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Analysis of the TSD spectra of polymers near the glass transition temperature using the fractional purification method

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Abstract. In this work, the thermally stimulated spectroscopy methods are applied to PET films exposed to UV rays for the analysis of electrically active defects parameters in these materials, such as activation energy (E_a) and relaxation time, or frequency factor (ω). To obtain these parameters the methods of thermally stimulated currents and thermally stimulated currents thermal sampling were used. To determine the relaxation parameters using the methods of thermally stimulated currents, various mathematical methods of data processing were used. The Eyring equation and the compensation law were found to be the most correct for PET films. The value of the activation energy determined with their help for the PET exposed to UV rays turned out to be 1.07 eV, and the value of effective frequency factor $\omega = 1/\tau_0 = 5 \times 10^{10}$ c^{-1}.

Keywords: electrets, polyethylene terephthalate, thermally stimulated depolarisation currents, thermally stimulated depolarisation currents thermal sampling.

Introduction

Methods of thermal analysis have been widely used since the 1970s due to the highly informative results. Due to its applicability to a wide range of dielectrics, various interpretations of current methods are of particular interest, allowing us to determine such parameters of electrically active defects in these materials as activation energy (E_a) and relaxation time, or frequency factor (ω), as well as to draw conclusions about the nature of relaxation processes and changes in the thermodynamic characteristics of the system.

The paper analyses the results of a study of polyethylene terephthalate (PET) films by the methods of thermally stimulated currents (TSC) and thermally stimulated currents thermal sampling (method of fractional purification) (TSC-TS), conclusions are drawn about the effectiveness of various methods for processing experimental results obtained by these methods in the field of polymer glass transition temperature.

Materials and methods

TSC and TSC-TS methods

The thermally stimulated relaxation currents method (TSC) in the short-circuit mode with linear cooling involves the following techniques: a sample placed between two electrodes (i. e., being in the short-circuit mode) is polarised at a temperature higher than the glass transition temperature. Then the sample is cooled with an applied field to "freeze" the resulting state. After that, the field is removed and the object of study is heated according to a linear law (Fig. 1).

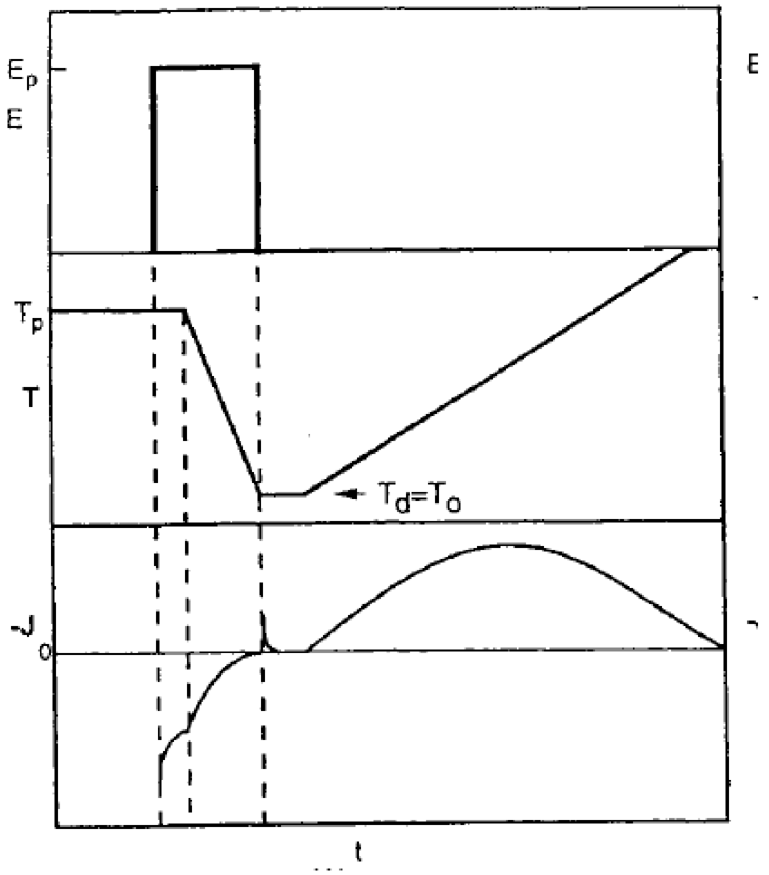

Fig. 1. Mode of operation of the TSC method

A thermally stimulated depolarisation current flows in a circuit. By taking readings using an electrometer and a thermocouple, the current dependence on temperature is obtained. On the graphs of these dependencies, it is possible to identify peaks; their height and location provide information about the mechanism of electrical relaxation and the parameters of electrically active defects. This method sometimes indirectly allows us to calculate the change in the entropy of the system by abnormally high values of the frequency factor and activation energy (Shabanova et al. 2020).

