Thermally stimulated discharge currents in poly(vinyl alcohol) thermoelectrets

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(Received 20 August 1979)

The depolarization currents in poly(vinyl alcohol) thermoelectrets have been measured by thermally stimulated discharge (t.s.d.) current techniques. The polarization is found to be uniform. The activation energy and the relaxation time have been calculated under different polarizing conditions. The formation of heterocharge is explained by dipole alignment and migration of charge over microscopic distances with trapping.

INTRODUCTION

When a dielectric material is subjected to simultaneous application of an electric field and thermal radiation, it develops electric charges of opposite sign on its sides. Such a polarized sample is known as a *Thermoelectret*. The polarization thus obtained in the dielectric is found to decay with time. At room temperature, the decay progresses rather slowly. However, it can be stimulated by heating the electret: the stored charge is released, and the discharge current thus produced can be measured as a function of temperature to obtain a 'current glow peak'. This is a 'thermally stimulated discharge' (t.s.d.) method and has been used by many investigators[1–5] for quantitative analysis of the electret effect.

In t.s.d. current measurements, the spectrum may consist of one or more glow peaks. A single glow peak in the thermal spectrum of shellac wax electrets has been reported by Pillai *et al*[5]. For PVC (SR_{11}) electrets[6], the t.s.d. spectrum consists of two distinct peaks. Perlman[1] has reported a more complex spectrum for carnauba wax electrets, which consist of three overlapping peaks. The peaks can be isolated by the 'peak cleaning method' as applied by Perlman and Creswell[7].

Bucci and Fieschi[8] have developed a theory to account for these peaks when they are due to a uniform dipole orientation. The peak temperature (T_M) at which the maximum current occurs is independent of the polarizing field and temperature, but varies for space-charge. Turnhout[9] has observed that the peak positions are independent of the polarizing field, temperature and time but are dependent strongly on the heating rate. He found that a shift in the peak position to higher or lower temperature depends on the increase or decrease in the heating rate.

The t.s.d. method allows precise analysis of a single relaxation process and enables determination of the dipolar relaxation time and activation energy. The total charge stored should increase linearly with the applied field for uniform polarization and non-linearly for space-charge.

THEORY

Bucci and Fieschi's[8] dipolar theory for ionic thermocurrents has been generalized by Perlman[1], Turnhout[9] and Gross[10]. Following Perlman[1], the theory relevant to the experiments is briefly given.

A dielectric polarized in the electric field E_p and temperature T_p develops an initial polarization P_0. At any instant, the rate of decay of polarization P with time can be expressed as:

$$\mathrm{d}P/\mathrm{d}t = -P/\tau \tag{1}$$

where τ is the relaxation time which is a function of temperature. From equation (1), the P is given by:

$$P = P_0 \exp\left[-\int(\mathrm{d}t/\tau)\right] \tag{2}$$

For freely rotating dipoles, P_0 is given by the Langevin function. When $\mu E_p << kT_p$, P_0 can be expressed as:

$$P_0 = (N\mu^2 E_p)/(3kT_p) \tag{3}$$

where N is the dipole concentration, μ is the dipole moment and k is Boltzmann's constant.

The discharge current J is the rate of change of polarization:

$$J = -(P_0/\tau)\exp\left[-\int(\mathrm{d}t/\tau)\right] \tag{4}$$

For dipolar relaxation, the dielectric loss is maximum at the resonance frequency, the reciprocal of which is the relaxation time τ given by:

$$\tau = \tau_0 \exp\left(\frac{U}{kT}\right) \tag{5}$$

where τ_0 is a constant and U is the activation energy. The uniform heating rate of the dielectric may be expressed as:

$$T = A + Bt \tag{6}$$

where A and B are costants.

