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The effect of annealing time on thermally stimulated discharge current of corona-charged ethyl cellulose

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Abstract Short circuit thermally stimulated discharge current (TSDC) has been recorded in corona-charged ethyl cellulose foil samples at different annealing time. An analysis of the data reveals significant changes in the TSDC curves of the samples as a function of annealing time. The possible relaxation processes accounting for the changes are discussed, not only a shift of peak temperature of the observed peak to higher temperatures, but also a lowering in its height has been observed with increase in annealing time. Peak temperature higher than 343 K did not arise even for the annealing time of 240 h. The activation energy (A) has been found to increase, while the trapped charge carrier n_t decrease with increase in annealing time. Linear relationship between ln A and n_t indicated an exponential distribution of traps.

Keywords Annealing time · Electret · Mobility · Charge released · Temporary traps · Permanent traps

Introduction

Charge trapping and transport in highly insulating polymers have been of considerable interest due to the usefulness of charged material, commonly called electret, in an increasing number of applications [1–3]. Quite apart from this, research on charge trapping in polymers has opened up new approaches to the investigation of solid-state properties of materials. This was aided by the development of number of new methods, including thermally stimulated discharge current (TSDC) in short and open-circuit configurations, designed for the investigations of charged dielectrics. TSDC is a powerful technique that helps in the understanding of the charge storage, charge decay, and structure of polymers (i.e., semi-crystalline polymers, co-polymers, polymer blends, and polymer nanocomposites), because it is a more sensitive alternative than other thermal analysis techniques like differential scanning calorimetry and dynamic mechanical analysis for detecting the transitions that depend on changes in mobility of molecular scale structural units [4–7].

Thermally stimulated discharge current allows arriving at detailed information about energetic and spatial distribution of traps in dielectrics able to hold charges active for the prolonged period [8–11]. The technique further makes it possible to investigate the effect of physical aging (annealing) of the charged polymer on the charge storage, its distribution and transport in the material [12–15].

However, no detailed information are available in the literature on the effect of annealing on charge storage and transport in ethyl cellulose (EC). In view of the above, the effect of annealing time on TSDC spectra of negatively charged EC has been undertaken in present study.

Experimental

Ethyl cellulose used in this study was supplied by Redox and manufactured by Loba Chemical, Mumbai (India), and

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all the samples of EC were prepared by using the solution grown method. The analytical grade chloroform used as a solvent was procured from Merck India Ltd, New Delhi. Foil samples of EC were obtained by "solution grown method." The samples were outgassed at 313 K for 24 h. Circular samples of 6 cm in diameter and 30 μm of thickness have been prepared. The each sample was unilaterally vacuum aluminized over central circular area of 3.5 cm in diameter, have been used for this study.

The measurements have been made on unmetalized surface of the samples which was negatively corona charged in air at room temperature for 1 min through a dc-biased grid, which was mounted 0.5 cm above the sample-supporting plate (i.e., the plate on which the sample was placed) and 4 cm below the corona needle, for controlling the initial surface potential of the sample. All the samples were charged with negative corona voltage of 10 kV and positive grid voltage of 500 V.

The unmetalized surface of the sample was earthed temporarily just after polarization to reduce the effect of stray charges. The samples were then short-circuited over a range of time from 1/6 to 240 h allowing the samples to isothermally discharge at room temperature. The sample was then mounted in the measuring cell placed in a programmable oven, and TSDC in short circuit configuration was recorded at a linear heating rate of 3 K min^{-1} with Keithley electrometer (i.e., model number 610 C).

