plot of ln I vs. E yields a straight line having a slope $\frac{e\delta}{2kT}$, from which the separation distance $s$ between traps can be obtained. The separation distance between traps appears to increase with increasing temperatures above 100 °C. At around the glass-transition temperature of polyester the conduction current shows a high value of the separation distance $s$. Table 7.2 shows the values of the separation distance calculated at various poling temperatures of 70°, 100°, 140°, and 200 °C with aluminum electrodes and for limited temperatures of 140° and 200 °C with silver electrodes. Similar results were reported by Govinda Raju [16] in aramid paper (Nomex 410) where the separation distance between traps is in the range of 4.4 to 10 nm depending on the temperatures, higher temperatures yielding higher values for both thicknesses of 76 and 127 μm. The large separation distance between traps obtained in N-P-N dielectric is possibly due to the presence of different layers and they are about 4 times higher than the values obtained in aramid paper (Nomex 410) by itself [16].

Thermally assisted tunnelling corresponds to thermal activation of electrons over the metal-dielectric interface barrier with the presence of the applied field to reduce the barrier height. Hanscomb and Calderwood [6] suggested that the thermally assisted tunnelling is the preferred mechanism of conduction in polyimides. In the case of field
assisted thermionic emission from the cathode to dielectric, the current density $J_t$ may be expressed by Schottky equations (4.4) and (4.5). The zero electric field emission current density according to eqn. (4.4) is given by eqn. (4.6), and is obtained by extrapolating the straight line joining the current data points to $Y$-axis as shown in Fig. 7.14. This yields the emission constant $A$, which is observed to be temperature dependent. The obtained values of the emission constant $A$ are in the range of $(220 - 870) \times 10^{-7} \text{Acm}^{-2}\text{K}^{-2}$ at temperatures ranging between $70^\circ$ to $140^\circ$C, which is much lower than the expected value of $120 \text{Acm}^{-2}\text{K}^{-2}$ for Schottky emission [6]. Hence, Schottky emission can be ruled out as one of the mechanisms responsible for the conduction current in composite polyamide dielectrics.

A plot of $\ln I_o$ vs. $1/T$ according to eqn. (4.6) also yields a reasonably straight line as shown in Fig. 7.15. From the slope the effective work function between the Fermi level of the metal cathode and the conduction band insulator can easily be calculated and is found to be $1.1 \text{eV}$, which is in a good agreement with Baker and Yager [17] who concluded that the conduction mechanism in linear polyamides is due to protons with an activation energy of $1.29 \text{eV}$.

The Poole-Frenkel effect is a bulk effect and it is based on the field lowering of the barrier surrounding the charge carriers. However, the barrier in this case is that for thermal excitation of trapped electrons into the conduction band of the insulator. The current density in this case is expressed by the Poole-Frenkel effect [68] as given by eqn. (4.7).
Figure 7.14 Isochronal currents as a function of $E^{1/2}$ at various constant temperature for 152.4 μm thick paper of N-P-N; electrode material-Al.
Figure 7.15 Plot of \( \ln I \) as a function of \( 1000/T \) in N-P-N sample with Al electrodes; sample thickness=152.4 \( \mu m \).
Both eqns. (4.4) and (4.7) show that a plot of \( \ln I \) vs. \( E^{1/2} \) also yields a reasonably good straight line as shown in Fig. 7.14. For Schottky emission the slope, which is equal to \( \beta_s/kT \). \( \beta_s \) the Schottky coefficient can be calculated and hence the high frequency permittivity \( \varepsilon_{\omega(s)} \) from eqn. (4.5). The calculated dielectric constant at high frequencies \( \varepsilon_{\omega(s)} \) in N-P-N was observed in the range of 0.28 ± 0.1, as shown in Table 7.2, which is obviously wrong. For the Poole-Frenkel effect, however, the dielectric constant at high frequencies \( \varepsilon_{\omega(p)} \) would be four times these values [6], due to the fact that \( \beta_p = 2\beta_s \), which is around 1.2 ± 0.5. This value is low when compared with the static permittivity of 3.4. Hence, while Schottky emission effect mechanisms are ruled out, the Poole-Frenkel effect may be an acceptable process going along with ionic hopping mechanism. This suggests that the conduction process is a bulk effect due to thermal excitation of trapped electrons into the conduction band of the insulator, and the ionic conduction occurs due to the drift of ions under the influence of the applied electric fields.

**Table 7.2 Summary of the conduction current results in N-P-N.**

<table>
<thead>
<tr>
<th>( T (^\circ C) )</th>
<th>( s \ (nm) )</th>
<th>( \varepsilon_{\omega(s)} )</th>
<th>( \varepsilon_{\omega(p)} )</th>
<th>( A \times 10^7 ) ( (\text{Acm}^{-2}\text{K}^{-2}) )</th>
<th>Electrode Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>30.6</td>
<td>0.29</td>
<td>1.16</td>
<td>219.56</td>
<td>Al</td>
</tr>
<tr>
<td>100</td>
<td>18.8</td>
<td>0.39</td>
<td>1.56</td>
<td>382.89</td>
<td>=</td>
</tr>
<tr>
<td>140</td>
<td>23.5</td>
<td>0.38</td>
<td>1.52</td>
<td>869.83</td>
<td>=</td>
</tr>
<tr>
<td>200</td>
<td>37.2</td>
<td>0.17</td>
<td>0.66</td>
<td>195.95</td>
<td>=</td>
</tr>
<tr>
<td>140</td>
<td>22.5</td>
<td>0.47</td>
<td>1.89</td>
<td>-</td>
<td>Ag</td>
</tr>
<tr>
<td>200</td>
<td>25.3</td>
<td>0.41</td>
<td>1.65</td>
<td>-</td>
<td>=</td>
</tr>
</tbody>
</table>
Chapter 8

THERMALLY STIMULATED POLARIZATION (TSP)
AND DEPOLARIZATION (TSD) CURRENTS IN
COMPOSITE POLYAMIDES

8.1 INTRODUCTION

A variation of the technique for the measurement of the charging current isothermally is
to measure the current as a function of temperature of the material which is allowed to
increase linearly while a constant electric field is applied. Measurement of these currents,
also known as thermally stimulated polarization (TSP) currents, has several advantages
[1], one of which is that the measured current reveals how the orientation of the dipoles
is proceeding. A search for an optimum poling temperature is eliminated and over heating
of the specimen is avoided.

