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Analysis of thermally stimulated discharge data on amorphous semiconductors

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This paper deals with the most common methods of interpretation of the thermally stimulated discharge (TSD) spectrum. TSD due to dipole disorientation, calculation of activation energies using initial rise method, graphical integration, and methods based on the variation of heating rates are described in some detail. It will be argued that calculation of activation energies from these methods strictly holds for relaxation of a single well-defined frequency. For a distributed relaxation, methods based on the variations of the heating rates are more appropriate, but certain difficulties may arise.

1. Introduction

Theories involved in thermally stimulated discharge (TSD) were described in a previous paper [1]. The purpose of this paper is to describe the most common methods used for the interpretation of the TSD spectrum, including the initial rise method and the graphical integration method.

2. Analysis of TSD

2.1. TSD due to dipole disorientation

2.1.1. Single relaxation time

The discharge of the frozen-in dipole polarization, $P(t)$, in a short-circuited polar electret under a linear heating rate, r, is considered here. Assuming that the polarization $P(t)$ decays with a single temperature-dependent relaxation frequency, $\alpha(T)$, according to the Debye rate equation we have

$$\frac{dP(t)}{dt} + \alpha(T)P(t) = 0 \qquad (1)$$

Integration of the above yields

$$P(t) = P_e \exp\left[-\int_{t_d}^{t} \alpha(T)\,dt\right] \qquad (2)$$

where t_d is the time of commencement of TSD.

P_e is the attained equilibrium polarization before the start of the TSD and could be expressed by

$$P_e = Np\overline{\cos\theta} \qquad (3)$$

where N is the density of dipoles, p is the electric dipole moment and θ is the angle the dipoles subtend with the applied field. For a low concentration of dipoles, the average orientation can be expressed as

$$\overline{\cos\theta} = \frac{pE_p}{3kT_p} \qquad (4)$$

The current density, $j(t)$, due to the decay of the polarization is

$$j(t) = \frac{-dP(t)}{dt} = \alpha(T)P(t) \qquad (5)$$

Using Equation 2, this can be expressed as

$$j(t) = \alpha(T)P_e \exp\left[-\int_{t_d}^{t} \alpha(T)\,dt\right] \qquad (6)$$

In a TSD run, the temperature, T, is raised at a rate $r = dT/dt$, and the released current is expressed as

$$j(T) = \alpha(T)P_e \exp\left[-\frac{1}{r}\int_{T_d}^{T} \alpha(T)\,dT\right] \qquad (7)$$

using the conditions that at the start of the run, $t = t_d$ and $T = T_d$.

The relaxation frequency for the dipole disorientation, $\alpha(T)$ is often envisaged to follow an Arrhenius shift

$$\alpha(T) = \alpha_0 \exp(-A/kT) \qquad (8)$$

where α_0 is the characteristic relaxation frequency ($T \rightarrow \infty$) and A is the activation energy for dipole disorientation. Equation 8 can be applied to describe the temperature shift of the relaxation frequency of well-characterized dipole groups normally associated with the β-type of relaxations. For dipole groups where disorientations are brought about by the segmental and cooperative movements of segments of the main chains, the frequency shift can be better described by the WLF shift (applicable for $T > T_g$)

$$\alpha(T) = \alpha_g \exp[2.303\, C_1(T - T_g) \times (C_2 + T - T_g)^{-1}] \qquad (9)$$

where for most amorphous polymers [2, 3] $\alpha_g = 7\times10^{-3}\,\mathrm{s}^{-1}$, $C_1 = 17.44$ and $C_2 = 51.6$ K.

Combining Equations 7 and 8 results in the following expression for the TSD current density:

$$j(T) = \alpha_0 \exp[-A/kT] P_e \times \exp\left[-\frac{1}{r}\int_{T_d}^{T} \alpha(T)\,\mathrm{d}T\right] \qquad (10)$$

or substituting for P_e using Equations 3 and 4

$$j(T) = \frac{\alpha_0 N p^2 \varepsilon_0 E_p}{3kT_p} \exp[-A/kT] \times \exp\left[\frac{-\alpha_0}{r}\int_{T_d}^{T} \exp(-A/kT')\,\mathrm{d}T'\right] \qquad (11)$$

Equation 11 describes the depolarization current density released due to a dipolar depolarization in a shorted electret. The first exponential, which dominates the expression at low temperatures, describes the initial increase of the depolarization current as the frozen-in dipoles gradually become disoriented. The second exponential which dominates at high temperatures will gradually depress the current released until a maximum output current is reached, after which the currently rapidly falls as the induced polarization is exhausted. The current peak is thus asymmetric, having a steeper slope on its high temperature side. The theory of TSD due to dipolar disorientation as described above, can be extended to include systems with a distribution in relaxation times [3–6].

