Journal of Thermal Analysis, Vol. 50 (1997) 441-453

ELECTRICAL SIMULATION OF THERMALLY STIMULATED DEPOLARIZATION CURRENT EXPERIMENTS

J. Bayard, J. Grenet, C. Cabot, M. Jutigny and E. Dargent

Laboratoire LECAP, Faculté des Sciences de Rouen, F-76821, Mont Saint Aignan Cedex, France

Abstract

In this paper we present an electrical model of simulation. This model is used to simulate Thermally Stimulated Depolarization Current measurements. The time constant of the model shows the same temperature behaviour as that observed for amorphous materials. The computations by means of SPICE software give results which are very close to be behaviour laws used in the theory of relaxation in amorphous materials.

Keywords: SPICE software, Thermally Stimulated Depolarization Current

Introduction

It is well known that the structural relaxations which principally occur during physical aging inside ill-ordered materials, (glasses, polymers) are strongly temperature dependent.

Indeed, during the production of an amorphous material by melt-quenching, a rapid decrease in temperature, in a temperature range near the glass transition (T_g), induces an increase in the viscosity so large that the initial thermodynamic state is frozen-in.

The diagram of Fig. 1 allows us to represent the evolution of enthalpy H (or any other extensive variable: V,...) *vs.* temperature during the production, aging and reheating of an amorphous material. Above T_g (from A to B), the low viscosity permits a structural relaxation fast enough for the enthalpy to follow the equilibrium law. The large increase in viscosity below T_g leads to a freezing of the structure. The actual enthalpy H (curve B→C) diverges from the extrapolated equilibrium law (dashed line) and has a very small variation. By isothermal annealing at a temperature $T_A<T_g$, a slow evolution (C→D→E) takes place, which corresponds to relaxation towards equilibrium.

The relaxation process, at temperature T, can be described by the following equation:

$$\left(\frac{dH}{dt}\right)_T = -\frac{H-H_e}{\tau} \qquad (1)$$

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

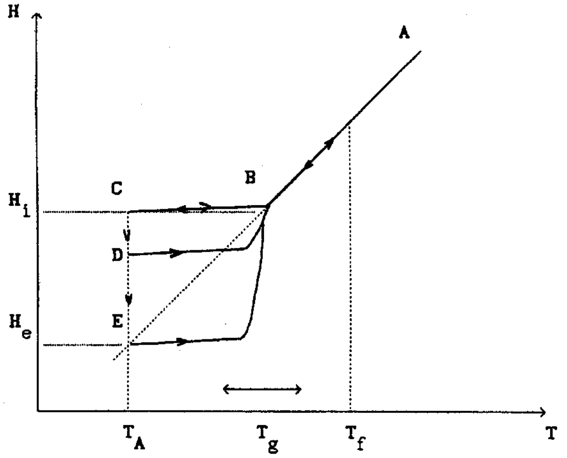


Fig. 1 Enthalpy *H* *vs.* time *t* for glassy materials

which takes into account that the relaxation rate is proportional to the deviation of the actual enthalpy from the equilibrium value H_e, and in inversely proportional to the relaxation time τ.

In order to describe the physical dependence of the relaxation rate on both temperature and structure (i.e. the departure from equilibrium), the relaxation time τ is assumed to take a simple form, used previously by most authors [1],

$$\tau = \tau_e \exp[-c(H - H_e)] \tag{2}$$

where $\tau_e = a\exp(\Delta E/kT)$, a, c and ΔE are constants and k is the Boltzman constant.

So, all thermal analysis methods are particularly convenient to study the aging behavior and to determine the connected time constants. Among these methods, the most commonly used are: Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analysis (DMTA), Dielectric Thermal Analysis (DETA).

Although the Thermally Stimulated Depolarization Current (TSDC) method is scarcely used, it is a powerful tool to study low molecular motions in amorphous materials.

