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Theoretical and experimental analysis methods of the piezostimulated current curves for the determination of the dielectric relaxation time versus pressure and temperature

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The dependence of the dielectric relaxation on pressure and temperature can be examined from the variations of the depolarization current of the dielectric, which has been previously subjected to an electric field and high hydrostatic pressure, during the pressure-decrease phase. This is the piezostimulated-current (PSC) method. Different analysis methods of the PSC curves are given in this study. They enable the characteristic parameters of the dielectric to be determined, including the activation volume ΔV, the activation enthalpy ΔH, the activation energy ΔE, and the pre-exponential term τ_0 of the Arrhenius-type relaxation time: $\tau = \tau_0 \exp[(P\Delta V + \Delta E)/\kappa T]$. An example is given, with results obtained from experiments on 6-polyamide. Good agreement exists between the values determined by different methods of analysis.

I. INTRODUCTION

We described in our previous work[1-3] the principle of piezostimulated current (PSC), which enabled us to obtain the characteristic parameters of the dielectric samples studied, such as the activation volume ΔV, the activation enthalpy ΔH, and the activation energy ΔE of the polarizable units contained in the samples used.

We shall review briefly the experimental procedure adopted to record the PSC curves, which comprises three main phases:

(i) The dielectric material is first polarized by an electric field $\mathcal{E}$ at temperature T_p, and at atmospheric pressure P_a, for a sufficiently long time relative to the relaxation time $\tau(T_p, P_a)$ to allow polarization to reach its equilibrium value $\mathcal{P}_0$.

(ii) The pressure is increased to its maximum value $P_{\max}$ where the relaxation time $\tau(T, P_{\max})$ becomes considerable. The electric field $\mathcal{E}$ is then suppressed without any change in the state of the polarization obtained previously.

(iii) The pressure is then lowered at constant speed $b = dP/dt$ while maintaining the temperature constant. The dielectric remains short-circuited. The depolarization current and pressure decrease are simultaneously recorded as functions of time. The previous polarizable units can reorient. Their rearrangement is shown by the presence of one or more peaks in the depolarization-current curve. These peaks are called piezostimulated-current peaks or PSC peaks.

II. PIEZOSTIMULATED-CURRENT PEAK ANALYSIS

In order to analyze the PSC peak, the electrical model of the measuring circuit is a dielectric sample which is charged or discharged through an electrometer having a sufficiently low impedance, compared to that of the sample.

The variation of polarization $\mathcal{P}$ as a function of time during the application of the electric field $\mathcal{E}$ is given by the following classical relationship:

$$\tau(t)\frac{d\mathcal{P}(t)}{dt} + \mathcal{P}(t) = \epsilon\epsilon_0\mathcal{E}, \tag{1}$$

where ϵ is the dielectric permittivity and ϵ_0 is the vacuum permittivity. During the short-circuit $\mathcal{E} = 0$, the preceeding relation becomes

$$\tau(t) = -\frac{\mathcal{P}(t)}{d\mathcal{P}(t)/dt}. \tag{2}$$

Assuming that pressure and temperature vary as monotonic functions, we obtain

$$\tau(P, T) = \mathcal{P}(P, T)/j(P, T). \tag{3}$$

Supposing that the pressure varies linearly with time $P = P_0 + bt$, where $b = dP/dt$ is a negative constant, the value of the current density is

$$j(t) = -\frac{d\mathcal{P}(t)}{dt} = -\frac{d\mathcal{P}(t)}{dP}\frac{dP}{dt} \tag{4}$$

or

$$j(P) = -b\frac{d\mathcal{P}(P)}{dP}. \tag{5}$$

Relations (3) and (5) can be expressed as the following equation:

$$\frac{d\mathcal{P}(P)}{\mathcal{P}(P)} = -\frac{1}{b}\frac{dP}{\tau(P)}, \tag{6}$$

where T is a constant. After integration, this equation enables the polarization of the sample to be known at any time for a given pressure P, during the decrease in pressure:

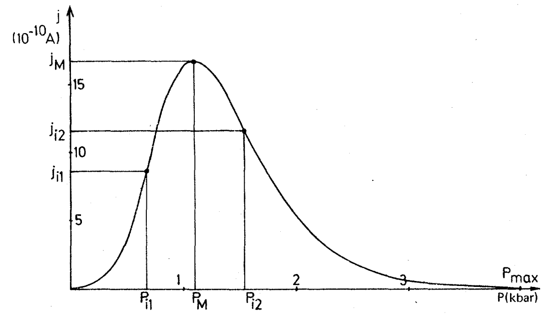

FIG. 1. Theoretical shape of a piezostimulated-current peak obtained with a computer by the relation (10) for the following given values: $\tau_0 = 10^{-2}$ sec; $\Delta V = 10 \times 10^{-29}$ m^3; $b = 4\times 10^5$ Pa sec^{-1}; $T = 320$ °K; $P_{max} = 4\times 10^8$ Pa; $\Delta E = 3\times 10^{-20}$ J; $\mathcal{P}_0 = 5\times 10^{-7}$ C. (j_{i1}, P_{i1}) and (j_{i2}, P_{i2}) are the coordinates of the inflexion points. (j_M, P_M) are the coordinates of the maximum of the PSC peak, P_{max} = 4000 bars (maximum freezing pressure).

$$\mathcal{P}(P) = \mathcal{P}_0 \exp \int_{P_{max}}^{P} - \frac{dP'}{b\tau(P')} \tag{7}$$

$\mathcal{P}_0$ is the value of $\mathcal{P}$ corresponding to $P = P_{max}$. Taking into account Eq. (7), the current density in (3) can be expressed, when T is constant, as

$$j(P) = \frac{\mathcal{P}_0}{\tau(P)} \exp \int_{P_{max}}^{P} - \frac{dP'}{b\tau(P')} . \tag{8}$$

If we consider an Arrhenius type relaxation time given by Williams,[4,5]

$$\tau(P, T) = \tau_0 \exp \frac{\Delta H}{kT} = \tau_0 \exp\left(\frac{P\Delta V + \Delta E}{kT}\right) , \tag{9}$$

where $\Delta H = P\Delta V + \Delta E$ is the activation enthalpy, Eq. (8) becomes:

$$\begin{aligned} j(P) = \frac{\mathcal{P}_0}{\tau_0} \exp\left(-\frac{\Delta H}{kT}\right) & \\ \times \left(\exp\left\{\frac{kT}{b\Delta V\tau_0}\left[\exp\left(-\frac{\Delta E}{kT}\right)\right]\right.\right. & \\ \left.\left. \times \left[\exp\left(-\frac{P\Delta V}{kT}\right) - \exp\left(\frac{-P_{max}\Delta V}{kT}\right)\right]\right\}\right) . & \end{aligned} \tag{10}$$

Thus we obtain the expression of a PSC peak whose shape, determined theoretically by (10), is given in Fig. 1.

III. MATHEMATICAL PROPERTIES OF THE $j(P)$ FUNCTION

A study of particular points of the $j(P)$ function, such as its maximum and its inflexion points, enables the characteristic parameters ΔV and ΔE of the dielectric material under study to be determined later.

A. P_M and j_M coordinates of the maximum of $j(P)$

For the pressure P_M corresponding to the maximum of $j(P)$, it is sufficient to solve the equation $dj(P)/dP = 0$. This gives

$$\frac{d\tau(P_M)}{dP} + \frac{1}{b} = 0 . \tag{11}$$

From Eqs. (9)–(11) we obtain, respectively,

$$P_M = \frac{kT}{\Delta V} \ln\left(-\frac{kT}{b\tau_0\Delta V}\right) - \frac{\Delta E}{\Delta V} \tag{12}$$

and

$$j_M = -\frac{\mathcal{P}_0 b\Delta V}{kT} \times \exp\left[1 - \frac{kT}{b\Delta V\tau_0}\exp\left(-\frac{P_{max}\Delta V + \Delta E}{kT}\right)\right] . \tag{13}$$

