

ON THE EVALUATION OF THE RELAXATION PARAMETERS OF SOME DIELECTRIC MATERIALS

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There were studied the procedures used to evaluate the relaxation parameters of the dielectric materials, corresponding to restricted intervals of frequencies (200 Hz ... 100 kHz, or less, by means of the method of dielectrics spectroscopy), or to restricted intervals of temperatures (80 ... 300 K, in frame of the method of thermally stimulated depolarization currents (TSDC)), respectively. There were studied: a) the choice of the zero-order approximations of the correlation parameters, b) the selection of the experimental results corresponding to a unique dielectric relaxation, c) the convergence speed of the iterative procedure, d) the compatibility of some studied theoretical models relative to the existing experimental data. The obtained results allow for the optimization of the data processing used for the evaluation of the dielectric relaxation parameters for restricted domains of frequencies or temperatures.

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1. Introduction

Taking into account the mathematical intricacies corresponding to the continuous relaxation time distributions $g(\tau)$ [1], or even to the generalized Christensen's theory [2] of multiple (N) relaxations:

$$D_i + \sum_{k=1}^N a_{k,ij} \frac{d^k D_j}{dt^k} = \sum_{k=0}^N b_{k,ij} \frac{d^k E_j}{dt^k} \quad (i, j = x, y, z) \quad (1)$$

(where D_i , E_j are the corresponding components of the electrical induction and field strength, respectively), the selection and the data processing of the experimental data corresponding to a unique dielectric relaxation is studied by this work. That is why the main goal of this work is to improve: a) the choice (accuracy) of the zero-order approximations of the dielectric relaxation correlation parameters, b) the existing procedures of selection of the experimental data corresponding – for restricted intervals of frequencies (the complex dielectric constant dispersion) or temperatures (the thermally stimulated depolarization currents (TSDC) method) – to a unique dielectric relaxation, as well as: c) to apply (and test) the improved procedures to the evaluation of the relaxation parameters of some dielectric materials, and of the accuracy of these evaluations, inclusively.

The most important studied models of the dielectric relaxation were those of R. H. Cole and K. S. Cole [3]:

$$\varepsilon'(\omega) = \varepsilon_1(\omega) - i \cdot \varepsilon_2(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^\beta} \quad , \quad (2)$$

that of S. Havriliak and S. Negami [4]:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = [1 + (i\omega\tau)^\beta]^{-\gamma} \quad , \quad (3)$$

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and the TSDC model of R. Chen [5]-[9]:

$$\ln I(T) = \ln I_M + \frac{E}{k} \left(\frac{1}{T_M} - \frac{1}{T} \right) \left[T_M E_2(x_M) - T \cdot E_2(x) \right], \quad (4)$$

where T_M is the temperature for which the TSDC intensity reaches its maximum value, $E_2(x)$ is the exponential integral function:

$$E_2(x) = \int_1^{\infty} \frac{e^{-xt}}{t^2} dt = e^{-x} - x(-Ei(-x)), \quad (5)$$

and $x = E/(kT)$, $x_M = E/(kT_M)$, E being the activation energy.

2. Experimental

The analyzed experimental data referring to the complex dielectric constant dispersion were obtained using a capacitance bridge General Radio 1615, under a voltage of 3 V, the accuracy being: a) between 0.01% for $f \leq 1$ kHz and $(3 \cdot 10^{-5}\% + 0.2\% \cdot C_{\mu F}) \times f_{kHz}^2$ for $f = 10 \dots 100$ kHz and $C = 100 \dots 1000 \mu F$ – for the electrical capacities (and for ϵ_1 , implicitly) and: b) of about 2% for the losses factor $D = \tan \delta / f$ (and for ϵ_2 , implicitly) [10,11].

The studied TSDC measurements were made on a “home made” system [12]. The currents were measured with a TAKEDA RIKEN electrometer (measuring sensitivity 1×10^{-15} A). The accuracy of the temperature continuous control was of ± 0.1 K, while the deviations from linearity of the ramp generator $T = f(t)$ were under 1.25% and the correlation coefficients $r(T, t)$ were larger than 0.995.