The fractional purification mode (TSC-TS method) is largely similar to the previous mode (TSC). The initial high temperature at the polarised sample is also selected. Then the cooling begins to a temperature, usually denoted by the depolarisation temperature, which does not differ too much from the highest temperature (T_{max}). Thus, the polarisation takes place in a narrow "window" of temperatures, which allows us to observe only those processes and transitions that fall into this window. Then the sample is cooled with the field turned off to the "freezing" temperature (Fig. 2) and after that the dependence of the TSC-TS current on the temperature during heating is removed. The fractional purification method provides a unique opportunity to determine the nature of complex transitions in compounds (this is especially interesting in cases where the transitions overlap and it is important to identify each transition separately).

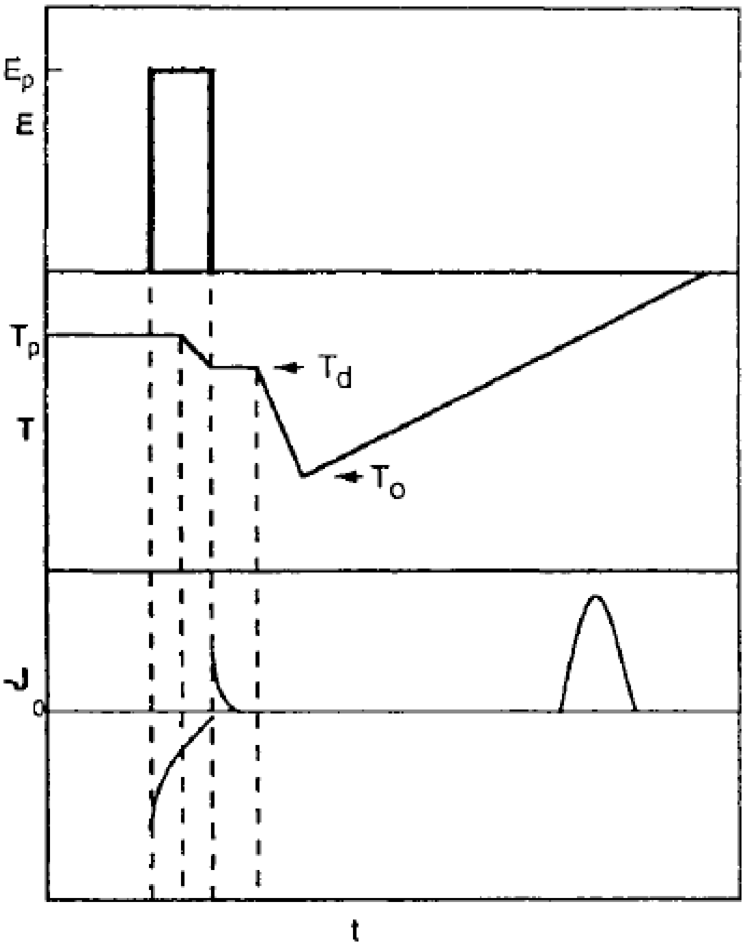

Fig. 2. Mode of operation of the TSC-TS method

In the experimental part of the work, films of polyethylene terephthalate with a thickness of 30 microns were used. PET is a polymer that is a complex thermoplastic polyester of terephthalic acid and ethylene glycol with a glass transition temperature in the region of 80 °C. PET films are a composition consisting of amorphous and crystalline phases. PET in the amorphous state is characterized by a mutual disorderly arrangement of chains of macromolecules with single separate formations of an ordered structure. The crystal state of PET is characterised by the presence of crystallites in the material, i. e. folded bundles of macromolecules in the form of folded bundles. The size of the crystallites in the films is about 5–10 nm, and the degree of crystallinity is about 40–50%.

Calculation methods

To determine the relaxation parameters using the methods of thermally stimulated currents, several mathematical data processing methods may be used. If the polarisation occurred during continuous linear cooling, the method of varying the heating rates (the Bogan-Butte method), the Tikhonov regularisation method or the initial rise method (the Garlick-Gibson method) is used. The first two methods correctly determine the parameters of electrically active defects in the case of a single relaxation in the temperature range that does not affect the glass transition region. The method of initial rise a priori uses values in the temperature range below the glass transition, but it is the least informative and accurate.

