Space Charge Limited Currents and Trap Distribution in PVC Stabilized with Lead Stearate

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The current-voltage characteristics at different temperatures had been studied for PVC stabilized with lead stearate. At low voltages, Ohm's law is seen to be followed, while at high voltages space-charge-limited current was observed. The obtained results were interpreted in terms of a Schottky emission type of conduction operating over the temperature range studied. By using an analytical method the density of states is calculated.

Keywords: Current-voltage relationship; PVC; temperature effect; trap distribution

INTRODUCTION

Oriented fibers of commercial polyvinyl chloride crystallize in an orthorhombic unit cell (space group Pc am) with *a*-, *b*- and *c*- dimensions 10.6, 5.4 and 5.1°A respectively [1]. There are two chains per unit cell which are syndiotactic in the planar zigzag confirmation [2]. A lack of order was found in the *c*-direction [3]. Apart from the uncertainties with respect to crystallinity, indications have been found for the formation of a so called mesophase in the non-crystalline regions

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of PVC [2]. Some specific interactions of the chlorine atoms are though [3] to be on the basis of this additional structural order, but the exact origin and corresponding molecular structure are still not well understood.

Lead salts are used primarily in the stabilization of flexible PVC compounds used as electrical insulation over wire. They are also employed to some extent in expanded flexible PVC sheets, certain other opaque non-electrical compositions, are beginning to be employed in the stabilization of rigid, industrial profiles, *etc*. Generally, the increase use of lead salts as stabilizers for the preventions of dischlorination and cracking in rigid PVC during its hydrochlorination at 150–200°C was revised by Heine [4]. Lead stearate is used [5], mainly in conjugation with other salts, but its action appears to be largely that of a lubricant [5].

$$(CH_3(CH_2)_{16}COO)_2Pb + 2HCl \longrightarrow PbCl_2 + 2CH_3(CH_2)_{16}COOH$$
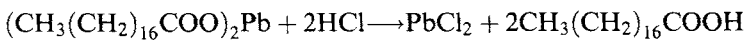
The aim of the present work is to study the space-charge-limited-current (SCLC) and trap distribution in PVC stabilized with lead sterate to obtain information about the energy distribution of states.

EXPERIMENTAL

Polyvinyl chloride (PVC) used in the present work was obtained from Polymer Laboratories Ltd., with average molecular weight $M_W = 2 \times 10^5$. The polymer and 10 wt.% of the stabilizer (lead sterate) were mixed together in a small container and molted in an electric furnace. The melt is filled up in the space between the silver (aluminum or gold) coated brass electrodes of diameter 10 mm. The distance between the electrodes was 0.1 mm. For the measurements of the thermally stimulated discharge current (TSDC), the sample was polarized at temperature 373 K for 1 hr with the application of different polarizing fields, and cooled down to room temperature under the same conditions. The sample was then held in the short circuit state for 30 min to clear the parasitic charge. The depletion current was then measured upon heating at 1 k/min to temperature above T_P. The current was measured with Keithly 614 C electrometer.

RESULTS AND DISCUSSION

Typical space charge limited current (SCLC) characteristics at different temperatures for PVC stabilized with lead sterate are reported in Figure 1 in the form of log I – log V. The figure exhibits two regions: a small ohmic region at low electric fields where I is proportional to V, and a SCLC region where I is proportional to $V^{2.7}$. The ohmic behavior can be understood on the basis of the reasonable assumption that, at low voltages, there is a negligible injection of carriers from the electrode and the initial current is governed by the intrinsic free carriers in the material. The current will be ohmic until the injected free carriers density becomes comparable with the thermally generated carrier density. SCLC sets in that voltage for which the intrinsic current equals to the SCLC. On the other hand, the current in the second region cannot be described on the basis of the trap filled limited current (TFLC), because the present samples have a slightly high thickness.

