

## Thermal depolarisation current study of electron irradiated fluorinated ethylene propylene

S J WALZADE, J P JOG and S V BHORASKAR

Department of Physics, University of Poona, Pune 411 007, India

MS received 20 June 1980; revised 9 September 1980

**Abstract.** Thermally stimulated current (TSC) studies have been reported in the co-polymer of tetrafluoro ethylene and hexafluoropropylene films. Depolarisation current peaks are obtained at  $\alpha_1$ ,  $\alpha_2$  and  $\beta$  relaxation temperatures of the polymer and the detrapping process is explained on the basis of its molecular motion. A cross-over electron energy of 18 keV is observed where the nature of TSC spectra undergoes a remarkable change. This is explained in relation to the surface states in FEP. Five groups of trapping levels,  $0.25 \pm 0.08$ ,  $0.57 \pm 0.10$ ,  $1.07 \pm 0.1$ ,  $1.3 \pm 0.25$  and  $2.3 \pm 0.4$  eV are obtained.

**Keywords.** Depolarisation; trapping; molecular motion; surface states; fluorinated ethylene propylene; thermally stimulated current.

### 1. Introduction

Despite the fact that the thermally stimulated current (TSC) measurements in fluorinated ethylene propylene (FEP) have been widely studied using various methods (Sessler and West 1962, 1968; Perlman and Reedyk 1968; Murphy and Fraim 1968; Tyler *et al* 1955; Reiser *et al* 1969; Seiwatz and Brophy 1965) for charging, little of information is available on the charge release process and its relation to the molecular motions of polymer. An attempt is therefore made to understand the charge release process in FEP. The low energy electron bombardment with non-penetrating (range of electrons less than the foil thickness) beam of electrons is used for charging the FEP foils. From the experimental results a correlation has been found between the charging of the films and the surface states in the polymer. Earlier studies on electron bombarded teflon FEP (Turnhout 1975) shows that there are at least two possible traps for the charges in this polymer and the thermal release of charges from these traps is related to the molecular motion in the host polymer. By analysing our experimental results, it is found that trapped charges in this polymer are released at least at three different temperatures, characteristic of its molecular motions and there are at least five trapping levels for low energy electron irradiated samples.

This paper reports the results of short circuit TSC of 250  $\mu\text{m}$  teflon FEP after open circuit irradiation with electrons ranging between 3–30 keV. Two well-defined peaks are obtained near glass transition temperature for the foils irradiated below an energy of 18 keV electrons. A change in the nature of spectra has been observed at and above the electron energy of 18 keV. This has been explained in terms of the range of incident electrons and the surface states in the polymer.

## 2. Experimental

Samples used were 250  $\mu\text{m}$  thick films of teflon FEP type A (EI duPont de Nemours and Company) which contained about 10 to 18 mole % of HFP. Each sample was cut into a size of  $2.5 \times 2.5$  cm and one of the surfaces was provided with vacuum evaporated aluminium electrode having 10 mm diameter. The metallised surface was kept in contact with an aluminium electrode of 10 mm diameter. The non-metallised surface of the sample was then exposed to the monoenergetic electron beam of cross-section 3 mm ranging in energy between 3 to 30 keV. The focussed electron beam was obtained from a gun with an accelerating system. The beam could be deflected in X-Y direction using ferrite cored deflection coils. The beam current was monitored by deflecting it over a Faraday collector, which was positioned near the front surface. The rear surface of the sample was backed by an electrode kept at earth potential during electron irradiation.

All the samples were irradiated over an area of  $7.07 \times 10^{-2}$   $\text{cm}^2$  with a beam current of  $3.5 \times 10^{-8}$  amp for 2 min at a pressure  $< 10^{-5}$  Torr. The irradiated samples were removed from the vacuum chamber and stored in short circuit in atmosphere. Results of short circuit TSC measurements are reported for samples short circuited and stored for 2 hr. The thermal depolarisation was carried out by sandwiching the sample between two metal electrodes inside a separate thermostatic oven with a linear heating rate of  $6.44^\circ\text{C}/\text{min}$  using a linear temperature programmer. The temperature was recorded with chromel-alumel thermocouple kept in close contact with the sample. A vibrating reed electrometer amplifier type EA 811 was used as a current detector and the current temperature plot was obtained on an X-Y chart recorder.