Results and discussion

Thermally stimulated discharge current thermograms of negatively corona-charged samples annealed for different time after charging are shown in Figs. 1 and 2. It has been observed that the current in each case is of negative

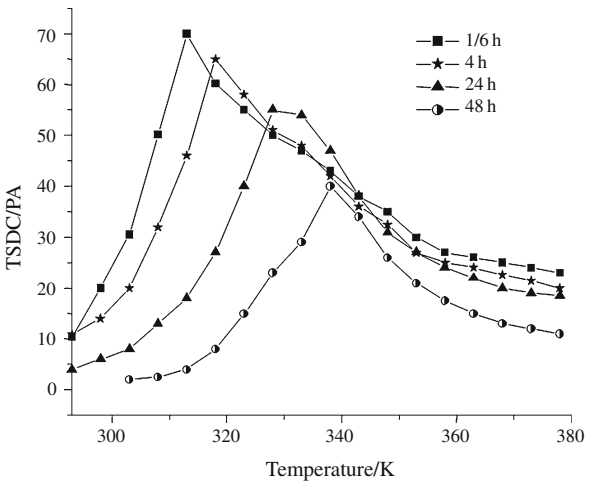

Fig. 1 TSDC thermograms of ethyl cellulose samples annealed for different times (i.e., 1/6, 4, 24, and 48 h)

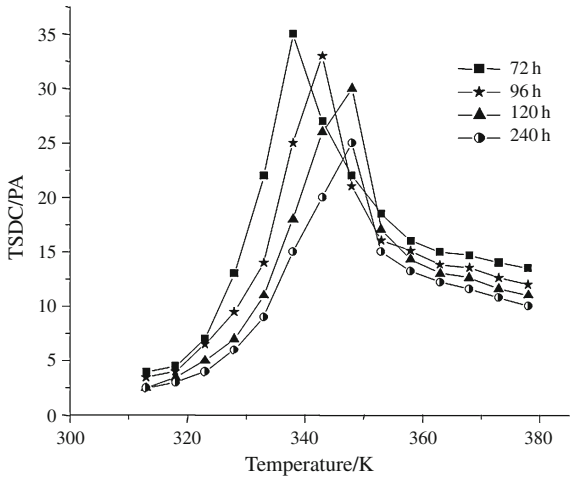

Fig. 2 TSDC thermograms of ethyl cellulose samples annealed for different times (i.e., 72, 96, 120, and 240 h)

polarity (i.e., opposite to that of charging current and never changes polarity during TSDC run).

Every thermogram has been found to be characterized by a single peak. The peaks for sample annealed at different times have been found to be located in the temperature range of 313–348 K. As the annealing time increases the peak intensity decreases and peak temperature moves to higher temperatures. It is further observed that for annealing time exceeding 120 h, the peak does not shift toward higher temperature, and the peak temperature for such annealing time remains the same as that of the peak obtained with the annealing time of 120 h. The observed negative polarity of current and no change of the polarity can be understood as follows:

From Poisson's equation, the continuity equation and the short circuit condition [$F(x,\ t)\ \mathrm{d}x = 0$], neglecting carrier diffusion, we obtain the following equations for the discharging current originating due to space-charge carriers $n(x,\ t)$ [15–17].

$$J_d = \frac{\varepsilon\mu}{2\mathrm{d}}[F^2(d,t) - F^2(0,t)] \tag{1}$$

$$F(0,t) = -\frac{1}{\varepsilon}\int en(x,t)\mathrm{d}x \tag{2}$$

$$F(d,t) = \frac{1}{\varepsilon}\int en(x,t)\mathrm{d}x \tag{3}$$

or

$$J_d(t) = ex(x_0,t)\frac{\mathrm{d}x_0}{\mathrm{d}t}, \tag{4}$$

where ε the permittivity, μ the carrier mobility, e the charge of carrier, d the distance between electrodes, $n(x,\ t)$ the density of space-charge carriers, and $F(x,\ t)$ the internal field. The field $F(x,\ t)$ is zero at some point x_0 (known as zero-field point). Beyond x_0, the field changes the sign.

