Effect of electrode material on thermally stimulated discharge and dark current in polystyrene

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Thermally stimulated discharge (*TSD*) currents excited at 110°C by 117 V in 20 μm thick polystyrene (PS) films in contact with Al, Zn, Pb, Cd, Cu and Ni have been measured keeping the other electrode as Al. *TSC* parameters are observed to change with the choice of electrode material. Maximum charge is stored by PS films in contact with Cu. The observed polarization is explained in terms of detrapping of charges injected from the electrodes with subsequent space-charge formation. The dependence of dark current at 50°C in metal–PS–Al systems on applied voltage in the range 3–117 V has also been investigated. Current density–square root voltage plots are observed to have straight portions at high field values. Zero field current density extrapolated from these plots and *TSC* activation energy are found to vary with metal work function qualitatively in a similar manner.

INTRODUCTION

The importance of carrier injection[1–4] for the explanation of electrical properties of organic solids has been long recognised. It is only in recent years that the possibility of technological application of electrification of polymers due to their contacts with metals has been discovered. The availability of new measuring techniques such as photo current[5,6] and thermally stimulated discharge (*TSD*) current[7,8] has freshened interest in achieving a better understanding and application of the phenomena. Polystryene (PS) is a cheap promising insulator and there is no report on contact electrification of PS using different metal contacts and utilizing *TSD* current techniques which have proven to be especially well suited to the study of polymers[9,10]. Hence, it is worthwhile to investigate electret forming characteristics of PS films in contact with metals providing a range of work functions.

In this paper, *TSD* currents and steady state current–voltage (J–V) characteristics of PS in contact with Al, Zn, Pb, Cd, Cu and Ni are reported to demonstrate the electrode effect on injection in the polymer.

EXPERIMENTAL

20 μm thick PS films were grown on Al, Zn, Pb, Cd, Cu and Ni substrates by immersing them isothermally in PS solution in cyclohexanone. The substrate acted as one electrode and the other of Al (area = 1 cm^2) was pressed on the film in a laid-on electrode assembly. Electrets were formed by a thermal method under identical conditions of temperature, voltage and time, viz., 110°C, 117 V, 30 min. The polarizing temperature is above the glass-transition temperature (100°C) of PS and the voltage applied is fairly high. Thermo-electrets were stored for 2 min to eliminate stray charges and then were heated at a rate of 5° per min. A Keithley 600B electrometer was used to measure the current.

J–V characteristics of PS films on different metal substrates were traced using a guarded electrode to avoid surface effects. Below 50°C, it was difficult to measure the small currents generated by voltage application in the measuring set-up. The film was kept at 50°C for about 2 h and then a voltage was applied and the transient behaviour of the current was noted. Voltage application gave a current which was found to decrease to a much lower value in a matter of 2 or 3 min and then very slowly attain an almost steady value in half an hour. The same procedure was followed to observe the steady value of current at each step of voltage increment.

RESULTS

TSC thermograms of PS electrets formed by incorporating Al, Zn, Pb, Cd and Cu as electrode materials are shown in *Figure 1*. The initial slope of current was found to change with the other electrode system. The activation energy of the process involved was calculated by the initial rise method of Garlick and Gibson[11]. Relaxation times were evaluated according to Bucci *et al.* theory[12]. Charge released during the discharge was estimated by integrating current vs. temperature (time) curve. *TSC* parameters are listed in *Table 1*. In all the cases of electrode variation, a *TSC* peak arises well above the glass-transition temperature of PS and lies in between 155°–162°C except in the case of Al as the two

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electrodes are similar. This observation suggests that peak temperature when the polymer film is poled above its glass-transition temperature is a characteristic of the polymer and does not depend on the choice of metal forming the electrode. The intensity of the peak and the charge released are at a minimum for the configuration Al–PS–Al and maximum for the configuration Cu–PS–Al. Carrier free-life-time is least and most affected by temperature for PS in contact with Cu. Current–voltage characteristics of PS at 50°C using different metal electrodes in J–$V^{1/2}$ form are shown in *Figure 2.* All the curves are convex towards the current-axis. At low voltages they seem to originate from the same point and diverge more and more as the voltage is increased and have considerable linear portions.