## 3. Theory

Creswell and Perlman (1970) developed a complete theory to account for the TSC peaks, in surface charged dielectrics. The externally measured current (with no applied field) is given by

$$J = \frac{\mu e^2 \delta^2 n_{t0}^2 \tau}{2\epsilon d \tau_0} \exp \left[ -\frac{E}{kT} - \frac{2}{\beta \tau_0} \int_{T_0}^T \exp \left( -\frac{E}{kT} \right) dT \right] \quad (1)$$

where  $\mu$  is the mobility of charge carrier,  $e$  the electronic charge,  $\delta$  penetration depth,  $n_{t0}$  the initial density of electrons in traps,  $\tau$  the relaxation time,  $\epsilon$  the dielectric constant,  $d$  the thickness of the sample,  $\tau_0$  the time constant,  $E$  the depth of trapping level and  $\beta$  is the heating rate.

The relaxation time is given by

$$\tau_T = \tau_0 \exp (E/kT) \quad (2)$$

where  $\tau_0$  is given by

$$\frac{2kTm^2}{\beta E \exp (E/kT_m)}, \quad (3)$$

where  $T_m$  is the temperature at which the maximum current occurs.

The initial rise method of Garlick and Gibson (1948) was used for calculating the activation energies, as the low temperature tail of (1) gives

$$\log J = \text{const.} - \frac{E}{kT} \quad (4)$$

The activation energy can be determined from the semilog plot of current versus  $1/T$ .

## 4. Results and discussion

### 4.1 Relation to molecular motion

The intrinsic electrical behaviour of FEP was observed by the spontaneous TSC measurements for virgin samples. This method was found suitable for detecting the possible structural transitions in any sample (Walzade *et al* 1978). This is illustrated in the TSC spectrum of virgin  $\text{NaNO}_2$  crystal in figure 1(a). A current peak is obtained at the ferroelectric transition temperature at  $163^\circ\text{C}$ . Similar ferroelectric transition was also obtained in other ferroelectric samples (Walzade *et al* 1978). In figure 1 the TSC spectrum for untreated FEP is shown with and without the bias voltage applied across the sample. In figure 1(a) the spontaneous current starts rising near the glass transition temperature, which is located by the break in the log of current versus  $1/T$  plot (a typical plot is given in figure 2). This has revealed the presence of two transitions,  $a_1$  and  $a_2$  respectively, around  $180^\circ\text{C}$  and  $80^\circ\text{C}$ . These transitions are associated with the well-known leather-to-rubber and glass-to-leather transitions in this polymer (Cowie 1973). The  $80^\circ\text{C}$  transition agrees with the  $77^\circ\text{C}$  glass transition reported by Turnhout (1975) and that at  $180^\circ\text{C}$  corresponds to the transition at which  $\delta$ -peak has been reported by Turnhout. Figure 1(b)

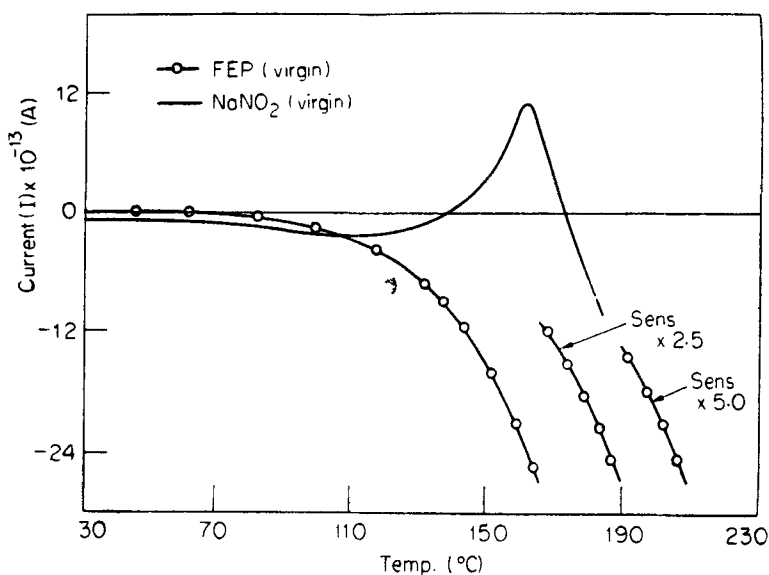


Figure 1(a). TSC of untreated FEP without any bias voltage and single crystal of  $\text{NaNO}_2$ .