The observed variation between the current and the square root of the applied voltage, Figure 2, suggests a conduction mechanism in which charge carriers are released by thermal activation over a
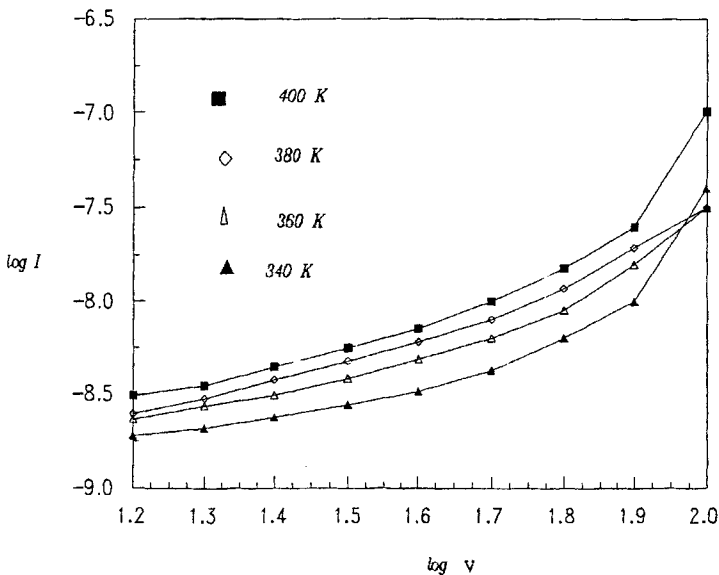
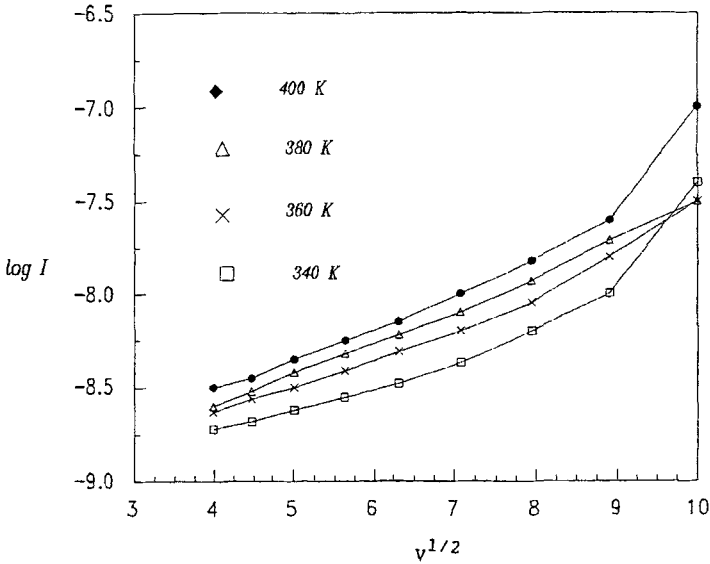FIGURE 1   Typical log I vs. log V curves for stabilized PVC at different temperatures.

FIGURE 2 Plots of log I vs. $V^{1/2}$ for PVC stabilized with lead sterate at different temperatures.

coloumbic potential barrier that is decreased by the applied electric field. The physical nature of such a potential barrier can be interpreted in two basic ways. It can be considered as a charge carrier injection into the polymer from the contact electrode *via* field-assisted lowering of the metal-polymer potential barrier *i.e.*, Schottky-Richardson (SR) emission, taking the classical imaginary force into consideration (Schottky emission). Alternatively, charge carriers can be released due to ionization of impurity centers in the polymer (Poole-Frenkel effect). For deciding whether it is Schottky or Poole-Frenkel process, the slopes of the linear portion of the plots, Figure 2, are compared with the theoretically calculated value using the Schottky relation [4]

$$\beta_{PF} = 2\beta_S = 2\left(\frac{e^3}{4\pi\varepsilon\,\varepsilon_o}\right)^{1/2} \tag{1}$$

where e is the electronic charge, ε_o is the vacuum permittivity and ε is the dielectric constant of the material. If the value of β, obtained from the slope of the straight line portion of the plot in Figure 2, is close to β_S obtained theoretically, from Eq. (1), the process is that of Schottky

emission. If, on the other hand, the value of β obtained from slope is twice large as β_S the process is that of Poole-Frenkel. The experimental value of β is found to be close to that calculated theoretically. So it is concluded that the Schottky type of conduction is dominant.

From another point of view, the obtained coincidence of β values is not sufficient evidence for the detection of the conduction mechanism. The actual conduction mechanism may be well determined by study the effect of different electrode materials on the current-voltage characteristics, since the Schottky emission is electrode dependent, while the Poole-Frenkel is independent of the electrode material [5]. Also, a study of the thermally stimulated discharge currents (TSDC), as a function of the polarizing field, determines the actual conduction mechanism [6, 7].

