Thermally stimulated current and electrical conduction in metal (1)–ethyl cellulose–metal (1)/(2) systems

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Abstract. Depolarization current characteristics of solution grown pure ethyl cellulose (EC) films of about 20 μm thickness have been studied as a function of electrode materials at constant poling field (5×10^4 V/cm) and poling temperature 40°C. Thermally stimulated current (TSC) thermograms of EC consists of two well resolved peaks (located at 60°C and 140°C) for Al–Al system, which are attributed to the deorientation of strongly attached ethoxy groups of glycosidal units and diffusion of space charges either at electrodes or due to their thermal release at higher temperatures from the defect levels. For dissimilar electrode combinations (Al–Ag/Cu/Au/Sn/Pb), an indication of peak of lower magnitude at around (50–70°C) alongwith a higher temperature peak (140–155°C), have been observed. TSC parameters are found to change with the choice of electrode material. The dependence of dark current at 40°C in metal–ethyl cellulose–metal systems on applied voltage in the range $(2.0–5.0) \times 10^4$ V/cm has also been studied. The results of current–voltage measurement on EC have been interpreted to show that the Schottky–Richardson mechanism is the controlling transport mechanism. Zero field current density extrapolated from I–$E^{1/2}$ plots are found to vary with metal work function.

Keywords. Thermally stimulated current; electrical conduction; ethyl cellulose; space charge relaxation; dipolar orientation; Schottky–Richardson mechanism.

1. Introduction

Thermally stimulated discharge (TSD) of polymers has become a widely used experimental technique for the investigation of various material parameters such as charge storage properties, determination of the mean depth of the internal charge, activation energies of traps and the trap structure of the material. The importance of carrier injection (Gutman and Lyons 1967; Koton 1968; Lampert and Mark 1970) for the explanation of electrical properties of organic solids has been long recognized. It is only in recent years that the possibility of technological application of electrification of polymers due to their contacts with metal has been discovered (Shrivastava et al 1981). The availability of new measuring techniques such as photocurrent (Wintle 1974) and thermally stimulated discharge (TSD) current (Turnhout 1975) has freshened interest in achieving a better understanding and application of the phenomena. Many studies and reviews (Pulfrey 1972; Kryozewski 1975; Khare and Srivastava 1992a, 1994; Khare et al 1994a) have been devoted to the problem of contacts and surface charge influence but there is controversy

about the causes of the polarity and amount of charge transferred under given conditions.

Ethyl cellulose (EC) is a thermally stable polymer that exhibits excellent chemical resistance and good mechanical properties and probably there is no report on contact electrification of EC using different metal contacts. Hence, it is worthwhile to investigate electret forming characteristics of EC in contact with metals providing a range of work functions. In view of this an analysis of the thermally stimulated current (TSC) and steady state current–voltage (I–V) characteristics of EC polarized under identical conditions with a special reference to the nature of the electrode metals has been made to elucidate the electrode effect on injection in the polymer.

2. Experimental

The isothermal immersion technique was utilized for preparing thin films of ethyl cellulose (EC). The solution was prepared in a glass beaker by first dissolving 2·1 g EC in 30 ml of chemically pure chloroform at room temperature and continuously stirred for 30 min by means of a teflon-coated magnetic stirrer. Thereafter, it was stirred and heated to 40°C to yield a homogeneous solution. The glass beaker containing the solution was

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then immersed in a constant temperature oil bath. Ultrasonically cleaned vacuum metallized microscopic glass slides were immersed vertically into the solution for a period of about 30 min. After deposition of the film the glass slide was taken out and dried in an oven at 40°C for 24 h. This was followed by room temperature outgassing at 10^{-5} torr for a further period of 24 h. Aluminium, copper, silver, lead, tin and gold metals were vacuum deposited on the upper surface of the film to obtain a sandwich configuration. The following electrode combinations were used—Al–Al, Al–Ag, Al–Cu, Al–Pb, Al–Sn and Al–Au. The preparation of electrodes and measurement of thickness were the same as reported earlier (Khare and Srivastava 1992; Khare *et al* 1994b). The voltage was applied from a high voltage unit EC-4800 D and current was recorded with an electrometer (Keithley 600B), which was carefully shielded and grounded to avoid ground loops or extraneous electrical noise, at a linear heating rate of 4 K/min. The thickness of the sample was of the order of 20 μm which was estimated by measuring the capacitance of the fabricated sandwiches taking the value of dielectric constant ε of ethyl cellulose as 3.