DISCUSSION

Dipolar processes[8,9] and charge detrapping mechanisms[7,13] are generally invoked to interpret the occurrence of a *TSC*-spectra. PS is a nonpolar polymer and the dipolar contribution[14] calculated from Debey's equation does not respond to the high value of charge released. Moreover, the dipolar peaks remain uninfluenced by the choice of electrode material[8] which is contrary to the present observation ruling out dipole re-orientation. Our previous work[15] on *TSD* of PS films has revealed that the peak current varies linearly with the square root of the field applied during polarization suggesting carrier injection. Consequently, the interpretation of depolarization appears to be reasonably possible in terms of charge detrapping of a space-charge built-up due to carriers injected from the electrodes[16]. At high fields, the charges are injected from the electrodes into the polymer film and are then trapped. It is only at temperatures above the glass-transition of PS that the molecular chains are sufficiently agitated to release the charges stored in them. The amount and sign of charge injected depends on the relative work function of the metal–polymer interface, i.e. the difference in energy

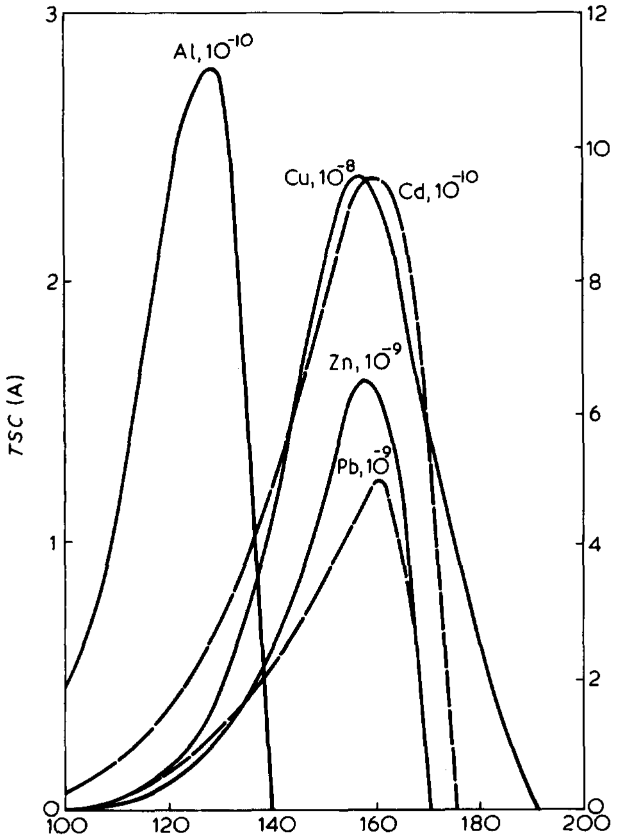

Figure 1 *TSC* **of PS films on different metals. Biasing temperature, 110°C; biasing voltage, 117V; biasing time, 30 min. Broken lines (— — — —) refer to right hand scale**

