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Assessment of activation energies of transitions by thermally stimulated discharge current (TSD) experiments

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SUMMARY

The thermally stimulated discharge currents are very sensitive to the changes in molecular mobility of polar particles. Using the short-circuit arrangement without an air gap the depolarisation current can be described easily, if the A activation energy is known. There are many methods to determinate the activation energy, but these require either complicated experimental work or are limited in accuracy. The present method makes possibile the calculation of A from a single TSD experiment with an accuracy of 2% or better.
The demonstration shows the resolution of different transitions in unplasticized PVC.

INTRODUCTION

The thermally stimulated discharge current method (known also as depolarisation spectroscopy) is very powerfull to study polymers and polymer compounds. The experimental technique is not too complicated (1,2), in spite of this it is not widely used. There are different techniques, which are sensitive to different processes taking place in the polymer sample during the depolarisation (1). The most commonly used is the short-circuit method, since it is less sensitive to the changes in conductivity of the sample. Its efficiency is 100% for dipole reorientation and fairly high for Maxwell-Wagner polarisation, too. The experimental technique will be written just briefly here. The arrangement shows the Fig.1. below. The sample is heated to the polarising temperature, the polarising field is turned on, and the sample will be polarised for a given period

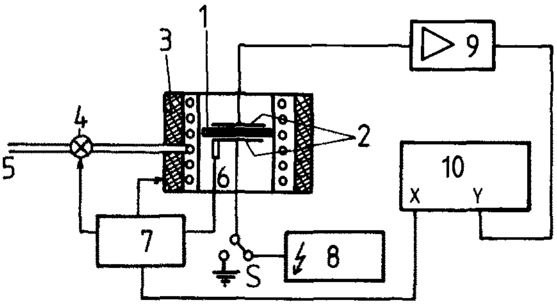

Figure 1.

Block diagram of the TSD apparatus
1. Sample
2. Electrodes
3. Heater
4. Magnetic valve
5. Liquid nitrogen inlet
6. Temperature sensor
7. Temperature programmer
8. High voltage D.C. supply
9. D.C. amplifier
10. X – Y recorder

The switch S is grounded when the external field is off.

After that the sample will be cooled down at a determined rate to T_o under voltage. After removing the polarising field the short circuit current of the sample will be recorded using a well determined b heating rate. The most important quantities as a function of the time are outlined in Fig.2.

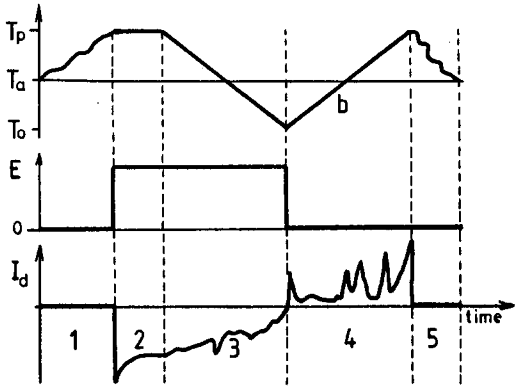

Figure 2.

Temperature, electric field and current during the TSD experiment

1. Pre-heating
2. Polarizing at T_p
3. Cooling down to T_o
4. Heating and recording of TSD current
5. Cooling to ambient temperature

b is the heating rate

The method was used among others for investigations of inorganic crystals (7,8), polycarbonate (6), copolymers and blends (1,5), PVC (1,11,13,14) and chlorinated polyethylene (12).

THEORETICAL

The theory of thermally stimulated currents have been summarised by vanTurnhout (1), Aoki and Brittain (6). The relaxation time of the dipoles in a dielectric can be approximated by the Arrhenius equation:

$$\tau(T) = \tau_o \exp(A/RT) \qquad (1)$$

where τ_o is constant preexponential factor.
At the T_p polarising temperature and during the forming a P polarisation developes near the P_o in the given field E. Shorting the electret, the depolarisation current density is:

$$j(t,T) = -P(t,T)/\tau(t) \qquad (2)$$

using a constant b heating rate.

$$T = T_o + bt \qquad (3)$$

the depolarisation current can be expressed as

$$I(T) = \frac{P_o \mathcal{A}}{\tau_o} \exp\left[-\frac{A}{RT} - \left(\frac{1}{b\tau_o}\right)\int_{T_o}^{T} \exp\left(-\frac{A}{RT}\right) dT\right] \qquad (4)$$

At the T_m $dI/dT=0$. Differentiating eq.4. τ_o can be expressed as:

$$\tau_o = \frac{RT_m^2}{b\ A \exp(A/RT_m)} \qquad (5)$$

By substitution $s = A/RT$ in eq.4.:

$$I_{(s)} = \frac{P_0\mathcal{A}}{\tau_0} \exp \left[-s + \frac{A}{\delta R \tau_0} \int_{s_0}^{s} \exp(-s)\ s^{-2}\ ds\right] \qquad (6)$$