In addition, according to the obtained data, mathematical modelling alone is seldom enough to separate non-cooperative processes, and often this task remains unresolved in principle.

The Garlick-Gibson method is based on the fact that at sufficiently low temperatures, the change in charge carriers localised at the capture centres is small compared to the relative change in the concentration of free charge carriers. As shown by theoretical studies at sufficiently low temperatures ($T \approx T_0$), the nature of the dependence of the depolarisation currents does not depend either on the order of the kinetics of the relaxation process or on the heating rate. Thus, in the initial section, the TSD current curves have an exponential dependence on temperature and have the form:

$$j(T) \simeq j_0 e^{-\frac{W}{kT}} \tag{1}$$

So, if we construct the initial section of the current obtained by TSC method in the Arrhenius coordinates ($\ln j \sim 1/kT$), the dependence is linearised. The slope of such a straight line enables calculation of the activation energy.

Tikhonov's method of regularising algorithms provides information about the functions of the activation energy distribution of electrically active defects. This method is based on solving the problem of finding the distribution function of the activation energy for given experimental current values. This problem is incorrect according to Hadamard (small errors at the input give large errors in the results) and is solved by the proposed Tikhonov numerical method. The solution algorithm is described in detail in (Gorohovatskij, Temnov 2007).

The advantages of this method are that it allows us to solve a one-dimensional problem finding a distribution function. This method also takes into account the order of kinetics, but it will be suitable for solving the problem only within the strict framework of a certain model and will give erroneous values when going beyond this framework (for example, this method is not sensitive to changes in entropy and it is impossible to separate such processes with its help).

For an ideal Debye relaxation with a single relaxation frequency, the relaxation times $\tau(T)$ can be obtained from the experimental TSC-TS spectra (the method of thermal dots or fractional purification) using the standard Bucci-Fieschi-Guidi method (Bucci et al. 1966) or the "BFG" method. The relaxation times ($\tau(T)$) for a single Debye relaxation are determined by the equation (Bucci et al. 1966; van Turnhout 1971):

$$\tau(T) = \frac{P(T)}{J(T)}, \tag{2}$$

where $P(T)$ is the remaining polarisation at an arbitrary temperature T. The TSC-TS current spectra are integrated numerically to obtain $P(T)$ (Bucci et al. 1966):

$$\tau(T) = \frac{1}{\beta} \frac{\int_T^{T_m} J(T')\,dT'}{J(T)}, \tag{3}$$

where β is the heating rate, T_m is the temperature at which the entire charge was released, and $J(T)$ is the depolarisation current at a given temperature T. The polarisation $P(T)$ in this case is usually found as follows:

$$\beta P(T) = \int_T^{T_m} J(T')\,dT' = \int_{T_0}^{T_m} J(T')\,dT' - \int_{T_0}^{T} J(T')\,dT' = \beta P_0 - \int_{T_0}^{T} J(T')\,dT', \tag{4}$$

where P_0 is easily determined by numerically integrating the region of the entire experimental TSC-TS spectrum.

For distributed relaxation times, it is known that the BFG method gives underestimated values of the activation energy E_a (van Turnhout 1971), although with sufficiently narrow polarisation windows used in the TSC-TS method, this is not so significant and can be corrected by introducing some empirical correction (Teyssedre, Lacabanne 1995), taking into account the fact that P_0 in the case of the relaxation time distribution is somewhat larger than in the case of a single relaxation time. Taking into account such an amendment leads to the equation:

$$\beta P(T)=\frac{\beta P_0}{1,3}-\int_{T_0}^{T} J(T')\,dT' \tag{5}$$

The modified value of $P(T)$ is then used in equation (2) and, at a heating rate of several degrees per minute, gives for most polymers a relaxation time value lying in the range of $10^1 < \tau < 10^4$ c. The temperature dependence of the relaxation time is used later for the analysis of relaxation data:

$$\tau(T)=\tau_0 \exp\left(\frac{E_a}{RT}\right), \tag{6}$$

where τ_0 is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant. Unfortunately, in many cases, for example, near the glass transition temperatures of polymers, the use of equation (6) leads to sufficiently high values of E_a and unrealistic values of relaxation times (less than 10–20 s).

