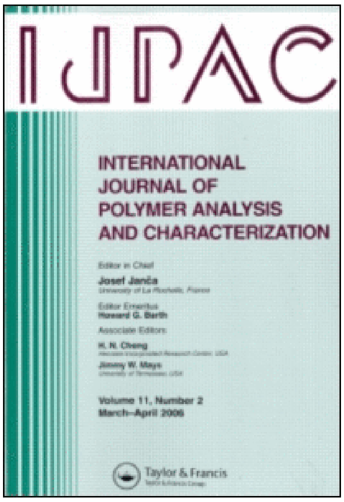

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

# Study of the Effect of Annealing and Physical Aging on PVC by the Thermally Stimulated Currents Methods

M. W. Khemici[a]; A. Gourari[a]; M. Bendaoud[a]
[a] Physics of Materials Laboratory, Research team: Dielectric Materials, Faculty of Physics, University of Science & Technology Houari Boumedienne "USTHB", El-Alia (Algiers), Algeria

**To cite this Article** Khemici, M. W. , Gourari, A. and Bendaoud, M.(2006) 'Study of the Effect of Annealing and Physical Aging on PVC by the Thermally Stimulated Currents Methods', International Journal of Polymer Analysis and Characterization, 11: 1, 101 — 114

**To link to this Article: DOI:** 10.1080/10236660500486440

**URL:** http://dx.doi.org/10.1080/10236660500486440

*International Journal of Polymer Anal. Charact.*, 11: 101–114, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1023-666X print
DOI: 10.1080/10236660500486440

# Study of the Effect of Annealing and Physical Aging on PVC by the Thermally Stimulated Currents Methods

**M. W. Khemici, A. Gourari, and M. Bendaoud**
Physics of Materials Laboratory, Research team: Dielectric Materials,
Faculty of Physics, University of Science & Technology Houari Boumedienne
"USTHB", El-Alia (Algiers), Algeria

**Abstract:** The thermally stimulated currents technique has been used to determine different relaxation and transition modes in polyvinyl chloride (PVC). The influence of thermal annealing has also been studied. For each temperature of annealing, the activation enthalpy and the relaxation times were evaluated and calculated. A compensation phenomenon was observed. Empirical formulas that relate the temperature of compensation to the crystallinity rate of the material were introduced. Furthermore, the influence of physical aging on the mode of relaxation located in the vicinity of the glass transition was investigated.

**Keywords:** Polyvinylchloride; Aging; Thermally stimulated currents method

## INTRODUCTION

The effect of rubber annealing and physical aging on the microstructure of polyvinyl chloride (PVC) was investigated in this study. The thermally

Received 30 August 2005; Accepted 14 November 2005.

The authors would like to express their gratitude to N. Doulache of USTHB (Algeria), S. Kerrache of Tsukuba University (Japan), and A. Boukemedja of IAP Institute (Algeria) for helpful collaboration.

Address correspondence to M. W. Khemici, Physics of Materials Laboratory, Faculty of Physics, USTHB, BP 32 El-Alia, CP 16111, Algeria. E-mail: wafikkhemici@yahoo.fr

stimulated currents (TSC) technique permitted the determination of different relaxation and transition modes in the material. TSC measurements were used to study the relaxation properties of dielectric materials in the solid state, mainly because they allow working in ranges of very low equivalent frequencies, as well as resolving transitions that cannot be detected or separated using other techniques, such as fractional polarization or partial cleaning.[1–6]

The TSC technique consists in subjecting the material to a constant electrical field, which orients sensitive dipoles.[7] The temperature is then decreased (with the electrical field maintained) in order to reduce internal motion, thus trapping the polarized dipole in the material. The electric field is then switched off and the sample reheated, allowing thermal energy to release the "trapped" molecular motions. As a result, a small current is observed, corresponding to one or more types of relaxations.

The aim of this work is to analyze the nature of the TSC spectrum in amorphous PVC, evaluate the relaxation time and the enthalpy of relaxation of the elementary processes, and determine the effect of rubber annealing and physical aging.

The elementary processes (individual modes of relaxation) are obtained around the glass-rubber transition $\alpha$ peak by using the thermal windowing technique (thermal sampling or peak cleaning method).[8]

The plot of $\log(\tau) = \mathrm{f}(1/T)$, where $\tau$ is the relaxation time, indicates a compensation phenomenon that demonstrates the existence of an order within the material in its amorphous phase.[9] This compensation phenomenon is observed for each temperature of annealing. An empirical formula is introduced that relates the rate of crystallinity to the temperature of compensation.