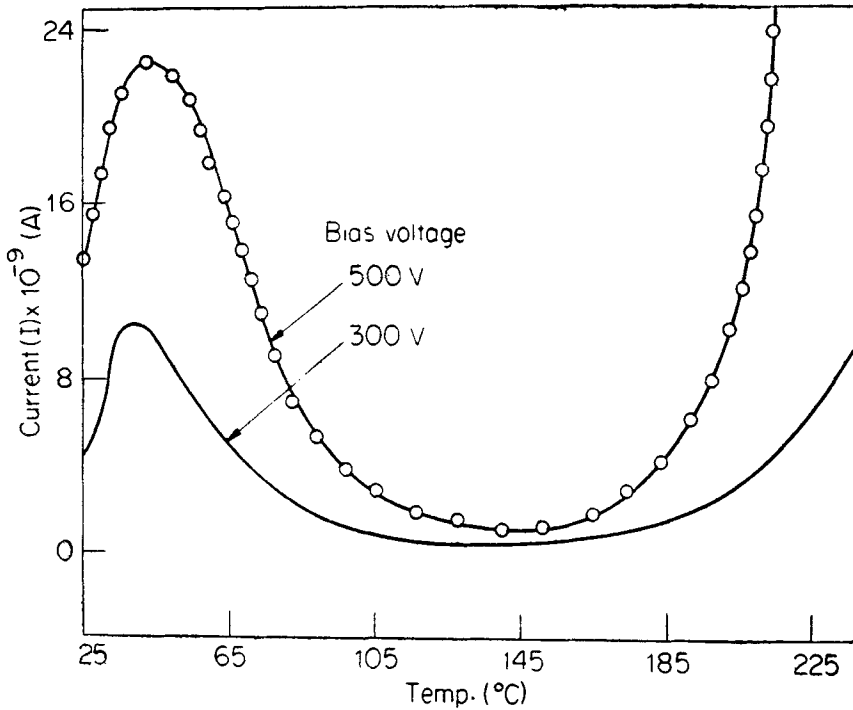


Figure 1 (b). TSC of untreated FEP with bias voltage.

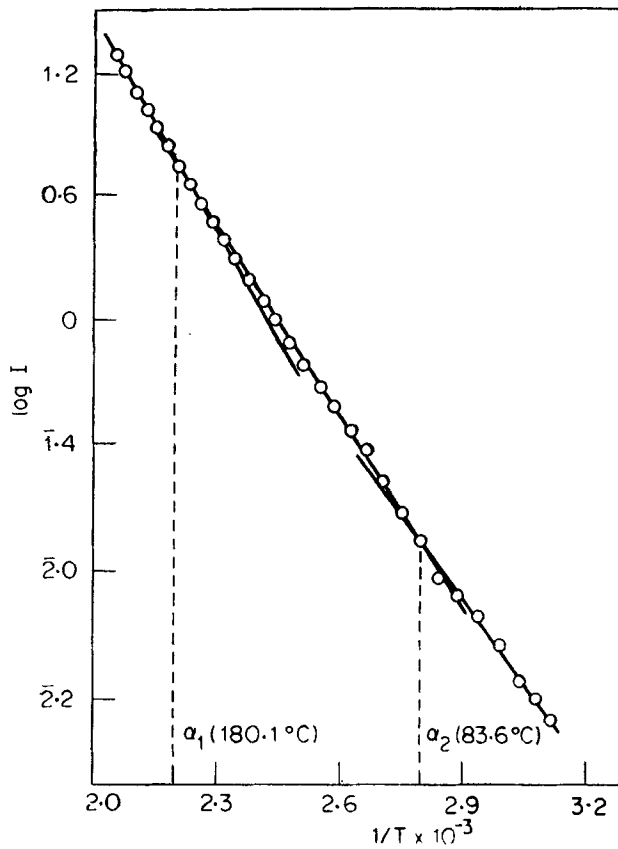


Figure 2. Plot of  $\log I$  versus  $1/T$  for untreated FEP without applied bias voltage, showing  $\alpha_1$  and  $\alpha_2$  transitions.