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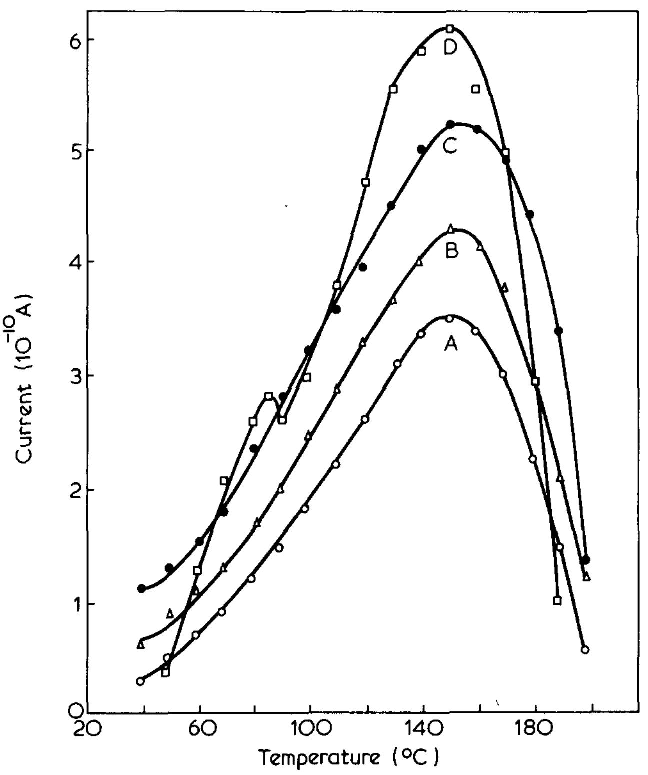

Figure 1 Discharge current *versus* temperature. A, E_p = 6 kv cm^{-1}; B, E_p = 8 kV cm^{-1}; C, E_p = 10 kV cm^{-1}; D, E_p = 12 kV cm^{-1}

Combining equations (3)–(6), J may be expressed as:

$$J(T) = \frac{N\mu^2 E_p}{3kT_p\tau_0} \exp\left[-\frac{U}{kT} - \frac{1}{B\tau_0}\int_{T_0}^{T} \exp\left(-\frac{U}{kT}\right) \mathrm{d}T\right] \quad (7)$$

On differentiating equation (7), the temperature T_M at which the maximum current flows can be written as:

$$\tau_0 = (kT_M^2)/[BU \exp\,(U/kT_M)] \quad (8)$$

The low temperature tail of equation (7) may be written as:

$$\ln J(T) = \text{constant} - U/kT \quad (9)$$

U may be determined from a semi-log plot of $J(T)$ *versus* $1/T$: this is the 'initial rise method' of Garlick and Gibson[11]. Using this value of U and equations (5) and (8), the value of τ at T_M and at room temperature, say 300K, may be calculated.

The activation energy and relaxation time can also be determined using Bucci's[8] whole curve method.

From equation (5), one may write:

$$\ln\tau = \ln\tau_0 + U/kT \quad (10)$$

which gives:

$$\tau = \frac{\int_{t(T)}^{\infty} J(t')\mathrm{d}t'}{J(T)} \quad (11)$$

The integral in equation (11) can be estimated accurately by graphically integrating the curve. A plot of ln τ *versus* $1/T$ should be a straight line if a uniform process is operative. The slope and intercept of this line determine U and τ_0.

EXPERIMENTAL

In the present investigations, the t.s.d. technique has been used to calculate the activation energy and relaxation time for poly(vinyl alcohol) thermoelectrets. Samples of poly (vinyl alcohol) were taken as solid slabs of 1 cm^2 cross-sectional area and 1 mm thickness. The sample holder consisted of two brass electrodes. A thin mica sheet with a 1 x 1 cm cavity at its centre to hold the sample was fixed on one of these brass plates. Thermoelectrets were prepared by applying an electric field of 10 kV cm^{-1} and temperatures varying from 140–185°C with 2 h polarizing time to these samples, for a run of experiments. For another set of experiments, the polarizing temperature was kept constant at 160°C for 2 h polarizing time and electric fields of 6, 8, 10 and 12 kV cm^{-1} were applied.

