Thermally stimulated discharge currents in poly(vinyl formal) films

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Thermally stimulated discharge currents (t.s.d.c.) of pure poly(vinyl formal) films of thickness 42.5 μm grown by the solution growth technique have been studied as a function of polarizing field and polarizing temperature. The temperature corresponding to a peak in t.s.d.c. is found to be independent of polarizing field but dependent on the polarizing temperature. Activation energies and relaxation parameters are evaluated.

(Keywords: poly(vinyl formal) films; t.s.d.c.)

INTRODUCTION

Thermally stimulated discharge current (t.s.d.c.)[1,2] studies in electret materials give information about the charge storage mechanism. Charge storage may be due to either dipolar orientation or space charge. In polar materials the main contribution is due to orientation of aligned dipoles, whereas in non-polar materials it is due to space charge. Hence in the present investigations, an attempt has been made to study the charge storage mechanism in a weakly polar substance (poly(vinyl formal)). A detailed study of the t.s.d.c. on poly(vinyl formal) films as a function of polarizing field strengths and polarizing temperatures was made and is reported here.

EXPERIMENTAL

Pure poly(vinyl formal) films of thickness 42.5 μm were grown by the solution growth technique[3], which involved the isothermal immersion of the substrate in the polymer solution. A 10% (by volume) poly(vinyl formal) solution was prepared by dissolving 5 g of poly(vinyl formal) in 50 cm^3 of the solvent. The solvent was a mixture of benzene and ethanol in the ratio 3:2. The pure poly(vinyl formal) films were grown on thoroughly cleaned aluminium substrates. They were dried in an oven for about 48 h at a temperature well below the softening temperature. The thickness of the films in the present investigations was measured by using a semi-micro balance (Mettler H51AR). It was checked by the capacitance measurement method by assuming the dielectric constant[4] of poly(vinyl formal). The measurements made by each method were found to be in good agreement.

The t.s.d.c's were studied in these polymer films in the sandwich configuration. The substrate itself acted as one of the electrodes and another aluminium electrode of area 1 cm^2 was pressed against the polymer films, with the help of a screw. Sufficient care was taken to keep the same amount of pressure on the films for all measurements. The films were polarized in a thermostat at different polarizing temperatures (T_p) of 304, 336 and 367 K by using 2, 6, 10 and 14 V batteries for a constant period of poling time, 4.2×10^3 s. After that the films were cooled to room temperature slowly, with the polarizing field kept on. Then the electret was short circuited to remove any stray surface charges. The t.s.d.c. spectra were measured while keeping the electret in an evacuated shielded assembly and the output was fed into an ECIL EA 815 Electrometer amplifier. The electrets were heated to a temperature of 400 K at constant heating rate (β) of 0.08 K s^{-1}.

A guard ring was also used around the top electrode to study whether it had any effect. But within the experimental limits, it was found to have no effect on the t.s.d.c. measurements.

RESULTS

The t.s.d.c. spectra for poly(vinyl formal) films poled at 367 K for different polarizing fields (E_p) are shown in *Figure 1*. For a given polarizing temperature, the temperature corresponding to the t.s.d.c. peaks is independent of polarizing field strength, but the maximum current and charge associated with them are found to increase with the increase in field strength. The temperature at which the t.s.d.c. vanishes is found to be in the range 385 K–395 K.

Figure 2 shows the t.s.d.c. spectra for a given field strength of 3.29 kV/cm and different polarizing temperatures. It is found that the temperature corresponding to the peak current shifts from 356 K to 385 K as the polarizing temperature increases from 304 K to 367 K. The maximum currents and the charge associated with them are seen to increase with the increase in polarizing temperature. It is also found that the rate of fall of t.s.d.c. after reaching the peak current as a function of increase in temperature is more rapid with the increase in polarizing temperature.

Figures 3 and *4* indicate the variation of maximum peak current and the charge released, respectively, as a function of polarizing field for an electret polarized at three different temperatures.