In our experiments, the condition $\Delta H = P_{max}\Delta V + \Delta E \gg kT$ holds (for example, $T = 293$ °K, $P_{max}\Delta V + \Delta E = 100kT = 10^{-19}$J). Therefore, Eq. (13) can be written

$$j_M = -\mathcal{P}_0 b\Delta V/2.718kT . \tag{14}$$

B. $P_{i1}, P_{i2}, j_{i1}, j_{i2}$ coordinates of $j(P)$ inflexion points

The second special property of $j(P)$ is the existence of two inflexion points (j_{i1}, P_{i1}) and (j_{i2}, P_{i2}) which can be determined by the solution of

$$\frac{d^2 j(P)}{dP^2} = 0 ,$$

$$\frac{1}{\tau(P)}\left(\frac{2d\tau(P)}{dP} + \frac{1}{b}\right)\left(\frac{d\tau(P)}{dP} + \frac{1}{b}\right) - \frac{d^2\tau(P)}{dP^2} = 0 . \tag{15}$$

Assuming that τ takes the previous form, we have

$$P_{i1} = \frac{kT}{\Delta V}\ln\left(\frac{-0.764}{2b}\frac{kT}{b\Delta V\tau_0}\right) - \frac{\Delta E}{\Delta V} , \tag{16}$$

$$P_{i2} = \frac{kT}{\Delta V}\ln\left(\frac{-5.236}{2b}\frac{kT}{b\Delta V\tau_0}\right) - \frac{\Delta E}{\Delta V} , \tag{17}$$

which gives

$$P_{i2} - P_{i1} = 1.924kT/\Delta V . \tag{18}$$

In writing

$$P_M - P_{i1} = 0.962\ kT/\Delta V = P_{i2} - P_M \tag{19}$$

it is found that P_M is the median of the $P_{i1}P_{i2}$ interval. Bearing in mind the previous observations, $\Delta H \gg kT$, and relations (16) and (17) the j_{i1} and j_{i2} values are

$$j_{i1} = -0.191\mathcal{P}_0 b\Delta V/kT , \tag{20}$$

$$j_{i2} = -0.260\mathcal{P}_0 b\Delta V/kT. \tag{21}$$

And comparing with j_M,

$$j_{i1} = 0.519 j_M, \quad j_{i2} = 0.709 j_M. \tag{22}$$

IV. PSC PEAK EXPLOITATION METHODS

It is possible to determine the law of variation of relaxation time $\tau(P, T)$ from the PSC peaks, obtained at different temperatures T, by knowing ΔV and ΔE. Several methods can be adopted for the analysis of these peaks.

A. Area method

The relaxation time $[\tau(P)]_T$ for a given temperature T is defined, in accordance with (3), by

$$[\tau(P)]_T = [\mathcal{P}(P)]_T/[j(P)]_T.$$

The value of $[j(P)]_T$ is directly deduced from the current $j(t)$ and pressure $P(t)$ curves recorded during the pressure decrease, and by means of the change of t in P from the rate $b = dP/dt$. With regard to $[\mathcal{P}(P)]_T$, it is sufficient to determine the area of the $j(P)$ curve included between the considered pressure and the end of the pressure decrease. From the two preceeding expressions, $[\tau(P)]_T$ can be graphically represented. If the formula (9) is considered, the slope of $[\ln\tau(P)]_T$ gives the value of ΔV. By recording the PSC at different temperatures, the values of ΔH and consequently ΔE are determined. We shall continue in the same way with all the methods, to be described later in detail, to obtain the analytical expression of the general law of $\tau(P, T)$.

B. Initial slope method

The current density (10) can be expressed by the product of two exponential functions. In the initial part of the curve used with this method, the pressure is equal to $P_{\max}$. The preceeding expression is therefore reduced to

$$j(P) = \frac{\mathcal{P}_0}{\tau_0}\exp\left(\frac{-P\Delta V - \Delta E}{kT}\right). \tag{23}$$

In this case ΔV can be determined from the slope of $\ln j(P)$ for $P = P_{\max}$ and for a given temperature T.

