THERMALLY STIMULATED SHORT-CIRCUITED CURRENT IN PLASMA-POLYMERISED POLYACRYLONITRILE

ABSTRACT

An appreciable amount of thermally stimulated short-circuited current is observed during heating and cooling between 30°C and 160°C from unpoled plasma-polymerised polyacrylonitrile thin film sandwiched by aluminium electrodes. The observed current is attributed to the space charges accumulated at the vicinity of the outer electrode producing a charge gradient towards the inner. The disorientation of dipoles also contributes to the thermally stimulated current. The temperature activation energy of 1.4 eV indicates that charges are formed from the covalent bond of the carbon atoms. An additional current is also developed which is associated with the electrodes of dissimilar thicknesses. Observations are made by the application of low fields and the relative magnitudes of the various components are discussed.
4.10 INTRODUCTION

Extensive studies have been reported on the short-circuited current of poled [1-4] and unpoled [1,5-7] polymers to obtain information about the behaviour of trapped charges and dipole relaxation process. Thermo-electric and electromechanical effects have also been studied in detail on a variety of polymers [6,7]. It is understood from the thermally stimulated depolarisation current (TSD) studies of polyvinylidene fluoride that the dipole orientation in this polymer is reversible [8-10]. The existence of large piezoelectric and pyroelectric coefficients have extended its application to transducers [11] and thermal sensors [12]. All the interesting properties of polyvinylidene fluoride originate from the preferential orientation of the dipoles.

Polyacrylonitrile (PAN), which has been investigated here in detail, also possesses a permanent dipole moment and is expected to show similar electrical properties [1]. The TSD current spectrum of PAN shows three different peaks, centered around 90°C, 145°C and 190°C and these peaks are characterised by various physical techniques. They are due to loss of preferred orientation of dipoles, the onset of chain segmental mobility ionic diffusion, and solvent diffusion [4,13]. Trapped space charges and residual
solvent molecules also contribute to a broad and strong peak [1] at the vicinity of $195^\circ C$. These peaks are suppressed on repeated heating cycles. Persistent polarisation due to stretching has also been reported [14]. The structural and dipolar properties of the polymers are known to depend on the history of the material, namely, method of polymerisation, stretching details and poling parameters. Considering the increased application of polymers as electrets in recent years, it is felt important to undertake an extensive investigation on the short-circuited current in plasma-polymerised PAN thin films. As a part of the studies, the short-circuited current for the temperature range $30^\circ C$ to $160^\circ C$ on PAN films of different thicknesses using aluminium electrodes, is reported here.

4.20 Experimental

All the measurements are made on plasma-polymerised PAN films sandwiched by vacuum deposited aluminium electrodes. Initially, known amount of aluminium is evaporated in a vacuum and is deposited on ultrasonically cleaned glass slides. PAN thin film is now deposited on the electrode coated glass slide by plasma-polymerisation method. This substrate is transferred to the high vacuum unit and the thermally evaporated outer free electrode is prepared. The details of
preparation of Al-PAN-Al sandwich specimen have been discussed in section 2.24. The sandwich structure thus prepared for short-circuited current studies are schematically shown in Fig.2.09 (a and b). For the thickness measurement of the polymer film separate samples are prepared simultaneously with the specimen and Fizeau fringes method is adopted. The details of Fizeau fringes method are discussed in section 2.32. From the mass of the aluminium taken for evaporation, the thickness of electrodes are estimated.

4.21 Thermally stimulated short-circuited current measurement

The Al-PAN-Al sandwich specimen is transferred to a specially designed chamber which is kept at a pressure of $10^{-3}$ torr. The description of conductivity chamber has been given in section 2.40. Proper electrical connections are made using copper block pressure contacts. For the present investigations, one of the electrodes is connected to the Electrometer amplifier (ECIL-EA-815) while the other is earthed. The electrical connections for the measurement of short-circuited current is shown in Fig.4.01. Before making the thermally stimulated short-circuited current measurements, the short-circuited specimen is heated in vacuum to $160^\circ C$ at the rate of $1^\circ C/min.$ maintained for one
Fig. 4.01. Electrical connection for short-circuited current measurements: IB - inner bound electrode, OF - outer free electrode, S - double pole double throw switch, EA - electrometer amplifier.