The aim of this paper is to establish an electrical model which allows, by simulation, a large set of experimental parameters of TSDC to be determined. In the range of T_g the quantity $(H-H_e)$ approaches zero and τ assumes approximately the value τ_e. In order to simulate the variations of the time constant τ_e with temperature, we propose in the first part a circuit diagram of an experimental set-up built with current devices and its simulation carried out by the SPICE software. In the second part, we propose the simulation of a set-up whose time constant τ_e follows Eq. (2) but which is quite difficult to build with usual devices. Finally, we compare simulated results with experimental ones obtained for amorphous polyethylene terephthalate.

Theoretical development

Although rather old [2], (the first theoretical developments of the TSDC method were proposed thirty years ago by Bucci and Fieschi [3]), the method has become useful since the seventies, to study the storage and the flow charge mechanisms in semi-conductors and insulators, and now, it is used for the characterization of molecular motions occurring in polymers [4–6].

Represented in Fig. 2, the essence of the TSDC method can be given as follows. Polarization is done during t_p (2 min) at temperature T_p, chosen in such a

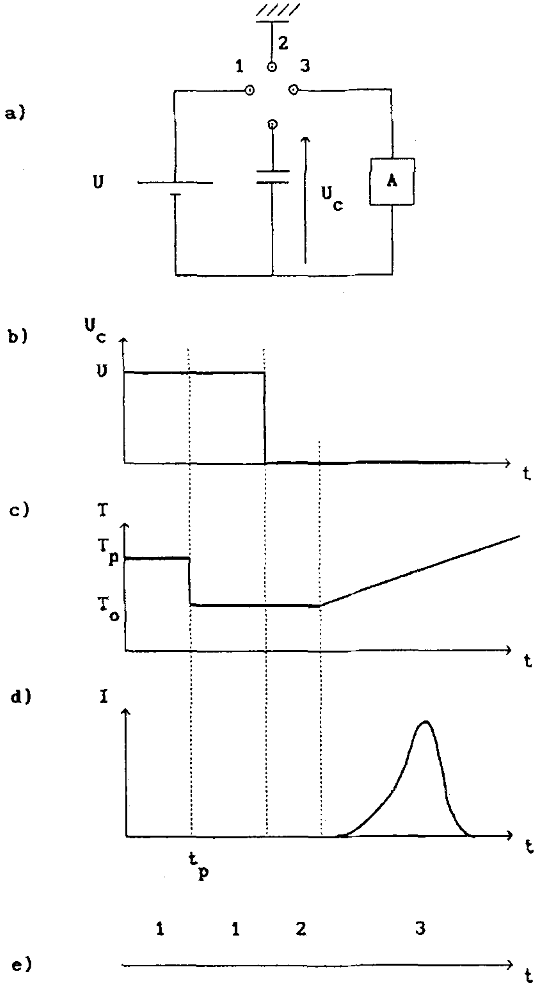


Fig. 2 TSDC method a) Block diagram of the TSDC experimental apparatus. b) Voltage applied to the material *vs.* time. c) Temperature *vs.* times. d) Depolarization current *vs.* time. e) Position of switch *vs.* time

way that no isothermal crystallization appears and under an electric field of 10^6 V m^{-1}. Then, the sample is cooled to T_o=–150°C, the electric field is cut off and the depolarization current is measured during reheating up to T_p at 10°C min^{-1}.

In its simplest expression, the depolarization of a dielectric is given by:

$$P = P_e \exp\left(\frac{\Delta E}{kT}\right) \tag{3}$$

where P_e is polarization at saturation, T the temperature and ΔE the activation energy.

Then, the polarization behaviour can be simulated by an RC network (Fig. 3) whose differential equation:

$$\tau\frac{\mathrm{d}v}{\mathrm{d}t} + v = 0 \tag{4}$$

has RC as time constant.

