Use of the Dielectrometer for the Determination of the Complex Dielectric Constant in the Microwave Region in Organic High Polymers at Various Temperatures

MARIO CALAMIA, *Centro Studi per l'Elettronica e le Telecommunicazioni del C.N.R. presso l'Istituto di Elettronica dell'Università di Pisa, Italy,* and ENZO BUTTA and VITTORIO FROSINI, *Centro Nazionale di Chimica delle Macromolecole del C.N.R. Sezione VI presso l'Istituto di Chimica Industriale ed Applicata dell'Università di Pisa, Italy*

Synopsis

A commercial type dielectrometer has been utilized for determining the complex dielectric constant of insulating materials as a function of temperature. For low-temperature measurements, modifications of the apparatus have been made, by which the lower section of the guide, containing the specimen, is insulated from the upper section by means of a Teflon disk, in order to permit measurements under vacuum without difficulties arising from moisture condensation. Taking into account the modifications made, relations between the experimentally measured quantities and the complex dielectric constant have been elaborated, an error analysis made, and best conditions to perform experimental measurements determined. For high- and medium-loss materials, in the low-temperature range, an accuracy of the order of 1% in ϵ' and of 10% in ϵ'' have been calculated. Better results can be obtained for measurements at high temperature. The apparatus performance and the accuracy of measurements have been checked through measurements of the complex dielectric constant of different polar polymers at frequencies of the order of 9×10^9 Hz, at temperatures between -150 and $200°C$. The experimental results are in good agreement with literature data derived from experimental measurements with other techniques and with the behavior expected on the basis of the results from radiofrequency measurements through considerations of molecular mobility in relation to molecular structure.

General

In microwave techniques there is an ever-increasing demand for dielectrics with determined properties for the most varied applications. Dielectric lenses to focus electromagnetic waves, dielectric antennas, wideband matching junctions, black bodies for wave guides, radome dielectrics, etc. are already in wide spread use. It is, therefore, important to know accurately the dielectric behavior of different materials in the microwave region in a wide range of temperature.

With the present research, we initiated an investigation of the dielectric behavior at very high frequency of organic high polymers in relation to

their chemical constitution, physical state, and thermal and mechanical treatments.

For the execution of the experimental measurements we made use of a dielectrometer (Model 3, Serial N.37 of the Central Research Laboratories Inc., Minnesota), suitably modified for the execution of measurements at low temperature under vacuum.

WORKING PRINCIPLE OF THE DIELECTROMETER

The method employed in the dielectrometer, described by Roberts and von Hippel,[1] is based on the principle that any admittance which closes a transmission line can be expressed as function of the admittance characteristic of the line, through determination of the values and of the positions, with respect to the terminal admittance, of the maxima and minima of the electric field.[2,3]

The dielectrometer consists of a klystrom oscillator, square pulse-modulated at 2 kc./sec., which feeds, for the operation in the 8.6 kMHz range, a short circuited circular pipe working on the TE_{11} mode. Standing waves so generated are explored through a slotted line. Measurements are made on a guide representing the transmission line, with and without the specimen inserted, which constitutes its terminal admittance.

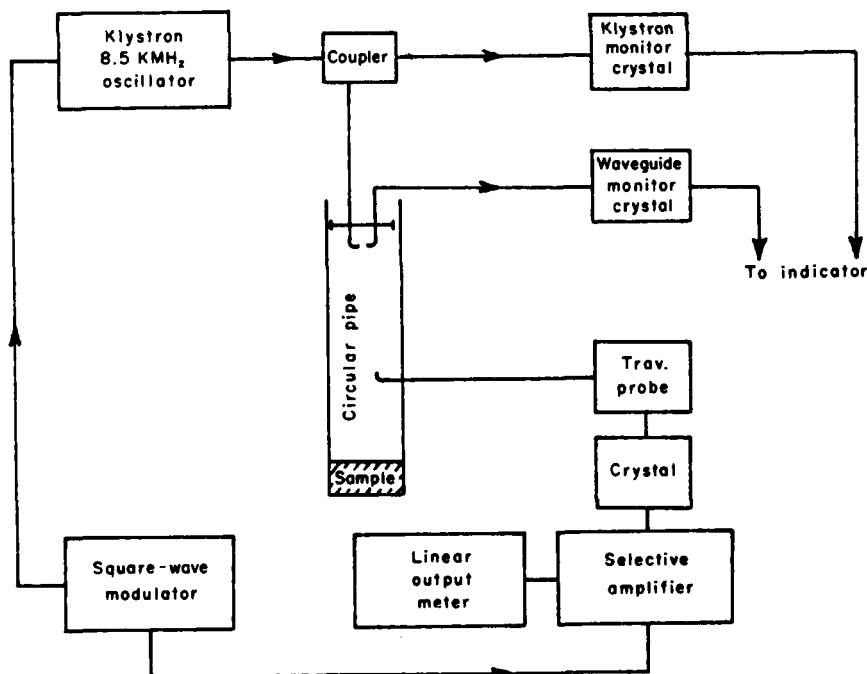Figure 1 shows a simplified diagram of the dielectrometer; Figure 2
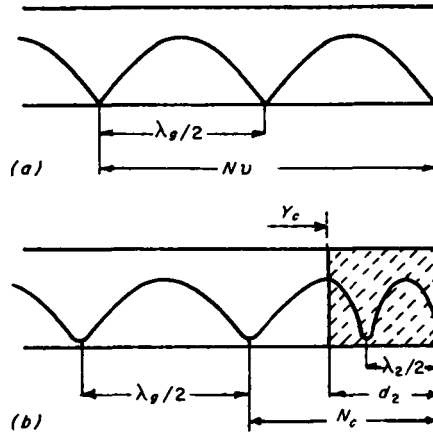

Fig. 1. Diagram of microwave dielectrometer.

Fig. 2. Standing wave pattern (a) in the empty guide and (b) in the guide containing the specimen.

describes the standing wave pattern, both for the empty guide and for the guide partially filled with the specimen under examination. Here,

$$y_c = Y_c/Y_{01} = (Y_{02}/Y_{01}) \coth \gamma_2 d_2 \tag{1}$$

where Y_c = input admittance of the sample, Y_{02} = admittance characteristic of the sample, γ_2 = propagation constant of the sample, and d_2 = thickness of the sample, while y_c is Y_c normalized with respect to the admittance characteristic of the empty guide Y_{01}.

Moreover, for nonmagnetic materials $(\mu = \mu' - j\mu'' = 1 - jo)$ $(\mu = $ magnetic permeability)

$$\gamma_2^2 = (2\pi/\lambda_c)^2 - \omega^2 \mu_0 \epsilon_0 (\epsilon' - j\epsilon'') \tag{2}$$

where λ_c is the cut-off wave length determined by the propagation mode and by the guide dimensions and $f = \omega/2\pi$ is the work frequency.

A knowledge of y_c allows, then, through eqs. (1) and (2), determination of the relative complex dielectric constant $\epsilon^* = \epsilon' - j\epsilon''$.

y_c can be determined through measurements of some quantities in the part of the guide not filled by the specimen. If this is considered as terminal admittance of an empty guide section, we have:[3]

$$y_c = \frac{1 - j R \cot U}{R - j \cot U} \tag{3}$$

where

$$U = [(\Delta + d_2)/\lambda_g] 2\pi \tag{4}$$

$\Delta = N_v - N_c$ being the shift of the node towards the termination caused by the specimen (Fig. 2) and λ_g = wavelength for the empty guide. Then the standing wave ratio R is

$$R = \sqrt{1 + \cosec^2 (\Delta x/\lambda_g)\pi} \tag{5}$$

Δx being the distance between the double power points on the right and on the left of a node.