The peak temperature, T_m, for the current peak can be found by differentiating Equation 10 and also substituting for $\alpha(T)$ from Equation 8 we have

$$T_m = \left[\frac{rA}{k\alpha_0}\exp(A/kT_m)\right]^{1/2} \qquad (12)$$

From the above it can be seen that T_m will shift towards a higher temperature if a higher heating rate, r, is employed. Also for a fixed heating rate, the position of the peak (i.e. along the temperature axis) will be an increasing function of A, the activation energy for disorientation as well as the natural relaxation time, $1/\alpha_0$, for the process. An interesting conclusion that can be drawn from Equation 12 is that T_m is independent of the forming conditions, E_p and T_p, provided the equilibrium polarization has been attained.

2.1.2. Distribution of relaxation times

In the essentially non-crystalline polymeric solid, different conformations that the macromolecules may adopt, will result in an environment that can offer differing resistances to the disorientating or rotating dipoles in different areas of the bulk. The dipoles then will have to surmount different activation energies resulting in different relaxation frequencies, $\alpha_i(T)$. Assuming that they still obey an Arrhenius shift, this can be written as

$$\alpha_i(T) = \alpha_0 \exp(A_i/kT) \qquad (13)$$

Different relaxation frequencies may also arise from different values of α_0, for which we have

$$\alpha_i(T) = \alpha_{0i} \exp(A/kT) \qquad (14)$$

A distribution of the type described by Equation 13 is usually encountered in β-type of relaxations. The type described by Equation 14 is more likely to arise from relaxations associated with movements of the dipolar groups that move in unison with the micro-Brownian motions of the main chain segments, like the α-relaxation near T_g [7]. Here different masses for the relaxing segments are most likely to be involved.

Assuming that distributions in α_0 or A are continuous, their contributions towards the polarization, $P(t)$, could be expressed as

$$P(t) = P_e \int_0^{\infty} f(\alpha_0) \times \exp\left[-\alpha_0 \int_{t_d}^{t} \exp(-A/kT)\,\mathrm{d}t\right]\mathrm{d}\alpha_0 \qquad (15)$$

for a distribution in α_0. For a distribution in A, this can be written as

$$P(t) = P_e \int_0^{\infty} g(A) \exp\left[-\alpha_0 \int_{t_d}^{t} \exp(-A/kT)\,\mathrm{d}t\right]\mathrm{d}A \qquad (16)$$

The distributions are also normalized such that

$$\int_0^{\infty} f(\alpha_0)\,\mathrm{d}\alpha_0 = \int_0^{\infty} g(A)\,\mathrm{d}A = 1 \qquad (17)$$

The corresponding expressions for the current can be found by differentiating Equations 15 and 16 which yields

$$j(t) = P_e \exp(-A/kT) \int_0^{\infty} \alpha_0 f(\alpha_0) \times \exp\left[-\alpha_0 \int_{t_d}^{t} \exp(-A/kT)\,\mathrm{d}t\right]\mathrm{d}\alpha_0 \qquad (18)$$

and

$$j(t) = P_e\alpha_0 \int_0^{\infty} g(A) \exp\left[[-A/kT] - \alpha_0 \times \int_{t_d}^{t} \exp(-A/kT)\right]\mathrm{d}A \qquad (19)$$

The equations above also show that the TSD currents are independent of the forming conditions provided that the fullest possible polarization has been reached. If this condition is not achieved, say due to too short a polarization time, t_p, or too low a temperature, T_p, then an effective distribution can be defined by [8, 9]

$$f^*(\alpha_0) = f(\alpha_0)FS(\alpha_0) \tag{20}$$

or

$$g^*(\alpha_0) = g(A)FS(A) \tag{21}$$

where $FS(\alpha_0)$ or $FS(A)$ refers to the "filling state" of the polarization. For a completely filled state, i.e. one where the electret has been polarized to its equilibrium polarization value, P_e, the parameter FS equals unity.

2.2. Calculation of activation energies

In theory, the activation energy of non-distributed relaxation process can be calculated from a single TSD curve by means of some characteristic elements of the peak such as its half-width, inflection point or initial part of the current rise. Other methods based on utilizing the whole current–temperature curve or that which uses several heating rates are also available. Most of these methods, except for the one using the whole of the TSD plot, were derived from methods based on the early works of thermoluminescence or thermally stimulated conductivity [10, 11].