The thermally stimulated depolarization (TSD) method has become one of the
most powerful tools for the evaluation of various properties, such as molecular
depolarization [54,92,93] and carrier transport [1,94], in a relatively short time.

Electrical polarization in polar and semi-polar polymers can be due to several
molecular phenomena. One of these is the ability of the molecules to rearrange themselves
in the presence of an applied d.c. field at temperatures high enough where the relaxation
times for such molecular motions are short. The other phenomenon is the electrical
polarization that might arise from the drift of ionic impurities towards electrodes of opposite charge.

Finally, the results of windowing polarization, which is basically a modified technique of the TSD current method, first introduced by Lacabanne and Chatain [96] are also presented.

The results of thermally stimulated polarization (TSP) and Depolarization (TSD) currents with the windowing polarization (TSWP) currents are discussed in this dissertation for the first time with a thickness of 152.4 μm. Electric field strengths ranging from 0.33 to 19.69 MVm⁻¹ with aluminum and silver electrodes, which were vapour deposited with a thickness of 50 nm, are employed.

The influence of poling electrical fields, heating rates, field polarities, and electrode materials on both (TSP) and (TSD) currents were investigated in composite polyamides (N-P-N). The results of the separation of polarization and conduction currents, using (TSP) current techniques with different heating rates, are also described for the first time in this chapter. Results of windowing polarization (TSWP) currents are introduced for N-P-N for the first time with silver electrodes and at a constant polarization field of 19.69 MVm⁻¹ in the polarization temperature ranging from 60 to 140 °C in steps of 10 °C.
8.2 EXPERIMENTAL PROCEDURE

8.2.1 Thermally Stimulated Polarization and Depolarization Currents

The study of TSD currents involve independent control of the poling field and thermal profiles of the specimen under study [1,16].

Measurements of TSD and TSP currents were carried out on composite polyamides having a radius of 44 mm and a thickness of 152.4 μm. Before using the samples they were heat treated for 12 hours at 200 °C to remove any moisture content and to improve reproducibility of results. Two different electrode materials, aluminum and silver of 50 nm thickness were vacuum deposited on the samples at a pressure of 10⁻⁶ torr. The low voltage electrode, which was provided with a guard ring which was also vapour deposited and was employed to reduce effects due to stray fields, was connected to a Keithley 610C electrometer for measuring the current flow.

Figure 3.3, in chapter 3, shows the schematic arrangement of the experimental set up used for TSP and TSD current measurements. The experimental procedures for TSP currents are shown in Fig. 3.4 which consist of raising the temperature linearly at a constant rate while the electric field is applied to the sample. The experimental steps are discussed in chapter 3.

Figure 3.5, in chapter 3, shows the experimental procedures used for TSD current measurements in N-P-N. The sample is placed between the two electrodes and poled at a temperature of 70 °C with an applied electric field $E_p$ for 60 min. then the temperature is reduced to 0 °C while the field is still applied. At the end of this formation period the field is cut-off and the two electrodes were short circuited for 30 min. to allow the
charges to be stored in the trapping sites; this is called the storage or annealing time. The temperature of the sample was then increased at a linear rate of 1 to 2 Kmin⁻¹, and the TSD current was measured using the experimental set up shown in Fig. 3.3.

8.2.2 Windowing Polarization (TSWP)

Figure 3.6, in chapter 3, shows the schematic of the experimental procedure of windowing polarization using TSD current techniques. The sample is polarized first at temperature $T_p$ for a time $t_p$, which is equal 60 min. in these studies, to allow only certain fragments of dipoles to orient. The sample temperature is then reduced to $T_d$, which is 10 °C below the polarization temperature $T_p$, then the polarizing field is cut-off and the temperature is retained constant at $T_d$ for a time period of $t_d = t_p$; this allows depolarization of another fragment of the oriented dipoles. At the end of this time (i.e. $t_d$) the sample temperature is reduced to $T_o \ll T_d$ and then is reheated at a constant linear rate of 2 Kmin⁻¹. TSD currents for windowing polarization are measured using the same equipment and experimental set up used in Figure 3.3 (chapter 3).
8.3 RESULTS AND DISCUSSION

8.3.1 Effect of Electric Fields and Electrode Materials on TSD Spectra

Figure 8.1 shows the influence of various poling applied fields ranging from 0.66 to 13.12 MVm\(^{-1}\) on the TSD currents in N-P-N sample with aluminum electrodes. The samples were poled at a temperature of 70 °C for 60 min. The storage time was 30 min. at 0 °C. TSD currents were obtained with a heating rate of 2 Kmin\(^{-1}\). The TSD current peaks are observed to increase with poling fields up to 9.84 MVm\(^{-1}\) with evidence of an appreciable shift in the peak temperature. The current peaks were in the temperature range of 96 to 110 °C. For higher electric fields of 13.1 MVm\(^{-1}\) the TSD current peak ceased to increase any further. The currents are also observed to rise again at T ≥ 160 °C, strongly suggesting the existence of a second peak at T > 200 °C. The increase of TSD currents at such high temperatures could be another confirmation to the change of mechanisms; from dipolar polarization to the conduction current mechanism, as has been observed earlier in the studies of charging and discharging currents in this material, where the change from a dipolar to interfacial polarization occurs at a temperature of 140 °C.

Figure 8.2 shows the influence of various poling fields on the TSD current spectrum in a sample with silver electrodes. The observed TSD currents with silver electrodes were lower by an order of magnitude than the TSD currents observed with aluminum electrodes at lower fields. The TSD current peaks were at a constant temperature of 114 °C, which is a little higher than the peak temperatures observed with aluminum electrodes at low fields. Furthermore, the second current rise at T > 160 °C is nonexistent with the silver electrodes.
Figure 8.1  TSD currents in N-P-N sample with a thickness of 152.4 μm and β=2 Kmin⁻¹. The poling temperature is 70 °C for 60 min. and the poling field as shown on each curve, in MVm⁻¹. Electrode material-Al.
Figure 8.2  TSD Currents in N-P-N sample with a thickness of 152.4 µm and $\beta = 2 \, \text{Kmin}^{-1}$ poling temperature is 70°C for 60 min. and the poling field as shown on each curve, in MVm$^{-1}$. Electrode material-Ag.
According to eqn. (2.28), a plot of ln I vs. 1000 / T yields a straight line having a slope (ξ / k), from which the activation energy of these current peaks can be evaluated. Figure 8.3 shows these plots for the TSD current spectra shown in Fig. 8.1 with poling fields of 0.66, 6.56, and 13.12 MVm⁻¹. Activation energies of 1.12 ± 0.24 eV are observed with a heating rate of 2 Kmin⁻¹ in N-P-N sample with aluminum electrodes and 0.4 ± 0.08 eV obtained with silver electrodes, for the same range of field applied. Govinda Raju [16] observed an activation energy of 0.6 ± 0.1 eV at a heating rate of 1 Kmin⁻¹ in aramid paper (Nomex 410) with silver electrodes having a thickness of 127 μm. No data are available in N-P-N for comparison.