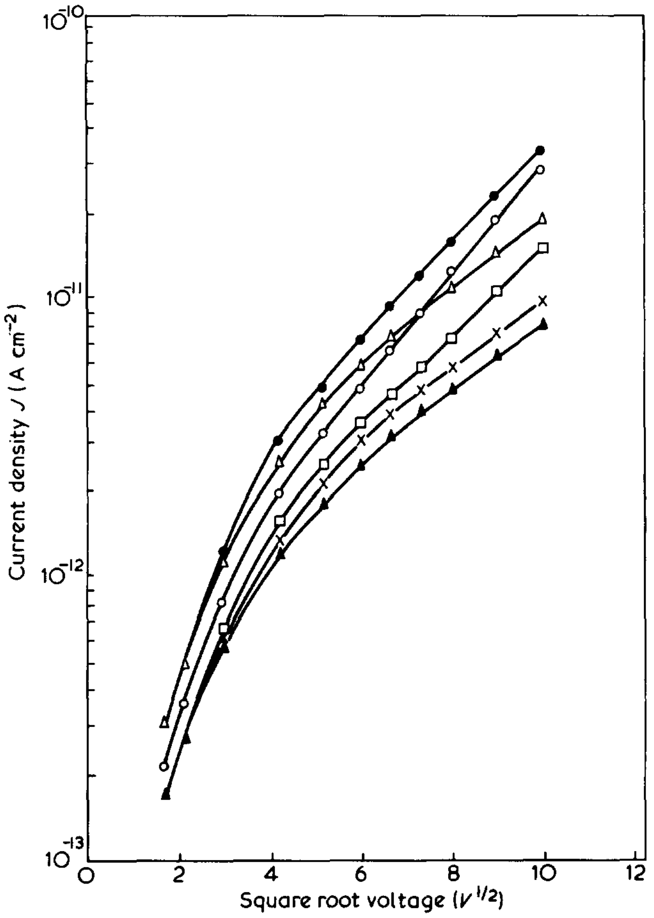

Figure 2 ***J–V*$^{1/2}$ characteristics of PS films on different metals. (●), Zn; (○), Cd; (△), Cu; (□), Pb; (x), Ni; (▲), Al. Temperature = 50°C**

Table 1 ***TSC*** **Parameters of PS films in contact with different metals**

Electrode material	Al	Pb	Zn	Cu	Bu
Peak temperature (°C)	128	160	155	162	160
Activation energy (eV)	0.98	0.85	1.10	0.84	1.40
Natural relaxation time (s)	3.5×10^{-10}	2.6×10^{-6}	2.0×10^{-11}	4.8×10^{-8}	7.4×10^{-15}
Relaxation time at peak temperature (s)	182	186	178	240	145
Relaxation time at 300K (s)	3.2×10^{6}	5.0×10^{8}	5.9×10^{7}	5.8×10^{6}	2.5×10^{9}
Peak current (A)	2.8×10^{-10}	5.0×10^{-9}	9.8×10^{-9}	9.8×10^{-10}	2.4×10^{-8}
Charge released (C)	1×10^{-7}	2×10^{-6}	6×10^{-7}	5×10^{-7}	1×10^{-5}

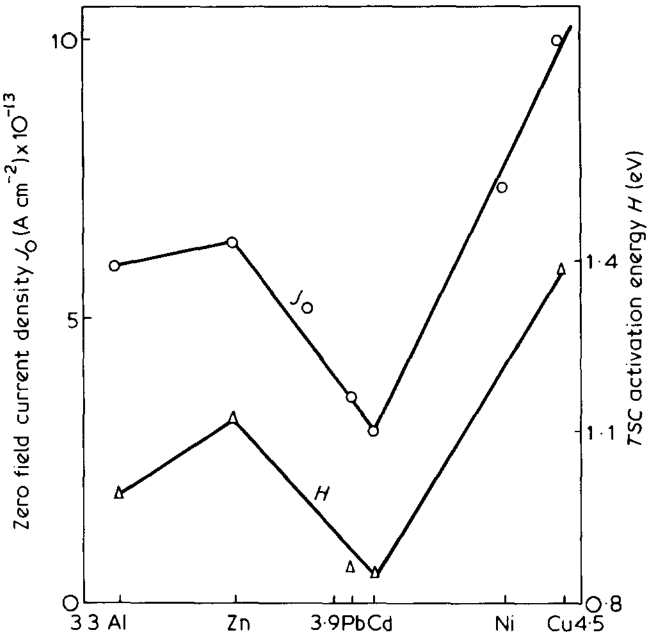

Figure 3 Zero field current density and *TSC* activation energy *versus* work function of the metal

between the Fermi level in metal and the bottom of the conduction band in the insulator. Therefore, the *TSC* parameters are changed when the electrode forming material is changed.