Figure 3 shows the $I-V$ characteristics for PVC stabilized with lead sterate at 360 K for different electrode materials (Ag, Al, and Au). It is clear from this figure that, the $I-V$ characteristics are greatly affected by changing the electrode material. It is noticed also that the current has a maximum value for the sample with Ag electrode, while for Au
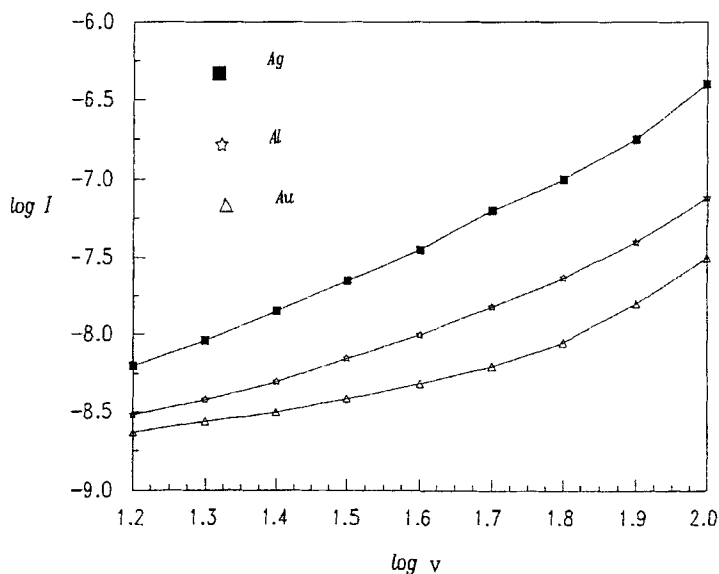

FIGURE 3   Variation of log I as a function of voltage at 360 K for different electrode materials.

electrode the current is low. This behavior can be described according to the work function of the metal electrodes and also the theory of Schottky emission (described elsewhere) [8]. This confirming that the Schottky emission type of conduction is the dominant one.

In the TSDC measurements, the obtained current peak may be due to the dipole orientation around the main chains [7], (or due to the micro-Brownian motion of the chains themselves), or migration of space charge carriers over microscopic distances, releases from the traps with subsequent retrapping [8]. If the trapping centers are of Poole-Frenkel type, the temperature corresponding to the current peak is dependent of the polarizing field [7]. But if the current peak is independent of the polarizing field, the conduction must be of Schottky type. In the present case, it is observed in Figure 4 that the temperature corresponding to the current peak is independent of the polarizing field which emphasises the previous suggestion, that the conduction is of Schottky type.

In Figure 2, it is noticed that at high temperatures (380 and 400 K), the slope of the straight line is higher than that expected for Schottky emission. This behavior can be explained on the basis that some of the
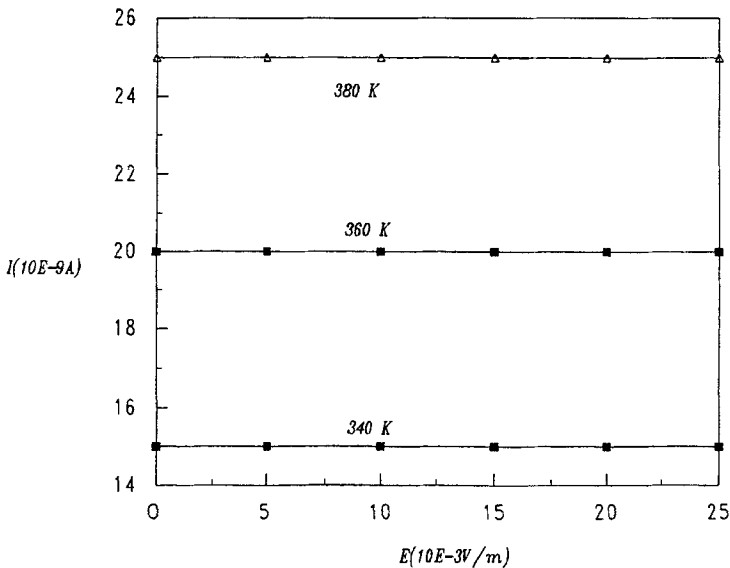

FIGURE 4   Variation of the thermally stimulated discharge current peak with polarizing field at different temperatures.

injected charge carriers is getting trapped in the shallow traps present in the polymer, and their release is controlled by a Poole-Frenkel mechanism, thus one can say that charges are build-up near the electrodes. In order to obtain directly the trap distribution $N(E)$ from the SCLC measurements, one may follow the analytic method primarily proposed by Pfister [8] and subsequently developed by Manfredotti et al. [9], Stockmanny [10] and Weisfield [11]. In the so-called simplified theory of the one-carrier SCLC flow, the following assumptions are made as: (i) the diffusion current is neglected and the cathode is an inifinite reservoir of electrons available for injection, (ii) the distribution of impurities and the electron mobility μ are spatially uniform and independent of electric field; and (iii) the trap occupancy is determined by the position of quasi-Fermi level E_F, and the density of free electrons is described by Boltzmann statistics.