presents the current thermogram of virgin FEP in the presence of the applied electric field. A current peak is observed around  $40^{\circ}\text{C}$ , the peak height increases with increasing bias voltage. This peak should relate to the characteristic structural transition in FEP and we name this as the  $\beta$  transition in FEP (Jog *et al* 1979). However no peak in the current is observed at  $\alpha_1$  and  $\alpha_2$  transitions even when bias is applied. At the  $\beta$ -relaxation the sample undergoes a transition from one stable state to the other stable state while at the  $\alpha_1$  and  $\alpha_2$  transitions the sample passes through a metastable leathery state into an unstable rubbery state. The current in the sample therefore continuously increases during and after this transition and no current peak is observed. The  $\beta$ -transition in FEP may be very similar to the transition in polytetrafluoro ethylene observed at  $19^{\circ}\text{C}$  by D'Ilario and Giglio (1974) where the helical macromolecule changes its repeat unit from 13  $\text{CF}_2$  groups arranged in 6 turns to 15  $\text{CF}_2$  groups in 7 turns. The activation energy of  $0.44\text{ eV}$  was calculated for in  $\beta$ -relaxation process in our experiments which is in close agreement with the allowed energies of activation for any process inside the glassy region (Birks 1960).

Having known the possible structural transitions in FEP, its impact on the charge release from the filled traps can be seen from figure 3. These are the TSC spectra of electron irradiated FEP foils under different electron energies ranging from 3 to 30 keV. Several peaks are revealed in the TSC spectra corresponding to the different trapping sites in the foil. A prominent feature observed is that a broad bump exists at and around  $41^{\circ}\text{C}$  for each foil irradiated with electrons of 3 to 15 keV energies (figure 3a). This temperature is very close to the  $\beta$ -transition temperature of the sample. Again another peak occurs near the  $\alpha_2$ -transition of the polymer for each of these samples. The peaks are distributed between  $75^{\circ}\text{C}$  to  $85^{\circ}\text{C}$ . The peak height at

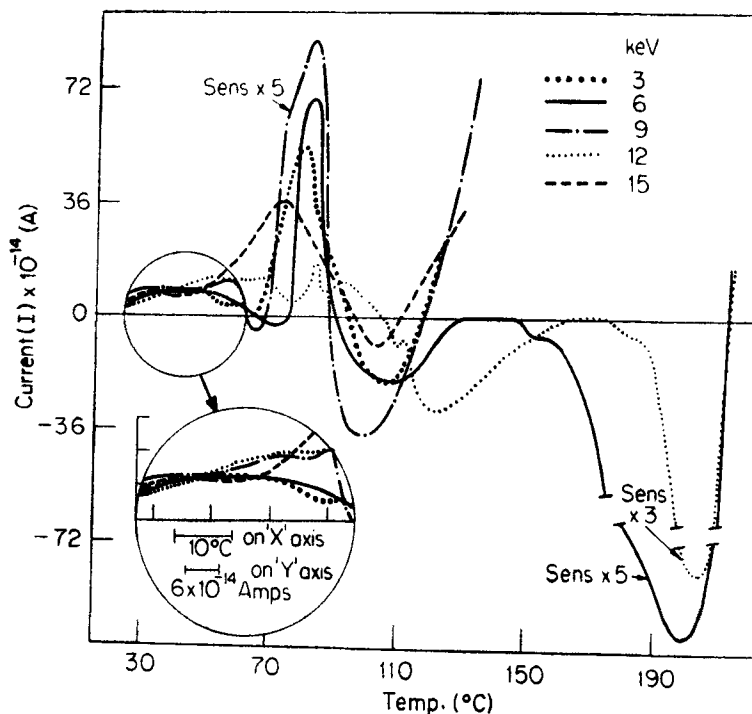


Figure 3 (a). TSC of electron irradiated FEP for electron energies of 3 to 15 keV,