In wide gap insulators and polymers with π-electrons, intrinsic carrier generation is not possible. Charge transfer from the metal depends on the electron levels in which the carriers shift freely under the influence of the applied field. The energy on this level may be given by[17]:

$$E_b = E_g = (I_g - p^+) - (A_c + p^-) = I_c - A_c \quad (1)$$

where I_g is the ionization energy, A_c is the electron affinity, p^+ and p^- are the polarization energies and I_c is the ionization energy of a molecule of the dielectric. E_b corresponds to the energy gap E_g. In case of PS, $E_b = E_g \approx 4$–5 cV. From this data intrinsic generation of free carriers resulting from Boltzmann's factor is negligible at temperatures below polymer decomposition. It lends more emphasis to the importance of the metal electrode which is the origin of the carriers responsible for conduction and surface charges. Electrons must overcome the potential barrier (designated by χ)

$$\chi^- = \varphi - A_c \quad (2)$$

while holes are given by

$$\chi^+ = I_c - \varphi \quad (3)$$

where φ is the metal work function. The emission current is described by Richardson's equation:

$$J_0 = AT^2 \exp\left(-\frac{\chi}{kT}\right) \quad (4)$$

where J_0 is the current density, A is a constant, T is the absolute temperature and k is Boltzmann's constant.

In the light of above discussion, J–$V^{1/2}$ plots may be interpreted in terms of Richardson–Schottky (RS) field-assisted thermionic injection of carriers from metal electrodes. The RS mechanism has also been suggested in other studies on polyethylene terephthalate, polytetrafluorethylene and poly N-vinylcarbazole[18–20]. The simple RS theory does not give a good fit to the experimental data and various explanations have been advanced to explain this. Schug *et al.*[21] have concluded that the electric field in the RS effect is determined by the trapped space-charge moderated by the Poole–Frenkel effect[22]. Taylor and Lewis[23] have assumed a more generalised form of the potential barrier rather than the Coulombic barrier usually employed in treatments of the RS effect. They obtained consistent agreement with experimental results in studies on polyethylene and polyethylene terephthalate and concluded that the potential barrier chosen referred to the cathode-dielectric interface and is probably determined by a space-charge layer in the dielectric. It has been suggested that such space-charge layers are charged up by the absorption current[23,24]. The classical RS effect predicts a current–voltage relationship of the form:

$$J = AT^2 \exp\left(-\frac{\chi}{kT}\right) \exp(\beta_s V^{1/2}) \quad (5)$$

with

$$\beta_s = \frac{e}{kT}\left(\frac{e}{4\pi\varepsilon\varepsilon_0 d}\right)^{1/2} \quad (6)$$

where d is the film thickness, ε is the dielectric constant, ε_0 is the permittivity of free space and e is the electronic charge. For zero field, equation 5 reduces to equation 4 and the current density depends on the potential barrier at a constant temperature. The zero field current density (J_0) was extrapolated by extending the linear portion of the J–$V^{1/2}$ plot backward to meet the current axis.

Zero field current density and *TSC* activation energy have been plotted against metal work function in *Figure 3*. The variation of the two quantities with metal work function is seen to be qualitatively equivalent. Excluding Al (identical electrodes), the plots consist of two straight lines inclined oppositely to the work function-axis. Negatively sloped lines have been obtained for the contact materials: Zn, Pb and Cd, which have comparatively low work functions. For the contact materials Ni and Cu whose work functions are comparatively higher, positively sloped lines have been obtained. This shows clearly the effect of electrode material on carrier injection in PS and shows that charge carrier injection into the polymer film decreases with the increase in metal work function. A similar conclusion[25] has also been drawn by us previously when working with the photo-depolarization of PS films in contact with different metals. This is in accordance with the findings of Takai *et al.*[6] and Goodman and Neill[26].

CONCLUSION

TSD and dark current measurements of PS films in contact with Al, Zn, Pb, Cd, Ni and Cu reveal a strong dependence of these currents on the electrode forming material which is the source of charge carriers responsible for conduction and observed polarization of the polymer. There are two stages of charging of the polymer. The first stage of charging of PS films, as a result of contact with the metal, is charge injection which decreases with the increase in metal work function. The second stage is entrapment of these charges in the border layer.

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