## EXPERIMENTAL SECTION

### Material and Samples Preparation

The measurements were carried out on polyvinyl chloride (PVC) (4000 M) with K value 65–67 and polymerization degree, DP, 970–1070[10] supplied by Cabel (Algiers, Algeria). The sample appeared as a white powder, which was pastilled under 18 tonnes/cm$^2$ pressure. A sample of 1 mm thickness and 1.2 cm$^2$ surface area was thus obtained.

The sample with electrodes shorted was put in the measurement chamber, which was filled with inert nitrogen and maintained at a constant pressure of 300 torr (394 mbar). The current was measured with an electrometer (Keithley 610 C) and recorded using an X-Y plotter. The platinum temperature sensor Pt100, which was mounted on a holder adjacent to the sample, allowed the temperature to be measured with a precision of 0.1°C. A heating rate of 8°C/min was used. The complex TSC spectrum was obtained by submitting the sample to a constant electrical field $E_p = 3 \times 10^5$ V/m for two minutes at a temperature of polarization $T_p = 82$°C. The sample was then cooled to liquid nitrogen temperature at about $T = -175$°C. The electrical field was then suppressed at around 0°C and the electrodes short-circuited for 15 min. Finally, the sample was heated again at 8°C/min to 140°C and the depolarization current recorded.

To study in more detail the relaxation mode, the peak cleaning method was used by resolving the complex peak into an elementary spectrum with thermal windows of 5°C. The differential scanning calorimetry (DSC) measurements were performed in a TA Instrument Q10 differential scanning calorimeter. The temperature of the instrument was calibrated with indium. The same indium sample was used for the heat flow calibration. The calibrations were performed during heating at 10°C/min. The sample was placed in a sealed aluminum cupel, with the powder of PVC fragments having a maximum contact area with the cupel. The recording of the spectra of DSC transition was performed for heating rates of about 10°C/min.

## Basic Considerations for Peak Analysis

The obtained complex spectrum is a contribution of many dipole families; the peak cleaning method was used to separate each family of dipoles characterized by a unique relaxation time and activation energy. The obtained peak is called an *elementary peak*.[11]

For an elementary peak subjected to an electrical field at temperature T, the sample acquires a polarization P as:

$$\frac{dP}{dt} = -\frac{P}{\tau} \qquad (1)$$

where $\tau$ is the relaxation time and t is the time.

After resolving this equation, it is found that:[12]

$$P(t) = P_0 \exp\left[-\int_0^t \frac{dt'}{\tau[T(t')]}\right] \qquad (2)$$

where $\tau$ is the relaxation time, which is dependent on the temperature T, which in its turn depends on the time t′; $P_0$ is given by the equation:

$$P_0 = \frac{N\mu^2}{3kT_p} E_p \qquad (3)$$

where k is the Boltzmann cgonstant, N is the number of dipoles per unit volume, $\mu$ is the dipolar moment, $T_p$ is the temperature of polarization, and $E_p$ is the intensity of the electrical field of polarization.

The variation of polarization is translated into a density of electrical current J(T).

The Arrhenius formula is applied to describe the dependence of the relaxation time $\tau$ on the temperature:

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta H}{kT}\right) \tag{4}$$

where ΔH is the activation energy, $\tau_0^{-1}$ is the characteristic frequency factor for a vacancy jump from one lattice site to another, T is the temperature, and k is the Boltzmann constant.

The expression of the density of current J(T) is:

$$J(T) = \frac{P_0}{\tau_0} \exp\left(-\frac{\Delta H}{kT}\right) \exp\left[-\frac{1}{\tau_0}\int_0^t \left(-\frac{\Delta H}{kT(t')}\right) dt'\right] \tag{5}$$

where $P_0$, $\tau_0$, ΔH, k, T, and t′ were defined in Equations (1)–(4), and t is a time.

In the range of temperatures where the material is in an iso-configurational state, the plotting of the inverse of the temperature versus the logarithm of the relaxation time gives a linear variation. Eyring[13] demonstrated this relation based on a model of two lattice sites separated by a barrier of energy. Also, Hoffman, Williams, and Passaglia[14] demonstrated a linear relation between the enthalpy and the entropy of activation:

$$\Delta H = \Delta H_0 + T_c \Delta S \tag{6}$$

where $\Delta H_0$ is a constant related to the polymer, ΔS is the entropy, and $T_c$ (called the compensation temperature) is the temperature at which the free enthalpy ΔG becomes equal to $\Delta H_0$. Therefore, the Arrhenius equation becomes:

$$\tau(T) = \tau_c \exp\left\{\frac{\Delta H}{k}\left(\frac{1}{T} - \frac{1}{T_c}\right)\right\} \tag{7}$$

where ΔH, k, T, and $T_c$ were defined above, and $\tau_c$ is given by:

$$\tau_c = \tau_0 \exp\left(\frac{\Delta H}{kT_c}\right) \tag{8}$$

The plotting of $\log(\tau_0)$ versus ΔH gives a linear relationship.