C. Curve-fitting method

This method consists of choosing from amongst all the possible values of ΔV, ΔE, and τ_0, by means of a computer, those values that give an identical shape of curve $[j(P)]_T$ of expression (10) as that of the experimental curve.

D. Maximum-current j_M method

Relation (14) directly provides the activation volume

$$\Delta V = 2.718kTj_M/b\mathcal{P}_0. \tag{24}$$

$\mathcal{P}_0$ can be obtained from the total area within the limits of the current and the time axis.

E. $j(P)$-inflexion-points method

Equation (18) enables us to calculate ΔV from two pressures P_{i1} and P_{i2} corresponding to the inflexion points;

$$\Delta V = 1.924kT/(P_{i2} - P_{i1}). \tag{25}$$

The position on the curve of the inflexion points is sometimes difficult to determine. To locate them precisely, Eq. (22) can be utilized to give their positions relative to that of maximum:

$$j_{i1} = 0.519 j_M$$

and (26)

$$j_{i2} = 0.709 j_M.$$

It is noticeable that P_M is the middle of the $P_{i_1}P_{i_2}$ interval, and consequently, ΔV is given by

$$\Delta V = 0.962kT/|P_M - P_{ip}| \tag{27}$$

with

$p = 1$ or $p = 2$.

V. EXPERIMENTAL RESULTS

Curve 1 in Fig. 2 shows the PSC shape obtained on 6-polyamide material with our high-pressure bomb.[6,7] The various methods of analysis mentioned above have been applied to the experimental curves and give the different values of ΔV in Table I. The ΔH value is given by the slope of the curve $\ln\tau(1/T)$ determined from PSC peaks plotted at the different temperatures, 20, 35, and 49 °C,[3] $\Delta H = 3.71 \times 10^{-20}$J. The value of ΔE, deduced from the relation $\Delta H = P\Delta V + \Delta E$ for $P = 1500$ bars and ΔV (average) = 6.04 is obtained as follows: $\Delta E = 2.80 \times 10^{-20}$J.

ΔE is defined as the minimum energy required to lift the dipolar molecule over the potential barrier separating the two equilibrium positions[8] at atmospheric pressure. ΔH is a function of P, while ΔE does not depend on P. τ_0 is the value obtained from the curve $\ln\tau(1/T)$ for $1/T = 0$, $\tau_0 = 0.15$ sec. Finally, the average value of the re-

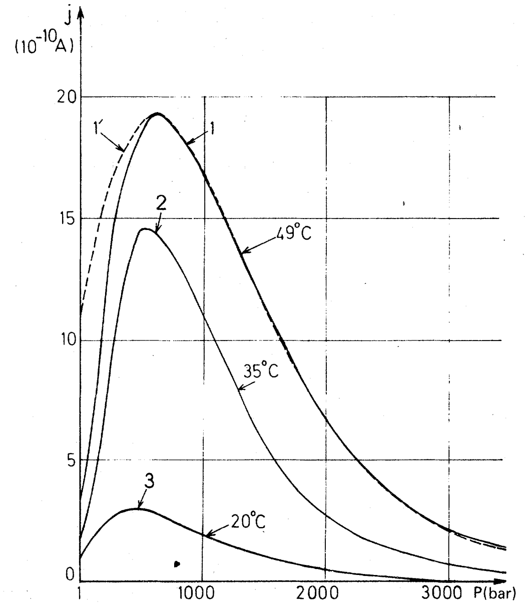

FIG. 2. 1, 2, 3: experimental PSC curves plotted at different temperatures (49, 35, and 20 °C) and with a pressure decrease b = 4 bars sec^{-1}. 1′: PSC curve obtained by the curve-fitting method. Studied dielectric material: 6-polyamide. Characteristics of the sample: thickness, 40 μm; diameter, 20 mm; crystallinity, 20%.