To understand the mechanism responsible for the t.s.d.c., spectra were analysed in terms of the existing theory of the initial-rise method[5]. In *Figure 5* the variation

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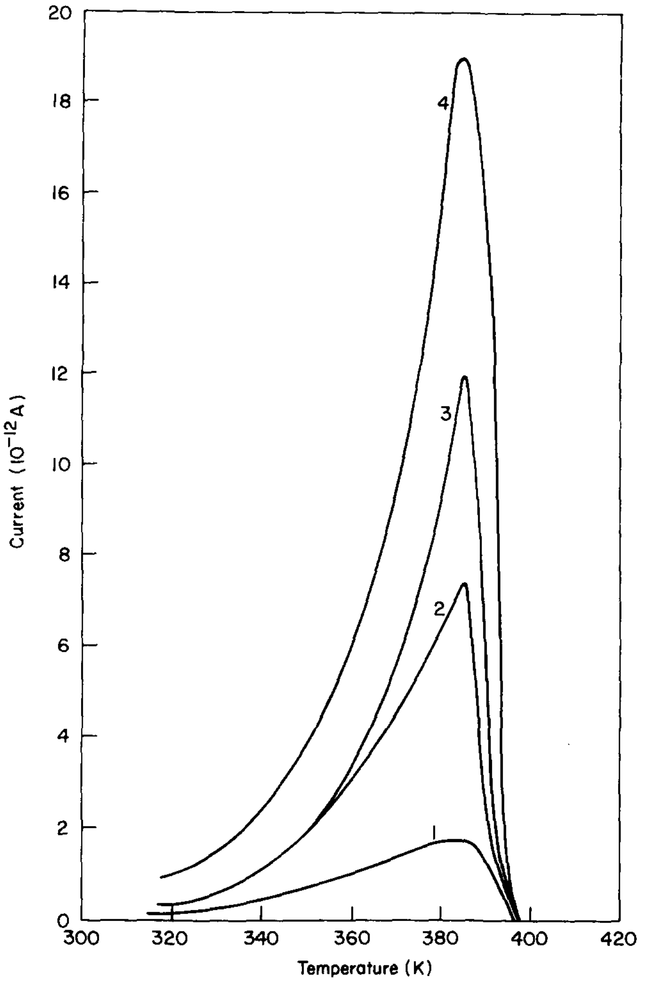

Figure 1 T.s.d.c. spectra of poly(vinyl formal) films polarized at 367 K by using field strengths of (1) 0.47 kV/cm, (2) 1.41 kV/cm, (3) 2.35 kV/cm and (4) 3.29 kV/cm with $\beta = 0.08$ K s^{-1}