3. Improvement of the procedures of data selection

The use of the center coordinates (ϵ_{1c} , ϵ_{2c}) and of the radius r of the Cole arc to the evaluation of the zero-order approximations of the Cole-Cole parameters was studied in frame of our work [10]. In order to avoid the supplementary errors introduced by the evaluation of the parameters ϵ_{1c} , ϵ_{2c} and r , we studied later [13] also the possibilities to obtain these zero-order approximations starting from the inflexion points of the plots $\epsilon_2 = f(\ln \omega)$ [for the complex dielectric constant dispersion] and $I = f(T(t))$ [for the thermally stimulated depolarization currents], respectively.

Taking into account that the accuracy of the evaluations of the experimental plots maxima and minima is considerably better than that corresponding to the evaluation of the inflexion points, this work studied the procedure of obtainment of the zero-order approximations starting from the angular frequency $\omega_M = 2\pi f_M$ corresponding to the maximum of the $\epsilon_2(\omega)$ dependence and from the frequency $f_c = \omega_c / (2\pi)$ corresponding to the minimum of the $ctg \delta(f)$ plot.

The frequency dependence of the cotangent of the losses angle being (for the Cole-Cole correlation):

$$ctg \delta = \frac{\sqrt{\epsilon_0 \epsilon_\infty}}{(\epsilon_0 - \epsilon_\infty) \sin(\pi\beta / 2)} \left[\sqrt{\frac{\epsilon_\infty}{\epsilon_0}} \cdot (\omega\tau)^\beta + \sqrt{\frac{\epsilon_0}{\epsilon_\infty}} \cdot (\omega\tau)^{-\beta} \right] + \frac{\epsilon_0 + \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} ctg(\pi\beta / 2), \quad (6)$$

we obtained the relations:

$$\sqrt{\frac{\epsilon_\infty}{\epsilon_0}} \cdot (\omega_c \tau)^\beta = 1, \quad \text{therefore:} \quad \sqrt{\frac{\epsilon_0}{\epsilon_\infty}} = \left(\frac{f_c}{f_M} \right)^\beta \quad (7)$$

and:

$$(ctg \delta)_{\min} = \frac{2\sqrt{\varepsilon_0 \varepsilon_\infty}}{(\varepsilon_0 - \varepsilon_\infty) \sin(\pi\beta/2)} + \frac{\varepsilon_1(f_M)}{\varepsilon_{2M}}, \quad (8)$$

equivalent to:

$$\frac{2}{\sin(\pi\beta/2)} \left[\left(\frac{f_c}{f_M} \right)^\beta - \left(\frac{f_M}{f_c} \right)^\beta \right]^{-1} = (ctg \delta)_{\min} - \frac{\varepsilon_1(f_M)}{\varepsilon_{2M}}. \quad (9)$$

The logical scheme (algorithm) of the new evaluation procedure involves the steps:

a) evaluation of the relaxation time τ , by means of the relation:

$$\tau = \frac{1}{\omega_M}, \quad (10)$$

b) the determination of the zero-order approximation of the Cole-Cole parameter β , by means of the numerical solution of the implicit (in β) equation (9),

c) the evaluation of the Cole-Cole parameters ε_0 and ε_∞ , as parameters of the regression lines $\varepsilon_1 = f(\omega)$ and $\varepsilon_2 = F(\omega)$, with known values (the above zero-order approximations) of the relaxation time τ and of the Cole-Cole parameter β .

In following, the ratio $r = f_{i1}/f_M = f_M/f_{i2}$ of the frequencies f_{i1} , f_{i2} corresponding to the inflexion points of the $\varepsilon_2 = F(\ln f)$ plot, relative to the frequency f_M corresponding to the maximum of this plot is calculated by means of the expression [13]:

$$r = \left\{ \frac{1}{2} \left[\cos\left(\frac{\pi\beta}{2}\right) + \sqrt{8 + \cos^2\left(\frac{\pi\beta}{2}\right)} + \sqrt{4 + 2\cos^2\left(\frac{\pi\beta}{2}\right) + 2\cos\left(\frac{\pi\beta}{2}\right)\sqrt{8 + 2\cos^2\left(\frac{\pi\beta}{2}\right)}} \right] \right\}^{\frac{1}{\beta}}. \quad (11)$$

The accomplished calculations pointed out that – if the Cole-Cole parameters β' , β'' corresponding to the neighbor relaxations do not differ too much relative to the β parameter value corresponding to the studied dielectric relaxation – the domain corresponding to the studied (mono)relaxation is not necessarily restricted to the interval (f_{i1}, f_{i2}) between the corresponding inflexion points of the $\varepsilon_2 = F(\ln f)$ plot (as it was initially assumed [14]), being possible to involve in this domain also the experimental data referring to the “external” frequencies $f \notin (f_{i1}, f_{i2})$ if these frequencies (f) differ considerably relative to the frequencies f'_m, f''_m corresponding to the neighbor $\varepsilon_2 = F(\ln f)$ minima of the considered dielectric relaxation.