## RESULTS AND DISCUSSION

Figure 1 represents the DSC thermogram of the sample of amorphous PVC. It shows the glass transition as a step covering a temperature

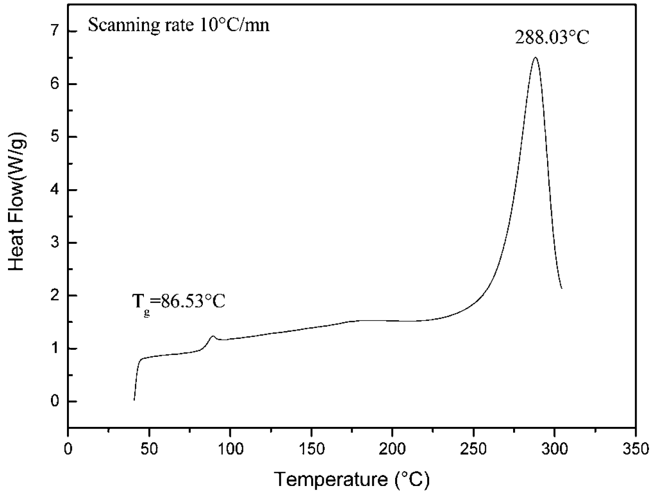

Figure 1. DSC spectrum of amorphous polyvinyl chloride (PVC) samples; scanning rate 10°C/min, PVC mass used 10 mg.

interval from 73 to 100°C. The glass transition is defined as the midpoint temperature of the heat flow rise in the transition, which is about 86°C. The melting point of the sample is about 288°C.

## α-Relaxation Mode

It is well known that either a single peak with well-defined characteristics or a broad peak including several overlapping peaks can be observed in TSC spectra of the investigated material. Figure 2 displays a typical TSC spectrum of PVC powder. The behavior of the α peak as a function of the polarizing field $E_p$ displays a linear dependence, which is shown in the inset of Figure 2. The temperature of the peak maximum seems not to be affected by the change of the electrical field, remaining constant at about 83°C. Ahmed and Fahmy[15] obtained a temperature of the peak very close to our data (82°C and 83°C); the intensity of the maximum current of the peak they obtained is also comparable in magnitude to that found in this work.

The α peak is a complex spectrum attributed to glass transition and to the α relaxation in the material.[15–17] The latter is clearly detected in most amorphous polymers. The significant movements of the atoms of the main chain associated with this transition indicate that the latter is due to the amorphous segments animated with disordered ones.[18,19]

To study this relaxation mode in more detail, the α relaxation peak has been experimentally resolved into a set of elementary spectra using

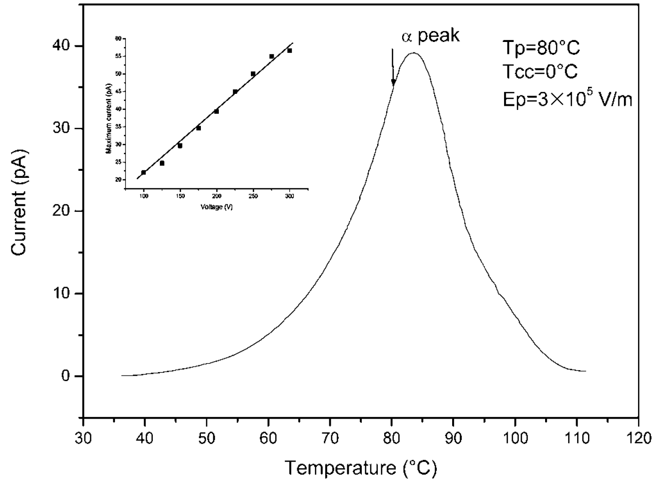

**Figure 2.** TSC spectrum scan of PVC sample polarized at $T_p = 80°C$ and $t_p = 2\,min$, heating rate 8°C/min. (Inset: maximal current versus polarization field.)

the peak cleaning method with a thermal window of 5°C, as shown in Figure 3.

Each of these elementary relaxation curves can be mathematically transformed into their Arrhenius representation and plotted as log(τ) versus 1/T, which expresses the variation of the relaxation time versus temperature as shown in the individual lines in Figure 4. The activation