2.2.1. Initial rise method

This method is credited to Garlick and Gibson [12] and is based on the fact that the second integral term in the $j(T)$ expression (Equation 11) is negligible at temperatures $T < T_m$. Thus, differentiating with respect to $1/T$, the following expression for the initial portion of the current rise is obtained:

$$\frac{\mathrm{d}}{\mathrm{d}(1/T)} \ln j(T) = -A/k \tag{22}$$

where A is the activation energy. By plotting $\ln j(T)$ versus $1/T$, A can be determined. This procedure is generally advocated to be satisfactory and is widely used. It does not necessitate a linear heating rate nor a precise knowledge of the absolute temperature.

The approximation that at $T < T_m$ the TSD current can be simplified into $j(T) = \text{constant} \exp[-A/kT]$ may not be true if the magnitude of the TSD signal in the rising portion of the plot is large when compared to the peak height. When this happens, then the plot of $\ln j(T)$ versus $1/T$ ceases to be linear and a value of A (obtained from the slope) has to be corrected as

$$A_{\text{corrected}} = (1 + 0.74d_1 + 0.092d_2)A - (2d_1 + 0.22d_2)kT_m \tag{23}$$

where A is the value obtained from the least-squares-fitted plot of $\ln j(T)$ versus $1/T$ with experimental values of $j(T)$ that had been culled between two values of the current $j(T_2)$ and $j(T_1)$ where $T_1 < T_2 < T_m$. The parameters d_1 and d_2 are defined as

$$d_1 = \frac{j(T_1)}{j(T_m)} \tag{24a}$$

$$d_2 = \frac{j(T_2)}{j(T_m)} \tag{24b}$$

The ranges of applicability of Equation 23 are $d_2 \leqslant 0.5$, $d_2/d_1 \geqslant 5$, and

$$10 \leqslant \frac{A_{\text{corrected}}}{KT_m} \leqslant 100 \tag{25}$$

2.2.2. Graphical integration method

From Equation 5, the relaxation time can be written as [13, 14]

$$\tau(T) = \frac{P(T)}{j(T)} = \frac{1}{r}\left[\int_T^\infty J(T')\,\mathrm{d}T'\right]\frac{1}{J(T)} \tag{26}$$

or

$$\ln \tau(T) = \ln\left[\frac{1}{r}\int_T^\infty J(T')\,\mathrm{d}T'\right] - \ln J(T) \tag{27}$$

Assuming an Arrhenius shift for $\tau(T)$, we have

$$\ln \tau(T) = \ln \tau_0 + A/kT \tag{28}$$

The quantity $\tau(T)$ can be calculated by using Equation 27 where we have taken the integral term to be easily evaluated by graphical integration of the area of the TSD peak from $T \rightarrow \infty$. Knowing $\ln \tau(T)$ and plotting it against $1/T$, a straight line may be obtained, yielding the activation energy A. This straight line is usually called the BFG plot after Bucci *et al.* [13]. Like the initial rise method this procedure does not presume a linear heating rate, but unlike the former it utilizes data from the whole of the TSD peak. The BFG plot is to be preferred if the TSD plots exhibit large parasitic background currents which may be difficult to eliminate from the small current signal portion of the initial rise.

2.2.3. Methods based on the variation of heating rates

These methods are based on the shifts of the TSD current maximum with the heating rates employed. Several ways of plotting the results have been proposed [15, 16]. It can be readily seen from Equation 12 that

$$A = \frac{kT_{m_1}T_{m_2}}{T_{m_1} - T_{m_2}} \ln\left(\frac{r_1 T_{m_2}^2}{r_2 T_{m_1}^2}\right) \tag{29}$$

i.e. if the heating rate is changed from r_1 to r_2, the activation energy for the relaxation can be calculated from the corresponding shift of the peak temperature T_{m_1} to T_{m_2}.

A better procedure utilizing a series of heating rates, r (resulting in corresponding T_ms), was also suggested by Hoogenstraaten whereby the plot of $\ln(T_m^2/r)$ against $1/T_m$ should yield a straight line, from the slope of which the activation energy can be found [17]. The accuracy of these methods will depend on the accurate control of the heating rates employed and also on the magnitude of the actual shifts of the T_ms. Therefore it can be seen from Equation 12 that the method is less suitable for relaxations with large activation energies, A, because the shifts of the current maxima will be smaller and experimentally more difficult to measure.

Several other methods to calculate the activation energy based on utilizing the shape or symmetry of the TSD peak can also be found [18–21]. More recently, a new procedure has been proposed for a more accurate determination of the activation energy [22].

2.3. Calculation of other relaxation parameters

If the activation energy for the relaxation is known by applying the procedure described above, then the characteristic frequency factor $\alpha_0 = 1/\tau_0$ can be calculated from Equation 12 if T_m is noted from the experimental peak. α_0 can also be directly determined from the BFG plot (Section 2.2.2).

