5. PYROELECTRICITY

5.1 INTRODUCTION

The pyroelectric effect is the change in the polarisation of a crystal when it undergoes variation in its temperature. Pyroelectricity can be divided into two types, namely primary and secondary pyroelectricity. If the sample temperature is changed without letting the sample change its shape and size, then it is primary pyroelectricity. The secondary pyroelectricity is a direct result of piezoelectricity. Interest in the pyroelectric properties of polymeric materials are due to two reasons. First, polymeric materials are used in the place of crystalline or ceramic materials in many pyroelectric applications such as infra-red detectors, electrically calibrated radio meters and thermal imaging devices. Second, the pyroelectric coefficient has become a valuable tool in the study of the mechanisms of the polarisation of polymers.

5.2 THEORY

The pyroelectric effect is the development of electric polarisation in a crystal due to a change in temperature. This effect, in principle, should appear in all crystals with non-centrosymmetry and with any of the following ten structural space groups, $C_1$, $C_{1h}$, $C_2$, $C_{2h}$, $C_3$, $C_{3v}$, $C_4$, $C_6$, $C_{6v}$, and $S_4$ [1-2]. These crystals have unique polar axis along which spontaneous polarisation exists. However, a required polar axis can be introduced in an originally isotropic material by the application of an electric field [3]. The electric dipoles aligned in the direction of polar axis produce a polarisation along the polar axis. However, an external field is not normally observed because of the presence of mobile charge carriers or stray charges present on the surface of the material, which neutralise the polarisation. If the temperature of the material is changed,
polarisation also changes and this change in polarisation overcomes the compensation charges and produces an observable electric field. If the crystal is made into a capacitor by providing the surface perpendicular to the polar axis with electrodes, then the redistribution of compensating charges causes a current flow in an external circuit connecting the electrodes.

The change in polarisation \( dP \) of a crystal due to the change in its temperature \( dT \) is given by,

\[
dP = P \ dt \quad (5.1)
\]

where the constant ‘\( P \)’ is called the pyroelectric coefficient of the crystal.

If a temperature change in the crystal is due to the absorption of radiation, the observed pyroelectric effect is equivalent to the direction of the incident radiation. The current ‘\( i \)’ in the external circuit depends on the area ‘\( A \)’ of the radiation receiving electrode and the rate of change of polarisation with temperature and is given by \([4]\),

\[
i = (A \ dP/dT) \ (dT/dt) \quad (5.2)
\]

The power ‘\( w \)’ absorbed by the crystal due to the change in the incident radiation, is

\[
w = JA \ t \ \rho \ C \ (dT/dt) \quad (5.3)
\]

where \( J \) is the mechanical equivalent of heat, ‘\( t \)’, the thickness, ‘\( \rho \)’ the density and ‘\( C \)’ its specific heat at constant stress. Hence

\[
i = (dP/dt) \ (w / \rho JC) \quad (5.4)
\]
Equation (5.4) indicates the necessity of high volume resistivity, low density, low specific heat for the pyroelectric material. Also the thickness of the material should be of minimum possible value, preferably less than the thermal diffusion length to ensure a uniform heating. In general, polymers have most of these desirable properties. A polymer is a homogeneous mixture of crystalline and amorphous regions and on a macroscopic scale, it has no polarisation. However, polarisation can be introduced by mechanical stretching and/or by poling i.e., applying an electric field at high temperatures. Two physical models have been proposed to account for the appearance of pyroelectricity. They are (1). dipolar model and (2). space charge model.

In order to explain piezo and pyroelectricity, Broadhurst et al [5] developed a dipolar model with compensating surface charges and suggested that pyroelectricity originates from the dimensional changes of the polymer due to its temperature change. This model is applicable to crystalline and semicrystalline polymers with polar groups. The polarisation in this material can be written as,

\[ P = (N/V) \mu <\cos\theta> \]  \hspace{1cm} (5.5)

where 'N' is the number of dipoles in the crystal of volume 'V' and '\( \mu <\cos\theta> \)' is the effective dipole moment at an angle '\( \theta \)' with respect to the direction of polarisation P. Assuming dipole-dipole interaction and spherical cavity field, \( \mu \) can be expressed in terms of high frequency relative permittivity \( \varepsilon_{\infty} \) and intrinsic dipole moment \( \mu_0 \) of the polymer. The polarisation P then becomes

\[ P_0 = \left[ (\varepsilon_{\infty} + 2) / 3 \right] (N/V) \mu_0 <\cos\theta> \]  \hspace{1cm} (5.6)

where '\( P_0 \)' is the frozen-in polarisation. The pyroelectric coefficient can be obtained from this expression as
where \( \alpha \) is the volume thermal expansion coefficient, \( \phi \) the mean square torsional displacement of the vibrating dipole and \( \nu \) the Gruneisen constant for the torsional frequency of the dipole. The thermal vibrations of dipole orientations are considered as an additional effect in this case and are dependent on temperature.