Fig. 4.02. The electrical connection for ISC with applied voltage: IB - inner bound electrode, OF - outer free electrode, EA - electrometer amplifier.
hour and then cooled to room temperature at the same rate for removing condensed monomer vapours and charges, if any. Each specimen is subjected to heating and cooling before final readings are recorded. In general, it is observed that logarithmic short-circuited current against temperature curve during the first heating and cooling operation is very much different from the subsequent curves. However these subsequent readings show only very small changes among themselves. The readings reported here are for the second heating and cooling operation. The short-circuited current for different specimens of Al-PAN-Al is recorded for the temperature range 30°C - 160°C.

4.22 Parameters controlling the short-circuited current

From the preliminary investigations, it is found that the important parameters on which the short-circuited current depends are the film thickness of the inner bound and outer free electrodes and the range of temperature. From the observations on the direction of the short-circuited current, it is possible to classify the specimens into two groups (1) specimens for which the outer free electrode is thicker than the inner (2) specimen for which the inner bound electrode is thicker than the outer. The investigations presented here are mainly centered on the magnitude and direction of short-circuited current as a function of electrode
thickness and temperature. In the present study, effort is not given to correlate the thickness of PAN thin film with short-circuited current. Different specimens with thicknesses ranging from 700Å to 1500Å are presented to illustrate the validity of the observed effect. Special effort is not taken to study the specimens having thicknesses below 700Å because most of them are short-circuited on heating.

4.23 Thermally stimulated current in low applied fields

In order to have a better insight into the mechanism of short-circuited current, particularly to illustrate the current reversibility when two exponentially varying currents are added vectorially, the potential of the outer free electrode is raised by an external voltage and the resulting thermally stimulated current is studied. For such studies, the positive terminal of the external voltage source is given to the outer free electrode and the negative terminal is earthed. The electrometer amplifier is connected to the inner bound electrode (Fig. 4.02). The current flowing through the sandwich structure is recorded for heating and cooling processes. The investigations are also made by increasing the field across the specimen.

4.30 RESULTS OF THE EXPERIMENTS

From the initial results, it is clearly understood that two main mechanisms drive the process of short-circuited
Fig. 1.02. The logarithmic short-circuited current vs. temperature for Al-PAN-Al when the inner Al electrode is thicker. (A) is the current when the electrometer is connected to the outer Al electrode and (B) the current when electrometer is connected to the inner bound electrode.

The thicknesses of inner electrode is 1200Å, the outer electrode is 600Å and the PAN is 1200Å. (− log J implied that the current flows from the outer electrode to the inner in the opposite direction).
current. Depending on the relative thicknesses of the inner bound electrode or outer free electrode the direction of the current generated due to one mechanism is reversed while the direction of current due to other is maintained. These processes are classified and explained to understand the mechanism. For specimens with the inner bound electrode thicker than the outer free electrode, it is found that the current is flowing from the outer free electrode to the inner bound one in the external circuit when inner bound electrode is thicker. In Fig.4.03, the short-circuited current when the electrometer is connected to the outer electrode (n) and also when the electrometer is connected to inner electrode (b) is recorded against temperature. The current is recorded for every alternate intervals of temperature on heating and cooling processes. The symmetric curves A and B ensure that the short-circuited current is a bulk process of the material rather than a surface process. Unlike the reversible pyroelectric materials [8], on the cooling cycle, the direction of the current is not reversed, but log J vs. T curve retained the same form with a decrease of one to two orders of magnitude forming a closed loop as shown in Fig.4.03. In Fig.4.04, the short-circuited current against temperature for Al-PIN-Al films when the inner bound electrode is thicker, is presented for various
Fig. 4.04. The short-circuited current Vs. temperature for Al-PAN-Al films when the inner electrodes are thicker. ● and ▲ are the curves on heating and cooling when the thickness of the inner electrode is 2950 Å, the outer electrode 730 Å and the PAN 1360 Å and 1120 Å respectively. X is the curve on heating when the thickness of the inner electrode is 730 Å, the outer electrode 550 Å and the PAN 700 Å. (-log J implies that the current flows from the outer electrode to the inner in the external circuit. The arrow shows the direction of the closed loop).
thicknesses of PAN. The short-circuited current on heating and cooling forms a closed loop.