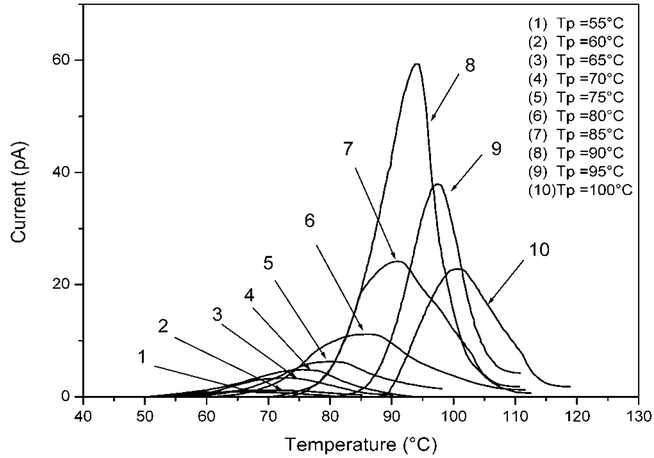

**Figure 3.** TSC peak profile for amorphous PVC sample obtained by thermal windowing technique, polarization window $\Delta T = 5°C$, $T_p$ varies from 55 to 100°C, polarization field $3 \times 10^5\,V/m$, heating rate 8°C/min.

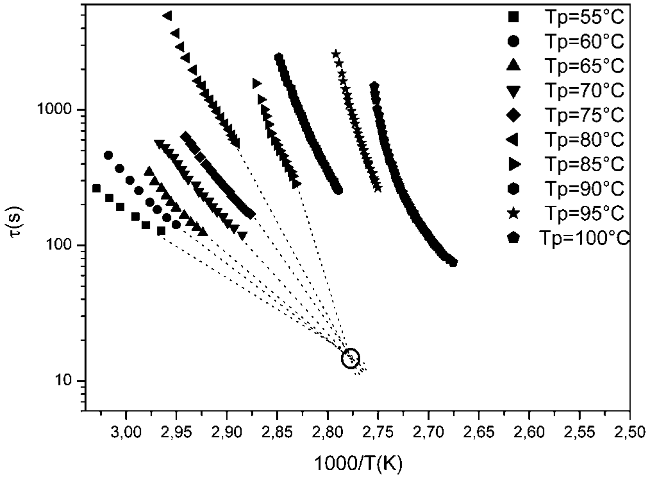

**Figure 4.** Arrhenius plot of the relaxation times obtained from TSC measurement for $\alpha$ peak. Dashed lines are fits according to the Arrhenius equation. The graph shows a positive compensation around T = 86.93°C, $\tau = 15\,$s.

energy and $\tau_0$ are calculated assuming a dipolar origin using the Arrhenius equation (Equation (8)). The partial integration method is used, and the results are reported in Table I.

The value 2.15 (eV) of the activation enthalpy in the vicinity of the glass transition is characteristic of a main relaxation mode.[17] The existence of a compensation phenomenon[20,21] is observed for the $\alpha$ relaxation mode. Indeed, from the Arrhenius diagram (Figure 4), it is observed that most of the lines converge towards a single point. Its coordinates give the parameters ($T_c = 86.93$°C, $\tau_c = 15\,$s), which represent respectively the temperature and time compensations. Furthermore, the linear evolution

**Table I.** Specific parameters for $\alpha$ relaxation process involved in the release of the current, determined by the peak integration method

| $T_p$ (°C) | $T_M$ (°C) | ΔH (EV) | $\tau_0$ (s) |
|---|---|---|---|
| 55 | 65 | 0.98 | $3.06 \times 10^{-14}$ |
| 60 | 70 | 1.53 | $2.70 \times 10^{-22}$ |
| 65 | 72 | 1.65 | $6.92 \times 10^{-24}$ |
| 70 | 76 | 1.70 | $2.38 \times 10^{-24}$ |
| 75 | 81 | 1.78 | $2.74 \times 10^{-25}$ |
| 80 | 86 | 2.15 | $3.57 \times 10^{-30}$ |
| 85 | 91 | 2.78 | $8.38 \times 10^{-39}$ |
| 90 | 93 | 3.23 | $1.11 \times 10^{-44}$ |
| 95 | 98 | 4.71 | $1.33 \times 10^{-64}$ |

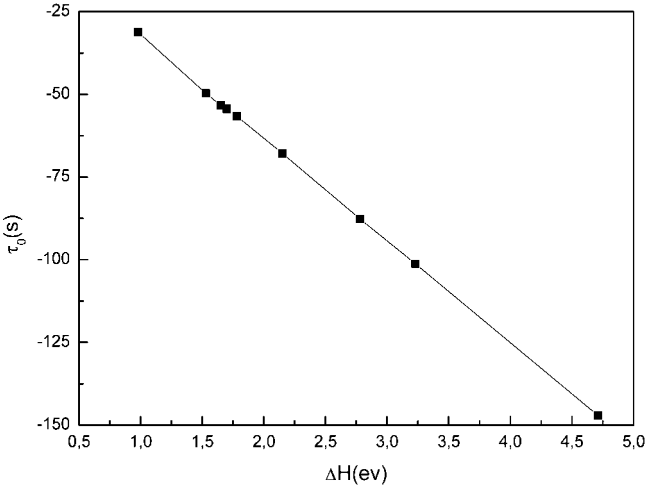

**Figure 5.** Illustration of the compensation phenomenon observed with the $\alpha$ peak.

of $\log(\tau)$ versus $\Delta H$ confirms the existence of such phenomenon characterizing the mobile amorphous phase (Figure 5). This phenomenon is associated with the existence of an order in the amorphous phase of the material.[20] Ahmed and Fahmy[15] obtained by TSC in PVC a compensation temperature of about 86°C. This last value of $T_c$ is in a good agreement with the value obtained in this work.