The TSD current peaks, observed in Fig. 8.4, are expected to be linearly dependent on the poling applied fields in the range of 0.66 to 13.12 MVm⁻¹ and 3.28 to 13.12 MVm⁻¹ for aluminum and silver electrodes respectively if the polarization is due to dipolar orientation and nonlinear for space charge [16,48,52,55] and interfacial polarization. Figure 8.4 shows that the magnitude of the current peaks are in fact linear with poling fields in N-P-N sample with silver electrode materials. Thus, the dipolar mechanism might be operative with silver electrode materials. However, in the case of aluminum electrodes the polarization was uniform up to a field about 6.56 MVm⁻¹ and non-uniform for higher fields, this is clear from Fig. 8.4, and might be due to the formation of space charge [52] or due to the accumulation of charges between the boundaries of crystalline and amorphous regions and/or between the different layers in the sample.

The charge released to the external circuit provides another means of deciphering the mechanism involved. For polarization due to dipoles the total released charge should
Figure 8.3  Arrhenius diagram of TSD current spectra at poling fields of 0.66, 6.56, and 13.12 MVm$^{-1}$ in N-P-N sample with aluminum electrodes.
Figure 8.4  Peak current as a function of poling field in N-P-P sample. Top curve for Al electrodes, bottom curve for Ag electrodes.
increase linearly with applied fields, as shown in Fig. 8.4 with silver electrodes, and nonlinearly for space charge and/or interfacial polarization [16,48] at higher fields where the charge released tends to saturate because of the number of additional charges that is released to the external circuit which does not increase proportionately. Figure 8.5 shows the results of the total charge released to the external circuit as a function of the applied fields in a sample with aluminum and silver electrodes. The total charge released to the external circuit from a sample with silver electrodes shows a linear dependency on the applied fields in the range of 3 to 13 MVm\(^{-1}\) the nonlinearity may occur at higher fields. Whereas for aluminum electrodes the linear dependency ceased at a poling field of 6.56 MVm\(^{-1}\) and for higher poling fields the total charge released tends to saturate.

Figure 8.6 shows the comparison of the TSD current spectra with aluminum and silver electrodes obtained at poling fields of 6.56 and 13.12 MVm\(^{-1}\). The TSD current spectra observed with aluminum electrodes are much higher than those with silver electrodes. This dependency could suggest that there is an electrode polarization or blocking mechanism that might be operative. These mechanisms usually occur in ionic materials, which is the case in Nomex 410 by itself [16], and in N-P-N.

### 8.3.2 Effect of Poling Temperatures on TSD Currents

Figure 8.7 shows the influence of different poling temperatures on the TSD current spectra in N-P-N sample with aluminum electrodes at a constant poling field of 6.56 MVm\(^{-1}\) and a heating rate of 2 Kmin\(^{-1}\). The TSD current peaks, shown in Fig. 8.7, tend to shift to higher temperatures as the poling temperature increases. Perlman [52] who
Figure 8.5 Charge released to the external circuit as a function of poling field strength. 152.4 μm thick paper. Top curve for Al electrodes, Bottom for Ag electrodes.
Figure 8.6 TSD currents in 152.4 μm N-P-N sample with β = 2 Kmin⁻¹. Comparison between Al and Ag electrodes. The poling temperature is 70 °C and poling field as shown on each curve, in MVm⁻¹.
Figure 8.7  Effect of poling temperatures on TSD currents in N-P-N sample charged with a constant field of 6.56 MVm\(^{-1}\). Heating rate (\(\beta\)) = 2 Kmin\(^{-1}\). Sample thickness = 152.4 μm. Electrode material-Al.
investigated the thermal current spectra in Carnauba Wax electrets observed similar results with different poling temperatures. At poling temperatures of 70 and 110 °C the peaks are observed at the same temperatures within ± 5%. It is also noted that at lower poling temperatures a complete dipolar orientation is observed with fast reacted dipoles which could arise from the disorientation of a polar side group. As the poling temperature increases, the peaks due to fast reacted dipoles become less pronounced and they appear as a small shoulder in the TSD current spectra. This could be another proof that the dipolar polarization mechanism is operative at temperatures less than 140 °C.

The TSD current peaks observed at higher poling temperatures of 140 and 160 °C could be attributed to the dipolar polarization of heavier or more rigid dipoles with larger relaxation times. These dipoles disorient only at higher temperatures where the mobility is high.

8.3.3 Effect of Electric Field Polarities on TSD Currents

Figure 8.8 shows the influence of poling field polarities on the TSD current Spectra in a sample with aluminum electrodes at a poling field and temperatures of 0.66 MVm⁻¹ and 70 °C respectively. The lack of dependency on the poling field polarities is very well demonstrated in Fig. 8.8. Hence, the injection of charges from the cathode are eliminated, which confirms the earlier finding from conduction currents in chapter 7, that the Schottky mechanism is not operative in this material. The increase of the TSD currents at T ≥ 170 °C (Fig. 8.8) with a positive field is attributed to the ionic conduction which is enhanced with positive field polarities and decreased in the case of negative field polarities.
Figure 8.8  Effect of applied electric field polarities on the TSD current spectra in N-P-N sample charged at constant field of ± 0.66 MVm⁻¹ at a poling temperature of 70 °C. Heating rate (β) = 2 Kmin⁻¹. Sample thickness = 152.4 μm. Electrode material-Al.
8.3.4 Effect of Rate of Heating (β) on TSD Currents

The influence of rate of heating on the TSD current spectra in a sample with aluminum electrodes at a poling field of 6.56 MVm$^{-1}$ and temperature 70 °C is shown in Fig. 8.9. The rates of heating were 2, 3, and 4 Kmin$^{-1}$. An increase in the rate of heating is observed to shift the peak to higher temperatures with an increase in magnitude of the peak current. The rate of heating β and temperature at which the current peak is observed, $T_m$, are related by [1,16]

$$T_m = \sqrt{\frac{\tau \beta \xi}{k}}$$  \hspace{1cm} (8.1)

in which $\tau$ is the relaxation time at $T_m$ and $\xi$ the activation energy. Equation (8.1) shows that for a Debye Type of relaxation process, the maximum temperature, $T_m$, increases with increasing $\beta$ as observed in Fig. 8.9.