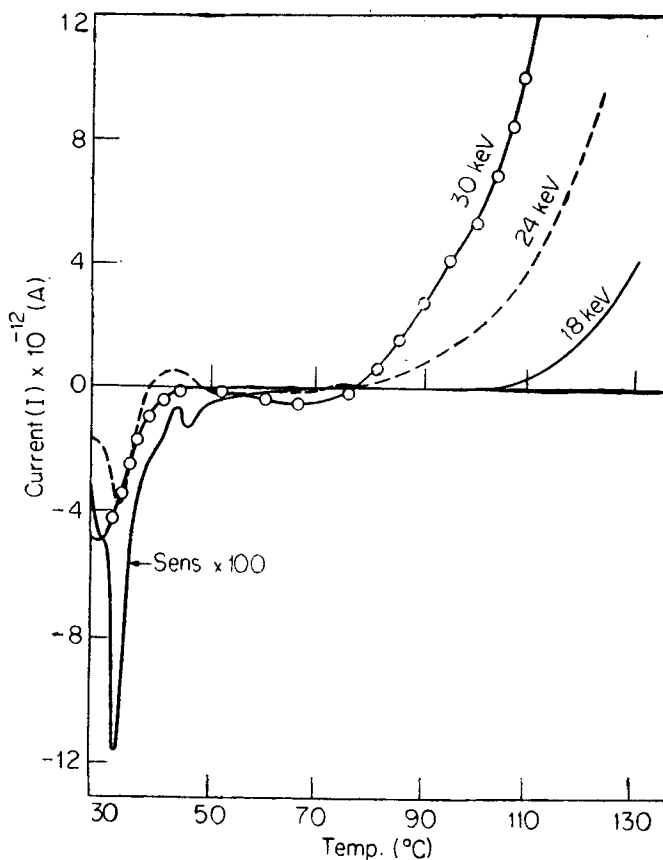


Figure 3 (b). TSC of electron irradiated FEP for electron energies of 18 to 30 keV.

transition increases with increasing electron energy from 3 to 9 keV. The high temperature peak named as  $\rho$ -peak by Turnhout (1975) is seen at 196°C and 204°C corresponding to the beam energies of 6 and 12 keV respectively. This peak is not obtained for other energies and may be treated as an ill-defined peak (Turnhout 1975). Our experiments with TSC of nitrogen ion implanted FEP also resulted in a peak around 180°C (Jog *et al* 1980). We believe this is the  $\alpha_1$ -transition which should be treated as the true glass-transition temperature in FEP, where the actual molecular motion begins. At  $\alpha_2$  transition the sample seems to undergo a transition from glass to leather state (Cowie 1973) and where the segmental motions around the main chain begin. On the other hand at  $\alpha_1$  the main chain itself may be in motion around the helical axis. The thermograms obtained by Turnhout (1975) actually start decaying around this temperature. This kind of  $\alpha_1$ -relaxation process can be distinguished only when its effect is not masked by the high conductivity. This is because due to the increased molecular motions around  $\alpha_1$ -transition, the conductivity of intrinsic carriers predominates over that due to the excess carriers.

Current peaks also appear on the negative side between 93 to 124°C. No particular transition in FEP has been detected in this region either in our observations or those reported by other workers. However it seems reasonable that once the glassy state is overcome chain segments in the polymer are in motion although rather slowly. The trapped charges are released due to the commencement of rotation of particular

segmental group. Moreover the activation energies for these peaks are distributed around an average of 1.66 eV. This leads us to the conclusion that there is a definite trapping site related to the segmental defects.

#### 4.2 Surface states

A change in the nature of the spectra is encountered at and above the irradiation energy of 18 keV. The number of peaks is sharply reduced and a single peak appears on the negative current side. The positive currents seen in figure 3(b) are due to positive charges flowing through the dielectric in the direction from front to the rear electrode or due to negative charges flowing in the opposite direction. Negative current in the case of foils irradiated at and above 18 keV may be due to the negative charge carriers flowing from the front towards the rear electrode. The reason for this behaviour may be understood more clearly by assuming the presence of surface and near states in the polymer. Figure 4 shows the range of electrons in FEP type A, as has been reported by Gross *et al* (1974). The average range of electrons having energies below 15 keV lies below 2  $\mu\text{m}$ . It is felt that the centroid of electrons of energies below and around 15 keV get trapped in the surface and near surface traps. In fact such surface traps in electron irradiated FEP have been detected at and around 1.8  $\mu\text{m}$  by Seggern (1979) in his TSC measurements. The result therefore seems to be less speculative. Similar surface traps ranging between 0 to 4 eV have been measured by Murata (1979) while studying the photoelectric emission