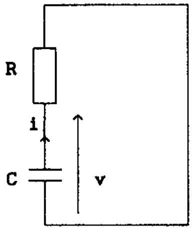


Fig. 3 Network used for the computation of the current

In fact, in a vitreous material, because of structural relaxation, the time constant depends on the temperature and structure. Then, following Tool [7], it is usual to separate the temperature dependence $f(T)$ and the structural variation $g(\varepsilon)$ (cooperative effects). In this model, used in many previous works [1], the relaxation time can be given by:

$$\ln(\tau) = \ln(a) + \frac{\Delta E}{kT} - c(H - H_e) \tag{5}$$

where the constants a, ΔE and c depend on the material; H is the enthalpy at the aging time t and H_e the enthalpy when the aging is achieved. Hereafter we consider that, in a small range of temperature around the glass transition temperature T_g, the enthalpy deviation can be neglected in Eq. (5). Therefore the relaxation time should be given by:

$$\tau = \tau_o \exp\left(\frac{\Delta E}{kT}\right) \tag{6}$$

To take into account the temperature dependence of the physical relaxation time (Eq. (6)), the value of R of the RC network must depend on temperature as follows:

$$R = R_o \exp\left(\frac{\Delta E}{kT}\right) \qquad \text{with} \quad R_o = \frac{\tau_o}{C} \tag{7}$$

If it is possible to use such a device, it is very difficult to assure a large range of variation of R_o and ΔE to test the model. This difficulty could be overcome by expanding, at the first order, Eq. (6) around a temperature T_c. (T_c is an arbitrary value in the range of T_g).

$$\tau = \tau_o \exp\left(\frac{\Delta E}{kT_c}\right)\exp\left(\frac{-\Delta E}{kT_c^2}T\right) = \tau_b \exp(-bT) \tag{8}$$

It follows that:

$$R = R_b \exp(-bT) \qquad \text{with} \quad R_b = \frac{\tau_b}{C} \tag{9}$$

Figure 4 shows the new circuit diagram of the electronic simulator in which the resistor R is given by input impedance Z_e of the network inside the broken line.

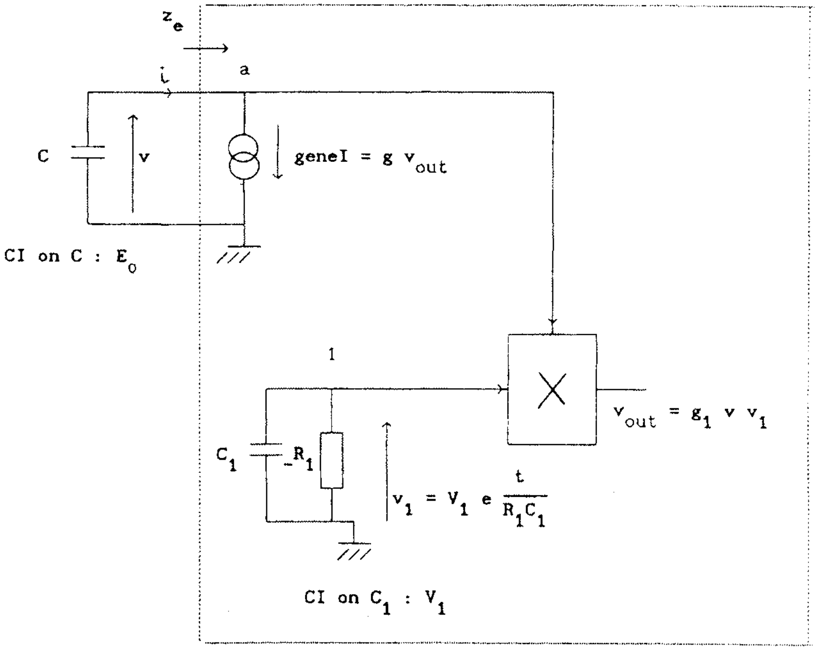


Fig. 4 Circuit diagram of the experimental apparatus

In this network, the voltage-controlled current source is monitored by the output voltage of the multiplier M:

$$\text{geneI} = g v_{\text{out}} \qquad \text{with} \qquad v_{\text{out}} = g_1 v v_1 \tag{10}$$