The small loss in the empty guide has been neglected in deriving eq. (3), that is, the approximation

$$\gamma_g \simeq j\, 2\pi/\lambda_g \tag{6}$$

has been made. The measurement, therefore, of Δ, Δx, and λ_g, by means of the dielectrometer, allows, because of eq. (3), the determination of y_c and, hence, through eqs. (1) and (2), of $\epsilon^* = \epsilon' - j\epsilon''$.

Determination of the Complex Dielectric Constant as a Function of Temperature

The use of the dielectrometer for the determination of the complex dielectric constant at high temperature does not require any modification of the apparatus; it is necessary, however, to account for elongation of the guide as a result of temperature variations.

For low-temperature measurements, on the other hand, some problems are involved, first of all as a result of condensation of atmospheric moisture. Preliminary attempts to eliminate this inconvenience by flushing dry nitrogen through a small hole made into the sample gave no satisfactory results. Good results, however, were obtained when measurements were made
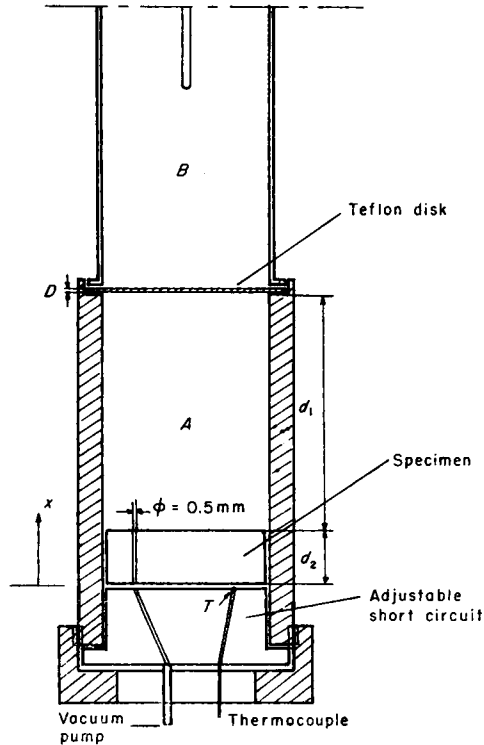

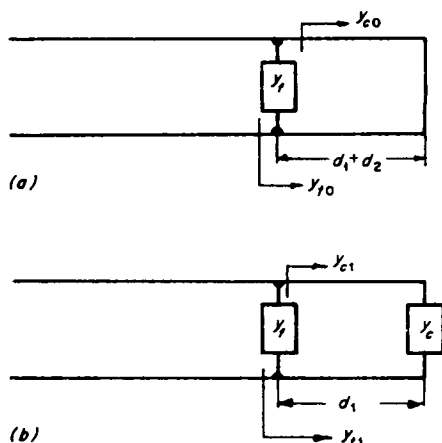Fig. 3. Schematic representation of the terminal section of the guide.

Fig. 4. Equivalent circuit (a) of the empty guide and (b) of the guide containing the sample.

under vacuum (residual pressure of 4–5 μ Hg). However, the presence of the slot, for the insertion of the probe, made it impossible to evacuate the whole guide in this case; this difficulty was overcome by insulating the terminal part of the guide, i.e., the portion in which the specimen was placed, by means of a Teflon disk, and evacuating this section only. A simplified diagram of the modified guide section is shown in Figure 3.

The presence of the thin Teflon sheet modifies the conditions in which measurements are carried out. An analysis of the new situation is then necessary and the relationships must be rederived.

Figure 4 shows the equivalent circuits of the modified guide, with and without the specimen inserted. Here d_2 is the thickness of the sample, $d_1 + d_2$ is the length of the guide section insulated by Teflon, D is the thickness of the Teflon sheet; then Y_f = equivalent admittance of the Teflon sheet, Y_c = input equivalent admittance of the sample when $x = d_2$; Y_{c0} and Y_{c1} = equivalent admittance without and with the sample, respectively, for $x = d_1 + d_2$; Y_{t0} and Y_{t1} = equivalent admittance without and with the sample, respectively, for $x = d_1 + d_2 + D$; Y_{01} and Y_{02} = characteristic admittances of the empty guide and of the specimen, respectively; $y_{ik} = (Y_{ik}/Y_{01})$ = admittance normalized with respect to the characteristic admittance of the empty guide.

Without insertion of the sample, neglecting the losses in the empty guide we have

$$y_{c0} = -j \cot (2\pi/\lambda_g) (d_1 + d_2) \tag{7}$$

$$y_{t0} = y_f + y_{c0} = y_f - j \cot (2\pi/\lambda_g) (d_1 + d_2) \tag{8}$$

On neglecting the losses in Teflon (tan $\delta = \sim 10^{-4}$), eq. (3) can be written ($\Delta x = 0$ from which $R = \infty$):

$$y_{t0} = -j \cot U \tag{9}$$

which yields, in our case,

$$U = [(\Delta + d_1 + d_2 + D)/\lambda_g] \, 2\pi \tag{10}$$

From eqs. (9) and (8):

$$y_f = y_{f0} - y_{c0}$$
$$= -j\left[\cot \frac{2\pi}{\lambda_g} (\Delta + d_1 + d_2 + D) - \cot \frac{2\pi}{\lambda_g} (d_1 + d_2)\right] \tag{11}$$

With the sample inserted:

$$Y_c = Y_{02} \coth \gamma_2 d_2 \tag{12}$$

and

$$y_{c1} = \frac{Y_{02} \coth \gamma_2 d_2 \cos \dfrac{2\pi}{\lambda_g} d_1 + jY_{01} \sin \dfrac{2\pi}{\lambda_g} d_1}{Y_{01} \cos \dfrac{2\pi}{\lambda_g} d_1 + jY_{02} \coth \gamma_2 d_2 \sin \dfrac{2\pi}{\lambda_g} d_1} \tag{13}$$

which, for $d_1 = (2n + 1) \, \lambda_g/4$, gives:

$$y_{c1} = (Y_{01}/Y_{02}) \tanh \gamma_2 d_2 \tag{14}$$

Moreover,

$$y_{f1} = y_f + y_{c1} \tag{15}$$

The knowledge of y_{f1} [y_f being already known from eq. (11)] allows computation of y_{c1}, hence of γ_2 and, for eq. (2), of

$$\epsilon^* = \epsilon' - j\epsilon''$$

for any value of the temperature.

By means of the above calculations we have shifted y_c, modified by the presence of the Teflon sheet, to the abscissa $x = d_1 + d_2 + D$.

From λ_g, Δx, and Δ, measured in the region B, we obtain y_{f1}, expressed by eq. (3)

$$y_{f1} = \frac{1 - j R \cot U}{R - j \cot U} = \frac{R + j \tan U}{1 + jR \tan U} \tag{16}$$

where R is given by eq. (5) while

$$U = (2\pi/\lambda_g) \, (d_1 + d_2 + D + \Delta) \tag{17}$$

Examination of Measurements and Relative Errors

y_f in eq. (11) is computed as the difference between two cotangents. It is advisable, therefore, that $(\Delta + d_1 + d_2 + D)$ and $(d_1 + d_2)$ assume values near $(2n + 1) \, \lambda_g/4$, in order that the relative values of the cotangents be found in the region of lowest slope.

For evacuating the region A, a small hole (0.5 mm. diameter) was made through the sample. The presence of such a hole actually causes changes in the absolute values of the dielectric constant of the material under examination;[4] however, such variations are negligible.

The guide is subject to length variations as a result of temperature changes. Considering that the guide section used for the experimental measurements is about 400 mm. long and that the linear thermal coefficient of copper (of which the guide is made) is $\alpha = 16.8 \times 10^{-6}/°C.$, we obtain, for a temperature change of 180°C., a total length change of $l = 1.21$ mm., which cannot be neglected. Therefore, we carried out determinations of the position of a node using the empty guide (with the Teflon sheet inserted), as function of temperature, while the Δ value relative to the inserted specimen was determined as function of this position change.