When the outer free electrode is thicker than the inner bound electrode, the current flows from the inner bound electrode to the outer free electrode at the initial temperatures and reverses at elevated temperature. In Fig.4.05, logarithmic short-circuited current is plotted against temperature for a specimen whose outer free electrode is thicker. In the heating cycle, the current is increased exponentially up to 60°C and then decreased sharply. The current is reversed at 75°C. In the figure, the short-circuited current is recorded against temperature when the electrometer is connected to outer free electrode (A) and also when the same is connected to the inner bound electrode (B). In the process of cooling the short-circuited current decreases exponentially with temperature. Unlike the heating cycle, in this case, the current reversal is observed only at the vicinity of the room temperature. The symmetric variation of curves A and B indicates that the observed short-circuited current is a bulk process of the material rather than the surface process. In Fig.4.06 the short-circuited current of Al-PAN-Al with the outer free electrode thicker for different thicknesses of PAN is plotted against temperature in the heating and the
Fig. 4.05. Short-circuited current Vs. temperature for Al-PAN-Al films when the outer free electrode is thicker. (A) is the current when the electrometer is connected to the outer electrode and (B) the current when the electrometer is connected to the inner bound electrode. The thickness of the inner bound electrode is 650Å, the outer electrode is 2500Å and the PAN is 1200Å. (−log J implies that the current flows from the outer electrode to the inner in the external circuit).
Fig. 4.06. The short-circuited current Vs. temperature for Al-PAN-Al films when the outer electrodes are thicker. ○ and ▲ are the curves on heating and cooling when the thickness of the inner electrode is 730 Å, the outer electrode 2950 Å and the PAN 1420 Å and 1120 Å respectively. (-log J implies that the current flows from the outer electrode to the inner in the external circuit. The arrow shows the direction of the closed loop).
cooling cycles. It can be seen from the figure that the current variation in the heating and cooling processes form a closed loop.

4.31 Effect of application of field across the specimen

In order to have a better insight into this anomalous process of current reversibility, the potential of the outer free electrode is raised in the positive direction for those samples which do not show a current reversibility on heating. In Fig. 4.07, (A) the typical results when the potential of the outer electrode is raised to produce a mean field of $3 \times 10^4$ V/cm in the P...N is presented. On heating, the current initially increases and reaches a maximum at about $60^\circ$C. On further heating, the current drops sharply and at about $70^\circ$C the direction of short-circuited current reverses. In the cooling cycle, the current drops exponentially and at about $65^\circ$C, the direction of the current again reverses. It reaches a maximum at $60^\circ$C and decreases to room temperature current. One of the notable features is that the low temperature current peaks, one on heating and the other on cooling, show a difference in magnitude of two orders. For comparison, the short-circuited current of Al-P...N-Al specimen with thicker outer free electrode is also plotted in the figure.
Fig. 4.07. ○ is the short-circuited current on heating and cooling for Al-PAN-Al film whose the inner electrode is 550Å, the outer electrode 730Å and the PAN 700Å. ▲ is the curve on heating and cooling when the potential of the outer electrode (730Å) is raised in the positive direction to produce a mean field of $3 \times 10^7 \text{V/cm}$ across the PAN film (1120Å); the thickness of inner electrode is 750Å.
(Fig. 4.07,  ). It can be observed that on heating, the two samples show identical curves while on cooling, the curves are different.

It is important to study the variation of current with temperature at higher fields. By applying higher fields, the current reversibility as shown in Fig. 4.07 is not observed till 160°C, but on cooling the current abruptly goes to the negative side and decreases on cooling. A typical plot is shown in Fig. 4.08 when the potential of the outer electrode is raised to produce a field of $5 \times 10^4$ V/cm across the PAN film. In the figure $A$–$B$ shows the current variation on heating and $B$–$C$ gives the current reversal on cooling. On further cooling the current decreases and at $D$ it reverses as shown in figure. At room temperature, it again reaches $A$. But when the specimen is heated again from the point $D$, Fig. 4.08, $B$–$C$–$D$ form a closed cycle and the loop is repeated on heating and cooling from 75°C to 160°C.