laxation time in 6-polyamide as a function of the pressure and temperature can be expressed by the following relation:

$$\tau(P, T) = 0.15 \exp[(60.4 \times 10^{-30} P + 2.80 \times 10^{-20})/kT].$$

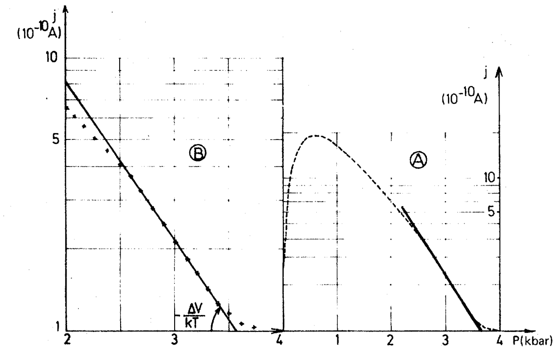

FIG. 3. Diagram A shows the experimental PSC curve obtained with 6-polyamide at 49° C. The full line of the curve is the part in which the initial slope method is used. It is enlarged in detail in diagram B.

VI. REMARKS

It is noticeable that the value of ΔV calculated by the area method in the table is different from the others. This can be explained by the imprecision in the determination of the polarization value $\mathcal{P}_0$ resulting from the value (which is not negligible) at the tail of the depolarization current curve.

With regard to the curve-fitting method, in the range of $500 < P < 4000$ bars the theoretical curve 1′ in Fig. 2 superposes with the experimental one, 1. The difference of two curves observed in the pressure range of $1 < P < 500$ bars is due to the diminution of decreasing rate of pressure b. We have noted from experiments that, for the lower range of pressure, it is difficult to maintain b strictly constant without having appreciable temperature variations. To obtain more desirable

TABLE I. Values of ΔV for several exploitation methods.

	Exploitation methods	Utilized relations	$\Delta V (10^{-29}\ \mathrm{m}^3)$
1	Area method[a]	Slope of $\ln\tau(P) \rightarrow \Delta V/kT$	5.05
2	Initial slope[b]	Slope of $\ln j(P) \rightarrow \Delta V/kT$	6.04
3	Curve fitting[c]	$j(P)$ and computer	6.00
4	Maximum current	$\Delta V = 2.718 kT j_M / b \mathcal{P}_0$	6.54
5	Inflexion points	$\Delta V = \dfrac{0.962 kT}{\lvert P_M - P_{ip} \rvert}$ $p = 1$, or 2	6.58

[a] Reference 3.
[b] Figure 3.
[c] Figure 2.

results in the theoretical and experimental curves, it is necessary to lower the rate of the pressure decrease to a small extent.

VII. CONCLUSION

The characteristic parameters of the polymers such as the activation volume ΔV, the activation enthalpy ΔH, the activation energy ΔE, and the preexponential factor τ_0 can be determined from the piezostimulated-current peaks. The results obtained with 6-polyamide, for example, at maximum freezing pressure of 4000 bars and at temperatures of 20, 35, and 49 °C have shown good agreement between the different methods used to determine ΔV.

Thereafter, the values of ΔH, ΔE, and τ_0 can be deduced graphically or from the relations established previously. This enables an analytical expression to be given describing the variations of relaxation time, as a function of pressure and temperature for the material studied.

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[1] Bui Ai, P. Destruel, Hoang Thê Giam, and R. Loussier, Phys. Rev. Lett. 34, 84 (1975).

[2] Bui Ai, P. Destruel, Hoang Thê Giam, and R. Loussier, C. R. Acad. Sci (Paris) 279, 321 (1974).

[3] Bui Ai, Hoang Thê Giam, and P. Destruel, J. Electrostatics 3, 83 (1977).

[4] G. Williams, Trans Faraday Soc. 60, 1548 (1964).

[5] G. Williams, Trans Faraday Soc. 61, 1564 (1965).

[6] Bui Ai, P. Destruel, Hoang Thê Giam, and R. Loussier, Rev. Sci. Instrum. 45, 1180 (1974).

[7] R. Loussier, thesis (Université Paul Sabatier, 1974) (unpublished).

[8] H. Frohlich, in *Monographs on the Physics and Chemistry of Materials*, 2nd ed. (Oxford U. P., London, 1958).