The position $d_1 = (2n + 1) \lambda_g/4$, which allows substitution of eq. (13) with eq. (14) is necessary, for it determines the most suitable d_1 value to minimize the error in z (see Appendix A); it is also quite useful for simplifying the computation of y_{c1}, allowing us to employ the calculation program already prepared for the CEP digital computer (see Appendix B). If it could not be possible to realize this condition, it would be advisable to approach it as much as possible. However, $d_1 = (2n + 1) \lambda_g/4$ is valid for a certain value of d_1, but it is no longer valid when the temperature is varied. In fact, the maximum length change which may occur in the guide section A, limited on the upper end by the Teflon sheet and on the lower end by the specimen under examination, when the lowest temperature ($-150°C.$) is reached, can be evaluated as about 0.04 mm.

The substitution of eq. (13) with eq. (14) thus causes an error in the determination of the complex dielectric constant, which, however is quite negligible (see Appendix A). In addition, the measured Δn has been corrected to account for wall losses in the wave guise.

EXPERIMENTAL MEASUREMENTS

We proceeded, first of all, to the determination of y_f, expressed by eq. (11), obtaining:

$$y_f = 0.912 \text{ ohm}^{-1} \tag{18}$$

This value has been determined through successive measurements, changing each time $d_1 + d_2$, in order to realize to the best the approach to the condition $d_1 = (2n + 1) \lambda_g/4$.

For low-temperature measurements, we put $\lambda_g = 58.52$ mm., $d_1 = 307.3$ mm. The condition is then satisfied for $n = 10$. Moreover D is 1.65 mm. For ϵ' values smaller than 4 and by using eq. (A-20) to choose $K = 1$ as demonstrated in appendix A, it was convenient to chose d_2 so that: $0.3 < d/\lambda_g < 0.38$. Among possible values for d_2, one very near to $0.3 \lambda_g$ was chosen, in order to be able to make use of a thin specimen and so reduce local temperature differences. We used, therefore, the value $d_2 = 17.5$ mm.

As expected, $|y_{c1}|$ values so found varied between about 0.3 and 0.5. In this case, the error in $\Delta|z|/|z|$ does not exceed 1%. This indicates an error in ϵ' lower than 0.5%, while the error in ϵ'' may reach about 50% for materials of very low loss $\tan \delta = 10^{-4}$. The accuracy for ϵ'' increases noticeably when medium- or high-loss materials are considered. Ob-

viously, the errors of the instrument must be added to those due to the modifications carried out for low-temperature measurements. We can conclusively say that, for medium-loss materials, the largest errors are of the order of 1.5% for ϵ' and of the order of 10% for ϵ''. The situation, as already explained, becomes much better when high-loss materials are examined.

Before proceeding to the execution of experimental measurements, the node shift caused by temperature variations was determined. The results were very near the calculated values.

Low-temperature measurements were carried out by inserting the lower section of the guide into a cylindrical lead block having a longitudinal central hole of diameter slightly larger than that of the guide. The lead block was placed into a Dewar flask provided with a circular cover made of insulating material, suitably drilled to allow passage of the guide. The cooling was carried out by gradual introduction of liquid nitrogen, cooling rates being of the order of 10°C./hr. The specimen temperature was controlled by means of a Fe-Constantan thermocouple located very close to the sample (Fig. 3). During the measurements, the guide portion was kept under vacuum (residual pressure of about 4–5 μ Hg), in order to avoid, as already explained, moisture condensation.

For high-temperature measurements, the guide was placed in a tubular oven furnished with a thermoregulator.

RESULTS

In order to control the performance of the apparatus and the accuracy of the experimental results, some typical high polymers (amorphous linear, semicrystalline linear, and amorphous crosslinked), all polar, were examined over a wide range of temperature (from about -150 to about 200°C.).

Samples of poly(methyl methacrylate), poly-ϵ-caprolactam, poly(vinyl acetate), and samples of an epoxy resin with different rent crosslink densities, were considered. The main characteristics of these samples are reported in Table I. Samples 1, 2, and 3, the linear (thermoplastic) polymers, were shaped in the form of circular plates (24.45 mm. diameter, 17.5 mm. thickness), by molding at temperatures above the corresponding softening or melting points, in an inert atmosphere (dry nitrogen, practically free of oxygen) and then ground on a lathe. Finally, to eliminate residual stresses due to thermal history and work hardening, the various samples were annealed at suitable temperatures (about 20–30°C. below the corresponding softening or melting points), for about 24 hr. and allowed to cool very slowly to room temperature. The annealing treatment was carried out under vacuum.

The epoxy resin samples (thermosetting) were shaped by pouring the mixture of uncured liquid resin with the hardener into suitable molds kept at room temperature or above in an inert, dry atmosphere. Sample A was prepared by addition of 20% (by weight) of curing agent and cured at high temperature (140°C. for 3 hr.). Sample B was prepared by addi-

TABLE I

Polymer Samples

No.	Polymer	Source	$[\eta]$, dl./g.	$\overline{M}$	d_{20}, g./cm.^{3}	T_g, °C.	T_m, °C.
1	Poly(methyl methacrylate)[a]	Rohm & Haas	0.35	75,000	1.190	108	—
2	Poly-ε-cap- rolactam[b]	Organico	—	21,000	1.146	5	196
3	Poly(vinylace- tate)[c]	—	1.267	360,000	1.180	30	—
4	Epoxy resin (Araldit)[d]	Ciba	—	—	—	—	—

[a] Medium fraction obtained by dissolution of polymer in acetone and subsequent precipitation with methanol.

[b] Molecular weight determined by a titration of a solution of the polymer in phenol–methanol mixture (70/30 in weight) with aqueous HCl (amine endgroup determination) and by titration of a solution in hot benzyl alcohol with KOH in ethylene glycol (carboxyl group determination).

[c] Intrinsic viscosity determined in acetone at 25°C.

[d] Epichlorhydrin–bisphenol A epoxy resin, crosslinked with diethylenetriamine (DETA). The glass transition points, T_g, have been determined through determinations of the sound velocity at different temperatures. The values so obtained are practically the same as those deduced from dilatometry.

tion of 40% of hardner, cured for 8 hr. at room temperature, and finally kept for 3 hr. at 140°C.

In Figure 5 the experimental values of the real part of the dielectric complex constant ϵ' and of the dissipation factor tan δ for poly(methyl methacrylate) are reported as functions of temperature between −150 and
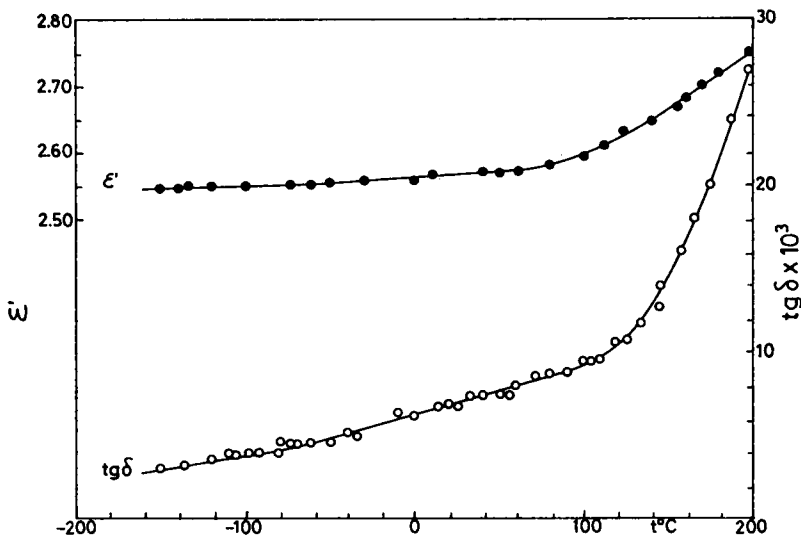