The last elementary peak, which is isolated at $T_{max} = 101°C$, represents a different behavior than those isolated at lower temperatures. In fact, the Arrhenius plot of Figure 4 shows a nonlinear variation. This peak is resolved using the Williams-Landel-Ferry equation:[22]

$$\tau(T) = \tau_{0v} \exp\left(\frac{1}{\alpha_f (T - T_\infty)}\right) \tag{9}$$

where $T_\infty$ is a temperature whose determination allows a linearization of $\log(\tau) = f(1000/T - T_\infty)$, $\alpha_f$ is the free volume dilatation coefficient, and $\tau_{0v}$ is an pre-exponential factor. The value of $T_\infty = 32°C$ seems to be the best for the linearization of $\log(\tau) = f(1000/T - T_\infty)$. The parameters $\alpha_f$ (free volume dilatation coefficient) and $\tau_{0v}$ are reported in Table II.

**Table II.** Vögel parameters related to the peak isolated at $T_{max} = 101°C$ with $T_p = 100°C$, heating rate of 8°C, and polarization field $E_p = 3 \times 10^5$ V/m

| $T_p$ (°C) | $T_{max}$ (°C) | $T_\infty$ (°C) | $\tau_{0v}$ (s) | $\alpha_f$ ($K^{-1}$) |
|---|---|---|---|---|
| 100 | 101 | 32 | $6.87 \times 10^{-11}$ | $5.97 \times 10^{-4}$ |

**Table III.** Various temperatures of annealing $T_a$ from 90° to 140°C with an increment of 10°C; all samples were stabilized for $t_a = 20$ min at the annealing temperature $T_a$

| | Sample | | | | | |
|---|---|---|---|---|---|---|
| | $PVC_1$ | $PVC_2$ | $PVC_3$ | $PVC_4$ | $PVC_5$ | $PVC_6$ |
| $T_a$ (°C) | 90 | 100 | 110 | 120 | 130 | 140 |

## Study of Rubbery Annealing Effect

To bear out the effect of rubbery annealing on amorphous PVC, the sample was heated from room temperature to temperature $T_a$, definitely higher than the glass transition temperature $T_g$. In this temperature range, the material is in what is known as the rubbery state. As long as the temperature is held at $T_a$, this state is maintained during a time interval $\Delta t_a = 20$ min, which corresponds to the duration of rubbery annealing, which can vary. The application of this process on an amorphous polymer produces a semicrystalline polymer.[23] This procedure is called "cold" crystallization[24] due to the ordered structure obtained from the glass state. In this work, annealing of six samples was studied. For every sample, isochronal annealing was conducted at various temperatures $T_a$ (Table III).

The complex spectra obtained for each sample are given in Figure 6, which shows a diminution of the maximal current of the $\alpha$ relaxation mode. This reduction is due to the appearance of a crystalline phase in the material at its amorphous state.[25,26] Consequently, some segments of the main chain are more ordered, they have less mobility, and the $\alpha$ peak decreases. In a similar work on PVC by TSC, Fahmy and Ahmed[27] noticed a decrease of the magnitude of current as the time and temperatures of annealing increased. This was due to the increase in the rate of crystallinity $\chi$ in the material as confirmed by X-ray spectrum.[27] As described above, for each temperature of annealing, the complex spectra are resolved in elementary spectra. The Arrhenius representation ($\log(\tau)$ versus $1/T$) was plotted for each temperature of annealing. The appearance of the compensation phenomena can be seen. Knowing the temperature of compensation $T_c$ and the temperature of glass transition, the rate of crystallinity in the materials can be estimated using the deduced empirical formula:

$$\chi = \frac{T_c\,(^\circ C) - T_g\,(^\circ C)}{T_c\,(^\circ C)} \tag{10}$$

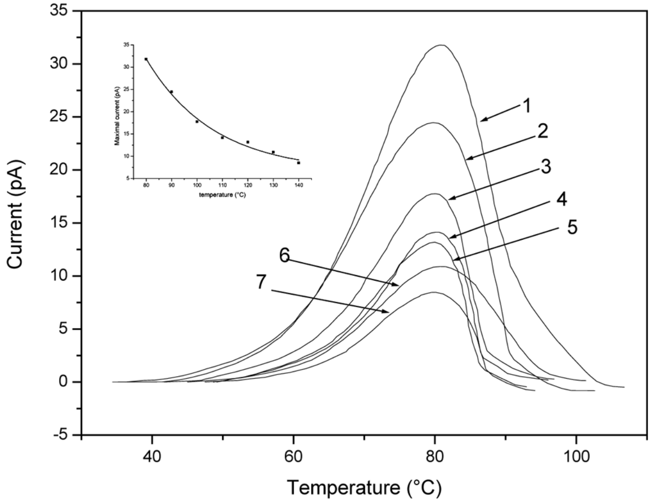

**Figure 6.** Effect of rubbery annealing on the relaxation peak ($\alpha$) for different temperatures $T_a$: (1) no annealing, (2) $PVC_1$ $T_a = 90°C$, (3) $PVC_2$ $T_a = 100°C$, (4) $PVC_3$ $T_a = 110°C$, (5) $PVC_4$ $T_a = 120°C$, (6) $PVC_5$ $T_a = 130°C$, (7) $PVC_6$ $T_a = 140°C$. Polarization temperature $T_p = 80°C$, heating rate $8°C/min$, $E_p = 3 \times 10^5\ V/m$. (Inset: plotting of the maximal current versus temperature of annealing.)

where $T_c$ is the temperature of compensation and $T_g$ is the temperature of glass transition.

Table IV reports the value of the crystallinity rate according to the empirical formula (Equation (10)) with different values of annealing temperature and compensation temperature.

## Study of Physical Aging Effect

To study the effect of physical aging, the sample was heated to a temperature just above the temperature of glass transition in order to make clear

**Table IV.** Rate of crystallinity ($\chi$%) and temperature of compensation for various temperatures of annealing $T_a$ 90° to 140°C with an increment of 10°C; all samples were stabilized for $t_a = 20$ min

| | $T_a$ (°C) | | | | | |
|---|---|---|---|---|---|---|
| | 90 | 100 | 110 | 120 | 130 | 140 |
| $T_c$ (°C) | 93 | 97.3 | 100.13 | 103 | 106 | 110.2 |
| $\chi$ (%) | 7.53 | 11.61 | 14.11 | 16.50 | 18.87 | 21.96 |

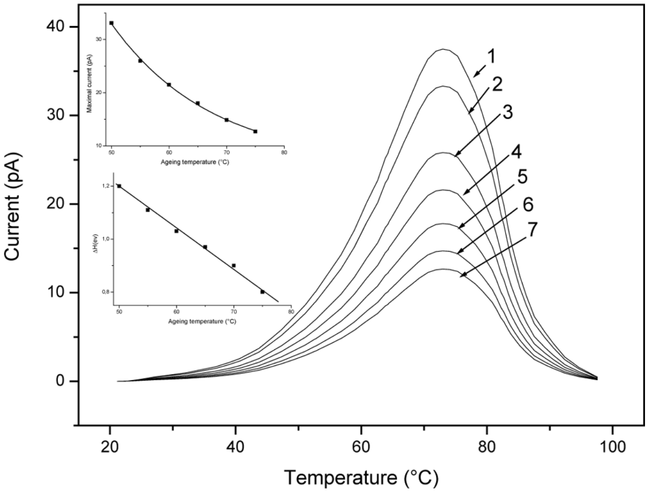

**Figure 7.** Effect of physical aging on the relaxation peak ($\alpha$) for different temperatures $T_{ag}$: (1) no aging, (2) $T_{ag} = 50°C$, (3) $T_{ag} = 55°C$, (4) $T_{ag} = 60°C$, (5) $T_{ag} = 65°C$, (6) $T_{ag} = 70°C$, (7) $T_{ag} = 75°C$. Polarization temperature $T_p = 70°C$, heating rate 8°C/min, $E_p = 3 \times 10^5$ V/m. (Insets: plotting of the maximal current versus temperature of aging and plotting of the activation enthalpy versus temperature of aging.)

the thermal history of the material. Subsequently, the sample was stabilized at an aging temperature $T_{ag}$ below the temperature of glass transition for a certain time called *aging time* $t_{ag}$. The aging time was then fixed to 20 min and the temperature of aging $T_{ag}$ was varied. Figure 7 shows the complex spectrum of the $\alpha$ mode for various temperatures of aging. As can be seen in Figure 7, the effect of the physical aging is characterized by a decrease in the amplitude of the $\alpha$ peak maximum. In the higher inset of Figure 7, the variation of the maximum current is shown, and the enthalpy of activation is evaluated using the initial rise method (Equation (5)); the lower inset of Figure 7 shows a plot of enthalpy of activation versus temperature of aging. Table V reports the values of maximal current, polarization, and the activation enthalpy for each aging temperature $T_{ag}$.