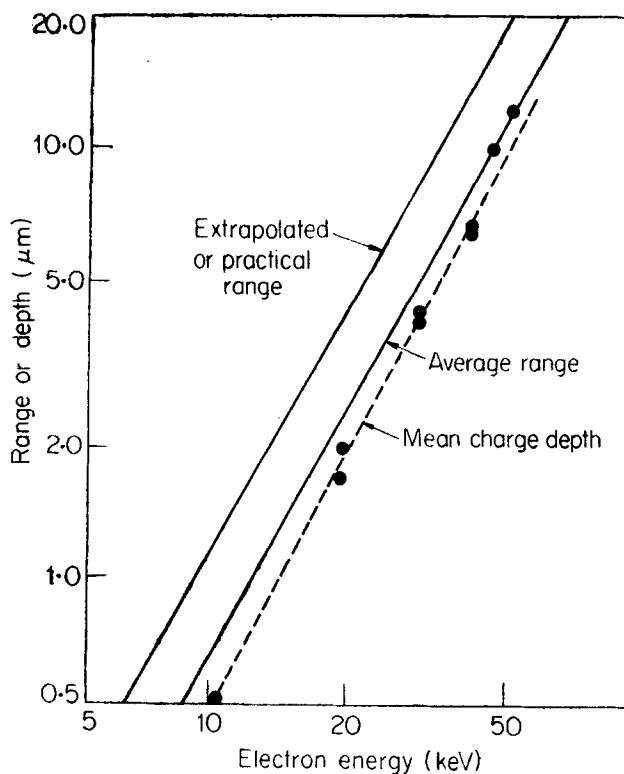


Figure 4. Range of electrons compared with mean charge depth in teflon FEP (type A) (Gross 1974)

from several irradiated polymers. The possibility of distribution of surface states may be due to the non-uniform structure of the spatial arrangement as well as the adsorbed gaseous layers in the polymer.

It is difficult to describe the nature of the surface and near surface traps. These traps can be caused by chemical impurities, oxidation products, broken chains and absorbed molecules. The detected surface and near surface traps in the range of 0-1.5  $\mu\text{m}$  can be caused by known effects during the history of the foil (Seggern 1979). For example it is known that an applied strain to the foil creates dislocations in PTFE. These dislocations can change the crystalline character of the material and allow impurities to penetrate deeper into the polymer. Even oxidation and other chemical reactions can occur in deeper regions.

It seems, therefore, highly probable for electrons ranging within the spatial depth of near surface states to get trapped in the surface traps. The trapping in these states becomes less probable as the range of the incident electrons increases beyond this spatial depth. Indirectly this experiment thus gives an idea about the spatial depth of the near surface states in FEP which comes out to be roughly 2.0  $\mu\text{m}$  corresponding to range of 18 keV electrons.

### 3. Activation kinetics

The peak temperature in TSC and the activation energies corresponding to the different peaks, the total stored charge under the peak, and the relaxation time at the room temperature are calculated from the experimental data and listed in table 1.

Table 1. Activation kinetics calculated from figure 3.

Beam energy keV	Peak No.	Peak temp. $T_m$ $^{\circ}\text{C}$	Activation energy eV	Charge released coulomb $Q \times 10^{-12}$	No. of charge carriers N $\times 10^7$	Relaxation time at R.T. sec.
3	1	41	0.26	20.81	12.99	952.00
	2	83	1.32	70.43	43.96	$49.82 \times 10^4$
	3	106	2.39	30.41	18.98	$33.56 \times 10^9$
6	1	41	0.33	19.21	11.99	850.76
	2	72	1.44	1.60	00.99	$215.04 \times 10^3$
	3	85	0.50	57.62	35.90	$1009.24 \times 10^1$
	4	107	1.09	43.22	26.97	$1546.60 \times 10^4$
	5	196	1.27	605.10	377.71	$314.00 \times 10^3$
9	1	61	0.18	32.01	19.98	$202.00 \times 10^1$
	2	85	1.16	192.09	119.90	$293.60 \times 10^{-3}$
	3	93	0.96	144.07	89.93	$18.80 \times 10^{-1}$
12	1	67	0.20	43.54	27.17	$235.60 \times 10^1$
	2	85	2.23	7.04	4.39	$1311.00 \times 10^5$
	3	95	0.68	16.52	10.31	116.00
	4	124	1.08	80.55	50.28	$675.60 \times 10^4$
	5	204	1.25	181.40	113.23	$201.33 \times 10^8$
15	1	75	0.55	111.41	69.54	$707.40 \times 10^1$
	2	104	2.79	6.40	3.99	$331.20 \times 10^9$
18	1	32	1.91	4258.13	2658.01	273.00
	2	45	1.58	640.32	399.70	$384.80 \times 10^1$
24	1	32	0.61	16.00	9.99	664.20
30	1	28	0.29	22.92	14.30	535.00