Starting from the Poisson equation together with the current flow equation using the above assumptions, one obtains [5, 8]

$$n_\Lambda = -(d/\mu e(2 - m)(I/V))$$ (2)

and

$$n_t = \varepsilon\,\varepsilon_o(V/d^2)((2 - m)(1 - m) + 1)$$ (3)

where n_Λ, n_t are respectively, the free electron density and the total charge density at the collecting contacts, and

$$m = \frac{d(\ln V)}{d(\ln I)}, \quad l = \frac{d^2(\ln V)}{d(\ln I)^2}$$

If the gap-state density $N(E)$ varies slowly and continuously over the energies of the order of kT, so zero-temperature Fermi-Dirac statistics can be applied, and if the contribution of free carriers is neglected, the charge density can be written as [12]

$$n_t = e \int_{E_{FO}}^{E_F} N(E)dE$$ (4)

Differentiating Eq. (4) and using Eqs. (2), (3), one obtains

$$N(E_F) = \frac{\varepsilon\varepsilon_o}{ekTd^2} V \left(\frac{(2m - 3)1 + s}{(2 - m)(1 - m) + 1} + m \right)(2 - m)$$ (5)

where

$$s = \frac{d^3(\ln V)}{d(\ln I)^3}$$

The position of the quasi-Fermi level E_F calculated from its thermal equilibrium value E_{FO}, is given by the relation [4]

$$E_F - E_{FO} = kT(\ln(V(2 - m)/J) - \ln(V_\Omega/I_\Omega)) \qquad (6)$$

where the current density J_Ω is given by the Ohm's law

$$J_\Omega = en_o\mu(V_\Omega/d)$$

and n_o is the thermal equilibrium density of free electrons.

In order to evaluate $N(E)$ and E_F from Eqs. (5), (6), the log V against log I data is fitted locally point by point to a cubic function. The best fit was obtained by adjusting the smoothing parameters in such way that the first calculated derivative is the same as the experimental slope. The density of state distribution reported in Figure 5 exhibits the energy
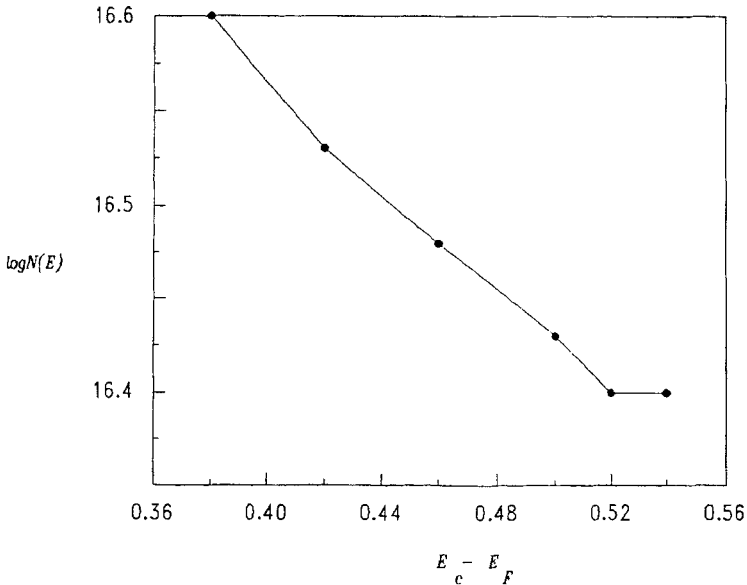

FIGURE 5   Density of gap-state distribution $N(E)$ calculated by means of Eqs. (5) and (6).

distribution of the density of states has approximately the same profile for all the samples with values between $(2-4) \times 10^{16}\,\mathrm{eV^{-1}\,cm^{-3}}$.

CONCLUSION

From the forgoing results, one can conclude the following:

1. The dominant charge carriers generation mechanism in PVC stabilized with lead sterate is Schottky one.
2. The density of states distribution $N(E)$ has been found in the range $2-4 \times 10^{16}\,\mathrm{eV^{-1}\,cm^{-3}}$.

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