4.40 DISCUSSION

The origin of short-circuited current in $M$–$I$–$M$. structures is described elsewhere [6,7]. On the contact of the polymer with a metal, the electrons are usually transferred between the polymer and metal mainly because of
Fig. 4.0. $\bullet$ is the curve on heating and cooling when the potential of the outer electrode (730 A) is raised in the positive direction to produce a mean field of 5x10 V/cm across the PAN (1360Å); the thickness of the inner electrode is 295Å. $\circ$ is the curve when the specimen is reheated from 75°C.
the difference in the work functions, which will in turn bend the conduction band due to the space-charges. If the work functions are temperature dependent, a transient current flows in the external circuit which depends on the rate of change of temperature \([6]\). Also an electrochemical current will be produced \([7]\) when the temperature of the system is increased. For all the above observations, the two electrodes are to be of different metals and hence they may not be applicable to \(\text{Al-PAN-Al}\). However, even with electrodes of the same metal a thermo-electric current is possible, the magnitude of which in the present investigation will be very small as compared to the observed current and can also be neglected. It may be inferred from the behaviour of the thermally stimulated current, that the unreacted monomer vapours are not contributing to the observed current. The thermally stimulated depolarisation current peaks observed by Comstock et al \([1]\) at \(95^\circ\text{C}\) and \(185^\circ\text{C}\) and attributed to the dipole orientations and residual charges might have been superposed on the large space-charge current generated from \(\text{Al-PAN-Al}\) specimen.

4.41 Thermally released space-charge induced current

Several processes contribute to the thermally stimulated current in insulators. Immobilised and
thermally released space-charges produce a thermally stimulated current in insulators. In polar insulators the disorder of the dipoles may also contribute a thermally stimulated current. The possible mechanism that explains the observed thermally stimulated current is outlined below by taking into consideration the magnitude and the direction of the short-circuited current. From the direction of the current shown in Figs. 4.03 and 4.04, the observed short-circuited current is not due to the surface charges but associated with the bulk of the polymer film. Hence whatever changes found in the electrometer connected to one electrode is observed in the other one as a mirror image. Hence from the direction of the current, it may be inferred that the trapped negative charge density is maximum at the vicinity of the outer electrode. Due to the irradiation of electrons and ions having the energy of the order of 1 KeV, shallow trapped holes and electrons are possibly formed in the specimen enhancing the conductivity of the system. The space-charge field in the specimen may orient the polar side group-CN towards the outer electrode [1]. When the specimen is short-circuited, charge migration of the space-charges and the disorientation of dipoles develop a current in the external circuit. At room temperature, the relaxation time is very large and trap modulated mobility is very small. As charges move
in the system, they may either get trapped again or recombine with the opposite charges. The blocking of electrons by aluminium electrodes may prevent the motion of the charge carriers from the electrodes to the insulator so that recombination of charges is minimum. As mobility and relaxation time vary exponentially with temperature, the thermally stimulated short-circuited current increases exponentially as shown in Figs.4.03 and 4.04. The steady exponential increase of current with temperature indicates that the relaxation time of the permanent dipoles and space-charges are widely distributed in plasma-polymerised PAN as it has been reported for styrene [15]. The reappearance of current on repeating the experiment shows that only a part of the charge is untrapped on heating. Thus it is plausible to assume that thermally stimulated short-circuited current mainly arises from the untrapping and conduction of real charges in plasma polymerised PAN. However, the contribution from the disorientation of the dipoles is not to be ignored. As the specimen is cooled, the decrease in current of one to two orders may be an indication to the reversible polarisation of the dipoles at a lower rate explaining the closed loop as shown in the figure.
4.42 The short-circuited current induced by electrodes of dissimilar thicknesses