8.3.5 Relaxation Time (τ)

The TSD Current measurements provide a remarkable technique for investigating the relaxation time arising from single and distributed relaxations. The relaxation process having a characteristic time $\tau$ is given by eqn. (8.2)

$$\tau (T) = \frac{-P(T)}{j(T)} = \frac{1}{\beta} \int \frac{j(T')}{T_p} dT'$$  \hspace{1cm} (8.2)
Figure 8.9 Effect of rate of heating on the TSD current spectra in N-P-N sample charged at a poling field of 6.56 MVm\(^{-1}\) at a poling temperature of 70 °C. Sample thickness = 152.4 μm, Electrode material-Al.
which provides a convenient technique for calculating the relaxation times using all the data points in the TSD curve in contrast to eqn. (8.1) which uses only the value of maximum temperature.

The integral of the current density in the numerator of eqn. (8.2) was calculated using the numerical method of the Trapezoid rule. The integral is carried from the initial temperature $T_o$ to the final temperature $T$. The relaxation time is then obtained simply by dividing the total area by the current density at the initial temperature $T_o$.

Figure 8.10 shows the plot of $\ln \tau$ vs. $1000/T$ in N-P-N sample with aluminum and silver electrodes at poling field of 6.56 MVm$^{-1}$ using eqn. (8.3)

$$\ln \tau (T) = \ln \tau_o + \frac{E_a}{kT}$$ (8.3)

The relaxation times were decreasing with increasing temperature as expected with both aluminum and silver electrodes. The activation energy in the sample with aluminum electrodes is 1.34 eV in the temperature range of 30° to 80 °C. For higher temperatures the data for the relaxation times did not fit a straight line and hence the activation energy cannot be determined by using equation (8.3). The relaxation times with silver electrodes show only one slope which decreases linearly with increasing temperatures. This is attributed to the broadness of the TSD current peaks which suggests multiple relaxation processes due to the different reactions of different dipoles. The activation energy obtained with silver electrodes is 0.28 eV which is much lower than that obtained with aluminum electrodes.


**Figure 8.10** Relaxation time as a function of 1000/T in N-P-N sample with 152.4 μm thick paper obtained under constant poling field of 6.56 MVm\(^{-1}\) and a poling temperature of 70 °C at \(\beta = 2 \text{ Kmin}^{-1}\). for both Al and Ag electrode materials.
Typical relaxation times of $16.2 \times 10^5$ and $19.3 \times 10^3$ s. are obtained with aluminum and silver electrodes respectively at a room temperature of 26 °C. Table 8.1 shows some typical values of relaxation times as a function of temperature obtained from TSD current spectra at a poling field of 6.56 MVm$^{-1}$ with aluminum and silver electrodes.

**Table 8.1** Typical relaxation times obtained from TSD current studies with aluminum and silver electrodes.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\tau_{Al}$ ($\times 10^3$ s)</th>
<th>$\tau_{Ag}$ ($\times 10^3$ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>1619.50</td>
<td>19.32</td>
</tr>
<tr>
<td>50</td>
<td>47.27</td>
<td>12.78</td>
</tr>
<tr>
<td>70</td>
<td>2.16</td>
<td>5.60</td>
</tr>
<tr>
<td>130</td>
<td>0.63</td>
<td>0.55</td>
</tr>
<tr>
<td>190</td>
<td>0.28</td>
<td>0.21</td>
</tr>
</tbody>
</table>
8.4 THERMALLY STIMULATED POLARIZATION (TSP) CURRENTS

In contrast to charging and discharging currents, which were measured to observe the time-dependent polarization effect [26], thermally stimulated polarization (TSP) currents are measured with the temperature of the sample being increased at a linear rate in the presence of the applied electric field. Therefore, in addition to the current peaks due to dipolar disorientation or filling of traps, the conduction current now can be observed to increase steadily at high temperatures [20]. This technique provides valuable information about the relative importance of the conduction current in the dielectric. Hence, the fast neutralization of stored charges can be avoided [1]. The various influences of poling electric fields, heating rates, field polarities, and electrode materials on the TSP currents are studied for the first time.

8.4.1 Effect of Poling Electric Fields on TSP Currents

Figure 8.11 shows typical TSP currents in a sample with aluminum electrodes at poling fields $0.33 \leq E \leq 6.56 \text{ MVm}^{-1}$ at a heating rate of $2 \text{ Kmin}^{-1}$. The currents increase with temperature, for all electric fields studies. At $200 \text{ °C}$ the environmental chamber is switched to an isothermal mode and the current is observed to increase with time for a periods as large as 50 minutes. The upper curves of Fig. 8.11 show these isothermal measurements. Typically at an electric field of $6.56 \text{ MVm}^{-1}$ the current at $130 \text{ °C}$ is $172.9 \times 10^{10} \text{ A}$ increasing to $150.6 \times 10^{8} \text{ A}$ at $200 \text{ °C}$. The current measurements are continued in the isothermal mode for a period of 60 minutes during which time the current increased from $150.6 \times 10^{8} \text{ A}$ to $365.1 \times 10^{8} \text{ A}$, a factor of 2.4 higher.
Figure 8.11 Typical TSP current spectra in N-P-N sample charged at poling fields in the range of $0.33 \leq E \leq 6.56 \text{ MVm}^{-1}$. at $\beta = 2 \text{ Kmin}^{-1}$. Electrode material-Al.
The same qualitative behaviour is observed at other electric fields.