The exponential behaviour of Z_e is obtained by means of a $(-R_1C_1)$ parallel network with the initial condition V_1:

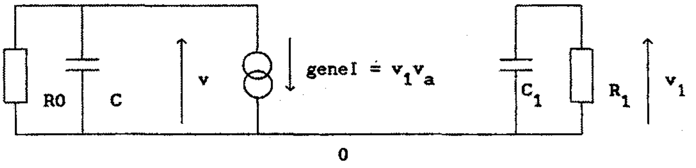
$$v_1 = V_1 \exp\left(\frac{t}{R_1 C_1}\right) \tag{11}$$

Indeed, the input impedance is given by:

$$Z_e = \frac{v}{i} = \frac{v}{g g_1 v V_1 \exp(t/R_1 C_1)} = \frac{1}{g g_1 V_1} \exp\left(-\frac{t}{R_1 C_1}\right) \tag{12}$$

Now, it is sufficient to assume that the temperature depends linearly on time (like in TSDC, $T=T_{\text{ini}}+rt$ with the temperature rate r) to obtain the behaviour described in Eq. (8).

If this network is not difficult to construct (the different elements are available from usual devices), the principal interest does not lie in its realization but in its response to variations in the values of the built-in components. So, instead of a physical apparatus, we have simulated it by means of the SPICE software. The simulation electrical diagram and the connected program are given in Fig. 5.



```
RO        a    0    1e30

C         a    0    0.2n

geneI     a    0    poly(2) (1,0) (a,0) 0 0 0 0 1

C1        1    0    14u

R1        1    0    -1e6

.IC            V(a) = 100

.IC            V(1) = 0.125e-12

.tran          1 120

.probe

.end
```

Fig. 5 Electrical diagram used in the simulator

In addition to the R_1, C_1, genel, and C devices, we notice the presence of an extra resistor R_0. The value (10^{30} Ohm) of this resistor imposed by the software (all nodes of the network must be connected to ground by a finite resistor), was chosen in order to keep the characteristics of the electrical scheme.

For instance, the set of values indicated in Fig. 5, simulates an experimental set-up whose time constant is:

$$\tau = \tau_b \exp(-bt) = 1600 \exp\left(-\frac{t}{14}\right) \tag{13}$$

The simulated current shown in Fig. 6, has the same shape as an experimental TSDC curve.

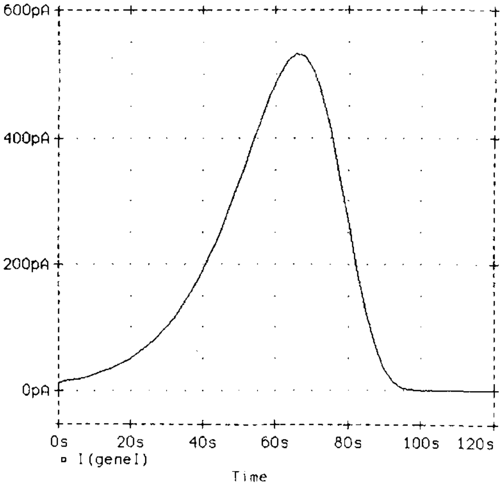


Fig. 6 Current depolarization *vs.* time obtained by the computation

In a TSDC experiment, the time constant τ is determined from the depolarization current $i(t)$ as follows [9]:

$$\tau(t) = \frac{\int_t^{\infty} i(t')\mathrm{d}t'}{i(t)} \tag{14}$$

The duration of computation of the time constant from Eq. (14) is very important, so we prefer calculating this value from Eq. (15).

$$\tau(t) = R(t)C = \frac{v(t)}{i(t)}C = -\frac{v(t)}{\frac{\mathrm{d}v(t)}{\mathrm{d}t}} \tag{15}$$