For all these polarized samples, the t.s.d. current measurements were taken using a Keithley electrometer 610 C. The electrets were heated at a constant heating rate of 1°C min^{-1} and the currents were measured from room temperature to a temperature well above the polarizing temperature.

RESULTS

Figure 1 shows the thermal current spectra for four samples prepared at 160°C for 2 h polarizing time and for polarizing fields varying from 6–12 kV cm^{-1}. The spectrum consists of a sharp peak corresponding to a peak temperature T_M around 151°C. When the polarizing field is 12 kV cm^{-1}, a small additional peak at 85°C is also observed. The peak positions are found to be independent of the polarizing field strength. The slight shift in the position of the peaks may be due to small variations in the heating rate. In *Figure 2*, the peak current I_m and the total charge released during the depolarization of the samples are plotted as a function of the polarizing field. The peak current and the charge released are proportional to the polarizing field within the experimental range.

In *Figure 3*, the depolarization current is plotted *versus* temperature for samples prepared at different polarizing temperatures and for fixed values of electric field and polarizing time. When T_p is 140° and 160°C, the spectrum consists of a single peak. However, for poly(vinyl alcohol) samples polarized at 185°C, the spectrum has two peaks corresponding to 85° and 150°C.

For the determination of activation energy and relaxation time using the initial rise method of Garlick and Gibson[11], ln $J(T)$ *versus* $1/T$ is plotted in *Figure 4*. The activation energy is calculated making use of equation (9). The relaxation time at T_M and at 27°C is calculated using equation (5).

Figure 5 shows a plot of ln (charge/current) *versus* $1/T$. The activation energy and the relaxation time are calculated using Bucci's[8] whole curve method, from the slopes and the intercepts of the lines. The results are summarized in *Table 1*.

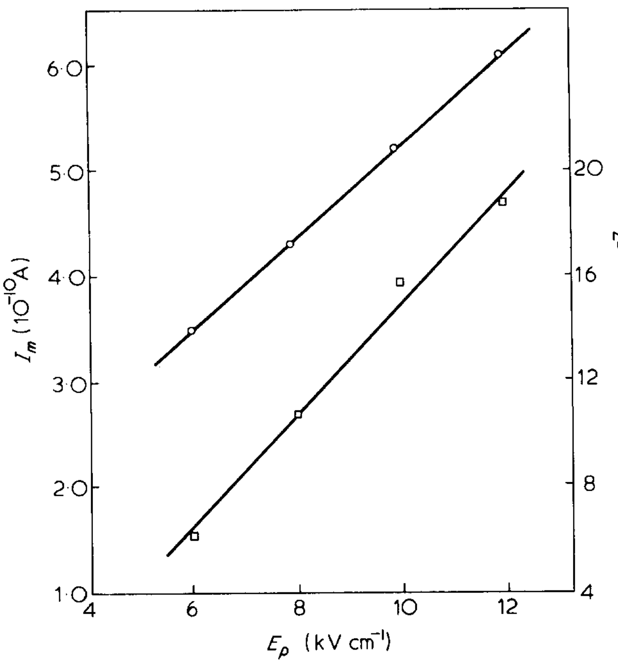

Figure 2 Peak current *versus* polarizing field, ○; total charge released *versus* polarizing field, □