8.4.2 Effect of Electrode Materials on TSP Currents

Figure 8.12 shows the TSP currents obtained at various poling fields of 13.1, 16.4, and 19.7 MVm$^{-1}$ in N-P-N sample with silver electrodes at a heating rate of 2 Kmin$^{-1}$. Comparing the characteristics of these curves with those obtained with aluminum electrodes Fig. 8.11, the influence of the electrode materials can be observed. The rate of increase of the TSP currents, shown in Fig. 8.12, was smaller than that with aluminum electrodes. This supports the results obtained from TSD current measurements where the spectra with aluminum electrodes were observed to increase faster leading to narrower peaks with higher activation energy. The TSD currents obtained with silver electrodes on the other hand were observed to increase at a much slower rate leading to broader peaks and hence lower activation energy. Figure 8.12 also shows clearly the dividing temperature between the dipolar polarization and the conduction current mechanism which becomes the dominant at $T > 130$ °C.
Figure 8.12 TSP current spectra in N-P-N sample with poling fields of 13.1, 16.4, and 19.7 MVm$^{-1}$ at $\beta = 2$ Kmin$^{-1}$. Sample thickness = 152.4 $\mu$m. Electrode material-Ag.
8.4.3 Effect of Electric Field Polarities on TSP Currents

The influence of polarities on the TSP current in N-P-N sample with aluminum electrode at an electric field of ± 2.63 MVm⁻¹ and a rate of heating of 2 Kmin⁻¹ is shown in Fig. 8.13. No appreciable dependency on the field polarities are observed in N-P-N polymer.

8.4.4 Effect of Rate of Heating (β) on TSP Currents

Figure 8.14 shows the TSP currents in a sample with aluminum electrodes at poling fields of 2.63 and 6.56 MVm⁻¹ and a heating rate of β = 1 and 2 Kmin⁻¹. The TSP currents with a higher heating rate shows higher current magnitudes which is in agreement with the theory [1].
Figure 8.13 Effect of polarities on the TSP current in N-P-N sample at constant poling field of ±2.63 MVm\(^{-1}\) and \(\beta = 2\) Kmin\(^{-1}\). Sample thickness = 152.4 μm. Electrode material-Al.
Figure 8.14 Effect of heating rate on the TSP current spectra in N-P-N sample charged at a poling field of 2.63 and 6.56 MVm$^{-1}$ at different heating rates of ($\beta$) = 1 and 2 Kmin$^{-1}$. Sample thickness = 152.4 $\mu$m; electrode material-Al.
8.4.5 SEPARATION OF POLARIZATION AND CONDUCTION CURRENT

The experimental technique has been discussed in section 5.5 chapter 5. Figure 8.15 shows the results of separation of polarization and conduction currents in N-P-N sample with silver electrodes and an applied electric field of 13.1 MVm\(^{-1}\). This study is performed with three different heating rates of $\beta = 2$, 3, and 4 Kmin\(^{-1}\).

Figure 8.15 shows that the current during the second cycle at lower temperatures is much smaller than that during the first cycle, the difference between the two currents decreasing as the temperature increases. At 200 °C the two currents become almost equal. Similarly, results were obtained at $\beta = 3$ and 4 Kmin\(^{-1}\). These results clearly demonstrate that at lower temperatures the currents observed during the second cycle is lower because the dipoles are already oriented. The polarization currents which are obtained from subtracting the currents of the second cycle from those of the first cycle are also shown in Fig. 8.15 by the broken curve. These results are in agreement with the earlier results shown in section 8.3.2 where at a poling temperature greater than 140 °C the observed peaks were at 174 °C. For a lower poling temperature of 70 °C only fast dipoles are oriented and the current peaks in the range of 94 to 112 °C with aluminum electrodes and at 114 °C with silver electrodes. The activation energies for the first and second cycle at $T \leq 130$ °C are 0.30 and 0.86 eV respectively whereas for $T \geq 130$ °C the activation energies were 1.50 and 1.53 eV for the first and second cycle respectively.

Figure 8.16 shows the polarization currents obtained with three different heating rates of $\beta = 2$, 3, and 4 Kmin\(^{-1}\). respectively. The calculated activation energies were obtained from the slope of ln I vs. 1000/T using eqn.'(8.3). Figure 8.17 shows the plot
Figure 8.15 Separation of polarization and conduction currents using TSP techniques in N-P-N sample charged at a constant applied field of 13.1 MVm⁻¹ at $\beta = 2$ Kmin⁻¹. Sample thickness = 152.4 μm; electrode material-Ag.
of ln I vs. 1000/T, the calculated activation energies were 1.27, 1.43, and 1.66 eV for 
$\beta = 2, 3, \text{ and } 4 \text{ Kmin}^{-1}$ at $T \geq 130 \text{ °C}$ respectively. The activation energies for $T \leq 130$ 
°C were 0.24, 0.24, and 0.19 eV for $\beta = 2, 3, \text{ and } 4 \text{ Kmin}^{-1}$, respectively.

Application of the theory discussed in chapter 3, section 3.1, yields the quantities 
shown in Table 8.2. For a more accurate analysis it is therefore essential to use all of the 
experimental data in the ln I vs. T curve as shown in Fig. 8.15 and the calculation of the 
relaxation time at each temperature obtained according to eqn. (8.2). The results of these 
calculations are shown in Fig. 8.18.

The activation energies obtained for these relaxation times were $0.23 \pm 0.02$ eV 
for $T \leq 130$ °C and for $T \geq 130$ °C the activation energies were $1.97 \pm 0.18$ eV for $\beta = 
2, 3, \text{ and } 4 \text{ Kmin}^{-1}$. No dependence of the activation energy on $\beta$ was observed in both 
temperature ranges. No data are available for comparison.