In the present case EC thermoelectrets were formed by a thermal method under identical polarizing conditions of temperature (T_p), higher field (E_p) and time (t_p), viz. 40°C, 5.0×10^4 V/cm and 120 min but with different metal electrodes, namely copper, silver, lead, tin and gold, having different work functions. Thermoelectrets were shorted for 5 min to eliminate stray charges. The method of polarization of sample and measurement of TSC and steady current were same as reported earlier (Khare and Srivastava 1992; Khare *et al* 1993).

Below 40°C it was difficult to measure the small currents generated by voltage application in the measuring set up. The film was kept at 40°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 2–5 min and then very slowly attain an almost steady value in a few hours. The same procedure was followed to observe the steady value of current at each step of voltage increment.

The depolarization kinetic data, activation energy (E), charge released (Q) and relaxation time (τ_0) for the observed peaks have been calculated using initial rise method of Garlick and Gibson (1948), Simson's rule and Bucci *et al* (1966) theory, respectively (table 1).

3. Results and discussion

Thermally simulated current (TSC) thermograms of ethyl cellulose (EC) samples formed by incorporating aluminium, copper, silver, lead, tin and gold as electrode metals with polarizing field, $E_p = 5.0 \times 10^4$ V/cm at $T_p = 40$°C are shown in figure 1. In all the cases of electrode variation, an indication of peak at lower temperatures at around 50–70°C along with a broad TSC lying in between 140–155°C have been observed. For Al–Al system, TSC thermograms are characterized with two peaks located at 60° and 140°C, respectively. Current–voltage $(I–V)$ characteristics of EC at 40°C with polarizing fields $(2.0–5.0) \times 10^4$ V/cm using different metal electrodes in $I-E^{1/2}$ form are shown in figure 2. It is clear from figures 1 and 2 that the current through the sample is greater when the upper electrode aluminium is replaced by silver, copper, tin, lead or gold.

The TSC thermograms are characterized by various peaks, due to dissipation of charges arising because of polarizations during charging process. The polarization of the material may arise due to various mechanisms, the important of which are dipole orientation, charge displacement, molecular and domain structures, macro/microscopic displacement of ions with subsequent trapping, surface and space charge polarization etc. The trapping centres originate in the transition of the crystalline state into amorphous regions, in the rearrangement of molecules in the polymer chain and from the presence of impurities and defects in the materials. The various defects, in addition to giving rise to their own characteristic trapping levels, can also combine with other trapping centres present around them, and thus they can modify qualitatively as well as quantitatively the TSC spectra observed under polarizing conditions. EC is known to be a partial polar polymer. Its main chain is C–O–C. The side groups also have a structure of the form C–O–C but they differ in electronegative nature from the main chain. The electronegativity of the main chain bond arises from the difference in the electronegativity of carbon and oxygen atoms; however, the electronegativity of the side groups arises from the difference in electronegativity of $H_2C–O–C_2H_5$ and $C–O–C_2H_5$ bonds in the side chains. The slight polar nature of the polymer is due to the difference in electronegativity of the main chain and the side groups. The dipolar relaxation is maximum around the glass transition temperature (T_g). Its T_g lies in the temperature range 60–75°C for its atactic form and around 80°C for high molecular weight ethyl cellulose. In view of above characteristic of the polymer, it is expected to get first peak around 60–80°C. This peak seems to be due to the orientation of strongly attached ethoxy groups of glycosidal units. The relaxation process has been found to be associated with an activation energy of 0.18 eV and related to the segmental rotations or translations of the main chain (Khare *et al* 1996). It remains unaffected with heating rate and storage time (Khare and Srivastava 1993). The peak current is almost linearly dependent on poling field. It is suggestive of the dipolar polarization (Khare *et al* 1992). The second peak appears on the higher temperature side of the TSC thermograms. This peak may be considered due to space charge polarization arising out of localization of bulk