From Figs. 4.05 and 4.06 it is observed that the thickness of the inner bound electrode and outer free electrode develop an additional contribution to the observed short-circuited current. For thermally stimulated current studies the specimens are heated by specially designed copper blocks mounted symmetrically at the ends of the substrates. The heating is therefore due to the conduction along the length of the films. The thickness of aluminium electrodes and, to a lesser degree, the thickness of the PAN with much smaller thermal conductivity therefore control the quantity of heat conducted. Thus, the polymer film sandwiched by the two electrodes of dissimilar thicknesses when heated with copper blocks develop a temperature gradient across the film with thicker electrode always at a higher temperature. The average heating and cooling rate is maintained at 1°C/min. Since the cooling takes place by radiation, the temperature gradient across the film on cooling is relatively very small with inner electrode always at a higher temperature and the disorder exhibited by the specimen during thermally stimulated current studies is not significant. Hence in the sandwich system a temperature gradient will be developed during the process of heating and this temperature gradient may
develop an additional component to the short-circuited current [16]. The mobility and detrapping of the electrons are increased in the region of the thicker outer electrode which has a larger concentration of trapped electrons. But the temperature in the region of the inner bound electrode will be less. Hence, mobility of the charge carriers in that region will be small. The activated electrons at the vicinity of the outer free electrode move from the outer free electrode to the inner one giving a current in the external circuit. Also due to the large expansion coefficient of aluminium electrodes, the PAN surface which has a lower expansion coefficient might have been strained on heating. It is reported that as the PAN film is strained, the dipoles formed due to the nitrile side group may rotate inducing a charge on the surface [1]. Thus in Al-PAN-Al as the temperature is increased, the observed current of $C_E \frac{dT}{dx}$ can be considered to be a function of the temperature gradient and the surface strain. Within the specimen the charges migrate towards the inner bound electrode resulting in a current of magnitude $C_D$ which is an exponential function of temperature. Hence the total electron current $C$ is given by $C = C_D - C_E \frac{dT}{dx}$. At the initial temperatures, $C_E \frac{dT}{dx}$ will be predominant and hence the net electron current will be from the outer free electrode to the inner
one in the external circuit producing a peak current density of $5 \times 10^{-9}$ A/cm$^2$ at 65°C. As the temperature increases $C_D$ predominates and the direction of current reverses as seen in the Figs. 4.05 and 4.06. On the contrary, when the inner bound electrode is thicker, the magnitude of $C_E(dT/dx)$ will be very small due to low concentration of trapped electrons at the vicinity of the inner electrode and the resulting current will be approximately $C_D$. Hence, as seen before, there is no current maximum at the initial temperatures. If the positive charges were trapped in the vicinity of the inner electrode, the direction of $C_E(dT/dx)$ would have been opposite to $C_D$ and the current would have been reversed when the inner electrode is thicker. Hence in plasma-polymerised PAN, the negative charge gradient with a maximum at the outer electrode can explain the observed thermally stimulated current. It can also be inferred that there are no positive charges trapped at the inner bound electrode.

4.43 Vector addition of short-circuited currents due to trapped charges and due to electrodes of nonidentical thicknesses

To test the vector addition of $C_D$ and $C_E(dT/dx)$ in the thermogram of the specimen whose outer free electrode is thicker, a current is generated using external sources
in place of $C_E\frac{dT}{dx}$ in a sample whose inner bound electrode is thicker. For that, a field of $3\times10^4$ V/cm is applied on the outer thinner electrode to oppose the current due to the trapped charges. When the potential of the M-I-M structure is raised, an ohmic current $C_\alpha$ and a polarisation current $C_p$ due to the motion of space charges and orientation of dipoles will be developed in the direction of the field [17,18]. For a system with a thinner outer free electrode, $C_E\frac{dT}{dx}$ will be very small compared to $C_D$. Hence the total current $C$ towards the direction of the field is given by $C = C_\alpha + C_p - C_D$. As the temperature increases, all the contributions to the observed current increases and at the temperature of $70^\circ C$, $C_D$ dominates and the direction of the total current reverses as shown in the Fig.4.07. In the cooling cycle the polarisation current $C_p$ will be zero because the specimen is poled with maximum amount of dipoles and space charges. Hence the total current will be $C = C_\alpha - C_D$. At about $65^\circ C$, $C_\alpha$ becomes relatively large and the direction of the current will be towards the field. Hence the low temperature peak in the cooling process is less by two orders than the one in the heating cycle which may be due to the absence of $C_p$. On comparing Fig. 4.07(▲) and Fig.4.07(●), it is clear that the current reversibility is due to the additional contribution of short-circuited current which is in the opposite
direction of $C_D$ and in the case of Fig.4.07(●), it is explained on the basis of a temperature gradient due to the electrodes of dissimilar thicknesses and a trapped charge accumulation at the vicinity of outer electrode. In the cooling cycle of the specimen with thicker outer free electrode, only $C_D$ will be predominant at higher temperatures while at the vicinity of room temperature the current due to reversible polarisation will be slightly higher. Hence Fig.4.07 (●) shows a current reversal at the vicinity of room temperature in the cooling cycle. The decrement of short-circuited current by one to two orders may be an indication of reversible polarisation which leads to a short-circuited current in the next heating cycle.