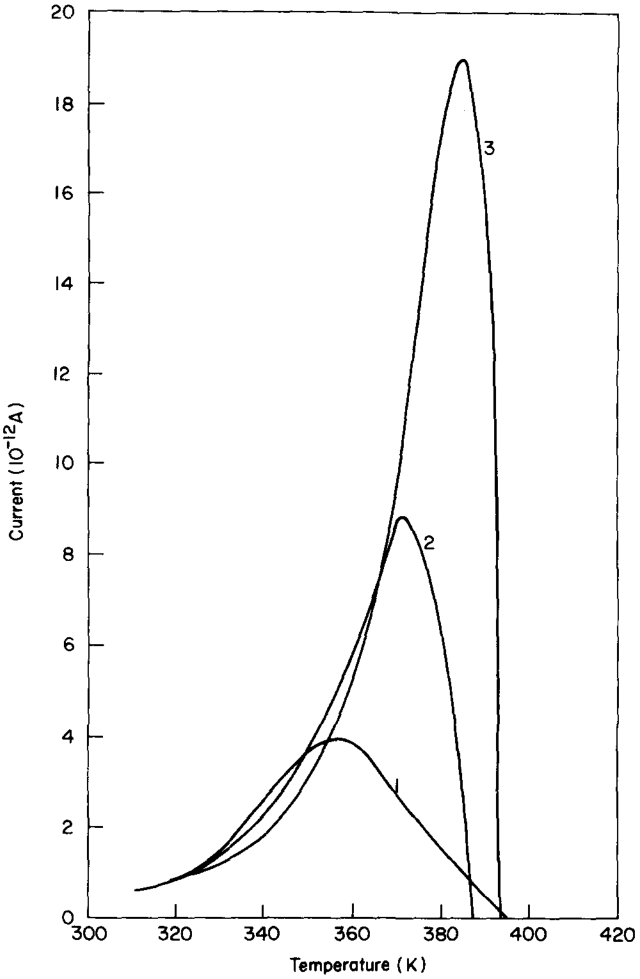

Figure 2 T.s.d.c. spectra of poly(vinyl formal) films polarized at (1) 304 K, (2) 336 K and (3) 367 K by using field strength of 3.29 kV/cm with $\beta = 0.08$ K s^{-1}

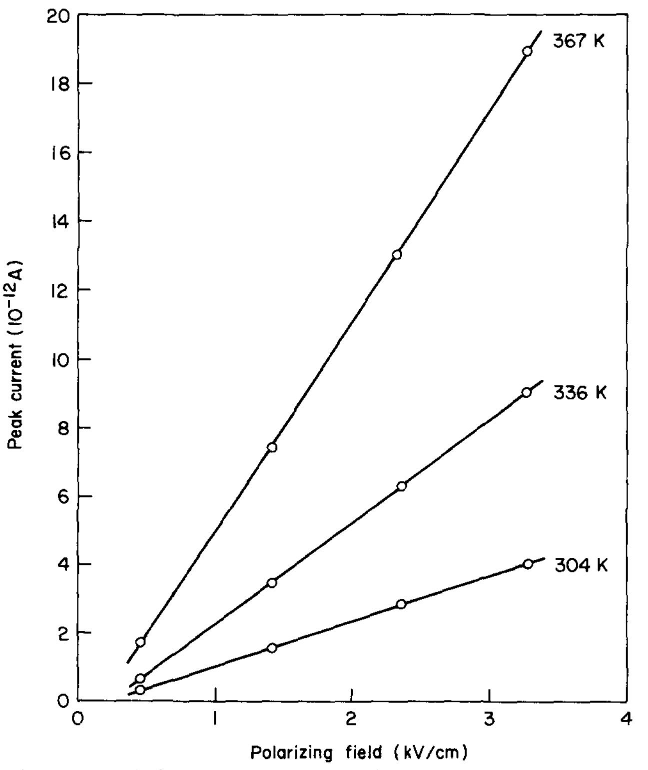

Figure 3 Variation of the peak current of t.s.d.c. spectra as a function of polarized field strengths for an electret polarized at different temperatures with $\beta = 0.08$ K s^{-1}