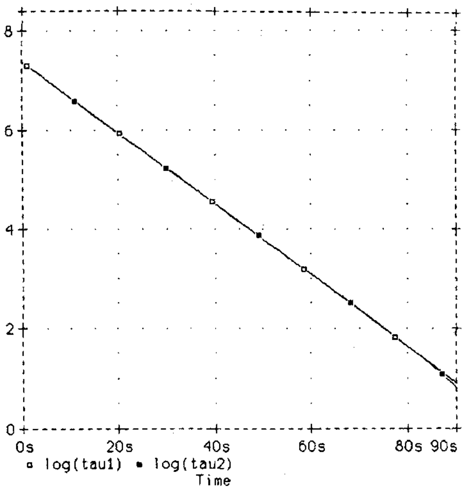


Fig. 7 Variation of τ *vs.* time

$$\tau_1(t)=\frac{1}{\text{geneI}}\int_t^{\infty}\text{geneI}\,\mathrm{d}t=\frac{1}{\text{geneI}}\int_0^{\infty}\text{geneI}\,\mathrm{d}t-\frac{1}{\text{geneI}}\int_0^{t}\text{geneI}\,\mathrm{d}t \qquad \tau_2(t)=-\frac{v(\mathrm{a})}{\frac{\mathrm{d}v(\mathrm{a})}{\mathrm{d}t}}$$

The variations of τ with time calculated by both Eqs (14) and (15) displayed in Fig. 7, show that

* the two ways used to determine τ lead to identical results,

* the calculated values $(\tau b)_{\mathrm{cal}}$ and $(b)_{\mathrm{cal}}$ (τ_{bcal}=1600.06 s, b_{cal}=0.0716 s^{-1}) are in good agreement with the theoretical ones (τ_b=1600 s, b=0.0714 s^{-1}).

In spite of this good agreement, the use of this model is not very suitable. Indeed, the variations of the time-constant τ with temperature are described by the law $\exp(-bT)$ (Eq. (8)) whereas τ varies as $\exp(\Delta E/kT)$ in TSDC discussions.

However, the interesting fact is the behaviour of the electrical model rather than its realization, so we propose hereafter a new scheme, which is more difficult to build, but whose time constant varies with temperature similarly to the TSDC behaviour and follows Eq. (6): $\exp(\Delta E/kt)$.

To reach this goal, we build the following schematic diagram: (Fig. 8)

a) the simulator (C, geneI) of the time constant is still placed between nodes 0 and a (as in the previous set-up) but the voltage controlled current source is now monitored by a mathematical function given by the simulator software SPICE instead of a physical voltage:

$$\text{geneI}=\frac{1}{\tau_0}vC\exp\left(-\frac{\Delta E}{kT}\right) \tag{16}$$

Then, the impedance equivalent to the current source is equal to:

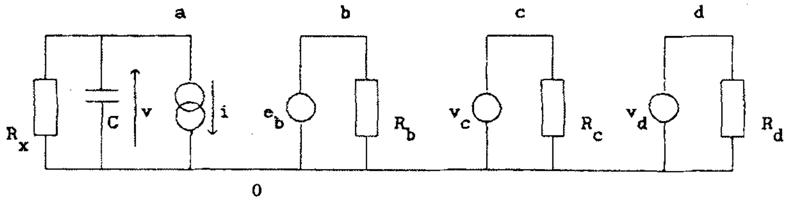
$$R=\frac{\tau_0}{C}\exp\left(\frac{\Delta E}{kT}\right) \tag{17}$$

and follows Eq. (6).

b) Compared to the old diagram, in this new diagram, we have added a function e_b between the nodes 0 and b. This simulated voltage allows the variation of τ with temperature to be described by the following expression:

$$e_b = T_{\text{ini}} + rt$$

with r=heating (or cooling) rate, t=time, T_{ini}=initial temperature.