generated and/or injected charge carriers in various available traps distributed energetically and spatially over the bulk of the sample. The joint motion/deorientation of the backbone chains of EC may be considered to contribute to some extent to this peak. The charge released from the trap levels at temperatures greater than T_g are very well documented previously (Dubey *et al* 1990; Khare *et al* 1992; Khare and Srivastava 1993). An indication of peak of smaller magnitude (around 50–70°C) alongwith a broad TSC peak around 140–155°C have been found for dissimilar electrode combinations. These are space charge peaks modified by the type of metal (Shrivastava *et al* 1979), probably because the various metal–polymer interfaces possess different charge exchange rates, which change the space charge storage and current released by diffusion. The first stage of charging is carrier injection and the second stage is the entrapment of these charges in the border layer (Hino and Yamashita 1974). Consequently, the interpretation of depolarization appears to be reasonably possible in terms of charge detrapping of a space-charge build up due to carriers injected from the electrodes (Shatzkes

1978). At high fields, the charges are injected from the electrodes into the polymer film and then trapped. It is only at temperatures above the glass transition of EC that the molecular chains are sufficiently agitated to release the charge stored in them (Khare *et al* 1994c). The amount and sign of charge injected depends on the relative work function of the metal–polymer interface, i.e. the difference in energy 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. It also seems possible that the dipolar peak either gets masked by the space charge peak or its contribution to the total polarization is very small (Khare *et al* 1994a).

The absence of peak at 60°C in Al–Sn and Al–Pb combinations may be due to oxidation of Pb and Sn metal electrodes. The ethoxy group being weakly electronegative and the oxide layer electropositive, will neutralize each other's effects to some extent. It is probably for this reason that in these two particular electrode combinations, the peak at 60°C is suppressed and only small humps are observed.
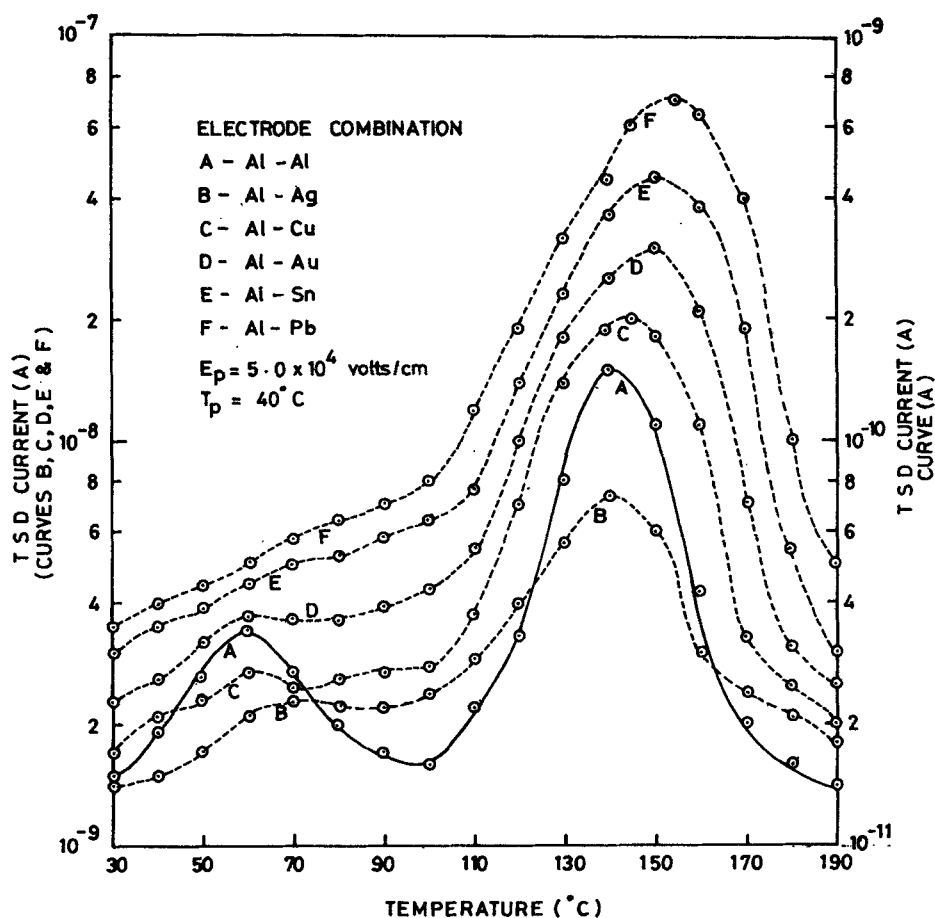
Figure 1. Effect of electrode materials on thermally stimulated current for ethyl cellulose samples with polarizing field $E_p = 5 \cdot 0 \times 10^4$ V/cm at polarizing temperature $T_p = 40°C$.