Wada and Hayakawa [6] proposed a space charge model for pyroelectricity in which they made use of the established fact that charges may be injected into a dielectric material from the electrodes when an electric field is applied. These charges, which get trapped in the localised states for a considerable time even after the removal of the field, contributed to the pyroelectricity in materials possessing heterogeneity in the dielectric or elastic properties.

5.3 MEASUREMENTS

The experimental set up for the measurement of pyroelectric current is similar to that used in TSDC measurements. The first irreversible thermal run is a measure of the absorbed charges during the poling process. All the subsequent thermal cycles give the reversible or true pyroelectric current. Similarly as above, the sample was heated at a constant rate at a particular temperature and cooled at the same rate. The constant heating rate used was about 0.521 K/sec.

The pyroelectric effect of cellulose acetate films was studied in a vacuum of 10^{-3} Torr by measuring the pyroelectric current under different polarising fields,
polarising temperatures and dopant concentrations. After polarisation, the films were subjected to a number of heating cycles. The first cycle, which is irreversible, is associated with thermally stimulated discharge currents while the subsequent cycles, gives rise to pyroelectric current [7-8].

Pyroelectric current was measured in samples polarised at different polarising temperatures ($T_p$) of 303 and 343 K and different polarising fields ($E_p$) of $1.18 \times 10^6$ V/m ($E_{p1}$), $2.35 \times 10^6$ V/m ($E_{p2}$), $3.50 \times 10^6$ V/m ($E_{p3}$) & $4.71 \times 10^6$ V/m ($E_{p4}$) for a fixed period of $3.6 \times 10^3$ sec. The pyroelectric coefficient [$P$] was computed from the measured pyroelectric current using the formula

$$P = -I / A\beta$$

where 'I' is the pyroelectric current, 'A', the area of the electrode and 'β' is the heating rate. The sign of $P$ was taken as positive for pyroelectric currents with the same polarity as the first depolarisation current.

5.4 RESULTS AND DISCUSSION

5.4.1 Results

Figs 5.1 and 5.2 show the variation of the pyroelectric coefficient in undoped CA films polarised at two temperatures (303 and 343 K) for different polarising field strengths.

The pyroelectric coefficient showed a behaviour with negative values at low temperatures and positive values at high temperatures. The temperature at which the pyroelectric coefficient changed sign from negative to positive value (transition temperature) was from 365 K onwards. At polarising temperature 303 K, the transition temperature was ranging from 365 to 390 K for different polarising fields. This temperature increases with the increase in field $E_p$. On further increasing the polarising temperature to 343 K, this transition
Fig. 5.1 Variation of pyroelectric coefficient with temperature in pure 4% CA film at $T_p = 303$ K for various polarising fields.

$T_p = 303$ K

$\beta = 0.521$ K/sec.

- $E_{P1}$
- $E_{P2}$
- $E_{P3}$
- $E_{P4}$

Pyroelectric coefficient ($\times 10^{-8}$ C cm$^{-2}$ K$^{-1}$)

Temperature (K)
Fig 5.2 Variation of pyroelectric coefficient with temperature in pure 4% CA film at $T_p = 343$ K for various polarising fields.
temperature range becomes narrow (i.e., from 370 to 383 K). Both these samples showed a peak in the negative pyroelectric coefficient, which is in agreement with the β peak observed in TSDC studies.

Another interesting feature of the pyroelectricity in CA was that the samples polarised at lower temperatures showed larger pyroelectricity. As the polarising temperature was increased, the magnitude of \( P \) decreased. Thus, the pyroelectric activity induced by poling is closely related to the degree of crystallinity of the samples before poling. Similar results were reported for PTrFE by Oka and Koizumi [9-11].

For the samples with 0.05% dopant (see Figs. 5.3 and 5.4), a significant change in the magnitude of the pyroelectric coefficient for the entire temperature range was observed. In this case, the negative peak disappeared and also a small peak at about 330 K is observed at all fields, the pyroelectric coefficient then decreases and show a sudden hike at around 370 K. It should be noted that, for this sample the value of glass transition temperature (\( T_g \)) is 373 K. Thereafter \( P \) increases with the increase in temperature. On increasing the \( T_p \) to 343 K, a decrease in peak height was noticed. Also for the entire temperature range the magnitude of \( P \) is low when compared with samples polarised at room temperature (303 K). In this sample also, a sudden increase in \( P \) value was noticed around the \( T_g \) of the sample with the increase in temperature.