$$\text{geneI} = \frac{v}{R_0}\, e^{-\frac{\Delta E}{k\,V(2)}} \qquad e_b = 300 + 10 * \text{time} / 60$$

$\uparrow T_{ini}$ $\uparrow$ *heating rate 10K/min*

```
Rx      a    0    1e30
                                              -12
                                   τ  = 0.2 10          ΔE = 1eV
                                    0
C       a    0    0.2n              ↓                    ↓

geneI   a    0    value = {v(a)* 0.2n / (0.2p * v(c)) * exp(-11594*v(d)/v(b))}

.IC             v(a) = 100

Rb      b    0    1e30

eb      b    0    value = {300 + 10 * time /60}

                                ↑
vc      c    0    DC 1     heating rate 10K/min

Rc      c    0    1e30

vd      d    0    DC 1

Rd      d    0    1e30

.step           vc list 1 2 4 8

.tran           1 600

.probe

.end
```

Fig. 8 New block diagram of simulation

c) The simulated voltages v_c, v_d allow the variations (function .step of SPICE) of physical (τ_o, ΔE) parameters which depend on the nature of the material.

The block diagram of simulation is presented in Fig. 8 and the SPICE program is given for the following set of experimental values:

C_o 0.2 nF
τ_o 0.2 ps (* 1, 2, 4, 8)
ΔE 1 eV
r 10 K $\min^{-1}$
T_{ini} 300 K
Duration of experiment = 600 s (function .tran of SPICE).

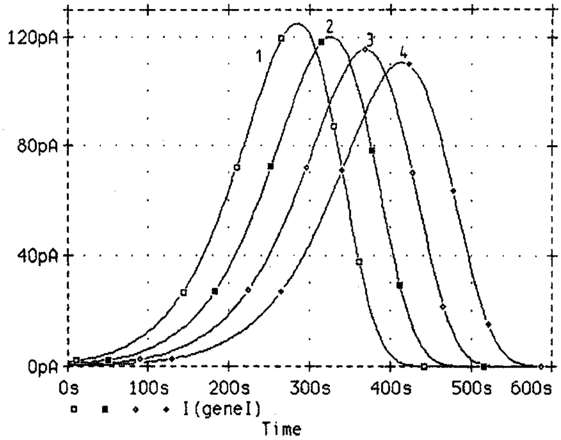


Fig. 9 Current depolarization *vs.* time 1) τ_o=0.2 ps, 2) τ_o=0.4 ps, 3) τ_o=0.8 ps, 4) τ_o=1.6 ps

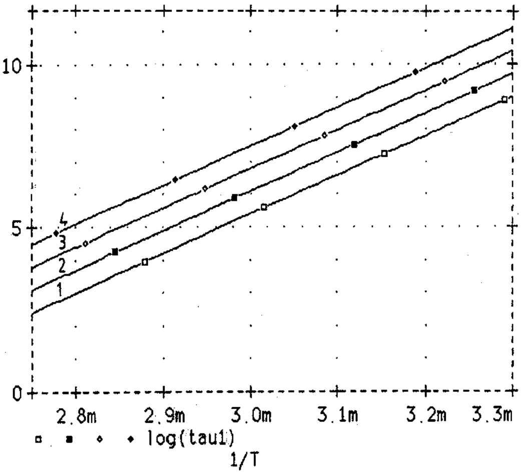


Fig. 10 Variations of lnτ *vs.* 1/*T* (obtained from Fig. 8). 1) τ_o=0.2 ps, 2) τ_o=0.4 ps, 3) τ_o=0.8 ps, 4) τ_o=1.6 ps

The resistor R_x plays the same part as in the first set-up, whereas R_b, R_c and R_d are imposed by another restrain of SPICE software (two devices at least must be connected to a node).