The equilibrium polarization, P_e, for the electret may also be obtained by integrating the area underneath the $j(T)$ curve, assuming that there was no loss or change of polarization during the cooling and isothermal stages of the TSD run, i.e.

$$\begin{aligned} P_e &= P(T_p) \\ &= P(T_d) \end{aligned} \tag{30}$$

Hence

$$P_e = \int_{T_d}^{\infty} j(T)\,dT \tag{31}$$

Also using the relation for the relaxation strength

$$\begin{aligned} \Delta\varepsilon &= \varepsilon_s - \varepsilon_\infty \\ &= \frac{P_e}{\varepsilon_0 E_p} \end{aligned} \tag{32}$$

where E_p is the field applied during formation. From the above equation and using Equations 3 and 4 we can relate the experimentally observed quantity, $\Delta\varepsilon$, with the molecular parameters, N, the dipole density and p, the dipole moment. This is expressed as

$$\Delta\varepsilon = \frac{Np^2}{3\varepsilon_0 k T_p} \tag{33}$$

where T_p is the temperature of formation of the electret. If either quantity N or p, is known, then the other can be calculated using Equation 33. The obvious condition is that P_e is adequately described by the Langevin equation and that it is recovered fully during the TSD.

2.4. Activation energy for distributed processes

The methods described previously to calculate the activation energy only holds strictly for relaxations of a single, well-defined frequency. For a distributed relaxation, the initial rise method for the calculation of the activation energy would theoretically yield too low a value by over emphasizing the role of the components with the slowest relaxation times. The graphical integration method will also have the same systematic error as a result of taking into account too high a number of components.

It has been shown that the initial rise method can still be applied to the case where there is a symmetrical distribution in $1/\alpha_0$ [5]. Up to the lower half-width temperature, the TSD current was shown to obey, approximately

$$\ln J(T) \sim \text{const} - \frac{WA}{kT} \tag{34}$$

where W is a constant whose value will depend on the type of the distribution describing $1/\alpha_0$. Equation 34 will also show that A can still be calculated by the initial rise plot.

The methods based on the variations of the heating rates are still theoretically applicable, without modification, for the distributed process. This is so because the peak of the TSD current plot is determined essentially by the components with the average value of the activation energy. However, a problem would exist in the exact determination of T_ms and their shifts due to the broad nature of the TSD plots of the distributed systems.

The determination of other relaxation parameters, such as the characteristic frequency, equilibrium polarization and relaxation strength, is little affected by the existence of a distribution in relaxation times. The quantities can still be approximated by the equations of Section 2.2 [23].

2.5. Charge motion model

Assuming that the decay of a uniform distribution of the excess charges obeys first order kinetics with a single relaxation time, then the classical methods (initial rise, variable heating rate methods) used to evaluate the TSD parameters are still applicable. This follows from the similar functional relationship of the $j(T)$ expression for the different decay processes that was briefly discussed in the preceding sections.

For a spatially non-uniform distribution of space charges, a modification to the graphical integration method has been proposed so that [24]

$$\left[\int_{T_d}^{T} j(T')\,dT'\right]\left[\int_{T}^{\infty} j(T')\,dT'\right]^{-1} \tag{35}$$

is plotted against $1/T$ to yield the effective activation energy for the decay (compare with the BFG plot of Section 2.2.2). Another method has been discussed where the quantity in the following equation is plotted against $1/T$ [15]

$$\left[T_m^2 \int_{T_d}^{T} j(T')\,dT'\right]\left[T^2 \int_{T}^{\infty} j(T')\,dT'\right]^{-1} \tag{36}$$

It should be noted that the methods mentioned above are applicable in the low-temperature region of the current plots. The linearity of the latter plot is also suggested as a good test for the applicability of the charge motion model. The linearity of this plot is unique to the decay of a space charge polarization via their self-drift.

In the charge motion model, it is also expected that the activation energy calculated from TSD data will be closely related to that for the dark conductivity mechanism in the medium and as such the method can be used as a good complement to the traditional current–voltage–temperature method, particularly when blocking electrodes could not be avoided [25, 26].

3. Conclusion

In this paper, the most common methods of analysis of TSD were described. In view of the complexity of the charge storage mechanisms in insulators and the uncertainties associated with their physical structures in general, the interpretation of their TSD spectrums has to be carried out with some knowledge about the possible underlying microscopic processes involved. This is important because most models usually adopted for describing dipolar, ionic and electronic processes predict similar functional relationships which can lead to TSD peaks that look deceptively similar. The interpretation of the TSD results will be greatly facilitated if relevant factors such as physical structure, chemical content, thermodynamic behaviour, etc., are reasonably well known from other complementary experiments.

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