We see that the closer the aging temperature is to the glass transition temperature, the more the maximum of the $\alpha$ peak decreases. This is due to the mobility of the chain near the glass transition temperature.[28] The diminution of the activation enthalpy is observed in the main material.[2] Several studies demonstrate the diminution of the specific volume and the activation enthalpy when the materials become aged.[29] It has been noticed that in PVC and for aging temperatures between 39.5° and 80°C, the Young modulus increases with the time of aging.[28] This result

**Table V.** Values of maximal current, polarization, and enthalpy of activation for each aging temperature $T_{ag}$ varying from 50 to 75°C with an increment of 10°C; all samples were stabilized for $t_{ag} = 20\,\text{min}$, $E_p = 3 \times 10^5\,\text{V/m}$, $T_p = 70°\text{C}$

| $T_{ag}$ (°C) | $I_{max}$ (pA) | Polarization ($10^{-5}\,\text{Cb/m}^2$) | ΔH (eV) |
|---|---|---|---|
| 50 | 33.1 | 3.73 | 1.20 |
| 55 | 25.96 | 2.9 | 1.11 |
| 60 | 21.49 | 2.42 | 1.03 |
| 65 | 18 | 1.99 | 0.97 |
| 70 | 14.86 | 1.65 | 0.90 |
| 75 | 12.7 | 1.42 | 0.80 |

confirms the diminution of the molecular mobility, and as it is related to the structural relaxation, the free volume in the material decreases. The diminution of the activation enthalpy leads to the diminution of the entropy S. The material evolves from the metastable state, with higher configurational entropy and enthalpy, to the equilibrium state. This situation followed the collapse of the configurational rearrangement for the temperature below the glass transition temperature, at which the equilibrium state would not be attainable.[23]

## CONCLUSION

The thermal relaxation behavior of PVC has been investigated by the TSC technique over a wide range of temperatures. The measurement reveals the existence of a relaxation mode around the glass temperature. The α peak obtained at $T_{max} = 80°\text{C}$ is attributed to the dielectric manifestation of the glass transition. The complex spectrum has been resolved into elementary peaks, characterized by one relaxation time. The Arrhenius diagram shows a linear dependence between $\log(\tau)$ and $1/T$. The enthalpy of activation ΔH is then deduced, and the value of $\Delta H = 2.15$ (eV) around $T_{max} = 86°\text{C}$ characterizes the glass transition. The appearance of the compensation phenomenon has been seen. It is attributed to the existence of an order within the material in its amorphous phases. The investigation has been extended to the effect of rubber annealing on α relaxation mode. The latter is characterized by a diminution of the maximum current due to the growth of the crystallinity fraction in the material. The rate of crystallinity is estimated using an empirical formula. Then, the effect of physical aging is studied over the α mode. A diminution is noticed in the maximum current of the α peak as well as in the activation enthalpy. This diminution is due to the evolution of the polymer from a metastable state to a stable state in the presence of residual mobility. However, if the temperature of aging is far below the glass transition temperature (more than 40°C), the materials would never attain the equilibrium state and the motion would be stopped because of the increasing mobility.

## REFERENCES

[1] Bordun, O. M. (1999). Thermally stimulated depolarization in $Bi_4Ge_3O_{12}$ single crystals and thin films. *Phys. Status Solidi A* **176**, 1089–1091.

[2] Gourari, A. (1995). Contribution à l'étude des propriétés physico-thermiques de la série méthacrylique par courants thermiquement stimulés. Ph.D. diss., University of Sciences and Technologies, Algiers.

[3] Pintilie, I., D. Petre, L. Pintilie, C. Tivarus, M. Petris, and T. Botila. (2000). Investigation of trapping levels in standard nitrogenated and oygenated Si p-n junction by thermally stimulated currents. *Nucl. Instrum. Methods A* **439**, 303–309.

[4] Gourari, A. and M. Bendaoud. (1993). Mise en évidence d'une transition liquide-liquide dans les poly méthacrylates par des mesures de courants thermiquement stimulés. *J. Chim. Phys.* **90**, 2007–2019.

[5] Gourari, A., M. Bendaoud, C. Lacabanne, and R. Boyer. (1985). Influence of tacticity on $T_\beta$, $T_g$ and $T_{ll}$ in PMMA by the methods of thermally stimulated current (TSC). *J. Polym. Sci. Phys.* **23**, 889–916.

[6] Saffel, J. R., A. Matthiesen, R. McIntyre, and J. P. Ibar. (1991). Comparing thermally stimulated current (TSC) with other thermal analytical methods to characterize the amorphous phases of polymers. *Thermochim. Acta* **192**, 243–264.

[7] Lavergne, C. and C. Lacabanne. (1993). A review of thermo-stimulated current. *IEEE Elec. Insul. Mag.* **9**(2), 5–21.