Considering one type of carrier, i.e., electron in the present case due to negative corona charging of the samples, the most likely distribution of injected homo space charge just after charging will be such that its density $n(x, t)$ drops with increasing value of x. This will be because of charge distribution due to corona charging depends upon the charging voltage and temperature. It has been reported that negative corona charging at room temperature with the corona voltage as used in the present case (i.e., 10 kV) often results in a surface or near-surface charge [18, 19]. For such charge, distribution on the zero-field point x_0 (i.e. Fig. 3) will evidently be near the front electrode. Thus, in this case $F(0, t)$ will be larger than $F(d, t)$. The field on the front electrode side of x_0 drives carriers toward this electrode and that on the rear electrode side of x_0 will drive them away from the front electrode, resulting into currents I_1 and I_2. Clearly, the observed TSDC will be opposite to the charging current, i.e., of negative polarity as expected from Eq. 1.

The observed negative polarity of TSDC can also be understood in terms of the charge distribution, the charge carriers trapped between the zero-field plane and the front electrode may reach this electrode during TSDC run without significant detrapping, while the carriers on the other side of the zero-field plane will be subjected to detrapping before they can reach the rear electrode. Thus, the current I_1 will be greater than I_2 which will provide a current peak of negative polarity.

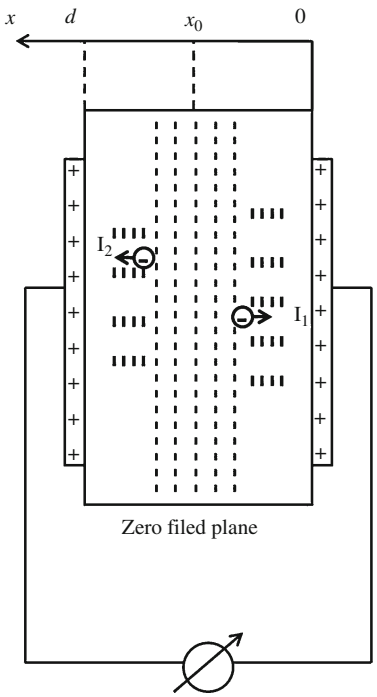

Fig. 3 Schematic representation of zero-field plane

The loss of space-charge carriers released from shallow traps due to compensation by ohmic conduction is small during isothermal discharge of sample at room temperature for short annealing time of 1/6 h. It will leave the large number of thermally released carriers from shallow traps to drift toward the front electrode and hence to give rise a prominent peak of high intensity located at 313 K for short period of annealing time of 1/6 h (Fig. 1). As the annealing time becomes longer, an increasing amount of space charge captured in shallow traps is released and neutralized by recombining with the carriers responsible for the ohmic conduction during the isothermal discharge of the sample. Under such situation, the observed TSDC is mainly due to the carriers trapped in deeper traps, and hence, the peak starts to move toward higher temperatures corresponding to the charge released from deeper and deeper traps. The intensity of the peak gradually decreases as it moves to higher temperature. Such decrease in peak intensity may be attributed to the gradual decrease of charge released from traps and subsequent increase of energetic trap depth. The shifting of peak temperature to higher temperatures with increase in annealing time indicates the possibility of population shift of carriers from shallow to deeper traps during annealing.

In the present case, the peak temperature has been found to increase with increase in annealing time up to 120 h, and then the peak appears at the same temperature for all annealing times greater than the time of 120 h. This observation indicates that thermal energy supplied to the sample over the range of TSDC is not sufficient to release the carriers from the traps, which are energetically deeper than the traps releasing the carriers for the peak at 343 K. Such deeper traps may be considered as inactive (i.e., not contributing the observed TSDC) traps, while the traps, which contribute to the observed TSDC for various annealing times are considered as the active traps.

The activation energy value (A) calculated using initial rise method for different peaks is given in Table 1.