### Table 8.2 Summary of relaxation time obtained at different heating rates.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\beta = 2 \text{ Kmin}^{-1}$</th>
<th>$\beta = 3 \text{ Kmin}^{-1}$</th>
<th>$\beta = 4 \text{ Kmin}^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>30</td>
<td>186577.7</td>
<td>123223.0</td>
<td>92098.0</td>
</tr>
<tr>
<td>50</td>
<td>243701.9</td>
<td>154464.4</td>
<td>115289.1</td>
</tr>
<tr>
<td>70</td>
<td>13433.9</td>
<td>82648.3</td>
<td>61573.2</td>
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<tr>
<td>90</td>
<td>80452.4</td>
<td>49159.9</td>
<td>36503.7</td>
</tr>
<tr>
<td>110</td>
<td>55892.2</td>
<td>36630.1</td>
<td>26793.8</td>
</tr>
<tr>
<td>130</td>
<td>47476.3</td>
<td>30029.9</td>
<td>30285.8</td>
</tr>
<tr>
<td>150</td>
<td>16659.2</td>
<td>6754.7</td>
<td>7087.8</td>
</tr>
<tr>
<td>170</td>
<td>1961.4</td>
<td>973.2</td>
<td>437.7</td>
</tr>
<tr>
<td>190</td>
<td>186.3</td>
<td>89.0</td>
<td>121.6</td>
</tr>
</tbody>
</table>
Figure 8.16 Polarization currents in N-P-N sample charged at a constant poling field of 13.1 MVm\(^{-1}\) and \(\beta = 2, 3, \text{ and } 4 \text{ Kmin}^{-1}\). Sample thickness = 152.4 \(\mu\text{m}\); electrode material-Ag.
Figure 8.17 Plots of $\ln I$ as a function of $1000/T$ for the curves shown in Fig. 8.16.
Figure 8.18 Relaxation time obtained from TSP studies as a function of $1000/T$ in N-P-N sample with a thickness of 152.4 $\mu$m charged at a constant poling field of 13.1 MVm$^{-1}$. Electrode material-Ag.
8.5 WINDOWING POLARIZATION (TSWP)

The influence of molecular orientation on the polarization phenomenon in this composite polyamide dielectric was investigated using the new technique proposed by Lacabanne [95,96], which is called windowing polarization. The experimental set up and procedures are discussed in chapter 3.

The use of this technique also eliminates the traditionally tedious peak cleaning technique and partial heating method, which are commonly used to find the multiple hidden overlapped TSD current peaks caused by multiple relaxation frequencies of different masses and shapes of dipoles.

The studies of TSWP were conducted on N-P-N samples coated with silver electrodes and the window temperatures were in the range of 60° to 140 °C and the polarization window was 10 °C. For poling temperatures greater than 140 °C no peaks were observed up to 200 °C. Figure 8.19 shows the peaks of the TSWP current with silver electrodes. The peaks were observed to shift to higher temperatures as the window temperature increases up to 130 °C. This confirms the earlier findings from the studies of charging/discharging currents, low frequency dielectric loss factor, and TSP currents, that the dipolar polarization is the operative mechanism up to T = 130 °C. The solid curve shows that the TSWP current at temperature of 130-140 °C increases up to T=198 °C, with the peak temperature exceeding the highest temperature adopted in this study.

Application of the relaxation time theory discussed in chapter 2, section 2.1, at each polarizing window yields the calculated values shown in Table 8.3. These values for the relaxation times are obtained from the TSWP current data shown in Fig. 8.20 using
Figure 8.19 TSWP current spectra for N-P-N sample charged at 9.84 MVm\(^{-1}\) with different polarizing window temperatures of 10 °C. Sample thickness = 152.4 μm, electrode material-Ag.
Figure 8.20 Relaxation time as a function of 1000/T for the polarizing currents shown in Fig. 8.19 in N-P-N sample with silver electrodes.
The calculated activation energies for each polarizing window are obtained from the relaxation time using eqn. (8.3). Table 8.3 shows the obtained values of the activation energies and they are observed to be in range of 1.01 to 1.55 eV. These values are considered to be due the intramolecular cohesion which are responsible for the primary bonds, and they are usually stronger and much greater than 0.5 eV, due to the sharing or exchanging of valence electrons from the s- or p- orbitals. The intermolecular cohesion is due to secondary bonding which is much weaker and smaller than 0.5 eV [98].

Figure 8.21 shows the plot of the obtained activation energies against polarizing window temperatures. It is clearly demonstrated that the activation energies of the relaxation times are temperature dependent and they are increased with increasing temperatures and thus the dipolar polarization mechanism is thermally activated.

<table>
<thead>
<tr>
<th>Window Polarizing Temperature</th>
<th>Activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (°C)</td>
<td>$\xi$ (eV)</td>
</tr>
<tr>
<td>130-120</td>
<td>1.55</td>
</tr>
<tr>
<td>120-110</td>
<td>1.54</td>
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<tr>
<td>110-100</td>
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<tr>
<td>70-60</td>
<td>1.01</td>
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</table>

Table 8.3 Summary of the calculated activation energies in N-P-N.
Figure 8.21 Activation energies as a function of poling temperatures in N-P-N sample with Ag electrodes. Poling field is 9.84 MVm\(^{-1}\). Sample thickness = 152.4 µm and β = 2 Kmin\(^{-1}\).
Chapter 9

SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

9.1 SUMMARY AND CONCLUSIONS

The concluding remarks of this dissertation are summarized in this chapter along with the suggestions for future research topics in high temperature polymers, which are considered as an extension to the studies conducted in this dissertation.

In chapter 4 the study of the conduction currents in Teflon (PTFE) were investigated over a wide range of electric fields up to 246 kV/cm, and in the temperature range of 40-200 °C, with silver electrodes. The results of this investigation eliminated both Schottky and Poole-Frenkel theories as the explanation for the conduction process in PTFE. However, electronic and ionic space charge were found to be present in PTFE and each dominated at different temperature levels. Ionic space charge dominated at T < 120 °C and electric fields less than 246 kV/cm. At T > 120 °C and electric fields greater than 100 kV/cm electronic space charge was the dominant one. The ionic separation distance between traps was increased with decreasing temperature from 200° - 80 °C. At T < 80 °C the separation distance between traps decreased with decreasing temperature for 50 μm thickness and for 150 μm the transition temperature was 120 °C.

In chapter 5 the investigation of the charging/discharging currents and thermally
stimulated polarization (TSP) currents in aromatic polyamides, known as aramid paper or Nomex 410, were considered with various parameters such as electrode materials, sample thickness, poling electric fields, poling temperatures, etc. The results show that the charging/discharging currents are dissimilar at all electric fields and temperatures measured. The mechanism responsible for charge decay is due to dipolar orientation and ionic hopping at a temperature of 70 °C, and changes to an interfacial polarization at a high temperature of 200 °C. The effects of electrode material and sample thickness were considered, and no appreciable dependency on either were observed. The low frequency dielectric loss factor obtained from the discharging current results show two dipolar relaxation frequencies at $T \leq 190$ °C, and these correspond to relaxation times of $1.6 \times 10^3$ s and $2 \times 10^4$ s. At $T = 200$ °C. The dielectric loss factor increases very rapidly with frequency, which is another manifestation of interfacial polarization.