Fig. 5. Dielectric constant and dissipation factor as functions of temperature in poly-(methyl methacrylate) ($f = 8.60 \times 10^9$ Hz).
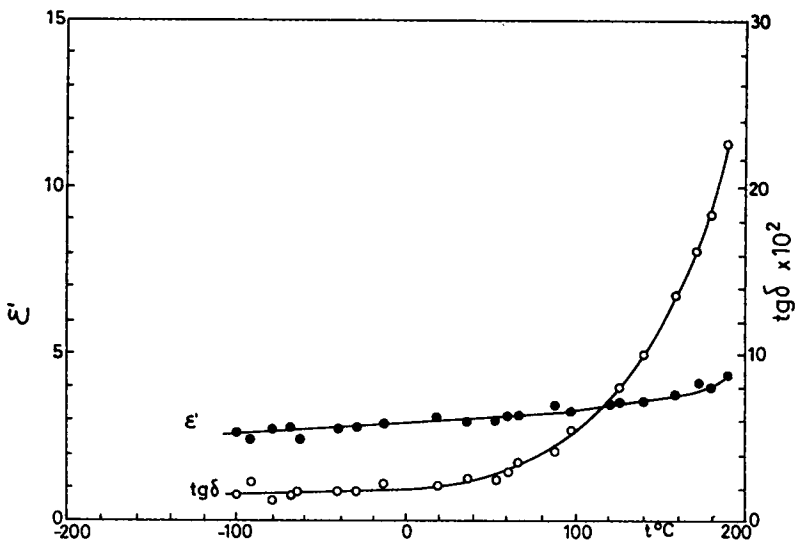
Fig. 6. Dielectric constant and dissipation factor as functions of temperature in poly-ε-caprolactam ($f = 8.60 \times 10^9$ Hz).

200°C. At the lowest temperature reached in the experiments, ϵ' is equal to 2.55, remaining practically constant, with increasing temperature up to about $-70°C$. At higher temperatures, it tends to increase, at first slowly, between -70 and about 100°C., and then more rapidly, with increasing temperature.

The dissipation factor is equal to 4.0×10^{-3} at the lowest temperature, and increases progressively with increasing temperature, reaching values of the order of 30×10^{-3} at about 200°C. The thermal coefficient of the dissipation factor $(d \tan \delta/dT)$, which is very low between -150 and $-70°C.$, exhibits two successive increases, one at about $-70°C.$ and another, of larger intensity, at about 110°C., at practically the same temperatures at which the increases of the thermal coefficient of the dielectric constant are observed.

In Figure 6, the values of ϵ' and of $\tan \delta$ determined in poly-ε-caprolactam samples, between -100 and 200°C. are reported against temperature. The dielectric constant at the lowest temperature is equal to 2.50 and tends to increase with increasing temperature, reaching a value of 5.0 at 200°C. The dissipation factor at the lowest temperature of measurements has a value of 1.5×10^{-2}; it remains practically constant with increasing temperature up to about 40°C., but increases markedly (nearly exponentially), with increasing T at still higher temperatures.

In Figure 7, the values of ϵ' and of $\tan \delta$ for the three poly(vinyl acetate) samples are reported as functions of temperature between -150 and 140°C. Sample 3A has been completely dried; samples 3B and 3C contain 0.5 and 1.0% water, respectively. In the dry sample, the dielectric constant at $-150°C.$ is 3.0 and remains practically constant up to about
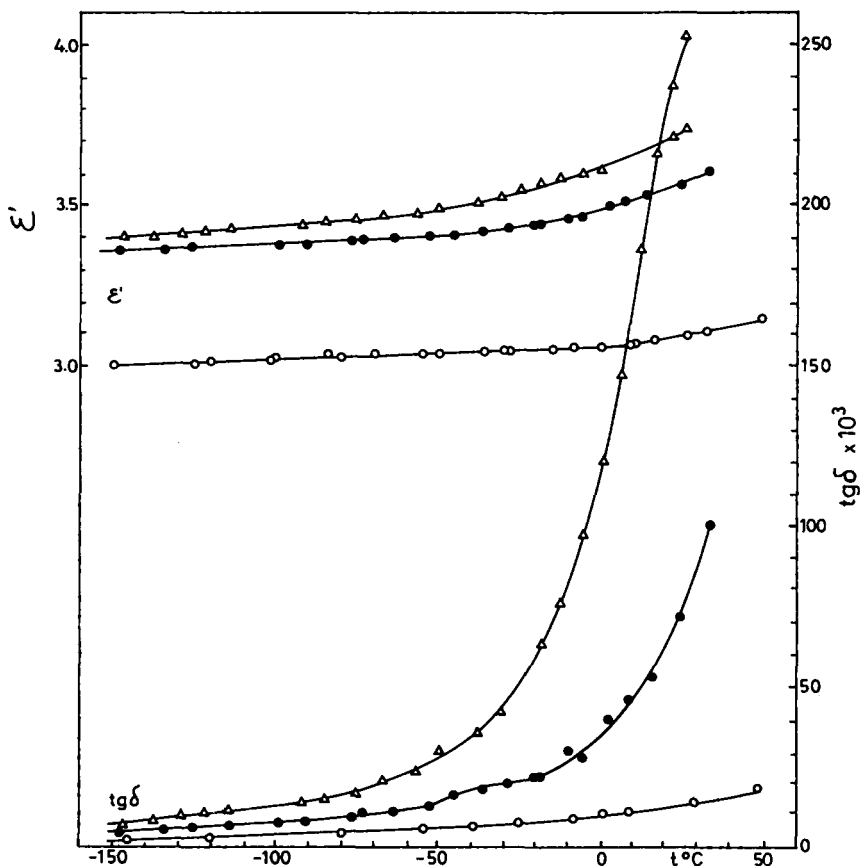
Fig. 7. Dielectric constant and dissipation factor as functions of temperature in poly-(vinyl acetate) ($f = 8.60 \times 10^9$ Hz).

40°C.; at higher temperatures, it tends to increase with increasing temperature. The dissipation factor at −150°C. is 1.5×10^{-3}, increases approximately linearly to room temperature, and then exhibits a more marked increase of values with increasing temperature.

Sample 3B, which contains 0.5% by weight of water, shows behavior which is similar to that of the corresponding dry sample, both with respect to the variation of the dielectric constant or the dissipation factor with increasing temperature; however, at each temperature, in the range explored, the values of both ϵ' and tan δ are always larger than those for the dry sample, while the transition point, i.e., the temperature at which sudden increases of the thermal coefficients of these two quantities are observed, is shifted towards lower temperature.

The same phenomena, much more accentuated, are observed for sample 3C, which contains still larger amounts of water.