On increasing the dopant concentration further to 0.1%, at \( T_p = 303 \) K (Fig.5.5), the magnitude of \( P \) value was found to be increasing. The peak value of \( P \) was also noticed around 330 K. At glass transition temperature (\( \approx 370 \) K) of the sample, a sudden hike in \( P \) was noticed at all the fields. On increasing the polarising temperature (\( T_p = 343 \) K), the magnitude of the pyroelectric coefficient did not show any appreciable increase with the increase in temperature (see Fig. 5.6).
Fig. 5.3 Variation of pyroelectric coefficient with temperature in 0.05% nickel doped CA film at $T_p = 303$ K for various polarising fields.

0.05% DOPED CA

$T_p = 303$ K
$\beta = 0.521$ K/sec.

- $E_{P1}$
- $E_{P2}$
- $E_{P3}$
- $E_{P4}$

Fig. 5.3 Variation of pyroelectric coefficient with temperature in 0.05% nickel doped CA film at $T_p = 303$ K for various polarising fields.
Fig. 5.4 Variation of pyroelectric coefficient with temperature in 0.05% nickel doped CA film at $T_p = 343$ K for various polarising fields.
Fig. 5.5 Variation of pyroelectric coefficient with temperature in 0.1% nickel doped CA film at $T_p = 303$ K for various polarising fields.
Fig. 5.6 Variation of pyroelectric coefficient with temperature in 0.1% nickel doped CA film at $T_P = 343$ K for various polarising fields.
Further increase of dopant concentration to 0.15% results with the appearance of negative peak as observed in the undoped film, which is depicted in Figs. 5.7 and 5.8. This peak also appears around 330 K. In this case the \( P \) value changes from negative to positive side at the temperature around the glass transition temperature of the material \( (T_g = 371 \text{ K}) \). The magnitude of \( P \) decreases with the increase of polarising temperature \( (T_p = 343 \text{ K}) \).

5.4.2 Discussion

The origin of pyroelectricity in polymer electrets may be due to any one or a combination of more than one of the following processes: (i) orientation of permanent dipoles [5], (ii) polarisation due to displacement of ions and (iii) charge injection from the electrodes [12]. The first process is generally called as dipolar orientation process whereas, the other two are termed as space charge dominated processes.

Das Gupta and Duffy [13] explained the origin of pyroelectricity in polyvinylidene fluorides as due to dipolar orientation by observing the sign of pyroelectric current as opposite to that of charging current. Hayashi and Kubo [14] explained the origin of pyroelectricity in terms of space charge by observing the dependence of pyroelectric coefficient on electrode materials of different work functions.

In the present work, where the temperature range of pyroelectric studies is confined to 303 to 450 K. Based on the results, the samples are grouped in two, and in the first the undoped sample and 0.15% nickel doped sample showing negative pyroelectric coefficient in the low temperature range and positive pyroelectric coefficient in the high temperature range. The second consists of the 0.05% and 0.1% Nickel doped samples showing positive pyroelectric coefficient in the entire temperature range. In both these categories, a hike in pyroelectric coefficient at high and low temperature region was observed. This
Fig. 5.7 Variation of pyroelectric coefficient with temperature in 0.15% nickel doped CA film at $T_p = 303$ K for various polarising fields.
Fig. 5.8 Variation of pyroelectric coefficient with temperature in 0.15% nickel doped CA film at $T_p = 343$ K for various polarising fields.
suggests the possibility of two different mechanisms for pyroelectric activity in these films. In the low temperature region, the peak value (both the negative and positive) of pyroelectric coefficient may be due to dipolar orientation process whereas the hike in the pyroelectric coefficient in the high temperature range is due to the space charge polarisation. The observation of negative pyroelectric coefficient and their corresponding peaks at low temperature support the theory of dipolar orientation [10]. At high temperatures, it is believed that the origin of pyroelectricity is due to the injection of charge carriers from the electrodes into the dielectric.

In conclusion, the present study reveals the pyroelectric nature of pure and nickel doped cellulose acetate. As discussed above, pyroelectricity in first category of samples differ from those in other pyroelectric fluorocarbon polymers such as PVDF [15-16] and PVF [17-18]. Here, $P$ changes the sign upon heating and the transition temperature of $P$ does not depend on the poling temperature, but depends on the glass transition temperature of the samples. In this respect the pyroelectricity is considered to be anomalous because the temperature dependence of $P$ in other pyroelectric polymers like PVDF, PVF does not show any negative pyroelectric coefficient.

When the polymer is doped with nickel, there is a possibility of creation of more charges and dipoles in the polymer. This results in a increased pyroelectric activity. As the dopant concentration is increased the number of charge carriers created in the dielectric is also increased thus enhancing the pyroelectric current. For larger dopant concentrations, however, there is a possibility of formation of molecular aggregates of the dopant in the polymer, which may result in a comparatively smaller pyroelectric activity.
References