Let $A/\delta R\tau_0=B$ and $P_0\mathcal{A}/\tau_0=C$. The integration leads to a well convergent infinite series.

$$I_{(s)} = C \cdot \exp \left(-s - B\left[\exp(-s)(s^{-2}-2s^{-3}+6s^{-4}\ \ldots)\right]_{s_0}^{s}\right) \qquad (7)$$

If s is large, greater than 10, the first three terms give an approximation of about 2%, which is reasonable for practical use. The values of s are generally over 20, in this case the largest error is within 0.3%, which is negligable. The eq.7. can be easily calculate by computer. This approximation well describes the every single transition observed in a measured TSD curve. Since a real polymer contains different kinds of polare groups, a measured TSD curve is always complex, consists of multiple transitions. In case of the short-circuit method the external electric field on the sample is near zero during the depolarisation. It is assumed, that the individual processes do not influence one another.

$$I_{d(t)} = \sum_{i=1}^{n} I_{d(T)_n} \qquad (8)$$

The calculation of τ_0 is simple using the eq.5., there are many existing methods to acquire the activation energy.
The first exponential of eq.4. dominates at low tempetatures, so:

$$I_{(T)} = \text{const.}\ \exp(-A/RT) \qquad (9)$$

This so called initial rise method can be used to $I < 0.05 \cdot I_m$ and in the case of single transition only.
From eq.5. can be deduced

$$A = R\ \frac{\ln(T_{m(1)}^2/\delta_1)-\ln(T_{m(2)}^2/\delta_2)}{1/T_{m(1)} - 1/T_{m(2)}} \qquad (10)$$

The maximum of the depolarisation current is shifted to higher temperatures, when the δ heating rate is increased. By estimating the T_m at two (or more) different rates, the activation energy of processes can be calculated from eq.10.
Let us view the shape of depolarisation current peaks. The Fig.3. shows calculated TSD currents of transitions having the same activation energy but different T_m. The transitions become broader with the increasing of T_m.
In the Fig.4. calculated TSD peaks of different activation energy and the same T_m are plotted. The currents both in the Fig.3. and in the Fig.4. are calculated using a negligable low T_0. Representing the depolarisation current as a function of reciprocial temperature uniform curves are obtained if the activation energy is constant. It means that the TSD curves can be normalised using $1/T^* = 1/T - 1/T_m$ and if it is necessary, $I^* = I/I_m$. It is preferable to represent I in logaritmic scale.

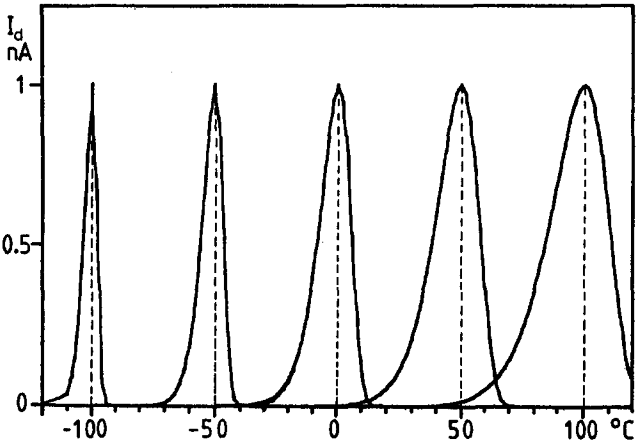

Figure 3.

Calculated TSD currents of transitions having the same activation energy (100 kJ/mol) and different Tm

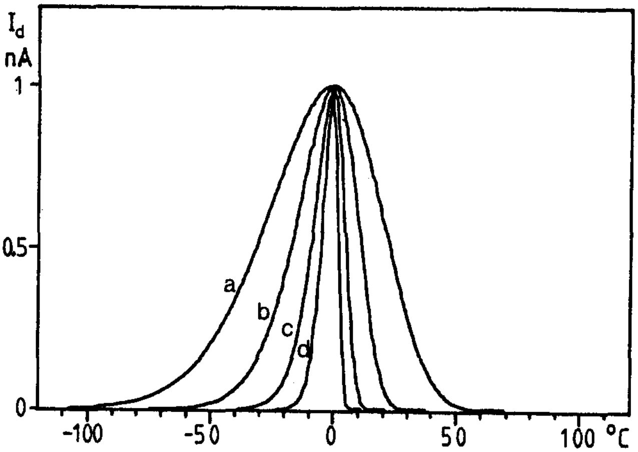

Figure 4.