In Figure 8 the values of ϵ' and of tan δ measured between O and 200°C. in the samples 4A and 4B of the cured epoxy resin are reported against
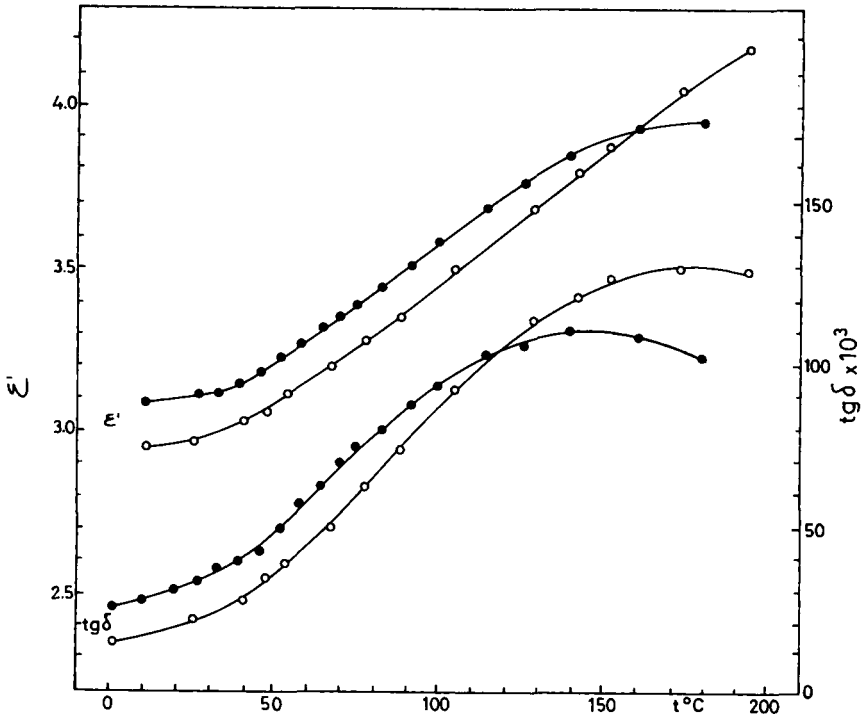
Fig. 8. Dielectric constant and dissipation factor as functions of temperature in cured epoxy resin ($f = 8.60 \times 10^9$ Hz).

temperature. Sample 4A shows a value of ϵ' equal to about 3.0 at 0°C.; it tends to increase with increasing temperature, reaching a value of 4.2 at 200°C. The dissipation factor, on the contrary, which is 15×10^{-3} at 0°C., increases with increasing temperature, passing through a very flat maximum at about 180°C. The dielectric behavior of sample 4B is analogous to that, already described, of sample 4A; the former, however, presents values of the dielectric constant always higher than those of the latter, except at high temperature. The maximum loss temperature for sample 4B is shifted towards lower temperatures (about 150°C.) as compared with sample 4A, while the dissipation factor value corresponding to the maximum is lower.

DISCUSSION OF RESULTS

Considering first the experimental results for poly(methyl methacrylate), we observe that at room temperature the dielectric constant in the microwave region is considerably higher than the square of the refractive index ($n_D^2 = 2.25$). Evidently, since in high polymers the contribution of the atomic polarization is quite negligible, the difference observed between the experimental ϵ' value and the contribution of the electronic polarization ($\epsilon_\infty = n^2$) is to be ascribed to the partial orientation, with the applied electric field, of the permanent dipoles present along macromolecular chains.

The glass transition point T_g of poly(methyl methacrylate) is at about 110°C.[6]; we must exclude, therefore, for this polymer at room temperature the possibility of cooperative motions of chain segments associated with internal rotation around C—C bonds of the main chain (α relaxation effect or "dipoloelastic relaxation"), as the backbone chains are in a state of conformational rigidity below T_g. The higher value of the experimental dielectric constant as compared with the optical dielectric constant (n_D^2) is then associable with the manifestation of some orientational polarization, due to the possibility of local motions of side chain ("β process"), (in this case, by polar methoxycarbonyl groups), characterized by mean relaxation times sufficiently short to give place to dielectric losses in the microwaves region. These suggestions are in agreement with what is at present known concerning the molecular mobility of polymers of the methacrylic series in the rigid (glassy) state. The progressive small increase of the dielectric constant with increasing temperature observed between room temperature and about 100°C. can be related with the progressive increase of the mean kinetic energy of chain segments. The marked increase of ϵ', observed above 100°C. is, on the contrary, due to the excitation of cooperative motions of chain segments, which enhances the orientational facility of the polar groups in the branches.

By comparing the experimental results for the dielectric losses in the microwave region for poly(methyl methacrylate) with those obtained for this same polymer in the radiofrequency range,[7] it can be observed that, while in the latter case both α and β processes are characterized by a loss peak (at some temperature above or below the glass transition point, respectively, the exact location depending on frequency), in the present case, no maxima are found in the dissipation factor versus temperature curves. This is to be ascribed, evidently, to the fact that both α and β loss maxima tend to move with increasing frequency towards higher temperatures, which, for the examined polymer, in the microwave region, fall above the decomposition point of the material.

The observations made on poly(methyl methacrylate) may be extended to poly-ϵ-caprolactam and poly(vinyl acetate), for which α and β processes have also been found in radiofrequency measurements.[8-10] In the case of poly(vinyl acetate) samples containing water, the shift of the transition temperature towards lower values with increasing water content, is ascribed to the plasticizing effect of water molecules, which, through the weakening of intermolecular forces, favors conformational changes of side chains.[11]

Somewhat different behavior is exhibited by epoxy resins, for which a dielectric loss maximum is found at temperature above T_g. This difference is attributable mainly to the fact that, as the latter materials are densely crosslinked, they do not soften when warmed above the glass transition point; therefore, sufficiently high temperatures can be reached in measurements, passing through the range at which the dielectric loss achieves its maximum value.

CONCLUSIONS

The present experimental results are in a very good agreement with those found by other authors using different experimental techniques for the same materials in the microwave region,[12,13] and with predicted behavior of the examined materials in the microwave region on the basis of the results from radiofrequency measurements, through considerations concerning molecular mobility in relation to molecular structure.

The described method seems to be, therefore, suitably applicable to the investigation of the microwave dielectric characteristics of different materials, and in particular of polar high polymers, over a wide range of temperature.

APPENDIX A: MINIMIZATION OF THE ERROR MADE NEGLECTING BY THE VARIATIONS IN GUIDE LENGTH WITH VARYING TEMPERATURE

Determination of the Error in $z = \gamma_2 d_2 \coth \gamma_2 d_2$

From eq. (13) we obtain:

$$\gamma_2 d_2 \coth \gamma_2 d_2 = \frac{2\pi d_2}{\lambda_g} \frac{1 + j\, y_{c1} \cot\, (2\pi/\lambda_g) d_1}{\cot\, (2\pi d_1/\lambda_g) - j\, y_{c1}} \qquad \text{(A-1)}$$

Let us put:

$$z = \gamma_2\, d_2 \coth \gamma_2\, d_2 \qquad \text{(A-2)}$$

$$y_{c1} = \alpha + j\beta \qquad \text{(A-3)}$$

Once d_2 and λ_g are fixed, eq. (A-1) can be written:

$$|z|\, e^{j\varphi} = f(\alpha,\beta,d_1) \qquad \text{(A-4)}$$

where $|z|$ and φ are the module and the argument of z, respectively; and $f(\alpha,\beta,d_1)$ is a generally complex function.