Another method of empirical analysis, which is usually used and can give more physically realistic parameters, at least in the case of non-cooperative relaxations at not very high temperatures, is based on the equation of activated Eyring states. In this case, this equation is used:

$$\tau(T)=\frac{h}{kT}\exp\left(\frac{\Delta H}{RT}\right)\exp\left(-\frac{\Delta S}{R}\right), \tag{7}$$

where k is Boltzmann's constant, h is Plank's constant, and ΔH, ΔS and $\Delta G = \Delta H - T\Delta S$ are the enthalpy of the activated states, entropy and free energy, respectively. It follows that the construction of a graph corresponding to equation (7) in Arrhenius coordinates $ln(1/\tau T) \sim 1/T$ allows us to calculate the enthalpy and entropy, and only then the activation energy per mole of the substance $E_a = \Delta H - T\Delta S$ and τ_0.

When interpreting the data of fractional purification, the so-called compensation law, or the "isokinetic" effect, can also be used (Ibar 1993). Compensation equation

$$\tau_0=\tau_c \exp\left(-\frac{E_a}{RT_c}\right) \tag{8}$$

assumes the presence of a compensation temperature T_c, at which all relaxations are observed for the same time τ_c , or in other words, a linear dependence between the activation energy of "individual" relaxations and $\ln(\tau_0)$. The construction of this dependence again in the Arrhenius coordinates $\ln(\tau_0) \sim E_a/R$ makes it possible to determine both the compensation temperature T_c, and τ_c.

Substitution (8) in (6)gives

$$\tau(T)=\tau_c \exp\left(\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_c}\right)\right), \tag{9}$$

which in its form is in principle similar to the Eyring equation (7) and allows us to find all the parameters of the relaxation process.

Results

Figure 3 shows the results of temperature dependence of depolarisation currents for PET films exposed to UV light, obtained by TSC method. The graphs show characteristic current maximums located in the glass transition region.

Using the Tikhonov's regularising algorithms method, the parameters of electrically active defects were calculated. The results are presented in Table 1.

It can be noticed that the values of the activation energy and the frequency factor are abnormally high. As mentioned above, this calculation method does not take into account the change in entropy, which leads to an error.

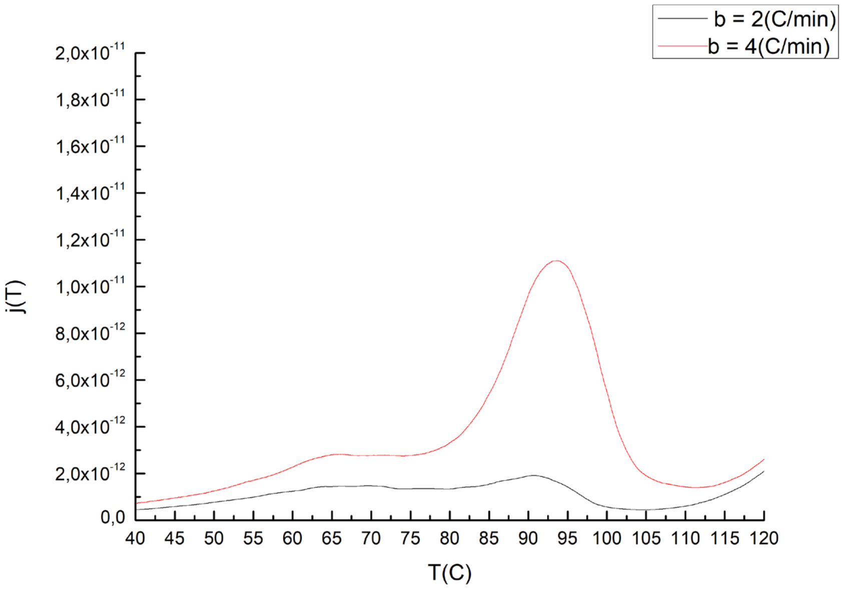

Fig. 3. Depolarisation currents for PET films. (2 and 7 indicate the heating rate in °C / min, respectively)

Table 1. Results obtained by Tikhonov's regularising algorithms method

Heating Rate, °C / min	**T_m(°C)**	**log (τ_0)**	**E_a(eV)**
2	90.6	−54	3.9
4	92.6		

Fig. 4 shows the results of temperature dependence of depolarisation currents for PET films exposed by UV light, obtained by TSC-TS method. The relaxation parameters were calculated using the methods described above. The values obtained using equation (6) are presented in Table 2. The values obtained using equation (7) are presented in Table 3. An illustration of the compensation law for PET films is the graphs of BFG-relaxations constructed in Arrhenius coordinates (Fig. 5).