In wide gap insulators and polymers with n-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 (Baessler 1972)

$$E_b = E_g = (I_g - p^+) - (A_c + p^-) = I_c - A_c, \tag{1}$$

where I_g is the ionization energy, A_c the electron affinity, p^+ and p^- are the polarization energies and I_c the ionization energy of a molecule of the dielectric. The observed relation between the current and voltage points to a conduction mechanism in which the charge carriers are released by thermal activation over a coulombic potential barrier that is decreased by the electric field. The potential barrier can be one of the two types; (i) barrier between electrodes and dielectric taking the classic image force into consideration (Schottky emission), and (ii) barriers due to trapping centres in the dielectric (Poole–Frenkel effect). Taylor and Lewis (1971) assumed a more generalized form of the potential barrier rather than a Coulombic barrier usually employed in treatment of the RS effect.

They concluded that the potential barrier chosen is referred to the cathode–dielectric interface and probably is determined by a space-charge layer in the dielectric. Such space-charge layers are charged up by the absorption current. In the present case, I–$E^{1/2}$ plots may be interpreted in terms of Richardson–Schottky (RS) field assisted thermionic injection of carriers from metal electrodes.

The primary source of charge carriers is the electrode contacts. Carriers are generated in the bulk on account of thermal ionization of impurities and absorbed water molecules. Nath and Kumar (1980) have shown injection of holes in cellulose acetate film. Hole injection results in depletion of layer of negative charges creating a field at the interface between the electrode and film surface. When two metals are brought in close contact, a potential difference of work function $\phi_2 - \phi_1$, is created between the two metals. The semi-insulating polymer differs from a metal, however, in that an electric field may exist within the interior of the semi insulator. For this reason the contact potential drop between the metal and the semi-insulator may take place within the material rather than at the contact interfaces. Along with the field, there may exist a depletion in the accumulation of charges in
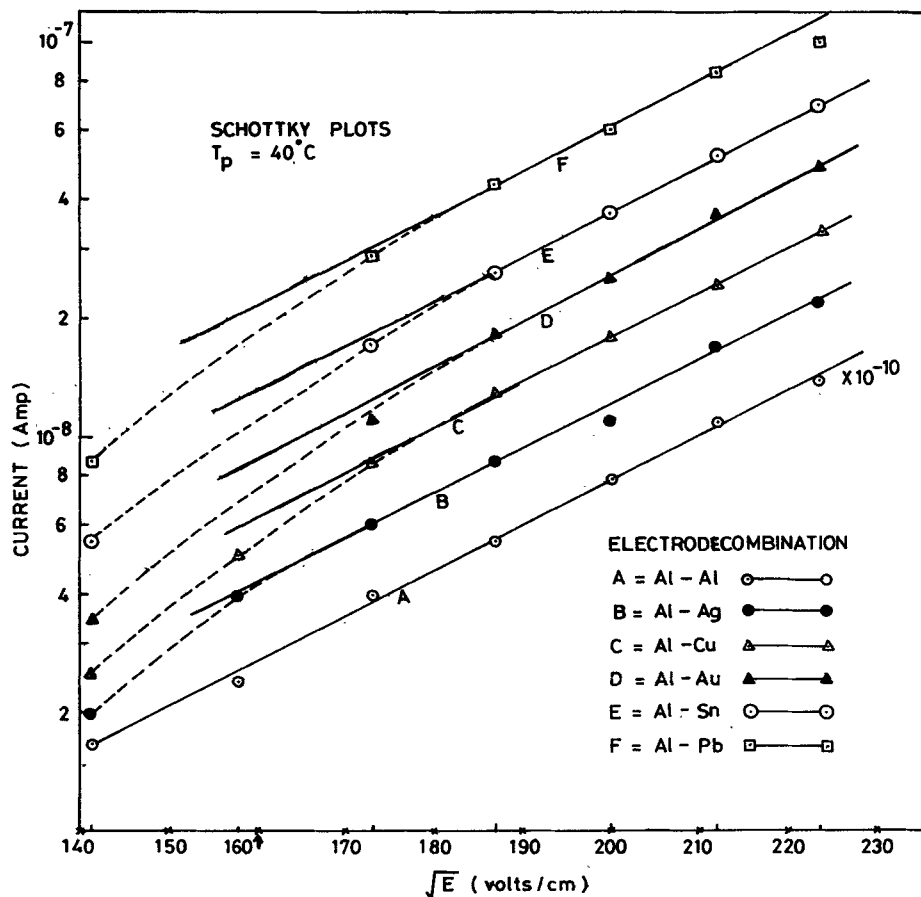