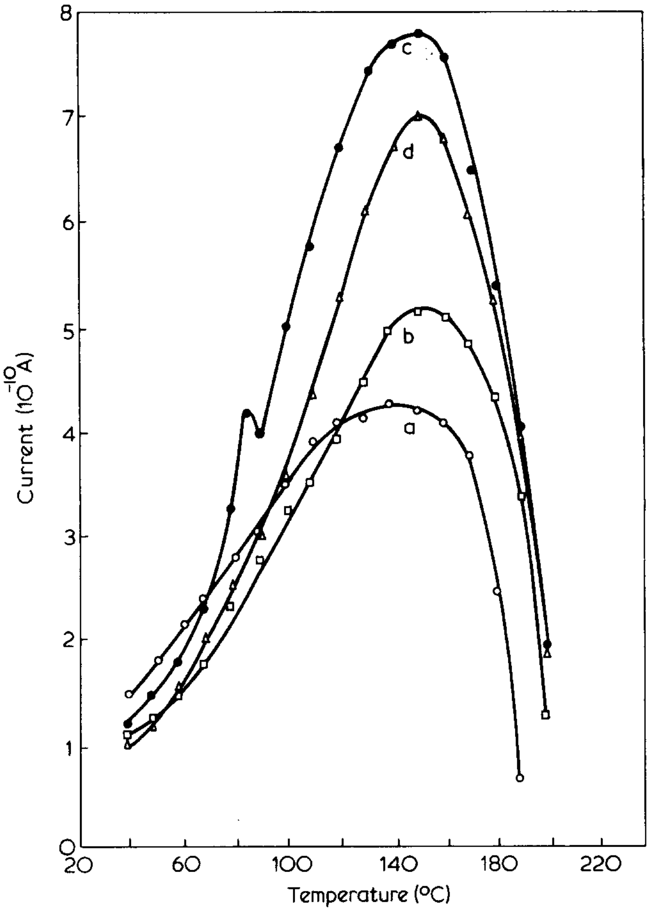

Figure 3 Discharge current *versus* temperature. a, T_p = 140°C, t_p = 2 h; b, T_p = 160°C, t_p = 2 h; c, T_p = 185°C, t_p = 2 h; d, T_p = 160°C, t_p = 3 h

DISCUSSION

According to the two charge theory of electrets of Gross[12], the electret homocharge is due to transfer of charges across the electrode–dielectric interface during the polarization process. The heterocharge is known to be an internal volume effect. A non-uniform volume polarization may be attributed to the space-charge build-up associated with the migration of ions inside the dielectric over macroscopic distances, or charge injection from the electrodes. A uniform polarization is understood generally to be due to the dipole alignment and/or migration of charge over microscopic distances with trapping.

The current and charge measurements indicate that the polarization in poly(vinyl alcohol) thermoelectets is uniform. Therefore, the heterocharge cannot result from space-charge due to charge injection from the electrodes or macroscopic ion displacement. However, at the glass-transition temperature, interatomic restraints are reduced sufficiently to permit a non-elastic displacement of neighbouring molecules under an applied electric stress. This may be the reason for a small current peak around 85°C in the current spectrum. The most plausible mechanism responsible for the heterocharge is alignment of dipoles. At the same time, even the complete alignment