Calculated TSD currents of transitions having $\vartheta_m = 0°C$ and different activation energy

a. 25
b. 50
c. 100 and
d. 200 kJ/mol

If the normalised curves are equal, their shape depend on the activation energy only. The A can be calculated from their selected points e.g. the half width. The Fig.5. demonstrates the calculated lnI vs. 1/T curves of different transitions having Im=1000 pA and A=100 kJ/mol. By numerical solving of $I_{(T)}=I_m/2$ the T_l and T_u values were determined. It has been found that the activation energy can be expressed in J/mol as

$$A = 20 \frac{1}{1/T_l - 1/T_u} \tag{11}$$

or

$$A = 12 \frac{1}{1/T_l - 1/T_m} \tag{12}$$

Taking into consideration that the depolarisation current rapidly descends on the side of higher temperature. In the case of a complex spectrum the descending side is more distorted by the consecutive transition, for which it is prefered to use eq.12. The constants are independent on the b heating , rate. The T_m and I_m increase caused by the increasing of b, however the full charge of the transition remains constant.

$$Q = \int_{t_o}^{t} I dt \quad \text{i.e.} \quad Q = 1/b \int_{T \ll T_m}^{T \gg T_m} I dT \tag{13}$$

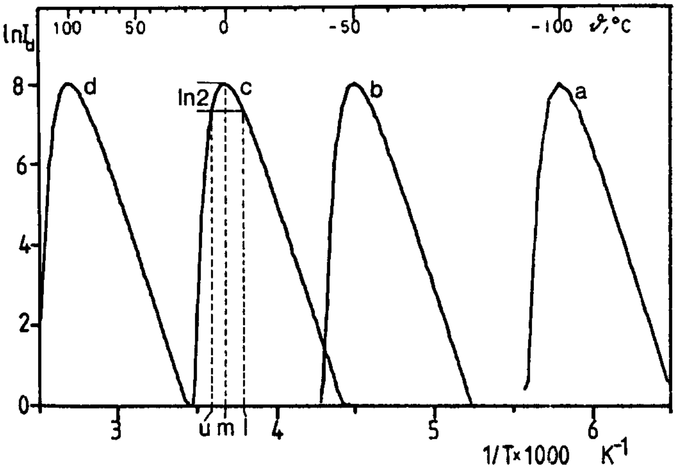

Figure 5.

lnI vs. 1/T diagrams of TSD peaks of 100kJ/mol activation energy having different ϑ_m
a. −100
b. −50
c. 0 and
d. +100 °C

The letters u, m and l show the 1/Tu, 1/Tm and 1/Tl respectively

The relaxation strength of a transition can be also easily calculated by

$$\text{Relaxation strength} = \sigma/E\varepsilon_0 \qquad (14)$$

where $\sigma=Q/\mathcal{A}$.

EXPERIMENTAL

Sample preparation

The tested formulation contained the most necesary additives only:

PVC ONGROVIL S-5070[1]	100	w.parts
Tin stabilizer	1	"
Paraffin type lubricant	0.15	"

The components were mixed on a roll-mill at 158 °C for 2 minutes, then pressed about 0.4 mm thick plates. Disks of 54 mm diameter were die-cut. For electrodes Graphit 33[2] conductive spray was used.

Apparatus

For investigations of PVC (and other polymers) a home-made apparatus is used as a part of MULTIRELAX[3]. The least measurable current is 10^{-13} A limited by noise and drift, therefore a fairly large electrode area was chosen.

The main data are:

Polarising voltage	1210 V
Heating and cooling rate	1 K/min
Sample/electrode diameter	54/38 mm

In the present work polarising temperature and time was 115 °C and 30 min. respectively. Starting temperature ϑ_0= −120 °C was chosen. The depolarisation current was recorded by an X − Y recorder.

Calculations

Calculations were carried out by EMG 666 computer connected with a Videoton NE 2000 plotter. The recorded values were inputed manually into the computer.

Assuming a linear connection between the current and area as

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1. K-value 70, Product of Borsodi Vegyi Kombinat, Hungary
2. Product of Kontakt Chemie, Rastatt FRG.
3. Assembled by Plastic Research Institute, Budapest

well as the polarising field, the recorded currents were transformed to 30 cm^2 electrode area and 1 kV/mm field. The apparent activation energies were determined by eq.12.

RESULTS AND DISCUSSION

The measured TSD curve of an U-PVC sample is shown on Fig.6. Considering the final period as initial part of a transition, it was evaluated by the eq.9. Substracting the calculated values from the measured curve, the data of the 95°C peak were determined. It was calculated by eq.7. and also substracted. This procedure was used consecutively to find transitions A and B, as well.