Figure 2. Log I vs $\sqrt{E}$ plots (Schottky plots—similar and dissimilar electrode system).

the surface layers (Khare and Srivastava 1992b). The work function of the metals used for contacts is lower compared to that of the work function of the polymeric material which creates an accumulation layer at the interfaces and leaves charged donors in the bulk. This in turn creates fields at the interfaces of the metal–polymer system (Khare *et al* 1994d). Suppose an insulator has a large energy gap with its Fermi level located above the mid gap and there is no surface state, then after contact with a metal surface, the electron transfer at contact equalizes both Fermi levels. The barrier height depends on the relative values of metal work function and the electron affinity of the insulator (Takai *et al* 1975). The surface state (Wintle 1977) is one of the

factors which affects injection phenomena. Donor-like surface states located between the conduction band and Fermi level, after contact tend to bend the band edge towards the Fermi level, making electron injection from the metal much easier. On the other hand, acceptor like surface states located between the valence band and Fermi level act as a stepping-stone for electrons injected from the valence band of the insulator to the metal, thus, enhancing hole injection (Shrivastava *et al* 1979). Electrons must overcome the potential barrier (x) given by
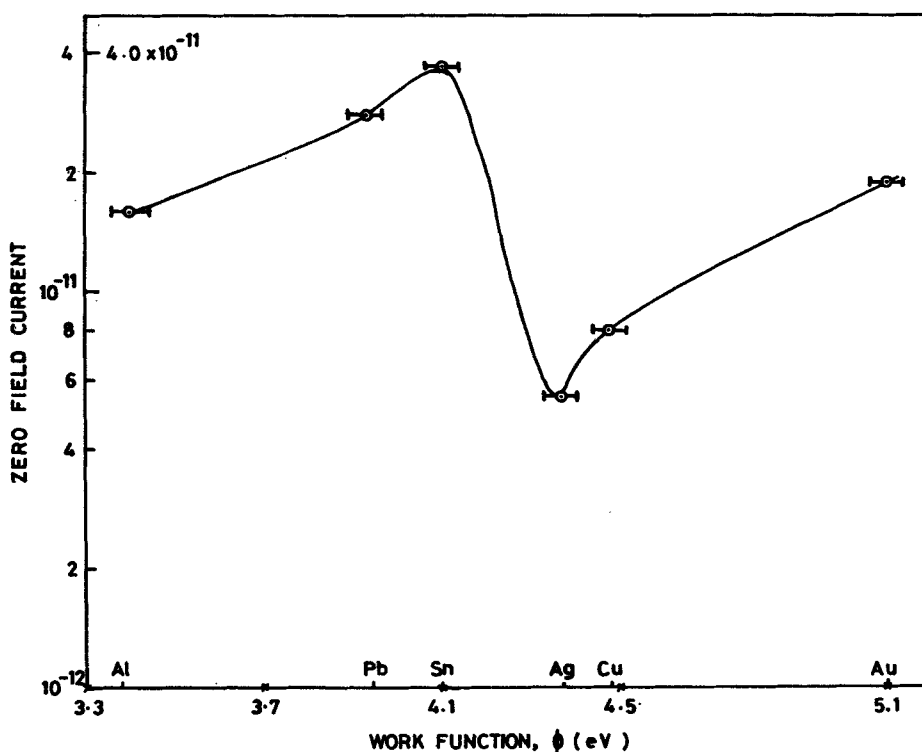
$$x^- = \phi - A_c,$$