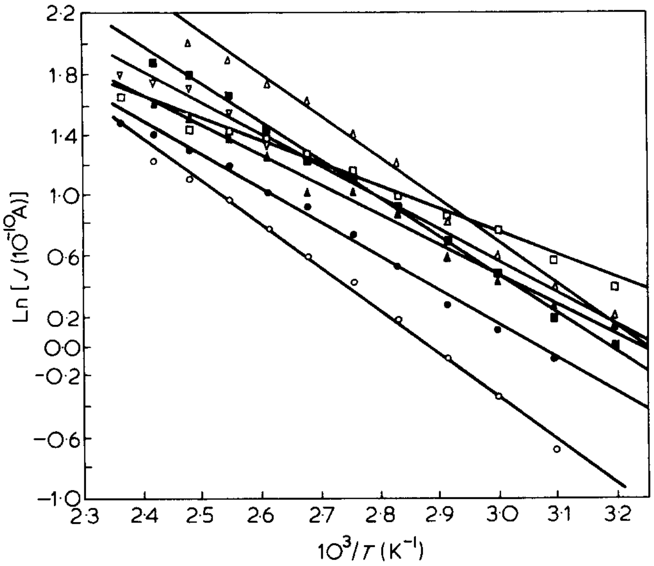

Figure 4 Ln *J(T) versus* 1/*T*. ○, A; □, a; ●, B; ▲, C, b; △, c; △, D; ■, d

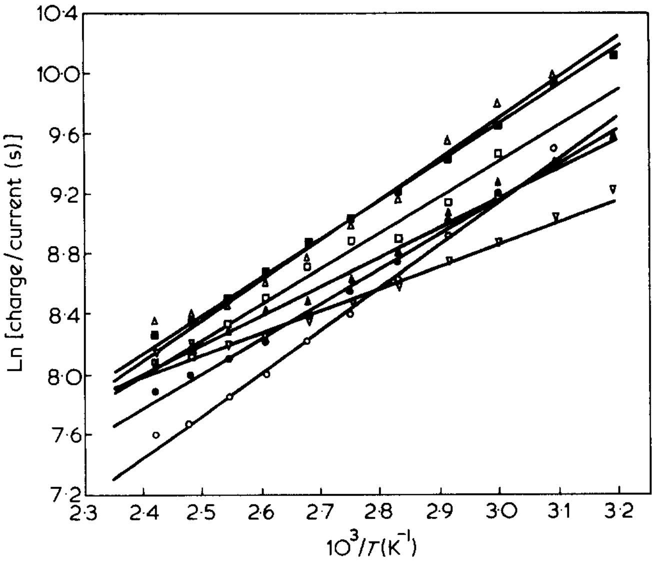

Figure 5 Ln charge/current *versus* 1/*T*. ○, A; △, a; ●, B; ▲, C, b; △, c; □, D; ■, d

Table 1 Summary of results obtained from poly(vinyl alcohol) thermoelectrets

Polarizing time (h)	2.0	2.0	2.0	2.0	2.0	2.0	3.0
Polarizing temperature (°C)	160	160	160	160	140	185	160
Polarizing field (kV cm^{-1})	6	8	10	12	10	10	10
Peak temperature (°C)	150	152	154	150	144	150	152
Peak current, I_m ($\times 10^{-10}$ A)	3.5	4.3	5.2	6.1	4.3	7.8	7.0
Garlick's initial rise method							
Activation energy, U ($\times 10^{-1}$ eV)	2.49	1.69	1.69	1.82	1.29	2.40	2.09
τ_0 (s)	3.99	54.74	55.26	34.28	187.21	5.36	14.94
Relaxation time corresponding to $T = T_M$ ($\times 10^{-3}$ s)	3.71	5.52	5.56	5.07	6.92	3.85	4.47
Relaxation time corresponding to T = 300K ($\times 10^{4}$ s)	6.12	3.78	3.91	3.94	2.83	5.72	4.81
Bucci's whole curve method							
Total charge ($\times 10^{-7}$ C)	6.29	10.80	15.80	18.90	15.00	32.40	25.60
Activation energy, U ($\times 10^{-1}$ eV)	2.45	2.02	1.69	2.07	1.25	2.24	2.28
τ_0 ($\times 10^{-2}$ s)	5.39	9.25	13.66	11.47	16.19	10.96	11.88
Relaxation time corresponding to T = 300K ($\times 10^{6}$ s)	6.96	2.28	0.94	3.40	0.21	6.36	7.97

of dipoles may not be sufficient to produce the observed charge. Therefore, it is suggested that, in addition to the dipole alignment, the heterocharge is due to the thermal excitation of the trapped charge carriers. A distribution of localized energy levels or charge traps exists in the polymer. The trapped carriers are excited thermally and contribute to electrical conduction. Under the effect of local fields, these charge carriers migrate over microscopic distances and are recaptured. If the recapture time is small in comparison to the lifetime in traps, the rate of decay of polarization or the current density depends on the rate of release from the traps. Under these conditions, the thermal current may also be represented as in equation (7).

ACKNOWLEDGEMENT

RS gratefully acknowledges financial assistance given by U. G. C., India.

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