The TSP current results on aramid paper show that the TSP current increases with increasing temperature slowly up to 100 °C and more rapidly at higher temperatures. The TSP currents also show an increase with time up to 60 min. after the temperature reaches the maximum of 200 °C. This increase is attributed to the interfacial polarization of the material at high temperatures. The separation of the conduction and polarization currents is achieved using several cycles of TSP current techniques. A relaxation time of $6.3 \times 10^4$ s at room temperature and an activation energy of 0.84 eV were obtained. The total polarization obtained at 2 Kmin$^{-1}$ in aramid paper is 1.73 $\mu$Cm$^{-2}$.

In chapter 6 the results of the TSD currents of positively corona charged aramid paper showed that the various peaks are due to different trapping levels. As the poling
time increases, the charges are trapped in deeper traps causing the peaks to shift to higher temperatures during the release of charges. The influence of poling voltage on TSD currents, which is to increase the current with increasing voltage, is attributed to the ionic nature of the aramid paper. No dependency on the sample thickness is observed while some dependency on the electrode materials is observed with silver electrodes showing some kind of, undetermined as yet, blocking process.

The wide angle X-ray diffraction results show mainly four peaks observed in aramid paper with a shift in the same peaks as corona voltage increased. The peak intensities are higher in samples exposed to higher annealing temperature suggesting an improvement in the polymer crystallization. The Infrared spectroscopy analysis results in aramid paper show that the intensities of the absorption band at 2925 and 2852 cm\(^{-1}\), which is assigned to NH frequency, decreased as the poling corona voltage increases, and finally disappeared when the sample is exposed to a corona voltage of 33 kV. Suggesting that the charge in the dipole moment as NH deformation frequencies take place in the direction parallel to the chain. The vibration which occur at 1743 Cm\(^{-1}\) absorption band is assigned to C = O vibration disappears completely due to the large dipole moment.

The absorption band at 1743 cm\(^{-1}\) which is assigned to C = O bending is increased in its intensities in a sample exposed to a higher annealing temperature of 300 °C.

In chapter 7 the results of charging/discharging currents, the loss factor in the low frequencies, and the conduction currents in composite polyamides (N-P-N) are presented. The results show that the charging and discharging currents are dissimilar at all fields and temperatures measured, and both decay with time according to I=I_0 \times e^{-\alpha t}. The decay constant
n observed during charging is much smaller than that during discharging where two slopes are obtained. The rate of decay depends both on time duration and temperature. At times less than $10^3$ s the value of $n$ decreases with increasing temperature, where $n$ was in the range of 0.7 - 0.4. However, for $t > 10^3$ s and $T \leq 130$ °C $n$ is in the range of 1.0 - 0.97. For $t > 10^3$ s and $T > 130$ °C the value of $n$ is much smaller in the range of 0.5 - 0.2 due to the change from a dipolar to interfacial polarization mechanism which occurs at a transition temperature of 130 °C. The dependency on the electrode materials suggests the presence of electrode polarization as the second dominant mechanism.

The low frequency loss factor results in composite polyamides show one broad peak at each temperature up to 130 °C, which was confirmed to be due to dipolar polarization. Above 130 °C the loss factor is observed to increase significantly with temperature which is characteristic of interfacial polarization mechanisms. The results of the conduction current tests confirm that both Poole-Frenkel and ionic hopping mechanisms are present, where the Poole-Frenkel effect is due to the bulk effect caused by the thermal excitation of trapped electrons into the conduction band of the insulator and the ionic conduction occurs due to the drift of defects under the influence of the applied electric fields.

In chapter 8 the results of thermally stimulated polarization (TSP) and depolarization (TSD) currents with the results of windowing polarization (TSPW) currents in composite polyamides are presented for the first time in this dissertation. The results of (TSD) currents show that the fast dipoles are oriented at lower poling temperature while the slow dipoles are at higher poling temperatures. The TSD current peaks are
observed to increase linearly with poling fields in samples with silver electrodes up to the fields and temperature investigated while the samples with aluminum electrodes show a decrease in the current peaks at higher fields. This might suggest that samples with silver electrodes may behave similarly at higher fields. Thus, the dipolar mechanism might be operative at lower fields while the non-linear behaviour is attributed to space charge and/or interfacial polarization. The TSD current peaks shift to higher temperatures as the poling temperature increases, which suggests the presence of multiple relaxation times. No dependency on the field polarities are observed in N-P-N samples. The TSP currents in N-P-N samples show an increase with temperature. The separation of conduction and polarization currents is achieved by the use of TSP current techniques with different heating rates of 2, 3, and 4 Kmin⁻¹. The results show that higher heating rates give higher currents with the peaks being shifted to lower temperature.

The windowing polarization method is adopted in the N-P-N materials to evaluate the distribution of relaxation time for the dipolar process which is present for T < 140 °C. The observed results indicate several peaks with different activation energies. These peaks are thermally activated and they are observed to increase with increasing poling window temperatures.
9.2 SUGGESTIONS FOR FUTURE RESEARCH

Various techniques have been applied to identify the fundamental mechanisms responsible for charge storage and decay in aromatic and composite polyamides insulating materials for the first time. However, there are still some questions which should be addressed by including the following:

1) The influence of insulating gases (e.g. He, Ar, and Ne) on conduction currents, charging/discharging currents, TSD, and TSP currents should be investigated.

2) Corona charging techniques should be investigated using different experimental arrangements and with negative polarities in both aramid and composite polyamides.

3) The study of both X-ray diffraction and Infrared spectroscopy analysis should also be included in the investigation of composite polyamides.

4) Other various electrode materials such as gold should be investigated, especially the one which are less sensitive to oxidation.

5) The TSD, TSP, and TSWP experiments should also be conducted starting from temperatures below zero (e.g. -80 °C) to observe the lower temperature relaxation process.