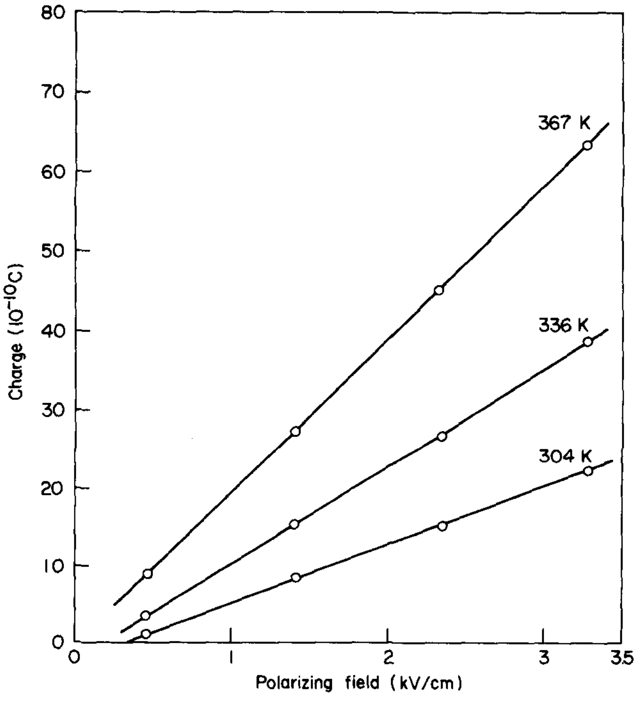

Figure 4 Variation of the charge released as a function of polarized field strength for an electret polarized at different temperatures, T_p, with $\beta = 0.08$ K s^{-1}

of log $I(T)$ values from the initial rise of the peak as a function of $1000/T$ for an electret polarized at 367 K is shown. From the slopes of the graphs, the activation energies are evaluated. From the values of the activation energies, the characteristic relaxation times τ_0, τ_{300} and τ_m are evaluated and represented in *Table 1*. By using Bucci–Fieschi theory[6], which involves the whole-curve method, the log of (remaining charge/current) on the electret as a function of inverse temperature for an electret polarized at 367 K with polarizing field 3.29 kV/cm is also shown in *Figure 5*. Activation energies evaluated by using this modified theory are also summarized in *Table 1*. The parameters evaluated by each theory are found to be fairly in good agreement.

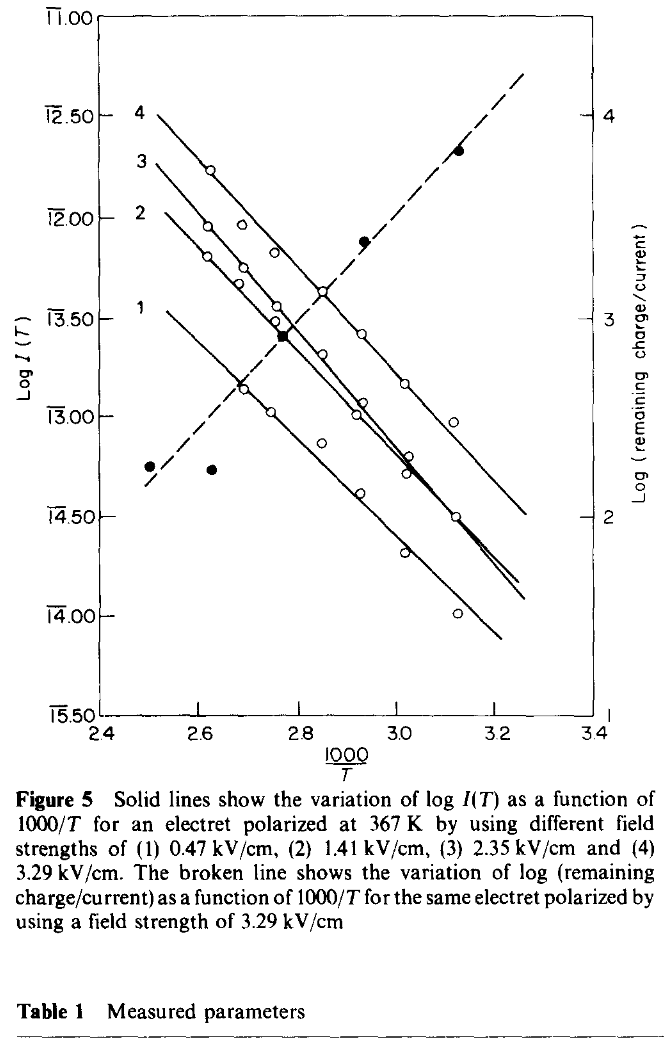

Figure 5 Solid lines show the variation of log $I(T)$ as a function of $1000/T$ for an electret polarized at 367 K by using different field strengths of (1) 0.47 kV/cm, (2) 1.41 kV/cm, (3) 2.35 kV/cm and (4) 3.29 kV/cm. The broken line shows the variation of log (remaining charge/current) as a function of $1000/T$ for the same electret polarized by using a field strength of 3.29 kV/cm