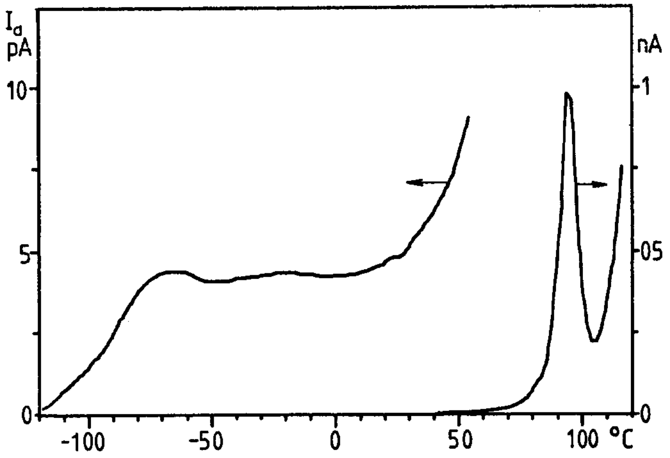

Figure 6.

Measured TSD current of U-PVC

Heating rate:
b = 1 K/min

Polarizing field:
E = 1 kV/mm

Area of electrodes:
$\mathscr{A}$ = 30 cm^2

The transitions found shows the Fig.7. and the data of each transitions are summarised in Tab.1. The transition signed by C can be ordered to the main segmental movement in PVC i.e. the α relaxation. Its activation energy (340 kJ/mol) is lower than the values found in the literature. This can be explained by structural bases or experimental irregularity, namely small thermal gradient in the sample.

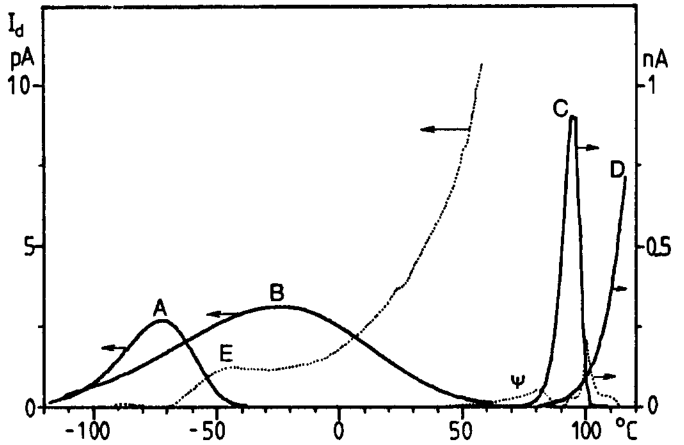

Figure 7.

Separated TSD peaks of U-PVC calculated from TSD current shown in the Fig.6. Data of each transitions are summarised in Tab. 1.

Dotted line:
Remained part after substraction of calculated currents from the measured curve

Table 1. Transitions in U-PVC detected by TSD

Transition	A $kJmol^{-1}$	ϑ_m °C	I_m pA	τ_o s	Q pAs	Relaxation strength $\sigma/E\varepsilon_o$
A β_1	22	-72	2.7	$1.78\ 10^{-3}$	5767	0.22
B β	11	-20	3.1	$1.56\ 10^{-3}$	17559	0.66
C α	340	+95	940	$1.14\ 10^{-46}$	499301	18.8
E β_2	~ 50	-46	1	$1.05\ 10^{-10}$	1195	0.045
D α_1	160	const. in eq. 9 : $2.58\ 10^{24}$ pA				

The transition signed by B is the β relaxation process. In consequence of very low effective frequency (2) the resolution of the β transition is well detectable. In addition to transitions A and B a new peak can be assumed signed by E. It is undeniably present, however its data are unsure.

The dotted line shows the remaining part after substraction of calculated currents of transitions A,B,C and D from the measured curve. A broad transition is visible signed by ψ. This ψ relaxation process is in connection of extra free volume in PVC (15), so it must be dependent on the processing conditions, too. This problem and the influence of additives will be analysed in an other paper.

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List of symbols

A	activation energy	$J\ mol^{-1}$
$\mathcal{A}$	area	cm^2
b	heating rate	$K\ s^{-1}$
E	electric field	$V\ m^{-1}$
ε_o	permittivity of vacuum	$8.85\ 10^{-12}\ F\ m^{-1}$
I	current	A; pA
I_d	depolarisation current	pA
j	current density	$A\ m^{-2}$
k	Boltzmann's constant	$1.38\ 10^{-23}\ J\ K^{-1}$
l	thickness of the sample	m
P	polarisation	$As\ m^{-2}$
R	gas constant	$8.314\ J\ mol^{-1}K^{-1}$
σ	charge density	$As\ m^{-2}$
T	temperature in Kelvin	K
ϑ	temperature in centigrades	°C
t	time	s
τ	relaxation time	s
Q	charge	As
U	voltage	V

Indicies for temperatures

p	polarizing or forming temperature
o	at start of discharge
m	at peak maximum
l	at half intensity of a peak below T_m (lower half)
u	at half intensity of a peak above T_m (upper half)

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