From Fig. 9 which displays the behaviour of the simulated current *vs.* time (or *vs.* temperature: the time axis and temperature axis are equivalent by: $T=T_{ini}+rt$), we calculate the time constant by Eq. (15) (as in a TSDC experiment). According to the model and to the initial value of τ_o, Fig. 10 which collects the variations of $\ln\tau$ *vs.* $1/T$, shows a set of straight lines whose slopes are equal to 1 eV. In the same way, varying the activation energy ΔE leads to a set of converging straight lines.

Comparison with TSDC results

A TSDC measurement can be carried out in two ways: whole (or complex) polarization or fractional polarization.

a) the complex spectrum, obtained following the method described in Fig. 1, is characteristic of the behaviour of the whole of the sample.

b) in the fractional polarization method [9], an elementary spectrum is characteristic of the relaxations occurring in the temperature range between the polarization temperature T_p and the depolarization temperature T_d.

The methods lead to parameters τ_o of about 10^{-45} and 10^{-13}, respectively.

We compare the simulated experiments with a TSDC elementary spectrum measured for an amorphous polyethylene terephthalate (PET) sample.

Figure 11 shows the elementary spectrum obtained for T_p=50°C, T_d=45°C, V=450 V and r=10 K min^{-1}. From this curve, the semi-logarithmic plot of τ *vs.* $1/T$ shows a linear behaviour in the temperature range 40–70°C (Fig. 12). The

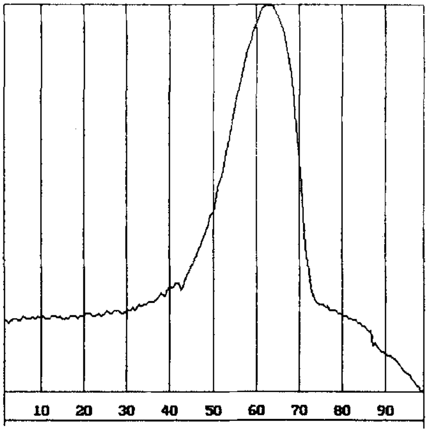
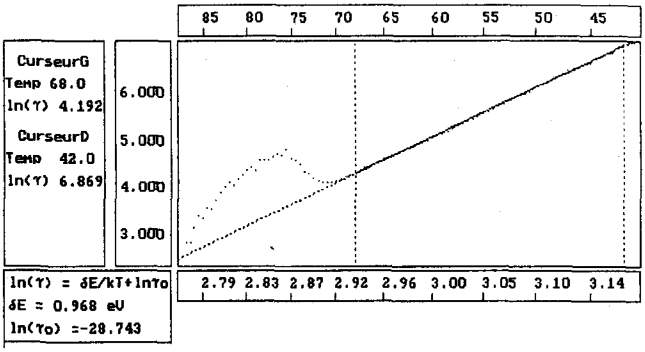


Fig. 11 Elementary spectra obtained for amorphous polyethylene terephthalate (T_p=50°C, T_d=45°C, V=450 V, r=10 K min^{-1})


CurseurG
Temp 68.0
ln(τ) 4.192
CurseurD
Temp 42.0
ln(τ) 6.869

ln(τ) = δE/kT+lnτo
δE ≈ 0.968 eV
ln(τo) =-28.743

Fig. 12 Variation of τ *vs.* $1/T$ (obtained from Fig. 11)