DISCUSSION

According to Pearlman[7], the t.s.d.c. peaks have the same temperature dependence if the polarization is uniform and is either due to a dipolar orientation process or migration of charge carriers through microscopic distances with subsequent trapping. Also, in both of the cases the temperature corresponding to the maximum current is independent of polarizing field strength and polarizing temperature, but varies for space charge. In the present investigations, the shape of the t.s.d.c. spectra of poly(vinyl formal) suggest that either or both of these mechanisms may be at work. But the peak temperature is independent of polarizing field strength and strongly depends on the polarizing temperature. The charge associated with the electrets varies linearly with the polarizing field strength, indicating that a uniform polarization process is operative in the present investigations. This is further supported by the linear dependence of the peak current on the polarizing field strength.

The peak temperatures of t.s.d.c. spectra are found to be in the range 356 K–385 K. The possibility of attributing[8] the observed charge in the electret to the glass transition (glass transition temperature of poly(vinyl formal) is 378 K) is ruled out because no depolarization current was observed in the unpolarized specimens on heating. Also, previously depolarized specimens did not give currents corresponding to the peak on reheating, indicating that the dipolar orientation process is responsible for the t.s.d.c. spectra. But the dependence of peak temperature on polarizing temperature suggests that there may be some contribution from the migration of charge carriers through microscopic distances. But this is not due to the charge injected from the electrodes, since bulk-limited conduction was observed[9] in poly(vinyl formal) films in the entire temperature range of present study.

The activation energies evaluated by both methods (initial-rise method 0.49 ± 0.04 eV and Bucci–Fieschi method 0.58 ± 0.02 eV) are in fairly good agreement and of the same order as that of the energy required for molecular motion from one equilibrium to another in high molecular weight polymers[10]. This value of activation energy is also very small compared to the 1 eV typically required for the movement of ions[11]: hence the simultaneous action of the dipolar orientation process due to the alignment of dipolar molecules attached to the main polymer chain along with the migration of

Table 1 Measured parameters

Temperature of polarization (K)	Polarizing field (kV/cm)	Peak temperature (K)	Peak current (10^{-12} A)	Activation energy (eV)	Relaxation parameters τ_m (10^2 s)	τ_0 (10^{-4} s)	τ_{300} (10^4 s)	Total charge (10^{-10} C)	Activation energy from Bucci–Fieschi method (eV)
304	0.47	356	0.25	0.46	3.06	1.48	0.45	0.94	0.59
304	1.41	356	1.55	0.46	3.06	1.48	0.45	6.87	0.59
304	2.35	356	3.40	0.46	3.06	1.48	0.45	17.81	0.59
304	3.29	356	4.00	0.46	3.06	1.48	0.45	22.50	0.50
336	0.47	370	0.63	0.46	3.30	2.80	0.86	3.12	0.59
336	1.41	370	3.00	0.46	3.30	2.80	0.86	13.12	0.59
336	2.35	370	7.10	0.46	3.30	2.80	0.86	23.12	0.59
336	3.29	370	9.00	0.46	3.30	2.80	0.86	39.37	0.59
367	0.47	385	1.75	0.46	3.58	5.21	1.62	8.75	0.59
367	1.41	385	7.50	0.55	2.92	0.21	2.76	27.50	0.59
367	2.35	385	12.00	0.59	2.68	0.04	3.89	32.50	0.59
367	3.29	385	19.00	0.59	2.68	0.04	3.89	63.75	0.59

electrons/holes released from the valence band through microscopic distances with subsequent trapping. The opposite charge carriers in the trap may form dipoles and may contribute to the t.s.d.c. spectra[12].

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