[8] Devautour, S., J. Vanderschuren, J. C. Guitini, F. Henn, and J. V. Zanchetta. (1997). Analysis of thermally stimulated currents measured on ionic conductors. *J. Appl. Phys.* **82**, 5057–5062.

[9] Nogales, A. and B. B. Sauer. (1998). Cooperative motion in PVC studied by thermally stimulated currents: Comparison with A.C. dielectric derivative analysis. *J. Polym. Sci. B* **36**, 913–918.

[10] Endo, K. (2002). Synthesis and structure of poly(vinyl chloride). *Prog. Polym. Sci.* **27**, 2021–2054.

[11] Alegria, A., L. Goitiandia, and J. Colmenero. (1996). On the interpretation of TSDC results in the study of the α-relaxation of amorphous polymers. *J. Polym. Sci.* **34**, 2915–2923.

[12] Heitz, R. J. and H. Szware. (1980). Thermally current of depolarisation and distribution of dielectric relaxation times. *Appl. Phys.* **15**, 687–696.

[13] Eyring, E. (1936). Viscosity plasticity and diffusion as examples of absolute reaction rates. *J. Chem. Phys.* **4**, 283–291.

[14] Hoffman, J. D., G. Williams, and E. Passaglia. (1966). Analysis of the α, β and γ relaxations in polychlorotrifluorethylene and polyethylene: Dielectric and mechanical properties. *J. Polym. Sci. C* **14**, 173–214.

[15] Ahmed, M. T. and T. Fahmy. (1999). Distributed relaxations in PVC/PEMA polymer blends as revealed by thermostimulated depolarization current. *Polym. Test.* **18**, 589–599.

[16] Ferreira, L. G. F., M. T. Figueiredo, S. N. Fedosov, and J. A. Giacometti. (1998). The thermally stimulated polarization in dye doped polystyrene explained via the Williams-Watts $\alpha$-$\beta$ relaxation model. *J. Phys. D Appl. Phys.* **31**, 2051–2056.

[17] Perez, J. (1992). *Physique et Mécanique des Polymères Amorphes: Technique et Documentation*. Paris: Lavoisier Publication, pp. 291–339.

[18] Boyer, R. F. (1977). Transition and relaxations. In *Encyclopedia of Polymer Science, and Engineering, Supplement 2*, New York: John Wiley, pp. 746–832.

[19] Dargent, E., E. Bureau, L. Delbreilh, A. Zumailan, and J. M. Saiter. (2005). Effect of macromolecular orientation on the structural relaxation mechanisms of poly(ethylene terephthalate). *Polymer* **46**, 3090–3095.

[20] Neagu, E. R. and R. Neagu. (2003). Comments on the compensation effect observed in thermally stimulated depolarization current analysis. *Thermochim. Acta* **395**, 183–189.

[21] Grenet, J., J. M. Saiter, and M. E. Godard. (2002). Arguments in support of a critical length in polymethyl(a-n-alkyl)acrylate by TSDC investigations. *J. Non-Cryst. Solids* **307**, 232–237.

[22] Williams, G., R. Landel, and J. D. Ferry. (1955). The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. *J. Am. Chem. Soc.* **77**, 3701–3707.

[23] Alves, N. M., J. F. Mano, E. Balaguer, J. M. Meseguer, and J. L. Gomez Ribelles. (2002). Glass transition and structural relaxation in semi-crystalline poly(ethylene terephthalate): A DSC study. *Polymer* **43**, 4111–4122.

[24] Connor, M. T., M. C. Garcia, D. R. Gutiérrez, F. J. Rueda, and B. Calleja. (1997). Cold crystallization studies on PET/PEN blends as revealed by microhardness. *J. Mater. Sci.* **32**, 5615–5620.

[25] Benrekaa, N., A. Gourari, M. Bendaoud, and K. Ait-hamouda. (2004). Analysis of thermally stimulated current and effect of rubbery annealing around glass-rubber transition temperature in polyethylene terephthalate. *Thermochim. Acta* **413**, 39–46.

[26] Teyssèdre, G. and C. Lacabanne. (1995). Some consideration about the analyses of thermostimulated depolarisation peaks. *J. Phys. D Appl. Phys.* **28**, 1478–1487.

[27] Fahmy, T. and M. T. Ahmed. (2001). Thermal induced structural change investigations in PVC/PEMA polymer blend. *Polym. Test.* **20**, 477–484.

[28] Verdu, J. (1994). Vieillissement physique. *Traité plastiques, Technique de l'ingénieur* **A 3**, 150.

[29] Bernes, A. (1993). Transition et relaxations diélectriques dans le polystyrène amorphe interprétation microstructurale, Ph.D. diss., Toulouse, France.