After a long, but not complicated, elaboration of the preceding relations, we obtain, for the relative deviation of $d|z|/|z|$:

$$\frac{d|z|}{|z|} = \frac{2\pi}{\lambda_g} \cdot \frac{1}{\sin^2 \frac{2\pi}{\lambda_g} d_1} \left[\frac{\beta - |y_{c1}|^2 \cot \frac{2\pi}{\lambda_g} d_1}{1 + |y_{c1}|^2 \cot^2 \frac{2\pi}{\lambda_g} d_1 - 2\beta \cot \frac{2\pi}{\lambda_g} d_1} \right.$$

$$\left. + \frac{\beta + \cot \frac{2\pi}{\lambda_g} d_1}{|y_{c1}|^2 + \cot \frac{2\pi}{\lambda_g} d_1 + 2\beta \cot \frac{2\pi}{\lambda_g} d_1} \right] d(d_1) \quad \text{(A-5)}$$

For a loss-free dielectric we have:
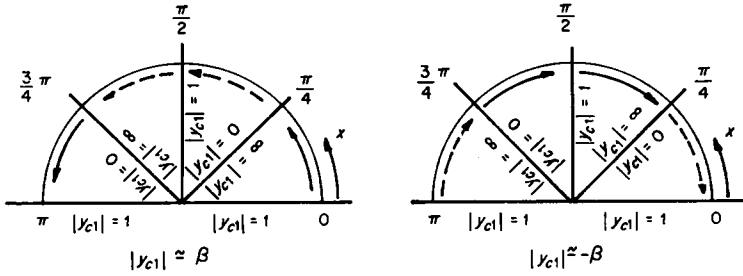
$$y_{c1} = j\beta \qquad \text{(A-6)}$$

Fig. A1. Shifts of relative minima (- -) and maxima (——) with varying y_{c_1}.

while, in general, for low and medium-loss dielectrics we have:

$$|\alpha| \ll |\beta| \tag{A-7}$$

In first approximation, we can therefore put:

$$|y_{c1}| \simeq \pm \beta \tag{A-8}$$

Equation (A-5) gives rise, therefore to the relations:

$$\frac{\Delta|z|}{|z|} = \pm 0.418 \frac{1}{\sin^2 x} \frac{|y_{c1}|}{1 \pm |y_{c1}| \cot x} + \frac{1}{|y_{c1}| \pm \cot x} \tag{A-9}$$

in which we pass from infinitesimal to finite increments and put:

$$x = (2\pi/\lambda_g)d_1 \tag{A-10}$$

and $\lambda_g = 60$ mm., $d_1 = 0.04$ mm., in agreement with conclusions in the text.

After having determined the behavior of eqs. (A-9) and chosen the most suitable value for $|y_{c1}|$, we shall verify that such a choice is convenient also as regards the relative angular deviation, $\Delta\varphi/\varphi$.

From the investigation of the functions (A-9), which, for brevity, is here neglected, we deduce that the abscissas of the absolute values of the minima are given as follows.

For $|y_{c1}| \simeq \beta$

$$\tan 2x = \frac{|y_{c1}|^2 - 1}{2\ |y_{c1}|} \tag{A-11}$$

For $|y_{c1}| \simeq -\beta$

$$\tan 2x = \frac{1 - |y_{c1}|^2}{2|y_{c1}|} \tag{A-12}$$

Figure A1 shows a circular diagram, which puts in evidence, the shifts of the relative minima and maxima, when $|y_{c1}|$ varies from zero to infinity.

Figure A2 gives, for illustrative purposes, the functions (A-9) for some particular values of $|y_{c1}|$. The curves relative to $|y_{c1}|$ values intermediate between those considered can be easily deduced from the graph. It should be noted that, for any $|y_{c1}|$ value, the absolute values of the minima are in any case equal to 0.836.
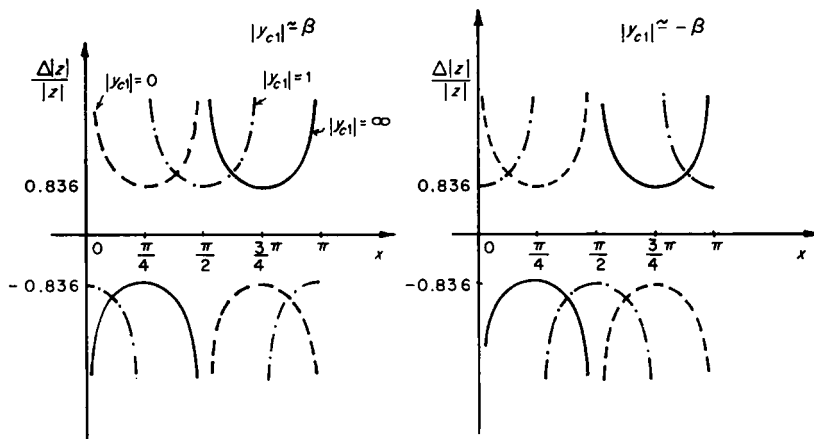
Fig. A2. Behavior of $\Delta|z|/|z|$: (- -) for $|y_{c1}| = 0$ (— ·—) for $|y_{c1}| = 1$, and (———) for $y_{c1} = \infty$ as function of $x = (2\pi/\lambda_g)d_1$.

The choice:

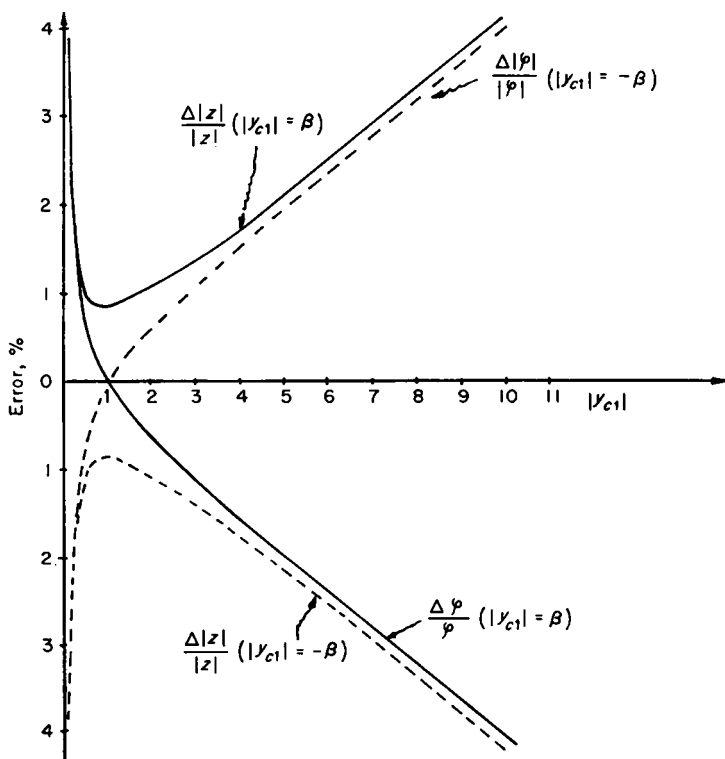$$d_1 = (2n + 1) \lambda_g/4 \qquad\qquad (\text{A-13})$$

Fig. A3. Behavior of $\Delta|z|/|z|$ and $\Delta\varphi/\varphi$ as functions of $|y_{c_1}|$ for $d_1 = (2n + 1) \lambda_g/4$.
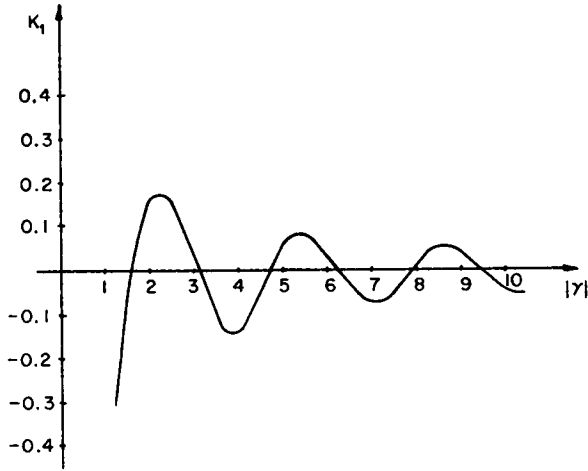
Fig. A4. First-approximation behavior of K_1 as functions of $|\gamma|$.

depends on the considerations made in the text. The functions (A-9), because of eq. (A-13), become:

$$\left[\frac{\Delta|z|}{|z|}\right]_{d_1 = (2n+1)\lambda_0/4} = \pm\, 0.418 \left(|y_{cl}| + \frac{1}{|y_{cl}|}\right) \qquad \text{(A-14)}$$

with

$$|y_{cl}| \simeq \pm\beta$$

Moreover, for the relative angular deviation, in the conditions (A-13) we obtain, relative to the first quadrant:

$$\left[\frac{\Delta\varphi}{\varphi}\right]_{d_1 = (2n+1)\lambda_0/4} \simeq \pm\, 0.418 \left(\frac{1 - |y_{cl}|^2}{|y_{cl}|}\right) \qquad \text{(A-15)}$$

with

$$|y_{cl}| \simeq \pm\beta$$

The functions (A-14) and (A-15) are shown in Figure A3. From these we obtain: (a) for $|y_{cl}| = 1$, the lowest percentage deviation is obtained, that is,

$$\Delta|z|/|z| = 0.84\%$$

and

$$\Delta\varphi/\varphi = 0\% \qquad \text{(A-16)}$$

(b) for $0.2 < |y_{cl}| < 5$, the error on both curves is lower than 2%.