When higher potential is applied to the specimen whose outer free electrode is thinner, the thermogram obtained (Fig.4.08) is different from what is observed before. When the potential of outer thinner electrode is raised to produce a field of $5 \times 10^4$ V/cm, the current $C$ will be towards the field (Fig.4.08, □-□). In this case $C_n + C_p$ is field dependent and hence very large. At higher temperatures, thermally stimulated charges are formed and move in the field resulting in a sharp increase in current above $120^\circ$C. The current due to the space-charges
as well as reorientation of dipoles is given by Goro Sawa et al [7] as

\[ C_p = \frac{SV}{d} \frac{\partial}{} \frac{\partial \varepsilon}{\partial T} \]  

where \( \beta = \frac{dT}{dt} \) and \( \frac{\partial \varepsilon}{\partial T} \) is the change in dielectric constant with temperature. For plasma polymerised PAN the quantities in the above expression are positive on heating while \( C_p \) becomes negative on cooling. Thus on cooling, the direction of the total current \( C \) reverses (Fig.4.08, B-C). On further cooling, at about 75°C, the ohmic current \( C_\Omega \) dominates showing a current reversal as seen in Fig.4.08,(D). It is also found that the point D shifts on changing the applied field. When the applied field is of the order of \( 10^5 \)V/cm, the \( C_\Omega \) and \( C_p \) are appreciably large and hence the influence of \( C_D \) is unobserved. In such cases the current reversal is not observed. At low fields the cyclic nature of the current with temperature may be due to the to and fro motion of space charges and the reorientation of dipoles. Since this process is repeatable, it can be assumed that the recombination rate of space charges is very small.

4.44 Energy levels of trapped charges

The temperature activation energy is calculated to be \( \sim 1.4 \) eV from the expression \( \log J = C - \frac{E}{kT} \) using
the low temperature tail of the short-circuited current [19] shown in Figs. 4.03 and 4.04. It is in good agreement with the energy required to create charge carriers in a structure consisting principally of C-C bonds [20]. Hence it is clear that trap levels are situated at \( \sim 1.4 \text{ eV} \) below conduction band. From the absorption spectra of PAN discussed in chapter III, it is found that the absorption band starts from the frequency close to the above energy level (1.7 eV). Hence it is clear that the absorption takes place at the trap centers. It is concluded that negative charges are trapped at the covalent bonds of the carbon atoms most probably in the termination process and released on heating.

4.50 ORIGIN OF SHORT-CIRCUITED CURRENT

The short-circuited current generated from plasma-polymerised unpoled Al-PAN-Al sandwich system may originate from the accumulation of negative trapped charges in the vicinity of the outer electrode and the preferential orientation of dipoles due to the rotation of \(-\text{CN}\) side groups towards the outer electrode. The electrons are trapped at the tail ends of the polymer chain and they form a negatively charged molecule of charge \( e^- \). From the behaviour of the current, it is inferred that the degree
of polymerisation will be maximum near the inner electrode and minimum near the outer. Hence the electrons may trap at different levels in the process of plasma polymerisation with a maximum of trapped charges at the outer electrode producing a gradient towards the inner. The space charge gradient might have been due to the decrease in the pressure in the vacuum chamber in the process of polymerisation. From the study of the additional current produced due to nonuniform heating as well as the surface strain of the specimen, it is inferred that no positive charges are trapped at the vicinity of inner electrode. Since the activation energy is $\sim 1.4$ eV, it is concluded that the charges are formed from the covalent bond of the carbon atoms and this supports the formation of electrons from the tail ends of the molecules. These types of sandwich systems can store a large amount of negative charges and can be used as electrets and thermal current sources.
REFERENCES