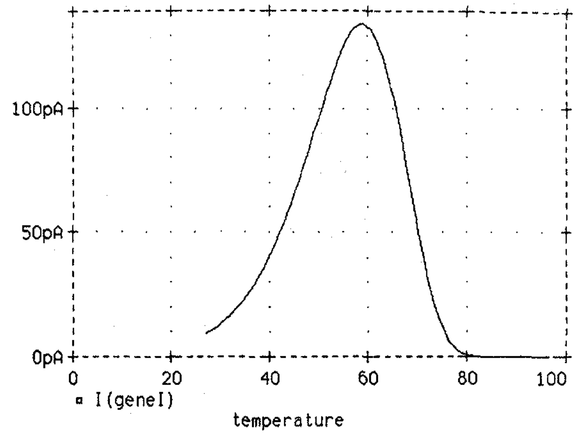


Fig. 13 Current variation *vs.* time obtained by the simulator

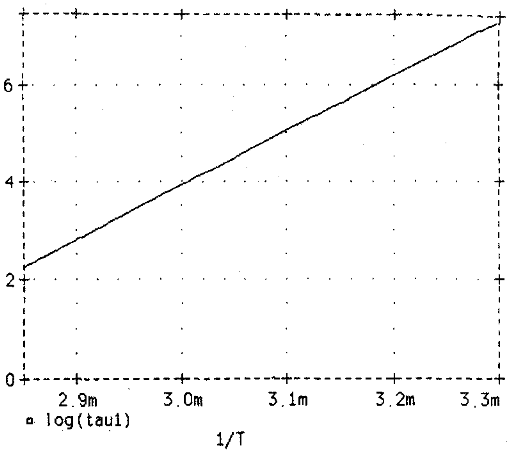


Fig. 14 Variation of τ *vs.* $1/T$ (obtained by the simulator)

left part of the curve in Fig. 12 must be cut because it corresponds to a numerical divergence in the computation of Eq. (15) (0/0 term). Then Eq. (2): $\ln\tau = \Delta E/kT + \ln\tau_o$, leads to: $\Delta E = 0.968$ eV; $\ln\tau_o = -28.7$.

Now, these experimental values are used in the software of simulation described in Fig. 8 (instead of arbitrary ones).

Then, not only the simulated current curve (Fig. 13) has the same shape as the real one, but also the variations of τ *vs.* $1/T$ (Fig. 14) lead to $\tau_o = -29.7$ s and $\Delta E = 0.969$ eV. The good agreement of these results shows that the block diagram described in Fig. 8 allows the simulation of concrete TSDC experiments in a very reliable manner.

Conclusion

In this paper, we describe an electrical model whose time constant shows the same behaviour as amorphous materials. In the first section we propose a scheme (and its simulation by means of the SPICE software) of an electrical set-up whose relaxation time law is equal to exp(−bt). In the second section, we describe a program which allows the simulation of an electrical model whose relaxation time is given by $\tau_o \exp(\Delta E/kT)$. In this case, the shape of the τ *vs.* temperature curve is very close to the behaviour law used in the theories of relaxation in amorphous materials. Then, the response of this second model compared to experimental results obtained for amorphous polyethylene terephthalate (PET) shows the similarity of the values of τ_o and ΔE (measured on PET and simulated by means of this set-up). This good agreement proves the reliability of the model of simulation. Nevertheless, for complex spectra it remains a slight divergence between calculated and experimental results in the range of lower temperatures (below T_g). Indeed, the lower the temperature below T_g, the greater the effect of the structural term $H-H_e$. So, this term is not negligible in the behaviour of the time constant. Hence, in future simulations it will be necessary to introduce the structural dependence.

References

1 J. P. Larmagnac, J. Grenet and P. Michon, J. Non-Crystalline Solids, 45 (1981) 157.
2 H. Frei and G. Groetzinger, Physik. Z., 37 (1936) 720.
3 C. Bucci and R. Fieschi, Phys. Rev. Letters, 12 (1964) 16.
4 B. Sauer, R. Beckerbauer and L. Wang, J. Polym. Sci., Polym. Phys., part B, 31 (1993) 1861.
5 A. Bernes, D. Chatain and C. Lacabanne, Polymer, 33 (1992) 4682.
6 B. Sauer and P. Avakian, Polymer, 33 (1992) 5128.
7 A. Tool, J. Amer. Ceram. Soc., 29 (1946) 240.
8 E. Dargent, J. J. Santais, J. M. Saiter, J. Bayard, J. Grenet, J. Non-Crystalline Solids, 172–174 (1994) 1062.
9 Topics in Applied Physics, Vol. 37, P. B. Braunlich editor.