Determination of the Error in $\gamma_2 d_2 = |\gamma| \exp j\Gamma$

From eq. (A-2) we obtain, putting $\gamma_2 d_2 = |\gamma| \exp j\Gamma$:

$$\frac{d|\gamma|}{|\gamma|} + jd\Gamma - \frac{2e^{j\Gamma}}{\sinh(2|\gamma|\, e^{j\Gamma})}\, [d|\gamma| + j|\gamma|\, d\Gamma] = \frac{d|z|}{|z|} + jd\varphi$$

and also

$$\frac{d|\gamma|}{|\gamma|} = K_1 \frac{d|z|}{|z|} - K_2 \, d\varphi \qquad (A\text{-}18)$$

$$d\Gamma = K_2 \frac{d|z|}{|z|} + K_1 \, d\varphi \qquad (A\text{-}19)$$

where

$$K_1 = f_1(|\gamma|, \Gamma)$$
$$K_2 = f_2(|\gamma|, \Gamma)$$

with $|K_2| \ll |K_1|$ for the most frequently occurring $|\gamma|$ and Γ values. In first approximation, it is therefore possible to neglect K_2, and hence the effects that $d\varphi$ and $d|z|/|z|$ exert on $d|\gamma|/|\gamma|$ and $d\Gamma$, respectively. We then obtain:

$$K_1 = \frac{\sin 2|\gamma|}{\sin 2|\gamma| - 2|\gamma|} \qquad (A\text{-}21)$$

whose behavior is represented in Figure A4. It can be seen from the graph reported in Figure A4 that, for $|\gamma| > \pi/2$, the errors in $d|\gamma|/|\gamma|$ and $d\Gamma$ decrease rapidly till below 10% of the corresponding errors in $d|z|/|z|$ and $d\varphi$.

Determination of the Error in $\epsilon^* = \epsilon' - j\epsilon''$

From eq. (2) we have:

$$\frac{d\epsilon'}{\epsilon'} = 2\frac{d|\gamma|}{|\gamma|}\left[\frac{1}{1 + \left(\dfrac{2\pi}{\lambda_c}\right)^2 \dfrac{1}{|\gamma|^2 \cos 2\Gamma}}\right.$$

$$\left. - 2\, d\Gamma \frac{1}{\cot 2\Gamma + \left(\dfrac{2\pi}{\lambda_c}\right)^2\left(\dfrac{1}{|\gamma|^2 \sin 2\Gamma}\right)}\right] \qquad (A\text{-}22)$$

$$\frac{d\epsilon''}{\epsilon''} = 2\frac{d|\gamma|}{|\gamma|} + 2 \cot 2\Gamma \, d\Gamma \qquad (A\text{-}23)$$

The error in ϵ' is, therefore, of the same order of that in $d|\gamma|/|\gamma|$ and $d\Gamma$, while particular attention requires the error in ϵ''.

If $d\Gamma \neq 0$, the former can reach very high values when Γ tends to $\pi/2$, that is, in very low-loss materials.

Optimum Length for the Sample

We saw that for $|y_{cl}|$, given $0.2 < |y_{cl}| < 5$, the relative error in $|z|$ and φ is lower than 2%. Because of eq. (A-23), it is moreover desirable to get as close as possible to the condition $|y_{cl}| = 1$.

We shall make now an indicative analysis, in order to determine to a first approximation, the most convenient length for the sample. From eq. (14) for loss-free materials, we have:

$$\left| y_{cl} \right| = \frac{\lambda_2}{\lambda_g} \left| \tan \frac{2\pi d_2}{\lambda_g} \right| \tag{A-24}$$

from which

$$\frac{d_2}{\lambda_g} = \frac{1}{2\pi} \frac{\lambda_2}{\lambda_g} \left[\arctan \left| y_{cl} \right| \frac{\lambda_g}{\lambda_2} + K\pi \right] \tag{A-25}$$
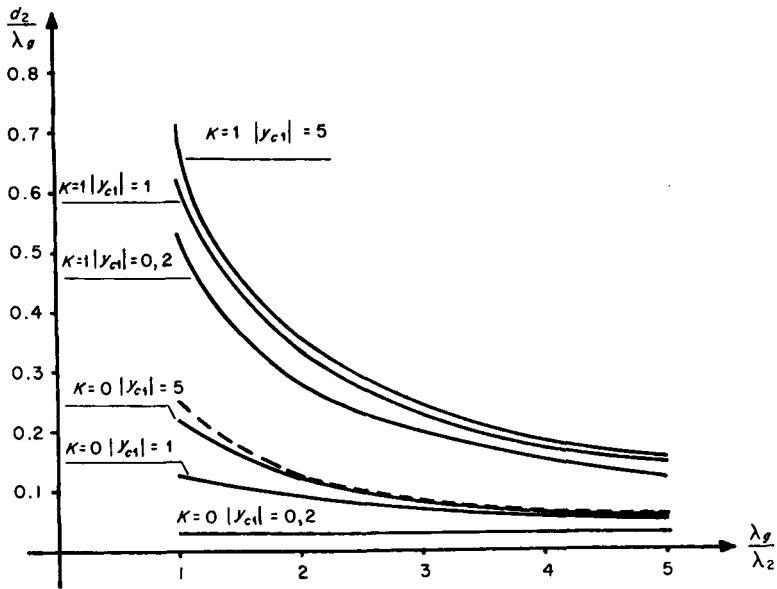
with $K = 0, 1, 2, \ldots$

Fig. A5. Plots of (——) (d_2/λ_g) as function of K and y_{cl} and y_{cl}; (- -) limiting (d_2/λ_g) curve to minimize the error in z.

In Figure A5 the function (A-25) is given for different $\left| y_{cl} \right|$ values, taking $K = 0$ and $K = 1$. From the examination of eq. (A-20) we saw that the minimization of the error in $\left| \gamma \right|$ and Γ requires that

$$\left| \gamma \right| > \pi/2$$

and, hence, in absence of loss

$$2\pi \, d_2/\lambda_2 > \pi/2 \tag{A-26}$$

That is,

$$d_2/\lambda_g > \lambda_2/4\lambda_g \tag{A-27}$$

In Figure A5, function (A-27) is reported for in the particular case in which both sides are assumed to be equal. Because of eqs. (A-25) and (A-27), we obtain:

$$\frac{1}{2\pi} \cdot \frac{\lambda_2}{\lambda_g} \arctan |y_{cl}| \frac{\lambda_g}{\lambda_2} + \frac{1}{2} K \frac{\lambda_2}{\lambda_g} > \frac{1}{4} \frac{\lambda_2}{\lambda_g} \qquad (A\text{-}28)$$

For $K = 0$ and $|y_{cl}|$ for $0.2 < |y_{cl}| < 5$, as can be readily seen from Figure A5, such a relation cannot be satisfied. For $K = 1$, on the contrary, it is satisfied, whatever the first term of the left-hand side of eq. (A-28) may be. This allows us to minimize the final error in $\gamma_2 d_2$, fixing $K \geq 1$, in an independent way, determining the most convenient $|y_{cl}|$ value.