As it concerns the TSDC method, taking into account that zero-order approximations of the uniqueness parameters have to be easily and accurately evaluated, we have chosen as such parameters: the temperature T_M to which the TSDC intensity reaches its maximum value I_M and the activation energy (in agreement with work [15]). Starting from the results of the work [13], we obtained now that the ratios $y_1 = T_{i1}/T_M$ and $y_2 = T_{i2}/T_M$ (of the temperatures T_{i1}, T_{i2} corresponding to the inflexion points of the TSDC $I = f(T)$ plot, relative to T_M), fulfill the implicit equation:

$$y_k^2 \exp \left[x_M \left(\frac{1}{y_k} - 1 \right) \right] = \frac{1}{2} \left(3 \pm \sqrt{5 + \frac{8}{x_M y_k}} \right), \quad (12)$$

where $k = 1, 2$, and:

$$x_M = \frac{E}{kT_M}, \quad (13)$$

E being the activation energy. One obtains so that the domain corresponding to a unique (studied) TSDC relaxation involves the interval ($T_{i1} = y_1 \cdot T_M$, $T_{i2} = y_2 \cdot T_M$) as well as its neighbor temperatures T , sufficiently far from the temperatures T_m' , T_m'' for which the TSDC intensity reaches its minimum values around T_M .

4. Some features of the data processing procedure

In order to evaluate the parameters of the studied dielectric relaxation, we used – starting from the above obtained zero-order approximations – the last versions [16], [17] of the gradient method:

$$\bar{C}^{(I+1)} \equiv \bar{p}^{(I+1)} - \bar{p}^{(I)} = -\bar{d} \left(\bar{J}^{(I)T} \cdot \bar{W} \cdot \bar{J}^{(I)} \right)^{-1} \cdot \bar{J}^{(I)T} \cdot \bar{W} \cdot \left(\bar{t}_{calc.}^{(I)} - \bar{t}_{exp.} \right), \quad (14)$$

where $\bar{p}^{(I)}$ is the vector of material (dielectric relaxation) parameters in the I-th iteration, \bar{d} is the diagonal matrix of the eventual damping coefficients, $\bar{t}_{calc.}^{(I)}$ and $\bar{t}_{exp.}$ are the vectors of the calculated (in the I-th iteration) and experimental values of the test parameters, respectively, \bar{W} is the matrix of weights associated to the experimental values $\bar{t}_{exp.}$, while:

$$J_{ij}^{(I)} = \frac{\partial t_{calc.}^{(I)}}{\partial p_j^{(I)}} \quad (15)$$

are the elements of the Jacobean matrix $\bar{J}^{(I)}$, and $\bar{J}^{(I)T}$ is the transposed of this matrix.

In order to evaluate also the convergence speed of the used gradient method, we have found that – assuming a uniform distribution inside the confidence interval – the expression of the Claude Shannon's information entropy: $S_I = -\log \varphi(I) + \text{const.}$, will lead to the following expression of the apparent information amount, received during the I-th iteration:

$$I_I = S_{I-1} - S_I = \log_2 (s_{I-1} / s_I), \quad (16)$$

where s_I is the square mean error after the I-th iteration.

Similarly, the amount of “real” information received in the I-th iteration is:

$$\mathfrak{S}_I = \log_2 \left(\frac{s_{I-1} - s_\infty}{s_I - s_\infty} \right), \quad (17)$$

where s_∞ is the limit of the square mean error after a large number ($I \gg 1$) of convergent iterations.

At the end of the iterative procedure, the square mean errors affecting each of the dielectric relaxation parameters were evaluated applying the Gauss' errors propagation formula to the expression (14).