6) The charging/discharging and conduction currents should also be investigated under vacuum to eliminate the effect of air humidity on the conduction process.
Publication Cited in Support of the Dissertation


A.1 Electrical and Physical Properties of Teflon (PTFE) [2]

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<th>Property</th>
<th>Teflon (PTFE)</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>Glass transition temperature, T_g, °C</td>
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<td>Melting or maximum service temperature, °C</td>
<td>327</td>
</tr>
<tr>
<td>Coefficient of linear expansion, cm/cm°C</td>
<td>9.9 x 10^-5</td>
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<td>Dielectric constant at 60 Hz, room temperature</td>
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</tr>
<tr>
<td>(ASTM D 150-78)b</td>
<td></td>
</tr>
<tr>
<td>tan δ at 60 Hz, room temperature (ASTM D 150-78)</td>
<td>2 x 10^-4</td>
</tr>
<tr>
<td>Arc resistance, s [ASTM D 495-73 (1979)]</td>
<td>&gt;200</td>
</tr>
<tr>
<td>Dielectric strength, V/mil (ASTM D 149-75)</td>
<td>400 to 500</td>
</tr>
<tr>
<td>Volume resistivity, Ω.cm (ASTM D 257-78)</td>
<td>1 x 10^19</td>
</tr>
<tr>
<td>Water absorption, % (ASTM D 570-77)</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Tensile Strength, MPa X 145 for psi (ASTM D 638-77a)</td>
<td>17 to 45</td>
</tr>
</tbody>
</table>

\*ASTM Standards:
- ASTM D 149-75_ASTM Test for Dielectric Breakdown Voltage and Dielectric Strength of Electrical Insulating Material at commercial power frequencies.
- ASTM D 257-78_ASTM Test for D-C Resistance or Conductance of Insulating Materials.
- ASTM D 570-77_ASTM Test for Water Absorption of Plastics.
- ASTM D 638-77a_ASTM Test for Tensile Properties of Plastics.
### A.2 Electrical and Physical properties of Nomex 410 (Aramid Paper)[91]

<table>
<thead>
<tr>
<th>Property</th>
<th>Nomex 410 (10 Mil Paper)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile, kg/mm² (psi)</td>
<td>11.8 (17,000)</td>
</tr>
<tr>
<td>Modulus, kg/mm² (psi)</td>
<td>300 (430,000)</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>20</td>
</tr>
<tr>
<td>Moisture Absorption, %</td>
<td></td>
</tr>
<tr>
<td>Dielectric constant, 1kHz, 25°C</td>
<td>2.9, 2.7 @ 60 Hz</td>
</tr>
<tr>
<td>Dissipation factor, Ω·cm</td>
<td>0.014, 0.006 @ 60 Hz</td>
</tr>
<tr>
<td>Volume resistivity, Ω</td>
<td>1.5 x 10¹⁶</td>
</tr>
<tr>
<td>Surface resistivity, Ω</td>
<td>1 x 10¹⁶</td>
</tr>
<tr>
<td>Dielectric strength, V/μm (V/mil)</td>
<td>31 (800)</td>
</tr>
<tr>
<td>Flammability, U.L.Rating</td>
<td>V-0</td>
</tr>
<tr>
<td>Melt point, °C</td>
<td>None</td>
</tr>
<tr>
<td>Glass transition temperature,</td>
<td>273</td>
</tr>
<tr>
<td>T&lt;sub&gt;b&lt;/sub&gt;, °C</td>
<td></td>
</tr>
<tr>
<td>Thermal rating U.L., °C</td>
<td></td>
</tr>
<tr>
<td>Mechanical</td>
<td>220</td>
</tr>
<tr>
<td>Electrical</td>
<td>220</td>
</tr>
<tr>
<td>Shrinkage, % 30 min., 150°C</td>
<td>0.5 @ 300 °C</td>
</tr>
<tr>
<td>120 min., 400°C</td>
<td></td>
</tr>
<tr>
<td>Hydrolytic stability</td>
<td>Degraded in strong acid</td>
</tr>
<tr>
<td>Specific gravity, gm/cm³</td>
<td>0.96</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>Excellent</td>
</tr>
<tr>
<td>Tear-initial, kg/cm (gm/mil)</td>
<td>273 (700)</td>
</tr>
<tr>
<td>Tear-propagating, kg/cm (gm/mil)</td>
<td>38 (100)</td>
</tr>
<tr>
<td>Special claims</td>
<td>Excellent Thermal Stability, Mechanical Toughness</td>
</tr>
</tbody>
</table>
A.3 Electrical and Physical properties of Polyester [2]

<table>
<thead>
<tr>
<th>Property</th>
<th>Polyester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/ml</td>
<td>1.39</td>
</tr>
<tr>
<td>Glass transition temperature, $T_g$, °C</td>
<td>69</td>
</tr>
<tr>
<td>Melting or maximum service temperature, °C</td>
<td>250 to 265</td>
</tr>
<tr>
<td>Coefficient of linear expansion, cm/cm°C.</td>
<td>$1.7 \times 10^5$</td>
</tr>
<tr>
<td>Dielectric constant at 60 Hz, room temperature</td>
<td>3.0 to 4.56</td>
</tr>
<tr>
<td>(ASTM D 150-78)$^b$</td>
<td></td>
</tr>
<tr>
<td>tan δ at 60 Hz, room temperature</td>
<td>0.3 to $1.5 \times 10^2$</td>
</tr>
<tr>
<td>(ASTM D 150-78)</td>
<td></td>
</tr>
<tr>
<td>Arc resistance, s</td>
<td>115 to 135</td>
</tr>
<tr>
<td>[ASTM D 495-73 (1979)]</td>
<td></td>
</tr>
<tr>
<td>Dielectric strength, V/mil</td>
<td>380 to 500</td>
</tr>
<tr>
<td>(ASTM D 149-75)</td>
<td></td>
</tr>
<tr>
<td>Volume resistivity, $\Omega$.cm</td>
<td>$1.0 \times 10^{15}$</td>
</tr>
<tr>
<td>(ASTM D 257-78)</td>
<td></td>
</tr>
<tr>
<td>Water absorption, %</td>
<td>0.15 to 0.6</td>
</tr>
<tr>
<td>(ASTM D 570-77)</td>
<td></td>
</tr>
<tr>
<td>Tensile Strength, MPa X 145 for psi</td>
<td>41 to 90</td>
</tr>
<tr>
<td>(ASTM D 638-77a)</td>
<td></td>
</tr>
</tbody>
</table>

* The ASTM standards as described in section A.1.
BIBLIOGRAPHY


VITA AUCTORIS

NAME: Mohamed Abdulbari A. Sussi.

PLACE OF BIRTH: Tripoli, Libya.

YEAR OF BIRTH: June 13, 1958.

EDUCATION:


Concordia University, Montreal, Quebec, Canada, 1984 - 1985, M.Eng., 1986 - 1988, Research and Teaching Assistant.

University of Windsor, Windsor, Ontario, Canada, 1988 - 1992, Ph.D.