APPENDIX B: DESCRIPTION OF THE CALCULATION PROGRAM FOR THE ELABORATION OF DIELECTROMETER DATA IN THE CEP SYMBOLIC PROGRAM

From eqs. (1), (3), and (6) we obtain:

$$\frac{\tan h\gamma_2 d_2}{\gamma_2 d_2} = \frac{\lambda_g}{2\pi d_2} \cdot \frac{\tan U - jR}{1 + j\dfrac{\tan U}{R}} \qquad (B\text{-}1)$$

where the symbols have the meanings indicated in the text. We indicate the left side of eq. (B-1) as $\delta_1 + j\delta_2$ and the NAC ACADEL program gives δ_1 and δ_2 on the basis of λ_g, d, and Δx data. With such δ_1 and δ_2 values, we deduce from the tables of

$$\frac{\tanh (\gamma'_2 + j\,\gamma''_2)d_2}{(\gamma'_2 + j\,\gamma''_2)d_2} \qquad (B\text{-}2)$$

largely approximate values of $(\gamma'_2 + j\gamma''_2)d_2$. As known, the function (B-2) has many values, in the sense that the same $\delta_1 + j\delta_2$ may be obtained for different $(\gamma'_2 + j\gamma''_2)d_2$ values. The latter can be, however, improved by means of the NAC AMISOL program. This is extremely useful, reducing in a few seconds, the maximum error, intended as module of the difference between the left and the right sides of eq. (B-1), to a few 10^{-5} units. The $\gamma_2 d_2$ values, so optimized, introduced in the ulterior NAC ACCOMP program permit calculation of $\epsilon^* = \epsilon' + j\epsilon''$ on the basis of eq. (2).

The above described programs have been opportunely utilized also for the solution of the equations obtained in the determination of ϵ^* as function of temperature. Equation (16) allows the calculation of y_a; the NAC ACADEL program, with the input of λ_g, Δ, Δx, and $d = d_1 + d_2 + \Delta$ data, gives:

$$\delta'_1 + j\,\delta'_2 = j\,\frac{\lambda_g}{2\pi d} \cdot y_a \qquad (B\text{-}3)$$

from which

$$y_{n} = -\frac{\lambda_g}{2\pi d} \cdot \frac{\delta'_2 + j\delta'_1}{\delta_1'^2 + \delta_2'^2} \tag{B-4}$$

Once y_f is determined from eq. (14) we have, by use of eq. (15)

$$\frac{\tanh \gamma_2 d_2}{\gamma_2 d_2} = -j\frac{\lambda_g}{2\pi d_2}(y_n - y_f) \tag{B-5}$$

Once the right side of eq. (B-5) is calculated, we proceed in the way above described to the calculation of $\epsilon^* = \epsilon' - j\epsilon''$.

References

1. S. Roberts and A. R. von Hippel, *J. Appl. Phys.*, **17**, 610 (1946).

2. A. R. von Hippel, *Dielectric Materials and Applications*, Wiley, New York, 1958.

3. Instruction Manual, Microwave Dielectrometer, Model 2, C.R.L. Inc., Red Wing, Minnesota, June 1951.

4. M. Calamia, G. Franceschetti, and A. Langella, Atti della LXV Riunione AEI, Palermo, Italy.

5. G. Franceschetti and S. Silleni, *Alta Frequenza*, **33**, 7133 (1964).

6. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, p. 23.

7. I. Koppelman, *Proceedings of the International Conference on Physics of Non-crystalline Solids, Delft, July 1964*, Prins, North-Holland, Amsterdam, 1965, pp. 255–269.

8. H. A. Stuart, *Die Physik der Hochpolymeren*, Vol. IV, Springer, Berlin, 1956, pp. 552–553.

9. Y. Ishida, M. Matsuo, and K. Yamafuji, *Kolloid-Z.*, **180**, 108 (1962).

10. D. McCall and E. Anderson, *J. Chem. Phys.*, **32**, 237 (1960).

11. E. Butta, V. Frosini, and P. L. Magagnini, *Chim. Ind. (Milan)*, **46**, 209 (1964).

12. G. P. Mikhailov and A. M. Lobanov, *Fizik Dielektrikov*, Akad. Nauk S.S.S.R., Moscow, Sbornik, 1960, p. 91.

13. E. Amrhein, *Proceedings of the International Conference on Physics of Non-crystalline Solids, Delft, July 1964*, Prins, North-Holland, Amsterdam, 1965, pp. 283–293.

Résumé

Un diélectromètre commercial a été utilisé en vue de déterminer la constante diélectrique complexe de matériaux isolants en fonction de la température. Pour les mesures à basses températures, des modifications de l'appareil ont été apportées en isolant la section inférieure du guide qui contient le spécimen, la section supérieure au moyen d'undisque en téflon afin d'effectuer des mesures sous vide en éliminant les difficultés résultant de la condensation de l'humidité. En tenant compte de ces modifications, les relations entre les quantités mesurées expérimentalement et la constante diélectrique complexe ont été reprises, les erreurs d'analyse ont été déterminées de même que les conditions optimum pour effectuer des mesures expérimentales. Pour des matériaux à pertes élevée et moyenne, dans le domaine des basses températures, la précision est de

l'ordre de 1% en ce qui concerne ϵ' et de 10% pour ϵ''. De meilleurs résultats peuvent être obtenus avec des mesures à températures élevées. La performance de l'appareil et la précision des mesures ont été contrôlées par des mesures de constante diélectrique complexe des différents polymères polaires à des fréquences de 9×10^9 Hz à des températures entre $-150°C$ à $200°C$. Les résultats expérimentaux sont en accord convenable avec les données de la littérature, résultant de mesures expérimentales utilisant d'autres techniques et avec le comportement attendu en se basant sur les résultats des mesures de radiofréquences et des considérations concernant la mobilité moléculaire en rapport avec la structure moléculaire.

Zusammenfassung

Ein handelsübliches Dielektrometer wurde zur Bestimmung der komplexen Dielektrizitätskonstanten von Isolationsmaterialien in Abhängigkeit von der Temperatur verwendet. Für Tieftemperaturmessungen wurde der Apparat durch Isolierung des unteren, die Probe enthaltenden Teils vom oberen Teil durch eine Teflonscheibe modifiziert, sodass die Messungen unter Vakuum ausgeführt werden konnten und die aus der Feuchtigkeitskondensation entstehenden Schwierigkeiten beseitigt wurden. Die ausgeführten Modifikationen wurden bei der Neuermittlung der Beziehungen zwischen den experimentell bestimmten Grössen und der komplexen Dielektrizitätskonstanten berücksichtigt, eine Fehleranalyse durchgeführt und die besten experimentellen Messbedingungen ermittelt. Für Stoffe mit hohem und mittlerem Verlust wurde im Tieftemperaturbereich eine Genauigkeit in der Grössenordnung von 1% in ϵ' und 10% in ϵ'' erreicht. Bessere Ergebnisse können bei höheren Temperaturen erhalten werden. Die Brauchbarkeit des Apparats und die Genauigkeit der Messungen wurde durch Messung der komplexen Dielektrizitätskonstanten verschiedener polarer Polymerer bei Frequenzen zwischen -150 und $200°C$ überprüft. Die Versuchsergebnisse stimmen mit den nach anderen Verfahren erhaltenen Literaturdaten sowie mit dem auf Grund von Radiofrequenzmessungen und Betrachtungen über die Molekülbeweglichkeit in Beziehung zur Molekülstruktur zu erwartenden Verhalten gut überein.