5. Results

Table 1 presents the values (in binary information units, bits) of the apparent I_I and “real” \mathfrak{S}_I information amounts, respectively, corresponding to the successive iterations of the gradient method applied to the data processing of the TSDC experimental data for a poly-phenylene-vinylene (PPV) foil with no mechanical treatment, maintained for a hour at $t = 300^\circ\text{C}$ before the measurement of the current intensity [18].

Table 1. Apparent I_I and “real” \mathcal{J}_I information amounts (bits), corresponding to successive iterations of the gradient method applied to the data processing of the TSDC experimental data for a PPV foil.

Iteration order, I	I_I (bits) when there are changed only values				\mathcal{J}_I (bits) when there are changed only values			
	E	I_M	T_M	E, I_M, T_M	E	I_M	T_M	E, I_M, T_M
1	0.0013	0.0052	0.52	0.77	8.934	0.671	6.993	7.6807
2	2.6×10^{-6}	0.0088	0.005	0.005	5.931	≈ 10	9.145	14.035
3	1.4×10^{-8}	0	8.6×10^{-6}	$\approx 10^{-7}$	0	0	4.917	0.5849
4	0	0	2.3×10^{-7}	5×10^{-8}	0	0	0	0

From Table 1 it results that: a) the maximum information amounts are obtained when all uniqueness (correlation) parameters are adjusted concomitantly, b) the convergence speed of the gradient method applied to the TSDC data processing is very high, the solutions being obtained after only approx. 3 iterations. A similar high convergence speed (as well as values of the information amounts of the same magnitude order) was found for the gradient method applied to the dielectric spectrometry data processing, if the zero-order approximations of the uniqueness (correlation) parameters were properly chosen.

Starting from the frequency dependence (3) of the complex dielectric constant pointed out by S. Havriliak and S. Negami [4], these authors have found the existence of some temperature intervals (of about 50 K width) where the parameters $\epsilon_0, \epsilon_\infty, \beta$ and γ present linear temperature dependencies. This quantitative hypothesis was used also [19] for the Cole-Cole correlation [which is a particular case (for $\gamma=1$) of the Havriliak-Negami correlation] and considerably wider temperature intervals. In order to test this hypothesis, we completed our previous calculations [10] by evaluations of the accuracy of the Cole-Cole parameters estimations (by means of the gradient method) for 9 different temperatures, between 140 K and 250 K, as well as of the relative square mean errors $s_{rel}(\epsilon_1), s_{rel}(\epsilon_2)$ corresponding to the theoretically calculated (by relation (2)) real and pure imaginary parts of the complex dielectric constant (see Table 2).

Analyzing the results synthesized by Table 2, one finds that: a) excepting the relative mean error corresponding to the pure imaginary part ϵ_2 of the dielectric constant at $T = 198.8$ K, all other theoretically evaluated square mean errors are less than the corresponding experimental ones (see Section 2), therefore the Cole-Cole model is compatible relative to the experimental data, b) there is an obvious nonlinear temperature dependence of the Cole-Cole parameters, illustrated also by Figure 1, where the confidence intervals corresponding to each temperature were indicated by means of segments (in fact, the 2 ascending parts (145 ... 170 K and 210 ... 250 K, respectively) of the $\beta = f(T)$ plot from Fig. 1 correspond to different dielectric relaxations [10c]), c) the accuracy of the gradient method evaluations of the Cole-Cole parameters is satisfactorily, excepting the evaluations of the relaxation times, whose calculated values have to be checked also by means of the expression of the zero-order approximation: $\tau = 1/\omega_M$.

Table 2. The standard confidence intervals and the relative square mean errors of the real ϵ_1 and pure imaginary ϵ_2 parts of the complex dielectric constant, for a commercial (du Pont) sample of semi-crystalline (43%) sample of polyethylene-terephthalate (CPET).