Peak cleaning experiments were carried out wherever it was found necessary for isolating the multiple current peaks. We found five dominant groups of trapping levels:  $0.25 \pm 0.08$  eV,  $0.57 \pm 0.10$  eV,  $1.07 \pm 0.1$  eV,  $1.33 \pm 0.25$  eV,  $2.33 \pm 0.4$  eV. This classification was made by taking the average value of all those levels which lie close to each other. The number of peaks reduces as one reaches higher electron energies. The shape of the individual peak was assumed to be Gaussian for those which were not symmetric to the superposition. The highest total charge under the peak is observed for film irradiated at an energy of 18 keV. The results indicate that the available trapping sites inside the bulk of the polymer are less as compared to the surface regions. The single peak obtained for irradiated energies of 18, 24 and 30 keV occurs around 30°C. Experiments are in progress to further investigate these surface traps.

### Acknowledgements

The authors wish to thank Professors M R Bhiday and A S Nigavekar for providing the encouragement and necessary facilities. Thanks are due to the Council of Scientific and Industrial Research, New Delhi for financial assistance. SJW and JPJ are thankful to the University Grants Commission, New Delhi for fellowships.

### References

- Birks J B 1960 *Progress in dielectrics* (London: Heywood and Company) Vol. 2, p. 58  
Bucci C and Fieschi R 1966 *Phys. Rev.* **148** 816  
Cowie J M G 1973 *Polymers: chemistry and physics of modern materials* (London: Billing and Sons)  
Creswell R A and Perlman M M 1970 *J. Appl. Phys.* **41** 2365  
D'Ilario L and Giglio E 1974 *Acta Crystallogr.* **B30** 372  
Garlick G F J and Gibson A F 1948 *Proc. Phys. Soc. (London)* **60** 574  
Gross B, Sessler G M and West J E 1974 *J. Appl. Phys.* **45** 2841  
Jog J P, Ogale S B, Walzade S J, Ogale A S, Bhoraskar S V, Bhiday M R and Bhoraskar V N 1980 *Pramana* **14** 343  
Jog J P, Walzade S J and Bhoraskar S V 1979 *Nucl. Phys. Solid State Phys. Symp.* (Madras)  
Murata Y 1979 *Jpn. J. Appl. Phys.* **18** 1  
Murphy P V and Fraim F W 1968 *J. Audio Eng. Soc.* **16** 458  
Perlman M M and Reedyk C W 1968 *J. Electrochem. Soc.* **115** 45  
Perlman M M 1971 *J. Appl. Phys.* **42** 2645  
Reiser A, Lock M W B and Knight J 1969 *Trans. Faraday. Soc.* **65** 2168  
Seggern H V 1979 *J. Appl. Phys.* **50** 2817  
Seiwatz H and Brophy J J 1965 Annual Report, Conference on Electrical Insulation (unpublished)  
Sessler G M and West J E 1962 *J. Acoust. Soc. Am.* **34** 1787  
Sessler G M and West J E 1968 *J. Electrochem. Soc.* **115** 836  
Turnhout J V 1975 *Thermally stimulated discharge of polymer electrets*, (Amsterdam: Elsevier)  
Tyler R W, Webb J H and York W C 1955 *J. Appl. Phys.* **26** 61  
Walzade S J, Jog J P and Bhoraskar S V 1978 *Nucl. Phys. Solid State Phys. Symp.* (Bombay) **C21**  
708