It is notable the slope of individual lines obtained at different polarisation temperatures increases as they approach the glass transition temperature, and their extrapolation falls into one point in the frequency-temperature space, which is determined by two compensation parameters: τ_c and T_c (their values are shown on the graph). Substituting these values in (8) allows us to determine the value log (τ_0) = −13,3 which agrees fairly well with the data in Table 3.

Conclusion

In this paper, methods for obtaining parameters of electrically active defects by processing the results of TSC and TSC-TS measurements were investigated. A comparison of the obtained data showed that when processing the results of thermal activation spectroscopy of relaxation processes in the polymer glass transition region, the use of the Eyring equation or the compensation law proves the most accurate.

The value of the activation energy determined with their help for the PET exposed to UV rays turned out to be 1.07 eV, and the value of effective frequency factor $\omega = 1/\tau_0 = 5 \times 10^{10}$ c^{-1}.

Conflict of interest

The authors declare that there is no conflict of interest, either existing or potential.

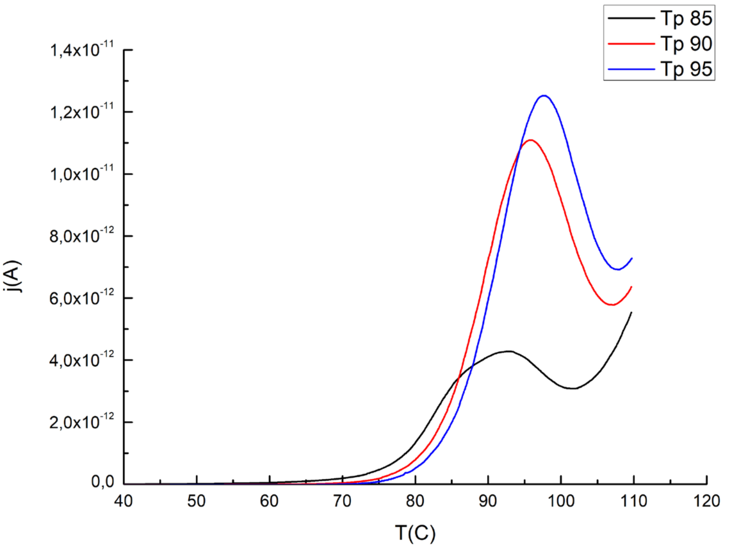

Fig. 4. Depolarisation currents for PET films (TSC-TS) (95, 90 and 85 indicate the polarisation temperatures in °C / min, respectively)

Table 2. Results obtained using equation (6)

T_p(°C)	T_m(°C)	$\log(\tau_0)$	E_a (eV)
85	92.8	−21.5	1.68
90	95.9	−30.7	2.35
95	97.7	−30.2	2.33

Table 3. Results obtained using equation (7)

T_p(°C)	Tm(°C)	ΔH (kcal/mol)	ΔS (cal/K)	E_a (eV)	$\log(\tau_0)$
85	92.8	38.06	37.46	1.07	−6.6
90	95.9	53.54	79.25	1.08	−13.4
95	97.7	53.04	77.19	1.07	−12.1

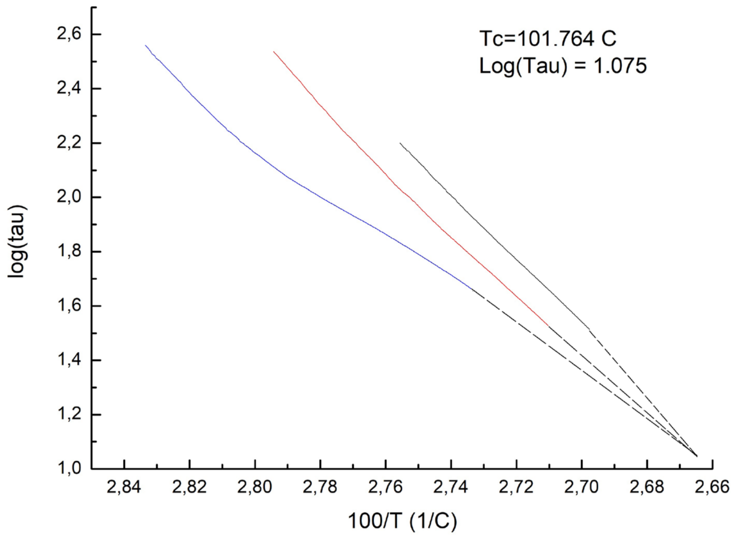

Fig. 5. An illustration of the compensation law for PET films

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