while holes are given by

Figure 3. Zero field current vs metal work function for EC films.

Table 1. Depolarization kinetic data of electrode variation in ethyl cellulose films ($E_p = 5.0 \times 10^4$ volts/cm, $T_p = 40°C$).

Electrode combination	Peak temperature (°C)	Peak current (A)	Activation energy (eV)	Relaxation time τ_0 (sec)	Charge released Q (Coul)
Al–Al	60	3.2×10^{-11}	0.18	4.789×10^{-11}	6.222×10^{-11}
	140	1.5×10^{-10}	0.32	8.698×10^{-10}	1.576×10^{-10}
Al–Ag	140	7.2×10^{-9}	0.48	9.978×10^{-10}	3.321×10^{-9}
Al–Cu	145	2.0×10^{-8}	0.52	3.957×10^{-9}	2.234×10^{-8}
Al–Au	150	3.0×10^{-8}	0.56	6.998×10^{-9}	8.768×10^{-8}
Al–Sn	150	4.4×10^{-8}	0.59	7.345×10^{-9}	7.764×10^{-7}
Al–Pb	155	7.0×10^{-8}	0.62	8.372×10^{-9}	9.957×10^{-7}

$$x^+ = I_c - \phi \, , \tag{2}$$

where ϕ is the metal work function, A_c the electron affinity and I_c the ionization energy of a molecule of the dielectric.

In the present case the magnitude of TSC and steady state current was found to be higher in dissimilar electrode than similar electrode combinations. This shows the effect of materials of electrodes on the current of the sample sandwiched between them. The observations are consistent with the proposed R–S mechanism in which the carriers are injected over the field-dependent polymer–electrode interfacial barrier. The emission current is described by Richardson's equation

$$J_0 = AT^2 \, \exp\left(-\frac{x}{kT}\right), \tag{3}$$

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

The classical RS effect predicts a current–voltage relationship of the form

$$J = AT^2 \, \exp\left(-\frac{x}{kT}\right) \exp(\beta_s V^{1/2}) \, , \tag{4}$$

with

$$\beta_s = \frac{e}{kT} \left(\frac{e}{4\pi \, \varepsilon \, \varepsilon_0 \, d}\right)^{1/2}, \tag{5}$$

where d is the film thickness, ε the dielectric constant, ε_0 the permittivity of the free space and e the electronic charge. For zero field, (4) reduces to (3) 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 I–$E^{1/2}$ plot backwards to meet the current axis. The values of J_0 vs metal work function have been plotted in figure 3. The negative slope of the line when EC makes contact with Ag which signifies that the electron injection decreases for Al–Ag electrode combination and so the zero field current decreases. The possible meaning that may be attached to the positively sloped line which is obtained when ethyl cellulose will be in contact with copper, tin, lead and gold is that, hole injection into the polymer film increases with the increase in metal function (Khare 1994) and hence zero field current also increases.

4. Conclusion

Thermally stimulated current and conduction current of ethyl cellulose films reveal a strong dependence on the electrode forming material which is the source of charge carriers responsible for conduction and observed polarization of the polymer.

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