Table 1 Summary of the TSDC parameters

Sample	Annealing time t_r/h	Peak temperature T_m/K	Activation energy A/eV	Trapped charge carrier concentration $n_t/10^{18}/m^{-3}$
1	1/6	313	0.52	7.90
2	4	318	0.61	7.10
3	24	327	0.75	5.60
4	48	333	0.94	3.58
5	72	338	1.10	2.80
6	96	343	1.23	2.33
7	120	348	1.25	2.17
8	240	348	1.25	1.81

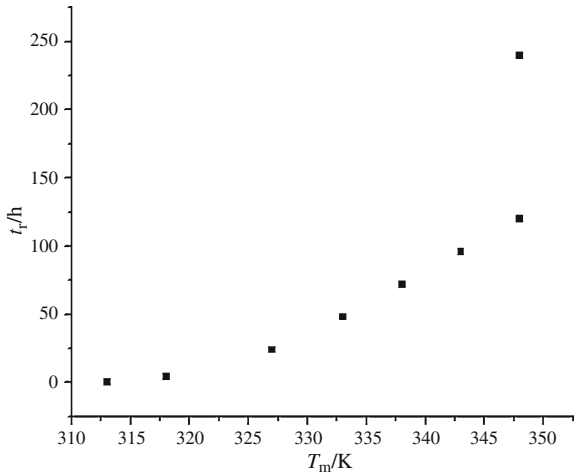

Fig. 4 Dependence of peak temperature T_{max} on annealing time t_r of ethyl cellulose samples

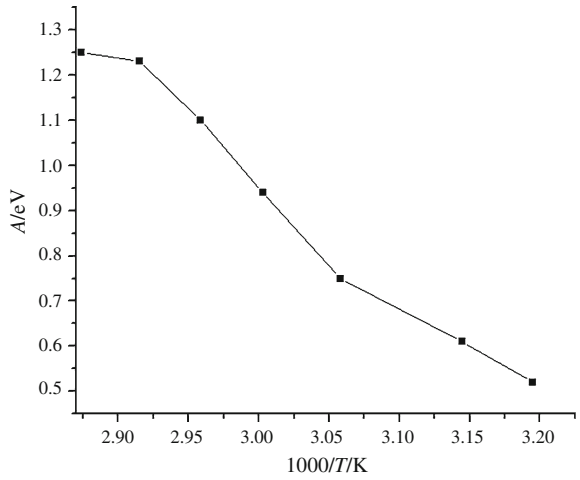

Fig. 6 Variation of activation energy against $1{,}000/T_{max}$

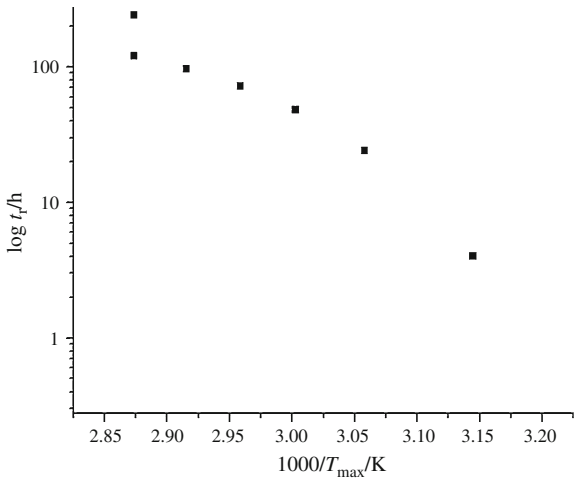

Fig. 5 Log t_r versus $1{,}000/T_{max}$ plot for corona-charged ethyl cellulose

The value of A has been found to increase with increasing value of annealing time.

The temperature at which the TSDC curves (i.e., Fig. 4) attain maximum value was plotted as a function of annealing time (t_r). It is seen that for annealing times longer than 4 h, it obeys almost Arrhenius relationship and the logarithm of t_r plotted against the $1{,}000/T_{max}$ (peak temperature) has a slope corresponding to an activation energy value of 1.16 eV (Fig. 5). Although this activation energy falls within the range of those obtained for individual TSDC curves, the peak shift observed in our corona-poled samples cannot be accounted for in terms of a delayed radiation-induced conductivity as proposed for electron-beam charged Teflon FEP electrets by Sessler and West [14]. This is to be expected that since the surface and bulk conductivities can be affected by the charging techniques. The Arrhenius behavior of annealing time is further justified by plotting activation energy (A) versus $1{,}000/T_{max}$ characteristics (Fig. 6).