$T(K)$	$\epsilon_0 \pm s(\epsilon_0)$	$\epsilon_\infty \pm s(\epsilon_\infty)$	$\beta \pm s(\beta)$	$\tau \pm s(\tau), ms$	$s_{rel}(\epsilon_1), \%$	$s_{rel}(\epsilon_2), \%$
141.14	2.9947±0.1288	2.6822±0.0277	0.1192±0.0179	5679.5±24063	0.0189	1.9718
147.8	2.8568±0.0271	2.6928±0.0120	0.1852±0.0150	1.6940±1.1502	0.0074	1.1457
159.31	2.8411±0.0302	2.6974±0.0143	0.2334±0.0319	0.1502±0.0841	0.0031	0.8127
168.9	2.8734±0.0688	2.6680±0.0217	0.1785±0.0532	0.0525±0.0691	0.0155	0.3720
198.8	3.1289±0.1094	2.6056±0.0299	0.1115±0.0273	1.7417±3.4018	0.2727	2.4174
218.75	3.2904±0.4302	2.5364±0.1487	0.0955±0.0672	1.7429±11.770	0.0159	0.6099
228.0	3.1651±0.0621	2.5753±0.0564	0.1279±0.0263	0.0047±0.0018	0.2018	0.5975
238.5	3.1215±0.0279	2.5813±0.0542	0.1500±0.0218	0.0072±0.0039	0.0093	0.7212
248.31	3.0742±0.0092	2.6527±0.0294	0.2033±0.0161	0.0054±0.0019	0.0135	0.4776

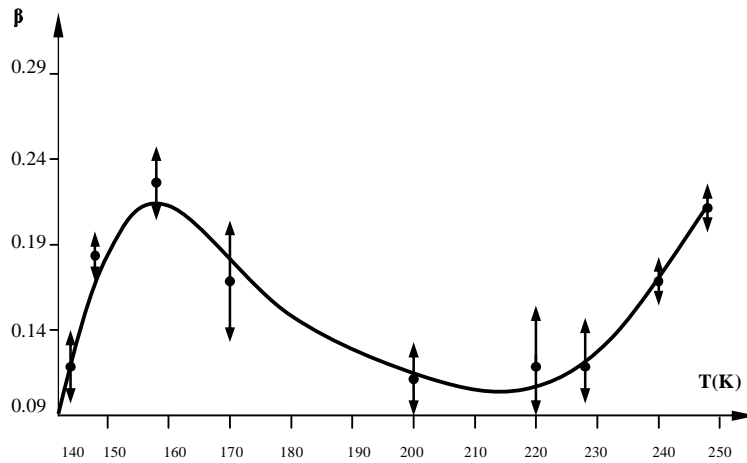


Fig. 1. The temperature dependence of the Cole-Cole parameter β , compared with the experimental confidence intervals, for a semi-crystalline (43%) sample of polyethylene - terephthalate (CPET)

6. Conclusions

The present work has introduced new procedures for the obtainment of the zero-order approximations of the dielectric relaxation parameters, preferring the evaluation of the extreme values of the parameters of some experimental plots and the numerical solution of some implicit equations. Taking into account that the accuracy of the above indicated determinations is considerably better than that corresponding to the parameters of the Cole-Cole arc, or to evaluation of the coordinates of the inflexion points of certain experimental plots, the new introduced procedure represents an improvement of the numerical techniques used for the evaluation of the dielectric relaxation parameters.

The convergence speed of the used gradient method was studied by means of the information amounts obtained in each iteration. It was found that: a) the maximum values of the information amounts correspond to the concomitant adjustment (fit) of all uniqueness (correlation) parameters, b) the gradient method used to evaluate the dielectric relaxation parameters is very fast, the final solutions being obtained in approx. 3 iterations, if the zero-order approximations were properly (accurately) chosen. The accuracy of the dielectric relaxation parameters evaluations is good for ε_0 , ε_∞ , E (the activation energy), β and γ (Havriliak's parameters), being rather mediocre (or even poor) for the evaluations of the relaxation times τ .

The use of the determined confidence intervals: a) confirms the compatibility of the studied theoretical models relative to the existing experimental data (see [19] for a detailed study of the compatibility criteria), and: b) invalidate the Smith-Boyd hypothesis [20] referring to the linear temperature dependencies of the Cole-Cole parameters on wide temperature intervals, confirming so the qualitative results (without use of the confidence intervals, unlike the present work) of the paper [21].

The future investigations will try to find the eventual validity – for restricted frequency intervals – of some frequency power dependencies of the tangent of dielectric losses, somewhat similar to those pointed out for magnetic materials [22] and to the fractal size power laws found for certain electrical capacitors [23].

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