It has already been mentioned that the intensity of the observed peaks (Figs. 1 and 2) gradually decreases with increase in annealing time indicating the gradual decrease of charge released during TSDC with increasing value of annealing time. Such observation may be understood in terms of the charge holding by different active traps. For mono-molecular recombination process, when free-carrier life time (τ) is constant, and for TSDC with weak detrapping of carriers, the concentration n_t of charge carriers captured by traps is given by [20]

$$n_t = 2.7 J_m k T_m^2 / edbA, \tag{5}$$

where J_m is the maximum value of the current density, e the electronic charge, k the Boltzmann constant, T_m the peak temperature, b the heating rate, A the activation energy, and d the sample thickness. The value of n_t is calculated by using Eq. 5 as given in Table 1. It is seen that n_t decreases as the annealing time increases. Such observation supports the appearance of peak of smaller intensity; it may be due to the decrease in charge released from traps with increasing value of annealing time.

Log–log plot of activation energy A versus charge concentration n_t for the EC samples is presented in Fig. 7. A straight line was obtained. Such dependence of A on n_t seems to indicate the logarithmic distribution of traps in energy and in this case one can write

$$\ln A(t) = \ln A_0 - n_t/n_0. \tag{6}$$

It can explain why the low-temperature peaks are stronger than those located at higher temperatures (Figs. 1 and 2).

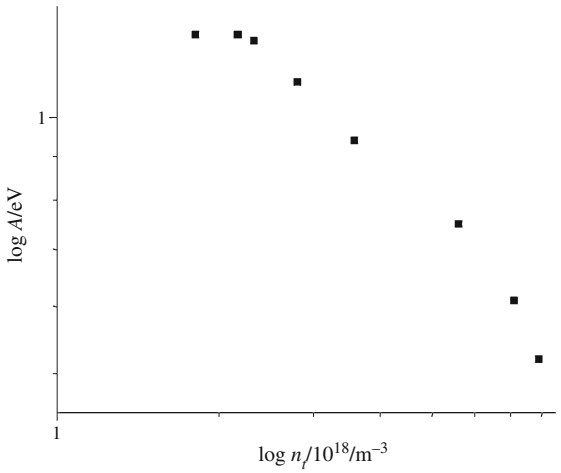

Fig. 7 Logarithmic plot of activation energy A versus charge carrier concentration for corona-charged ethyl cellulose samples annealed for different times

Conclusions

The effect of annealing time on the TSDCs of negatively corona-charged EC foil samples has been investigated, and the observed TSDCs have been found to be strongly dependent on the annealing time of short-circuited samples at room temperature. The observed polarity of TSDCs opposite to that of charging current, which was explained in terms of the homo space charge in near injecting surface region. The shifting of peak position to higher temperatures and decrease in peak intensity with increase in annealing time have been explained in terms of the neutralization of charge released from shallow traps due to ohmic conduction during annealing and contribution of charge released from increasingly deeper traps to the observed TSDCs. The stabilization of the peak at 348 K for annealing time longer than 120 h is suppose to be due to no contribution of charge during thermal cycle by the traps energetically deeper than the trap contributing to the above peak. Activation energy value (A) has been found to increase, while the trapped charge carrier concentration (n_t) was found to be decrease with increase in annealing time. Both these observations indicated the involvement of more and more deeper traps toward the contribution for the observed TSDCs with increase in annealing time. The linear relationship between ln A and log n_t indicated an exponential distribution of energetic traps in polymer matrix.

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